Organophosphorus Chemistry. Part XI.[1] Reactions of Dimethyl- and Bis(trifluoromethyl)-phosphine with Olefins, and Photochemical Reaction of Ethyl(bistrifluoromethyl)phosphine with Ethylene

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Dimethylphosphine gives two-way addition with vinyl fluoride under u.v. irradiation forming the 1-fluoroethyl- and 2-fluoroethyl-dimethylphosphines in high yield in the ratio 8:92. With 1,1-difluoroethylene it gives a high yield of 1,1-difluoroethyl- and 2,2-difluoroethyl-dimethylphosphines in the ratio 28:72, but with propene only dimethyl-n-propylphosphine is produced. Bis(trifluoromethyl)phosphine gives only one adduct with each olefin. In all cases the product, or the major product where two are formed, is that predicted on the basis of formation of the most stable intermediate radical. Neither bis(trifluoromethyl)phosphine nor phosphine react with 1,1,3,3,3-pentafluoropropene under u.v. irradiation. Dimethylphosphine reacts as a nucleophile with this olefin during irradiation or in the dark to give a mixture of *cis*- and *trans*-1-dimethylphosphino-1,3,3,3-tetrafluoropropene. Irradiation of ethylbis(trifluoromethyl)phosphine and ethylene gives ethyltrifluoromethyl-3,3,3-trifluoropropylphosphine, the first example of photochemical addition of a trialkylphosphine to an olefin.

FREE-RADICAL addition of phosphine,[2] dimethylphosphine,[1] and bis(trifluoromethyl)phosphine[1] gives two-way addition with trifluoroethylene, the proportion of attack on the CF_2 group decreasing along the series $Me_2PH > H_2PH > (CF_3)_2PH$.

$$R_2PH + CF_2{:}CHF \xrightarrow{\text{u.v.}} \underset{\text{(I)}}{R_2P{\cdot}CHF{\cdot}CHF_2} + \underset{\text{(II)}}{R_2P{\cdot}CF_2{\cdot}CH_2F}$$

Phosphine gives only one 1 : 1 adduct with 1,1-difluoroethylene,[3] and the reactions of dimethylphosphine and bis(trifluoromethyl)phosphine with this and other olefins are now reported.

TABLE 1

N.m.r. parameters of alkylphosphines

	Chemical shifts (p.p.m.)					Coupling constants (Hz)[a]						
	δMe_2P[b]	δP[c]	$\delta\alpha H$[b]	$\delta\beta H$[b]	δF[d]	J_{MeP}	$J_{\alpha HP}$	$J_{\beta HP}$	J_{HFgem}	J_{HFvic}	J_{FP}	$J_{\alpha H\beta H}$
$Me_2P{\cdot}CH_2{\cdot}CHF_2$[e]	5·7	60·8	4·8	0·8	29·4	3·3	0·9	3·3	57·5	19·0	11·0	5·0
$Me_2P{\cdot}CF_2{\cdot}CH_3$	5·7	28·2		5·1	20·8	3·5		7·5		20·5	72·5	
$Me_2P{\cdot}CH_2{\cdot}CH_2F$	5·75	57·2	5·0	2·2	133·6	3·0	0·9	9·2	48	22	14·0	7·4
	$\delta(CF_3)P$[d]					J_{CF_3P}						
$(CF_3)_2P{\cdot}CH_2{\cdot}CHF_2$[f]	−23·0		4·2	0·7	35	78	2·0	6·4	56	18	27	4·0
$(CF_3)_2P{\cdot}CH_2{\cdot}CH_2F$[g]	−21·2	4·0	4·4	2·2	139	75·8	1·1	14·3	47	23·4	31·4	6·5
$CF_3(Et)P{\cdot}CH_2{\cdot}CH_2{\cdot}CF_3$[h]	−18·0				−8·7	62				9·7	4·0	

[a] Signs not determined. [b] +ve values to high field of external benzene. [c] +ve values to high field of external H_3PO_4. [d] +ve values to high field of external trifluoroacetic acid. [e] J_{CH_3-F} 0·6 Hz. [f] J_{CF_3-F} 2·8 Hz. [g] J_{CF_3-F} 3·5 Hz, $J_{CF_3-\beta H(?)}$ 0·6 Hz. [h] ^1H spectrum was complex, centred at δ_{Benz} 5·13 p.p.m.

Bis(trifluoromethyl)phosphine.—U.v. irradiation of equimolar mixtures of bis(trifluoromethyl)phosphine with vinyl fluoride or 1,1-difluoroethylene gave the corresponding 1 : 1 adducts in excellent yield. These were readily identified by n.m.r. spectroscopy as the 2-fluoroethyl- and 2,2-difluoroethyl-bis(trifluoromethyl)-phosphines respectively. The former showed the characteristically large (47 Hz) doublet splitting in the ^1H spectrum and corresponding triplet in the ^{19}F spectrum for the CH_2F group. The latter showed the similarly characteristic doublet (56 Hz) in the ^{19}F spectrum and triplet in the ^1H spectrum for the CHF_2 group. The spectra were fully analysable by first-order methods (see Table 1) and are completely in accord with the structures shown. No trace of any isomer could be detected by n.m.r. or by g.l.c.

$$CH_2{:}CFX + (CF_3)_2PH \xrightarrow{\text{u.v.}} \underset{\text{(III)}}{(CF_3)_2P{\cdot}CH_2{\cdot}CHFX}$$

a; X = H: (IIIa) 88%
b; X = F: (IIIb) 93%

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[1] Part X, R. Fields, R. N. Haszeldine, and N. F. Wood, *J. Chem. Soc. (C)*, 1970, 744.

