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Addition of sulphenyl halides and thiocyanates to alkenyl-metal compounds. Structures of [1-chloro-2-(4-methyl-2-nitrophenyl)ethyl]-triphenylstannane and [2-(2-nitrophenyl)-1-thiocyanatoethyl]triphenylstannane

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Abstract

The crystal and molecular structures of $Ph_3SnCHClCH_2SC_6H_3NO_2$-2-Y-4 (II, Y = Me) and $Ph_3SnCH(SCN)CH_2SC_6H_4NO_2$-*o* (III) have been determined. Compounds II and III are adducts of $Ph_3SnCH{=}CH_2$ and the appropriate sulphenyl chloride and thiocyanate. Both compounds are monomeric and contain slightly distorted tetrahedral tin atoms. The intra-molecular Sn---S(R) distances in II (Y = Me) and III are 3.67 and 3.58 Å, respectively. The solid state conformations are staggered and have dihedral angles Sn–C–C–S of 56.6 and 57.4° in II (Y = Me) and III, respectively, and Cl–C–C–S in II and S–C–C–S in III 176.0° and 174.1°, respectively. From ^3J(H–H) and $^3J(^{119}Sn–^1H)$ values, the solid state conformation of II (Y = Me) is calculated to be populated in solution for approximately 1/3rd of the time at 25°C.

Introduction

Sulphenyl halides and thiocyanates [1,2] take part in electrophilic additions to alkenes [1,3] as well as substitution reactions with arenes [4] and organometallic compounds. Among the carbon–metal bonds cleaved by electrophilic sulphenyl compounds, RSX, are electron-rich aryl–tin bonds (*e.g.* *p*-$MeOC_6H_4$–Sn) and

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allyl–tin bonds, [5] eq. 1. For other alkenyl–tin compounds, such as vinyl–, [6] eq. 2, and 3-butenyl–tin compounds, [7] additions and/or cleavages result.

$$R'Sn\equiv + RSX \rightarrow R'SR + X\text{–}Sn\equiv \qquad (1)$$

(R′ = allyl or aryl)

$$R_3'SnCH{=}CH_2 + RSX \rightarrow R_3'SnX + CH_2{=}CHSR + \underset{\text{(I)}}{R_3'SnCHXCH_2SR} \qquad (2)$$

Adducts from $R_3'SnCH{=}CH_2$ were assigned the Markownikov structure (I) from the ^1H NMR (100 MHz) spectra, although resolutions of the central CH–CH protons in (I) were not completely achieved [6]. This plus a report [8] that $Me_3SiCH{=}CH_2$ forms *anti*-Markownikov adducts, $Me_3SiCHSRCH_2Cl$, with RSCl led us to reinvestigate the structures of adducts (I). We now report an X-ray crystallographic study of two compounds, *viz.* $Ph_3SnCHClCH_2SC_6H_3NO_2$-2-Y-4 (II, Y = Me) and $Ph_3SnCHSCNSC_6H_4NO_2$-*o* (III), adducts of $Ph_3SnCH{=}CH_2$ with 2-NO_2-4-YC_6H_4SCl and *o*-$NO_2C_6H_4SSCN$, respectively. Confirmation of our original assignment of the structures was obtained.

In addition to the solid state study, more detailed NMR spectra (^1H, ^{13}C and ^{119}Sn) of II have been obtained, in order to estimate populations of the conformers of II in solution.

Experimental

Compounds II and III were obtained as previously reported [6] and were recrystallised from EtOH. Melting points were as previously reported. NMR Spectra were obtained using a Bruker 250 MHz spectrometer (Table 1).

Crystal structure determinations

Data were collected on a Nicolet P3 automated diffractometer, using monochromated Mo-K_α radiation and a graphite monochromator.

Compound II (Y = Me)

Crystal data. $C_{27}H_{24}ClNO_2SSn$, $M = 580.703$, triclinic, space group $P\bar{1}$, $a = 7.780(15)$, $b = 8.370(12)$, $c = 19.544(32)$ Å, $\alpha = 92.67(12)$, $\beta = 89.98(14)$, $\gamma = 95.99(13)°$, $Z = 2$, $V = 1264(4)$ Å^3, $D_x = 1.525$ kg m^{-3}, $F(000) = 584$, μ(Mo-K_α) = 1.22 mm^{-1}, $\lambda = 0.71069$ Å, T = room temperature.

Data collecting and processing. Yellow crystal, 0.04 × 0.38 × 0.88 mm. The cell dimensions were obtained from setting angles of 14 reflections with $2\theta \simeq 20°$.

Data were collected using the $\theta/2\theta$ method for 2θ in the range 0–50° for the set of unique reflections with $0(-11, -25) \leq h(k, l) \leq 10(11, 25)$. Pre-scan intensities ($I_p$) were used to select scan rates in the range 5.33 to 58.6° $2\theta/\text{min}^{-1}$, the limiting values corresponding to $I_p < 150$ and $I_p > 2500$ respectively. The 2θ scan width varied from 2.4 to 2.75° depending on 2θ for the reflection. The resulting data contained 4470 unique reflections of which 1193 were classed as unobserved $[I < 3\sigma(I)]$ and not considered further. The intensities of two standard reflections monitored at intervals of 50 measurements showed no significant variation and no absorption correction was applied.

