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SYNTHESIS AND STEREOCHEMISTRY OF ACIDOLYSIS OF SOME CYCLOHEPT-2-ENYLSTANNANES AND -SILANES

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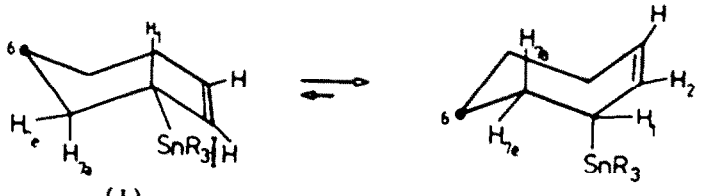
ABSTRACT

A range of methyl-substituted cyclohept-2-enyltrimethylstannanes and trimethylsilanes have been synthesised and characterised by ^{1}H, ^{13}C and ^{119}Sn (or ^{29}Si) nmr spectroscopy. Key conformational characteristics of some of these compounds are discussed. Acidolysis of these stannanes and silanes (with CF_3COOD) proceeds cleanly to provide the ^{2}H-substituted methylcycloheptene resulting from allylic rearrangement i.e. regiospecific γ-attack by the electrophile (S_E'). Detailed examination of the ^{2}H nmr spectra of the methylcycloheptenes establishes a highly preferred, if not specific, γ-*anti* mode of electrophile delivery. Thus, this γ-*anti*-S_E' process may form the basis of synthetically useful applications in what is sometimes an awkward ring system for functionalisation.

INTRODUCTION: The reaction of allylsilanes and -stannanes with electrophiles generally proceeds with allylic transposition (S_E' reaction)[1] and delivery of the electrophile (other than sulphur dioxide)[2] to the π-face *anti* to the carbon-silicon or -tin bond i.e. *anti*-stereochemistry.[3] These generalisations apply to acyclic systems, as well as to some cyclopentenyl and most cyclohexenyl derivatives. Those cases of variable stereochemistry are attributable to the nature of the electrophile, steric factors and ring size.[3] To provide information on this latter aspect, and in anticipation that the S_E' process, if stereochemically reliable, may have synthetic value in the sometimes awkward seven and medium-ring systems, we have examined the stereochemistry of the S_E' process with a range of methyl-substituted cyclohept-2-enylsilanes and -stannanes and are able to report such acidolyses adhere faithfully to the γ-*anti* substitution mode.[4]

RESULTS AND DISCUSSION: To assist in the assignment of relative configurations of the various methyl substituted cyclohept-2-enyl derivatives likely to be encountered, the parent compounds cyclohept-2-enyltriphenylstannane and -trimethylstannane were synthesised from the allylic chloride and triphenyltin- and trimethyltinlithium reagents. Key aspects of their ^{1}H and ^{13}C nmr spectra were assigned, accepting that cycloheptene adopts overwhelmingly the chair conformation.[5] The nmr data require these stannanes to prefer a conformation with a quasi-*axial* tin group (II) a situation confirmed for the solid by an X-ray structural determination[6] for cyclohept-2-enyltriphenylstannane.

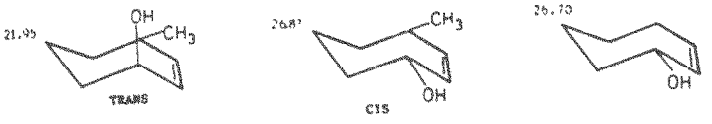


(I) (II)

The 400 MHz ^1H spectrum of cyclohept-2-enyltrimethylsilane[7] is rather compressed and lacks the chemical shift differences between *axial* and *equatorial* protons so obvious in the spectra of the stannanes. This could suggest that more than one conformation is significant for the silane, and we conclude that in the silane, a conformation resembling (I) probably coexists with (II) to a significant degree. This information[6] for the stannanes and silane provides the basis for identifying the stereoisomers of the methyl-substituted cyclohept-2-enylstannanes and silanes.

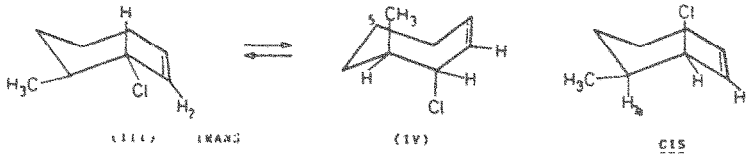
4- and 7-Methylcyclohept-2-enyltrimethylstannanes:

Reaction of the monoepoxide of cyclohepta-1,3-diene with methylcyanocuprate[3,8] affords *trans*-4-methylcyclohept-2-enol on the basis of ^1H and ^{13}C nmr spectra, and comparisons with those of the *cis*-isomer, obtained (70:30) by oxidation (of *trans*) and reduction with $LiAlD_4$ to assist in ^{13}C nmr assignments. A particularly diagnostic feature in the ^{13}C spectrum is shielding of C_6 in the *trans* isomer (21.95 ppm) compared with the *cis* (26.87 ppm) and ascribable to the γ-gauche effect of hydroxyl.



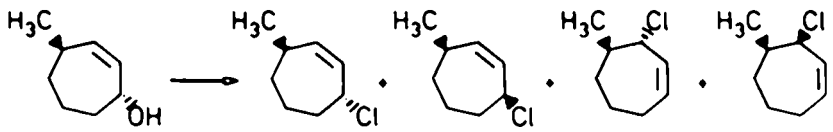
The coupling pattern for H_{7a} (and others) requires the *trans* stereochemistry with a quasi-*axial* hydroxyl group.

Treatment of this *trans*-alcohol with thionyl chloride provided a four component mixture of the allylic chlorides (M^+ = 146, 144 *ca* 3:1) in the ratio of 19:5:15:61 in order of elution (OV101). The major and minor isomers were clearly the rearranged 7-methylcyclohept-2-enylchlorides on the basis of their lower field ^{13}C signals for *C*-Cl at 65.73 and 66.08 ppm, due to the deshielding β-methyl effect. The unrearranged chlorides exhibited analogous signals at 59.89 and 60.15 ppm. Mechanistic considerations[8] would indicate the major isomer was *trans*-7-methylcyclohept-2-enylchloride and the minor (~ 5%) the *cis*-7-methyl isomer. The coupling patterns exhibited by H_1 confirmed this.



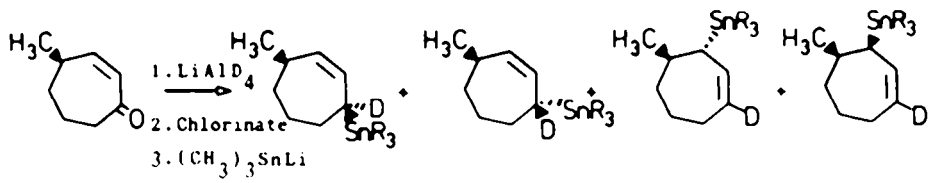
In the minor isomer, this proton was a slightly broadened doublet ($J_{H1\text{-}H2}$; 7 Hz) at δ 4.49 (~ 10^0) with very small coupling to H7a (- ~ 100^0). H_1 in the major isomer (~ 60%) (δ 4.34) appears as a doublet of doublets ($W_{\frac{1}{2}}$ = 14 Hz, J = 7 Hz and 5.4 Hz) and this pattern is difficult to explain on the basis of (III) above. A significant population of (IV) would influence the coupling in the observed direction. (In (III) serious Cl-H_2 and Cl-CH_3 interactions occur) whereas in (IV) there is an important *gauche* butane type interaction). The high field resonances for CH_3 (20.25 ppm) and C_5 (23.16 ppm) indicate a significant level of (IV). There is strong evidence (vide infra) that *trans*-7-methylcyclo- hept-2-enyltrimethylstannane utilises a conformation of the (IV) type.

