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THE REACTIONS OF DIPHENYLLITHIOARSINE AND DIPHENYLARSINE WITH ALDEHYDES

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Summary

Diphenyllithioarsine reacts with aldehydes (RCHO, R = CH_2CH_3, $CH(CH_3)_2$, and Ph) to form lithium salts of α-hydroxyalkylarsines. Protonation of the lithium salts gives α-hydroxyalkylarsines. Diphenylarsine reacts with aldehydes below room temperature in the absence of solvents to produce white solids. The reactions are rapid in the presence of acid catalysts. Proton and carbon-13 NMR, infrared and Raman spectra show that the products are diphenyl-(α-hydroxyalkyl)arsines, $Ph_2AsCHOHR$. These compounds are thermally unstable. In organic solvents, equilibrium is established between the α-hydroxyalkylarsines and the aldehyde and diphenylarsine.

Introduction

The few reported reactions between arsines (R_nAsH_{3-n}, $n = 1, 2$) and aldehydes and ketones to produce α-hydroxyalkylarsines [$R_nAs(CR_2OH)_{3-n}$] employed starting materials with perfluoroalkyl groups attached to the arsenic atom or the carbonyl group [1]. These fluorinated hydroxyalkylarsines, including the recently reported diphenylhexafluoro-2-hydroxy-2-propylarsine [2], are relatively stable compounds but have a tendency to lose the hydroxyalkyl group. It has been shown that phenylarsine reacts with aldehydes to yield 1,3-dioxa-5-arsacyclohexanes [1] rather than phenylbis(α-hydroxyalkyl)arsines [3,4]. Diphenyllithioarsine reacts with quinones or aromatic ketones to give only tetraphenyldiarsine [5]. The reactions of diphenylarsine and diphenyllithioarsine with aldehydes have now been investigated to ascertain whether

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α-hydroxyalkylarsines can be prepared. These compounds would be valuable starting materials for the synthesis of other substituted organoarsenic compounds.

Experimental

All preparations were performed in a well ventilated hood under an atmosphere of dry nitrogen. Diphenyllithioarsine was prepared by the reaction of triphenylarsine with lithium wire in tetrahydrofuran [5]. The phenyllithium formed in this reaction was destroyed by addition of t-butyl chloride. Diphenylarsine was then obtained by acid hydrolysis of diphenyllithioarsine. Vacuum distillation gave diphenylarsine (85% yield, b.p. 114°C/0.5 mmHg, ^{1}H NMR: δ 4.68 [1H, s], 7.02—7.50 [10H, m] ppm). Aldehydes and ketones were obtained commercially and distilled prior to use. Proton NMR spectra were obtained on a Varian HA-100 spectrometer with internal tetramethylsilane as a reference. Carbon-13 spectra were obtained on a JEOL PFT-100/Nicolet 1080 Fourier transform spectrometer. Infrared spectra were recorded with a Beckman IR-8 spectrophotometer. Raman spectra were taken on a Cary Model 82 Raman spectrometer using the 5145 Å line from a Coherent Radiation Model 53 argon ion laser and the 5208 and 5308 Å lines from a Coherent Radiation Model 52 krypton ion laser.

Reactions of aldehydes with diphenyllithioarsine

The aldehyde RCHO (R = CH_3CH_2, $(CH_3)_2CH$, or Ph, 0.03 mol) dissolved in 10 ml of THF was added at room temperature to the dark red solution of diphenyllithioarsine in THF prepared from triphenylarsine (9.2 g, 0.03 mol) and lithium wire. The solution became almost colorless. After protonation with 15 ml of 2 *M* hydrochloric acid, the organic layer was evaporated under vacuum at 0° C to give white solids. Further attempts to purify the white reaction products by vacuum distillation at higher temperature resulted in the loss of the aldehyde and the isolation of only diphenylarsine.

