Stereochemical Aspects of Sulfur Dioxide Insertion into Cyclohex-2-enylstannanes

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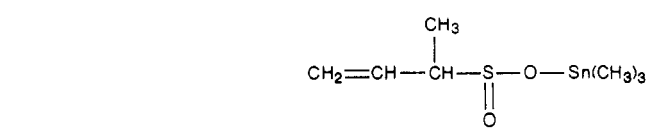
Sulfur dioxide insertion into a range of (4-alkylcyclohex-2-enyl)-, (5-alkylcyclohex-2-enyl)-, and (6-alkylcyclohex-2-enyl)stannanes has been studied for the solvents chloroform and methanol, and the reaction proceeds γ-regiospecifically (with allylic rearrangement) to provide the *O*-sulfinate. For chloroform solvent, syn stereospecificity was observed (and hence sulfur dioxide insertion is less sensitive to steric factors than trifluoroacetolysis) whereas for methanol solvent (despite γ-regiospecificity) insertion is not stereospecific, possibly reflecting the importance of methanol coordination at tin, reducing the necessity for intramolecular coordination and the consequential operation of the γ-syn stereocourse. Comparisons of the results for acidolysis and sulfur dioxide insertion of cyclohex-2-enylstannanes demonstrate that S_E' reactions lack a unique, stereoelectronically enforced stereochemical outcome and that factors such as the nature of the electrophile, solvent, steric factors, etc. may operate to render γ-syn and γ-anti stereocourses of comparable energies.

Introduction

In the preceding paper,[1] we demonstrated that γ-anti acidolysis was highly preferred for cyclohex-2-enyl metallics, unless severe steric factors operated, in which circumstances γ-syn substitution becomes competitive. We also opined that the syn/anti stereo competition could be regulated if a suitable appendage of the electrophile could coordinate with (and hence stabilize) the departing metallo group, via a cylic ensemble (S_Ei'), leading to syn substitution. These requirements appeared likely to be met by the sulfur dioxide insertion reaction into carbon–tin bonds, aspects of which are well-established, particularly the production of *O*-sulfinate products[2] and complete rearrangement[3] of allylic moieties attached to tin, as shown.

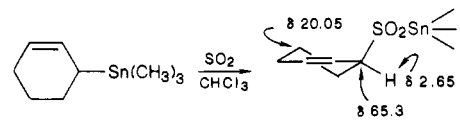


Kinetic,[4] substituent effect,[4] and other studies support an electrophilic mechanism for insertion, and possible O···Sn interaction in the transition state, as part of the cyclic ensemble alluded to above. We now wish to present in detail[5] our examination of the stereochemical aspects of sulfur dioxide insertion into cyclohex-2-enylstannanes, which establish a highly preferred (if not stereospecific) mode of γ-syn insertion for noncoordinating solvents (e.g. chloroform) and confirm the absence of a stereochemical rule for S_E' processes.

Results and Discussion

Treatment of cyclohex-2-enyltrimethylstannane (in chloroform) with gaseous sulfur dioxide produced a very viscous gel or semisolid, which, without further purification, analyzed adequately for the monoinsertion product, and infrared spectra confirmed the *O*-sulfinate structure. The ^{13}C NMR spectrum established that insertion occurred between the cyclohexenyl ring and tin, as $^{119,117}Sn$ spin coupling to ring carbons was not now observed, whereas that to methyl carbons (525 and 502 Hz) was. The presence of seven signals only (excluding Sn–C satellites about $(CH_3)_3Sn$) confirmed monoinsertion.

Scheme I



The ^{13}C NMR spectrum was assigned by comparison with that of the deuteriated analogue (^2H equally distributed between C_1 and C_3), and these data were of value in stereochemical conclusions when the (alkylcyclohex-2-enyl)stannanes are employed. (^{119}Sn NMR measurments on some insertion products were conducted, but these signals were quite broad and variable with concentration and of very limited diagnostic value).

The ^1H NMR spectrum was characterized by a downfield shift of the $(CH_3)_3Sn$ resonance (to δ 0.54 ($^2J_{^{119,117}Sn-H}$ = 69.8; 66.9 Hz)) and of C*H*SO_2Sn (δ 2.65 ($w_{1/2} \approx 13$ Hz)), compared with the corresponding proton shifts in the starting stannane.[3,4] The increased value of $^2J_{Sn-H}$ (from ca. 54 Hz) is characteristic of a pentacoordinate $(CH_3)_3Sn^{IV}$ system,[2] probably achieved by aggregation in solution. The width and shape of C*H*SO_2Sn suggests a predominately quasi-equatorial proton,[6] and the shielding of C_5 (20.05 ppm compared with 22.9 ppm for C_4 of cyclohexene) supports a quasi-axial sulfinate group. Reaction of cyclohex-2-enyltriphenylstannane proceeded in an analogous fashion (no phenyltin insertion), and for the product, the C*H*SO_2Sn signal resonated at δ 2.56 ($w_{1/2} \approx 14$ Hz), now to *higher* field of C*H*Sn in the starting stannane (δ 2.89). This unusual shielding has been attributed to the orientation of the phenyl groups in an aggregated product species.[2,7]

Insertion into (5-Alkylcyclohex-2-enyl)stannanes. Reaction of (5-methylcyclohex-2-enyl)trimethylstannane

(1) Wickham, G.; Young, D.; Kitching, W. *Organometallics*, preceding paper in this issue.
(2) For leading references see: Kitching, W.; Fong, C. W. *Organomet. Chem. Rev., Sect. A* **1970**, *5*, 281. Also: Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 32.
(3) Fong, C. W.; Kitching, W. *J. Organomet. Chem.* **1970**, *22*, 107.
(4) Fong, C. W.; Kitching, W. *J. Am. Chem. Soc.* **1971**, *93*, 3791. Fong, C. W.; Kitching, W. *J. Organomet. Chem.* **1973**, *59*, 213.
(5) For previous communications see: Young, D.; Kitching, W. *J. Org. Chem.* **1983**, *48*, 614; *Tetrahedron Lett.* **1983**, *24*, 5793.
(6) For analogous examples see: Wickman, G.; Young, D.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 4884.
(7) Fong, C. W. Ph.D. Thesis, University of Queensland, 1971.

