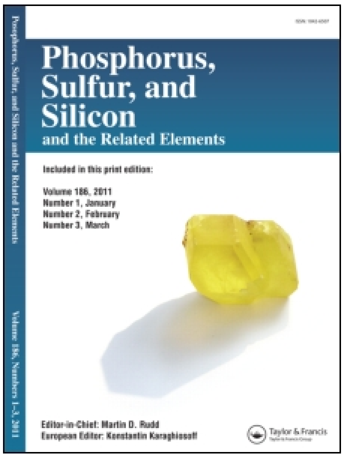

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ORGANOGERMANIUM(IV) O,O,ALKYLENEDI-THIOPHOSPHATES

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ORGANOGERMANIUM(IV) *O,O*,ALKYLENEDITHIOPHOSPHATES

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Tri- and di-organogermanium(IV) *O,O*-alkylenedithiophosphates $R_{4-n}Ge(S_2PO_2G)_n$ (where R = Ph, Bu, Et, G = $—C(CH_3)_2C(CH_3)_2—$, $—CH_2C(CH_3)_2CH_2—$, $—CH—CH_3CH_2C(CH_3)_2—$, $n = 1, 2$) were synthesized by treatment of organogermanium(IV) chlorides with ammonium *O,O*-alkylenedithiophosphates in benzene. These are volatile, liquids except the phenyl ones which are solids. All of these are miscible in organic solvents and monomeric in refluxing benzene. Like dialkyldithiophosphate derivatives of organogermanium these cyclic ones also appear to be tetrahedral with the ligands behaving as unidentate ones.

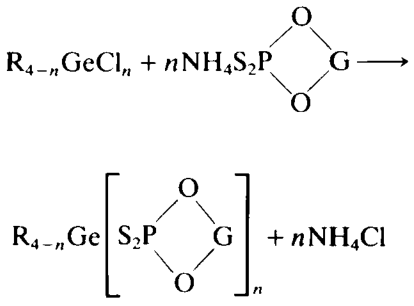
Key words: Organogermanium, dithiophosphates, volatile, unidentate, tetrahedral, spectral studies.

INTRODUCTION

In continuation of previous studies on organotin(IV) and organosilicon(IV) *O,O*-alkylenedithiophosphates,[1–4] reported here are the synthesis and characterisation of some tri- and di-organogermanium(IV) *O,O*-alkylenedithiophosphates.

RESULTS AND DISCUSSION

Organogermanium(IV) *O,O*-alkylenedithiophosphates have been prepared by the reaction of organogermanium(IV) chlorides with ammonium *O,O*-alkylenedithiophosphates in a stoichiometric ratio in dry benzene.



where R = n-Bu, Ph, Et

$G = —CH(CH_3)CH_2C(CH_3)_2—$, $—C(CH_3)_2C(CH_3)_2—$ and $—CH_2C(CH_3)_2CH_2—$; $n = 1, 2$.

TABLE I

Reactions of triorganogermanium(IV) chlorides with *O,O*-alkylenedithiophosphates

