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Novel 3,3′-(Alkanediyl)bis-(2,2,2-triaryl-1-oxa-2-stiba-3-azabenzo[d]cyclohex-5-enes)

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ABSTRACT

The hitherto unreported compounds of general structure 3,3′-(alkanediyl)bis-(2,2,2-triaryl-1-oxa-2-stiba-3-azabenzo[d]cyclohex-5-ene) have been synthesized in 48–56% yields by the cyclization of the tetrasodium salt of N,N′-bis(2-hydroxybenzyl)-1,2-diaminoethane(II) or of N,N′-bis(2-hydroxybenzyl)-1,3-diaminopropane(II) with* R_3SbBr_2 *(R = phenyl, p-tolyl, or mesityl). The tetrasodium salts were prepared by the reactions of the corresponding amines with sodium hydride. The amines (II and II*), in turn, were obtained by the sodium borohydride reduction of N,N′-bis(salicylidene)-1,2-diaminoethane and N,N′-bis-(salicylidene)-1,3-diaminopropane, respectively. The heterocyclic compounds are air stable and moisture insensitive. These compounds have been characterized by elemental analyses, molecular weight determinations, and by IR, far IR,* ^1H*, and* ^{13}C *NMR spectral studies. © 1996 John Wiley & Sons, Inc.*

INTRODUCTION

Although the majority of the published reports on group 15 heterocycles are concerned with those derived from nitrogen, a wide range of analogous ring systems containing the heavier group 15 heteroatoms is also known [1]. Some of these heterocycles, e.g., 1,3-oxazines, have gained importance because of their biological and pharmacological activity [2–7]. Six-membered heterocycles containing N, P, and O as heteroatoms have found application as antineoplastic agents [8], in bone marrow purging [9], in cancer research [10], and in the manufacture of multilayered controlled-release transdermal patches [11]. Some heterocycles containing N, As, and O are also known [12,13]. Regarding the heterocycles containing N, Sb, and O, only a few such heterocycles containing a five-membered ring have been reported [14,15]. However, we have found no report on six-membered rings containing N, Sb, and O as heteroatoms in the literature, and hence we thought it to be of interest to synthesize a few such compounds. We are reporting a new class of compounds that contain two six-membered rings with N, Sb, and O as heteroatoms attached through an alkanediyl group.

RESULTS AND DISCUSSION

Six-membered heterocyclic compounds containing N, Sb, and O, viz., 3,3′-(alkanediyl)bis-(2,2,2-triaryl-1-oxa-2-stiba-3-azabenzo[d]cyclohex-5-enes) have been synthesized by the reactions of R_3SbBr_2 (R = Ph, p-tolyl, or mesityl) with the tetrasodium salts of the amines (II or II*) in dry THF as depicted in Scheme 1. The stoichiometry of the reaction has been confirmed by the amount of precipitated sodium bromide isolated. The heterocyclic compounds are obtained as white solids soluble in organic solvents such as 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 (Table 1).

The IR spectra of N,N′-bis(2-hydroxybenzyl)-

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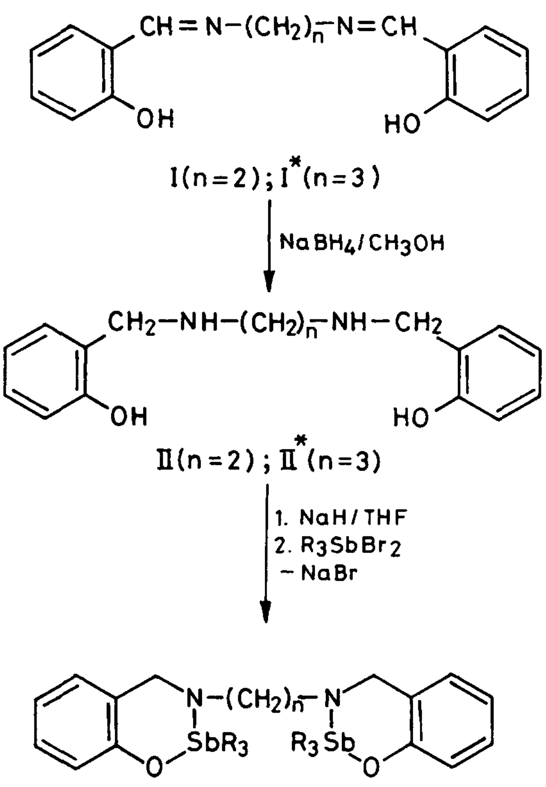