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Scheme II

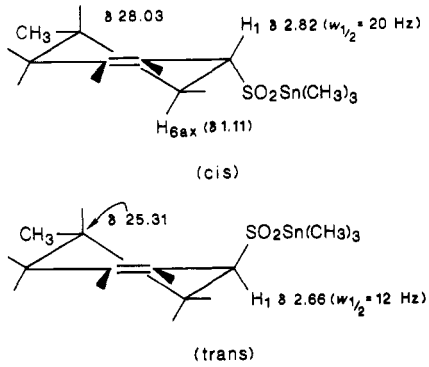
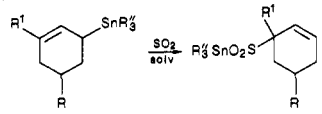


Table I



entry	R	R^1	R″	cs/trans[a]	solv	cis/trans[a]
1	CH_3	H	CH_3	59:41	$CDCl_3$	59:41
2	CH_3	H	CH_3	71:29	$CDCl_3$	67:33
3	CH_3	H	CH_3	29:71	$CDCl_3$	25:75
4	CH_3	H	CH_3	30:70	$CDCl_3$	34:66
5	CH_3	H	CH_3	58:42	CD_3OD	ca. 39:61
6	CH_3	H	CH_3	36:64	CD_3OD	ca. 31:69
7	CH_3	H	Ph	22:78	$CDCl_3$	23:77
8	CH_3	H	Ph	81:19	$CDCl_3$	83:17
9	CH_3	CH_3	CH_3	72:28	$CDCl_3$	31[b]:69[b]
10	CH_3	CH_3	CH_3	64:36	$CDCl_3$	36[b]:64[b]
11	CH_3	CH_3	CH_3	64:36	CD_3OD	65:35
12	$(CH_3)_3C$	H	CH_3	24:76	$CDCl_3$	26:74
13	$(CH_3)_3C$	H	CH_3	62:38	$CDCl_3$	61:39

[a] Ratios of starting stannanes and product sulfinates were determined by ^1H, ^{119}Sn, and ^{13}C NMR spectroscopy. [b] Refers to orientation of methyl groups.

(cis/trans = 59:41) with sulfur dioxide in chloroform provided the monoinsertion product as a viscous gel, consisting, on the basis of the ^{13}C NMR spectrum, of two isomeric sulfinates (60:40). The signals were assigned by consideration of the data for the parent sulfinate, other 5-methylcyclohex-2-enyl derivatives, and certain deuteriated sulfinates. The major sulfinate (59%) was assigned as the *cis* diastereomer, primarily on the basis of the shielding of C_5 in the minor isomer ($\Delta\delta = 2.72$), attributable to the γ-shielding effect on the sulfinate group.

The ^1H NMR spectrum confirmed these assignments firstly because H_1 in the major sulfinate was considerably broader, indicative of a quasi-axial proton.[6] This orientation was required by the appearance of H_{6ax} (δ 1.11) as a quartet ($J \approx 12$ Hz), requiring three large couplings (to H_{6e}, H_5, and H_1). Reaction of a predominately trans stannane mixture resulted in the trans rich sulfinate mixture. The results are shown below in Table I (entries 1–4) and confirm syn insertion consistent with the S_Ei' description.

The regiochemistry (not assessable in the unlabeled 5-alkyl system) was examined by utilizing a predominantly (*cis*-5-methylcyclohex-2-enyl)trimethylstannane (68%) which was ^2H labeled at C_3 (vinylic; 58%) and C_1 (allylic; 42%) whereas the label was equally distributed between C_1 and C_3 in the minor (32%) trans stannane.[6] A combination of ^2H and ^{13}C NMR spectra confirmed that for the cis stannane, SO_2 insertion was accompanied by allylic rearrangement and as noted before syn stereochemistry. (The ^2H signals in the sulfinate product were at δ 2.73 (ca. 66%) and 5.76 (ca. 34%).) A further assay of the regiochemistry was conducted by employing (3,5-dimethylcyclohex-2-enyl)trimethylstannane (cis/trans = 72:88). The ^1H NMR spectrum of the insertion product exhibited two vinylic proton signals and none for $CHSO_2Sn$, indicating complete allylic rearrangement accompanied insertion into both the cis and trans stannanes. The ^{13}C NMR spectrum consisted of two sets of signals ca. 69:31 for the sulfinate isomers, and these spectra were assigned by comparisons with spectra of the (5-methylcyclohex-2-enyl)sulfinates, and *cis*- and *trans*-3,5-dimethylcyclohexene and other model compounds. A full discussion is presented elsewhere,[8] but it was concluded that the minor sulfinate (with C_6 to lower field by 2.54 ppm than in the major sulfinate) was the cis isomer (i.e. the methyl groups are cis). Other aspects of the ^{13}C and ^1H NMR spectra were in line with this analysis.

