

## Chelated Organotin (IV) Compounds of Substituted Benzophenones†

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Substituted tin (IV) derivatives of 2-hydroxybenzophenone and 2-hydroxy-4-methoxybenzophenone have been prepared. These include the dichloro-, dibromo-, dimethyl-, di-*n*-butyl-, di-*n*-octyl-, tri-*n*-butyl- and triphenyl- tin chelates of the ligands. Evidences for their coordinated structures have been obtained from infrared, PMR and UV spectra. The molecular weights of these compounds have been determined and possible structures assigned to them.

CHELATED tin(IV) compounds are formed (a) by effecting the Sn-C(phenyl) cleavage by a chelating ligand<sup>1</sup>, or (b) by reacting the sodio derivative of a ligand with a halo tin compound<sup>2-8</sup>. Derivatives of salicylaldehyde,  $\beta$ -diketones, fluoro diketones, 8-hydroxyquinoline, diphenylphosphinic acid etc. have been reported. Acetylacetone as a chelating ligand has been studied in detail<sup>9-14</sup>. Tin derivatives of substituted benzophenones are not reported. In this paper are reported the results of our attempts on the synthesis and characterisation of chelated organotin (IV) compounds of substituted benzophenones.

### Materials and Methods

The reactions were carried out in dry nitrogen atmosphere. Solids were separated from liquids either by centrifuging or by filtration in sintered glass apparatus using a positive pressure of nitrogen. Dried solvents were freshly distilled before use.

(a) *Preparation of bis-2-oxy-benzophenone dichlorostannane* — Sodium methoxide, prepared from sodium (0.23 g; 0.01 mol) and methanol (10 ml), was mixed with 2-hydroxybenzophenone (1.98 g, 0.01 mol) in benzene (30 ml) and refluxed for 30 min. The dry sodio derivative was isolated by removing methanol and benzene under reduced pressure at 40-50°. Stannic chloride (1.30 g; 0.005 mol) dissolved in benzene (50 ml) was added to the dry sodio derivative and the mixture refluxed for 2 hr. The contents were cooled, NaCl that separated was removed by centrifuging and the clear solution concentrated *in vacuo* till crystals appeared. The flask was cooled, and the crystals were washed with hexane and dried *in vacuo* at 50-60°; yield 2.32 g (80%). Molecular weight by ebullioscopy in benzene, found 600; calc. 585. Other chloro- and bromo- and diorganotin(IV) derivatives of 2-hydroxybenzophenone and 2-hydroxy-4-methoxybenzophenone were similarly prepared, and are given in Tables 1 and 2.

(b) *Preparation of 2-oxy-benzophenone triphenylstannane* — 2-Hydroxybenzophenone (1.98g; 0.01 mol) in benzene (50 ml) was refluxed with triphenyltin

hydroxide (3.67 g, 0.01 mol) using a partial take off condenser. The water formed in the reaction and the solvent were removed by distillation, the solid dried under reduced pressure, taken up in benzene, filtered and the clear solution concentrated under reduced pressure till crystallization. The crystals were removed, washed with hexane and solvent removed *in vacuo*; yield 4.1 g (75%); molecular weight by ebullioscopy in benzene, found 555 (calc. 547).

Other organotin compounds were similarly prepared (Tables 1 and 2).

### Results and Discussion

It is known that in the presence of an HCl acceptor the chlorine/bromine atoms of stannic chloride/bromide can be replaced by bidentate chelating ligands containing potential hydroxy groups. With 2-hydroxybenzophenone, the product thus obtained is the *bis*-chelated dichloro/dibromo stannane. The reaction has been successfully extended to organotin chlorides such as dimethyl dichlorostannane, di-*n*-butyldichlorostannane, di-*n*-octyl-dichlorostannane, tri-*n*-butylchlorostannane and triphenyl-chlorostannane. Chelated tin compounds are also prepared as above from a similar ligand, 2-hydroxy-4-methoxybenzophenone. The technique of azeotropic removal of water formed in the reaction between the ligands and organotin oxides/hydroxides is also employed to obtain similar chelated compounds. The products are yellow to orange solids, soluble and monomeric in boiling benzene. The new compounds prepared from typical experiments are listed in Tables 1 and 2.

