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THE REACTION OF PHENYLARSINE WITH ALIPHATIC ALDEHYDES

PREPARATION OF 2,4,6-TRIALKYL-5-PHENYL-1,3-DIOXA-5-ARSACYCLOHEXANES

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Summary

Phenylarsine and aliphatic aldehydes RCHO (R = CH_3, C_2H_5, C_3H_7) reacted in a 1/3 molar ratio in the presence of a catalytic amount of hydrochloric acid to produce 2,4,6-trialkyl-5-phenyl-1,3-dioxa-5-arsacyclohexanes. The structure of these compounds has been ascertained by NMR, IR and mass spectral methods.

Introduction

Only very few organic arsenic compounds containing an α-hydroxyalkyl group have been prepared. Raver and co-workers [1] obtained $RAs(CH_2OH)_2$ and $(CH_3)RAsCH_2OH$ (R = HCF_2CF_2) from the appropriate arsines and formaldehyde in an acid catalyzed reaction. The hydroxymethylarsines decomposed on distillation in vacuum. Cullen [2] succeeded in adding dimethylarsine and methylarsine to the carbonyl group of hexafluoroacetone. From the neat reagents at room temperature the compounds $(CH_3)_2AsC(OH)(CF_3)_2$ and $CH_3As(H)C(OH)(CF_3)_2$ were isolated. Their thermal stability seems to be low also. Our recent attempts to synthesize α-hydroxyalkylarsenic derivatives from non-fluorinated starting materials produced only tetraphenyldiarsine from diphenyllithioarsine and aromatic ketones [3] and thermally unstable adducts which could not be isolated from diphenylarsine and aliphatic aldehydes [4]. It was, therefore, surprising that Adams and Palmer [5,6] had isolated and purified by vacuum distillation bis(α-hydroxyalkyl)arylarsines, which one would expect to be rather unstable. These authors obtained their compounds from reactions of arylarsines and aliphatic aldehydes employing concentrated hydrochloric acid as catalyst. In view of the chemical behavior of the few known α-hydroxyalkylarsines the identity of the compounds prepared by Adams and Palmer appeared doubtful to us. In order to clarify this

apparent discrepancy between the reported structures and chemical properties of bis(α-hydroxyalkyl)arylarsines the reactions of phenylarsine with aliphatic aldehydes were reinvestigated.

Experimental

Acetaldehyde, propionaldehyde and butyraldehyde were obtained from Fisher Scientific. Before use, their purity was checked by ^{1}H NMR. When NMR signals of the trimeric aldehyde were found, the aldehydes were purified by distillation. Benzenearsonic acid was purchased from Eastman Organic Chemicals. Phenylarsine was prepared by reduction of benzenearsonic acid [6]. Phenylarsine (10% solution in carbon tetrachloride) exhibited ^{1}H NMR signals at 7.02-7.57 ppm (5H) and 3.55 ppm (2H).

Elemental analyses were performed either by Galbraith Laboratories, Knoxville, Tennessee, or by Chemalytics, Inc., Tempe, Arizona.

All experiments were conducted under nitrogen. The nuclear magnetic resonance spectra of the compounds in carbon tetrachloride solutions were obtained either on a Varian Associates Model T-60 or HA-100 spectrometer. Tetramethylsilane served as internal standard. The infrared spectra of the neat liquids between KBr plates were measured on a Beckman IR-8 spectrophotometer. The mass spectra were recorded on a CEC 21-110B mass spectrometer with the probe at 30-35°C and the ion source at 200°C. The samples were ionized with 70 eV electrons.

2,4,6-Trimethyl-5-phenyl-1,3-dioxa-5-arsacyclohexane

Phenylarsine (3.1 g, 0.02 mol) was placed into a nitrogen filled one-necked 50 ml flask equipped with a magnetic stirrer and a dropping funnel. The flask was cooled in an ice bath. After addition of four drops of concentrated hydrochloric acid, acetaldehyde (2.6 g, 0.06 mol) was dropped in to the stirred phenylarsine over a 15 min period. The reaction mixture, which was kept in the ice bath, was stirred for an additional 3 h. The oily mixture was shaken with anhydrous potassium carbonate, filtered into a distillation flask and vacuum-distilled. The low boiling fractions were discarded. The product (47% yield), a clear, colorless oil boiled at 109-113°C/ 1.5 Torr. Anal. found: C, 53.32; H, 6.49. $C_{12}H_{17}AsO_2$ calcd.: C, 53.74; H, 6.39%. n_D^{25} 1.5546 (lit. [6] 1.5619).

