Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

STUDIES OF ORGANOMETALLIC COMPOUNDS THE FIVE-MEMBERED RING STRUCTURE OF ORGANOTIN CONTAINING DICARBOXYLIC ESTERS*

SUMIO MATSUDA, SHOICHI KIKKAWA AND IWAO OMAE
Department of Applied Chemistry, Osaka University, Suita, Osaka (Japan)

(Received July 25th, 1967; in revised form March 18th, 1969)

SUMMARY

Bis[(1,2-dialkoxycarbonyl)ethyl]tin dihalides (II) were synthesized by the direct method; the reaction between tin foil and dialkyl halosuccinates in the presence of accelerators. Besides the main products, [(1,2-dialkoxycarbonyl)ethyl]tin hydroxydibromide (III) was obtained as by-product.

It was considered that (II) had two stereoisomers with a six-coordination containing 2 five-membered ring structures in which the oxygen atom of the C=O at the γ-position with respect to the tin atom was coordinated to the tin atom. These isomers could be isolated with appropriate solvents and the by-products (III) on the basis of IR or NMR spectra, had the five-coordination with tridentate ligand in which the C=O group at the γ-position was coordinated to the tin atom and another C=O group in the β-position formed a hydrogen bond to the OH group.

However, only one product (unstable in the air) was obtained by the direct reaction between other dialkyl halodibasic acid esters and tin foil.

The properties of the direct reaction products were compared with those of hydrostannation of the unsaturated dicarboxylic ester with tri-n-butyltin hydride and of the subsequent bromination. The brominated products were considered to have the five-membered ring structure with the C=O at the γ-position coordinated to the tin atom, also on the basis of IR and NMR spectra.

In view of these observations, it is concluded that those coordinations where the C=O at the γ-position coordinates to the tin atom must be caused by the electronegativity of the attached halogen atoms.

INTRODUCTION

Grignard[5] or Wurtz[6] reaction methods have rarely been available for syntheses of organotin compounds containing functional groups. Generally speaking, these methods cannot be applied when reactive functional groups are present, and these compounds have been synthesized mainly by the hydrostannation method reported by Van der Kerk *et al.*[7-9].

Recently, a new method of synthesis of alkyltin compounds was developed

---

* This paper is the summarized report of four articles published in Japanese[1-4].

in our laboratory[10–15] using the direct reaction between alkyl halides and tin foil in the presence of accelerators such as magnesium, 1-butanol, tetrahydrofuran and butyl iodide. Attempts were made to synthesize organotin compounds containing dicarboxylic esters by this direct reaction. Elementary analyses and molecular weight data showed that the reaction products of tin and dialkyl halosuccinates obviously corresponded to $X_2Sn\!-\!\left[\begin{array}{l}\mathrm{CHCOOR}\\ |\\ \mathrm{CH_2COOR}\end{array}\right]_2$. However, as they showed wide melting ranges even after repeated recrystallisations, they were assumed to be mixtures of stereoisomers and separations were tried with different solvents. The products could be separated into two species of pure isomers with an ethanol–ether mixed solvent.

On the bases of physical methods such as IR and NMR spectra, etc., these stereoiosomers contained 2 five-membered ring structures in which the oxygen atoms of the C=O groups at the γ-position with respect to the tin atom coordinated to the tin atom.

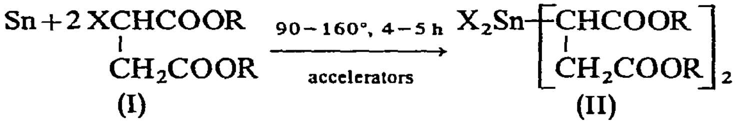
The hydrostannation of unsaturated dicarboxylic esters with the tri-n-butyltin hydride and subsequent bromination was also carried out.

The reason for the formation of the five-membered ring structure was investigated by comparing the IR and NMR spectra of the hydrostannation products, the bromination products of hydrostannation and the products of the direct reaction.

An X-ray diffraction study[16,17] showed that direct reaction products had the five-membered ring structure previously described.

