

ORGANOTIN COMPLEX COMPOUNDS OF *N*-SUBSTITUTED BENZOHYDROXAMIC ACIDS

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Summary

A number of diorganotin derivatives of *N*-substituted benzohydroxamic acids have been synthesized. Some of these compounds have been converted into halo derivatives of diorganotin hydroxamates (R_2SnXL , where $LH = N$ -phenylbenzohydroxamic acid (PBHA) and $R = Ph$, $X = SCN, Cl, I$; $R = Bu$, $X = SCN$). Halogen derivatives of phenyltin bis(*N*-phenylbenzohydroxamates) ($PhSnX(PBHA)_2$, where $X = Cl, Br, I$) have also been prepared. When refluxed with methanol both the diphenylhalotin and monophenylhalotin derivatives gave the same type of haloalkoxy-organotin derivatives ($PhSnX(OMe)L$, where $X = SCN, Cl, Br, I$, $LH = PBHA$; $X = Cl$, $LH = O-TBHA$), benzene being liberated in the former case and ligand (LH) in the latter. Diphenylchlorotin *N*-phenylbenzohydroxamate was found to disproportionate to phenylchlorotin bis(*N*-phenylbenzohydroxamate) and triphenyltin chloride.

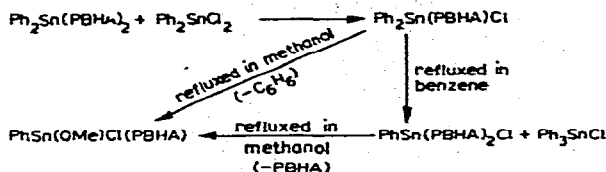
Introduction

Like oxines and β -ketoesters, substituted hydroxylamines have been proved to be suitable ligands for organotin complex compounds [1]. Harrison et al. have prepared some triorganotin derivatives of *N*-substituted and unsubstituted benzohydroxamic acids and have discussed the structure of *O*-trialkyltin hydroxylamines [2-3]. In an attempt to prepare triphenyltin benzohydroxamate they obtained tetraphenyltin and assumed that diphenyltin bis(benzohydroxamate) was formed but they could not isolate it [2]. We now report the preparation of certain diorganotin derivatives of *N*-substituted benzohydroxamic acids; though the dimethyltin bis(*N*-methylacetohydroxamate) was synthesized and its crystal structure determined [4] during our investigation. We have also isolated three new classes of organotin compounds of *N*-substituted hydroxamic acids, viz.: (a) R_2SnLX , (b) $RSnL_2X$ and (c) $RSnLX(OMe)$ ($R = Ph, Bu$; $LH = N$ -

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phenylbenzohydroxamic acid (PBHA); X = Cl, Br, I, SCN).

Some interesting interconversions of the following types have been observed:



Experimental

Materials. *N*-Substituted benzohydroxamic acids were prepared by standard procedures [5]. All solvents were purified and dried. The petroleum ether used had b.p. 60–80°C. Triphenyltin chloride [6], diphenyltin dichloride [7], diphenyltin diiodide [8], and dibutyltin dithiocyanate [9] were prepared by literature methods. Dibutyltin dichloride (Fluka) was recrystallized from benzene. Mercuric chloride (B.D.H.), mercuric bromide (E.M.) and mercuric iodide (E.M.) were used after drying in an air oven at 110°C. Triphenyltin *N*-phenylbenzohydroxamate was prepared as described by Harrison [2] and crystallized from methanol m.p. 133°C). Found: C, 65.98; H, 4.73% (lit. [2] m.p. 115.5–116.5°C; found: C, 65.9; H, 4.7%). All melting points are uncorrected.

Preparation and properties of organotin hydroxamates and their halogen derivatives

The other diorganotin bis(*N*-substituted benzo-hydroxamates) were prepared by following one of the two methods described below for the diphenyltin bis(*N*-phenylbenzohydroxamate).

