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New reactions of fluoroepoxides. Cleavage by trialkyl phosphites

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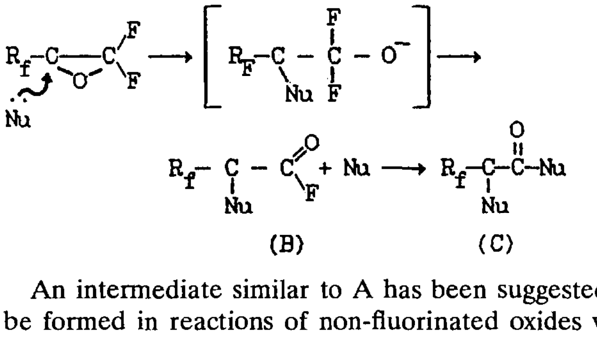
Abstract

Mono-, di- and tri-substituted fluorine-containing α-oxides have been shown to enter into reactions with trialkyl phosphites which proceed through cleavage of the C–C and C–O bonds in the epoxide ring. The trialkoxyphosphorus ylides **II**, **V**, **VII** and **VIII** were obtained from the epoxides **I**, **IV**, **VII** and **XVI**. Triethoxyfluorocarbonylfluorophosphorane (**IIIb**) has been isolated and characterized. Further conversions of **IIIb** have been studied and the formation of trialkoxyphosphorus ylides **XXIV** containing a fluorine atom in the position α to the phosphorus atom has been noted. It has been shown that when propylene oxide reacts with triethyl phosphite, vinyl ethers are obtained through the intermediate formation of tetrafluoroethylidenetriethoxyphosphorane (**XX**).

Introduction

Fluoro-olefin oxides are well known as capable of interacting readily with nucleophilic reagents. The basic scheme for these reactions assumes that the first step in the process is attack by the nucleophile on the carbon atom of the epoxide ring leading to a bipolar intermediate A, which is stabilized by eliminaton of the fluoride anion and formation of a carbonyl fluoride B. Interaction of compound B with a second molecule of the nucleophile gives the final product C which contains two fragments of the nucleophile. When Nu = F$^-$, only isomerization of the α-oxide takes place, according to eqn. (1) [1].



(1)

An intermediate similar to A has been suggested to be formed in reactions of non-fluorinated oxides with trivalent phosphorus compounds. In particular, with trialkyl phosphites, the bipolar intermediate A can be stabilized via three routes, viz. (a) deoxygenation with elimination of trialkyl phosphate; (b) intramolecular alkylation of the O-anion by the phosphorus cation and the formation of reaction products of a type similar to those from Arbuzov's reaction, and (c) stabilization via alkyl halide elimination (where possible) resulting in the formation of β-ketophosphonates [2, 3].

The reactions of fluoro-olefin oxides with esters of trivalent phosphorus acids have not been reported previously. In accordance with the data mentioned above, it may be expected that such reactions would differ from the other nucleophilic reactions of fluoro-olefin oxides.

Experimental

NMR spectra were obtained using Perkin-Elmer R-32 (^{1}H, 90 MHz; ^{19}F, 84.6 MHz) and Bruker WP-200 SY (^{19}F, 188.3 MHz; ^{31}P, 81.0 MHz) spectrometers; chemical shifts are reported in ppm from the external standards $(CH_3)_4Si$ (^{1}H, δ scale), CF_3COOH (^{19}F, upfield direction taken as positive) and 85% H_3PO_4 (^{31}P, δ scale). Designations: s, singlet; d, doublet; t, triplet; q, quartet; sp, septet; m, multiplet; br, broadened. IR spectra (cm^{-1}) were obtained with a UR-20 spectrophotometer using thin layers, mass spectra on Varian MAT CH-8 and VG 7070E mass spectrometers (ionizing energy, 70 eV); *m/z*, relative abundance (%), assumed assignment, as well as M* and assumed transition are presented. Preparative GLC (PGLC) was undertaken using a QF-1 column with Chromosorb W (length, 4 m; diameter, 25 mm).