Structure analysis and refinement. The structure was solved initially in the non-centrosymmetric space group $P1$ in which the Sn positions were obtained from SHELXS-86 [9] and all other non-H were obtained from a series of structure factor and difference map calculations. This model was refined by a series of full matrix least squares calculations minimising $\Sigma w(|F_o| - |F_c|)^2$ with unit weights and all atoms vibrating isotropically. At this stage it became apparent that the structure was in fact centrosymmetric and all further calculations were carried out in the space group $P\bar{1}$. Further refinement in this space group with all non-H vibrating anisotropically, including H in calculated positions with common U_{iso} for alkyl and aryl H as separate groups and with weights defined as $1/[\sigma^2(F) + 0.006F^2]$ gave $R = 0.053$ and $R_w = 0.057$ for 3277 reflections and 303 refined parameters when the maximum Δ/σ was 0.15 (Z/c for Sn) but generally an order of magnitude less for positional and thermal vibration parameters and 0.45 for one of the rotational parameters of the methyl group which was refined as a rigid body. The difference map then showed no feature in excess of ± 1.5 eA^{-3}. Calculations were carried out on the Bull DPS8 computer (CP6 operating system) of the Computing Centre of the University of Aberdeen using SHELX76 [9]. The scattering factors used were those supplied with the program.

Compound III

Crystal data. $C_{27}H_{22}N_2O_2S_2Sn$; $M = 589.305$; space group $P\bar{1}$, $a = 7.919(5)$, $b = 11.415(10)$, $c = 17.424(16)$ Å, $\alpha = 117.29(7)$, $\beta = 104.45(6)$, $\gamma = 96.32(6)°$; $V = 1308(2)$ Å^3, $Z = 2$, $D_c = 1.50$ kg m^{-3}, $D_m = 1.52$ g cm^{-3}, $F(000) = 592$, μ(Mo-K_α) $= 1.16$ mm^{-1}, $\lambda = 0.71069$ Å, T = room temperature.

Data collection and processing. Pale yellow crystal, $0.5 \times 0.7 \times 0.2$ mm. The intensities of 4615 unique reflections were measured with $2\theta < 50°$ as ω–2θ scans and 3948 had $F > 6\sigma(F)$ and were used for subsequent analysis. Range of hkl $0 \leq h < 10$, $-15 \leq k < 15$, $-22 \leq l < 22$. Data were collected for Lorentz and polarization effects; absorption was ignored. Two reference reflections, monitored periodically, showed no significant variation in intensities.

The position of the tin atom was located from the three-dimensional Patterson function while the remaining non-hydrogen atoms were located from successive difference Fourier maps, using SHELX76 [9]. Hydrogen atoms were located but given ideal geometry with C–H = 1.00(2) Å and allowed to ride on attached carbons. Full-matrix least-square calculation on F with anisotropic thermal parameters for the Sn, S, N, O and C atoms and isotropic thermal parameters for the H atoms converged at $R = 0.032$, $R_w = 0.035$. Atomic scattering factors were from SHELX76 [9]. Final $w = 1.000/[\sigma^2(F) + 0.00100\ F^2]$; final $\Delta\rho_{max} = 0.48$, $\Delta\rho_{min} = -0.41$ e Å^{-3}.

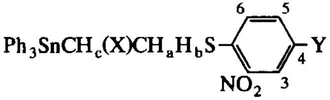
Results and discussion

Solid state structures of II (Y = Me) and III

The molecular structure and numbering system of II (Y = Me) are shown in Fig. 1. The atomic positions and bond lengths and valency angles for II (Y = Me) are in Tables 2 and 3. Corresponding data for III are in Tables 4 and 5. The molecular structure and numbering system of III are shown in Fig. 2.

Table 1

NMR spectral data for $Ph_3SnCHXCH_2SAr$ in $CDCl_3$ solution at 20°C



X, Y	^{1}H NMR									
	$\delta(H_a)$ $[JH_a{-}H_b]$ $[[J^{119}Sn{-}H_a]]$	$\delta(H_b)$ $[JH_b{-}H_c]$ $[[J^{119}Sn{-}H_b]]$	$\delta(H_c)$ $[JH_a{-}H_c]$ $[[J^{119}Sn{-}H_c]]$	$\delta(H_3)$ $[JH_3{-}H_5]$	$\delta(H_4)$	$\delta(H_5)$ $[JH_5{-}H_6]$	$\delta(H_6)$ $[J^{119}Sn{-}H]$	Ph_3Sn		Others
								$\delta(o\text{-}H)$	$\delta(m- + p-H)$	
Cl, Me	3.70 [13.8] [[57.2]]	3.64 [7.3] [[35.2]]	4.39 [8.3] [[17.6]]	7.96 [1.7]	– –	7.29 [8.3]	7.19	7.65m [50]	7.45m	2.41(Me)
	3.48[a] [13.7][a] [[77]][a]	3.37[a] [7.7][a] [[28.6]][a]	4.18[a] [7.7][a] [[16.5]][a]	7.51[a] [*ca.* 2][a]	– –	6.49[a] [8.4][a]	6.69[a]	7.64[a]	7.16[a]	1.70[a](Me)
	4.04[b] [13.7][b] –	3.90[b] [6.3][b] –	4.89[b] [8.7][b] [[22.0]][b]							
Cl, NO_2	3.79 [13.6] [[37.2]]	3.72 [6.4] [[21.6]]	4.35 [8.7] [[19.0]]	9.00 [2.5]	– –	8.23 [8.9]	7.34	7.63m	7.46m	
Cl, H	3.81 [13.8] [[56.0]]	3.66 [7.2] [[35.2]]	4.41 [8.3] [[17.6]]	8.16 [1.3][c]	7.13–7.31m			7.67m	7.46m	
SCN, H	3.90 [13.2] [[62]]	3.50 [9.7] [[43.8]]	3.68 [4.2] –	8.15 [1.4][c]	7.25–7.38m			7.58m	7.42m	
SCN, H[d]	4.13[d] [14.3][d]	3.57[d] [11.2][d]	3.76[d] [5.0][d]							