[2] R. Fields, H. Goldwhite, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc. (C)*, 1966, 2075.

[3] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1963, 1083.

As expected from our previous work with such compounds,[4] and in accord with other work reported recently,[5] the tertiary phosphines were readily hydrolysed by sodium hydroxide in aqueous dioxan, each giving two equivalents of fluoroform. Like 2,2-difluoroethylphosphonous dichloride,[6] 2,2-difluoroethylbis(trifluoromethyl)phosphine also gave a high (73%) yield of acetylene.

$$(CF_3)_2P{\cdot}CH_2{\cdot}CHF_2 \xrightarrow{\text{aq.NaOH}} \underset{98\%}{2CHF_3} + \underset{73\%}{CH{:}CH}$$

In contrast, the 2-fluoroethyl group of 2-fluoroethylbis(trifluoromethyl)phosphine remained intact and attached to phosphorus, since neither fluoride ion nor volatile fragments, apart from fluoroform, were detectable.

$$(CF_3)_2P{\cdot}CH_2{\cdot}CH_2F \xrightarrow{\text{aq.NaOH}} 2CHF_3 + \underset{\text{not isolated}}{[CH_2F{\cdot}CH_2{\cdot}P(OH)_2]}$$

The successive bromination and pyrolysis of the tertiary phosphines, which had previously been applied successfully[1] to the products from bis(trifluoromethyl)phosphine and trifluoroethylene, was completely unsuccessful with (IIIb), giving a complex mixture containing hydrogen bromide, silicon tetrafluoride, bromotrifluoromethane, fluoroform, and at least nine other major components, but no bromo-1,1-difluoroethanes. We have reported previously[1] that this procedure is ineffective with dimethylphosphinofluoroalkanes, and it now appears that all three α-carbon atoms must carry at least one fluorine for a clean cleavage reaction.

Dimethylphosphine.—Dimethylphosphine reacted smoothly under u.v. irradiation with vinyl fluoride and with 1,1-difluoroethylene, to give 1 : 1 adducts in good yield. With 1,1-difluoroethylene the major component of the two-component mixture of adducts was readily purified and identified by its n.m.r. (Table 1) and mass spectra as 2,2-difluoroethyldimethylphosphine. The minor product could not be purified from traces of the major, but the n.m.r. spectra (Table 1), after subtraction of peaks known to be due to the 2,2-difluoroethyl compound, strongly suggested the presence of 1,1-difluoroethylbis(trifluoromethyl)phosphine. The ^1H spectrum showed a doublet of triplets, and the ^{19}F spectrum a doublet of quartets for the $CH_3{\cdot}CF_2{\cdot}P$ system, although the signals due to the Me_2P group were obscured by those of the other isomer. An authentic sample of 1,1-difluoroethyldimethylphosphine was therefore preprepared from sodium dimethylphosphide and 1-bromo-1,1-difluoroethane, and was identical with the minor compound obtained above.

$$Me_2PH + CH_2{:}CF_2 \longrightarrow \underset{(IV)}{Me_2P{\cdot}CF_2{\cdot}CH_3} + \underset{(V)}{Me_2P{\cdot}CH_2{\cdot}CHF_2}$$

$$Me_2PNa + CH_3{\cdot}CF_2Br \xrightarrow{120^\circ} (IV)$$

The isomer ratio [(IV) : (V) 28 : 72] was measured by repeated integration of the well-separated ^{19}F n.m.r. absorptions, since accurate calibration of the g.l.c. equipment with the high-boiling, spontaneously inflammable pure compounds proved impracticable. The ratio was reproducible within 2% in separate irradiations.

Irradiation of dimethylphosphine and vinyl fluoride also gave a good yield of a mixture which, from analysis and from its n.m.r. spectra, was found to contain only the two expected 1 : 1 adducts, in the ratio, determined as before from the ^{19}F n.m.r. spectrum, of 92 : 8. A pure sample of the major component was obtained by fractionation *in vacuo*, and was identified as 2-fluoroethyldimethylphosphine.

The ^1H n.m.r. spectrum consisted of a doublet, characteristic of the Me_2P group, a large doublet (*J* 48 Hz) of doublets of triplets for the CH_2F group, and a doublet of triplets of doublets for the CH_2 group of the $P{\cdot}CH_2{\cdot}CH_2F$ system. The ^{19}F signal was a triplet (48 Hz) of triplets of doublets, confirming the assignments. The mass spectrum showed a strong molecular ion (*m*/*e* 108), and strong fragment ions at *m*/*e* 75 (C_3H_8P), 61 (C_2H_6P), and 62 (C_2H_7P). Rearrangement involving migration of fluorine to phosphorus, reported recently[7] for some fluoroalkyldiphosphines, probably accounts for the strong peak at *m*/*e* 80 (C_2H_6PF), and possibly for several others (*e.g.* *m*/*e* 79).

