$$E_t = x_t\epsilon_x + z_t\epsilon_z = x_t\epsilon_x + (x_0 - x_t)\epsilon_z$$

since z is equal to the decline in x. When terms are combined it is seen that

$$z_t = \frac{E_t - E_0}{\epsilon_z - \epsilon_x}$$

while $x_t = x_0 - z_t$.

In general, the rate constants were calculated by fitting the usual second-order rate equation to the concentrations as a function of time. In the azide additions, however, the UV method was so sensitive that adequate rate measurements were obtained with 1% or less change in the concentrations of the reactants, and the rate constants could be determined by the zero-order approximation

$$k = \frac{1}{t}\left(\frac{\Delta z}{x(x + c)}\right)$$

where $c = [\text{olefin}]_0 - x_0$.

The rate constants for the substituted phenyl azides are shown in Table III, and some of the data used in determining them are given in Table IV.

Acknowledgment. We thank the Robert A. Welch Foundation and the National Science Foundation for support of this work.

Supplementary Material Available: Tables of IR and NMR spectral data of the triazoline adducts reported in Table V (3 pages). Ordering information is given on any current masthead page.

Synthesis and Electrophilic Cleavage of Some Verbenylstannanes

David Young and William Kitching*

Chemistry Department, University of Queensland, Brisbane 4067, Australia

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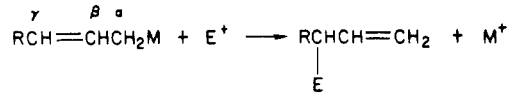
Trifluoroacetolysis of the allylic *cis*- and *trans*-verbenylstannanes yields a mixture of *cis*- and *trans*-δ-pinenes, confirming regiospecific γ-substitution. Analysis of the product distribution confirms the view that any inherent preference for γ-anti substitution (anti-S_E' process) is not so strong that steric effects on both reagent approach and product development cannot influence the balance between syn and anti stereocourses. Sulfur dioxide insertion (chloroform solvent) proceeds readily with the *trans*-stannane to provide the rearranged (tertiary) "δ-pinenylsulfinate" in a stereospecific syn fashion (syn-S_E' process). *cis*-Verbenylstannane is less reactive but is transformed to the same sulfinate. The verbenylstannanes were acquired by trimethyl- and triphenylstannylation (with (trimethyltin)lithium and (triphenyltin)lithium in tetrahydrofuran) of predominantly (~90%) *trans*-verbenyl chloride.

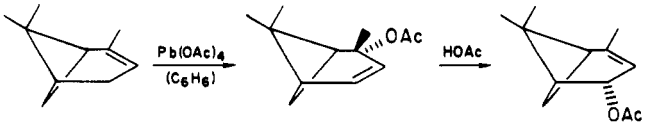
Electrophilic substitution of allyl derivatives of main group metals is a topic of considerable interest and quite attractive because of its γ-regiospecificity as shown below.[1,2] As part of a general program concerned primarily



with the formation and cleavage of allylic derivatives of silicon and tin, we have reported on the stereochemical aspects of these reactions with cyclohex-2-enyl derivatives.[3,4] While this work was progressing, the absence of a stereochemical generality with respect to the S_E' process (electrophilic substitution with allylic rearrangement) became obvious,[1,4] and examination of further structurally diverse allylic systems was required to identify the chief factors regulating stereochemistry. It appeared to us that terpene-based systems, because of their availability and diverse structural features and possiblity of transformation (via allylic metal derivatives) into useful derivatives,[2] warranted examination. In this paper we discuss the characterization of some verbenylstannanes and details of their substitution reactions with acid and sulfur dioxide, while subsequent reports will focus on the carvone- and piperitone-derived allylic stannanes and silanes.[5] While this work was proceeding, we became aware that Russian workers, particularly Kashin and Reutov,[6] had prepared and examined some tin derivatives in this series. Our studies of the verbenylstannanes, while more extensive, agree generally with the Russian findings.