Table 1 (continued)

^{13}C NMR and ^{119}Sn NMR

X, Y	CHX [J^{119}Sn–^{13}C]	δ^{13}C							*ipso*-C	*o*-C	*m*-C [J^{119}Sn–^{13}C]	*p*-C	δ^{13}C Others	δ^{119}Sn
		CH$_2$	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$						
Cl, Me	44.9 [378]	39.9	131.5	146.6	126.3	136.0	134.4	127.0	136.3 [536]	137.1 [38.7]	128.7 [52.4]	129.5 [11.8]	20.4(Me)	−128.6 (−127.2 [b]) (−123.7 [a])
Cl, H	44.7 [376]	39.8	133.4	146.4	125.0	126.2	133.4	126.6	136.3 [537]	137.1 [36.8]	128.8 [53.2]	129.5 [11.8]		
Cl, NO$_2$	44.1	40.3	144.0	145.4	121.8	145.1	127.0	126.8	135.8	137.1 [36.9]	129.0 [53.8]	129.9 [12.0]		
SCN, H	29.5 [256]	36.6 [6.7]	133.8	146.1	125.3	126.2	133.8	126.3	134.8 [553]	137.0 [38.7]	129.0 [55.4]	129.9 [12.1]	113.0(SCN)	−111.1

[a] In C_6H_6 solution. [b] In C_5D_5N solution. [c] [$J(H_3–H_4)$] 8.3 Hz. [d] Data for $IPh_2SnCHSCNCH_2SC_6H_4NO_2$-*o*.

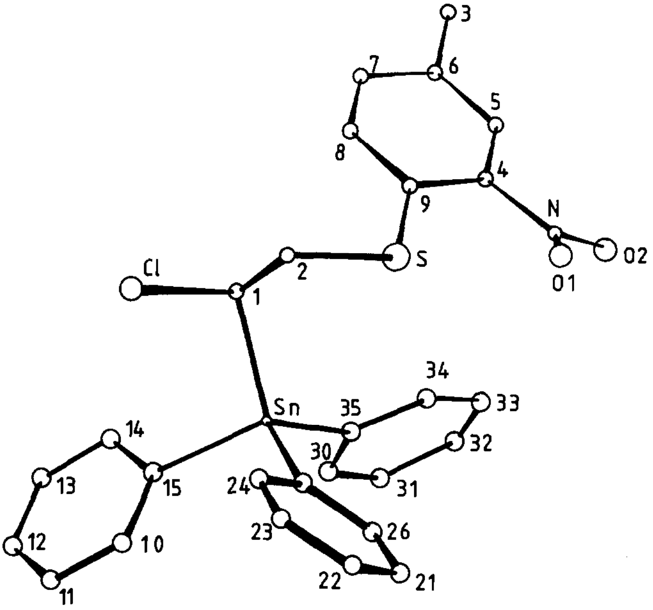


Fig. 1. Molecular structure of II (Y = Me).

The atomic arrangements determined by crystallography confirm those deduced from an earlier ^1H 100 MHz NMR study [6]. The Markownikov addition of RSX to $R'_3SnCH{=}CH_2$ contrasts with the reported anti-Markownikov addition to $Me_3SiCH{=}CH_2$ [8]. Compounds II (Y = Me) and III are monomeric species, with the geometry about tin in both cases only slightly distorted from tetrahedral. For II (Y = Me) the C–Sn–C bond angles are in the range 106.5 to 113.2°, with the C–Sn bond lengths between 2.125(8) to 2.134(7) Å for Ph–Sn and 2.186(8) Å for the alkyl–Sn bond. For (III) the C–Sn–C bond angles show a slightly larger range — 104.6 to 118.2° — with the C–Sn bond lengths varying from 2.125(3) to 2.139(3) Å for Ph–Sn and 2.204(3) Å for the alkyl–Sn bond. All the C–Sn bond lengths are in the normal range for such bonds.

Intramolecular Sn---S distances are 3.67 Å in II (Y = Me) and, in III, 3.58 (to SR) and 3.18 Å (to SCN). These values are much larger than the sum of covalent radii (2.44 Å) but are within the sum of the van der Waal radii (4.05 Å). Examples of Sn–S single bond lengths are 2.42 Å in $\overline{SCH_2CH_2SCH_2S}Sn\underline{SCH_2CH_2SCH_2S}$ (IV) [10] and 2.413(3) Å in $Ph_3SnSC_6H_4{}^tBu$-*p* [11]. Intramolecular coordinate Sn–S linkages were found to be 3.13 Å in (IV), [10] 3.097(4) and 3.118(4) Å in $(ClMe_2\overline{SnCH_2CH_2CH_2)_2S}$ [12] and 3.195(4) Å in $ClPh_2\overline{SnCH_2CH_2CH_2S}C_6H_4$ Me-*p* [13]; for these three compounds, evidence for Sn–S bonding was apparent from the bond angles about Sn.