Although stereochemical determinations were not as straightforward in this system, it is clear that SO_2 insertion is highly regioselective for both isomeric stannanes and yields the less stable tertiary allylic sulfinates. (Excess sulfur dioxide induced a slow decomposition of these compounds.) (See Table I, entries 9 and 10.)

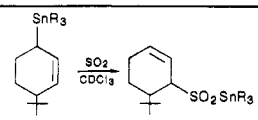
(*cis*-5-Methylcyclohex-2-enyl)- and (*trans*-5-methylcyclohex-2-enyl)triphenylstannanes reacted cleanly with SO_2 in chloroform, and the ^1H and ^{13}C NMR spectra of the sulfinates permitted straightforward stereochemical assignments. $CHSO_2Sn$ signals appeared at δ 2.21 ($w_{1/2}$ = 14 Hz) (trans) and 2.05 ($w_{1/2}$ = 28 Hz) (cis), somewhat to higher field than the corresponding signals for the trimethyltin derivatives. Highly stereoselective syn insertion occurred, with the trans stannane reacting marginally faster than the cis (^1H NMR monitoring) (Table I, entries 7 and 8).

Reaction of predominantly (*cis*-3,5-dimethylcyclohex-2-enyl)triphenylstannane with SO_2 (in chloroform) provided sulfinates that were very unstable. ^{13}C signals which could be assigned to the products (and the signals for decomposition products) indicated that both isomeric sulfinates were tertiary. The primary evidence for this conclusion was the position of the methyl signals at quite high field (δ 17.77 (major) and 17.36), which compared well with those for the insertion products of (*cis*-3,5-dimethylcyclohex-2-enyl)- and (*trans*-3,5-dimethylcyclohex-2-enyl)trimethylstannanes at 16.80 (cis) and 17.94 ppm (trans). The major sulfinate was tentatively assigned trans stereochemistry (i.e. *trans*-methyl groups).

The reactions of the nearly conformationally homogeneous (*cis*-5-*tert*-butylcyclohex-2-enyl)- and (trans-5-*tert*-butylcyclohex-2-enyl)trimethylstannanes with SO_2 in chloroform proceeded with the same γ-syn stereopath that characterized the 5-methyl compounds. Stereochemical conclusions were based on ^{13}C and ^1H NMR assignments as outlined for the 5-methyl compounds, with particular emphasis on the C_5 chemical shifts ($\Delta\delta$ = 3.10 ppm; higher field C_5 being trans) and width of the H_1 signals as before. In the cis isomer H_{6ax} was identified (δ 1.07) as a quartet ($J \approx 11.8$ Hz). The regiochemistry of this reaction was examined by using a deuteriated derivative, and the cis isomer (with unequal ^2H distributions between positions 1 (46%) and 3 (54%)) at least reacts with high γ-selectivity. Examination of a reaction after the addition of approximately 0.5 equiv of SO_2 revealed nearly identical reactivities for the cis and trans isomers. This was of interest and indicated that the γ-syn mode observed with both the (cis-5-methylcyclohex-2-enyl)- and (*trans*-5-methylcyclohex-2-enyl)stannanes was not dependent on conformational mobility.[5] Additionally, the γ-syn insertion

(8) Young, D. Ph.D Thesis, University of Queensland, 1986.

Table II



entry	R	cis/trans	cis/trans
1	CH_3	33:67	36:64
2	CH_3	71:29	73:27
3	Ph	13:87	16:84
4	Ph	64:36	68:32

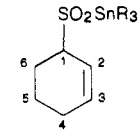
into *cis*-5-*tert*-butyl stannane at about the same rate as for the trans stannane (with quasi-axial tin group) was somewhat surprising as the cis isomer would require more geometrical reorganization to permit a cyclic transition state apparently favored for this insertion in chloroform. This would require the C–Sn bond to be substantially perturbed with bond lengthening and significant rehybridization (formal sp^3 toward sp^2) at the carbon bearing tin, permitting the tin atom to be incorporated and enjoying O–Sn stabilizing within a cyclic coordinative ensemble (Table I, entries 12 and 13).

Insertion into (4-Alkylcyclohex-2-enyl)- and (6-Alkylcyclohex-2-enyl)stannanes. (*cis*-4-*tert*-Butylcyclohex-2-enyl)- and (*trans*-4-*tert*-butylcyclohex-2-enyl)trimethylstannane reacted cleanly with SO_2 in chloroform to yield the rearranged sulfinates. (Table II, entries 1 and 2). That the products were the rearranged (6-*tert*-butylcyclohex-2-enyl)sulfinates was confirmed by a number of features in the ^1H and ^{13}C NMR spectra. For example, the ^{13}C shifts of the *tert*-butyl groups were to lower field than those for 4-*tert*-butyl derivatives, indicating the proximity effect of the $(CH_3)_3SnOSO$ moiety. The chemical shifts of ring carbons also required the rearranged structure. The $CHSO_2Sn$ ^1H signals for the isomeric sulfinates were relatively narrow (δ 3.14 (br t, $w_{1/2} \approx 11.7$ Hz), 2.73 (br d, $w_{1/2} = 10.2$ Hz)), and by monitoring it was clear that the δ 2.7o signal developed from the trans stannane, which reacted ca. 5–8 times as fast as the cis stannane. ^1H NMR comparisons with *cis*- and *trans*-6-methylcyclohex-2-enyl chlorides confirmed the assignment of the δ 3.14 signal to the cis isomer. This was supported by the C_5 chemical shift in this isomer (19.51 ppm), some 2.4 ppm to higher field of the corresponding signal of the trans isomer, again reflecting the shielding γ-effect of the $SO_2Sn(CH_3)_3$ group.

