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### SYNTHESES AND SPECTROSCOPIC STUDIES OF 2-ALKYLENE DITHIOPHOSPHATO-1,3,2- DIOXARSOLANES AND -ARSENANES

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## SYNTHESES AND SPECTROSCOPIC STUDIES OF 2-ALKYLENE DITHIOPHOSPHATO-1,3,2- DIOXARSOLANES AND -ARSENANES

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Compounds of the type  $\overline{\text{OGOAsS}_2\text{POG}'\text{O}}$  [where  $\text{G} = \text{—CMe}_2\text{CMe}_2\text{—}$ ,  $\text{—CH}_2\text{CMe}_2\text{CH}_2\text{—}$ ,  $\text{G}' = \text{—CMe}_2\text{CMe}_2\text{—}$ ,  $\text{—CH}_2\text{CMe}_2\text{CH}_2\text{—}$ ,  $\text{—CH}_2\text{CH}_2\text{CHMe—}$ , and  $\text{—CMe}_2\text{CH}_2\text{CHMe—}$ ] have been synthesized by the reactions of ammonium salts of alkylene dithiophosphates with 2-chloro-1,3,2-dioxarsolanes and -arsenanes. The new derivatives are yellow crystalline solids, soluble in common organic solvents, monomeric in nature, and are characterized by elemental analyses, molecular weight measurements, IR and multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ) spectroscopic data.

**Key words:** 2-Chloro-1,3,2-dioxarsolanes and -arsenanes; ammonium salt of alkylene dithiophosphate.

### INTRODUCTION

O,O'-dialkyl and alkylene dithiophosphoric acids contain both the  $\text{—SH}$  as well as the  $\text{P=S}$  group and thus may behave either as unidentate or a bidentate ligand in the adduct formation with transition<sup>1–3</sup> as well as non-transition<sup>4–6</sup> elements. Although a large number of alkylene dithiophosphate derivatives of arsenic (III) have been synthesized,<sup>7–9</sup> derivatives of dioxarsolanes and -arsenanes appears to be limited.<sup>10–12</sup>

In continuation of earlier investigations from our laboratory on organic<sup>11–12</sup> and dialkyl dithiophosphato derivatives<sup>10</sup> of dioxarsolanes and -arsenanes, it was considered of interest to investigate the reactions of alkylene dithiophosphate with 2-chloro-1,3,2-dioxarsolanes and -arsenanes and get a comparative view of them with open chain derivatives.

### RESULTS AND DISCUSSION

2-Alkylene dithiophosphato-1,3,2-dioxarsolanes and -arsenanes have been synthesized by reacting the ammonium salts of alkylene dithiophosphates with 2-chloro-1,3,2-dioxarsolanes and -arsenanes.

$\overline{\text{OGOAsCl}} + \text{NH}_4\text{S}_2\overline{\text{POG}'\text{O}} \rightarrow \overline{\text{OGOAsS}_2\text{POG}'\text{O}} + \text{NH}_4\text{Cl} \downarrow$  [ $\text{G} = \text{—CMe}_2\text{CMe}_2\text{—}$ ,  $\text{G}' = \text{—CMe}_2\text{CMe}_2\text{—}$  (I),  $\text{—CH}_2\text{CMe}_2\text{CH}_2\text{—}$  (II),  $\text{—CMe}_2\text{CH}_2\text{CHMe—}$  (III),  $\text{—CH}_2\text{CH}_2\text{CHMe—}$  (IV),  $\text{G} = \text{—CH}_2\text{CMe}_2\text{CH}_2\text{—}$ ,  $\text{G}' = \text{—CMe}_2\text{CMe}_2\text{—}$  (V),  $\text{—CH}_2\text{CMe}_2\text{CH}_2\text{—}$  (VI)].

The reactions were complete within ~4–6 hrs at ambient temperatures. The new derivatives are light yellow crystalline solids, soluble in common organic solvents, monomeric in nature and exhibit high sensitivity towards atmospheric moisture.

