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PART 19. FREE-RADICAL ADDITION OF DIALKYL PHOSPHITES TO POLYFLUORO-OLEFINS

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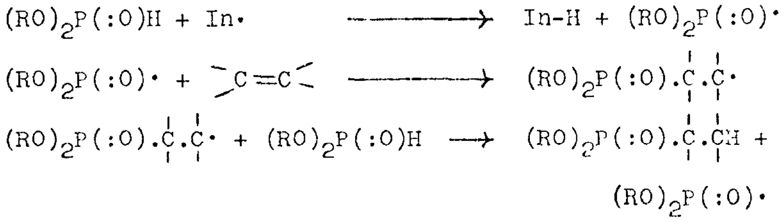
An improved procedure for the peroxide-catalysed addition of dialkyl phosphites to tetrafluoroethylene is described, and the reactions of diethylphosphite with chlorotrifluoroethylene, 1,1-difluoroethylene, perfluoropropene, and 3,3,3-trifluoropropene have been investigated and found to yield diethyl 2-chloro-1,1,2-trifluoroethylphosphonate, diethyl 2,2-difluoroethylphosphonate, an 80:20 mixture of diethyl 2H-hexafluoro-n-propylphosphonate and diethyl 1H-hexafluoropropyl-2-phosphonate, and diethyl 3,3,3-trifluoropropyl-1-phosphonate, respectively.

Free-radical addition of a dialkyl phosphite to an olefin (Scheme 1) usefully yields dialkyl alkylphosphonates [2,3],

Scheme 1



$$(RO)_2P(:O)H + In\cdot \longrightarrow In\text{-}H + (RO)_2P(:O)\cdot$$

$$(RO)_2P(:O)\cdot + {>}C{=}C{<} \longrightarrow (RO)_2P(:O).\overset{|}{\underset{|}{C}}.\overset{|}{\underset{|}{C}}\cdot$$

$$(RO)_2P(:O).\overset{|}{\underset{|}{C}}.\overset{|}{\underset{|}{C}}\cdot + (RO)_2P(:O)H \longrightarrow (RO)_2P(:O).\overset{|}{\underset{|}{C}}.\overset{|}{\underset{|}{C}}H + (RO)_2P(:O)\cdot$$

(In• = initiating radical)

but although fluoro-olefins react smoothly with phosphine [4,5] and with secondary alkylphosphines and fluoroalkylphosphines [6,7], dialkyl phosphites give only low and variable yields of dialkyl polyfluoroalkylphosphonates, $R_fP(:O)(OR)_2$ [8-11]. A study of the effect of reaction variables on adduct yields in the peroxide-catalysed addition of dimethyl and diethyl phosphite to tetrafluoroethylene, now reported, has given a satisfactory reproducible procedure which has been applied to reactions of diethyl phosphite with a range of fluoro-olefins.

Optimisation of the Dialkyl Phosphite-Tetrafluoroethylene Reaction

No reaction occurs when tetrafluoroethylene and diethyl phosphite are heated in the dark unless a free-radical initiator is present. With di-*t*-butyl peroxide in a metal autoclave, the rate of olefin consumption varies widely from experiment to experiment and is often extremely slow, as noted previously [9]. Conditioning the reactor by a series of preliminary runs gives marked improvement [*cf*.experiments 2, 3 and 4 (Table 1) where olefin consumption rises from 23% after 23 h to 98% after 4 h in successive, essentially identical, experiments], but such improvement fails if subsequent runs are long-delayed (Table 1, expt. 5).

High and reproducible olefin consumption rates are, however, obtained by use of a Pyrex inner vessel or liner to minimise contact with metal. Thus with an approximately 3·1:0.05 molar ratio of phosphite : olefin : peroxide, olefin conversions invariably exceeded 70% after 6 h at 130 °C, and were improved to $\geqslant$95% by rocking (Table 1, expt. 6).

Distillation, preferably through a spinning-band column at low pressure to maintain stillpot temperature at $<$100 °C, gave the 1:1 adduct, diethyl 1,1,2,2-tetrafluoroethylphosphonate in 30-35% yield; telomers $H[CF_2.CF_2]_n.P(:O)(OEt)_2$ ($n > 1$) were invariably formed.

