phases are very difficult to detect in the presence of large amounts of other phases[4].

Cholesterol, the chief ingredient of gall stones, is a chemically complex molecule with several side chains. It has triclinic symmetry and its content varies from 57.3 to 99.7% of the dry substance[5]. Three forms of cholesterol have been reported in literature[1,6,7]. However, difficulties[6] occur in differentiating these forms. Cholesterol and cholesterol monohydrate are readily interchangeable, suggesting that water can enter and leave the lattices without difficulty. Cholesterol deposits freshly removed from man were invariably found to be cholesterol monohydrate[8], suggesting that cholesterol is originally laid down as monohydrate. When cholesterol monohydrate crystallised in man is kept in air for some time, it loses its water and transforms into anhydrous cholesterol. Thus anhydrous is formed from monohydrate, but whether this is always the case or whether it is deposited as such is not yet understood. Besides the formation of an anhydrous crystal form, the x-ray powder patterns reported by Bogren and Larsen[7] also indicated that cholesterol was transformed into an amorphous state when water left the lattice.

Cholesterol is almost insoluble in water[9]. It is, therefore, remarkable that crystals of anhydrous cholesterol undergo a transition into monohydrate in the presence of water. Crystals of the hydrate are stable up to five years under certain conditions, whereas samples consisting of very small crystallites have been found, where a large part is transformed after a few days.

Calcium carbonate as aragonite has been found only in one stone whereas calcite is present in the nucleus and outer layers with other crystalline compounds in three stones. Vaterite could not be detected in any of the stones.

Indication of apatite in the nucleus and the other layers of five stones has also been noticed. Due to small crystallite size, the apatite gives diffuse and weak patterns. On the basis of its strongest lines in the region of 2.82 to 2.88 A, it has been identified.

The incidence of gall stones increases with advancing years and the disease has a high frequency in females in all ages. In our series the female-to-male ratio was 6.5:1. This ratio was similar to that observed by others[10-12]. This disease in females is highest between 50 and 59 years and in males between 70 and 79 years. The maximum number of patients have been found in the age group of 36 to 40 years and the majority of them (70.6%) were vegetarians. This conforms to the general dietary habits of Meerut area. In the majority of the patients the fat intake was comparatively high. The consumption of high calorie diet with a large amount of fat containing saturated fatty acid has been supposed to be the cause for the formation of stones.

Authors thank Dr. A. M. Nagar, Department of Surgery, L.L.R.M. Medical College, Meerut for supplying the gall stones.

1. Sutor, D. J. and Wooley, S. E., *Gut*, 1969, **10**, 681.
2. Sutor, D. J., *Gut*, 1970, **11**, 618.
3. Lonsdale, K., *Nature* (*London*), 1968, **217**, 56.
4. Sutor, D. J., *Br. J. Urol.*, 1968, **40**, 29.
5. Nishimura, C., *Ch. Ztbl. I.*, 1939, 2441.
6. Sutor, D. J. and Wooley, S. E., *Gut*, 1971, **12**, 55.
7. Sutor, D. J. and Gaston, P. J., *Gut.*, 1972, **13**, 64.
8. Bogren, H. and Larson, K., *Biochem. Biophys. Acta*, 1963, **75**, 65.
9. Ekwall, P. and Mandell, I., *Acta Chem. Scand.*, 1961, **15**, 1404.
10. Horn, G., *Br. Med. J.*, 1956, **2**, 732.
11. Rains, A. F. J. H., *Gallstone*, William Heinmann Medical Book Ltd., (Pergamon Press, Oxford, U.K 1964.
12. Friedman, G. G., *J. Chronic Disease*, 1966, **19**, 273.

REACTION OF TETRAPHENYLDITIN DIACETATE WITH N-PHENYL-BENZOHYDROXAMIC ACID AND 8-HYDROXYQUINOLINE

B. PRADHAN* AND A. K. GHOSH
Department of Chemistry, North Bengal University, Darjeeling 734 430, India.
* Present Address: Department of Chemistry, Raiganj University College, Raiganj 733 134, India.

ABSTRACT

The Sn—Sn bond in tetraphenylditin 1,2-diacetate is cleaved when reacted with N-phenyl-benzohydroxamic acid (PBHA); but the bond is retained when reacted with 8-hydroxyquinoline (Ox). In the former the characterised product is diphenyl tin *bis* (N-phenyl-benzohydroxamate) and in the latter the product has been characterised as diacetate ditin *bis* (oxinate).

