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Synthetic and Mechanistic Aspects of Preparation of Phosphinito- and Phosphito-mercuries

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ABSTRACT: *A >P—O$^-$ (**1**) type of anion has been used as an efficient synthetic precursor of four-coordinated compounds: $R_2P(O)$—Hg—$(O)PR_2$ (**5**) and $R_2P(O)$—Hg—Bz (**3**) (R = alkoxy, alkyl, aryl). They were obtained in good yield. Bis(t-butylphenylphosphinito-P)mercury (meso and rac) (**5c,d**) selectively decomposed into 1,2-di-t-butyl-1,2-diphenyldiphosphane 1,2-dioxide (meso and rac) (**6c,d**). Furthermore, some mechanistic aspects of the synthesis of mentioned compounds are elaborated.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:234–237, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20409

INTRODUCTION

Phosphinito- and phosphito-mercuries (**5**) are a well-known class of compounds [1–4]. Reaction between $R_2P(O)$—H and mercuric oxide [1] is the only procedure reported in the literature for the synthesis of type **5** compounds. The reaction was reported to proceed very slowly. They are a potential source of $R_2P(O)^\bullet$-type radicals. From a theoretical point of view, phosphorus-centered radicals, which have a lone pair in the molecular plane and an unpaired electron perpendicular to the plane, like $>P^\bullet$ radicals, are expected to dimerize and form a P—P bond [3a,5]. This is not obvious for $>P(O)^\bullet$ or $>P(S)^\bullet$ species in which the phosphorus is pyramidal. The cleavage of the P—Hg bond has been reported during heating [4a–d] or irradiation [6]. There is no radical evidence for P—Hg bond fission. This could support the radical cage mechanism.

RESULTS AND DISCUSSION

Type **5** compounds are still not fully explored. To increase their accessibility, a reaction between **1** and HgX_2 (X = Cl, OAc) was studied. The configuration of R_2PO derivatives depends on the cation. The three-coordinated form is found mainly in alkali metals or silver counterion [7], but the four-coordinated form is predominant in mercury [2a].

Compounds of type **3** have not been reported previously.

A reaction between **1** and benzylmercury chloride (**2**) was performed. It was monitored by TLC and NMR techniques. The reaction proceeds very fast under mild condition in darkness (Scheme 1). Isolation of **3** is always accompanied by symmetric side products, namely dibenzylmercury (**4**) and type **5** compounds (Scheme 2).

Higher concentration of nucleophile **1** did not give a significantly higher yield of **3**. Type **3** compounds are labile and decomposed in daylight in the solution (Scheme 2). They do not react with anion **1**.

The presence of symmetric compounds **4** and **5** in the reaction mixture can be considered as evidence of existence of the Schlenck-type equilibrium

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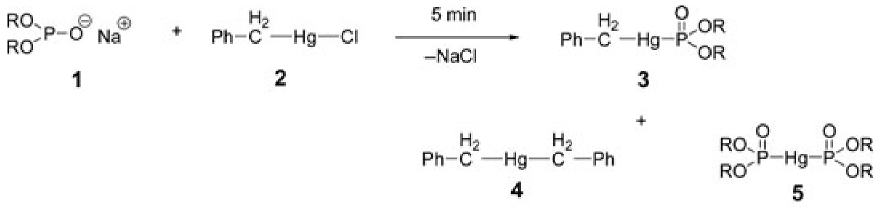
This paper is dedicated to Prof. Andrzej Chimiak.



Entry		R	Yield (%)			
			2	3	4	5
1	**a**	Et	29	65	3	3
2	**b**	Pr^i	35	60	2.5	2.5

SCHEME 1 Reaction between **1** and **2** in darkness. Yields were determined by ^{1}H and ^{31}P NMR spectroscopic methods.

$$2\,\mathbf{3a} \rightleftharpoons \mathbf{4} + \mathbf{5a}$$

Entry	Time (h)	Yield (%)		
		3a	4	5a
3	2	62	19	19
4	4	50	25	25
5	168	22	39	39

SCHEME 2 Symmetrization of **3a** in daylight. Yields were determined by ^{1}H and ^{31}P NMR spectroscopic methods.

(Scheme 5). To verify it, a reaction between **4** and three equivalents of $HgCl_2$ has been carried out (Scheme 3).