THE PRODUCTS OF THE DIRECT REACTION BETWEEN TIN FOIL AND CARBOXYLIC HALOESTERS

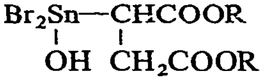
Dialkyl halosuccinates (I) (R=Et) reacted with tin foil in the presence of the accelerators described above as in reaction (1):



$$\mathrm{Sn}+2\underset{\text{(I)}}{\begin{array}{l}\mathrm{XCHCOOR}\\ |\\ \mathrm{CH_2COOR}\end{array}} \xrightarrow[\text{accelerators}]{90-160°,\ 4-5\ \text{h}} \underset{\text{(II)}}{X_2Sn\!-\!\left[\begin{array}{l}\mathrm{CHCOOR}\\ |\\ \mathrm{CH_2COOR}\end{array}\right]_2} \qquad (1)$$

(R=alkyl group; X=halogen atom)

The elementary analyses and molecular weight data indicated that crystals of (II) were obtained. However, even after many recrystallisations from ethanol, the melting point range (X=Br, 106–114°; X=I, 91.5–102.5°) remained unchanged but two crystal species were isolated by fractional crystallization from an ethanol–ether mixed solvent. These showed the same elementary analyses and molecular weight data as (II), and the melting points were: 114–115°, 122–123° (X=Br) and 99–101°, 118.5–119.5° (X=I), respectively. In addition colorless crystals of melting point 139° were obtained from the filtrate when the crude crystals (II) (X=Br) after standing for three weeks were recrystallised with ethanol. The results of elementary analyses and molecular weight were in good agreement with the calculated values for



$$\begin{array}{ll}\mathrm{Br_2Sn}\!-\!\!\!&\mathrm{CHCOOR}\\ \ \ \ |&|\\ \ \ \mathrm{OH}&\mathrm{CH_2COOR}\end{array}$$

(III) (R=Et).

Reaction (1) was also carried out with other ester groups and two species of stereoisomers were isolated as described above. The details of these reactions are shown in Tables 1 and 2, and the properties of the products in Table 3.

Very small amounts of by-products (III) were also obtained from reaction (1) when the alkyl groups of ester (I) were n-propyl and n-butyl; the melting points were 128° and 126.5–127°, respectively. These products had the molecular formula (III) (R=n-Pr, n-Bu) since the elementary analyses and molecular weight data were identical with the calculated values for (III).

TABLE 1

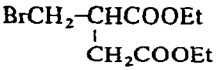
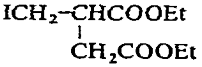
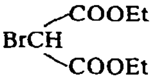
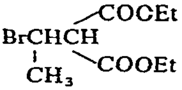
DIRECT REACTIONS BETWEEN TIN AND DIALKYL HALOSUCCINATES[a]

Dialkyl halosuccinates	Reaction temp. (°C)	Reaction time (h)	Tin conversion[b] (%)	Yield (%)
ClCHCOOMe CH$_2$COOMe	150±5	5	5	—
ClCHCOOEt CH$_2$COOEt	160±3	4	5	—
ClCHCOO-n-Pr CH$_2$COO-n-Pr	160±3	4	1	—
BrCHCOOMe CH$_2$COOMe	110±3	4	99	20.7
BrCHCOOEt CH$_2$COOEt	110±3	4	99	63.6
BrCHCOO-n-Pr CH$_2$COO-n-Pr	110±3	4	96	—[c]
BrCHCOO-n-Bu CH$_2$COO-n-Bu	110±3	4	82	—[c]
BrCHCOO-n-Oct CH$_2$COO-n-Oct	110±3	4	9	—
ICHCOOMe CH$_2$COOMe	90±3	4	97	<5
ICHCOOEt CH$_2$COOEt	90±3	4	97	72.8
ICHCOO-n-Pr CH$_2$COO-n-Pr	90±3	4	98	<5
ICHCOO-n-Bu CH$_2$COO-n-Bu	90±3	4	99	—

[a] All reactions were carried out with 2.2 moles of ester to tin and 0.3 wt.% of magnesium to tin and 3 wt.% of n-butanol, n-butyl iodide and tetrahydrofuran to ester as accelerators. [b] Tin conversion shows the ratio of consumed tin to the initial amount of tin foil. [c] The products were established to be present in the reaction mixtures by infrared spectra, but could not be isolated in crystalline form.

