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Organosilicon(IV) O,O-Alkylenedithiophosphates

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Abstract

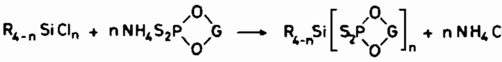
Tri- and di-organosilicon O,O-alkylenedithiophosphates, $R_{4-n}Si[S_2PO_2G]_n$ (where R = Ph, Me, G = $-C(CH_3)_2\cdot C(CH_3)_2-$, $-CH_2C(CH_3)_2CH_2-$, $-CHCH_3CH_2C(CH_3)_2-$, n = 1,2) were synthesized by treatment of organosilicon(IV) chlorides with ammonium O,O-alkylenedithiophosphates in benzene. The compounds are volatile, yellow oily liquids, miscible with common organic solvents and monomeric in refluxing benzene. Like dialkyldithiophosphate derivatives of organosilicon(IV), these cyclic chain derivatives appear to be tetrahedral, the ligand behaving as unidentate.

Introduction

In continuation to our studies on organotin(IV) O,O-alkylenedithiophosphates [1–3], we report here the synthesis and characterisation of some tri- and di-organosilicon(IV) O,O-alkylenedithiophosphates.

Results and Discussion

Organosilicon(IV) O,O-alkylenedithiophosphates were prepared by empolying the following route:

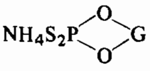


where R_3 = Ph_2Me, Me_3; n = 1. R_2 = PhMe, Me_2; n = 2. G = $-C(CH_3)_2C(CH_3)_2-$, $-C(CH_3)_2-CH_2CH-CH_3-$ and $-CH_2C(CH_3)_2CH_2-$.

These reactions are facile and proceed readily at room temperature. However, the reactants were refluxed in benzene for 4–5 h to ensure completion of the reaction. The desired product could be isolated by evaporation of solvent under reduced pressure, after filtering off the precipitated ammonium chloride.

These organosilicon(IV) O,O-alkylenedithiophosphates (Tables I and II) are oily liquids which could be further purified by distillation under reduced pressure. They are miscible with common organic solvents and show a monomeric nature in refluxing

TABLE I. Reactions of Triorganosilicon(IV) Chloride with Ammonium O,O-alkylenedithiophosphates in 1:1 Molar Ratio

Reactants (g)		Product[a] B.P./mm (°C) (physical state)	Yield (%)	Analysis (Found (Calcd.))	
R_3SiCl R=	 G=			% Si	% S
$(C_6H_5)_2CH_3$ 3.14	$-C(CH_3)_2-C(CH_3)_2-$ 3.11	$(C_6H_5)_2CH_3SiS_2\overline{POC(CH_3)_2C(CH_3)_2O}$ 112–120/0.8	92	6.41 (6.88)	15.22 (15.68)
$(C_6H_5)_2CH_3$ 1.63	$-C(CH_3)_2-CH_2-CHCH_3-$ 1.61	$(C_6H_5)_2CH_3SiS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$ 98–100/1.4	84	6.69 (6.88)	15.62 (15.68)
$(C_6H_5)_2CH_3$ 2.21	$-CH_2C(CH_3)_2)CH_2$ 2.05	$(C_2H_5)_2CH_3SiS_2\overline{POCH_2C(CH_3)_2CH_2O}$ 108–115/0.5	92	6.99 (7.12)	16.10 (16.24)
CH_3 1.45	$C(CH_3)_2CH_2CHCH_3$ 3.28	$(CH_3)_3SiS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$ 120–122/2.2	84	9.65 (9.88)	22.40 (22.52)
CH_3 1.39	$-C(CH_3)_2C(CH_3)_2-$ 3.04	$(CH_3)_3SiS_2\overline{POC(CH_3)_2C(CH_3)_2O}$ 85/2.0	84	9.70 (9.88)	22.49 (22.52)

[a] All the products are yellow oily liquids.

