

A NEW ROUTE TO [2-(ALKOXYCARBONYL)ETHYL]TIN DERIVATIVES AND A STUDY OF THEIR STRUCTURES*

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SUMMARY

Mixtures of methyl halide and β -halopropionates were brought into reaction with tin foil in the presence of additives. Distillation of such reaction mixtures afforded methyl[2-(alkoxycarbonyl)ethyl]tin dihalides. Starting from these compounds, some organotin derivatives having 2-(alkoxycarbonyl)ethyl groups were prepared. The identities of the derivatives were established by means of elementary analysis, infrared absorption spectroscopy and proton magnetic resonance spectroscopy. From the results of IR and NMR studies, it was concluded that a halogen substituent on the tin atom favors the formation of a five membered ring in which the oxygen atom of the carbonyl group coordinates to the tin atom.

INTRODUCTION

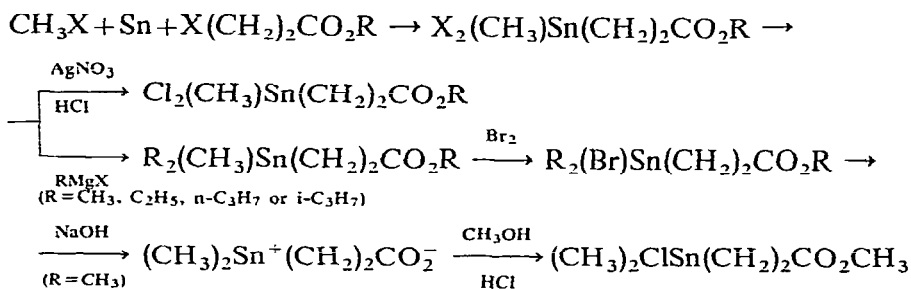
Hydrostannation^{2,3} is one of the most important preparative methods for the syntheses of functionally substituted organotin compounds. Little attention has been paid to direct syntheses of these compounds except for a few reports^{4,5} on the direct reaction between an active α -substituted alkyl halide and tin powder.

It was found that direct reactions between tin foil and ω -haloesters, $X(\text{CH}_2)_n\text{CO}_2\text{R}$ ($n=1, 2, 3$ or 4) proceed in the presence of a few additives⁶ which are effective in the reaction of tin foil with alkyl halides. Many organotin halides of the types, $X_2\text{Sn}[(\text{CH}_2)_n\text{CO}_2\text{R}]_2$ ($n=1, 2$ or 4)^{7,8,9} have been obtained.

Recently functionally monosubstituted organotin compounds, $\text{CH}_3\text{X}_2\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{R}$ could be obtained by the direct reaction of tin foil with methyl halides and β -halopropionates in the presence of additives⁶ and starting from these compounds new organotin compounds such as $\text{R}_{3-n}\text{X}_n\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{R}$ ($n=0, 1$ or 2) were prepared by alkylation of halogens bonded to tin with Grignard reagents followed by bromination and so on.

These reaction processes are shown schematically below.

* This paper is a reorganized report of the article published in Japanese¹ and unpublished results.



The authors also suggest on the basis of IR spectra that the various kinds of compounds such as $\text{X}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{R})_2$,⁷ $\text{X}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{COR})_2$,¹⁰ and $\text{X}_2\text{Sn}[\text{CH}(\text{CO}_2\text{R})\text{CH}_2\text{CO}_2\text{R}]_2$,^{11,12} prepared with direct syntheses in their laboratories have a five membered ring structure in which the carbonyl oxygen atom coordinates to the tin atom. Lately, the correctness of five membered ring formation has been proven in the case of $\text{Br}_2\text{Sn}[\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5]_2$ by X-ray diffraction analysis¹³.

The systematic arguments concerning the structure of methyl[2-(alkoxycarbonyl)ethyl]tin derivatives given in this paper are supported not only by the carbonyl stretching vibration of IR spectra but also by the values of $^{119}\text{SnCH}_3$ coupling constants which are very sensitive to the nature of the bonding.

Judging from NMR and IR data, it was concluded that when a methyl group in $\text{R}_2\text{CH}_3\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{R}$ was substituted by halogen, the oxygen atom in the carbonyl group coordinated to the tin atom forming a five membered ring.

In the present paper, the syntheses are described in the experimental part and structural arguments are presented under results and discussion.