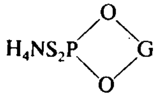
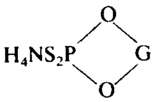
Reactants (g)					Analysis found (calcd.)	
R_3GeCl R =	 G =	Molar ratio	Product B.P./mm (°C) M.P. (Physical state)	Yield %	% Ge	% S
C_6H_5 0.41	$—(CH_3)_2CH_2CHCH_3—$ 0.31	1:1	$(C_6H_5)_3GeS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$ (White sticky solid)	90	14.30 (14.10)	12.23 (12.43)
C_6H_5 0.87	$—C(CH_3)_2C(CH_3)_2—$ 0.68	1:1	$(C_6H_5)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$ (White solid) 181	92	14.05 (14.10)	12.65 (12.43)
n-C_4H_9 0.89	$—(CH_3)_2CH_2CHCH_3—$ 0.86	1:1	$(C_4H_9)_3GeS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$ (Colourless liquid) 186/0.8	94	16.04 (15.97)	14.00 (14.07)
n-C_4H_9 1.02	$—C(CH_3)_2C(CH_3)_2—$ 0.87	1:1	$(C_4H_9)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$ (Colourless liquid) 184–185/1.2	92	16.21 (15.97)	14.01 (14.07)
n-C_4H_9 1.04	$—CH_2C(CH_3)_2CH_2—$ 1.30	1:1	$(C_4H_9)_3GeS_2\overline{POCH_2(C(CH_3)_2CH_2O}$ (Colourless liquid) 96/0.5	73	21.42 (21.31)	18.80 (18.78)
C_2H_5 1.36	$—C(CH_3)_2C(CH_3)_2—$ 1.64	1:1	$(C_2H_5)_3GeS_2\overline{PO(CH_3)_2C(CH_3)_2O}$ (Colourless liquid) 141–143/0.5	97	19.77 (19.58)	17.29 (17.27)
C_2H_5 1.12	$—(CH_3)_2CH_2CHCH_3—$ 1.46	1:1	$(C_2H_5)_3GeS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$ (Yellow liquid) 155–156/0.3	95	19.81 (19.58)	17.24 (17.27)
C_2H_5 0.86	$—CH_2C(CH_3)_2CH_2—$ 1.11	1:1	$(C_2H_5)_2GeS_2\overline{POCH_2C(CH_3)_2CH_2O}$ (Yellow oily liquid) 166–170/0.2	95	20.59 (20.35)	17.81 (17.94)

TABLE II

Reactions of diorganogermanium(IV) dichloride with ammonium *O,O*-alkylenedithiophosphates in 1:2 molar ratio

Reactants (g)					Analysis found (calcd.)	
R_3GeCl R =	 G =	Molar ratio	Product B.P./mm (°C) M.P. (Physical state)	Yield %	% Ge	% S
C_6H_5 0.53	$—CHCH_3CH_2C(CH_3)_2$ 0.95	1:2	$(C_6H_5)_2Ge[S_2\overline{POCHCH_3CH_2C(CH_3)_2O}]_2$ (White solid) 175	91	11.30 (11.19)	19.63 (19.73)
C_6H_5 0.65	$—CH_2C(CH_3)_2CH_2—$ 1.19	1:2	$(C_6H_5)_2Ge[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$ (White sticky solid)	89	11.86 (11.69)	20.68 (20.62)
n-C_4H_9 0.54	$—C(CH_3)_2(CH_3)_2—$ 0.97	1:2	$(C_4H_9)_2Ge[S_2\overline{POC(CH_3)_2C(CH_3)_2O}]_2$ (White solid) 88	85	12.11 (11.92)	21.01 (21.03)
n-C_4H_9 0.82	$—C(CH_3)_2CH_2CHCH_3—$ 1.47	1:2	$(C_4H_9)Ge[S_2\overline{POC(CH_3)_2CH_2CHCH_3)O}]_2$ (Yellow liquid 170–175/0.8	87	12.07 (11.92)	21.09 (21.03)
n-C_4H_9	$—CH_2C(CH_3)_2CH_2—$ 1.21	1:2	$(C_4H_9)_2Ge[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$ (Yellow liquid) 120–126/0.6	92	12.65 (12.50)	21.09 (22.04)

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

Organogermanium(IV) *O,O*-alkylenedithiophosphates are liquids except the phenyl ones (Tables I and II). They were purified by distillation under reduced pressure, and volatility is in the same order as that of corresponding dialkyldithiophosphate derivatives. They are miscible with common organic solvents and show a monomeric nature in refluxing benzene. These organogermanium(IV) *O,O*-alkylenedithiophosphates are stable towards moisture and air and resemble organotin(IV) *O,O*-alkylenedithiophosphates in this regard.

INFRARED SPECTRA

Infrared spectra of these organogermanium(IV) *O,O*-alkylenedithiophosphates have been recorded as neat liquids in the region 4000–200 cm^{-1} and those of solid samples as Nujol mulls. Some important characteristic IR bands are listed in Table III.

