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A SULFOTROPIC MOLECULAR REARRANGEMENT OF DIPHENYLPHOSPHINYL DIORGANODITHIOARSINATES. FORMATION OF DIORGANOARSENIC(III) DIPHENYLDITHIOPHOSPHINATES

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Summary

The reaction of chlorodiphenylphosphine with sodium organodithioarsinates, NaS_2AsR_2 (R = Me, Ph) yields diorganoarsenic(III) diphenyldithiophosphinates $R_2As-S-P(S)Ph_2$ (instead of the expected diphenylphosphinyl dithioarsinates $Ph_2P-S-As(S)R_2$) as a result of a rearrangement involving migration of sulfur from arsenic(V) to phosphorus(III). This is confirmed by infrared and NMR spectroscopic data. An alternative preparation of the phenyl derivative based upon the direct reaction of $Ph_2P(S)SH$ with $(Ph_2As)_2O$ provides additional proof.

Introduction

Organodithiophosphorus anions (dithiophosphates, $(RO)_2PS_2^-$ and dithiophosphinates, $R_2PS_2^-$) exhibit a variety of coordination patterns towards metals, which can be classified as monodentate, bidentate and bridging. The most interesting results are obtained when the dithiophosphorus ligand is attached to a nontransition metal atom or to an organometallic moiety (see for a review ref. 1). Although dithioarsinates, $R_2AsS_2^-$ are closely related to their phosphorus analogs, they have been much less used as ligands. Transition metal organodithioarsinates have been studied to some extent [2a–2e], and the only nontransition metal derivatives reported are those of antimony, bismuth [2f], indium, thallium and lead [2g] dithioarsinates; some organo-tin [3], -lead [4], -germanium [4], and -silicon [5] derivatives were recently reported.

We have extended this work to a study of the reaction of chlorodiphenylphosphine with sodium dimethyl- and diphenyl-dithioarsinate.

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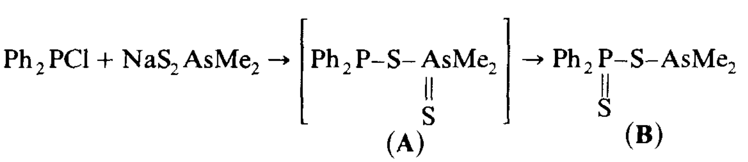
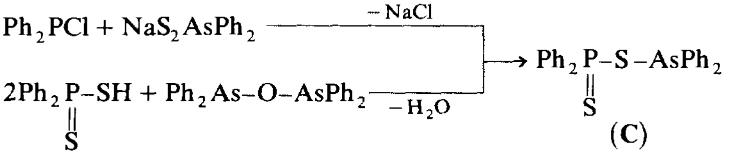
Results and discussion

The reaction of chlorodiphenylphosphine with sodium dimethyldithioarsinate was expected to give the diphenylphosphinyl thioester (**A**) of dimethyldithioarsinic acid; instead, the compound obtained was the isomeric dimethylarsenic(III) diphenyldithiophosphinate (**B**), whose identity was established with the aid of infrared and NMR spectra (eq. 1). The formation of **B** can be explained by migration of a sulfur atom from arsenic(V) to phosphorus(III), which can be described as a sulfotropic rearrangement. Although the intermediate **A** was not isolated, there is some evidence about its presence in solution, therefore **B** can be regarded as a rearrangement product.



$$Ph_2PCl + NaS_2AsMe_2 \rightarrow \left[\underset{(\mathbf{A})}{Ph_2P\text{-}S\text{-}\underset{\underset{S}{\|}}{As}Me_2} \right] \rightarrow \underset{(\mathbf{B})}{Ph_2\underset{\underset{S}{\|}}{P}\text{-}S\text{-}AsMe_2} \qquad (1)$$

Similarly the reaction of chlorodiphenylphosphine with sodium diphenyldithioarsinate gave a rearranged product **C**, which was also synthesized directly, by an alternative route, from diphenylarsenic(III) oxide and diphenyldithiophoshinic acid (eq. 2). The two samples of **C**, obtained in these reactions were shown to be identical (elemental analysis, infrared and NMR spectra). The ability of phosphorus(III) to extract a sulfur from a dithioarsinate was previously observed in a reaction of triphenylphosphine with rhenium tetracarbonyl dimethyldithioarsinate $[(CO)_4ReS_2AsMe_2]$, which gave thiotriphenylphosphine $SPPh_3$, but the other products of this reaction were not identified [6].



