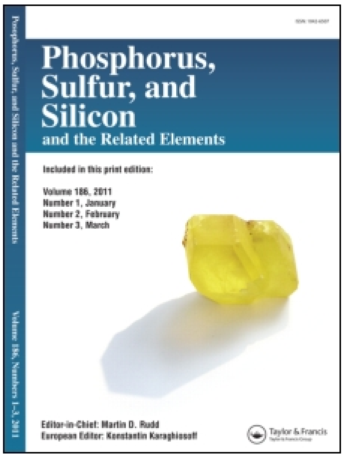

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Properties of Alkylene (Dialkyl) Dithiophosphate Derivatives of Thionyl Chloride

Neelam Harkut[a]; A. Keshawat[a]; Padam N. Nagar[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Harkut, Neelam , Keshawat, A. and Nagar, Padam N.(2006) 'Synthesis and Properties of Alkylene (Dialkyl) Dithiophosphate Derivatives of Thionyl Chloride', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 9, 2177 — 2185

To link to this Article: DOI: 10.1080/10426500600614725

URL: http://dx.doi.org/10.1080/10426500600614725

Phosphorus, Sulfur, and Silicon, 181:2177–2185, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500600614725

Taylor & Francis
Taylor & Francis Group

Synthesis and Properties of Alkylene (Dialkyl) Dithiophosphate Derivatives of Thionyl Chloride

Neelam Harkut
A. Keshawat
Padam N. Nagar
Department of Chemistry, University of Rajasthan, Jaipur, India

Alkylene (dialkyl) dithiophosphate derivatives of thionyl chloride of the general formula $\overline{OGOP}(S)SS(O)Cl$ *and* $(RO)_2(S)SS(O)Cl$ *where* $G = —CH_2(CH_3)_2CCH_2—$, $—CH_2CH_2CH(CH_3)—$, $—C(CH_3)_2CH_2CH(CH_3)—$ *and* $R = i\text{-}C_3H_7$, *have been synthesized by reacting thionyl chloride with alkylene / dialkyl dithiophosphates in a 1:1 molar ratio in refluxing benzene. A similar reaction in a 1:2 molar ratio yields the corresponding products of the type* $(\overline{OGOP}S_2)_2S{=}O$ *and* $[(RO))_2PS_2]_2S{=}O$. *It is interesting to note here that the sulfur atom of the thionyl chloride has been retained in the product, which is evidenced by sulfur analysis. The products thus obtained are light yellow colored semi solid (1:1 products) and orange colored liquids (1:2 products); and are soluble in common organic solvents. These new compounds have been characterized by elemental analysis, molecular weight measurements, and spectroscopic [IR and NMR (*^1H *and* ^{31}P*)] studies. These compounds are found to be biologically active against bacteria* S.aureus *and* E.coli.

Keywords 2-[(R)-chlorosulfinyl]thio-diisopropyl-1,3,2-dioxaphosphinane-2-sulfide; O,O,O′,O′-tetra isopropyl[sulfinylbis(thio)]bis(phosphonothioate); ammonium alkylene (dialkyl)dithiophosphate; thionyl chloride

INTRODUCTION

Dialkyl phosphonates, dialkyl thiophosphonates,[1] dialkyl dithiophosphates, and O, O′-alkylene dithiophosphates are well known for their utility as active pesticides. The metal derivatives of alkylene dithiophosphates have also been reported from our laboratory during the last 15 years.[2–5] Recently Bhasin et al.[6,7] reported novel macrocyclic complexes of nickel(II) having tetraoxatetrathio tetraaza ligands in 24–28

Received September 5, 2005; accepted December 30, 2005.

