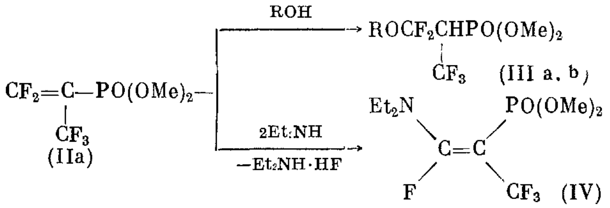
HEXAFLUOROISOPROPYLIDENE AND PENTAFLUOROISOPROPENYL DERIVATIVES OF PHOSPHORUS.

COMMUNICATION 2. ELECTROPHILICITY OF PENTAFLUOROISOPROPENYLPHOSPHONATE ESTERS AND THE REACTIONS OF PHOSPHORYLHEXAFLUOROISOPROPYL ANIONS

A. A. Kadyrov and E. M. Rokhlin UDC 542.91:547.1'118'161

Alkenylphosphonate esters are similar in their reactivity to α,β-unsaturated carbonyl compounds [1]. In our previous work [2], we showed that perfluoromethacrylate esters $CF_2 = C(CF_3)CO_2R$ (I) readily react with various nucleophiles to form addition products and/or "vinylog" substitution products. Pentafluoroisopropenylphosphonate esters (II) [3] behave similarly.

Thus, the action of alcohols on dimethyl ester (IIa) gives alkoxyesters (IIIa,b), while the action of diethylamine gives enaminoester (IV)

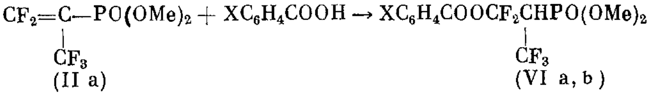


(IIa) (III a, b) (IV)

R = Me (a), Et (b).

The competitive reaction of esters (I) and (II) with ethanol showed approximately the same reactivity of these compounds and the formation of equal amounts of ester (IIIb) and $EtOCF_2CH(CF_3)CO_2Me$ (V).

Similar to perfluoromethacrylate esters [2], phosphonate ester (IIa) reacts with carboxylic acids to yield adducts (VIa,b) as shown by ^{19}F NMR spectroscopy:

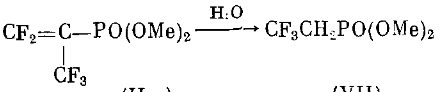


$$CF_2{=}\underset{CF_3}{\underset{|}{C}}{-}PO(OMe)_2 + XC_6H_4COOH \rightarrow XC_6H_4COOCF_2\underset{CF_3}{\underset{|}{C}}HPO(OMe)_2$$

(II a) (VI a, b)

X = H (a), *m*-Cl (b).

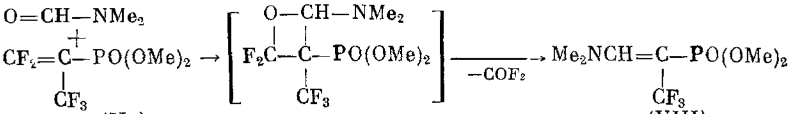
The hydrolysis of ester (IIa) leads to a trifluoroethylphosphonate ester (VII):



$$CF_2{=}\underset{CF_3}{\underset{|}{C}}{-}PO(OMe)_2 \xrightarrow{H_2O} CF_3CH_2PO(OMe)_2$$

(II a) (VII)

The reaction of ester (IIa) with dimethylformamide yields enaminoester (VIII):



$$\begin{matrix} O{=}CH{-}NMe_2 \\ + \\ CF_2{=}\underset{CF_3}{\underset{|}{C}}{-}PO(OMe)_2 \end{matrix} \rightarrow \left[\begin{matrix} O{-}CH{-}NMe_2 \\ |\quad\; | \\ F_2C{-}\underset{CF_3}{\underset{|}{C}}{-}PO(OMe)_2 \end{matrix}\right] \xrightarrow[-COF_2]{} Me_2NCH{=}\underset{CF_3}{\underset{|}{C}}{-}PO(OMe)_2$$

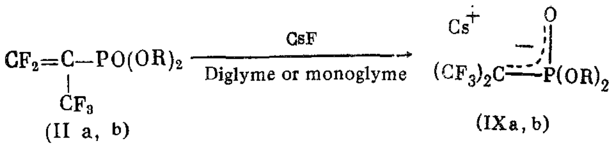
(IIa) (VIII)

Analogous reactions of perfluoromethacrylate acid derivatives are very common [2, 4].