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Preparation of fluorocarbonyltriethoxyphosphorane (IIIa) and hexafluoroisopropylidenetrimethoxyphosphorane (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 °C). The reaction mixture was refluxed for 2 h (−78 °C) until boiling of the oxide **I** was over when the system was allowed to stand at 20 °C for 30 min. On freezing (−60 °C), white crystals of product **IIIa** were obtained and separated by decanting, m.p. 0 °C (decomp.). ^{19}F NMR (diglyme, −30 °C) δ: −77.9 (dd, COF); 1.3 (ddm, PF, $J_{CF-P}=199$ Hz, $J_{F-P}=864$ Hz, $J_{F-F}=7.0$ Hz ppm. Carbonyl fluoride **IIIa** decomposed at 0 °C evolving CO (as indicated by I_2O_5) and formed phosphorane **VIa** (^{19}F NMR δ: −15.1 [d, $J_{P-F}=733$ Hz] ppm). On standing for 1 month, product **VIa** converted into dimethylfluorophosphate **XIIIa** and tetramethoxyphosphonium hexafluorophosphate (**XVa**). Compound **XIIIa**: ^{19}F NMR δ: 8.8 (d, $J_{F-P}=974$ Hz) ppm. Compound **XVa**: ^{19}F NMR δ: −4.4 (d, $J_{P-F}=705$ Hz) ppm (cf. refs. 4 and 5). Distillation of the ether solution decantated from product **IIIa** gave 4.0 g (50% of phosphorane **IIa**, b.p. 78–79 °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 °C). The reaction mixture was refluxed for 2 h (−78 °C) until the boiling of oxide **I** ceased, when after warming to 20 °C the mixture was allowed to stand for 30 min at 20 °C. After evaporating the ether *in vacuo* at 0 °C, mixture A was obtained. Distillation of the latter gave 5.2 g (60%) of phosphorane **IIb**, b.p. 76–78 °C/0.01 mmHg (cf. refs 6 and 7). MS: 316 (17, M^+); 297 (11, M^+-F); 289 (11, $M^+-C_2H_3$); 261 (24, $M^+-C_2H_3-C_2H_4$); 233 (100, $M^+-C_2H_3-C_2H_4$); 232 (32, $M^+-C_2H_4$); 212 (25, $M^+-C_2H_4-HF$); 93 (33, $C_2H_5PHO_2^+$); 65 (73, $H_2PO_2^+$); 45 (32, $C_2H_5O^+$); 29 (73, $C_2H_5^+$).

Phosphorane **IIIb** was detected by ^{19}F NMR spectroscopy (−20 °C) in a sample of mixture A in addition to the phosphorus ylide **IIb**. Compound **IIIb**: ^{19}F NMR (−20 °C) δ: −79.7 (dd, COF); −2.2 (dd, PF, $J_{CF-P}=206.8$ Hz, $J_{F-P}=864$ Hz, $J_{F-F}=7.7$ Hz) ppm. Carbonyl fluoride **IIIb** decomposed at room temperature to evolve CO (as indicated by I_2O_5) and form phosphorane **VIb**: ^{19}F NMR δ: −18.2 (d, $J_{F-P}=728$ Hz) ppm. On standing for 1 month, product **VIb** converted into diethylfluorophosphate **XIIIb** and tetraethoxyphosphonium hexafluorophosphate (XVb) (as established by ^{19}F NMR spectra). Compound **XIIIb**: ^{19}F NMR δ: 4.0 (d) ppm. ^{31}P NMR δ: 75.6 (d, $J_{P-F}=968$ Hz) ppm. Compound **XVb**: ^{19}F NMR δ: −4.7 (d) ppm. ^{31}P NMR δ: 2.0 (ws, p^+); −144.6 (h P^-, $J_{P-F}=708$ Hz) ppm (cf. refs. 4 and 8).

