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# Synthesis and characterisation of organotin(IV) derivatives of benzilmonohydrazone

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Some new tri- and di-organotin(IV) derivatives of benzilmonohydrazone have been prepared by the reaction of the corresponding tri- and di-organotin(IV) chlorides with the sodium salt of benzilmonohydrazone (prepared *in situ*) in 1:1 and 1:2 molar ratios, respectively, in refluxing benzene. These derivatives have been characterised by elemental analyses, molecular weights, conductivity measurements, melting points determinations, and IR and NMR ($^1H$ and $^{119}Sn$) spectral studies. All the complexes are monomeric and non-electrolytic in nature, and are soluble in most of the organic solvents. IR and NMR spectral data of these complexes show the bidentate behaviour of benzilmonohydrazone and five-coordinate and six-coordinate structures for triorganotin(IV) and diorganotin(IV) derivatives, respectively.

Organotin(IV) chelates with nitrogen, oxygen and sulphur donor ligands[1-3] have received much attention during the last few years. Hydrazones, an important class of chemical substances, are being used extensively for the treatment of several diseases and have applications in synthetic and analytical chemistry.[4] Their importance as herbicides, insecticides, rodenticides, and plant growth regulators is well-known.[5] The use of hydrazones for the treatment of leprosy, leukaemia and other diseases has also been reported.[6] Hydrazones have also been used as extractants for atomic absorption spectrometry of several metal ions.[7] Moreover, they are valuable synthones for a wide variety of chemicals of practical use.[8] Thus in view of the pharmacological importance of benzilmonohydrazone and the promising results obtained for some organotin(IV) derivatives as cancer therapeutic agents[9-11], and, in continuation of our studies on organotin(IV) derivatives[12], we report herein the synthesis and characterisation of oganotin(IV) complexes of benzilmonohydrazone.

## Experimental

All the reactions were carried out under moisture-free conditions. Benzene, petroleum ether and isopropanol were dried by standard methods[13]. Benzil and hydrazine hydrate (both AR grade) were used as such without further purification. IR spectra were recorded using KBr pellets on Perkin-Elmer 377 spectrophotometer in the range 4000-400 $cm^{-1}$. The $^1H$ NMR spectra were recorded on a JEOL JNM FX 90 Q spectrophotometer in $CDCl_3$ using TMS as internal standard. $^{119}Sn$ (at 37.06-38.08 MHz) spectra were measured on a JEOL FX 100 spectrometer. Chemical shifts are recorded in δ (ppm) relative to TMS. Molecular weights were measured on Knauer Vapour Pressure Osmometer in dilute (20 g $l^{-1}$) $CHCl_3$ solution at room temperature. Microanalyses were performed using Coleman-Carbon, Hydrogen and Nitrogen analysers for C, H and N, respectively. Tin and chlorine were estimated gravimetrically by literature method[13] and are in good agreement with the calculated values (Table 1). Conductance measurements in DMF were made at room temperature using a Digisum Electronic conductivity bridge.

### *Reaction of tributyltin(IV) chloride with the sodium salt of benzilmonohydrazone in 1:1 molar ratio*

Benzilmonohydrazone (m.pt. 152°C) was prepared by the literature method[14] by mixing methanolic solution of benzil (10.50g, 50 mmol) to a 75 ml of 80% hydrazine hydrate. A weighed quantity of sodium metal (0.12g, 5.00 mmol) and 20 ml of isopropanol were taken in a round bottom flask fitted with a water condenser and a guard tube and refluxed for about half an hour till a clear solution of sodium isopropoxide was obtained. After cooling, a weighed amount of ligand (1.12g, 5.00 mmol) was added and the mixture was further refluxed for two hours. After cooling, a weighed amount of tributyltin(IV) chloride (1.63g, 5.00 mmol) was added and contents were again refluxed with constant stirring for two hours. The