2,4,6-Triethyl-5-phenyl-1,3-dioxa-5-arsacyclohexane

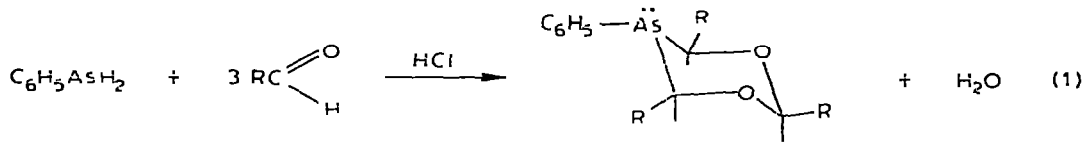
Phenylarsine (3.1 g, 0.02 mol) and propionaldehyde (3.5 g, 0.06 mol) produced a 55% yield of the triethyl derivative boiling at 130-132°C/1.2 Torr. Anal. found: C, 57.86; H, 7.34. $C_{15}H_{23}AsO_2$ calcd.: C, 58.07; H, 7.47%. n_D^{25} 1.5394 (lit. [6] 1.5425).

2,4,6-Tripropyl-5-phenyl-1,3-dioxa-5-arsacyclohexane

Phenylarsine (3.1 g, 0.02 mol) and butyraldehyde (4.3 g, 0.06 mol) reacted to give a 33% yield of the tripropyl derivative boiling at 164-166°C/1.3 Torr. Anal. Found: C, 61.58; H, 8.44. $C_{18}H_{29}AsO_2$ calcd.: C, 61.36; H, 8.30%. n_D^{25} 1.5222 (lit. [6] 1.5271).

Results and discussion

The reaction between phenylarsine and an aliphatic aldehyde employed in a 1/3 molar ratio proceded according to eqn. 1 with formation of 2,4,6-trialkyl-5-phenyl-1,3-dioxa-5-arsacyclohexanes (I). These acid catalyzed re-



(I)

actions between the neat reagents produced the heterocycles I in yields varying from 33 (R = C_3H_7) to 55% (R = C_2H_5). The compounds were isolated by vacuum distillation as clear, colorless oils. The propyl derivative is particularly viscous. The compounds do not appear to be very oxygen sensitive. They will, however, oxidize to benzenearsonic acid on extended exposure to air. All operations were consequently conducted under an atmosphere of nitrogen. The reaction mixtures were cooled with an ice-water bath, since at higher temperatures phenylarsine is reported to be oxidized by aldehydes to arsenobenzene [6].

Initially, a molar ratio of phenylarsine to aldehyde of 1/2 was used in attempts to prepare bis(α-hydroxyalkyl)phenylarsines. After the products had been identified as the heterocycles I, the molar ratio required by eqn. 1 was employed producing higher yields.

Distillation of the reaction mixtures containing the heterocycles I produced, in most cases, low boiling fractions. Proton NMR spectra of these fractions established that they were mixtures of phenylarsine and the trimers of the respective aldehydes. The spectral peaks coincided with NMR data for pure phenylarsine and with literature values for 2,4,6-trimethyl- and 2,4,6-triethyl-1,3,5-trioxacyclohexanes [7].

The proton NMR data of the 5-phenyl-2,4,6-trialkyl-1,3-dioxa-5-arsacyclohexanes, which are assumed to exist in the chair configuration, are summarized in Table 1. The 100 MHz proton NMR spectrum of the trimethyl derivative of

TABLE 1

PROTON NMR SPECTRAL DATA FOR 2,4,6-TRIALKYL-5-PHENYL-1,3-DIOXA-5-ARSACYCLOHEXANES (I)

R	Chemical shift, ppm (TMS = 0)			
	C_6H_5	CH(ring)	CH_2	CH_3
CH_3	7.90-7.61(m), 7.56-7.14(m)[a]	5.26-4.08(m)[b]		1.72-1.12(m)[e]
C_2H_5	7.90-7.72(m), 7.57-7.39(m) 7,37-7.17(m)[a]	5.04-4.05(m)[b]	2.04-1.38(m)[c]	1.16-0.82(m)[c]
C_3H_7	7.92-7.70(m), 7.58-7.38(m) 7.36-7.18(m)[a]	5.05-4.10(m)[b]	2.08-1.20(m)[d]	1.16-0.74(m)[e]

[a] 5 protons. [b] 3 protons. [c] 6 protons. [d] 12 protons. [e] 9 protons.

