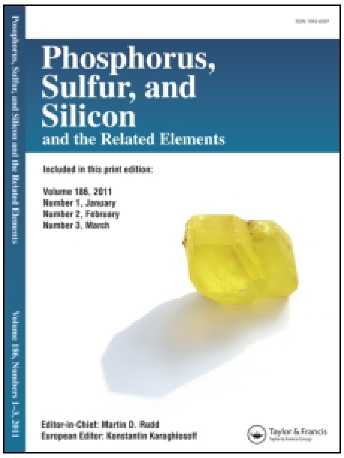

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Synthesis and Characterisation of Additional Products of Phenylarsenic(III) Dimethoxide With Substituted Benzothiazolines

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Synthesis and Characterisation of Additional Products of Phenylarsenic(III) Dimethoxide With Substituted Benzothiazolines

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Phenylarsenic(III) dimethoxide derivatives of substituted benzothia-zolines having the general formula $PhAs(OMe)_2[\overline{N(H)C_6H_4SC}R(R)']$ *where* $R = CH_3$, $R' = CH_3$ *(1),* $R = C_2H_5$, $R' = C_2H_5$ *(2),* $R = H$, $R' = C_6H_5$ *(3),* $R = CH_3$, $R' = C_6H_5$ *(4)* $R = CH_3$, $R' = C_6H_4CH_3$*-4 (5),* $R = CH_3$, $R' = C_6H_4Cl$*-4 (6), have been synthesized by the reaction of* $PhAs(OMe)_2$ *(prepared in situ) with substituted benzothiazolines in a 1:1 molar ratio in refluxing benzene solution. These newly synthesized complexes have been characterized by elemental analysis and molecular weight measurements. The spectral studies IR,* ^1H*, and* ^{13}C *NMR show the formation of the additional products in which the nitrogen atom of the benzothiazoline-ring coordinate to the central arsenic atom. A distorted trigonal bipyramidal geometry around arsenic atom has been tentatively proposed for these derivatives.*

Keywords Additional products; phenylarsenic(III) dimethoxide; spectral studies; substituted benzothiazoline

INTRODUCTION

Benzothiazoline ring generally opens up in the presence of metal ions to give corresponding metal Schiff-base complexes.[1–5] However, in some reactions, (for example, in the reaction of $SnCl_4$[6], $AsCl_3$[7], $SbCl_3$[7], and $BiCl_3$[7]) with benzothiazoline are reported to form addition products.

A survey of the literature reveals that although $SnCl_4$[6] forms additional complexes with benzothiazolines, the ring opens up when the chlorine atom in $SnCl_4$ is partially replaced by methyl/phenyl groups.[1]

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In view of the above, it was thought worthwhile to synthesize some new benzothiozoline derivatives with $PhAs(OMe)_2$. The results of these studies are being reported in this article.

RESULTS AND DISCUSSION

The interaction of $PhAs(OMe)_2$ (prepared in situ by the reaction of $PhAsCl_2$ and NaOMe in a 1:2 molar ratio) with substituted benzothiazolines in a 1:1 molar ratio in refluxing benzene solution leads to the formation of corresponding additional compounds instead of substituted compounds.

$$\mathrm{PhAsCl_2 + 2Na^+O^-Me \longrightarrow PhAs(OMe)_2 + 2NaCl \downarrow}$$

$$\mathrm{PhAs(OMe)_2 + [\overline{N(H)C_6H_4SC}R(R')] \xrightarrow{C_6H_6} PhAs(OMe)_2[\overline{N(H)C_6H_4SC}R(R')]}$$

Where $R = CH_3$, $R' = CH_3$ (1); $R = C_2H_5$, $R' = C_2H_5$ (2); R=H, $R' = C_6H_5$ (3), $R = CH_3$, $R' = C_6H_5$ (4) $R = CH_3$, $R' = C_6H_4CH_3$-4 (5), $R = CH_3$, $R' = C_6H_4Cl$-4 (6);

These compounds are found to be yellow-to-crimson solids.

It is interesting to mention that the reaction of $PhAs(OMe)_2$ (prepared in situ) and substituted benzothiazolines even in a 1:2 molar ratio also yields the simple 1:1 additional product.

IR SPECTRA

The IR spectra of these compounds exhibit a strong absorption band in the region of 3310–3350 cm^{-1} due to a νNH stretching band.[8] The nNH bending[8] mode appears in the region of 1620–1665 cm^{-1}. A shift of ~40 cm has been observed in the position of νNH stretching band towards lower frequency in comparison to its position in the corresponding free ligands. This shift in its position indicates the coordination of the benzothiazoline ligand with the arsenic atom through the nitrogen atom.

