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The Preparation and Dynamic Stereochemistry of Oxyarsoranes Containing Five- and Six-membered Ring Systems

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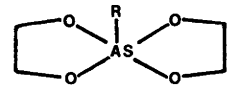
The exchange reactions of a series of acyclic oxyarsoranes with pinacol and 2,2-dimethyl-1,3-propanediol are reported. The general result of these reactions is the formation of five- or six-membered cyclic oxyarsoranes. Mixing of the arsorane $R-As(OCH_3)_4$ ($R=OCH_3$, CH_3, Ph) with the diol compound in molar ratio 1:2 leads to the quantitative formation of a spiro-arsorane. The same components in molar ratio 1:1 form the monocyclic arsorane quantitatively only in the case where the diol is pinacol and $R=OCH_3$. When $R=CH_3$ and Ph a mixture of products is obtained, including the spiro and probably also the monocyclic compound. It is concluded that the bis-ring compound is thermodynamically more stable than the mono-ring compound whether the ring is five- or six-membered. On the other hand, the spiro arsoranes derived from pinacol are generally more stable than those derived from 2,2-dimethyl-1,3-propanediol. The synthesized oxyarsoranes have been studied by variable temperature NMR in the temperature range -100 °C to 30 °C and the results interpreted in terms of pseudorotation processes. Comparison with available data on phosphorus compounds shows that there is close correspondence between the kind of pseudorotation processes undergone by analogous compounds of arsenic and phosphorus.

In a previous paper [1] we reported the preparation and variable temperature NMR spectra of oxyarsoranes of the type $R_nAs(OCH_3)_{5-n}$,

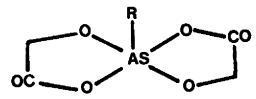
1 $n=1$ $R=OCH_3$
2 $n=1$ $R=CH_3$
3 $n=1$ $R=Ph$
4 $n=2$ $R=CH_3$
5 $n=2$ $R=Ph$
6 $n=3$ $R=Ph$

The main emphasis of the present work has been to investigate the extent to which these compounds participate in exchange reactions with 1,2- and 1,3-diols. If cyclic oxyarsoranes resulted, we were interested in examining the intramolecular bond bending processes in these compounds, using NMR as a tool.

While there is no report in the literature on cyclic oxyarsoranes containing six-membered rings (although synthesis of such compounds has been attempted),[2] oxyarsoranes of types I and II have been known for a long time.[3,4] These very stable spirocyclic compounds are



I



II

generally made by allowing 1 mol of the appropriate arsonic acid to react with 2 mol of the 1,2-dihydroxy compound, the water formed being removed either by performing the reaction in acetic anhydride or by azeotropic distillation from a proper solvent, *e.g.* benzene.[2]

The role of pseudorotation processes in I, II,[5,6] and analogous phosphorus compounds [7,8] has been studied by variable temperature NMR. In the present work such studies are extended to monocyclic derivatives and to spirooxyar-

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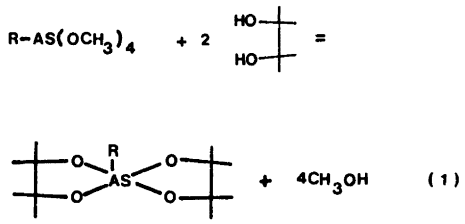
soranes containing six-membered rings. The results obtained are discussed in relation to the data on corresponding phosphorus compounds recently reported by Denney and co-workers.[9]

RESULTS AND DISCUSSION

Exchange reactions involving 1,2-diols. The reaction of one mol of *1*, *2*, or *3* with 2 mol of pinacol leads to the formation of spiroarsoranes according to reaction (1). The occurrence of this

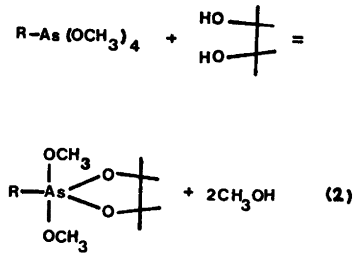


7 R = OCH_3
8 R = CH_3
9 R = Ph

reaction is not surprising when the known stability of these compounds is taken into account. However, the reaction above opens a new route to their preparation.

