Characterization of (Z)-Cyclooct-2-enylstannanes

Kerry G. Penman and William Kitching*

Department of Chemistry, The University of Queensland, Queensland, Australia 4072

Giuseppe Tagliavini

Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Universita di Padova, via Marzolo 1, 35131 Padova, Italy

Received September 19, 1990

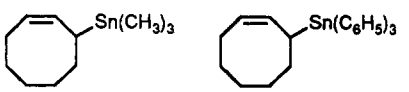
(*Z*)-Cyclooct-2-enyltrimethylstannanes and -triphenylstannanes have been synthesized and characterized by ^1H and ^{13}C NMR spectra, which indicate a predominating unsymmetrical chair–boat arrangement. A mixture of the cis and trans isomers of both the (4-methylcyclooct-2-enyl)- and (8-methylcyclooct-2-enyl)trimethylstannanes (allylic stannanes) results from a sequence commencing with methylcyanocuprate opening of the monoepoxide of 1,3-cyclooctadiene, which is considered to afford regio- and stereoselectively *trans*-4-methylcyclooct-2-enol. Chlorination of this alcohol with both thionyl chloride and *N*-chlorosuccinimide/dimethyl sulfide has been conducted and the structures of the chlorides established by NMR methods and use of [1-$^2H_1$]-4-methylcyclooct-2-enol. Trimethylstannylation of the chloride mixtures provides the four possible allylic stannanes, with one of the rearranged 8-methyl isomers slightly predominating. NMR spectra of various fractions from preparative gas chromatography have been obtained, and full assignment of the ^{13}C NMR spectra of the isomers is reported. Acidolysis of these fractions (with CF_3COOD) proceeds rapidly to yield mixtures of ^2H-substituted 3- and 4-methylcyclooctenes, but only one diastereomer of each system appears to be formed, on the basis of the ^{13}C NMR spectra. This implies that electrophile approach to the π-face at the γ-carbon is not influenced by the orientation of the C–Sn bond but is probably dictated by the predominant molecular conformation.

Introduction

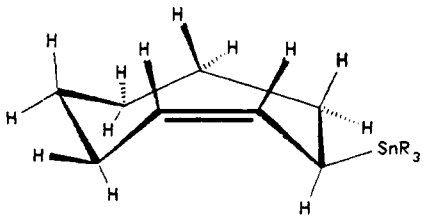
In previous papers, we reported the synthesis, characterization, and some substitution reactions of various alkyl-substituted cyclohex-2-enyl- and cyclohept-2-enyltrimethylstannanes.[1-3] These allylic stannanes underwent S_E' reactions with acid, sulfur dioxide, and aldehyde–Lewis acid systems, and the stereochemistry was deduced in certain cases. As a continuation of these studies, we have synthesized a series of allylic stannanes based on the cis (or *Z*) cyclooctene ring system, and characterized them by NMR methods. This study, along with another,[4] provides useful sets of ^{13}C NMR shifts for cyclooctenes and is a companion to a detailed study of various metal derivatives of trans (or *E*) cyclooctene and their reactions.[5]

Results and Discussion

The simple allylic stannanes, cyclooct-2-enyltrimethyl- and cyclooct-2-enyltriphenylstannanes (**1** and **2**), were prepared and their spectra assigned to provide base data for consideration of the various methyl-substituted derivatives.



1 **2**



1 was obtained by treating the allylic chloride, from cyclooct-2-enol and thionyl chloride, with $(CH_3)_3SnLi$ in the normal way[6] and was purified by Kugelrohr distillation and preparative gas chromatography. The infrared and low-field ^1H NMR spectra were in agreement with those for one of the products resulting from free radical addition of $(CH_3)_3SnH$ to 1,3-cyclooctadiene.[7] Stannane **2** was surprisingly difficult to purify, and a crystalline sample for X-ray analysis was not obtained. Reaction of cyclooct-2-enyl chloride with $(C_6H_5)_3SnLi$ in THF provided mainly **2**, but side products were difficult to remove. As an alternative, we quenched cyclooct-2-enyllithium, prepared by the method of Schlosser,[8] with $(C_6H_5)_3SnCl$. This route appeared cleaner, and repeated column chromatography provided **2** as a viscous oil, which was not crystalline at 20 °C. This sample was sufficiently pure for spectral examination. The ^{119}Sn shifts for **1** (+2.20 ppm) and **2** (−119.6 ppm), relative to internal $(CH_3)_4Sn$ were appropriate for such allylic stannanes.[6]

The ^{13}C NMR assignments for **1** (Table I) were based on chemical shift comparisons with those of cyclooctene[4,9] and the magnitudes of ^{119}Sn–^{13}C coupling constants.[10] The only possible ambiguity concerns C-4 (25.97 ppm) and C-6 (25.40 ppm), but the measurable ^{119}Sn coupling about the 25.97 ppm signal is consistent with the assignment and supported by data for the triphenylstannane **2**. The salient point from the spectrum regarding the preferred conformation of **1** is the large *vic*-^{119}Sn coupling (to C-7) of 70 Hz, which requires an almost 180° dihedral angle between the coupled nuclei,[10] as does the deshielding γ-effect of $Sn(CH_3)_3$ (at C-7) of ca. 3.1 ppm.[11] From similar con-

(1) Kitching, W.; Penman, K. G.; Jones, M. A.; Valle, G.; Tagliavini, G.; Ganis, P. *Organometallics* **1989**, *8*, 785.
(2) Wickham, G.; Young, D.; Kitching, W. *Organometallics* **1988**, *7*, 1187.
(3) Kitching, W.; Penman, K. G.; Laycock, B.; Maynard, I. *Tetrahedron* **1988**, *44*, 3819.
(4) Penman, K. G.; Kitching, W.; Wells, A. P. *J. Chem. Soc., Perkin Trans. 1*, in press.
(5) Penman, K. G.; Kitching, W. Research in progress.
(6) Wickham, G.; Young, D.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 4884.
(7) Fish, R. H.; Kuivila, H. G.; Tyminski, I. J. *J. Am. Chem. Soc.* **1967**, *89*, 5861.
(8) Schlosser, M.; Hartmann, J. *Angew. Chem., Intg. Ed. Engl.* **1973**, *12*, 508.
(9) Read, G.; Shaw, J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2287.
(10) Doddrell, D.; Burfitt, I.; Kitching, W.; Bullpitt, M.; Lee, G.; Mynott, R. L.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640.
(11) Kitching, W.; Marriott, M.; Adcock, W.; Doddrell, D. *J. Org. Chem.* **1976**, *41*, 1671.