INTRODUCTION

IN recent years, coordination compounds of organo monotin moieties have been extensively studied. But coordination compounds of organoditin compounds have not been studied in detail due to the cleavage of Sn—Sn bond by various reagents. An attempt is made here to prepare coordination com-

pounds of ditin moieties by bidentate chelating agents like oxine and N-phenyl-benzohydroxamic acid.

Experimental

Tetraphenyl ditin 1,2-diacetate was prepared following the method of Sawyer *et al.*[1] by reacting dried ether solution of diphenyl ditin dihydride with glacial acetic acid in nitrogen medium. Tetraphenyl ditin 1,2-diacetate (1.33 g) was taken in benzene and to it was added 0.8 g of N-phenyl-benzohydroxamic acid and the mixture was heated around 80–85° C for 10 min. The product after recrystallization from methanol gave fine white crystals (0.51 g) of m.p. 160° C. On the other hand, when tetraphenyl ditin 1,2-diacetate and 8-hydroxyquinoline (1:2 mole ratio) taken in benzene was heated to boiling point and shaken fine yellow crystals resulted having a m.p. 224–230° C. On crystallization twice from benzene this showed a m.p. of 235° C and mixed with diphenyltin *bis* oxinate (m.p. 252° C) had m.p. of 210–215° C. Analysis of this compound gave:

C = 41.0, H = 3.0, N = 5.1, Sn = 36.6

Calculated for $C_{22}H_{18}N_2O_6Sn_2$: C = 41.0, H = 2.8

N = 4.4 and Sn = 36.9%.

Results and Discussions

It has been found that diphenyl tin *bis* (N-phenyl-benzohydroxamate) is obtained when tetraphenyl-ditin 1,2-diacetate is reacted with any equivalent of the PBHA. This reaction can be taken as the cleavage of the Sn—Sn bond by the hydroxamic acid ligand which can act as an oxidising agent[2]. Similar Sn—Sn bond cleavage reactions by many common reagents which are acid and oxidising are known[3]. The cleaved product, diphenyltin bis (N-phenyl-benzohydroxamate) has been characterised by analytical, IR and UV data[4].

On the other hand, when tetraphenyl ditin 1,2-diacetate is reacted with 8-hydroxyquinoline (1:2 mole ratio), the compound obtained has analytical data which conform to the formula:

$[(OAc)_2Sn_2(OX)_2]_n$

in which Sn—Sn bond is retained. There are very few reactions of ditins in which Sn—Sn bond is retained. One such reaction is that of Ph_6Sn_2 with acetic acid to yield $(AcO)_6Sn_2$[5]. The formulation of $[(OAc)_2Sn_2(OX)_2]_n$ is supported by IR and UV data. The IR spectra of 1,1,2,2-tetraphenyl-1,2-diacyloxy ditin compounds have been studied[6]. For the acetate compound, the band at 1530 cm^{-1} has been assigned to ν_{as}(COO) vibration. The symmetric stretching vibration of ν_s(COO) has been assigned at 1405 cm^{-1}. A structure with the two-acetate ligands, bridging the two tin atoms has been proposed. In the spectrum of the present compound, these two bands have been missing and a new intense band at 1620 cm^{-1} has appeared. Monomeric diorganotin *bis* acetate, $R_2Sn(OAc)_2$ (R = CH_3, C_3H_7, C_4H_9) has been shown to give ν_{as}(COO) at 1607 cm^{-1} which is attributed to a chelating acetate group. For $Sn(OAc)_4$, the bands at 1625 cm^{-1} and 1725 cm^{-1} have been interpreted as (COO) vibrations involving a chelating and an ester like configuration respectively. Also the ν_{as}(C=O) stretching band of CH_3COOEt at 1741 cm^{-1} is shifted to 1613 cm^{-1} upon coordination of the C=O group through the oxygen atom to the Sn atom[7]. Hence, in the present compound, the acetate group is not a bridging one as in the parent ditin compound, but a chelating one.