Diethyl Phosphite-Fluoro-olefin Reactions

Diethyl phosphite was similarly treated with chlorotrifluoroethylene, 1,1-difluoroethylene, perfluoropropene, and 3,3,3-trifluoropropene. Almost complete conversions (90-99%) of olefin were observed routinely after 6-12 h at 130-150 °C, with the exception of perfluoropropene which reacts more slowly.

The structures of the 1:1 adducts obtained (see Table 1) were established by n.m.r. spectroscopy (Table 2) and are wholly consistent with a free-radical mechanism initiated by addition of the $(EtO)_2P(:O)\cdot$ radical to the fluoro-olefin. Only in the case of hexafluoropropene was a mixture of isomeric 1:1 adducts detected, the predominant isomer arising by addition of $(EtO)_2P(:O)\cdot$ at the terminal CF_2-group, the site also preferred by the $H_2P\cdot$ radical [4].

As an alternative to peroxide catalysis, photochemical initiation was briefly investigated using 1,1-difluoroethylene and a 3:1 excess of diethyl phosphite, but although most of the olefin had reacted after 24 h, only a low yield (ca. 22%) of 1:1 adduct was obtained together with numerous unidentified by-products.

Experimental

Conventional vacuum transfer techniques were used for gaseous materials. Distillation: 1 m Haage spinning band column, fitted with a stainless steel band (Column A), or a 30 cm Podbielniak column packed with Heligrid (Column B); Column A used unless otherwise stated. N.m.r. spectroscopy: Perkin-Elmer R10, operated at 60 MHz for ^1H, 56.46 MHz for ^{19}F, and 24.29 MHz for ^{31}P. Mass spectrometry: A.E.I. MS/2H. Analytical g.l.c.: Perkin-Elmer Models 154 and 116; Pye Model 104 Fractometers.

Reaction of Dialkyl Phosphites with Fluoro-olefins. - (a) General Procedure. A solution of di-*t*-butylperoxide in the dialkyl phosphite was placed in a Pyrex liner, which was then put into a silver-lined autoclave (300 ml). After pressure test and degassing, the fluoro-olefin was admitted *in vacuo*, and the autoclave was heated and rocked vigorously about an horizontal axis. After reaction the unreacted olefin was taken into the vacuum system, and the autoclave dismantled to obtain liquid products. See Tables 1 and 2.

Control experiments showed that there was no reaction in the absence of initiator, and concurrent nucleophilic attack did not occur.

TABLE 1. Reactions between dialkyl phosphites and fluoro-olefins

Expt.	$(RO)_2P(:O)H$ R (mol)	Olefin[a] (mol)	$(^tBuO)_2$ (mmol)	Vessel[b]	Temp. (^oC)	Duration (h)	Olefin consumed	R_f	$R_fP(:O)(CR)_2$ B.p. (^oC/p)	Yield[c]
1.	Me (1.091)	C_2F_4 (0.376)	15	A	130	4	55 (%)	$CHF_2.CF_2$	67-70/10mmHg	40
2.	Et (1.095)	C_2F_4 (0.375)	14	A	130	23	23	-	-	-
3.	Et (1.095)	C_2F_4 (0.375)	21	A	130	16.5	32	-	-	-
4.	Et (1.095)	C_2F_4 (0.375)	21	A	130	4	98	$CHF_2.CF_2$	83-5/10mmHg	33
								$CHF_2.(CF_2)_3$	100-2/10mmHg	11
5.[d]	Et (1.095)	C_2F_4 (0.375)	21	A	130	6	6	-	-	-
6.	Et (0.725)	C_2F_4 (0.249)	14	B	130	6	96[e]	$CHF_2.CF_2$	83-5/10mmHg	33
7.	Et (0.725)	$\overset{*}{C}F_2$:CFCl (0.249)	14	B	130	6	94	$CHFCl.CF_2$	96-9/10mmHg	12
8.	Et (0.725)	$\overset{*}{C}H_2:CF_2$(0.249)	14	B	130	6	99	$CHF_2.CH_2$	91-3/10mmHg	49
								$CHF_2.CH_2.CF_2.CH_2$	83-4/3mmHg	3
9.	Et (0.725)	$\overset{*}{C}F_2:\overset{*}{C}F.CF_3$ (0.249)	14	B	150	12	70	[f] $CF_3.CHF.CF_2$ (80%) $CF_3.CF(CHF_2)$ (20%)	86-7/10mmHg	68
10.	Et (0.495)	$\overset{*}{C}H_2:CH.CF_3$ (0.165)	9.2	B	130	6	99	$CF_3.(CH_2)_2$	79-80/5mmHg	39

[a] Site of attack shown by asterisk.