This has been further supported by the appearance of a new band in the region of 429–435 cm^{-1} assigned to ν(As$\leftarrow$S) stretching mode.[9] The ν(As-C) stretching mode[10] has been observed in the region 470 ± 5 cm^{-1}.

The bonds due to the aromatic ring appeared at their usual positions.

^{1}H NMR SPECTRA

The ^{1}H NMR spectra of ligands exhibit a broad signal in the region of δ 3.48–4.76 ppm, which is assigned to the NH proton. This indicates the

TABLE I ^{1}H NMR Spectral Data of Phenylarsenic(III)dimethoxide of Substituted-Benzothiazoline (δ pmm)

S.	PhAs(OMe)$_2$-[NHC$_6$H$_4$SCR(R′)]						C_6H_5—As + $C_6H_4\begin{smallmatrix}/N—\\ \backslash S—\end{smallmatrix}$
no.	R	R′	–NH–	R	R′	(OCH$_3$)$_2$	
1	CH$_3$	CH$_3$	4.20 (bs)	1.26 (s)	2.15 (s)	2.61 (s)	6.59–8.08 (m)
2	C$_2$H$_5$	C$_2$H$_5$	3.77 (bs)	1.44(q) CH$_2$, J = 9.31 Hz 1.07 (t) CH$_3$s J = 8.18 Hz	3.18(q) CH$_2$, J = 9.42 Hz 2.39 (t) CH$_3$, 8.27 Hz	2.84 (s)	6.29–7.79 (m)
3	H	C$_6$H$_5$	4.32 (bs)	1.33 (s)	6.31–8.78 (m)	3.68 (s)	6.41–8.49 (m)
4	CH$_3$	C$_6$H$_5$	3.20 (bs)	1.26 (s)	5.73–8.17 (m)	2.59 (s)	5.73–8.17 (m)
5	CH$_3$	C$_6$H$_4$-CH$_3$-4	4.88 (bs)	2.13 (s)	2.44 (s) CH$_3$ 6.98–9.07 (m) C$_6$H$_5$	3.56 (s)	6.98–9.07 (m)
6	CH$_3$	C$_6$H$_4$-Cl-4	4.15 (bs)	1.28 (s)	7.07–8.07 (m)	2.18 (s)	7.07–8.07 (m)

(s) = singlet, (t) = triplet, (q) = quartet, (m) = multiplet, (bs) = broad singlet, and (J) = coupling constant.

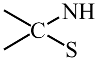
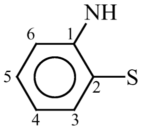
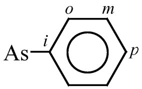
presence of a benzothiazoline ring in the ligands rather than Schiff's base. This signal has also been observed in the spectra of the compounds as a broad singlet in the range of δ 3.20–4.88 pp. This supports the formation of the additional product. A small upfield shift of ~0.5–1.0 ppm in the position of the NH proton signal has been observed in the compounds signal has been observed in the compounds. This small shift in compounds in comparison to its position in the parent ligand indicates that the coordination takes place through the nitrogen atom of the NH group of ligand moiety toward arsenic atom.

The proton signals for the alkyl groups $\left(\begin{smallmatrix}NH\\S\end{smallmatrix}\!>\!C\!<\!\begin{smallmatrix}R\\R'\end{smallmatrix}\right)$ in the spectra of complexes appear in the range of δ 1.26–4.07 pm. An upfield shift (~1.2 ppm) has been observed in the position of signals in the compounds in comparison to their position in the spectra of corresponding ligands. This further supports the involvement of a nitrogen atom of the ligand moiety in the coordination.

The spectra of the ligand as well as the compound no. (1) and (2) and two set of signals have been observed for the alkyl-group protons attached to a carbon atom. This may be due to their different orientation in space.

In the spectra of compound nos. (3)–(6), the signals due to the alkyl group protons appear at their usual position. The presence of the OMe proton signal in the spectra of the compounds (1–6) appears in the range of δ 2.18–3.68 ppm as a singlet. This further supports the formation of an additional compound.

