

THE PREPARATION AND PROPERTIES OF SOME TRIVINYLTIN CARBOXYLATES

VALERIO PERUZZO, GUALTIERO PLAZZOGNA AND GIUSEPPE TAGLIAVINI

Institute of Analytical Chemistry, University of Padua, I-35100-Padua (Italy)

(Received April 2nd, 1970)

SUMMARY

Trivinyltin carboxylates $(\text{CH}_2=\text{CH})_3\text{SnOOCR}'$ ($\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{Cl}, \text{CF}_3$) have been prepared by an electrochemical procedure, in which tetravinyltin reacts with mercury(I) ions generated electrolytically in methanol containing the appropriate sodium carboxylate as supporting electrolyte.

The new compounds obtained are appreciably soluble in THF, less soluble in chloroform, and much less soluble in carbon tetrachloride. Their IR spectra in solid, Nujol mulls and in solution reveal that the compounds are polymers, containing five-coordinated tin atoms in a trigonal bipyramidal structure with bridging carboxylate groups. The Sn-C region bands, either in solid or in solution, show that the three vinyl groups do not lie in the equatorial plane.

Molecular weight determinations show that depolymerization occurs in chloroform, in which the compounds are unassociated except for the acetate, which is trimeric.

INTRODUCTION

While several alkenyltin compounds are known^{1,2}, no trivinyltin carboxylates have previously been prepared.

We have recently made trimethyltin carboxylates by means of a new electrochemical procedure³, and have now used this procedure to prepare trivinyltin carboxylates of general formula $(\text{CH}_2=\text{CH})_3\text{SnOOCR}'$, where R' is $\text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{Cl}$, or CF_3 .

EXPERIMENTAL

Tetravinyltin, purchased from Fluka (Switzerland) was used without further purification.

Methanol and sodium carboxylates were reagent grade from C. Erba (Milan) or Schuchardt (München).

IR spectra were recorded on a Perkin-Elmer Model 621 or 457 equipped with KBr optics using the prepared compounds dispersed in Nujol or in KBr discs. IR spectra in chloroform solution have been run on a Beckmann IR 9 instrument equipped with KBr optics.

Melting points (uncorrected) were taken with a Büchi apparatus (Switzerland) using open capillaries.

Molecular weights were determined in chloroform and THF with a Mechrolab Model 301A vapour phase osmometer.

The electrochemical apparatus has been previously described³: the two electrodes consist of a mercury pool anode (5 cm diameter) and a platinum cathode.

Electrochemical preparation of trivinyltin carboxylates

The general procedure was as follows. A current of 25 mA was passed for about 12 h through a 0.1 M NaOOCR' methanolic solution (150 ml) containing tetravinyltin (2 ml, 11×10^{-3} mole). After the current was switched off, the anodic solution was distilled. The organotin compound was then separated from the crude residue by dissolving it with an appropriate solvent (THF for R' = CH₃, C₂H₅, CH₂Cl; cyclohexane for R' = CF₃). Further purification was made by crystallizing the product from THF. Attempts to prepare the trivinyltin formate were unsuccessful.

Table 1 lists the analytical data and the physical properties of the compounds obtained, which are all new.

TABLE 1

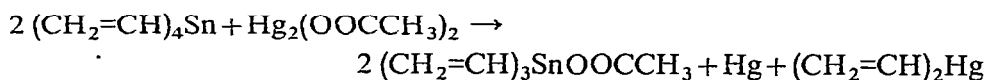
ANALYTICAL AND PHYSICAL DATA OF THE TRIVINYLTIN CARBOXYLATES

Compound	M.p. (°C)	Analysis, found (calcd.) (%)					Yield ^a (g)
		C	H	Cl	F	Sn	
(CH ₂ =CH) ₃ SnOOCCH ₃	161–162 ^b 159–160	36.85 (37.11)	4.63 (4.67)			45.70 (45.85)	0.55
(CH ₂ =CH) ₃ SnOOC C ₂ H ₅	137–138	39.49 (39.61)	5.06 (5.17)			43.20 (43.49)	0.24
(CH ₂ =CH) ₃ SnOOCCH ₂ Cl	127–128	32.20 (32.75)	3.59 (3.78)	11.81 (12.08)		40.72 (40.56)	0.42
(CH ₂ =CH) ₃ SnOOC CF ₃	127–129	30.29 (30.71)	2.74 (2.90)		18.48 (18.22)	38.02 (37.94)	0.48

^a The figures represent the quantities (g) of the purified product. ^b M.p. of the product obtained by chemical procedure.

