

Organotin N-Phenyl-*p*-nitrobenzo- hydroxamates

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Nine new organotin N-phenyl-*p*-nitrobenzohydroxamates of the types R_2SnL_2 and R_2SnXL (where R = methyl, butyl; X = Cl, Br, I, SCN; and LH = N-phenyl-*p*-nitrobenzohydroxamic acid) have been synthesised and characterised on the basis of their elemental analyses, molar conductance, IR and PMR spectral data. Tentative structures of these compounds have been discussed.

The chemistry of organotin derivatives of hydroxamic acids presents many interesting aspects; these compounds are also reported to exhibit fungicidal activity against a variety of fungi¹. As only one organotin derivative of N-phenyl-*p*-nitrobenzohydroxamic acid has been reported earlier², we thought it worthwhile to prepare some new organotin N-phenyl-*p*-nitrobenzohydroxamates. The preparation of compounds of the types R_2SnL_2 and R_2SnXL (R = methyl, butyl; X = Cl, Br, I, SCN; and LH = N-phenyl-*p*-nitrobenzohydroxamic acid) and their characterisation through various physico-chemical studies are reported here.

N-phenyl-*p*-nitrobenzohydroxamic acid was prepared according to the method of Tandon *et al.*³. Dibutyltin bis-(N-phenyl-*p*-nitrobenzohydroxamate) was prepared according to the method of Pradhan and Ghosh².

Two typical procedures of preparation of organotin N-phenyl-*p*-nitrobenzohydroxamates are described here.

Preparation of dimethylchlorotin-N-phenyl-*p*-nitrobenzohydroxamate

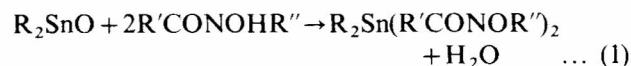
Dimethyltin bis-(N-phenyl-*p*-nitrobenzohydroxamate) (2.0 g) was dissolved in benzene (20 ml) and dimethyltin dichloride (0.8 g) was added to it. The mixture was refluxed over a water-bath for 10 min and the solution was evaporated to a pasty mass. Shining yellow crystals (2 g) were obtained after the addition of methanol. The compound was purified from the same solvent (m.p. 107-110°C) [Found: Sn, 27.2; N, 5.83. Cal. Sn, 26.9; N, 6.3%].

Preparation of dimethyliodotin N-phenyl-*p*-nitrobenzohydroxamate

Dimethylchlorotin N-phenyl-*p*-nitrobenzohydroxamate (1.0 g) was dissolved in benzene (20 ml) and dry potassium iodide (0.3 g) was added to it. The mixture was warmed over a water-bath with frequent shaking for one hour; the solution was filtered and concentrated to a pasty mass. The compound was isolated and purified as stated above (m.p. 85-87°C) [Found: Sn, 22.5; N, 5.07. calc. Sn, 22.3; N, 5.2%].

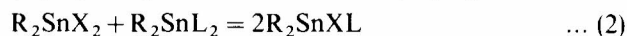
IR spectra of the compounds were recorded on a Beckman IR-20 spectrophotometer in nujol. PMR data and elemental analyses were obtained through the technical services of the RSIC, Lucknow. The PMR spectra in $CDCl_3$ were recorded at 90 MHz with TMS as the internal standard. Molar conductances measured in benzene by a Philips conductance bridge (Model No. 303) showed their non electrolytic nature ($\Lambda_m = 4.7$ to $15.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

N-Phenyl-*p*-nitrobenzohydroxamic acid contains one labile hydrogen per molecule and this hydrogen attacks the organotin oxides in the equilibrium reaction to give water along with the organotin derivative (Eq. 1),

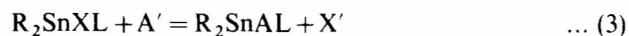


(where R = Me; R' = *p*-substituted phenyl group; R'' = Ph).

The halo ligand compounds of diorganotin moiety with N-phenyl-*p*-nitrobenzohydroxamic acid have been prepared either by disproportionation reaction (Eq. 2) or by metathesis reaction (Eq. 3),



where X = Cl, Br, SCN; R = Bu)



(where A = Br, I; R = Me; LH = N-phenyl-*p*-nitrobenzohydroxamic acid).

For all the diorganotin compounds, the $\nu C=O$ frequency shifts from 1610 in the ligand to $1555 \pm 15 \text{ cm}^{-1}$ in the complexes. The hydrogen bonded $\nu(OH)$ frequency that appears at 3170 cm^{-1} in the free ligand disappears in the organotin derivatives. The $\nu(N-O)$ mode shifts from 915 cm^{-1} in the ligand to $920-930 \text{ cm}^{-1}$ in the organotin derivatives. All these facts indicate strong coordination of the ligand to the organotin moieties. In the present study, $\nu Sn-C$ and $\nu Sn-O$ modes are not assigned as the ligand itself contains a number of bands in the regions ~ 500 and $600-800 \text{ cm}^{-1}$. The bands at 1515 and 1350 cm^{-1} have been assigned to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes. For

dimethyltin bis-(N-phenyl-*p*-nitrobenzohydroxamate), a distorted octahedral structure is assigned⁴.

