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ALCOHOLYSIS OF (2-METHOXYCARBONYL)ETHYLTIN COMPOUNDS

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Summary

Under acid or base catalysis, di(2-alkoxycarbonylethyl)tin dichlorides of various R groups, $(ROCOCH_2CH_2)_2SnCl_2$, can be prepared conveniently in high yield by alcoholysis of $(CH_3OCOCH_2CH_2)_2SnCl_2$ in various alcohols, ROH ($R = C_2H_5$, C_4H_9, iso-C_4H_9, C_5H_{11}, $C_6H_5CH_2$, $C_4H_9CH(C_2H_5)CH_2$). When excess acid or base is present in the aqueous solution, $(ROCOCH_2CH_2)_2SnCl_2$ eliminate ROH and precipitate as $C_6H_8O_4Sn$ regardless of the R group. $C_6H_8O_4Sn$ can be converted into various $(ROCOCH_2CH_2)_2SnCl_2$ derivatives on dissolving in alcoholic HCl solutions.

Introduction

Di(alkoxycarbonylalkyl)tin dihalides, R_2SnX_2, are commercially important as intermediates in the synthesis of non-toxic organotin stabilizers for halogenated polymers such as PVC [1,2]. For example, di(alkoxycarbonylalkyl)tin mercaptoesters can be prepared from the corresponding dihalides by the following reaction:

$$R_2SnCl_2 + 2HSCH_2\overset{\overset{O}{\|}}{C}OCH_2\overset{\overset{CH_2CH_3}{|}}{C}H(CH_2)_3CH_3 + 2NaHCO_3$$

$$\rightarrow R_2Sn\left(SCH_2\overset{\overset{O}{\|}}{C}OCH_2\overset{\overset{CH_2CH_3}{|}}{C}H(CH_2)_3CH_3\right)_2 + 2NaCl + 2H_2O$$

R = alkoxycarbonylalkyl

The preparation of di(2-alkoxycarbonylethyl)tin(IV) halides (hereafter called estertin halides) have been of particular interest because the reactions may involve hydrostannation of α,β-unsaturated carbonyl compounds under mild conditions [3–6].

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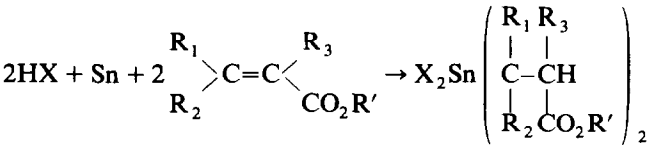


$(R_1, R_2, R_3 = H \text{ or alkyl})$

However, it appears that the yield of the estertin product in the reaction decreases drastically as the bulk of the R′ group increases. The yields for $R' = CH_3$ and C_2H_5 were reported to be 94% and 60%, respectively, and no product of $R' = C_4H_9$ was isolated at all [4].

It is known that different alkyl groups may cause a change in the properties of the stabilizers in the form of $(alkyl)_2Sn[SCH_2CO_2C(C_2H_5)H(CH_2)_3CH_3]_2$ [1]. One would therefore like to investigate how R′ group in $[R'O_2C-\underset{|}{C}-\underset{|}{C})_2Sn\langle$ affects the properties of estertin stabilizers. For these reasons we are interested in preparing various estertin compounds $(R'OCOCH_2CH_2)_2SnX_2$ by other means, and we report our results on alcoholysis.

Experimental

Preparation of diestertin dichlorides, $(ROCOCH_2CH_2)_2SnCl_2$

These compounds with $R = CH_3$, C_2H_5, C_3H_7 and C_4H_9 were prepared following the method described by Hutton and Oakes [5]. Metallic tin was reacted with $ROCOCH{=}CH_2$ and dry HCl in ethyl ether solution. The yield was 98–99% for $R = CH_3$, 78% for $R = C_2H_5$, 55% for $R = C_3H_7$, and < 10% for $R = C_4H_9$.

