



**Preparation of fluorocarbonyltriethoxyphosphorane (IIIa) and hexafluoroisopropylidenetriethoxyphosphorane (IIa)**

To a mixture consisting of 6.4 g oxide **I** and 5 ml dry diethyl ether, 7.4 g trimethyl phosphite was added dropwise with stirring and cooling ( $-30^{\circ}\text{C}$ ). The reaction mixture was refluxed for 2 h ( $-78^{\circ}\text{C}$ ) until boiling of the oxide **I** was over when the system was allowed to stand at  $20^{\circ}\text{C}$  for 30 min. On freezing ( $-60^{\circ}\text{C}$ ), white crystals of product **IIIa** were obtained and separated by decanting, m.p.  $0^{\circ}\text{C}$  (decomp.).  $^{19}\text{F}$  NMR (diglyme,  $-30^{\circ}\text{C}$ )  $\delta$ :  $-77.9$  (dd, COF);  $1.3$  (ddm, PF,  $J_{\text{CF-P}} = 199$  Hz,  $J_{\text{F-P}} = 864$  Hz,  $J_{\text{F-F}} = 7.0$  Hz ppm. Carbonyl fluoride **IIIa** decomposed at  $0^{\circ}\text{C}$  evolving CO (as indicated by  $\text{I}_2\text{O}_5$ ) and formed phosphorane **Vla** ( $^{19}\text{F}$  NMR  $\delta$ :  $-15.1$  [d,  $J_{\text{P-F}} = 733$  Hz] ppm). On standing for 1 month, product **Vla** converted into dimethylfluorophosphate **XIIIa** and tetramethoxyphosphonium hexafluorophosphate (**XVa**). Compound **XIIIa**:  $^{19}\text{F}$  NMR  $\delta$ :  $8.8$  (d,  $J_{\text{F-P}} = 974$  Hz) ppm. Compound **XVa**:  $^{19}\text{F}$  NMR  $\delta$ :  $-4.4$  (d,  $J_{\text{P-F}} = 705$  Hz) ppm (cf. refs. 4 and 5). Distillation of the ether solution decanted from product **IIIa** gave 4.0 g (50% of phosphorane **IIa**, b.p.  $78-79^{\circ}\text{C}/2$  mmHg (cf. ref. 6).

**Preparation of hexafluoroisopropylidenetriethoxyphosphorane (IIb)**

Triethyl phosphite (9.9 g) was added dropwise to a mixture of 6.4 g perfluoroisobutene oxide (**I**) and 5 ml dry diethyl ether under stirring and cooling ( $-30^{\circ}\text{C}$ ). The reaction mixture was refluxed for 2 h ( $-78^{\circ}\text{C}$ ) until the boiling of oxide **I** ceased, when after warming to  $20^{\circ}\text{C}$  the mixture was allowed to stand for 30 min at  $20^{\circ}\text{C}$ . After evaporating the ether *in vacuo* at  $0^{\circ}\text{C}$ , mixture A was obtained. Distillation of the latter gave 5.2 g (60%) of phosphorane **IIb**, b.p.  $76-78^{\circ}\text{C}/0.01$  mmHg (cf. refs 6 and 7). MS: 316 (17,  $\text{M}^+$ ); 297 (11,  $\text{M}^+ - \text{F}$ ); 289 (11,  $\text{M}^+ - \text{C}_2\text{H}_3$ ); 261 (24,  $\text{M}^+ - \text{C}_2\text{H}_3 - \text{C}_2\text{H}_4$ ); 233 (100,  $\text{M}^+ - \text{C}_2\text{H}_3 - \text{C}_2\text{H}_4$ ); 232 (32,  $\text{M}^+ - \text{C}_2\text{H}_4$ ); 212 (25,  $\text{M}^+ - \text{C}_2\text{H}_4 - \text{HF}$ ); 93 (33,  $\text{C}_2\text{H}_5\text{PHO}_2^+$ ); 65 (73,  $\text{H}_2\text{PO}_2^+$ ); 45 (32,  $\text{C}_2\text{H}_5\text{O}^+$ ); 29 (73,  $\text{C}_2\text{H}_5^+$ ).

Phosphorane **IIIb** was detected by  $^{19}\text{F}$  NMR spectroscopy ( $-20^{\circ}\text{C}$ ) in a sample of mixture A in addition to the phosphorus ylide **IIb**. Compound **IIIb**:  $^{19}\text{F}$  NMR ( $-20^{\circ}\text{C}$ )  $\delta$ :  $-79.7$  (dd, COF);  $-2.2$  (dd, PF,  $J_{\text{CF-P}} = 206.8$  Hz,  $J_{\text{F-P}} = 864$  Hz,  $J_{\text{F-F}} = 7.7$  Hz) ppm. Carbonyl fluoride **IIIb** decomposed at room temperature to evolve CO (as indicated by  $\text{I}_2\text{O}_5$ ) and form phosphorane **Vlb**:  $^{19}\text{F}$  NMR  $\delta$ :  $-18.2$  (d,  $J_{\text{F-P}} = 728$  Hz) ppm. On standing for 1 month, product **Vlb** converted into diethylfluorophosphate **XIIIb** and tetraethoxyphosphonium hexafluorophosphate (**XVb**) (as established by  $^{19}\text{F}$  NMR spectra). Compound **XIIIb**:  $^{19}\text{F}$  NMR  $\delta$ :  $4.0$  (d) ppm.  $^{31}\text{P}$  NMR  $\delta$ :  $75.6$  (d,  $J_{\text{P-F}} = 968$

