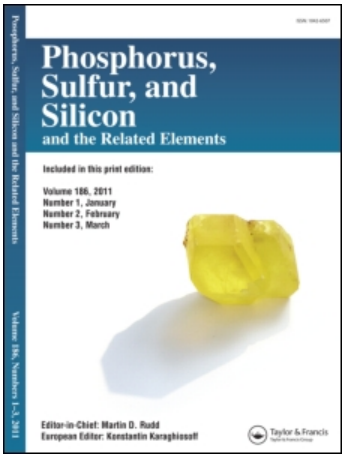

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Synthesis and Spectroscopic Properties of Mixed Aryloxide-Glycolate Derivatives of Arsenic(III)

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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF MIXED ARYLOXIDE-GLYCOLATE DERIVATIVES OF ARSENIC(III)

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The reaction in 1:1 molar ratio of $\overline{OGOA}sCl$, *where* $G = CH_2CH_2$, $CHMeCHMe$, CMe_2CMe_2, $CHMeCH_2CMe_2$, *and* $CMe_2CH_2CH_2CMe_2$, *and substituted phenols ArOH (Ar =* $C_6H_3Me_2$*-2,6;* $C_6H_3Pr^i$*-5-Me-2;* $C_6H_3Pr^i$*-2-Me-5 and* $C_6H_3Pr^i_2$*-2,6), in the presence of one equivalent of triethylamine in benzene afford volatile colorless liquids of the type* $\overline{OGOA}sOAr$. *All these derivatives have been characterized by elemental analyses, molecular weight measurements, and spectroscopic [IR, NMR(*^1H *and* ^{13}C*)] studies.*

Keywords: Arsenic(III) derivatives; aryloxides; aryloxide-glycolate derivatives

During the past two decades there have been unprecedented developments in the aryloxo chemistry of metals,[1–3] resulting in the synthesis and characterization of many novel compounds and studies on their catalytic activity. Furthermore, a number of interesting types of antimony[3–6] and bismuth[3,7,8] aryloxides have been synthesized (by a variety of methods) and characterized. The chemistry and structural features of fascinating types of bismuth aryloxide complexes[3,7,8] have been reviewed by Whitmire et al.[7,8] Interestingly, there is still a paucity of preparative, analytical, and physicochemical data for aryloxo complexes of arsenic(III). Furthermore, only a limited number of mixed glycolate-ligand derivatives of arsenic(III) are known,[9–11]

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and derivatives of arsenic(III) containing both glycolate and aryloxide groups are unknown even today.

We, therefore, report for the first time in this article the synthesis and spectroscopic properties of mixed glycolate-aryloxide derivatives of arsenic(III).

EXPERIMENTAL

All synthesis and manipulations were preformed under a moisture free environment. Benzene, toluene, and hexane (BDH) were dried by refluxing over sodium benzophenone ketyl and distilled prior to use. Glycols were dried by refluxing over $Al(OPr^i)_3$ followed by distillation. Triethylamine was dried by keeping over potassium hydroxide (KOH) pellets for ~48 h, followed by distillation at 89°C/760 mm. Chloro(glycoxo)arsines, $\overline{OGOA}sCl$ (G = CH_2CH_2,CHMeCHMe, $CHMe_2$ CMe_2, $CHMeCH_2CMe_2$, $CMe_2CH_2CH_2CMe_2$) were prepared by the procedure described in the literature[11] and distilled prior to use. Chloride was determined by Volhard's method. Arsenic was determined iodometrically[12] using KI and starch as an indicator. Elemental (C, H) analyses were performed by the Microanalytical Laboratory of RSIC (CDRI), Lucknow.

IR spectra of the compounds were recorded as Nujol mull on a Nicolet Magna 550 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on JEOL FX-90Q spectrometer in $CDCl_3$ and CCl_4 respectively. Molecular weights were determined in benzene on a Gallenkamp ebulliometer.

Preparation of $\overline{OCHMeCH_2CMe_2OA}sOC_6H_3Me_2$-2,6 (2f)

To a benzene (~30 ml) solution of $\overline{OCHMeCH_2CMe_2OA}sCl$ (2.63 g, 11.64 mmol) and $HOC_6H_3Me_2$-2,6 (1.42 g, 11.65 mmol) was added a solution of triethylamine (1.17 g, 11.64 mmol) in benzene (~40 ml), and the resulting reaction mixture was stirred at room temperature for ~6 h, followed by refluxing for ~2 h. The precipitated Et_3NHCl was removed by filtration. Removal of the volatile components from the filtrate, followed by distillation under reduced pressure (b.p. 104°C/0.5 mm) affords colorless liquid in 78% yield. Adopting a procedure similar to (**2f**) other derivatives listed below also have been prepared from appropriate reactants with their amounts actually used are given in brackets.