The minor component could not be purified, and the best n.m.r. spectra obtainable showed only a peak at +115·8 p.p.m. (^{19}F), consistent with the $CHF{\cdot}P$ group, in which the fine structure could not be sufficiently resolved for unambiguous assignment. An attempt to prepare 1-fluoroethyldimethylphosphine by treatment of 1-bromo-1-fluoroethane with sodium dimethylphosphide gave only a small amount of material with ^{19}F

$$CH_3{\cdot}CH_2F \xrightarrow{Br_2/\text{u.v.}} CH_3{\cdot}CHBrF \xrightarrow{Me_2PNa} CH_3{\cdot}CHF{\cdot}PMe_2$$

n.m.r. absorption at 117 p.p.m., and peaks at *m*/*e* 108 ($Me_2PC_2H_4F$), and 47 (C_2H_4F), consistent with the formation of 1-fluoroethyldimethylphosphine in low yield. Ethylene (2%), and vinyl fluoride (10%) were also obtained. A mixture of sodium, dimethylphosphine, and vinyl fluoride in xylene failed to react during one week *in vacuo* at 120°.

Mechanism.—The proportions of attack on the vinylic carbon atoms of the olefins studied are as follows:

	$\overset{*}{C}HF{:}CF_2$		$\overset{*}{C}H_2{:}CF_2$		$\overset{*}{C}H_2{:}CHF$	
$Me_2P{\cdot}$	48	52 [1]	72	28	92	8
$PH_2{\cdot}$	85	15 [2]	100	0 [3]		
$(CF_3)_2P{\cdot}$	98	2 [1]	100	0	100	0

These results are consistent with the concept that a radical R· will attack the olefins to give preferentially

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[4] R. Fields, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc.* (*C*), 1970, 197.

[5] K. Gosling, D. J. Holman, J. D. Smith, and B. N. Ghose, *J. Chem. Soc.* (*A*), 1968, 1909.

[6] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1964, 572.

[7] R. G. Cavell and R. C. Dobbie, *J. Chem. Soc.* (*A*), 1968, 1406.

the radicals $RCHF{\cdot}CF_2{\cdot}$, $RCH_2{\cdot}CF_2{\cdot}$, and $RCH_2{\cdot}CHF{\cdot}$ which are more stable intermediates than $RCF_2{\cdot}CHF{\cdot}$, $RCF_2{\cdot}CH_2{\cdot}$, and $RCHF{\cdot}CH_2{\cdot}$ respectively. The difference in stability between these pairs of radicals is not high when only fluorine and hydrogen are present as substituents on the radical carbon, however, and under such near-balanced circumstances other effects, particularly the change in the electrophilic character of the attacking phosphorus radical caused by variation in its substituents, and possibly steric effects, can be discerned. The $Me_2P{\cdot}$ radical is less electrophilic ('more nucleophilic') than $(CF_3)_2P{\cdot}$ and can hence attack the CF_2 group of the olefins $CHF{:}CF_2$ and $CH_2{:}CF_2$, and the CHF group of vinyl fluoride (the sites for nucleophilic attack on these olefins), more readily than can the particularly electrophilic radical $(CF_3)_2P{\cdot}$. The more susceptible these olefins are towards nucleophilic attack, the more does their direction of free-radical addition depend upon any diminution in the electrophilic character of the attacking phosphorus radical by its substituents, as well as on the relative stabilities of the new intermediate radicals produced by the addition reaction. Presumably $(CF_3)_2P{\cdot}$ has a larger steric requirement than $Me_2P{\cdot}$, and this too will enhance the trend in direction of addition caused by the electronic effect discussed above.

It is unlikely that in these experiments any attack by molecular dimethylphosphine (as nucleophile) took place. 1,1-Difluoroethylene and dimethylphosphine failed to react at all in the dark at 100°, and vinyl fluoride and dimethylphosphine were recovered unchanged after being kept at 50° (the ambient temperature in the irradiation enclosures), and, in the presence of sodium and xylene, at 120°, in the dark.

The photochemical reaction of dimethylphosphine with propene gives only dimethyl-n-propylphosphine:

$$Me_2P{\cdot} + MeCH{:}CH_2 \longrightarrow Me_2P{\cdot}CH_2\dot{C}HMe \xrightarrow{Me_2PH} \underset{(95\%)}{Me_2P{\cdot}CH_2{\cdot}CH_2Me}$$

Isopropyldimethylphosphine, the other possible 1 : 1 adduct, was prepared from isopropylphosphonous dichloride[8]

$$Pr^i_2Cd + 2PCl_3 \longrightarrow Pr^iPCl_2 \xrightarrow{2MeMgI} \underset{(27\%)}{Pr^iPMe_2}$$

and was shown not to have been formed in the reaction with propene. Bidirectional radical attack on propene, an olefin susceptible to electrophilic attack, is thus not observed with the less electrophilic $Me_2P{\cdot}$ radical, and any tendency for this radical to attack the CH group of propene must be more than offset by the relatively marked difference in radical stability between $RCH_2{\cdot}\dot{C}HMe$ and $RCHMe{\cdot}\dot{C}H_2$. Enhancement of electrophilic character in the attacking radical, *e.g.*, by use of $(CF_3)_2P{\cdot}$, merely increases by the electronic effect the already strong trend to attack on the terminal CH_2 group of propene, and only n-propylbis(trifluoromethyl)-phosphine is formed.[4]

