Journal of Fluorine Chemistry, 11 (1978) 441–454
© Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands
Received: November 16, 1977

ORGANOPHOSPHORUS CHEMISTRY. PART 20. REACTIONS OF PHENYLTETRAFLUOROETHYLPHOSPHINE WITH AMMONIA AND ALKYL AMINES: EVIDENCE FOR INTERMEDIATE PHOSPHA-ALKENES*

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

Phenyl-1,1,2,2-tetrafluoroethylphosphine reacts rapidly at low temperatures with an excess of methylamine, dimethylamine, or diethylamine to give the corresponding amine hydrofluoride and mixtures of N-methyl or N,N-dialkyl phenyl-(E)-1,2-difluorovinylphosphinous amides and N-methyl or N,N-dialkyl phenyl-1,2,2-trifluoroethylphosphinous amides. The mixtures are unchanged by further treatment with the corresponding free amine. With an excess of ammonia in the liquid phase the phenyltetrafluoroethylphosphine gives, almost quantitatively, ammonium fluoride and phenyl-(E)-1,2-difluorovinylphosphinous amide, which polymerises when kept to an air- and thermally-stable polymer. With an excess of trimethylamine the tetrafluoroethylphosphine yields an intractable solid and the amine hydrofluoride. These reactions are discussed on the basis of a phospha-alkene mechanism.

INTRODUCTION

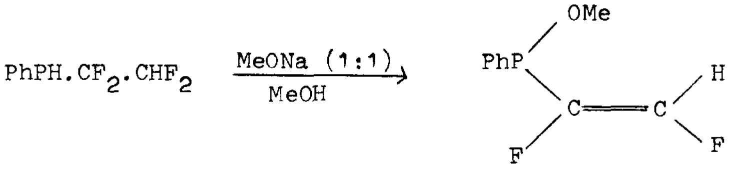
Reactions of primary and secondary polyfluoroalkylphosphines with amines [2-4] or alkoxides [2,5] can be interpreted on the basis of two alternative mechanisms.

---

*Part 19: Ref. [1].

The first postulates the intermediate formation of short-lived phospha-alkenes, a type of intermediate first suggested to arise in the alkaline aqueous hydrolysis of bis(tetrafluoroethyl)phosphine [6], and recently observed by microwave spectroscopic analysis of the pyrolysis products of phosphines [7]. The second mechanism is based upon a nucleophilically initiated hydride ion shift from phosphorus to α- carbon, and was first proposed to account for negligible deuterium incorporation during NaOD/D_2O hydrolysis of chloromethylphosphinic acid [8].

We recently reported [5] that the mixed secondary phosphine $PhPH.CF_2.CHF_2$ reacts with an equimolar amount of methanolic sodium methoxide to give a mixture of the 1,2-difluorovinylphosphinite (I) and the 1,2,2-trifluoroethylphosphinite (II)

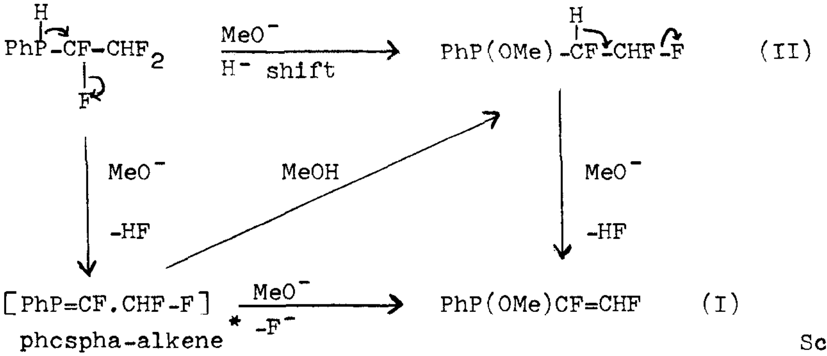


(I) (28)

+

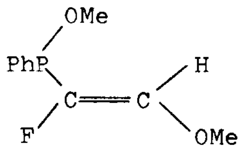
$PhP(OMe).CHF.CHF_2$ (II) (3)

The saturated product (II) can arise either directly from the phosphine by a hydride ion shift, or indirectly via methanol addition to a phospha-alkene. The unsaturated product (I) can also arise by either mechanism: it may be formed by methoxide attack on the phospha-alkene with displacement of fluoride ion, or via base-catalysed dehydrofluorination of (II) (Scheme 1)

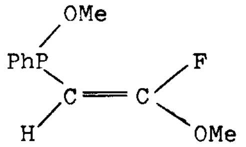


Scheme 1

Strong evidence for the phospha-alkene route to (I) would have been provided if the trifluoroethylphosphinite (II) had proved to be stable to the reagents used. However, the mixture of (I) and (II) reacted further with an excess of sodium methoxide, yielding the methoxyfluorovinylphosphinite (III), a product also obtained, together with a trace of the isomer (IV), by treating the phosphine directly with an excess of methoxide.



