TRIALKYLSILYL ESTERS OF POLYFLUOROACYLPHOSPHONIC ACIDS

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UDC 541.91:547.1'118'128

Heteroorganic compounds that simultaneously contain silicon, phosphorus and fluorine have hardly been studied. Only some (triorganylsilyl)fluorophosphates have been described [1], which are characterized by a hydrolytic and thermal instability and possess biological activity. We were the first to synthesize some trialkylsilyl esters of polyfluoroacylphosphonic acids of type $R_FCOP(O)(OSiR_3)_2$ (R_F = either the per- or the polyfluoroalkyl group, and R = alkyl), and study their IR and NMR (H and ^{19}F) spectra.

The most convenient method for the preparation of the alkyl [2, 3] and trialkylsilyl [4, 5] esters of acylphosphonic acids is based on the reaction of the neutral esters of phosphorous acid with acyl halides (Arbuzov reaction). We studied the reaction of the tris(trialkylsilyl)phosphites with trifluoroacetyl chloride and α-hydrohexafluoroisobutyroyl chloride, which leads to the formation of the corresponding bis(trialkylsilyl)per(poly)fluoroacylphosphonates in 31-52% yield: $(R_3SiO)_3P + R_FCOCl \rightarrow (R_3SiO)_2P(O)COR_F + R_3SiCl$.

$$R_F = CF_3,\quad (CF_3)_2CH$$

The obtained compounds (Table 1) are viscous colorless liquids with a weak specific odor. All of the compounds have low refractive index values when compared with the indices of the organic [2, 3] and organosilicon [6] α-ketophosphonates. Bis(triethylsilyl)-α-hydrohexafluoroisobutyroyl phosphonate and bis(trimethylsilyl) trifluoroacetyl phosphonate exhibit an exaltation of the molecular refraction,* which is in agreement with the literature data for acyl phosphonates [3]. We were unable to obtain bis(triethylsilyl) trifluoroacetyl phosphonate in the analytically pure state, probably due to the impossibility of separating the secondary close-boiling compounds, in particular bis(triethylsilyl)phosphite, by conventional procedures.

In the IR spectra of the obtained compounds are present bands in the 1720-1730 (C=O), 1260-1280 (P=O), 970 and 1060-1080 (P−O−Si) cm^{-1} regions, and intense bands at 1000, 1100 and 1400 cm^{-1}, which were assigned to the vibrations of the C−F bond [6, 8]. A change of the alkyl radicals on the silicon atom fails to cause a shift of the characteristic frequencies of the C=O and P=O groups. At the same time, a shift of the $\nu_{P=O}$ toward lower frequencies (more than 20 cm^{-1}), and of $\nu_{C=O}$ toward higher frequencies (<5 cm^{-1}), is observed when the CF_3 group is replaced by $(CF_3)_2CH$. A shift of the P=O frequency in the IR spectra of the exo-substituted bis(trialkylsilyl)aroyl phosphonates is determined by the inductive effect of the substituent, whereas the shift of the C=O frequency is associated with the total electronic effect (I + M + C) of the substituent in the aromatic ring; the P=O shift toward high frequencies increases with increase in the −I effect of these substituents [9]. A similar phenomenon is observed in the IR spectra of the bis(trialkylsilyl)polyfluoroacyl phosphonates, and specifically for $CH_3COP(O)[OSi(C_2H_5)_3]_2$ (ν, cm^{-1}): 1700 (C=O), 1260 (P=O) [5], while for $CF_3COP(O)[OSi(C_2H_5)_3]_2$: 1726 (C=O), 1270 (P=O).