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1353-1359, June, 1983. Original article submitted September 1, 1982.

0568-5230/83/3206-1224$07.50

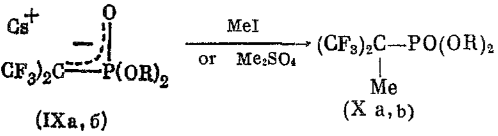
As a consequence of the high electrophilicity of the double bond, pentafluoroisopropenylphosphonate esters (II) readily add fluoride anions. The action of CsF in polar aprotic solvents at reduced temperatures yields solutions of cesium salts (IX)



$$CF_2{=}C(CF_3){-}PO(OR)_2 \xrightarrow[\text{Diglyme or monoglyme}]{CsF} Cs^+\,[(CF_3)_2C\overset{-}{=}P(O)(OR)_2]$$

R = Me (a), Et (b).

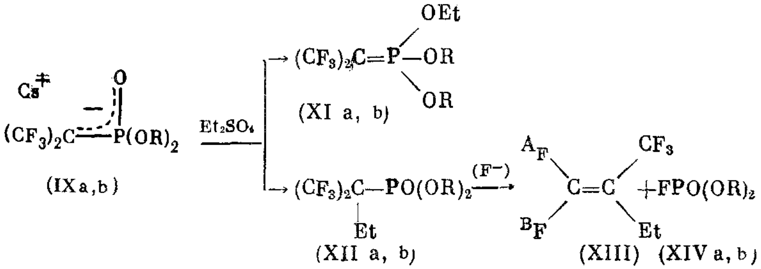
The mesomeric cation in salts (IX) is capable of alkylation. The results of this reaction depend on the steric requirements. Thus, ^{19}F NMR spectroscopy was used to demonstrate that methylation proceeds at the carbon atom with formation of α-methylphosphonate esters (X)



$$Cs^+\,[(CF_3)_2C\overset{-}{=}P(O)(OR)_2] \xrightarrow[\text{or } Me_2SO_4]{MeI} (CF_3)_2C(Me){-}PO(OR)_2$$

R = Me (a), Et (b),

The ethylation of salts (IX) is more difficult to accomplish and not only the carbon atom, but also the "phosphoryl" oxygen atom undergoes attack, leading to hexafluoroisopropylidenetrialkoxyphosphoranes (XIa,b) in addition to α ethyl-substituted esters (XII) which are unstable under the reaction conditions and decompose to give 2-ethylpentafluoropropene (XIII) and dialkyl fluorophosphates (XIV)

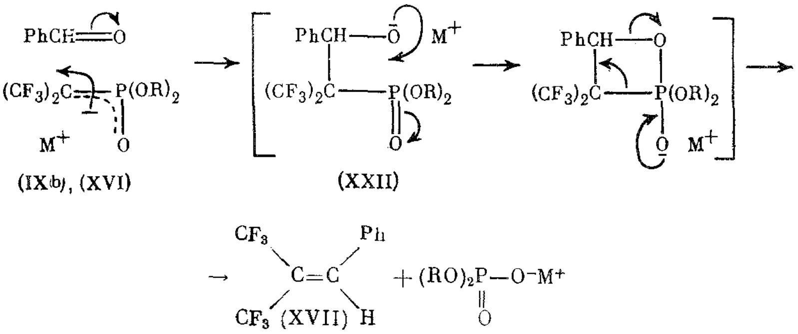


R = Me (a), Et (b).