Treatment with N-chlorosuccinimide-dimethylsulphide (NCS-DMS) proceeds in an S_N2-like fashion[8] to provide predominantly *cis*-4-methylcyclohept-2-enylchloride (~ 70%), on the basis of ^1H and ^{13}C nmr spectra. (δ 1.05 (d, J = 7 Hz) CH_3 and δ 4.68 ($W_{\frac{1}{2}}$ = 18 Hz, J ~ 9.5 Hz) CHCl). These results are summarised below and the ^{13}C shifts of all new compounds are in Table 1.



$SOCl_2$	24	9	67	>2
(Repeat)	19	15	61	5
NCS-DMS	15	70	11	4

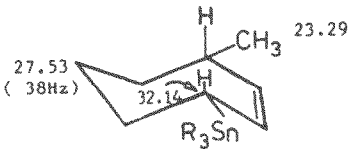
Trimethylstannylation of the chloride mixture was performed as described previously,[8] and led to a four component mixture of stannanes, the composition of which was not strongly dependent on the chloride mixture employed. The thionyl chloride derived chloride mixture provided a 49:16:10:25 blend (in order of elution), with ^{119}Sn shifts of +1.88, -1.48, -6.31 and -14.38 ppm relative to $(CH_3)_4Sn$. The ^{119}Sn shift of cyclohept-2-enyltrimethyl stannane is +1.55 ppm and indicated that the major isomer with δ Sn = +1.88 ppm was probably the *trans*-4-methyl isomer on the basis of quasi-axial $Sn(CH_3)_3$ in both cases. Structural assignments for the four stannanes were conducted in the following way. 4-Methylcyclohept-2-enone was reduced with $LiAlD_4$ and the resulting 1-^{2}H-alcohol was converted to the chloride and trimethylstannylated. The *cis* and *trans*-4-methyl isomers would exhibit, in their ^{119}Sn spectra, large (~ 14 Hz) geminal ^2H-^{119}Sn couplings, whereas the *cis* and *trans*-7-methyl isomers would not (^2H now located at C-3).[8] The ^{119}Sn signals at δ +1.76 ($J_{^2H-Sn}$ = 13.5 Hz) and δ -6.36 (J = 15 Hz) must represent the *cis* and *trans*-4-methyl isomers whereas those at δ -1.55 and δ -14.42 (with barely resolvable ^2H-Sn couplings) correspond to the 7-methyl isomers. In addition, in the ^{13}C nmr spectrum, Cl (bearing Sn) is substantially to lower field in the 7-methyl isomers (~ 40-43 ppm) compared with the 4-methyl pair (~ 33 ppm) because of the deshielding β-methyl effect. Distinction within these isomeric subsets was based on values of ^{119}Sn-^{13}C couplings (^3J) alluded to above, and certain ^1H nmr data, particularly of the major isomer (δ_{Sn} = +1.88 ppm) which was obtained in >85% isomeric purity by careful preparative gas chromatography. These aspects are summarised below.



$\delta Sn(ppm)^a$	-6.36	+1.76	-1.55	-14.42
J_{Sn-D}(Hz)	15	13.5	nr[b]	nr
isomer	III	IV	V	VI

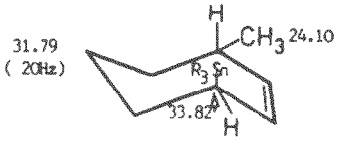
[a] Relative to $(CH_3)_4Sn$. [b] nr = not resolved

Important ^{13}C nmr parameters are located below on the preferred conformations of isomers (III)-(VI), and perhaps except for (V) little comment is necessary. (Values in parentheses are ^{119}Sn-^{13}C coupling constants (Hz)).



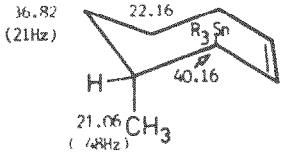
δ_{Sn} = -6.36

(III)



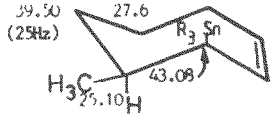
δ_{Sn} = +1.76

(IV)



δ_{Sn} = -1.55

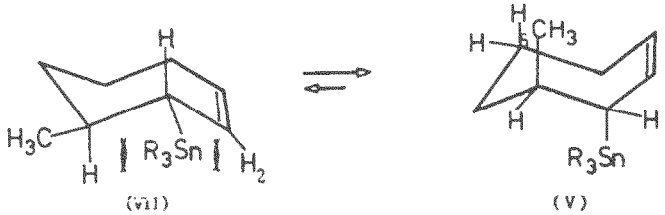
(V)



δ_{Sn} = ~ 14.42

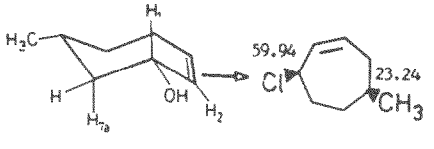
(I)

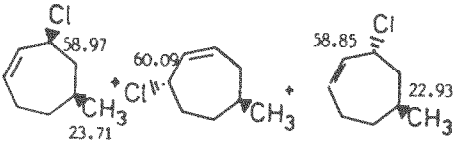
The *trans*-7-methyl isomer exhibited some spectral parameters which were very difficult to explain in terms of a predominantly diequatorial conformation (VII) below, but which indicated (V) to be predominant. A full discussion of this and related matters will be presented elsewhere.[6] The full details of the ^{13}C nmr spectra of the compounds are in Table 1.



(VII) (V)

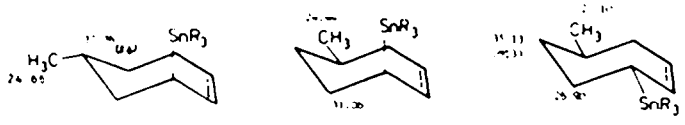
5- and 6-Methylcyclohept-2-enyltrimethylstannanes were also acquired. Methylcuprate addition to cyclohepta-2,6-dienone provided 6-methylcyclohept-2-enone, which on reduction led very predominantly (>90%) to *cis*-6-methylcyclohept-2-enol, on the basis of ^1H and ^{13}C nmr spectra. For example H_{7a} was a clean quartet (including one large coupling to H_1) and H_1 lacks a large coupling to H_2. Reactions of this *cis*-alcohol with both $SOCl_2$ and NCS-DMS were conducted to give different isomeric mixtures. Conversion of the 1-deuterio alcohol with NCS-DMS demonstrated the major chloride was unrearranged[8] and on mechanistic considerations and analysis of the ^1H and ^{13}C nmr spectra demonstrated it to be the *trans*-6-methyl isomer. Analysis of the ^1H and ^{13}C spectra, along the lines outl ned previously, provided the summary below. Key ^{13}C data are in Table 1.