Thus, both (*cis*-4-*tert*-butylcyclohex-2-enyl)- and (*trans*-4-*tert*-butylcyclohex-2-enyl)stannanes undergo strict γ-syn SO_2 insertion, and the slightly slower rate of the trans stannane may reflect some impedance of SO_2 approach to the γ-carbon but insufficient to promote detectable γ-anti substitution for this solvent ($CHCl_3$). By contrast, steric hindrance to γ-anti acidolysis of this *trans*-4-*tert*-butyl stannane resulted in predominant γ-syn cleavage.[1] These observations may again suggest that carbon–tin bond perturbation is advanced in the transition state, whereas carbon–sulfur bond formation is lagging or reflects sulfurs' ability to form bonds at larger distances.

Similar observations apply to insertion into the (*cis*-4-*tert*-butylcyclohex-2-enyl)- and (*trans*-4-*tert*-butylcyclohex-2-enyl)triphenylstannanes (for chloroform solvent) (Table II, entries 3 and 4). The ^{13}C NMR spectra were of interest in that the trans triphenylstannyl sulfinate consisted two diastereomers in approximately equal amounts. The spectrum (assigned by INEPT sequence etc.) exhibited a particularly large chemical shift difference ($\Delta\delta$ = 6.0 ppm) for C_6 in the diastereomers, which arise from the chiral sulfur center present in a monomeric *O*-sulfinate. We presume aggregation in this sulfinate (by bridging O–S(R)–O groups with consequential achiral sulfur) is hindered by the adjacent *tert*-butyl group.

Table III. Trimethyl- and Triphenylstannyl Cyclohex-2-enylsulfinate Derivatives



compd no.	R	substitutn	stereoisomer
1	Me		
2	Ph		
3	Me	5-Me	cis
4	Me	5-Me	trans
5	Ph	5-Me	cis
6	Ph	5-Me	trans
7	Me	1,5-Me_2	cis[a]
8	Me	1,5-Me_2	trans[a]
9	Me	5-*t*-Bu	cis
10	Me	5-*t*-Bu	trans
11	Me	6-*t*-Bu	cis
12	Me	6-*t*-Bu	trans
13	Ph	6-*t*-Bu	cis
14	Ph	6-*t*-Bu	trans
15	Me	4-Me	cis
16	Me	4-Me	trans
17	Me	6-Me	cis
18	Me	6-Me	trans

[a] Stereochemistry refers to the two methyl groups.

As detailed elsewhere,[9] (*cis*-4-methylcyclohex-2-enyl)- and (*trans*-4-methylcyclohex-2-enyl)trimethylstannanes were obtained as mixtures with the *cis*- and *trans*-6-methyl isomers. Examination of the regio- and stereochemistry of insertion into this four-component mixture appeared a daunting task, but fortunately key regions of the ^1H and ^{13}C NMR spectra were well-resolved and permitted unequivocal conclusions. Reaction of stannane mixture A1 below with SO_2 (in $CDCl_3$) produced a four-component sulfinate mixture S1, and detailed scrutiny of the ^1H and ^{13}C NMR spectra led to Scheme III below. The 6-methyl sulfinates were identified by their lower field C_1 shifts (71.33 and 70.48 ppm) compared with those of the 4-methyl sulfinates (65.50 and 65.24 ppm), the difference ascribable to the deshielding β-methyl effect. Similarly, the CH_3–C shifts of the 6-methyl sulfinates are to higher field, reflecitng the shielding γ-effect of the $SO_2Sn(CH_3)_3$ group, which would be more severe in the *cis*-6-methyl isomer (19.36 and 16.22 ppm compared with 21.09 ppm for the 4-methyl isomers). Further differentiation within the 4-methyl and 6-methyl stereoisomer pairs was based on the position and shape of the $CHSO_2Sn\equiv$ ^1H shifts (Figure 1) as well as trends in the ^{13}C chemical shifts. For example, the 4-methyl isomers exhibited such signals closer together (δ 2.63 and 2.70) and with different $w_{1/2}$ values (11 and 17 Hz, respectively) than the 6-methyl pair (δ 2.45 ($w_{1/2} \approx 9$ Hz) and 2.76 ($w_{1/2} \approx 16$ Hz)). These trends parallel those for the corresponding chlorides.[9]

The above approaches to sulfinate identification were supplemented in the following way. As described in detail elsewhere,[9] 4-methylcyclohex-2-enol-*1-d* was chlorinated and trimethylstannylated to yield stannane mixture A2 below. In the resulting sulfinate mixture S2, *two* signals in the $CHSO_2$ region (δ 2.76 and 2.43) (ratio 1.55:1) were observed and on the basis of γ-insertion must correspond to the (*cis*-6-methylcyclohex-2-enyl)- and (*trans*-6-methylcyclohex-2-enyl)sulfinates as shown in Scheme III.

(9) Young, D.; Kitching, W.; Wickham, G. *Aust. J. Chem.* **1984**, *37*, 1841.

