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The Preparation and ^1H Nuclear Magnetic Resonance Spectra of Some Acyclic Oxyarsoranes

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It has been shown that compounds of the type $R_nAs(OCH_3)_{5-n}$, $R = CH_3$ or Ph, $n = 0$, 1, 2, 3, can be prepared by allowing the corresponding halides of trivalent arsenic to add bromine and thereafter react with sodium methoxide in methanol solution. Their variable temperature ^1H NMR spectra have been examined down to -100 °C and the results interpreted in terms of pseudorotation processes among structures with trigonal bipyramidal geometry. $Ph_2As(OCH_3)_3$ was the only compound which showed NMR nonequivalence of the methoxy groups at low temperatures.

While pentasubstituted phosphorus compounds containing one or more P–O bonds have been studied rather extensively,[1–3] the research done on analogous arsenic compounds is rather limited.[1] A considerable amount of work has also been done on pentacovalent antimony compounds having Sb–O bonds.[1] On the other hand there is strong evidence that pentacovalent arsenic compounds play an important role as reactant intermediates in reactions involving nucleophilic attack on tetracoordinated arsenic. On this background we considered it valuable to attempt synthesis of pentasubstituted arsenic compounds with one or more As–O bonds (oxyarsoranes). Given the existence of oxyarsoranes, variable temperature NMR provides a possible technique for examining their ability to undergo pentatopal isomerizations (Berry pseudorotation or turnstile rotation).[1] Hopefully, the comparison with corresponding phosphorus and antimony derivatives may lead to some generalisations regarding intramolecular processes in pentasubstituted compounds of group V elements. In the present work we consider the preparation and NMR spectra of oxyarsoranes with acyclic substituents. Oxyarsoranes incorporating five- and six-membered ring systems will be the subject of a later investigation.

Some pentacoordinated arsenic compounds with *O*-alkyl- and F-substituents have been synthesized by Hass.[4–8] For example, $As(OCH_3)_5$ was obtained as one of the products from the reaction between $O=As(OCH_3)_3$ and $Pr-NH_2$.[4] However, the sequence of reactions leading to this compound can not be regarded as established and the yield is low. Alternative reaction routes are therefore desirable. The dynamic stereochemistry, in terms of pseudorotation processes, has not been considered for the above mentioned compounds.[4–8]

RESULTS AND DISCUSSION

The oxyarsoranes *1*–*6* (Table 1) were conveniently prepared according to the general reactions:

$$R_nAsX_{3-n} + Br_2 = R_nAsX_{3-n}Br_2$$

$$R_nAsX_{3-n}Br_2 + (5-n)\ Na^+OCH_3^- = R_nAs(OCH_3)_{5-n} + (5-n)\ Na^+ + (3-n)X^- + 2Br^-$$

$R = CH_3$, Ph
X = Cl, Br, I

The reactions were performed by allowing bromine to drop into a methanol solution containing the appropriate trivalent arsenic compound and sodium methoxide in the proper ratio (see experimental section for further details). The yield in the case of *1*, *2*, and *3*

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seemed to be quantitative. *1–6* are thermally stable substances, and were, with the exception of *6*, distilled at reduced pressure. As can be expected for compounds having As-O bonds, the prepared oxyarsoranes are very readily hydrolyzed. Detailed studies on the hydrolytic stability of the compounds *1–6* have not been performed, but it appears that the hydrolytic stability decreases as the number of R groups increase, regardless of whether R is methyl or phenyl. The compounds *1*, *2* and *3* (Table 1) have been stored for more than a year at ambient temperature and appear to be completely stable. They can be handled under normal atmospheric conditions without difficulty. The reaction scheme given above offers a new and simple way of preparing this type of oxyarsoranes.

^{1}H NMR data for the arsoranes *1–6* are listed in Table 1. With the exception of compound *5* there is no essential change in spectral behaviour on cooling down to −60 °C in deuteriochloroform solution. *1–4* were also recorded in carbon disulfide at −100 °C, but no qualitative change in their NMR spectra resulted.

Assuming the oxyarsoranes to have the structure of a trigonal bipyramid (TBP), the substituents can exist in two different environments, apical and equatorial. If the TBP structure is rigid, one would expect for *1*, two different signals with relative intensity 2:3. The observation of five equivalent methoxy groups is in accordance with fast intramolecular pseudorotation, *i.e.* the activation energies for the relevant intramolecular processes are low. The observed NMR equivalence of the methoxy groups could also be explained if the chemical shift difference between apically and equatorially situated substituents is small. In this case, the temperature required to observe splitting of the NMR signal would not be obtainable, even if the activation energy for the pseudorotation process is considerable, say 15 kcal mol^{-1}. The fact that a single signal results at low temperatures whether the solvent is deuteriochloroform or carbon disulfide does not support this explanation. The NMR equivalence of substituents in pentacoordinated compounds of the type AsY_5, seems to be general. Thus the fluorines in AsF_5 [9,10] and the methyl groups in $As(CH_3)_5$ [11] and $As(p\text{-}CH_3\text{-}C_6H_4)_5$ [12] give rise to only one signal in their respective NMR spectra, even at low temperatures.