Monoestertin trichlorides were obtained as by-products from the reactions described above. Crude product mixtures were extracted out by warm chloroform and the monoestertin compounds were purified by fractional recrystallization in ethyl ether.

Preparation of $C_6H_8O_4Sn$

To 100 ml of 10–15% NaOH aqueous solution was added 36.4 g of di(2-methoxycarbonylethyl)tin dichloride. Stirring for 3 h under refluxing temperature gave $C_6H_8O_4Sn$ as white precipitate in 95% yield. Elemental analysis showed this molecular formula (Found: C, 27.58; H, 3.14; Sn, 45.17. $C_6H_8O_4Sn$ calc.: C, 27.38; H, 3.24; Sn, 45.04%). The mass spectral data were consistent with the formula: *m/e* 262(20), 235(13), 220(10), 191(100), 72(86), 55(46), 28(32). Because of the insolubility of this compound in all solvents tried, no NMR spectral data were available. Compound $C_6H_8O_4Sn$ decomposes gradually at temperatures above 180°C.

Preparation of diestertin dichlorides via $C_6H_8O_4Sn$

A typical reaction can be described as follows: 26.4 g of $C_6H_8O_4Sn$ was added to 100–150 ml of ROH and the suspension was mixed thoroughly. A suitable amount of concentrated HCl was added dropwise until all the $C_6H_8O_4Sn$ was consumed. When water and ROH were removed by heating, the estertin compound $(ROCOCH_2CH_2)_2SnCl_2$ was obtained in good yield (Table 1). All products were purified by vacuum distillation and consistent mass spectra and elemental analysis were obtained.

TABLE 1

ESTERTIN COMPOUNDS PREPARED FROM $C_6H_8O_4Sn$ AND DIRECT ALCOHOLYSIS

Solvent	$(ROCOCH_2CH_2)_2SnCl_2$		ν(C=O) (cm^{-1})	Chemical Shift (δ, ppm)	Yield (%) [a]	Yield (%) [b]
C_2H_5OH	$R = C_2H_5$	m.p. 132–133°C	1630	1.32(t, CH_3, 6H), 1.92(t, $SnCH_2$, 4H) 2.92(t, $O{=}\overset{|}{C}{-}CH_2$, 4H), 4.28(q, OCH_2, 4H)	92	90
n-C_4H_9OH	R = n-C_4H_9	orange oil	1660	1.12(t, CH_3, 6H), ~1.4(m, CH_2, 8H) 1.86(t, $SnCH_2$, 4H), 2.86(t, $O{=}\overset{|}{C}{-}CH_2$, 4H) 4.10(t, OCH_2, 4H)	92	100
iso-C_4H_9OH	R = iso-C_4H_9	pale yellow liq.	1660	0.94(d, CH_3, 12H), 1.88(t, $SnCH_2$, 4H) ~2.1(m, CH, 2H), 2.90(t, $O{=}\overset{|}{C}{-}CH_2$, 4H) 4.00(d, OCH_2, 4H)	88	100
$C_5H_{11}OH$	$R = C_5H_{11}$	viscous liq.	1660	0.90(t, CH_3, 6H), ~1.4(m, $-(CH_2)_3-$, 12H) 1.88(t, $SnCH_2$, 4H), 2.88(t, $0{=}\overset{|}{C}{-}CH_2$, 4H) 4.20(t, OCH_2, 4H)	91	–
$C_6H_5CH_2OH$	$R = C_6H_5CH_2$	viscous liq.	1670	1.88(t, $SnCH_2$, 4H), 2.84(t, $O{=}\overset{|}{C}{-}CH_2$, 4H) 5.34(s, $PhCH_2$, 4H), 7.28(s, Ph, 10H)	92	–
$C_4H_9\overset{C_2H_5}{\overset{|}{C}}HCH_2OH$	$R = C_4H_9\overset{C_2H_5}{\overset{|}{C}}HCH_2$	yellow oil	1660	0.86(t, CH_3, 12H), ~1.24(m, $-\overset{CH_2-}{\overset{|}{C}}H-(CH_2)_3-$, 18H) 1.88(t, $SnCH_2$, 4H), 2.88(t, $O{=}\overset{|}{C}{-}CH_2$, 4H) 4.10(d, OCH_2, 4H)	88	100

[a] Yield from $C_6H_8O_4Sn$. [b] Yield from direct alcoholysis. s: singlet, d: doublet, t: triplet, q: quartet m: multiplet.