Results and Discussion

α-Pinene was converted to predominantly *trans*-verbenol according to the procedure described by Whitham.[7] This involves reaction with lead tetraacetate (in benzene) to form *cis*-3-pinen-2-yl acetate which undergoes ready allylic isomerization (with acetic acid) to *trans*-verbenyl acetate, followed by saponification. (eq 1). In our hands,



(1)

α-pinene, $[\alpha]_D$ +51° (c, 5.31, CH_3OH), was converted in 38% overall yield to an alcohol mixture ($[\alpha]_D$ +116.6° (c 2.07, $CHCl_3$)) which comprised *trans*-verbenol (87%) and

(1) See, for example: Fleming, I.; Terrett, N. K. *Pure Appl. Chem.* **1983**, *55*, 1707.
(2) Sukurai, H. *Pure Appl. Chem.* **1982**, *54*, 1.
(3) Wickham, G.; Young, D.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 4884. Wickham, G.; Kitching, W. *J. Org. Chem.* **1983**, *48*, 614.
(4) Young, D.; Kitching, W.; Wickham, G. *Tetrahedron Lett.* **1983**, *24*, 5789.
(5) Young, D.; Jones, M.; Kitching, W. *Aust. J. Chem.*, in press.
(6) Kashin, A. N.; Bakunin, V. N.; Beletskaya, I. P.; Reutov, O. A. *J. Org. Chem. (USSR)* **1982**, *18*, 1969. Kashin, A. N.; Bakunin, V. N.; Beletskaya, I. P.; Reutov, A. O. *J. Org. Chem. (USSR)* **1982**, *18*, 1973.
(7) Whitham, G. H. *J. Chem. Soc.* **1961**, 2232. See also: Mori, K. *Agric. Biol. Chem.* **1976**, *40*, 415. Morc, K.; Mizumachi, N.; Matsui, M. *Agric. Biol. Chem.* **1976**, *40*, 1611.

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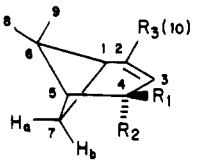
Table I. Carbon-13 Chemical Shifts[a] of Some Pinene Derivatives (Chart I)

	carbon number										
compd	1	2	3	4	5	6	7	8	9	10[b]	$Sn(CH_3)_3$
1	47.6	146.8	119.3	73.1	nl	38.8	35.3	26.8	~22.2	nl[d]	
2	47.9*	148.1	118.8	70.0	46.9*	45.9	28.4	26.5	20.3	22.5	
3	47.1	148.9	117.7	62.7	48.9	39.6	36.6	26.8	20.3	22.3	
4	47.3	148.1	117.8	62.3	48.6	45.6	29.4	26.5	20.3	22.3	
5[c]	47.0	140.4	119.2	34.6	44.7	36.9	33.2	26.6	23.1*	22.2*	-8.90
	(19)	(54)	(34)	(373, 358)	(26?)	(27)	(48)				(318, 303)
6[c]	46.9	140.0	119.6	32.0	44.9	36.4	29.8	26.4	20.8	22.91	-10.4
	(18)	(51)	(41)	(371, 355)	(22)	(41)	(13)			(10)	(316, 303)
7[c]	47.1	142.5	118.2	37.2	44.8	37.3	33.2	26.4	20.8	22.9	
	(20)	(59)	(40)	(395, 377)	(22)	(~20)	(52)				
8[c]	46.8	141.6	118.6	35.3	44.8	36.5	30.3	26.4	20.5	23.1	
	(20)	(55)	(44)	(~387)	(~22)	(68)	(~18)				
9[c]	41.6	125.8*	140.1*	69.5	48.2	43.0	29.4	27.1	24.0	11.7	0.8
											(~474)
10	42.2	129.7	134.4	40.4	48.4	37.9	35.2	27.4	23.8	18.3	
11	42.7	129.9	135.7	35.7	47.6	41.1	28.2	26.6	20.9	18.5	

[a] Chemical shifts are referenced to the central peak of the $CDCl_3$ triplet at 77.00 ppm. [b] C-10 represents CH_3 (either R_1, R_2, R_3). [c] Values in parentheses are ^{119}Sn, ^{117}Sn–^{13}C coupling constants. Asterisked values may be reversed. The values for *cis*-verbenol (compound 1) and *trans*-verbenol (compound 2) were obtained from the ca. 90:10 trans:cis mixture. Distinction between C-9 and C-10 in most entries was based on the unambiguous shift of C-9 (20.9 ppm) in *trans*-δ-pinene (entry 11). [d] nl = not located.