In $(cyclohexyl)_3SnCH_2SC_6H_4Cl$-*p* (V), the intramolecular Sn---S separations were found to be 3.29(1) and 3.26(1) Å in the two independent molecules within the crystal. The bond angles around tin are essentially tetrahedral, being between 105.6(13) and 113.6(12)° and 106.1(11) and 113.2(7) Å [14]. Compound V, like III, has a sulphur atom on a *α*-carbon atom, relative to tin. In such compounds the S

Table 2

Atoms coordinates and equivalent isotopic temperature factors ($\times 10^3$) for compound II (Y = Me) with e.s.d.s in parentheses

	x	y	z	U_{eq} [a]
Sn	4811(1)	6884(1)	2040(1)	40(1)
Cl	8564(3)	8695(3)	2441(1)	83(1)
S(1)	3759(3)	9594(2)	3482(1)	51(1)
C(1)	6456(10)	8200(10)	2829(4)	52(2)
C(2)	5889(10)	9753(9)	3119(4)	52(2)
N(1)	789(9)	8196(11)	4391(4)	68(2)
O(1)	586(9)	9350(12)	4069(4)	103(3)
O(2)	−388(9)	7200(13)	4541(5)	113(3)
C(3)	4435(13)	5996(11)	6108(4)	64(3)
C(4)	2560(8)	7952(9)	4612(4)	45(2)
C(5)	2667(10)	7102(9)	5197(4)	51(2)
C(6)	4269(10)	6860(8)	5462(4)	46(2)
C(7)	5716(9)	7525(9)	5103(4)	45(2)
C(8)	5591(9)	8310(9)	4515(4)	44(2)
C(9)	3967(8)	8558(8)	4244(3)	40(2)
C(10)	6517(11)	5726(11)	712(4)	61(2)
C(11)	7526(14)	4773(14)	304(5)	81(3)
C(12)	8508(12)	3750(14)	581(6)	85(4)
C(13)	8432(12)	3537(13)	1275(6)	82(4)
C(14)	7463(11)	4446(12)	1688(5)	69(3)
C(15)	6457(9)	5562(9)	1415(4)	45(2)
C(20)	1970(11)	8399(11)	1295(4)	61(2)
C(21)	1214(14)	9505(14)	891(5)	78(3)
C(22)	2279(16)	10749(13)	631(5)	79(3)
C(23)	4026(15)	10925(11)	764(5)	73(3)
C(24)	4723(12)	9844(10)	1174(5)	63(3)
C(25)	3709(10)	8570(9)	1439(4)	49(2)
C(30)	2921(10)	3558(10)	2265(4)	56(2)
C(31)	1757(12)	2384(10)	2549(5)	69(3)
C(32)	640(13)	2809(12)	3037(5)	74(3)
C(33)	602(12)	4387(13)	3228(5)	76(3)
C(34)	1715(9)	5601(10)	2939(4)	55(2)
C(35)	2929(8)	5170(8)	2462(3)	40(2)

[a] $U_{eq} = \frac{1}{3}[\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j]$.

atom has of necessity to be relatively close to Sn (*i.e.* within 3.1 to 3.4 Å, assuming reasonable values for bond lengths and angles). The SCN unit in III is almost linear [175.2(5) Å] with S–C and C–N bond lengths of 1.685(4) and 1.140(6) Å, respectively. These bond lengths are similar to those found in p-$H_2NC_6H_4SCN$ [1.704(4) and 1.132(5) Å] [15] and in $NCSCH_2SCN$ [1.677(9) and 1.194(12) Å] [16]. The Sn---N(CS) intramolecular distance in III is 4.434(5)°.

Although the β-sulphur atoms in both II (Y = Me) and in III [*i.e.* S(1)] are further away from their respective tin atoms than is the α-sulphur atom in III, they could more comfortably interact with tin. As can be seen in Fig. 3, the solid state conformations of II (Y = Me) and (III) are staggered, and have the Sn and β-S atoms in *gauche* arrangements; the dihedral angles Sn–C(1)–C(2)–S(1) are 56.6 and 57.4° for II (Y = Me) and III, respectively, as well as 174.1° for S(2)–C(1)–C(2)–S(1) in III and 176.0° for S–C(1)–C(2)–Cl in II (Y = Me). (The S–C–C–

Table 3

Bond lengths (Å) and valency angles (°) with e.s.d.s in parentheses for II (Y = Me)