(III)



(IV)

Both (III) and (IV) could arise by addition-elimination sequences from (I), but the failure to recover (II) leaves the mechanism of the phosphine's initial reaction with a nucleophile unresolved.

Reactions now reported between the phosphine $PhPHCF_2CHF_2$ and ammonia, methylamine, and secondary alkylamines are most readily interpreted on the basis of the phospha-alkene mechanism.

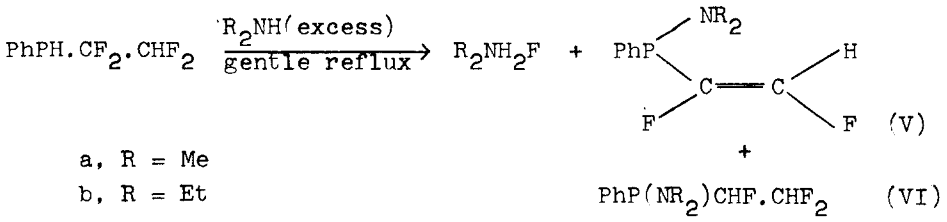
RESULTS AND DISCUSSION

Reactions with Secondary Amines

When the secondary phosphine was added to a large excess of dimethylamine or diethylamine at a temperature slightly below the boiling point of the amine, an exothermic reaction instantly occurred which was conveniently moderated by permitting the amine to reflux. The phosphorus-containing product from both reactions proved to be a not readily separated mixture of two components, identified as the N,N-dialkyl phenyl-(E)-1,2-difluorovinylphosphinous amide (Va,b) and the N,N-dialkyl phenyl-1,2,2-trifluoroethylphosphinous amide (VIa,b).

---

* For simplicity, only the uncharged canonical form is shown of a phospha-alkene $-P{=}C< \longleftrightarrow -\overset{+}{P}-\overset{-}{C}<$



(V)

(VI)

a, R = Me

b, R = Et

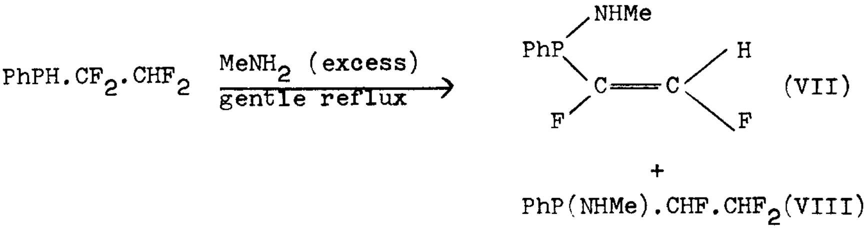
These reactions therefore resemble those leading to (I) and (II), described above, in that a saturated product (VI) is the major component (61% yield when R = Me, 39% when R = Et). The (E)-geometry of the minor, unsaturated, component (V) (12% yield when R = Me, 15% when R = Et) is also the same as that of (I).

Although the (V)/(VI) mixtures were not separated, because their thermal instability precluded preparative gas chromatography, they were readily characterised by n.m.r. spectroscopic analysis of the mixtures. The (E)-geometry of the vinyl group in (V) is unambiguously established by consideration of (i) the high value of the H-F coupling constant ($^{2}\underline{J}_{HF}$ = 73.6 - 76.2 Hz), which indicates a geminal CHF arrangement, and (ii) the low value of the vicinal F-F coupling constant ($^{3}\underline{J}_{FF}$ = 16.4 - 18.3 Hz) which indicates a cis-FC:CF structure [9]. These values agree closely with those reported for (I) (74 and 17.5 Hz respectively) [5]. The nature of the trifluoroethyl substituent in (VIa) is demonstrated just as forcibly by the observation that the CHF ^{19}F resonance, when observed at 94.1 MHz, appears as two distinct multiplets, an observation only to be interpreted as revealing diastereoisomerism due to two chiral centres (phosphorus and α- carbon), a well-known phenomenon in phosphine chemistry [10], which is also a feature of the 94.1 MHz spectrum of (II). A $CH_2F.CF_2.P$ arrangement is thereby precluded.

In contrast to their alkoxy counterparts (I) and (II), the phosphinous amides (V) and (VI) were unaffected by further treatment with secondary amine, an observation which has an important bearing on the mechanistic argument (see below).