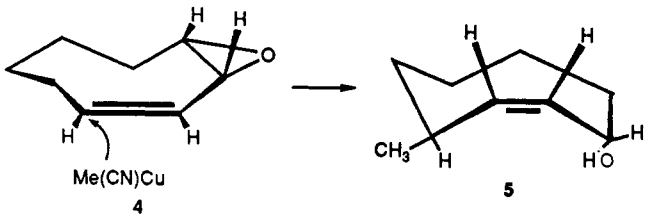
0276-7333/91/2310-1320$02.50/0

Table I. Carbon-13 NMR Data[a] for Cyclooct-2-enyl Derivatives

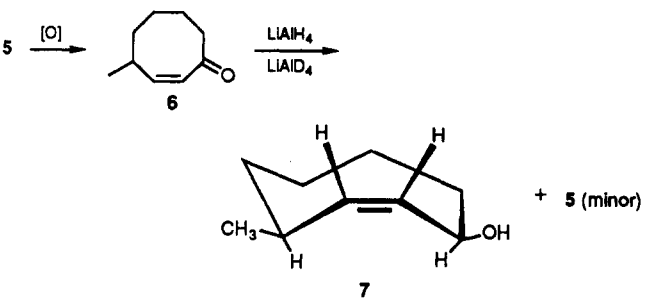
	carbon no.								
compd	1	2	3	4	5	6	7	8	other
1[b]	26.65 (365)	133.84 (34)	125.59 (57)	25.97 (7.5)	29.01 (14)	25.40 (n.o.)	29.25 (70)	31.53 (13)	−11.03 (309)
2[b]	27.57 (402)	132.34 (~35)	128.50 (n.l.)	26.05 (~7)	29.11 (13)	25.73 (n.o.)	28.44 (73)	32.44 (17)	*c*
4[d]	58.01	134.26	122.43	*25.46*	*28.94*	*25.03*	*27.19*	53.61	
5	68.96	131.06	135.46	32.88	34.96	25.75	22.52	36.05	22.68
6[d]	204.78	132.18	148.66	*32.66*	*33.28*	*23.98*	*22.88*	*42.49*	22.86
7	69.60	133.44	134.04	31.19	38.46	25.55	23.70	38.77	21.78
calc	70.28	133.11	134.95	31.28	38.38	25.77	24.13	38.87	
trans-**11**	63.65	133.10	129.84	27.32	29.03	22.64	32.56	41.35	18.33
cis-**11**	64.47	133.53	131.92	27.85*	27.83*	23.17	37.65*	37.98*	19.54
trans-**12**[d]	59.32	129.06	136.96	*31.68*	*35.20*	*24.35*	*24.55*	*37.53*	22.63
cis-**12**[d]	57.77	131.14	135.81	*31.61*	*38.48*	*25.47*	*25.56*	*40.75*	21.94
calc	57.99	130.77	135.99	*31.12*	*38.27*	*25.53*	*25.78*	*40.53*	
15[b,d]	26.12 (n.l.)	130.67 (24.4)	130.21 (59.6)	*26.56*	*26.58*	*30.62* (~8)	35.93 (53)	37.86 (16)	20.53 (20.6), −9.98 (308)
16[b,d]	24.68 (n.l.)	133.05 (47)	127.80 (52)	*30.21* (*10.7*)	*31.26* (*12*)	*31.59* (*17*)	*31.72* (*72*)	*37.47* (*24.4*)	23.59, −10.73 (307)
17[b,d]	23.19 (n.l.)	134.14 (32)	126.96 (60)	*29.39* (*~11*)	*30.58*	*33.9*	*35.62*	*36.11* (*~17*)	23.27 (~14), −9.70 (304)
18[b]	24.13 (n.l.)	131.26 (23.7)	136.47 (61)	31.15	39.20 (6.1)	26.03 (6)	28.05	32.92 (14.5)	22.62, −11.20 (310)
calc	27.68	132.03	132.28	31.01	38.38	25.36	29.78	31.71	

[a] For $CDCl_3$ solvent and referenced to the central peak of the $CDCl_3$ triplet taken as 77.00 ppm. [b] Values in parentheses are $^{119}Sn-^{13}C$ coupling constants (Hz), and those for $^{117}Sn-^{13}C$ are about 4% smaller. n.l. = not located. n.o. = not observed. [c] Aromatic resonances at 128.21 (11), 128.43 (45), 137.34 (32), and 138.25 (n.l.). [d] No attempt made to assign resonances grouped together (in italics), and calculated chemical shifts are based on assumed additivity of substituent-induced shifts. Asterisked signals may be interchanged.

Scheme I



Scheme II



siderations, the assignments shown for **2** in Table I were arrived at and shown to be correct from the $^{13}C-^{1}H$ correlated spectrum, which was dependent on assignment of the ^{1}H NMR spectrum of **2**, which was possible by spin-decoupling methods. These ^{1}H NMR assignments are listed in the Experimental Section. For **2**, a large *vic*-^{119}Sn coupling to C-7 (73 Hz) is observed, and a positive γ-effect of 2.3 ppm indicates a γ-anti array of C-7 and the tin nucleus.[10,11] The above observations are accommodated by **3** or a similar arrangement[12] as the important conformation of **1** and **2**. **3** is also consistent with certain $^{1}H-^{1}H$ coupling constants. For example, H-1 in **2** would be expected to experience a large and a moderate coupling to the H-8 pair, as is observed (13 and 5 Hz).