Chemical preparation of the trivinyltin acetate

The trivinyltin acetate was also prepared by treating tetravinyltin with mercury(I) acetate in methanol at room temperature⁴. The products were trivinyltin acetate, metallic mercury and divinylmercury, and the overall reaction may be formally represented as:



Treatment of the organomercurial product with mercury(II) chloride gave vinylmercury chloride (m.p. 184°, lit.⁵ 185–186).

Solubility and molecular weights in chloroform and THF

The new carboxylates are appreciably soluble in THF, less soluble in chloroform (the solubility of the acetate at room temperature is of the order of 16 mg/ml, that of the other compounds is about 6–7 mg/ml), and much less soluble in carbon tetrachloride.

Molecular weights data have been obtained in chloroform for all the compounds and in THF for the acetate. Table 2 lists the obtained results, which also gives

TABLE 2
MOLECULAR WEIGHTS OF TRIVINYLTIN CARBOXYLATES (37°)

Compound	Solvent	Concn. (mg/ml)	Mol. wt. found	Mol. wt. formal	i^a	
$(\text{CH}_2=\text{CH})_3\text{SnOOCCH}_3$	THF	16.95	267.7	258.86	1.034	
		8.47	251.0		0.969	
		4.23	266.1		1.027	
		2.11	259.8		1.003	
	CHCl_3			258.5 ^b		0.998
		11.65	914.1	258.86	3.531	
		8.32	900.7		3.479	
		4.16	826.3		3.192	
$(\text{CH}_2=\text{CH})_3\text{SnOOCCH}_2\text{H}_5$	CHCl_3		790.3 ^b		3.053	
		5.00	331.0	272.89	1.212	
		2.50	326.6		1.196	
		1.25	322.0		1.179	
$(\text{CH}_2=\text{CH})_3\text{SnOOCCH}_2\text{Cl}$	CHCl_3		320.0 ^b		1.172	
		6.25	307.6	293.31	1.048	
		3.12	326.6		1.022	
		1.56	294.0		1.002	
$(\text{CH}_2=\text{CH})_3\text{SnOOCF}_3$	CHCl_3		292.8 ^b		0.998	
		6.25	475.7	312.84	1.520	
		3.12	429.8		1.373	
		1.56	368.4		1.177	
			354.0 ^b		1.131	

^a $i = \text{Mol. wt. found/mol. wt. formular.}$ ^b Extrapolated value (concn. $\rightarrow 0$).

values of the ratio i , of the observed molecular weight to the formular weight. It will be seen that in chloroform the compounds are not associated except for the acetate, which is trimeric. The acetate is essentially monomeric in THF, however.

Infrared spectra

The IR spectra of the examined trivinyln tin carboxylates are the same in KBr discs or in Nujol mulls. The (C=C) stretch occurs in all cases at 1585 cm^{-1} , as in trimethylvinyln tin⁶ and tetravinyln tin⁷. The spectra show the $\delta(=\text{CH}_2)$ vibration at $1390\text{--}1400 \text{ cm}^{-1}$, the $\delta(=\text{CH}-)$ vibration at 1248 cm^{-1} , the $\pi(=\text{CH}_2)$ vibration at $995\text{--}1000 \text{ cm}^{-1}$ and the $\pi(=\text{CH}-)$ vibration at 948 cm^{-1} in agreement with values

