

Synthesis and Spectral Characterization of 2-Oxo-1,3,2-dioxarsenanes

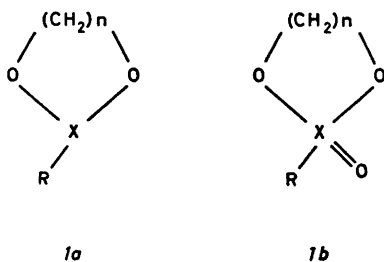
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This paper reports a synthesis of 2-oxo-1,3,2-dioxarsenanes from acyclic arsonic acid esters and 2,2-dimethyl-1,3-propanediol. Two of the compounds were also obtained by addition of the diol to arsonic acid dichlorides in the presence of pyridine. NMR spectroscopic behaviour of the compounds is consistent with conformational preference of axially oriented As=O. Attempts to prepare 2-oxo-1,3,2-dioxarsolanes were unsuccessful. The high chemical reactivity and thermodynamic instability of these compounds is explained in terms of an arsonale effect.

While trivalent phosphorus and arsenic compounds *1a* (X=P, As) have been known for a long time, the corresponding 2-oxo compounds *1b* have been prepared and studied for X=P only.



The chemistry of the latter compounds shows great variety and has been thoroughly investigated in later years.^{1,2}

The preparation of the corresponding arsenic compounds (*1b*, X=As) would be of considerable interest, particularly since these offer a possibility to test whether the models,² by which the chemical behaviour of *1b*, X=P

has been interpreted, also apply to corresponding arsenic-containing heterocycles. Another aspect which has been given some attention³ is the conformation which these molecules (*1b*, X=P) adopt, in solution and in the solid state. Conformational studies on trivalent arsenic compounds have lately appeared in the literature.⁴ It is clearly of interest to extend these studies to include the conformational behaviour of the pentavalent arsenic compounds *1b*.

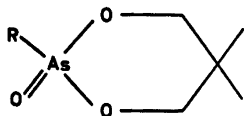
We now report the preparation and spectral characterization of three 2-oxo-1,3,2-dioxarsenanes. We also give the results from attempted preparations of the corresponding 2-oxo-1,3,2-dioxarsolanes.

RESULTS AND DISCUSSION

Possible methods for the preparation of the cyclic esters *1b*, X=As are: (1) Direct esterification of the appropriate arsonic acid with diols, (2) reaction of arsonic acid dihalides with diols in the presence of a suitable base, (3) oxidation of the corresponding trivalent compounds, (4) reaction between dihalides and the disilver salt of an arsonic acid, and (5) transesterification of acyclic arsonates with diols.

From the fact that arsonanes like R–As(OCH₃)₄ very readily undergo exchange reactions with 1,2- and 1,3-diols with the formation of bis-ring compounds,⁵ we figured that 2-oxo-1,3,2-dioxarsenanes could possibly be prepared by allowing the acyclic arsonates R–AsO(OCH₃)₂ to react with a 1,3-diol (method 5).

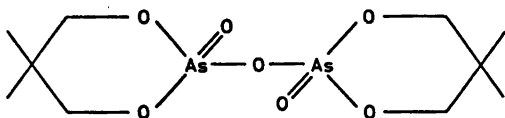
This synthetic route proved to be successful, no formation of the spirocyclic compound being observed. From 2,2-dimethyl-1,3-propanediol and $R-\text{AsO}(\text{OCH}_3)_2$ ($R = \text{CH}_3$, Ph, OCH_3) compounds **2a**, **2b** and **2c** were obtained. While **2a** and **2b** could be distilled at reduced pressure, attempted distillation of **2c** led to the formation of a high boiling substance.



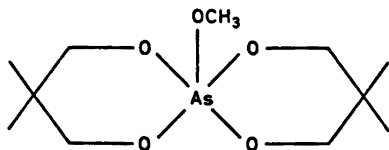
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2a, $R = \text{CH}_3$; **2b**, $R = \text{Ph}$; **2c**, $R = \text{OCH}_3$.

