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Metal-Induced Rearrangement of Benzothiazoline Ring: Synthesis and Characterization of Some New Organoantimony(V) Derivatives of N, O, and S Atom Containing Schiff Base Ligands

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ABSTRACT: *Some new triphenylantimony(V) derivatives of Schiff bases having the composition* $Ph_3S\overline{b[SC_6H_4N:C(R)CH:CO}COOCH_3]$ *have been synthesized by the equimolar reactions of* Ph_3SbBr_2 *with newly synthesized benzothiazoline ligands,* $H\ \overline{NC_6H_4SC}(R)CH:C(OH)COOCH_3$ *(where* $R=C_6H_5(H_2L^1)$, $4\text{-}BrC_6H_4(H_2L^2)$, $4\text{-}ClC_6H_4(H_2L^3)$, $4\text{-}CH_3OC_6H_4(H_2L^4)$, $4\text{-}CH_3C_6H_4(H_2L^5)$*). The reaction proceeds with the rearrangement of benzothiazoline ring. All the derivatives have been characterized by elemental analyses, molecular weight measurements and their plausible structures have been proposed on the basis of IR and NMR (*^1H *and* ^{13}C*) spectral studies.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:70–75, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20260

INTRODUCTION

Benzothiazoline ring is reported to open in the presence of metal ion, and rearrangement of the ring yields corresponding metal derivatives of Schiff bases [1–2]. However, in certain cases the ring opening does not take place and only addition compounds are formed, for example, when the reaction of $AsCl_3$[3], $SbCl_3$[3], and $BiCl_3$[3] is carried out with benzothiazoline, the opening of ring does not take place and simple 1:1 addition products are obtained. Even when $PhAsCl_2$[4] is used, simple addition product is obtained. However, when the reaction is carried out with Ph_3Bi [1], Me_3SnOH [2], and $Me_3Sn(OEt)$ [2], rearrangement of the ring takes place and substituted products are obtained.

In view of the above, it was considered worthwhile to use organoantimony(V)alkoxide for the synthesis of benzothiazoline derivatives. Since the alkoxy group is more labile, it may react with NH proton to lead the pathway for the opening of the ring. Moreover, the presence of antimony atom in higher oxidation state may also facilitate the opening of the ring. In the present communication, we report the synthesis and characterization of organoantimony(V) derivatives of Schiff bases formed by the rearrangement of benzothiazoline in the presence of organoantimony(V) moiety.

RESULTS AND DISCUSSION

Reactions of $Ph_3Sb(OPr^i)_2$ with corresponding benzothiazoline ligands in 1:1 molar ratio in refluxing benzene solution proceed with rearrangement of benzothiazoline ring and, thus,

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yield the triphenylantimony(V) derivatives, $\mathrm{Ph_3\overline{Sb[SC_6H_4N : C(R)CH : CO}COOCH_3]}$.

$$\begin{aligned}&\mathrm{Ph_3Sb(OPr^{\it i})_2}\\&\qquad+\mathrm{H\overline{NC_6H_4SC}(R)CH: C(OH)COOCH_3} \xrightarrow[\text{Reflux}]{\mathrm{C_6H_6}}\\&\mathrm{Ph_3\overline{Sb[SC_6H_4N: C(R)CH: CO}COOCH_3]} + \mathrm{2Pr^{\it i}OH} \uparrow\end{aligned}$$

where $\mathrm{R = C_6H_5}$, $\mathrm{4\text{-}BrC_6H_4}$, $\mathrm{4\text{-}ClC_6H_4}$, $\mathrm{4\text{-}CH_3OC_6H_4}$, $\mathrm{4\text{-}CH_3C_6H_4}$.

Isopropanol produced in the reaction was fractionated off azeotropically with benzene. The amount of liberated isopropanol in the azeotrope was monitored regularly to check the progress and the completion of the reaction.

After stripping off the volatile components under reduced pressure at the room temperature, colored viscous compounds are obtained. These compounds are found to be soluble in common organic solvents such as benzene, chloroform, etc. Ebullioscopic molecular weight measurements in benzene solution reveal the monomeric nature of these derivatives. These compounds have been further characterized by IR and NMR (^{1}H and ^{13}C) spectral studies. The results of these studies are described in the following section.