Sn-C(1)	2.186(8)	C(8)-C(9)	1.410(9)
Sn-C(15)	2.128(7)	C(10)-C(11)	1.399(14)
Sn-C(25)	2.125(8)	C(10)-C(15)	1.387(11)
Sn-C(35)	2.134(7)	C(11)-C(12)	1.337(16)
Cl-C(1)	1.823(8)	C(12)-C(13)	1.378(17)
S-C(2)	1.797(8)	C(13)-C(14)	1.364(14)
S-C(9)	1.773(7)	C(14)-C(15)	1.403(12)
C(1)-C(2)	1.502(11)	C(20)-C(21)	1.418(14)
N-O(1)	1.201(13)	C(20)-C(25)	1.373(12)
N-O(2)	1.217(12)	C(21)-C(22)	1.378(16)
N-C(4)	1.482(10)	C(22)-C(23)	1.375(17)
C(3)-C(6)	1.496(11)	C(23)-C(24)	1.389(13)
C(4)-C(5)	1.382(11)	C(24)-C(25)	1.379(12)
C(4)-C(9)	1.376(9)	C(30)-C(31)	1.399(12)
C(5)-C(6)	1.387(11)	C(30)-C(35)	1.385(11)
C(6)-C(7)	1.405(10)	C(31)-C(32)	1.350(14)
C(7)-C(8)	1.359(10)	C(32)-C(33)	1.359(15)
C(34)-C(35)	1.390(10)	C(33)-C(34)	1.404(13)
C(15)-Sn-C(1)	106.5(3)	C(25)-Sn-C(1)	108.7(3)
C(35)-Sn-C(1)	112.2(3)	Cl(1)-C(1)-Sn	106.8(4)
C(2)-C(1)-S	117.1(5)	C(25)-Sn-C(15)	109.2(3)
C(35)-Sn-C(15)	106.8(3)	C(10)-C(15)-Sn	120.8(6)
C(14)-C(15)-Sn	121.8(6)	C(35)-Sn-C(25)	113.2(3)
C(20)-C(25)-Sn	120.6(6)	C(24)-C(25)-Sn	120.9(6)
C(30)-C(35)-Sn	119.3(5)	C(34)-C(35)-Sn	122.5(5)
C(2)-C(1)-Cl	106.6(5)	C(9)-S-C(2)	104.4(3)
C(1)-C(2)-S	115.0(5)	C(4)-C(9)-S	122.5(5)
C(8)-C(9)-S	122.1(5)	O(2)-N-O(1)	123.3(9)
C(4)-N-O(1)	118.7(8)	C(9)-C(4)-N	120.2(6)
C(4)-N-O(2)	117.9(8)	C(7)-C(6)-C(3)	122.3(7)
C(5)-C(4)-N(1)	115.6(7)	C(6)-C(5)-C(4)	120.1(7)
C(5)-C(6)-C(3)	121.6(7)	C(7)-C(6)-C(5)	116.1(7)
C(9)-C(4)-C(5)	124.2(7)	C(9)-C(8)-C(7)	121.0(6)
C(8)-C(9)-C(4)	115.4(6)	C(12)-C(11)-C(10)	121.4(10)
C(8)-C(7)-C(6)	123.1(7)	C(13)-C(12)-C(11)	119.6(10)
C(15)-C(10)-C(11)	119.9(8)	C(15)-C(14)-C(13)	121.1(9)
C(14)-C(15)-C(10)	117.4(7)	C(22)-C(21)-C(20)	118.2(9)
C(14)-C(13)-C(12)	120.4(10)	C(23)-C(22)-C(21)	121.1(10)
C(25)-C(20)-C(21)	121.4(8)	C(25)-C(24)-C(23)	121.4(8)
C(24)-C(25)-C(20)	118.5(8)	C(32)-C(31)-C(30)	120.0(9)
C(24)-C(23)-C(22)	119.4(9)	C(33)-C(32)-C(31)	119.6(10)
C(35)-C(30)-C(31)	121.3(8)	C(35)-C(34)-C(33)	118.9(8)
C(34)-C(35)-C(30)	118.2(7)	C(34)-C(33)-C(32)	121.9(9)

halogen dihedral angles in $ICH_2CH_2SSSCH_2CH_2I$ are also almost 180°; [17]). Some of the angles involving the β-S atoms, S(1), in III are C(15)-Sn---S(1) = 155.2(1), C(25)-Sn---S(1) = 80.8(1), C(35)-Sn---S(1) = 89.3(10) and C(1)-Sn---S(1) = 50.7(1)°. Corresponding values in II (Y = Me) are C(15)-Sn---S = 155.5(2), C(25)-Sn---S 83.7(2), C(35)-Sn---S 85.7(2) and C(1)-Sn---S 49.0(2). These values and the solid state conformation point to some Sn---S(β) interaction.

Table 4

Coordinates and equivalent isotropic temperature factors ($\times 10^3$) for III with e.s.d.s in parentheses

	x	y	z	U_{eq} [a]
Sn	1603(1)	1033(1)	2855(1)	47(1)
S(1)	−2564(1)	−1559(1)	1760(1)	68(1)
S(2)	−264(1)	1745(1)	1339(1)	72(1)
N(1)	−2075(5)	−4314(4)	1606(3)	78(1)
N(2)	−3054(7)	843(5)	−333(3)	113(2)
O(1)	−2408(5)	−3455(4)	2239(3)	92(1)
O(2)	−1444(7)	−5216(5)	1652(3)	131(2)
C(15)	3549(4)	2647(3)	3002(2)	50(1)
C(10)	3882(6)	3981(4)	3697(3)	63(1)
C(11)	5145(7)	5027(4)	3797(3)	76(1)
C(12)	6095(6)	4744(5)	3201(3)	77(1)
C(13)	5786(6)	3434(5)	2502(3)	74(1)
C(14)	4517(5)	2381(4)	2405(3)	61(1)
C(25)	407(4)	1868(3)	3890(3)	53(1)
C(20)	713(5)	1541(4)	4584(3)	65(1)
C(21)	24(7)	2129(6)	5284(3)	86(1)
C(22)	−1006(7)	3031(6)	5299(4)	91(2)
C(23)	−1322(6)	3363(5)	4621(3)	83(1)
C(24)	−623(5)	2792(4)	3927(3)	63(1)
C(35)	2982(4)	−351(3)	3059(2)	51(1)
C(34)	2132(6)	−1569(4)	2940(3)	69(1)
C(33)	3122(7)	−2364(5)	3172(3)	79(1)
C(32)	4964(7)	−1918(6)	3546(4)	88(2)
C(31)	5814(7)	−723(6)	3656(5)	105(2)
C(30)	4831(6)	55(5)	3409(4)	83(1)
C(1)	−490(5)	269(4)	1511(3)	55(1)
C(2)	−2364(5)	−227(4)	1478(3)	68(1)
C(9)	−2568(5)	−3034(4)	767(3)	63(1)
C(4)	−2372(5)	−4239(4)	765(3)	63(1)
C(5)	−2471(7)	−5424(5)	−7(4)	86(1)
C(6)	−2762(8)	−5426(6)	−825(4)	99(2)
C(7)	−2931(8)	−4249(6)	−841(4)	100(2)
C(8)	−2828(6)	−3072(5)	−72(3)	77(1)
C(3)	−1954(6)	1158(4)	341(3)	73(1)