Its ^1H NMR spectrum was in agreement with structure **3**. The tendency of the $\text{As}-\text{OCH}_3$ grouping to form an

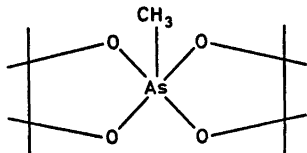


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$\text{As}-\text{O}-\text{As}$ bond was recently observed⁵ for the oxyarsorane **4**. There is also some evidence that phosphorus compounds akin to **2c** undergo a similar reaction, forming pyrophosphates.^{6,5}



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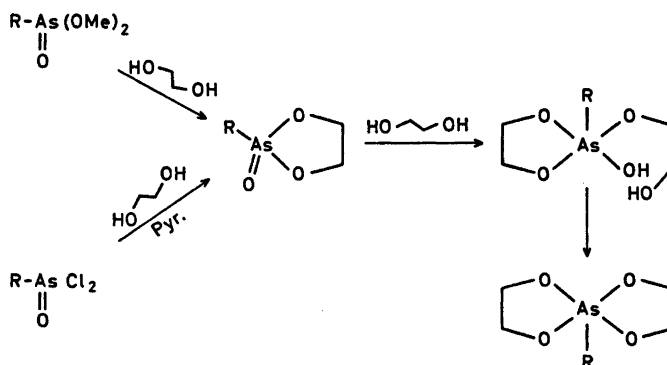
Method 5 was also investigated as a possible route to 2-oxo-1,3,2-dioxarsolanes. Treatment of methyl dimethylarsionate with 2,3-dimethylbutane-2,3-diol led, however, to the spirocyclic compound **5**.

Direct esterification of arsonic acids with 1,2-diols is known to yield the corresponding bis-ring compounds as sole products.⁸ Method **3** (oxidation) was lately attempted,⁹ but SeO_2 oxidation of 2-methyl-1,3,2-dioxarsolanes led to methylarsonic acid anhydride together with the bis-ring compounds. The reaction took the same course with dioxarsolanes derived from ethane-1,2-diol, butane-2,3-diol, and 2,3-dimethylbutane-2,3-diol. Addition of a 1,2-diol to the reaction mixture led to incorporation of that diol in the resulting spirocyclic compound, and this observation was taken as evidence for the intermediate formation of a cyclic arsonic acid ester.

In another synthetic approach (method 2) we reacted phenylarsonic acid dichloride with 1,2-diols in the presence of pyridine, but once more distillation provided the spirocyclic compounds. Also method 4 failed to give any of the desired 2-oxo-1,3,2-dioxarsolanes.

Some evidence for the formation of a 2-oxo-1,3,2-dioxarsolane was obtained, however, from GLC/MS analysis of the reaction mixture from methyl dimethylarsionate and 2,3-dimethylbutane-2,3-diol in 1:1 molar ratio. Apart from observing the bisring compound, a product giving ions at $m/e = 222$ (M^+), 221 ($\text{M}^+ - \text{H}$), 207 ($\text{M}^+ - \text{CH}_3$) and 149 ($\text{M}^+ - \text{CH}_3 - \text{C}_3\text{H}_6\text{O}$) was observed. The present findings indicate that 2-oxo-1,3,2-dioxarsolanes may be prepared, but that they are unstable both in the chemical and thermodynamic sense. These results were by no means unexpected considering the high chemical reactivity of the corresponding 2-oxo-1,3,2-dioxaphospholanes and the relatively low bond energy for $\text{As}=\text{O}$ as compared to $\text{P}=\text{O}$ (390 and 650 kJ mol^{-1} , respectively). It must be concluded that 2-oxo-1,3,2-dioxarsolanes in contrast to 2-oxo-1,3,2-dioxarsenanes are strained compounds. Thus, it may be appropriate to speak of an arsolane effect in analogy with the phospholane effect⁸ by which the high chemical reactivity of 2-oxo-1,3,2-dioxaphospholanes is rationalized.

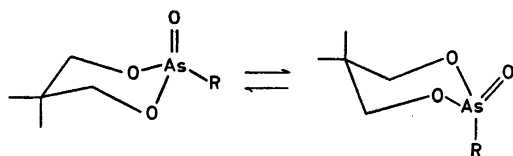
Our failure to isolate 2-oxo-1,3,2-dioxarsolanes is probably due to the reaction sequence shown in Scheme 1.