Scheme III

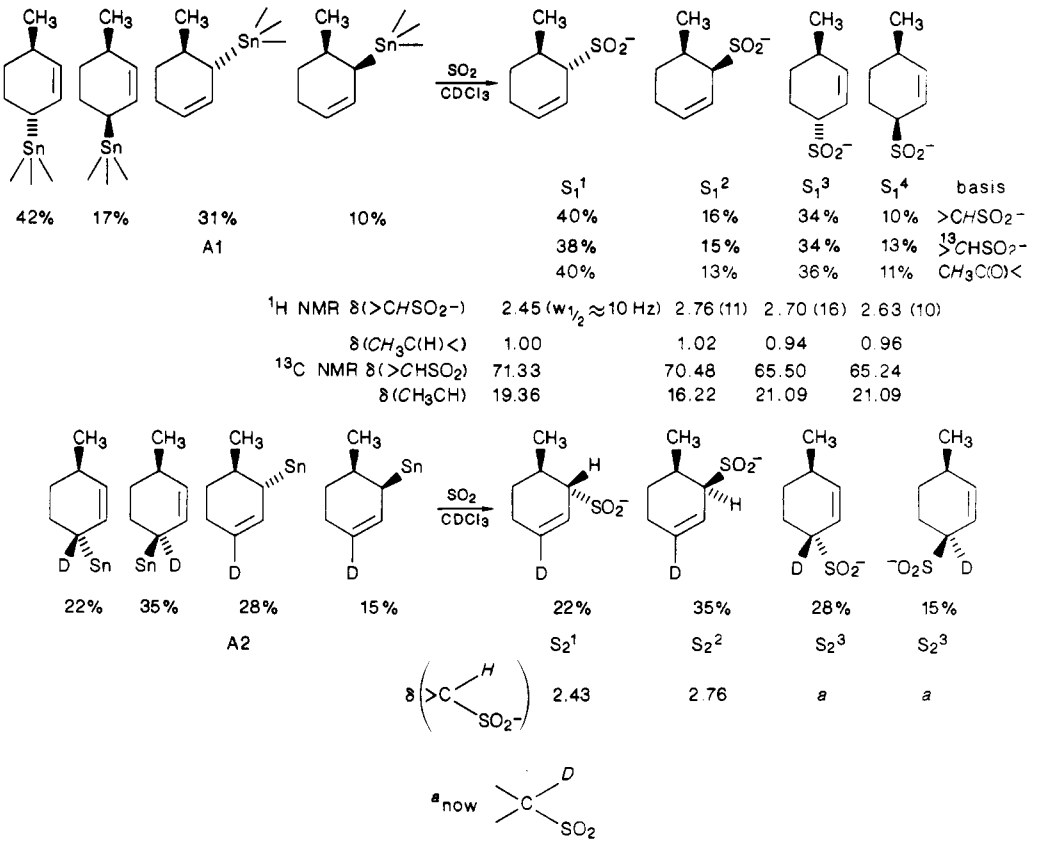


Table IV. Carbon-13 NMR Data for Various Cyclohex-2-enylsulfinates

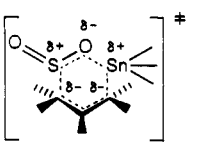
	carbon number							
compd	1	2	3	4	5	6	SnR_3	others
1	65.30	121.73	132.67	24.87	20.05	22.12	1.33[a]	
2	63.92	121.20	131.85	24.58	19.81	20.31	*b*	
3	66.35	121.32	132.17	33.77	28.03	30.23	1.21[a]	22.12
4	66.15	121.52	132.40	33.50	25.31	30.37	1.21[a]	21.69
5	64.64	120.92	130.95	33.47	27.60	27.97	*b*	21.84
6	64.26	120.92	131.28	32.87	24.62	28.52	*b*	21.03
7	61.67	127.34	131.29	33.56	24.87	38.97	1.18[a]	22.04, 16.80
8	62.37	128.78	130.88	34.06	25.49	36.43	1.18[a]	22.12, 17.94
9	67.20	121.32	132.64	26.72	43.04	23.76	1.33[a]	27.13, 32.36
10	67.20	121.70	133.08	26.72	39.94	23.76	1.33[a]	27.04, 32.22
11	67.00	120.39	133.03	27.37	19.51	47.84	1.29[a]	28.82, 32.98
12	66.23	122.07	133.03	27.27	21.87	40.05	1.29[a]	28.74, 33.65
13	66.08	119.69	134.40	27.17	19.33	47.64	*b*	32.66, 28.62
14[c]	64.46	120.39	134.09	25.27	23.11	45.98	*b*	33.27, 28.06
				24.48	21.78	39.89	*b*	27.36
15	65.25	120.98	138.76	30.02	28.18	21.13	1.36[a]	21.18
16	65.54	120.81	138.62	30.02	29.31	20.90	1.36[a]	21.18
17	70.53	121.19	131.39	23.10	27.98	28.59	1.36[a]	16.15
18	71.43	120.22	132.06	22.35	27.15	26.75	1.31[a]	19.28

[a] Chemical shifts in ppm are referenced to the central peak of the $CDCl_3$ triplet at 77.00 ppm. Values of $^{119}Sn-^{13}C$ coupling constants in $(CH_3)_3Sn$ derivatives ranged from 511 to 525 Hz and $^{117}Sn-^{13}C$ couplings from 488 to 502 Hz. [b] Typical shifts for $(C_6H_5)_3SnOSO$ are 141.49 (761.7 Hz; ipso carbon), 136.64 (47.6 Hz; ortho carbon), 128.11 (71.6 Hz; meta carbon), and 129.90 ppm (0.0 Hz; para carbon). [c] This compound consists of two diastereomers in equal proportions.