Address correspondence to Neelam Harkut, University of Rajasthan, Department of Chemistry, Jaipur, 302004, India. E-mail: neelam_gats2005@rdiffmail.com

membered rings and alkylene dithiophosphate derivatives of macrocyclic complexes of nickel(II) having N_2S_2 donors in 14–20 membered rings. In these publications, their catalytic, antimicrobial, and some biocidal aspects have also been reported. In view of their strong pesticidal activity, the organic derivatives[5,8,9] of alkylene dithiophosphates have attracted the attention of chemists. It has also been reported in the literature that asymmetric phosphorus containing disulphides and sulphonylthio has been synthesized by reacting dialkyl dithiophosphates with alkylsulphurus acid chorides (ROS(O)Cl).[10] In these derivatives, the sulphuryl (S=O) group is retained in the products. In view of the previous as well as a survey of literature that reveals that the title reactions had not been reported, it was considered of interest to extend the investigations to the syntheses and biological activity determinations of alkylene/dialkyl dithiophosphate derivatives of thionyl chloride.

RESULTS AND DISCUSSION

The reaction of thionyl chloride with alkylene/dialkyl dithiophosphate in a 1:1 (Eqs. (**1**) and (**3**)) and 1:2 (Eq. (2) and (4)) molar ratio have been carried out in refluxing benzene for ~10 h.

$$(i\text{-}C_3H_7O)_2P(S)SNH_4 + SOCl_2 \rightarrow (i\text{-}C_3H_7O)_2P(S)SS(O)Cl + NH_4Cl\downarrow \tag{1}$$

$$2(i\text{-}C_3H_7O)_2P(S)SNH_4 + SOCl_2 \rightarrow \{(i\text{-}C_3H_7O)_2P(S)S\}_2S{=}O + 2NH_4Cl\downarrow \tag{2}$$

$$\overline{OGOP}\,(S)SNH_4 + SOCl_2 \rightarrow \overline{OGOP}(S)S(O)Cl + NH_4Cl\downarrow \tag{3}$$

$$2\overline{OGOP}\,(S)SNH_4 + SOCl_2 \rightarrow \{\overline{OGOP}(S)S\}_2S{=}O + 2NH_4Cl\downarrow \tag{4}$$

where G = $-CH_2(CH_3)_2CCH_2$, $-CH_2CH_2CHCH_3-$, $-C(CH_3)_2CH_2\text{-}CHCH_3-$, and R = $i\text{-}C_3H_7$

It is interesting to mention here that the sulfur atom of the thionyl chloride had been retained in the products. These derivatives are light yellow colored semisolids (1:1) and orange colored liquids (1:2) that are soluble in benzene, chloroform, and methanol, and are found to be monomeric in nature. These compounds are stable on storage for a long time and show no tendency to convert into disulfides or polysulfides on storage.

IR Spectra

A comparison of the IR spectra of alkylene/dialkyl dithiophosphate thionyl chloride derivatives with starting materials shows the following characteristic changes (Table I).

1. A sharp sulphuryl (S=O) absorption band in these derivatives appeared in the range 1152–1140 cm^{-1} for 1:1 derivatives and 1135–1125 cm^{-1} for 1:2 derivatives.
2. Two strong absorption bands in the region 1075–1010 cm^{-1} and 840–810 cm^{-1} have been observed and are assigned to ν(P)O—C and νP—O(C) vibrations. In 1:1 derivatives, one absorption band at 790–780 cm^{-1} for νS—Cl band has been observed, while in 1:2 derivatives the νS—Cl absorption band from the region 790–780 cm^{-1} disappeared. On this basis, tentatively the formation of (S—S=O) is established.
3. A sharp absorption band in the region 660–685 cm^{-1} for νP=S and for νP—S at 580–565 cm^{-1} has been observed.
4. A new absorption band appeared at 430–450 cm^{-1} that was assigned for νS—S band in 1:1 derivatives and 450–437 cm^{-1} for 1:2 derivatives.

NMR (^{1}H and ^{31}P) Spectra

^{1}H NMR spectra of the previously discussed derivatives show signals due to dialkyl and alkylene protons of 1,2 and 1,3 glycol rings. A multiplet has been observed in the range δ4.5–5.2 ppm for —CHO and —CH_2O protons which is due to long range coupling of the magnetically active phosphorus atom (Table II).