Spectroscopic Studies

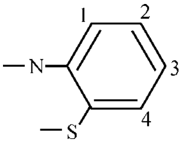
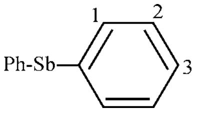
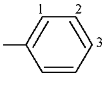
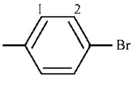
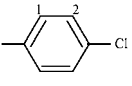
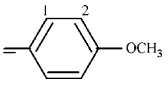
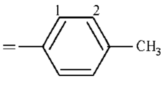
Infrared Spectra. A comparative study of IR spectra of these complexes with those of free ligands shows the disappearance of NH absorption band, which was observed as a broad band in the range 3225–3325 cm^{-1} in the spectra of free ligands. The spectra also show the bands in the range 1590–1606, 425–430, and 390–409 cm^{-1}, which have been assigned to ν(C=N), ν(Sb—S) [5], and ν(Sb ← N) [6], respectively. The IR data indicate the removal of NH proton. The presence of ν(C=N) and ν(Sb—S) bands indicates the rearrangement of benzothiazoline ring and subsequent formation of Sb ← N and Sb—S bonds. A broad band observed at 3638–3417 cm^{-1} in the spectra of free ligands, which has been assigned to ν(O—H) group absorption band, is found to be absent in the spectra of the corresponding organoantimony(V) derivatives. This indicates that this group (—OH) is deprotonated during complex formation. This has also been supported by the appearance of ν(Sb—O) [7] absorption band at 755–763 cm^{-1} in the spectra of these complexes. The ν(Sb—C) mode of vibrations appears in the range 449–472 cm^{-1} in these complexes [7].

^{1}H NMR Spectra. The signal observed at δ 3.90–4.40 ppm in the spectra of free ligands and assigned to NH group is found to be absent in the spectra of corresponding organoantimony(V) derivatives. This indicates the deprotonation of NH group. Appearance of =CH and —OH signals in the spectra of free ligands indicates enolization of these ligands. Disappearance of —OH signal and a downfield shift in the position of =CH signal in the corresponding complexes indicate the involvement of >C—OH group in bonding. Methyl(ester) group protons are observed as singlet in the range δ 2.30–2.59 ppm. The substituted phenylene ring protons are observed in the range δ 7.04–7.85 ppm. The phenyl ring protons attached to the central antimony atom appear as complex pattern in the range δ 7.11–8.17 ppm in these derivatives (Table 1).

^{13}C NMR Spectra. Some useful information about the mode of bonding and the geometry of these derivatives has been obtained on the basis of a comparative study of ^{13}C NMR spectra of these derivatives with the spectra of free ligands. The signal observed at δ 158.68–160.07 ppm in the spectra of free ligands, and has been assigned to CN—R signal, shows a downfield shift (~4 ppm) on complexation. This indicates the rearrangement of benzothiazoline ring on complexation and consequent formation of Schiff base derivatives with the formation of Sb←N and Sb—S bonds. Formation of these bonds is further supported by a downfield shift in the position $\mathrm{C_1}$ and $\mathrm{C_2}$ carbon signals of $\mathrm{—NC_6H_4S—}$group, respectively (Table 2). The signals of >C—O and =CH group carbons also show a downfield shift on complexation, indicating the participation of >C—O group in bonding. The signal observed at δ 24.84–25.70 ppm has been assigned to $\mathrm{CH_3}$(ester) signal. The $\mathrm{—NC_6H_4S—}$group carbons have been observed in the range δ 121.0–153.85 ppm. The >C=O(ester) group signal has been observed in the range δ 194.87–196.96 ppm. Absence of any shift in the position of this signal on complexation indicates that this group does not participate in bonding. A new set of four signals appears in the range δ 127.27–152.37 ppm has been assigned to phenyl ring carbons attached to the central antimony atom.

On the basis of the above spectroscopic evidences, it is clear that the ligands behave as bifunctional tridentate moiety in these complexes. In view of the monomeric nature of the tridentate ligand moiety and the presence of three phenyl rings on central antimony atom, the octahedral geometry shown in Fig. 1 seems to be highly plausible for these derivatives.

TABLE 1 ^{1}H NMR Spectral Data (δ, ppm) of the Complexes, $\mathrm{Ph_3S\overline{b[SC_6H_4N{:}C(R)CH{:}CO}COOCH_3]}$