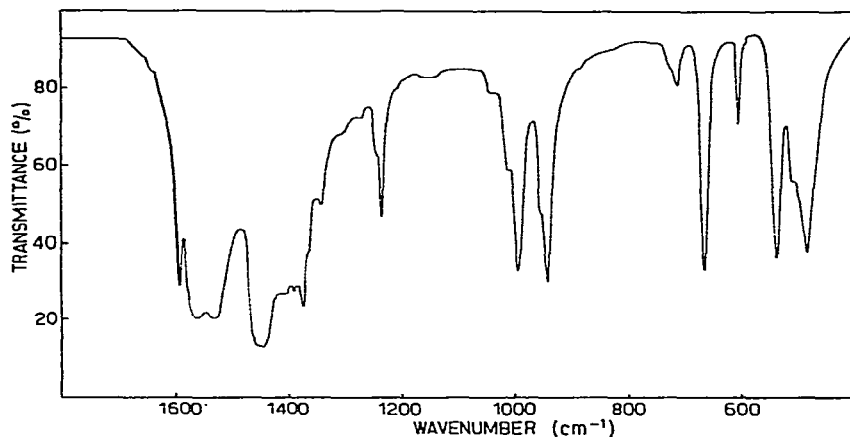


Fig. 1. IR spectra of trivinyltin acetate in Nujol mull (optics KBr).

previously found for a vinyl group bonded to a metal⁸. Fig. 1 shows an IR spectrum of trivinyltin acetate dispersed in Nujol mull in the region 1800–400 cm^{-1} .

The IR spectra of all the compounds in chloroform have the vinyl bands at the same wave numbers as in the solid state.

Assignments for the asymmetric and symmetric stretching vibrations of the carboxylic group have been made. Tables 3 and 4 list these frequencies (wave numbers,

TABLE 3

IR SPECTRA IN NUJOL MULLS AND IN SOLID (KBr DISCS)

Wave numbers, cm^{-1} .

Compound	Carboxylic region		Sn-C region
	ν_a	ν_s	
$(\text{CH}_2=\text{CH})_3\text{SnOOCCH}_3$	1565 s, 1540 s	1420 s	540 m, 510 (sh), 485 m
$(\text{CH}_2=\text{CH})_3\text{SnOOCCH}_2\text{H}_5$	1555 s, 1525 s	1420 s	540 m, 510 (sh), 485 m
$(\text{CH}_2=\text{CH})_3\text{SnOOCCH}_2\text{Cl}$	1595 s, 1555 s	1420 s	540 m, 510 w, 485 m
$(\text{CH}_2=\text{CH})_3\text{SnOOCF}_3$	1670 s	1190 s	540 m, 510 m, 475 m

TABLE 4

IR SPECTRA IN CHLOROFORM SOLUTION, OPTICS KBr, 1 MM

Wave numbers, cm^{-1} .

Compound	Concn. (mg/ml)	Carboxylic region		Sn-C region
		ν_a	ν_s	
$(\text{CH}_2=\text{CH})_3\text{SnOOCCH}_3$	8.3	1645 vs, 1618 s	1315 vs	540 m, 515 (sh), 485 m
$(\text{CH}_2=\text{CH})_3\text{SnOOCCH}_2\text{H}_5$	5.0	1630 vs, 1580 s	1375 s	540 m, 515 (sh), 475 m
$(\text{CH}_2=\text{CH})_3\text{SnOOCCH}_2\text{Cl}$	6.2	1670 vs	1350 s	545 m, 515 w, 485 m
$(\text{CH}_2=\text{CH})_3\text{SnOOCF}_3$	6.2	1710 s, 1655 vs		545 m, 515 m, 485 m

cm^{-1}) found for the examined compounds in solid or Nujol mulls and in chloroform solution respectively. The frequencies which can be attributed to the Sn-C bond vibrations are listed in the same Tables. It will be seen that the frequency related to the carboxylic asymmetric stretching vibration increases, either in solid or in solution, on increasing the electronegativity of the R' group in $(\text{CH}_2=\text{CH})_3\text{SnOOCR}'$ compounds. The trend for the frequency of the carboxylic symmetric stretching vibrations is opposite to that observed for the asymmetric one. The greatest separation between the two bands is observed for the trivinyltin trifluoroacetate. In addition, from the comparison of the (COO) frequencies, it appears that the carboxylic asymmetric stretching vibration values are higher in chloroform than in the solid state. On the other hand the carboxylic symmetric vibration values are lower in solution than in the solid.