In the decoupled ^{31}P NMR spectra of the derivatives (1–4), only one ^{31}P signal is observed for each compound in the range δ92.14–88.25 ppm. Similarly in decoupled ^{31}P NMR spectra of derivatives (5–8), only one ^{31}P signal is observed in the range δ104.55–99.87 ppm. An upfield shift is observed for these derivatives in comparison to parent dialkyl/alkylene dithiophosphates (^{31}P NMR = δ 93–78 ppm). On the basis of previously discussed and elemental analysis, the formation of P—S—S(O)— chemical linkage has been established.

EXPERIMENTAL

During the experiment, precautions were taken to exclude moisture. Alkylene/dialkyl dithiophosphate were synthesized by the reported methods.[3] Sulfur was estimated gravimetrically as barium sulphate (messenger method).[11] Thionyl chloride was distilleld

TABLE I IR Spectral Data of Alkylene/dialkyl Dithiophosphate Derivatives of Thionyl Chloride

S. no.	Compounds	ν(P)—O—C	νP—O—(C)	Ring vibrations	ν P=S	νP—S	νS—Cl	ν S=O
1	$(i\text{—}C_3H_7O)_2P(S)SS(O)Cl$	1010	810	—	670	570	790	1140
2	$OCH_2CH_2CH(CH_3)OP(S)SS(O)Cl$	1070	830	975	680	580	855	1150
3	$OC(CH_3)_2CH_2CH(CH_3)OP(S)SS(O)Cl$	1060	840	977	682	578	865	1152
4	$OCH_2(CH_3)_2CCH_2OP(S)SS(O)Cl$	1060	840	970	685	575	860	1150
5	$\{(i\text{-}C_3H_7O)_2P(S)S\}_2S{=}O$	1010	810	—	668	560	—	1125
6	$\{OCH_2CH_2CH(CH_3)OP(S)S\}_2S{=}O$	1070	835	975	670	570	—	1130
7	$OC(CH_3)_2CH_2CH(CH_3)CHOP(S)S\}_2S{=}O$	1065	840	965	675	565	—	1135
8	$\{OCH_2(CH_3)_2CCH_2OP(S)S\}_2S{=}O$	1070	840	970	672	565	—	1130

TABLE II NMR ^{1}H and ^{31}P Spectral Data of Alkylene/dialkyl Dithiophosphate Derivatives of Thionyl Chloride

S. no.	Compounds	^{1}H (δ, ppm)	^{31}P(δppm)
1	$(i\text{-}C_3H_7O)_2P(S)SS(O)Cl$	1.42–1.6, d (J = 15 hz), 12H(CH_3)	88.25
2	$OCH_2CH_2CH(CH_3)OP(S)SS(O)Cl$	1.45,d (J = 19.5 hz),3H(CH_3); 2.2–2.9, m, 2H(CH_2); 4.5-4.9, m, 3H(OCH, OCH_2)	91.87
3	$OC(CH_3)_2CH_2CH(CH_3)OP(S)SS(O)Cl$	1.8–2.2, m, 11H(CH_3,CH_2); 4.6–5.1, m, 1H(CHO)	90.67
4	$OCH_2(CH_3)_2CCH_2OP(S)SS(O)Cl$	1.2, S, 6H(CH_3); 4.5, d (J = 18 hz), 4H(CH_2O)	92.14
5	$\{(i\text{-}C_3H_7O)_2P(S)S\}_2S{=}O$	4.2–4.5, m, 4H(OCH); 1.92, d (J = 13.5 hz), 24H(CH_3)	99.87
6	$\{OCH_2CH_2CH(CH_3)OP(S)S\}_2S{=}O$	1.41, d (J = 17.5 hz), 6H(CH_3); 1.51–1.55, m, 4H(CH_2); 4.38–4.9, m, 6H(OCH_2)	104.55
7	$OC(CH_3)_2CH_2CH(CH_3)CHOP(S.)S\}_2S{=}O$	1.39–1.41, m, 22H(CH_3); 5.21, S, 3H(CHO)	103.4
8	$\{OCH_2(CH_3)_2CCH_2OP(S)S\}_2S{=}O$	1.35, S, 12H(CH_3); 4.2–4.5, d (J = 18 hz), 8H(OCH_2)	102.35

before use (b.p = 92°C). IR spectra were recorded in nujol mull (4000–200 cm^{-1}) on a FT IR spectrophotometer model Megna -IR-550 MOCOLAC-USA. Carbon and hydrogen analysis was performed on a Perkin Elmer CHN/O analyser. ^1H NMR spectra were recorded on a 90 MHz JEOL FX 90 spectrometer using TMS as an external reference. Molecular weights were determined by the kanauer vapour pressure osmometer using a $CHCl_3$ solution at 45°C. The experimental detail of a representative compound is described below. Analytical results are summarized in (Table III).