Preparation of α-carbethoxytrifluoroethylidenetriethoxyphosphorane (V)

To 3.8 g ethyl α-trifluoromethyl-β,β-difluoroglycidoate (**IV**), 8.0 g triethyl phosphite was added dropwise at 0–5 °C. The reaction mixture was stirred for 1 h at 20 °C and distilled to afford 6.5 g of a mixture of triethyl phosphite and triethoxydifluorophosphorane (**VIb**) (b.p. 50–53 °C/1 mmHg) and 3.2 g (65%) phosphorane **V** (b.p. 130–132 °C/0.01 mmHg). MS: 320 (34, M^+); 301 (8, M^+-F); 293 (43, $M^+-C_2H_3$); 275 (43, $M^+-OC_2H_5$); 265 (43, $M^+-C_2H_3-C_2H_4$); 237 (64, $M^+-C_2H_3-C_2H_4$); 209 (43, $M^+-C_2H_3-C_2H_4$); 191 (71, $M^+-C_2H_3-C_2H_4-H_2O$); 171 (64, $M^+-C_2H_3-C_2H_4-H_2O-HF$); 121 (89, $(C_2H_5)_2PO_2^+$); 93 (64, $C_2H_5PHO_2^+$); 65 (50, $H_2PO_2^+$); 45 (29, $C_2H_5O^+$); 29 (100, $C_2H_5^+$). Analysis: Found: C, 41.1; H, 6.36; F, 17.7; P, 9.4%. $C_{13}H_2FN_2OP$ requires: C, 41.3; H, 6.30; F, 17.8; P, 9.7%.

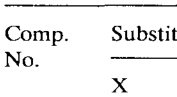
Preparation of α-dimethylphosphoryltrifluoroethylidenetriethoxyphosphorane (VIII)

Triethyl phosphite (0.39 g) and dimethyl α,β-epoxypentafluoroisopropylphosphonate (**VII**) (0.14 g) were mixed at 20 °C. Compounds **VII** (see Table 1), **VIb** [−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}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 °C, the mixture heated gradually up to −10 °C, allowed to stand at this temperature for 30 min and

TABLE 1. NMR data for compounds of the type



Comp. No.	Substituents			^{19}F NMR data	
	X	Y	Z	δ_{CF_3COOH} (ppm)	J_{CF_3-P} (Hz)
IIa	CF_3	OMe	OMe	−31.9	7.3
IIb	CF_3	OEt	OEt	−32.9	7.3
V	COOEt	OEt	OEt	−31.3	5.8
VIII	$PO(OMe)_2$[a]	OEt	OEt	−37.0	7.0
IX	CF_3	OEt	NEt_2[b]	−34.4	6.1

[a] $J_{CF_3-PO(OMe)_2}=12.6$ Hz.

[b] 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 hexafluoroisopropylidenethoxybis(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. ^{1}H NMR δ: 1.1 (m, CH_3); 3.0 m, $CH_2{-}N$); 4.1 (m, CH_2O) ppm. $^{31}P\{^1H\}$ NMR δ: 44.7 h, $J_{P-CF_3}=6.1$ Hz) ppm. MS: 370 (0.5, M^+); 351 (7, M^+-F); 325 (4, $M^+-OC_2H_5$); 222 (6, $M^+-C_2H_5OPN(C_2H_5)_2$); 186 (18, $C_2H_5OPF_2N(C_2H_5)_2{}^+$) 158 (32, $HOPF_2N(C_2H_5)_2{}^+$); 148 (100, $C_2H_5OPN(C_2H_5)_2{}^+$); 120 (41, $HOPN(C_2H_5)_2{}^+$); 72 (46, $(C_2H_5)_2N^+$). Analysis: Found: C, 41.6; H, 6.81; P, 8.4; N, 7.7%. $C_{13}H_2FN_2OP$ 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 $Et_3N{\cdot}BF_3$ 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. ^{1}H NMR δ: 1.12 (br t, CH_3); 3.91 (br dq, CH_2, $J_{CH_3-CH_2}=6.4$ Hz, $J_{CH_2-P}=12$ Hz) ppm. $^{31}P\{^1H\}$ NMR δ: 13.8 (br t, $J=12.2$ Hz) ppm. ^{19}F NMR δ: −15.8 (m, F); −20.2 (m, F); −22.9 (m, CF_3) ppm. MS: 322 (1, M^+); 303 (7, M^+-F); 250 (3, $M^+-N(C_2H_5)_2$); 202 (3, $M^+-C_2H_5F-N(C_2H_5)_2$); 191 (18, $M^+-C_2F_5$); 138 (16, $(C_2H_5)_2NPFO^+$); 72 (100, $(C_2H_5)_2N^+$). Analysis: Found: C, 42.5; H, 7.6%. $C_{11}H_{20}F_5N_2OP$ requires: C, 41.0; H, 6.36%.

