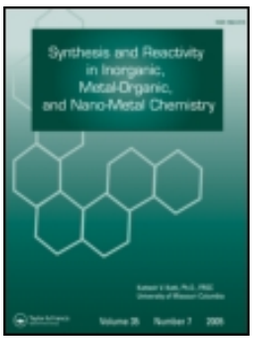

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N-BENZOIN-*o*-MERCAPTOANILINE AS AN EFFICIENT SYNTHON FOR ORGANOTIN(IV) COMPOUNDS

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ABSTRACT

α-Benzoin reacted with *o*-aminothiophenol to give a diprotic ONS Schiff base H_2L. The preparation of organotin(IV) compounds of N-benzoin-*o*-mercaptoaniline *via* monoanion and dianion intermediates is reported. All of the newly synthesized compounds have been characterized by elemental analyses and spectral (IR, ^{1}H, ^{13}C and ^{119}Sn NMR) studies. Metal coordination occurs *via* deprotonation of the OH and SH groups, depending upon the reaction conditions.

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INTRODUCTION

The ability of heavier main group elements to accommodate more than eight electrons in their valence shell, forming hypervalent or hypocoordinated compounds, is well established. The chemistry of such compounds in all its different facets has been regularly reviewed over the years.[1] Well-known exemplary series of di- and triorganotin halides with various nitrogen and oxygen/sulfur-containing ligands[2,3] have been found to possess significant biological and pharmacological activities and are used as fungicides,[4,5] bactericides,[6,7] tuberculostatic[8] and anticarcinogenic agents.[9] Complexes of tridentate and tetradentate Schiff bases using benzoin as the basic nucleus have been reported.[10–12] Hypervalent tin compounds attract interest from both the structural and reactivity point of view.[13] Certain penta-coordinated and hexa-coordinated organotin(IV) complexes[14] have been reported in the literature as having interesting stereochemistry.[15] Thus, in view of the above and in continuation of our studies on organotin(IV) derivatives,[16–19] we report here the syntheses and characterization of some new organotin(IV) complexes of N-benzoin-*o*-mercaptoaniline.

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere and analytical grade chemicals were used. Solvents were purified and dried according to standard procedures.[20] All melting points are uncorrected. The progress of the reaction was monitored by TLC on silica gel. Elemental analyses were performed by the Central Drug Research Institute, Lucknow. Tin and chloride in the complexes were determined by gravimetric and Messenger's methods, respectively.[21] Infrared spectra were recorded on a Perkin-Elmer model 377 spectrometer in the range 4000–200 cm^{-1}. NMR spectra were recorded on a Bruker AC 200 instrument at 200 (^{1}H), 74 (^{119}Sn) and 50.32 (^{13}C) MHz at the National Chemical Laboratory, Pune. Chemical shifts are quoted in ppm relative to TMS for ^{1}H and ^{13}C, and relative to tetramethyltin for the ^{119}Sn nucleus as an internal standard in DMSO-d_6.

The ligand N-benzoin-*o*-mercaptoaniline[22] was synthesized by the condensation of benzoin (10.6 g, 0.05 mol) and *o*-aminothiophenol (6.25 g, 0.05 mol) dissolved in 25 mL dry ethanol in 1:1 molar ratio; yield 8.97 g (56%), m. p.149 °C. IR (KBr, cm^{-1}): 3426 ν(OH), 2526 ν(SH) 1622 ν(C=N); ^{1}H NMR (200 MHz, DMSO-d_6): δ 6.64–7.21 (m, 14H, Ar-H), 5.84 (s, 1H, OH), 9.76 (s, 1H, SH), 4.12 (s, 1H, CH); Anal. Calcd. for $C_{20}H_{17}NOS$ (319): C, 75.25; H, 5.33; N, 4.39; S, 10.03. Found: C, 75.08; H, 5.12; N, 4.04; S, 9.87.

