Silafunctional Compounds in Organic Synthesis. 32.[1] Stereoselective Halogenolysis of Alkenylsilanes: Stereochemical Dependence on the Coordination State of the Leaving Silyl Groups

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Halogenation of (*E*)-1-octenyltrimethylsilane (**1**), -trifluorosilane (**2**), and -pentafluorosilicate(2-) (**3**) by iodine chloride, bromine, and *N*-bromosuccinimide has been examined in nonpolar solvents, mostly carbon tetrachloride, and in polar solvents, mostly dimethylformamide, in the dark. Cleavage reactions of **1** proceed uniformly with inversion of configuration to form (*Z*)-1-octenyl halides, while **3** is cleaved with retention of configuration to form (*E*)-1-octenyl halides. A dual selectivity is observed with **2**: inversion in nonpolar solvents and retention in polar solvents. Further spectral and mechanistic studies on **2** have provided a general rule for correlation between the stereochemical courses of the halogen cleavage reactions and the coordination states of the silicon center at the stage of attacking by electrophiles. Thus, while attack on ordinary tetracoordinate silicon compounds (trans addition) followed by nucleophilic attack on silicon (anti elimination) leads to inversion, attack on extracoordinate silicon species immediately followed by cleavage of the activated silicon–carbon bond results in retention of the olefin geometry. On the basis of the new aspect, one-pot synthesis of (*E*)- and (*Z*)-alkenyl bromides from acetylene has been achieved in combination with hydrosilation by triethoxysilane.

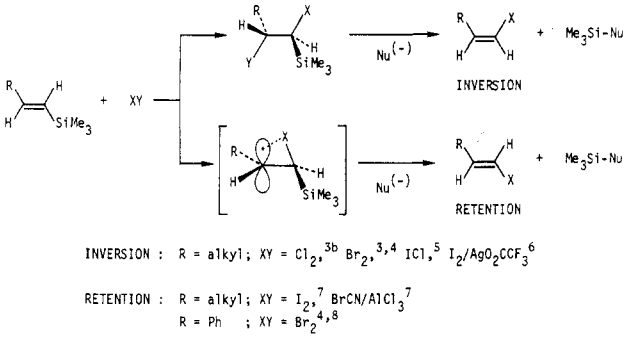
In this report we demonstrate that the stereoselectivity of the halogenolysis of alkenylsilanes is greatly dependent upon the nature of the leaving silyl group, especially the coordination state of the silicon.

Vinylsilanes have now been recognized as useful synthetic reagents, since the carbon–silicon bonds are readily cleaved by various electrophiles in a regio- and stereoselective manner.[2] Halogen cleavage reactions have provided efficient methods for the stereoselective synthesis of (*E*)- and (*Z*)-alkenyl halides. The stereoselectivity has been known to be dependent upon the nature of the reagent and the structure of the alkenyl group, as seen from the literature data summarized in Scheme I.[3-8] These stereochemical results have been explained as follows.[2a] Net inversion of the geometry may result from the trans addition of halogen and the subsequent trans elimination of halogenosilane induced by nucleophiles such as fluoride ions, while retention observed in several cases may arise from a rapid elimination of the silyl group from the intermediate carbonium ion prior to its capture by nucleophiles owing to the poor nucleophilicity of the counterions present and/or relatively high stability of carbonium ions formed.

It should be pointed out here that the leaving silyl group has been restricted to the trimethylsilyl group in all of this previous work.[9] It is easily anticipated, however, that the nature of the silyl group should also be an important factor in the determination of the stereoselectivity. The anticipation originates from the following qualitative analysis of electrophilic cleavage reactions of the carbon–silicon bond.

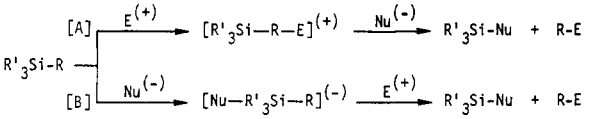
A priori, there would be two extreme cases in electrophilic cleavage reactions, depending on the timing of the interaction with an electrophile and a nucleophile, as shown in Scheme II.[10] In route A, the reaction may be initiated by electrophilic attack on the organic group in the first step followed by nucleophilic attack on silicon. In the other case, route B, the carbon–silicon bond may be activated by extra coordination via nucleophilic attack on silicon in the first step and then cleaved by an electrophile in the second step. A contrasting and complementary electronic effect may be envisaged in these two routes. Thus, in route A, the presence of electronegative substituents on silicon should diminish the reactivity of the carbon–silicon bond, while in route B, the more the electronegative groups on silicon, the easier would be the

Scheme I[a]



[a] For clarity, only the (*E*)-alkenylsilane is presented.