Interaction of hexafluoropropene oxide with triethyl phosphite

A mixture consisting of 50 g (300 mmol) $P(OEt)_3$ 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**: ^{1}H NMR δ: 1.35 (t, $2CH_3$, $J_{CH_3-CH_2}=9$ Hz); 4.03 (m, $2CH_2$) ppm. $^{13}C\{^1H\}$ 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. ^{19}F NMR δ: 2.2 (dt) (a); 92.5 (tqq) (b); 68.0 (dqq) (c); −9.7 (dd) (d) ($J_{ab}=9.7$ Hz, $J_{ac}=12.1$ Hz, $J_{bc}=19.5$ Hz, $J_{bd}=2.4$ Hz, $J_{cd}=7.6$ Hz) ppm. IR (cm^{-1}): 2990; 2900; 1780; 1760; 1380; 1360. MS: 388 (2.3, $M^+-C_2H_4$); 366 (2.4, $M^+-C_2H_5F$); 358 (18, $M^+-2C_2H_4$); 338 (14, $M^+-C_2H_4-C_2H_5F$); 319 (12, $M^+-C_2H_4F-C_2H_5F$); 289 (13, $M^+-2C_2H_4-CF_3$); 269 (20, $M^+-HF-2C_2H_4-CF_3$); 230 (16, $M^+-C_2H_5OH-2CF_3$); 129 (100, $C_4H_5F_4$); 128 (38, $C_4H_4F_4$); 109 (55, $C_4H_4F_3$); 70 (2 CF_3); 45 (4, C_2H_5O). Analysis: Found: C, 34.8; H, 2.44; F, 53.9%. $C_{12}H_{10}F_{12}O_2$ requires: C, 34.8; H, 2.43; F, 55.0%.