EXPERIMENTAL

All melting points were uncorrected and were determined using micro melting point apparatus. Molecular weight determinations were carried out in a thermistor osmometer (Mechrolab Osmometer Model 301). Benzene was used as a solvent.

Infrared spectra were run on a Hitachi EPI-2G, EPI-G2 and a Hitachi EPI-L spectrophotometer both equipped with gratings covering the range 4000 to 250 cm^{-1} . NMR spectra were recorded using a JNM-3H-60 spectrometer. All NMR spectral data of [2-(alkoxycarbonyl)ethyl]tin derivatives prepared in this paper are collected in Table 4.

Materials

β -Halopropionates were prepared by addition¹⁴ of gaseous hydrogen bromide to acrylates and the corresponding iodides were synthesized according to the Finkelstein reaction¹⁵. Properties of these halides are described below. Methyl β -bromopropionate b.p. 59–60°/13 mm (lit.¹⁴ 66°/18 mm) n_D^{20} 1.4588; ethyl β -bromopropionate b.p. 78–79°/19 mm (lit.¹⁴ 77–79°/19 mm), n_D^{20} 1.4536; methyl β -iodopropionate b.p. 67–68°/10 mm, n_D^{20} 1.4536, ethyl β -iodopropionate b.p. 81°/10 mm (lit.¹⁶ 85°/13 mm).

Methyl halides were of commercial grade. Tin foil was obtained from Tokyo Fine Chemicals Co. Ltd. and Chugoku Toryo Co. Ltd.

Reaction of the mixture of methyl halide and β -halopropionate with tin foil

A mixture of tin foil (20 g, 0.168 mole), β -halopropionate (0.202 mole), methyl halide (0.202 mole) and a catalytic amount of magnesium, butyl iodide and tetrahydrofuran was heated at 135–165° in a stainless autoclave of 100 ml. Methyl bromide was used by sealing it in the reaction tube.

In the case of iodides, direct reaction proceeded without additives but magnesium was used in this experiment because its presence accelerated the reaction. After 3–5 hours the tin foil was almost completely consumed and the reaction mixture was distilled. A typical example of the results is described below for the case of methyl bromide and methyl β -bromopropionate.

Fraction 1, –74°/3.0 mm (14.5 g); fraction 2, intermediate part (4.0 g); fraction 3, 140–155°/10⁻³ mm (10.0 g); residue (20.7 g).

The gas chromatograms of fraction 1 displayed three peaks which were assigned respectively to trimethyltin bromide, dimethyltin dibromide and methyl β -bromopropionate. The amount of dimethyltin dibromide was determined quantitatively. Fraction 3 was redistilled and the fraction described in Table 1 solidified at room temperature. The solid compound which was recrystallized from petroleum ether was confirmed to be (CH₃)Br₂Sn(CH₂)₂CO₂CH₃ by the elemental analysis and so on. From the residue dissolved in methanol, there crystallized Br₂Sn(CH₂CH₂CO₂CH₃)₂ as was confirmed by IR spectra and its melting point 140–141° (lit.¹⁷ 138–140°).

The results of the direct reaction experiments are tabulated in Tables 1 and 2.

TABLE 1

DIRECT REACTION OF X(CH₂)₂CO₂R AND CH₃X WITH TIN FOIL

X	R	(CH ₃) ₂ SnBr ₂ ^a (%)	X ₂ CH ₃ Sn(CH ₂) ₂ CO ₂ R		M.p. (°C)	n _D ²⁰
			B.p. (°C/10 ⁻³ mm)	Yield (g)		
Br	CH ₃	26.6	121–124	7.0	75–77	
	C ₂ H ₅	25.1	120–124	9.0	52–54	
I	CH ₃	31.0	130–140	11.0		1.6563
	C ₂ H ₅	29.8	143–146	10.5		1.6383

^a Based on consumed tin.