A strong band in the region 680–725 cm^{-1} appears to be due to ν (P═S) stretching vibrations and this band is almost in the same range as observed in free acids.[5] Bands in the region 560–600 cm^{-1} have been assigned tentatively to ν (P—S) asymmetric and symmetric stretching vibrations.[6]

Two characteristic bands in the region 1020–1100 cm^{-1} and 800–890 cm^{-1} have been observed and assigned to ν (P)—O—C and ν P—O—(C) stretching vibrations respectively.[6–8] The (P)—O—C stretching modes are most probably coupled with the motions of atoms in their vicinity.[9]

The bands present in the region 920–970 cm^{-1} may be assigned to dioxaphospholanes and dioxaphosphorinane ring vibrations.[10,11]

The Ge—C stretching vibrations have been assigned in the region 330–370 cm^{-1} on the basis of earlier assignments.[12,13] In triphenylgermanium(IV) chloride the asymmetric and symmetric Ge—C stretching modes appear at 335 and 303 cm^{-1} respectively[14] and do not show any significant changes on being bonded to the dithiophosphate group.

All these assignments were made tentatively on the basis of earlier reports.[7,8,15,16]

MAGNETIC RESONANCE SPECTRA

The ^1H NMR spectra of new derivatives have been recorded in CCl_4 or CS_2 and values of observed chemical shifts are tabulated in Table IV.

The signals due to protons of butyl, ethyl and phenyl protons attached to germanium appear as multiplets. These multiplets tend to be mixed with proton signals of the ligand. Resonances which can be assigned to phenyl, butyl and ethylgermanium protons fall in the ranges of δ 7.2–7.9, 0.7–2.0 and 1.0–2.1 ppm, respectively.

TABLE III

Infrared spectral data (cm^{-1}) of organogermanium(IV) *O,O*-alkylenedithiophosphates

Compound	ν (P)O—C	ν P—O—(C)	Ring vibration	ν (P=S)	ν (P—S)
$(C_4H_9)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	1020	860	920	710	600
$(C_4H_9)_3GeS_2\overline{POCH_2C(CH_3)_2CH_2O}$	1070	850	970	725	590
$(C_4H_9)_3GeS_2\overline{POCH_2C(CH_3)_2CH_2O}$	1020	800	930	680	—
$(C_2H_5)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	1020	860	920	710	600
$(C_2H_5)_3GeS_2\overline{POCHCH_3CH_2C(CH_3)_2O}$	1050	890	970	725	590
$(C_6H_5)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	1100	860	930	720	600
$(C_4H_9)_2Ge[S_2\overline{POCHCH_3CH_2C(CH_3)_2O}]_2$	1075	870	950	700	580
$(C_4H_9)_2Ge[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$	1060	—	930	690	560
$(C_6H_5)_2Ge[S_2\overline{POCHCH_3CH_2C(CH_3)_2O}]_2$	1020	890	920	680	590

TABLE IV

Proton nuclear magnetic resonance spectra data of few organogermanium(IV) *O,O*-alkylenedithiophosphates

S. No.	Compound	Chemical shift δ (ppm)
1	$(C_6H_5)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	1.4, S, 12H (CH_3) 7.2–7.8, m, 15H(Ge—C_6H_5)
2	$(C_6H_5)_3GeS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$	7.2–7.9, m, 15H(Ge—C_6H_5) 4.2–5.0, m, 1H(CHO) 0.8–2.2, m, 11H(CH_2, CH_3)
3	$(C_4H_9)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	0.7–1.6, m, 39H(Ge—C_4H_9, CH_3) 0.7–1.0, t, 9H(terminal methyl protons of butyl geranium group)
4	$(C_4H_9)_3GeS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$	0.7–2.0, m, 38H(Ge—C_4H_9, CH_3, CH_2) 4.6–5.0, m, 1H(CHO)
5	$(C_2H_5)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	1.0–1.6, m, (Ge—C_2H_5, CH_3)
6	$(C_2H_5)_3GeS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$	1.0–2.1, m, 26H(Ge—C_2H_5, CH_2, CH_3) 4.6–5.0, m, 1H(CHO)
7	$(C_2H_5)_3GeS_2\overline{POCH_2C(CH_3)_2CH_2OO}$	0.5–1.3, m, 21H(Ge—C_2H_5, CH_3) 3.6–3.9, d, 4H(OCH_2)
8	$(C_6H_5)_2Ge[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_2$	1.0–2.0, m, 22H(CH_3, CH_2) 4.4–4.9, m, 2H(CHO) 7.4–8.2, m, 10H(Ge—C_6H_5)
9	$(C_4H_9)_2Ge[S_2\overline{POC(CH_3)_2(CH_3)_2O}]_2$	0.9–2.3, m, 42H(Ge—C_4H_9, CH_3)
10	$(C_4H_9Ge[S_2\overline{POC(CH_3)_2CH_2CHCH_3O}]_2$	0.7–2.2, m, 40H(Ge—C_4H_9, CH_2, CH_3) 4.3–5.2, m, 2H(CHO)