TABLE 2

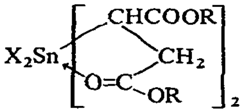
DIRECT REACTIONS BETWEEN TIN AND DICARBOXYLIC ESTERS[a]

Dicarboxylic esters	Reaction temp. (°C)	Reaction time (h)	Tin conversion (%)	Yield (%)
 $BrCH_2\text{-}\underset{CH_2COOEt}{CHCOOEt}$	120±10	3	10	—
 $ICH_2\text{-}\underset{CH_2COOEt}{CHCOOEt}$	120±10	3	49	—
 $BrCH{<}^{COOEt}_{COOEt}$	100±5	0.5	99	50
 $\underset{CH_3}{BrCH}CH{<}^{COCEt}_{COOEt}$	160±5	3	6	—

[a] All reactions were carried out with the same ratio of reagents and accelerators as reaction (1).

TABLE 3

PRODUCTS (II) FROM TIN AND DIALKYL HALOSUCCINATES



R	X	M.p. (°C)	Sn (%) found (calcd.)	C (%) found (calcd.)	H (%) found (calcd.)	X (%) found (calcd.)	Mol. wt. found (calcd.)
Me	Br	130–131		25.31 (25.34)	3.13 (3.19)	27.97 (28.10)	
Me	Br	157.5–158.5	20.99 (20.87)	25.29 (25.34)	3.14 (3.19)	28.03 (28.10)	579 (569)
Me	I	164.5–165.5		21.64 (21.74)	2.58 (2.74)	38.83 (38.30)	
Et	Br	114–115	18.93 (19.00)	30.58 (30.75)	4.02 (4.19)	25.50 (25.58)	623 (624)
Et	Br	122–123	18.97 (19.00)	30.83 (30.75)	4.21 (4.19)	25.47 (25.58)	632 (624)
Et	I	99–101	16.61 (16.51)	26.99 (26.73)	3.44 (3.62)		
Et	I	118.5–119.5	16.68 (16.88)	26.73 (26.73)	3.50 (3.62)		
n-Pr	I	77–78		31.17 (30.99)	4.47 (4.42)		

Reaction (1) was tried with all kinds of combination of accelerators and magnesium was found to be the most effective. The reactivity of (I) towards tin increased in the order: Cl < Br < I and significantly decreased when the carbon number of the alkyl groups of (I) was above that of n-butyl.

The direct reactions of diethyl bromomalonates (IV), diethyl halomethylsuccinates (V) and diethyl haloethylmalonate (VI) were carried out as reaction (1). The details are given in Table 2.

The order of reactivity of esters towards tin was, (IV) > (V) > (VI), and a crystalline product was isolated only with (IV), but it was very unstable in air.

Typical IR spectra of products (II) and (III) mentioned above are shown in Figs. 1 and 2.

A strong C=O absorption in the infrared spectra of (I) was observed only at 1740 cm^{-1}, but those of the two crystal species of (II) were found separately at 1710 cm^{-1} and about 1660 cm^{-1}, both in the solid state (Fig. 1) and in organic solvents.

As molecular weight measurements suggested that (II) was evidently in the monomeric state in organic solvents, the strong absorption at 1660 cm^{-1} must be due to a marked shift of the carbonyl stretching vibration, which was expected from the coordination of the oxygen atom of the C=O in the groups at the γ-position with respect to the tin atom. The other strong absorption found at 1710 cm^{-1} was assigned to the C=O stretching of the ester group at the β-position. This is one reason for believing that both crystal species of (II) had the six-coordination structure with the five-membered ring structure as in (VII).

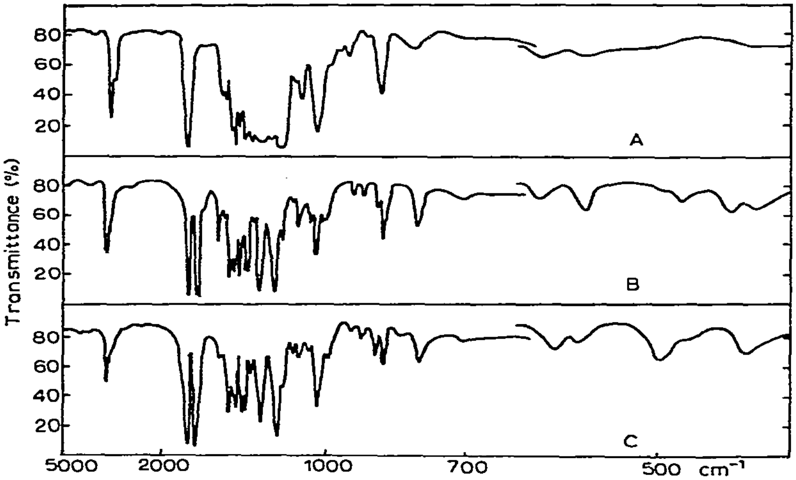


Fig. 1. Infrared spectra. (A) (I) (R=Et; X=Br); (B) (II) (R=Et; X=Br; m.p. 114–115°); (C) (II) (R=Et; X=Br; m.p. 122–123°).

