SUMMARY

In recent years Organotin Chemistry has attracted much research effort as a result of the application of a good number of organotin compounds as PVC stabilisers, insecticides, pesticides, etc. During the last few years many workers have studied these organotin complex compounds of chelating ligands specially of oximes, 8-hydroxyquinoline and β-diketones. The present investigation is concerned mainly with the preparation of different types of organotin complex compounds of another potential bidentate chelating agent, the N-substituted benzohydroxamic acids, and their characterisation by analytical, UV, IR and NMR spectral data.

In the first place, a very short introduction of organotin compounds has been given, followed by a brief description on the nature of bonding and other related properties required to explain the chemical behaviour of organotin compounds in a general way. Next, the preparation and properties of some known organotin complex compounds have been discussed. These include organotin adducts formed from mono-, di- and triorganotin compounds; different types of organotin oxinates; organotin tropolonates, kojates and dithiocarbamates; organotin acetylacetonates and other β-diketonates; organotin oximates and hydroxamates; and organotin alkoxides. Some structural aspects of organotin complexes containing penta-, hexa- and hepta- coordinated tin have also been briefly discussed. Cleavage of tin-carbon bonds, in polar and non-polar solvents, involving symmetrical tetraalkyltin has been discussed, which is followed by

some specific cleavage reactions of symmetrical and unsymmetrical alkyl and aryl organotin compounds in different environments. Finally, nature of the present ligand, N-substituted benzohydroxamic acids, has been briefly discussed.

After this short review, experimental details of the present investigation have been given. First, the preparations of some known compounds which have been required for the present investigation have been given. These were prepared by standard procedures and modified where necessary.

All the triphenyltin N-substituted benzohydroxamates, Ph_3SnL (where L = N-phenylbenzohydroxamic acid, N-phenylparachlorobenzohydroxamic acid, N-phenylparanitrobenzohydroxamic acid, N-orthotolylbenzohydroxamic acid, N-parachlorophenylbenzohydroxamic acid), has been prepared by either azeotropic distillation of water from a mixture of bistriphenyltin oxide and the ligand or neutrallisation by aqueous ammonia of a mixture of triphenyltin chloride and the ligand. Diorganotin bis(N-substituted benzohydroxamates), R_2SnL_2, have similarly been prepared. Compounds prepared in this series include diphenyltin bis(N-phenylbenzohydroxamate), diphenyltin bis(N-paratolylbenzohydroxamate), diphenyltin bis(N-orthotolylbenzohydroxamate), diphenyltin bis(N-phenylparachlorobenzohydroxamate), diphenyltin bis(N-phenylparanitrobenzohydroxamate), diphenyltin bis(N-ethylparachlorobenzohydroxamate), dibutyltin bis(N-phenylbenzohydroxamate), dibutyltin bis(N-phenylparachlorobenzohydroxamate), dibutyltin bis(N-parachlorophenylbenzohydroxamate), dibutyltin bis(N-ethylparachlorobenzohydroxamate). All the tri- and diorganotin derivatives prepared here are moisture-stable white crystalline or amorphous solids except those derived from N-phenylparanitrobenzohydroxamic acid, which are beautiful yellow crystalline solids.

Triphenyltin N-substituted benzohydroxamates are all penta-coordinated compounds with Sn-O moiety. So, it is expected that these compounds should react with mercuric halides to undergo phenyl-tin cleavage and produce, like oxinates, the compounds of the type, e.g. for PBHA, $PhSnX(PBHA)_2$ along with the phenylmercuric halides and triphenyltin halides. Thus, reactions of triphenyltin N-phenylbenzohydroxamate with mercuric chloride, mercuric bromide and mercuric iodide gave quantitative yield of the respective phenyltin halide bis(N-phenylbenzohydroxamates) together with phenylmercuric halides and triphenyltin halides. Possible mechanism of this conversion has been given. In fact, all the compounds of this series have been prepared by this method. Phenyltin thiocyanate bis(N-phenylbenzohydroxamate) has been prepared from the corresponding chloride by the displacement of chloride by thiocyanate. Other compounds of this series are: phenyltin chloride bis(N-phenylparanitrobenzohydroxamate), phenyltin bromide bis(N-phenylparanitrobenzohydroxamate), phenyltin iodide bis(N-phenylparanitrobenzohydroxamate), phenyltin bromide bis (N-phenylparachlorobenzohydroxamate) and phenyltin iodide bis(N-phenylparachlorobenzohydroxamate).