TABLE 2

NMR DATA OF DIESTERTIN *S,S'*-BIS-(2-ETHYL HEXYL THIOGLYCOLATE)

$(ROCOCH_2CH_2)_2Sn(EHT)_2$ [a]		Chemical Shift (δ, ppm)	Yield(%)
$R = CH_3$	yellow oil	0.88(t, CH_3, 12H), 1.28(m, -CH-$(CH_2)_3$-, 18H) 1.68(t, $SnCH_2$, 4H), 2.82(t, O=C-CH_2, 4H) 3.42(s, SCH_2, 4H), 3.68(s, OCH_3, 6H), 4.01(d, OCH_2, 4H)	95
$R = C_2H_5$	pink oil	0.88(t, CH_3, 12H), 1.24(m, CH_3-CH_2O, -CH-$(CH_2)_3$-, 24H) 1.66(t, $SnCH_2$, 4H), 2.80(t, O=C-CH_2, 4H), 3.22(s, SCH_2, 4H), 4.10(m, OCH_2, 8H)	92
$R = C_4H_9$	pale yellow liq.	0.88(m, CH_3, 18H), 1.30(m, -$(CH_2)_2$-, -CH-$(CH_2)_3$-, 26H) 1.68(t, $SnCH_2$, 4H), 2.80(t, O=C-CH_2, 4H), 3.42(s, SCH_2, 4H), 4.04 (m, OCH_2, 8H)	90
$R = C_6H_5CH_2$	yellow oil	0.88(t, CH_3, 12H), 1.28(m, -CH-$(CH_2)_3$-, 18H) 1.68(t, $SnCH_2$, 4H), 2.84(t, O=C-CH_2, 4H), 3.42(s, SCH_2, 4H) 4.0(d, OCH_2, 4H), 5.10(s, $PhCH_2$, 4H), 7.30(s, Ph, 10H)	90

[a] EHT = $[SCH_2CO_2CCH_2(C_2H_5)H(CH_2)_3CH_3]_2$.

Preparation of diestertin S,S'-bis(2-ethylhexyl thioglycolate)

To a mixture of 0.1 mol of $(ROCOCH_2CH_2)_2SnCl_2$ and 0.2 mol of $HSCH_2COOC_8H_{17}$-i was added 100–150 ml of ROH. The reaction temperature was maintained at 50–60°C while 0.2 mol of $NaHCO_3$ was added slowly. The reaction was complete in 2–3 h. NaCl was removed by washing with water. The yields of various products are listed in Table 2. All the compounds $(ROCOCH_2CH_2)_2Sn[SCH_2CO_2CH_2C(C_2H_5)H(CH_2)_3CH_3]_2$ show a strong band of ν(C=O) at 1720–1740 cm^{-1}. Their molecular formulae were further confirmed by consistent mass spectra.

Spectra

NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 99.6 MHz. In all cases $CDCl_3$ was used as the solvent. IR spectra were obtained from a Perkin Elmer 580 spectrometer. Mass spectra were obtained using a JEOL MS 100 mass spectrometer operating at 12 eV.