Diphenyltin bis(N-phenylbenzohydroxamate)

(i) 11.56 g (0.04 mol) of diphenyltin oxide was dissolved in 150 ml of benzene and 17.04 g (0.08 mol) of *N*-phenylbenzohydroxamic acid was added. The mixture was refluxed for 4 h, then the light yellow solution was filtered. The filtrate was evaporated on a water bath to a pasty mass, which was crystallized from benzene/petroleum ether or, better from benzene/methanol. Yield 26.5 g (96%), m.p. 160°C.

(ii) 2.13 g (0.01 mol) of *N*-phenylbenzohydroxamic acid was dissolved in 25 ml of benzene and 1.72 g (0.005 mol) of diphenyltin dichloride was added with shaking. To the clear solution was added 2 ml of 25% aqueous ammonia. The mixture was filtered, and the organic layer separated. The solution was concentrated to a pasty mass on a water bath and boiled with methanol, to give fine white crystals (2.4 g), m.p. 160°C (yield 69%).

0.51 g of the same compound was obtained when 1.33 g of tetraphenylditin diacetate and 0.58 g of *N*-phenylbenzohydroxamic acid in benzene was refluxed for 10 min. The mixture was concentrated to a pasty mass, which was boiled with methanol.

Properties and analytical data of diorganotin bis(*N*-substituted benzohydroxamates) are given in Table 1.

TABLE I
 R_2SnL_2 COMPOUNDS: R = Ph, Bu; LH = *N*-SUBSTITUTED BENZOHYDROXAMIC ACID

R	LH	Solvent for crystallization or precipitation	Nature of the compound	M.p. (°C)	Analysis found (calcd.) (%)			
					C	H	H	Sn
C_6H_5	<i>N</i> -Phenylbenzohydroxamic acid	Benzene/petr. ether or benzene/methanol	Colourless crystals	160	65.08 (65.42)	4.53 (4.30)		16.98 (17.07)
C_6H_5	<i>N</i> - <i>para</i> -Tolylbenzohydroxamic acid	Petr. ether/methanol	White precipitate	166-167	66.26 (66.02)	4.76 (4.88)		16.39 (16.41)
C_6H_5	<i>N</i> -Phenyl- <i>para</i> -chlorobenzohydroxamic acid	Methanol	White crystals	189	59.78 (59.53)	3.97 (3.67)		15.41 (15.63)
C_6H_5	<i>N</i> -Phenyl- <i>para</i> -nitrobenzohydroxamic acid	Methanol	Ligh yellow crystals	196	58.00 (57.94)	3.66 (3.81)		15.02 (15.12)
C_6H_5	<i>N</i> -Ethyl- <i>para</i> -chlorobenzohydroxamic acid	Benzene/ethyl acetate	White crystals	222.6	53.93 (53.73)	4.29 (4.18)		17.45 (17.76)
Bu	<i>N</i> -Phenylbenzohydroxamic acid	Ethanol/benzene	Colourless crystals	106-107	62.42 (62.11)	5.84 (5.78)		17.73 (18.11)
Bu	<i>N</i> -Phenyl- <i>para</i> -chlorobenzohydroxamic acid	Methanol	White crystals	98-100	56.71 (56.20)	4.95 (4.99)		15.67 (16.39)
Bu	<i>N</i> - <i>para</i> -Chlorophenylbenzohydroxamic acid	Ethanol	White crystals	102-103	55.78 (56.20)	5.15 (4.96)		15.40 (16.39)
Bu	<i>N</i> -Ethyl- <i>para</i> -chlorobenzohydroxamic acid	Methanol	White leafy crystals	100	49.54 (49.86)	5.52 (5.71)		18.67 (18.89)

Phenylchlorotin bis(N-phenylbenzohydroxamate)

