

REACTIONS OF ALKYLPHOSPHORUS, ARSENIC, AND ANTIMONY HYDRIDES AND HALIDES WITH DIBENZYL MERCURY. AN IMPROVED PROCEDURE FOR CYCLOPOLYARSINES

ARNOLD L. RHEINGOLD* and PRANAB CHOUDHURY*

Department of Chemistry, State University of New York, Plattsburgh, NY 12901 (U.S.A.)

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Summary

Dibenzylmercury is a convenient and general reagent for the formation of homoatomic catenates from primary alkyl phosphines, arsines and stibines. From CH_3PH_2 , CH_3AsH_2 and $\text{C}_2\text{H}_5\text{AsH}_2$, the products are Hg^0 and the cyclopentamers, $(\text{CH}_3\text{P})_5$, $(\text{CH}_3\text{As})_5$ and $(\text{C}_2\text{H}_5\text{As})_5$, respectively. From CH_3SbH_2 , the solid, polymeric product, $(\text{CH}_3\text{Sb})_x$, is obtained. With $(\text{CH}_3)_2\text{AsH}$, both the condensation product, $(\text{CH}_3)_2\text{AsAs}(\text{CH}_3)_2$, and the substitution product, $(\text{CH}_3)_2\text{AsCH}_2\text{C}_6\text{H}_5$, are obtained. With dibenzylmercury, CH_3PCl_2 , CH_3AsCl_2 , and CH_3SbCl_2 give only the monosubstitution product $\text{CH}_3\text{E}(\text{Cl})\text{CH}_2\text{C}_6\text{H}_5$ (E = P, As or Sb) and HgCl_2 . With CH_3AsI_2 , disubstitution occurs giving (in addition to HgI_2) $\text{CH}_3\text{As}(\text{CH}_2\text{C}_6\text{H}_5)_2$, and with $(\text{CH}_3)_2\text{AsI}$, $(\text{CH}_3)_2\text{AsCH}_2\text{C}_6\text{H}_5$. In all cases the conversion of starting materials to the indicated products is very high.

Introduction

Dialkylmercury compounds have found application as effective reagents for coupling main-group hydrides in the formation of new element-element bonds. An 86% yield of hexaethyliditin is obtained from triethyltin hydride by the action of diethylmercury at 100°C (3–5 h reaction time) [1].

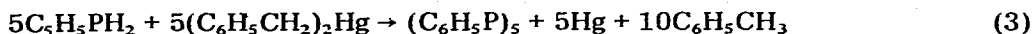


Dibenzylmercury affects the same conversion, but under more rigorous conditions and in lower yield. Triethylsilane and triethylgermane behave differently; dibenzylmercury with the former, gives $(\text{C}_2\text{H}_5)_3\text{SiHgC}_2\text{H}_5$, and with the latter, $(\text{C}_2\text{H}_5)_3\text{GeHgGe}(\text{C}_2\text{H}_5)_3$ [2]. Diarylmercury compounds do not produce coupling; rather an aryl group is substituted for hydrogen [3].

* Present address: Department of Chemistry, Cornell University, Ithaca, NY 14853.



Under mild conditions, dibenzylmercury readily converts phenylphosphine, $\text{C}_6\text{H}_5\text{PH}_2$ to pentaphenylcyclopentaphosphine, $(\text{C}_6\text{H}_5\text{P})_5$, in a 70–80% yield [4]; the yield compares favorably with that of other procedures [5].



Several organomercuric halides, RHgX , also show an ability to couple main group hydrides [6].

In contrast, the characteristic reaction of Group V chlorides with organomercury reagents is substitution, not coupling, i.e.,



Examples of this reaction are found for $\text{C}_6\text{H}_5\text{PCl}_2$ and $\text{C}_6\text{H}_5\text{AsCl}_2$, but no reactions of alkylidihalophosphines, arsines, or stibines have been reported [6].

