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Synthesis and Properties of *N*-Bromosuccinimide Derivatives of Ammonium Dialkyl/Alkylene Dithiophosphates

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Reactions of N-bromosuccinimide with ammonium salt of alkylene (dialkyl) dithiophosphates; [OGOP₂S₂NH₄; G = –CMe₂CMe₂–CH₂CMe₂CH₂–, CMe₂CH₂CHMe–, CH₂CH₂CHMe–; (RO)₂PS₂NH₄; R = C₂H₅, n-C₃H₇, i-C₃H₇] in 1:1 molar ratio in refluxing benzene solution yields red / brown-colored sticky liquids. These newly synthesized complexes have been characterized by physicochemical and spectroscopic techniques (MW, IR, and NMR [¹H and ³¹P]). The computational semi-empirical calculations (MOPAC6P/c) have also been studied for these complexes. On the basis of above studies, the formation of P-S-N chemical linkage has been established.

Keywords IR; NMR spectra; N-Bromo succinimide, 1-((dialkyoxyphosph-orothioyl)-thio)pyrrolidine-2,5-dione, 1-[(alkylene Dithiophosphate)]-2,5-dione

INTRODUCTION

A lot of work had been reported on organic, metal and organometal derivatives of O, O' alkylene/dialkyl dithiophosphates from our laboratories^{1–10} during the last decade. In continuation of our earlier investigations into the synthesis and properties of phenyl acetyl, p-methyl benzoyl,¹¹ 2-alkylene dialkyl dithiophosphato-2-oxo-1,3,2-dioxaphosphorinane¹² and phosphorus trichloride,¹³ and thio phosphoryl chloride¹⁴ derivatives of alkylene dithiophosphates, we are interested in extending the investigations on the derivatives of the above ligands with N-bromosuccinimide.

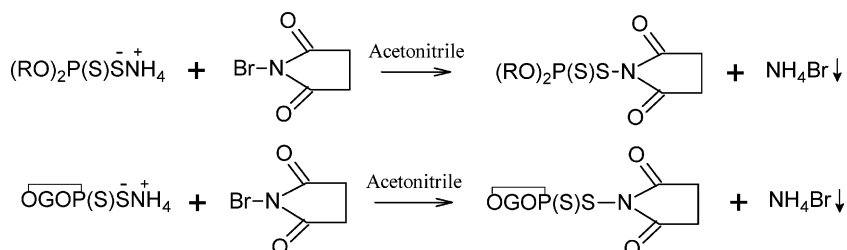
RESULTS AND DISCUSSION

Reaction of N-bromosuccinimide with ammonium dialkyl (alkylene) dithiophosphates have been carried out in the presence of anhydrous

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acetonitrile which was completed within 6 to 7 h (refluxing) with the precipitation of ammonium bromide.



These derivatives are reddish- or brown-colored sticky liquids. These are non-volatile even under reduced pressure and are miscible with common organic solvents. When heating these compounds, they tend to decompose. The above compounds are reddish- colored sticky liquids, so it could not be possible to have a single crystal X-ray data for correlation. The computational semi-empirical calculations (Mopac6p/c) for one representative complex 1-[(diethoxy phosphorothioyl)thio]pyrrolidine-2,5-dione have been studied. The molecular weight data corresponding with the results obtained. The molecular data indicates large deviation in the tetrahedral bond angle values for almost all the atoms. The data indicates good stability of the molecule ($\Delta H_f = -178.8$ K.Cal). The five-membered ring at nitrogen atom seems to be puckered, therefore, a distorted tetrahedral structure around phosphorus atom has been proposed. These computer-based calculations/data are also in good agreement with the analytical and spectroscopic (I.R, PMR, ^{31}P NMR) data obtained for these compounds.