As a consequence, a reaction between HgX_2 ($X = Cl$, OAc) and anion **1** was investigated. The procedure is efficient and fast (Scheme 4). Comparing phosphinylmercuries of types **3** and **5** with appropriate four-coordinated compounds of the $R_2P(O)–(O)PR_2$ type (**6**), that is, diphosphine dioxides (R = alkyl, aryl) and hypophosphoric acid esters (R = alkoxy), the chemical shift is significantly shifted to high frequencies in a similar manner as described in the literature [8].

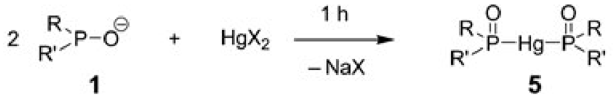
$$\mathbf{4} + HgCl_2 \longrightarrow 2\,\mathbf{2}$$

Entry	Time (h)	Yield (%)	
		4	2
6	1	35	65
7	19	0	100

SCHEME 3 Reaction between **4** and three equivalents of $HgCl_2$. Yields were determined by ^{1}H NMR spectroscopic method.

In contrast to bis(dialkoxyphosphinyl)-mercuries **5a,b** (entries 8–11), bis(*t*-butyl-phenyl-phosphinito-P)mercury (meso and rac) **5c,d** (entry 12) during isolation decomposed into 1,2-di-*t*-butyl-1,2-diphenyldiphosphane-1,2-dioxide (meso and rac) (**6c,d**).

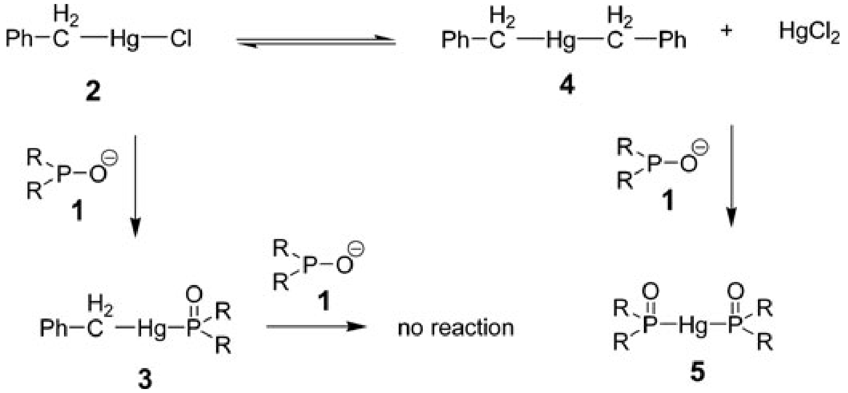
The starting material **2** and product **3** are labile. During synthesis and/or isolation, they are accompanied by symmetric side-products, for example, **4** and **5**. This additionally confirms the Schlenck-type equilibrium and symmetrization described here. For this reason, the data presented in Schemes 1–3 refer to yields determined from integration of appropriate ^{1}H and ^{31}P NMR spectra of the reaction mixture, which are different from the isolated amounts.



Entry		X	R	R′	Yield (%)
8	**a**	AcO	EtO	EtO	73
9	**b**	AcO	$\mathrm{Pr^iO}$	$\mathrm{Pr^iO}$	83
10	**a**	Cl	EtO	EtO	64
11	**b**	Cl	$\mathrm{Pr^iO}$	$\mathrm{Pr^iO}$	72
12	**c,d**	Cl	Ph	$\mathrm{Bu^t}$	84*

* the remains are 1,2-di-bu^t-1,2-diphenyldiphosphane 1,2-dioxide (**6c,d**)

SCHEME 4 Synthesis of **5**.



SCHEME 5 The Schlenck-type equilibrium as a proposed mechanism for the formation of **5** during the reaction of **1** with **2**.

CONCLUSION

A new strategy for the synthesis of the compounds of type **3** and **5** is presented. The method can be applied efficiently both for the derivatives substituted with the alkyl and/or aryl groups. The alkoxy group on the phosphorus decreases the efficiency of synthesis of **5** because of the electronic reasons. The presented method is a convenient and easy way to control general synthesis procedure, yielding symmetric and nonsymmetric mercury compounds. The isolation of compound **5** during the synthesis of compounds **3** suggests a possible existence of the Schlenck-type equilibrium. Compounds **3** are unstable and decomposed under the daylight. Therefore, the synthesis requires darkness. Bis(*t*-butyl-phenylphosphinito-P)mercury (**5c,d**) selectively decomposed into 1,2-di-*t*-butyl-1,2-diphenyldiphosphane 1,2-dioxide (**6c,d**).