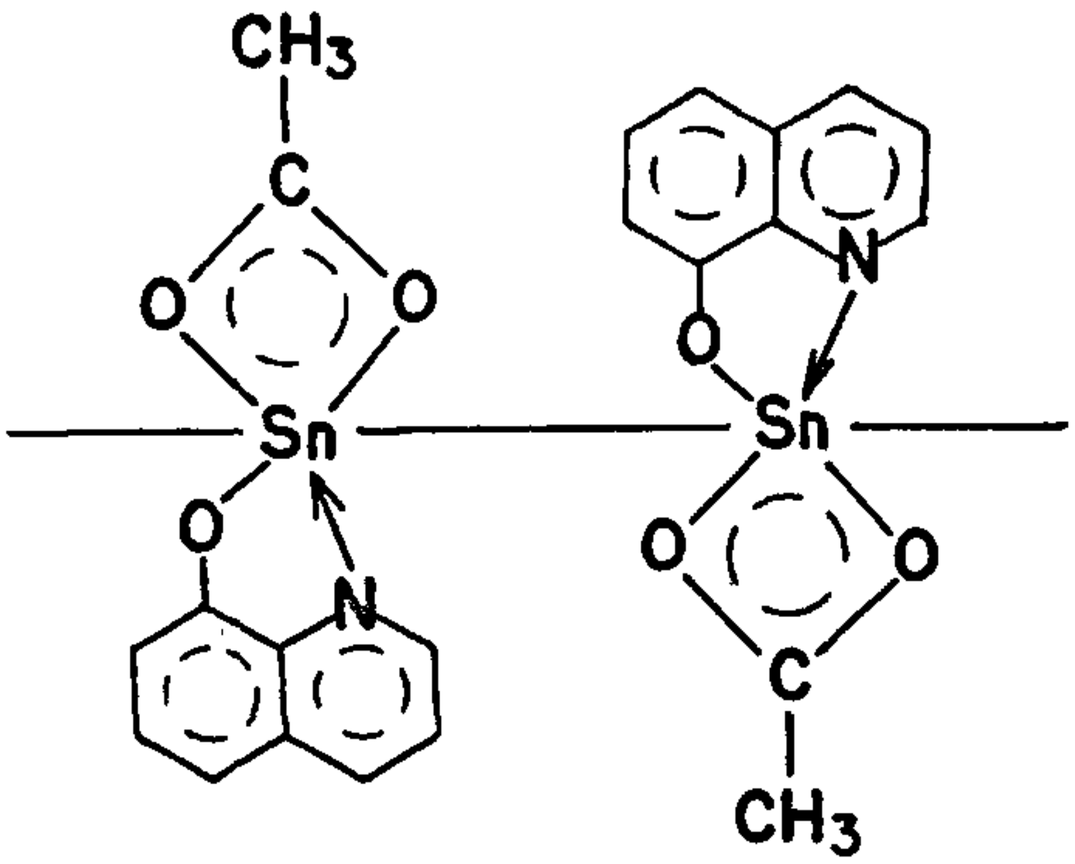
In $(CH_3)_2Sn(OX)_2$, the bands at 395 cm^{-1} and 517 cm^{-1} have been assigned as due to tin-nitrogen and tin-oxygen stretching vibrations respectively[8]. Similar band assignments have been made for the $R_2SnX(OX)$ compounds[9]. The present compound contains two strong bands at 390 cm^{-1} and 515 cm^{-1} which were absent in the tetraphenyl ditin 1,2-diacetate and hence these bands can be assigned as ν(N→Sn) and ν(Sn—O) modes respectively arising from the coordination of the oxine group to the Sn atom.

All the phenyl tin compounds have medium-to-intense absorption band at ~450 cm^{-1} which has been assigned to phenyl ring vibration[9]. Since the present compound has no absorption band between 390 and 490 cm^{-1} corresponding to the intense band at 450 cm^{-1} in the $Ph_4Sn_2(OAc)_2$ and $Ph_2Sn(OX)_2$ compounds, it can be suggested that the compound lacks the phenyl group. And this lack of phenyl group in dicarboxylic tin *bis* (oxinate) is responsible for the absence of any band at ~ 450 cm^{-1}. This is further supported by the fact that the present compound does not have any band at ~ 1065 cm^{-1} corresponding to the bands at 1072 cm^{-1} and 1061 cm^{-1} respectively of $Ph_4Sn_2(OAc)_2$ and $Ph_2Sn(OX)_2$. The band at ~1065 cm^{-1} has been assigned by Henry and Noltes as perturbed phenyl vibrational absorption characteristic of the phenyl group attached to tin[10]. Further, a medium to strong intensity band at ~ 3060 cm^{-1}, which is absent in the present compound, generally has been found to appear for phenyl groups[11].