Triphenyltin *N*-phenylbenzohydroxamate (2.55 g) and mercuric chloride (1.23 g) were refluxed together in 50 ml of benzene for 2 h. The hot solution was cooled and the leafy crystals of phenylmercuric chloride (1.4 g, m.p. 248–249°C) were filtered off. The filtrate was then evaporated to dryness, cooled and washed with hot petroleum ether several times, to yield a solid (m.p. 140–162°C). This was recrystallized several times from benzene to give crystals of m.p. 195°C (1.1 g). Analysis found: C, 58.53; H, 3.99; Sn, 18.11. $C_{32}H_{25}ClN_2O_4Sn$ calcd.: C, 58.58; H, 3.82; Sn, 18.15%. The petroleum ether solution yielded 0.4 g of triphenyltin chloride (m.p. 106°C).

Phenylbromotin bis(N-phenylbenzohydroxamate)

Triphenyltin *N*-phenylbenzohydroxamate (1.686 g) and mercuric bromide (1.081 g) were refluxed together in 50 ml of benzene for 2 h. Subsequent procedure was as for the chloride. Crystals of m.p. 183°C formed after adding ethanol to the cold benzene solution after concentration. Analysis found: C, 54.75; H, 3.75; Sn, 16.81. $C_{32}H_{25}BrN_2O_4Sn$ calcd.: C, 54.77; H, 3.56; Sn, 16.97%.

Phenyliodotin bis(N-phenylbenzohydroxamate)

Triphenyltin *N*-phenylbenzohydroxamate (2.81 g) and mercuric iodide (2.27 g) were refluxed together with occasional shaking in 50 ml of benzene for 2 h. Subsequent work-up was as described for the chloride. Crystallization as for the bromide yielded colourless crystals of m.p. 177–178°C. Analysis found: C, 51.26; H, 3.51; Sn, 15.72. $C_{32}H_{25}IN_2O_4Sn$ calcd.: C, 51.40; H, 3.35; Sn, 15.93%.

Diphenylchlorotin N-phenylbenzohydroxamate

To a solution of diphenyltin bis(*N*-phenylbenzohydroxamate) (20 g) dissolved in 15 ml of benzene, diphenyltin dichloride (9.9 g) was slowly added at 25°C with shaking. Benzene was then completely removed with a vacuum pump and the white pasty residue was washed with cold petroleum ether and dissolved in an excess of cold methanol. Residual methanol was then removed at the pump at room temperature and the concentrated solution was placed in the refrigerator. 24 g of fine white crystals m.p. 110–112°C were separated, which were similarly treated and the final crystallized product had a m.p. of 113°C. Analysis found: C, 57.78; H, 3.81; Sn, 22.75. $C_{25}H_{20}ClNO_2Sn$ calcd.: C, 57.64; H, 3.84; Sn, 22.86%.

Diphenyliodotin N-phenylbenzohydroxamate

Diphenyltin bis(*N*-phenylbenzohydroxamate) (1.39 g) was dissolved in 15 ml of hot benzene and diphenyltin diiodide (1.05 g) was added. The mixture was cooled and after addition of petroleum ether, kept in the refrigerator overnight to give 2.1 g of fine white crystals of m.p. 127–129°C. The product crystallized twice from the same solvent mixture; m.p. 132°C. Analysis found: C, 48.82; H, 3.27; Sn, 19.39. $C_{25}H_{20}INO_2Sn$ calcd.: C, 49.02; H, 3.26; Sn, 19.43%.

Diphenylthiocyanatotin N-phenylbenzohydroxamate

To a solution of diphenylchlorotin *N*-phenylbenzohydroxamate (2.1 g) in 15

ml of benzene was added an ethanol solution of potassium thiocyanate. The mixture was then shaken for 5 min, filtered and placed in the refrigerator overnight. Colourless square crystals (1.2 g) appeared, which on further crystallization afforded crystals of m.p. 158–159°C. Analysis found: C, 57.65; H, 3.75; Sn, 21.70. $C_{26}H_{20}SN_2O_2Sn$ calcd.: C, 57.45; H, 3.71; Sn, 21.91%.