TABLE 2

ANALYSIS OF X₂CH₃Sn(CH₂)₂CO₂R

X	R	Analysis found (calcd.) (%)			Mol. wt. found (calcd.)
		C	H	Sn	
Br	CH ₃	15.88 (15.78)	2.70 (2.65)	31.03 (31.18)	392 (381)
	C ₂ H ₅	18.37 (18.26)	3.14 (3.06)	29.64 (30.07)	395 (395)
I	CH ₃	12.46 (12.61)	2.18 (2.12)	24.84 (25.01)	485 (475)
	C ₂ H ₅	14.93 (14.75)	2.66 (2.48)	23.96 (24.30)	504 (489)

Preparation of derivatives of methyl[2-(alkoxycarbonyl)ethyl]tin dibromide

Since the derivatives of methyl[2-(alkoxycarbonyl)ethyl]tin dihalide mentioned in Table 3 were prepared by similar procedures, details concerning their preparation have been listed in Table 3 and representative examples are given here to illustrate the methods used.

TABLE 3

SOME ORGANOTIN DERIVATIVES OF METHYL[2-(ALKOXYCARBONYL)ETHYL]TIN DIBROMIDE

Compound	Preparative method	Yield (%)	B.p. (°C/mm)	n_D^{20}	Analysis found (calcd.) (%)		
					C	H	Sn
$(CH_3)_3\dot{S}n(CH_2)_2CO_2CH_3$	B	70	92-95/20	1.4690	33.78 (33.51)	6.71 (6.43)	46.81 (47.31)
$(CH_3)_3Sn(CH_2)_2CO_2C_2H_5$	B	90	99-101/20	1.4660	36.45 (36.27)	6.86 (6.85)	44.30 (44.80)
$(CH_3)_2ClSn(CH_2)_2CO_2CH_3$	D	31	^a		26.30 (26.56)	4.96 (4.83)	43.37 (43.75)
$CH_3(Cl_2)Sn(CH_2)_2CO_2CH_3$	A		^b		20.35 (20.58)	3.54 (3.46)	
$CH_3(Cl_2)Sn(CH_2)_2CO_2C_2H_5$	A		^c		23.42 (23.60)	4.20 (3.92)	38.79 (38.82)
$(CH_3)_2BrSn(CH_2)_2CO_2CH_3$	C		^d		22.51 (22.82)	4.30 (4.15)	37.41 (37.59)
$(CH_3)_2BrSn(CH_2)_2CO_2C_2H_5$	C		107-111/1.5		25.58 (25.49)	4.80 (4.58)	35.98 (35.99)
$(C_2H_5)_2CH_3Sn(CH_2)_2CO_2C_2H_5$	B	59	86-88/1.0	1.4732	41.08 (41.00)	7.59 (7.57)	
$(n-C_3H_7)_2CH_3Sn(CH_2)_2CO_2CH_3$	B	53	116-123/11	1.4768			43.30 (43.03)
$(n-C_3H_7)_2BrSn(CH_2)_2CO_2CH_3$	C	73	100-104/10 ⁻³		32.17 (32.30)	5.97 (5.69)	31.63 (31.92)
$(i-C_3H_7)_2CH_3Sn(CH_2)_2CO_2CH_3$	B	56	117-123/10		43.51 (43.03)	7.87 (7.88)	
$(i-C_3H_7)_2BrSn(CH_2)_2CO_2CH_3$	C	77	96-98/10 ⁻³		32.40 (32.30)	5.65 (5.69)	

^a M.p. 35.3-37.5°. ^b M.p. 84-85° (from CCl₄). ^c M.p. 62-63° (from Bu₂O). ^d M.p. 58-59° (from n-hexane).

(a). *Preparation of methyl[2-(methoxycarbonyl)ethyl]tin dichloride.* A solution of [2-(methoxycarbonyl)ethyl]methyltin dibromide (7.8 g, 0.02 mole) in methanol was added to a methanolic silver nitrate aqueous solution with stirring. Immediately a yellow precipitate of silver bromide formed and was removed by filtration. Then the mother liquor was acidified with excess hydrochloric acid and extracted with ethyl ether. After removal of solvent, the crystalline compound, Cl₂(CH₃)Sn(CH₂)₂-CO₂CH₃ (2.5 g) was obtained. An analytically pure sample was obtained by recrystallization from carbon tetrachloride.