Hz) ppm. Compound **XVb**:  $^{19}\text{F}$  NMR  $\delta$ :  $-4.7$  (d) ppm.  $^{31}\text{P}$  NMR  $\delta$ :  $2.0$  (ws,  $\text{P}^+$ );  $-144.6$  (h  $\text{P}^-$ ,  $J_{\text{P-F}} = 708$  Hz) ppm (cf. refs. 4 and 8).

**Preparation of  $\alpha$ -carbethoxytrifluoroethylidenetriethoxyphosphorane (V)**

To 3.8 g ethyl  $\alpha$ -trifluoromethyl- $\beta,\beta$ -difluoroglycidate (**IV**), 8.0 g triethyl phosphite was added dropwise at  $0-5^{\circ}\text{C}$ . The reaction mixture was stirred for 1 h at  $20^{\circ}\text{C}$  and distilled to afford 6.5 g of a mixture of triethyl phosphite and triethoxydifluorophosphorane (**Vlb**) (b.p.  $50-53^{\circ}\text{C}/1$  mmHg) and 3.2 g (65%) phosphorane **V** (b.p.  $130-132^{\circ}\text{C}/0.01$  mmHg). MS: 320 (34,  $\text{M}^+$ ); 301 (8,  $\text{M}^+ - \text{F}$ ); 293 (43,  $\text{M}^+ - \text{C}_2\text{H}_3$ ); 275 (43,  $\text{M}^+ - \text{OC}_2\text{H}_5$ ); 265 (43,  $\text{M}^+ - \text{C}_2\text{H}_3 - \text{C}_2\text{H}_4$ ); 237 (64,  $\text{M}^+ - \text{C}_2\text{H}_3 - \text{C}_2\text{H}_4$ ); 209 (43,  $\text{M}^+ - \text{C}_2\text{H}_3 - \text{C}_2\text{H}_4$ ); 191 (71,  $\text{M}^+ - \text{C}_2\text{H}_3 - \text{C}_2\text{H}_4 - \text{H}_2\text{O}$ ); 171 (64,  $\text{M}^+ - \text{C}_2\text{H}_3 - \text{C}_2\text{H}_4 - \text{H}_2\text{O} - \text{HF}$ ); 121 (89,  $(\text{C}_2\text{H}_5)_2\text{PO}_2^+$ ); 93 (64,  $\text{C}_2\text{H}_5\text{PHO}_2^+$ ); 65 (50,  $\text{H}_2\text{PO}_2^+$ ); 45 (29,  $\text{C}_2\text{H}_5\text{O}^+$ ); 29 (100,  $\text{C}_2\text{H}_5^+$ ). Analysis: Found: C, 41.1; H, 6.36; F, 17.7; P, 9.4%.  $\text{C}_{13}\text{H}_{12}\text{F}_2\text{N}_2\text{OP}$  requires: C, 41.3; H, 6.30; F, 17.8; P, 9.7%.

**Preparation of  $\alpha$ -dimethylphosphoryltrifluoroethylidenetriethoxyphosphorane (VIII)**

Triethyl phosphite (0.39 g) and dimethyl  $\alpha,\beta$ -epoxy-pentafluoroisopropylphosphonate (**VII**) (0.14 g) were mixed at  $20^{\circ}\text{C}$ . Compounds **VII** (see Table 1), **Vlb** [ $-18.2$  (d,  $J = 728$  Hz) ppm], **XIIIb** [ $4.0$  (d,  $J = 968$  Hz) ppm] and **XVb** [ $-4.7$  (d,  $J = 708$  Hz [4]) ppm] were identified by  $^{19}\text{F}$  spectral analysis of the mixture.

**Interaction of perfluoroisobutene oxide (I) with trimethylsilyl phosphites**

Perfluoroisobutene oxide (**I**) (8.0 g, 37 mmol) was added to trimethylsilyl phosphite (16.6 g, 29 mmol) at  $-70^{\circ}\text{C}$ , the mixture heated gradually up to  $-10^{\circ}\text{C}$ , allowed to stand at this temperature for 30 min and

TABLE 1. NMR data for compounds of the type

$$\begin{array}{c} \text{CF}_3 \\ \diagdown \\ \text{C} = \text{P} \begin{array}{l} \diagup \text{Y} \\ \diagdown \text{Z} \end{array} \\ \diagup \text{X} \end{array}$$

Comp. No.	Substituents			$^{19}\text{F}$ NMR data	
	X	Y	Z	$\delta_{\text{CF}_3\text{COOH}}$ (ppm)	$J_{\text{CF}_3-\text{P}}$ (Hz)
<b>IIa</b>	$\text{CF}_3$	OMe	OMe	$-31.9$	7.3
<b>IIb</b>	$\text{CF}_3$	OEt	OEt	$-32.9$	7.3
<b>V</b>	COOEt	OEt	OEt	$-31.3$	5.8
<b>VIII</b>	$\text{PO}(\text{OMe})_2^a$	OEt	OEt	$-37.0$	7.0
<b>IX</b>	$\text{CF}_3$	OEt	$\text{NEt}_2^b$	$-34.4$	6.1

<sup>a</sup> $J_{\text{CF}_3-\text{PO}(\text{OMe})_2} = 12.6$  Hz.