Reaction Between Ph_3SnCl and the Sodium Salt of N-Benzoin-*o*-mercaptoaniline in 1:1 Molar Ratio

A quantity of 0.086 g (3.58 mmol) of sodium hydride and 20 mL of dry isopropanol were placed in a 100 mL three-necked, round bottom flask equipped with an efficient magnetic stirrer, an addition funnel, a condenser and a two-way balloon system. It was stirred for about half an hour till a clear solution of sodium isopropoxide was obtained. Then 1.145 g (3.58 mmol) of N-benzoin-*o*-mercaptoaniline in 20 mL of dry benzene was added slowly, and the mixture was refluxed. After half an hour a light-violet color appeared which changed to dark yellow after three hours. Subsequently, a solution of 1.381 g (3.58 mmol) of triphenyltin(IV) chloride in 25 mL of dry benzene was added drop-wise at room temperature with a dropping funnel to the reaction vessel. After complete addition, the mixture turned greenish yellow. The content was further refluxed for 2 h to ensure the completion of the reaction during which no specific change was observed. The solution was then filtered to remove NaCl formed during the course of the reaction. Removal of the solvent from the filtrate under reduced pressure *via* a rotary evaporator gave the desired product, which was recrystallized from a 1:1 benzene-petroleum ether (40–60°) mixture. All other organotin(IV) derivatives of N-benzoin-*o*-mercaptoaniline were synthesized analogously as mentioned above. The pertinent data for this and other compounds are listed below.

$Ph_3Sn[SC_6H_4N{=}C(Ph)CH(OH)Ph]$ (1)

Yield 1.55 g (65%); m. p. 91–93 °C. IR (KBr, cm^{-1}): 3428 ν(OH), 1578 ν(C=N), 332 ν(Sn-S), 418 ν(Sn-N). ^{1}H NMR (DMSO-d_6, δ ppm): 6.84–7.32 (m, 29H, Ar-H), 5.76(s, 1H, OH), 4.26 (s, 1H, CH). ^{13}C NMR (DMSO-d_6, δ ppm): 124.6–141.3 (Ar-C),[23] 76.4 (C_7), 162.2 (C_8), 147.6 (C_9), 174.6 (C_{10}). ^{119}Sn NMR (DMSO-d_6, δ ppm): −196.2. Anal. Calcd. for $C_{38}H_{31}NOSSn$ (668): C, 68.26; H, 4.64; N, 2.09; S, 4.79; Sn, 17.81. Found: C, 68.12, H, 4.38; N, 1.87; S, 4.56; Sn, 17.45.

n-$Bu_3Sn[SC_6H_4N{=}C(Ph)\cdot CH(OH)Ph]$ (2)

Yield 0.83 g (62%); m. p. 93–95 °C. IR (KBr, cm^{-1}): 3430 ν(OH), 1574 ν(C=N), 336 ν(Sn-S), 422 ν(Sn-N). ^{1}H NMR (DMSO-d_6, δ ppm): 6.92–7.46 (m, 14H, Ar-H), 5.66 (s, 1H, OH), 4.22 (s, 1H, CH), 1.18–1.26 (m, 18H, CH_3), 0.88 (t, J = 8 Hz, 9H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 123.6–139.3 (Ar-C),[23] 76.8 (C_7), 162.6 (C_8), 146.8 (C9), 174.2 (C_{10}), 9.42–26.68

(*n*-Bu).[23] ^{119}Sn NMR (DMSO-d_6, δ ppm): −234.6. Anal. Calcd. for $C_{32}H_{43}NOSSn$ (608): C, 63.16; H, 7.07; N, 2.30; S, 5.26; Sn, 19.57. Found: C, 63.42, H, 7.38; N, 2.67; S, 5.56; Sn, 19.25.

$Me_2Sn[SC_6H_4N{=}C(Ph){\cdot}CH(OH)Ph]Cl$ (3)

Yield 1.47 g (68%); m. p. 81–83 °C. IR (KBr, cm^{-1}): 3422 ν(OH), 1580 ν(C=N), 340 ν(Sn-S), 426 ν(Sn-N). ^{1}H NMR (DMSO-d_6, δ ppm): 6.78–7.12 (m, 14H, Ar-H), 5.70 (s, 1H, OH), 4.12 (s, 1H, CH), 1.12 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 119.6–138.3 (Ar-C),[23] 76.2 (C_7), 162.1 (C_8), 146.8 (C_9), 174.8 (C_{10}), 6.44, 6.49 (Me). ^{119}Sn NMR (DMSO-d_6, δ ppm): −244.6. Anal. Calcd. for $C_{22}H_{22}NOSSnCl$ (503): C, 52.49; H, 4.37; N, 2.78; S, 6.36; Sn, 23.68, Cl, 7.06. Found: C, 52.72, H, 4.68; N, 2.47; S, 6.56; Sn, 23.25, Cl, 6.86.