While the reaction between *1* and ethylene glycol gave the spirocyclic compound, the reaction between *1* and catechol resulted in a green solution which gradually darkened and polymerized. A mixture of *2* and catechol in molar ratio 1:2 led, however, to the quantitative formation of the spiro-bis(1,2-phenylenedioxy)methylarsorane.

The reaction of *1*, *2*, and *3* with pinacol in 1:1 ratio takes a route which differs for each arsorane. *1* reacts quantitatively according to eqn. 2 (R = OCH_3).



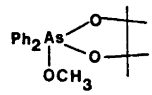
10 R = OCH_3

The product was thermally stable and could be distilled at reduced pressure.

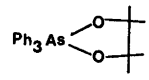
2 and *3* also undergo the above reaction, (eqn. 2) (R = CH_3 and Ph), but this is clearly not the only one taking place. In the case of *2* for instance, the NMR spectrum of the reaction mixture shows four signals in the As – CH_3 region. Thus there are at least four compounds present which contain the As – CH_3 group. However, both in the case of *2* and *3*, the spiroarsoranes *8* and *9* are observed (a pair of singlets in the C – CH_3 region). It thus appears that the bis-ring compounds are relatively more stable than the mono-ring compounds when R = CH_3 or Ph than is the case when R = OCH_3.

Clearly, steric hindrance plays a role with respect to what extent spiro and monocyclic compounds are formed when mixing $RAs(OCH_3)_4$ and a 1,2-diol. Thus while *1* and pinacol in 1:1 ratio gave the monocyclic compound *10* in quantitative yield, *1* and ethylene glycol in the same ratio resulted in a mixture of mono- and bis ring compounds.

Compounds *11* and *12* were prepared by allowing *5* and *6*, respectively, to undergo exchange reaction with pinacol.



11



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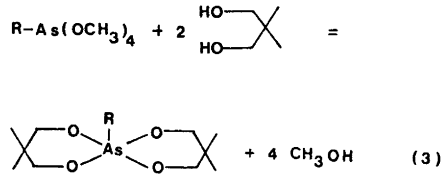
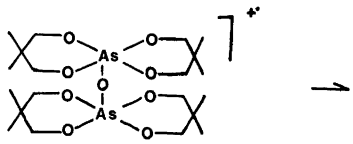
Synthesis of oxyarsoranes derived from 2,2-dimethyl-1,3-propanediol. The reactions of *1*, *2*, and *3*, respectively, with neopentyl glycol in molar ratio 1:2 yields the spirooxyarsoranes according to eqn. 3.



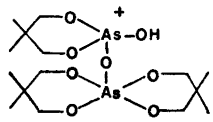
13 R = OCH_3
14 R = CH_3
15 R = Ph

While *14* and *15* could be distilled at reduced pressure, *13* was converted into a high boiling substance which solidified when left at room temperature. $As(OCH_3)_5$ was the only compound which could be isolated from the reaction mixture by distillation.

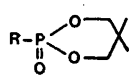
A possible structure for the nonvolatile compound is given by III. This structure is consistent with the finding that its ^1H NMR spectrum in deuteriochloroform solution shows two relatively broad singlets in the ratio 2:3 in the OCH_2- and $C-CH_3$ region, respectively. The presence of bis-ring units is also supported by an abundant ion at $m/e=279$ in its mass spectrum. Other abundant ions in the high mass region were observed at $m/e=489$, 403, 387, 301. The absence of a molecular ion is in accordance with what is found for other oxyarsoranes.[10] The ion at $m/e=489$ can be rationalized by the fragmentation



III



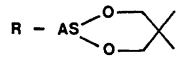
This fragmentation of the ring residue is of the same type as observed in arsoranes *14* and *15*[11] and in phosphorus compounds of the type[12]



It should be noted that the tendency of trivalent arsenic compounds to dimerize by forming an $As-O-As$ bond has been known for a long time.[13] However, the structure of the isolated compound has yet to be verified.