$\overline{OCH_2CH_2OA}sOC_6H_3Me_2$-2,6 (**2a**): $\overline{OCH_2CH_2OA}sCl$ (1.81 g, 10.62 mmol), Et_3N (1.074 g, 10.62 mmol), and $HOC_6H_3Me_2$-2,6 (1.29 g, 10.62 mmol)

$\overline{OCHMeCHMeOAs}OC_6H_3Me_2$-2,6 (**2b**): $\overline{OCHMeCHMeOAs}Cl$ (2.09 g, 10.55 mmol), Et_3N (1.07 g, 10.55 mmol), and $HOC_6H_3Me_2$-2,6 (1.29 g, 10.55 mmol)

$\overline{OCHMeCHMeOAs}OC_6H_3Pr^i_2$-2,6 (**2c**): $\overline{OCHMeCHMeOAs}Cl$ (2.12 g, 10.67 mmol), Et_3N (1.08 g, 10.67 mmol), and $HOC_6H_3Pr^i_2$-2,6 (1.90 g, 10.67 mmol)

$\overline{OCMe_2CMe_2OAs}OC_6H_3Me_2$-2,6 (**2d**): $\overline{OCMe_2CMe_2OAs}Cl$ (1.92 g, 8.49 mmol), Et_3N (0.859 g, 8.49 mmol), and $HOC_6H_3Me_2$-2,6 (1.04 g, 8.49 mmol)

$\overline{OCMe_2CMe_2OAs}OC_6H_3Pr^i_2$-2,6 (**2e**): $\overline{OCMe_2CMe_2OAs}Cl$ (2.31 g, 10.21 mmol), Et_3N (1.03 g, 10.21 mmol), and $HOC_6H_3Pr^i_2$-2,6 (1.82 g, 10.21 mmol)

$\overline{OCHMeCH_2CMe_2OAs}OC_6H_3Me_2$-2,6 (**2f**): $\overline{OCHMeCH_2CMe_2OAs}Cl$ (2.64 g, 11.64 mmol), Et_3N (1.17 g, 11.64 mmol), and $HOC_6H_3Me_2$-2,6 (1.42 g, 11.64 mmol)

$\overline{OCHMeCH_2CMe_2OAs}OC_6H_3Pr^i_2$-2,6 (**2g**): $\overline{OCHMeCH_2CMe_2OAs}Cl$ (2.38 g, 10.05 mmol), Et_3N (1.06 g, 10.5 mmol), and $HOC_6H_3Pr^i_2$-2,6 (1.87 g, 10.05 mmol)

$\overline{OCHMeCH_2CMe_2OAs}OC_6H_3Pr^i_2$-5-Me-2 (**2h**): $\overline{OCHMeCH_2CMe_2OAs}$-Cl (2.45 g, 10.82 mmol), Et_3N (1.09 g, 10.82 mmol), and $HOC_6H_3Pr^i$-5-Me-2 (1.62 g, 10.82 mmol)

$\overline{OCHMeCH_2CMe_2OAs}OC_6H_3Pr^i_2$-2-Me-5 (**2i**): $\overline{OCHMeCH_2CMe_2OAs}$-Cl (1.14 g, 5.03 mmol), Et_3N (0.509 g, 5.03 mmol), and $HOC_6H_3Pr^i$-2-Me-5 (0.755 g, 5.03 mmol)

$\overline{OCMe_2CH_2CH_2CMe_2OAs}OC_6H_3Me_2$-2,6 (**2j**): $\overline{OCMe_2CH_2CH_2CMe_2OAs}Cl$ (2.26 g, 8.87 mmol), Et_3N (0.898 g, 8.87 mmol), and HOC_6H_3Me-2,6 (1.01 g, 8.87 mmol)

RESULTS AND DISCUSSION

Equimolar reactions of the precursor chloro(glycoxo)arsines, $\overline{O\text{-}G\text{-}OAs}Cl$, with substituted phenols ArOH (see Experimental section) in the presence of Et_3N afford mixed glycolate-aryloxides of the type $\overline{O\text{-}G\text{-}OAs}OAr$:

$$\overline{OGOAs}Cl + Et_3N + ArOH \xrightarrow{C_6H_6} \begin{array}{c} O \\ G \end{array}\!\!\begin{array}{c} \diagup \\ \diagdown \end{array}\!\!\begin{array}{c} O \\ O \end{array}\!\!\begin{array}{c} \diagup \\ \diagdown \end{array}\!\!As\!\!\begin{array}{c} \diagup \\ \diagdown \end{array}\!\!O\!\!\begin{array}{c} \diagup \\ \diagdown \end{array}\!\!Ar + Et_3NHCl\downarrow \qquad (1)$$