<sup>b</sup>Compound **IX** was prepared from the hexafluoroacetone dimer in much the same way [6].

then warmed to 20 °C. Distillation gave 4.9 g (49.5%) diethyl pentafluoroisopropenylphosphonoate (**X**) [9], b.p. 63–65 °C/2 mmHg.

*Preparation of hexafluoroisopropylidenethoxy-bis(diethylamido)phosphorane (IX)*

To a solution consisting of 22.8 g (103 mmol) ethylbis(diethylamido) phosphite in 10 ml dry diethyl ether was added dropwise under stirring and cooling (–30 °C) a solution of 9.5 g (26 mmol) hexafluorothioacetone dimer in 10 ml anhydrous diethyl ether. After stirring for 1.5 h at 20 °C, the reaction mixture was distilled and phosphorus ylide **IX** (14.0 g, 74%) was obtained, b.p. 143–145 °C/0.1 mmHg. <sup>1</sup>H NMR δ: 1.1 (m, CH<sub>3</sub>); 3.0 m, CH<sub>2</sub>–N); 4.1 (m, CH<sub>2</sub>O) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR δ: 44.7 h, *J*<sub>P–CF<sub>3</sub></sub> = 6.1 Hz) ppm. MS: 370 (0.5, M<sup>+</sup>); 351 (7, M<sup>+</sup> – F); 325 (4, M<sup>+</sup> – OC<sub>2</sub>H<sub>5</sub>); 222 (6, M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>OPN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>); 186 (18, C<sub>2</sub>H<sub>5</sub>OPF<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup>); 158 (32, HOPF<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup>); 148 (100, C<sub>2</sub>H<sub>5</sub>OPN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup>); 120 (41, HOPN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup>); 72 (46, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N<sup>+</sup>). Analysis: Found: C, 41.6; H, 6.81; P, 8.4; N, 7.7%. C<sub>13</sub>H<sub>27</sub>N<sub>2</sub>OP requires: C, 42.1; H, 6.75; P, 8.6; N, 7.6%.

*Preparation of pentafluoroisopropylphosphonic acid bis-diethylamide (XII)*

A solution consisting of 7.7 g of product **IX** and 3.7 g adduct Et<sub>3</sub>N·BF<sub>3</sub> in 20 ml anhydrous diethyl ether was refluxed for 3 h. After evaporating the ether, the mixture was heated for 1 h at 90 °C. Then 20 ml anhydrous ether was added and the precipitate formed filtered. Distillation of the filtrate yielded 2.6 g (39%) of product **XII**, b.p. 91–92 °C/0.04 mmHg. <sup>1</sup>H NMR δ: 1.12 (br t, CH<sub>3</sub>); 3.91 (br dq, CH<sub>2</sub>, *J*<sub>CH<sub>3</sub>–CH<sub>2</sub></sub> = 6.4 Hz, *J*<sub>CH<sub>2</sub>–P</sub> = 12 Hz) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR δ: 13.8 (br t, *J* = 12.2 Hz) ppm. <sup>19</sup>F NMR δ: –15.8 (m, F); –20.2 (m, F); –22.9 (m, CF<sub>3</sub>) ppm. MS: 322 (1, M<sup>+</sup>); 303 (7, M<sup>+</sup> – F); 250 (3, M<sup>+</sup> – N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>); 202 (3, M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>F – N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>); 191 (18, M<sup>+</sup> – C<sub>2</sub>F<sub>5</sub>); 138 (16, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NPFO<sup>+</sup>); 72 (100, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N<sup>+</sup>). Analysis: Found: C, 42.5; H, 7.6%. C<sub>11</sub>H<sub>20</sub>F<sub>5</sub>N<sub>2</sub>OP requires: C, 41.0; H, 6.36%.

*Interaction of hexafluoropropene oxide with triethyl phosphite*

A mixture consisting of 50 g (300 mmol) P(OEt)<sub>3</sub> and 25 g (150 mmol) hexafluoropropene oxide was shaken in a autoclave for 100 h at 20 °C and then the reaction mixture was treated by water for 10 h at 20 °C. Distillation of the lower layer gave a mixture (12.5 g) of products **XVIII** and **XIX** (b.p. 172–175 °C) which were isolated by preparative GLC methods.