[b] A, 300 cm^3 Ag-lined autoclave; B, 300 cm^3 Ag-lined autoclave, fitted with 130 cm^3 glass inner vessel, rocked unless otherwise stated.

[c] Yields in mol % based on olefin consumed, estimated by g.l.c. unless otherwise stated.

[d] 6 weeks elapsed between runs 4 and 5, during which the autoclave was left assembled and evacuated.

[e] 96-99% conversions were obtained routinely under these conditions; an otherwise identical run in which the autoclave was static gave 73% conversion of C_2F_4.

[f] Mixture of isomers not separated.

(b) *Dimethyl 1,1,2,2-tetrafluoroethylphosphonate* (11.4 g, 54.3 mmol, 40% on olefin consumed) had b.p. 67-70 °C/10 mmHg (lit.[9], b.p. 72-4 °C/10 mmHg).

(c) *Diethyl 1,1,2,2-tetrafluoroethylphosphonate* (6.9 g, 29.1 mmol, 33% on olefin consumed) had b.p. 83-5 °C/10 mmHg (lit.[9], b.p. 87 °C/10 mmHg).

Diethyl 4*H*-octafluoro-*n*-butylphosphonate (1.6 g, 4.8 mmol, 11% on olefin consumed) b.p. 100-102 °C/10 mmHg (lit.,[9] b.p. 95-6 °C/5-6 mmHg) was also isolated by distillation.

(d) *Diethyl 2-chloro-1,1,2-trifluoroethylphosphonate*. The crude product, purified by distillation, b.p. 96-99 °C/10 mmHg, followed by preparative-scale g.l.c. (2 m MS550 Silicone 20% on 60-80 Celite at 150 °C), gave *diethyl 2-chloro-1,1,2-trifluoroethylphosphonate* (total yield estimated by g.l.c. : 6.70 g, 24.5 mmol, 12% on olefin consumed) (Found: C, 28.6; H, 4.6; Cl. 14.0; P, 12.2%; *M*$^+$, 254, 256. $C_6H_{11}ClF_3O_3P$ requires C, 28.3; H, 4.3; Cl, 14.0; P, 12.2%; *M*, 254 for ^{35}Cl), n_D^{20} 1.402, K_{max} 3509w, 3012m, 2950m, 1764w, 1479m, 1445m, 1396m, 1372m, 1342w, 1274s, 1198s, 1163s, 1115s, 1058s, 1015s, 980s, 952m, 844m, 780m, 735 cm^{-1}.

(e) *Diethyl 2,2-difluoroethylphosphonate*. Distillation of the crude material gave *diethyl 2,2-difluoroethylphosphonate* (total yield estimated by g.l.c. : 24.0 g, 0.119 mmol, 49% on olefin consumed) (Found: C, 35.3; H, 6.4; P, 16.9%; *M*$^+$, 202. $C_6H_{13}F_2O_3P$ requires C, 35.6; H, 6.4; P, 15.4%; M, 202) n_D^{20} 1.398, K_{max} 3012s, 2959m, 1481w, 1448w, 1412m, 1393s, 1370m, 1258s, 1242s, 1195m, 1164m, 1117s, 1099m, 1022s, 995s, 962s, 845-840m, 818m, 780m, 729w cm^{-1}, b.p. 91.5-93 °C/10 mmHg.

A colourless oil, (2.8 g) b.p. 83-4 °C/3 mmHg, purified by g.l.c. (2 m MS550 Silicone 20% on 60-80 Celite at 150 °C), gave *diethyl 2,2,4,4-tetrafluoro-n-butylphosphonate* (total yield estimated by g.l.c. 3.80 g, 14.3 mmol, 3% on olefin consumed) (Found: C, 35.9; H, 5.5%; *M*$^+$, 226. $C_8H_{15}F_4O_3P$

TABLE 2.