$$\begin{array}{l} Ph_2PCl + NaS_2AsPh_2 \xrightarrow{-NaCl} \\ 2Ph_2\underset{\underset{S}{\|}}{P}\text{-}SH + Ph_2As\text{-}O\text{-}AsPh_2 \xrightarrow[-H_2O]{} \end{array} \rightarrow \underset{(\mathbf{C})}{Ph_2\underset{\underset{S}{\|}}{P}\text{-}S\text{-}AsPh_2} \qquad (2)$$

Infrared spectra

A dimethyldithioarsinate with structure **A** is expected to exhibit an IR band near 480 cm^{-1} due to As=S double bond stretching, which is present in nontransition metal derivatives containing monodentate dimethyldithioarsinate groups, e.g. $Me_2As(=S)\text{-}S\text{-}AsMe_2$ [7] and $Me_2Sn[S\text{-}As(=S)Me_2]_2$ [3]. This band is absent in the spectrum of the diphenylphosphinyl derivative, suggesting structure **B**. The infrared spectrum of $Ph_2PS_2AsMe_2$ exhibits two bands (Table 1) at 530 and 640 cm^{-1}, which are also present in the spectrum of the acid $Ph_2P(=S)SH$ [8], and can be assigned to $\nu(P\text{-}S)$ and $\nu(P=S)$, respectively, again suggesting structure **B**. The band at 415 cm^{-1} (with a shoulder at 428 cm^{-1}) found in the infrared spectrum of our compound, and also observed in the spectrum of $Me_2Sn(S\text{-}As(=S)Me_2)_2$, is assigned to $\nu(As\text{-}S)$. The arsenic–carbon stretchings provide additional support in favor of structure **B**; thus, the shift of $\nu(As\text{-}C)$ bands from 603 and 625 cm^{-1} in NaS_2AsMe_2, to 572 and 585 cm^{-1} in our compound, can be explained by a conversion of Me_2As^{V} to Me_2As^{III} groups [7,9]. A normal coordinate analysis of $Me_2AsS_2^-$ anion established

TABLE 1

COMPARISON OF THE INFRARED SPECTRA OF $Ph_2PS_2AsR_2$ (R = Me, Ph) WITH THOSE OF RELATED COMPOUNDS

$Ph_2\underset{\underset{S}{\Vert}}{P}{-}S{-}AsMe_2$	$Ph_2\underset{\underset{S}{\Vert}}{P}{-}S{-}AsPh_2$	$Ph_2\underset{\underset{S}{\Vert}}{P}{-}SH$	$Me_2Sn(S{-}\underset{\underset{S}{\Vert}}{As}Me_2)_2$	$Me_2Sn(S{-}\underset{\underset{S}{\Vert}}{As}Ph_2)_2$	Assignment
415 m 428 sh	432 m	–	415 m	416 m	ν(As–S)
–	–	–	480 s	484 s	ν(As=S)
530 m	530 m	530 m	–	–	ν(P–S)
572 m	–	–	–	–	$\nu_s(As^{III}{-}C)$
585 m	–	–	–	–	$\nu_{as}(As^{III}{-}C)$
–	–	–	603 m	–	$\nu_s(As^{V}{-}C)$
–	–	–	625 m	–	$\nu_{as}(As^{V}{-}C)$
640 ms	645 ms	640 ms	–	–	ν(P=S)

that the ν(As–C) vibrations are not coupled with ν(As–S) modes and thus can be regarded as diagnostic [10]. In $Me_2As{-}SR$ compounds the ν(As–C) vibrations appear at 570–590 cm^{-1} [9].

The band at 432 cm^{-1} in the spectrum of compound **C** can be assigned to As–S single bond stretching, this band was observed in all the organometallic diphenyldithioarsinates investigated [4]. No band assignable to ν(As=S) is present in the spectrum of compound **C**.