The reaction of *1*, *2*, and *3* with 2,2-dimethyl-1,3-propanediol in molar ratio 1:1 did not result in a single compound. From NMR it could be concluded that several species were formed. The formation of monocyclic derivatives probably occurs to some extent, but they are in every case accompanied by others, even under very mild reaction conditions. In the case of *2* the spiro compound could be clearly detected from the NMR spectrum of the reaction mixture. The reaction mixtures resulting from *1* and *3* also gave NMR spectra consistent with the presence of the respective spiro-oxyarsoranes.

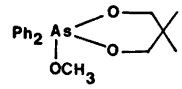
Preparation of monocyclic compounds derived from 2,2-dimethyl-1,3-propanediol was attempted by treating the trivalent arsenic compounds *16* – *18* with bromine and sodium methoxide.



16 R = Cl
17 R = CH_3
18 R = Ph

Distillation of the reaction mixtures obtained from *17* and *18* again lead to the isolation of the bis-ring oxyarsoranes. $As(OCH_3)_5$ was the only product isolated from the reaction of *16* with $Br_2/NaOCH_3$.

Compound *19* was formed by allowing *5* to react at room temperature with equivalent amounts of 2,2-dimethyl-1,3-propanediol.

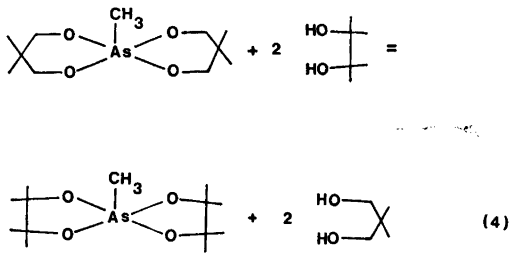


19

Relative stability of oxyarsoranes. The synthetic results seem to indicate that the spiro compounds, whether derived from pinacol or 2,2-dimethyl-1,3-propanediol are thermodynamically more stable than their acyclic analogues. Treatment of the spiro arsoranes with methanol did not lead to reversion to the acyclic compounds.

The greater stability of five-menbered cyclic oxyarsoranes as compared to those containing six-membered rings was clearly illustrated by the ^1H NMR spectrum of a deuteriochloroform solution of *14* and pinacol in molar ratio 1:2. The change in the NMR spectrum with time

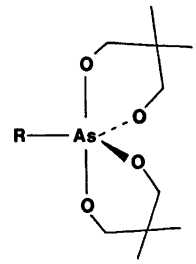
was in complete accordance with the exchange reaction shown in eqn. 4. This reaction went to completion within approximately 30 min. The main driving force for the reaction is probably a combination of crowding in the six-membered oxyarsoranes and the favourable angular situation present in oxyarsoranes containing five-membered rings.



NMR spectra of oxyarsoranes derived from 2,2-dimethyl-1,3-propanediol. ^{1}H spectral data at 25 °C for compounds *13* – *15* are given in Table 1. In all cases equivalency of O – CH_2- and C – CH_3 protons are observed. Whether the R substituent is apically or equatorially situated, a rigid trigonal bipyramidal structure would require that their respective NMR signals should be more complicated than simple singlets. The NMR results at room temperature can therefore be explained by assuming that these compounds undergo pseudorotation processes at a rate which is fast on the NMR time scale.

Cooling to −60 °C (deuteriochloroform) or −100 °C (methylene chloride or carbon disulfide) did not change the NMR spectrum of *13* essentially. A broadening of all three signals was, however, observed. *14* and *15* underwent qualitative changes on cooling. The C – CH_3 signal broadened and split into two signals of equal intensity. Similarly the methylene group split into a quartet.

The results obtained on compounds *14* and *15* mean that pseudorotation processes at these low temperatures are slow enough to be detected by NMR. The NMR spectra are consistent with the structure expected on grounds of electronegativity, *i.e.* the one in which the R group is in an equatorial position, IV.



IV

This structure would predict a NMR spectrum in which the methyl groups appear as two singlets and the methylene protons as two AB quartets. If overlapping of the AB quartets is assumed (a situation which must be considered very likely), the NMR results are in agreement with the structure pictured by IV.