Dibutylthiocyanatotin N-phenylbenzohydroxamate

A mixture of dibutyltin bis(*N*-phenylbenzohydroxamate) (2.19 g) and dibutyltin dithiocyanate (1.61 g) in 30 ml of benzene was refluxed on a water bath for 1 h, then concentrated to a very small volume and treated with petroleum ether to give 2.21 g of colourless square crystals (m.p. 77–78°C). Recrystallization gave crystals of m.p. 79–80°C. Analysis found: C, 52.12; H, 5.94; Sn, 23.51. $C_{22}H_{28}SN_2O_2Sn$ calcd.: C, 52.48; H, 5.61; Sn, 23.65%.

Phenyl(chloro)methoxytin N-phenylbenzohydroxamate

(a) When diphenylchlorotin *N*-phenylbenzohydroxamate was refluxed in methanol, fine white crystals began to separate. Refluxing was continued for 1 h, and the solution was then filtered hot and the precipitate washed several times with hot methanol. The crystals had a m.p. of 228°C (dec.) in a preheated bath. Analysis found: C, 50.57; H, 3.84; Sn, 25.18; Cl, 7.31; OCH_3 , 6.59. $C_{20}H_{18}ClNO_3Sn$ calcd.: C, 50.58; H, 3.75; Sn, 25.08; Cl, 7.48; OCH_3 , 6.53%.

(b) The same methoxy compound (identified by mixed m.p.) was obtained when phenylchlorotin bis(*N*-phenylbenzohydroxamate) was refluxed in methanol and the insoluble white solid was washed with hot methanol several times.

Phenylthiocyanatomethoxytin N-phenylbenzohydroxamate

This was prepared by refluxing diphenylthiocyanatotin *N*-phenylbenzohydroxamate in methanol for 2.5 h. The white solid was filtered hot and washed with hot methanol and had a m.p. of 230–231°C (dec.). Analysis found: C, 50.94; H, 3.77; Sn, 23.71. $C_{21}H_{18}SN_2O_3Sn$ calcd.: C, 50.70; H, 3.61; Sn, 23.94%.

Phenyl(bromo)methoxytin N-phenylbenzohydroxamate

This was obtained by refluxing a methanol solution of phenylbromotin bis(*N*-phenylbenzohydroxamate) for 3 h and filtering the white solid and washing with hot methanol. The solid had m.p. 235°C (dec.). Analysis found: C, 46.22; H, 3.59; Sn, 22.70. $C_{20}H_{18}BrNO_3Sn$ calcd.: C, 46.15; H, 3.46; Sn, 22.90%.

Phenyl(iodo)methoxytin N-phenylbenzohydroxamate

This was prepared by refluxing a methanol solution of diphenyliodotin *N*-phenylbenzohydroxamate/phenyliodotin bis(*N*-phenylbenzohydroxamate). The fine white crystals which were filtered off and washed with hot methanol, had m.p. 219–220°C (dec.). Analysis found: C, 42.52; H, 3.23; Sn, 20.90. $C_{20}H_{18}INO_3Sn$ calcd.: C, 42.40; H, 3.18; Sn, 21.02%.

Phenyl(chloro)methoxytin N-ortho-tolylbenzohydroxamate

This was prepared by refluxing a methanol solution of diphenylchlorotin *N*-ortho-tolylbenzohydroxamate. The white solid was filtered off and washed with hot methanol, m.p. 207°C (dec.). Analysis found: C, 51.20; H, 4.10; Sn, 24.07. $C_{21}H_{20}ClNO_3Sn$ calcd.: C, 51.53; H, 4.09; Sn, 24.34%.