TABLE II ^{13}C Spectral Data of Phenylarsenic(III)dimethoxide of Substituted Benzothiazoline (δ ppm)

S. no.	$PhAs(OMe)_2[\overline{NHC_6H_4SC}R(R'p)]$									
	R	R′		R	R′	$(—OCH_3)_2$			δ′	σR°
1	CH_3	CH_3	149.0	31.2	32.3	47.0	137.1 (1), 132.9 (2), 128.0 (3), 126.4 (4), 119.5 (5), 115.0 (6)	133.5, 131.6 128.6, 118.5	−10.1	−0.45
2	CH_3	C_6H_5	149.4	29.65	135.0 127.6 133.1 133.6	49.7	147.7 (1), 137.6 (2), 135.3 (3), 133.7 (4), 129.9 (5), 127.3 (6)	136.8, 133.9 128.7, 124.8	−3.9	−0.17
3	CH_3	C_6H_5-CH_3-4	153.9	22.50	134.5 128.9 129.7 124.7	47.2	144.7 (1), 144.2 (2), 132.5 (3), 130.8 (4), 131.0 (5), 125.7 (6)	141.2, 136.6 128.4, 121.8	−6.6	−0.29
4	CH_3	C_6H_4-Cl-4	153.9	26.50	137.0 123.2 132.7 135.0	49.7	148.6 (1), 140.3 (2), 139.5 (3), 129.9 (4), 128.6 (5), 123.4 (6)	139.5, 134.6 128.3, 123.6	−4.7	−0.21

Metal-Phenyl Carbon values are given in the order *ipso*, *ortho*, *meta* and *para*, respectively.

^{13}C NMR SPECTRA

A perusual of Table II shows that the ^{13}C NMR signal for the phenylene carbon attached to the nitrogen atom of compounds has been observed at about δ 149.00–153.90 ppm, whereas this signals in ligand has been observed at δ 141.50–153.85 ppm. A remarkable shift of $\sim$8.0 ppm in the position of carbon attached to a nitrogen atom in compounds in comparison to its position in the parent ligand supports the involvement of this nitrogen atom of the ligand in bonding. This shift confirms the coordination between the nitrogen atom of ligand moiety and arsenic atom.

In the compound no. (1), two set of signals have been observed for the methyl group at δ 31.23 and 32.30 ppm. In ligand these signals have been observed at δ 26.03 and 30.97 ppm. These two sets of signals for a similar alkyl group attached to the carbon atom in ligand and compound (1) due to their different orientation in space. In compounds (2–4) a signal for methyl carbons has been observed at their expected position in the range of 22.50–29.65 ppm.

The carbon atoms of the phenyl ring which are bonded to a nitrogen atom and arsenic phenyl ring carbon signal are observed at their expected positions (δ 115.0–148.60 ppm). The corrected chemical shift values, $\delta^{1\,11-12}$ calculated by the relation $\delta' = \delta\text{Cp-}\delta\text{Cm}$ (where δCp and δCm are the chemical shift values of a para and meta carbon of a phenyl ring) are found to be in the range of –3.9 to –10.1 ppm. These values have been correlated to the Hammet Tafts constant[12] by the relation $\delta^1 = 22.06\,\sigma\text{R}^\circ$ and are found to be in the range of $\delta - 0.17$ to -0.45 ppm. The negative values of δ' and σR° indicate the electron release from an arsenic atom towards the phenyl ring through dπ-Pπ conjugation and poor donor capability of the arsenic atom,[7] respectively.

In the view of the spectroscopic evidences (IR and NMR), it may be concluded that the ligand moiety behaves as a monodentate and binds to phenylarsenic(III) dimethoxide through a nitrogen atom. A distorted trigonal-bipyramidal structure in which the methoxide group occupy the axial position may be tentatively proposed for these compounds.

EXPERIMENTAL

Precautions have been taken to exclude moisture throughout the experiment. All the chemicals used were of reagent grade and purified before use. The substituted benzothiazolines have been synthesized by the condensation method[7] and were characterized by there m.p., elemental analysis, and IR and NMR spectral studies. Arsenic was estimated iodometrically.[13] Nitrogen and sulphur were estimated by Kjeldahl's[13] and Messenger's methods,[13] respectively. IR spectra were recorded as

TABLE III Synthetic and Analytical Data of Phenylarsenic(III)dimethoxide Complexes of Substituted-Benzothiazoline