Salts (IX), similar to the salts of other phosphate α-carbanions [5], participate in the Wittig–Horner reaction. Thus, the reaction of (IXa) with hexafluoroacetone yields tetrakis(trifluoromethyl)ethylene (XV)

$$\text{(IX a)} + O{=}C(CF_3)_2 \xrightarrow[-(MeO)_2POOCs]{} \underset{\text{(XV)}}{(CF_3)_2C{=}C(CF_3)_2}$$

By analogy, the reaction of benzaldehyde with (IXb) or methyltriethylammonium salt (XVI) [3] yields (XVII) which was shown by gas-liquid chromatography (GLC) and ^{19}F NMR spectroscopy to be identical to a previously described sample [6, 7]



$M^+ = Cs^+$, R = Et (IX b); $M^+ = Me\overset{+}{N}Et_3$, R = Me (XVI).

TABLE 1. ^{19}F NMR Spectra of $XCF_2CH(CF_3)PO(OMe)_2$*

Compound	X	Chemical shifts, ppm			J, Hz					
		F(A)	F(B)	CF_3	F(A)—F(B)	F(A)—CF_3	F(B)—CF_3	F(A)—H and F(A)—P	F(B)—H and F(B)—P	CF_3—H and CF_3—P
(IIIa)	MeO	−9,3	−8,0	−17,9	148	11,5	10,7	~7,3	9,6 and 10,7	8,1 and 11,8
(IIIb) †	EtO	−12,1	−10,1	−17,8	145	11,1	11,1	~6,6	7,5 and 11,7	7,7 and 9,4
(VIa) ‡	PhCOO	−13,9	−9,7	−18,0	169	12,0	10,5	9,0 and 12,2	5,3 and 13,5	6,8 and 9,0
(VIb) ‡	m-ClC_6H_4COO	−13,7	−9,7	−18,4	160	11,8	10,0	8,8 and 12,0	5,6 and 13,5	~7,9

---

*CF_2 gives an AB system with additional splitting to d.d.q., while CF_3 gives a d.d.d.d. pattern.

†In ethanol.

‡In ether.

TABLE 2. ^{19}F NMR Spectra of $(CF_3)_2CXPO(OR)_2$

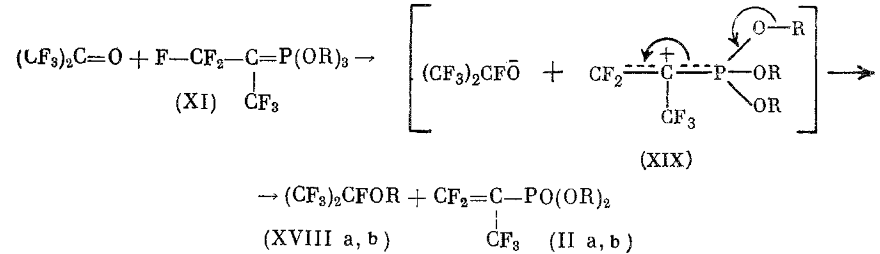
Compound	X	R	Solvent	CF_3 chemical shifts, ppm	J_{CF_3-P}, Hz
(Xa)	Me	Me	Monoglyme	−11,0 d	4,7
(Xb)	Me	Et	Diglyme	−11,9 d	4,0
(XIIa)	Et	Me	Monoglyme	−11,3 d	5,7
(XX) *	$\underset{\substack{\mid \\ \mathrm{OMe}}}{\mathrm{PhCH}}$	Me	CCl_4	−18,2 d.q and −20,8 d.q	4,1 and 5,4
(IXa)	Cs	Me	Monoglyme	−37,1 d	4,7
(IXb)	Cs	Et	Diglyme	−37,9 d	5,0

---

*The CF_3 groups are nonequivalent, $J_{CF_3-CF_3}$ = 9.8 Hz.

As expected, hexafluoroisopropylidenetrialkoxyphosphoranes (XI) are much less reactive relative to carbonyl compounds [7]. Hexafluoroacetone and benzaldehyde react with (XI) under more vigorous conditions than in the case of salts (XI) and in contrast to derivatives of perfluorocarboxylic acids [8], do not give Wittig reaction products.