Reactions of aldehydes with diphenylarsine

The aldehyde RCHO (R = CH_3CH_2, $(CH_3)_2CH$, or Ph, 0.01 mol) was added to diphenylarsine (2.3 g, 0.01 mol) at 0° C. A small amount of an acid catalyst was added (a few drops of conc. aqueous hydrochloric or tetrafluoroboric acid or a few crystals of *p*-toluenesulfonic acid). The solutions were stirred at 0° C and after several hours set to a white mass.

Attempted trapping of diphenyl(α-hydroxyalkyl)arsines and their lithium salts

Attempted trapping of the addition products of diphenyllithioarsine and aldehydes by *O*-alkylation with methyl iodide gave diphenylmethylarsine as the only arsenic containing product. Attempts to form diphenyl(methoxyalkyl)-arsines from the reactions of diazomethane with the addition compounds between diphenylarsine and aldehydes gave diphenylarsine and methyl alkyl ketones. The reactions of the addition products with trimethylchlorosilane did not lead to the isolation of the expected trimethylsilyl ethers.

Diphenyl(methoxymethyl)arsine

Chloromethyl methyl ether (3.8 ml, 4.0 g, 0.05 mol) dissolved in 10 ml of THF was added to a THF solution of diphenyllithioarsine (0.05 mol). The solution became colorless and the lithium chloride was extracted with 10 ml of water. Distillation of the separated organic layer gave diphenyl(methoxymethyl)-arsine (7.4 g, 45% yield, b.p. 138—140°C/0.5 mmHg, ^{1}H NMR: δ 3.33 [3H, s], 4.18 [2H, s], 7.03—7.50 [10H, m] ppm). (Found: C, 61.07; H, 5.52. $C_{14}H_{15}$-AsO calcd.: C, 61.33; H, 5.51%).

Results and discussion

The reactions of diphenyllithioarsine and diphenylarsine with aldehydes

The reactions of diphenyllithioarsine and diphenylarsine with aldehydes were carried out to obtain diphenyl(α-hydroxyalkyl)arsines. Addition of equal molar quantities of aldehyde to the dark red solutions of diphenyllithioarsine at room temperature caused rapid and almost complete decoloration. This indicates that addition of diphenyllithioarsine across the carbonyl has occurred with the formation of the lithium salts of diphenyl(α-hydroxyalkyl)arsines (I) (eq. 1). Protonation with hydrochloric acid and concentration of the organic

$$\underset{(R = CH_3CH_2,\ (CH_3)_2CH,\ C_6H_5)}{Ph_2AsLi + RCHO} \longrightarrow \underset{(I)}{Ph_2AsCHR\ (O^-\ Li^+)} \xrightarrow{H^+} \underset{(II)}{Ph_2AsCHR\ (OH)} \qquad (1)$$

layer at or below 0°C gave white solids. However all attempts to further purify these white solids by vacuum distillation resulted in the loss of aldehyde and the isolation of diphenylarsine.

Similar results were obtained with diphenylarsine. Reactions of neat alde-

$$\underset{(R = CH_3CH_2,\ (CH_3)_2CH,\ C_6H_5)}{Ph_2AsH + RCHO} \rightleftharpoons Ph_2AsCHR\ (OH) \qquad (2)$$

hydes with diphenylarsine at 0°C in the presence of a proton acid catalyst, *p*-toluenesulfonic acid, concentrated hydrochloric acid or tetrafluoroboric acid (eq. 2), resulted in the formation of a solid white mass within a few minutes to half an hour. *p*-Toluenesulfonic acid was the most effective catalyst, perhaps because of its greater solubility. In the absence of a proton source, the reactions proceed very slowly. When diphenylarsine and propionaldehyde or isobutyraldehyde were refluxed in THF in the presence of a trace of proton catalyst, tetraphenyldiarsine was isolated in 60% yield. Since oxygen was carefully excluded in these reactions, the aldehyde must have served as the oxidizing agent. However, since no evidence for the formation of diphenyl(α-hydroxyalkyl)arsines was found under these conditions, this reaction was not further investigated.