N.m.r. Data of Polyfluoroalkyl phosphonates, $R_fP(O)(OR)_2$[†]

$R_fP(:O)(OR)_2$		Chemical shifts[a] and multiplicities[b]							
		^1H				^{19}F			^{31}P
R	R_f	Me	OCH_2	α	β	α	β	CF_3	
Me	$CHF_2.CF_2$	2.8d	-	-	0.4ttd	52.2ddt	61.4dt	-	-3.8tm
Et	$CHF_2.CF_2$	5.4t	2.5dq	-	0.4_5ttd	52.6ddt	60.8dtd	-	c
Et	$CHF_2.CH_2$	5.3t	2.4dq	4.0dtd	0.3_5tdt	-	32.8ddt	-	-20.4m
Et	$CHFCl.CF_2$	5.1t	2.2dq	-	-0.2_5ddd	46.0ddd[d]	76.2dt	-	-1.4tm
Et	$CF_3.CHF.CF_2$[e]	5.3t	2.4dq	-	~ 1m	48.0ddddq[f]	138.0dtq	-3.4dtdd	-2.0t
Et	$CF_3.CF(CHF_2)$[e]	5.3t	2.4dq	-	~ 1m	121.6ddq	~55m	-4.0m	c
Et	$CF_3.CH_2.CH_2$	5.4t	2.6dq	4-5	4-5	-	-	-9.6tt	-27.4m

$R_fP(:O)(OR)_2$		Coupling constant moduli/Hz											
R	R_f	PH_α	PH_β	$POCH_n$	PF_α	PF_β	$H_\alpha H_\beta$	$H_\alpha F_\beta$	$H_\alpha CF_3$	$H_\beta F_\alpha$	$H_\beta F_\beta$	$H_\beta CF_3$	$F_\alpha F_\beta$
Me	$CHF_2.CF_2$	-	3.3	10.8	91.3	c	-	-	-	5.7	52.8	-	5.6
Et	$CHF_2.CF_2$	-	3.0	8.4	92.0	2.0	-	-	-	5.9	52.5	-	6.5
Et	$CHF_2.CH_2$	19.2	4.8	8.4	-	27.6	1~ 5	17.2	-	-	56.5	-	-
Et	$CHFCl.CF_2$	-	c	7.8	93.7	c	-	-	-	5.6, 12.2	47.1	-	16.9
Et	$CF_3.CHF.CF_2$[e]	-	c	c	93[g]	c	-	-	-	~11[g]	42.0	~11	c
Et	$CF_3.CF(CHF_2)$[e]	-	c	c	71.0	c	-	-	-	c	c	c	c
Et	$CF_3.CH_2.CH_2$	c	c	8.4	-	-	c	-	4.2	-	-	9.6	-

† Compare n.m.r. data for dimethyl and diethyl alkylphosphonates and fluoroalkylphosphorus compounds[7,12-15].

[a] ^1H in p.p.m. upfield of ext. benzene; ^{19}F in p.p.m. upfield of ext. $CF_3.CO_2H$

^{31}P in p.p.m. upfield of ext. 85% H_3PO_4.

[b] d = doublet, t = triplet, q = quartet, m = multiplet.

[c] Not measured. [d] AB pattern, δ = 404 Hz, J_{AB} = 316 Hz

[e] Spectra obtained using a 4:1 mixture of isomers.

[f] AB pattern, δ = 342 Hz, J_{AB} = 328 Hz, each component being a doublet of doublets of quartets of doublets.

[g] Average value quoted.

requires C, 36.1; H, 5.6%; *M*, 266) n_D^{20} 1.396, K_{max} 3500w, 2990s, 2935m, 2915m, 2870w, 1760w, 1484w, 1448m, 1423s, 1397m, 1375m, 1340m, 1315-1297m, 1258s, 1175s, 1120s, 1060s, 1030s, 985-865s, 877m, 847m, 795m, 770m, 740m, 709w cm^{-1}, ^{1}H n.m.r. bands at (p.p.m. rel. to ext. benzene) 0.5 ($C\underline{H}F_2$, tt, $^{2}\underline{J}_{HF}$ 56 Hz, $^{3}\underline{J}_{HH}$ *ca.* 5 Hz), 2.5_5 ($OC\underline{H}_2$, dq, $^{3}\underline{J}_{HP}$ 9 Hz), 3.9-4.1 ($2xC\underline{H}_2$, 2xdtq), 5.3_5 (Me, t), ^{19}F n.m.r. bands at (p.p.m. upfield of ext. $CF_3.CO_2H$) 8.3 ($P.CH_2.C\underline{F}_2$, ddt, $^{3}\underline{J}_{FP}$ 26 Hz), 37.5 ($CH\underline{F}_2$, dtt, $^{2}\underline{J}_{FH}$ 55 Hz).