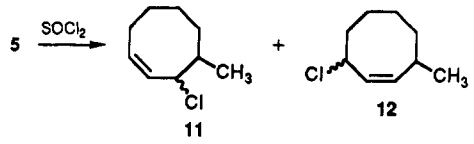
(4-Methylcyclooct-2-enyl)- and (8-Methylcyclooct-2-enyl)trimethylstannanes. Reaction of the monoepoxide of *cis*-1,3-cyclooctadiene (**4**) with methylcyanocuprate afforded ca. 95% of one isomer of 4-methylcyclooct-2-enol. The highly regio- and stereoselective opening of such epoxides with cyanocuprates has been employed by Mariano[13] and shown to operate in six- and seven-membered ring systems.[2,3] The alcohol formed was concluded to be *trans*-4-methylcyclooct-2-enol (**5**) on the basis of its ^{13}C and ^{1}H NMR spectra and a presumed mechanism for these apparent S_N2' reactions. Anet and Yavari[14] have reported that the preferred conformations of **4** are the twist-boat–chair and twist-boats, and the preferred direction of approach by the cuprate reagent would lead to **5**, as shown.

In the ^{1}H spectrum of **5** >C*H*OH appeared as an apparent quartet ($J \sim 6.5$–7.0 Hz) at δ 4.67, and this coupling pattern is best accommodated by **5** as the preferred conformation. Some distortion of the "chair–boat" arrangement[12] is required to accommodate couplings of ca. 7.0 Hz from H-2 and both H-8 to H-1. Average dihedral angles of 20 or 120–140° are required for these coupling constants. The general shape of this H-1 resonance is different from that for >C*H*X, where X = $Sn(C_6H_5)_3$, Cl, Br, and OH, in simple cyclooct-2-enyl derivatives, in which X would very predominantly occupy a *quasi*-equatorial site and experience one large *vic*-$^{1}H-^{1}H$ coupling. Oxidation of alcohol **5** with Jones reagent (Scheme II) provided the α,β-unsaturated ketone **6**, which was reduced with a mixture of $LiAlH_4/LiAlD_4$ to provide an ca. 2:1 mixture of allylic alcohols, with **5** being the minor component. The torsion angle between the planes of the carbonyl group and double bond in cyclooct-2-enone has been estimated[15] at 57° and for such a conformation of 4-methylcyclooct-2-enone comparable amounts of the epimeric alcohols **5** and **7** are not unexpected.

Comparison of the ^{13}C shifts for these alcohols (the spectra were completely assigned by consideration of chemical shifts and ^{2}H effects on the spectra) with the set calculated for the cis isomer (**7**), on the basis of additivity of substituent-induced shifts for –OH and $-CH_3$,[4] showed impressive agreement (see Table I) with those measured for the major reduction product. There may be an illusory component to this agreement, because of assumptions

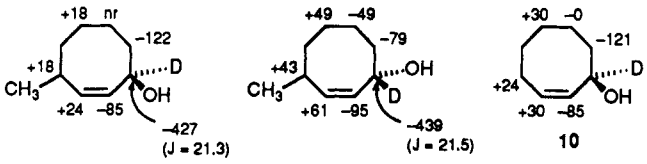
(12) (a) St. Jacques, M.; Brown, M. A.; Anet, F. A. L. *Tetrahedron Lett.* **1966**, 5947. (b) St. Jacques, M. Dissertation, University of California at Los Angeles, 1967; *Diss. Abstr.* **1968**, *B28*, 4076.
(13) Mariano, J. P.; Abe, H. *Synthesis* **1980**, 872.
(14) Anet, F. A. L.; Yavari, I. *Tetrahedron Lett.* **1975**, *19*, 1567.
(15) Heap, N.; Whitham, G. H. *J. Chem. Soc. B* **1966**, 164.

Scheme III



11 12

concerning conformations. Reduction of enone **6** with the mixture of $LiAlH_4/LiAlD_4$ provided **5** and **7** admixed with the [1-$^2H_1$ isotopomers, and the ^{13}C spectra of this mixture provided accurate measures of ^2H effects[4,9] on the spectra of **5** and **7**, thus leading to complete assignments. In addition, we had hoped that some long-range ^2H effects in the spectra would have assisted in confirming the stereochemistry of **5** and **7**. These effects are shown on **8** and



8 9 10

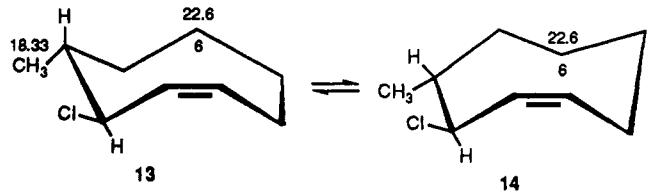
9, with **9** corresponding to the alcohol formed by methylcyanocuprate opening of epoxide **4**. The ^2H effects shown are in parts per billion (ppb), with negative values corresponding to high-field shifts caused by 1-^2H substitution. Values[4] for [1-$^2H_1$]cyclooct-2-enol are shown (on **10**) for comparison.

Alcohol **8**, believed to be the cis isomer, is characterized by ^2H effects on the spectra that are similar to those shown on **10**. This is understandable on the basis that the orientation of ^2H in **8** and **10** will be essentially the same, and one dominant conformation will describe **8**, with both $-CH_3$ and -OH being quasi-equatorial. However, the suspected trans isomer (**9**) exhibits positive four-bond isotope effects ($^4\Delta$) that are significantly larger. These positive $^4\Delta$ are of interest in their own right[4,16] but in this system probably reflect changes in the conformational equilibria induced by ^2H substitution,[16] and examination of models suggests that **9** may have comparable populations of two conformations of similar energy (in each, one of $-CH_3$ and -OH is quasi-equatorial and the other quasi-axial) based on a distorted boat–chair.[12] It is reasonable, then, that 1-^2H substitution will have a greater effect on the apparently more balanced conformational equilibria for **9** than on that for **8**, for which one dominant conformation will prevail. However, more detailed studies on these aspects are required.