n-$Bu_2Sn[SC_6H_4N{=}C(Ph){\cdot}CH(OH)Ph]Cl$ (4)

Yield 1.43 g (71%); m. p. 186–188 °C. IR (KBr, cm^{-1}): 3432 ν(OH), 1586 ν(C=N), 334 ν(Sn-S), 428 ν(Sn-N). ^{1}H NMR (DMSO-d_6, δ ppm): 6.78–7.12 (m, 14H, Ar-H), 5.66 (s, 1H, OH), 4.24 (s, 1H, CH), 1.22–1.34 (m, 12H, CH_2), 0.9 (t, J = 8Hz, 6H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 120.6–137.6 (Ar-C),[23] 76.9 (C_7), 162.8 (C_8), 146.3 (C_9), 174.2 (C_{10}), 9.44–26.49 (*n*-Bu).[23] ^{119}Sn NMR (DMSO-d_6, δ ppm): −254.6. Anal. Calcd. for $C_{28}H_{34}NOSSnCl$ (587): C, 57.24; H, 5.79; N, 2.39; S, 5.45; Sn, 20.28, Cl, 6.05. Found: C, 57.62, H, 5.48; N, 2.47; S, 5.66; Sn, 20.65, Cl, 6.46.

$Me_2Sn[SC_6H_4N{=}C(Ph){\cdot}CH(Ph)OH]_2$ (5)

Yield 0.78 g (68%); m. p. 87–89 °C. IR (KBr, cm^{-1}): 3426 ν(OH), 1576 ν(C=N), 338 ν(Sn-S), 424 ν(Sn-N). ^{1}H NMR (DMSO-d_6, δ ppm): 6.78–7.12 (m, 28H, Ar-H), 5.60 (s, 2H, OH), 4.12 (s, 2H, CH), 1.04 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 122.6–138.6 (Ar-C),[23] 76.2 (C_7), 162.1 (C_8), 146.7 (C_9), 174.8 (C_{10}), 6.34–6.39 (Me). ^{119}Sn NMR (DMSO-d_6, δ ppm): −344.6. Anal. Calcd. for $C_{42}H_{38}N_2O_2S_2Sn$ (786): C, 64.12; H, 4.83; N, 3.56; S, 8.15; Sn, 15.15. Found: C, 64.42, H, 4.46; N, 3.37; S, 8.46; Sn, 15.35.

n-$Bu_2Sn[SC_6H_4N{=}C(Ph){\cdot}CH(Ph)OH]_2$ (6)

Yield 0.61 g (62%); m. p. 95–97 °C. IR (KBr, cm^{-1}): 3434 ν(OH), 1584 ν(C=N), 340 ν(Sn-S), 426 ν(Sn-N). ^{1}H NMR (DMSO-d_6, δ ppm): 6.88–7.26

(m, 28H, Ar-H), 5.60 (s, 2H, OH), 4.32 (s, 2H, CH), 1.20–1.32 (m, 12H, CH_2), 0.96 (t, J = 8Hz, 6H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 122.6–138.6 (Ar-C),[23] 76.2 (C_7), 162.1 (C_8), 146.7 (C_9), 174.8 (C_{10}), 9.34–27.19 (*n*-Bu).[23] ^{119}Sn NMR (DMSO-d_6, δ ppm): −354.6. Anal. Calcd. for $C_{48}H_{50}N_2O_2S_2Sn$ (870): C, 66.21; H, 5.57; N, 3.22; S, 7.36; Sn, 13.69. Found: C, 66.62; H, 5.38; N, 3.47; S, 7.66; Sn, 13.35.