The inability to isolate α-hydroxyalkylarsines in pure form in the neat and solution reactions of either diphenyllithioarsine or diphenylarsine with aldehydes strongly suggests that the lithium salts (I) and the α-hydroxyalkylarsines

(II) are in equilibrium with the precursor aldehydes and arsine. Attempts were made to trap I and II. Addition of methyl iodide to the THF solutions from the reactions of diphenyllithioarsine and aldehydes gave no *O*-alkylation product and diphenylmethylarsine was the only arsenic-containing product isolated. Diphenylmethylarsine results from the direct reaction of diphenyllithioarsine with methyl iodide (eq. 1). It has been reported that diphenyllithioarsine reacts with 1,3-dichloropropane in THF to produce diphenyl(3-chloropropyl)arsine [6].

Similarly, diazomethane did not react with the α-hydroxyalkylarsines formed in the neat reactions of diphenylarsine with aldehydes. The characteristic yellow color of the ethereal solutions of diazomethane disappeared but only diphenylarsine and methyl alkyl ketones were isolated upon workup. The methyl alkyl ketones are the product of the reaction of diazomethane with the aldehydes in equilibrium with α-hydroxyalkylarsines [7]. Trimethylchlorosilane was treated with the lithium salt of the α-hydroxyalkylarsines. The NMR spectra of the reaction mixtures indicated that a silyl ether had formed. Attempts to isolate the silyl ether by vacuum distillation resulted in decomposition of the product. The *O*-methyl derivative of diphenyl(α-hydroxymethyl)arsine was prepared by the reaction of diphenyllithioarsine with chloromethyl methyl ether. Diphenyl(α-hydroxymethyl)arsine is a colorless oil, unreactive under the conditions used in the attempts to trap I and II. Therefore, lack of product stability is not the reason that trapping with either methyl iodide or diazomethane failed to give positive evidence for the presence of α-hydroxyalkylarsines.

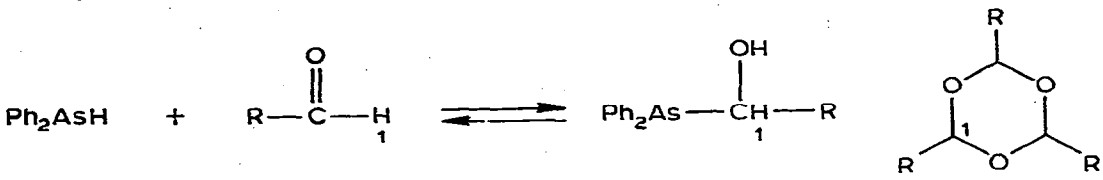
Spectroscopic characterization of diphenyl(α-hydroxyalkyl)arsines

Proton and carbon-13 magnetic resonance. Proton and carbon-13 spectra show that α-hydroxyalkylarsines are present and are in facile equilibrium with their precursor aldehyde and diphenylarsine. When equal molar amounts of diphenylarsine and an aldehyde were mixed neat in the absence of a proton catalyst, the approach to equilibrium occurred very slowly and resonance intensities were changing even after eight days. Equilibrium was not observed in these neat reactions because precipitation occurred before equilibrium was attained. When the reactions were followed with proton NMR in dilute solutions in benzene in the presence of a proton catalyst, equilibrium was attained much more rapidly. Table 1 presents proton chemical shifts and couplings for the reactions of diphenylarsine with propionaldehyde, isobutyraldehyde, and benzaldehyde. Also included in this table are the chemical shifts and couplings for the cyclic trimer of propionaldehyde and isobutyraldehyde. Figure 1 shows the proton spectrum for the reaction of isobutyraldehyde with excess diphenylarsine.