Scheme 1.

The present findings are also in agreement with the observation that spiroarsoranones containing five-membered rings are chemically more stable than the corresponding compounds containing six-membered rings.⁵

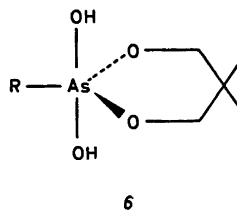
¹H NMR parameters for compounds *2a*–*c* are listed in Table 1. The spectra are consistent with the conformational equilibrium shown in eqn. (1), provided that the interconversion between conformational



states is fast on the NMR time scale. In this respect the spectral results are in analogy with those observed for the corresponding phosphorus compounds.² It should, however, be noted that while compounds *2a* and *2b* show nonequivalency for the OCH₂ as well as for the C–CH₃ hydrogens, this is not the case for *2c* (although the analogous phosphorus compound does show such nonequivalency).

The above-mentioned effect of the As–OCH₃ group seems to be rather general. Thus while the spirocyclic compounds derived from 2,3-dimethylbutane-2,3-diol and 2,2-dimethyl-1,3-propanediol show NMR nonequivalency both in the case of R = CH₃ and R = Ph, this is not observed when R = OCH₃, even at low temperatures.⁵

The nonequivalency observed for the OCH₂– and C–CH₃ signals for compounds *2a* and *2b* disappear in the presence of traces of water. On the basis of the very low hydrolytic stability of the compounds under study, the effect can be explained in terms of rapid water-catalyzed breaking and formation of As–O bonds. The equivalency of NMR signals can alternatively be explained by postulating the formation of a pentacoordinated intermediate with trigonal bipyramidal geometry, *6*.



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Table 1. ¹H NMR data for compounds *2a*–*c*. Chemical shifts (δ) are determined for 0.1 M solutions in CDCl₃ with internal TMS as standard. $J_{\text{H-C-H}}$ 11.5 Hz in compounds *2a*–*c*.

Compound	C–CH ₃		OCH ₂		As–CH ₃	Ph	OCH ₃
<i>2a</i>	0.85	1.22	3.73	4.38	2.08		
<i>2b</i>	0.88	1.32	3.83	4.52		7.6(<i>m,p</i>), 7.9(<i>o</i>)	
<i>2c</i>		1.05		4.0			3.88

The latter mechanism is similar to the one which has been put forward to explain the difficulties met with when attempting to resolve optically active arsinoxides. In this case, the formation of symmetrical oxide hydrates with TBP geometry, in which the apical positions are occupied by hydroxyl groups, is regarded to be responsible for the observed rapid racemization.⁷

If the conformational preference of 5,5-dimethyl-2-oxo-1,3,2-dioxarsenanes is similar to that of corresponding phosphorus compounds it is reasonable to expect an axially oriented As=O bond for *2a* and *2b*, whereas *2c* would be expected to prefer an equatorial As=O bond.^{3,10} Although this assumption cannot be verified by the data so far collected, the large chemical shift difference between the methylene protons in *2a* and *2b* (Table 1) indicates the operation of an anisotropy effect of the As=O bond similar to that observed for corresponding phosphorus compounds with axial P=O bonds. The chemical shift difference between the methylene protons in the corresponding 1,3,2-dioxarsenanes is 0.18 and 0.12 ppm as compared to 0.65 and 0.69 ppm for *2a* and *2b*, respectively.

Additional evidence for the axial orientation of the As=O bond in the case of *2a*, was obtained from an experiment in which increasing amounts of the shift reagent Eu(fod)₃ were added to a 0.1 M solution of *2a* in deuteriochloroform. Treatment of the induced chemical shifts as previously described for corresponding phosphorus compounds,¹⁰ led to an S₄/S₃ ratio of 2.0, thus indicating predominance of the conformer with axially oriented As=O.

EXPERIMENTAL

General. NMR spectra were recorded on Varian A60A and HA100-15D spectrometers. Mass spectral data were obtained using an A.E.I. MS 902 mass spectrometer and a Varian MAT 111 for combined GLC-MS.