The free energy of activation for the pseudorotation process leading to equivalence of the methyl groups can, knowing the coalescence temperature and the chemical shift difference between the two signals at low temperature, be estimated by means of the Eyring equation.[14] Using the values of T_c and $\Delta\nu$ listed in Table 1, the free energy of activation was found to be 11.9 kcal mol^{-1} and 12.8 kcal mol^{-1} for *14* and *15*, respectively.

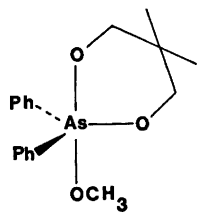
Table 1. ^{1}H NMR data [a] for oxyarsoranes derived from 2,2-dimethyl-1,3-propanediol.

Compound	δ (ppm downfield from internal TMS) [b] O – CH_2	C – CH_3	O – CH_3	As – CH_3	As – Ph	$\Delta\nu$(C – CH_3) [c] (Hz)	T_c [d] (°C)	$\Delta G^{\ddagger}$ [e] (kcal mol^{-1})
13	3.82	0.97	3.63					
14	3.86	0.99		2.02		8.4	−45	11.9
15	3.82	0.96			7.55 7.95	14.4	−24	12.8
19	3.89	0.93	3.17		7.42 7.80	45.0	+23	14.6

[a] Obtained on a JEOL JNM-C-60H spectrometer. [b] In deuteriochloroform solution at 25 °C. [c] Measured at −55 °C. [d] Coalescence temperature for ring methyl groups. [e] Free energy of activation at T_c.

The fact that compound *13* shows equivalence of methyl groups down to −100 °C can be interpreted in terms of a rather small free energy of activation for the relevant pseudorotation process. In contrast to what is the case for *14* and *15*, the R group in compound *13* is strongly electronegative. From the electronegativity rule[8] it can therefore be concluded that a transition state in which the R group adopts an apical position, is energetically more favourable in the case of *13* than in *14* and *15*. Consequently, if similar chemical shift differrences are assumed between the methyl groups, the coalescence temperature for *13* should be lower than for *14* and *15*. The failure of compound *13* to show a ^{1}H NMR spectrum in which the signals split up at low temperatures can alternatively be due to accidental identity of chemical shifts. The possibility of fast exchange of methoxy groups, catalyzed by traces of water, should also be considered.

NMR data for compound *19* are listed in Table 1. At 25 °C a singlet is observed for the methyl groups as well as for the methylene groups. Cooling caused the methylene signal to split into two signals of equal intensity, while the methyl signal remained a singlet, although broad. The NMR results are compatible with the most probable trigonal bipyramidal structure for the compound, namely the one in which the maximum number of oxygen substituents are apically situated, V.



V

In this structure the two methylene groups are non-equivalent while the methyl groups are equivalent. A similar NMR behaviour has already been noted for $Ph_2As(OCH_3)_3$.[1] This compound showed a low temperature NMR spectrum which was in agreement with a trigonal bipyramidal structure having the apical positions occupied by methoxy groups. The free energy of activation for the relevant pseudorotation process undergone by *19* was found to be 14.6 kcal mol^{-1}.

It should be noted that the NMR results from this investigation are very similar to those obtained by Denney and co-workers on analogous phosphorus compounds.[9] They found for example that while the ^{1}H NMR spectrum of the phosphorus ethoxy analogue of *13* did not change on cooling down to −65 °C, coalescence was observed for the analogues of *14* and *15*. Similarly, at −65 °C the NMR spectrum of the phosphorus-ethoxy analogue of *19* showed two distinct doublets for the methylene hydrogens and a singlet for the methyl groups. The correspondence in NMR behaviour between these closely related compounds of arsenic and phosphorus strongly indicate that the same type of structures are involved in the pseudorotation processes which they undergo.

NMR of oxyarsoranes derived from pinacol. The ^{1}H NMR spectra of compounds *7* – *9* have previously been studied by Goldwhite[5] and by Casey and Mislow.[6] At room temperature the ring methyl groups appeared as a pair of singlets in the case of *8* and *9*, while a single peak was observed for *7*. These results are in disagreement with what to expect from the energetically more favoured TBP configuration. According to the rules found valid for pentacoordinated phosphorus compounds, this configuration will be the one in which each of the five-membered rings is in an equatorial-apical position and at the same time the most electronegative substituents in apical positions. In the structure predicted from these rules, VI, there will be four different environments for the methyl groups. It should be noted that no further splitting of signals was observed on cooling down to −100 °C. On the other hand, the doublet found for *8* and *9*, collapsed to a singlet at higher temperatures (about 160 °C). As first pointed out by Goldwhite the pair of methyl signals observed for *8* and *9* can be rationalized by the occurrence of the pseudorotation process shown in Fig. 1.