The fourth series of organotin compounds, R_2SnXL (where R = Ph, X = Cl, I, SCN and LH = N-phenylbenzohydroxamic acid; R = Bu, X = SCN and LH = N-phenylbenzohydroxamic acid; R = Ph, X = Cl, I, LH = N-phenylparanitrobenzohydroxamic acid) have been synthesised. These compounds have been synthesized by the reaction of diorganotin dihalide with diorganotin bis(N-substituted benzohydroxamate). Diphenyltin thiocyanate N-phenylbenzohydroxamate has been obtained by displacement of chloride by thiocyanate of the corresponding chloride.

The fifth series of organotin compounds prepared here consists of novel compounds, the phenyltin halide methoxy N-substituted benzohydroxamates, $PhSnX(OMe)L$. The prepared compounds are: phenyltin chloride methoxy N-phenylbenzohydroxamate, phenyltin thiocyanate methoxy N-phenylbenzohydroxamate, phenyltin bromide methoxy N-phenylbenzohydroxamate, phenyltin iodide methoxy N-phenylbenzohydroxamate, phenyltin chloride methoxy N-orthotolylbenzohydroxamate. And, in one case instead of methoxy, the hydroxy compound, phenyltin chloride hydroxy N-phenylparanitrobenzohydroxamate has been obtained. These compounds have been easily obtained from the reaction of $Ph_2SnXL/PhSnXL_2$ in large excess of methanol.

Of these five series of organotin compounds of N-substituted benzohydroxamic acids, Ph_2SnXL (where X = Cl, SCN and LH = PBHA) has been found to undergo disproportionation reaction to give $PhSnXL_2$ and Ph_3SnX. Action of methanol on Ph_2SnXL (where X = Cl, SCN and LH = PBHA) and $PhSnXL_2$ (where X = Cl, Br, I and LH = PBHA; X = Cl and LH = N-phenylparanitrobenzohydroxamic acid) has also been studied.

Both Ph_2SnXL and $PhSnXL_2$ gave the same methoxy compound, PhSnX(OMe)L (PhSnX(OH)L where, LH = N-phenylparanitrobenzohydroxamic acid); but while the former gave C_6H_6 (which has been detected and estimated spectroscopically) as another product, the latter gave LH. In the former case the reaction goes completion within a short period.

The IR spectral data of the prepared compounds have been given. All the compounds show a shift of the ν(C = O) band to lower frequencies with a concomitant increase in the N-O frequencies. Also, the ν(O-H) frequency due to intramolecular hydrogen bonding in the ligand at ~3150 cm^{-1} is absent in the organotin derivatives. Thus, all these organotin derivatives have been suggested to be coordinated compounds, the carbonyl group of the ligand being coordinated intramolecularly to the tin atom. The triphenyltin derivatives have been suggested to have a penta-coordinated tin atom in a trigonal bipyramidal arrangement. The diorganotin bis(N-substituted benzohydroxamates) have been suggested to possess a hexa-coordinated octahedral arrangement around tin and in the case of $Bu_2Sn(PhCO.NOPh)_2$ the two butyl groups are probably cis. $PhSnXL_2$ compounds like R_2SnL_2 compounds have been suggested to possess an octahedral arrangement of groups around tin and when X = SCN, the bonding to tin is through the nitrogen atom of the group. While $Ph_2SnX(PBHA)$ (X = Cl, I) can have the penta-coordinated structure around tin, the $R_2Sn(NCS)(PBHA)$ (R = Ph, Bu) compounds have been suggested to have a dimeric hexa-coordinated structure with NCS bridging via the nitrogen atom in the solid. The phenyltin halide methoxy derivatives, PhSnX(OMe)L, have been suggested to be dimeric with hexa-coordinated tin atom and bridging $-OCH_3$ groups which is supported by the NMR data. Unfortunately, the molecular weights of these compounds could not be determined due to insufficient solubility of these compounds in common organic solvents.

The UV spectral data of some of these organotin derivatives of N-substituted benzohydroxamic acids have also been taken. All these compounds show strong absorptions and the longest wavelength absorption maxima of the free ligand have been shifted to the longer wavelength region suggesting that these are chelated in solution. Also, the stabilities of these five types of chelates (in the case of PBHA) have been compared from the UV spectral data in cyclohexane and the following stability sequence of these complexes has been suggested:

$$Ph_2Sn(PBHA)_2 > Ph_3Sn(PBHA) > Ph_2SnCl(PBHA) \simeq$$

$$PhSnCl(PBHA)_2 \simeq PhSnCl(OMe)(PBHA).$$

Finally, the action of chelating agents, e.g., N-substituted benzohydroxamic acids and 8-hydroxyquinoline on tetraphenylditin diacetate has been discussed. While N-substituted benzohydroxamic acids cleaved the Sn-Sn bond and formed diphenyltin bis(N-substituted benzohydroxamates) the 8-hydroxyquinoline gave a compound in which Sn-Sn bond remains intact but which is devoid of any phenyl groups.