Reaction with Methylamine

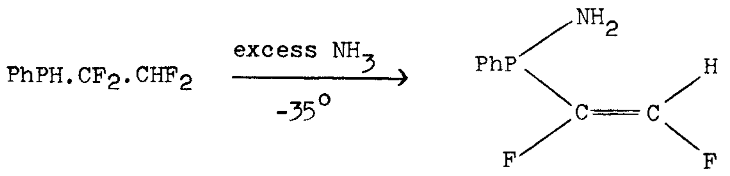
In a closely analogous reaction under very mild conditions (at -6 °C, in refluxing methylamine), the phosphine $PhPHCF_2CHF_2$ was converted by methylamine into a 75:25 mixture of N-methyl phenyl-(E)-1,2-difluorovinylphosphinous amide (VII) (63%; $^2J_{HF}$ = 75.6 Hz, $^3J_{FF}$ = 17.5 Hz) and N-methyl phenyl-1,2,2-trifluoroethylphosphinous amide (VIII) (21%).



Although the ^{19}F n.m.r. spectrum of the mixture of (VII) and (VIII), even at 94.1 MHz, was too complex to determine whether diastereoisomerism was displayed by (VIII), the chemical shifts (CH$\underline{F}$ at 138 and CH$\underline{F_2}$ at 48 p.p.m.) are almost identical to those of the corresponding N,N-dialkyl phosphinous amides (VI) (137-138 and 47.8-48.2 p.p.m., respectively). Methylammonium fluoride was also isolated: the amount indicates that the elimination of approximately 1.5 mol of HF per mol of secondary phosphine had occurred [formation of (VII) requires that 2 mol per mol of phosphine be eliminated]. Like the N,N-dialkyl phosphinous amides (V) and (VI) the mixture of (VII) and (VIII) was essentially unaffected by further treatment with refluxing methylamine.

Reaction with Ammonia

Even at -35 °C an instantaneous reaction occurred when the secondary phosphine was added to an excess of liquid ammonia. Ammonium fluoride was formed together with an organic material which, if isolated without delay by extraction at ambient temperature and in the absence of air, was obtained as pure phenyl-(E)-1,2-difluorovinylphosphinous amide (IX) (92%; $^2J_{HF}$ = 74.4 Hz, $^3J_{FF}$ = 18.6 Hz), with satisfactory mass and elemental analyses.



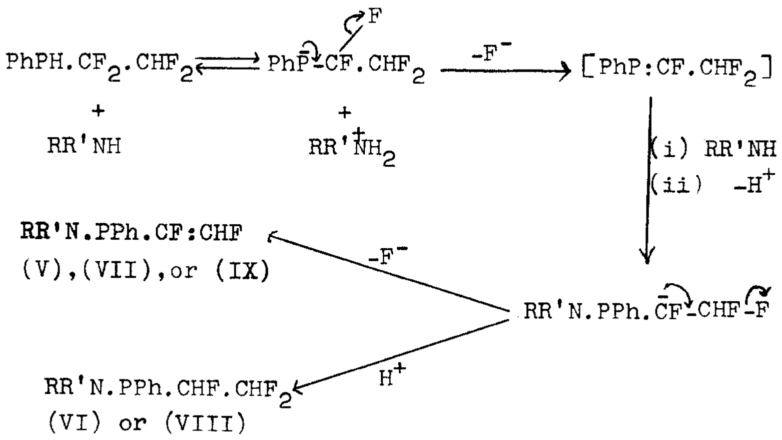
(IX)

In this reaction there was no trace of the corresponding trifluoroethylphosphinous amide $PhP(NH_2).CHF.CHF_2$ (X).

The vinylphosphinous amide (IX) polymerized with extreme readiness: even at ambient temperature in vacuo the polymerization was not significantly retarded by free-radical inhibitors. The polymer ($\underline{M}$, by osmometry in 1,2-dichloroethane solution, in the range 3500 - 4500) is a hard solid of similar elemental composition to the monomer (complete combustion was not readily achieved), and it is unaffected by water or by heating in air at up to 350 °C.

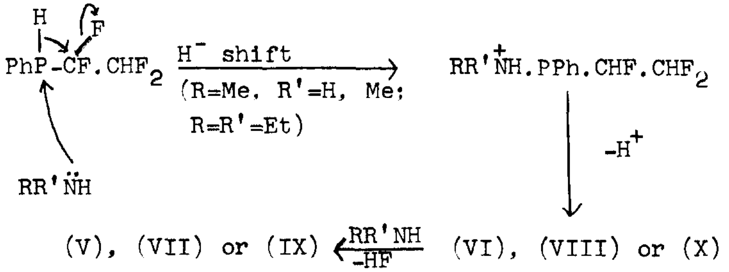
Mechanism

The reactions reported here strongly support the operation of the phospha-alkene mechanism in the formation of the vinyl phosphinous amides. In this mechanism, unlike that based on a hydride ion shift, formation of the unsaturated products (V), (VII) and (IX) requires that the nucleophilic attack occurs only after the formation of the phospha-alkene, when it is followed by or synchronised with, displacement of β-fluoride (Scheme 2).



