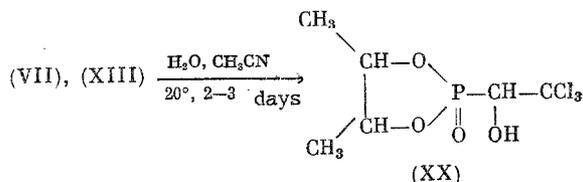


In the case of phosphoranes (VII) and (XIII), hydrolysis in acetonitrile leads to α -hydroxyphosphonate (XX) (δ P 12 ppm).



EXPERIMENTAL

The ^1H NMR spectra were taken on a Varian HA-100D spectrometer at 100 MHz and Tesla BS-467A spectrometer at 60 MHz. The IR spectra were taken on a UR-20 spectrometer. The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz.

Alkylene-(1,1,3-trihydroperfluoropropyl)phosphites. A mixture of 0.5 mole 1,1,3-trihydroperfluoropropanol and 0.5 mole Et_3N in 300 ml ether was added dropwise with stirring over 1 h to 0.5 mole alkylene chlorophosphite in 1 liter anhydrous ether at $0-5^\circ\text{C}$ and stirred for 2.5 h at 20°C . The precipitate was removed. Ether was evaporated off and subsequent distillation in vacuum gave phosphites (I)-(IV) (Table 1).

Reaction of Phosphite (I) with Chloral. a) A sample of 0.098 mole phosphite (I) in 20 ml CH_2Cl_2 was added dropwise to 0.19 mole chloral in 100 ml CH_2Cl_2 in an argon stream with stirring at from -20 to -30°C . The mixture was stirred at 20°C for 3 h. CH_2Cl_2 was removed in vacuum. The residue was maintained for 48 h at 0°C . The crystals were washed with cold CH_2Cl_2 (from -30 to -20°C) and dried in vacuum to give phosphorane (V) (Table 2).

b) The reaction was carried out by analogy to the above procedure but with a reverse order of addition (addition of the chloral to phosphite). Stirring for 3 h gave the precipitation of crystalline phosphorane (IX), which was filtered, washed with CH_2Cl_2 and dried in vacuum (see Table 2).

TABLE 1. Alkylene-(1,1,3-trihydroperfluoropropyl) phosphites (I)-(IV)

Compound	[O]	Yield, %	Bp, deg C (p, mm Hg)	n_D^{20}	$\delta\text{P, ppm}$	Chemical formula	Found / Calculated, %	
							C	H
(I)	$\begin{array}{c} \text{CH}_2\text{-O} \\ \\ \text{CH}_2\text{-O} \end{array}$	73	70(30)	1,3941	132	$\text{C}_5\text{H}_7\text{F}_4\text{O}_3\text{P}$	$\frac{27,29}{27,02}$	$\frac{3,35}{3,15}$
(II)	$\begin{array}{c} \text{CH}_3\text{CH-O} \\ \\ \text{CH}_3\text{CH-O} \end{array}$	92	73(12)	1,3885	136, 138	$\text{C}_7\text{H}_{11}\text{F}_4\text{O}_3\text{P}$	$\frac{33,83}{33,60}$	$\frac{4,47}{4,40}$
(III)		85	85(10)	1,4515	128	see [10] ref.	-	-
(IV)	$\begin{array}{c} \text{CH}_2\text{-O} \\ \\ \text{CH}_2\text{-O} \end{array}$	60	75(20)	1,3980	126	$\text{C}_6\text{H}_9\text{F}_4\text{O}_3\text{P}$	$\frac{30,29}{30,70}$	$\frac{3,92}{3,96}$

TABLE 2. 5-(1',1',3'-Trihydroperfluoropropoxy)-2,3-bis(trichloromethyl)-7,8-dimethyl-1,3,6,9-tetraoxa-5-phosphaspiro[4,4]nonanes (V), (VII), (VIII) and 5-(1',1',3'-Trihydroperfluoropropoxy)-2,3-bis(trichloromethyl)-7,8-dimethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4,4]nonanes (XI) and (XIII)

Compound	X	Mp, °C	Chemical formula	Found %		
				Calculated		
				C	H	P
(V)	Cl	77-79	C ₉ H ₉ Cl ₆ F ₄ O ₃ P	—	—	—
(VII)	Cl	103-105	C ₁₁ H ₁₃ Cl ₆ F ₄ O ₃ P	24,28	2,46	5,81
(VIII)	Br	111-113	C ₁₁ H ₁₃ Br ₆ F ₄ O ₃ P	24,22	2,38	5,68
				16,78	2,02	—
				16,25	1,60	—
(XI)	Cl	92-97	C ₉ H ₉ Cl ₆ F ₄ O ₃ P	—	—	5,99
(XIII)	Cl	113-115	C ₁₁ H ₁₃ Cl ₆ F ₄ O ₃ P	—	—	6,02
				24,76	2,79	5,52
				24,22	2,38	5,68