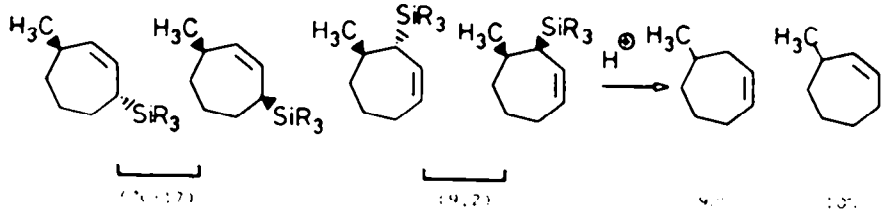
>C*H*Cl	δ 4.7	4.6	4.82	4.74
$SOCl_2$ →	~50	~30	~10	~10
NCS-DMS →	13	11	13	62

Trimethylstannylation of the chloride (derived from $SOCl_2$) provided three stannanes with δ_{Sn} of +2.60 (~ 50%) +1.77 (30%) and -4.23 ppm (~ 20%) and with essentially identical mass spectra (M⁺ 274; 5% (^{120}Sn)). Positive tin shifts are indicative of quasi-*axial* $Sn(CH_3)_3$, and using the deuteration technique and observation of J_{Sn-D}, it was confirmed that the +2.60 ppm signal (J_{Sn-D} = 12.9 Hz) corresponded to a 6-methyl isomer, whereas the remaining two signals must represent the isomeric 5-methylstannanes. These assignments are supported by chemical shift considerations, an INEPT spectrum and values of certain ^{119}Sn-^{13}C coupling constants. Certain features of the spectra of the *trans*-5-methyl isomer indicate that the di-equatorial arrangement drawn is probably not predominate, and are consistent with a substantial contribution of the diaxial conformer, as outlined previously in the companion series. Trimethylstannylation of the MCS-DMS-chloride provided *ca* 46:43:11 mixture of *trans*-6-methyl, and *cis* and *trans*-5-methyl isomers.

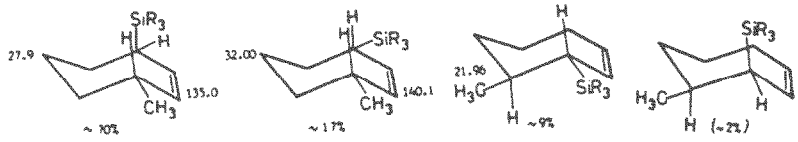


δ_{Sn}	+2.60	+1.77	-4.23
$\delta(CH_3)_3Sn(^{13}C)$	-9.00	-9.08	-9.54
(^1H)	+0.08	+0.075	+0.07
δ CH_3-CH	+0.96	+0.94	+0.90

Cyclohept-2-enylsilanes were generally acquired by reacting the cyclohept-2-enylphenyl ether with sodium and chlorotrimethylsilane in situ. Cyclohept-2-enyltrimethylsilane (δ_{Si} = +4.92 ppm relative to $(CH_3)_4Si$) has the ^{13}C shifts listed in Table 1. 4-Methylcyclohept- 2-enylphenylether provided four silanes (gc-ms) in the proportions 70:17:9:2 with δ_{29Si} of +4.48, 4.82, 4.04 and 2.78 respectively. Acid cleavage of this mixture produced very predominantly 4-methylcyclo- heptene (~ 90%) on the basis of ^{13}C nmr spectra, and hence the two most abundant isomers must have been *cis* and *trans*-4-methylcyclohept-2-enyl isomers.



In the ^1H nmr spectrum, the major isomer had vinyl-H signals at δ 5.30 and δ 5.54, such separation suggesting a 1,4-relationship of substituents. The ^{13}C spectrum of the mixture, along with an INEPT sequence, permitted the assignment of the important isomers (Table 1). (The assignments for the least abundant isomer (<4%) are tentative).

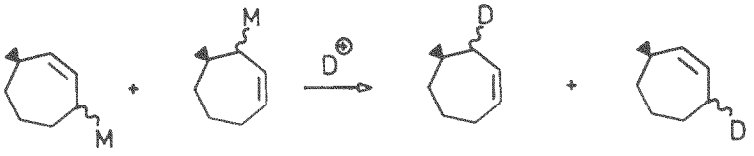


That the major silane was the *trans*-4-methyl isomer was indicated by (i) the higher field position (27.88 ppm) of C_8 reflecting the γ-shielding effect of $(CH_3)_3Si$ and (ii) the shielding of C_3 (135.00 ppm) is greater than in the second isomer (140.18 ppm) reflecting stronger σ-π shielding. The third isomer was concluded to be *trans*-7-methyl and the relatively high field position of the 7-CH_3 group (21.96 ppm) indicates a significant population of the diaxial conformer for the reasons detailed earlier. The fourth isomer (*cis*-7-methyl) was present in very low amount.

SUBSTITUTION WITH CF_3COOD: Treatment of the silanes and stannanes with CF_3COOD results in very rapid cleavage of the stannanes and somewhat slower reaction of the silanes to generate mono-^2H-cycloheptene (for the parent systems) and ^2H-substituted-methylcyclo-heptenes for the methyl-substituted systems. For stereochemical determinations of the substitution, it is necessary to establish the relative configurations of the product ^2H-substituted-methylcycloheptenes, as well as their relative proportions.

(*a*) *Mixtures of 4- and 7-Methylcyclohept-2-enylsilanes and -stannanes*

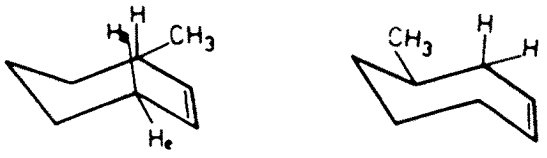
On the basis of regiospecific γ-substitution by D^+, the following would apply:



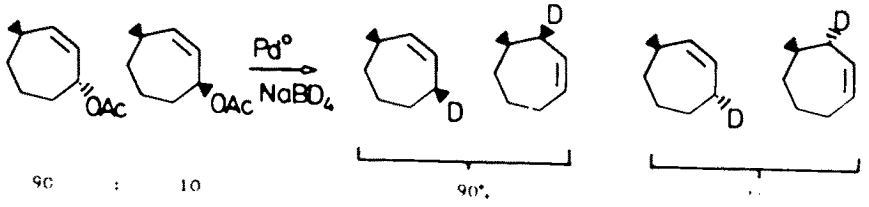
M = $Si(CH_3)_3$;$Sn(CH_3)_3$

i.e. the *cis* and *trans*-4-methyl isomers yield *cis* and *trans*-3-^2H-4- methylcycloheptene and *cis* and *trans*-7-methyl isomers yield *cis* and *trans*-7-^2H-3-methylcycloheptenes. Our aim was to use direct ^2H nmr spectroscopy (as we had previously)[10] to reveal stereochemical detail, and this would require assigning the ^1H nmr spectrum of 4-methylcycloheptene (H_3 region) and 3-methylcycloheptene (H_7 region) *or* acquiring specifically ^2H substituted methylcycloheptenes and thus directly establishing the relevant ^2H chemical shifts. We used a combination of both.