Derivatives **2a**–**2j** (Table I) are highly moisture-sensitive, colorless, volatile liquids (whereas, **2e** is a solid), soluble in common organic

TABLE I Preparative, Analytical, and Some Physical Data of New Arsenic(III) Compounds

Compound[a]	Empirical formula (Yield %)[b]	b.p. °C/mm (Yield %)[c]	Analysis (%) found (calcd.)			m.wt. found (Calcd.)
			As	C	H	
2a	$C_{10}H_{13}AsO_3$ (2.65, 97.67)	105/0.6 (71.5)	29.45 (29.26)	46.14 (46.91)	5.28 (5.11)	270 (256)
2b	$C_{12}H_{17}AsO_3$ (2.95, 96.7)	106/0.5 (88)	26.47 (26.38)	50.42 (50.74)	6.21 (6.03)	290 (284)
2c	$C_{16}H_{25}AsO_3$ (3.54, 96.6)	112/0.4 (87)	22.59 (22.03)	56.24 (56.51)	7.60 (7.41)	346 (340)
2d	$C_{14}H_{21}AsO_3$ (2.58, 97.6)	130/0.5 (75.8)	23.98 (24.01)	53.73 (53.89)	6.81 (6.76)	324 (312)
2e	$C_{18}H_{29}AsO_3$ (3.52, 93.7)	160/0.6 (77.8)	20.21 (20.35)	58.24 (58.62)	7.72 (7.94)	372 (368)
2f	$C_{14}H_{21}AsO_3$ (3.59, 97)	103/0.5 (78)	23.95 (24.01)	53.24 (53.89)	6.82 (6.76)	325 (312)
2g	$C_{18}H_{29}AsO_3$ (3.85, 99)	116/0.5 (72.2)	20.46 (20.35)	58.32 (58.74)	7.75 (7.94)	373 (368)
2h	$C_{16}H_{25}AsO_3$ (1.70, 98.2)	145/0.6 (74)	22.48 (22.03)	56.03 (56.51)	7.05 (7.41)	349 (340)
2i	$C_{16}H_{25}AsO_3$ (3.60, 97.7)	145/0.5 (80)	22.55 (22.03)	56.10 (56.51)	7.52 (7.41)	353 (340)
2j	$C_{16}H_{25}AsO_3$ (2.98, 96.85)	140/0.5 (70)	22.27 (22.03)	56.28 (56.51)	7.61 (7.41)	352 (340)

[a]All are colorless liquid, except **2e**, which is a solid.
[b]Refers to undistilled product.
[c]Refers to distilled product.

solvents (benzene, toluene, dichloromethane, carbon tetrachloride), and monomeric (ebullioscopically) in benzene.

SPECTROSCOPIC STUDIES

IR Spectra

Derivatives **2a–2j** (Table II) exhibit medium to strong absorptions in the regions 1029–1095 cm^{-1} and 1235–1279 cm^{-1} due to ν(C—O) alkoxide and ν(C—O) phenoxide respectively. An increase of ~7 cm^{-1} in the phenoxo ν(C—O) of the new derivatives supports for O-bonded phenoxo group to arsenic(III). The ν(C—C) has been observed in the region 838–882 cm^{-1}. The derivatives **2a–2j** show absorption bands in the regions 720–765 cm^{-1} and 444–448 cm^{-1} assignable to ring pulsation and ring vibration respectively. The appearance of new strong absorption band in the region 588–618 cm^{-1} may be assigned to ν(As—O).

TABLE II IR Spectral Data (cm^{-1}) for Arsenic(III) Compounds

Compound	νC—O glycolate (Phenolate)	νC—C	ν(As—O)	Ring pulsation	Ring vibration
2a	1044, s (1279, m)	882, m	588, s	765, m	488, s
2b	1048, m (1250, m)	853, s	617, s	720, s	459, s
2c	1073, s (1268, s)	838, s	574, s	764, m	444, s
2d	1095, s (1265, m)	882, m	574, m	735, s	452, s
2e	1074, m (1257, s)	852, m	574, s	735, s	459, s
2f	1044, s (1279, s)	838, m	588, s	765, s	466, m
2g	1036, s (1265, s)	846, m	558, s	749, m	459, m
2h	1029, m (1279, s)	867, s	588, s	735, s	474, m
2i	1044, m (1235, m)	867, s	570, s	735, s	473, s
2j	1044, m (1265, s)	838, s	558, s	765, m	444, m

m = medium; s = strong.