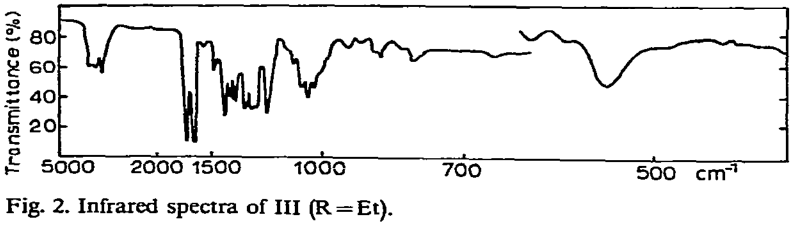
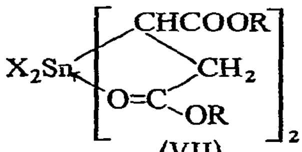
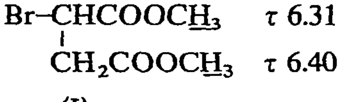


Fig. 2. Infrared spectra of III (R=Et).



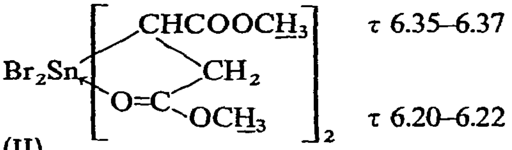
(VII)

NMR spectra of (I) and (II) (R = Me, X = Br) were also investigated. The chemical shifts of the methoxy proton bonded to the C=O at the β- and γ-positions with respect to the methin proton of (I) occurred at τ 6.31 and τ 6.40, respectively, but those for (II) at corresponding positions were τ 6.35–6.37 and τ 6.20–6.22, respectively.



$$\begin{array}{ll} \text{Br-CHCOOC}\underline{\text{H}}_3 & \tau\ 6.31 \\ \quad | & \\ \text{CH}_2\text{COOC}\underline{\text{H}}_3 & \tau\ 6.40 \end{array}$$

(I)



(II)

The relatively low field shift, as against that of the starting material (I), of the methoxy proton bonded to the C=O at the γ-position with respect to the methin proton (or tin atom) of (II) indicated that the C=O in the ester group at the γ-position with respect to the tin atom, coordinated equally to the tin atom, as already suggested by the IR spectra. This low field shift was a result of the shielding constant decreasing in proportion to the decrease in the electrons in the methoxy proton as the electrons shifted from the methoxy proton to the C=O at the γ-position to the tin atom.

Recently, the five-membered ring structure has been confirmed by an X-ray diffraction study of the direct reaction products (II) (R = Et, X = Br, m.p. 114–115°[16] and m.p. 122–123°[17]).

The IR-spectra (Fig. 2) of by-products (III) showed a strong C=O absorption at 1688–1685 cm^{-1} and 1645–1640 cm^{-1}. The hydrogen bond to the oxygen of the C=O group at the β-position with respect to the tin atom was expected because the band at 3390–3230 cm^{-1} was largely shifted to a lower frequency than an ordinary OH stretching vibration. In the far infrared using a KBr disk, a new strong band was present at 540–529 cm^{-1}. This was not observed in (II) and was assigned to the Sn–O stretching vibration. (III) were found to be monomeric in organic solvents by molecular weight determinations. The strong absorption of the C=O stretching vibration observed at 1645–1640 cm^{-1} was the same as that of the C=O absorption in the ester group at the γ-position in (II) which was largely shifted to a lower frequency compared with the C=O absorption at the β-position in (II). Accordingly, it was considered that the C=O in the ester group at the β-position formed a hydrogen bond to the hydrogen of Sn–OH.