EXPERIMENTAL

All reactions were carried out under argon atmosphere in anhydrous solvents (benzene and THF dried over benzophenone ketyl, CH_2Cl_2 and $CHCl_3$ dried over P_2O_5, and hexane was dried over sodium-potassium alloy). Chromatography was carried out on silica gel 60 (0.15–0.3 mm) Machery Nagel. NMR was preformed on Varian Gemini 500 MHz (all *J* values are given in Hz); IR on a Bruker IFS66 (KBr tablet); MS were acquired on a MASPEC II system [II32/99D9] in EI mode and if necessary liquid LSIMS technique was applied. Compounds **1c** and **2** were obtained according to procedures described in the literature [8] and [9], respectively.

Reaction of Sodium Salt of $R_2P(O)H$ (1) with 2 or (HgX_2)

$R_2P(O)H$ (5.0 mmol) was added to the suspension of NaH (0.133 g, 5.5 mmol) in THF (25 mL) and stirred until the disappearance of the bubbles of H_2. Subsequently, benzylmercury chloride (**2**) (1.635 g, 5.00 mmol) or HgX_2 ($X = OAc$, Cl) (2.5 mmol) in THF (25 mL) was slowly added. The reaction was carried out for 5 min at room temperature under darkness (entries 1 and 2; Scheme 1) or 16 h (entries 10–13; Scheme 4). Next, a sample of the reaction mixture was removed, and C_6D_6 was added. The solvents were evaporated, and the ^1H NMR and ^{31}P NMR spectra were recorded. Results are presented in Scheme 1. Next, aq. diethyl ether was added. The organic phase was dried with $MgSO_4$, and the solvent was evaporated. The crude product was purified by chromatography and/or crystallization.

Entry 1. Dibenzyl-mercury (**4**): ($CHCl_3$:hexane = 1:10); 0.134 g (0.4 mmol, 14%); mp 108–109°C; ^1H NMR ($CDCl_3$) $\delta = 2.26$ (s, CH_2, 4H), 6.60–7.0 (m, aromatic, 10H). Benzylmercury chloride (**2**): ($CHCl_3$:hexane = 1:10); 0.343 g (1.0 mmol, 21%); mp 104–105°C; ^1H NMR ($CDCl_3$) $\delta = 3.10$ (s, CH_2, 2H), 6.73–7.00 (m, aromatic, 5H). Benzyl(diethoxyphosphinyl)mercury (**3a**): ($CHCl_3$); 1.303 g (3.0 mmol, 61%); ^1H NMR ($CDCl_3$) $\delta = 1.31$ (t, $J_{H\text{–}H} = 14.0$ Hz, CH_3, 6H), 2.75 (d, $J_{H\text{–}H} = 14.5$ Hz, CH_2, 2H); 4.01–4.10 (m, CH_2, 4H), 7.00–7.20 (m, aromatic, 5H); ^{31}P NMR ($CDCl_3$) $\delta = 123.40$ (d, $J_{P\text{–}Hg} = 10284$ Hz); IR $\nu = 1200$ P=O, 1060 P—O—C cm^{-1}. Bis(diethoxyphosphinyl)-mercury (**5a**): (CH_2Cl_2:MeOH = 50:1); 0.147 g (0.3 mmol, 12%); mp 56.8–58.2°C; ^1H NMR ($CDCl_3$) $\delta = 1.20$ (t, $J_{H\text{–}H} = 6.0$ Hz, CH_3, 6H), 3.5–4.1 (m, CH_2, 4H); ^{31}P NMR ($CDCl_3$) $\delta = 107.75$ (d, $J_{P\text{–}Hg} = 18154$ Hz) [2a].

