PERKOV REACTION IN SERIES OF MIXED BIS(1,1,3-TRIHYDRO-PERFLUOROPROPYL) ALKYL PHOSPHITES

> I. V. Konovalova, E. N. Ofitserov, UDC 542.91:547.1'118 V. F. Mironov, and A. N. Pudovik

The attention of investigators has been attracted recently to organophosphorus compounds that contain either fluorinated alkyls or alkoxyls on the P(III) atom [1-6]. A sharp decrease in its nucleophilic properties and an increase in the electrophilic properties is characteristic for the P(III) in perfluoroalkyl phosphites [1, 2]. Thus, tris(perfluoroalkyl) phosphites are oxidized with great difficulty [3], and they enter into the Arbuzov [1,4,5] and Perkov [1] reactions. However, they form phosphoranes much more easily when reacted with halogens [2], and they also react more easily with chloral hydrate [1]. The insertion of even one P-C bond sharply increases the nucleophilicity of P(III) [6].

In the present paper we describe for the first time the synthesis of mixed bis(1,1,3-trihydroperfluoropropyl) alkyl phosphites and discuss their reaction with chloral. Ethyl bis(1,1,3-trihydroperfluoropropyl) phosphite was obtained by the following reactions:

 $\begin{array}{c} (\mathrm{Et}_{2}\mathrm{N})_{2}\mathbf{P}\mathrm{OEt}+2\mathrm{R}_{F}\mathrm{OH} & & \\ \mathrm{Cl}_{2}\mathrm{P}\mathrm{OEt}+2\mathrm{R}_{F}\mathrm{OH}+2\mathrm{NEt}_{3} & & \\ \mathrm{Cl}_{2}\mathrm{P}\mathrm{OEt}+2\mathrm{R}_{F}\mathrm{OH}+2\mathrm{NEt}_{3} & & \\ \mathrm{(R}_{F}\mathrm{O})_{2}\mathrm{P}\mathrm{Cl}+\mathrm{Et}\mathrm{OH}+\mathrm{NEt}_{3} & & \\ \mathrm{(I)} & & \\ \mathrm{R}_{F} & = \mathrm{CH}_{2}\mathrm{CF}_{2}\mathrm{CHF}_{2} & & \\ \end{array}$

The mixed 1-(dimethylphosphono)methyl bis(1,1,3-trihydroperfluoropropyl) phosphite was also obtained by the transesterification reaction of a tris(perfluoroalkyl) phosphite. The reaction proceeds at room temperature, but heating in vacuo is needed for completion (100°C, 40 mm, 2 h). The analogous reaction for $(EtO)_3P$ goes only at 160-200° [7]. The structure of the obtained mixed phosphites was proved spectrally ('H and ³¹P NMR, IR).

 $(\text{MeO})_{2}P(\text{O})\text{CH}_{2}\text{OH} + (\text{R}_{\text{F}}\text{O})_{3}P \rightarrow (\text{MeO})_{2}P(\text{O})\text{CH}_{2}\text{OP}(\text{OR}_{\text{F}})_{2} + \text{R}_{\text{F}}\text{OH}$ (II)

The reaction of these phosphites with chloral (III) (1:1) was studied. The reaction begins at -10 to 0°. In the ³¹P NMR spectrum of the reaction mixture of (I) + (III) at room temperature are recorded four signals with δ ³¹P, ppm: -43 (IV), -8 (V), -3 (VI), +140 (starting phosphite (I)). The +140 signal disappears with the further addition of chloral, while the signals at -43, -8, and -3 increase in intensity. Heating to 100° (3-5 min) leads to an increase in the intensity of the signal at -8 ppm and a decrease in the -43 ppm signal. Only the pure phosphate with δ ³¹P at -8 ppm can be isolated when the reaction mixture is distilled, whose constants and IR and PMR spectra correspond to the compound (RFO)₂P(O)OCH = CCl₂ (V) and coincide with the literature data [1]. The -43 ppm signal corresponds to a phosphorane with a P-C bond (IV) [8]. The phosphate with -3 ppm is formed both at 0 and at 25°. On the basis of these experimental data we proposed the reaction scheme given on the following page.

The compound with $\delta^{31}P$ -3 ppm can be assigned the structure of a phosphate, the direct oxidation product of phosphite (I) by chloral. The oxidation of P(III) derivatives by carbonyl compounds, including chloral, is known and can proceed either directly or via a phosphorane with P-O-C bonds [9, 10]. Direct oxidation occurs in the given case, since it is known that acyclic phosphoranes, containing a perfluoroalkoxy grouping, are stable and can even be vacuum-distilled [2], while the insertion of a ring should additionally stabilize the phosphorane structure

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V. I. Ul'yanov-Lenin Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1432-1434, June, 1983. Original article submitted September 9, 1982.