Spectral Studies

IR Spectra

The IR spectra of these derivatives show the following characteristic changes (Table I):

- 1) the $\nu\text{C}=\text{O}$ absorption band is present in the region $1700\text{--}680\text{ cm}^{-1}$; no change in its position has been observed;
- 2) the $\nu\text{P}\text{--}\text{S}\text{--}\text{N}$ absorption band present in the region $1270\text{--}1250\text{ cm}^{-1}$ has been shifted towards a lower wave number ($20\text{--}30\text{ cm}^{-1}$) for six-membered (dioxaphosphorinane) ring derivatives;
- 3) a strong absorption band present in the region $1125\text{--}1020\text{ cm}^{-1}$ and $905\text{--}865\text{ cm}^{-1}$ has been observed for $\nu(\text{P})\text{--}\text{OC}$ and $\nu\text{P}\text{--}\text{O}(\text{C})$ stretching vibrations, respectively;

TABLE I IR Spectral Data of N-Bromosuccinimide Derivatives of Ammonium Dialkyl/Alkylene Dithiophosphate

S. no.	Compounds	$\nu(\text{P})\text{O}-\text{C}$	$\nu\text{P}-\text{O}(\text{C})$	Ring vibrations	$\nu\text{P}=\text{S}$	$\nu\text{P}-\text{S}$	$\nu\text{C}=\text{O}$	$\nu\text{S}-\text{N}$
1	$\delta\text{CH}_2\text{CH}_2\text{CHMeOP}(\text{S})\text{SN}<\begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1120	900	950	660	580	1685	1240
2	$\overline{\text{OCH}_2\text{C}(\text{Me})_2\text{CH}_2\text{OP}(\text{S})\text{SN}<\begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}}$	1115	905	960	670	575	1680	1240
3	$\overline{\text{OC}(\text{Me})_2\text{CH}_2\text{CHMeOP}(\text{S})\text{SN}<\begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}}$	1115	905	950	670	575	1685	1235
4	$\overline{\text{OC}(\text{Me})_2\text{C}(\text{Me})_2\text{OP}(\text{S})\text{SN}<\begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}}$	1125	900	964	670	580	1690	1250
5	$(t\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{S})\text{SN}<\begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1020	875	—	650	560	1700	1230
6	$(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{S})\text{SN}<\begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1050	865	—	640	555	1682	1235
7	$(n\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{S})\text{SN}<\begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1025	885	—	650	550	1700	1230

- 4) the $\nu\text{N}-\text{Br}$ absorption band present in the region $912-866\text{ cm}^{-1}$ has disappeared, which supports the formation of $>\text{P}-\text{S}-\text{N}$ chemical linkage; and
- 5) the absorption band around $640-670\text{ cm}^{-1}$ has been observed for $\nu\text{P}=\text{S}$ vibrations and absorption band present in the region $550-580\text{ cm}^{-1}$ is due to $\nu\text{P}-\text{S}$ vibrations. Ring vibrations have been observed in the region $964-950\text{ cm}^{-1}$.

¹H NMR Spectra

¹H NMR spectra of these derivatives are listed in Table II. The spectra show the characteristic resonance for alkyl and glycoxy groups present on phosphorus. A multiplet at δ 4.7–4.9 ppm is assigned for glycoxy protons, which is due to long-range coupling of these protons with magnetically active phosphorus atoms. A singlet appears for CH_2 proton of succinimide ring at δ 1.1–1.5 ppm.

³¹P NMR Spectra

In the proton-decoupled ³¹P NMR spectra, only one ³¹P NMR signal has been observed for each compound (Table II). Only one sharp resonance signal appears at δ 8–62 ppm shows purity of these compounds. An upfield shift (δ 19–22 ppm) is observed for these derivatives in comparison to parent dialkyl (alkylene) dithiophosphates, which suggests the covalent nature of newly-formed sulfur-nitrogen linkage, as well as

TABLE II NMR ¹H and ³¹P Spectral Data of N-Bromo Succinimide Derivative of Ammonium Dialkyl/Alkylene Dithiophosphate