As a continuation of our studies of homoatomic organophosphorus, arsenic and antimony oligomers and polymers, we have broadened the application of dibenzylmercury in the synthesis of compounds containing E–E bonds. We also have characterized the reactions of dibenzylmercury with several primary and secondary methyl-Group V chlorides and iodides.

Experimental

Dibenzylmercury as obtained from Alfa Inorganics required two recrystallizations from benzene to obtain a white reagent free of metallic mercury. Methylphosphine [7], methylarsine [8], ethylarsine [8], dimethylarsine [8], and the methylhaloarsines [9] were prepared by literature methods. Methylstibine was prepared by the LiAlH_4 reduction of methyldichlorostibine in di-n-butylether [10]. Methyldichlorophosphine was obtained from the Ethyl Corporation. All reagents were found to be spectroscopically pure (IR, mass spectroscopy, PMR). Spectrograde benzene was distilled from sodium and stored over a molecular sieve. Spectrograde methylene chloride was dried over P_2O_{10} and distilled. C/H analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All PMR spectra are referred to internal TMS ($\delta = 0.00$).

Reactions with hydrides (methylphosphine, methylarsine, dimethylarsine, ethylarsine, methylstibine)

A quantity of hydride needed to achieve the stoichiometry of a particular reaction was distilled from a storage tube on an all-Pyrex vacuum line into a repeatedly degassed benzene or methylene chloride solution of dibenzylmercury to form approximately 10% solutions contained in medium-wall, 5 mm NMR tubes. After the addition of TMS, the tubes were sealed with a torch, and placed in a 60°C oven. Products and yields are given in Table 1. From methylstibine, a purple-black solid was obtained, $(\text{CH}_3\text{Sb})_x$. (Found: C, 8.91; H, 2.25. CH_3Sb calcd.: C, 8.77; H, 2.21%.)

TABLE 1
 REACTIONS OF PHOSPHORUS AND ARSENIC HYDRIDES AND CHLORIDES WITH
 DIBENZYL MERCURY

Reagent	Reaction conditions (60° C)	Products containing phosphorus, arsenic or antimony	Yield (%)
CH ₃ PH ₂	C ₆ H ₆ , 48 h	(CH ₃ P) ₅	Quant.
	CH ₂ Cl ₂ , 48 h	(CH ₃ P) ₅	Quant.
CH ₃ AsH ₂	C ₆ H ₆ , 48 h	(CH ₃ As) ₅	Quant.
	CH ₂ Cl ₂ , 30 h	(CH ₃ As) ₅	Quant.
CH ₃ SbH ₂	C ₆ H ₆ , 24 h	(CH ₃ Sb) _x	Quant.
C ₂ H ₅ AsH ₂ (CH ₃) ₂ AsH	C ₆ H ₆ , 30 h	(C ₂ H ₅ As) ₅	Quant.
	C ₆ H ₆ , 48 h	(CH ₃) ₂ AsAs(CH ₃) ₂	25
		(CH ₃) ₂ AsCH ₂ C ₆ H ₅	75
	CH ₂ Cl ₂ , 48 h	(CH ₃) ₂ AsAs(CH ₃) ₂	40
		(CH ₃) ₂ AsCH ₂ C ₆ H ₅	60
CH ₃ PCl ₂	C ₆ H ₆ , 30 days	CH ₃ P(Cl)CH ₂ C ₆ H ₅	Quant.
CH ₃ AsCl ₂	C ₆ H ₆ , 48 h	CH ₃ As(Cl)CH ₂ C ₆ H ₅	Quant.
CH ₃ SbCl ₂	C ₆ H ₆ , 5 h	CH ₃ Sb(Cl)CH ₂ C ₆ H ₅	Quant.
CH ₃ AsI ₂	C ₆ H ₆ , 1 h	CH ₃ As(CH ₂ C ₆ H ₅) ₂	88
(CH ₃) ₂ AsI	C ₆ H ₆ , 30 min	(CH ₃) ₂ AsCH ₂ C ₆ H ₅	Quant.