Scheme II



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[‡] Department of Industrial Chemistry.

(1) Part 31: Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090.
(2) (a) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.
(3) (a) Jarvie, A. W. P.; Holt, A.; Thompson, J. *J. Chem. Soc.* B **1969**, 852. (b) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424. (c) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1979**, *44*, 4623. (d) Fisher, R. P.; On, H. P.; Snow, J. T.; Zweifel, G. *Synthesis* **1982**, 127.
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(5) Miller, R. B.; McGarvey, G. *Synth. Commun.* **1978**, *8*, 291.
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(7) Chan, T. H.; Lau, P. W. K.; Mychajlowskij, W. *Tetrahedron Lett.* **1977**, 3317.
(8) Koenig, K. F.; Weber, W. P. *Tetrahedron Lett.* **1973**, 2533.
(9) Only one report has dealt with triphenylsilyl derivatives.[4]
(10) Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; pp 231-242.

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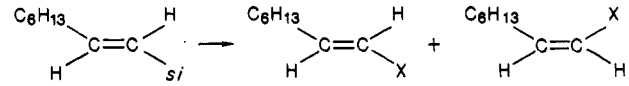
Table I. Halogenation of (*E*)-1-Octenyltrimethylsilane, -trifluorosilane, and -pentafluorosilicate(2-)



entry	*si*	reaction conditions[a]	yield (%)[b]	*E*/*Z*[b]
		Reaction with ICl; X = I		
1	$SiMe_3$ (1)	(1) CCl_4/0 °C–rt/2 h, (2) Al_2O_3[c]	45[d]	6/94
2		(1) DMF/0 °C/2 h, (2) Al_2O_3[c]	68	<1/>99
3	SiF_3 (2)	(1) CCl_4/0 °C/5 h, (2) DMF/0 °C	64[e]	<1/>99
4		DMF/0 °C–rt/2 h	76[e]	95/5
5	SiF_5^{2-} (3)	CCl_4/0 °C–rt/3 h	30[f]	83/17
6		DMF/0 °C–rt/3 h	57	>99/<1
		Reaction with Br_2; X = Br		
7	$SiMe_3$	(1) CCl_4/0 °C–rt/3 h, (2) Al_2O_3[c]	74	<1/>99
8		(1) DMF/0 °C/1 h, (2) Al_2O_3[c]	68	1/99
9	SiF_3	(1) CCl_4/rt/1 h, (2) DMF/0 °C	66	34/66
10		(1) DME/LiBr/0 °C–rt/4 h, (2) DMF/0 °C	45	1/99
11		DMF/0 °C–rt/3 h	66	81/19
12	SiF_5^{2-}	CCl_4/0 °C–rt/2 h	55	72/28
13		DMF/0 °C–rt/4 h	62	91/9
		Reaction with NBS; X = Br		
14	$SiMe_3$	THF/rt/3 h	19	50/50
15		THF/rt/5 h [NBS, 2 equiv]	50	35/65
16		THF/DMF (1 equiv)/rt/3 h	28	27/73
17		THF/DMP (1 equiv)/rt/5 h [NBS, 2 equiv]	61	25/75
18		THF/HMPA(1 equiv)/rt/5 h	25	22/78
19		NMP/50 °C/4 h	55	29/71
20		DMF/rt/5 h	51	10/90
21		DMF/rt/5 h [NBS, 2 equiv]	86	7/93
22	SiF_3	THF/rt/5 h	23	65/35
23		THF/DMF (1 equiv)/rt/3 h	31	72/28
24		THF/DMF (1 equiv)/rt/3 h [NBS, 2 equiv]	25	74/26
25		THF/HMPA (1 equiv)/rt/5 h	49	80/20
26		NMP/rt/5 h	82	87/13
27		NMP/rt/5 h [NBS, 2 equiv]	86	70/30
28		DMF/rt/3 h	45	90/10
29		DMF/0 °C–rt/5 h [NBS, 2 equiv]	67	88/12
30	SiF_5^{2-}	CCl_4/rt/4 h	77	91/9
31		DMF/rt/4 h	80	>99/<1