Results and discussion

In the synthesis of the organotin stabilizer, $R_2Sn[SCH_2CO_2CH_2C(C_2H_5)HC_4H_9]_2$ with R being an alkyl instead of an ester group, the reaction can be carried out

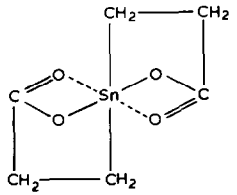
stepwise as follows [7],

$$R_2SnCl_2 \xrightarrow[\text{reflux}]{\text{5–10\% NaOH}} R_2SnO$$

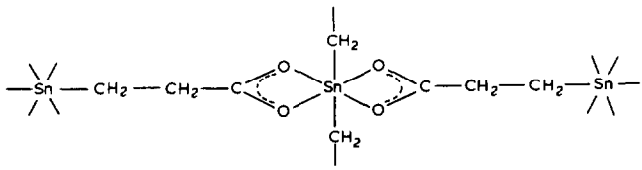
$$R_2SnO + HSCH_2COOC_8H_{17}\text{-i} \xrightarrow[\text{azotropic removal of } H_2O]{\text{benzene}} R_2Sn(SCH_2COOC_8H_{17}\text{-i})_2$$

However, when R is an ester the reaction of alkali with R_2SnCl_2 proceeds by a completely different pathway which yields quantitatively a white solid insoluble in water and organic solvents. For example, in the case of $(CH_3OCOCH_2CH_2)_2SnCl_2$, elemental analysis of the white precipitate indicates a molecular formula of $C_6H_8O_4Sn$ (I) instead of $(CH_3OCOCH_2CH_2)_2SnO$. The IR spectrum shows a carbonyl absorption at 1540 cm^{-1}.

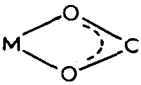
These results are consistent with those reported by Matsuda et al. [8] in their study of the direct synthesis of estertin compounds from β-halogenated esters. Based on the low frequency of the ν(C=O) band (Matsuda et al. reported a band at 1550 cm^{-1}), two possible structures for this white solid were proposed:



(A)



(B)

The absorption at 1540 cm^{-1} should be more properly assigned to the carboxylate group  having C_{2v} symmetry, accordingly, the metal carboxylate group would have coplanarity. This argument would make structure A stereochemically less likely.

At 150°C the mass spectrum of this white solid was obtained. The detailed mass spectral data are shown in Table 3. The mass peaks at *m/e* 262, 235, 220 and 191 all

TABLE 3

MASS SPECTRAL DATA OF $C_6H_8O_4Sn$

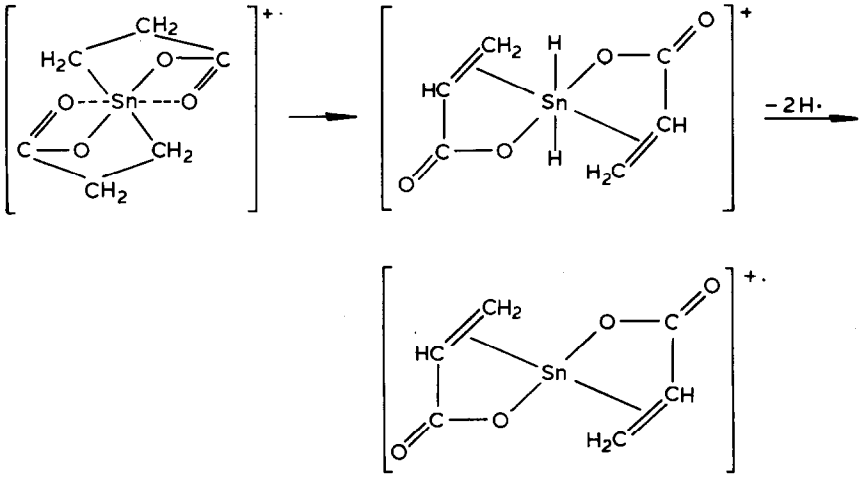
m/e	Assignment	Abundance
264	$(C_3H_4O_2)_2Sn^+$	[a]
262	$(C_3H_3O_2)_2Sn^+$	20
235	$(C_3H_3O_2)Sn(CO_2)^+$	13
220	$(C_3H_4O_2)Sn(CH_2)_2^+$	10
191	$(C_3H_3O_2)Sn^+$	100
72	$(CH_2)_2CO_2^+$	86
55	$(C_2H_3)CO^+$	46
44	CO_2^+	16
28	$C_2H_4^+$, CO^+, N_2^+	35

[a] See text.

contain isotope patterns typical of ions involving one Sn. The intense mass peak at *m/e* 72 corresponds to the fragment of CH_2CH_2COO. However, the parent ion of a compound of $C_6H_8O_4Sn$ should have *m/e* 264 instead of 262.