Compound **XVIII**: <sup>1</sup>H NMR δ: 1.35 (t, 2CH<sub>3</sub>, *J*<sub>CH<sub>3</sub>–CH<sub>2</sub></sub> = 9 Hz); 4.03 (m, 2CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR

δ: 118.8 [qd(270, 37.5)] (a); 93.0 [dq(200, 32)] (b); 140.9 [dd(27, 21)] (b); 145.0 [dq(261, 39)] (c); 121.6 [qd(285, 30)] (d); 75.4 (s) (e); 14.7 (s) (f) ppm. <sup>19</sup>F NMR δ: 2.2 (dt) (a); 92.5 (tqq) (b); 68.0 (dqq) (c); –9.7 (dd) (d) (*J*<sub>ab</sub> = 9.7 Hz, *J*<sub>ac</sub> = 12.1 Hz, *J*<sub>bc</sub> = 19.5 Hz, *J*<sub>bd</sub> = 2.4 Hz, *J*<sub>cd</sub> = 7.6 Hz) ppm. IR (cm<sup>–1</sup>): 2990; 2900; 1780; 1760; 1380; 1360. MS: 388 (2.3, M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>); 366 (2.4, M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>F); 358 (18, M<sup>+</sup> – 2C<sub>2</sub>H<sub>4</sub>); 338 (14, M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub> – C<sub>2</sub>H<sub>5</sub>F); 319 (12, M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>F – C<sub>2</sub>H<sub>5</sub>F); 289 (13, M<sup>+</sup> – 2C<sub>2</sub>H<sub>4</sub> – CF<sub>3</sub>); 269 (20, M<sup>+</sup> – HF – 2C<sub>2</sub>H<sub>4</sub> – CF<sub>3</sub>); 230 (16, M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>OH – 2CF<sub>3</sub>); 129 (100, C<sub>4</sub>H<sub>5</sub>F<sub>4</sub>); 128 (38, C<sub>4</sub>H<sub>4</sub>F<sub>4</sub>); 109 (55, C<sub>4</sub>H<sub>4</sub>F<sub>3</sub>); 70 (2 CF<sub>3</sub>); 45 (4, C<sub>2</sub>H<sub>5</sub>O). Analysis: Found: C, 34.8; H, 2.44; F, 53.9%. C<sub>12</sub>H<sub>10</sub>F<sub>12</sub>O<sub>2</sub> requires: C, 34.8; H, 2.43; F, 55.0%.

Compound **XIX**: <sup>1</sup>H NMR δ: 1.33 t, CH<sub>3</sub>, *J*<sub>CH<sub>2</sub>–CH<sub>3</sub></sub> = 7 Hz); 1.36 t, CH<sub>3</sub>, *J*<sub>CH–CH<sub>3</sub></sub> = 7 Hz); 4.1 (m, CH<sub>2</sub>) (g); 4.4 m, CH<sub>2</sub>) (h) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR δ: 119.0 [qd(270, 36)] (a); 91.1 [dk(203, 37.5)] (b); 140.0 [t, (24)] (c); 146.0 [dq(260, 40)] (d); 121.0 [qd(282, 30)] (e); 75.4 (c) (f); 14.7 (c) (g); 64.7 (c) (h); 13.4 (c) (i); 161.0 [d, (25)] (j) ppm. <sup>19</sup>F NMR δ: –2.7 (dd) (a); 85.1 (dqq) (b); 67.5 (dqq) (c); –9.5 (dd) (d) (*J*<sub>ab</sub> = 9.5 Hz, *J*<sub>ac</sub> = 9.0 Hz, *J*<sub>bc</sub> = 13.4 Hz, *J*<sub>bd</sub> = 2.8 Hz, *J*<sub>cd</sub> = 8.3 Hz) ppm. IR (cm<sup>–1</sup>): 2990; 2940; 2900; 1770; 1380. MS: 330 (1.2 M<sup>+</sup>); 302 (21, M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>); 274 (100, M<sup>+</sup> – 2C<sub>2</sub>H<sub>4</sub>); 257 (11, M<sup>+</sup> – OC<sub>2</sub>H<sub>5</sub> – C<sub>2</sub>H<sub>4</sub>); 256.39 (M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>OH – C<sub>2</sub>H<sub>4</sub>); 255 (22, M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>F – C<sub>2</sub>H<sub>4</sub>); 229 (11, M<sup>+</sup> – COOC<sub>2</sub>H<sub>5</sub> – C<sub>2</sub>H<sub>4</sub>); 210 (40, M<sup>+</sup> – COOC<sub>2</sub>H<sub>5</sub> – C<sub>2</sub>H<sub>4</sub>F); 205 (14, C<sub>2</sub>H<sub>5</sub>CF<sub>2</sub>CF(CF<sub>3</sub>)COOH); 146 (14, CF<sub>3</sub>CF=CFCH<sub>3</sub>); 128 (21, CH<sub>3</sub>CH=CFCH<sub>3</sub>); 109 (50, C<sub>4</sub>H<sub>4</sub>F<sub>3</sub>); 69 (9, CF<sub>3</sub>); 48 (17, C<sub>2</sub>H<sub>5</sub>O). Analysis: Found: C, 36.2; H, 3.0; F, 47.3%. C<sub>10</sub>H<sub>10</sub>F<sub>8</sub>O<sub>3</sub> requires: C, 36.4; H, 3.05; F, 46.0%.