The absence of any intense absorption band near 3600 in the IR spectrum† of 2-hydroxybenzophenone confirms the hydrogen bonded nature of the ligand even as a dilute solution in CCl<sub>4</sub>. Intramolecularly hydrogen bonded carbonyl band is seen around 1620-1640. In 2-hydroxy-4-methoxybenzophenone this band is seen at 1620. The  $\nu$  (C=O) is shifted to 1575 in dichloro- and dibromo- tin derivatives of 2-hydroxybenzophenone. In the case of corresponding 2-hydroxy-4-methoxybenzophenone derivatives, the  $\nu$  (C=O) band is observed at 1550. These observed

†IR  $\nu_{\max}$  cm<sup>-1</sup> UV  $\nu_{\max}$  in nm and NMR chemical shift in  $\delta$ (ppm).

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TABLE 1 — REACTION PRODUCTS OF 2-HYDROXYBENZOPHENONE\* (LH) WITH TIN(IV) COMPOUNDS

No.	Tin compd used	Product	Found (calc.) (%) <sup>b</sup>			m.p. (°C)
			C	H	Sn	
1	SnCl <sub>4</sub>	(C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>2</sub> SnCl <sub>2</sub>	53.71(53.46)	3.19(3.08)	20.24(20.33)	100(d)
2	SnBr <sub>4</sub>	(C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>2</sub> SnBr <sub>2</sub>	46.19(46.37)	2.78(2.67)	17.51(17.64)	232
3	Me <sub>2</sub> SnCl <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> Sn(C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>2</sub>	62.08(61.90)	4.85(4.42)	21.47(21.87)	Low melting solid
4	Bu <sub>2</sub> SnCl <sub>2</sub>	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>2</sub>	64.97(65.10)	5.91(5.74)	18.74(18.94)	-do-
5	Oct <sub>2</sub> SnO	(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> Sn(C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>2</sub>	68.00(68.22)	7.21(7.01)	15.91(16.77)	-do-
6	(Bu <sub>3</sub> Sn) <sub>2</sub> O	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> Sn(C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>2</sub>	61.77(61.65)	7.51(7.39)	24.32(24.40)	67
7	Ph <sub>3</sub> SnOH	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sn(C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>2</sub>	68.61(68.03)	4.58(4.39)	21.68(21.71)	99

(a) Sodio derivative of the ligand was used for SI Nos 1-6; molar ratio of the reactants 1:2 for SI No. 1-6 and 1:1 for SI No. 7.

(b) Satisfactory halogen analyses have been obtained for products at SI. Nos 1 and 2

TABLE 2 — REACTION PRODUCTS OF 2-HYDROXY-4-METHOXYBENZOPHENONE\* (LH) WITH TIN (IV) COMPOUNDS

No.	Tin compd used	Product	Found (calc.) (%) <sup>b</sup>			m.p. (°C)
			C	H	Sn	
1	SnCl <sub>4</sub>	(C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	52.39(52.19)	3.62(3.41)	18.42(18.44)	95
2	SnBr <sub>4</sub>	(C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> ) <sub>2</sub> SnBr <sub>2</sub>	45.69(45.85)	3.21(3.00)	16.11(16.20)	Low melting solid
3	Me <sub>2</sub> SnCl <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> (SnC <sub>14</sub> H <sub>11</sub> O <sub>3</sub> ) <sub>2</sub>	59.54(59.73)	4.89(4.64)	20.00(19.70)	168
4	Bu <sub>2</sub> SnCl <sub>2</sub>	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> ) <sub>2</sub>	57.18(57.33)	5.39(5.31)	15.76(15.77)	120
5	Oct <sub>2</sub> SnO	(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> Sn(C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> ) <sub>2</sub>	65.99(66.10)	7.23(7.01)	14.79(14.86)	161
6	(Bu <sub>3</sub> Sn) <sub>2</sub> O	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> Sn(C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> ) <sub>2</sub>	60.22(60.39)	7.39(7.35)	23.09(22.98)	Liquid
7	Ph <sub>3</sub> SnOH	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sn(C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> ) <sub>2</sub>	66.32(66.59)	4.52(4.50)	20.41(20.59)	91

(a) and (b) as in Table 1.

shifts in  $\nu$  (C=O) indicate coordination of the carbonyl of the ligand with metal. The phenolic C-O band, observed at 1250 in both the ligands shifts to higher frequency region in the above chelated tin halides suggesting metal-oxygen bond formation by replacement of phenolic proton. In these new compounds, the tin-chlorine vibrations appear around 340 as a single band suggesting a *trans* disposition of the two chlorine atoms with octahedral geometry.