It should be noted that *1* and methanol are participating in an exchange reaction which at 25 °C is fast on the NMR time scale. Thus while *1* in deuteriochloroform solution gives a resonance signal at δ 3.74 and methanol one at δ 3.47, a mixture of these two compounds does not give rise to two separate signals. Instead, one signal, having a chemical shift in between that of methanol and *1*, is observed. This result opens the possibility that traces of methanol present in the NMR tube can catalyze an intermolecular exchange of OCH_3 groups. As a consequence, NMR equivalence of substituents may result.

In the case of pentacovalent phosphorus compounds, the generalisation that the most electronegative substituents tend to occupy the apical positions in the TBP seems to be valid.[1–3] Assuming that this electronegativity rule also applies to pentacovalent arsenic compounds, a rigid TBP structure would predict the methoxy groups in *2* and *3* to show up in NMR as two signals in 1:1 ratio. The four equivalent methoxy

Table 1. ^{1}H NMR spectral data[a] for acyclic oxyarsoranes in deuteriochloroform solution at 25 °C.

Compound	Chemical shifts, δ[b]			
	O–CH_3	As–CH_3	As–Ph	
1 $As(OCH_3)_5$	3.74			
2 CH_3-$As(OCH_3)_4$	3.62	1.93		
3 Ph-$As(OCH_3)_4$	3.65		7.55,	7.85
4 $(CH_3)_2As(OCH_3)_3$	3.36	1.83		
5 $Ph_2As(OCH_3)_3$	3.24		7.58,	8.00
6 $Ph_3As(OCH_3)_2$	2.63		7.42,	8.08

[a] The spectra were recorded at 60 Mz, using a Jeol JNM-C-60H spectrometer. [b] Downfield from internal TMS.

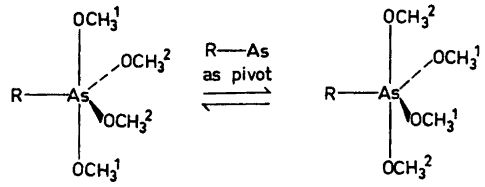


Fig. 1.

groups observed in both cases, down to −100 °C, are consistent with a low activation energy for the pseudodorotation process illustrated in Fig. 1 (R = CH_3, Ph).

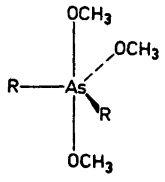
These results are in correspondence with those obtained previously for $PhAsF_4$ [9,13] and $PhP(OCH_2CH_3)_4$,[14] as the variable temperature NMR spectra of these substances showed only one signal for their respective substituents.

5 is the only oxyarsorane considered in this work which shows qualitative difference in its NMR spectrum at different temperatures. At room temperature the OCH_3 signal is very broad. Cooling causes splitting into two signals (δ 3.02, 3.98 at 40 °C) in the ratio 2:1, while heating results in a normally sharp singlet (δ 3.36 at 50 °C). The low temperature spectrum is in agreement with the structure predicted from the electronegativity rule, *i.e.* the one in which the two phenyl groups are occupying equatorial positions, I (R = Ph). This geometrical situation will have as a consequence that the equatorial methoxy group is less shielded than are the apical groups. The fact that the high intensity signal is at higher field than the low intensity signal is consistent with this deduction. The coalescence temperature for the process leading to equivalence of the methoxy groups was found to be 21 °C. From this temperature and the chemical shift difference between the two methoxy signals, 58 Hz, the free energy of activation (at the coalescence temperature) can be estimated.[15] This was found to be 14.4 kcal mol^{-1}. The variable temperature NMR spectrum of *5* is completely analogous to the one obtained for the related phosphorus compound, $Ph_2P(OCH_2CH_3)_3$.[14] The same kind of NMR behaviour is exhibited by the ^{19}F NMR spectrum of Ph_2AsF_3.

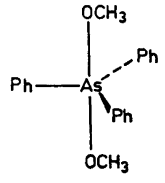
On this background one would expect compound *4* to have a NMR spectrum which on cooling changed in a manner similar to the one of *5*. This was not observed as both the methyl groups and methoxy groups each gave rise to only one signal over the temperature range studied. The result can either be explained by assuming accidental isochrony of the substituents or alternatively by postulating that the pseudorotation processes involved have activation energies which are too low to be detected by the NMR technique. There is also the possibility that traces of water can lead to exchange of methoxy groups at a rate which is rapid on the NMR time scale. It is interesting to note that $(CH_3)_2AsF_3$ has a ^{19}F NMR spectrum which is essentially invariant with temperature.[10] The single ^{19}F signal observed in this case has been attributed to an octahedral structure in which the arsenic compound acts as a Lewis acid towards the solvent molecule (acetone or acetonitrile). It is not likely that this interpretation applies to *4*, especially because of the absence of suitable donor molecules in this case.