Scheme 2

In contrast, a hydride ion shift requires (i) initial nucleophilic attack leading to the trifluoroethylphosphinous derivatives (VI), (VIII) or (X) (the latter was not detected), and (ii) subsequent formation of unsaturated products, which can only arise by base-catalysed elimination of HF from the trifluoroethyl group, a reaction shown not to occur in the separate experiment between (VI) or (VIII) and the corresponding amines (Scheme 3).



Scheme 3

Furthermore, the increasing preference for unsaturated products with decreasing basicity of the amine (Table 1) is difficult to reconcile with a hydride shift mechanism for the formation of (V), (VII) and (IX). The experiments described above do not, however, rule out the possibility that a hydride shift mechanism accounts for the formation of some or all of the saturated phosphinous amides (VI) and (VIII). Such a simultaneous operation of both mechanisms has been suggested previously, to account for observations made during the study of reactions between Grignard reagents and methyl chloromethylphosphinate [11].

Table 1

Product Distributions in Phosphine-Amine Reactions

Amine			Temp	% Yield of Products	
RR'NH	R	R'	T/K	RR'N.PPh.CF:CHF	RR'N.PPh.CHF.CHF$_2$
NH$_3$	H	H	238	92	-
MeNH$_2$	Me	H	267	63	21
Me$_2$NH	Me	Me	280	12	61
Et$_2$NH	Et	Et	298-328	15	39

In an attempt to resolve this remaining uncertainty, the secondary phosphine was treated with a large excess of trimethylamine, in the hope that the phospha-alkene $PhP:CF.CHF_2$, or a dimer or polymer derived from it, would be isolated. The expected by-product, trimethylammonium fluoride, was indeed produced but the phosphorus containing product was an involatile tar, the elemental composition of which did not correspond to any simple product.

Thus, although the phospha-alkene mechanism can account for all the products observed in the reactions between the phosphic $PhPHCF_2CHF_2$ and alkoxides, amines, and ammonia and is clearly the pathway followed when (V) and (VII) are formed, the experiment do not preclude the operation of the hydride shift mechanism as a contributing or exclusive route to (VI) and (VIII).

EXPERIMENTAL

Special techniques for manipulating the oxygen- and water-sensitive substances were described previously [5]. Phenyl-1,1,2,2-tetrafluoroethylphosphine was prepared by the method of Parshall <u>et</u> <u>al</u>. [12], modified as described previously [5]. Products were identified by i.r. (Perkin-Elmer 137 with NaCl optics and 257 with diffraction grating), n.m.r. (Perkin-Elmer R10, operated at 60 MHz for ^1H, and 56.46 MHz for ^{19}F, and Varian HA100 operated at 100 MHz for ^1H and 94.1 MHz for ^{19}F) using pure liquid samples unless otherwise stated (chemical shifts quoted in p.p.m. relative to ext. interchange samples of pure C_6H_6 and $CF_3.CO_2H$, for ^1H and ^{19}F, respectively, positive values indicating shifts to high field of the reference; spin-spin coupling constants quoted are moduli), and mass spectrometry (A.E.I. MS902). Analytical g.l.c. was achieved for liquid samples on Pye Unicam 104 fractometers (F.I. detector, 2 m. x 4.5 mm i.d. columns), and for gaseous samples on a Perkin-Elmer 116 fractometer (thermistor detector, 7 m. x 5 mm i.d. columns).