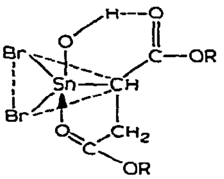
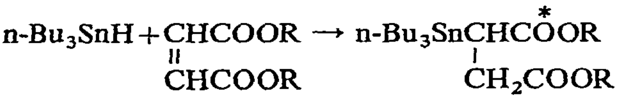


Fig. 3. VIII (R = Et, n-Pr, n-Bu).

Therefore, (III) were assumed to contain a five-coordination with a tridentate ligand in which one C=O group at the γ-position with respect to the tin atom, coordinated to the tin atom, and the other C=O group in the β-position formed a hydrogen bond to the OH group as shown in Fig. 3.

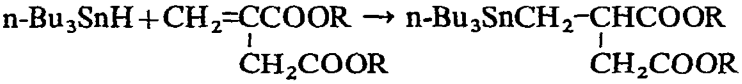
HYDROSTANNATION OF UNSATURATED DICARBOXYLIC ESTERS WITH TRI-n-BUTYLTIN HYDRIDE AND BROMINATION OF THE PRODUCTS

The hydrostannation of reactions (2)–(4) were carried out by a similar method to that of Van der Kerk *et al.*[8] in the ratio of 1 mole each of unsaturated dicarboxylic esters and tri-n-butyltin hydride and about 1.6 mole% of azobis(isobutyronitrile). Bromination (reactions (5)–(7)) of the products (IX, X, XI) were carried out using a solution of bromine (0.1 mole) in 40 ml of chloroform and a solution of the hydrostannation product (0.1 mole) in 40 ml of the same solvent and stirring for 3.5 h at room temperature[18].



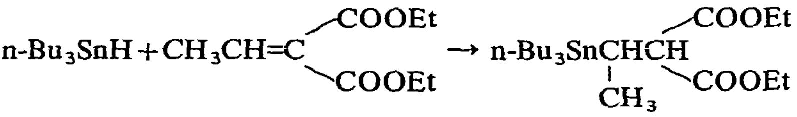
$$n\text{-Bu}_3\text{SnH}+\begin{array}{c}\text{CHCOOR}\\ \|\\ \text{CHCOOR}\end{array}\longrightarrow n\text{-Bu}_3\text{Sn}\begin{array}{l}\text{CHC}\overset{*}{\text{O}}\text{OR}\\ |\\ \text{CH}_2\text{COOR}\end{array} \qquad (2)$$

(IX) R = Me, Et, n-Pr, n-Bu



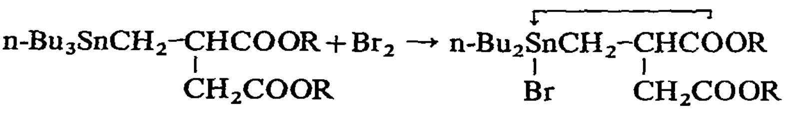
$$n\text{-Bu}_3\text{SnH}+\text{CH}_2{=}\begin{array}{l}\text{CCOOR}\\ |\\ \text{CH}_2\text{COOR}\end{array}\longrightarrow n\text{-Bu}_3\text{SnCH}_2\text{-}\begin{array}{l}\text{CHCOOR}\\ |\\ \text{CH}_2\text{COOR}\end{array} \qquad (3)$$

(X) R = Me, Et, n-Pr



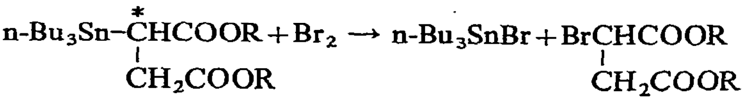
$$n\text{-Bu}_3\text{SnH}+\text{CH}_3\text{CH}{=}\text{C}\begin{array}{l}\diagup\text{COOEt}\\ \diagdown\text{COOEt}\end{array}\longrightarrow n\text{-Bu}_3\text{Sn}\begin{array}{l}\text{CHCH}\\ |\\ \text{CH}_3\end{array}\begin{array}{l}\diagup\text{COOEt}\\ \diagdown\text{COOEt}\end{array} \qquad (4)$$

(XI)