Despite the presence of three electron-acceptor substituents in all of the alkyl groups on the phosphorus atom, the reaction of (II) with (III) proceeds in a similar manner, but it is much slower. Heating is required for its completion (10 min, $80-90^{\circ}$). Even under these conditions the phosphorane with a P-C bond is recorded ($\delta^{31}P + 22, -42$ ppm, (VII)).

 $(\mathbf{R}_{\mathbf{F}}\mathbf{O})_{2}\mathbf{POCH}_{2}\mathbf{P}(\mathbf{O})(\mathbf{OMe})_{2} + \mathbf{CCl}_{3}\mathbf{CHO} \rightarrow (\mathbf{R}_{\mathbf{F}}\mathbf{O})_{2}\mathbf{P} \rightarrow \mathbf{O} + (\mathbf{V}) + (\mathbf{MeO})_{2}\mathbf{P}(\mathbf{O})\mathbf{CH}_{2}\mathbf{CI}$ $(\mathbf{II}) \qquad (\mathbf{III}) \qquad (\mathbf{III}) \qquad \mathbf{Cl}_{3}\mathbf{CHC} \qquad \mathbf{CHCCl}_{3} \qquad (\mathbf{VIII})$ $(\mathbf{VII}) \qquad \mathbf{O}$

Phosphonate (VIII) and phosphate (V) were isolated when the reaction mixture was fractionally distilled. The oxidation product was not detected.

EXPERIMENTAL

The PMR spectra were taken on Varian HA-100D (100 MHz) and Varian T-60 (60 MHz) instruments, the IR spectra were taken on Specord 75-IR and UR-20 instruments, and the ³¹P NMR spectra were taken on a KGU-3 NMR instrument (10.2 MHz).

Synthesis of Bis(1,1,3-trihydroperfluoropropyl) Ethyl Phosphite (I). a) To a mixture of 0.06 mole of $CHF_2CF_2CH_2OH$ and 0.06 mole of Et_3N in ether at 0° was added in drops 0.03 mole of EtOPC1₂, and the mixture was stirred for 30 min and the salt was filtered. The yield of (I) was 60%, bp 83-85° (13 mm), np^{2°} 1.3630. $\delta^{3}P$ +140 ppm. PMR spectrum (CC1₄, 60 MHz, δ , ppm): 3.93, 3.66 m (a superimposition of the quintet of the POCH₂ protons and the triplet of doublets of the CF₂CH₂O protons), 5.6 t.t (CHF₂), ('JFCH = 54, 'JFCCH = 4 Hz), 1.03 t (CH₃, 'JHCCH = 7.5 Hz). Found: C 28.47; H 3.38%. C₈H₁₁F₈PO₃. Calculated: C 28.40; H 3.25%.

b) To a mixture of 0.03 mole of EtOH and 0.03 mole of $Et_{9}N$ in ether at 0° was added in drops 0.03 mole of $(R_{\rm F}O)_{2}PC1$ in ether. The mixture was stirred for 30 min and the precipitate was filtered. Compound (I) was isolated in 55% yield by distillation.

c) To 0.03 mole of $EtOP(NEt_2)_2$ was added 0.061 mole of RFOH. The mixture was heated at 110-120° with removal of the Et_2NH by distillation. Product (I) was isolated in 70% yield (based on the amine).