Reactions with 1,1,3,3,3-*Pentafluoropropene*.—Somewhat surprisingly, in view of the known reaction of phosphine with hexafluoropropene,[3] both phosphine and bis(trifluoromethyl)phosphine failed to react with 1,1,3,3,3-pentafluoropropene, even after prolonged irradiation. However, recent work[9] has shown that this olefin undergoes other radical additions only slowly. The olefin was completely recovered from the reaction with phosphine; a small amount of reduction to 1,1,1,3,3-pentafluoropropane (3%) took place with bis(trifluoromethyl)phosphine, and some tetrakis(trifluoromethyl)biphosphine was formed.

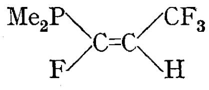
The olefin reacted rapidly with dimethylphosphine under u.v. irradiation, but also at a similar rate (based on recovery of the phosphine) in the dark at 50°. The major volatile product, which was shown by analysis, and by n.m.r. and mass spectrometry to have molecular formula $C_5H_7PF_4$, was formed almost quantitatively, based on consumed olefin (67% and 74% respectively) in each case. The i.r. spectrum showed a strong band close to 6 μm, and g.l.c. showed the presence of two components the proportions of which depended on the reaction conditions. The components were separated by g.l.c. and shown to be the *cis*- and *trans*-isomers of 1-dimethylphosphino-1,3,3,3-tetrafluoropropene (VI and VII). The n.m.r. parameters are in Table 2.

TABLE 2

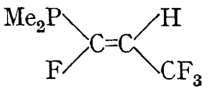
N.m.r. parameters of compounds (VI) and (VII)

	(VI)	(VII)[a]		(VI)	(VII)
Chemical shifts (p.p.m.)[b]					
Me$_2$P	5·63d	5·59d	H	0·95c	1·4d,d,q
CF_3	−22d,d,d	−19·2d,d,d	F	21·6c	19·4c
Coupling constants (Hz)					
CH_3–P	4·5	3·4	CF_3–H	7·8	7·7
P–H	15	3·2	F–H	20·8	37·0
CF_3–P	43·1	4·2	CF_3–F	12·0	17·0
P–F	33·4	37·0			

[a] δ_P 43·8 p.p.m. to high field of external H_3PO_4. [b] ^1H to high field of external benzene, ^{19}F, to high field of external trifluoroacetic acid; d doublet, q quartet, c complex multiplet.



(VI)



(VII)

Assignment of the stereochemistry to (VI) and (VII) has been made on the basis of the H–F coupling constants. $J(HF_{trans})$ usually falls in the range 12—53 Hz and $J(HF_{cis})$ 0—20 Hz; the observed values for (VI) and (VII) are 20·8 and 37 Hz respectively; with this assignment, $J(CF_3F_{cis})$ and $J(CF_3F_{trans})$ also fall in the usual ranges.[10] This assignment is also in accord with the

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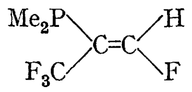
[8] (*a*) A. I. Razumov and Sim-Do-Khen, *Trudy Kazan. Khim.-Tekhnol. Inst. im S.M. Kirova*, 1954—1955, no. 19—20, 167; *Chem. Abs.*, 1957, **51**, 6503; (*b*) B. J. Perry, J. B. Reesor, and J. L. Ferron, *Canad. J. Chem.*, 1963, **41**, 2299.

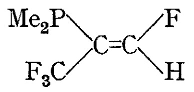
[9] R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1969, 991.

[10] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, 1966, vol. 2, p. 910.

observed boiling points and g.l.c. retention times of the isomers, since (VI), with CF_3 *trans* to F, will have the lower dipole moment. The proportion of (VII) increases with length of irradiation; irradiation of a sample of pure (VI) gave a mixture containing 52% of (VII) after 15 hours.

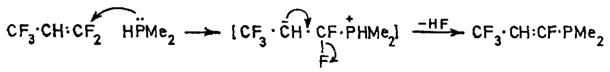
The other possible isomers, (VIII) and (IX), which could have been formed by attack on the $CH\cdot CF_3$ group (which would be contrary to the normal reactions of this olefin with nucleophiles), are excluded by the n.m.r. evidence, since both would require[10] J_{HF} in the range 72—85 Hz, considerably larger than the observed values.


(VIII)


(IX)

Attempts to hydrogenate the phosphinopropenes with Raney nickel and with hydrogen and palladium on alumina failed. Since the latter, in particular, readily hydrogenates fluoro-olefins, it seems that the lack of reactivity is due to the dimethylphosphino-group.

In view of the reaction conditions and of the relative inertness of the olefin to radical attack, the reaction of dimethylphosphine with 1,1,3,3,3-pentafluoropropene most likely takes place by a genuinely nucleophilic attack by dimethylphosphine, (*cf.* ref. 11) rather than attack by a ' relatively nucleophilic ' radical.