[a] $U_{eq} = \frac{1}{3}[\Sigma_i \Sigma_j a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j]$.

Solution conformations and NMR spectra

The ^{1}H, ^{13}C and ^{119}Sn NMR data for II and III are listed in Table 1; a ^{1}H-^{13}C COSY experiment aided the assignment for II (Y = Me). The protons on the β-carbon atom (H_a and H_b) are diastereotopic. The $\delta(H_a)$ and $\delta(H_b)$ and coupling constant values for II and III in Table 1 can be compared with values for the RSCl adducts of non-metallated alkenes: $PhCH_cClCH_aH_bSC_6H_4NO_2$-*p* [$\delta(H_a) = 3.60$, $J(H_a{-}H_c)$ 8.3 Hz; $\delta(H_b) = 3.72$, $J(H_b{-}H_c)$ 6.7 Hz] and *p*-$MeC_6H_4CH_cClCH_aH_bSC_6H_3(NO_2)_2$-2,4 [$\delta(H_a)$ 3.68, $J(H_a{-}H_c)$ 8.3 Hz; $\delta(H_b) =$ 3.78, $J(H_b{-}H_c)$ 6.8 Hz] [18]. As well as the solid state conformations (Fig. 3), others must be considered in solution (see Fig. 4). Estimations of the populations (a, b and c) of the three staggered conformations in solution can be attempted from the overall ^3J coupling constants [$J(H_a{-}H_c)$ and $J(H_b{-}H_c)$ [19] as well as $J(^{119}Sn{-}H_a)$ and $J(^{119}Sn{-}H_b)$], if values can be deduced for the individual cou-

Table 5

Bond lengths (Å) and valency angles (°) for III

Sn–C(1)	2.204(3)	C(10)–C(15)	1.384(5)
Sn–C(15)	2.139(3)	C(14)–C(15)	1.386(5)
Sn–C(25)	2.129(4)	C(11)–C(10)	1.384(6)
Sn–C(35)	2.125(3)	C(12)–C(11)	1.372(7)
C(9)–S(1)	1.776(4)	C(13)–C(12)	1.372(7)
C(2)–S(1)	1.803(4)	C(14)–C(13)	1.396(6)
C(1)–S(2)	1.841(4)	C(20)–C(25)	1.395(5)
C(3)–S(2)	1.685(4)	C(24)–C(25)	1.391(5)
O(1)–N(1)	1.207(5)	C(21)–C(20)	1.379(7)
O(2)–N(1)	1.218(5)	C(22)–C(21)	1.378(8)
C(4)–N(1)	1.468(5)	C(23)–C(22)	1.373(7)
C(3)–N(2)	1.140(6)	C(24)–C(23)	1.372(6)
C(34)–C(35)	1.374(5)	C(30)–C(35)	1.370(5)
C(33)–C(34)	1.392(6)	C(32)–C(33)	1.367(7)
C(31)–C(32)	1.359(7)	C(30)–C(31)	1.384(6)
C(2)–C(1)	1.506(5)	C(4)–C(9)	1.400(5)
C(8)–C(9)	1.404(6)	C(5)–C(4)	1.379(6)
C(6)–C(5)	1.384(7)	C(7)–C(6)	1.377(8)
C(8)–C(7)	1.369(8)		
C(25)–Sn–C(15)	108.9(1)	C(35)–Sn–C(15)	108.1(1)
C(35)–Sn–C(25)	108.5(1)	C(1)–Sn–C(15)	104.6(1)
C(1)–Sn–C(25)	108.2(1)	C(1)–Sn–C(35)	118.2(1)
C(9)–S(1)–C(2)	104.2(2)	C(3)–S(2)–C(1)	102.0(2)
O(2)–N(1)–O(1)	122.2(4)	C(4)–N(1)–O(1)	118.9(4)
C(4)–N(1)–O(2)	118.8(5)	C(10)–C(15)–Sn	121.1(3)
C(14)–C(15)–Sn	120.8(3)	C(14)–C(15)–C(10)	118.2(3)
C(11)–C(10)–C(15)	121.3(4)	C(12)–C(11)–C(10)	119.8(4)
C(13)–C(12)–C(11)	120.4(4)	C(14)–C(13)–C(12)	119.6(4)
C(13)–C(14)–C(15)	120.7(4)	C(20)–C(25)–Sn	120.0(3)
C(24)–C(25)–Sn	122.1(3)	C(24)–C(25)–C(20)	117.8(4)
C(21)–C(20)–C(25)	120.6(4)	C(22)–C(21)–C(20)	120.3(4)
C(23)–C(22)–C(21)	119.8(4)	C(24)–C(23)–C(22)	120.2(4)
C(23)–C(24)–C(25)	121.3(4)	C(34)–C(35)–Sn	123.9(3)
C(30–C(35)–Sn	117.7(3)	C(30)–C(35)–C(34)	118.1(3)
C(33)–C(34)–C(35)	121.0(4)	C(32)–C(33)–C(34)	119.9(4)
C(31)–C(32)–C(33)	119.5(4)	C(30–C(31)–C(32)	120.6(5)
C(31)–C(30)–C(35)	120.9(4)	S(2)–C(1)–Sn	103.2(2)
C(2)–C(1)–Sn	113.5(3)	C(2)–C(1)–S(2)	112.4(3)
C(1)–C(2)–S(1)	113.3(3)	C(4)–C(9)–S(1)	122.1(3)
C(8)–C(9)–S(1)	121.8(3)	C(8)–C(9)–C(4)	116.1(4)
C(9)–C(4)–N(1)	120.9(4)	C(5)–C(4)–N(1)	115.6(4)
C(5)–C(4)–C(9)	123.5(4)	C(6)–C(5)–C(4)	118.6(5)
C(7)–C(6)–C(5)	119.2(5)	C(8)–C(7)–C(6)	122.1(5)
C(7)–C(8)–C(9)	120.5(5)	N(2)–C(3)–S(2)	175.2(5)