(b). *Preparation of trimethyl[2-(methoxycarbonyl)ethyl]tin.* A Grignard reagent was prepared in the usual way starting from 14.2 g of methyl iodide and 2.4 g of magnesium in 70 ml of ether. To a solution of methyl[2-(methoxycarbonyl)ethyl]tin

dibromide (15.2 g, 0.04 mole) dissolved in 100 ml ethyl ether, was added dropwise with stirring the ether solution of methylmagnesium iodide prepared above. At the same time of dropping, the ether solution changed in color to yellow and began to reflux. Dropping was stopped when the ether solution was decolorized. At that time, there remained only a small amount of Grignard reagent solution in the separatory funnel. The reaction mixture was heated at reflux temperature for an additional 30 min period and was subsequently decomposed by ammonium chloride solution. The reaction product was then extracted with two 150 ml portions of ether. The IR spectrum of the residue obtained after evaporation of the dried ethereal extract did not show either $\nu(\text{C}=\text{O})$ frequency at 1680 cm^{-1} specific of starting materials or $\nu(\text{OH})$. The residue was subsequently fractionated *in vacuo*.

In this reaction, estimation of the end point of the Grignard reagent addition was most important, though it happened that in the case of methyl iodide this estimation was rather clear, but in another case it was necessary to determine the yield of Grignard reagent by acid titration methods¹⁸.

(c). *Preparation of dimethyl[2-(methoxycarbonyl)ethyl]tin bromide.* To a solution of trimethyl[2-(methoxycarbonyl)ethyl]tin (7.0 g, 0.028 mole) in 50 ml of chloroform, 4.48 g (0.028 mole) of bromine were added dropwise below 0° . The solid obtained after removal of the solvent was recrystallized from n-hexane.

Other monobromide derivatives listed in Table 3 were prepared in a similar way. In all cases, the methyl group bonded to the tin atom was fissioned first by bromine.

(d). *Preparation of dimethyl[2-(methoxycarbonyl)ethyl]tin chloride.* In order to effect saponification and dehalogenation of dimethyl[2-(methoxycarbonyl)ethyl]tin bromide, this compound (3.0 g) was refluxed with aqueous alcoholic alkali for one hour. Upon acidifying the reaction mixture with dilute hydrochloric acid, a white precipitate formed which was considered to have the structure, $(\text{CH}_3)_2\text{Sn}^+(\text{CH}_2)_2\text{CO}_2^-$ ¹⁹ as indicated by elemental analysis and a strong absorption at 1530 cm^{-1} in the infrared spectrum which is due to the CO_2 stretching vibration²⁰. (Found: C, 27.36; H, 4.68; Sn, 52.73. $\text{C}_5\text{H}_{10}\text{O}_2\text{Sn}$ calcd.: C, 27.07; H, 4.54; Sn, 53.75%.)

The compound treated with dilute hydrochloric acid at room temperature changed to a methanol soluble compound which seemed to be dimethyl[2-(hydroxycarbonyl)ethyl]tin chloride. The methanol solution was refluxed with continuous drying for 12 h in the presence of *p*-toluenesulfonic acid. After removal of solvent, the reaction product was distilled. The fraction b.p. $107\text{--}109^\circ/2.0\text{ mm}$ solidified at room temperature.

RESULTS AND DISCUSSION

Five membered ring structure

The infrared spectra of [2-(alkoxycarbonyl)ethyl]tin derivatives have been investigated. Of particular interest are the absorption bands in the carbonyl region. The $\nu(\text{C}=\text{O})$ stretching vibration measured under various conditions are summarized in Table 5.

Examination of the data in Table 5 shows that the value of the $\text{C}=\text{O}$ stretching vibration of $(\text{CH}_3)_3\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{CH}_3$ is lowered by $50\text{--}55\text{ cm}^{-1}$ when one methyl