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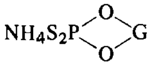
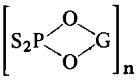
TABLE II. Reactions of Diorganosilicon(IV) Dichloride with Ammonium O,O-alkylenedithiophosphates in 1:2 Molar Ratio

Reactants (g)		Product^a B.P./mm (°C)	Yield (%)	Analysis (Found (Calcd.))	
R_2SiCl_2 R=	 $NH_4S_2P\langle O_2 \rangle G$ G=			% Sn	% S
$C_6H_5(CH_3)$ 2.45	$C(CH_3)_2C(CH_3)_2)$ 6.01	$C_6H_5(CH_3)Si[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$ 125–135/1.2	93	4.99 (5.18)	23.52 (23.61)
$C_6H_5(CH_3)$ 1.46	$C(CH_3)_2CH_2CHCH_3-$ 3.54	$C_6H_5(CH_3)Si[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_2$ 131–134/1.2	92	4.84 (5.18)	23.42 (23.61)
$C_6H_5(CH_3)$ 1.45	$-CH_2C(CH_3)_2CH_2-$ 3.26	$C_6H_5(CH_3)Si[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$ 107–110/0.9	81	5.58 (5.46)	24.81 (24.89)
C_6H_5 1.13	$-C(CH_3)_2-C(CH_3)_2-$ 2.05	$(C_6H_5)_2Si[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	93	4.62 (4.80)	21.10 (21.19)

^{a}All the products are yellow oily liquids.

TABLE III. Infrared Spectral Data (cm^{-1}) of Organosilicon(IV) O,O-alkylenedithiophosphates, $R_{4-n}Si$

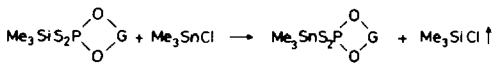


$R_{4-n}Si\left[S_2P\langle O_2 \rangle G\right]_n$

Compound	ν(P)–O–C	νP–O–(C)	Ring vibration	ν(P=S)	ν(P–S)	ν(Si–S)	ν(Si–C) ν (Si–CH$_3$)
$(C_6H_5)_2CH_3SiS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	1060	860	925	730	585	480 440	730 1255
$(C_6H_5)_2CH_3SiS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$	1060	800	980	705	590	490 450	745 1270
$(CH_3)_3SiS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	1015	870	925	700	600	455 435	1270
$(CH_3)_3SiS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$	1050	860	980	700	590	510	1270
$(C_6H_5)CH_3Si[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	1035	865	930	705	595	490	740 1270

benzene. Organosilicon(IV) O,O-alkylenedithiophosphates are extremely sensitive towards atmospheric moisture and tend to hydrolyse to give dithiophosphoric acids and organosilicon oxide.

In order to assess the relative stability of the Si–S and Sn–S bonds, trimethylsilicon(IV) O,O-alkylenedithiophosphates were treated with trimethyltin chloride. In these reactions the Si–S bond cleaved and the ligand moiety, transferred to tin trimethylsilicon(IV) chloride formed during the reaction, could be removed under vacuum at room temperature:



where G = $-C(CH_3)_2C(CH_3)_2-$ and $-CHCH_3CH_2$-$C(CH_3)_2-$.

Infrared Spectra

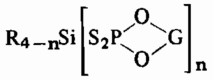
Infrared spectra of these derivatives were recorded in the region 4000–400 cm^{-1} as neat liquids; important IR absorbances are listed in Table III.

Two strong bands in the region 1015–1060 and 800–870 cm^{-1} were observed and assigned to ν(P)–O–C and νP–O–(C) stretching vibrations respectively [4–6]. The ν(P)–O–C stretching modes are most probably coupled with the motions of the atoms in the vicinity [7].

A characteristic band in the region 700–730 cm^{-1} appears to be due to ν(P=S) stretching vibrations, and this band is almost in the same range as observed in the free acids [8]. Bands of medium intensity in the region 585–600 cm^{-1} have been assigned tentatively to ν(P–S) asymmetric and symmetric stretching vibrations [4].

The stretching vibrations observed in the range 925–980 cm^{-1} can be assigned to dioxaphospholane and dioxaphosphorinane [9, 10].