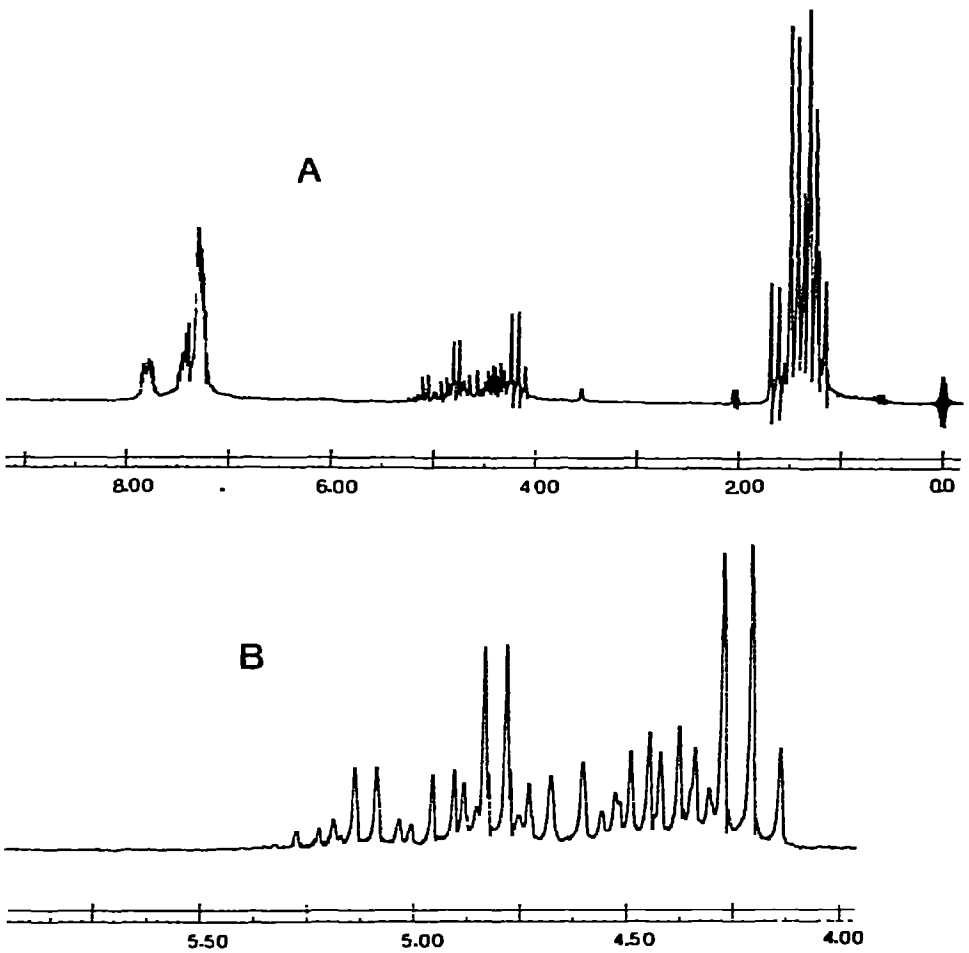


Fig. 1. A. 100 MHz NMR spectrum of 2,4,6-trimethyl-5-phenyl-1,3-dioxa-5-arsacyclohexane. B. NMR spectrum of annular protons of 2,4,6-trimethyl-5-phenyl-1,3-dioxa-5-arsacyclohexane.

compound I is reproduced in Figure 1A, and an expanded spectrum of the annular protons is shown in Figure 1B. Signals are found in three groups in the ranges 7-8 ppm (C_6H_5), 4-5 ppm (ring H atoms) and 0.7-2 ppm (alkyl groups). All of these signals appear as multiplets, indicating that various isomers differing with respect to equatorial or axial positions of the phenyl and/or alkyl groups were present in the samples. The three annular carbon atoms are asymmetric and the arsenic atom may also be a center of asymmetry. Keeping the phenyl group on the arsenic atom fixed in the equatorial position, eight isomers are possible, two pairs of which are mirror images. Thus, there are left six isomers, which should be distinguishable by NMR. Ring inversion from one chair form to the other would convert equatorial positions to axial positions and vice versa. Eight more isomers (conformers) all having the phenyl group in axial position would thus be generated. An inversion of the group on the arsenic atom, which probably does not occur even at the temperatures to which these compounds