[a] Reactions were carried out in the dark. rt = room temperature. [b] Determined by GLC, unless otherwise noted. [c] The Al_2O_3 treatment has been developed by Miller et al. (see ref 3b). [d] Octenyl chloride (*E*/*Z* = 14/86) was also formed in 9% yield. [e] Isolate yield. [f] (*Z*)-Octenyl chloride (*Z* > 99%) was also formed in 5% yield.

formation of extracoodinate silicon species and, in turn, the more favorable the cleavage reaction. Therefore, route A should be favored with traditional trimethylsily derivatives, while route B should be realized with silafunctional derivatives. In alkenyl–silicon compounds, we might anticipate different stereochemical outcomes.

The aforementioned halogen cleavage reactions of alkenyltrimethylsilanes fall into the category of route A. Some extreme cases of route B have been found in the chemistry of hexacoordinate organopentafluorosilicates(2–) which may be regarded as isolable intermediates in route B.[11] Thus, we have previously reported[12] that the bromine cleavage of alkenylpentafluorosilicates(2–) proceeds with retention of configuration, in sharp contrast to inversion observed in the corresponding trimethylsilyl chemistry mentioned above, demonstrating the first case of the dependency of the stereoselectivity on the coordination state of the silyl group. We present herein the detailed studies on cleavage reactions of (*E*)-1-octenyltrimethylsilane (1), -trifluorosilane (2), and -pentafluorosilicate(2–) (3) with ICl, Br_2, and NBS and deduce a general rule for the stereochemical dependence on the coordination state of silicon. It should be noted here that while 1 and 3 are regarded as a representative of respectively ordinary neutral tetracoordinate silicon compounds and coordinatively saturated electron-rich silicon compounds, 2 has an electropositive acidic tetracoordinate silicon center which is eager to interact with donating species and hence may exhibit a dual reactivity.

(*E*)-*n*-C_6H_{13}CH=CH-*si*
1, *si* = $SiMe_3$
2, *si* = SiF_3
3, *si* = SiF_5^{2-}/K^+_2

Results and Discussion

Halogenation of (*E*)-1-octenyl–silicon compounds 1–3 by ICl, Br_2, and NBS was examined in nonpolar solvents, mostly CCl_4, and in polar solvents, mostly DMF, in the dark. Table I summarizes the reaction conditions, yields of alkenyl halides, and the *E*/*Z* ratios. Significant features are as follows.

Reactions with ICl and Br_2. The trimethylsilyl derivative 1 gave (*Z*)-octenyl halides with inversion of stereochemistry via a two-step transformation, regardless of the nature of the solvent (entries 1, 2, 7, 8), in consonant with the previously reported results. In contrast, the hexacoordinate counterpart 3 gave directly (*E*)-octenyl halides with predominant to almost exclusive retention of configuration, regardless of the polarity of the solvent

(11) (a) Müller, R. *Z. Chem.* **1984**, *24*, 41; **1985**, *25*, 421. (b) Kumada, M.; Tamao, K.; Yoshida, J. *J. Organomet. Chem.* **1982**, *239*, 115.

(12) Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, R.; Murata, M.; Kumada, M. *Organometallics* **1982**, *1*, 355.

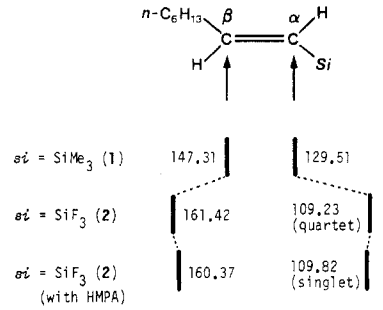


Figure 1. ^{13}C NMR chemical shifts of olefin carbons in **1** and **2** in $CDCl_3$ and in **2** in $CDCl_3$ together with 1 equiv of HMPA: δ from Me_4Si.