The spectra of alkyl- and phenyl-tin derivatives reported in Table 3 resemble those of chloro- and bromo-tin chelates. The ligand is acting as a bidentate chelate in these compounds, but the coordination appears to be slightly weaker in these cases as expected.

2-Hydroxybenzophenone shows UV absorption bands at 261 ( $\epsilon$  14700) and 340 nm ( $\epsilon$  4400) in CHCl<sub>3</sub>. However the symmetry forbidden  $n$ - $\pi^*$  transition band of the ligand is not observed probably due to superimposition of the secondary band of benzene ( $^1L_b \leftarrow ^1A$ ). The higher intensity band of the ligand around 261 is seen in the same position in the tin compounds with increased intensity. The longer wavelength band of the ligand at 340 is also retained in the tin compounds with increased intensity. However in the triphenyltin derivatives the intensities of these bands show a considerable decrease, probably due to steric hindrance from the phenyl groups. 2-Hydroxy-4-methoxybenzophenone displays two absorption bands at 288 ( $\epsilon$  16600) and 328 ( $\epsilon$  10200). This kind of batho-

TABLE 3 — IR AND NMR SPECTRA OF CHELATED TIN(IV) COMPOUNDS OF SUBSTITUTED BENZOPHENONES

Compound	$\nu$ (C=O) cm <sup>-1</sup>	$\nu$ C-O (phenolic) cm <sup>-1</sup>	Chemical shift ( $\delta$ ppm)			
			OMe	3-H	5-H	Other aromatic protons
(LH)	1620-1640	1250		6.62	6.92	7.45
Cl <sub>2</sub> SnL <sub>2</sub>	1575	1300				
Br <sub>2</sub> SnL <sub>2</sub>	1575	1270				
Me <sub>2</sub> SnL <sub>2</sub>	1590	1260				
Bu <sub>2</sub> SnL <sub>2</sub>	1590	1260				
Bu <sub>3</sub> SnL	1590	1280		6.68	6.85	7.60
Ph <sub>3</sub> SnL	1580	1300		6.93		8.00
(L, H)	1620	1250	3.87	6.20	6.53	7.53
Cl <sub>2</sub> SnL' <sub>2</sub>	1550	1280				
Br <sub>2</sub> SnL' <sub>2</sub>	1550	1280				
Me <sub>2</sub> SnL' <sub>2</sub> e	1580	1280				
Bu <sub>2</sub> SnL' <sub>2</sub>	1590	1280				
Oct <sub>2</sub> SnL' <sub>2</sub>	1580	1270				
Bu <sub>3</sub> SnL'	1580	1280	3.80	6.13	6.43	7.25
Ph <sub>3</sub> SnL'	1580	1280	3.77	6.13	6.43	7.25

LH = 2-Hydroxybenzophenone and

L'H = 2-hydroxy-4-methoxybenzophenone.

chromic shift is expected for 261 nm band when an electron releasing substituent is introduced in the 4-position of benzophenone as in  $\beta$ -resorcylic acid<sup>15</sup>. The longer wavelength band of 2-hydroxybenzophenone at 340 suffers a hypsochromic shift in 2-hydroxy-4-methoxybenzophenone and appear at 328. In the organotin compounds of this ligand, the position

of the two bands is the same, but the intensities are doubled as in 2-hydroxybenzophenone compounds. These observations are in line with those made by Ismail<sup>16</sup> in the case of organosilicon chelates of the same ligand.

In the PMR spectrum (CCl<sub>4</sub>) the hydroxyl proton of 2-hydroxybenzophenone appears as a singlet at 11.93. The 3-H and 5-H protons of the hydroxy substituted ring appears at 6.62 and 6.92 respectively. The remaining aromatic protons of the ligand resonate around 7.45. The hydroxyl proton signal of the ligand is absent in its compounds suggesting metal-oxygen bond formation. The 3-H protons in the tin compounds suffer deshielding due to coordination of carbonyl group to tin. Other aromatic protons are also slightly deshielded due to compound formation. These observations are similar to those observed by Okawara<sup>17</sup> in the case of acetylacetone and its tin derivatives. In 2-hydroxy-4-methoxybenzophenone, the hydroxyl proton signal is found at 12.53. In all its tin compounds this signal is missing. The methoxy protons and aromatic protons of the tin compounds are shielded compared to the free ligand probably due to high order of distortion of the two aromatic rings as a result of compound formation with tin.

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