Preparation of (i-$C_3H_7O_2PS(S)S(O)Cl$ from 1:1 Molar Ratio Reaction: 2-[(R)-chlorosulfinyl]thio-diisopropyl-1,3,2-dioxaphosphinane-2-sulfide

The ammonium salt of diisopropyldithiophosphate (3.01g) in dry benzene (~50 ml) was refluxed with thionyl chloride (1.56 g) for ~10 hrs. After removing the ammonium chloride, the solvent was distilled off under reduced pressure. A light yellow colored semi solid was obtained. The above procedure was adopted for all other preparations in (1:1) molar ratio. Relevant data are given in (Table-III).

Preparation of $\{(i\text{-}C_3H_7O)_2P(S)\}S_2S{=}O$ from 1:2 Molar Ratio Reaction: O,O,O′,O′-Tetra Isopropyl [sulfinylbis(thio)]bis (phosphonothioate)

The ammonium salt of diisopropyldithiophosphate (4.85 g) was taken up in ~50 ml of dry benzene. The thionyl chloride (1.25 g) in ~50 ml of benzene was added slowly with stirring and the mixture refluxed for ~10 hrs. The precipitated ammonium chloride was filtered off. The solvent was removed from the filtrate under reduced pressure to obtain the desired product as an orange colored liquid.

BIOLOGICAL SCREENING

The growing interest in the biochemical applications and an interest in better bactricides have promoted us to screen all the newly synthesized complexes against bacteria viz., *E. coli* and *S. aureus*. These microorganisms were chosen since they are known commercially and are pathogens for human beings. The activity was checked by adopting the following method.

TABLE III Synthetic and Analytical Data of Alkylene/dialkyl Dithiophosphate Derivatives of Thionyl Chloride

	Reactant (g)		Product	Found (Calculated) (in %)			M. Wt. Found
	OGOP(S)SNH$_4$/(RO)$_2$P(S)SNH$_4$						
S. no.	G= R=	SOCl$_2$	---g,----%	C	H	S	(Calculated)
1	i-C$_3$H$_7$—	1.56	(i-C$_3$H$_7$O)$_2$P(S)SS(O)Cl	23.77	3.62	30.88	290.1
	3.01		2.80, 72.41	(24.28)	(4.72)	(32.37)	(296.5)
2	—CH$_2$CH$_2$CH(CH$_3$)—	1.25	OCH$_2$CH$_2$CH(CH$_3$)OP(S)SS(O)Cl	17.79	2.59	35.51	259.2
	2.11		2.29, 82.10	(18.01)	(3.00)	(36.02)	(266.5)
3	—C(CH$_3$)$_2$CH$_2$CH(CH$_3$)—	0.99	OC(CH$_3$)$_2$CH$_2$CH(CH$_3$)OP(S)SS(O)Cl	23.79	3.72	31.41	—
	1.90		2.09, 85.50	(24.44)	(4.07)	(32.59)	(294.5)
4	—CH$_2$C(CH$_3$)2CH$_2$—	1.09	OCH$_2$C(CH$_3$)$_2$CH$_2$OP(S)SS(O)Cl	20.67	2.91	33.77	—
	1.96		1.97, 77.19	(21.39)	(3.56)	(34.22)	(280.5)
5	i-C$_3$H$_7$—	1.25	{(i-C$_3$H$_7$O)$_2$P(S)S}$_2$S=O	24.91	4.21	41.21	469
	4.85		4.13, 83.12	(25.31)	(3.78)	(40.50)	(474)
6	—CH$_2$CH$_2$CH(CH$_3$)—	1.05	{OCH$_2$CH$_2$CH(CH$_3$)OP(S)S}$_2$S=O	22.98	4.20	45.51	—
	3.54		2.97, 81.51	(23.18)	(3.86)	(46.37)	(414)
7	—C(CH$_3$)$_2$CH$_2$CH(CH$_3$)—	1.31	{OC(CH$_3$)$_2$CH$_2$CH(CH$_3$)OP(S)S}$_2$S=O	24.91	4.52	41.21	469
	5.04		3.95, 76.51	(25.53)	(5.10)	(40.85)	(470)
8	—CH$_2$C(CH$_3$)$_2$CH$_2$—	1.29	{OCH$_2$C(CH$_3$)$_2$CH$_2$OP(S)S}$_2$S=O	26.66	5.01	42.49	439
	4.66		3.97, 79.21	(27.14)	(4.52)	(43.43)	(442)