n		R
2	3	
IIIa	III*a	Phenyl
IIIb	III*b	p-Tolyl
IIIc	III*c	Mesityl

SCHEME 1

1,2-diaminoethane (II) and N,N'-bis(2-hydroxybenzyl)-1,3-diaminopropane (II*) show a strong absorption band for v(N–H) in the range 3280–3300 cm^{-1} and a weak, broad band in the range 2700–2810 cm^{-1} that may be assigned to the intramolecularly hydrogen bonded O–H group [16–18]. These bands are absent in the IR spectra of the heterocyclic compounds (IIIa,b,c and III*a,b,c), indicating O–Sb–N bond formation. The phenolic C–O stretching vibration that appears at 1252–1256 cm^{-1} in the amines (II and II*) undergoes a shift toward higher frequency (1260–1268 cm^{-1}) in the heterocycles, which further confirms the participation of oxygen in C–O–Sb bonding [19,20]. A similar trend has been observed for C–N stretching vibrations which appear at 1100–1102 cm^{-1} and 1106–1116 cm^{-1} in the amines (II and II*) and heterocyclic compounds, respectively, indicating C–N–Sb bonding. In the far IR spectra, a new band (not present in the reactants) observed in the heterocycles in the range 408–415 cm^{-1} may be attributed to the Sb–O stretching vibration [21–23]. Another band observed at 258–270 cm^{-1} may be assigned to Sb–N stretching [23]. However, Sb–Ar (X-sensitive t-vibration) bands also appear in the same region and indeed they are stronger in the heterocycles than those in R_3SbBr_2. The y mode bands of Sb–Ar appear in the region 460–497 cm^{-1}.

The ^1H NMR spectrum of the amine II shows the presence of the methylene protons of the $-CH_2CH_2-$ group at $\delta 2.8$ as singlet. Two types of methylene protons of the $-CH_2CH_2CH_2-$ group in the amine II* are observed as a triplet at $\delta 2.7$ and as a multiplet at $\delta 1.8$. The N–H/O–H signals are observed as broad signals at $\delta 5.6$ and $\delta 4.9$ in II and II*, respectively. The presence of these protons has been further confirmed by deuterium exchange with D_2O. The heterocyclic compounds do not exhibit signals due to O–H and N–H protons, confirming the deprotonation of secondary amines and hence the bonding of Sb to O and N. Two types of methylene protons in IIIa,b,c, appear at almost the same positions (at $\delta 3.9$–4.0 and $\delta 2.7$–2.8) as in II. Similarly, three types of methylene protons in III*a,b,c are observed at the same positions ($\delta 4.0$, $\delta 2.7$, and $\delta 1.7$–1.8) as those in II*. The methyl protons appear at $\delta 2.3$ and $\delta 2.4$ in IIIb and IIIb*, which contain the (p-tolyl)$_3$Sb group, whereas two types of methyl signals are observed at $\delta 2.3$ and $\delta 2.5$ for IIIc and at $\delta 2.3$ and $\delta 2.6$ for III*c, which contain the (mesityl)$_3$Sb group. The spectra show the correct integration ratio of the aromatic and CH_2 protons in the amines II and II* and of the aromatic, CH_2, and CH_3 protons in the heterocyclic compounds (IIIa,b,c and III*a,b,c).