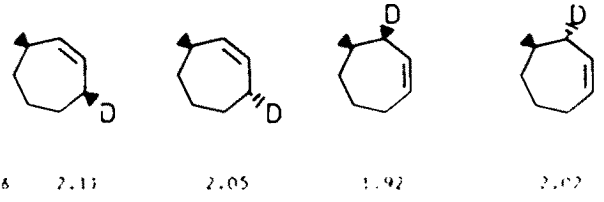
3-Methylcycloheptene was obtained from 3-chloro (or bromo)cycloheptene and $(CH_3)_2CuLi$, but 4-methylcycloheptene was obtained only as an *ca* 50:50 mixture with 3-methylcycloheptene by dehydration of 3-methylcycloheptanol.



The 400 MHz ^1H spectrum of 3-methylcycloheptene was consistent with a predominantly quasi-equatorial methyl group and this was supported by the ^{13}C nmr shifts, which showed little evidence for γ-shielding by an axial-methyl. Careful decoupling of this ^1H spectrum showed H_{7e} to be at lower field ($\underline{\delta\ 2.13}$) than H_{7a} ($\underline{\delta\ 2.07}$). Reaction of an *ca* 90:10 mixture of *trans* and *cis*-4-methyl-cycloept-2-enylacetate with $(Ph_3P)_4Pd^0$ and $NaBD_4$ provided a mixture (^{13}C) of 3- and 4-methylcycloheptene, and precedent would indicate that ^2H incorporation (replacement of acetate) would proceed with inversion of configuration,[11] leading to the following:

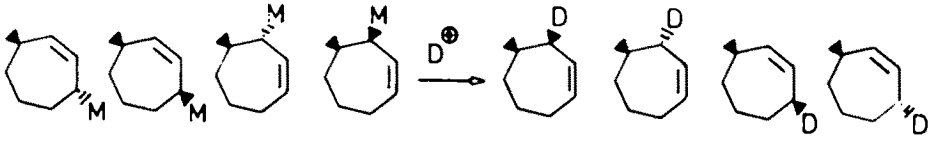


The ^2H nmr spectrum exhibited signals at δ 2.11 and δ 1.92 (together ~ 90% of intensity) and δ 2.05 and δ 2.02 (~ 10%). This information when combined with the shifts for H_{7e} (δ 2.13; *cis* to CH_3) and H_{7a} (δ 2.07; *trans* to CH_3) in 3-methylcycloheptene leads to the following (relative to internal $CDCl_3$ in $CHCl_3$ at δ 7.24).



δ 2.11 2.05 1.92 2.02

Although slight variations (± 0.02 ppm) are sometimes encountered, the ordering of the ^2H shifts among the four isomers is secure. The resolution of the four signals in the ^2H spectrum was a major blessing, and permitted direct analysis. The results of the cleavage of the 4- and 7-methylcyclohept-2-enylsilanes and stannanes are presented below.

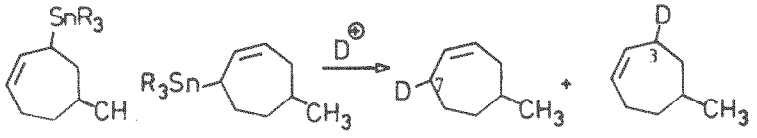


M.Sn$(CH_3)_3$							
47	10	11	32	50	10	11	30
51	10	16	23	52	13	18	17
85				85 (^2H and ^{13}C)			
M-Si$(CH_3)_3$							
71	17	10	2	70	18	9	4

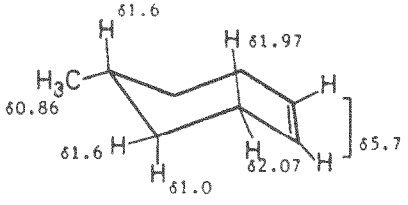
Irrespective of leaving group, an attractive consistency characterises these data. Firstly, the cleavages with CF_3COOD are regiospecific providing the rearranged cycloalkene with incorporation of a single ^2H, on the basis of ^{13}C, ^1H and ^2H nmr spectra. With respect to stereochemistry, the most economic rationale is that each reactant isomer experiences *anti* electrophilic attack i.e. S_E' (*anti*). This conclusion is particularly compelling when the result for the substitution of *trans*-4-methylcycloheptenylstannane is considered. Essentially only *cis*-3-^2H-4-methylcycloheptene (γ-*anti* attack) is detected by ^2H nmr.

Mixtures of 5- and 6-methylcyclohept-2-enylstannanes:

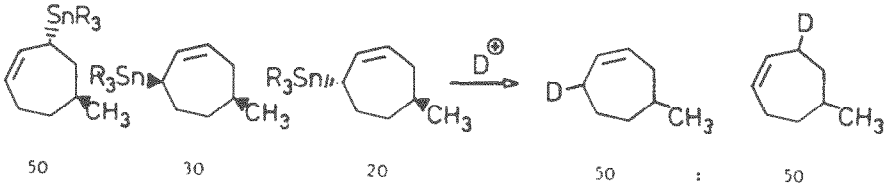
Acid cleavage of such mixtures would be anticipated to yield a mixture of 4- and 5-methylcycloheptene on the basis of S_E' cleavage (below) and stereochemical interpretation would require knowledge of the ^2H shifts- H_7 in the former and H_3 in the latter.



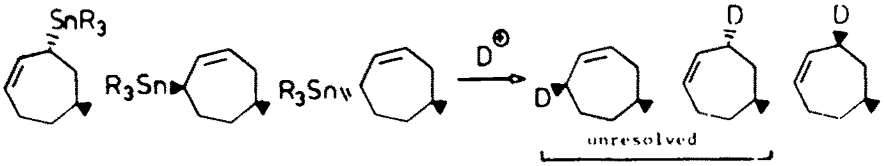
The ^{13}C shifts for 4-methylcycloheptene were established earlier, but the characterisation of the pure compound is incomplete.[12] 5-Methylcyclo- heptene (M = 110) was obtained by reduction of cycloheptene-5- carboxylic acid,[13] followed by tosylation and reduction again ($LiAlH_4$). The ^1H and ^{13}C nmr spectra attested to its symmetry, and the ^1H spectrum was readily assigned.



Although the ^{13}C nmr spectrum of 4-methylcycloheptene was easily assigned this compound was obtained as a mixture with 3-methyl- cycloheptene, and chromatographic separation was not possible.[12] Hence, accurate chemical shift data for H_7 were not available, but it is reasonable to expect these at *ca* δ 2.0. Even in the absence of this information, stereochemical analysis was still possible. The regiochemistry of the cleavage of a mixture of these stannanes was determined by ^{13}C nmr examination of the product cycloalkenes, as indicated below. Regiospecific γ-substitution operated.