As the reactions proceed, resonances due to the aldehydic hydrogen and the arsenic hydrogen (δ 4.99 ppm) decrease in intensity and new resonances appear that are characteristic of α-hydroxyalkylarsines, particularly the resonances due to the hydrogen on the carbon attached to arsenic and hydroxy (δ 4.57, 4.51, and 5.80 ppm) and a sharp singlet due to the hydroxy proton. The ratios of the sum of the integrated intensities of the aldehyde H(1) and the α-hydroxyalkylarsenic H(1) compared to the sum of the arsenic hydrogen and the hydroxy

TABLE 1

PROTON SHIFTS AND COUPLINGS [a]



Aldehyde			α-Hydroxyalkylarsine				Notes
H(1)	H(2)	H(3)	H(1)	H(2)	H(3)	OH	
R = CH_2CH_3							
9.38(3)	1.98(4)	0.80(3)	4.57(3)	1.74(cm)	1.04(3)	1.71(1)	neat
			4.76(3)	1.58(cm)	0.88(3)		trimer
R = $CH(CH_3)_2$							
9.36(bs)	2.02(7)	0.87(2)	4.51(2)	2.05(cm)	1.16(2), 1.23(2)	3.00(1)	neat
9.46(bs)	2.19(7)	0.96(2)	4.36(2)	2.00(cm)	1.08(2) 1.15(2)	2.28(1)	C_6H_6
			4.46(2)	1.94(cm)	0.94(2)		trimer
R = *Ph*							
9.75(1)			5.80(1)			3.50(1)	neat

[a] Chemical shifts in ppm downfield from TMS; figures in parenthesis represent multiplicity of resonances; bs = broad singlet; cm = complex multiplet.

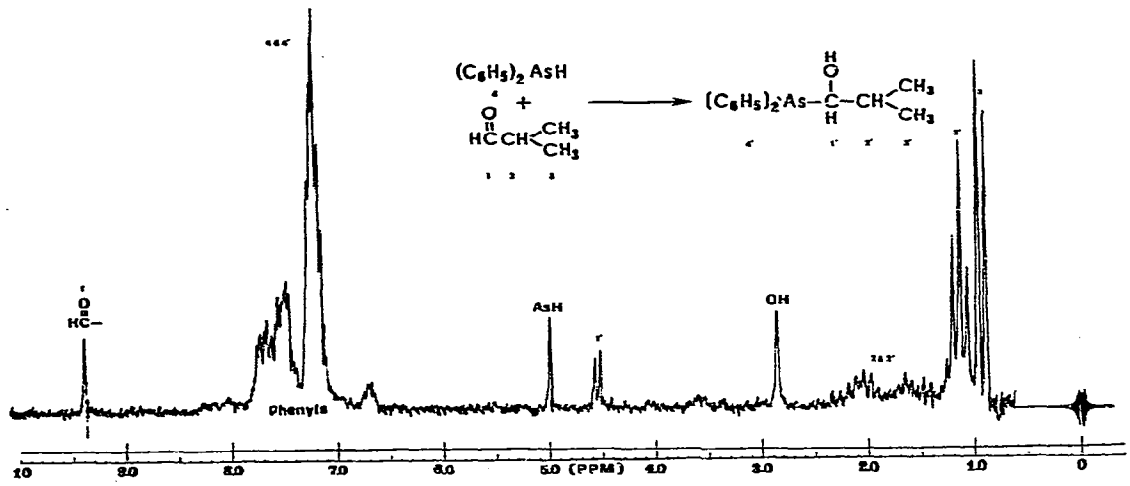


Fig. 1. ^{1}H NMR spectrum of the reaction of isobutyraldehyde with excess diphenylarsine.

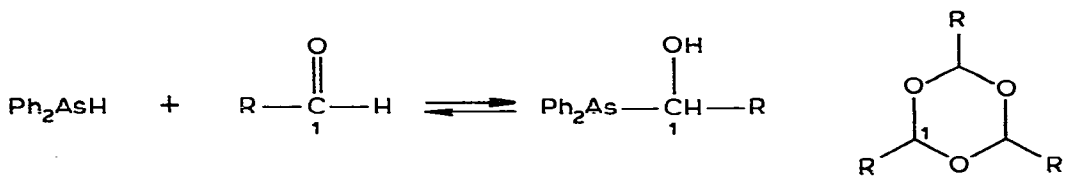
proton remained a constant as required by eq. 2.