(entries 5, 6, 12, 13), the stereoselectivity being higher in DMF than in CCl_4. The most remarkable results have been observed with the trifluorosilyl derivative **2**. Thus, the stereoselectivity changed dramatically from inversion in CCl_4 to retention in DMF (entries 3, 9, 10 vs. 4, 11). In the former case the alkenyl halides were formed only after addition of donating solvent DMF, while in the latter case the halides were obtained directly. It should also be noted that the low stereoselectivity in the Br_2 cleavage in CCl_4 (entry 9) was greatly improved by the addition of LiBr (entry 10).

Reactions with NBS. While the silicate **3** reacted readily with NBS regardless of the polarity of the solvent (entries 30, 31), the trimethylsilyl (**1**) and trifulorosilyl (**2**) counterparts were cleaved only in polar solvents, no reaction being observed in CCl_4 (entries 19–29). The stereochemical outcome was here again inversion with **1**, but retention with **2** and **3**. The stereoselectivity was higher in polar solvents such as DMF and NMP than in less polar solvents. The solvent effects observed with **1** and **2** are informative. Thus, the low selectivity in THF was greatly improved by addition of only 1 equiv of a polar solvent such as DMF and HMPA (entries 14 vs. 16, 18 and entries 22 vs. 25, 27). The use of 2 equiv of NBS improved the yields, keeping the selectivity nearly constant in the case of **1**. Far more important is that even in the inversion chemistry with **1** the halide was formed directly in one step, in contrast to the two-step transformation in the ICl and Br_2 cleavage reactions.

The most significant stereochemical aspects obtained herein are summarized as follows. Cleavage reactions of trimethylsilyl derivative **1** proceed uniformly with inversion of configuration, while pentafluorosilicate(2–) (**3**) is cleaved with retention of configuration. Trifluorosilyl counterpart **2** exhibits a dual selectivity: inversion in CCl_4 and retention in polar solvents. The elucidation of the mechanism for the dual reactivity of the trifluorosilyl derivative should be useful for establishing the general rule for the stereochemistry–coordination state correlation.

NMR Spectral Data of 1 and 2. The ^{13}C NMR spectra of **1** and **2** were taken for the purpose of the approximation of p coefficients of the π-HOMO and π^*-LUMO of the olefins.[13] Figure 1 indicates that **2** has a largely polarized double bond owing to the electron-withdrawing trifluorosilyl group and hence should exhibit a lower reactivity toward electrophiles in comparison with trimethylsilyl counterpart **1**. Addition of 1 equiv of HMPA to **2** caused a very slight perturbation in the chemical shifts, but, significantly, the direction of the perturbation implies the weakening of the electron-withdrawing ability of the trifluorosilyl group.

(13) For example, see: Martin, G. J.; Martin, M. L.; Odiot, S. *Org. Magn. Reson.* **1975**, *7*, 2.

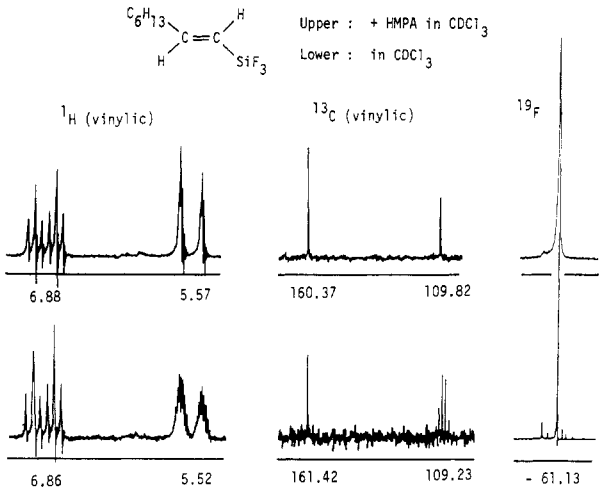


Figure 2. ^1H, ^{13}C, and ^{19}F NMR spectra of **2** in $CDCl_3$ (lower) and in $CDCl_3$ together with 1 equiv of HMPA (upper): δ from Me_4Si for ^1H and ^{13}C and from external CF_3COOD for ^{19}F.