*Interaction of hexafluoroisopropylidenetriethoxyphosphorane (IIb) with carbonyl fluoride*

To 3.16 g (100 mmol) of phosphorane **IIb** cooled to –100 °C was added 10 g (150 mmol) carbonyl fluoride. The reaction mixture was then heated gradually for 3 h to room temperature. Distillation of the lower layer gave 2.1 g of a mixture (b.p. 10–25 °C) containing 75% difluoride **XXIII**. <sup>19</sup>F NMR δ: –119.8 (h); –11.8 t, *J*<sub>CF<sub>3</sub>–CF</sub> = 9.8 Hz) ppm (cf. ref. 10) and 25% perfluoroisobutene [–17.6(m)] according to GLC and NMR data).

*Preparation of decaperfluoropentylidenetriethoxyphosphorane (XXIV)*

A mixture consisting of 9.4 g (57 mmol) P(OEt)<sub>3</sub> and 12.6 g (39 mmol) perfluorohexene oxide **XXV** was heated for 30 min to 45 °C and then allowed to stand at room temperature for 48 h. Distillation of the reaction mixture gave 6.1 g ylide **XXIV** containing significant

amounts of unidentified by-products, b.p. 89–94 °C/0.001 mmHg.  $^{19}\text{F}$  NMR  $\delta$ : 4.4 (d,  $\text{CF}_3$ ); 40.7 (m); 46.2 (m); 49.1 (m); 52.7 (m,  $3\text{CF}_2$ ); 73.8 (dm, CF) ppm.  $^{31}\text{P}$  NMR  $\delta$ : 44.5 (d,  $\text{C}=\text{P}$ ,  $J_{\text{F-P}}=56$  Hz) ppm. MS: 97 (6,  $\text{M}^+ - \text{F}$ ); 377 (55,  $\text{M}^+ - \text{F} - \text{HF}$ ); 349 (31,  $\text{M}^+ - \text{C}_2\text{H}_3 - 2\text{HF}$ ); 321 (100,  $\text{M}^+ - \text{F} - \text{HF} - 2\text{C}_2\text{H}_4$ ); 307 (3,  $\text{M}^+ - \text{F} - 2\text{C}_2\text{H}_5\text{O}$ ); 259 (13,  $\text{M}^+ - \text{HF} - \text{PO}(\text{OC}_2\text{H}_5)_2$ ); 219 (5,  $\text{CF}_3(\text{CF}_2)_3^+$ ); 109 (27,  $\text{C}_2\text{H}_5\text{OPHO}_2^+$ ); 93 (16,  $\text{C}_2\text{H}_5\text{PHO}_2^+$ ); 81 (23,  $\text{C}_2\text{F}_3^+$ ); 69 (17,  $\text{CF}_3^+$ ); 65 (53,  $\text{H}_2\text{PO}_2^+$ ); 45 (11,  $\text{C}_2\text{H}_5\text{O}^+$ ).

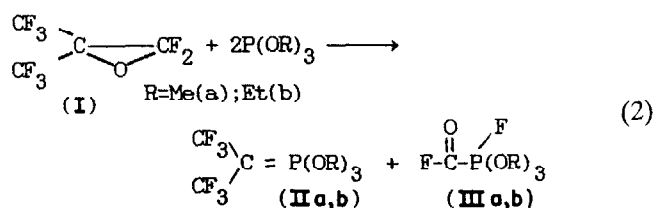
#### Interaction of perfluoro-2-methylpent-2-ene oxide (XVI) with triethyl phosphite

To 7.1 g (22 mmol) oxide XVI was added a solution consisting of 7.7 g (46 mmol) triethyl phosphite in 7 ml trifluoroacetic acid amide. The reaction mixture was refluxed for 23 h and then evaporated at low pressure (1 mmHg). The mixture (7.5 g) which gathered in a trap was distilled when 2.2 g (52%) ethyl perfluoropropionate (b.p. 75–76 °C) and diethyl phosphite (GLC, NMR analyses) were obtained. Distillation of the residue gave 4.9 g (69%) of product IIb, b.p. 70–74 °C/1 mmHg. On storing for 48 h, product IIb converts into ester X [11].