Phosphine and bis(trifluoromethyl)phosphine are considerably less powerful nucleophiles, and their failure to react as such under mild conditions is not surprising.

The Reaction of Ethylene with Ethylbis(trifluoromethyl)-phosphine.—Several reactions between bis(trifluoromethyl)phosphine and olefins, particularly where irradiation is prolonged, have given small amounts of high-boiling products as well as 1 : 1 adducts (see above, and ref. 1,4). Fluoroform is also formed in a number of reactions, indicating that P–C cleavage can occur. Ethylbis(trifluoromethyl)phosphine was therefore irradiated with ethylene in order to see whether a typical alkylbis(trifluoromethyl)phosphine would undergo further reaction with its olefin precursor. This resulted in the formation of ethyltrifluoromethyl-3,3,3-trifluoropropylphosphine in 79% yield. Presumably CF_3—P cleavage is followed by attack of one of the radicals on ethylene, and this is followed rapidly either by radical combination

$$\begin{tikzcd}
(CF_3)_2PEt \arrow[r] & CF_3\cdot\dot{P}Et + \dot{C}F_3 \arrow[r, "C_2H_4"] & {} \\
CF_3\cdot CH_2\cdot\dot{C}H_2 \arrow[d] & \text{or} & CF_3(Et)P\cdot CH_2\cdot\dot{C}H_2 \arrow[dll] \\
CF_3(Et)P\cdot CH_2\cdot CH_2\cdot CF_3 & &
\end{tikzcd}$$

or by abstraction of a $\dot{C}F_3$ group

$$CF_3\cdot\dot{P}Et \xrightarrow{C_2H_4} CF_3(Et)P\cdot CH_2\cdot\dot{C}H_2 \xrightarrow{(CF_3)_2PEt} CF_3(Et)P\cdot CH_2\cdot CH_2\cdot CF_3 + CF_3\cdot\dot{P}Et$$

The reaction is remarkably specific; only small amounts of fluoroform (3%) and trifluoropropane (2%) were formed, indicating that hydrogen abstraction is relatively inefficient. The other high-boiling product (3% yield) was tentatively identified from its mass spectrum as trifluoromethylbis(trifluoropropyl)phosphine, which may also be formed by hydrogen abstraction followed by radical combination.

$$CF_3(Et)P\cdot CH_2\cdot CH_2\cdot CF_3 \xrightarrow{R\cdot} CF_3\cdot P(CH_2\cdot CH_2\cdot CF_3)CH_2\cdot\dot{C}H_2 \xrightarrow{CF_3\cdot} CF_3\cdot P(CH_2\cdot CH_2\cdot CF_3)_2$$

EXPERIMENTAL

Preparation and manipulation of the phosphines, and irradiation experiments, were as described previously.[2,4] N.m.r. spectra were recorded on a Perkin-Elmer R.10 permanent magnet spectrometer at 35° and 60·0 (^1H), 56·46 (^{19}F), and 24·3 MHz (^{31}P), with spinning 5-mm. o.d. samples, i.r. spectra on a Perkin-Elmer Model 21 spectrometer with sodium chloride optics, and mass spectra on an AEI MS2 spectrometer at 70 ev, with direct sample entry for high-boiling materials; under these conditions, all the phosphines showed molecular ions. Molecular weights were measured by Regnault's method unless otherwise stated.

Reaction of Bis(trifluoromethyl)phosphine with 1,1-*Difluoroethylene.*—Bis(trifluoromethyl)phosphine (4·55 g., 26·8 mmole) and 1,1-difluoroethylene (1·71 g., 26·8 mmole) were irradiated *in vacuo* (60 hr. at 30°) to give (i) a trace of hydrogen, (ii) unchanged phosphine (0·61 g. 13%) and 1,1-difluoroethylene (0·13 g., 8%), (iii) fluoroform (0·03 g., 1%), (iv) 1,1-difluoroethane (0·01 g.), (v) 2,2-*difluoroethylbis(trifluoromethyl)phosphine* (5·40 g., 93% on olefin consumed) (Found: C, 20·75; H, 1·6%; *M*, 236. $C_4H_3F_8P$ requires C, 20·5; H, 1·3%; *M*, 234), b.p. (isoteniscope) 71·8°, L_V 7·27 kcal. mole^{-1}, Trouton's constant 21·1 cal. mole^{-1} deg.$^{-1}$, and (vi) high boiling material (*ca.* 0·05 g.).

Hydrolysis of 2,2-*Difluoroethylbis(trifluoromethyl)phosphine.*—The phosphine (0·97 g., 4·2 mmole) was kept *in vacuo* (80°, 8 hr.) with dioxan (10 ml.) and aqueous sodium hydroxide (40% w/v, freshly made from deoxygenated water, 30 ml.). The volatile products were dried over P_2O_5 and fractionated *in vacuo* to give acetylene (0·080 g., 73%) and fluoroform (0·57 g., 98%).

Reaction of Dimethylphosphine with 1,1-*Difluoroethylene.*—(a) *In the dark.* Dimethylphosphine (1·04 g., 16·8 mmole) and 1,1-difluoroethylene (1·07 g., 16·7 mmole) failed to react when kept in the dark *in vacuo* at 100° (48 hr.).

