

PROPERTIES OF THE β -CARBONYLALKYLTIN CHLORIDES: EVIDENCE FOR INTRAMOLECULAR COORDINATION

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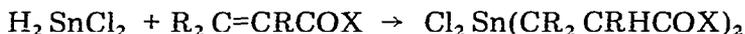
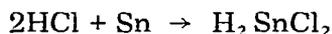
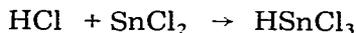
(Received February 12th, 1979)

Summary

The Mössbauer spectra and the solvent effect on the ^1H NMR spectra support the conclusions from infrared spectroscopy that the compounds $\text{Cl}_3\text{SnCR}_2\text{CRHCOX}$ and the $\text{Cl}_2\text{Sn}(\text{CR}_2\text{CRHCOX})_2$ ($\text{R} = \text{Me}$ or H ; $\text{X} = \text{Me}$, OH , or OAlkyl) are intramolecularly coordinated in both the solid state and in solution. The compounds $\text{Cl}_3\text{SnCR}_2\text{CRHCOX}$ ($\text{X} = \text{OH}$ or OAlkyl) react with *t*-butoxyl radicals in solution to show the ESR spectra of the displaced radicals $\cdot\text{CR}_2\text{CRHCOX}$.

Hutton et al. (AKZO company) have recently reported a novel route to β -carbonylalkyltin halides which are the precursors of an important family of stabilizers for polyvinyl chloride [1–3]. The IR and ^1H NMR spectra of these halides were interpreted as implying that in these compounds, the carbonyl group was intramolecularly coordinated to tin. We report here a variety of further evidence which emphasises the importance of this effect.

The compounds listed in Table 1 were prepared by the AKZO methods which are illustrated in the following equations.



The low vibrational frequency of the C=O group, which Hutton, Burley, and Oakes [3] showed to be independent of concentration for the trichloro compounds, has previously been the main evidence for intramolecular coordination [1–4].

The common ranges which are observed for the ^{119}Sn Mössbauer qua-

TABLE I

 β -CARBONYLALKYL TIN CHLORIDES

	M.p. ($^{\circ}$ C)	$\nu(\text{C=O})(\text{cm}^{-1})^a$	Mössbauer spectra ^b	
			$\delta/\text{mm s}^{-1}$	$\Delta E q (\text{mm s}^{-1})$
$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{H}$	125	1640	—	—
$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$	70	1665	1.352	2.003
$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	ca. 55	1650	1.164	2.040
$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{C}_4\text{H}_9$	53	1660	1.105	1.947
$\text{Cl}_3\text{SnCH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$	89	1650	—	—
$\text{Cl}_3\text{SnC}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3^c$	127	1675	1.779	2.145
$\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_2$	133	1685	1.354	3.445
$\text{Cl}_2\text{Sn}(\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_2$	60	1650	—	—
$\text{Cl}_2\text{Sn}(\text{C}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3)_2^d$	176	1685	2.195	4.003

^aNujol mull: cf. $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ 1730, $\text{CH}_3\text{CO}_2\text{CH}_3$ 1760, $(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$ 1725, $(\text{CH}_3)_2\text{CHCO}_2\text{Me}$ 1750 cm^{-1} . ^bAt 77 K, with respect to SnO_2 at room temperature.

^cMolecular weight measurements: concentration (mg cm^{-3}), m.w.:

In CHCl_3 : 6.48, 341; 13.0, 365; 19.4, 374; 25.9, 378.

In C_6H_6 : 6.48, 364; 13.0, 413; 19.5, 412; 25.9, 463.

Formula weight 324.

^dIn CHCl_3 : 7.76, 443; 15.5, 437; 23.3, 427; 31.0, 392.

In C_6H_6 : 7.74, 425; 15.6, 443; 23.3, 449; 31.3, 445.

Formula weight 388.

drupole coupling constants, $\Delta E q$, for compounds of various geometries are: tetrahedral RSnX_3 , 1.4–1.6; trigonal bipyramidal RSnX_4 (R equatorial), 1.7–2.0; tetrahedral R_2SnX_2 , 2.1–2.4; trigonal bipyramidal R_2SnX_3 (R_2 equatorial) 2.9–3.7; *trans*-octahedral R_2SnX_4 , 3.9–4.1 mm s^{-1} ; these values however are sensitive to deviations of the structures from regularity.

The values given in Table 1 for the β -carbonylalkyltin compounds are therefore inconsistent with tetrahedral four-coordination, but compatible with intramolecular coordination giving, in the solid state, trigonal bipyramidal geometry for the trichloro compounds, and trigonal bipyramidal or octahedral geometry for the dichloro compounds.

