Sterically Hindered Metal Alkenyls. Part 2.† Synthesis and Properties of Tin(IV) Alkenyls: Stereochemical Features and Energetics of Isomerisation of $SnMe_2[C(C_{10}H_7)=CMe_2]_2$

David J. Cardin* and Alice C. Sullivan
Department of Chemistry, Trinity College, University of Dublin, Dublin 2, Ireland

The compounds $SnMe_{4-n}R^1_n$ [n = 1 or 2; $R^1 = C(C_{10}H_{15})=CH_2$ ($C_{10}H_{15}$ = adamant-1-yl)], $SnMe_2R^2_2$ [$R^2 = C(C_{10}H_7)=CMe_2$ ($C_{10}H_7$ = naphth-1-yl)], and $SnBrR^1_3$ have been prepared and characterised by elemental analysis, i.r. and n.m.r. spectroscopy, and mass spectrometry. The compound $SnMe_2R^2_2$ exists as an unusual mixture of rotamers, which can be separated by crystallisation. The thermal conversion of one isomer into the other has been studied by variable-temperature n.m.r., and the energetics of isomerisation determined.

Tin alkenyls bearing very bulky α-substituents (larger than phenyl) have not previously been reported. In the preceding paper in this series we described transition-metal compounds having such ligands, where unusual reactivity was found for some cases. We now give details of tin derivatives with the ligands (adamant-1-yl)ethenyl (R^1) and 2-methyl-1-(naphth-1-yl)prop-1-enyl (R^2). No homoleptic species SnR_4 could be obtained in contrast both to 2-methyl-1-phenylprop-1-enyl[1] and to adamant-1-yl (tricyclo[3.3.1.1^{3,7}]dec-1-yl) as ligands.[2] The effect of the bulky substituents is clearly seen for the rotamers of $SnMe_2R^2_2$.

Results and Discussion

The compounds $SnMe_{4-n}R^m_n$ (n = 1 or 2, m = 1; n = 2, m = 2) were prepared, as shown in equation (1), from the tin chloride and the corresponding Grignard reagent in high yield.

$$SnCl_nMe_{4-n} + nMgR^mCl \longrightarrow SnMe_{4-n}R^m_n + nMgCl_2 \quad (1)$$

Attempts to form the tetra-alkenyls using $SnCl_4$ were unsuccessful, yielding a mixture from which the only isolated product using R^1 was the trialkenyl $SnBrR^1_3$, in low yield (12.4%). In this case the bromine originated from the 1,2-dibromoethane used to initiate the Grignard reaction. With R^2 no isolable product was obtained, nor when the lithium reagent of R^1 was employed. A survey of the available data on the synthesis of tetra-alkenyls of tin shows a monotonic variation of yield with ligand size, the principal factor being the bulk at the ligating carbon atom; R in SnR_4, yield (%): $CH=CH_2$, 74;[3] $CH=CMe_2$, 61;[1] $CPh=CMe_2$, 16;[1] $CPh=CPh_2$, 0;[4] R^1, 0; R^2, 0. The figures also show, however, a significant effect of the β-substituents.

The new compounds are air- and moisture-stable at room temperature: colourless liquids ($SnMe_3R^1$) or low melting solids. Selected physical and analytical data are given in Table 1, and spectroscopic details in Table 2.

Isomerisation of $SnMe_2R^2_2$.—The proton n.m.r. spectrum of this compound reveals two magnetically distinct sets of tin methyl groups, and similarly for one of the two methyl substituents on the alkenyl ligand, see Figure 1(*a*). This spectrum we interpret in terms of an equimolar (by integration) mixture of isomers, one having equivalent, and the other inequivalent tin methyls. The conformations shown in Figure 2 represent possible structures for these rotamers.

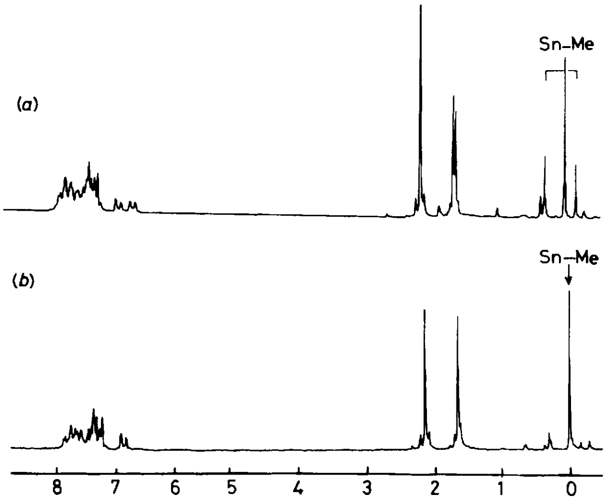

Figure 1. ^1H N.m.r. spectra of isomers of $SnMe_2R^2_2$ [(*a*) mixture, (*b*) single isomer]