Three bands occur in the Sn-C region and there are no appreciable differences between the band position in the solid and in solution (Fig. 2). There are some varia-

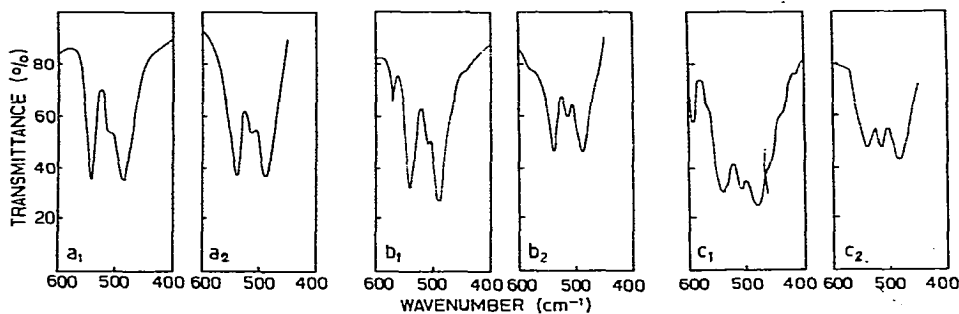


Fig. 2. IR spectra in the Sn-C region in Nujol mulls (index 1), and in chloroform solution (index 2): (a) acetate, (b) monochloroacetate, (c) trifluoroacetate.

tions in the intensities: the relative intensity of the 510 cm^{-1} band in solid (*cf.* Table 3) as well as that of the 515 cm^{-1} band in solution (*cf.* Table 4) increases on increasing the electronegativity of the R' organic group.

DISCUSSION

The IR spectra in the carboxylic region ($1700\text{--}1300\text{ cm}^{-1}$) and the Sn-C region ($600\text{--}400\text{ cm}^{-1}$) of most compounds⁹ of the type $\text{R}_3\text{SnOOCR}'$ (R and R', alkyl groups), and also X-ray diffraction studies, particularly on trimethyltin formate¹¹ and tribenzyltin acetate¹⁰, have shown that these compounds are polymeric in the solid state. They contain five-co-ordinated tin atoms in a trigonal bipyramidal structure, with bridging carboxylate groups and planar SnC_3 moieties. Depolymerization of the $(\text{R}_3\text{SnOOCR}')_n$ compounds occurs on dissolving in most organic solvents: (i) the (COO) asymmetric stretching vibration bands are found at higher wave numbers in solution than in the solid^{3,12-15}, (ii) two bands appear in the Sn-C region showing that the SnC_3 group is not planar in solution^{4,9,12-14}.

The carboxylic asymmetric stretching vibration values of the examined $(\text{CH}_2=\text{CH})_3\text{SnOOCR}'$ compounds, either in solid or in solution, change in the same way as those of trimethyltin carboxylates when the electronegativity of the R' groups is

TABLE 5

CARBOXYLIC ASYMMETRIC STRETCHING VIBRATIONS FOR TRIMETHYLTIN AND TRIVINYLTIN CARBOXYLATES ($R_3SnOOCR'$) IN SOLUTION AND IN THE SOLID STATE
Wave numbers, cm^{-1} .

R'	R (solution)			R (solid)		
	$-CH_3$ (CCl_4)	Ref.	$CH_2=CH-$ ($CHCl_3$)	$-CH_3$	Ref.	$CH_2=CH-$
CF_3	1720	14	1710, 1655	1680	14	1670
$CHCl_2$	1700	14		1615	14	
CH_2Cl	1690, 1685	3	1670	1630, 1621	15	1595, 1555
H	1655 ^a	3		1603, 1575	15	
CH_3	1650, 1648 ^b	3	1645, 1618	1564	15	1565, 1540
C_2H_5	1655, 1645	3	1630, 1580	1565, 1555	15	1555, 1525

^a In $CHCl_3$: 1650 and 1590 (ref. 3.) ^b In $CHCl_3$: 1640 (ref. 3.)

varied (*cf.* Table 5). It seems that the structure of the vinyltin compounds resembles that of their methyltins analogues, in that the tin atoms are five-co-ordinated in a trigonal bipyramidal structure involving bridging carboxylate groups. However, the configuration of the SnC_3 moiety cannot be the same as that in trimethyltin carboxylates, for all the compounds there is no change at all in the $Sn-C$ region on passing from the solid state to the solution. This is true not only for the acetate, which is trimeric, but also for the other compounds which are monomeric in chloroform. These spectroscopic data suggest that the three vinyl groups do not lie in the trigonal bipyramidal equatorial plane.