Table 1—Synthetic and analytical data of the complexes

| Sl. No. | Reactants*, g(mmol) | | | Yield, g (%) | Found (Calcd.), % | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Organotin chloride | Ligand | Sodium metal | | C | H | N | Sn | Cl |
| 1 | $Ph_3SnCl$ 1.92 (5.00) | 1.12 (5.00) | 0.12 (5.00) | 2.22 (77) | 66.68 (67.02) | 4.42 (4.54) | 4.96 (4.88) | 20.53 (20.77) | — |
| 2 | $Bu_3SnCl$ 1.63 (5.00) | 1.12 (5.00) | 0.12 (5.00) | 2.08 (81) | 60.97 (60.82) | 7.63 (7.41) | 5.32 (5.46) | 23.32 (23.19) | — |
| 3 | $Bu_2SnCl_2$ 1.52 (5.00) | 1.12 (5.00) | 0.12 (5.00) | 1.86 (76) | 53.94 (53.71) | 5.78 (5.90) | 5.43 (5.69) | 24.47 (24.21) | 7.46 (7.22) |
| 4 | $Bu_2SnCl_2$† 1.22 (4.00) | 1.79 (8.00) | 0.18 (8.00) | 2.00 (74) | 63.43 (63.62) | 5.64 (5.89) | 8.43 (8.24) | 17.77 (17.52) | — |
| 5 | $Me_2SnCl_2$ 1.10 (5.00) | 1.12 (5.00) | 0.12 (5.00) | 1.60 (79) | 47.31 (47.12) | 4.29 (4.17) | 6.62 (6.87) | 29.53 (29.20) | 8.98 (8.71) |
| 6 | $Me_2SnCl_2$† 1.10 (5.00) | 2.24 (10.00) | 0.24 (10.00) | 2.29 (77) | 60.37 (60.54) | 4.59 (4.71) | 9.67 (9.41) | 20.23 (20.00) | — |

*Molar ratio 1:1:1
†Molar ratio 1:2:2

precipitated sodium chloride was removed by filtration. Removal of solvent from the filtrate under reduced pressure yielded a brown coloured solid, [yield, 2.08g (81%)].

All other organotin(IV) derivatives of benzilmonohydrazone were synthesised analogously. The physical and spectral data of the complexes are listed in Table 2.

## Results and discussion

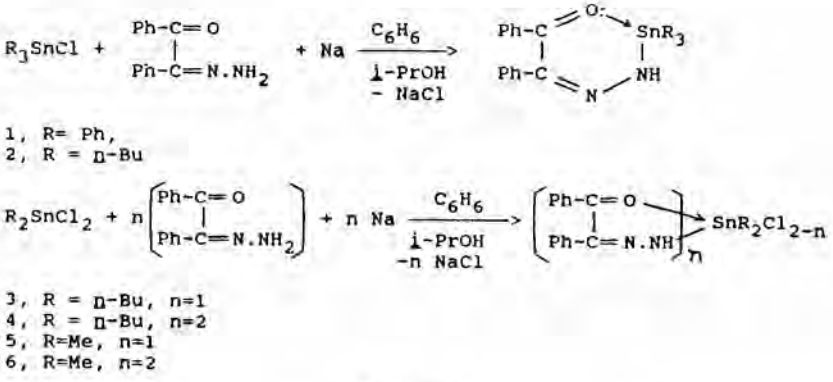
Triorganotin(IV) and diorganotin(IV) complexes of benzilmonohydrazone have been synthesized by the reaction of the corresponding triorganotin(IV) and diorganotin(IV) chlorides with the sodium salt of benzilmonohydrazone (prepared *in situ* by the reaction of sodium isopropoxide and benzilmonohydrazone) in 1:1 and 1:2 molar ratios, respectively (Scheme 1).

All the newly synthesized complexes are more or less soluble in common organic solvents like benzene, chloroform, carbon tetrachloride, DMF, DMSO, etc. They appear to be highly susceptible to even trace amounts of moisture[2]. Molecular weight determination in dil. $CHCl_3$ solution shows monomeric nature of these complexes. Molar conductance values (< 30 $ohm^{-1}$ $cm^2$ $mol^{-1}$) reveal their non-electrolytic[15] nature.