Reactions of Phenyl-1,1,2,2-tetrafluoroethylphosphine

(a) With ammonia. The phosphine (17.0 g, 80.95 mmol) was added dropwise under dry, oxygen-free, nitrogen, to liquid ammonia (14.8 g, 0.871 mol) with vigorous stirring at -35 °C in a flask fitted with a total reflux condenser maintained at -78 °C. An exothermic reaction occurred and a white precipitate formed immediately: the ammonia was allowed to reflux gently for 1 h after addition was completed. Unchanged ammonia (10.9 g, 0.64 mol) was recovered by evaporation, leaving a pale-yellow slush (20.7 g) which was extracted with dry ether (5 x 25 cm^3) under nitrogen to yield a residue (5.47 g, 148 mmol) identified as NH_4F and, after removal of ether from the extract at reduced pressure, an orange oil (14.1 g), which after 3 days at room temperature under nitrogen became a brown solid (Found: C, 45.4; H, 4.3%), m.p. range 108-113 °C: after washing with water to remove traces of NH_4F, the dried solid [Found: C, 52.5; H, 4.3; F, 17.1; N, 4.4: P, 16.9%; M (by osmometry in sym.-$C_2H_4Cl_2$), 3675-4250. $C_8H_8F_2NP$ requires C, 51.3; H, 4.3; F, 20.3; N, 7.5; P, 16.6%; M, 187] softened at 109-115 °C; it had i.r. bands at 3.0 w, 3.3 w, 6.0 w, 6.3 w, 7.0 m, 7.7 s, 8.0 s, 8.3 s, 8.9 s, 9.6 m, 9.8 w, 10.0 w, 13.5 s, and 14.5 s µm, and on thermal gravimetric analysis (Stanton Thermobalance, Pt-Rh type, heating rate 4.5 °C min^{-1}) in air lost 60% weight from 350 - 620 °C.

In a further experiment using ammonia (7.31 g, 0.43 mol) and the phosphine (10.0 g, 47.6 mmol), the raw slush was rapidly extracted with dry ether (5 x 25 ml), the extract freed from ether and the residue immediately sealed in vacuo and stored at -196 °C. The pale-yellow oil obtained was identified as phenyl-(E)-1,2-difluorovinylphosphinous amide (nc) (IX) (8.19 g, 43.8 mmol, 92% yield) [Found: C, 49.2; H, 4.1%; M^+, 187. $C_8H_8F_2NP$ requires C, 51.3; H, 4.3%: M, 187] λ_{max} (liq) 2.90 m, 2.98 m, 3.23 m, 3.25 m, 3.27 m, 3.33 w, 6.00 s, 6.29 w, 6.40 m, 6.75 m, 6.96 s, 7.24 w, 7.69 m, 8.38 m, 8.94 s, 9.26 s, 9.73 m, 10.01 m, 10.14 m, 12.20 s, 13.37 s, and 14.31 s µm, δ (^1H) at 60 MHz -0.8 to

-0.2 (Ph), 0.3 (ddd, $:C\underline{H}F$, $^{2}J_{HF}$ 74.4, $^{3}J_{HF}$ 19, $^{3}J_{HP}$ 4 Hz), and 4.7 (d, $N\underline{H}_2$, $^{2}J_{HP}$ 10.8 Hz), δ (^{19}F) at 56.46 MHz 64.4 (ddd, $:CH\underline{F}$, $^{3}J_{FP}$ 26.0, $^{3}J_{FF}$ 18.6 Hz) 72.2 (td, $:CP\underline{F}$, $^{2}J_{FP}$ 10.7 Hz). Attempts to distil the phosphinous amide at reduced pressure under nitrogen led to rapid formation of a brown gum. Samples stored *in vacuo* at ambient temperature solidified over a period of several days, even when radical polymerization inhibitor (mixed terpenes) was present.

(b) *With Methylamine*. The phosphine (15.3 g, 72.9 mmol) was similarly added to methylamine (22.6 g, 0.73 mol) at -8 °C during 1 h; an exothermic reaction occurred and a white precipitate formed. After a further 1 h at reflux (-6 °C), excess methylamine (16.1 g, 0.52 mol) [Found: *M* (Regnault), 31.3. Calc. for CH_5N; *M*, 31] was distilled out leaving a slush (21.4 g) which was immediately extracted under nitrogen with anhydrous ether (5 x 25 ml), giving residual methylammonium fluoride (6.11 g, 0.12 mol) and, after evaporation of the extract to dryness, a pale-yellow oil. The oil was stored *in vacuo* at -196° and then distilled (15 cm x 1 cm i.d. Vigreux column with partial take-off head) under nitrogen to give *N*-methyl phenyl-(*E*)-1,2-difluorovinylphosphinous amide (nc) (VII) (9.22 g, 45.9 mmol, 63%) as a 75:25 mixture with *N*-methyl phenyl-1,2,2-trifluoroethylphosphinous amide (nc) (VIII) (3.38 g, 15.3 mmol, 21%) (a small amount of an unidentified substance was also present in the mixture, but was ignored in estimating the yields) b.p. range 50-53 °C at 0.5 mmHg, which could not be separated by g.l.c. (2 m SE 30 at 150-200°) and was therefore analysed as a mixture (Found: C, 52.7; H, 5.4%. Calc. for a 75:25 mixture of $C_9H_{10}F_2NP$ and $C_9H_{11}F_3NP$: C, 52.5; H, 5.0) λ_{max} (liq) 2.92 m, 3.21 w, 3.25 m, 3.27 m, 3.32 w, 3.39 m, 3.43 m, 3.45 m, 3.55 m, 6.00 s, 6.28 w, 6.73 m, 6.86 w, 6.96 s, 7.22 m, 7.51 w, 7.68 m, 8.42 w, 8.56 s, 8.83 s, 9.71 m, 10.00 m, 10.27 w, 11.11 s, 12.22 s, 12.99 m, 13.40 s, and 14.31 s µm, and a dark tarry residue (1.41 g). N.m.r. analysis of the mixture yielded the following data: for the vinylphosphinous amide (VII) δ (^{1}H) at 60 MHz -0.35 (m, $\underline{Ph}P$), 0.4 (ddd, $:C\underline{H}F$,