While the low temperature spectrum of the phosphorus analogue of *4* has not been reported, the antimony analogue, $(CH_3)_2Sb(OCH_3)_3$, has been studied in detail. At −80 °C this compound showed two signals in the ratio 1:2 for the methoxy groups, an observation consistent with a structure similar to I. However, these results were, with support from molecular weight data, interpreted in terms of a dimer with octahedral structure.[16]

The NMR spectrum of compound *6* showed only one signal associated with the methoxy groups. This is in agreement with the favoured



I



II

structure in which the three phenyl groups are situated equatorially, II. There is no necessity of assuming the occurrence of fast pseudorotation processes in order to explain the observed NMR equivalence of methoxy groups, specially because the possible intramolecular processes would involve structures in which the most electronegative substituents are in equatorial positions and the least electronegative substituents in apical positions. In addition, the substantial shielding expected for the methoxy groups in II is in agreement with the high field signal found experimentally. In the case of *6*, there is, as far as NMR behaviour is concerned, complete analogy with related compounds. Thus the low temperature NMR spectra of Ph_3AsF_2,[10] $Ph_3P(OCH_2CH_3)_2$,[14] and $Ph_3Sb(OCH_3)_2$,[17] showed only one signal for the fluorine-, ethoxy-, and methoxy groups, respectively. The assumed TBP geometry has in the case of $Ph_3Sb(OCH_3)_2$ been confirmed by X-ray structure determination.[18]

In conclusion, the NMR behaviour of the oxyarsoranes considered in this study can be explained in terms of pseudorotation processes among structures having TBP geometry. There is, as far as the comparison goes, correspondence in the variable temperature NMR spectra between analogous compounds of arsenic and phosphorus. However, much work has to be done in order to determine the relative importance of the various factors governing the dynamic stereochemistry of oxyarsoranes. As a beginning, we will in future work consider oxyarsoranes containing five- and six-membered rings.

EXPERIMENTAL

Preparation of haloarsines

Diiodo(methyl)arsine was prepared by treatment of an alkaline solution of arsenic oxide with methyl iodide followed by reduction with sulfur dioxide.[19]

Dichloro(phenyl)arsine was synthesized according to Michaelis from triphenylarsine and trichloroarsine.[20]

Chlorodimethylarsine was prepared from cacodylic acid according to the procedure of Steinkopf and Mieg.[21]

Chlorodiphenylarsine was prepared from triphenylarsine and dichloro(phenyl)arsine as described by Pope and Turner.[22]

Preparation of oxyarsoranes

Pentamethoxyarsorane(1) was prepared as described previously,[23] b.p. 39 °C/2 mmHg.

Tetramethoxy(methyl)arsorane (2) was obtained by treatment of a solution of 1 mol of sodium in methanol with 0.25 mol diiodo (methyl)arsine followed by addition of 0.25 mol of bromine. The temperature of the reaction mixture was held at 0 – 5 °C during the additions. The methanol was distilled off at reduced pressure and the residue extracted with dry ether. The ether extract was freed from sodium bromide and the product distilled after evaporation of the solvent, b.p. 30 °C/0.03 mmHg.

Tetramethoxy(phenyl)arsorane(3) was obtained according to a procedure analogous to the one used for preparing *2*, b.p. 70 °C/0.01 mmHg.

Trimethoxydimethylarsorane (4). To a solution of 0.15 mol of sodium in 500 ml methanol 0.1 mol chlorodimethylarsine, and thereafter 0.1 mol of bromine was added. The reaction mixture was vigorously stirred during the additions and the temperature held at 0 °C. The reaction mixture was stirred at room temperature for 1 h after the addition was completed. Most of the methanol was distilled off and the product dissolved in ether. After evaporation of this solvent the product was distilled, b.p. 32 °C/0.2 mmHg. After brief exposure to the atmosphere the product is hydrolysed to a white solid, m.p. 195 °C, undepressed by admixture of an authentic sample of cacodylic acid.

Trimethoxydiphenylarsorane (5). This compound was prepared according to a procedure similar to the one used for *4*, b.p. 163 °C/1 mmHg. The product was readily hydrolysed when exposed to the atmosphere.

Dimethoxytriphenylarsorane (6). To a solution of sodium in methanol was added 0.05 mol triphenylarsine and thereafter 0.1 mol bromine. The temperature was held at 0 °C. Working up of the reaction mixture as described above for compound *4* resulted in a viscous material, which on exposure to air was hydrolysed to triphenylarsenic oxide. The NMR spectrum of the isolated material (Table 1) integrated in agreement with compound *6*.

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