were subjected during distillation, does not produce isomers not already accounted for earlier. Since the ring inversion barrier is generally low for cyclohexane-type systems, a maximum of six sets of signals representing distinct isomers and/or averaged environments of pairs of conformers could be expected. The presence of at least four isomers of the trimethyl compound is indicated by the resonances of the annular protons. Quartets at 4.81, 4.93, 5.11 and 5.25 ppm with a coupling constant of 5.1 Hz have been tentatively assigned to the OCHO protons whereas the quartets at 4.24 (6.7 Hz), 4.41 (6.9 Hz), 4.45 (7.0 Hz) and 4.63 ppm (7.4 Hz) were assigned to the AsCHO protons. These assignments are based on chemical shifts and coupling constants reported for 2,4,6-trimethyl-1,3-dioxacyclohexane [8] and 2,4,6-trimethyl-1,3,5-trioxacyclohexane [7]. Annular protons on the carbon atom joining the two oxygen atoms in these compounds have coupling constants with exocyclic methyl groups of $\approx$5 Hz. In this position, one would expect a minimal effect of the arsenic atom on the CH group and therefore a close correpondence between the three compounds. The exocyclic methyl absorptions in the arsenic compound exhibit smaller chemical shift differences than do the ones for the annular protons making analysis more difficult. The annular proton resonances in the triethyl and tripropyl derivatives of I indicate that fewer isomers were present.

The infrared spectra of the heterocycles I are transparent above 3200 cm^{-1} and exhibit a strong peak at 1100 cm^{-1} that can be associated with the COC group [9]. Peaks characteristic of monosubstituted benzene are apparent at 690 and 740 cm^{-1}.

The mass spectra of the trialkyl derivatives of I exhibit very weak molecualar ion peaks (M) of less than 0.5% relative abundance and a similarly weak peak corresponding to M—H. Significant peaks correspond to fragments formed by loss of RCHO, RCHOCHR and RCHORCHO. The most intense peak is found at *m/e* 152 representing C_6H_5As. The fragment C_6H_5AsCHR is responsible for the second largest peak. Vandewalle and co-workers [10] have examined the mass spectral behavior of 1,3-dioxacyclohexanes and have found that the molecular ion peaks are also generally weak in these compounds.

There can be no doubt that the compounds prepared from phenylarsine and aldehydes have the ring structure I. It is unlikely that Adams and Palmer [5,6] had synthesized the bis(α-hydroxyalkyl)phenylarsines in spite of their analyses, which were in agreement with their postulated structures. Their observation that methylmagnesium iodide did not react with their compounds is certainly an indication that hydroxyl groups were not present. These authors [6] also claimed that upon interaction of phenylarsine and aldehydes for two days in the presence of anhydrous hydrogen chloride 1,4-dioxa-2,5-diarsacyclohexanes were formed, which were not hydrolyzed by water, dilute acids or dilute bases. The AsOC group is in general easily hydrolyzed. The identity of these ring compounds is therefore also doubtful. The chemical behavior of these compounds is, however, in agreement with the 1,3-dioxa-5-arsacyclohexane structure I.

All attempts during this investigation to detect and isolate α-hydroxyalkylarsines have been unsuccessful. NMR spectral data cannot be used with any reliability to prove that α-hydroxyalkyl compounds were present in or absent from

the reaction mixtures. Since water is formed in the reaction leading to the heterocycles I and hydrochloric acid has been added as catalyst, an O—H resonance does not unequivocally prove the presence of the hydroxyalkylarsine. The alkyl resonances would very likely be overlapping with the complex spectral peaks of the heterocycles and would be difficult to discern, especially in the case that the hydroxy compounds were present in low concentrations. In fact, no NMR signals which could be assigned to the OH group were seen in the spectra of samples of crude reaction mixtures dissolved in carbon tetrachloride.

The addition of acetyl chloride to the reaction mixtures, which perhaps might convert any α-hydroxyalkylarsine present to the acetoxy derivative, did not give the desired products. Since the heterocycles I have been recognized as cyclic acetals, an attempt was made to set free the phenylbis(α-hydroxyalkyl)-arsine in a reaction with excess methanol. The only arsenic containing product, which was isolated, was phenylarsine. This result is indicative of the thermal instability of α-hydroxyalkylarsines and makes it almost certain that the compounds which were isolated by Adams and Palmer [5,6] were the heterocycles I.

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