Substitution with CF_3COOD of the mixtures of the isomeric stannanes was next conducted and direct ^2H nmr analysis provided the results summarised below.



48	34	18	80	20
34	29	37(prep. vpc)	60	40
46	43	11	45* , 45*	10

* [illegible]

Taken together, these data, consistent with an *anti* S_E' process, harmonise with the related 4- and 7-methyl series of cycloheptenyl derivatives discussed earlier, but whether this γ-*anti* substitution will characterise attack by more complex electrophiles is not clear. In the FMO approach to such substitutions of allylmetal systems, electrophile delivery occurs to that alkene face where the HOMO (π-orbital) is more concentrated[14] and this is *anti* to the interacting C-M σ-bond, and more distorted with a more polar C-M bond that is better aligned for σ-π interaction. In cyclohex-2-enyl metal systems, the degree of interaction between quasi-*axial* and quasi-*equatorial* C-M bonds (with the double bond) while significantly different, cannot be substantial as the relevant angles are comparable. In the cyclohept-2-enyl cases, the interactions differ substantially from the two orientations, as quasi-*equatorial* bonds lie almost in the nodal plane, with *ca* 75° for the quasi-*axial* arrangement. It is of interest to note that the major stereoisomers available and employed in this study have quasi-*axial* metal groups (i.e. *trans*-4-methyl, *cis*-7-methyl, *trans*-6-methyl and *cis*-5-methyl systems) or (on the basis of nmr evidence) adopt a conformation with such an arrangement (e.g. *trans*-7-methyl, *cis*-6-methyl systems)[6] through which reaction may be channelled. Thus, on this basis, stereospecific *anti* substitution is anticipated to be stereoelectronically highly preferred in these systems.

The regio and stereospecificity of acidolysis of these cyclohept-2-enyl derivatives is promising from a synthetic viewpoint if maintained for carbon electrophiles,[15] and found to apply in medium rings generally. We are extending such studies to the interesting cyclooctenyl systems.

ACKNOWLEDGEMENT: We acknowledge partial funding of this research by the Australian Research Grants Committee.

EXPERIMENTAL

Combined gas chromatography-mass spectrometry was performed on a Hewlett-Packard 5992B instrument, fitted with a 10 metre OV101 capillary column. Preparative gas chromatography was conducted with a Shimadzu GC-9A gas chromatograph fitted with a 2 metre OV101 column. High-field ^1H nmr spectra were obtained at either 300 MHz on a Bruker CXP-300 spectrometer or at 400 MHz on a JEOL-GX-400 spectrometer. 25 MHz ^{13}C, 15.24 MHz ^2H, 19.74 MHz ^{29}Si and 39.08 MHz ^{119}Sn spectra were obtained with the JEOL-FX 100 instrument. For extra dispersion, most ^2H nmr spectra were acquired at higher field using the 300 or 400 MHz (for ^1H) spectrometers. Any special conditions used in acquiring the ^{29}Si spectra have been detailed elsewhere.[16] Spectra other than ^2H spectra ($CHCl_3$ referenced to internal $CDCl_3$ at δ 7.24) pertain to $CDCl_3$ solvent (centre peak of triplet at δ 77.00 ppm). ^{119}Sn and ^{29}Si chemical shifts are referenced to internal $(CH_3)_4Sn$ and $(CH_3)_4Si$ respectively. ^{13}C nmr shifts are located in Table 1.

Trans-4-methylcyclohept-2-enol (bp 85°, 4 mm) was obtained (~ 90%) from the monoepoxide of cyclohepta-1,3-diene using the procedure of Marino and Abe.[9] δ ($CDCl_3$) 0.94 (3H, d, CH_3), 1.38 (m, H7a), 1.55 (m, H7e), 1.6-1.8 (4H, H_5 + H_6), 2.35 (m, H_4), 4.29 (br d, J ~ 7.5 $W_{\frac{1}{2}}$ ~ 16.5 Hz, H_1), 5.46-5.56 (2H, H_2,H_3). Mass spectrum: M^+126, 91 (49%), 108 (43%), 77 (49%), 55 (88%). This alcohol was oxidised (Jones reagent) and reduced with $LiAlD_4$ to provide a mixture of the 1-deuterio-*cis* (~ 70%) and *trans* (~ 30%)-4-methylcyclohepten-1-ols. The ^{13}C nmr shifts for these alcohols are located in Table 1.

Conversion of this alcohol (and of the deuterio analogues) to the allylic chlorides was conducted using both thionyl chloride ($SOCl_2$) and N-Chlorosuccinimide-dimethylsulfide (NCS-DMS), in the manner described in full elsewhere.[8] A mixture of four chlorides (ratio in the text) was identified by gc-ms with M^+ = 146, 144 (*ca* 3:1) and prominent ions at 109, 108 and 91. The chlorides were characterised by high-field ^1H and ^{13}C nmr methods (see Table 1). The key ^1H nmr resonances are listed below: *trans*-7-methylcyclohept-2-enylchloride: δ 1.06 (d, J = 7 Hz, CH_3) and δ 4.34 (d of d, $W_{\frac{1}{2}}$ ~ 14 Hz, J = 7 and 5.4 Hz, H_1); *cis*-7-methyl- chloride: δ 1.04 (d, CH_3) δ 4.49 (br d, J ~ 7 Hz, H_1); *trans*-4-methyl- chloride: δ 1.02 (d, J = 7 Hz, CH_3) and δ 4.67 (H_1 superimposed on H_1 of *cis*-4-methylisomer); *cis*-4-methylchloride: δ 1.05 (d, J = 7 Hz, CH_3) δ 4.68 (brd, J ~ 9.5 Hz, $W_{\frac{1}{2}}$ ~ 18.5 Hz, H_1).

Trimethylstannylation with $(CH_3)_3SnLi$ prepared in THF, of these (and subsequent) allylic chloride mixtures was carried out in the manner described fully elsewhere.[8] Mixtures of allylic stannanes resulted, which were characterised by high quality ^1H, ^{13}C and ^{119}Sn nmr spectra, the key features of which are discussed in the text. For example, trimethylstannylation of the allylchlorides resulted from *trans*-4-methylcycloheptenol and $SOCl_2$ provided a four component mixture (Kugelrohr, 55°/0.5 mm) of allylic stannanes (50:17:14:20) with ^{119}Sn shifts of +1.88 -1.48, -6.31 and -14.38 ppm relative to $(CH_3)_4Sn$. The ^{13}C shifts are listed in Table 1. Careful preparative gas chromatography provided a sample of the major isomer (>85% isomerically pure) with δ_{Sn} = + 1.88 ppm. Found: C, 47.50; H, 8.20. Calc. for $C_{11}H_{22}Sn$: C, 48.40; H, 8.12. ^1H nmr (400 MHz) of *trans*-4- methylcyclohept-2-enyltrimethylstannane: δ +0.09 (s, 9H, $(CH_3)_3Sn$), .95-1.0 (1H, H_{8a}), 1.04 (d, J = 6.5 Hz, CH_3), 1.15-1.3 (H_{6a}), 1.65-17.5 (2H), 1.9-2.0 (2H), 2.1-2.2 (m, CH_3CH), 2.4-2.46 (H_1, J_{Sn-H} = 92 Hz), 5.15-5.25 (1H) and 5.7-5.85 (1H). Careful analyses of coupling constant patterns etc, were consistent with the *trans*-arrangement.