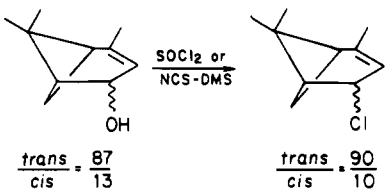
Chart I. Pinene Derivatives



		R_1	R_2	R_3
1	*cis*-verbenol	OH	H	CH_3
2	*trans*-berbenol	H	OH	CH_3
3	*cis*-verbenyl chloride	Cl	H	CH_3
4	*trans*-verbenyl chloride	H	Cl	CH_3
5	*cis*-verbenyltrimethylstannane	$Sn(CH_3)_3$	H	CH_3
6	*trans*-verbenyltrimethylstannane	H	$Sn(CH_3)_3$	CH_3
7	*cis*-verbenyltriphenylstannane	$Sn(C_6H_5)_3$	H	CH_3
8	*trans*-verbenyltriphenylstannane	H	$Sn(C_6H_5)_3$	CH_3
9	"δ-pinenylsulfinate"	CH_3	$SO_2Sn(CH_3)_3$	H
10	*cis*-δ-pinene	CH_3	H	H
11	*trans*-δ-pinene	H	CH_3	H

another component (13%) which was neither myrtenol nor *cis*-pin-3-en-ol. Consideration of its ^{13}C NMR spectrum indicated it to be *cis*-verbenol, and the ^1H NMR spectrum of the alcohol mixture confirmed this, as the minor signals agreed well with those reported for *cis*-verbenol, obtained by metal hydride reduction of verbenone.[8] (*trans*-Verbenol has >C*H*OH at δ 4.17 ($w_{1/2}$ = ~7.7 Hz) while *cis*-verbenol has >C*H*OH at δ 4.37).

Chlorination of the verbenol mixture with thionyl chloride (ether) provided in good yield (~80%) a chloride mixture (93:7) ([α]$_D$ +202° *c* 2.82, $CHCl_3$)) that was predominantly *trans*-verbenyl chloride, on the basis of ^1H and ^{13}C NMR spectra and similarities with the spectra of the verbenols. (The shielding γ-gauche effects of the hydroxyl and chloro groups in the verbenyl derivatives are particularly diagnostic.) The ^1H NMR spectrum of the major trans chloride was completely assigned and is characterized by >CHCl at δ 4.75 ($w_{1/2}$ ~6 Hz) with cis >CHCl at δ 4.91. On the basis of the presumed ion-pair mechanism[7] for allylic isomerization of *cis*-2-acetoxypin-3-ene to *trans*-verbenyl acetate, the result in this chlorination procedure is not surprising. Chlorination with *N*-chlorosuccinimide–dimethyl sulfide (NCS–DMS), a procedure that can exhibit high stereochemical inversion at carbon for the OH → Cl change,[3] also provided very predominantly the trans chloride. This result is not unanticipated, considering the presence of the *gem*-dimethyl bridge (eq 2). A full listing of the ^{13}C NMR data is presented in Table I.

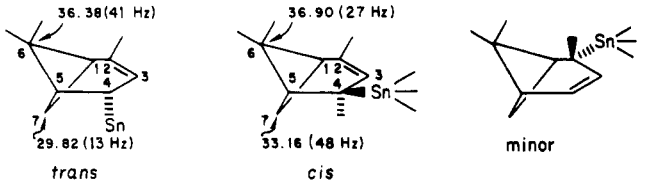


(2)

Trimethylstannylation. Slow addition of the verbenyl chloride mixture (93:7 = trans:cis) to a cold (0 °C) solution of $(CH_3)_3SnLi$ in tetrahydrofuran, provided, after Kugelrohr distillation (2 mmHg, 120 °C oven temperature), a stannane mixture in ca. 67% yield. The ^{119}Sn NMR spectrum revealed the presence of three stannanes with chemical shifts (relative to internal $(CH_3)_4Sn$) of -1.6 (2%), -7.2 (28%), and -7.9 (70%). The composition of a further preparation was 4%, 32%, and 64%, respectively, which had [α]$_D$ +73.0° ($CHCl_3$, *c* 2.06). GC–MS examination showed all three were $C_{13}H_{24}Sn$ derivatives, with M^+ (~1%) showing the characteristic cluster for the tin isotopes. The mass spectrum of the least abundant stannane correlated poorly (0.786) with those of the major isomers which correlated well (0.994). The ^{13}C and ^1H NMR