As the compounds under study are readily hydrolyzed, all reactions were carried out under dry, purified nitrogen.

Trimethyl arsenate was prepared by oxidation of trimethyl arsenite. The procedure was essentially that of Hass.¹¹ B.p. 65°C/2 mmHg, lit.¹¹ 70–75°C/3–5 mmHg.

Methyl dimethylarsenate and phenyl dimethylarsenate were prepared from the silver salts

of the corresponding arsonic acids on heating with methyl iodide. The silver salts were suspended in dry benzene and an equivalent amount of methyl iodide was added. The reaction mixture was vigorously stirred during the addition and was then heated under reflux for 5 h. Silver iodide was separated and the benzene removed on a rotary evaporator. Distillation of the residue through a short Vigreux column afforded the expected products in fair to good yields.

Phenyl dimethylarsenate, b.p. 96°C/0.01 mmHg, NMR (CDCl₃): δ 3.84 (6 H, s) and 7.5–7.9 (5 H) *n*_D²⁰ 1.5436. MS [IP 70 eV; *m/e* (% rel. int.)]: 200 (18, [M–CH₃O]), 182 (12), 170 (26), 169 (32), 153 (28), 152 (26), 137 (15), 123 (33), 109 (32), 108 (14), 107 (17), 106 (11), 91 (25), 78 (65), 77 (48). Methyl dimethylarsenate, b.p. 80°C/0.3 mmHg, *n*_D²⁰ 1.4699 (lit.¹² 97°C/10 mmHg, *n*_D²⁰ 1.469) NMR (CDCl₃): δ 1.98 (3 H, s) and 3.80 (6 H, s). MS: 153 (3.5, M–CH₃), 138 (9.9, M–CH₃O), 137 (14.9, M–OCH₃), 123 (100), 121 (4.4), 107 (34.0), 93 (21.1), 92 (5.2), 91 (31.5).

The 5,5-dimethyl-2-oxo-1,3,2-dioxarsenanes were prepared from the above-mentioned arsonates. To a stirred solution of 1.04 g (0.01 mol) of dry 2,2-dimethyl-1,3-propanediol in carbon tetrachloride 0.01 mol of the appropriate arsonate was added at ambient temperature. The reaction mixture was stirred for a couple of hours and the solvent evaporated under reduced pressure. The residue was fractionated at the lowest possible pressure. Attempts to distill the 2-methoxy derivative *2c* failed.

The compounds *2a* and *2b* were also prepared from the corresponding arsonic acid dichlorides and 2,2-dimethyl-1,3-propanediol together with an equivalent amount of pyridine. The reaction was monitored by the precipitation of pyridinium hydrochloride and by GLC; the starting materials had been consumed after 1–2 h. The reaction mixture was filtered and the solvent evaporated under reduced pressure. The residue was fractionated as in the above-mentioned procedure. 5,5-Dimethyl-2-oxo-2-methyl-1,3,2-dioxarsenane b.p. 110°C/0.005 mmHg (accompanied by sublimation) M.p. 85–95°C. NMR: see Table 1; MS [70 eV; *m/e* (% rel. int.)]: 208 (2, M), 193 (19, [M–CH₃]), 163 (63), 153 (15.5), 145 (62.5), 141 (23.6), 123 (63), 117 (17.2), 109 (23), 107 (39.6), 91 (35.2). Anal. C₈H₁₃AsO₃: C, H. 5,5-Dimethyl-2-oxo-2-phenyl-1,3,2-dioxarsenane b.p. 150°C/0.005 mmHg. For NMR data see Table 1. MS: 270 (10, M), 224 (14.7), 185 (33), 169 (100), 168 (16.3), 152 (97.8), 140 (33.1), 91 (42), 78 (21.1), 77 (41.2), 73 (41), 71 (38), 56 (80), 55 (64.5). Anal. C₁₁H₁₅AsO₃: C, H.

5,5-Dimethyl-2-oxo-2-methoxy-1,3,2-dioxarsenane. This compound could not be isolated by distillation. For NMR data see Table 1.

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