Entry 2. **4**: 0.306 g (0.8 mmol, 32%). **2**: 0.039 g (0.1 mmol, 2%). Benzyl(diisopropyloxyphosphinyl)-mercury (**3b**): ($CHCl_3$); 1.371 g (3.0 mmol, 60%); ^1H NMR ($CDCl_3$) $\delta = 1.15$ (d, $J_{H\text{–}H} = 8.0$ Hz, CH_3, 12H), 2.50 (d, $J_{P\text{–}H} = 14.0$ Hz, CH_2, 2H); 4.10–4.60 (m, CH, 2H), 6.40–7.90 (m, aromatic, 5H); ^{31}P NMR ($CDCl_3$) $\delta = 121.06$ (d, $J_{P\text{–}Hg} = 10767$ Hz); IR $\nu = 1200$ P=O, 1000 P—O—C cm^{-1}. Bis(diisopropyloxyphosphinyl)-mercury (**5b**): (CH_2Cl_2:MeOH = 50:1); 0.425 g (0.8 mmol, 32%); mp 111–114°C; ^{1}H NMR ($CDCl_3$) $\delta = 1.34$ (d, $J_{H–H} = 6.4$ Hz, CH_3, 12H), 4.72–4.79 (m, CH, 2H); ^{31}P NMR ($CDCl_3$) $\delta = 105.92$ (d, $J_{P–Hg} = 15570$ Hz) [4].

Entry 8. **5a**: 0.867 g (1.8 mmol, 73%).

Entry 9. **5b**: 1.110 g (2.1 mmol, 83%).

Entry 10. **5a**: 0.760 g (1.6 mmol, 64%).

Entry 11. **5b**: 0.963 g (1.8 mmol, 72%).

Symmetryzation of **3a** *in Daylight*

A sample of **3a** was dissolved in $CDCl_3$, and the ^{1}H and ^{31}P NMR spectra were recorded in time. Results are presented in Scheme 2.

Reaction between **4** *and Three Equivalents of $HgCl_2$*

$HgCl_2$ (3.0 mmol, 0.815 g) in THF (20 mL) was slowly added into the solution of $PhCH_2HgCH_2Ph$ (**2**) (1.0 mmol, 0.367 g) in THF (10 mL). The reaction was carried out at room temperature under darkness. The ^{1}H NMR spectrum of the reaction mixture was recorded in $CDCl_3$ solvent. Results are presented in Scheme 3.

*Reaction of Potassium Salt of t-Butylphenylphosphinic Acid Anion (***1c***) with $HgCl_2$*

Potassium (0.78 g, 20 mmol) was dissolved in a mixture of liquid ammonia (50 mL) and THF (50 mL). The reaction mixture was stirred until complete dissolution of the metal, then cooled to −78°C. *t*-Butylphenylphosphinic acid chloride (2.16g, 10 mmol) in THF (5 mL) was added and stirred at −78°C for additional 15 min. Next, the ammonia was evaporated at 10 mmHg, and solid $HgCl_2$ (1.36 g, 5 mmol) was added at room temperature. The reaction mixture was stirred for 45 min. The solvent was evaporated, and the crude product was purified by crystallization and chromatography.

Entry 12. 1,2-di-*t*-Butyl-1,2-diphenyldiphosphane 1,2-dioxide (**6c,d)** (mixture of meso and rac) [8b]. (CH_2Cl_2:MeOH = 50:1); 0.217 g (0.6 mmol, 12%). Bis(*t*-butyl-phenylphosphinito-P)mercury (**5c,d**) (mixture of meso and rac): (CH_2Cl_2:MeOH = 5:1) 2.365 g (4.2 mmol, 84%); ^{1}H NMR ($CDCl_3$) $\delta_1 = 1.00$ (d, $^3J_{P–H} = 18$ Hz, *t*-Bu, 9H), 7.20–7.66 (m, aromatic, 10H); $\delta_2 = 1.15$ (d, $J_{P–H} = 17$ Hz, = 15 Hz, *t*-Bu, 9H), 7.17–7.80 (m, aromatic, 10H); ^{31}P NMR ($CDCl_3$) $\delta_1 = 103.14$, $J_{P–Hg} = 3495$ Hz; $\delta_2 = 118.42$, $J_{P–Hg} = 3520$ H. MS: LSIMS (M + H)$^+$ 565(15%). HRMS (*m/z*) Calcd for $C_{20}H_{29}HgO_2P_2$ $(M + H)^+$; 565.135700; Found 565.135291.

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