TABLE 4
 NMR DATA OF [2-(ALKOXYCARBONYL)ETHYL]TIN DERIVATIVES^a

Compound	Chemical shifts τ (ppm)					Coupling constants J (Hz)			Solvent (wt. %)	
	e	a	b	c	d	$J(ab)$	$J(cd)$	$J(SnCH_3)$		
								¹¹⁷ Sn		¹¹⁹ Sn
(CH ₃) ₃ SnCH ₂ CH ₂ CO ₂ CH ₃	9.94	9.15	7.51	6.40		7.5		50.4	53.4	CCl ₄ (10)
(CH ₃) ₃ SnCH ₂ CH ₂ CO ₂ CH ₂ CH ₃	9.94	9.08	7.53	5.95	8.75	7.5	7.1	51.0	54.0	CCl ₄ (10)
(CH ₃) ₂ ClSnCH ₂ CH ₂ CO ₂ CH ₃	9.30	8.65	7.23	6.23		7.5		61.8	64.5	CCl ₄ (5)
(CH ₃) ₂ BrSnCH ₂ CH ₂ CO ₂ CH ₃	9.27	8.53	7.22	6.22		7.5		61.8	64.5	CCl ₄ (10)
	9.28	8.55	7.22	6.22		7.5		61.5	64.5	CCl ₄ (20)
(CH ₃) ₂ ISnCH ₂ CH ₂ CO ₂ CH ₂ CH ₃	9.14	8.45	7.29	5.82	8.69	7.2	7.1	60.3	63.6	CCl ₄ (10)
CH ₃ (Cl ₂)SnCH ₂ CH ₂ CO ₂ CH ₃	8.69		7.14	6.16		7.2		77.4	80.4	CCl ₄ (9)
CH ₃ (Br ₂)SnCH ₂ CH ₂ CO ₂ CH ₃	8.85	8.74	7.93	6.40		7.2		76.5	79.8	C ₆ H ₆ (10)
CH ₃ (Br ₂)SnCH ₂ CH ₂ CO ₂ CH ₂ CH ₃	8.54	8.11	7.14	5.69	8.64	7.5	7.1	75.6	79.2	CCl ₄ (10)
CH ₃ (I ₂)SnCH ₂ CH ₂ CO ₂ CH ₃	8.20	7.98	7.21	6.16		7.0		70.3	73.5	CCl ₄ (10)
CH ₃ (I ₂)SnCH ₂ CH ₂ CO ₂ CH ₂ CH ₃	8.23	8.02	7.25	5.73	8.65			70.8	73.8	CCl ₄ (10)
(n-C ₃ H ₇) ₂ CH ₃ SnCH ₂ CH ₂ CO ₂ CH ₃	10.02		7.54	6.40		7.5		48.6	50.4	CCl ₄ (10)
(n-C ₃ H ₇) ₂ BrSnCH ₂ CH ₂ CO ₂ CH ₃			7.28	6.26		7.2				CCl ₄ (10)
(i-C ₃ H ₇) ₂ CH ₃ SnCH ₂ CH ₂ CO ₂ CH ₃	10.10	9.05	7.52	6.39		7.2		46.8	48.6	CCl ₄ (10)
(i-C ₃ H ₇) ₂ BrSnCH ₂ CH ₂ CO ₂ CH ₃			7.29	6.24		7.5				CCl ₄ (10)

^a The hydrogen atoms are indicated as follows: e SnCH₃, a SnCH₂CH₂CH₂C, b SnCO₂RH₂CO₂R, c Sn(CH₂)₂CO₂CH₃ and d Sn(CH₂)₂CO₂CH₂CH₃.

TABLE 5

INFRARED DATA OF CARBONYL STRETCHING VIBRATIONS

Compound	$\nu(C=O)$ (cm ⁻¹)	Method
(CH ₃) ₃ Sn(CH ₂) ₂ CO ₂ CH ₃	1735	Neat
(CH ₃) ₂ ClSn(CH ₂) ₂ CO ₂ CH ₃	1680	KBr disk
(CH ₃) ₂ BrSn(CH ₂) ₂ CO ₂ CH ₃	1680	KBr disk
	1678	C ₆ H ₆ (10 wt %)
	1730 ^a	THF (10 wt. %)
	1670	
CH ₃ (Br ₂)Sn(CH ₂) ₂ CO ₂ CH ₃	1656	KBr disk
	1670	THF (10 wt. %)
(i-C ₃ H ₇) ₂ CH ₃ Sn(CH ₂) ₂ CO ₂ CH ₃	1740	Neat
(i-C ₃ H ₇) ₂ BrSn(CH ₂) ₂ CO ₂ CH ₃	1685	Neat
	1690	THF (10 wt. %)

^a A very weak shoulder.

group was replaced by a bromine atom [both in the solid state (KBr disk) and in benzene solution]. This decrease is observed for the other halogen substituted compounds in Table 5. This observation has been also seen in the case of analogous compounds described in the Introduction and can be explained as due to the lowering of the bond order in C=O resulting from intramolecular coordination to the tin atom.