Chlorination of allylic alcohol **5** with thionyl chloride in ether[3,6] led to a four-component mixture of the chlorides in the ratio 15:12:60:13 (capillary VPC), with each showing $M^+ = m/z$ 158 (6%) and 160 (2.1%) and prominent loss of Cl (m/z 123, 17%) and HCl (m/z 122, 25%). After careful distillation (Kugelrohr), the chlorides were examined by ^1H and ^{13}C NMR spectroscopy and could be placed in two groups of two on the basis of the chemical shift of >C–Cl. In the rearranged 8-methylcyclooct-2-enyl chlorides (**11**), the β-effect of the *vic*-CH_3 will cause a low-field shift of ca. 5–6 ppm. On this basis, signals at δ 63.65 (major isomer) and δ 64.47 correspond to the isomers of **11**, and those at δ 57.77 and δ 59.32 to the unrearranged isomers **12**. Cyclooct-2-enyl chloride shows >*C*–Cl at δ 57.13.[4]

These conclusions are supported by the methyl shifts, with isomers **11** exhibiting signals at δ 18.33 and δ 19.54,

Scheme IV



such high-field positions being due to the *vic*-chloro substituent[17] and also the likely *axial* orientation of CH_3 in one of the predominating conformations of the rearranged chlorides **11**. In the ^1H NMR spectra, the major isomer shows >C*H*Cl at δ 4.47 as a doublet of doublets (J = 8.4, 11 Hz), such a pattern being much simpler than that at δ 4.8, which then corresponds to an isomer of **12**.

Chlorination with *N*-chlorosuccinimide/dimethyl sulfide[18] was conducted also and provided two chlorides (ca. 90:10) with a trace of a third isomer. The major isomer was clearly one of **12** (^1H, ^{13}C NMR), and the shape of its >C*H*Cl resonance was very similar to that of cyclooct-2-enyl chloride. This correspondence is best accommodated by this major isomer being *cis*-4-methylcyclooct-2-enyl chloride (*cis*-**12**) anticipated also on the basis that this chlorinating agent behaves in an S_N2 fashion with allylic alcohols.[18] Chlorination of [1-$^2H_1$]-4-methylcyclooct-2-enol (with $SOCl_2$) confirmed that the major chloride was rearranged (i.e. one of **11**, as ^2H in this isomer was located at a vinylic site. The ^{13}C spectrum of this deuterated sample facilitated the assignments in Table I for *cis*- and *trans*-**11** and *cis*- and *trans*-**12**.

We conclude that the major chloride resulting from $SOCl_2$ chlorination of **5** is *trans*-**11** and arrangements **13** and **14** depict reasonable conformations for it. Although the methyl shift of 18.33 ppm may be accounted for by **13** (*vic*-gauche chloro effect),[17] the high-field position of C-6 (22.6 ppm, which is well upfield from the corresponding shift in 4-methylcyclooctene, 24.2 ppm) seems to require a significant population of **14**, with the γ-gauche effect of methyl at C-6. The ^1H NMR pattern for >C*H*Cl (d of d, J = 11, 8.5 Hz) is consistent with the conformation of either **13** or **14**, with a large coupling to H-8 (11 Hz) and a smaller coupling to H-2 (8.5 Hz). The corresponding *cis*-**11** was always present at a low level, and definite location of its >C*H*Cl resonance was not possible. However reasonable conformations indicate that a large coupling (~11 Hz) would not be present. Production of *trans*-**11** from trans alcohol **5** is consistent with information on $SOCl_2$ chlorinations.[18] The calculated shifts for cis chloride **12** agree exceptionally well with those observed for the major product from trans alcohol **5** with *N*-chlorosuccinimide/dimethyl sulfide, as expected for "S_N2-type" chlorination. Such agreement in shifts is reasonable, as in the cis isomer both $-CH_3$ and –Cl will presumably occupy sites they would in the respective monosubstituted compounds. Thus the four chlorides have been characterized by their ^{13}C NMR spectra (and some ^1H NMR data), which are assembled in Table I.

Trimethylstannylation. The chloride mixture described above was subjected to stannylation with $(CH_3)_3SnLi$ in THF,[6] and a mixture of the four possible methylcyclooct-2-enyltrimethylstannanes was formed, based on GC–MS and NMR examination of the product. All four showed very similar mass spectra, which exhibited weak molecular ions, M^+, at m/z 288 (3.0%) and 286

(16) For a general discussion see: Siehl, H. V. *Adv. Phys. Org. Chem.* **1987**, *23*, 62.

(17) Schneider, H.; Hoppen, V. *J. Org. Chem.* **1978**, *43*, 3866.

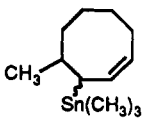
(18) Young, D.; Kitching, W.; Wickham, G. *Aust. J. Chem.* **1984**, *37*, 1841.

(2.5%) for the major tin isotopes, M − CH_3 (*m/z* 273, 2.6%), with the base peak at *m/z* 165 ($(CH_3)_3Sn$). The four isomers **15**–**18** were formed in the approximate proportions shown.

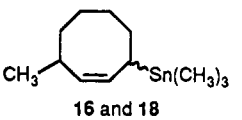
	isomer			
	15	**16**	**17**	**18**
%	33	30	14	22
$\delta_{^{119}Sn}$	−3.17	−0.78	−1.89	+3.10
$^{13}C_{Sn-CH_3}$	−9.98 (308)	−10.73 (307)	−9.70 (304)	−11.21 (310)

($\delta_{^{119}Sn}$ are relative to internal $(CH_3)_4Sn$. Values in parentheses are one-bond ^{119}Sn–C coupling constants. Order of elution (OV101) was **18** < **16** < **15** < **17**; i.e. **18** eluted first.)

At this stage it should be noted that cyclooct-2-enyltrimethylstannane shows δ_{Sn} = +2.20 ppm and δ_{Sn-CH_3} = −11.03 (309), indicating perhaps that **18** is one of the two unrearranged isomers, i.e. a 4-methylcyclooct-2-enyltrimethylstannane. Furthermore, on this basis, **16** is also probably unrearranged, so that the following groupings are suggested.