	$PhAs(OMe)_2[NHC_6H_4SCR(R')]$		Reactant gm/(mM)					Analysis (%)		
S. no	R	R′	Ligand	Na	$PhAsCl_2$	Molecular formula (% yield)	NaCl gm found (Calc.)	N found (Calc.)	S found (Calc.)	As found (Calc.)
1	CH_3	CH_3	0.75 (4.54)	0.20 (9.09)	1.01 (4.54)	$C_{17}H_{22}NO_2SAs$ (95)	0.52 (0.54)	3.54 (3.69)	8.53 (8.45)	19.68 (19.75)
2	C_2H_5	C_2H_5	0.58 (3.04)	0.14 (6.08)	0.68 (3.04)	$C_{19}H_{26}O_2NSAs$ (90)	0.32 (0.36)	3.40 (3.43)	7.83 (7.87)	18.23 (18.39)
3	H	C_6H_5	0.67 (3.14)	0.14 (6.26)	0.70 (3.14)	$C_{21}H_{22}NO_2SAs$ (85)	0.42 (0.42)	3.18 (3.27)	7.44 (7.50)	17.41 (17.53)
4	CH_3	C_6H_5	0.83 (3.66)	0.16 (7.33)	0.81 (3.66)	$C_{22}H_{24}NO_2SAs$ (90)	0.40 (0.42)	3.11 (3.17)	7.24 (7.26)	16.82 (16.97)
5	CH_3	$C_6H_4CH_3$-4	0.56 (2.32)	0.10 (4.65)	0.51 (2.32)	$C_{23}H_{26}NO_2SAs$ (80)	0.26 (0.26)	3.01 (3.07)	7.00 (7.03)	16.43 (16.45)
6	CH_3	C_6H_4Cl-4	1.28 (4.91)	0.22 (9.82)	1.09 (4.91)	$C_{22}H_{23}NO_2SAsCl$ (80)	0.56 (0.57)	2.88 (2.94)	6.70 (6.73)	15.70 (15.74)

Csl pellets or Nujolmull on a Perkin Elmer 577 and Nicolet DX-FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on a Jeol FX-90Q and Bruker DPX-300 MHz NMR spectrometer using TMS as an internal reference.

GENERAL METHOD OF PREPARATION OF COMPLEXES

Since all the compounds have been synthesized by a similar method, a preparative method for only one of these derivatives is described below in detail and the results of the rest along with their analytical data are being summarized in Table III.

SYNTHESIS OF $PhAs(OMe)_2[\overline{NHC_6H_4SC}(C_2H_5)_2]$

A weighed amount of freshly cleaned sodium metal (0.14 g, 6.08 mM) was treated with anhydrous methanol (~20 mL) to prepare sodium methoxide with constant stirring and heating for ~30 min. In the above solution, a benzene solution (~30 mL) of $PhAsCl_2$ (0.68 g, 3.04 mM) was added drop by drop and the reaction mixture was refluxed for ~2 h. After cooling the above, ~20 mL of benzene solution of $NHC_6H_4SC(C_2H_5)_2$ (0.58 g, 3.04 mM) was added to the reaction mixture and was refluxed again for ~4 h to ensure the completion of the reaction. The sodium chloride thus formed was filtered off. Excess of the solvent was removed under reduced pressure to yield a light brown solid compound. The solid compound was purified by precipitating the compound from the benzene pet-ether solution. After decanting off the solvent, compound was dried under vaccum (yield 92%). The compound has been analyzed for As, N, S, and NaCl, As = 18.23, N = 3.40, S = 7.83% and NaCl = 0.32%, Calculated for $C_{19}H_{26}NSO_2As$, As = 18.39, N = 3.43, S = 7.87% and NaCl = 0.36%.

REFERENCES

[1] B. S. Saraswat, G. Srivastava, and R. C. Mehrotra,. *J. Organomet. Chem.*, **137,** 301 (1977).

[2] H. Jadamus, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **3,** 928 (1964).

[3] H. Jadamus, Q. Fernando, and H. Freiser, *J. Am. Chem. Soc.*, **86,** 3056 (1964).

[4] L. F. Lindoy and S. E. Livingstone, *Inorg. Chem. Acta*, **1,** 365 (1967).

[5] L. Jain, B. S. Saraswat, and R. C. Mehrotra, *Indian J. Chem.*, **21A,** 583 (1982).

[6] E. N. Sakuntala, Ph.D. Thesis, University of Rajasthan, 1982.

[7] H. P. S. Chauhan, G. Srivastava, and R. C. Mehrotra, *Indian J. Chem.*, **23,** 436 (1984).

[8] G. N. Chremos and R. A. Zingaro, *J. Organomet. Chem.*, **22,** 647 (1970).

[9] G. O., Doak, G. G. Longman, and L. D. Freedman, *J. Organomet. Chem.*, **4,** 82 (1965).
[10] G. E. Maciel and J. J. Natterstud, *J. Chem. Phys.*, **42,** 2427 (1965).
[11] G. N. Bodner and L. J. Todd, *Inorg Chem.*, **13,** 360 (1974).
[12] P. J., Craig *Comprehensive Organometallic Chemistry*, (Wilikinson, F. G. A. Stone, and E. W. Abel) (Oxford: Pergamon Press), **2,** 979 (1982).
[13] A. I. Vogel, *A Text Book of Qualitative Analysis*, London: Longman, 1978.