The proportion of sulfinates in S2 were deterined by careful ^1H and ^{13}C NMR measurements. The ^{13}C NMR spectra of the four sulfinates were completely assigned with the aid of these deuteriated derivatives and a DEPT (polarization transfer) experiment (Table IV).

Clearly, each of the isomeric stannanes undergoes highly stereo- and regioselective γ-syn insertion of sulfur dioxide, with no detectable deterrent to this stereopath posed by the methyl group in the *cis*-4-methyl isomer. A partial reaction revealed roughly equal rates for the four stannanes, with formation of the *cis*-6-methyl sulfinate being marginally slower. For chloroform solvent, oxygen coordination probably serves to stabilize developing positive charge on the leaving $(CH_3)_3Sn$ group, and this can operate intramolecularly for a syn insertion, as shown below.

Scheme IV



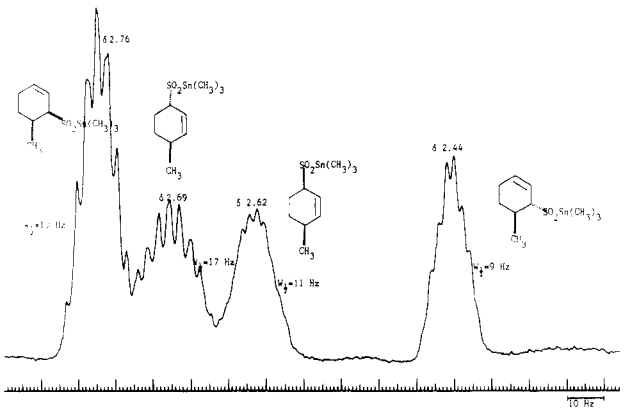


Figure 1. The 300-MHz ^1H NMR spectrum ($CDCl_3$ solvent) in the $CHSO_2Sn$ region of a mixture of the (*cis*-4-methylcyclohex-2-enyl)-, (*cis*-methylcylcohex-2-enyl)-, (*trans*-4-methylcyclohex-2-enyl)- and (*trans*-6-methylcyclohex-2-enyl)sulfinates arising from sulfur dioxide insertion into the precursor stannanes.

However, in the case of the pin-2-en-4-ylstannanes[10] steric effects can enforce apparent γ-anti insertion for chloroform solvent, but this proceeds very slowly compared with γ-syn insertion, perhaps highlighting the importance of internal coordination for this route in noncoordinating solvents.

If internal (O···Sn) coordination is a key energy lowering factor favoring γ-syn insertion, a change in solvent from chloroform to methanol—efficient coordination at tin[11]—would be anticipated to remove the necessity for cyclic coordination and hence reduce the advantage that the γ-syn route would otherwise enjoy. The choice of methanol as solvent revealed a complication—methanol-induced isomerization of the cyclohex-2-enylstannanes. This phenomenon has been investigated and reported elsewhere,[12] and the isomerization rate was concluded to be slow in comparison with insertion. Reaction of (*cis*-5-methylcyclohex-2-enyl)- and (*trans*-5-methylcyclohex-2-enyl)trimethylstannanes (dissolved in methanol for ca. 2 min before addition of SO_2) provided predominantly the trans sulfinate (ca 60–70%) irrespective of the starting cis/trans ratio. The cis sulfinate was demonstrated not to isomerize in some post-kinetic fashion, and hence the product distributions probably reflect kinetic control (Table I, entries 5 and 6).

This outcome therefore differs from the situation of γ-syn insertion for chloroform solvent. However, insertion under these conditions maintains high γ-regioselectivity, as the results for the (3,5-dimethylcyclohex-2-enyl)stannanes demonstrate (along with other systems) (Table I, entries 10 and 11).

This stereochemistry (with predominantly quasi-axial sulfinate) is opposite to that for chloroform solvent, and the production of the tertiary sulfinate indicates the stereochemistry reflects that of kinetic coontrol. The observation that both *cis*- and *trans*-5-methyl (and *tert*-butyl) provide predominantly the trans sulfinate suggests the tin group has little directing influence, and this stereochemistry may reflect "normal" axial electrophilic attack on cyclohexene. (*cis*-4-*tert*-butylcyclohex-2-enyl)- and (*trans*-4-*tert*-butylcyclohexenyl)stannanes provided exclusively the rearranged (*trans*-6-*tert*-butylcylcohex-2-enyl)sulfinate as determined by careful monitoring by ^1H and ^{13}C NMR. Under these conditions (SO_2 in CH_3OH) allyl anion involvement is excluded (such an intermediate would hardly provide only the 6-*tert*-butyl derivative), and the directing influence of the tin group is insufficient to overcome the steric obstacle to γ-syn cleavage of the cis stannane.

In summary, sulfur dioxide insertion for chloroform solvent indicates the existence of a γ-syn enforcing, coordinatively stabilized cyclic ensemble of allylic stannane and SO_2. When this internal coordination is replaced by external (solvent) methanol coordination, faithful γ-insertion still operates, but with no clear-cut stereochemistry. Thus SO_2 insertion when compared with acidolysis reveals the absence of a stereoelectronically dictated stereochemical rule for S_E' reactions.