15 and **17**



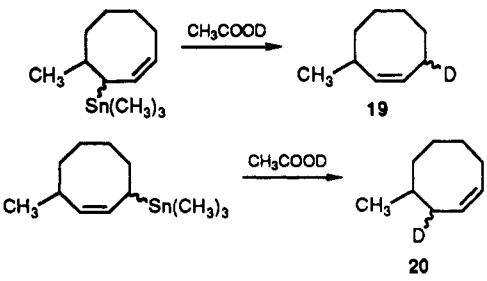
16 and **18**

Careful preparative gas chromatography provided a number of fractions in which there was substantial variation in the proportions of the four isomers. ^1H, and more diagnostically ^{13}C NMR spectra of these fractions allowed the identification of the four sets of signals. A DEPT sequence conducted on a fraction containing essentially only **15** and **18** identified the CH_2, CH, and CH_3 signals for these isomers. In this way, four sets of ten ^{13}C signals for **15**–**18** were located. **17** was least abundant, and there may be some reservations about one or two of the shifts. The signal at 20.53 ppm in the spectrum of **15** was identified as a CH_3 signal and was flanked by ^{119}Sn satellites (J = 20.6 Hz). This observation requires **15** to be an 8-methyl isomer, as otherwise an unacceptably large $^5J_{Sn-C}$ would exist in either **16** or **18**. The shift (20.53 ppm) is indicative also of the γ-gauche shielding effect of $Sn(CH_3)_3$[9,11] and confirms **15** as an 8-methyl isomer. One fraction was ca. 83% **15** and 13% **17**, and the 400-MHz ^1H NMR spectrum of this mixture exhibited a clean doublet of doublets (J = 11, 4 Hz) at δ 2.55, which was flanked by $^{119,117}Sn$ satellites ($J \sim 67$ Hz). This resonance must be >C*H*Sn, and the coupling to two *vic*-protons only further confirms **15** as an 8-methyl isomer. **15** was further characterized by CH_3–C*H* at δ 2.28 (multiplet), with vinylic protons exhibiting the expected pattern between δ 5.5 and 5.7, and $(CH_3)_3Sn$ at δ 0.059.

Cleavage studies with acid[2,3] confirm these conclusions, as such acidolysis of the two component mixture of **15** and **17** with CF_3COOD provided 3-methylcyclooctene (**19**) only, with no trace of 4-methylcyclooctene (**20**) in good-quality ^{13}C NMR spectra of the total reaction mixture. On the reasonable assumption that these allylic cyclooct-2-enylstannanes will experience S_E' acidolysis as other allylic stannanes unwaveringly do,[2,3] Scheme V presents the outcome. (Alternatively, if the spectroscopic data outlined above are accepted and **15** is undoubtedly an 8-methyl isomer, the result in Scheme V confirms its S_E' style of acidolysis).

Thus **15** and **17** must be the *cis*- and *trans*-8-methylcyclooct-2-enyltrimethylstannanes, and therefore **16** and **18** are the *cis*- and *trans*-4-methylcyclooct-2-enyltrimethylstannanes, speculated above on the basis of ^{119}Sn and CH_3–Sn shifts. (The cleavages of various stannane mixtures with CF_3COOD provide 3- and 4-methylcyclooctenes,[4] which are clearly regiospecifically monodeuterated (^{13}C NMR), as expected for S_E' cleavage, and it is almost certain that stereospecific introduction of ^2H has occurred also. This is discussed later.)

Scheme V

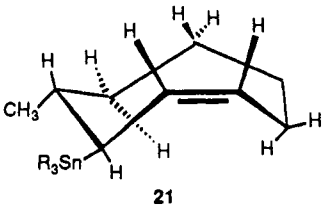


The "total stannane" product mixture was assayed to have the following composition:

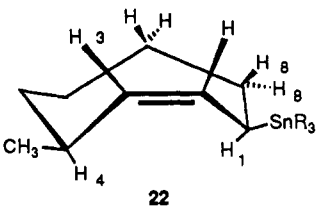
	isomer			
	15	**16**	**17**	**18**
% by VPC	40	30	11	19
% by Sn–C*H*$_3$ intens	35	33	11	20

Acid cleavage of this mixture provided 3- and 4-methylcyclooctene (**19** and **20**), and the ^{13}C NMR spectrum[4] showed about equal proportions of these hydrocarbons, with perhaps a slight preponderance of **20**. This result is consistent with **15** and **17** being the 8-methyl isomers (giving 3-methylcyclooctene (**19**)) and **16** and **18** being the 4-methyl isomers providing, on cleavage, 4-methylcyclooctene (**20**). Certainly **15** and **16** must be regioisomers to give this result.

The problem that next arises is the assignment of relative configurations within the **15**, **17** and **16**, **18** pairs. With respect to the former duo, **15** exhibits >C*H*Sn as a doublet of doublets (J = 11, 14 Hz), and as outlined in the case of the rearranged 8-methyl chlorides, the larger coupling of 11 Hz (J_{H1-H8}) is consistent with a *vic*-trans arrangement whereas unreasonable conformations would be required for this coupling to characterize the *vic*-cis isomer. The $^3J_{Sn-C}$ of 53 Hz (to C-7) requires[10] an average dihedral angle of ca. 160–170° as present in what appears to be the preferred conformation (**21**) of the *vic*-trans isomer. Thus



21

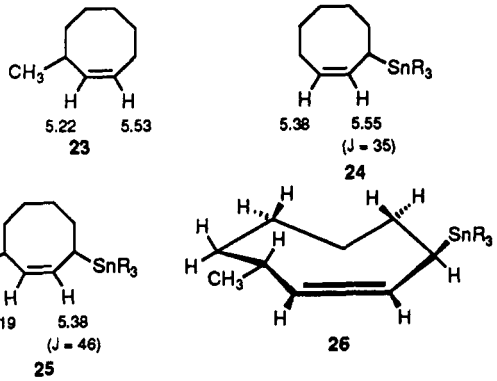


22

we conclude **15** is *trans*-8-methyl- and **17** is *cis*-8-methylcyclooct-2-enyltrimethylstannane.