Compound **XIX**: ^{1}H NMR δ: 1.33 t, CH_3, $J_{CH_2-CH_2}=7$ Hz); 1.36 t, CH_3, $J_{CH-CH}=7$ Hz); 4.1 (m, CH_2) (g); 4.4 m, CH_2) (h) ppm. $^{13}C\ \{^1H\}$ 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. ^{19}F NMR δ: −2.7 (dd) (a); 85.1 (dqq) (b); 67.5 (dqq) (c); −9.5 (dd) (d) ($J_{ab}=9.5$ Hz, $J_{ac}=9.0$ Hz, $J_{bc}=13.4$ Hz, $J_{bd}=2.8$ Hz, $J_{cd}=8.3$ Hz) ppm. IR (cm^{-1}): 2990; 2940; 2900; 1770; 1380. MS: 330 (1.2 M^+); 302 (21, $M^+-C_2H_4$); 274 (100, $M^+-2C_2H_4$); 257 (11, $M^+-OC_2H_5-C_2H_4$); 256.39 ($M^+-C_2H_5OH-C_2H_4$); 255 (22, $M^+-C_2H_4F-C_2H_4$); 229 (11, $M^+-COOC_2H_5-C_2H_4$); 210 (40, $M^+-COOC_2H_5-C_2H_4F$); 205 (14, $C_2H_5CFCF(CF_3)COOH$); 146 (14, $CF_3CF{=}CFCH_3$); 128 (21, $CH_3CH{=}CFCF_3$); 109 (50, $C_4H_4F_3$); 69 (9, CF_3); 48 (17, C_2H_5O). Analysis: Found: C, 36.2; H, 3.0; F, 47.3%. $C_{10}H_{10}F_8O_3$ 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**. ^{19}F NMR δ: −119.8 (h); −11.8 t, $J_{CF_3-CF}=9.8$ 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) $P(OEt)_3$ 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}F NMR δ: 4.4 (d, CF_3); 40.7 (m); 46.2 (m); 49.1 (m); 52.7 (m, $3CF_2$); 73.8 (dm, CF) ppm. ^{31}P NMR δ: 44.5 (d, C=P, $J_{F-P}=56$ Hz) ppm. MS: 97 (6, M^+-F); 377 (55, M^+-F-HF); 349 (31, $M^+-C_2H_3-2HF$); 321 (100, $M^+-F-HF-2C_2H_4$); 307 (3, $M^+-F-2C_2H_5O$); 259 (13, $M^+-HF-PO(OC_2H_5)_2$); 219 (5, $CF_3(CF_2)_3{}^+$); 109 (27, $C_2H_5OPHO_2{}^+$); 93 (16, $C_2H_5PHO_2{}^+$); 81 (23, $C_2F_3{}^+$); 69 (17, $CF_3{}^+$); 65 (53, $H_2PO_2{}^+$); 45 (11, $C_2H_5O^+$).

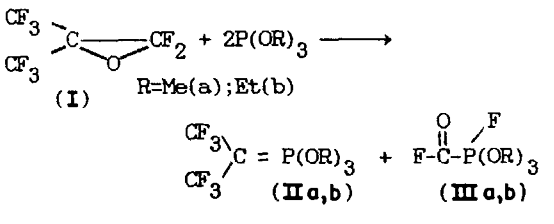
Interaction of perfluoro-2-methylpent-2-ene oxide (XVI) with triethyl phosphite

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

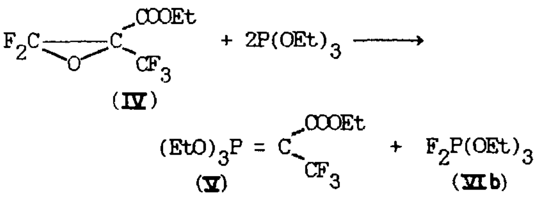
*Interaction of terminal disubstituted fluoro-olefin oxides with trialkyl phosphites**

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 fluorocarbonyltrialkoxyfluorophosphoranes **III** [eqn. (2)].



(2)

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



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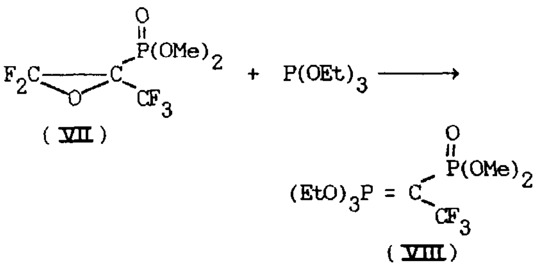
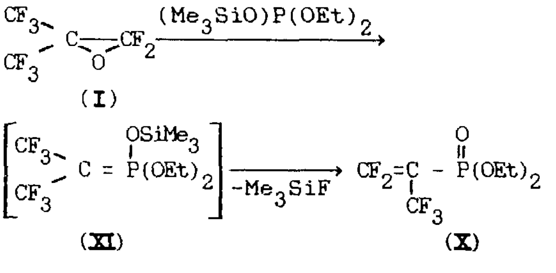
Dimethyl epoxypentafluoroisopropyl-2-phosphonate (**VII**) reacts with triethyl phosphite in a similar manner to form α-(dimethylphosphoryl)trifluoroethylidenetriethoxyphosphorane (**VIII**) [eqn. (4)].