Starting with the 1-deuterio alcohol mentioned above, the sequence provided four stannanes, with those ^{119}Sn signals at +1.88 (J = 13.5 Hz) and -6.31 (J = 15 Hz) ppm exhibiting large couplings to ^2H, indicative of a geminal relationship, whereas those at -148 and -14.38 ppm were broadened, but lacking resolved ^2H-splitting.

6-Methylcyclohept-2-enone was acquired efficiently by treating the known cyclohepta-2,6-dienone with $(CH_3)_2CuLi$ in the standard way. ^1H nmr: δ 1.03 (d, J Hz, CH_3), 1.55 (1H, m) 1.94 (1H, m), 2.1 (1H, m), 2.35-2.55 (3H, m), 2.65-2.75 (1H, m), 6.0 (1H, d, J ~ 12 Hz, Hz), 6.63 (d of t, H_3). ^{13}C nmr: 21.82, 28.15, 28.34, 34.69, 51.21, 132.55, 147.06, 202.73.

Cis-6-methylcyclohept-2-enol (>90% *cis*) resulted from reduction of the above enone with $LiAlH_4$ in the usual way. ^1H nmr: δ 0.95 (d, CH_3), 1.0 (H_{5a}), 1.32 (H_{7a}), 1.6 (H_{5e}), 1.71 (H_{6a}), 1.81 (H_{7e}), 1.96 (H_{4e}) 2.15 (H_{4e}), 4.35 (H_1), 5.71 (H_2, H_3). The multiplicities of the above signals were appropriate for the *cis*-isomer. In particular, H_{7a} was a clean quartet (a triplet would be expected for the *trans* isomer) and H_1 exhibits one large coupling (to H_{7a}) and H_2 lacks a significant coupling to H_1. Thus this alcohol has equatorial CH_3 (at position 6) and quasi-equatorial hydroxy groups. The *acetate* was made and examination of its spectra supports the *cis* arrangement. ^{13}C nmr (alcohol) 23.85, 26.64, 33.69, 34.32, 44.82, 70.41, 128.45, 138.70. Oxidation and reduction ($LiAlD_4$) provided the 1-deutero *cis* alcohol, and a minor set of peaks ascribable to the *trans*-alcohol were located: 22.00, 25.95, 26.14, 29.21, 42.57, ?, 129.42 and 135.05. In the *trans* alcohol, the γ-shielding effect of quasi-axial hydroxyl at C_6 (cf. 33.69 and 25.95 ppm) is clear. (The deuterated alcohol was chlorinated with NCS-DMS and the resulting predominant chloride was unrearranged).

Reaction of *cis*-6-methylcyclohept-2-enol with $SOCl_2$ led to the rearranged *cis*-5-methylcyclohept-2-enyl chloride (~ 60%) *cis*-6-methylcyclohept-2-enyl chloride (~ 40%), with a minor amount of a third isomer which was the *major* isomer resulting from the NCS-DMS reaction i.e. the *trans*-6-methyl-isomer. In both cases, a minor amount of the fourth allylic isomer, *trans*-5-methylcyclohept-2-enyl chloride was detectable by gc-ms, and actual ratios are outlined in the text. Mass spectrum: M^+ (146,144), 108 (35%), 109 (26%), 93 (64%), 91 (56%), 80 (24.5%), 79 (100%), 78 (24.5%), 77 (69.5%).

Trans-6-methylcyclohept-2-enylchloride (from NCS-DMS) was fully characterised by ^1H nmr; δ 0.97 (d, J ~ 7 Hz, CH_3), 1.22 (H_{5a}), 1.7 (H_{7a}), 1.83 (H_{5e}), 2.1 (H_{7e}), 2.1-2.5 (H_{5a}, H_{4a}, H_{4e}), 4.74 (t of d, H_1), 5.72-5.95 (H_2,H_3). The assignments of H_{7c} and H_{7a} were confirmed by comparisons with the ^2H substituted systems. The chloride mixture from the NCS-DMS procedure also exhibited methyl doublets at δ 0.90 and (two) at δ 0.94. Key ^1H resonances for the four isomers are as follows:

Trans-6-methyl: δ 0.97 (CH_3); 4.74 (H_1); *cis*-6-methyl: 0.945; 4.6: *cis*-5-methyl: 0.94; 4.7; *trans*-5-methyl: 0.90; 4.82. The ^{13}C nmr shifts are located in Table 1.

Trimethylstannylation of the $SOCl_2$ derived chloride mixture provided three stannanes with ^{119}Sn shifts of +2.60 ppm (~ 50%), 1.77 (30%) and -4.23 (~ 20%), and with essentially identical mass spectra. (M^+, 274 (^{120}Sn), 5%; 165 (100%) $(CH_3)_3Sn^+$). Examination of ^2H substituted stannane mixture (M^+, 275, 3.3%) established that the ^{119}signal at +2.60 ppm (J_{Sn-D} = 12.9 Hz) must correspond to a 6-methylcyclohept-2-enylstannane, whereas the other two (no resolved ^2H coupling) must be the *cis* and *trans*-5-methylstannane isomers. Further distinction was based on ^{13}C nmr parameters (see Table 1). In the ^1H nmr spectrum, $\delta_{Sn(CH_3)_3}$ were located at +.08 (~ 50%) +0.75 (~ 30%) and +.07 (~ 20%) with δ_{CH_3-Sn} 0.96 (~ 50%), 0.94 (31%) and 0.90 (~ 19%). Vinylic resonances were at δ 5.3-5.9. A different ratio of stannanes (~ 46:43:11) (in the sequence above) was obtained from the MCS-DMS derived chloride.

Cyclohept-2-enyltrimethylstannane resulted from trimethylstannylation of cyclohept-2-enylchloride (cyclohept-2-enol and $SOCl_2$); b.p. 30-35°/3 mm; M^+ 132,130 (5.5%, 2%) in the usual way. A pure sample was obtained by preparative gas chromatography and was stored under N_2 at -10°C. (M^+ = 260 (5.2%), ^{120}Sn with appropriate ion cluster for $C_{10}H_{20}Sn$). ^{13}C nmr: -9.15, 28.89, 30.31, 31.38, 31.85, 33.76, 125.79, 135.06. In the 400 MHz ^1H nmr spectrum, diagnostic absorptions were located at +.08 $Sn(CH_3)_3$, 2.39 (J_{H-Sn} ~ 90 Hz, H_1), 5.85 (J ~ 24 Hz, H_2) and 5.49 (J ~ 28 Hz, H_3). Other absorptions in the range δ 1.16 - 2.28. A fuller discussion of this compound and its spectra will be presented elsewhere.

