

Synthesis and infrared studies of tri- and diorganotin(IV) derivatives of benzoic acid

M. ADEDIRAN MESUBI

Department of Chemistry, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria

(Received 16 February 1982)

Abstract—Some triorganotin benzilates, R_3SnB ($R = CH_3, C_2H_5, C_3H_7$ and C_6H_5 , $B = (C_6H_5)_2C(OH)COO^-$) and diorganotin dibenzilates, R_2SnB_2 ($R = CH_3, C_2H_5$ and $n-C_4H_9$) have been synthesized and characterized by elemental analysis and i.r. spectra. The i.r. data indicate that the triorganotin benzilates are tetracoordinated monomers in the solid state thus suggesting that the steric hindrance between the benzilate ion and the organotin moiety is sufficient to prevent formation of polymers. The diorganotin dibenzilates on the other hand have a *cis*- R_2SnCl_2 or distorted octahedral structure.

INTRODUCTION

Although considerable amount of work has been done on the structure and bonding of organotin carboxylates using various techniques: X-ray[1-3], i.r.[4-7] and Mössbauer[8-10], the subject continues to attract interest as evident from the recent publications[11, 12]. The structure of organotin carboxylate depends on the nature of the acid and the organic groups attached to the tin atom. If there is sufficient steric interaction between the organotin moiety and the carboxylate ion, then tetracoordinated monomers are formed in the solid state[13]. Otherwise, the organotin carboxylates form polymers in the solid state with pentacoordinate tin atom in a trigonal bipyramidal configuration, the tin atoms being bridged by the carboxylate group.

There are a few reports of transition metal complexes of benzoic acid[14, 15] but no organotin derivatives have been studied in detail. Therefore, this paper describes the preparation and i.r. spectra of some organotin derivatives of benzoic acid in order to investigate their structure type either pentacoordinated polymers or tetra-coordinated monomers in the solid state.

EXPERIMENTAL

Synthesis of organotin benzilates

First, potassium benzilate was prepared by refluxing benzil with aqueous-alcoholic potassium hydroxide as described by VOGEL[16]. The organotin benzilates were then prepared by the interaction of the appropriate organotin chloride with equimolar quantity of potassium benzilate in ethanol. The mixture was refluxed for about 1 h, cooled to room temperature and filtered to remove the precipitated KCl. The solvent was removed under reduced pressure using a vacuum rotatory evaporator. Most of them gave yellow oils which solidified under high vacuum. The resulting solid was recrystallized from hot acetonitrile-ethanol mixture and dried in a vacuum desiccator over $CaCl_2$.

Physical measurements

The melting points were determined using an electrothermal melting point apparatus. Microanalyses were performed by MidWest MicroLab Ltd., Indianapolis.

The i.r. spectra were recorded using Nujol mulls between KBr plates and CsI pellets on Perkin-Elmer model 180 spectrophotometer of the Department of Chemistry, University of Guelph, Canada.

RESULTS AND DISCUSSION

All the organotin benzilates are white solids up to the transition temperature, but become reddish in the molten state. They decompose a few degrees above the transition temperature. The compounds are all air and moisture stable. Their melting points and analytical data are shown in Table 1. They are generally not soluble in the common organic solvents like chloroform, acetone, benzene.

Infrared spectra

The spectra in both nujol mulls and CsI pellets are essentially the same. The spectral regions of interest are the carbonyl frequency region, 1750-1300 cm^{-1} and the far i.r. region, 700-200 cm^{-1} . The stereochemistry of the benzilates can be inferred from the frequencies of the $\nu_a(OCO)$ and $\nu_s(Sn-C)$ stretching vibrations. The frequencies associated with these vibrations are shown in Table 2. The assignments have been made by comparison with frequencies of known organotin carboxylates and complexes in literature[5, 6, 17-19].

Triorganotin benzilates, R_3SnB

They all show strong absorption bands at 1640 cm^{-1} except for trimethyltin benzilate which has absorption bands at 1720 and 1630 cm^{-1} . These bands have been assigned to the $\nu_a(OCO)$ stretching vibration. In trimethyltin benzilate the $\nu_a(OCO)$ band is very broad but strong in intensity; it is so broad that the peaks at 1720 and 1630 cm^{-1} are not sharp. These bands probably overlap with those of the benzene ring which usually absorb in the range 1600-1500 cm^{-1} . The strong bands observed in the range 1322-1330 cm^{-1} are assigned to the $\nu_s(OCO)$ stretching vibrations.