The ^{13}C signal attributable to $ArCH_2$ is observed at $\delta 47.80$ and $\delta 46.25$ for the amines II and II*, respectively. These signals appear at nearly the same positions ($\delta 46.30$–47.81) as those in the corresponding heterocycles. The ^{13}C signal attributable to $-CH_2CH_2-$ appears at $\delta 52.53$ in II, which also remains nearly unchanged ($\delta 51.86$–52.49) in the corresponding heterocycles. Similarly, two ^{13}C signals attributable to the $-CH_2CH_2CH_2-$ group appear at $\delta 52.64$ and $\delta 29.54$ in II* and are observed at almost the same positions ($\delta 52.14$–52.64 and $\delta 29.42$–29.59) in the heterocycles. The ^{13}C signal of the methyl group in IIIb and IIIb* appears at $\delta 21.45$ and $\delta 21.30$, respectively, which contain the Sb(tolyl-p)$_3$ group, whereas two signals are observed at $\delta 20.96$ and $\delta 24.63$ for IIIc and at $\delta 20.86$ and $\delta 24.62$ for IIIc*, which contain the Sb(mesityl)$_3$ group. The ^{13}C signals for aromatic carbons appear in the range of 116.18–157.99 and 116.33–142.15 in the amines (II and II*) and the het-

TABLE 1 Elemental Analyses and Physical Properties of Amines and Heterocyclic Compounds

					Found (Calculated)				
n	*Compound*[a]	*Formula*	*Yield (%)*	*m.p. (°C)*	*%C*	*%H*	*%N*	*%Sb*	*Mol. Wt.*
2	II	$C_{16}H_{20}N_2O_2$	78	120	71.06 (70.59)	7.18 (7.35)	9.94 (10.29)	—	264 (272)
2	IIIa	$C_{52}H_{46}N_2O_2Sb_2$	51	102(d)	63.64 (64.10)	4.52 (4.73)	3.18 (2.88)	25.73 (25.01)	936 (973.5)
2	IIIb	$C_{58}H_{58}N_2O_2Sb_2$	48	136–8	66.06 (65.82)	5.76 (5.49)	3.07 (2.65)	23.86 (23.03)	1010 (1057.5)
2	IIIc	$C_{70}H_{82}N_2O_2Sb_2$	56	162(d)	68.14 (68.54)	6.57 (6.69)	2.07 (2.29)	20.82 (19.87)	1162 (1225.5)
3	II*	$C_{17}H_{22}N_2O_2$	80	108	71.59 (71.32)	8.02 (7.69)	10.24 (9.79)	—	275 (286)
3	IIIa*	$C_{53}H_{48}N_2O_2Sb_2$	49	114-6	64.94 (64.41)	5.11 (4.86)	2.96 (2.84)	25.26 (24.66)	935 (987.5)
3	IIIb*	$C_{59}H_{60}N_2O_2Sb_2$	52	120-2(d)	65.60 (66.08)	5.29 (5.60)	2.88 (2.61)	23.49 (22.73)	1018 (1071.5)
3	IIIc*	$C_{71}H_{84}N_2O_2Sb_2$	50	180(d)	68.27 (68.74)	6.54 (6.78)	2.62 (2.26)	20.30 (19.65)	1194 (1239.5)

[a] Structures of the compounds are given in Scheme 1.

erocyclic compounds (IIIa,b,c and III*a,b,c), respectively.

EXPERIMENTAL

The triarylantimony dibromides were prepared and purified by the methods reported in the literature [24–27]. The imines were obtained by the condensation of salicylaldehyde with the appropriate amines (1,2-diaminoethane and 1,3-diaminopropane) in ethanol [28,29]. Secondary amines were obtained by the reduction of imines with $NaBH_4$ in methanol by a reported method [30]. Solvents and other materials were dried and purified before use. Elemental analyses were carried out on a Perkin-Elmer 240 C elemental analyzer. Antimony was determined volumetrically by a reported method [31]. 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 (5-DX) 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.

Preparation

The heterocyclic compounds were prepared by the dropwise addition of R_3SbBr_2 (10 mmol in 50 mL THF) to a stirred solution of each tetrasodium salt of the amine (II or II*), Na_4L [prepared from H_4L + NaH (5 mmol: 20 mmol)] in 20 mL THF under a nitrogen atmosphere. After the complete addition, the mixture was refluxed for 2 hours. The resultant solution was then concentrated to dryness under vacuum at 40–50°C, and 30 mL benzene was added to the solid residue. Sodium bromide separated and it was filtered off and weighed. The filtrate was concentrated to obtain the heterocycles, which were recrystallized from a (20:80) benzene:hexane mixture.

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