(f) *Diethyl hexafluoropropylphosphonates*. A portion (69.0 g) of liquid reaction product (102 g) was distilled through Column B to remove diethylphosphite, then through Column A to give a fraction b.p. 86-7 °C/10 mmHg (11.3 g) apparently a single component by g.l.c. (2m SE30 and 2 m PEGA, 10% on 60-80 Celite, at 120 °C) but shown by n.m.r. (Table 2) to consist of an 80:20 mixture of *diethyl 2H-hexafluoro-n-propylphosphonate* and *diethyl 1H-hexafluoropropyl-2-phosphonate* (estimated total yield 18.2 g, 63 mmol, 68% based on olefin consumed) (Found: C, 29.5; H, 4.1; P, 11.0%; *M*$^{+}$, 288. $C_7H_{11}F_6O_3P$ requires C, 29.2; H, 3.8; P, 10.8%; *M*, 288) n_D^{20} 1.363, K_{max} 3510—3410w, 2993m, 2940w, 2925w, 2880w, 1483w, 1450w, 1397m, 1387m, 1378m, 1280s, 1218s, 1192s, 1180s, 1110s, 1065s, 1027s, 988m, 958m, 885w, 853w, 830m, 800w, 755w, 730w, 716w, 690m, 665w cm^{-1}. Structural identification was assisted by the following features in the ^{19}F n.m.r. spectrum of the mixture: (i) the major component has an asymmetric centre [CF_2-resonance an AB doublet of doublets, each A-component a doublet ($^{2}\underline{J}_{PF}$ 93 Hz) of ten line multiplets, analysed as a doublet of quartets of doublets (*J* values *ca.* 11, 11, and 5-6 Hz, respectively]; (ii) a $CF_3.CHF.CF_2.P$ group in this component is supported by the CF_3-resonance (doublet of triplets of doublets of doublets) and CHF-resonance (doublet, $^{2}\underline{J}_{FH}$ 42 Hz, of quartets of triplets); (iii) a $P.CF(CHF_2).CF_3$ group in the minor component is indicated by the CF-resonance (doublet, $^{2}\underline{J}_{FP}$ 71 Hz, of doublets of quartets with further fine structure). Integration of the CF_3-resonances of the two isomers was used to determine the isomer ratio.

(g) *Diethyl 3,3,3-trifluoropropyl-1-phosphonate*. Distillation of crude product (43.2 g) gave diethyl phosphite (26.2 g), and a fraction (4.6 g) b.p. 79-80 °C/5 mmHg shown by g.l.c. to consist of a single component identified as *diethyl 3,3,3-trifluoropropyl-1-phosphonate* (estimated total yield 7.5 g, 32.3 mmol, 39% on olefin) (Found: C, 36.2; H, 6.0; P, 13.5%; *M*$^+$, 234. $C_7H_{14}F_3O_3P$ requires C, 35.9; H, 6.0; P, 13.3%; *M*, 234) n_D^{20} 1.383, K_{max} 2990m, 2940w, 2915w, 2880w, 1484w, 1450m, 1421w, 1388m, 1374w, 1318m, 1275s, 1263s, 1240s, 1218s, 1166s, 1142s, 1100m, 1084s, 1060s, 1027s, 972s, 855m, 816m, 797m, 757w, and 720w cm^{-1}.

Photochemical addition.- A mixture of 1,1-difluoroethylene (3.20 g, 50 mmol) and diethyl phosphite (20.7 g, 0.150 mol) was irradiated in a sealed silica tube (340 ml) placed 20 cm from a 500 watt Hg-vapour Hanovia lamp for 24 h, to give 1,1-difluoroethylene (9% recovery) and a yellow liquid shown by g.l.c. (2 m PegA 10% on 60-80 celite at 125 °C) to contain diethyl phosphite, diethyl 2,2-difluoroethylphosphonate (estimated yield 22% on olefin consumed), diethyl 2,2,4,4-tetrafluorobutylphosphonate (*ca*. 1%) and several unidentified components.

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