IR spectra of benzilmonohydrazone and its organotin(IV) complexes have been studied in the range 4000-400 $cm^{-1}$. Tentative assignments have been made on the basis of earlier publications[16,17]. The spectrum of the ligand shows bands in the region 3440-3200, 1685 and 1590 $cm^{-1}$, which have been assigned to $\nu(NH_2)$, $\nu(C=O)$ and $\nu(C=N)$, respectively[18]. The disappearance of $\nu(NH_2)$ in the complexes indicates deprotonation of $NH_2$ and consequent coordination of nitrogen atom to tin metal. This is further supported by appearance of the bands in the region 490-450 $cm^{-1}$ which may be due to tin-nitrogen (Sn-N) bond[19]. The $\nu(C=O)$ modes of the ligand are shifted to lower wave number (30-40 $cm^{-1}$) in the complexes suggesting coordination of carbonyl oxygen to tin. This fact is further supported by the appearance of a new band in the region 570-440 $cm^{-1}$, which is ascribed to Sn-C and Sn-O stretching modes[20,21]. A band at 1590 $cm^{-1}$ in the ligand due to C=N group does not show any discernible shift in the spectra of

Table 2—Physical and spectral data of the complexes

| Sl No. | Compd Mol. wt, Calcd. (Found) | M.P., °C | IR, $cm^{-1}$ | | | | NMR, δ ppm | |
|---|---|---|---|---|---|---|---|---|
| | | | ν(C=O) | ν(C=N) | ν(NH) | ν(Sn-N) | PMR | $^{119}Sn$ |
| 1 | $C_{32}H_{26}N_2OSn$ 573 (596) | 168 | 1640 | 1590 | 3100-2800 | 450 | 5.80(s,1H,NH); 6.65-8.05(m,25H,arom.) | -187.60 |
| 2 | $C_{26}H_{38}N_2OSn$ 513 (536) | 142 | 1650 | 1585 | 3080-2825 | 475 | 0.65(s,9H,$CH_3$);1.10-1.80 (m,18H,$CH_2$); 5.65(s,1H,NH); 6.70-7.95(m,10H,arom.) | — |
| 3 | $C_{22}H_{29}N_2OSnCl$ 491.5(512) | 171 | 1645 | 1600 | 3110-2870 | 490 | 0.60(s,6H,$CH_3$);0.95-1.70 (m,12H,$CH_2$);5.60(s,1H,NH) 6.86-8.00(m,10H.arom.) | -192.63 |
| 4 | $C_{36}H_{40}N_4O_2Sn$ 679(698) | 186 | 1640 | 1595 | 3105-2820 | 465 | 0.64(s,6H,$CH_3$);0.90-1.85 (m,12H,$CH_2$);5.85(s,2H,NH); 6.72-7.98(m,20H,arom.) | -347.31 |
| 5 | $C_{16}H_{17}N_2OSnCl$ 407.5(422) | 162 | 1650 | 1580 | 3100-2800 | 470 | 0.72(s,6H,$CH_3$);5.85 (s,1H,NH);6.68-7.88 (m.,10H,arom.). | -189.36 |
| 6 | $C_{30}H_{28}N_4O_2Sn$ 595(624) | 176 | 1655 | 1590 | 3115-2820 | 485 | 0.72(s,6H,$CH_3$);5.75(s,2H,NH); 6.75-8.10(m,20H,arom.). | — |



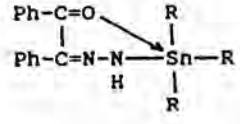

Scheme 1

complexes suggesting non-participation of C=N group in coordination.

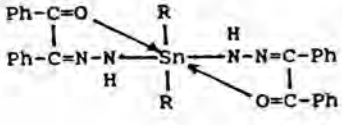
The $^1H$ NMR spectrum of the benzilmonohydrazone displays the $NH_2$ protons as a broad singlet at δ 4.15 ppm (exchangeable on deutaration[22]) and aromatic protons as multiplet at δ 6.65-8.10 ppm. The bonding through nitrogen of $NH_2$ group is supported by the high field shift of NH proton at δ 4.15 ppm in ligand to δ 5.60-5.85 ppm in complexes[19]. This is also supported by the peak integration which shows signal for one proton. The resonance due to $CH_2$ protons of butyl group is observed at δ 0.90-1.85 ppm, with a well defined triplet for $CH_3$ at δ 0.65 ppm ($J$=8 Hz). Methyl protons of dimethyltin(IV) derivatives appear as a sharp singlet at δ 0.72 ppm with double satellite resonances on each side of the main peak. These are due to coupling of methyl protons with $^{117}Sn$ and $^{119}Sn$ isotopes and the values vary with the coordination state of tin. For four coordinate dimethyltin(IV) compounds, $J(^{119}Sn\text{-}^1H)$ values[23] have been reported in the range 54-64 Hz. The $J$ values have been found to increase for the five, six or seven – coordinate compounds and have been observed in the range 71-116 Hz depending upon the stereochemistry[23]. The $^2J$ ($^{119}Sn\text{-}^1H$) values for dimethyltin(IV) derivatives of benzilmonohydrazone have been found to be *ca.* 85 Hz,

indicating hexacoordination for these complexes. The value of $^3J$ ($^{119}$Sn-$^1$H) (112 Hz) for *n*-BuSn complex suggests that the ligand acts as a bidentate moiety.