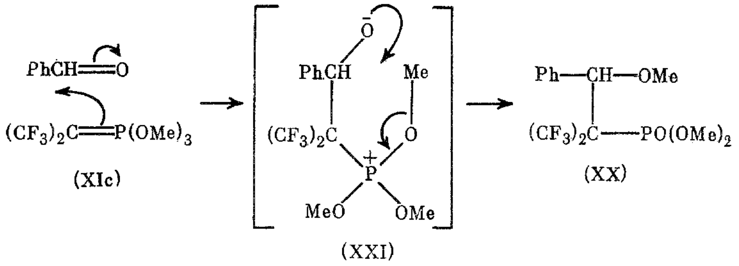
Hexafluoroisopropylidenetrialkoxyphosphoranes (XI) and hexafluoroacetone react to yield alkylheptafluoroisopropyl esters (XVIII) and pentafluoroisopropenylphosphonate esters (II).



R = Me (a), Et (b).

We might think that strongly electrophilic hexafluoroacetone behaves similarly to a Lewis acid such as BF_3 [3], abstracting a F^- anion from the phosphorane and the heptafluoroisopropylate anion formed is alkylated by the mesomeric carbocation (XIX). Thus, in contrast to the anion of salt (IX), not the carbon atom but rather the "allylic" fluoride atom undergoes electrophilic attack in the phosphorane upon the action of hexafluoroacetone.

On the other hand, the carbon atom is attacked in the reaction of benzaldehyde and phosphorane (XIc). However, instead of a Wittig reaction, we find a rearrangement with a methyl shift which leads to methoxyphosphonate ester (XX).



Apparently, this reaction involves intramolecular alkylation in the intermediate betaine (XXI) which contains a $\overset{+}{P}(OR)_3$ quasiphosphonium group which is an effective alkylating agent. The intermediate (XXII) in the reaction of salt (IX) with benzaldehyde contains a $PO(OR)_2$ group which displays less pronounced alkylating properties and, thus, the intramolecular attack of the O-anion is directed at the phosphorus atom, which leads to the Wittig–Horner reaction.

The scope of the reactions using salts (IX) likely can be expanded. This is also true for other reactions of pentafluoroisopropenylphosphonate esters. These esters, which have pronounced electrophilicity, may be seen as phosphorus analogs of perfluoromethacrylate esters.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were taken by É. M. Kagramanova on a Perkin-Elmer R-32 spectrometer at 90 and 84.6 MHz with TMS and CF_3CO_2H external standards. The ^{31}P NMR spectra were taken by P. V. Petrovskii on a Bruker HX-90 spectrometer at 36.43 MHz and Bruker WP-200SW spectrometer at 80.96 MHz with 85% H_3PO_4 as the external standard. The chemical shifts are given as ppm and on the δ scale for the ^1H and ^{31}P NMR spectra. The mass spectra were taken by E. I. Mysov on a Varian MAT CH-8 mass spectrometer; the m/z values and intensities (%) are given. The ^{19}F NMR spectra of (III) and (VI) are given in Table 1, while those for (IX), (X), (XII), and (XX) are given in Table 2.

Reactions of Pentafluoroisopropenylphosphonate Esters (IIa,b). With Alcohols. a) A sample of 1.41 g abs. methanol was added dropwise with cooling to about 20°C to a solution of 7.41 g ester (IIa) in 5 ml abs. ether. Distillation yielded 5.04 g (60%) dimethyl ester of α-hydro-β-methoxypentafluoroisopropylphosphonic acid (IIIa) with bp 75.5°C (1 mm). PMR spectrum: 3.49 s (CH_3OC), 3.66 d (CH_3OP), 3.6-4.2 m (CH), J_{CH_3O-P} = 12.0 Hz. Mass spectrum 272 (0.2), 253 (3), 252 (7), 144 (59), 125 (24), 110 (44), 109 (100), 79 (34). Found: C 26.8; H 3.87; F 34.9%. $C_6H_{10}F_5O_4P$. Calculated: C 26.5; H 3.70; F 34.9%.