$^2J_{\underline{H}F}$ 75.6 Hz, $^3J_{\underline{H}F}$ 16.8 Hz, $^3J_{\underline{H}P}$ 3.6 Hz), 4.6 (dd, MeN. $^3J_{\underline{H}P}$ 10.8 Hz, $^3J_{\underline{H}H}$ 5.1 Hz), 5.2 (dq, NH, $^2J_{\underline{H}P}$ 15.6 Hz) p.p.m., δ (^{19}F) at 56.46 MHz 61.8 (ddd, :CH$\underline{F}$, $^2J_{\underline{F}H}$ 74.5 Hz, $^3J_{\underline{F}P}$ 28.2 Hz, $^3J_{\underline{F}F}$ 17.5 Hz) and 66.0 p.p.m. (apparent q, PC$\underline{F}$, *Jq* *ca.* 17 Hz); and for the 1,2,2-trifluoroethylphosphinous amide (VIII) δ (^{1}H) at 60 MHz *ca.* -0.35 (Ph). 4.6 (MeN) and 5.2 p.p.m. (NH) (underlying the corresponding absorptions of the vinylphosphinous amide), δ (^{19}F) at 56.46 MHz 48.0 (CH$\underline{F}_2$), and 138 p.p.m. (CH$\underline{F}$). A freshly distilled sample of fraction (i) (0.44 g) shown by ^{19}F n.m.r. spectroscopy to consist of an 80:20 mixture of (VII) and (VIII) was recovered unchanged (^{19}F n.m.r., i.r.) after 4 h at -6 °C in contact with methylamine (21 mmol).