Table V. ^1H NMR[a] and Analytical Data[b] for Various Cyclohex-2-enylsulfinates

compd	^1H NMR data and anal. data
1	δ 0.54 (s, J = 69.8, 66.9 Hz, $(CH_3)_3Sn$), 1.42–2.04 (m, 6 H), 2.65 (m, $w_{1/2}$ = 13 Hz, H_1), 5.58 (H_3), 5.95 (H_2). Calcd for $C_9H_{18}O_2Ssn$: C, 34.98; H, 5.87. Found: C, 34.05; H, 5.68.
2	δ 1.22–2.00 (m, 6 H), 2.56 (m, $w_{1/2}$ = 14 Hz, H_1), 5.42 (H_2), 5.80 (H_3); mp 197–198.5 °C). Calcd for $C_{24}H_{24}O_2SSn$: C, 58.21; H, 4.89. Found: C, 58.69; H, 4.99.
3	δ 0.55 (s, $(CH_3)_3Sn$), 0.97 (d, J = 6.2 Hz, CH_3), 1.33–2.18 (m, 5 H), 2.82 (m, $w_{1/2}$ = 20 Hz, H_1), 5.57 (H_2), 5.92 (H_3). Calcd for $C_{10}H_{20}O_2SSn$: C, 37.18; H, 6.24; S, 9.93. Found: C, 37.73; H, 6.28; S, 10.06.
4	δ 0.55 (s, $(CH_3)_3Sn$); 0.90 (d, J = 6.5 Hz, CH_3), 1.33–2.18 (m, 5 H); 2.66 (m, $w_{1/2}$ = 12 Hz, H_1), 5.57 (H_2), 5.92 (H_3)
5	δ 0.94 (d, J = 6.7 Hz, CH_3), 0.90–1.78 (m, 5 H), 2.05 (m, $w_{1/2}$ = 28 Hz, H_1), 4.90 (H_2), 5.39 (H_3). Calcd for $C_{25}H_{26}O_2SSn$: C, 58.97; H, 5.15. Found: C, 56.59; H, 5.00.
6	δ 0.60 (d, J = 5.4 Hz, CH_3), 0.90–1.78 (m, 5 H), 2,21 (m, $w_{1/2}$ = 14 Hz, H_1), 4.90 (H_2), 5.39 (H_3)
7	δ 0.55 (s, $(CH_3)_3Sn$), 0.88 (d, J = 6.5 Hz, CH_3), 0.97 (s, CH_3), 1.25–2.16 (m, 5 H), 5.27 (H_2), 5.90 (H_3 (unstable)
8	δ 0.55 (s, $(CH_3)_3Sn$), 0.96 (d, J = 6.3 Hz, CH_3), 1.04 (s, CH_3), 1.25–2.16 (m, 5 H), 5.37 (H_2), 5.86 (H_3)
9	δ 0.57 (s, $(CH_3)_3Sn$), 0.86 (s, $(CH_3)_3C$), 1.07 (q, J = 11.8 Hz, H_{6a}), 1.27–2.19 (m, 4 H), 2.78 (m, $w_{1/2}$ = 23 Hz, H_1), 5.60 (H_2), 5.95 (H_3). Calcd for $C_{13}H_{26}O_2SSn$: C, 42.77; H, 7.18. Found: C, 43.06; H, 7.08.
10	δ 0.57 (s, $(CH_3)_3Sn$), 0.84 (s, $(CH_3)_3C$), 1.25–2.21 (m, 5 H), 2.70 (m, $w_{1/2}$ = 10 Hz, H_1), 5.58 (H_2), 5.98 (H_3)
11	δ 0.53 (s, $(CH_3)_3Sn$), 0.97 (s, $(CH_3)_3C$), 1.54 (m, H_6), 1.68 (m, H_{5a}), 2.0 (m, H_{4a}, H_{5e}), 2.14 (7, H_{4e}), 3.14 (m, $w_{1/2}$ = 11.7 Hz, H_1), 5.74 (H_2), 6.02 (H_3). Calcd for $C_{13}H_{26}O_2SSn$: C, 42.77; H, 7.18. Found: C, 42.40; H, 7.25.
12	δ 0.53 s, $(CH_3)_3Sn$), 0.88 (s, $(CH_3)_3C$), 1.50–2.20 (m, 5 H), 2.73 (m, $w_{1/2}$ = 10.2 Hz, H_1), 5.65 (H_2), 6.02 (H_3)
13 and 14	δ 0.88 (s, $(CH_3)_3C$), 0.94–1.98 (m, 6 H), 5.70 (H_2, H_3) (unstable)
15[c]	δ 0.56 (s, $(CH_3)_3Sn$), 0.96 (d, J = 7.3 Hz, CH_3), 2.62 (m, $w_{1/2}$ = 11 Hz, H_1). Calcd for $C_{10}H_{20}O_2SSn$: C, 37.18; H, 6.24. Found: C, 38.78; H, 6.48.
16[c]	δ 0.56 (s, $(CH_3)_3Sn$), 0.94 (d, J = 7.0 Hz, CH_3), 2.69 (m, $w_{1/2}$ = 17 Hz, H_1)
17[c]	δ 0.56 (s, $(CH_3)_3Sn$), 1.03 (d, J = 7.1 Hz, CH_3), 2.76 (m, $w_{1/2}$ = 10 Hz, H_1)
18[c]	δ 0.56 (s, $(CH_3)_3Sn$), 1.00 (d, J = 6.8 Hz, CH_3), 2.44 (m, $w_{1/2}$ = 9 Hz, H_1)

[a] Chemical shifts are relative to internal $CHCl_3$ at δ 7.24. Aromatic proton resonances (normally from δ 7.00–7.6.0) are not listed. [b] Microanalyses were performed on isomeric mixtures and are presented with the first isomer listed. [c] Other signals obscured in mixture.