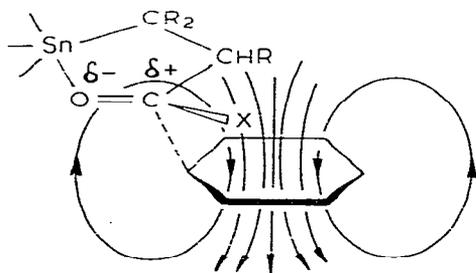
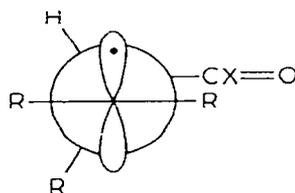
The measurements of the molecular weights of the compounds derived from mesityl oxide show that the monomer is also the principal species present in solution.

The proton NMR spectra of the β -carbonylalkyltin chlorides are listed in Table 2. We find that the chemical shifts are subject to a remarkably large upfield solvent effect compared with that of the corresponding protic compounds, when the solvent is changed from chloroform to benzene.

Solvent effects of this type are usually ascribed to the formation of a solvent (benzene)—solute (carbonyl compound) complex of a specific geometry, in which the magnetic field resulting from the induced aromatic ring current affects the protons of the carbonyl compound to a degree which depends on their location in the field [5].

In the β -carbonylalkyltin chlorides, coordination by the carbonyl oxygen to the tin renders the carbonyl carbon more electrophilic (see Fig. 1). This leads to an increase in the concentration of the benzene-carbonyl complex, and the time-averaged shielding effect of the induced field is increased.

The effects were smaller in chlorobenzene and negligible in nitrobenzene,

Fig.1. Anisotropic shielding of β -carbonylalkyltin compounds in benzene solution.Fig.2. Staggered conformation of β -carbonylalkyl radicals.

consonant with the reduced sensitivity of these compounds to electrophilic attack.

We have shown previously that alkyltin halides undergo bimolecular homolytic substitution by alkoxy radicals at the tin centre with the displacement of an alkyl radical which can be observed by ESR spectroscopy [6,7].



Di-*t*-butyl peroxide was photolysed in the presence of the β -carbonylalkyltin chlorides prepared here, and the radicals which were formed were monitored by ESR spectroscopy. The preferred solvent for these reactions is cyclopropane because of its low reactivity to *t*-butoxy radicals, but the carbonylalkyltin chlorides are not soluble enough in this solvent, and toluene had to be used instead.

The acids and esters containing a β -SnCl₃ group all gave strong spectra of the corresponding β -carbonylalkyl radicals, stronger than those obtained from the unsubstituted alkyltin chlorides; the background spectrum of solvent-derived benzyl radicals was relatively weak. On the other hand, the β -trichlorostannyl derivative of mesityl oxide showed only solvent-derived radicals. Although direct evidence is lacking, we think it is unlikely that *t*-butoxy radicals will react rapidly enough at 5-coordinate tin to give strong spectra of displaced alkyl radicals, and in the ketone derivative which shows the largest NMR solvent shift, the coordination is too strong to allow the $S_{\text{H}}2$ reaction to occur.

The dialkyltin dichlorides usually show stronger ESR spectra of the displaced alkyl radicals than do the alkyltin trichlorides [7] but no spectra could be observed from the bis(β -carbonylalkyl)tin dichlorides. Again it appears that,

TABLE 3

ESR CHARACTERISTICS OF β -CARBONYLALKYL RADICALS IN TOLUENE

Radical	$T(^{\circ}\text{C})$	$a(\text{H}_{\alpha})(\text{G})$	$a(\text{H}_{\beta})(\text{G})$
$\bullet\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	-50	22.5(2H)	28.0(2H)
	-90	22.5	29.1
$\bullet\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$	-40	22.5(2H)	29.0(2H)
	-80	22.5	30.0
$\bullet\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$	-18	22.2(2H)	28.8(2H)
	-54	22.2	29.9
$\bullet\text{CH}_2\text{CHMeCO}_2\text{Me}$	-40	21.8(2H)	26.8(1H)
	-90	21.8	28.2

with two chelating carbonyl groups, the concentration of 4-coordinate tin is too low to permit a rapid S_H2 reaction.

Details of the ESR spectra which were observed are given in Table 3, and are consistent with reports in the literature [8]. All showed a value of $a(H_\beta)$ which increased at low temperature, showing that all, like the β -ethoxycarbonylethyl radical [9] are most stable in the staggered conformation illustrated in Fig. 2.

Experimental

The organotin compounds were prepared by the published methods [1–3] and showed satisfactory analyses.

Infrared spectra were recorded on a Unicam SP1000 spectrometer, and NMR spectra with a Perkin–Elmer R12 instrument at 35°C. We are grateful to Dr. B.W. Fitzsimmons and I. Sayer for determining the Mössbauer spectra under the University of London Intercollegiate Research Service.

Molecular weights were measured using a Mechrolab Vapour pressure osmometer, Model 301A.

Samples for ESR spectroscopy were dissolved together with di-*t*-butyl peroxide in toluene in Suprasil silica tubes. The solutions were out-gassed and photolysed in the cavity of a Varian E4 ESR spectrometer by the technique which has been described [7].

Acknowledgement

We are grateful to the International Tin Research Council for the award of a Research Fellowship to Man-Wing Tse.

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