pling constants for each of the conformers. The populations of the conformations of $PhCH_cClCH_aH_bSC_6H_3(NO_2)_2$-2,4 have been previously calculated using values of $^3J_{trans}$(H–H) = 13.5 Hz and $^3J_{gauche}$(H–H) 2.5 Hz [19]. Using the same values (assumption 1) for II (Y = Me) in $CDCl_3$, relative populations of VI : VII : VIII were found to be 52 : 4 : 44 (a : b : c) at 25°C.

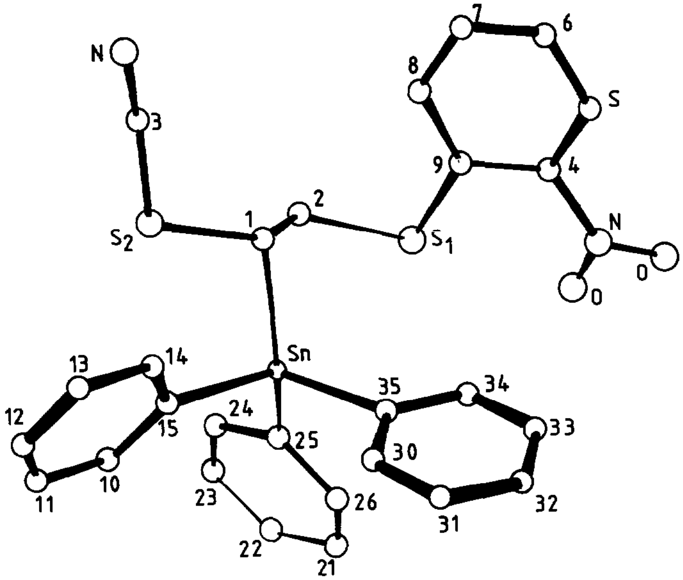


Fig. 2. Molecular structure of III.

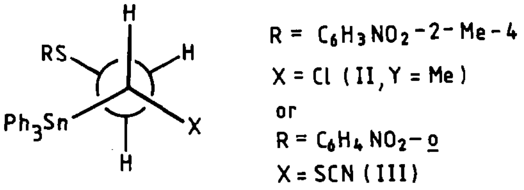


Fig. 3. Solid state conformation of II or III.

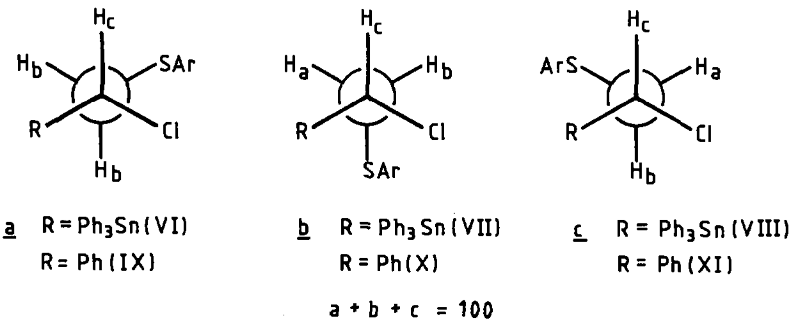


Fig. 4. Conformations of II and $PhCHClCH_2SAr$ in solution.

Table 6

Relative populations of II and $PhCHClCH_2SAr$ at 20°C

Compound	Solvent	VI	:	VII	:	VIII
II (Y = H)	$CDCl_3$ [a]	52± 8	:	12± 8	:	36± 8
II (Y = Me)	$CDCl_3$ [a]	52± 8	:	12± 8	:	36± 8
	C_6D_6 [b]	45± 3	:	12± 7	:	43± 4
	C_5D_5N [b]	53± 3	:	18± 9	:	30± 6
II (Y = NO_2)	$CDCl_3$ [b]	68±13	:	6± 2	:	26±11
		IX	:	X	:	XI
$PhCHClCH_2SC_6H_3(NO_2)_2$-2,4	$CDCl_3$ [c,d]	55	:	12	:	32
$PhCHClCH_2SC_6H_4NO_2$-*o* [b]	$CDCl_3$	53	:	9	:	38

[a] Based on ^3J(H-H) values [assumptions (1) and (2), see text] and on ^3J(Sn-H) values. [b] Based only on ^3J(H-H) values [assumptions (1) and (2)]. [c] [17]. [d] Based only on ^3J(H-H) values [assumption (1)] [16].