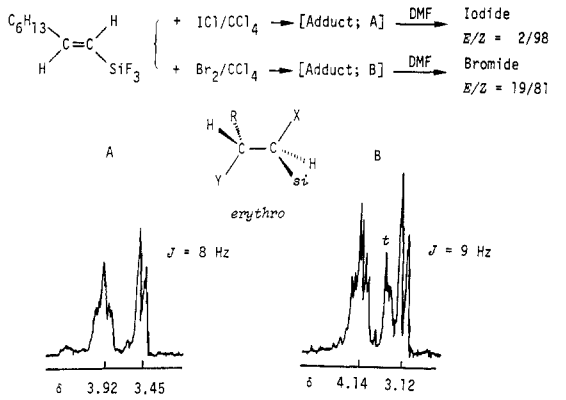


Figure 3. ^1H NMR spectra of adducts formed in ICl and Br_2 cleavage reactions of **2** in CCl_4. Signals marked t in B have been tentatively assigned to threo isomer.

Another significant spectral observation of **2** is a rapid intermolecular fluorine exchange in the presence of HMPA, as shown in Figure 2. Thus, in both the ^1H and ^{13}C NMR spectra, couplings with ^{19}F on silicon, i.e., ^3J(H–F) and ^2J(C–F), disappeared upon addition of 1 equiv of HMPA. In the ^{19}F NMR, the addition of HMPA caused broadening of the resonance. These spectral behaviors indicate that HMPA as a donor molecule[14] induces the fluorine exchange intermolecularly through penta- and hexacoordinate silicon species, the rate being fast on the NMR time scale. A trace amount of fluoride ion present in the mixture may play an important role in the exchange processes.[15]

Detection of Adducts in the ICl and Br_2 Cleavage of 2. Cleavage reactions of **2** with ICl or Br_2 in nonpolar solvent (CCl_4) were monitored by ^1H NMR. After several hours in the dark the vinylic proton signals were completely displaced by new signals diagnostic of the adducts. The δ 3–4 regions are reproduced in Figure 3. In the ICl adduct A, the double multiplet at δ 3.45 is assigned to the proton α to silicon (^3J(H–H) = 8 Hz and ^3J(H–F) = 2 Hz) and the multiplet centered at δ 3.92 assigned to the β-H, consistent with an erythro adduct[5,16b] arising from a high stereospecific trans addition. Similarly, in the Br_2 adduct

(14) Gutman, V. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 843.
(15) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983.
(16) (a) Fahey, R. C.; Schneider, H.-J. *J. Am. Chem. Soc.* **1968**, *90*, 4429. (b) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1469, 1477.

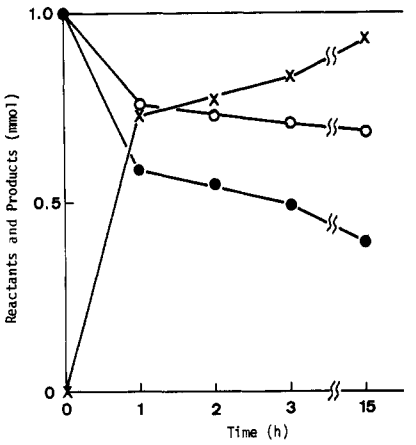
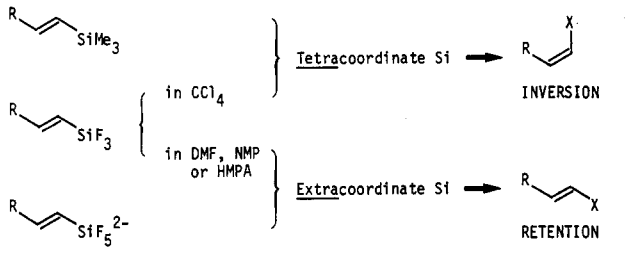


Figure 4. Competitive reactions of 1 (1 mmol) and 2 (1 mmol) with NBS (1.1 equiv) in HMPA (1 equiv)/THF in the dark: 1 (○), 2 (●), and octenyl bromide (×). The E/Z ratio of octenyl bromide remained to be 72/28 at each point.