Complex	*R*	*CH_3(ester)*	*=CH*		
R = 	7.64–7.67 (d) 7.45–7.55 (t) 7.59–7.60 (t)	2.30 (s)	8.67 (s)	7.69–7.72 (d) 7.16–7.29 (t) 7.16–7.29 (t) 7.89–7.94(d)	7.11–7.14 (d) 7.16–7.29 (t) 7.89–7.94 (t)
R = 	7.53–7.62 (d) 7.30–7.83 (d)	2.58 (s)	9.0 (s)	8.02–8.05 (d) 7.65–7.71 (t) 7.65–7.71 (t) 8.21–8.23 (d)	7.37–7.39 (d) 7.49–7.53 (t) 8.12–8.15 (t)
R = 	7.53–7.54 (d) 7.70–7.81 (d)	2.57 (s)	9.0 (s)	7.96–7.95 (d) 7.60–7.70 (t) 7.60–7.70 (t) 8.20–8.23 (d)	7.36–7.39 (d) 7.48–7.51 (t) 8.14–8.16 (t)
R* = 	7.57–7.61 (d) 7.73–7.85 (d)	2.59 (s)	9.03 (s)	7.78–7.92 (d) 7.52–7.56 (t) 7.52–7.56 (t) 8.21–8.25 (d)	7.12–7.15 (d) 7.49–7.54 (t) 8.15–8.17 (t)
R* = 	7.75–7.78 (d) 7.04–7.07 (d)	2.47 (s)	8.88 (s)	7.85–7.88 (d) 7.31–7.37 (t) 7.40–7.43 (t) 8.04–8.07 (d)	7.26–7.28 (d) 7.15–7.18 (t) 7.58–7.60 (t)

*—OCH_3 and —CH_3 group signals are observed as singlets at δ 3.78 and 2.25 ppm, respectively. s, singlet; d, doublet; t, triplet.

EXPERIMENTAL

Materials and Methods

Care was taken to exclude moisture throughout the experimental manipulations. All the chemicals used were of reagent grades. The solvents were dried by reported methods [8]. Aroyl pyruvates, $\mathrm{RC(O)CH{:}C(OH)COOCH_3}$ (where $\mathrm{R = C_6H_5}$, $\mathrm{4\text{-}BrC_6H_4}$, $\mathrm{4\text{-}ClC_6H_4}$, $\mathrm{4\text{-}CH_3OC_6H_4}$, $\mathrm{4\text{-}CH_3C_6H_4}$), have been synthesized by literature method [9]. The benzothiazoline ligands, $\mathrm{\overline{HNC_6H_4SC}(R)CH{:}\,C(OH)COOCH_3}$, have been synthesized by equimolar condensation reaction of aroyl pyruvate and 2-aminothiophenol in refluxing benzene solution [10]. The ligands were purified by distillation under reduced pressure before use. Nitrogen and sulfur were estimated by Kjeldhal's and Messenger's methods, respectively [11]. Triphenylantimony(V)bromide [12] and triphenylantimony(V)isopropoxide [13] were prepared by reported methods. Isopropanol liberated during the course of the reaction was estimated oxidimetrically using 1 N $K_2Cr_2O_7$ solution in 25% H_2SO_4 [14]. Antimony was determined iodometrically

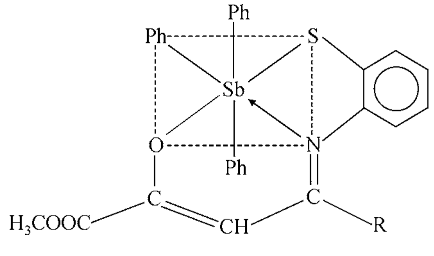
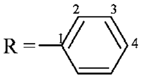
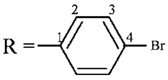
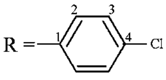
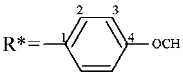
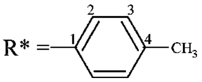


FIGURE 1 Proposed structure of the complexes, $\mathrm{Ph_3\overline{Sb[SC_6H_4N{:}\,C(R)CH{:}\,CO}COOCH_3]}$.

TABLE 2 ^{13}C NMR Spectral Data (δ, ppm) of the Complexes, $Ph_3\overline{Sb[SC_6H_4N:C(R)CH:CO}COOCH_3]$

Complexes	*R*	*=CH*	*CH_3(ester)*	*—NC_6H_4S—*	*=C—O*	*—C=O*	*—C=N*	*Sb—Ph*
	133.73 132.32 127.91 126.01	97.78	25.76	153.52 136.78 128.59 125.07 122.98 121.79	166.78	196.96	162.97	152.37 (i) 137.27 (o) 129.92 (m) 127.73 (p)
	133.84 132.77 129.44 126.60	97.51	24.84	153.05 136.37 128.21 126.14 123.76 121.62	166.35	194.87	163.5	151.55 (i) 137.67 (o) 130.02 (m) 127.55 (p)
	134.05 132.74 132.37 125.54	97.71	25.56	153.28 136.16 128.17 126.23 124.52 121.00	167.10	195.61	162.91	152.22 (i) 137.76 (o) 129.64 (m) 127.80 (p)
	134.02 131.07 125.87 140.10	97.98	26.05	153.36 136.12 127.21 124.97 123.59 121.96 153.85	167.18	195.74	163.10	152.01 (i) 137.86 (o) 129.99 (m) 127.83 (p)
	133.25 132.84 126.48 125.73	97.40	26.06	135.10 128.43 125.77 122.91 121.62	167.22	195.94	162.53	151.91 (i) 137.53 (o) 130.01 (m) 127.27 (p)

*—OCH_3 and —CH_3 group signals are observed at δ 55.15 and 28.27 ppm, respectively.