TABLE I  
Synthetic and analytical data of 2-alkylene dithiophosphato-1,3,2-dioxarsolanes and arsenanes

Com- pound no.	Reactants, g(mmole)			Product ..... g ..... %	M.P. °C	Analyses %		Molecular weight found ..... (calcd. ....)
	$\overline{\text{GOAsCl}}$ G = .....	$\overline{\text{OG'OPS}_2\text{NH}_4}$ G' .....				As found (calcd. ....)	S found (calcd. ....)	
I	$\text{—CMe}_2\text{CMe}_2$ 0.79 (3.48)	$\text{—CMe}_2\text{CMe}_2$ 0.80 (3.49)		$\overline{\text{OCMe}_2\text{CMe}_2\text{OAs}_2\text{POCMe}_2\text{CMe}_2\text{O}}$ 1.26	128	17.70 (17.63)	15.76 (15.91)	413.75 (402.22)
II	$\text{—CMe}_2\text{CMe}_2$ 0.93 (4.10)	$\text{—CH}_2\text{CMe}_2\text{CH}_2$ 0.89 (4.13)		$\overline{\text{OCMe}_2\text{CMe}_2\text{OAs}_2\text{POCH}_2\text{CMe}_2\text{CH}_2\text{O}}$ 1.42	136	19.41 (19.31)	16.21 (16.49)	—
III	$\text{—CMe}_2\text{CMe}_2$ 0.79 (3.48)	$\text{—CMe}_2\text{CH}_2\text{CHMe—}$ 0.77 (3.35)		$\overline{\text{OCMe}_2\text{CMe}_2\text{OAs}_2\text{POCMe}_2\text{CH}_2\text{CHMeO}}$ 1.27	*	17.71 (17.63)	15.68 (15.91)	363.18 (374.04)
IV	$\text{—CMe}_2\text{CMe}_2$ 1.37 (6.05)	$\text{—CH}_2\text{CH}_2\text{CHMe—}$ 1.22 (6.06)		$\overline{\text{OCMe}_2\text{CMe}_2\text{OAs}_2\text{POCH}_2\text{CH}_2\text{CHMeO}}$ 2.08	*	20.15 (20.02)	17.04 (17.11)	—
V	$\text{—CMe}_2\text{CMe}_2$ 1.12 (5.27)	$\text{—CMe}_2\text{CMe}_2$ 1.20 (5.24)		$\overline{\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OAs}_2\text{POCMe}_2\text{CMe}_2\text{O}}$ 1.90	126	19.39 (19.31)	16.38 (16.49)	363.3 (487.9)
VI	$\text{—CH}_2\text{CMe}_2\text{CH}_2$ 1.23 (5.79)	$\text{—CH}_2\text{CMe}_2\text{CH}_2$ 1.24 (5.76)		$\overline{\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OAs}_2\text{POCH}_2\text{CMe}_2\text{CH}_2\text{O}}$ 2.06	134	20.22 (20.13)	17.09 (17.20)	— —

\*Melting point is not sharp.

TABLE II  
IR spectral data of 2-alkylene dithiophosphato-1,3,2-dioxarsolanes and -arsenanes in  $\text{cm}^{-1}$

Compound no.	$\nu(\text{P})\text{—O—C}$	$\nu\text{P—O—(C)}$	Ring vibrations	$\nu\text{P—S}$	$\nu\text{P—S}$	$\nu\text{As—S}$
I	1050br	870s	960m	665m	540m	385w
II	1035br	865s	945m	660m	545s	390m
III	1005br	860m	945m	650s	530s	380m
IV	1040br	855s	940m	640m	545m	375w
V	1070br	880m	970m	680s	575m	390m
VI	1045br	860s	960m	645s	550s	385w

s = sharp; m = medium; br = broad; w = weak.