Scheme III

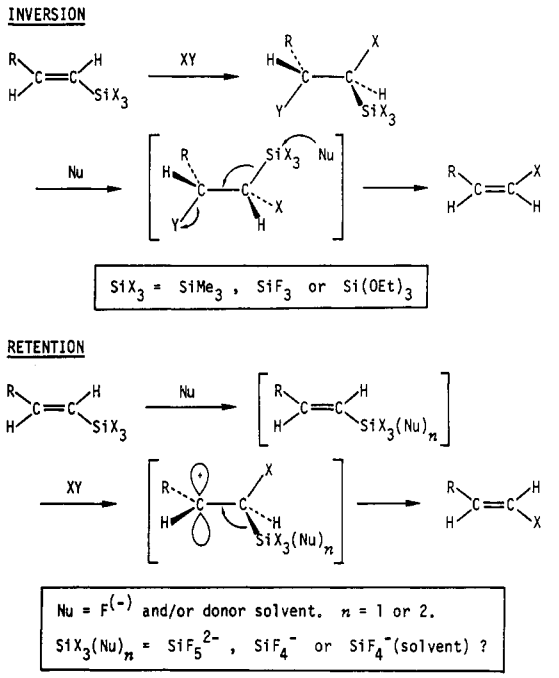


B, signals at δ 3.12 (^3J(H–H) = 9 Hz) and 4.14 are assignable to the α- and β-proton, respectively, of the erythro adduct, and a multiplet about δ 3.5 may be due to the α-proton of the thero isomer (the corresponding β-proton may be hidden in the 4.14 multiplet), indicative of a low stereospecificity of the bormine addition. Addition of DMF to these sample solutions caused the appearance of the signals due to the corresponding alkenyl halides at the expense of the signals of the adducts. GLC analysis showed the E/Z ratio to be 2/98 for 1-octenyl iodide and 19/81 for the bromide.

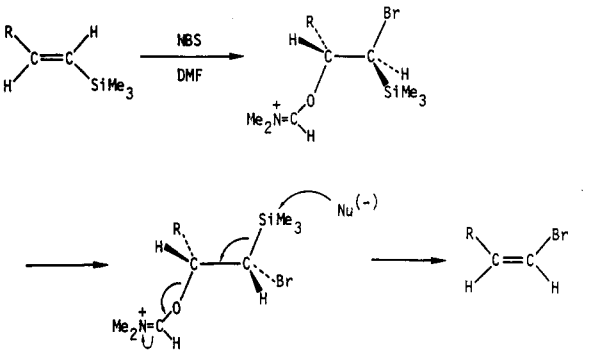
Competitive Reactions between 1 and 2. The reactivity order of 1 and 2 toward the NBS cleavage reactions was examined: in both cases the reaction proceeded in one step to produce the bromide directly (inversion with 1 and retention with 2). An equimolar mixture of 1 and 2 was allowed to react with 1 equiv of NBS in THF containing 1 equiv of HMPA. The reaction was followed by GLC. The results plotted in Figure 4 clearly indicate that 2 is about 1.8 times more reactive than 1. The isomer ratios, E/Z = 72/28, of the resulting bromide remained nearly constant during the reaction and are consistent with the values estimated from the individual experiments (see entries 18 and 25 in Table I). The observed reactivity order (1 < 2) is opposite to that expected simply from the electronic structures estimated by ^{13}C NMR (1 > 2) as mentioned above. The results, however, may be explained in terms of the activation of 2 through the formation of extracoordinate silicon species in the presence of HMPA (vide infra).

Correlation between the Stereochemical Courses and the Coordination States. As summarized in Scheme III, there seems to be a good correlation between the stereochemical courses of the halogen cleavage reactions and the coordination states of the silicon center at the stage of attacking by electrophiles. Thus, while attack on ordinary tetracoordinate silicon compounds followed by nucleophilic attack on silicon leads to inversion, attack on extracoordinate silicon species results in retention of the olefin geometry.

Scheme IV



Scheme V

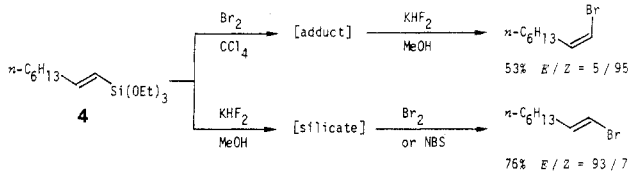


Mechanism of Inversion. All of the inversion chemistries may be explained by a traditional trans addition/anti elimination mechanism, as shown by the inversion route in Scheme I. A more generalized scheme is presented in Scheme IV. In the ICl and Br_2 cleavage reactions of trifluoro derivative 2 in nonpolar solvents, this mechanism has been confirmed by (1) the spectral detection of intermediate addition products and (2) the subsequent conversion of the adducts to alkenyl halides by the addition of DMF. The low stereoselectivity in the bromine cleavage of 2 in nonpolar solvent (entry 9, Table I) is attributable to the loss of stereospecificity of the addition step[16] owing to the less reactive double bond in 2 than in 1. This may be supported by the improved stereoselectivity upon addition of lithium bromide (entry 10, Table I).