^{1}H NMR Spectra

^{1}H NMR spectral data with peak assignment are presented in the Table III, which reveal the following: (1) Positions of the multiplets δ6.55–7.21 due to th aromatic protons of **2a–2j** remains almost unaltered; (2) chemical shifts of signals characteristic of glycolate moiety in the region δ1.13–5.03 are deshielded by ~0.22 ppm; and (3) the chemical shifts of the substituents on phenyl ring in the region δ1.17–3.32 remain almost unchanged.

^{13}C NMR Spectra

The ^{13}C NMR spectra (in CCl_4) of only four typical derivatives **2a**, **2b**, **2c**, and **2i** have been recorded. The characterstic chemical shifts and assigments for glycolate and substituents on aryl moieties are:

2a: δ67.28 (**C**H_2, Glycolate), 17.49 (**Me**$_2$-2,6, Phenyl group); **2b**: 76.59 (**C**HMe, Glycolate), 16.25 (CH**Me**, Glycolate), 17.49 (**Me**$_2$-2,6, Phenyl group); **2c**: 85.21 (**C**Me_2, Glycolate); 23.67 (C**Me**$_2$, Glycolate), 72.42 (**C**HMe_2, Phenyl group), 26.67 (CH**Me**$_2$, Phenyl group); **2i**: 75.78

TABLE III ^{1}H NMR Spectral Data (δ, ppm) for Arsenic(III) Compounds

Compound	Aromatic-H	Me/Pr^i (ArOH)	Glycolate moiety
2a	6.78–7.45	2.25 (s, **Me**$_2$-2,6)	4.18 (m, C**H**$_2$)
2b	6.75–7.35	2.28 (s, **Me**$_2$-2,6)	4.51 (m, C**H**Me), 1.13 (d, J = 6.2 Hz, CH**Me**)
2c	6.95–7.45	3.29 (sept, J = 6.2 Hz, C**H**Me$_2$) 1.16 (d, J = 6.2 Hz, CH**Me**$_2$)	4.58 (m, C**H**Me), 1.25 (d, J = 6.2 Hz, CH**Me**)
2d	6.75–7.38	2.25 (s, **Me**$_2$–2,6)	1.36 (s, C**Me**$_2$)
2e	6.97–7.38	3.26 (sept., J = 6.2 Hz, C**H**Me$_2$), 1.24 (d, J = 6.2 Hz, CH**Me**$_2$)	1.49 (s, C**Me**$_2$)
2f	6.68–7.29	2.26 (s, **Me**$_2$–2, 6)	1.27 (s, C**Me**$_2$), 1.35 (d, J = 6.2 Hz, CH**Me**), 4.99 (m, C**H**Me), 1.66 (m, C**H**$_2$)
2g	6.82–7.19	3.31 (sept, J = 6.2 Hz, C**H**Me$_2$), 1.17 (d, J = 6.2 Hz, CH**Me**$_2$)	1.27 (s, C**Me**$_2$), 1.30(d, J = 6.2 Hz, CH**Me**), 4.91 (m, C**H**Me), 1.66 (m, C**H**$_2$)
2h	6.66–7.38	3.18 (sept, J = 6.2 Hz, C**H**Me$_2$), 1.20 (d, J = 6.2 Hz, CH**Me**$_2$), 2.31 (s, **Me**)	1.27 (s, C**Me**$_2$), 1.36 (d, J = 6.2 Hz, CH**Me**), 5.03 (m, C**H**Me), 1.66 (m, C**H**$_2$)
2i	6.75–7.45	2.84 (sept, J = 6.2 Hz, **CH**Me$_2$), 1.20 (d, J = 6.2 Hz, CH**Me**$_2$), 2.25 (s, **Me**)	1.27 (s, C**Me**$_2$), 1.35 (d, J = 6.2 Hz, CH**Me**), 5.03 (m, C**H**Me), 1.66 (m, C**H**$_2$)
2j	6.72–7.19	2.22 (s, Me$_2$–2,6)	2.31 (s, C**Me**$_2$), 1.43 (m, C**H**$_2$)

(C**Me**$_2$, Glycolate), 74.92 (**C**HMe, Glycolate), 63.32 (**C**H$_2$, Glycolate), 26.92 (CH**Me**, Glycolate), 74.75 (**C**HMe$_2$, Phenyl group), 23.78 (CH**Me**$_2$, Phenyl group). In all these derivatives signals due to aromatic carbon atoms appear at δ 120.47–152.53.

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