TABLE IV Antibacterial Screening Data of the Alkylene/dialkyl Dithiophosphate Derivatives of Thionyl Chloride. Inhibition (mm) After 24 h (conc. in ppm)

		E. coli		*S. aureus*	
S. no.	Compounds	500	1000	500	1000
1	$(i\text{-}C_3H_7O)_2P(S)SS(O)Cl$	3	5	6	7
2	$OCH_2CH_2CH(CH_3)OP(S)SS(O)Cl$	10	16	13	15
3	$OC(CH_3)_2CH_2CH(CH_3)OP(S)SS(O)Cl$	11	13	16	19
4	$OCH_2(CH_3)_2CCH_2OP(S)SS(O)Cl$	8	14	14	15
5	$\{(i\text{-}C_3H_7O)_2P(S)S\}_2S{=}O$	4	5	6	8
6	$\{OCH_2CH_2CH(CH_3)OP(S)S\}_2S{=}O$	7	8	10	12
7	$OC(CH_3)_2CH_2CH(CH_3)CHOP(S)S\}_2S{=}O$	12	13	11	13
8	$\{OCH_2(CH_3)_2CCH_2OP(S)S\}_2S{=}O$	6	7	9	10

Inhibitions Zone Technique

The activity against bacteria was evaluated by the paper disc method. All compounds were dissolved in methanol in different concentrations. Paper discs of Whatman paper No.1 with a diameter of 5 mm were soaked in these solutions. These discs were placed on the medium previously seeded with organisms in petri dishes. These discs were stored in an incubator at 30 ± 2°C. The inhibition zone around each disc was measured (in mm) after 24–30 h. Bactericidal activities of the compounds against *E. coli* and *S. aureus* have been recorded in (Table IV). The inhibition zone record of the compounds clearly indicate that these are highly active against *S. aureus* and moderately active against *E. coli.*

REFERENCES

[1] P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **77,** 207 (1993).

[2] R. C. Mehrotra, G. Srivastava, and B. P. S. Chauhan, *Coord. Chem. Revs.*, **55,** 207 (1984).

[3] P. N. Nagar, In *The Chemistry and Applications of Alkoxy Aryloxy and Allide Derivatives of Elements*, pp. 351–365 (SIOC, R.B.S.A, Jaipur, India, 2003).

[4] C. Fest and K. J. Schmidt, *The Chemistry of Organophosphorus Pesticides, 2nd ed.*, (Springer Verlag, New York, 1982).

[5] A. Chaturvedi, C. S. Sharma, and P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **179,** 1793 (2004).

[6] C. P. Bhasin and D. G. Panchal, *Phosphorus, Sulfur, and Silicon*, **179,** 1545 (2004).

[7] C. P. Bhasin, A. G. Gupta, and M. P. Gongiwala, *J. Indian. Chem. Soc*, **81,** 1073 (2004).

[8] C. S. Sharma, M. K. Sharma, and P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **1,** 177 (2002).

[9] B. A. Khaskin, *Russian Chemical Reviews*, **8,** 53 (1984).

[10] W. Dabkowski, J. Michalski, and C. Radziejewski, *Phosphorus, Sulfur, and Silicon*, **375,** 8 (1980).

[11] A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis* (ELBS IV Edition, London, 1973).