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NOTE

ORGANOMETALLIC ACETYLENES OF PHOSPHORUS, ARSENIC AND ANTIMONY. SYNTHESIS AND SPECTRAL DATA OF TRIS(3,3-DIMETHYL-1-BUTYNYL) DERIVATIVES*

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Trialkynylphosphines, arsines and stibines have been synthesized and investigated during the past five years[1,2]. Phosphorus derivatives have been studied in detail[3]. In an earlier publication, we reported that tert-butyl groups stabilize the organometallic acetylenes[4]. Since the trialkynyl derivatives of the fifth main group are not very stable (the triethynyl compounds are explosive), we prepared the corresponding tris(3,3-dimethyl-1-butynyl) derivatives to establish the possibility of a similar stabilizing effect in these compounds.

Synthesis and reactions of these compounds may be represented by the following equations where M = P, Sb or As:

$$MCl_3 + 3\ LiC{\equiv}C{-}C(CH_3)_3 \xrightarrow{THF} [(CH_3)_3C{-}C{\equiv}C]_3M + 3\ LiCl \qquad (1)$$

$$\begin{tikzcd} {[(CH_3)_3C{-}C{\equiv}C]_3P} \arrow[dr, "H_2O_2", "Acetone"'] & & (2a) \\ & {[(CH_3)_3C{-}C{\equiv}C]_3PO} & (2b) \\ POCl_3 + 3\ LiC{\equiv}C{-}C(CH_3)_3 \arrow[ur, "THF"] & & \end{tikzcd}$$

$$[(CH_3)_3C{-}C{\equiv}C]_3P + S_8 \xrightarrow{CS_2} [(CH_3)_3C{-}C{\equiv}C]_3PS \qquad (3)$$

The products were obtained in excellent yields; however, the corresponding bismuth derivative could not be isolated. The physical properties and analytical data are summarized in Table 1.

These compounds can be stored at room temperature and are not sensitive to light in contrast to the corresponding Group IVb derivatives. Their thermal stability is remarkable. All three compounds, prepared by equation (1), melt without

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TABLE 1

DATA AND ANALYSES OF ORGANOMETALLIC DERIVATIVES

Product	Yield (%)	M.p. (°C)	Mol.wt.[a] found (calcd.)	C (%) found (calcd.)	H (%) found (calcd.)
$[(CH_3)_3C{-}C{\equiv}C]_3P$	98	83–84	274 (274)	78.70 (78.79)	9.76 (9.92)
$[(CH_3)_3C{-}C{\equiv}C]_3As$	99	62–63	306 (318)	67.82 (67.92)	8.27 (8.55)
$[(CH_3)_3C{-}C{\equiv}C]_3Sb$	91	65–66	361 (365)	59.42 (59.21)	7.86 (7.65)
$[(CH_3)_3C{-}C{\equiv}C]_3P{=}O$	98	141–142	292 (290)	74.45 (74.45)	9.49 (9.37)
$[(CH_3)_3C{-}C{\equiv}C]_3P{=}S$	88	112–113	302 (306)	70.60 (70.55)	9.10 (8.88)

[a] In benzene.

decomposition and recrystallize on cooling. The same three derivatives even sublime readily between 90°–110°/0.05 mm. A DTA study showed no signs of decomposition up to fairly high temperatures: P: 283°; As: 260°; and Sb: 270°. The observed melting point temperatures for the phosphine oxide and sulfide are: 336° and 305°. The endotherms observed at these temperatures are probably not caused by decomposi-