### IR Spectra

The IR spectra (Table III) of the newly synthesized derivatives show the following characteristic features:

- (i) Appearance of a new absorption band of medium intensities in the region  $390\text{--}375\text{ cm}^{-1}$  indicates the formation of a metal-sulfur bond.<sup>3,5,10,13</sup>
- (ii) The absorption bands present in the region  $1070\text{--}1005\text{ cm}^{-1}$  and  $880\text{--}855\text{ cm}^{-1}$ , are assigned to  $\nu(\text{P})\text{—O—C}$  and  $\nu\text{P—O—(C)}$  stretching modes, respectively.<sup>14</sup>  $\nu(\text{P})\text{—O—C}$  stretching modes may probably be overlapped with  $\nu\text{As—O—(C)}$  stretching modes.
- (ii) Absorption bands of medium intensities present in the region  $575\text{--}530\text{ cm}^{-1}$  have been assigned to  $\nu\text{P—S}$  asymmetric and symmetric vibrations.
- (iv) The absorption band due to  $\nu\text{P=S}$  vibrations show a chemical shift of  $15\text{--}20\text{ cm}^{-1}$  towards lower frequencies in comparison to the position in the IR spectra of alkylene dithiophosphates which may be due to  $\text{P=S} \rightarrow \text{As}$  coordination.<sup>9</sup>

### NMR Spectra

#### $^1\text{H}$

The  $^1\text{H}$  NMR spectra of these compounds show characteristic resonances of the corresponding glycoxy groups present on phosphorus and arsenic. A singlet is observed at  $\delta 1.38\text{--}1.41\text{ ppm}$  due to methyl protons but, in the case of compounds III and IV, a multiplet is observed due to overlapping of methyl and methylene protons (Table III).

#### $^{13}\text{C}$

The  $^{13}\text{C}$  NMR spectra of a few representative compounds have been recorded in  $\text{CCl}_4$  (Table III). They do not show any noticeable change from the corresponding values of alkylene dithiophosphate and dioxarsolanes and -arsenanes. The chemical shifts are very close to those found in the parent compounds. The resonance signals of  $\text{—CO}$  and methyl carbons appear in the range of  $\delta 75.81\text{--}89.78\text{ ppm}$  and  $\delta 21.32\text{--}23.92\text{ ppm}$ , respectively.

TABLE III  
NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ ) spectral data ( $\delta$  . . . ppm) of newly synthesized compound

Compound no.	$^1\text{H}$	$^{13}\text{C}$				$^{31}\text{P}$
		$-\text{CH}_3$	$-\text{CH}_2-$	$-\text{C}-$	$\text{OC}$	
I	1.38, s, 24H ( $\text{CH}_3$ )	23.91 (s)	—	—	89.78 (d) $J = 6.12$ Hz	103.46
II	1.38, s, 18H ( $\text{CH}_3$ ); 3.54–3.72, d, 4H( $\text{OCH}_2$ ); $J = 16.4$ Hz	21.32 (s)	—	32.31 (s)	75.81 (d) $J = 7.2$ Hz	91.28
III	1.26, –1.72, m, 21H ( $\text{CH}_3 + \text{CH}_2$ ); 4.56–4.87, m, 1H ( $\text{OCH}$ )	22.55 (d) $J = 9.87$ Hz 29.19 (d) $J = 9.82$ Hz	33.91, d $J = 11.02$ Hz	—	49.81 (d) $J = 2.53$ Hz	86.09
IV	1.16, –1.41, m, 17H ( $\text{CH}_3 + \text{CH}_2$ ); 3.67, d, 2H ( $\text{OCH}_2$ ); $J = 16.1$ Hz; 4.51–4.83, m, 1H ( $\text{OCH}$ )	—	—	—	—	89.71
V	1.41, s, 18H ( $\text{CH}_3$ ); 3.43–3.61, d, 4H ( $\text{OCH}_2$ ); $J = 16.74$ Hz	22.02 (s)	—	32.86 (s)	82.29 (d)	102.87
VI	1.39, s, 12H ( $\text{CH}_3$ ); 3.57–3.75, d, 8H ( $\text{OCH}_2$ ); $J = 16.6$ Hz	—	—	—	—	92.33