(4)

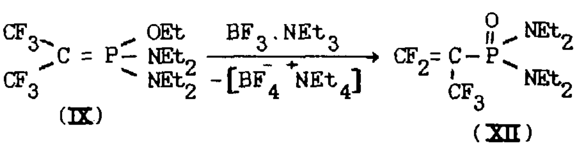
Trialkoxyphosphorus ylides containing a trifluoromethyl group at the ylide carbon atom exhibit a quite characteristic chemical shift for groups such as CF_3 in the ^{19}F NMR spectra, and this facilitates control of the reaction to a considerable extent (Table 1).

Cleavage of fluoro-olefin oxides by silylated phosphites can also be used for the synthesis of some fluoro-containing α,β-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)].



(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 $BF_3 \cdot NEt_3$ provides another route to the preparation of **X** [8]. Compound **IX** can also enter into similar reactions [eqn. (6)].



(6)

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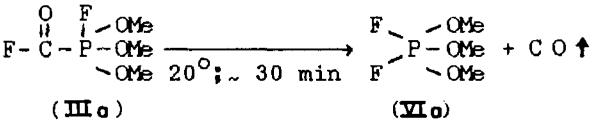
*For a preliminary note, see ref. 9.

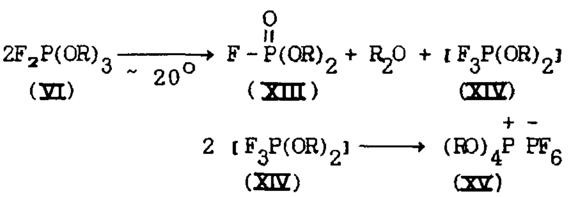
Fluorocarbonylfluorophosphoranes (III)

The reaction of perfluoroisobutene oxide with phosphorane led to the formation of **IIIa** which was isolated and identified by ^{19}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 fluorocarbonyltrialkoxyphosphoranes (**III**) has been assumed in the reaction of trialkyl phosphites with carbonyl fluoride [4] [eqn. (7)].



$$\underset{(\mathrm{IIIa})}{\mathrm{F{-}C(O){-}P(F)(OMe)_3}} \xrightarrow{20^\circ;\ \sim 30\ \mathrm{min}} \underset{(\mathrm{VIa})}{\mathrm{F_2P(OMe)_3}} + \mathrm{CO}\uparrow \qquad (7)$$

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



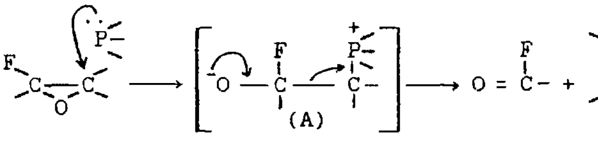
$$\underset{(\mathrm{VI})}{2\mathrm{F_2P(OR)_3}} \xrightarrow[\sim 20^\circ]{} \underset{(\mathrm{XIII})}{\mathrm{F{-}\overset{O}{\overset{\|}{P}}(OR)_2}} + \mathrm{R_2O} + \underset{(\mathrm{XIV})}{[\mathrm{F_3P(OR)_2}]}$$

$$2\,\underset{(\mathrm{XIV})}{[\mathrm{F_3P(OR)_2}]} \longrightarrow \underset{(\mathrm{XV})}{(\mathrm{RO})_4\overset{+}{\mathrm{P}}\ \overset{-}{\mathrm{PF_6}}} \qquad (8)$$

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

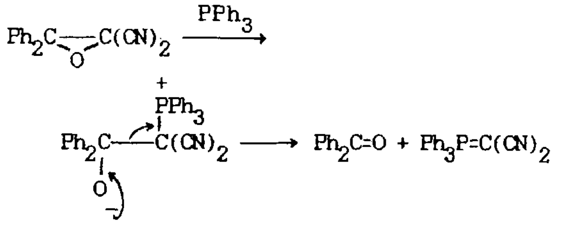
Cleavage mechanism of α-oxides

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)].