The H and ^{19}F NMR spectra of the obtained compounds also corroborate their structure. The resonance of the protons of the alkyl groups on the silicon atom in the NMR spectra of the bis(trialkylsilyl)-α-hydroperfluoroisobutyroyl phosphonates is depicted by a compressed (due to $J_{AB}/\nu_{AB} > 0.5$) multiplet of the A_3B_2 type with a center at δ 1 ppm (C_2H_5Si), or a single intense peak with a chemical shift of 0.32 ppm (CH_3Si). The signal of the methine proton in the $(CF_3)_2CHCO$ grouping is observed further downfield (5.24 ppm), which represents a septet, caused by the spin−spin coupling of the proton with the six magnetically equivalent ^{19}F nuclei ($^3J_{HF}$ = 7.6 Hz). The NMR spectra of the bis(trialkylsilyl) trifluoroacetyl phosphonates have a similar character, but do not contain the signals of the CH group [for bis(trimethylsilyl) trifluoroacetyl phosphonate, δ_{CH_3} 0.33 ppm, and $^4J_{HP} \leq 0.5$ Hz]. The NMR spectra of the ethyl groups in the $OSi(C_2H_5)_3$ grouping were

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*The values of the bond refractions were taken from Fogel [7].

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 399-402, February, 1973. Original article submitted February 8, 1972.

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TABLE 1. Bis(trialkylsilyl)polyfluoroacyl Phosphonates $R_FCOP(O)(OSiR_3)_2$

R_F	R	Yield %	Bp. °C (p, mm of Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	Found, % Si	Found, % P	Found, % F	Empirical formula	Calculated, % Si	Calculated, % P	Calculated, % F
CF_3	CH_3	46,3	128—129(7)	1,4122	1,1109	72,31	70,44	17,03	10,11	16,0	$C_8H_{18}O_4Si_2PF_3$	17,42	9,61	17,6
$(CF_3)_2CH$	CH_3	43,3	76—77(2)	1,3818	1,1845	79,39	79,03	13,49	8,12	29,2	$C_{10}H_{19}O_4Si_2PF_6$	13,89	7,66	28,2
$(CF_3)_2CH$	C_2H_5	52,2	117—118(2)	1,4073	1,1528	104,36	102,89	11,15	6,49	—	$C_{16}H_{31}O_4Si_2PF_6$	11,49	6,34	—

discussed in more detail by us previously [10, 11]. The presence of trifluoromethyl groupings in the studied compounds were corroborated by their ^{19}F NMR spectra. Thus, the ^{19}F NMR spectrum of bis(trimethylsilyl)-α-hydrohexafluoroisobutyroyl phosphonate represents a doublet of doublets, located further downfield (δ_F 0.25 ppm) relative to the signal of the internal standard, namely 1,2-dibromotetrafluoroethane (F-114B2). The multiplet nature of the signal is probably caused by the spin–spin coupling of the ^{19}F nuclei with the methine proton ($^3J_{FH}$ = 7.4 Hz) and the ^{31}P nucleus ($^4J_{FP}$ = 4.3 Hz). It is interesting to mention that the signal of the trifluoromethyl group in the ^{19}F NMR spectrum of bis(trimethylsilyl) trifluoroacetyl phosphonate is shifted relative to the peak of the standard upfield by 8.7 ppm.

As was postulated, the obtained organosilicon phosphorus compounds possess biological activity, and also the ability to impart antiadhesion and noninflammable properties to textile and paper materials.

EXPERIMENTAL METHOD

The IR spectra were obtained on a Nippon–Bunko DS-301 instrument in the 4000-600 cm^{-1} region with an accuracy of ±1 cm^{-1}. The NMR and ^{19}F NMR spectra were obtained on NMR-5535-TsLA and JNM-3 instruments at an operating frequency of 40 MHz (pure liquids), and at 80 MHz on a Tesla B-487B spectrometer (25% solutions in CCl_4, using HMDS, cyclohexane and 1,2-dibromotetrafluoroethane (F-114B2) as the internal standards.