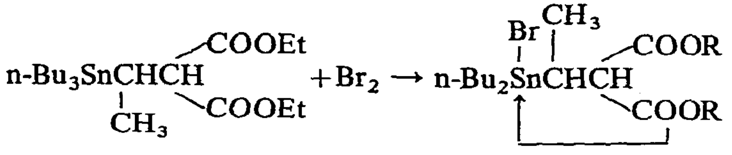


$$n\text{-Bu}_3\text{SnCH}_2\text{-}\begin{array}{l}\text{CHCOOR}\\ |\\ \text{CH}_2\text{COOR}\end{array}+\text{Br}_2\longrightarrow n\text{-Bu}_2\begin{array}{l}\text{Sn}\\ |\\ \text{Br}\end{array}\text{CH}_2\text{-}\begin{array}{l}\text{CHCOOR}\\ |\\ \text{CH}_2\text{COOR}\end{array} \qquad (5)$$

(XII)



$$n\text{-Bu}_3\text{Sn-}\begin{array}{l}\overset{*}{\text{C}}\text{HCOOR}\\ |\\ \text{CH}_2\text{COOR}\end{array}+\text{Br}_2\longrightarrow n\text{-Bu}_3\text{SnBr}+\text{Br}\begin{array}{l}\text{CHCOOR}\\ |\\ \text{CH}_2\text{COOR}\end{array} \qquad (6)$$



$$n\text{-Bu}_3\text{Sn}\begin{array}{l}\text{CHCH}\\ |\\ \text{CH}_3\end{array}\begin{array}{l}\diagup\text{COOEt}\\ \diagdown\text{COOEt}\end{array}+\text{Br}_2\longrightarrow n\text{-Bu}_2\overset{\text{Br}}{\underset{\uparrow}{\text{Sn}}}\overset{\text{CH}_3}{\text{C}}\text{HCH}\begin{array}{l}\diagup\text{COOR}\\ \diagdown\text{COOR}\end{array} \qquad (7)$$

(XIII)

TABLE 4

HYDROSTANNATION PRODUCTS OF UNSATURATED DICARBOXYLIC ESTERS WITH TRI-n-BUTYLTIN HYDRIDE

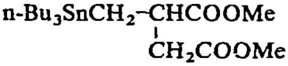
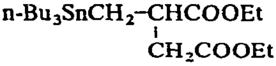
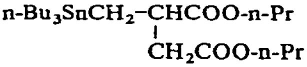
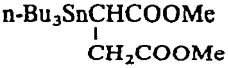
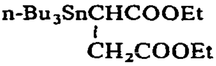
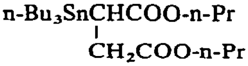
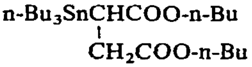
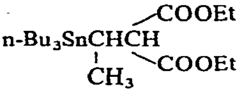
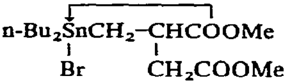
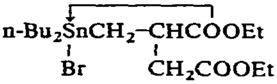
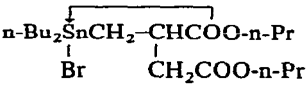
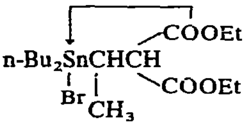
Product	Boiling range °C (mm)	Sn (%) found (calcd.)	C (%) found (calcd.)	H (%) found (calcd.)	Mol.wt. found (calcd.)	n_D^{20}	Yield (%)
 $n\text{-}Bu_3SnCH_2\text{-}\underset{CH_2COOMe}{CHCOOMe}$	85–95 (0.005)	26.44 (26.43)	50.80 (50.80)	8.73 (8.53)	450 (449)	1.4788	65
 $n\text{-}Bu_3SnCH_2\text{-}\underset{CH_2COOEt}{CHCOOEt}$	125–135 $(10^{-3}$–0.007)	24.65 (24.94)	53.02 (52.83)	8.91 (8.81)	469 (477)	1.4738	65
 $n\text{-}Bu_3SnCH_2\text{-}\underset{CH_2COO\text{-}n\text{-}Pr}{CHCOO\text{-}n\text{-}Pr}$	140–150 (0.003)	23.34 (23.49)	54.97 (54.67)	9.19 (9.18)	499 (505)	1.4738	79
 $n\text{-}Bu_3Sn\underset{CH_2COOMe}{CHCOOMe}$	122–127 $(< 10^{-3})$	27.57 (27.27)				1.4799	61
 $n\text{-}Bu_3Sn\underset{CH_2COOEt}{CHCOOEt}$	124–128 $(< 10^{-3})$	25.53 (25.62)	51.93 (51.86)	8.85 (8.70)		1.4777	86
 $n\text{-}Bu_3Sn\underset{CH_2COO\text{-}n\text{-}Pr}{CHCOO\text{-}n\text{-}Pr}$	125–128 $(< 10^{-3})$	23.86 (24.16)	54.02 (53.79)	9.54 (9.03)		1.4599	59
 $n\text{-}Bu_3Sn\underset{CH_2COO\text{-}n\text{-}Bu}{CHCOO\text{-}n\text{-}Bu}$	128–135 $(< 10^{-3})$	22.83 (22.85)	55.39 (55.62)	9.72 (9.32)		1.4582	77
 $n\text{-}Bu_3Sn\underset{CH_3}{CH}CH(COOEt)_2$	140–145 $(< 10^{-3})$	24.86 (24.87)	52.75 (52.85)	8.95 (8.87)		1.4765	78