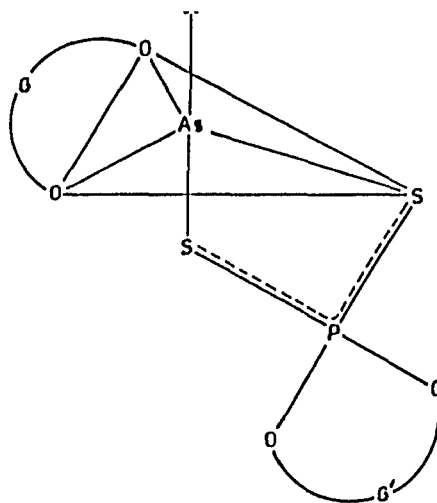


FIGURE 1 Trigonal bipyramidal geometry of 2-alkylene dithiophosphato-1,3,2-dioxarsolanes and -arsenanes.

### $^{31}\text{P}$

The  $^{31}\text{P}$  { $^1\text{H}$ } NMR spectra were measured in benzene and are summarized in Table III. The chemical shift of 1,3,2-dithiophospholanes is 92.0 ppm while that for 1,3,2-dithiophosphorene is 75.0–77.0 ppm; thus, a pronounced effect of the ring size on  $^{31}\text{P}$  chemical shift is exhibited.<sup>15</sup> The complexes show a low field shift of ~8–10 ppm with respect to the parent dithio acids. This is indicative of a bidentate mode of bonding of the ligand moiety in these complexes,<sup>3,9,13</sup> which is further supported by IR spectral data.

Based on the above mentioned observations a trigonal bipyramidal structure has been tentatively assigned for these complexes (Figure 1).

### EXPERIMENTAL

Stringent precautions were taken to exclude moisture throughout all the experimental manipulations. 2-chloro-1,3,2-dioxarsolanes and the ammonium salt of alkylene dithiophosphate have been synthesized by the methods reported in the literature.<sup>15</sup> Arsenic and sulfur were estimated by the Iodometric method<sup>16</sup> and Messenger's method,<sup>16</sup> respectively. Molecular weights were measured in chloroform using a Knauer vapour pressure osmometer, IR spectra were recorded on a Perkin Elmer-577 spectrophotometer in the range of 4000–200  $\text{cm}^{-1}$  using CsI cells.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$ ,  $^{13}\text{C}$  in  $\text{CCl}_4$  and  $^{31}\text{P}$  in  $\text{C}_6\text{H}_6$  on a JEOL FX 90 Q spectrophotometer using TMS (for  $^1\text{H}$  and  $^{13}\text{C}$ ) and  $\text{H}_3\text{PO}_4$  (for  $^{31}\text{P}$ ) as the external standards.

**Reaction of 2-chloro-1,3,2-dioxarsolanes with ammonium salt of alkylene dithiophosphates.** To a solution of  $\text{OCMe}_2\text{CMe}_2\text{OAsCl}$  (0.79 g, 3.48 mmole) in benzene was added  $\text{OCMe}_2\text{CMe}_2\text{OPS}_2\text{NH}_4$  (0.80 g, 3.49 mmole) and the mixture was refluxed for ~6 hrs. The precipitated  $\text{NH}_4\text{Cl}$  (0.18 g, Calcd. 0.18 g) was removed by filtration, the solvent was removed from the filtrate *in vacuo* to afford a light yellow product (1.26 g, 90% yield) Calcd. for  $\text{C}_{12}\text{H}_{24}\text{O}_4\text{PS}_2\text{As}$ : S, 15.91; As, 17.63; M, 402.22. Found: S, 15.76; As, 17.70; M, 413.75.

Since the same method was applied for synthesis of all these derivatives, the results of the remaining experiments have been summarized in Table I.

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