Infrared and ultraviolet spectra

The infrared spectra were recorded on a Beckman IR-20 infrared spectrophotometer equipped with KBr optics, using Nujol mulls. The ultraviolet spectra were recorded on a Beckman DU-2 UV spectrophotometer, using 1 cm cells. The C=O and N—O IR frequencies of representative compounds are given in Table 2, which also lists the absorption maxima and molecular extinction coefficients.

Disproportionation reaction of diphenylchlorotin *N*-phenylbenzohydroxamate

Diphenylchlorotin *N*-phenylbenzohydroxamate (1 g) was refluxed in benzene for 11 h. The benzene was completely evaporated and the pasty residue was crystallized from a mixture of benzene and petroleum ether. Crystals of m.p. 185–190°C (0.6 g) separated and after recrystallization these were shown to be phenylchlorotin bis(*N*-phenylbenzohydroxamate) (identified by mixed m.p.). Triphenyltin chloride (m.p. 106°C) was obtained from the mother liquor.

Reaction of phenylchlorotin bis(*N*-phenylbenzohydroxamate) with methanol

Phenylchlorotin bis(*N*-phenylbenzohydroxamate) (0.5 g) was refluxed in methanol for 5 h. The white precipitate (0.23 g) was filtered off and shown to be phenyl(chloro)methoxytin *N*-phenylbenzohydroxamate (by mixed m.p.). The filtrate was concentrated to give crystals of m.p. 195°C (0.15 g), which were identified as the starting material. The mother liquor was evaporated to dryness and the solid residue from a mixture of benzene/petroleum ether. The crystals (0.09 g, m.p. 122°C) were identified as the ligand.

Reaction of diphenylchlorotin *N*-phenylbenzohydroxamate with methanol

Diphenylchlorotin *N*-phenylbenzohydroxamate was dried at the pump and washed with cold methanol. The methanol washings showed no characteristic absorptions for free benzene in the UV region of the spectrum. Then the washed

TABLE 2
SPECTRAL DATA OF REPRESENTATIVE COMPOUNDS

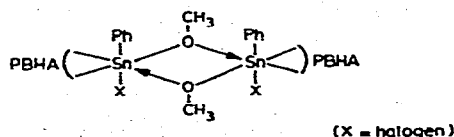
Compound	IR (cm ⁻¹) data (Nujol mulls)		Solvent	UV data	
	$\nu(\text{C=O})$	$\nu(\text{N-O})$		λ_{max} (nm)	log ϵ_{max}
PhCO · NOHPh	1635s	920s	Cyclohexane	275	3.81
			Dichloromethane	271	3.87
			Methanol	265	3.94
Ph ₂ Su(PhCO · NOPh) ₂	1520s	930s, 910m	Cyclohexane	298	—
			Dichloromethane	289	4.08
Ph ₂ SnCl(PhCO · NOPh)	1535s	930s, 910m	Cyclohexane	289	3.75
			Dichloromethane	279	3.82
			Methanol	269	3.90
PhSnCl(PhCO · NOPh) ₂	1530s	935s, 915m	Cyclohexane	287	—
			Methanol	271	4.11
PhSnCl(OMe)(PhCO · NOPh)	1532s	943s	Cyclohexane	285	—
			Methanol	271	—

crystals were refluxed in methanol for 1 h and the methanol was distilled off. The insoluble white residue was identified as the phenyl(chloro)methoxytin *N*-phenylbenzohydroxamate (m.p. 228°C (dec.)). The distillate showed the expected UV absorptions (234, 239, 243, 248, 254, 260 and 268 nm) and the liberated benzene was quantitative (the estimation was based on use of a standard solution of benzene in methanol at 254 nm).

Results and discussion

As shown in Table 2, the infrared carbonyl stretching frequencies are lowered by approximately 100 cm^{-1} in all the compounds compared to that in the free ligand. Harrison [1] has suggested strong intramolecular coordination via the carbonyl oxygen for triorganotin hydroxamates to account for the lowering of the carbonyl stretching frequency of these complexes (ca. 75 cm^{-1}). Similar intramolecular coordination can be suggested for our compounds.