Careful examination of the isotope pattern about *m/e* 262 indicates that the peaks at 264 and 266 are clearly much more intense than the theoretical intensities of the corresponding isotope peaks of mass 262 involving one Sn atom. It is therefore quite certain that there is a mass peak (*m/e* 264) of weak intensity hidden in the much more intense peak of *m/e* 262.

Assuming that the mass peak at *m/e* 264 corresponds to an ion with structure as shown, the facile pathway for the loss of two hydrogen atoms can be rationalized as follows:



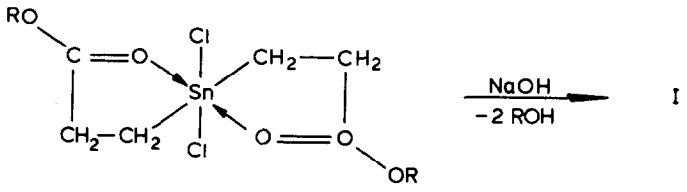
Fragmentation by losing two radicals accompanied by valency change [$Sn^{IV} \rightarrow Sn^{II}$] is a common mechanism in the mass spectrum of Sn^{IV} compounds [9]. Besides, β-H elimination involved in σ-π rearrangements is also one of the common phenomena observed in organometallic chemistry.

The same phenomenon is observed in the peaks at *m/e* 191. A weak peak at m/e 193 is hidden in the $M+2$ and $M+4$ isotope peaks of 191. These two peaks originate from (264 − 71) and (262 − 71) respectively. It is interesting to note that elimination of 71 ($-CH_2{=}CHCO_2-$) instead of 72 ($-CH_2CH_2CO_2-$) occurred in such fragmentations. This seems to support our proposed mechanism described above.

It is worth noting that monoestertin trichloride reacts with alkali to form $(C_3H_4O_2)SnCl_2$, which shows very similar behavior in its mass spectrum. For example, the highest mass peak, *m/e* 226, and the most intense peak, *m/e* 155, are derived from successive losses of HCl and $C_3H_3O_2$ (71) from the parent ion, respectively. They both show typical isotope patterns that agree with theoretical calculation.

However, it is believed that the observation of an ion peak at *m/e* 264 does not necessarily specify a monomeric structure of I. In this particular case, the insolubility (hence, no NMR spectrum available) of $C_6H_8O_4Sn$, the lack of sharp melting point and the IR spectrum discussed above, seem to be more compelling evidence for a polymeric structure.

Apart from the exact structure, we have found interesting reactions associated with the diestertin dichlorides. They undergo base hydrolysis with loss of ROH to give the same compound I regardless of the nature of R,