(b) *Photochemically.* Dimethylphosphine (2·37 g., 38·1 mmole) and 1,1-difluoroethylene (2·43 g., 38·0 mmole) were irradiated *in vacuo* (22 hr., mechanically shaken) to give (i) hydrogen (1·5 mmole), (ii) recovered 1,1-difluoroethylene (0·64 g., 26%) and dimethylphosphine (0·49 g., 20%), (iii) 1,1-difluoroethane (*ca.* 1%), (iv) a mixture (3·50 g., 99% on olefin consumed) of 1,1- and 2,2-difluoroethyldimethylphosphines [Found: C, 37·7; H, 7·3%; *M*(mass

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[11] J. E. Bissey, H. Goldwhite, and D. G. Rowsell, *J. Org. Chem.*, 1967, **32**, 1542.

spec.) 126. Calc. for $C_4H_9F_2P$: C, 38·1; H, 7·2%; *M*, 126], shown by ^{19}F n.m.r. and g.l.c. to be in the ratio 1,1-isomer : 2,2-isomer, 28 : 72. The mixture was fractionated *in vacuo* to give 2,2-*difluoroethyldimethylphosphine* (2·37 g.) [Found: C, 38·0; H, 7·1%; *M* (mass spec.), 126], b.p. (isoteniscope) 89·3° ± 0·5°, L_V 8·2 kcal. mole^{-1}, Trouton's constant 22·6 cal. deg.$^{-1}$ mole^{-1}, and a mixture (0·87 g.) of the 1,1- and 2,2-difluoro-isomers.

Preparation of 1,1-*Difluoroethyldimethylphosphine*.—Sodium wire (1·0 g.), dimethylphosphine (2·48 g., 40·0 mmole), and sodium-dried xylene (30 ml.) were kept *in vacuo* in a Pyrex tube equipped with a Teflon screw-valve at 120° (24 hr.). Hydrogen (17·4 mmole) was removed, 1-bromo-1,1-difluoroethane (5·40 g., 37·3 mmole) was condensed in, and the mixture was kept at 120° (24 hr.) to give 1,1-difluoroethylene (0·23 g., 9%), acetylene (0·03 g., 3%), unchanged 1-bromo-1,1-difluoroethane (2·52 g., 46%) and dimethylphosphine (0·04 g., 2%), and 1,1-*difluoroethyldimethylphosphine* (0·80 g., 32% on bromodifluoroethane consumed) (Found: C, 38·4; H, 7·0%; *M*, 126), b.p. (isoteniscope) 83·5° ± 0·5°, L_V 6·96 kcal. mole^{-1}, Trouton's constant 19·5 cal. deg.$^{-1}$ mole^{-1}, shown to be pure by g.l.c.

Reaction of Bis(*trifluoromethyl*)*phosphine with Vinyl Fluoride*.—Bis(trifluoromethyl)phosphine (4·73 g., 27·8 mmole) and vinyl fluoride (1·28 g., 27·8 mmole) were irradiated (44 hr.) to give a trace of hydrogen, fluoroform and 1,1,1,3-tetrafluoropropane, unchanged vinyl fluoride (0·18 g., 14%) and bis(trifluoromethyl)phosphine (0·72 g., 15%), a small amount (0·25 g.) of unidentified high-boiling liquid, and 2-*fluoroethylbis*(*trifluoromethyl*)*phosphine* (4·55 g., 88% on olefin consumed) (Found: C, 22·3; H, 1·7%; *M*, 214. $C_4H_4F_7P$ requires C, 22·2; H, 1·8%, *M*, 216), b.p. (isoteniscope) 84°, L_V 7·68 kcal. mole^{-1}, Trouton's constant 21·5 cal. deg.$^{-1}$ mole^{-1}.

Hydrolysis of 2-*Fluoroethylbis*(*trifluoromethyl*)*phosphine*.—The phosphine (1·17 g., 5·4 mmole) was treated with aqueous sodium hydroxide and dioxan (80°, 3 hr.) as described above, to give fluoroform (0·73 g., 97%) as the only volatile product. The aqueous residue gave a negative test for fluoride ion.

Reaction of Dimethylphosphine with Vinyl Fluoride.—Dimethylphosphine (2·64 g., 42·6 mmole) and vinyl fluoride (1·98 g., 43·0 mmole) were irradiated (48 hr.) to give hydrogen (0·003 g.), unchanged vinyl fluoride (0·23 g., 11%) and dimethylphosphine (0·11 g., 4%), and a mixture (4·00 g., 97% on olefin consumed) of 2-fluoroethyl- and 1-fluoroethyl-dimethylphosphine (Found: C, 44·4; H, 9·2. Calc for $C_4H_{10}FP$: C, 44·4; H, 9·3%), in the ratio 92 : 8 (^{19}F n.m.r.). Repeated fractionation *in vacuo* gave a sample of the pure 2-*fluoroethyl isomer* [Found: C, 44·2; H, 9·0%, *M* (mass spec.), 108], b.p. 103—104°/770 mm.Hg.

Dimethylphosphine (0·84 g., 13·5 mmole) and vinyl fluoride (0·64 g., 13·9 mmole) were recovered unchanged after 48 hr. (50°) in the dark.