TABLE 2

SPECTRAL DATA OF THE COMPOUNDS

IR[a] (as KBr pellets)					PMR (τ)[c]
Compound	C≡C stretch (cm^{-1})	CH_3 wag. and C–C stretch (cm^{-1})[6]	M–C stretch[a] (cm^{-1})[5]	P=X stretch[b] (cm^{-1})	
$[(CH_3)_3C{-}C{\equiv}C]_3P$	2175 s 2207 m	777 s 947 m	576 s 602 m		8.73
$[(CH_3)_3C{-}C{\equiv}C]_3As$	2155 s 2189 s	752 s 919 m	495 s 542 w		8.74
$[(CH_3)_3C{-}C{\equiv}C]_3Sb$	2149 s 2176 s	747 s 912 m	479 s 550 w		8.74
$[(CH_3)_3C{-}C{\equiv}C]_3P{=}O$	2186 s 2212 vs 2233 sh	792 s 967 s	576 sh 610 vs	1235 vs	8.66
$[(CH_3)_3C{-}C{\equiv}C]_3P{=}S$	2177 vs 2200 sh 2218 s	790 s 958 s	556 m 588 s	689 ms	8.67

[a] M = P, As, Sb. [b] X = O, S. [c] CCl_4 as solvent; TMS as internal standard; τ for $(CH_3)_3C$– protons; $\tau = 8.79$ for $(CH_3)_3C{-}C{\equiv}CH$.

TABLE 3

MASS SPECTRA OF THE COMPOUNDS

Compound	Parent ion (*m/e*)	Fragments (*m/e*)			
		$-CH_3$	$-(CH_3)_2$	$-(CH_3)_3$	$-(CH_3)_3C$
$^{31}P[C\equiv C-C(CH_3)_3]_3$	274	259	244	229	217
$^{75}As[C\equiv C-C(CH_3)_3]_3$	318	303	288	273	261
$^{121}Sb[C\equiv C-C(CH_3)_3]_3$	364	349	334	319	307
$^{123}Sb[C\equiv C-C(CH_3)_3]_3$	366	351	336	321	309

tion of these compounds but by their sublimation at atmospheric pressure. The oxidation of tris(3,3-dimethyl-1-butynyl)phosphine with peroxide was readily accomplished. Treatment with sulfur gave the corresponding phosphine sulfide. The attempted oxidation of the arsenic derivative with peroxide yielded a 50/50 mixture of starting material and the arsine oxide (indicated by PMR). Oxidation under more drastic conditions gave a high molecular weight oil (661). No reaction could be induced with sulfur using similar conditions to those described above. The starting material was recovered quantitatively. Spectral data for the compounds synthesized are given in Tables 2 and 3.

EXPERIMENTAL

Molecular weights were determined with a Mechrolab Osmometer Model 301A. The differential thermal data were obtained with a DuPont Model 900 differential thermal analyzer. The infrared spectra were recorded on a Beckmann IR-9 Spectrophotometer, the PMR spectra on a Varian A-60 Spectrometer, and the mass spectra using a CEC Model 21-110B.

The preparation of 3,3-dimethyl-1-butynyllithium and the synthesis of the tris(3,3-dimethyl-1-butynyl) derivatives was conducted under the same conditions as reported in our recent paper on the synthesis of Group IVb tetrakis(3,3-dimethyl-1-butynyl) compounds using the trichlorides of phosphorus, arsenic and antimony[4].

Oxidation of tris(3,3-dimethyl-1-butynyl)phosphine

A solution of 1.08 g of tris(3,3-dimethyl-1-butynyl)phosphine in 30 ml of acetone was treated with a slight excess of a 30% hydrogen peroxide solution. The mixture was stirred for 2 h at room temperature and then at 50° for 1 h. Evaporation of the solvent and subsequent sublimation of the remaining solid yielded 1.15 g of a white substance. This product was identical with the one synthesized in 97% via the reaction of phosphorus oxytrichloride and 3,3-dimethyl-1-butynyllithium in tetrahydrofuran at −78°.

Reaction of tris(3,3-dimethyl-1-butynyl)phosphine and sulfur

A mixture of 0.7 g of tris(3,3-dimethyl-1-butynyl)phosphine and 0.5 g of sulfur was refluxed for 5 h in 30 ml of carbon disulfide. The solvent was evaporated and the excess sulfur removed by treating the residue with acetone and charcoal. Filtration and evaporation of the solvent followed by drying of the residue yielded 0.68 g of the phosphine sulfide as a white solid.

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