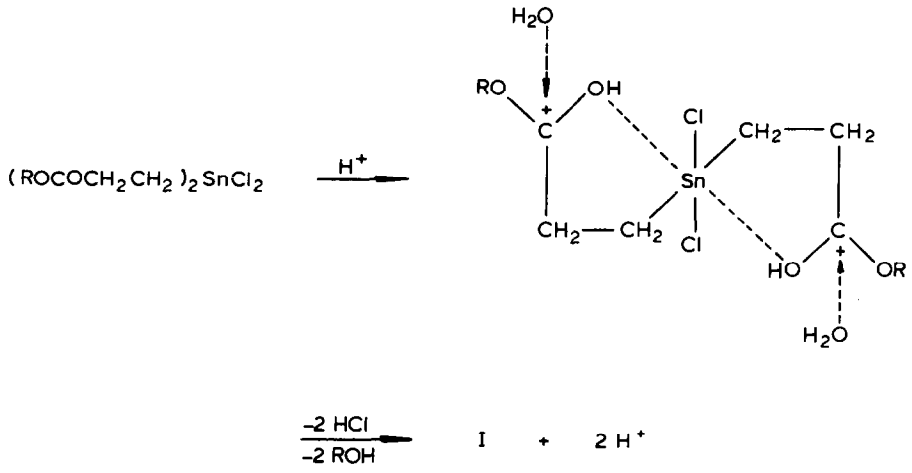


and the reverse reaction, i.e., the reaction of I with various alcohols in an acidic medium should reform the corresponding estertin dichlorides, depending on the nature of the alcohol.

$$Sn(CH_2CH_2CO_2)_2 \xrightarrow[ROH]{HCl} (ROCOCH_2CH_2)_2SnCl_2$$

Thus, hydrolysis of $(ROCOCH_2CH_2)_2SnCl_2$ ($R = CH_3$, C_2H_5, C_4H_9) in NaOH solution gave the same white precipitate I, while the addition of HCl to I in ROH ($R = CH_3$, C_2H_5, n-C_4H_9, iso-C_4H_9, t-C_4H_9, n-C_5H_{11}, iso-C_8H_{17}, $PhCH_2$), resulted in the corresponding estertin compounds $(ROCOCH_2CH_2)_2SnCl_2$, with ROH reactivity being primary > secondary > tertiary.

It was quite surprising to observe that when the estertin $(RO_2CCH_2CH_2)_2SnCl_2$ was treated with dilute hydrochloric acid the same white solid, $Sn(CH_2CH_2CO_2)_2$, was formed. The solid compound, of course, dissolved in excess hydrochloric acid to form $(HO_2CCH_2CH_2)_2SnCl_2$. It appears that the tin atom acts as an extra center for intramolecular hydrolysis in addition to the normal acidic hydrolysis of ester groups.



Because the formation of I from $(CH_3OCOCH_2CH_2)_2SnCl_2$ is almost quantitative, the chemistry described above provides a facile way to synthesize various types of estertin dihalides via esterification of I. In fact, the stabilizer estertin mercaptoesters $(ROCOCH_2CH_2)_2Sn(SCH_2COOC_8H_{17}\text{-}i)_2$ with various R groups can be

synthesized directly from I without isolating the corresponding dihalide:

$$I + 2ROH + 2HCl + 2HSCH_2COOC_8H_{17}\text{-i} \xrightarrow{2NaHCO_3}$$

$$(ROCOCH_2CH_2)_2Sn(SCH_2COOC_8H_{17}\text{-i})_2 + 2NaCl + 2H_2O$$

The results are summarized in Table 2. This reaction can be followed most conveniently by NMR spectroscopy (Fig. 1). The characteristic resonance of HS- of the starting material $HSCH_2COOC_8H_{17}$-i, a triplet at δ 2.0 ppm, is seen to disappear as the thio group is bonded to tin. Also, the signal due to the methylene group adjacent to SH changes from a doublet (δ 3.23 ppm) to a singlet (δ 3.41 ppm).

As is mentioned earlier, when the monoestertin trichloride, $(CH_3OCOCH_2CH_2)SnCl_3$, reacted with aqueous NaOH a similar white precipitate was formed. The compound has a molecular formula $(CH_2CH_2CO_2)SnCl_2$, suggested by its mass spectrum.