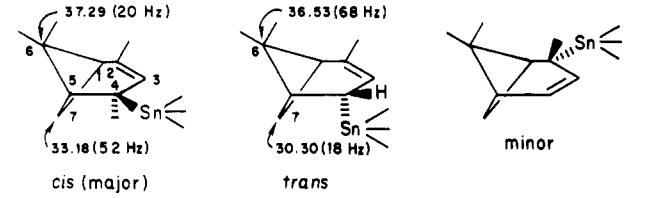
(8) Cooper, M. A.; Salmon, J. R.; Whittaker, D.; Scheidegger, U. *J. Chem. Soc. B* **1967**, 1259.

spectra of the mixture established the major stannanes to be the *cis*- and *trans*-verbenyltrimethylstannanes, and distinction between them appeared straightforward on the basis of the angular (Karplus-type) dependence of vic-^{119}Sn–^{13}C coupling.[9] In the present case, C_7 and C_6 in the trans isomer should have a smaller and larger coupling (to ^{119}Sn) than C_7 and C_6 in the cis isomer, considering the angle differences. (Computed couplings[9] are trans isomer,



55 Hz (C_6) and 8 Hz (C_7); cis isomer, 17 Hz (C_6) and 55 Hz (C_7).) Thus the major stannane is trans, a conclusion concordant with the higher field shift of C_7 in this isomer. (γ-Gauche effect of $Sn(CH_3)_3$.[9]) Other aspects of the ^{13}C and ^1H NMR spectra are unexceptional. (Complete assignment of the ^{13}C spectra was achieved by considering chemical shifts, ^{119}Sn–^{13}C couplings, and various polarization transfer sequences to distinguish the carbon types.) The identity of the minor stannane is not certain, but the presence of a few percent of α-pinene following acidolysis (γ-cleavage) would be consistent with the tertiary stannane above.

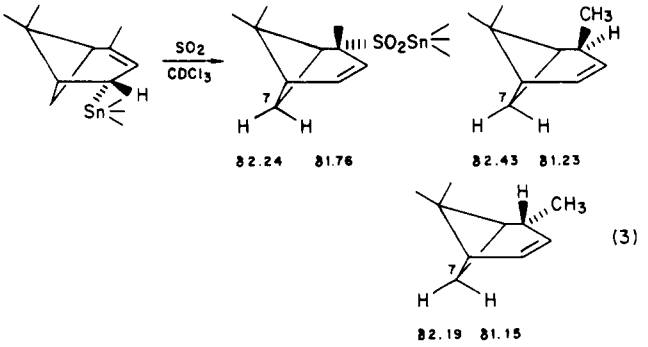
Triphenylstannylation of the predominantly trans (84%) verbenyl chloride was conducted utilizing 1.5 equiv of $(C_6H_5)_3SnLi$ prepared in the customary fashion in tetrahydrofuran. The crude stannane mixture had ^{119}Sn NMR shifts of −127.7 (59%), −131.5 (29%), and −139.0 (12%), whereas the purified stannane (60% yield; $[\alpha]_D$ +7.2 ($CHCl_3$, *c* 1.71)) was shown by a GC–MS procedure to consist of two structurally similar compounds (r = 0.986) in 61% and 36% abundance with a further minor component (3%). As before the major isomers were identified on the basis of their ^{13}C NMR spectra which were completely assigned. That the major stannane was the cis



isomer followed from the vic-^{119}Sn–^{13}C couplings of 52 Hz (C_7) and 20 Hz (C_6), whereas the related isomer (ca. 30%) had analogous couplings of 18 and 68 Hz. The identity of the minor isomer (ca. 3%) is uncertain, and as acidolysis of the triphenylstannanes resulted in highly preferred phenyl cleavage, no structural information was provided.