The NBS cleavage of 1 in polar solvents with inversion may also proceed by an addition–elimination process. The typical NBS/DMF case is shown in Scheme V. The activation of NBS by DMF[17] may be the first requisite for the cleavage. The attack by the active bromine cation at the α-carbon may be followed by the capture of the β-carbocation by DMF as a weak nucleophile to form an

(17) Mitchell, R. H.; Lai, Y.-H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733.

Scheme VI



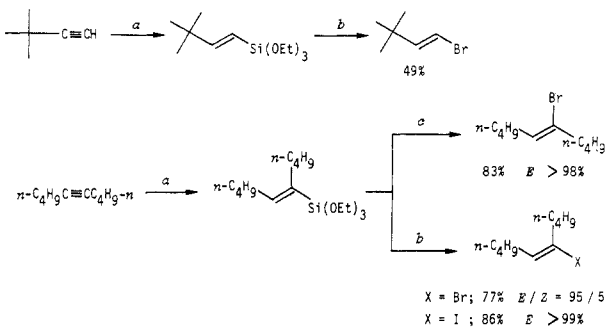
adduct,[18] which may undergo a facile anti elimination of the DMF and the silyl group induced by a weak nucleophile such as a succinimide anion to form (*Z*)-octenyl bromide. NMP and HMPA may play a similar role to afford moderate stereoselectivities, but THF has no such properties showing lower or no stereoselectivities.

Mechanism of Retention. All of the retention chemistries of trifluorosilane **2** as well as silicate **3** may involve the electrophilic attack on hypervalent silicon species, as shown in Scheme IV. Thus, the attack by a halogen cation on the activated double bond may be followed by cleavage of the highly activated silicon–carbon bond. The activation of both of the σ and the π bond in silicates has already been suggested theoretically.[12] The formation of hypervalent silicon species from **2** in the presence of DMF or HMPA has been confirmed spectroscopically as mentioned above. Under these circumstances, the least reactive **2** should be transformed into the extremely reactive species under rapid equilibration conditions. Although the concentration of such species is very low, the cleavage reaction would proceed only through such reactive species to afford the same stereochemical outcome as the silicates. The observed reactivity order (**1** < **2**) toward NBS in the presence of HMPA may also have reflected the change of the coordination state of **2**.

Synthetic Utility. The present aspects of the stereochemical dependence on the coordination state of silicon have provided a new basic concept for the synthetically useful reactions of silafunctional compounds. Thus, as mentioned above, both of the *E* and *Z* isomers of 1-octenyl halides have been prepared from the common (*E*)-octenyltrifluorosilane (**2**) by merely changing the order of treatment with an electrophile and a nucleophile (entries 3, 4, 10, and 11 in Table I). This idea has now been extended to triethoxysilyl counterparts. As shown in Scheme VI, (*E*)-1-octenyltriethoxysilane (**4**) could be transformed into (*E*)- and (*Z*)-octenyl bromide by alternate treatment with bromine and KHF_2. Thus, bromination in CCl_4 afforded an adduct which was treated with KHF_2 in methanol to form the *Z* isomer. Alternatively, (*E*)-**4** was stirred with an excess amount of KHF_2 in methanol overnight to form a white insoluble silicate which was converted to *E* bromide by the addition of bromine or NBS.