As a means of examining this suggestion of five membered ring formation, the $J(^{119}\text{SnCH}_3)$ coupling constants were measured. In Fig. 1 these values are plotted

against the number of halogen atoms. As shown in Fig. 1, there is little difference for the $J(^{119}\text{SnCH}_3)$ value between tetramethyltin²¹ and trimethyl[2-(methoxycarbonyl)ethyl]tin but where halogen is bound to tin, there is a considerable difference for $J(^{119}\text{SnCH}_3)$ values between halogen substituted derivatives and corresponding methyltin halide²¹. These observations are accounted for by the isovalent rehybridization theory of Bent²², *i.e.* when electronegative carbonyl groups coordinate to the central tin atom, the percentage of *s*-character of the more positive tin-methyl bond will be increased, so the values of $J(^{119}\text{SnCH}_3)$ of the halogen substituted derivatives are increased compared to methyltin halides.

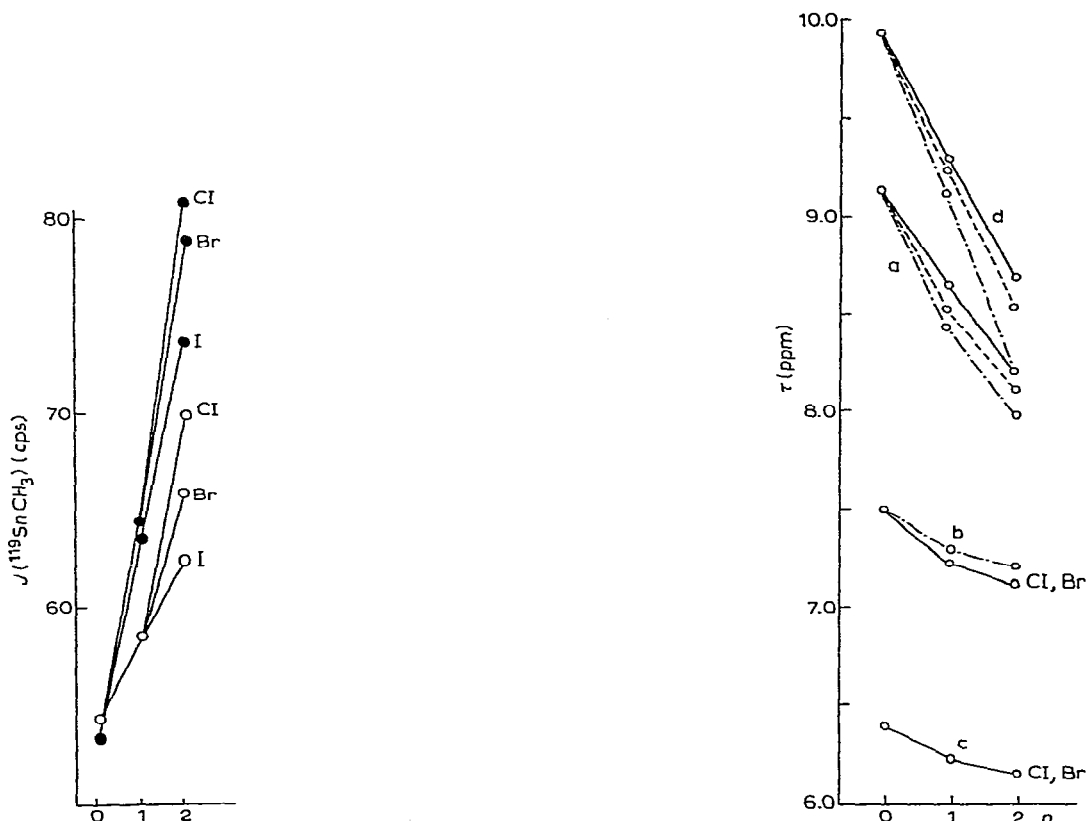


Fig. 1. The relation between $J(^{119}\text{SnCH}_3)$ coupling constants and number of halogen substituents n of both $(\text{CH}_3)_{3-n}\text{X}_n\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{CH}_3$ (●) and $(\text{CH}_3)_{4-n}\text{SnX}_n$ ²¹ (○).

Fig. 2. The relation between methylene and methyl group chemical shift values and number of halogen substituents n of $(\text{CH}_3)_{3-n}\text{X}_n\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{CH}_3$; — chloride, - - - bromide, ····· iodide.