TABLE IV. Proton Nuclear Magnetic Resonance Spectral Data of few Organosilicon(IV) O,O-alkylenedithiophosphates,



$R_{4-n}Si\left[S_2P\overset{O}{\underset{O}{\diamond}}G\right]_n$

Compound	Chemical shift δ (ppm)
$(C_6H_5)_2CH_3SiS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	0.9, s, 3H (Si–CH_3) 1.5, s, 12H (CH_3) 7.2–7.8, m, 10H (Si–C_6H_5)
$(C_6H_5)_2CH_3SiS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$	1.0, s, 3H (Si–CH_3) 1.3–2.0, m, 11H (CH_2, CH_3) 7.3–8.0, m, 10H (Si–C_6H_5)
$(CH_3)_3SiS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	1.4, s, 12H (CH_3) 0.2, s, 9H (Si–CH_3)
$(CH_3)_3SiS_2\overline{POC(CH_3)_2CH_2CIICH_3O}$	0.3, s, 9H (Si–CH_3) 1.2–2.3, m, 11H (CH_2, CH_3) 4.5–5.2, m, 1H (CHO)
$(C_6H_5)CH_3Si[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	1.0, s, 3H (Si–CH_3) 1.5, s, 24H (CH_3) 7.3–7.9, m, 5H (Si–C_6H_5)
$(C_6H_5)CH_3Si[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	0.5, s, 3H (Si–CH_3) 0.6, s, 12H (CH_3) 3.5–3.8, d, 8H (OCH_2)
$(C_6H_5)_2Si[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$	1.3, s, 24H (CH_3) 6.9–7.9, m, 10H (Si–C_6H_5)

The absorption bands in the region 425–510 cm^{-1} may be attributed to ν(Si–S) vibrations [11]; the Si–C and Si–CH_3 bands appear as bands of weak and strong intensity in the regions 730–745 and 1255–1270 cm^{-1}, respectively [4].

Magnetic Resonance Spectra

The ^1H NMR spectra of these derivatives were recorded in CCl_4 and chemical shift values are tabulated in Table IV.

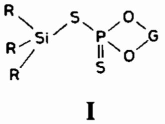
The spectra show all the characteristic resonances of ligand protons in the usual positions. The phenyl protons attached to silicon appear as multiplets in the range δ 6.9–7.9 ppm, while methyl protons attached to silicon appear as singlets in the range δ 0.2–0.3 ppm. In the phenyl methyl silicon(IV) O,O-alkylenedithiophosphates the methyl and phenyl protons appear at δ 0.5–1.0 ppm and 6.7–8.0 ppm as singlets and multiplets respectively.

The ^{29}Si NMR of only one derivative, PhMeSi-$[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$ was recorded and the value of the ^{29}Si chemical shift was −0.21 ppm. This value of chemical shift can be best interpreted in terms of four coordinate silicon [13, 14] in these derivatives, the ligands therefore behaving as monodentate.

Structural Information

In contrast to the lowering of ~30 cm^{-1} in the ν(P=S) absorption in IR spectra of the chelated derivatives of O,O-alkylenedithiophosphoric acid with a number of metals [15–17], and similar to the corresponding open chain dialkyldithiophosphate derivatives, these organosilicon alkylenedithiophosphates do not show any discernible change in the position of the ν(P=S) absorption. In view of the above and the monomeric nature of the products, ester type structure can be suggested for these derivatives. The observed ^{29}Si chemical shift values also confirm the tetrahedral environment around silicon in which ligand moieties are bonded through ester type linkages.

On the basis of the above findings and by analogy to dithiocarboxylate [18], dithiocarbamate [19] and dithiophosphate [4] derivatives of organosilicon(IV), the following molecular structures are proposed for the new derivatives.



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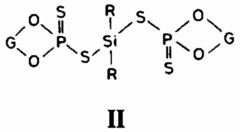

II

Experimental

The O,O-alkylenedithiophosphoric acids and their ammonium salts were prepared by a reported method. Sulfur was estimated as barium sulfate and silicon as the oxide.

Molecular weights were determined ebullioscopically. ^1H and ^{29}Si NMR spectra in $CDCl_3$ were recorded using TMS as standard. IR spectra were recorded as a neat liquid.

Reaction of Organosilicon(IV) Chloride with Ammonium O,O-alkylenedithiophosphates in Approximate Molar Ratios

A solution of organosilicon(IV) chloride was added to the suspension of ammonium O,O-alkylenedithiophosphate in benzene. The mixture was stirred for 3–4 h, then the solid was allowed to settle. After titration, the solvent was evaporated under reduced pressure to leave an oily yellow liquid which was purified by distillation under reduced pressure.

Details of the synthesis of individual compounds are given in Tables I and II.

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