NMR spectra

The ^1H NMR spectrum of $Ph_2PS_2AsMe_2$, recorded in CCl_4, exhibits two peaks, at δ 1.42 ppm and δ 1.32 ppm. These can be assigned to a $(CH_3)_2As^{III}{-}S$ group [8]. When ^1H NMR spectroscopy was used to monitor the formation of $Ph_2PS_2AsMe_2$ (by recording the spectrum of the reaction mixture in CCl_4 solution, from room temperature to 70°C) three peaks were observed, at δ 2.00, 1.42 and 1.32 ppm. The peak at 2.00 ppm is due to proton resonances in a $(CH_3)_2As^{V}{=}S$ group [3,4,5,7]. As the reaction proceeds the intensity of the δ 2.00 ppm peak decreases and finally dissapears, while the peak at δ 1.42 ppm increases. The peaks due to phenyl protons

TABLE 2

^1H NMR AND ^{31}P NMR SPECTRA

Compound	$\delta(^1H)$ (ppm) [a]	$\delta(^{31}P)$ (ppm) [b]
$(C_6H_5)_2\underset{\underset{S}{\Vert}}{P}{-}S{-}As(CH_3)_2$	CH_3: 1.42; 1.32 s C_6H_5: 7.37–7.92 m	61.2
$(C_6H_5)_2\underset{\underset{S}{\Vert}}{P}{-}S{-}As(C_6H_5)_2$		
	Sample I [c] C_6H_5: 7.20–7.95 m	62.1
	Sample II [d] C_6H_5: 7.20–7.95 m	61.7

[a] In CCl_4 solution; relative to TMS as internal standard. [b] Relative to 85% H_3PO_4. [c] Sample prepared from Ph_2PCl and NaS_2AsPh_2. [d] Sample prepared from $Ph_2P(S)SH$ and $(Ph_2As)_2O$.

(δ 7.37 to 7.92 ppm with J(P–H) 12 Hz) are as expected, and offer no further information.

The ^{31}P NMR spectra exhibit the peaks listed in Table 2, and are in agreement with the presence of S–P(=S)Ph$_2$ groups. Thus, the ^{31}P NMR peaks for related compounds are as follows: δ 65.9 ppm for Ph$_2$P(S)SMe [11], and δ 64.4 ppm for Ph$_2$P(S)Cl [12].

Experimental

The reagents used were prepared by published methods: NaS$_2$AsMe$_2$ [2a,2b], NaS$_2$AsPh$_2$ [2c], Ph$_2$P(S)SH [8], (Ph$_2$As)$_2$O [13]. Clorodiphenylphosphine was a commercial sample.

Reaction of chlorodiphenylphosphine with sodium dimethyldithioarsinate

Sodium dimethyldithioarsinate (0.88 g, 0.004 mol) in 20 ml dry ethanol was treated with a solution of 0.88 g (0.004 mol) chlorodiphenylphosphine, in 15 ml CCl$_4$. The sodium chloride which separated was filtered off and the filtrate was evaporated under vacuum to leave a viscous oil, which crystallized after several days of storage in a vacuum desiccator to give $(CH_3)_2AsS_2P(C_6H_5)_2$ as a crystalline solid, m.p. 68–70°C. Yield: 0.98 g, (68%). Found: C, 47.45; H, 4.48; As, 20.71. $C_{14}H_{16}AsPS_2$ calcd.: C, 47.94; H, 4.51; As, 21.18%.

Reaction of chlorodiphenylphosphine with sodium diphenyldithioarsinate

Sodium diphenyldithioarsinate (0.95 g, 0.003 mol) and chlorodiphenylphosphine (0.66 g, 0.003 mol) were mixed (1/1 molar ratio) in 40 ml CCl$_4$ at room temperature. After 30 min the sodium chloride was filtered off and the solvent was evaporated in vacuum. The residual oil crystallized on storage (ca. 2 weeks) to give solid $(C_6H_5)_2AsS_2P(C_6H_5)_2$, m.p. 78-80°C. Yield 1.15 g (80%). Found: C, 59.84; H, 4.00; As, 15.18. $C_{24}H_{20}AsPS_2$ calcd.: C, 60.25; H, 4.18; As, 15.69%.

Reaction of diphenyldithiophosphinic acid with diphenylarsenic oxide

A solution of diphenyldithiophosphinic acid (0.75 g, 0.003 mol) in 15 ml benzene was treated with 1.42 g (0.003 mol) diphenylarsenic oxide in 25 ml benzene. The mixture was heated under reflux and the water formed was removed as azeotrope and collected in a Dean–Stark trap. After evaporation of the solvent in vacuum, a viscous oil was obtained, which crystallized after several days, to give 1.35 g (93% yield) of $(C_6H_5)_2AsS_2P(C_6H_5)_2$, m.p. 78–80°C. The mixed melting point with a sample from the previous preparation was not depressed. Found: C, 59.87; H, 4.01; As, 15.24. $C_{24}H_{20}AsPS_2$ calcd.: C, 60.25; H, 4.18; As, 15.69%.

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