The IR spectrum of the thiocyanate complex, viz. dibutylthiocyanatotin N-phenyl-*p*-nitrobenzohydroxamate is similar to these of the corresponding halide complexes except the presence of an intense band at 2010 cm^{-1} and a weak band at 1975 cm^{-1} . The ambidentate ligand SCN can either coordinate to tin through S and N or it can act as a bridge. The ligand has a number of absorptions in the region where $\nu\text{C}-\text{S}$ occurs ($780\text{--}860\text{ cm}^{-1}$); hence, mode of bonding of the thiocyanate group has been characterised on the basis of $\text{C}\equiv\text{N}$ stretching frequency only, which shows that the CNS group is linked to tin atom through the nitrogen atom⁵. Mullins and Curan⁶ have shown that $\text{Ph}_2\text{Sn}(\text{SCN})\text{OX}$ [where $\text{HOX}=8\text{-hydroxyquinoline}$] does not contain any NCS bridging in the solid state and they have suggested a penta-coordinated tin atom having *cis*-arrangement of the hydrocarbon groups in the compound. But, in the case of dibutylthiocyanatotin N-phenyl-*p*-nitrobenzohydroxamate, the IR spectrum shows a very strong band at 2010 cm^{-1} and a weak band at 1975 cm^{-1} indicating that the coordination of SCN group to tin is through N-atom. In view of the presence of second band for $\text{C}\equiv\text{N}$ mode, which is absent in other thiocyanato complexes⁶, where SCN is not involved in bridging, a dimeric hexa-coordinated structure may be proposed in the present case. The NCS bending mode could not be ascertained in a conclusive manner due to the presence of some bands of the ligand and organotin moieties in the same region. Further detailed studies are necessary to confirm the structure.

PMR data of the ligand as well as those of some of the organotin compounds are given in Table 1. Compared to Me_2SnCl_2 , where the methyl protons appear at $\delta 1.2\text{ ppm}$ ⁷, the methyl protons of the dimethyltin bis-(N-phenyl-*p*-nitrobenzohydroxamate) are shielded and appear at $\delta 0.8\text{ ppm}$. This shielding may be due to increased electron density on the tin atom via electron donation from the ligand. The sharp

Table 1—Physical Characteristics and Analytical Data of the Organotin Compounds

Compound (Colour, m.p., °C)	Found (Calc), %		
	C	H	N
Dibutylchlorotin N-phenyl- <i>p</i> -nitrobenzohydroxamate (Pale yellow; 130)	48.7 (47.9)	5.56 (5.15)	5.12 (5.3)
Dibutylbromotin N-phenyl- <i>p</i> -nitrobenzohydroxamate (Yellow; 120)	44.65 (44.2)	5.2 (4.7)	4.56 (4.9)
Dibutyliodotin N-phenyl- <i>p</i> -nitrobenzohydroxamate (Yellow; 102-103)	40.06 (41.5)	2.5 (2.7)	5.0 (4.6)
Dibutylthiocyanatotin N-phenyl- <i>p</i> -nitrobenzohydroxamate (Yellow; 210)	46.84 (48.17)	5.88 (4.92)	6.29 (7.6)
Dimethyltin bis-(N-phenyl- <i>p</i> -nitrobenzohydroxamate) (Yellow; 237)	50.8 (50.68)	4.14 (3.62)	—
Dimethylbromotin N-phenyl- <i>p</i> -nitrobenzohydroxamate (Pale yellow; 96-98)	36.6 (37.03)	2.9 (3.08)	5.0 (5.74)

PMR data: Ligand, $\delta 7.13\text{--}8.05\text{ ppm}$ (aromatic protons); dibutyltin bis-(N-phenyl-*p*-nitrobenzohydroxamate), $\delta 7.12\text{--}8.0\text{ ppm}$ (aromatic protons) and $\delta 0.78\text{--}1.4\text{ ppm}$ (alkyl protons), ratio 1 : 1; compound 5, $\delta 7.15\text{--}7.98\text{ ppm}$ (aromatic protons), $\delta 0.8\text{ ppm}$ (alkyl protons), ratio 1 : 3.

singlet for methyl protons of this compound indicates magnetically equivalent methyl groups, suggesting a possible *trans*-disposition of the methyl groups⁸.

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