Table 1. Melting points and analytical data for the organotin benzilates

Compound	Melting point (°C)	Analysis found (calcd.)% C H	
(CH ₃) ₃ SnB	55–60	52.21 (52.36)	5.17 (4.99)
(C ₂ H ₅) ₃ SnB	78–80	55.45 (56.35)	6.06 (5.75)
(C ₃ H ₇) ₃ SnB	75–80	58.12 (58.71)	6.80 (6.99)
(C ₆ H ₅) ₃ SnB	> 250	66.58 (61.98)	4.55 (4.27)
(CH ₃) ₂ SnB ₂	164–171	59.72 (60.75)	4.69 (4.64)
(C ₂ H ₅) ₂ SnB ₂	170–179	60.87 (61.57)	5.12 (5.00)
(C ₄ H ₉) ₂ SnB ₂	139–146	63.94 (62.89)	5.43 (5.88)

Table 2. Relevant i.r. frequencies (cm⁻¹) for the organotin benzilates

Compound	$\nu_a(\text{OCO})$	$\nu_s(\text{OCO})$	$\nu(\text{OH})$	$\nu_a(\text{Sn-C})$	$\nu_s(\text{Sn-C})$	$\nu(\text{Sn-O})$
(CH ₃) ₃ SnB	1720, 1630 vs	1330 vs	3440 br	552 s	528 m	330 w
(C ₂ H ₅) ₃ SnB	1640 s	1327 s	3380 br	525 m	490 w	330 w
(C ₃ H ₇) ₃ SnB	1640 s	1330 s	3380 v.br	520 m	504 w	332 w
(C ₆ H ₅) ₃ SnB	1640 vs	1322 vs	3450 br	280 s*	225 ^b †	330 m
(CH ₃) ₂ SnB ₂	1721 s, 1642 vs, br	1335 s, br	3444 br	530 w	510 w	300 m
(C ₂ H ₅) ₂ SnB ₂	1721 s, 1640 vs br	1345 vs, br	3404 s	550, 535 m	502 m	300 s
(C ₄ H ₉) ₂ SnB ₂	1720 s, 1630 vs br	1344 vs br	3404 s	540, 532 m	507 m	290 s

vs, very strong; s, strong; m, medium; w, weak; br, broad; v.br, very broad.

ν_a asymmetric stretching vibration.

ν_s symmetric stretching vibration.

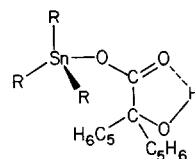
* $\nu_a(\text{Sn-Ph})$. † $\nu_s(\text{Sn-Ph})$.

The above frequencies for the $\nu_a(\text{OCO})$ bands are much higher than those usually associated with polymeric structures [11–13]. These high frequencies are consistent with monomeric tetra-coordinated organotin carboxylates. Shown in Table 2 are the frequencies observed for the $\nu_a(\text{Sn-C})$ and $\nu_s(\text{Sn-C})$ bands which are of weak to medium intensity. The presence of both $\nu(\text{Sn-C})$ bands suggests the absence of a planar SnC_3 configuration and hence the absence of pentacoordinated tin atom. A plausible structure consistent with these observations is shown in Scheme 1.

A broad band observed at about 3330–3440 cm⁻¹ has been assigned to the $\nu(\text{OH})$ stretching vibration. The broadening of the band and the lowering of the frequency from its usual value of about 3640 cm⁻¹ is attributed to the intramolecular hydrogen bonding with the free carbonyl oxygen as indicated in structure I.

Diorganotin dibenzilate, R_2SnB_2

The spectra are characterized by two well distinct $\nu_a(\text{OCO})$ bands, one at 1720–1721 cm⁻¹ and the other at 1642–1630 cm⁻¹. Except for the dimethyltin dibenzilate, the $\nu_a(\text{OCO})$ bands at 1720 cm⁻¹ are sharp but the ones at 1642–1630 cm⁻¹ are relatively broad in all the diben-



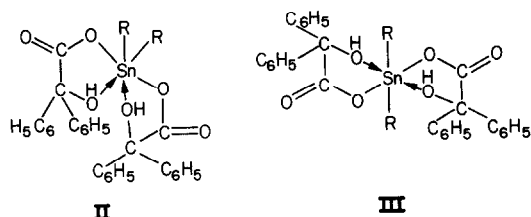
I

Scheme 1.

zilatates. Also, the $\nu_s(\text{OCO})$ bands observed in the range 1335–1345 cm⁻¹ are broad compared with those of the triorganotin benzilates.