With respect to these stannylation reactions, overall inversion accompanies triphenylstannylation, a result in keeping with the "S_N2" behavior of this reagent.[10] There is clearly some stereoleakage, and formation of the third (presumed tertiary) stannane could indicate significant syn-S_N2' displacement on the trans chloride. In contrast, the predominance of the trans-trimethylstannane (from trans chloride) requires an intermediate of some type but its nature has not been investigated. Halide displacement by $(CH_3)_3SnLi$ is well-established to be more prone to free radical and anion involvement than triphenylstannylation.[10]

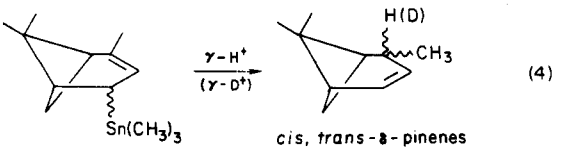
Sulfur Dioxide Insertion. Treatment of the trimethylstannane mixture (69.5% trans:28.2% cis) with SO_2 in deuteriochloroform or methanol resulted in rapid consumption of the trans isomer, whereas several treatments with SO_2 are required for complete consumption of the cis isomer. Nevertheless, only one sulfinate is formed ($[\alpha]_D$ −100.3 (*c* 1.06, CH_3OH)) which lacks a $>CHSO_2^-$ absorption, as appropriate for the δ-pinenyl (tertiary) sulfinate. This is consistent with the ^{13}C NMR spectrum, although distinction between the isomeric tertiary sulfinates is not straightforward. However, the highly preferred syn mode of insertion of chloroform solvent,[11] and the anticipated impeding effect of the *gem*-dimethyl bridge for this mode in the *cis*-stannane, harmonizes with the facile reaction of the *trans*-stannane. We therefore consider the sulfinate to be as shown below (eq 3), but it is supported by the H_7



endo shift of δ 1.76 (decoupling) which is considerably deshielded when compared with H_7 endo in both *cis*- and *trans*-δ-pinenes and reflects the deshielding 1,3-interaction of the $SO_2Sn(CH_3)_3$ group. (H_7 endo appears as a relatively "clean" doublet.) The pathway from *cis*-stannane to the same sulfinate described above apparently involves a less favorable anti-SO_2 insertion, evidence for which has been provided from studies of insertion in methanol solvent[11] where the need for "internal" O-coordination from SO_2 to the leaving Sn≡ group is replaced by methanol coordination.[12] The above analysis is consistent with the observation that only the *minor* triphenylstannane, concluded to be trans, reacts with SO_2, with the cis isomer experiencing prohibitive impedence to the favored syn mode of insertion.

Trifluoroacetolysis of Trimethylstannanes. Kashin and co-workers[6] have examined the acidolysis with hydrochloric and trifluoroacetic acids in various solvents and concluded that the *trans*-stannane reacted slightly faster than the *cis*-stannane and that *cis*-δ-pinene was the major cleavage product from either stannane isomer. A small proportion of α-pinene was reported as a product.

On the basis of γ-acidolysis of the verbenylstannanes, the δ-pinenes would be the anticipated product hydrocarbons, (eq 4), but full ^{13}C and ^1H NMR spectra of these



compounds were not available. Abraham[13] has presented

(9) Doddrell, D.; Burfitt, I.; Kitching, W.; Bullpitt, M.; Lee, C.; Mynott, R. J.; Considine, J. L.; Kuivila, H.; Sarma, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640.

(10) Kitching, W.; Harvey, K.; Olszowy, H. A. *J. Org. Chem.* **1982**, *47*, 1893.

(11) Young, D.; Kitching, W. *J. Org. Chem.* **1983**, *48*, 615. Young, D.; Kitching, W. *Tetrahedron Lett.* **1983**, *24*, 5793.

(12) Young, D. Ph.D. Thesis, University of Queensland, 1985.

(13) Abraham, R. J.; Cooper, M. A.; Salmon, J. R.; Whittaker, D. *Org. Magn. Reson.* **1972**, *4*, 489.