Cyclohept-2-enyltrimethylsilane: The reaction of cyclohept-2-enylchloride with phenol and anhydrous potassium carbonate in acetone, provided cyclohept-2-enylphenylether (M^+, 188, (19%); 94 (100%)). ^{13}C nmr: δ ($CDCl_3$) 26.51, 27.49, 28.54, 33.10 and 77.17, 115.65, 120.48, 129.40, 130.79, 135.76, 157.66. This ether (1.1 g; 5 mmol) and chlorotrimethylsilane (1.3 g, 12 mmol) in toluene (~ 4 cc) were added (N_2) to refluxing toluene (5 cc) which contained metallic sodium slivers (0.35 g, 15.2 mmol). As the dropwise addition proceded, local red colorations appeared and finally changed to purple. After further reflux (12 hours) a white solid had precipitated. After cooling, and cautious destruction of the excess sodium (NH_4Cl solution), pentane was added, and the mixture filtered (Celite). The organic phase was washed (30 cc H_2O) dried, and the pentane removed on a rotary evaporator. At this stage, vpc analysis showed three components and gc-ms identified them as phenoxysilane, the allylsilane and an unidentified much slower eluting component. Chromatography (neutral alumina; pentane elution) provided essentially pure allyl-silane as a clear oil (0.17 g, 20%). Mass spectrum: M^+, 168 (8.2%) $C_{10}H_{20}Si$ with correct ion cluster patterns) 94 (C_7H_{10}, 22%); 73 ($Si(CH_3)_3$, 100%). ^1H nmr: 0.01 (9H, S, CH_3), 1.75 (7H, br m) 2.10 (2H, br m), 5.70 (2H, "AB quartet", vinyl H). ^{13}C nmr: δ ($CDCl_3$): -2.25, 28.11, 28.43, 28.96, 30.69, 31.65, 129.91, 132.74. δ ^{29}Si + 4.92 ppm.

4- and 7-Methylcyclohept-2-enylphenylethers were obtained from the allylic chlorides, (*trans*-4-methylcyclohept-2-enol and $SOCl_2$) phenol and base as described previously, as a 71:10:17:2 mixture in *ca* 30% yield. Mass spectrum: M^+ 202 ($C_{14}H_{18}O$); 108 (C_8H_{12}), 77 (C_6H_5 (100%)). The isomers showed ^{13}C shifts at 75.03, 77.49 (major) 81.20, 82.49 for *C*-O.

4- and 7-Methylcyclohept-2-enyltrimethylsilanes were obtained from the above phenylethers in the manner described for cyclohept-2-enyltrimethylsilane itself. In this way, 0.45 g of a 17:70:10:2 mixture of the allylicsilanes was required by preparative gas chromatography. Mass spectrum: M^+ (182, 3.6% (^{28}Si); 108 (39.9%); 79 (10.4%), 73 (100%). (Mass spectra of the four isomers were essentially identical and displayed the appropriate ion cluster patterns). ^1H nmr: .005 (major) -0.02, -0.02 ($Si(CH_3)_3$); 0.98 (major), 1.00 (neat), 0.97 (CH_3); 1.1-1.30 and 1.45-1.87 (7H, complex ion); 2.35 (1H *br*) and 5.30, 5.54 (2H, vinyl H). The ^{13}C shifts are discussed in the text and located in Table 1. ^{29}Si (nmr): 4.48 (major); 4.82 (next); 4.04 and 2.78 (minor).

3-Methylcycloheptene was obtained from cyclohept-2-enyl chloride (or bromide) and $(CH_3)_2CuLi$ and purified by preparative gas chromatography.[12] A mixture of *3- and 4-methylcycloheptene* resulted from dehydration (distillation from $KHSO_4$) of 3-methylcycloheptanol, which in turn was acquired by conjugate addition ($(CH_3)_2CuLi$) to cyclohept-2-enone. *3-Methylcyclo- heptene*: ^1H nmr: δ 1.02 (CH_3); 1.25 (H_{4a}); 1.3 (H_{6a}); 1.55 (H_{5a}); 1.57 (H_{4e}); 1.66 (H_{6e}), 1.92 (H_{5e}); 2.07 (H_{7a}); 2.13 (H_{7e}); 5.5 (H_2); 5.7 (H_3). Important aspects of the ^1H nmr of 4-methylcycloheptene are discussed in the text, and ^{13}C nmr shifts are located in Table 1.

5-Methylcycloheptene[12] was readily obtained from the known 5-carboxycycloheptene[13] by reduction to the hydroxymethyl derivative, followed by tosylation and further reduction. (Mass spectrum: M^+ = 110). ^1H nmr: δ 0.86 (CH_3), 1.0 (H_{4a}); 1.6 (H_{4e} + H_5); 1.97 (H_{3a}) 2.07 (H_{3e}); 5.7 ($H_{1,2}$). ^{13}C nmr: 23.63, 27.03, 35.14, 37.31, 132.27.

Reduction of the acetate of 4-methylcyclohept-2-enol with $NaBD_4$ and $[(C_6H_5)_3P]_4Pd$[14] was performed in the reported fashion,[15,21] and the ^2H nmr spectrum is discussed in the text.

Acidolyses of the cyclohept-2-enylsilanes and -stannanes were conducted by adding CF_3COOH or CF_3COOD (in slight excess) to solutions of the silanes or stannanes in chloroform, as described fully elsewhere[3(c)]. The cleavage reactions were clean leading to cycloalkene and the trimethylsilyl or stannyl salt, based on high quality ^1H, ^2H and ^{13}nmr spectra which formed the basis of the regio- and stereo-chemical conclusions.

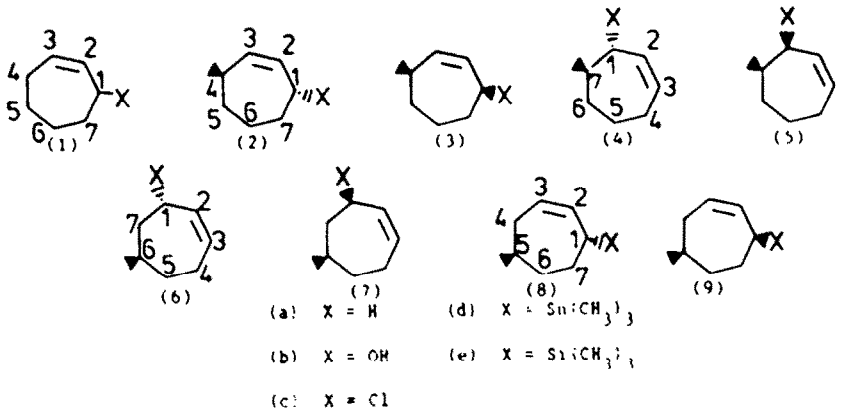
TABLE 1

^{13}C, ^{119}Sn, ^{29}Si NMR SHIFTS OF SOME CYCLOHEPT-2-ENYL DERIVATIVES[a]