(c) With Dimethylamine. The phosphine PhPHCF$_2$CHF$_2$ (15.0 g, 71.4 mmol) was added dropwise under dry nitrogen to vigorously stirred dimethylamine (32.1 g, 0.71 mol) at 5 - 7 °C in a flask fitted with a total reflux condenser at -78 °C vented to a -144° trap. An exothermic reaction occurred and a white precipitate formed; after the addition (1 h) gentle reflux was maintained for 1 h. Dimethylamine (550 mmol) was then removed leaving a pale-yellow residue (22.2 g) which was extracted with anhydrous ether (5 x 25 cm^3) under nitrogen. The residue was identified as dimethylammonium fluoride (5.09 g, 78 mmol). The extract was freed from ether by evaporation at low pressure and then distilled under nitrogen to give (i) a fraction (12.1 g) b.r. 69 - 77 °C at 0.5 mmHg, shown spectroscopically to consist of a 17:83 mixture (Found: C, 53.4; H, 6.3%. Calc. for a 17:83 mixture of $C_{10}H_{12}F_2NP$ and $C_{10}H_{13}F_3NP$: C, 51.8; H, 5.5%) of *N*,*N*-dimethyl phenyl-(*E*)-1,2-difluorovinylphosphinous amide (Va) (nc) (estimated yield 1.91 g, 8.9 mmol, 12%) and *N*,*N*-dimethyl phenyl-1,2,2-trifluoroethylphosphinous amide (VIa) (nc) (estimated yield 10.2 g, 43.4 mmol, 61%), and (ii) a tarry residue (2.7 g). Thermal instability of fraction (i) prevented g.l.c. separation and it was therefore analysed as a mixture, λ_{max} (liq) at 3.25 w, 3.27 w, 3.36 m, 3.42 m sh, 3.46 m, 3.51 m, 3.57 m, 6.02 m, 6.74 m, 6.90 m, 6.97 m, 7.09 w sh, 7.24 m, 7.35 w, 7.82 m, 8.41 m, 8.71 s, 8.93 m, 9.26 s, 9.42 m, 9.61 s, 10.15 s, 11.21 w, 12.27 w, 12.97 m, 13.48 s, 14.33 s and 15.04 w µm, n.m.r. (Va) δ (^{1}H) at 60 MHz *ca.* -0.45 [m, Ph, masked by corresponding band in (VIa)], 0.3 (ddd, $=\mathrm{C\underline{H}F}$, $^2J_{HF}$ 73.6 Hz, $^3J_{HF}$ 16.8 Hz, $^3J_{HP}$ 4 Hz), and *ca.* 4.3 p.p.m. ($\mathrm{Me_2N}$, also masked), δ (^{19}F) at 56.46 MHz 60.4 (ddd, $=\mathrm{CH\underline{F}}$, $^3J_{FP}$ 29.6 Hz, $^3J_{FF}$ 16.4 Hz) and 63.8 p.p.m. (apparent q, $\mathrm{PC\underline{F}}$, J_q *ca.* 16.5 Hz), and for (VIa) δ (^{1}H) at 60 MHz -0.45 (m, Ph), 0.9 (tm, $\mathrm{C\underline{H}F_2}$, $^2J_{HF}$ *ca.* 55 Hz), 1.8 (dm, $\mathrm{C\underline{H}F}$, $^2J_{HF}$ *ca.* 48 Hz) and 4.3 p.p.m. (m, $\mathrm{NMe_2}$), δ (^{19}F) at 56.46 MHz 48.2 (m, $\mathrm{CH\underline{F}_2}$) and 137.6 p.p.m. (m, $\mathrm{CH\underline{F}}$). At 94.1 MHz, the ^{19}F resonances due to (VIa) were sufficiently well-resolved to reveal diastereoisomerism as follows. Major isomer (70%): $\mathrm{CH\underline{F}_2}$ (AB type; A, dddd; B, apparent dq), J_{AB} = 292 Hz; δ_{AB} = 230 Hz; $\mathrm{CH\underline{F}}$ (ddtd), $^2J_{PF}$ 71, $^2J_{HF}$ 47.4, $^3J_{FF}$ 19, and $^3J_{HF}$ 9.2 Hz. Minor isomer (30%): $\mathrm{CH\underline{F}_2}$ (dddd), $^2J_{HF}$ 54.6, $^3J_{FF}$ 16.5, $^3J_{HF}$ 15.1 (or 19.8), and $^3J_{PF}$ 19.8 (or 15.1) Hz: $\mathrm{CH\underline{F}}$ (dddt) $^2J_{PF}$ 125, $^2J_{HF}$ 47.6, $^3J_{FF}$ 16.2 and $^3J_{HF}$ 10.6 Hz. After an otherwise identical reaction at 0 °C the composition of fraction (i) b.r. 70-74 °C at 0.5 mmHg was found to be 5:95, corresponding to estimated yields of (Va) and (VIa) of 4% and 67% respectively. A sample of this fraction (0.5 g) kept for 4 h at 7° alone and then at 7° for 4 h in contact with dimethylamine (1.05 g) was spectroscopically unchanged (i.r., ^{19}F n.m.r., m.s.).