Kawasaki et al. [10] has assigned the $520\text{--}530\text{ cm}^{-1}$ bands to $\nu(\text{Sn}\text{--}\text{OCH}_3)$ in methoxy(acetylacetonato)tin dihalides. It has also been suggested that there are characteristic absorption bands associated with the 4-membered $\overline{\text{OSnOSn}}$ ring system which frequently occurs in dimeric tin compounds [11]. Absorptions in the region $531\text{--}481\text{ cm}^{-1}$ have been assigned to this ring system in the methoxy-bridged acetylacetonates [12]. In the present methoxy compounds the band occurs at $480\text{--}490\text{ cm}^{-1}$ suggesting $\overline{\text{OSnOSn}}$ bonding. Due to the low solubility of the methoxy compounds, it was not possible to determine the molecular weight. The compounds are sparingly soluble in common organic solvents and are also moisture stable. The structure of the methoxy compounds can be written by analogy with that of the methoxy-bridged acetylacetonates [12].



The organotin oxinates have been shown [13] to be chelated in solution (since the peak in oxine in the UV region shifts to longer wavelengths in the complexes) and the order of the stability constant of the oxinates has been deduced from the band shifts in non-polar solvents [13]. Following the same arguments we conclude from the data in Table 2 that our organotin hydroxamates are chelated compounds, and that the sequence of the stability constants is: $\text{Ph}_2\text{Sn}(\text{PBHA})_2 > \text{Ph}_2\text{SnCl}(\text{PBHA}) \approx \text{PhSnCl}(\text{PBHA})_2 \approx \text{PhSn}(\text{OMe})\text{Cl}(\text{PBHA})$.

Diphenylchlorotin *N*-phenylbenzohydroxamate, which is assumed to be pentacoordinated, disproportionates to the more stable hexacoordinated phenylchlorotin bis(*N*-phenylbenzohydroxamate) and triphenyltin chloride in benzene. The same compound when refluxed with methanol gave the methoxy derivative, which was also obtained when phenylchlorotin bis(*N*-phenylbenzohydroxamate) was refluxed in methanol. In the former case benzene was liberated, and in the latter case ligand separated. Hence the methoxy compound must be phenylchloromethoxytin *N*-phenylbenzohydroxamate which is consistent with the analytical data. The structure is probably as shown.

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References

- 1 P.G. Harrison, *J. Organometal. Chem.*, **38** (1972) C5.
- 2 P.G. Harrison, *Inorg. Chem.*, **12** (1973) 1545.
- 3 P.G. Harrison and T.J. King, *J. Chem. Soc. Dalton*, (1974) 2298.
- 4 P.G. Harrison, T.J. King and J.A. Richards, *J. Chem. Soc. Dalton*, (1975) 826.
- 5 A.K. Majumdar, *N-Benzoylphenylhydroxylamine and its analogus*, Pergamon Press, London, 1972.
- 6 H. Gilman and S.D. Rosenberg, *J. Amer. Chem. Soc.*, **74** (1952) 5580.
- 7 H. Gilman and L.A. Gist Jr., *J. Org. Chem.*, **22** (1957) 368.
- 8 R.H. Bullard and W.B. Robinson, *J. Amer. Chem. Soc.*, **49** (1927) 1368.
- 9 D. Seyferth and E.G. Kochow, *J. Amer. Chem. Soc.*, **77** (1955) 1302.
- 10 Y. Kawasaki and R. Okawara, *J. Inorg. Nucl. Chem.*, **27** (1965) 1168.
- 11 R.C. Poiler, *The Chemistry of Organotin Compounds*, Logos Press Limited, 1970, p. 230.
- 12 Y. Kawasaki, T. Tanaka and R. Okawara, *J. Organometal. Chem.*, **6** (1966) 95.
- 13 K. Kawakami and R. Okawara, *J. Organometal. Chem.*, **6** (1966) 249.