The equivalency of methyl signals at higher temperatures was explained by assuming the

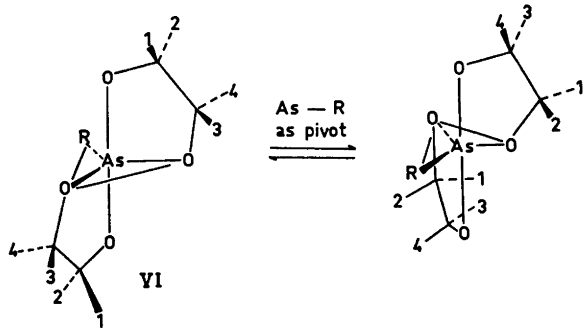
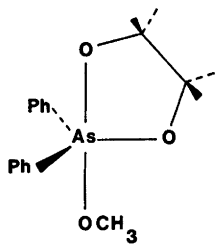


Fig. 1. Pseudorotation process.

existence of two additional successive pseudorotation processes.[5]

The free energies of activation reported by Casey and Mislow for compounds *8* and *9*, 21.8 kcal mol^{-1} and 22.8 kcal mol^{-1}, respectively, are very much larger than those obtained for the corresponding 2,2-dimethyl-1,3-propanediol derivatives. This behaviour is very similar to what observed for analogous compounds of phosphorus.[6] The effect can be explained, as pointed out by Holmes,[16] in terms



of different degree of strain in the transition state associated with the pseudorotation process leading to NMR equivalency of chemical shifts. As the transition state for this process requires diequatorial ring oxygens, it follows that less strain is to be expected in compounds containing a six-membered ring as compared to a five-membered one.

The observation that the NMR spectrum of *7* shows a singlet both at low and high temperature was explained by Goldwhite in terms of rapid interchange of ligands. However, Casey and Mislow attributed this observation to accidental isochrony of the ring methyl groups.[6]

In connection with the present work we were able to verify the latter explanation by utilizing the lanthanide chemical shift reagent Eu(fod)$_3$.[15] The addition of this compound to a carbon tetrachloride solution of *7* resulted in two downfield shifted singlet absorptions for the ring methyl groups. Presumably, the effect was due to a pseudocontact shift caused by the europium reagent upon complexation with the oxygens in *7*.

NMR data for compounds *10* and *12* are given in Table 2. No splitting of ring methyl signals was observed on cooling down to −100 °C in methylene chloride or carbon disulfide solution. The expected structure for these compounds would be the one in which the five-membered ring spans an apical-equatorial position, thus leading to two types of methyl groups. However, the methyl groups would be interchanged by a pseudorotation with the As−OCH$_3$ and As−Ph axis, respectively, as pivot. If this process is fast on the NMR time

Table 2. ^{1}H NMR data for oxyarsoranes derived from pinacol.

Compound	δ (ppm downfield from internal TMS)[a]					
	C−CH$_3$		O−CH$_3$	As−CH$_3$	As−Ph	
7	1.27		3.78			
8	1.19	1.24		2.03		
9	1.03	1.31			7.41	8.10
10	1.25		3.77			
11	1.14		3.37		7.38	8.00
12	1.11				7.34	7.64

[a] In deuteriochloroform solution at 25 °C.

scale, equivalency of ring signals will result. It may be recalled that this pseudorotation process is of the same type as the one discussed above for explaining the two methyl signals observed for *8* and *9*.

The variable temperature spectrum of compound *11* is similar to that observed in the case of *19*, Table 2. At room temperature the ring methyl groups appear as a singlet. Cooling results in gradually broadening and finally splitting into two signals. These observations indicate that the expected structure, VII, at low temperatures has a life time long enough to be detected by NMR. From the coalescence temperature (−39 °C) and the chemical shift difference between the ring methyl groups (18.2 Hz at −55 °C), the free energy of activation for the process leading to equivalency of methyl groups was estimated to be 11.8 kcal mol^{-1}.