S. no.	Compounds	¹ H (δ ppm)	³¹ P (δ ppm)
1	$\text{OCH}_2\text{CH}_2\text{CHMeOP}(\text{S})\text{SN} \begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1.40, d, 3H(CH ₃); 2.7–3.1, m, 2H(CH ₂) 4.7–4.9, m, 3H(OCH ₂ , OCH); 1.5, s, 4H(CH ₂)	59.12
2	$\text{OCH}_2\text{C}(\text{Me})_2\text{CH}_2\text{OP}(\text{S})\text{SN} \begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1.5, s, 6H(CH ₃); 4.2, d, 4H(CH ₂ O) 1.1–1.5, s, 4H(CH ₂)	59.71
3	$\text{OC}(\text{Me})_2\text{CH}_2\text{CHMeOP}(\text{S})\text{SN} \begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	2.1–2.5, m, 11H(CH ₃ , CH ₂); 5.2–5.4, m, 1H(CHO), 1.7, s, 4H(CH ₂)	60.32
4	$\text{OC}(\text{Me})_2\text{C}(\text{Me})_2\text{OP}(\text{S})\text{SN} \begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1.7, s, 12H(CH ₃); 1.6, s, 4H(CH ₂)	62.51
5	$(i\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{S})\text{SN} \begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1.42–1.53, d, 12H(CH ₃); 1.6, s, 4H(CH ₂)	55.61
6	$(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{S})\text{SN} \begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1.45–1.72, t, 6H(CH ₃); 4.9–5.3, m, 4H(OCH ₂); 1.7, s, 4H(CH ₂)	58.71
7	$(n\text{-C}_3\text{H}_7\text{O})_2\text{P}(\text{S})\text{SN} \begin{smallmatrix} \text{C}(\text{O})-\text{CH}_2 \\ \text{C}(\text{O})-\text{CH}_2 \end{smallmatrix}$	1.4–1.52, t, 6H(CH ₃); 2.01–3.1, m, 4H(CH ₂); 4.8–5.5, m, 4H(OCH ₂); 1.6, s, 4H(CH ₂)	57.32

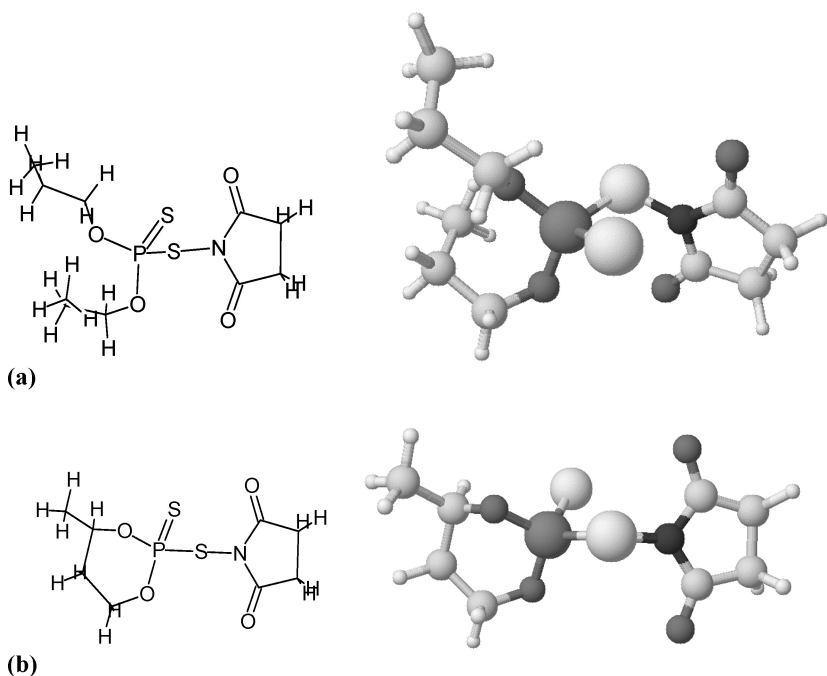


FIGURE 1 (a) 1-[(dipropoxyphosphorothioyl)thio]pyrrolidine-2,5-dione; (b) 1-[(4-methyl-2-sulfido-1,3,2-dioxaphosphinan-2-yl)thio]pyrrolidine-2,5-dione.

absence of any coordinating tendencies in above derivatives. Thereby, it appears a unidentate nature of dithiophosphate moiety.

