Acta Chemica Scandinavica A 31 (1977) 845—848

NMR Studies on Cyclic Arsenites. ^{13}C NMR Spectra of Seventeen 1,3,2-Dioxarsenanes

DAGFINN W. AKSNES

Department of Chemistry, University of Bergen, Allégaten 70, N-5014 Bergen-Univ., Norway

^{13}C chemical shifts have been measured for five 2-substituted 1,3,2-dioxarsenanes and twelve of their ring-substituted methyl derivatives. A variety of general trends are observed in the ^{13}C NMR data and a comparison with related heterocyclic systems has been made.

The substituent at arsenic has a marked influence on the ring carbon shieldings. By comparing compounds differing only in the 2-substituent it is seen that the shielding at C(4,6) increases in the series Ph, Br, Cl, OPh, and OMe. However, the shift effect of these substituents except Ph, on the C(5) carbon is opposite that for C(4,6).

On the introduction of an equatorial 4- or 6-methyl group the ring carbon atoms experience lowfield α_e, β_e, and γ_e shifts of 5.6 – 6.2, 6.5 – 6.6, and 0.2 – 0.5 ppm, respectively. An axial 6-methyl group produces similar deshielding effects at the α and β carbons whereas the γ carbon is shielded. 5-*gem*-Dimethyl substitution produces significantly smaller lowfield shifts than substitution at C(6).

The ^{13}C nucleus of a single equatorial methyl group at C(4,6) resonates near 24 ppm from TMS regardless of the substituent at arsenic. Furthermore, the ^{13}C signal of an axial methyl group appears downfield from the signal of an equatorial methyl group.

Recently increasing attention has been paid to ^{13}C NMR spectra of various heterocyclic ring systems.[1] The reported ^{13}C NMR studies on 1,3-dioxanes,[2,3] trimethylene sulfites [4,5] and 1,3,2-dioxaphosphorinanes [6–8] which are of particular relevance to this work, constitute a very useful addition to previous ^{1}H NMR studies.

In favourable cases [4,9] ^{13}C chemical shifts are an order of magnitude more sensitive to steric factors than ^{1}H chemical shifts. Furthermore, quite often certain substituent trends are sufficiently well defined that even relatively small shielding differences offer valuable assistance in signal identification and may lead to definitive stereochemical assignments.[1–4,9]

As part of our NMR studies on cyclic arsenites we have investigated the ^{13}C NMR spectra of a series of 1,3,2-dioxarsenanes. Previous NMR studies [10–14] have been confined to proton spectra and the present paper reports the first ^{13}C NMR investigation on these compounds.

EXPERIMENTAL

The syntheses of the cyclic arsenites have been described in previous papers.[12–14]

The seventeen compounds were examined in deuteriochloroform solutions (*ca.* 30 % v/v) at ambient probe temperature. A small amount of TMS was added to the samples and used as internal standard whereas deuteriochloroform served as internal ^{2}H lock signal source.

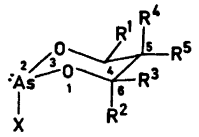
The ^{13}C NMR spectra of all compounds except III and XV, were recorded in 10 mm o.d. tubes on a Jeol FX 60 spectrometer operating at 15.04 MHz. The ^{13}C NMR spectra of III and XV were run in 5 mm o.d. tubes at 25.05 MHz on a Jeol FX 100 spectrometer. A spectral width of 2.5 or 4 kHz and a data memory size of 8 K were used.

Off-resonance decoupling was used for the purpose of signal identification.

RESULTS AND DISCUSSION

The studied compounds and the obtained ^{13}C chemical shift data are summarized in Table 1. The ^{13}C chemical shifts were obtained under proton-noise decoupling conditions. The assignment of the resonance signals due to C(4) and C(6) followed from the downfield inductive effect of the ring oxygen atoms and intensity considerations. For the methyl compounds off-

Table 1. ^{13}C NMR chemical shifts (ppm from TMS) of 1,3,2-dioxarsenanes measured in deuteriochloroform solution.