TABLE 5

SUBSTITUTION PRODUCTS FROM THE ACTION OF BROMINE ON THE HYDROSTANNATION PRODUCTS

Product	Boiling range °C (mm)	Sn (%) found (calcd.)	C (%) found (calcd.)	H (%) found (calcd.)	X (%) found (calcd.)	Mol.wt. found (calcd.)	n_D^{20}	Yield (%)
 $n\text{-}Bu_2\underset{Br}{Sn}CH_2\text{-}\underset{CH_2COOMe}{CHCOOMe}$	151–155 $(< 10^{-3})$	25.40 (25.14)	38.02 (38.17)	6.18 (6.14)			1.4787	82
 $n\text{-}Bu_2\underset{Br}{Sn}CH_2\text{-}\underset{CH_2COOEt}{CHCOOEt}$	155–157 (0.04)	24.05 (23.80)	40.89 (40.80)	6.70 (6.60)	16.44 (16.00)	493 (500)	1.5013	67
 $n\text{-}Bu_2\underset{Br}{Sn}CH_2\text{-}\underset{CH_2COO\text{-}n\text{-}Pr}{CHCOO\text{-}n\text{-}Pr}$	155–164 $(< 10^{-3})$.	22.77 (22.47)	43.33 (43.21)	6.90 (7.09)			1.5006	37
 $n\text{-}Bu_2\underset{Br}{Sn}\underset{CH_3}{CH}CH(COOEt)_2$	153–157 $(< 10^{-3})$	23.46 (23.74)	40.88 (40.83)	6.76 (6.65)			1.5004	52

The yields and properties of the products are shown in Tables 4 and 5.

C=O stretching vibrations of reaction products (IX) in reaction (2) were observed at 1738 and 1710 cm^{-1}. The band at 1710 cm^{-1} was at the same frequency as the C=O* of the ester group at the β-position with respect to the tin atom in (II) and was shifted to a considerably lower frequency compared with that of the other esters. It was therefore considered that the C=O* was a partial polarization.

An n-butyl group in (IX) and (X) was substituted by a bromine atom in reactions (5) and (7), but the Sn–C* bond in (IX) was disrupted by a bromine atom in reaction (6) showing that the Sn–C* bond was partially polarized on the basis of the same reasoning as that proposed by Van der Kerk *et al.*[19].

IR and NMR spectral data of (X)–(XIII) (R = Et), are shown in Fig. 4 (comparing the data of (X) and (XI) with those of (XII) and (XIII).

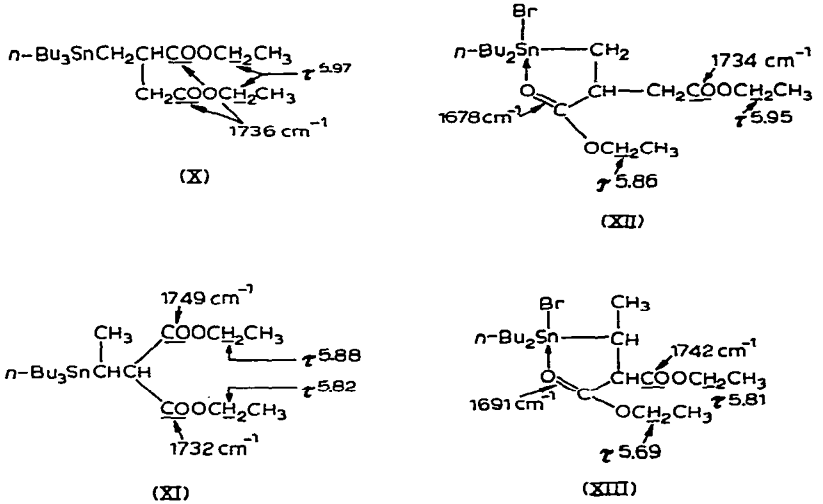


Fig. 4. The infrared frequencies of the C=O stretching vibration and the nuclear magnetic resonance shielding value for the ethoxymethylene proton of (X)–(XIII).