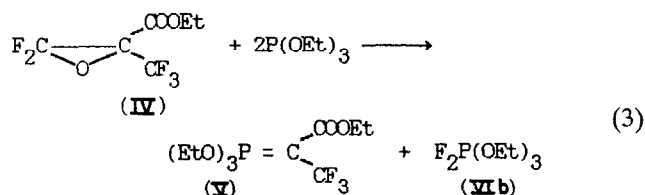
## Results and discussion

#### Interaction of terminal disubstituted fluoro-olefin oxides with trialkyl phosphites\*

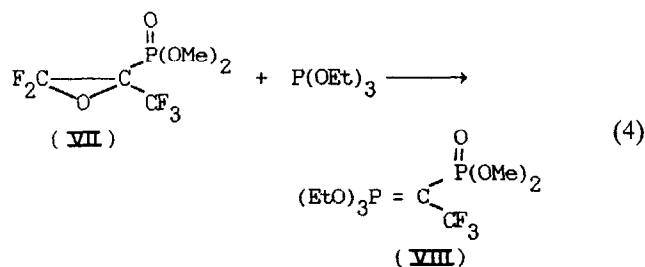
We have found that the interaction of perfluoroisobutene oxide (I) with trialkyl phosphites under mild conditions results in the formation of the isopropylidenetrialkoxyphosphoranes II as reported previously [6] together with unstable fluorocarbonyltrialkoxyposphoranes III [eqn. (2)].



Similarly, the reaction of ethyl  $\alpha$ -trifluoromethyl- $\beta,\beta$ -difluoroglycidoate (IV) with triethyl phosphite gives  $\alpha$ -carbethoxytrifluoroethylidenetriethoxyphosphorane (V); unstable triethoxydifluorophosphorane (VIb) was also isolated [eqn. (3)].

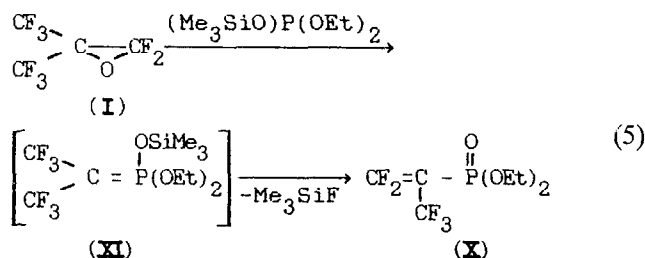


Dimethyl epoxypentafluoroisopropyl-2-phosphonate (VII) reacts with triethyl phosphite in a similar manner to form  $\alpha$ -(dimethylphosphoryl)trifluoroethylidenetriethoxyphosphorane (VIII) [eqn. (4)].

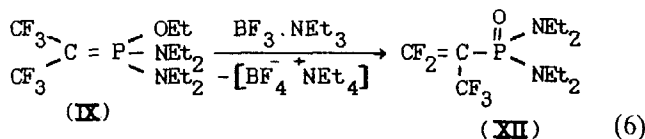


Trialkoxyphosphorus ylides containing a trifluoromethyl group at the ylide carbon atom exhibit a quite characteristic chemical shift for groups such as  $\text{CF}_3$  in the  $^{19}\text{F}$  NMR spectra, and this facilitates control of the reaction to a considerable extent (Table 1).

Cleavage of fluoro-olefin oxides by silylated phosphites can also be used for the synthesis of some fluoro-containing  $\alpha,\beta$ -unsaturated phosphonates. Thus, in the case of perfluoroisobutene oxide, diethyl pentafluoroisopropenylphosphonate (X) was obtained from the intermediate phosphorus ylide XI as a result of the elimination of trimethylfluorosilane [eqn. (5)].



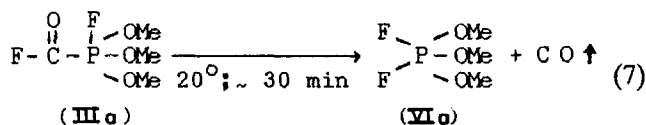
The possibility of such cleavage had been demonstrated in the reaction between the hexafluoroacetone dimer and trimethylsilyl phosphites [7]. Elimination of alkyl fluoride from phosphorus ylide II by the action of  $\text{BF}_3 \cdot \text{NEt}_3$  provides another route to the preparation of X [8]. Compound IX can also enter into similar reactions [eqn. (6)].



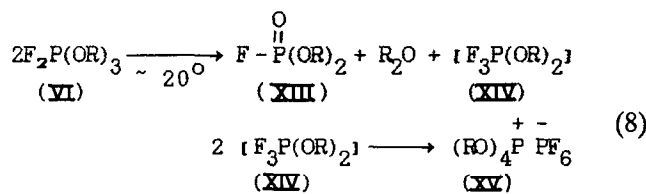
\*For a preliminary note, see ref. 9.

### Fluorocarbonylfluorophosphoranes (III)

The reaction of perfluoroisobutene oxide with phosphorane led to the formation of **IIIa** which was isolated and identified by  $^{19}\text{F}$  NMR spectroscopy. The compound **IIIa** is a white crystalline solid, which decomposes rapidly at room temperature evolving CO and forming trimethoxydifluorophosphorane (**VIa**)\*. The intermediate formation of fluorocarbonyltrialkoxyposphoranes (**III**) has been assumed in the reaction of trialkyl phosphites with carbonyl fluoride [4] [eqn. (7)].