Reactions with halides (methyldichlorophosphine, methyldichloroarsine, methyldiiodoarsine, dimethyldiiodoarsine, and methyldichlorostibine)

Degassed benzene solutions of dibenzylmercury and the halide were combined in stoichiometric molar ratios in an evacuated reaction tube to form 10% solutions, the tubes sealed and held at 60° C. Attempts to isolate the products (in each case CH₃E(Cl)CH₂C₆H₅) of the reactions of the chlorides by distillation led to the formation of further products not in evidence in the PMR spectra of the reaction mixture, the apparent result of substituent scrambling. The problem was most severe for the antimony derivative, least for phosphorus.

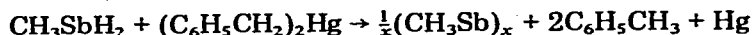
From methyldiiodoarsine, methyldibenzylarsine (b.p. 128° C, 0.5 mmHg) was obtained by distillation of the product from HgI₂. (Found: C, 65.53; H, 6.71. C₁₅H₁₈As calcd.: C, 65.93; H, 6.64%.) From dimethyldiiodoarsine, dimethylbenzylarsine (b.p. 70° C, 3.0 mmHg) was similarly obtained. (Found: C, 56.91; H, 6.66. C₉H₁₃As calcd.: C, 55.07; H, 6.68%.)

All results are summarized in Table 1.

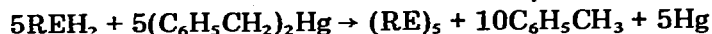
Results and discussion

The compounds CH₃PH₂, CH₃AsH₂ and C₂H₅AsH₂ were converted in essentially quantitative yields in both benzene and methylene chloride to their respective cyclopentamers by the action of dibenzylmercury. Only the solid, purple-black polymeric product, (CH₃Sb)_x, was obtained from CH₃SbH₂. This conversion also was quantitative. No cyclooligomers of antimony containing primary or secondary alkyl groups are known*. We can speculate that this solid product is an analog of the ladder-structure polymer, (CH₃As)_x [12].

* A solid cyclotetramer is known containing t-butyl substitution [11].



As followed by PMR, all reactions are complete in 1–2 days at 60°C. The overall reaction for methylphosphine, methylarsine and ethylarsine is the same as that reported for phenylphosphine (eq. 3) [5] i.e.,



(E = P, R = CH₃; E = As, R = CH₃ or C₂H₅).

The reaction has many attractions as a preparative procedure for the cyclopentaarsines. Of the alternative procedures, the reduction of an alkylarsonic acid by hypophosphorous acid is most commonly employed [13]. Not only does this reaction proceed in low yield, but also requires very careful attention to separation and purification procedures, including distillation, to obtain a product free from reactants and other reaction products. Distillation (at elevated temperatures) has been implicated as a source of ill-behaved samples of pentamethylcyclopentaarsine [14]. With the present procedure, decantation from a coalesced droplet of mercury directly affords a solution of the cyclopentamer in high purity (based upon the almost complete absence of omnipresent high-field NMR impurity peaks)*. Low-temperature removal of the benzene (or methylene chloride)/toluene mixture provides a product requiring no further workup. It is noteworthy that no evidence for the formation of any solid modifications of pentamethylcyclopentaarsine accompanies this synthesis, neither the amorphous red-brown modifications, nor the purple-black ladder polymer [12]. The cyclopentamers were identified by their characteristic NMR patterns [16], (CH₃Sb)_x by elemental analysis.

