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# 2,2,2-Triaryl-4-oxo-1,3,2-benzoxazastibinines

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ABSTRACT: *The hitherto unreported 4-oxo-1,3,2-benzoxazastibinines* **2** *have been synthesized by the cyclization of disodium salt of salicylanilide (***1***) with $Ar_3SbBr_2$ (Ar = Ph, p-tolyl, or mesityl). These compounds have been characterized by elemental analyses, molecular weight determination, and by IR, far IR, $^1H$, and $^{13}C$ NMR spectral studies.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:622–624, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10202

## INTRODUCTION

1,3-Oxazines have gained importance because of their biological and pharmacological activity [1]. Introduction of phosphorus in the oxazine ring at 2-position yields compounds that find applications in cancer research [2–7]. Some heterocycles containing N, As, and O are also known [8,9]; however, fewer reports are available on heterocycles containing N, Sb, and O. Only a few such heterocycles containing five-membered rings have been reported [10,11]. We have synthesized six-membered benzoxazastibinines [12,13] and have recently reported the synthesis of oxazastibinanes [14]. Oxo derivative of 1,3-oxazine [1], 1,3,2-benzoxazaphosphinine [15], and 1,3,2-benzoxazaphosphorine [16] are known in literature; however, there is no report available on the oxo derivative of 1,3,2-benzoxazastibinines. We report here an efficient route to 4-oxo-1,3,2-benzoxazastibinines.

## RESULTS AND DISCUSSION

4-Oxo-1,3,2-benzoxazastibinines **2** have been synthesized in 75–80% yields by the reaction of $Ar_3SbBr_2$ (Ar = Ph, *p*-tolyl, or mesityl) with the disodium salt of salicylanilide in dry THF (Scheme 1). The amount of precipitated sodium bromide confirmed the stoichiometry of the reaction. The products are obtained as white solids, which are soluble in organic solvents like benzene, chloroform, THF, and diethyl ether and are stable toward atmospheric oxygen and moisture. The elemental analyses of these compounds correspond to the assigned formulas, and vapor pressure osmometry measurements indicate that these compounds are monomeric in chloroform.

The structures have been confirmed by detailed spectroscopic analysis. The IR spectra of **1** show multiple bands for N—H stretching in the region 3330–3070 cm$^{-1}$ and the band for N—H bending (amide II band) at 1562 cm$^{-1}$ [17]. A weak broad band observed at 2938–2898 cm$^{-1}$ may be assigned to intramolecularly hydrogen bonded O—H [18–20]. The IR spectra of **2** show the absence of these bands indicating N—Sb—O bond formation. The carbonyl absorption (amide I band) in **1** appears at 1636 cm$^{-1}$ but this band in **2** shifts to higher frequency, indicating the formation of tertiary amide [17]. The phenolic C—O stretching vibration appearing at 1242 cm$^{-1}$ in salicylanilide undergoes a shift toward higher frequency in benzoxazastibininones, corroborating

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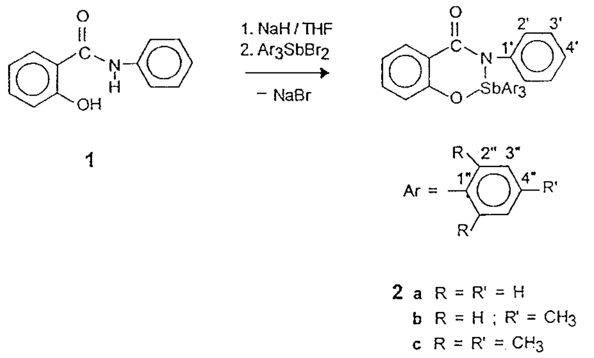

**SCHEME 1**

the participation of oxygen in C—O—Sb bonding [21,22]. Similar trend has been observed for C—N stretching vibration indicating C—N—Sb bonding [12–14].

In the far IR region of **2** there are some additional peaks that are not present in the reactants. A new band present in the region 404–410 $cm^{-1}$ may be assigned to Sb—O stretching vibration [23–25]. Another band observed in the range 250–280 $cm^{-1}$ may be attributed to Sb—N stretching [25]. However, Sb—Ar (X-sensitive t vibration) also appears in the same region and indeed these bands are stronger in the heterocyclic compounds compared to those in triarylantimony dibromides. The *y*-mode of Sb—Ar appears in the region 460–495 $cm^{-1}$.

The $^1H$ NMR data of **1** showed the N—H and O—H protons at $\delta$ 8.0 and $\delta$ 11.9. The presence of these protons has been confirmed by deuterium exchange with $D_2O$. The spectra of **2** do not exhibit signals due to N—H and O—H protons implying the bonding of antimony to nitrogen and oxygen.

The methyl protons in the spectrum of ($p$-tolyl)$_3$SbBr$_2$ appear at $\delta$ 2.4 and these protons appear at the same position in **2b**. The two methyl groups are observed at $\delta$ 2.3 and $\delta$ 2.5 in **2c**; these groups are found at $\delta$ 2.3 and $\delta$ 2.7 in Mes$_3$SbBr$_2$.