b) Treatment of ester (IIa) with excess abs. ethanol yields a solution of the dimethyl ester of α-hydro-β-ethoxypentafluoroisopropylphosphonic acid (IIIb) (the ^{19}F NMR spectrum is given in Table 1).

c) A mixture of equimolar amounts of ester (IIa), methyl perfluoromethacrylate (Ia), and abs. ethanol in abs. ether yielded a solution containing ester (IIIb) and methyl α-hydro-β-ethoxypentafluoroisobutyrate (V) [−12.5 d.t. (CF_3), −5.3 m (CF_2), $J_{CF_3-CF_2}$ = 9.8 Hz, J_{CF_3-CH} = = 8.3 Hz [4]] in approximately equal amounts, and the starting esters (Ia) and (IIa).

With Diethylamine. A solution of 4.52 g Et_2NH in 20 ml abs. ether was added to a solution of 7.43 g ester (IIa) in 20 ml abs. ether with stirring and cooling to −35°C. After 15 h at about 20°C, the mixture was treated with abs. benzene. Distillation of the filtrate gave 6.58 g (73%) dimethyl ester of α-trifluoromethyl-β-fluoro-β-diethylaminovinylphosphonic acid (IV) with bp 99°C (1 mm). PMR spectrum: 1.05 t (CH_3C), 3.52 d (CH_3O), 3.2-3.5 m (CH_2), $J_{CH_3-CH_2}$ = 7.0 Hz, J_{CH_3O-P} = 12.0 Hz. ^{19}F NMR spectrum: −27.4 d.d. (CF_3), −31.2 d.q. (CF), J_{CF_3-CF} = 18.8 Hz, J_{CF_3-P} = 3.4 Hz, J_{CF-P} = 22.6 Hz. ^{31}P NMR spectrum: 17.89 d.h.q., J_{P-CF} = = 23.2 Hz, J_{P-OCH_3} = 12.5 Hz, J_{P-CF_3} = 3.1 Hz (confirmed by double heteronuclear resonance). Mass spectrum: 293 (24), 274 (24), 258 (22), 224 (58), 198 (27), 184 (100), 164 (40), 131 (16), 110 (27), 109 (43), 79 (32). Found: C 36.6; H 5.34; F 25.4; N 4.78%. $C_9H_{16}F_4NO_3P$. Calculated: C 36.9; H 5.50; F 25.9; N 4.78%.

With Carboxylic Acids. a) Equimolar amounts of ester (IIa) and m-$ClC_6H_4CO_2H$ in abs. ether gave a solution of the dimethyl ester of α-hydro-β-(m-chlorobenzoyloxy)pentafluoroisopropylphosphonic acid (VIb).

b) By analogy, a solution of the dimethyl ester of α-hydro-β-benzoyloxypentafluoroisopropylphosphonic acid (VIa) was obtained.

With Water. A sample of 0.55 g water was added with stirring and cooling to −10°C to a solution of 7.31 g ester (IIa) and 10.28 g $Et_3N{\bullet}BF_3$ in 8 ml abs. ether. After 15 h at about 20°C, an additional 10.30 g $Et_3N{\bullet}BF_3$ in 10 ml abs. ether and 0.55 g water were added. The mixture was maintained for 1 h and, then, distillation of the ethereal extract gave 0.60 g (10%) dimethyl ester of 2,2,2-trifluoroethylphosphonic acid (VII) with bp 59°C (2 mm). PMR spectrum: 3.07 d.q. (CH_2), 3.80 d (CH_3), $J_{CH_2-CF_3}$ = 10.9 Hz, J_{CH_2-P} = 19.3 Hz, J_{CH_3-P} = = 11.2 Hz. ^{19}F NMR spectrum: −19.3 d.t. (CF_3), J_{CF_3-P} = 13.7 Hz, and $J_{CF_3-CH_2}$ = 10.9 Hz. Mass spectrum: 192 (18), 162 (22), (22), 161 (7), 131 (5), 110 (10), 109 (62), 97 (16), 79 (100), 69 (21), 64 (11). Found: C 26.0; H 4.18; F 27.6; P 15.7%. $C_4H_8F_3O_3P$. Calculated: C 25.0; H 4.20; F 29.7; P 16.1%.