Compound	Substituents X	R^1 [a]	C(4)	C(5)	C(6)	4-Me [c]	5-Me	6-Me	2-OMe
I	Cl		62.85	30.32	62.85				
II	Br		64.26	30.21	64.26				
III	OMe		61.30	31.19	61.30				49.80
IV	OPh		62.01	30.65	62.01				
V	Ph		64.45	34.05	64.45				
VI	Cl	$R^1=Me$	69.07	36.84	63.28	23.65			
VII	OMe		67.01	37.73	61.81	23.96			49.80
VIII	OPh		67.64	37.29	62.18	23.91			
IX	Cl	$R^1=R^3=Me$	69.67	43.89	69.67	23.63		23.63 (eq)	
X	OMe		66.16	44.87	66.16	24.74		24.74 (eq)	49.15
XI [b]	Cl	$R^1=R^2=Me$	67.72	39.93	67.72	23.57		23.57 (ax)	
XII	OMe		62.46	41.43	68.44	23.89		24.22 (ax)	49.61
XIII	Cl	$R^1=R^2=R^3=Me$	65.85	46.20	77.58	23.84		33.07 (ax) 28.33 (eq)	
XIV	OMe		62.94	48.01	74.59	24.11		33.80 (ax) 28.93 (eq)	49.43
XV [b]	Cl	$R^4=R^5=Me$	71.99	32.94	71.99		22.14 (ax) 22.14 (eq)		
XVI	OMe		70.63	33.27	70.63		23.00 (ax) 21.90 (eq)		49.83
XVII	OPh		71.15	33.01	71.15		22.81 (ax) 21.77 (eq)		

[a] $R^1=H$ unless otherwise stated. [b] The observed chemical shifts are the result of rapid exchange of chlorine. [c] The 4-methyl group is equatorial.

resonance decoupling together with empirically established trends of methyl substitution on carbon resonances,[3,9,15] aided the signal assignments.

The empirical approach used in this work is similar to the methods applied in ^{13}C NMR spectroscopy by many authors to rationalize, if not always to explain, experimental results. A variety of general trends can be observed in the data of Table 1, and a comparison with similar data for the related phosphites,[6–8] sulfites [4,5] and dioxanes [2,3] should be made.

Previous ^1H NMR studies [11–14] have shown that the 1,3,2-dioxarsenane ring has a chair conformation and that the preferred orientation of the 2-substituent at arsenic is axial. Furthermore, Arbuzov *et al.* report,[16] in a study based on measurements of dipole moments and Kerr constants, that the As–Cl bond is axial in 2-chloro-4-methyl-1,3,2-dioxarsenane. Supporting evidence for a predominantly axial orientation of the 2-methoxy group is found in the remarkably similar ^{13}C chemical shift values observed for this group in the 2-methoxy-1,3,2-dioxarsenanes and their axially 2-substituted phosphorus analogues.[7] (The ^{13}C signal of the *P*-OCH_3 group appears *ca.* 1 ppm upfield in the equatorially substituted stereoisomer).

The substituent at arsenic has a marked influence on the ring carbon shieldings. By comparing compounds differing only in the 2-substituent it is seen that the shielding at C(4) and C(6) increases in the series Ph, Br, Cl, OPh, and OMe. An axially oriented substituent at arsenic is *gauche* related to the C(4,6) carbon atoms and should give rise to a maximal γ effect.[9,15] However, the steric γ ef-

Table 2. ^{13}C NMR chemical shifts of α, β, and γ ring carbons in methyl substituted 2-chloro-, 2-methoxy- and 2-phenoxy-1,3,2-dioxarsenanes relative to the unsubstituted parent compounds (possessing the same 2-substituent).

Compound	Substituents [a]	ΔC(4)	ΔC(5)	ΔC(6)
VI	2-Cl-4-Me	6.2	6.5	0.4
VII	2-OMe-4-Me	5.7	6.5	0.5
VIII	2-OPh-4-Me	5.6	6.6	0.2
IX	2-Cl-4,6-*cis*-di-Me	6.8	13.6	6.8
X	2-OMe-4,6-*cis*-diMe	4.9	13.7	4.9
XI	2-Cl-4,6-*trans*-diMe	4.9	9.6	4.9
XII	2-OMe-4,6-*trans*-diMe	1.2	10.2	7.1
XIII	2-Cl-4,6,6-triMe	3.0	15.9	14.7
XIV	2-OMe-4,6,6-triMe	1.6	16.8	13.3
XV	2-Cl-5,5-diMe	9.1	2.6	9.1
XVI	2-OMe-5,5-diMe	9.3	2.1	9.3
XVII	2-OPh-5,5-diMe	9.1	2.4	9.1

[a] The 4-methyl group is equatorial.

fect cannot account for the large downfield shifts produced by phenyl and bromine in comparison with methoxy.