Preparation of 1-*Bromo*-1-*fluoroethane*.—Ethyl fluoride (1·99 g., 41·5 mmole) (prepared from ethyl toluene-*p*-sulphonate and anhydrous potassium fluoride[12] at 200°) and bromine (6·86 g., 43 mmole) were irradiated[13] (14 hr. at 130°) to give hydrogen bromide (2·19 g., 63%), unchanged ethyl fluoride (0·81 g., 41%), and 1-bromo-1-fluoroethane (2·55 g., 82% on ethyl fluoride consumed) (Found: *M*, 126. Calc. for C_2H_4BrF: *M*, 127), ^1H n.m.r. −1·96 p.p.m. [d, $J(HF_{vic})$ 22·0 of d, $J(HH_{vic})$ 5·4 Hz, intensity 3] and −6·5 p.p.m. from tetramethylsilane [d, $J(HF_{gem})$ 50·7 Hz of q, intensity 1], ^{19}F n.m.r. 47·6 p.p.m. (d of q). Little reaction took place between hydrogen bromide and vinyl fluoride in the dark at 150° (24 hr.). After a further 24 hr. at 250° in the dark, the product was a mixture of 1-bromo-1-fluoroethane (85%) and 1-bromo-2-fluoroethane (15%) [^{19}F n.m.r. +137 p.p.m., t, $J(HF)_{gem}$ 44·5, of t, $J(HF_{vic})$ 20·6 Hz].

Reaction of 1-*Bromo*-1-*fluoroethane with Sodium Dimethylphosphide*.—Sodium dimethylphosphide was prepared from dimethylphosphine (2·27 g., 36·6 mmole) as described above, and kept *in vacuo* at 120° (48 hr.) with 1-bromo-1-fluoroethane (4·65 g., 36·6 mmole), to give vinyl fluoride (0·17 g., 10%), ethylene (0·02 g., 2%), unchanged 1-bromo-1-fluoroethane (0·56 g., 12%) and dimethylphosphine (0·06 g., 3%), and a fraction (0·3 g.) which contained two components. The major (80%) showed ^{19}F absorption at −62·2 p.p.m. (d, *J* 564 Hz of septets, *J* 11·4 Hz) and the minor (20%) absorption at 117·4 p.p.m. The mass spectrum showed strong peaks at *m*/*e* 80 (Me_2PF), 65 (MePF), and 47 (C_2H_4F), and a weaker peak at *m*/*e* 108 ($Me_2PC_2H_4F$).

Reaction of Dimethylphosphine with Propene.—Dimethylphosphine (3·00 g., 48·5 mmole) and propene (2·28 g., 54·2 mmole) were irradiated (72 hr.) to give hydrogen (0·002 g., 4%), unchanged propene (0·33 g., 14%) and dimethylphosphine (0·056 g., 2%), and *dimethyl-n-propylphosphine* (4·60 g., 95% on olefin consumed) [Found: C, 57·4; H, 12·2%; *M* (mass spec.), 104. $C_5H_{13}P$ requires C, 57·7; H, 12·5%; *M*, 104], b.p. 100—101°/741 mm. Hg; ^1H n.m.r. 5·6 p.p.m., d[$J(Me_2P)$ 3·6 Hz] superposed on complex absorption between 5·2 and 6·0 p.p.m. from benzene; ^{31}P 55 p.p.m.

Preparation of Isopropyldimethylphosphine.—Di-isopropylcadmium was treated with phosphorus trichloride to give isopropylphosphonous dichloride, b.p. 88°/198 mm. (lit.,[8b] b.p. 88°/202 mm.), ^{31}P n.m.r. −201 p.p.m. Methyl iodide (90 g., 0·64 mole) was added to magnesium turnings (13 g.) in ether (140 ml.); when reaction was complete the mixture was cooled (−20°) and isopropylphosphonous dichloride (30 g., 0·21 mole) was added in a nitrogen atmosphere. The mixture was heated under reflux (1 hr.), cooled, and 2N-sulphuric acid (100 ml.) was added. Extraction and distillation gave *isopropyldimethylphosphine* (6·0 g., 27%) (Found: C, 57·5; H, 12·2%; *M*, 106. $C_5H_{13}P$ requires C, 57·7; H, 12·5%; *M*, 104), b.p. 93−94°, ^{31}P n.m.r. 38 p.p.m., ^1H n.m.r. complex absorption 1·8 to 0·6 p.p.m. to low field of Me_4Si, with a strong doublet (*J* 2·8 Hz) at −0·65 p.p.m.

The ^{31}P chemical shifts for dimethyl-n-propyl- and dimethylisopropyl-phosphine were in good agreement with those predicted from the reported[14] 'group contributions.'

Reaction of Bis(*trifluoromethyl*)*phosphine with* 1,1,3,3,3-*Pentafluoropropene*.—Irradiation (12 days) of bis(trifluoromethyl)phosphine (4·03 g., 23·7 mmole) and 1,1,3,3,3-pentafluoropropene (2·84 g., 21·5 mmole) gave hydrogen (0·003 g., 12%), fluoroform (0·33 g., 10%), 1,1,1,3,3-pentafluoropropane (0·1 g., 3%), tetrakis(trifluoromethyl)biphosphine, probably with other polyphosphines (0·54 g., 13%), unchanged olefin (2·76 g., 97%) and phosphine (2·22 g., 55%), and a yellow solid which inflamed in air (*ca.* 1 g.).