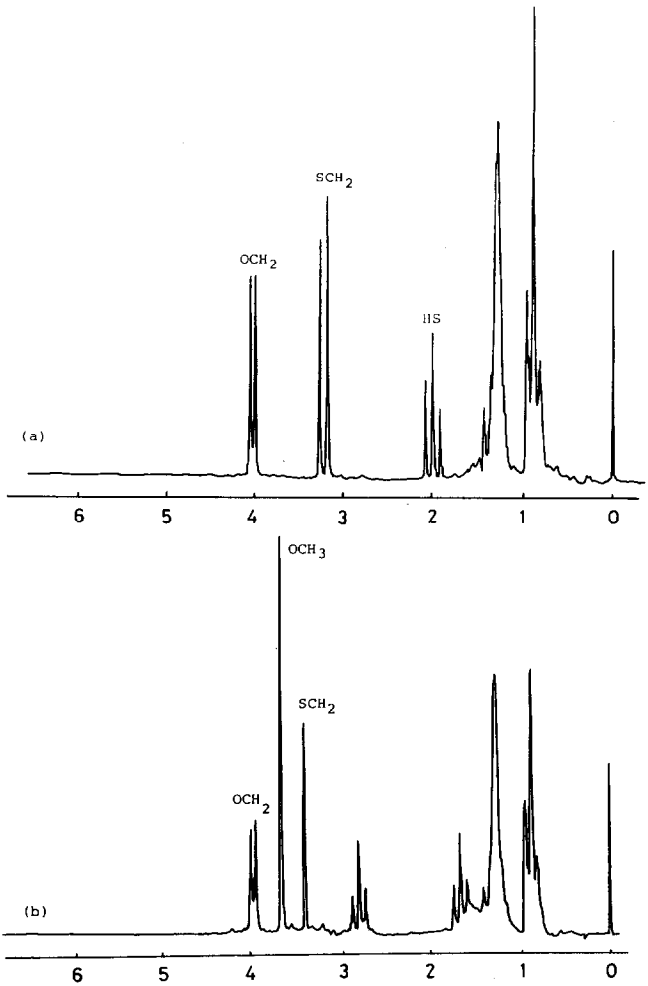


Fig. 1. ^1H NMR spectra of (a) $HSCH_2CO_2CH_2C(C_2H_5)H(CH_2)_3CH_3$ and (b) $(CH_3OCOCH_2CH_2)_2Sn[SCH_2CO_2CH_2C(C_2H_5)H(CH_2)_3CH_3]_3$.

When $(CH_2CH_2CO_2)SnCl_2$ is treated with $HSCH_2COOC_8H_{17}$-i in CH_3OH under the same reaction conditions as those described above, $(CH_3OCOCH_2CH_2)Sn[SCH_2CO_2CH_2C(C_2H_5)H(CH_2)_3CH_3]_3$ is formed. This compound shows complex peaks at about δ 3.8 and 4.1 ppm in the NMR spectrum in addition to the peaks corresponding to OCH_2CH_2Sn, (δ 2.12, 2.92 ppm, A_2B_2), $-CHCH_2CH_3$ and $-(CH_2)_3CH_3$ (δ 0.84–2.0 ppm) and $-OCH_3$ (δ 3.68 ppm, singlet) (Fig. 2). If these resonances correspond to $-SCH_2-$ and $-OCH_2-$, respectively, they should appear as a singlet and a doublet, respectively. When the spectrum is taken at 50°C, the complex peaks do merge into a singlet at δ 3.76 ppm and a doublet at δ 4.08 ppm. It is obvious that hindered rotation is involved, possibly caused by intramolecular interaction among the three bulky thio chains.

Since elimination of an alcohol is an essential step in either acidic or basic medium in forming $Sn(CH_2CH_2CO_2)_2$, which can then be converted to the estertin compound in the corresponding alcohol, it is thought that direct alcoholysis of estertin compounds without formation of $Sn(CH_2CH_2CO_2)_2$ should be possible if the elimination of alcohol is suppressed by carrying out the reaction in the alcohol.

$$(ROCOCH_2CH_2)_2SnCl_2 + R'OH \xrightarrow[\text{or } OH^-]{H^+} (R'OCOCH_2CH_2)_2SnCl_2 + ROH$$