Bis(trimethylsilyl) Trifluroacetyl Phosphonate. Through a solution of 20.0 g of tris(trimethylsilyl)phosphite at 40° was bubbled 5.0 liter (27.6 g) of trifluoroacetyl chloride. Here the reaction mixture heated up to 70° and 5.7 g (78%) of the formed trimethylchlorosilane was removed, bp 55-58° (755 mm); n_D^{20} 1.3900; d_4^{20} 0.8585. Fractional distillation of the residue gave: bis(trimethylsilyl) trifluoroacetyl phosphonate and 8.5 g of a fraction with bp 88-93° (7 mm); n_D^{20} 1.4145; d_4^{20} 1.098, which represented (based on the elemental analysis data, the IR spectra, the boiling point and the n_D^{20}) a mixture of unreacted tris(trimethylsilyl)phosphite and bis(trimethylsilyl)phosphite, contaminated with fluorine containing products.

Bis(triethylsilyl) Trifluoroacetyl Phosphonate. In a similar manner, from 10.0 g of tris(triethylsilyl)phosphite and 9.3 g of trifluoroacetyl chloride were obtained 3.0 g (31.3%) of bis(triethylsilyl) trifluoroacetyl phosphonate [bp 123-126° (5 mm); n_D^{20} 1.4436; d_4^{20} 1.070. Found: Si 15.21; P 8.68%; MR 100.6. $C_{14}H_{30}O_4Si_2PF_3$. Calculated: Si 13.85; P 7.62%; MR 94.3]; 3.1 g of unidentified fraction with bp 145-148° (5 mm); n_D^{20} 1.4440; d_4^{20} 1.0560, and 1.9 g (54.4%) of triethylchlorosilane; n_D^{20} 1.4305; d_4^{20} 0.8963. In the IR spectrum of the desired product was detected a weak band at 2400 cm^{-1}, characteristic for the P–H bond [8], which probably testifies to the presence of bis(triethylsilyl)phosphite [5].

Bis(trimethylsilyl)-α-hydrohexafluoroisobutyroyl Phosphonate. To 20.0 g of tris(trimethylsilyl)phosphite at 40° was added in drops 19.0 g of freshly distilled α-hydrohexafluoroisobutyroyl chloride in 15 min. Here the temperature rose, with the simultaneous distillation of a mixture of $(CH_3)_3SiCl$ and unreacted α-hydroperfluoroisobutyroyl chloride, the redistillation of which gave: 1.5 g of a fraction with bp 40-55° (760 mm); n_D^{20} 1.360; d_4^{20} 0.901; 7.6 g of a fraction with bp 55-57° (760 mm); n_D^{20} 1.3632; d_4^{20} 1.0215, and 3.3 g of a fraction with bp 58-61° (760 mm); n_D^{20} 1.370; d_4^{20} 1.2980 (for α-hydroperfluoroisobutyroyl chloride [12]: bp 57-59° (750 mm); n_D^{20} 1.3086; d_4^{20} 1.5492).

Fractional distillation of the residue gave bis(trimethylsilyl)-α-hydroperfluoroisobutyroyl phosphonate and 4.1 g of an unidentified fraction with bp 63-70° (2 mm); n_D^{20} 1.3930; d_4^{20} 1.1528.

Bis(triethylsilyl)-α-hydroperfluoroisobutyroyl Phosphonate. To 10.0 g of tris(triethylsilyl)phosphite at 40° was added in drops 9.0 g of freshly distilled α-hydroperfluoroisobutyroyl chloride in 3 min. The reaction mixture assumed an opalescence and the temperature rose to 65°. The system was rapidly, but carefully evacuated in order to remove the formed $(C_2H_5)_3SiCl$ and unreacted α-hydroperfluoroisobutyroyl chloride. Fractional distillation gave bis(triethylsilyl)-α-hydrohexafluoroisobutyroyl phosphonate and 1.1 g of an unidentified fraction with bp 90-105° (2 mm); n_D^{20} 1.4180.

CONCLUSIONS

The previously unknown neutral trialkylsilyl esters of polyfluoroacylphosphonic acids were synthesized. Their IR and NMR spectra were studied.

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