With Dimethylformamide. Maintenance of a mixture of 7.19 g ester (IIa) and 1.10 g DMF for 15 days at about 20°C and distillation yielded 2.65 g (70%) dimethyl ester of α-trifluoromethyl-β-dimethylaminovinylphosphonic acid (VIII) with bp 92-93°C (0.01 mm) which was shown by ^{19}F NMR spectroscopy to contain a considerable amount of an unidentified impurity with a broad singlet at −27.3. PMR spectrum: 3.11 br.s. (CH_3N), 3.56 br.d. (CH_3O), 7.33 br.d. (CH), J_{CH_3O-P} = 11.2 Hz, J_{CH-P} = 17.0 Hz. ^{19}F NMR spectrum: −34.6 br.d. (CF_3), J_{CF_3-P} = 5.6 Hz. ^{31}P {^1H} NMR spectrum (in ether): 25.67 q, J_{P-CF_3} = 7.1 Hz. Mass spectrum: 247 (50), 232 (6), 228 (14), 227 (14), 216 (11), 212 (36), 207 (33), 203 (11), 138 (100), 131 (49), 112 (33), 110 (47), 109 (31), 95 (21), 79 (27). Found: C 34.0; H 5.23; F 22.7; N 5.58; P 12.5%. $C_7H_{13}F_3NO_3$. Calculated: C 34.0; H 5.30; F 23.1; N 5.67; P 12.5%.

With Cesium Fluoride. a) A solution of 9.49 g ester (IIa) in 5 ml abs. monoglyme was added slowly with stirring at from −15° to −20°C to a suspension of 6.90 g freshly roasted CsF in 10 ml abs. monoglyme. After 30 min at −15°C, a solution was obtained largely containing the cesium salt of the dimethyl ester of α-hydrohexafluoroisopropylphosphonic acid (IXa).

The ^{19}F NMR spectrum did not change upon storage for one month at −78°C. The salt decomposes to a considerable extent over two days at about 20°C and 2-methylpentafluoropropene (identified according to its ^{19}F NMR spectrum [9]) was found among the decomposition products.

b) By analogy, 0.90 g CsF and 1.43 g ester (IIb) in 3 ml abs. diglyme at −10°C yields a solution of the cesium salt of the diethyl ester of α-hydrohexafluoroisopropylphosphonic acid (IXb) which contains small amounts of unidentified impurities. ^{31}P {^1H} NMR spectrum (at

$-10°C$): 27.8 h, J_{P-CF_3} = 4.9 Hz. This salt is stable in solution at $-78°C$ but almost completely decomposes over 20 days at about 20°C.

Reactions of the Cesium Esters of α-Hydrohexafluoroisopropylphosphonic Acid (IXa,b). Methylation. a) An equimolar amount of dimethyl sulfate was added to a monoglyme solution of salt (IXa) to give a solution of the dimethyl ester of α-methylhexafluoroisopropylphosphonic acid (Xa).

b) Treatment of a solution of salt (IXb) in diglyme with an approximately equimolar amount of MeI yields the diethyl ester of α-methylhexafluoroisopropylphosphonic acid (Xb).

Ethylation. a) A monoglyme solution of salt (IXa) was treated with an equimolar amount of diethyl sulfate. The reaction does not proceed at ~20°C. After 30 min at 60°C, distillation at ~20 mm and ~20°C gave a mixture of monoglyme and 2-ethylpentafluoropropene (XIII). The residue in the filtrate yielded a solution which was shown by ^{19}F NMR spectroscopy to contain the dimethyl ester of α-ethylhexafluoroisopropylphosphonic acid (XIIa) as well as hexafluoroisopropylidenethoxydimethoxyphosphorane (XIa) (-33.3 d, J_{CF_3-P} = 7.3 Hz) and dimethyl fluorophosphate (XIVa) (+8.6 d, J_{F-P} = 968 Hz [10,11]).