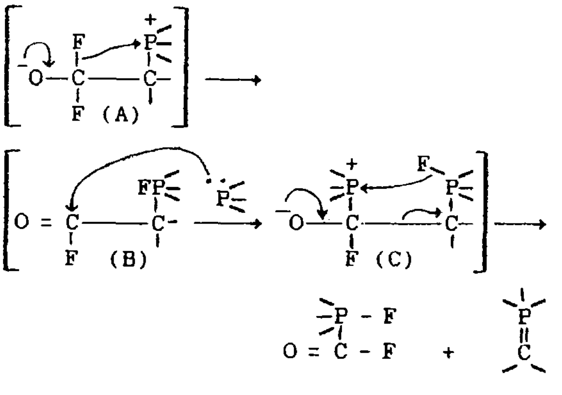
(9)

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)].



(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 C(O)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)].



(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† to form vinyl ethers

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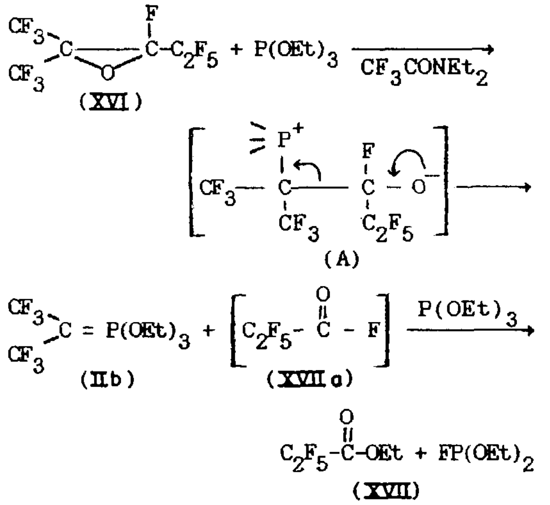
*Corresponding to the triethoxy-substituted carbonyl fluoride **IIIb** whose structure and further conversions were demonstrated by means of ^{19}F NMR spectroscopy.

†Compounds **IV** result from the reaction of COF_2 with $P(OR)_3$, but attempts to establish the formation of their precursors **III** were unsuccessful [4].

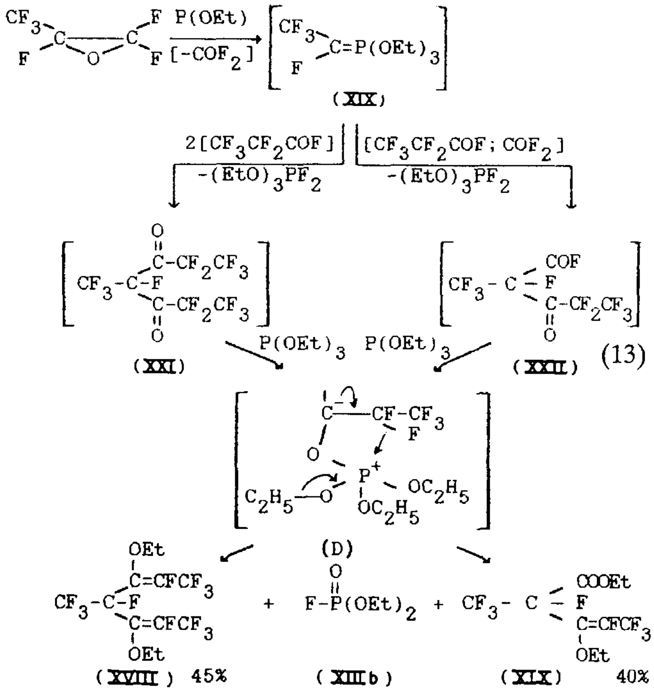
*For a preliminary note, see ref. 14.