The high $\nu_a(\text{OCO})$ frequencies observed above indicate the presence of uncoordinated carbonyl groups. The presence of both $\nu_a(\text{Sn-C})$ and $\nu_s(\text{Sn-C})$ bands observed in the range 530–550 and 502–510 cm⁻¹, respectively which are of weak to medium intensity implies a bent C–Sn–C configuration. Thus on the basis of these infrared data the following *cis*- $\bar{R}_2\text{SnB}_2$ octahedral structure (I) or distorted octahedral structure (III) has been proposed for the diorganotin dibenzilates (see Scheme 2).

Except for the dimethyltin dibenzilate, the $\nu(\text{OH})$ band observed in the range 3404–344 cm⁻¹ are relatively sharper than those observed for the triorganotin benzilates. This seems to indicate that there is very little or no hydrogen bonding in the



Scheme 2.

dibenzilates. This interpretation is consistent with the proposed structure (II or III).

CONCLUSION

The i.r. data presented in this paper show that both triorganotin and diorganotin benzoates are nonpolymeric in the solid state. Apparently the benzoate ion is bulky enough to prevent the formation of polymers in the solid state.

Acknowledgements—The University of Ilorin is gratefully acknowledged for financial support through the Senate Research Grant. The author is also grateful to Professor H. C. CLARK of the University of Guelph, Canada for financing the cost of the microanalysis and for permission to use his research facilities.

REFERENCES

- [1] N. W. ALCOCK and R. E. TIMMS, *J. Chem. Soc. A* 1873 (1968).
- [2] B. Y. K. HO, J. A. ZUBIETA and J. J. ZUCKERMAN, *Chem. Commun.* 88 (1975).
- [3] P. G. HARRISON, *Am. Chem. Soc. Advan. Chem. Ser.* 157, 258 (1976).
- [4] A. K. SAWYER, *Organotin Compounds*, Vol. 3, Chap. 12. Dekker, New York (1972).
- [5] N. W. G. DEBYE, D. E. FENTON, S. E. ULRICH and J. J. ZUCKERMAN, *J. Organomet. Chem.* 28, 339 (1971).
- [6] R. OKAWARA and M. WADA, *Adv. Organomet. Chem.* 5, 137 (1967).
- [7] R. C. POLLER, *The Chemistry of Organotin Compounds*, Chap. 14. Lagos (1970).
- [8] B. F. E. FORD, B. V. LIENGME and J. R. SAMS, *Chem. Commun.* 1333 (1968).
- [9] D. W. ALLEN, J. S. BROOKS, R. FORMSTONE, A. J. CROWE and P. J. SMITH, *J. Organomet. Chem.* 156, 359 (1978).
- [10] R. C. POLLER and J. N. R. RUDDICK, *J. Organomet. Chem.* 39, 121 (1972).
- [11] S. CALOGERO, D. A. CLEMENTE, V. PERUZZO and G. TAGLIAVINI, *J. Chem. Soc. Dalton Trans.* 7, 1172 (1979).
- [12] A. J. CROWE, R. HILL, P. J. SMITH, J. S. BROOKS and R. FORMSTONE, *J. Organomet. Chem.* 204, 47 (1981).
- [13] M. A. MESUBI, *Spectrochim. Acta* 32A, 1327 (1976).
- [14] A. C. RANADE, C. I. JOSE and A. B. BISWAN, *Proc. Int. Conf. Spectros.*, Bombay 2, 348 (1967).
- [15] B. K. SENGUPTA, S. P. MOULIK and K. DEY, *J. Inorg. Nucl. Chem.* 32, 1052 (1970).
- [16] A. J. VOGEL, *A Textbook of Practical Organic Chemistry*, 3rd edn. Longman, London (1956).
- [17] J. OTERA, Y. KAWASAKI and T. TANAKA, *Inorg. Chim. Acta* 1, 294 (1967).
- [18] E. V. VAN DEN BERGHE, G. P. VAN DER KELEN and J. ALBRECHT, *Inorg. Chim. Acta* 2, 89 (1968).
- [19] R. CEFALU, R. BOSCO, F. BONATI, F. MAGGIO and R. BARBIERI, *Z. Anorg. Allg. Chem.* 376, 180 (1970).