With respect to distinction between the 4-methyl isomers, **16** and **18**, useful information is located in the 400-MHz ^1H spectrum of a fraction that was ca. 80% **18** and 15% **16**. The vinylic proton pattern for **18** consisted of an apparent triplet of doublets (J = 2 × 11 Hz, 1.5 Hz) at δ 5.38 flanked by ^{119}Sn satellites (46 Hz) (H-2) and a doublet of doublets with a fine coupling at δ 5.19 ($J \sim$ 11, 8, 1 Hz) lacking ^{119}Sn coupling (H-3). The general appearance and chemical shift spread suggest both H-1 and H-4 occupy quasi-axial sites, i.e. the cis isomer. This is reinforced by comparisons with the vinylic proton patterns of 3-methylcyclooctene (**19**) and parent allylic stannane

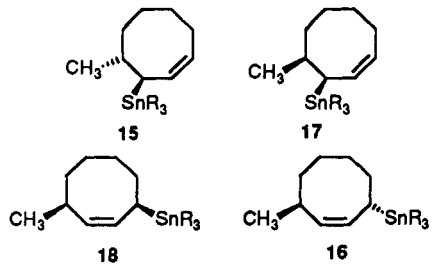
1, as shown below on **23–25**.



>C*H*Sn in **18** could be located because of its flanking ^{119}Sn satellites (J = 55 Hz), and the signal resulted from couplings of ca. 11, 8, and 4 Hz. We associate these with couplings to ^{1}H-8, H-2, and H-8, respectively, as in **22**. Reasonable conformations of the *trans*-4-methyl isomer cannot provide these couplings. We conclude that **18** is the *cis*-4-methyl isomer, as represented in **22**, and its δ_{Sn} of +3.10 ppm is close to that of **1** (+2.20 ppm), as expected for similar orientations of the tin group. On this basis, **16** must be the *trans*-4-methyl isomer, which has a remarkably large spread in the vinylic proton absorption, with one reasonance centered at δ 4.7 (J_{Sn-H} = 27 Hz) being shifted well upfield from the other (δ 5.61). The latter resonance appears to have $J_{Sn-H} \not> 12$ Hz. The δ 4.7 resonance was shown to arise from H-3 (by decoupling experiments), and its high-field shift suggests strong $\sigma-\pi$ electron donation from the C–Sn bond,[6] which also accounts for the ^{119}Sn coupling, which is absent about H-3 in the cis isomer. A conformation of the trans isomer favoring $\sigma-\pi$ interaction is shown in **26**, and it is clear that the Sn–C–C–H-2 dihedral angle is close to 90°, thus accounting for the nonobservable ^{119}Sn–H-2 coupling. (Note that in the *cis*-4-methyl isomer **18**, such coupling (46 Hz) is readily identified, and here the relevant angle is ~30°).

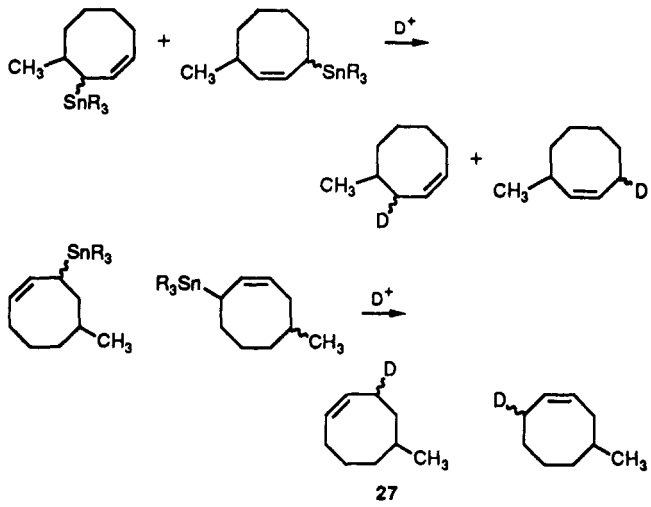
Arrangement **26** also accounts for the shielded nature of C-3 (127.8 ppm) compared with C-3 (131.26 ppm) in the cis isomer **18**. A further consequence of **26** should be appreciable ^{119}Sn coupling to C-7, and depending on the exact orientation of the tin group and nonbonded interactions (e.g. H-4···H-8), this could be of the order of 50–70 Hz. The resonance at 31.72 ppm, associated with **16** has a ^{119}Sn coupling of ca. 70 Hz, which magnitude rules out other than a *vic*-^{119}Sn–^{13}C coupling.

Thus we assign the following structures to isomers **15–18**:



Stannane Cleavage with CF_3COOD. With the relative stereochemistry of the stannanes **15–18** established, the intention was to examine the stereochemistry of CF_3COOD cleavage, such a determination requiring establishing the relative stereochemistry of the centers bearing $-CH_3$ and $-^{2}H$ in the product [$^{2}H_1$]-3- and 4-methylcyclooctenes. Reaction of various stannane mixtures with CF_3COOD ($CDCl_3$ solvent) proceeded very rapidly, and the ^{13}C spectra established that ^{2}H was located

Scheme VI



27

at one carbon site only in each methylcyclooctene. In the case of 3-methylcyclooctene this was C-4, because the spectrum of unlabeled 3-methylcyclooctene has been completely assigned by a ^{1}H–^{13}C correlated spectrum.[4] 4-Methylcyclooctene has been generated in the presence of both 3-methylcyclooctene (present series of stannanes) and 5-methylcyclooctene (from acid cleavage of a mixture of 5- and 7-methylcyclooct-2-enyltrimethylstannanes),[19] and its signals have been located. The situation is summarized in Scheme VI, and the acquisition of regiospecifically ^{2}H-labeled 3-, 4-, and 5-methylcyclooctenes has permitted complete assignment of their ^{13}C spectra and measurement of some interesting ^{2}H effects on the ^{13}C shifts.[4]