$Me_2Sn[SC_6H_4N{=}C(Ph){\cdot}CH(Ph)O]$ (7)

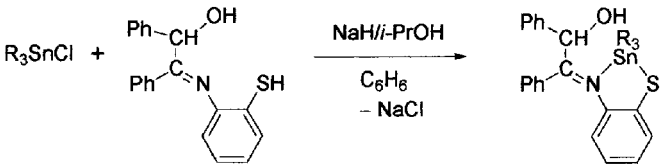
Yield 0.60 g (66%); m. p. 140–141 °C. IR (KBr, cm^{-1}): 1620 ν(C=N), 336 ν(Sn-S), 485 ν(Sn-O). ^1H NMR (DMSO-d_6, δ ppm): 6.72–7.32 (m, 14H, Ar-H), 4.32 (s, 1H, CH), 1.02 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 121.6–138.3 (Ar-C),[23] 76.4 (C_7), 156.5 (C_8), 142.2 (C_9), 174.9 (C_{10}), 6.36, 6.32 (Me). ^{119}Sn NMR (DMSO-d_6, δ ppm): 135.6. Anal. Calcd. for $C_{22}H_{21}NOSSn$ (466): C, 56.65; H, 4.51; N, 3.00; S, 6.87; Sn, 25.53. Found: C, 56.42; H, 4.78; N, 3.37; S, 6.46; Sn, 25.25.

n-$Bu_2Sn[SC_6H_4N{=}C(Ph){\cdot}CH(Ph)O]$ (8)

Yield 0.79 g (68%); m. p. 157–159 °C. IR (KBr, cm^{-1}): 1626 ν(C=N), 337 ν(Sn-S), 488 ν(Sn-O). ^1H NMR (DMSO-d_6, δ ppm): 6.88–7.29 (m, 14H, Ar-H), 4.16 (s, 1H, CH), 1.18–1.27 (m, 12H, CH_2), 0.86 (t, J = 8Hz, 6H, CH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 122.2–139.6 (Ar-C),[23] 76.9 (C_7), 156.1 (C_8), 142.7 (C_9), 174.3 (C_{10}), 9.64–27.24 (*n*-Bu).[23] ^{119}Sn NMR (DMSO-d_6, δ ppm): 132.6. Anal. Calcd. for $C_{28}H_{33}NOSSn$ (550): C, 61.09; H, 6.00; N, 2.55; S, 5.82; Sn, 21.63. Found: C, 61.42; H, 5.88; N, 2.87; S, 5.66; Sn, 21.35.

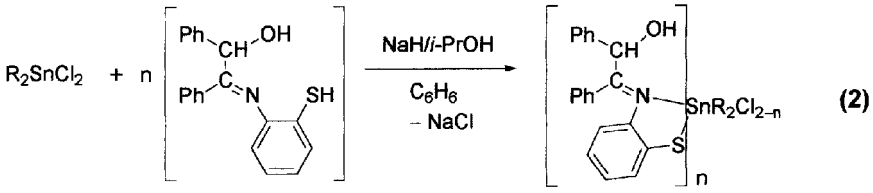
RESULTS AND DISCUSSION

Triorganotin(IV) and diorganotin(IV) derivatives of N-benzoin-*o*-mercaptoaniline have been synthesized by the reaction of corresponding tri- and diorganotin(IV) chlorides with the conjugate base of the ligand (prepared *in situ*) in desired molar ratios employing the following routes.



(1)

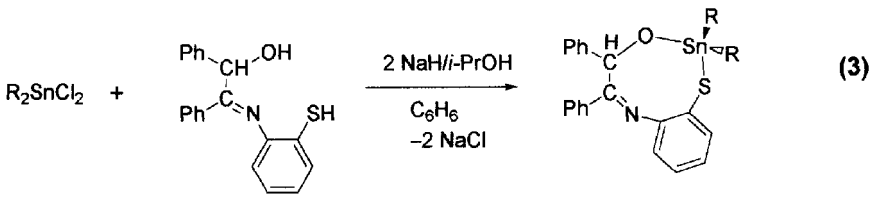
R = Ph (**1**); R = *n*-Bu (**2**).



(2)

n = 1, R = Me (3); n = 1, R = *n*-Bu (4); n = 2, R = Me (5); n = 2, R = *n*-Bu (6).

Similarly, the disodium salt of the ligand was treated with R_2SnCl_2 in 1:1 molar ratio to give a cyclic compound.