The phenyl group produces a significant downfield shift on C(5) as well. In contrast, all the other 2-substituents give rise to a shift effect on C(5) opposite that for C(4,6). The relatively small ^{13}C chemical shift range measured for C(5) can be largely ascribed to the remote δ effect.[15,17]

The chemical shift effect of methyl substitution is obtained by comparing the ^{13}C chemical shifts of the methyl derivatives with the corresponding parent compounds (Table 2).

On the introduction of an equatorial 4-methyl group to the basic ring system the C(4), C(5), and C(6) ring carbon atoms of compounds VI – VIII experience α_e, β_e, and γ_e deshielding effects of 5.6 – 6.2, 6.5 – 6.6, and 0.2 – 0.5 ppm, respectively. Similar α_e deshielding effects of an equatorial 4-methyl group have been reported for 1,3-dioxane (7.3 ppm),[3] trimethylene sulfite (6.7 – 7.0 ppm)[4,5] and methyl cyclohexanes (6.0 ppm).[15]

The *ca.* 6.5 ppm β_e deshielding effect on C(5) in the 4-methyl substituted arsenanes VI – VIII is again similar to the 7.3 ppm downfield shift observed in the corresponding 1,3-dioxane[3] and trimethylene sulfite.[4,5] Mason[18] has proposed that a diamagnetic term comparable in magnitude to the paramagnetic terms is contributing to the α carbon shifts. This is a possible explanation of why the α_e and β_e shifts are roughly equal in magnitude.

The observed downfield shifts for IX and X are similar to those reported for the analogous 4,6-*cis*-dimethyl substituted 2-methoxy-1,3,2-dioxaphosphorinane[7] and trimethylene sulfite.[4] The results for these related ring systems indicate when compared with the corresponding mono-4-methyl substituted derivatives, that the shift effect of the two equatorial methyl groups is roughly additive as expected.

The ^{13}C NMR shifts for XI and XV show that a process which leads to exchange of the nuclear magnetic environments of the asymmetric C(4,6) ring carbons and/or methyl carbons, is taking place. In accordance with previous ^{1}H NMR results,[12,14,19] this process is believed to be an intermolecular chlorine exchange.

The observed α_a and β_a deshielding effects of the axial 6-methyl group in XII are consistent with similar results for the related sulfites ($\alpha_a \approx 6-14$ and $\beta_a \approx 5$ ppm).[4] Replacement of both hydrogen atoms on C(6) by methyl shifts the C(6) resonance downfield by *ca.* 14 ppm in the trimethyl derivatives XIII and XIV, as compared with 33.5 ppm in the corresponding sulfite (axial S=O).[4] In 1,3-dioxanes[3] and cyclohexanes,[15] however, *gem*-dimethyl substitution produces a significantly smaller downfield shift on the α carbon (*ca.* 4 ppm).

It is interesting to note that C(4) of compounds XI – XIV is shielded by 2 – 4 ppm relative to the corresponding 4,6-*cis*-dimethyl derivatives IX and X. Similar upfield shifts have also been observed for similarly substituted sulfites[4] and dioxanes.[3] We believe, in agreement with Buchanan *et al.*[4] that steric interactions between the axial methyl group on C(6) and the axial hydrogen atom on C(4) are likely to be causing this shielding (γ effect).

It is notable that the α carbon bearing the axial methyl group suffers a considerably larger downfield shift in the arsenites and sulfites as compared with dioxanes and cyclohexanes. However, the β and γ ring carbons appear to be similarly affected by the axial methyl group in these four six-membered ring systems.

The ^{13}C NMR data for compounds XV – XVII and 2-methoxy-5,5-dimethyl-1,3,2-dioxaphos-

phorinane [7] show that *gem*-dimethyl substitution at C(5) produces a significantly smaller shift effect than substitution at C(4,6). This observation may be a reflection of the much less hindered environments of C(5) compared with C(4,6).

Apparently the ^{13}C nucleus of a single equatorial methyl group at C(4) or C(6) resonates near 24 ppm (from TMS) regardless of the substituent at arsenic.

