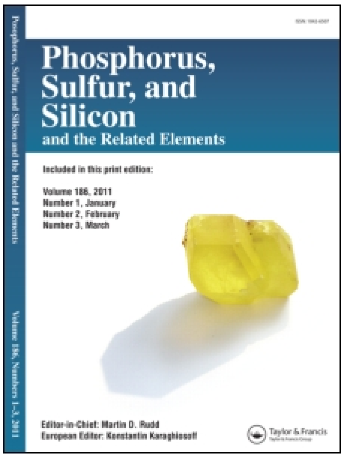

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Dialkylphosphonate and Thiophosphonate (Open Chain and Cyclic) Derivatives of Arsenic(III) and Tin(IV)

R. C. Mehrotra[a]; G. Srivastava[a]; P. N. Nagar[a]
[a] Chemical Laboratories, Rajasthan University, Jaipur, India

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DIALKYLPHOSPHONATE AND THIOPHOSPHONATE (OPEN CHAIN AND CYCLIC) DERIVATIVES OF ARSENIC(III) and TIN(IV)

R.C. MEHROTRA, G. SRIVASTAVA and P.N. NAGAR
Chemical Laboratories, Rajasthan University, Jaipur-302004
(India)

Dialkylphosphonates[1] and -thiophosphonates[2] are versatile ligands but except for a few brief reports[3-9] the chemistry of their derivatives with group IV and V elements remains unexplored. The corresponding derivatives of cyclic phosphonates and thiophosphonates[10] are virtually unknown.

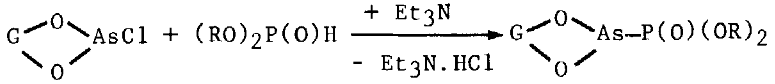
In view of their ambident nature, the modes of bonding in the derivatives of dialkylphosphonates and thiophosphonates with different types of metals and organometallic moieties present interesting possibilities. The formation of both metal-phosphorus and metal-X-phosphorus (X = O or S) bonded derivatives has been postulated in a few publications[11,12], but in most cases, the supporting evidence appears to be inconclusive. The present communication describes the work carried out during last 4 years on the derivatives of the above ligands and their cyclic analogues with arsenic(III) and tin(IV).

The reactions[13] described in the following 5 groups typify the synthetic routes adopted during the present investigations :

$$\text{(I)}\quad (R'O)_{3-n}AsCl_n + n(RO)_2P(O)H \xrightarrow[-\ nEt_3N.HCl]{+\ nEt_3n}$$

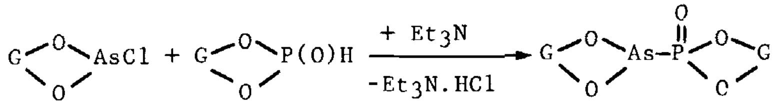
$$(R'O)_{3-n}As\ [P(O)(OR)_2]_n \qquad \text{(A)}$$

(II)



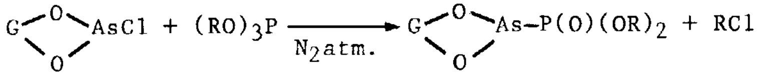
(B)

(III)



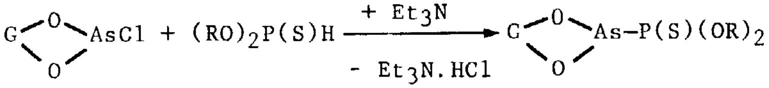
(C*)

(IV)



(D)

(V)



(E)

Where

R = Me, Et, n-Pr, i-Pr, n-Bu, t-Bu, Allyl ; R' = i-Pr;

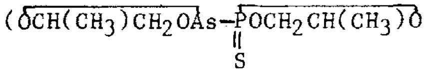
G = $\overset{}{\underset{|}{C}}H_2-\underset{|}{C}H_2$, $CH_3-\underset{|}{C}H-\underset{|}{C}H_2$, $(CH_3)_2.\underset{|}{C}-CH_2-\underset{|}{C}H-CH_3{}^{*}$

$(CH_3)_2\underset{|}{C}-\underset{|}{C}(CH_3)_2$, $\underset{|}{C}H_2-C=C-\underset{|}{C}H_2$.

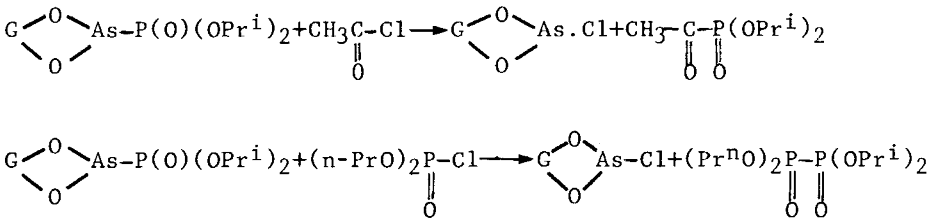
Compounds (A-E) are coloured oily products except (C^*) which is a crystalline solid. These tend to decompose at ambient temperatures and are soluble in common organic solvents. Alkoxy derivatives are moisture sensitive while tris-derivatives are water stable. The stability of these newly synthetized derivatives appears to follow the order :

Me < Et < n-Pr << i-Pr > n-Bu

2-Dialkylthiophosphonato-1,3,2-diox-arsolanes and -arsenanes, however, appear to be less stable than the corresponding 2-dialkylphosphonato-1,3,2-diox-arsolanes and -arsenanes. The cyclic-thiophosphonate derivative, e.g. $(\overline{OCH(CH_3)CH_2OAs}-\underset{\parallel \atop S}{\overline{P}OCH_2CH(CH_3)O})$ was also obtained by the above route.



I.R. spectra of these derivatives (A-D) show a sharp absorption band at 1250-1275 cm^{-1} which is characteristic of free phosphoryl (P=O) groups. I.R. spectra of compounds (E) show the presence of free thiophosphoryl (P=S) band at 650 cm^{-1}. A new sharp band observed at 550-580 cm^{-1} has been tentatively assigned to a ν As-P band. ^1H NMR spectra show disappearance of the P-H signal at 6.8-7.2 δ (ppm) and appearance of signals characteristic for alkoxy protons present on both phosphorus and arsenic. ^{31}P NMR spectra of a few representative compounds show characteristic resonance peaks in the region of P(V). All the above studies lead to the conclusion that the products are arsenic-phosphorus bonded derivatives, which is also corroborated by the mode of cleavage of the As-P bond in compounds (B&D) by acetyl chloride and dialkyl phosphorochloridate, as represented below :



Similar studies have been extended to organotin moieties and a large number of derivatives, $R_nSn[P(X)(OR)_2]_{4-n}$ have been synthesized. These are volatile liquids, soluble in common organic solvents, and show monomeric behaviour in benzene. The appearance of ν P=O absorption band in the I.R. spectra and, e.g. multiplicity of ^{31}P resonance in NMR spectra in derivatives of the type $(RO)_2P(O)Sn\leqslant$ indicates the possibility of tin-phosphorus direct linkage.

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