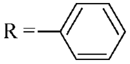
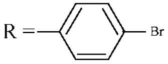
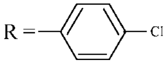
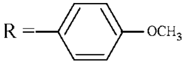
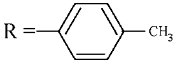
[11]. Molecular weights of these complexes have been determined ebullioscopically in benzene solution using Beckman's thermometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90 Q (90 MHz) or Brucker DPX (300 MHz) spectrometer, respectively, in $CDCl_3$ solution using TMS as an internal (^1H NMR) or external (^{13}C NMR) reference. IR spectra were recorded as neat film using CsI optics on Nicolet DX FTIR-550 spectrometer.

Since a similar method has been used for the synthesis of these complexes, therefore, the synthetic detail of only one representative complex is given. Synthetic and analytical data of the other analogous complexes are being compiled in Table 3.

Synthesis of $Ph_3\overline{Sb[SC_6H_4N:C(R)CH:CO}COOCH_3]$

A weighed amount of sodium metal (0.26 g, 11.31 mmol) was added to ~20 mL of well-dried isopropanol, and the mixture was stirred for ~1 h. A benzene solution of Ph_3SbBr_2 (2.90 g, 5.65 mmol) was added to it. The reaction mixture was refluxed for about 1 h. Sodium bromide thus precipitated during the reaction was filtered off and the removal of excess solvent from the filtrate at reduced pressure yields a solid $Ph_3Sb(OPr^i)_2$. A benzene solution of $Ph_3Sb(OPr^i)_2$ was addedto a benzene solution of the ligand, $H\overline{NC_6H_4SC}(R)CH:C(OH)COOCH_3$ (1.77 g,

TABLE 3 Synthetic and Analytical Data of the Complexes, $Ph_3Sb[SC_6H_4N{:}C(R)CH{:}COCOOCH_3]$

	Reactants, g (mmol)					*Elemental Analyses (%) Found (Calcd.)*			
Complex	*Na*	*Ph_3SbBr_2*	*Ligand*	*Molecular Formula, Color, Physical State and Yield (%)*	*Pr^iOH (g) Found (Calcd.)*	*Sb*	*N*	*S*	*Molecular Weight Found (Calcd.)*
	0.26 (11.31)	2.90 (5.65)	H_2L^1:1.77 (5.65)	$C_{35}H_{28}NO_3SSb$, dark yellow, viscous, 82.28	0.66 (0.68)	18.13 (18.32)	2.07 (2.11)	4.78 (4.83)	642 (664)
	0.34 (14.79)	3.79 (7.39)	H_2L^2:2.90 (7.39)	$C_{35}H_{27}NO_3BrSSb$, brown, viscous, 85.72	0.87 (0.89)	16.18 (16.38)	1.86 (1.88)	4.27 (4.31)	725 (743)
	0.41 (17.83)	4.57 (8.91)	H_2L^3:3.10 (8.91)	$C_{35}H_{27}NO_3ClSSb$, brown, viscous, 83.78	1.02 (1.07)	17.27 (17.42)	1.96 (2.00)	4.52 (4.59)	684 (699)
	0.39 (16.96)	4.35 (8.48)	H_2L^4:2.91 (8.47)	$C_{36}H_{30}NO_4SSb$, dark brown, viscous, 80.87	0.99 (1.02)	17.38 (17.53)	1.98 (2.02)	4.57 (4.62)	675 (694)
	0.32 (13.92)	3.57 (6.96)	H_2L^5:2.28 (6.96)	$C_{36}H_{30}NO_3SSb$, brown, viscous, 81.26	0.80 (0.84)	17.71 (17.95)	2.02 (2.06)	4.67 (4.73)	662 (678)

5.65 mmol). This reaction mixture was refluxed for ~5 h on a fractionating column. The isopropanol liberated during the course of the reaction was continuously fractionated off periodically and estimated oxidimetrically to monitor the progress as well as completion of the reaction. After the completion of the reaction, the excess amount of the solvent was removed under reduced pressure to afford a colored, viscous compound. For purification, this compound was dissolved in least amount of benzene and then petroleum ether (40–60°C) was added to it till the viscous compound begins to separate. The mixture was placed at −10°C overnight. After decanting off the solvent, a viscous compound was obtained, which was finally dried under vacuum.

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