The absorption of the C=O at the γ-position in (XII) and (XIII) in which tin is bonded to one halogen atom, shifted by 40–60 cm^{-1} to a lower frequency compared with those of (X) and (XI) in Fig. 4, but absorption of C=O at the δ-position was almost the same in these compounds. Similarly, in the NMR spectra, the ethoxymethylene proton which is bonded to C=O at the γ-position, shifted 0.1 ppm downfield (comparing (XII) or (XIII) with (X) or (XI)), but those at the δ-position were almost unchanged. Therefore, (XII) and (XIII) obtained from reactions (5) and (7), have an inner complex containing the same five-membered ring structure as (VII) and (VIII). (XIII) has two C=O-groups at the γ-position with respect to the tin atom, but only one C=O coordinates to the tin atom (Fig. 4) as only one C=O was shifted to a lower frequency or shielding value of the ethoxymethylene proton, in the IR or NMR spectra.

A comparison of the hydrostannation products and the bromination products shows that the latter differ from the former in that the C=O stretching vibration at the γ-position shifts to a lower frequency in the IR spectra, and the chemical shift of the ethoxymethylene proton bonded to the C=O group at the γ-position shifts downfield in the NMR spectra. These shifts must be a result of the C=O at the γ-postion coordinating to the tin atom. Hence, the oxygen atom of the C=O at the γ-position can coordinate to the tin atom because tin becomes electropositive when bonded by the electronegative halogen atom. These coordinations are very little affected by steric hindrance.

REFERENCES

1 S. Matsuda, S. Kikkawa and I. Omae, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 69 (1966) 646.
2 I. Omae, S. Matsuda, S. Kikkawa and R. Sato, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 70 (1967) 705.
3 I. Omae, S. Onishi and S. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 70 (1967) 1755.
4 I. Omae, S. Matsuda and S. Kikkawa, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kobyo Kagaku Zasshi)*, 70 (1967) 1759.
5 E. Kranse and G. Renwarz, *Ber.*, (1927) 1582.
6 P. R. Austin, *J. Amer. Chem. Soc.*, (1932) 3726.
7 G. J. M. van der Kerk, J. G. A. Luijten and J. G. Noltes, *Chem. Ind. London*, (1956) 352.
8 G. J. M. Van der Kerk and J. G. Noltes, *J. Appl. Chem. (London)*, 9 (1959) 106.
9 W. P. Neumann, *Angew. Chem.*, 20 (1964) 849.
10 S. Matsuda and H. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 63 (1960) 114.
11 H. Matsuda and S. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 63 (1960) 1958, 1965.
12 H. Matsuda, H. Taniguchi and S. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 64 (1961) 541.
13 H. Matsuda, G. Nakamura and S. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 64 (1961) 1948.
14 H. Matsuda, J. Hayashi and S. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 64 (1961) 1951.
15 S. Matsuda and H. Matsuda, *Bull. Chem. Soc. Japan*, 35 (1962) 208.
16 M. Yoshida, T. Ueki, N. Yasuoka, N. Kasai, M. Kakudo, I. Omae, S. Kikkawa and S. Matsuda, *Bull. Chem. Soc. Japan*, 41 (1968) 1113.
17 T. Kimura, T. Ueki, N. Yasuoka, N. Kasai, M. Kakudo, I. Omae, S. Kikkawa and S. Matsuda, *The 21st Annual Meeting of the Chemical Society of Japan, Osaka*, I, p. 176 (1968).
18 G. J. M. Van der Kerk and J. G. Noltes, *J. Appl. Chem. (London)*, 9 (1959) 179.
19 G. J. M. Van der Kerk and J. G. Noltes, *J. Appl. Chem. (London)*, 9 (1959) 113.