b) A sample of 2.20 g diethyl sulfate was slowly added with stirring at $-10°C$ to a solution of salt (IXb) obtained from 3.86 g ester (IIb) and 2.40 g CsF in 7 ml abs. monoglyme. After maintenance for 1.5 h at 55°C, distillation yielded 1.70 g of a mixture with bp 45-60°C (1 mm) which was shown by ^{19}F NMR spectroscopy to contain hexafluoroisopropylidenetriethoxyphosphorane (XIb) (-33.1 d, J_{CF_3-P} = 7.5 Hz) in addition to unidentified impurities. A solution containing considerable amounts of 2-ethylpentafluoropropene (XIII) [-16.7 d.d. (CF_3, -1.5 br.d.q. (F^A), +6.1 d.q.t. (F^B), $J_{F^A-F^B}$ = 26.3 Hz, $J_{F^A-CF_3}$ = 22.4 Hz, $J_{F^B-CF_3}$ = 11.1 Hz, $J_{F^B-CH_2}$ = 2.1 Hz [9]] and diethyl fluorophosphate (XIVb) (3.8 d, J_{F-P} = 968 Hz [10]) was obtained in the trap at $-78°C$.

The Wittig-Horner Reaction. a) A sample of 6.8 g hexafluoroacetone was introduced into a monoglyme solution containing 4.44 g salt (IXa). After 1 h at ~20°C, distillation over conc. H_2SO_4 yielded 1.22 g (36%) tetrakis(trifluoromethyl)ethylene (XV) with bp 54-55°C. ^{19}F NMR spectrum: -16.8 s [12]. Mass spectrum: 300 (1), 281 (42), 231 (23), 181 (35), 143 (16), 93 (14), 69 (100).

b) A solution of salt (IXb) in diglyme was treated with excess benzaldehyde. Maintenance at about 20°C for two days yielded a solution containing a considerable amount of benzylidenehexafluoropropane (XVII) identified by gas-liquid chromatography relative to an authentic sample [6] in addition to unidentified impurities. ^{19}F NMR spectrum: -20.6 q (CF_3^A), -14.9 d.q (CF_3^B), $J_{CF_3-CF_3}$ = 7.5 Hz, $J_{CF_3^B-H}$ = 1.7 Hz. The action of excess benzaldehyde at ~20°C on a solution of the methyltriethylammonium salt of the dimethyl ester of α-hydrohexafluoroisopropylphosphonic acid (XVI) in monoglyme obtained from hexafluoroisopropylidenetrimethoxyphosphorane (XIc) and triethylamine [3] also gives olefin (XVII).

Reactions of Hexafluoroisopropylidenetrialkoxyphosphoranes (XIb,c). With hexafluoroacetone. a) A mixture of 3.54 g phosphorane (XIb) and 2.26 g hexafluoroacetone was heated in a sealed ampul for 12 h at 85-90°C. The ampul was opened. Unreacted hexafluoroacetone and ethyl heptafluoroisopropyl ether (XVIIIb) (identified by its ^{19}F NMR spectrum) were trapped at $-78°C$ and reduced pressure. Distillation of this mixture over sulfuric acid gave 1.63 g (68%) ether (XVIIIb) with bp 45-46°C [13]). PMR spectrum: 1.17 t (CH_3), 3.93 q (CH_2), $J_{CH_3-CH_2}$ = 6.4 Hz. ^{19}F NMR spectrum: 3.3 d (CF_3), 61.5 unresolved h (CF), J_{CF_3-CF} = 1.9 Hz. Distillation of the reaction mixture gave 1.54 g (50%) 90% pentafluoroisopropenylphosphonate ester (IIb) with bp 43-44°C (1 mm). ^{19}F NMR spectrum: three characteristic multiplets at -19.9, -21.6, and -23.2 ppm [3]. There was also a fraction with bp 45-60°C (1 mm) (1.06 g) which was shown by ^{19}F NMR spectroscopy to contain ester (IIb), phosphorane (XIb), diethyl ester of α-ethylhexafluoroisopropylphosphonic acid (XIIb), and the diethyl ester of α-hydrohexafluoroisopropylphosphonic acid in 1.0:0.4:0.3:0.3 mole ratio.

b) By analogy, phosphorane (XIc) yielded ester (IIa) [3] and methyl heptafluoroisopropyl ether (XVIIIa) identical to a known sample [14]. ^{19}F NMR spectrum: +2.2 unresolved d (CF_3), +44.4 unresolved h (CF), J_{CF_3-CF} ≈ 1.5 Hz.