An elaborate empirical formula to determine ^3J(H-H) has been developed by Pachler [20]. This formula (eq. 3) takes account of both the electronegativities (E_X) of the substituents (X) on the CH-CH moiety and the spatial arrangements of these substituents, in terms of θ:

$$\begin{aligned}^3J(\text{H-H}) = {} & (7.48 - 0.74\Sigma\ \Delta E_X) - (2.03 - 0.17\Sigma\ \Delta E_X)\cos\theta \\ & + (4.60 - 0.23\Sigma\ \Delta E_X)\cos 2\theta + (0.06\Sigma \pm \Delta E_X)\sin\theta \\ & - (0.62\Sigma \pm \Delta E_X)\sin 2\theta. \qquad (3)\end{aligned}$$

where $\Delta E_X = (E_X - E_H)$ and the sign of $\pm\Delta E_X$ depends on the spatial arrangement of the substituent, X, relative to the coupling protons.

Use of this equation (assumption 2) provides relative populations of II (Y = Me) in $CDCl_3$ of 44:20:36 for VI:VII:VIII.

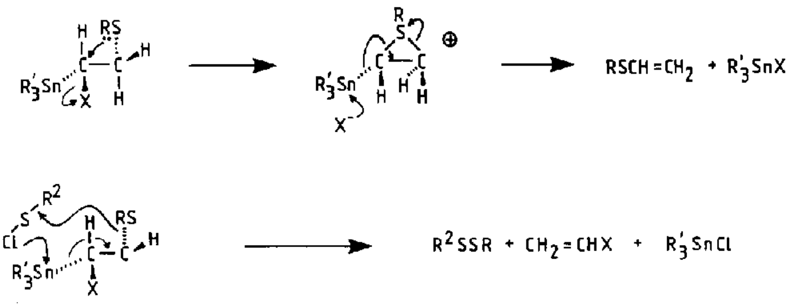
Values of $^3J(^{119}\text{Sn}-^1\text{H})$ of 170 Hz (J_t^{Sn}) and 15 Hz (J_g^{Sn}) have been derived for Sn-C-C-H dihedral angles of 180° and 60° respectively in alkyl- and cycloalkylstannanes [21]. Assuming that these apply also with the functionally substituted alkyltriphenylstannane II (Y = Me), the $J(^{119}\text{Sn}-^1\text{H}_a)$ and $J(^{119}\text{Sn}-^1\text{H}_b)$ values of 57.2 and 35.2 Hz provide relative populations of VI:VIII:VIII of 60:12:28. Combining the three calculations, the values obtained are (52 ± 8):(12 ± 8):(36 ± 8) for VI, VII and VIII at 25°C. The differences between the three calculations point to the problems in choosing suitable J values for the conformers. However despite this, the results do provide useful indications of the relative populations.

Table 7

^{1}H NMR spectral data for II (Y = Me) in $CDCl_3$ at various temperatures [a]

Temp. (°C)	H_c	H_b	H_a	$J(H_a-H_b)$	$J(H_a-H_c)$	$J(H_a-H_c)$	$J(^{119}Sn-H_c)$	$J(^{119}Sn-H_b)$	$J(^{119}Sn-H_a)$
−30	4.46	3.56	3.92	14.00	7.75	8.45	17.3	32.7	70.2
0	4.42	3.61	3.84	13.89	8.24	7.70	17.4	34.6	62.3
24	4.39	3.65	3.79	13.79	8.33	7.22	17.6	35.6	57.2

[a] Relative populations of conformers, (VI):(VII):(VIII) using assumption (1), see text = 45:1:54 (−30°), 52:1:47 (0°) and 52:4:44 (25°C).



Scheme 1.

They show, for example, that the most hindered VII conformer is the least populated conformation and that the solid state conformation is only populated for *ca.* 1/3 of the time in solution. This provides a further pointer to the weakness of the tin (β)–sulphur intramolecular interaction. From ^{1}H NMR spectral data for II (Y = Me) at other temperatures (Table 7), it can be calculated that the population of conformer VIII slightly increases as the temperature is lowered at the expense of both VI and VII. This is found no matter which assumption is used in the calculation. Calculated populations for other II are listed in Table 6.

Reactions of II

As shown previously [6], adducts (I, X = Cl or Br), slowly decompose on standing in solution to R'_3SnX and CH_2=CHSR, while on reaction with sulphenyl halides, CH_2=CHX is eliminated (Scheme 1).

The ideal geometry for both reactions in Scheme 1 has the S–C(H_2) bond (i) in a *cisoid* arrangement with the Sn–C(HCl) bond, for concerted formation of CH_2=CHX and (ii) in a *transoid* arrangement with the C–X bond for formation of CH_2=CHSR. The solid state conformation is thus suitable for these reactions. Although this conformation is only occupied for *ca.* $\frac{1}{3}$rd of the time in solution, low conformational barriers will enable II to react, as in Scheme 1, *via* (VIII).

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