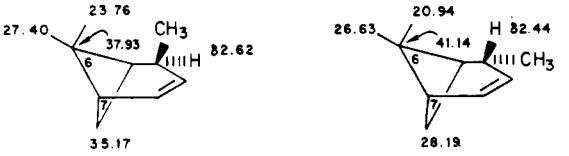
Table II. ^{1}H NMR Data of Some Pinene Derivatives[a] (Chart I)

	proton number										
compd	1	2	3	4	5	7a	7b	8	9	10	$Sn(CH_3)_3$
1	1.87		nl	4.37	nl	2.34					
2	1.92		5.35	4.17	2.05	2.13	1.27	1.25	0.78	1.62	
4	2.02		5.34	4.75	2.35	2.35	1.57	1.32	0.88	1.71	
5	nl		5.28	nl	nl	nl	nl	1.24	0.79	1.63	0.04 (56, 53.5)
6	1.92		5.19 (20.3)	2.12	2.29	2.29	1.04	1.22	0.81	1.63	0.02 (56.6, 54)
7	1.95		5.54 (22.6)	3.35 (95.5)	2.60 (~20)	2.45	1.32	1.19	0.82	1.69	
8	1.95		5.49 (~17)	3.18 (81.2)	2.45?	2.32	1.32	1.23	0.90	1.69	
9	2.17	6.38	5.26		1.90	2.24	1.76	1.32*	0.95	1.06*	0.55 (68.5, 65.8)
10	2.07	6.08	5.51	2.62	2.02	2.43	1.27	1.26	0.98	1.06	
11	2.12	6.09	5.40	2.44	1.84	2.19	1.15	1.26	0.88	0.96	

[a] nl = not located. Values in parentheses are ^{119}Sn, ^{117}Sn–^{1}H coupling constants. Chemical shifts quoted are relative to $CHCl_3$ = δ 7.24 in $CDCl_3$ and refer to center of multiplet. Assignments made in most cases by spin-decoupling, and chemical shifts refer to centers of multiplets. For typical values of ^{1}H–^{1}H couplings in pinene derivatives see ref 13 and references therein. A tabulation of ^{1}H chemical shifts and coupling constants for 1 and 2 may be found in ref 8.

the ^{1}H shifts of cis-δ-pinene, and summarized ^{1}H data are available for both isomers in the report of Bessiere-Chretien.[14] Zweifel and co-workers had described syntheses and partial ^{1}H NMR data of both isomers some years ago,[15] Professor Zweifel kindly made available samples of both isomers, and these have been completely characterised by 300-MHz ^{1}H and ^{13}C NMR spectra and GC–MS behavior. Although there are some significant differences in the ^{1}H NMR spectra, the shielding γ-gauche and deshielding δ-effects of the 4-methyl group in the isomers are particularly diagnostic.

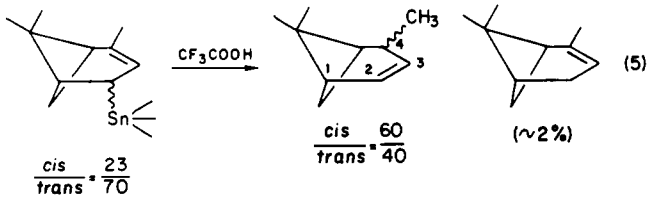
The key ^{13}C and ^{1}H NMR assignments for *cis*- and *trans*-δ-pinene are shown below, and these permitted easy



analysis of the products of the acidolysis reactions. (In *cis*- and *trans*-pinanes, C_7 resonates at 34.4 and 25.1 ppm, respectively.[16,17])

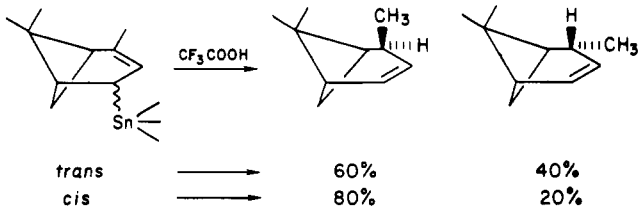
Although the mass spectral behavior of α- and *cis*- and *trans*-δ-pinenes are similar, the order of elution on a 25-m OV1 column is *trans*-δ- followed by *cis*-δ- and α-pinene.