The ^{13}C signal of an axial methyl group at C(6) appears downfield from the signal of an equatorial methyl group at C(4,6) in XII – XIV and the analogous sulfites.[4] The remote δ effect [9,17] is probably responsible for this downfield shift.

Similarly, the ^{13}C signal of an axial methyl on C(5) appears at lower field than the geminal equatorial methyl signal in XVI and XVII and the corresponding phosphites [7] and dioxanes.[3] This is, however, the reverse of what is observed in methyl cyclohexanes [15] (upfield γ effect). In the three series of heterocyclic compounds the axial methyl group at C(5) has no *syn*-axial hydrogen atoms with which to interact but rather appears to be deshielded by the ring oxygen atoms. Similar shielding effects are apparently operating on the methyl protons as well since the proton signal of the axial methyl group appears downfield for the equatorial methyl signal in these heterocyclic compounds.[13,14,19–21]

Acknowledgements. The author is indebted to Mrs. Grete Wöien, Chemical Institute, University of Oslo, and førsteamanuensis Jostein Krane, Department of Chemistry, University of Trondheim, for their assistance in recording the ^{13}C NMR spectra.

REFERENCES

1. See, for example, Eliel, E. L., Bailey, W. F., Kopp, L. D., Willer, R. L., Grant, D. M., Bertrand, R., Christensen, K. A., Dalling, D. K., Duch, M. W., Wenkert, E., Schell, F. M. and Cochran, D. W. *J. Am. Chem. Soc. 97* (1975) 322, and references therein.
2. Jones, A. J., Eliel, E. L., Grant, D. M., Knoeber, M. C. and Bailey, W. F. *J. Am. Chem. Soc. 93* (1971) 4772.
3. Kellie, G. M. and Riddell, F. G. *J. Chem. Soc. B* (1971) 1030.
4. Buchanan, G. W., Stothers, J. B. and Wood, G. *Can. J. Chem. 51* (1973) 3746.
5. Albriktsen, P. *Acta Chem. Scand. 27* (1973) 3889.
6. Bentrude, W. G., Yee, K. C., Bertrand, R. D. and Grant, D. M. *J. Am. Chem. Soc. 93* (1971) 797.
7. Haemers, M., Ottinger, R., Zimmermann, D. and Reisse, J. *Tetrahedron 29* (1973) 3539.
8. Bentrude, W. G. and Tan, H.-W. *J. Am. Chem. Soc. 95* (1973) 4666.
9. Stothers, J. B. *Carbon-13 NMR Spectroscopy*, Academic, New York 1972; Levy, G. C. and Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley, New York 1972.
10. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand. 26* (1972) 4170.
11. Samitov, Y. Y., Taceeva, N. K., Chadaeva, N. A. and Kamai, C. H. *Chemistry of Heterocyclic Compounds*, (Russian) 1973, No. 4, p. 457.
12. Aksnes, D. W. *Acta Chem. Scand. A 28* (1974) 1175.
13. Aksnes, D. W. and Tögersen, S. *Acta Chem. Scand. A 29* (1975) 376.
14. Aksnes, D. W., Andersen, J. and Bergesen, K. *Acta Chem. Scand. A 30* (1976) 327.
15. Dalling, D. K. and Grant, D. M. *J. Am. Chem. Soc. 89* (1967) 6612; *94* (1972) 5318.
16. Arbuzov, B. A., Anonimova, I. V., Vul'fson, S. G., Yuldasheva, L. K., Chadaeva, N. A. and Vereshchagin, A. N. *Phosphorus 5* (1974) 17.
17. Grover, S. H., Guthrie, J. P., Stothers, J. B. and Tan, C. T. *J. Magn. Reson. 10* (1973) 227.
18. Mason, J. *J. Chem. Soc. A* (1971) 1038.
19. White, D. W., Bertrand, R. D., McEwen, G. K. and Verkade, J. G. *J. Am. Chem. Soc. 92* (1970) 7125.
20. Maroni, P. and Gorrichon, J.-P. *Bull. Soc. Chim. Fr.* (1972) 785.
21. Cazaux, L. and Maroni, P. *Bull. Soc. Chim. Fr.* (1972) 773.

Received June 13, 1977.