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



(12)

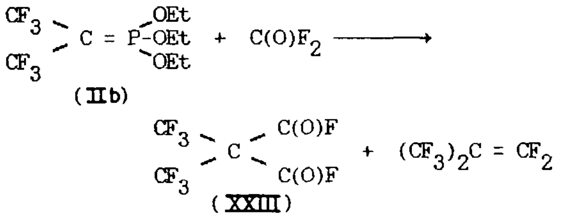
XVIII and **XIX** in yields of 45% and 40%, respectively (the basis of the amount of perfluoropropene oxide taken) [eqn. (13)].



(13)

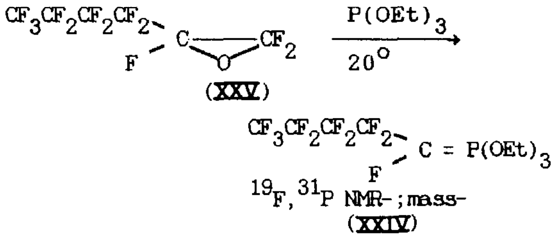
Clearly, in this case the reaction proceeds through the intermediate formation of a trialkoxyphosphorus ylide, i.e. tetrafluoroethylydenetriethoxyphosphorane (**XX**), which interacts further with both COF_2 and perfluoropropanoate fluoride, formed as a result of the partial isomerization of hexafluoropropene oxide*. The dicarbonyl compounds **XXI** and **XXII**, obtained by bisacylation of phosphoranes, can be converted into 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)].



(14)

Formation of the trialkoxyphosphorus ylide **XXIV** containing a fluorine atom at the ylide carbon atom, like ylide **XX**, has been established by ^{19}F and ^{31}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)].



(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 olefinoxides, 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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*Compound **XVIIa** is the sole product of interaction between hexafluoropropene oxide and $P(NEt_2)_3$.

References

1 P. Tarrant, C.O. Allison, K.P. Barthold and E.C. Stamp, *Fluorine Chem. Rev., 5* (1971) 77; P. Tarrant and E.C. Stamp, *Zh. Vses. Khim. Ova, 15* (1970) 34.

2 R.S. Edmundson, in D. Barton and W.D. Ollis (eds.), *Comprehensive Organic Chemistry,* Pergamon, Oxford, 1979, Vol. 2, Chap. 10.3.

3 C. Herzig and J. Gasteiger, *Chem. Ber., 115* (1982) 601.

4 A.F. Gontar', E.G. Bykhovskaya, A.S. Vinogradov and I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1981) 2632.

5 L. Kolditz, K. Leman and W. Wieker, *Z. Anorg. Allg. Chem., 360* (1968) 259.

6 W.I. Middleton and W.H. Sharkey, *J. Org. Chem., 30* (1965) 1348.

7 J. Heinc and C.-V. Roschenthaler, *Chem.-Ztg., 110* (1986) 91.

8 A.A. Kadyrov and E.M. Rokhlin, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1981) 2583.

9 A.A. Kadyrov, E.M. Rokhlin and I.K. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1981) 2653.

10 D.C. England, *US Pat. 3 733 357;* [*Chem. Abs., 79* (1973) 41 977].

11 W.J. Linn and E.J. Ciganek, *J. Org. Chem., 34* (1969) 2146.

12 N.P. Gambaryan, E.M. Rokhlin, Ju.V. Zeifman, Cheng Ching-Jun and I.L. Knunyants, *Angew. Chem., 78* (1966) 1008.

13 A.Yu. Volkonskii, E.I. Mysov and E.M. Rokhlin, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1984) 1356.

14 A.A. Kadyrov, E.M. Rokhlin, M.V. Galakhov and E.I. Mysov, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1989) 489.

15 S.A. Lermontov, I.M. Rakov and I.V. Martunov, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1990) 2848.

16 I.L. Knunyants, U. Utebaev, E.M. Rokhlin, E.P. Lur'e and E.I. Mysov, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1976) 875.