A reasonable anticipation[3] would have been that S_E' cleavage of isomeric mixtures of the allylic stannanes would provide diastereomeric [$^{2}H_1$]methylcyclooctenes, and in the case of [3-$^{2}H_1$]-5-methylcyclooctene (**27**) this was evidenced by two clearly resolved triplets to the high-field side of the C-3 signal of the cooccurring unlabeled 5-methylcyclooctene. ($^{1}\Delta$ = −334 and −373 ppb, each with J_{C-D} ~ 19.3 Hz.) (^{2}H incorporation is not 100%, and this permits accurate "internal" measures of ^{2}H-induced effects in the spectra.) For **27**, resonance duplication for carbons more remote from the deuteration site was also observed. However, in contrast, the spectra of the [$^{2}H_1$]-substituted 3- and 4-methylcyclooctenes showed no evidence for the presence of diastereomers, the >C-D triplets were not unusually broadened, and no longer range effects were identified. The most economical interpretation of this is that one diastereomer only of [8-$^{2}H_1$]-3-methyl- and [3-$^{2}H_1$]-4-methylcyclooctenes results from CF_3COOD cleavage of mixtures of **15–18**. This implies that electrophile access is restricted to one π-face in the γ-carbon region, as a result of the molecular conformation, and that the orientation of the C–Sn bond in **15** and **17** for example (or in **16** and **18**) cannot overcome this conformationally enforced direction of electrophile approach. A similar situation seems to apply in the epoxidation of 3-methylcyclooctene,[20] although models fail to reveal why the various cyclooctenylstannanes should behave so differently. We have reported that in specifically ^{2}H-substituted 3- and 4-methylcyclooctenes, four-bond downfield ^{2}H effects ($+^{4}\Delta$) in the ^{13}C spectra can be measured,[4] and we had hoped to correlate the presence of such effects with the orientation of ^{2}H in the assumed preferred conformations of the me-

(19) Penman, K. G.; Kitching, W. Research in progress.
(20) Cope, A. C.; Woo., G. L. *J. Am. Chem. Soc.* **1963**, *85*, 3601.

thylcyclooctenes. This approach does not, at this stage appear as decisive as we had hoped, and syntheses of certain diastereomers e.g. of [8-$^2H_1$]-3-methylcyclooctene, are currently being undertaken to establish more reliably the orientational dependence of these ^2H effects.

The ^{13}C chemical shifts of compounds discussed are located in Table I, except for the methylcyclooctenes which have been presented elsewhere[4] in a more general discussion of the ^{13}C NMR data of a range of cyclooctyl derivatives.

Experimental Section

^1H NMR spectra were recorded at 400 MHz in the FT mode on a JEOL JNM-GX400 spectrometer, and chemical shifts were referenced to internal tetramethylsilane (0.0 ppm) or residual $CHCl_3$ solvent (7.24 ppm). ^{13}C NMR spectra were recorded at 100 MHz, and chemical shifts were referenced to the center peak of the solvent ($CDCl_3$) at 77.00 ppm. Combined gas chromatography–mass spectrometry was conducted on a Hewlett-Packard 5992B instrument using OV101 or BP5 capillary columns. Preparative gas chromatography was performed on a Shimadzu gas chromatograph Model GC-9A equipped with OV101 and C-20M columns. Accurate mass determinations were conducted on a Kratos mass spectrometer at Flinders University, South Australia, by Dr. M. J. Thompson and Ms. R. Parry.

Synthesis of Compounds. Cyclooct-2-enyltrimethylstannane. Following the method outlined in detail elsewhere,[6] cyclooct-2-enyl chloride was added slowly to a cooled (0 °C) stirred solution of $(CH_3)_3SnLi$ prepared in THF. Standard workup provided an oil, which was distilled (Kugelrohr oven, 85 °C/0.5 mm) to provide the title stannane in moderate yield (40%). Mass spectrum: m/z 274 (M^+, 2.2%, ^{120}Sn), 169 (M − CH_3, 17.4), 165 ($(CH_3)_3Sn$, 100), 151 ($(CH_3)_2SnH$, 11.4), 135 (29.3), 120 (10.2). (Tin-containing ions exhibited excellent agreement with the calculated isotopic cluster patterns.) ^1H NMR, δ_H: 0.05 (s, 9 H, $(CH_3)_3Sn$), 1.3–1.85 (m, 10 H), 2.10–2.27 (m, 1 H), 5.35–5.45 (m, 1 H), 5.45–5.60 (m, 1 H). For the ^{13}C NMR data see the Discussion and Table I. The IR and low-field ^1H NMR data were in agreement with those for one of the products resulting from radical addition of $(CH_3)_3SnH$ to 1,3-cyclooctadiene.[7] The title stannane underwent extremely rapid cleavage with CF_3COOD to yield [3-$^2H_1$]cyclooctene, as anticipated for an allylic trimethylstannane. ^{119}Sn NMR, δ_{Sn}: +2.20.

Cyclooct-2-enyltriphenylstannane. To cyclooctene (1.0 g, 9.1 mm) dissolved in dry pentane (20 mL) under a dry N_2 atmosphere was added potassium *tert*-butoxide (1.0 g) and *n*-butyllithium (4.0 mL of a 15% solution in hexane).[8] The reaction mixture was allowed to stir for 30 min, and then triphenyltin chloride (3.5 g) dissolved in dry THF (10 mL) was added quickly. After 1 h, water (100 mL) was added and the mixture extracted with ether (3 × 100 mL), separated, and dried ($MgSO_4$). Removal of ether (rotary evaporator) left a white solid and oil which were taken up in pentane and filtered. The filtrate was evaporated and the residue chromatographed on silica gel, eluting with pentane. In this way, about 50 mg of the target stannane was obtained, and the purity was assessed at ca. 95% on the basis of its ^{13}C, ^1H, and ^{119}Sn NMR spectra. Repeated attempts at crystallization from a variety of solvents failed, and only a waxy solid was obtained. Cleavage with acid provided cyclooctene as well as some benzene, the latter resulting from phenyl cleavage. Extensive homonuclear decoupling allowed virtually complete assignment of the 400-MHz ^1H NMR spectrum, which was used, with the ^1H–^{13}C correlated spectrum, to assign the ^{13}C NMR spectrum. ^1H NMR, δ_H (400-MHz): 1.37 (m, 1 H, H-5), 1.5 (m, 1 H, H-6), 1.65 (br s, 4 H, 2 × H-7, H-6, H-5), 2.02 (m, 2 H, 2 × H-8), 2.22 (m, 1 H, H-4), 2.32 (m, 1 H, H-4), 3.12 (m, 1 H, H-1), 5.62 (m, 1 H, H-3), 5.83 (m, 1 H, H-2). For ^{13}C NMR data see the Discussion and Table I. ^{119}Sn NMR, δ_{Sn}: −119.6. The corresponding values for cyclohex-2-enyl- and cyclohept-2-enyltriphenylstannanes are −130.3 and −130.5 ppm, respectively.[1]

4-Methylcyclooct-2-enol. Treatment of the known monoepoxide of 1,3-cyclooctadiene with methylcyanocuprate using the procedure of Mariano and Abe[13] provided ca. 95% of a single isomer concluded to be trans on the basis of the ^1H and ^{13}C NMR spectra discussed in the text.