(3)

R = Me (7); R = *n*-Bu (8).

This synthesis involves the initial formation of the dianion which attacks R_2SnCl_2 leading to the formation of compounds **(7)** and **(8)** with elimination of NaCl. All these compounds are soluble in common, coordinating organic solvents.

Infrared Spectra

The IR spectra of the complexes have been compared with the ligand and from the shifts in frequency and/or from the intensity lowering, the coordination sites have been ascertained. The IR spectrum of the ligand shows bands in the regions 3426, 2526 and 1622 cm^{-1} assignable to ν(OH), ν(SH) and ν(C=N), respectively. The presence of OH vibrations in complexes **(1)** to **(6)** shows that the OH groups are intact, non-ionized and uncoordinated, whereas in complexes **(7)** and **(8)** they disappear forming Sn-O bonds, which is further supported by the appearance of new bands in the region 485–488 cm^{-1}, ascribable to the Sn-O mode.[18,19,24] The absence of a band around 2600 cm^{-1} in the spectra of all the complexes indicates that the SH group loses the thiol proton to form a covalent bond between the sulfur and tin in all the complexes. This fact is further supported by the appearance of new bands in all the complexes around 335 cm^{-1}, which may

be assigned to the ν(Sn-S) mode.[24] A strong band at 1622 cm^{-1} assignable to ν(C=N) in the ligand, is shifted to the lower frequency side (by about 45 cm^{-1}) in the spectra of complexes **(1)** to **(6)** indicating the coordination of the C=N group to tin,[19] while in compounds **(7)** and **(8)** a band at 1620 and 1626 cm^{-1} is observed suggesting that the C=N groups are intact and uncoordinated.

Nuclear Magnetic Resonance Spectra

The ^{1}H NMR spectra of the complexes exhibit the usual features. The signal of the OH group at 5.84 ppm in the ligand is found almost at the same position in the compounds **(1)** to **(6),** indicating that the OH group is intact and uncoordinated. The signal of the -OH group disappears completely in the spectra of complexes **(7)** and **(8),** thus showing deprotonation of the OH group and consequently tin-oxygen bond formation. The methyl protons attached to tin appear as a sharp singlet in the region 1.02–1.12 ppm. The resonances due to the butyl tin protons are observed in the region 0.86–1.34 ppm. The spectral features and integrations are consistent with the various stoichiometries and bonding sites as inferred from the infrared spectra.

The compounds were dissolved in $CDCl_3$ for the recording of ^{13}C NMR spectra, which is a good diagnostic tool for determining the bonding mode. On coordination, the resonances of the carbon atoms attached to the C=N and thiol sulfur shift some 20–25 ppm downfield, suggesting the bidentate nature of the ligand. Compounds **(1)**, **(2)**, **(3)** and **(4)** show $^{1}J(^{119}Sn\text{-}^{13}C)$ values of 562, 613.4, 567 and 622.2 Hz, respectively and these are characteristic of 5-coordinate tin. Compounds **(5)** and **(6)** exhibit tin-carbon couplings $^{1}J(^{119}Sn\text{-}^{13}C)$ of 672 and 686 Hz, respectively, comparable to six-coordinated organotin(IV) derivatives. The value of the coupling constants for compounds **(7)** and **(8)** are strongly indicative of four-coordinated structures.

^{119}Sn NMR spectra of all compounds have been recorded; they exhibit a sharp ^{119}Sn resonance in the region −354.6 to 135.6 ppm. The ^{119}Sn NMR spectra of the compounds **(1)** to **(4)** give signals in the region −196.2 to −254.6 ppm, and compounds **(5)** and **(6)** show signals at −344.6 and −354.6 ppm, respectively suggesting penta-coordinated[19] and hexa-coordinated[18] states around the tin atom. Compounds **(7)** and **(8)** display sharp ^{119}Sn resonances at 135.6 and 132.6 ppm, respectively, showing tetra-coordinated tin.[24]

Thus, on the basis of the above studies and the reports already available in the literature, it becomes clear that the ligand is behaving in

a bidentate manner. Therefore, tetra-, penta- and hexa-coordinated environments around the tin atom may be tentatively proposed for the resulting complexes.

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