The $^{119}$Sn NMR chemical shift of some derivatives have been observed between –187.60 and –447.31 for five- and six- coordinate organotin(IV) compounds[24,25], arising out of intramolecular carbonyl coordination. $^{119}$Sn NMR data show that triorganotin(IV) complexes are penta-coordinated, whereas diorganotin(IV) complexes in 1:1 molar ratio are penta-coordinated and in 1:2 molar ratio are hexa-coordinated.



(I)



(II)

Thus, based on the above observations five (I) and six (II) coordinated structures can tentatively be proposed for triorganotin(IV) and diorganotin(IV) derivatives respectively.

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**References**

1 Mehrotra R C, Srivastava G & Saraswat B S, *Rev Silicon Germanium Tin Lead Comp*, 6 (1982) 171.
2 Singh M S, Rao R J & Samuel A, *Natt Acad Sci Lett*, 19 (1996) 114.
3 Dixit P & Tandon J P, *Synth react inorg met-org Chem*, 18 (1988) 439.
4 Goyal R N, *J sci ind Res*, 51 (1992) 948.
5 Garg H G & Prakash C, *J med Chem*, 14 (1971) 175.
6 (a) Sosnovsky G & Rao N V M, *Cancer Lett*, 29 (1985) 309.
(b) Mohan M, Gupta M P, Chandra L & Jha N K, *Inorg chim Acta*, 151 (1988) 61.
7 Arpadyn S, Karadzhova I, Tsalev D, Uzunova M, Stratis J A & Tossidis I A, *Analyst*, 113 (1988) 1699.
8 Ruyuchen G, Baozhongcai P & Guaweihi N, *Synthesis*, (1991) 783.
9 Cardin C J & Roy A, *Inorg chim Acta*, 107 (1985) 57.
10 Huber F, Vornefeld M, Preut H, Vonangerer C & Rusi G, Appl organomet Chem, 7 (1992) 6.
11 Bouale M, Mounierpiret J, Dlesemans M, Williams R & Gielen M, Inorg chim Acta, 200 (1992) 249.
12 Raju M D, Tripathi U N & Singh M S, *Main Group Met Chem*, 20 (1997) 497.
13 Furniss B S, Hannaford A J, Smith P W G & Tatchell A R, *Vogel's Text book of practical organic chemistry*, 5th edn (Longman, London) (1989).
14 Nenitzescu C D & Solomonica E, *Org Synth*, II (1950) 496.
15 Greary W L, *Coord Chem Rev*, 13 (1971) 47.
16 Aggrawal. R C & Varaprasad Rao D S S, *Indian J Chem*, 20A (1981) 855.
17 Aggrawal R C & Varaprasad Rao D S S, *Indian J Chem*, 21A (1982) 735.
18 Nakamoto K, Infrared spectra of Inorganic and coordination compounds, (Wiley, New York) (1970).
19 Saxena A, Molley K C, Zukerman J J & Tondon J P, *J organomet Chem*, 63 (1982) 71.
20 (a) Sharma R K, Singh R V & Tandon J P, *J inorg nucl Chem*, 43 (1981) 410.
21 (b) Malhotra R, Kumar S & Dhindsa S, *Indian J Chem*, 36A (1997) 321.
22 Gupta A K, Sharma S, Chauhan H P S & Rao R J, *Synt react inorg met-org Chem*, 2 (1991) 497.
23 Audoye P, Comues R C, Gaset A & Gorrihen J P, *Can J Chem*, 60 (1982) 1150.
24 Petrosyan V S, *Prog NMR Spectroscopy*, 11 (1977) 115.
25 Juckerman J J, *Adv Organomet Chem*, 9 (1970) 21.
26 Holecek J, Nadvorlik M, Handlir K & Lycka A, *J organomet Chem*, 315 (1986) 299.