The $^{13}C$ signal of methyl group appears at $\delta$ 21.40 in **2b** almost at the same position as in ($p$-tolyl)$_3$SbBr$_2$. Two methyl signals are observed at $\delta$ 20.81 and $\delta$ 23.92 in **2c**, whereas these signals appear at $\delta$ 20.76 and $\delta$ 25.98 in Mes$_3$SbBr$_2$. The C=O group appears in the range $\delta$ 165.07–165.82 and the aromatic carbons appear in the range $\delta$ 117.10–160.96 in these heterocycles. The assignment of signals in the $^{13}C$ NMR spectra was made on the basis of low intensity signals as quaternary carbons and by comparing the spectrum of heterocycle with the spectra of ($p$-tolyl)$_3$SbBr$_2$, Mes$_3$SbBr$_2$, salicylanilide, and related compounds and by using standard correlations.

## *EXPERIMENTAL*

The triarylantimony dibromides were prepared and purified by the methods reported [26–29]. Solvents and other materials were dried and purified before use. The purity of the sample was checked by TLC. Elemental analyses were carried out on a Perkin-Elemer 240C elemental analyzer. Antimony was determined volumetrically [30]. Molecular weights of the compounds were determined in chloroform using a Knauer vapor pressure osmometer.

IR spectra in the range 4000–400 $cm^{-1}$ were recorded as KBr pellets on a Nicolet (5DX) FT IR spectrophotometer. Far IR spectra were recorded in polyethylene in the range of 700–50 $cm^{-1}$ on a Perkin-Elmer 1700X Far IR FT spectrophotometer. The $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ on a Jeol JNM FX-100 FT-NMR spectrometer using TMS as an internal standard. All melting points are uncorrected and have been measured in open glass capillaries.

### *2,2,2-Triaryl-4-oxo-1,3,2-benzoxazastibinines* **2**

$R_3SbBr_2$ (5 mmol in 50 ml THF) was added dropwise to a stirred solution of the disodium salt of **1** prepared from **1** (5 mmol) and NaH (10 mmol) in THF under nitrogen atmosphere. The mixture was refluxed for 2 h. The resultant solution was then taken to dryness under vacuum at 40–50°C, and 30 ml of benzene was added to the residue. Sodium bromide separated out was filtered off and weighed. The filtrate was concentrated to obtain compound **2**, which was recrystallized from a benzene–hexane mixture.

**2a:** Colorless solid, mp 127–128°C (d). Found C, 65.44; H, 4.15; N, 2.87; Sb, 22.34; Mol. wt. 549; $C_{31}H_{24}NO_2Sb$ requires C, 65.99; H, 4.26; N, 2.48; Sb, 21.60%; Mol. wt. 563.8. $\nu$ 1664 (C=O), 1452 (C—N), 1258 (C—O), 408 (Sb—O), 460 (Sb—Ar, *y*-mode), 263 (Sb—N + ts(Sb—Ar)) $cm^{-1}$; $\delta_H$ (100 MHz, $CDCl_3$): 6.5–8.2 (m arom-H); $\delta_C$ (25 MHz, $CDCl_3$): 165.07 (C4), 160.31 (C8a), 138.17 (C1′), 137.54 (C4″), 134.30 (C1″), 133.59 (C7), 132.48 (C2″), 130.10 (C3″), 129.54 (C3′), 128.02 (C5), 123.02 (C4′), 121.73 (C4a), 121.16 (C6), 120.32 (C2′), 117.10 (C8).

**2b:** Colorless, mp 134–135°C (d). Found C, 66.88; H, 4.69; N, 2.60; Sb, 20.78; Mol. wt. 592, $C_{34}H_{30}NO_2Sb$ requires C, 67.36; H, 4.95; N, 2.31; Sb, 20.10%, Mol. wt. 605.8. $\nu$ 1664 (C=O), 1452 (C—N), 1281 (C—O), 404 (Sb—O), 494 (Sb—Ar, *y*-mode), 280 (Sb—N + ts(Sb—Ar)) $cm^{-1}$; $\delta_H$ (100 MHz, $CDCl_3$): 2.4 (s, 9H, 3$CH_3$), 6.0–8.1 (m, 21H, arom-H) $\delta_C$ (25 MHz, $CDCl_3$): 165.23 (C4), 160.66 (C8a), 141.22 (C4″), 138.18 (C1′), 136.12 (C1″), 133.28 (CH), 133.24

(CH), 130.58 (C3″), 129.36 (C3′), 127.78 (C5), 122.92 (C4′), 121.80 (C4a), 121.12 (C6), 120.38 (C2′), 117.44 (C8), 21.40.

**2c:** Colorless solid, mp 170–172°C (d). Found C, 69.06; H, 6.23; N, 2.40; Sb, 18.42; Mol. wt. 658; $C_{40}H_{42}NO_2Sb$ requires C, 69.59; H, 6.09; N, 2.03; Sb, 17.65%; Mol. wt. 689.8. $\nu$ 1650 (C=O), 1450 (C—N), 1258 (C—O), 410 (Sb—O), 495 (Sb—Ar, *y*-mode), 250 (Sb—N + ts(Sb—Ar)) $cm^{-1}$; $\delta_H$ (100 MHz, $CDCl_3$): 2.3 (s, 9H, $3CH_3$), 2.5 (s, 18H, $6CH_3$), 6.8–7.9 (m, 15H, arom-H); $\delta_C$ (25 MHz, $CDCl_3$): 165.82 (C4), 160.96 (C8a), 145.52 (C4″), 141.64 (Cl″), 140.28 (C2″), 139.06 (C1′), 132.54 (C7), 130.82 (C3″), 129.48 (C3′), 127.96 (C5), 123.08 (C4′), 121.91 (C4a), 121.10 (C6), 120.26 (C2′), 117.14 (C8), 23.92, 20.81.

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