Not only does previous work show that triorganotin groups in trigonal bipyramidal structures are normally planar⁹, but theoretical predictions¹⁶⁻¹⁸ also suggest that ligands of lesser electronegativity tend to occupy equatorial positions. We suggest that the vinyl group has a tendency to occupy an axial position to assist $p_\pi-d_\pi$ bonding between the α -carbon atom and the tin atom. Such $p_\pi-d_\pi$ bonding has proposed for phenyl groups bound to tin¹⁹ and for vinyl groups linked to silicon²⁰.

Further work on the structure of these compounds is in progress in our laboratories.

ACKNOWLEDGMENT

We gratefully acknowledge support of this work by CNR-Roma, under Research Grant N. 69.00540 1152508 and NATO Research Grant N. 374.

REFERENCES

- 1 R. K. INGHAM, S. D. ROSENBERG AND H. GILMAN, *Chem. Rev.*, 60 (1960) 459 and references therein.
- 2 M. DUB, *Organometallic Compounds*, Vol. 2, Springer-Verlag, Berlin, 2nd ed., 1967 and references therein.
- 3 V. PERUZZO, G. PLAZZOGNA AND G. TAGLIAVINI, *J. Organometal. Chem.*, 18 (1969) 89.
- 4 G. PLAZZOGNA, V. PERUZZO AND G. TAGLIAVINI, *J. Organometal. Chem.*, 16 (1969) 500.
- 5 D. SEYFERTH, *J. Org. Chem.*, 22 (1957) 478.

- 6 I. V. OBRIMOV AND N. A. CHUMAEVKII, *Zh. Strukt. Khim.*, 5 (1964) 137; Chem. Abstr., 60 (1964) 12784.
- 7 A. D. KAESZ AND F. G. A. STONE, *Spectrochim. Acta*, 15 (1959) 360.
- 8 K. NAKAMOTO, in M. TSUTSUI (Ed.), *Characterization of Organometallic Compounds*, Interscience, New York, 1969, p. 77.
- 9 R. OKAWARA AND M. WADA, *Advan. Organometal. Chem.*, 5 (1967) 137 and references therein.
- 10 N. W. ALCOCK AND R. E. TIMMS, *J. Chem. Soc. A*, (1968) 1873.
- 11 See ref. 52 of ref. 9.
- 12 P. B. SIMONS AND W. A. G. GRAHAM, *J. Organometal. Chem.*, 8 (1967) 479.
- 13 M. J. JANSSEN, J. G. A. LUITEN AND G. J. M. VAN DER KERK, *Recl. Trav. Chim. Pays-Bas*, 82 (1963) 90.
- 14 E. V. VAN DEN BERGHE, G. P. VAN DER KELEN AND J. ALBRECHT, *Inorg. Chim. Acta*, 2 (1968) 89.
- 15 R. E. HESTER, *J. Organometal. Chem.*, 23 (1970) 123.
- 16 R. J. GILLESPIE AND R. S. NYHOLM, *Quart. Rev. (London)*, 11 (1957) 339.
- 17 R. J. GILLESPIE, *J. Chem. Educ.*, 40 (1963) 295.
- 18 R. J. GILLESPIE, *J. Chem. Soc.*, (1963) 4672.
- 19 J. CHATT AND A. A. WILLIAMS, *J. Chem. Soc.*, (1954) 4403.
- 20 J. J. EISCH AND J. T. TRAINOR, *J. Org. Chem.*, 28 (1963) 487.

J. Organometal. Chem., 24 (1970) 347-353