With Benzaldehyde. A mixture of 1.11 g phosphorane (XIc) and 0.50 g benzaldehyde was heated for 20 h at 85-95°C to yield a mixture which was shown by ^{19}F NMR spectroscopy to contain largely the dimethyl ester of 1,1-bis(trifluoromethyl)-2-methoxy-2-phenylethylphosphonic acid (XX), ester (Xa), and the methyl ester of α-hydrohexafluoroisopropylphosphonic acid in 5.5:3:1.5 mole ratio. Distillation yielded 0.48 g (30%) ester (XX) with bp 110-120°C (1 mm). PMR spectrum (in CCl_4): 3.23 s (CH_3OC), 3.85 d ($^ACH_3OP$), 3.89 d ($^BCH_3OP$), 4.86 d (CH), ∿7.5 m (C_6H_5), $J_{CH_3^A-P}$ = 12.4 Hz, $J_{CH_3^B-P}$ = 12.6 Hz, J_{CH-P} = 6.8 Hz. Mass spectrum: 380 (9), 271 (26), 121 (100), 110 (45), 109 (37).

CONCLUSIONS

1. Esters of pentafluoroisopropenylphosphonic acid are similar in their electrophilic reactivity to esters of perfluoromethacrylic acid. Their reactions with alcohols and carboxylic acids give addition products while their reactions with diethylamine give vinylog substitution products. Their reactions with dimethylformamide give the product of the replacement of the $CF_2=$ group by the $Me_2NCH=$ group.

2. The mesomeric carbanions obtained by the addition of the fluoride anion to esters of pentafluoroisopropenylphosphonic acid readily undergo alkylation and react with carbonyl compounds in the Wittig–Horner reaction.

LITERATURE CITED

1. E. N. Tsvetkov, Dissertation, Moscow (1970).
2. E. M. Rokhlin, E. G. Abduganiev, and U. Utebaev, Usp. Khim., 45, 1177 (1976).
3. A. A. Kadyrov and E. M. Rokhlin, Izv. Akad. Nauk SSSR, Ser. Khim., 2583 (1981).
4. U. Utebaev, Dissertation, Moscow (1976).
5. W. S. Wadsworth, Organic Reactions, 25, 73 (1977).
6. Yu. V. Zeifman, L. A. Simonyan, Z. V. Safronova, and N. P. Gambaryan, Izv. Akad. Nauk SSSR, Ser. Khim., 1367 (1981).
7. D. J. Burton and Y. Inouye, Tetrahedron Lett., 3397 (1979).
8. A. Yu. Volkonskii, E. M. Rokhlin, E. I. Mysov, Izv. Akad. Nauk SSSR, Ser. Khim., 477 (1982).
9. I. L. Knunyants, E. G. Abduganiev, S. T. Kocharyan, M. V. Urushadze, V. A. Livshits, Yu. E. Aronov, and E. M. Rokhlin, Izv. Akad. Nauk SSSR, Ser. Khim., 110 (1971).
10. A. A. Neimysheva, Dissertation, Moscow (1970).
11. I. Ruppert, Z. Anorg. Allg. Chem., 477, 59 (1981).
12. H. H. Evans, R. Fields, R. N. Hazeldine, and M. Illingworth, J. Chem. Soc., Perkin Trans., 1, 649 (1973).
13. West German Patent No. 1,298,514 (1969); Chem. Abstr., 71, 60701 (1969).
14. US Patent No. 3,962,460 (1976); Chem. Abstr., 85, 142632 (1976).