^{31}P NMR of a few samples have been recorded (Table V). The ^{31}P NMR chemical shifts of complexes occur in the range 78.6–102.2 ppm. The chemical shift difference between the ligand and the complexes is much less. Such small changes can well be attributed to bond polarity and to the electron releasing nature of the alkyl group on germanium, which effects π-bonding with phosphorus.[17] It is therefore difficult to comment on the nature of the ligand in these organogermanium(IV) *O,O*-alkylenedithiophosphates only on the basis of such small chemical shift differences.

TABLE V

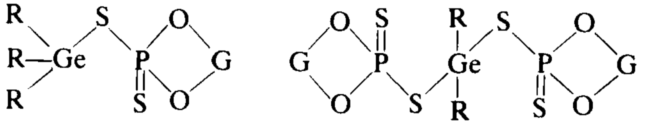
^{31}P NMR data of triorganogermanium(IV) *O,O*-alkylenedithiophosphates

S. No.	Compound	Chemical shift δ (^{31}P) ppm
1	$(C_6H_5)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	96.75
2	$(C_4H_9)_3GeS_2\overline{POC(CH_3)_2C(CH_3)_2O}$	102.16
3	$(C_2H_5)_3GeS_2\overline{POC(CH_3)_2CH_2CHCH_3O}$	78.97

STRUCTURAL INFORMATION

The organogermanium(IV) derivatives do not show any discernible change from the ν (P=S) absorption of the corresponding ligand, as lowering of about ~25 cm^{-1} is observed in the IR spectra of the chelated derivatives of *O,O*-alkylenedithiophosphoric acid with a number of metals.[18–21] The ^{31}P NMR resonances were observed for these derivatives in the region δ 78.5–102.16 ppm. This points out unidentate behaviour of ligand, since the resonances for the free ligands also appear in the same range (negligible difference).

In view of the above and the monomeric nature of the compounds, the following ester type structures can be suggested for these derivatives:



It may not be out of place to mention here that closely related compounds, such as organogermanium(IV) dithiocarboxylates,[22,23] -dithiocarbamates[14] and -dialkyldithiophosphates,[6,24] have also been assigned an ester type structure on the basis of IR and NMR spectral data.

EXPERIMENTAL

The *O,O*-alkylenedithiophosphoric acid and their ammonium salts were prepared by a reported method.[5] Sulfur was estimated as barium sulfate and germanium as the oxide.

Molecular weights were determined ebullioscopically ^{1}H and ^{31}P NMR spectra in $CDCl_3$ were recorded using TMS and H_3PO_4 as references, respectively. IR spectra were recorded as a neat liquids or Nujol mulls.

Reaction of Organogermanium(IV) chloride with ammonium-O,O-alkylenedithiophosphates in desired molar ratio. A solution of organogermanium(IV) chloride was added to the suspension of ammonium *O,O*-alkylenedithiophosphate in benzene. The mixture was stirred for 3–4 hrs, then the solid was allowed to settle. After filtration, the solvent was evaporated under reduced pressure to leave an oily yellow liquid which was purified by distillation under reduced pressure. If one uses excess of dithiophosphate, further reaction does not occur.

Details of the synethesis of individual compound are given in Tables I and II.

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