Chemical shift

The graphical presentation of the chemical shift data of $(\text{CH}_3)_{3-n}\text{X}_n\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{CH}_3$ are given in Fig. 2. The trend of chemical shift for methyl (d) and methylene (a) groups directly bonded to the tin atom do not follow the expected trend according to electronegativity of the halogen, but these experimental data can

be explained by the contribution of the diamagnetic anisotropy term of the halogen-tin bond in the same manner as the chemical shift of methyltin halides discussed by Van der Kelen *et al.*^{21,23}. However, it has been found that this neighbouring anisotropy effect does not play an important role in the chemical shift of a methylene (b) group next to a carbonyl group since there is the negative shift decreasing in the order $\text{Cl} \approx \text{Br} > \text{I}$.

A comparison of the chemical shift values of the methoxy group protons in the compounds collected in Table 4 shows that the shielding is lower for halogen substituted derivatives than for non-halogen substituted derivatives (τ about 6.40 ppm). This observation could be explained by a lower electron density at the OCH_3 group on account of the coordination of the carbonyl oxygen to the tin atom.

Infrared spectra in the region $600\text{--}250\text{ cm}^{-1}$

In Table 6 the infrared spectra of some [2-(methoxycarbonyl)ethyl]tin derivati-

TABLE 6

INFRARED DATA OF $(\text{CH}_3)_3\text{-}_n\text{X}_n\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{CH}_3$ RECORDED IN THE REGION FROM 600 TO 250 cm^{-1}

<i>n</i>	X	Absorption (cm^{-1})
0		524 s, 512 m, 425 w, 350 vw, (br)
1	Cl	576 w (br), 548 s, 516 w, 460 m, 365 vs, 272 vs
	Br	570 w (br), 544 s, 514 w, 460 m, 367 vs
2	Cl	577 m, 560 s, 522 m, 461 m, 377 vs, 319 vs, 294 vs
	Br	580 m, 550 s, 513 m, 458 m, 370 vs

ves are summarized in that range. In those compounds which have two or three methyl groups bonded to the tin atom, two absorption bands are observed between 550 cm^{-1} and 500 cm^{-1} , in agreement with the linear relationship between $J(^{119}\text{Sn}-\text{CH}_3)$ values and $(\text{Sn}-\text{C})_{\text{asym}}$ and $(\text{Sn}-\text{C})_{\text{sym}}$ frequencies for some methyltin compounds, as suggested by Brown²⁴. Therefore the two absorption bands may be assigned to $(\text{Sn}-\text{C})_{\text{asym}}$ (strong absorption) and $(\text{Sn}-\text{C})_{\text{sym}}$ (weak absorption) respectively. As for chloride derivatives, the strong absorptions observed near 300 cm^{-1} may be considered to be Sn-Cl stretching vibrations²⁵.

Structural configuration

Because of the intramolecular coordination of the carbonyl oxygen to the tin atom, four possible conformations (for trigonal bipyramidal structures) may be considered in both monohalide and dihalide derivatives $[(\text{CH}_3)_2\text{XSn}(\text{CH}_2)_2\text{CO}_2\text{R}]$ and

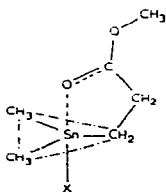


Fig. 3. The most probable configuration of $(\text{CH}_3)_2\text{XSn}(\text{CH}_2)_2\text{CO}_2\text{CH}_3$.

$\text{CH}_3(\text{X}_2)\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{R}$]. In the former case, the structure illustrated in Fig. 3 would be most probable because the more electronegative groups adopt axial positions in R_3MX_2 compounds ($\text{M} = \text{metal}$) as a consequence of the maximization of s -character in the bond to carbon (Bent's generalization)²⁶.

In the latter case, on the basis of these considerations it would seem likely for the two halogen atoms to adopt axial positions but as shown in Table 6, the fact that strong absorptions of $\nu(\text{Sn}-\text{Cl})_{\text{antisym}}$ and $\nu(\text{Sn}-\text{Cl})_{\text{sym}}$ are observed respectively at 319 cm^{-1} and 294 cm^{-1} , excludes a linear structure of SnCl_2 . Therefore the structure where one of the alkyl groups in Fig. 3 is displaced by a halogen atom is considered highly probable.

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