^1H NMR, $\delta(CDCl_3)$: 0.95 (3 H, d, J = 6 Hz, CH_3), 1.3–1.65 (6 H, m), 1.65–1.78 (2 H, app q, H-8), 1.9 (1 H, br, OH), 2.62 (1 H, m, CH_3CH), 4.67 (1 H, app q, $J \simeq$ 6.6 Hz, CHOH), 5.3 (1 H, H-3) and 5.4 (1 H, H-2) as "AB" pattern (J = 12.5 Hz) with fine coupling. The ^{13}C spectrum is discussed in the text and in Table I. Mass spectrum: m/z 140 (M^+, 2.3%), 122 (25.3), 107 (26.7), 97 (30.0), 96 (28.3), 93 (40.6), 81 (52.9), 79 (50.6), 70 (56.3), 67 (49.3), 57 (36.4), 55 (100). HRMS Calcd for $C_9H_{16}O$: 140.1201. Observed: 140.1205. Calcd for (M + NH_4^+ − H_2O) (NH_3, CI): 140.1439. Observed: 140.1435. Oxidation of this alcohol with Jones reagent provided 4-methylcyclooct-2-enone characterized by its ^{13}C spectrum ($\delta(CDCl_3)$: 22.86, 22.88, 23.98, 22.66, 33.28, 42.49, 132.18, 148.66, and 204.78), its reduction with $LiAlH_4$ to a mixture of the trans alcohol described above (33%), and its cis epimer (~66%), whose ^{13}C NMR spectrum has been assigned and listed in Table I. In the ^1H NMR spectrum (obtained for the mixture), the characteristic signals for the cis alcohol are δ 2.4 (CH_3CH), δ 4.52 (CHOH), δ 5.42 (H-2), and δ 5.16 (H-3). Reduction of enone **6** with $LiAlD_4$ provided the 1-$^2H_1$ analogues of **5** and **7**, whose ^{13}C spectra provided the assignments for **5** and **7**.

4- and 8-Methylcyclooct-2-enyl Chlorides (11 and 12). Conversion of alcohol **5** to the allylic chlorides was conducted by using both thionyl chloride in ether and *N*-chlorosuccinimide/dimethyl sulfide in the manner described fully elsewhere.[18] A mixture of four chlorides resulted in the former case and two in the latter. All showed M^+ (160, 158 (3:1)) and ions corresponding to the loss of Cl and HCl, as expected. No attempt was made to separate these reactive chlorides whose ^{13}C NMR spectra were completely assigned (Table I). Chlorination of the 1-$^2H_1$ derivatives of the alcohols provided $^2H_1$-substituted chlorides whose ^{13}C spectra facilitated the assignments listed in Table I. The 400-MHz ^1H spectra of the chloride mixture were obtained with the following key ^1H resonances: *trans*-**11** δ_{CH_3} 1.145 (d, J = 6.8 Hz) and 4.47 (d of d, J = 11, 8.5 Hz, CHCl); *cis*-**11** 1.17 (d, J = 6.3 Hz, CH_3); *trans*-**12** 0.99 (d, J = 6.8 Hz, CH_3) and 4.80 (m, CHCl); *cis*-**12** 1.04 (d, J = 5.9 Hz, CH_3) and 4.80 (m, CHCl).

Trimethylstannylation with $(CH_3)_3SnLi$ prepared in THF, was conducted in the manner described fully elsewhere,[6] and Kugelrohr distillation (85–90 °C/0.5 mm) provided the stannane fraction. The four possible allylic stannane isomers were resolved on capillary GC examination, and all exhibited very similar mass spectra. Mass spectrum: m/z 288 (M^+, 3.0%), 286 (2.5) (for major Sn isotopes), 273 (M − CH_3, 2.6), 165 ($(CH_3)_3Sn$, 100). GC/HRMS (EI) Calcd for $C_{12}H_{24}{}^{120}Sn$: 288.0900. Observed: 288.1048. (CI(NH_3) Calcd for $C_{12}H_{25}{}^{120}Sn$ (M + 1): 289.0978. Observed: 289.1453. The ^{13}C and ^{119}Sn chemical shifts are listed in Table I and discussed in the text, as are key aspects of the 400-MHz ^1H NMR spectra of some of the mixtures obtained by preparative gas chromatography. The characteristic Sn–CH_3 singlet (with ^{119}Sn coupling of ca. 52 Hz) and C–CH_3 doublet (J ~ 6.6 Hz) resonances for the four isomers are as follows: **15**, 0.063 and 0.833; **17**, 0.062 and 0.900; **16**, 0.046 and 0.928; **18**, 0.033 and 0.970. Note that **15** and **17** have been concluded to be the *trans*- and *cis*-8-methyl isomers, and **16** and **18**, the *trans*- and *cis*-4-methyl isomers, respectively.

Acidolyses of the various mixtures of the (methylcyclooct-2-enyl)trimethylstannanes were conducted by adding CF_3COOH or CF_3COOD (in slight excess) to solutions of the stannanes in chloroform, as described elsewhere.[2] These cleavage reactions were exceptionally clean, leading to methylcyclooctenes (regiospecifically deuterated) and trialkyltin salt, on the basis of high-quality ^1H, ^2H, and ^{13}C NMR spectra. A full discussion of the ^{13}C NMR spectra of the various methylcyclooctenes has been presented as part of another report.[4]

Acknowledgment. We are grateful to the Australian Research Council for partial support of this work.