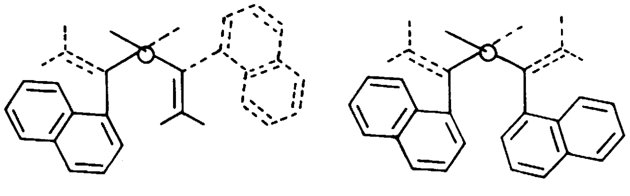
(*a*) (*b*)

Figure 2. Proposed conformations for rotamers of $SnMe_2R^2_2$

In agreement with this interpretation, slow crystallisation of this product from hexane afforded a material having the ^1H n.m.r. spectrum shown in Figure 1(*b*), which we accordingly assign the structure of isomer (*a*) in Figure 2, because of the methyl pattern. The species $SnMe_2R^2_2$ is unique in organotin chemistry, in that the rotamers are magnetically distinct at room temperature, and may be readily separated. Previous reports of stereoisomerism in organotin compounds relate to chiral[5–7] molecules, or those having diastereotopic groups.[8] To our knowledge the only isomeric separations have been achieved in the classic case of asymmetric molecules obtained by the isolation of intermediate diastereomers.[9]

On warming solutions of isomer (*a*) in a variety of solvents, isomerisation begins, and ultimately a 50:50 mixture of rotamers is obtained. This can be readily followed in the ^1H

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† Part 1 is the preceding paper.

Table 1. Physical and analytical data for the new tin alkenyls

Compound	M.p. (°C)	Yield(%)	Mass spectrometric data		Analysis(%)*	
			*m/e**	Assignment	C	H
$SnMe_3[C(C_{10}H_{15})=CH_2]$	—	78.5	324(324)	P^+	—	—
$SnMe_2[C(C_{10}H_{15})=CH_2]_2$	60—62	71.8	455(470)	$(P - Me)^+$	66.5(66.3)	8.25(8.6)
$SnBr[C(C_{10}H_{15})=CH_2]_3$	166	12.4	521(682)	$(P - R^1)^+$	61.95(63.3)	7.7(7.5)
$SnMe_2[C(C_{10}H_7)=CMe_2]_2$	68—71	87	—	—	70.7(70.5)	6.5(6.5)

* Calculated values in parentheses.

Table 2. Spectroscopic data for the new tin alkenyls[a]

Compound	δ/p.p.m.		$^nJ(^{117,119}Sn-H)/Hz$		δ(Sn*Me*)/p.p.m.	$^3J(^{117,119}Sn-H)/Hz$		ν(C=C)/cm $^{-1}$
	$=CR'_{cis}$	$=CR'_{trans}$	$=CR_{cis}$	$=CR_{trans}$				
$SnMe_3[C(C_{10}H_{15})=CH_2]$	5.1, 5.12	5.62, 5.64	68	68[b]	0.06	50.04,	52	1 590[c]
$SnMe_2[C(C_{10}H_{15})=CH_2]_2$	5.16, 5.18	5.68, 5.7	56	56[b]	0.03	48.04,	50.04	1 590[d]
$SnBr[C(C_{10}H_{15})=CH_2]_3$	5.32	5.85	110	*[b]	—	—		1 580[e]
$SnMe_2[C(C_{10}H_7)=CMe_2]_2$[f]	1.7, 1.8	2.4	—	—[g]	−0.32, 0.00, 0.5	—		1 615[e]
$SnMe_2[C(C_{10}H_7)=CMe_2]_2$[h]	1.7	2.4	6	11[g]	0.00	51		1 615[e]

[a] Spectra recorded in $CDCl_3$ solutions with $SiMe_4$ as internal standard; R^1=H or Me. [b] $n = 3$. [c] Neat. [d] Nujol mull. [e] KBr disc. [f] 50:50 mixture of rotamers, tin satellites not all observed. [g] $n = 4$. [h] Single isomer.

n.m.r. spectrum, most conveniently by observing the tin methyl resonances, the spectrum changing continuously from that shown in Figure 1(*b*) to that of (*a*). Analysis of the kinetics by ^1H n.m.r. spectroscopy in $C_6D_5NO_2$ at 353 K using the Eyring equation* gave $\Delta G\ddagger$ = 109.75(±0.84) kJ mol^{-1}. While there are no other data relating to this type of barrier for organometallic compounds, it is interesting to note that the value lies near the upper limit observed for the barrier to rotation about the central single bond in a number of substituted biphenyls (*ca.* 80—115 kJ mol^{-1}). In principle, isomer (*a*) can be resolved into enantiomers (Figure 2). Not surprisingly, measurement of the specific rotation for carefully crystallised samples revealed no significant degree of enantiomeric separation.