Reaction of Phosphite (II) with Chloral. A sample of 0.06 mole phosphite in 20 ml CH₂Cl₂ was added dropwise to 0.13 mole chloral in 100 ml CH₂Cl₂ with stirring at -10°C over 30 min in an argon stream and then stirred for 2 h at 20°C. The crystalline precipitate of phosphorane (XIII) was filtered, washed and dried. After removal of CH₂Cl₂, the filtrate crystallized upon storage for 48 h at 0°C. The crystals were washed with 10:1 pentane-ether and dried to give phosphorane (VII). The constants for (VII) and (XIII) are given in Table 2.

Reactions of Phosphite (II) with Bromal. This reaction was carried out by a procedure analogous to that given above. After 6 h at 0°C, the colorless oil obtained crystallized. The crystals were washed with 4:1 pentane-ether at -10°C and dried to give phosphorane (VIII).

Hydrolysis of Phosphoranes (VII) and (XIII). The phosphorane was dissolved in acetonitrile and maintained in the air for 48-72 h. The crystalline precipitate was separated, washed and dried to give (XX), mp 224-224.5°C, ν_{OH} 3200 cm⁻¹, δ_H(CH) 4.78 ppm, ²J_{PCH} = 11 Hz (CF₃CO₂H). Found: C, 25.19; H, 3.35; P, 11.48%. Calculated for C₆H₁₀Cl₃O₄P: C, 25.39; H, 3.53; P, 11.3%.

Reaction of Phosphite (VI) with Chloral. A sample of 0.011 mole chloral was added dropwise to 0.01 mole phosphite with stirring at ≤50°C. The mixture was heated at 100°C for 30 min. The yield of 1,1,3-trihydroperfluoropropyl-2,2-dichloro-vinyl-3-chloropropyl phosphate (XVII) was 100%, n_D²⁰ 1.4390, ν_{C=C} 1655 cm⁻¹, δ_H(=CH) 7.33 ppm, ³J_{POCH} = 5 Hz. Found: P, 8.00%. Calculated for C₈H₁₀Cl₃F₄O₄P: P, 8.08%.

CONCLUSION

For the first time, stable pentaalkoxyphosphoranes were isolated in addition to phosphoranes with P-C bond in the reactions of alkylene-(1,1,3-trihydroperfluoropropyl)phosphites with chloral or bromal.

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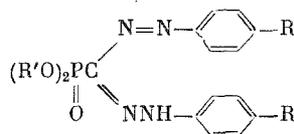
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ESR SPECTRA OF PHOSPHORUS-CONTAINING TETRAZONYL
RADICALS

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UDC 543.422.27:541.515:547.1'118

The reaction of dialkylphosphorylacetaldehydes with aryldiazonium salts gives 1,5-diaryl-3-(dialkoxyphosphoryl)formazanes (I)-(III) [1]:



$R' = Et$, $R = NO_2$ (I); $R' = Me$, $R = NO_2$ (II); $R' = Me$, $R = Br$ (III).

In order to confirm the structure of the products formed, we carried out an ESR study of the free radicals obtained by the oxidation of solutions of (I)-(III) using PbO_2 .

The oxidation of formazanes by lead dioxide in the presence or absence of oxygen readily

gives tetrazonyl radicals [2].

Solutions of (I)-(III) in toluene with PbO_2 were studied. In order to improve the solubility of (I)-(III), the samples were prepared in the presence of pyridine. The solutions were evacuated to 10^{-3} mm Hg. The ESR spectra were taken on an ER-9 spectrometer at $-20^\circ C$.

The hyperfine structure of the ESR spectra of the radicals obtained in the oxidation of (I)-(III) consists of nine broad lines due to coupling of the unpaired electron with the four equivalent nitrogen nuclei shown in Fig. 1 (a_N (I) = 6.2, a_N (II) = 5.7, a_N (III) = 6.9 Oe). Hyperfine splitting by other magnetic nuclei was not observed. The lack of coupling with the phosphorus atom may occur since the contributions to the spin density on the phosphorus atom due to spin polarization by N^2 and N^4 compensate each other [3] and the coupling constants due to the protons of the phenyl rings are less than the linewidth ($\delta H \sim 3.0$ Oe). Paramagnetic products were not detected in the electrochemical oxidation of (I)-(III).

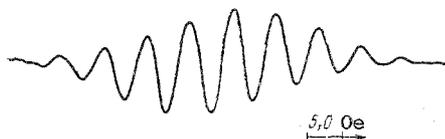


Fig. 1. ESR spectrum of the radical obtained in the oxidation of (I) by PbO_2 in toluene at $-20^\circ C$.

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