COMPOUND	CARBON NUMBER								^{119}Sn or ^{29}Si shift	
(Chart)	1	2	3	4	5	6	7	Other		
(1a)	29.1	132.4	132.4	29.1	27.4	32.1	27.4			
(2a)	28.9	130.6	139.4	34.5	35.9	30.6	27.0	23.1		
(4a)	40.6	130.7	132.7	28.8	26.2	37.0	32.6	23.6		
(6a)	27.0	132.3	132.3	27.0	35.1	37.3	35.1	23.6		
(1b)	72.0	137.9	129.9	28.6	26.8*	26.7*	36.6			
(1c)	60.1	133.8*	133.0*	28.1	26.5*	26.1*	36.3			
(1d)	33.8 (324)	135.0 (40)	125.8 (49)	28.9* (13?)	31.4* (25?)	31.9 (20)	30.3 (13)		-9.2 (301)	+1.55
(1e)	31.7	132.7	129.9	30.7*	28.1*	28.4*	29.0*		-2.3	+4.92
(2b)	70.0	134.0	137.2	34.3*	32.9*	21.9	35.7	22.0		
(3b)	71.7	136.2	137.1	34.5*	35.3*	26.9	36.4*	23.2		
(2c)	59.9	129.8	141.7	36.1*	33.6*	23.9	35.3*	22.9		
(3c)	60.2	133.1	139.2	36.7*	33.8*	26.1	34.8*	22.8		
(4c)	65.7	131.1	133.9	27.9	23.1	33.4	38.5	20.3		
(5c)	66.1	131.3	135.8	27.9	25.0	33.3	37.5	19.8		
(2d)	33.8	133.4 (40)	132.9 (48)	36.2 (12)	37.8	31.8 (19.6)	30.3 (~12)	24.1;	-9.1	+1.76
(3d)	32.1	132.9	132.4	32.5 (~12)	35.9 (~12)	27.5 (38)	30.5	23.3;	-9.7	-6.36
(4d)	40.2	132.3?	124.9 (50)	29.7 (~12)	22.2	36.9 (21)	33.1 (~15)	21.1; (48)	-10.2	-1.55
(5d)	43.1 (324)	134.7 (40)	126.5 (48)	29.3	27.6	39.5 (25)	37.6	25.1;	-7.1	-14.42
(2e)	32.9	130.7	135.0	33.7	37.1	27.7*	27.9*	23.6;	-2.0	+4.48
(3e)	30.1	131.2	140.2	34.4	36.1	32.0	28.1	23.4;	-3.1	+4.82
(4e)	40.9	130.5	126.9	29.0*	29.1*	29.4*	35.4	22.0;	-1.2	+4.04
(7b)	70.4	138.7	128.5	26.6	34.3	33.7	44.8	23.9		
(6c)	58.6	131.3	135.8	26.3	34.9	30.4	43.3	22.9		
(7c)	59.0	131.1	136.0	26.4	34.1	?	46.3	23.7		
(9c)	59.9	132.0	133.3	35.1*	33.6*	32.7*	36.2	23.2		
(8c)	60.1	[	very	minor	isomer			]		
(6d)	32.4 (325)	135.2 (39)	125.9 (50)	28.8 (14)	37.0* (12)	37.8 (24)	40.3* (19)	24.7;	-9.0 (302)	+2.60
(9d)	33.5 (324)	135.4 (40)	124.5 (50)	39.2 (14)	34.9 (15)	37.7	31.1 (20)	24.4;	-9.1 (303)	+1.77
(8d)	32.4	135.0 (37)	123.6 (~48)	40.3?	32.1 (8.5)	35.1 (13?)	26.9 (16)	21.1;	-9.5 (303)	-4.23

[a] ^{13}C shifts are for $CDCl_3$ solvent. The central peak of the $CDCl_3$ triplet has been taken as +77.00 ppm. ^{119}Sn shifts ($CDCl_3$ solution) are relative to $(CH_3)_4Sn$ as zero, and ^{29}Si shifts are relative to $(CH_3)_4Si$ as zero. Asterisked peaks may require interchange and values in parentheses refer to ^{119}Sn-^{13}C couplings. The shifts for compound (3b) refer to the 1-^2H-alcohol and small ^2H effects on some shifts are not corrected. Refer to Chart 1 for compound structure.

CHART 1



(a) X = H (d) X = $Sn(CH_3)_3$
(b) X = OH (e) X = $Si(CH_3)_3$
(c) X = Cl

(For X = H, the above numbering, strictly speaking, is inappropriate. However for conciseness of presentation it is retained and should be followed in reference to the table of chemical shifts).

REFERENCES

1. See, for example, Mangravite, J.A., *Organomet. Chem. Revs.*, 1979, 7, 45; Chan, T.H.; Fleming, I., *Synthesis*, 1979, 761.
2. Young, D.; Kitching, W., *J. Org. Chem.*, 1983, 48, 614.
3. (a) Fleming, I.; Terrett, N.K., *Pure Appl. Chem.*, 1983, 55, 1707. (b) Hayashi, T.; Matsumoto, Y.; Ito, Y., *Organometallics*, 1987, 6, 884 and references therein. (c) Wickham, G.; Young, D.; Kitching, W., *Organometallics*, (1987) Accepted for publication.
4. For a preliminary report of some of this information see Kitching, W.; Laycock, B.; Maynard, I.; Penman, K., *J. Chem. Soc. Chem. Commun.*, 1986, 954.
5. Meto, M.; DiLauro, C.; Califano, S., *Spectrochim. Acta Ser. A*, 1970, 26, 1489; St.-Jacques, M.; Vaziri, C., *Can. J. Chem.*, 1971, 49, 1256.
6. Ganis, P.; Kitching, W.; Tagliavini, G. (1988). Manuscript in preparation.
7. Maynard, I., 1985, B.Sc. (Hons) Thesis, University of Queensland.
8. Young, D.; Kitching, W.; Wickham, G., *Aust. J. Chem.*, 1984, 37, 1841.
9. Marino, J.P.; Abe, H.; *Synthesis*, 1980, 872.
10. Young, D.; Kitching, W.; Wickham, G., *Tetrahedron Lett.*, 1983, 24, 5789.
11. Keinan, E.; Greenspoon, N., *Tetrahedron Lett.*, 1982, 23, 241.
12. Pinchas, S.; G.I.-Av. E.; Altman, B.; Shabtai, J., *Spectrochim. Acta*, 1965, 21, 783; Shaktai, J., *J. Chromatogr.*, 1965, 18, 302.
13. Stork, G.; Landesman, H.K., *J. Am. Chem. Soc.*, 1956, 78, 5129.
14. Kahn, S.D.; Pau, C.F.; Chamberlan, A.R.; Hehre, W.J., *J. Am. Chem. Soc.*, 1987, 109, 650.
15. Acetylation of a cyclohept-2-enylsilane has been reported but the stereochemistry was not determined. See Magnus, P.; Cooke, F.; Sankar, T., *Organometallics*, 1982, 1, 562.
16. Wickham, G.; Kitching, W., *Organometallics*, 1983, 2, 541.
17. Young, D.; Jones, M.; Kitching, W., *Aust. J. Chem.*, 1986, 39, 563.