Experimental

Experiments were performed under argon or nitrogen gases in solvents freshly distilled from appropriate drying agents. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Carbon, hydrogen, and halogen analyses were obtained from the Microanalytical Laboratory, University College Dublin or Canadian Microanalytical Service, Vancouver. Infrared spectra were recorded on Perkin-Elmer 298 or 599 spectrophotometers and ^1H n.m.r. spectra on a Bruker WP 80 Fourier-transform instrument.

[1-(*Adamant*-1-*yl*)*ethenyl*]*trimethyltin*(IV), $SnMe_3[C(C_{10}H_{15})=CH_2]$.—1-(Adamant-1-yl)ethenylmagnesium chloride [60 cm^3 of a 0.208 mol dm^{-3} solution in tetrahydrofuran (thf, 12.4 mmol] was added dropwise at room temperature to a solution of trimethyltin chloride (2.37 g, 11.8 mmol) in thf (30 cm^3). The mixture was stirred at 80 °C (5 h) and then at room temperature (10 h). Removal of volatiles under vacuum was followed by extraction of the product into hexane and filtration to remove $MgCl_2$. The hexane filtrate was concentrated and the resultant colourless oil purified (by distillation under vacuum) of contaminants (adamant-1-yl)ethene and 1-(adamant-1-yl)-1-chloroethene at 30 (0.1 mmHg) and 40 °C (0.1 mmHg) respectively affording the desired *product* (3.01 g, 78.5%); *m/e*; 324 (P^+), 309 [$(P-Me)^+$], 294 [$(P-2Me)^+$], 278 [$(P-3Me)^+$].

Bis[1-(*adamant*-1-*yl*)*ethenyl*]*dimethyltin*(IV), $SnMe_2[C(C_{10}H_{15})=CH_2]_2$.—1-(Adamant-1-yl)ethenylmagnesium chloride (59 cm^3 of a 0.016 mol dm^{-3} solution in thf, 19.48 mmol) was added dropwise at room temperature to dimethyltin dichloride (1.79 g, 9.74 mmol) in thf (50 cm^3). The reaction mixture was held at reflux (48 h). The thf was removed under vacuum and the residue extracted with hexane (50 cm^3) and filtered. Concentration of the hexane solution afforded long white *needles* (3.34 g, 71.8%).

Tris[1-(*adamant*-1-*yl*)*ethenyl*]*bromotin*(IV), $SnBr[C(C_{10}H_{15})=CH_2]_3$.—To 1-(adamant-1-yl)ethenylmagnesium chloride (50 cm^3 of a 0.2 mol dm^{-3} solution in benzene, 10 mmol) and magnesium bromide (excess) was added dropwise, with stirring, a solution of tin(IV) chloride (0.29 cm^3, 2.25 mmol) in benzene (20 cm^3) at room temperature. The reaction mixture was held at reflux (36 h). A heavy white precipitate was filtered from the cooled benzene solution. The filtrate was concentrated and thoroughly washed with hexane affording a white *powder* (0.212 g, 12.4%).

Dimethylbis[2-*methyl*-1-(*naphth*-1-*yl*)*prop*-1-*enyl*]*tin*(IV), $SnMe_2[C(C_{10}H_7)=CMe_2]_2$.—A solution of dimethyltin dichloride (1.285 g, 5.6 mmol) in thf (15 cm^3) was added dropwise at 0 °C to 2,2-dimethyl-1-(naphth-1-yl)ethenylmagnesium chloride (50 cm^3 of a 0.25 mol dm^{-3} solution in thf, 12.5 mmol). The reaction mixture was held at reflux (24 h), and then cooled. The thf was removed under vacuum and the residue extracted with hexane and filtered. Concentration of the filtrate afforded a white solid (2.49 g, 87%). Slow crystallisation of the white solid obtained from hexane afforded microcrystalline clumps of one pure *isomer*, m.p. 124 °C (Found: C, 70.25; H, 6.50. $C_{30}H_{32}Sn$ requires C, 70.5; H, 6.50%).

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* $k = \kappa(kT/h)\exp(-\Delta G^{\ddagger}/RT)$.

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