In the reaction of isobutyraldehyde with diphenylarsine, C(1) becomes chiral and the methyls become diastereotopic upon formation of the α-hydroxyalkylarsine. These methyls are observed as a deceptively simple triplet due to the overlap of the nonequivalent methyl doublets (^3J(H(2)—H(3)) = ^3J(H(2)—H(3′)) = 6.8 Hz, Fig. 1). The formation of the cyclic trimer of the aldehyde did not compete effectively with the formation of the α-hydroxyalkylarsine. A doublet slightly downfield from the α-hydroxyalkylarsine H(1) doublet appeared only in the reaction of diphenylarsine with isobutyraldehyde in benzene, indicating the formation of a small amount of cyclic trimer. However, the proton resonances for the cyclic trimers are very close to the resonances for the α-hydroxyalkylarsines, so that it is difficult to estimate the amount of trimer formation from proton NMR. The equilibrium constant for the reaction of diphenylarsine with isobutyraldehyde (eq. 2) dissolved in benzene was determined by integration of the aldehyde-H, As-H and the methine-H of the hydroxyalkylarsine (K = 1.2 ± 0.1). Small amounts of the aldehyde trimer produce a methine doublet which interferes with the precise determination of the equilibrium constant because of overlap with the methine signal of the hydroxyalkylarsine.

Similar changes were observed in the carbon-13 spectra as the reactions proceeded (Table 2 and Fig. 2). The resonances in the α-hydroxyalkylarsines due to the carbon attached to arsenic and oxygen, C(1), appeared at δ 76.3, 81.5

TABLE 2

CARBON-13 CHEMICAL SHIFTS [a]



Aldehyde			α-Hydroxyalkylarsine			Notes
C(1)	C(2)	C(3)	C(1)	C(2)	C(3)	
R = CH_2CH_3 (2 3)						
202.2	37.2	6.3	76.3	28.8	11.2	neat
			101.9	27.6	7.8	trimer
R = $CH(CH_3)_2$ (2 3)						
205.1	41.6	16.3	81.5	33.9	21.5 19.6	neat
204.2	41.3	16.0	81.3	33.8	21.3 19.4	C_6H_6
			104.6	32.9	16.7	trimer
R = *Ph*						
192.5			77.8			neat

[a] Chemical shifts in ppm downfield from TMS.