Trifluoroacetolysis ($CHCl_3$) of a stannane mixture consisting of 28.2% *cis*- and 69.5% *trans*-verbenylstannanes (together with ca. 2% of the suspected tertiary δ-pinenyl derivative) resulted in the following product distribution, based on GC–MS and ^{13}C NMR examination of the product mixture (eq 5).



This clean conversion demonstrated γ-substitution[1] (see below) and monitoring the reaction (300-MHz ^{1}H NMR; disappearance of $(CH_3)_3Sn$ signals) demonstrated that the trans isomer reacts faster (ca. 3–5 times) than the cis. Cleavage with $CF_3COOD/CHCl_3$ was conducted and a 32/64 = *cis*/*trans*-stannane mixture (ca. 4.0% of suspected tertiary stannane) provided predominantly *cis*-δ-pinene (cis/trans = 64/36 by GC). The ^{2}H NMR spectrum consisted of signals at δ 2.60 (66%), 2.43 (23%), and 2.14 (~11%) which agree with the shifts for H_4 in *cis*- and *trans*-δ-pinenes and α-pinene,[13] respectively. Thus all evidence requires essentially exclusive γ-proton addition, presumably directed by the trimethylstannyl group. Proton addition β to the stannyl group to form a tertiary cyclobutylcarbinyl cation is clearly less favored.

In the hope of acquiring the pure *trans*-stannane, suspected to be more stable, we attempted Lewis acid (freshly sublimed $AlCl_3$; C_6D_6) induced isomerization of the cis–trans mixture, but this was not successful, although Kashin and co-workers[6] report such isomerization to be relatively facile. Based on the observation that the *cis*-verbenylstannane reacts sluggishly with SO_2, we selectively destroyed most of the trans isomer in this way and obtained a stannane mixture now rich in the cis isomer (cis/trans = 61/39). Trifluoroacetolysis of this mixture provided ca. 73% *cis*- and 27% *trans*-δ-pinenes, and combined with the earlier results (for the trans-rich stannane mixture) requires the *cis*-verbenylstannane to produce more *cis*-δ-pinene than does the *trans*-stannane. It may be concluded that the following operates



(Notice that γ-syn and γ-anti acidolysis of the *trans*- and *cis*-stannanes respectively lead to *cis*-δ-pinene, so that the favored mode differs for the stannane isomers.)

We have demonstrated previously that trifluoroacetolysis of cyclohex-2-enylstannanes follows a highly preferred γ-anti stereocourse[3] but that steric effects in the γ-region (e.g., δ-substituents) can exert a substantial influence, so that with *cis*-4-*tert*-butylcyclohex-2-enylstannane, γ-syn cleavage is dominant.[4] With respect to cleavage of the verbenylstannanes, several likely preference for γ-anti trifluoroacetolysis of allylic stannanes, (ii) steric

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impedance of electrophile approach by the *gem*-dimethyl bridge, and (iii) development of tetrahedral character at C_4 with approach trans to the *gem*-dimethyl bridge displaces the C_4-methyl group toward the congested region of this bridge. In the case of *trans*-verbenylstannane, factor i is opposed by ii, but in the cis isomer i is opposed by iii. The outcome thus depends on the relative importance of these factors, and the production of comparable amounts of *cis*- and *trans*-δ-pinenes from each isomer suggests that the major influence directing γ-proton addition is the *gem*-dimethyl bridge but that in the *cis*-stannane isomer this is reinforced by the inherent γ-anti preference, leading to ca. 80% *cis*-δ-pinene. That acidolysis of *cis*-stannane does not produce solely *cis*-δ-pinene (anti attack) (cooperative effect of factors i and ii indicates the significance of factor iii. Work currently underway in other bicyclic systems should provide more insight into the relative importance of factors influencing the stereochemistry of S_E' processes, particularly where exo,endo and syn-anti competition can be examined.

Experimental Section

Compounds. Predominantly *trans*-verbenol was obtained as described by Whitham[7] and converted to the **verbenyl chlorides** with either thionyl chloride or *N*-chlorosuccinimide/dimethyl sulfide as described previously[3] for cyclohex-2-enol. The chlorides were fully characterized by their ^{13}C and ^1H NMR spectra (Tables I and II). Anal. Calcd for $C_{10}H_{15}Cl$: C, 70.4; H, 8.9. Found: C, 70.9; H, 9.0.