On the basis of above spectral [IR, NMR (^1H , ^{31}P)] and other physicochemical evidence, the formation of [P—S—N] chemical bond has been established, and Figure 1 has been tentatively assigned for the above derivatives.

EXPERIMENTAL

Solvents were dried by standard methods. Ammonium salt of dialkyl/alkylene dithiophosphate were prepared by the methods reported in the literature.¹⁴ Sulfur was estimated gravimetrically as barium sulfate (messenger method).¹⁵ Molecular weights were determined by the "Knaur Vapor pressure Osmometer" using a chloroform solution at 45°C. IR spectra were recorded in Nujol mull. (4000–200 cm^{-1}) on a FT IR spectrophotometer model Megna-IR-550 MICOLAC-USA. Carbon and hydrogen analysis were performed on a Perkin Elmer CHN/O analyzer. ^1H NMR spectra were recorded in CDCl_3 solution on a 90 MHz

TABLE III Synthetic and Analytical Data of N-Bromo Succinimide Derivatives of Ammonium Dialkyl/Alkylene Dithiophosphate

S. S. No.	Reactant g (mM)		Product g, %	Found/(Calculated) (in %age)			M. wt Found (Calculated)
	OGOP(S)SNH ₄ /(RO) ₂ P(S)SNH ₄			C	H	S	
	G=	R=					
1	—CH ₂ CH ₂ CHMe— 1.37 (6.81)	1.15 (6.46)	OCH ₂ CH ₂ CHMeOP(S)SN 1.35, 70.41	33.21 (34.16)	3.81 (4.27)	21.92 (22.77)	277 (281)
2	—CH ₂ C(Me) ₂ CH ₂ — 1.34 (6.23)	1.05 (5.89)	OCH ₂ C(Me) ₂ CH ₂ OP(S)SN 1.84, 88.51	37.01 (36.61)	5.12 (4.74)	22.10 (21.69)	— (295)
3	—C(Me) ₂ CH ₂ CHMe— 1.33 (5.80)	0.98 (5.50)	OC(Me) ₂ CH ₂ CHMeOP(S)SN 1.80, 82.21	39.01 (38.83)	4.83 (5.38)	21.11 (20.71)	— (309)
4	—C(Me) ₂ C(Me) ₂ — 1.70 (7.42)	1.25 (7.02)	OC(Me) ₂ C(Me) ₂ OP(S)SN 1.75, 76.66	37.91 (38.83)	4.52 (5.38)	21.11 (20.71)	305 (309)
5	i-C ₃ H ₇ — 1.80 (7.79)	1.31 (7.35)	(i-C ₃ H ₇ O) ₂ P(S)SN 1.75, 72.61	39.01 (38.58)	6.11 (5.78)	21.11 (20.57)	— (311)
6	C ₂ H ₅ — 1.22 (8.86)	1.01 (5.67)	(C ₂ H ₅ O) ₂ P(S)SN 1.36, 80.28	34.15 (33.92)	5.16 (4.91)	23.03 (22.61)	279 (283)
7	n-C ₃ H ₇ — 1.71 (7.40)	1.25 (7.02)	(n-C ₃ H ₇ O) ₂ P(S)SN 2.04, 87.61	39.15 (38.58)	6.81 (5.78)	21.37 (20.57)	— (311)

JEOL FX 90 spectrometer using TMS as an internal reference. ^{31}P NMR was recorded in C_6H_6 using H_3PO_4 as an external reference (CDRI Lucknow). The experimental details of representative compounds are described in the following sections. Analytical results are summarized in Table III.

Preparation of $\text{OC}(\text{Me})_2\text{CH}_2\text{CHMeOP}(\text{S})\text{SNC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})$

An anhydrous acetonitrile solution (50 ml) of N-bromosuccinimide (0.98 g) was added into the suspension of ammonium salt of hexylene dithiophosphate (1.33 g) and refluxed for 6 to 7 h. Ammonium bromide precipitated within the course of reaction, was filtered off, and the solvent was removed under reduced pressure. A red/brown colored sticky liquid product (1.8 g, 82.21%) was isolated. Synthetic and analytical data are given in Table III.

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