Reaction of Phosphine with 1,1,3,3,3-*Pentafluoropropene*.—Phosphine (0·76 g., 22·3 mmole) and 1,1,3,3,3-penta-

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fluoropropene (2·97 g., 22·5 mmole) were recovered quantitatively after 72 hr. at 80° in the dark. After irradiation (17 days), phosphine (1·52 g., 44·6 mmole) and 1,1,3,3,3-pentafluoropropene (5·94 g., 45·0 mmole) were recovered quantitatively, apart from the formation of yellow solid polyphosphine (*ca.* 0·1 g.) and hydrogen (0·4 mmole, 2%).

Reaction of Dimethylphosphine with 1,1,3,3,3,-*Pentafluoropropene*.—(a) *Photochemical.* Dimethylphosphine (1·87 g., 30·2 mmole) and 1,1,3,3,3-pentafluoropropene (4·00 g., 30·2 mmole) were irradiated (4 hr.) to give hydrogen (0·4 mmole, 3%), unchanged dimethylphosphine (0·21 g., 11%) and olefin (1·31 g., 33%), a mixture of *cis*- and *trans*-1,3,3,3-tetrafluoro-1-dimethylphosphinopropene (3·47 g., 98% on olefin consumed), and an involatile semisolid material (*ca.* 0·5 g.) which smelled strongly of dimethylphosphine, and gave a positive reaction for fluoride ion.

The mixture of dimethylphosphinopropenes was separated (Aerograph Autoprep, 20 ft. didecyl phthalate at 90°) to give cis-1-*dimethylphosphino*-1,3,3,3-*tetrafluoropropene* (VI) [Found: C, 34·4; H, 3·9%; *M* (mass spec.), 174. $C_5H_7F_4P$ requires C, 34·5; H, 4·0%; *M*, 174], b.p. (isoteniscope) 89·3° ± 0·5°, L_V 7·78 kcal. mole^{-1}, Trouton's constant 21·4 cal. deg.$^{-1}$ mole^{-1}, λ C=C 6·04s μm, and trans-1-*dimethylphosphino*-1,3,3,3-*tetrafluoropropene* (VII) [Found: C, 34·5; H, 4·1%; *M* (mass spec.), 174], b.p. (isoteniscope) 112·3° ± 0·5°, L_V 7·92 kcal. mole^{-1}, Trouton's constant 20·6 cal. deg.$^{-1}$ mole^{-1}, λ C=C 6·00m μm. Samples of the pure isomers were used to calibrate the g.l.c. apparatus, and the isomer ratio of the original mixture was thus found to be (VI) : (VII) 66 : 34.

(b) *Thermal.* Dimethylphosphine (1·60 g., 25·8 mmole) and 1,1,3,3,3-pentafluoropropene (3·28 g., 24·8 mmole) were kept *in vacuo* at 50° (15 hr.) to give unchanged phosphine (0·05 g., 3%) and olefin (0·84 g., 26%), a grey solid (*ca.* 1·0 g.), and a mixture of *cis*- and *trans*-1-dimethylphosphino-1,3,3,3-tetrafluoropropenes (3·17 g., 98% on olefin consumed), shown by g.l.c. to be in the ratio 81 : 19.

Irradiation of cis-1-*Dimethylphosphino*-1,3,3,3-*tetrafluoropropene*.—The *cis*-isomer (VI) (0·10 g.) was irradiated (15 hr.) to give a mixture (0·05 g.) of the *cis*- and *trans*-isomers, shown by g.l.c. to be in the ratio 48 : 52, and a brown involatile solid (*ca.* 0·05 g.).

Reaction of Ethylbis(trifluoromethyl)phospine with Ethylene.—The phosphine (1·73 g., 8·7 mmole) and ethylene (0·25 g., 8·9 mmole) were irradiated *in vacuo* (35 days) to give (i) a mixture (1·3 mmole) of fluoroform (3% yield), ethylene (3%), 1,1,1-trifluoropropane (2%), and a trace of phosphorus trifluoride, (ii) *ethyltrifluoromethyl*-3,3,3-*trifluoropropylphosphine* (1·27 g., 65% on olefin consumed), [Found: C, 32·2; H, 4·1%; *M* (mass spec.) 226. $C_6H_9F_6P$ requires C, 31·9; H, 4·0%; *M*, 226], b.p. (isoteniscope) 92°, L_V 8·28 kcal. mole^{-1}, Trouton's constant 22·6 cal. deg.$^{-1}$ mole^{-1}, and (iv) a mixture (0·3 g.) containing ethyltrifluoromethyl-3,3,3-trifluoropropylphosphine (0·2 g.) and a compound (0·1 g.) tentatively identified from its mass spectrum [*m/e* 294 ($C_7H_8F_9P$), 225 ($C_6H_8F_6P$)] as trifluoromethylbis(3,3,3-trifluoropropyl)phosphine.

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