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Experimental Section

Compounds and the Reactions. The cyclohex-2-enylstannanes were prepared and characterized as described previously.[6,9,13] Reactions with sulfur dioxide in chloroform or methanol were conducted (at 0 °C), normally in NMR tubes, and examined directly by ^1H and ^{13}C spectroscopy. The solvent was then removed, and the viscous gel or white solid remaining represented essentially pure insertion product (the cyclohex-2-enylsulfinate). IR spectroscopy established *O*-sulfinato products.[3,4] The key ^{13}C and ^1H NMR spectra are located in Tables IV and V.

NMR Spectra. These were acquired by utilizing the conditions and solvents described fully in the preceding paper.

Registry No. 1, 113353-45-0; 2, 113353-46-1; 3, 113353-47-2; 4, 113378-70-4; 5, 113353-48-3; 6, 113353-49-4; 7, 113353-50-7; 8, 113353-51-8; 9, 113353-52-9; 10, 113353-53-0; 11, 89633-90-9; 12, 89633-91-0; 13, 113353-54-1; 14, 113353-55-2; 15, 89633-99-8; 16, 89633-98-7; 17, 89633-97-6; 18, 89633-96-5; SO_2, 7446-09-5; (*cis*-5-methylcyclohex-2enyl)trimethylstannane, 74089-88-6; (*trans*-5-methylcyclohex-2-enyl)trimethylstannane, 74089-89-7; (*cis*-5-methylcyclohex-2-enyl)triphenylstannane, 83269-35-6; (*trans*-5-methylcyclohex-2-enyl)triphenylstannane, 83269-36-7; (*cis*-3,5-dimethylcyclohex-2-enyl)trimethylstannane, 83269-39-0; (*trans*-3,5-dimethylcyclohex-2-enyl)trimethylstannane, 83269-40-3; (*cis*-5-(1,1-dimethylethyl)cyclohex-2-enyl)trimethylstannane, 84537-09-7; (*trans*-5-(1,1-dimethylethyl)cyclohex-2-enyl)trimethylstannane, 84537-11-1; (*cis*-4-(1,1-dimethylethyl)cyclohex-2-enyl)trimethylstannane, 89633-88-5; (*trans*-4-(1,1-dimethylethyl)cyclohex-2-enyl)trimethylstannane, 89633-89-6; (*cis*-4-(1,1-dimethylethyl)cyclohex-2-enyl)triphenylstannane, 89634-12-8; (*trans*-4-(1,1-dimethylethyl)cyclohex-2-enyl)triphenylstannane, 89634-11-7.

Chemistry of Heavy Carbene Analogues R_2M (M = Si, Ge, Sn). 12.[1] Concerted and Nonconcerted Insertion Reactions of the Germylene Me_2Ge into the Carbon–Halogen Bond

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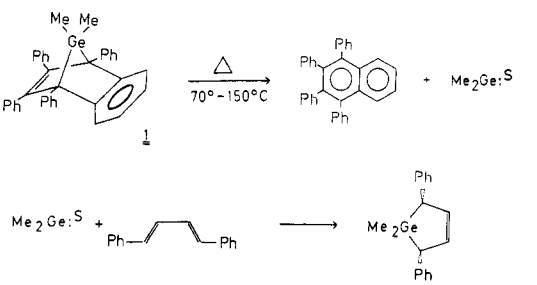
During the reaction of Me_2Ge with CCl_3X (X = Cl, Br), $PhCH_2X$ (X = Br, I), and Ph_2CHCl, ^1H CIDNP is observed in the products of net insertion of Me_2Ge into the carbon–halogen bond and in Me_2GeX_2 (X = Cl, Br). It is concluded that a two-step radical reaction takes place by an abstraction–recombination mechanism. No reaction takes place with alkyl halides that have a C–X bond dissociation energy of more than about 70 kcal/mol. Me_2Ge is generated thermally at 70–95 °C or photochemically from the 7-germabenzonorbornadiene 1 and reacts in both cases in the singlet state. The activation energy for forming Me_2Ge from 1 is 19 kcal/mol for the reaction with CCl_4. Insertion products are also formed with the alkenyl halides CH_2=$CHCH_2X$, PhCH=CHX (X = Cl, Br), and 2-bromobut-2-ene, but without showing CIDNP effects. Since Me_2GeX_2 was not found either, Me_2Ge reacts in these cases in a nonradical manner. It does not react with 1-chlorocyclohexene, but it does react with Me_2GeX_2 under formation of digermanes and/or oligogermanes without CIDNP.

Introduction

Carbenes, R_2C:, play an important role as intermediates in organic chemistry. Similarly, the chemistry of the heavy carbene analogues, the silylenes R_2Si,[3] the germylenes R_2Ge,[4] and the stannylenes R_2Sn,[5] has received much attention in recent years. In principle, the heavy carbene analogues undergo the same types of reactions as the carbenes—addition and insertion—but there are characteristic differences that are still in need of investigation. A question that is still of great interest is the spin state of the reacting intermediate (singlet or triplet). For example, dimethylgermylenes generated by thermolysis from the 7-germabenzonorbornadiene 1[6] or pentamethyldigermane[7] have been shown to undergo concerted 1,4-additions to 1,3-dienes (eq 1), indicating a singlet state for the reacting species.



(1)

Carbenes are known to undergo insertion into the carbon–hydrogen bond. From the beginning of carbene chemistry, two different reaction mechanisms were discussed. The first is a concerted one, meaning that the insertion occurs in a single step without further reaction intermediates via a three-center-type transition state (eq

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