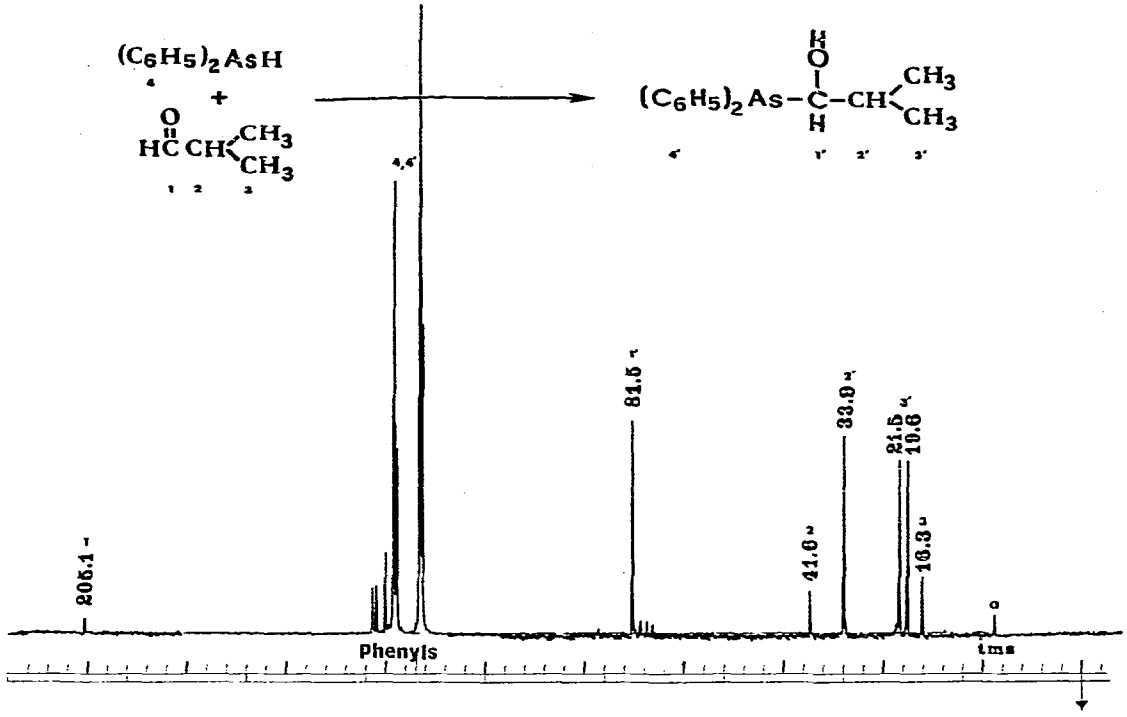


Fig. 2. ^{13}C NMR spectrum of the reaction of isobutyraldehyde with excess diphenylarsine.

and 77.8 ppm. In the reaction of isobutyraldehyde with diphenylarsine, the diasterotopic methyls appear at δ 21.4 and 19.4 ppm. Unlike the corresponding proton chemical shifts, C(1) of the α-hydroxyalkylarsines is well separated from C(1) for the cyclic trimers. Except for a small amount of cyclic trimer formed in the reaction of isobutyraldehyde with diphenylarsine, no resonances were observed in the carbon-13 spectra for the formation of the cyclic trimer in the other reactions of aldehydes with diphenylarsine.

Raman and infrared spectra. The Raman (R) and infrared (IR) spectra of the solid addition compound between diphenylarsine and propionaldehyde were recorded. In these spectra, the carbonyl stretch (1747 cm^{-1} (R) and 1740 cm^{-1} (IR)) [9] and the As—H stretch (2074 cm^{-1} (R) and 2070 cm^{-1} (IR)) [10] were not present. Further, the first overtone of the aldehyde stretch (3510 cm^{-1} (IR) was also absent. However, a band at 3410 cm^{-1} which may be attributed to a hydrogen bonded O—H stretch was observed. The disappearance of the absorption for the fundamental of the carbonyl supports the argument that the absorption at 3410 cm^{-1} is not a shifted first overtone of the carbonyl but is due to an O—H stretch.

The infrared spectrum of the addition compound between diphenyldeuteroarsine (Ph_2AsD) and propionaldehyde was obtained by cooling the aldehyde/arsine mixture in the IR cell and then adding a few drops of tetrafluoroboric acid. This spectrum showed an O—H stretch at 3410 cm^{-1}, due to the protons from the catalyst, and a weak broad absorption at 2580 cm^{-1}, due to the O—D stretch [12]. The infrared spectrum of a cooled mixture of diphenyldeutero-

arsine and propionaldehyde without a proton catalyst was observed for several days. Only a very weak absorption formed in the 3400 cm^{-1} region. However, after 50 h, the carbonyl and As—D absorptions had decreased in intensity and two strong absorptions appeared at 2550 and 2650 cm^{-1}, the expected region for the O—D stretching vibration [12].

Conclusion

The results of this investigation show that diphenyllithioarsine and diphenylarsine react with aldehydes to add As—Li and As—H across the carbonyl in a manner similar to that reported for the reaction of fluoroalkylarsines with carbonyl compounds [2]. The diphenyl(α-hydroxyalkyl)arsines formed are rather unstable. They cannot be recrystallized or distilled. Upon heating they decompose to the starting materials. Above room temperature in the presence of acid catalysts, diphenylarsine is oxidized to tetraphenyldiarsine. In solution, the diphenyl(α-hydroxyalkyl)arsines are in equilibrium with diphenylarsine and the aldehyde.

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