Synthesis of 1-(Dimethylphosphono)methyl Bis(1,1,3-trihydroperfluoropropyl) Phosphite (II). To 0.05 mole of $(R_{FO})_{3}P$ was added 0.05 mole of $(CH_{3}O)_{2}P(O)CH_{2}OH$. The mixture was heated at 100° (40 mm, 2 h) and the residue was distilled. The yield of (II) was 37%, bp 112-113° (0.05 mm), np^{2°} 1.3930. $\delta^{3}P$ (ppm): 140, 22 ($^{3}J_{PP}$ = 15 Hz). PMR spectrum (100 MHz, C₆H₆, δ , ppm): 5.46 t.t. ($F_{2}CH$, $^{2}J_{HCF}$ = 53, $^{3}J_{HCCF}$ = 5 Hz), 3.84 t.d. ($CF_{2}CH_{2}OP$, $^{3}J_{POCH}$ = 7, $^{3}J_{FCCH}$ = 13 Hz), 3.26 d (POCH₃, $^{3}J_{POCH}$ = 11 Hz), 3.76 d.d (degenerate, PCH₂OP, $^{3}J_{POCH}$ = $^{2}J_{PCH}$ = 7 Hz). IR spectrum (ν , cm⁻¹): 790-810, 1020-1040, 1080-1130 (POC + CF), 1230, 1260 (CF + P=O), 1455 [δ (CH)], 2860, 2960, 3000 (CH). Found: C 25.15; H 3.40%. C₉H₁₄F₈P₂O₆. Calculated: C 25.00; H 3.24%. Reaction of Bis(1,1,3-trihydroperfluoropropy1) Ethyl Phosphite (I) with Chloral (III). A mixture of 0.05 mole of phosphite (I) and 0.06 mole of chloral, prepared at 20°, was heated for 10 min at 80-90° and then distilled. We isolated phosphate (V), bp 132-134° (10 mm), $np^{2°}$ 1.3840. Found: C 22.92; H 2.01%. C₈H₇Cl₂F₈PO₄. Calculated: C 22.80; H 1.66%, cf. [1].

<u>Reaction of 1-(Dimethylphosphono)methyl Bis(1,1,3-trihydroperfluoropropyl) Phosphite</u> (<u>II) with Chloral (III)</u>. A mixture of 0.03 mole of phosphite (II) and 0.06 mole of chloral, prepared at 20°, was heated for 10 min at 80-90° and then distilled. We isolated: 1) dimethyl α -chloromethylphosphonate (VIII), bp 102-103° (12 mm), np^{2°} 1.4360, δ^{31} P 20 ppm. PMR spectrum (60 MHz, CCl₄, δ , ppm): 1.84 d (POCH₃, ³J_{PCOH} = 11 Hz), 1.76 d (PCH₂Cl, ²J_{PCH} = 10.5 Hz); 2) bis(1,1,3-trihydroperfluoropropyl) 2,2-dichlorovinyl phosphate (V), bp 48-51° (0.05 mm).

CONCLUSIONS

Mixed bis(1,1,3-trihydroperfluoropropyl) alkyl phosphites react under mild conditions with chloral to simultaneously give stable phosphoranes with a P-C bond and vinyl phosphates.

LITERATURE CITED

- 1. A. V. Fokin, A. F. Kolomiets, V. A. Komarov, A. I. Rapkin, K. I. Pasevina, and O. V. Verenikin, Izv. Akad. Nauk SSSR, Ser. Khim., 163 (1979).
- 2. L. N. Markovskii, N. P. Kolesnik, and Yu. G. Shermolovich, Zh. Obshch. Khim., <u>49</u>, 1764 (1979).
- 3. A. V. Fokin, Yu. N. Studnev, A. I. Rapkin, K. I. Pasevina, and A. F. Kolomiets, Izv. Akad. Nauk SSSR, Ser. Khim., 1641 (1981).
- 4. I. G. Maslennikov, L. N. Kirichenko, A. V. Gabaradzhiu, L. S. Koshcheeva, A. N. Lavrent'ev, and E. G. Sochilin, Zh. Obshch. Khim., 50, 1648 (1980).
- 5. I. G. Maslennikov, A. N. Lavrent'ev, N. Ya. Kuz'mina, and L. N. Kirichenko, Zh. Obshch. Khim., 51, 1567 (1981).
- 6. I. G. Maslennikov, A. N. Lavrent'ev, G. N. Prokof'eva, and T. B. Alekseeva, Zh. Obshch. Khim., 52, 529 (1982).
- 7. B. E. Ivanov, L. A. Kudryavtseva, T. A. Zyablikova, T. G. Bykova, and É. L. Gol'dfarb, Izv. Akad. Nauk SSSR, Ser. Khim., 1497 (1971).
- 8. T. Kh. Gazizov, Yu. I. Sudarev, É. I. Gol'dfarb, and A. N. Pudovik, Zh. Obshch. Khim., 46, 924 (1976).
- 9. A. N. Pudovik, I. V. Gur'yanova, V. P. Kakurina, and N. P. Anoshina, Zh. Obshch. Khim., 41, 1227 (1971).
- A. N. Pudovik, I. V. Konovalova, V. P. Kakurina, L. A. Burnaeva, and T. A. Komissarova, Zh. Obshch. Khim., 43, 257 (1973).