Indeed, transesterification proceeds smoothly under either acid or base catalysis. Starting with the methyl estertin (R = CH_3), the equilibrium can be shifted toward the right hand side by removing the methanol produced continuously at the

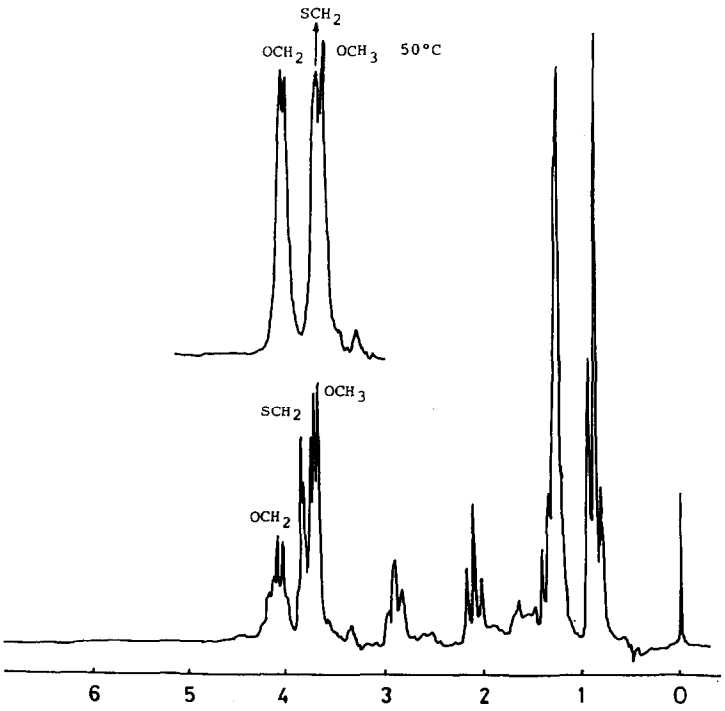


Fig. 2. ^1H NMR spectrum of $CH_3OCOCH_2CH_2Sn[SCH_2CO_2CH_2C(C_2H_5)H(CH_2)_3CH_3]_3$.

refluxing temperature of of R'OH. In fact when alcohols of higher boiling point are used, alcoholysis can be achieved even without a catalyst. For example, in 2-ethylhexanol (b.p. 185°C) the conversion of $(CH_3OCOCH_2CH_2)_2SnCl_2$ to $[CH_3(CH_2)_3CH(C_2H_5)CH_2OCOCH_2CH_2]_2SnCl_2$ is quantitative without any addition of acid or base. When a catalyst is present the conversion rate is high even in alcohols of low boiling point, e.g., 90% conversion in ethanol. The results of alcoholysis in various alcohols are shown in Table 1.

In general, conversion of alcoholysis increases with increasing boiling-point of the alcohol, but decreases with an increase in branching of the alcohol, i.e., primary alcohol > secondary alcohol ≫ tertiary alcohol. For example, the conversion of $(CH_3OCOCH_2CH_2)_2SnCl_2$ to $(t\text{-}C_4H_9OCOCH_2CH_2)_2SnCl_2$ was less than 10%. Steric effects are certainly responsible for the poor yield. In the case of the acid-catalyzed reaction in $t\text{-}C_4H_9OH$, the alcoholysis is further hampered by the formation of isobutene. It seems likely that the mechanisms of the acid- and base-catalyzed alcoholysis of estertin compounds are quite similar to those of organic esters. The effects of acid and base on estertin compounds can be summarized as follows:

$$(CH_3OCOCH_2CH_2)_2SnCl_2 + ROH \xrightarrow{H^+ \text{ or } OH^-} (ROCOCH_2CH_2)_2SnCl_2 + CH_3OH$$

$$\uparrow \text{HCl, ROH}$$

$$(CH_3OCOCH_2CH_2)_2SnCl_2 + H_2O \xrightarrow{H^+ \text{ or } OH^-} \quad I + CH_3OH$$

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