Denney and co-workers have prepared a number of oxyphosphoranes derived from ethylene glycol.[9] The variable temperature NMR behaviour is analogous to what has been observed for the oxyarsoranes. Compound *11* is, however, an exception as the NMR spectrum of the phosphorus-ethoxy analogue was essentially unchanged on cooling to −60 °C.

Recently, an X-ray structure determination of bis-ring oxyphosphoranes derived from catechol and the analogous dithiol, initiated an alternative interpretation of the variable temperature NMR spectra obtained for spirocyclic phosphorus compounds.[16] It was shown that the NMR data obtained by Denney and co-workers could be interpreted in terms of a square pyramidal structure. From what was said above regarding the similarity in spectral behaviour between analogous compounds of phosphorus and arsenic, it is evident that the variable temperature NMR spectra obtained for the spiro oxyarsoranes can be interpreted with reference to a square pyramidal geometry for the molecule. It should be mentioned, however, that X-ray studies on cyclic oxyphosphoranes similar to the oxyarsoranes under discussion points to TBP geometry in the former compounds.[17,18] In view of these results we have interpreted the ^1H NMR spectra on the basis of a trigonal bipyramidal structure. Presumably, further work will better define the factors determining the configuration of these compounds.

EXPERIMENTAL

Instrumental. The NMR spectra were recorded on a JEOL JNM-C-60H spectrometer. Mass spectra were obtained on a JEOL JMS-D100 instrument.

Syntheses

The acyclic arsoranes *1*, *2*, *3*, *5*, and *6* were prepared as described previously.[19,1]

General procedure for the exchange reaction between an acyclic oxyarsorane and a diol. To a carbon tetrachloride or methylene chloride solution of the acyclic arsorane was added the appropriate amount of the dihydroxy compound. The reaction mixture was left for a few hours or overnight at room temperature and the volatile components thereafter pumped off at 1 mmHg. The residue was dissolved in a proper solvent and examined by NMR. In the cases where the residue was a solid or thermally stable liquid the following physical data were obtained:

10 (b.p. = 75 °C/1 mmHg)
12 (m.p. = 93 − 96 °C)
14 (b.p. = 104 °C/2 mmHg)
15 (b.p = 131 °C/0.1 mmHg)

An attempt to distill compound *13* led to the isolation of $As(OCH_3)_5$ and a fraction boiling at 110 °C/1 mmHg. However, most of the reaction mixture (about 80 % by volume) was left in the distillation flask. On cooling it turned into a wax-like solid. Recrystallisation from petroleum ether resulted in a hygroscopic material. Its ^1H NMR spectrum in deuteriochloroform solution showed two relatively broad singlet absorptions, at δ 0.09 and 3.95.

Preparation of 16, 17 *and* 18. These 1,3,2-dioxarsenanes were prepared according to well known methods[20] and purified by fractionation under vacuum.

Reaction of 16, 17 *and* 18 *with bromine/sodium methoxide.* To a methanol solution containing 0.02 mol of *16* was added 0.06 mol of sodium methoxide and thereafter dropwise 0.02 mol of bromine. After the volume of the reaction had been reduced the formed salt was separated by filtration. Distillation afforded a fraction boiling at 40 − 41 °C/1 mmHg. Its ^1H NMR spectrum in deuteriochloroform solution showed a single absorption at δ 3.74. On this basis the compound was identified as $As(OCH_3)_5$. The distillation residue, about 50 % by volume, was not subjected to further analysis.

Similarly, distillation of the filtrate resulting from reacting 0.0312 mol of *17* with 0.0624 mol of sodium methoxide and 0.0312 mol of bromine

led to the isolation of a fraction with boiling point 104 °C/2 mmHg. Its ^{1}H NMR spectrum was identical to the one obtained for compound *14*.

From 0.0353 mol of *18* was as described above obtained a filtrate which was distilled at reduced pressure. A fraction boiling at 120 °C/0.01 mmHg which had the same NMR characteristics as compound *15* was isolated.

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