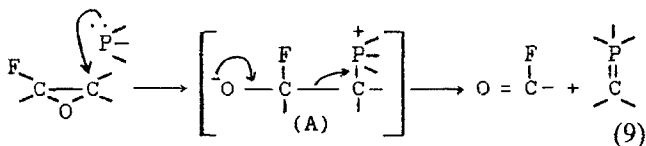
The trialkoxydifluorophosphoranes **VI** are also quite unstable<sup>†</sup>. On standing, they undergo disproportionation to form dialkylfluorophosphates **XIII**, dialkyl ethers and very unstable dialkoxyposphoranes **XIV**; the latter convert into stable tetraalkoxyposphonium hexafluorophosphates **XV** virtually immediately [eqn. (8)].



The structure of salt **XV** which has been described previously [5] was established by  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopy.

### Cleavage mechanism of $\alpha$ -oxides

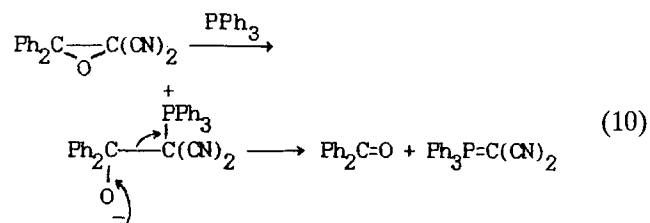
The results obtained show that cleavage appears to proceed according to the general pattern of nucleophilic reactions with olefin oxides. The reaction commences with a nucleophilic attack by a phosphite molecule on the central carbon atom of the oxide; this leads to opening of the fluorine-containing oxide ring to form a bipolar intermediate **A**. Then, however, the betaine **A** undergoes cleavage to give the phosphorus ylide and carbonyl fluoride; the latter product reacts with the second trialkyl phosphite molecule [eqn. (9)].



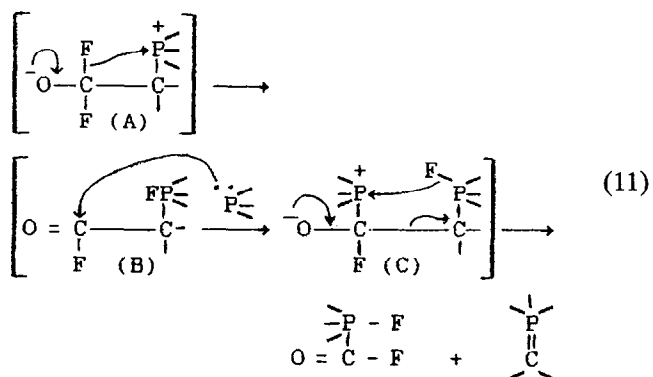
\*Corresponding to the triethoxy-substituted carbonyl fluoride **IIIb** whose structure and further conversions were demonstrated by means of  $^{19}\text{F}$  NMR spectroscopy.

<sup>†</sup>Compounds **IV** result from the reaction of  $\text{COF}_2$  with  $\text{P}(\text{OR})_3$ , but attempts to establish the formation of their precursors **III** were unsuccessful [4].

A similar decomposition has been shown as being possible in the reaction of diphenyldicyanoethylene with triphenyl phosphine leading to benzophenone and dicyanomethylenephosphorane [11] [eqn. (10)].



Obviously, it would be unwise to exclude another route to C—C bond cleavage, viz. migration of a fluorine atom in intermediate **A** from the carbon to the phosphorus atom, leading to carbonyl fluoride **B**, followed by nucleophilic attack by the second trialkyl phosphite molecule on the carbon atom of the  $\text{C}(\text{O})\text{F}$  group in product **B** to yield the intermediate bipolar adduct **C** (1:2). Decomposition of **C** results in the final products of the reaction [eqn. (11)].



### Interaction of trisubstituted fluoro-olefin oxides with trialkyl phosphites

Trialkyl-substituted perfluoro-2-methylpent-2-ene oxide (**XVI**) reacts with triethyl phosphite in a similar manner to other fluoro-olefin oxides. The use of the corresponding solvent (trifluoroacetic acid amide) and elevated temperature (c. 60 °C) are necessary to achieve this reaction. As a result, **IIb** and ethyl pentafluoropropanoate (**XVII**) were obtained [eqn. (12)] (see following page).

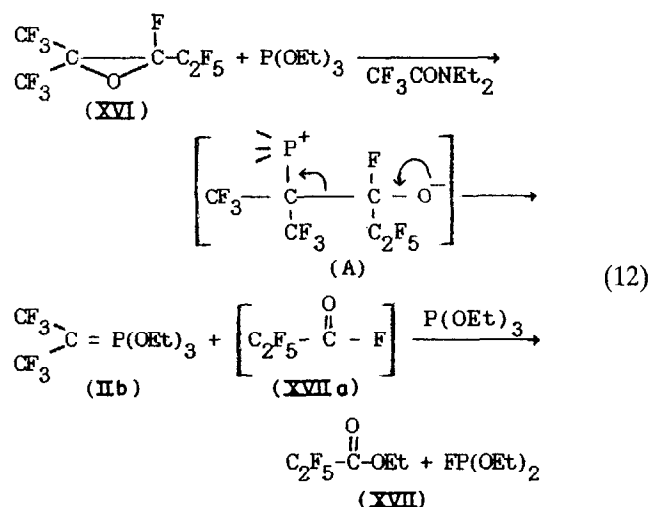
In this case, the bipolar compound **A** appears to be converted into phosphorane **IIb** and perfluoropropanoate fluoride, the latter reacting with triethyl phosphite to give ester **XVII** and diethylfluorophosphite.