Trimethylstannylation, employing $(CH_3)_3SnLi$ in tetrahydrofuran, was conducted as described previously.[3] Thus treatment of a 93:7 trans/cis verbenylchloride sample with $(CH_3)_3SnLi$ provided the stannane mixture described in the text in ca. 67% yield after Kugelrohr distillation (2 mmHg, oven temperature 120 °C). Anal. Calcd for $C_{13}H_{24}Sn$: C, 52.2; H, 8.1. Found: C, 51.4; H, 8.0. The ^{119}Sn, ^1H, and ^{13}C NMR spectra of the stannanes are described in the text and/or summarized in Tables I and II.

Triphenylstannylation of the verbenyl chlorides was conducted with an excess (1.5 equiv) of (triphenylstannyl)lithium in tetrahydrofuran as described previously. The crude product was dissolved in warm ethanol in which hexaphenylditin was very poorly soluble. The required stannane (60%) formed a very viscous oil. Anal. Calcd for $C_{28}H_{30}Sn$: C, 69.3; H, 6.2. Found: C, 70.2; H, 6.8. The ^{119}Sn, ^1H, and ^{13}C NMR spectra are described in the text. *cis*- and *trans*-δ-pinenes were kindly provided by Professor G. Zweifel and were fully characterized by ^1H and ^{13}C NMR and combined GC-MS.

Reactions with sulfur dioxide in chloroform or methanol and trifluoroacetic acid ($CDCl_3$) were conducted directly in 10-mm NMR tubes. The reaction products were examined directly by NMR spectroscopy and combined gas chromatograph-mass spectrometry (and comparison with authentic samples) where appropriate.

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Synthetic Studies Aimed at the Dolastanes. An Attempted A + C → ABC Approach

Daniel T. Belmont[1] and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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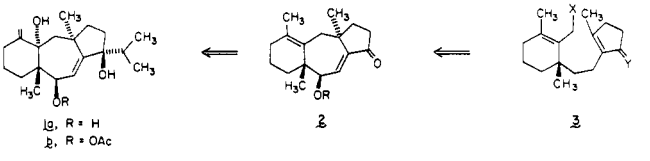
The dolastanes are marine diterpenes whose molecular array of fused 6-7-5 alicyclic rings is distinctive. As part of a program directed toward the synthesis of representatives of these bioactive natural products, the possibility of elaborating their framework by intramolecular cyclization to form the central seven-membered ring has been examined. An expedient two-step route to keto ester **8** was developed. This intermediate proved receptive to copper-promoted conjugate addition of allylmagnesium bromide and [(*E*)-2-(trimethylsilyl)vinyl]lithium. The acetal **21** to be subsequently derived from these adducts could be conveniently crafted into the highly functionalized 2-cyclopentenones **27**. Central to the synthetic strategy was the need for intramolecular C-C bond formation within **27**. Because we were singularly unsuccessful in achieving the desired end result, this particular approach appears unsuited for gaining access to the dolastanes.

The dolastane family consists of a small group of tricyclic diterpenes of marine origin having a uniquely distinctive linear 6-7-5 array of fused alicyclic rings. Dolatriol (**1a**) and its 6-acetate (**1b**) were the first members to be characterized.[2] Of particular note are the impressive cytotoxic properties of **1a**, which markedly inhibits the growth of P-388 lymphocytic leukemia. The location of its three allylic hydroxyl groups and the relative stereochemistry of its five stereogenic centers were defined by three-dimensional X-ray analysis of **1b**.[3] To this time, no reports have appeared describing efforts aimed at the preparation of this class of diterpenes. Our first attempts to assemble the tricyclic nucleus of **1** took the form of the socalled A + C → ABC route. Key compounds in this retrosynthetic analysis are suitably activated derivatives of the bicyclic diene **3**. Although lacking in precedent, the expectation was that bond formation could be achieved within **3** under the proper anionic or cationic conditions,



1a, R = H
1b, R = OAc
2
3

perhaps with good stereocontrol at the site of the incipient

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