Under identical conditions, (C₆H₅CH₂)₂Hg and dimethylarsine, (CH₃)₂AsH, combined in benzene or methylene chloride to give two arsenic-containing products: tetramethyldiarsine, (CH₃)₂AsAs(CH₃)₂, the anticipated coupled product (eq. 4) and benzyldimethylarsine (eq. 5). The total conversion of dimethylarsine to these products was quantitative in both solvents; the product ratios are given in Table 1. The course of this reaction combines the reactivities of triethyltin hydride with diethylmercury (coupling, eq. 1) and diphenylmercury (substitution, eq. 2).



Tetramethyldiarsine [17] and benzyldimethylarsine were identified by their PMR spectra (Table 2). This reaction would appear to have limited preparative value under the conditions tested.

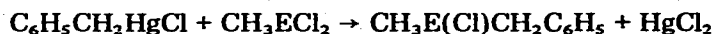
Substitution is the only reaction observed when chloride replaces hydride; both CH₃PCl₂ and CH₃AsCl₂ behaved similarly when combined with (C₆H₅CH₂)₂Hg in benzene. Substitution of both chlorides, even with a substantial excess of dibenzylmercury, was not observed.

* The high-field impurity peaks have been identified as a variable mixture of catena (methylarsenic) and oxidized forms of the cyclooligomer [15].

TABLE 2

¹H NMR SPECTRA OF SOME BENZYL-SUBSTITUTED DERIVATIVES OF GROUP V (P, As AND Sb) IN BENZENE

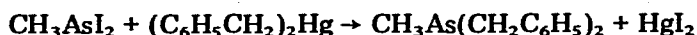
CH ₃ EXY ^a			δ(CH ₂ C ₆ H ₅)	δ(CH ₃)	Coupling constants (Hz)
E	X	Y			
P	Bz	Cl	2.86(d)	1.10(d)	J(PCH ₃), 9.6; J(PCH ₂), 6.6
As	Bz	Cl	2.92(s)	1.03(s)	
Sb	Bz	Cl	2.98(s)	0.93(s)	
As	Bz	Me	2.53(s)	0.68(s)	
As	Bz	Bz	3.00(m)	0.98(s)	J(AB), 12.5
			2.74(m)		

^a Me = CH₃, Bz = CH₂C₆H₅.

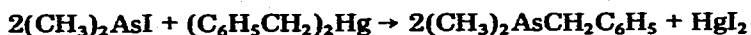
(E = P or As)

Although the conversion was again essentially quantitative, the reactions of the chlorides are much slower than those of the corresponding hydrides: for E = P, 30 days at 60° C is required before the last PMR-visible traces of starting material have disappeared; for E = As, 3 days. Benzylmethylchloro-phosphine, -arsine, and -stibine were identified by their PMR spectra (Table 2). A small quantity of benzyl chloride also was identified by its PMR spectrum (δ 2.42) in these reactions. Mercuric chloride was removed as a white solid in correct stoichiometric quantities. Scrambling of substituents during isolation procedures (worst for E = Sb, least for E = P) produced products not in evidence in PMR spectra of the reaction mixture prior to workup. The redistribution may be promoted by the presence of HgCl₂.

No evidence for the replacement of both chlorines to form dibenzyl derivatives was seen. When the halogen was iodine, however, only the dibenzyl product was obtained even when CH₃AsI₂ was in large excess.



The yield was 88%. The slow rate of As atom inversion at 30° C [18,19] produced a non-equivalency of the benzyl CH₂ protons in the product's NMR spectrum and their appearance as an AB pattern (Table 2). The conditions for observing non-equivalence of benzyl CH₂ protons has been thoroughly discussed [20-22]. Dimethyldioarsine was quantitatively converted to (CH₃)₂AsCH₂-C₆H₅ under similar conditions.



In this case, the benzyl CH₂ protons are equivalent.

It is possible to state with assurance that in no instance in this series of reactions were any soluble products containing mercury formed in NMR-detectable quantities. The absence of ¹⁹⁹Hg (16% natural abundance) satellites for all NMR resonances (except (C₆H₅CH₂)₂Hg) is conclusive.

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