### Interaction of monoalkyl-substituted fluoro-olefin oxides with trialkyl phosphites\*

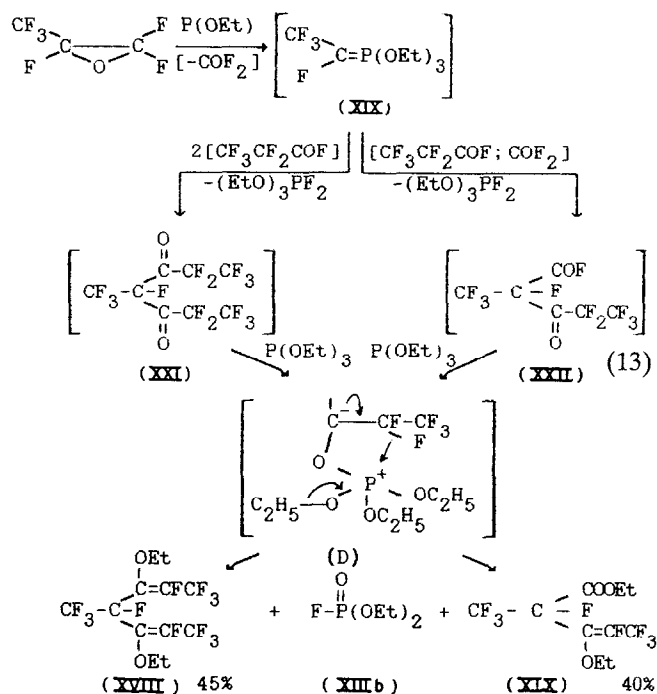
Perfluoropropene oxide reacts with triethyl phosphite in a more complicated manner<sup>†</sup> to form vinyl ethers

\*For a preliminary note, see ref. 14.

<sup>†</sup>Direct fluorination of trialkyl phosphites by perfluoropropene oxide [15] appears not to be a correct explanation.



**XVIII** and **XIX** in yields of 45% and 40%, respectively (the basis of the amount of perfluoropropene oxide taken) [eqn. (13)].

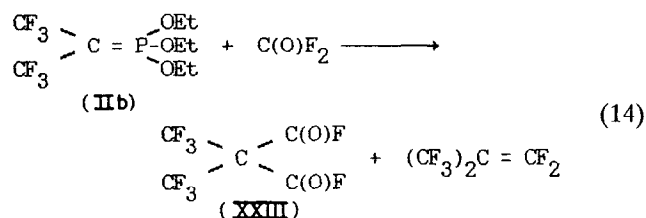


Clearly, in this case the reaction proceeds through the intermediate formation of a trialkoxyphosphorus ylide, i.e. tetrafluoroethylenetriethoxyphosphorane (**XX**), which interacts further with both  $\text{COF}_2$  and perfluoropropanoate fluoride, formed as a result of the partial isomerization of hexafluoropropene oxide\*. The dicarbonyl compounds **XXI** and **XXII**, obtained by bisacylation of phosphoranes, can be converted into

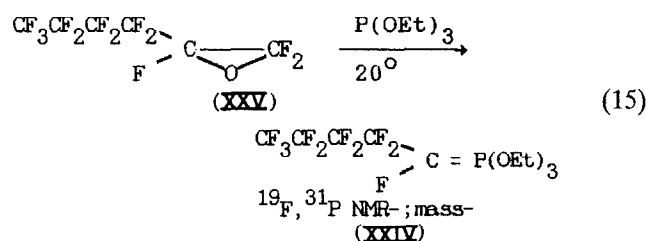
\*Compound **XVIIa** is the sole product of interaction between hexafluoropropene oxide and  $\text{P(NEt}_2)_3$ .

the vinyl ethers **XVIII** and **XIX** via intermediate of type D [12, 16].

A possibility of such bisacylation has been demonstrated by the reaction of phosphorane **IIb** with difluorophosgene, resulting in the formation of bis-trifluoromethylmalonate difluoride (**XXIII**) together with perfluoroisobutene (Wittig reaction product) [13] [eqn. (14)].



Formation of the trialkoxyphosphorus ylide **XXIV** containing a fluorine atom at the ylide carbon atom, like ylide **XX**, has been established by  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopy and mass spectrometry in the reaction of perfluorohex-1-ene with triethyl phosphite. However, product **XXIV** is unstable and rapidly decomposes at room temperature [eqn. (15)].



## Conclusions

The results obtained show that the reaction of fluoroolefin oxides with trialkyl phosphite proceeds according to the general pattern established in the nucleophilic reactions of olefin oxides, but leads to cleavage of the both the C—C and C—O bonds in the oxide rings. These conversions lead to the possibility of preparations and synthetic applications of trialkoxyphosphorus ylides which were hitherto unavailable.

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