(d) With Diethylamine. The phosphine $\mathrm{PhPHCF_2CHF_2}$ (14.3 g, 68.1 mmol) was added dropwise under nitrogen to vigorously stirred diethylamine (50.3 g, 690 mmol), at 25 °C. After addition (90 min) the mixture was gently refluxed (55-60 °C, 30 min). Worked up as described in (c), the products were diethylamine (520 mmol), diethylammonium fluoride (8.01 g, 86 mmol), and an ether-soluble oil which was distilled under nitrogen to give (i) a fraction (8.59 g) b.r. 82-91 °C at 0.5 mmHg, shown spectroscopically to be a 32:68 mixture (Found: C, 57.6: H, 6.9%. Calc. for a 30:70 mixture of $C_{12}H_{16}F_2NP$ and $C_{12}H_{17}F_3NP$: C, 56.2: H, 6.5%) of *N*,*N*-diethyl phenyl-(*E*)-1,2-difluorovinylphosphinous amide (nc) (Vb) (est. yield 2.44 g, 10.0 mmol, 15%) and *N*,*N*-diethyl phenyl-1,2,2-trifluoroethylphosphinous amide (nc) (VIb) (est. 6.15 g, 23.4 mmol), (ii) a fraction (0.82 g) b.p. 91-96 °C at 0.5 mmHg, shown to consist mainly ($>$90%) of (VIb) (est. total yield 26.4 mmol, 39%) but containing an unidentified substance (λ_{max} at 14 µm), and (iii) an involatile residue (5.7 g). Fraction (i) was analysed without further separation: λ_{max} (liq) at 3.25 w, 3.27 w, 3.37 m, 3.41 m, 3.49 m, 6.02 m, 6.23 w, 6.69 w, 6.73 m, 6.83 m, 6.95 m, 7.25 m, 7.31 m sh, 7.41 w, 7.70 m, 8.33 m, 8.47 m, 8.70 m, 8.94 s, 9.26 s, 9.71 s, 10.0 m sh, 10.26 w, 10.73 m, 11.17 w, 12.22 m, 12.58 m, 13.37 s, 14.29 s, and 15.15 w µm, n.m.r. (Vb) δ(^{1}H) at 60 MHz ca. -0.5 [Ph, masked by corresponding band in (VIb)], *ca.* 0.1 (ddd, $=C\underline{H}F$, $^2\underline{J}_{HF}$ 76.2 Hz, $^3\underline{J}_{HF}$ 17.9 Hz, $^3\underline{J}_{HP}$ 4Hz), 3.8 (CH_2N) and 5.8 p.p.m. ($\underline{Me}CH_2$), ^{19}F (56.46 MHz) at δ 61.2 (ddd, $=CH\underline{F}$, $^3\underline{J}_{FF}$ 18.3 Hz, $^3\underline{J}_{FP}$ 33.9 Hz) and 64.4 p.p.m. (apparent q, $PC\underline{F}$ $\underline{J}_q$ 18 Hz), and for (VIb) δ (^{1}H) at 60 MHz -0.5 (Ph), 0.7 (tm, $C\underline{H}F_2$, $^2\underline{J}_{HF}$ 55 Hz), 1.7 (dm, $C\underline{H}F$, $^2\underline{J}_{HF}$ 47 Hz), 3.8 (NCH_2) and 5.8 p.p.m. ($NCH_2\underline{Me}$), δ (^{19}F) at 56.46 MHz 47.8 ($CH\underline{F}_2$) and 137 p.p.m. ($CH\underline{F}$). A sample of fraction (i) (0.52 g) was unaffected (i.r., n.m.r.) by (i) treatment for 2 h at 56 °C *in vacuo* or by (ii) treatment with diethylamine (19 mmol) at 56 °C for 2 h, although the pale-yellow colour of the liquid intensified in both experiments.

(e) *With Trimethylamine.* The phosphine $PhPHCF_2CHF_2$ (15.1 g, 71.9 mmol) was added dropwise under nitrogen to vigorously stirred trimethylamine (63.2 g, 1.07 mol) at 1 - 3 °C over 40 min; no immediate reaction was apparent. Volatile products (trimethylamine, 0.99 mol) were removed *in vacuo* leaving a pale-yellow oil which, at 10 - 25 °C, reacted vigorously with evolution of heat. The mixture was extracted with diethyl ether (negligible extraction) and then with chloroform (5 x 25 cm^3). The residue was identified as trimethylammonium fluoride (2.34 g, 30 mmol); the extract was evaporated to give an involatile unidentified tar (15.9 g) (Found: C, 44.6; H, 5.0%).

REFERENCES

1 R.N. Haszeldine, D.L. Hobson, and D.R. Taylor, J. Fluorine Chem., 8, 115 (1976).

2 H. Goldwhite, R.N. Haszeldine, and D. G. Rowsell, J. Chem. Soc., 6875 (1965).

3 M. Green, R.N. Haszeldine, B. R. Iles and D. G. Rowsell J. Chem. Soc., 6879 (1965).

4 M. Green and R.N. Haszeldine, Brit. Pat. 1 121 301 (1968).

5 R.N. Haszeldine, D. R. Taylor, and E. W. White, J. Fluorine Chem., 10, 27 (1977).

6 G. M. Burch, H. Goldwhite, and R. N. Haszeldine, J. Chem. Soc., 572 (1964).

7 M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, Chem. Comm., 513 (1976).

8 C. E. Griffin, E. H. Uhing, and A. D. F. Toy, J. Amer. Chem. Soc., 87, 4757 (1965).

9 J. W. Emsley and L. Phillips in J. W. Emsley, J. Feeney and L. H. Sutcliffe (eds.), Progress in Nuclear Magnetic Resonance Spectroscopy, Vol 7, Pergamon, Oxford, 1971, p. 1; R. Fields in E.F. Mooney (ed.), Annual Reports of N.m.r. Spectroscopy, Academic Press, 1972, Vol 5a, p. 99.

10 W. E. McEwen in M. Grayson and E. J. Griffiths (eds.), Topics in Phosphorus Chemistry, Interscience, New York, 1965, Vol. 2, p.1; A. Rauk, L. C. Allen, and K. Mislow, Angew. Chem. Internat. Edn., 9, 400 (1970).

11 H. Goldwhite and D. G. Rowsell, J. Amer. Chem. Soc., 88, 3572 (1966).

12 G. W. Parshall, D. C. England, and R. V. Lindsey, J. Amer. Chem. Soc., 81, 4801 (1959).