Catenated metal-metal bonds of group IV metals absorb as Chromophores in the near ultraviolet, and, in the organo distannanes there is intense absorption around 245 nm in cyclohexane which is associated with the Sn—Sn bond and is independent of the presence of aromatic groups[12]. The UV spectra of $Ph_4Sn_2(OAc)_2$ and of the present compound in cyclohexane both show absorption maxima at 242–43 nm suggesting that the present compound contains a Sn—Sn bond. The extinction could not be determined due

to insufficient solubility of the compound in cyclohexane. But in the chloroform solution this compound shows absorption maxima at 259 nm ($\log \epsilon_{max} = 4.79$) and a broad band at 385 nm ($\log \epsilon_{max} = 3.50$) the compound in UV and visible region of the spectra in $CHCl_3$ solution clearly demonstrates the presence of the chelating oxinate groups[13] in the present compound.

Hence, the present compound can be assumed to have a structure (figure 1) consisting chelating acetate and oxinate groups in conforming with the analytical data.



ACKNOWLEDGEMENT

The authors thank the authorities of the University of North Bengal for facilities and financial support including a fellowship to BP.

1. Sawyer, A. K. and Kuivila, H. G., *J. Am. Chem. Soc.*, 1960, **82,** 5958.
2. Blakeley, J. H. and Ryan, D. E., *Analyst*, 1964, **89,** 721.
3. Gilman, H., Atwell, W. H. and Cartiledge, F. K., *Adv. Organometal Chem.*, 1966, **4,** 1.
4. Pradhan, B. and Ghosh, A. K., *J. Organometal Chem.*, 1977, **131,** 23.
5. Wiberg, E. and Behringer, H., *Z. anorg. Chem.*, 1964, **329,** 290.
6. Plazzogna, G., Peruzzo, V. and Tagliavini, G., *J. Organometal Chem.*, 1970, **24,** 667.
7. Lappert, M. F., *J. Chem. Soc.*, 1962, 542.
8. Kawakami, K. and Okawara, R., *J. Organometal Chem.*, 1966, **6,** 249.
9. Poller, R. C. and Ruddick, J. N. R., *J. Chem. Soc*, .(A) 1969, 2273.
10. Henry, M. C. and Noltes, J. G., *J. Am. Chem. Soc.*, 1960, **82,** 555.
11. Hague, D. N. and Prince, R. H., *J. Chem. Soc.*, 1965, 4690.
12. Creemers, H. M. J. C. and Noltes, J. G., *J. Organometal Chem.*, 1967, **7,** 237.
13. Datta, D., Ph.D. Thesis, North Bengal University, 1970.

SYNTHESIS AND ANTHELMINTIC ACTIVITY OF 1-(5′-SUBSTITUTED PHENOXY METHYL, 1′,3′,4′-THIADIAZOL-2′-YL), 2-METHYL-4-SUBSTITUTED BENZYLIDENE IMIDAZOL-5-ONES

J. S. SHUKLA AND KANCHAN AGARWAL
Department of Chemistry, Lucknow University, Lucknow 226 007, India.

ABSTRACT

A number of 1-5′-substituted phenoxy methyl 1′,3′,4′-thiadiazol-2′-yl), 2-methyl-4-substituted benzylidene imidazol-5-ones have been prepared by the condensation of 2-amino-5-substituted phenoxy methyl 1,3,4-thiadiazole with 2-methyl-4-substituted benzylidene azlact-5-ones. They have been screened for their cestodicidal activity against *H. nana* infection in rats.

INTRODUCTION

THE therapeutic properties of a number of thiadiazoles[1-4] and imidazolones[5-9] against infection in gastro-intestinal tract are well documented. In view of the important cestodicidal activity displayed by thiadiazole derivatives, it was considered worthwhile to prepare the compounds containing both the thiadiazole and imidazole nucleus. The present communication describes the synthesis of various 1-(5′-substituted phenoxy methyl 1′,3′,4′-thiadiazol-2′-yl), 2-methyl-4-substituted benzylidene imidazol-5-ones.

1-Substituted phenoxy methyl thiosemicarbazide(1) on cyclodehydration with conc. H_2SO_4 gives the corresponding 2-amino-5-substituted phenoxy methyl 1,3,4-thiadiazole(2) which on condensation with various 2-methyl-4-substituted benzylidene azlact-5-ones yields the corresponding 1-(5′-substituted phenoxy methyl 1′,3′,4′-thiadiazol-2′-yl),