These results suggested a one-pot stereoselective synthesis of both isomers of alkenyl bromides from acetylenes in combination with hydrosilation with triethoxysilane. Terminal acetylenes, however, unfortunately could not be generally employed in this approach because of a rather low stereo- and regioselective hydrosilation.[19,20] Only 3,3-dimethyl-1-butyne afforded fairly good results, but a route to only the *E* bromide was achieved (Scheme VII). In contrast, an internal acetylene, which underwent a highly selective hydrosilation to give an (*E*)-alkenyltriethoxysilane exclusively, was transformed into both *E* and *Z* isomers of bromide by the one-pot synthesis (Scheme VII). Similarly, an (*E*)-alkenyl iodide was also prepared, but several attempts with variation of the silyl groups (trimethoxysilane), halogenating agents (I_2 or ICl), and nucleophiles (KF, KHF_2, MeONa, or alumina) for the one-pot synthesis of the *Z* iodide failed.

Scheme VII[a]



[a] (a) $HSi(OEt)_3/H_2PtCl_6{\cdot}6H_2O$ catalyst; (b) (1) KHF_2/MeOH, (2) NBS (or Br_2) or I_2; (c) (1) Br_2/CCl_4, (2) KHF_2/MeOH.

Although the synthetic applications of the present one-pot procedure are restricted to internal, symmetrical acetylenes, the new processes should be useful as an alternative to the existing hydrometalation–halogenation procedures. It may be worthwhile to make a brief comparison here. The hydroboration–halogenation methods[21] have provided routes to (*E*)-alkenyl iodides[21c] and (*Z*)-alkenyl bromides[21d] through (*E*)-alkenylboronic acids and to (*Z*)-alkenyl iodides and (*E*)-alkenyl bromides via (*Z*)-alkenylboronic esters.[21f] While the iodides are formed with retention of geometry of alkenylboronic acids by treatment with alkali followed by iodine, in the bromide case the successive treatments with bromine and alkali result in inversion. In proposed mechanisms, the former retention case involves the halogen attack on alkenylborate anionic species, while in the latter inversion case trans addition of bromine to neutral alkenylboronic acid is followed by trans elimination of boron and bromine moieties. Thus, there is a close mechanistic resemblance between the boron and our silicon chemistry. Stereoselective synthesis of (*E*)-alkenyl bromides and iodides has been achieved by a sequence of cis hydroalumination and halogenation with retention of geometry.[22] All of (*E*)- and (*Z*)-1-alkenyl chlorides, bromides, and iodides are available from (trimethylsilyl)acetylenes via a hydroalumination–halogenation–desilylation process.[22c] Hydrozirconation has made possible the synthesis of only the *E* isomer of alkenyl bromides and chlorides.[23]

Our silicon methods have opened up for the first time efficient routes to both *E* and *Z* isomers of alkenyl bromides from the common *E* hydrosilation product. Refine-

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(20) The $H_2PtCl_6{\cdot}6H_2O$-catalyzed reaction gave a mixture of three isomers, (*E*)-, (*Z*)-*n*-$C_6H_{13}CH{=}CHSi(OEt)_3$, and *n*-$C_6H_{13}C[Si(OEt)_3]{=}CH_2$, in the ratio of 71/11/18. With $RhCl(PPh_3)_3$ as catalyst, allylsilane derivatives *n*-$C_5H_{11}CH{=}CHCH_2Si(OEt)_3$ were also formed in substantial amounts. Details will be reported elsewhere.

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ment of the regio- and stereoselectivity of the hydrosilation of terminal acetylenes with triethoxysilane remains to be achieved for establishing the generality of the present methodology.

Experimental Section

^{1}NMR, IR, and MS facilities have been described in our previous paper,[12] ^{13}C and ^{19}F NMR spectra were recorded on a JEOL FX-100 spectrometer. GLC analyses were performed on a Shimadzu GC-4B gas chromatograph, equipped with a 3-m glass column packed with 30% silicone DC 550 on Celite 545 with a hydrogen carrier flow rate of 60 mL/min. Compound, retention time, and column oven temperature were as follows: (*Z*)- and (*E*)-octenyl chloride, 5.9 and 6.6 min, 100 °C; (*Z*)- and (*E*)-octenyl bromide, 4.5 and 5.0 min, 120 °C; (*Z*)- and (*E*)-octenyl iodide, 6.5 and 7.0 min, 140 °C; (*Z*)- and (*E*)-5-bromo-5-decene, 4.2 and 4.6 min, 180 °C; (*E*)-5-iodo-5-decene, 3.8 min, 200 °C; (*E*)-1-bromo-3,3-dimethyl-1-butene, 4.2 min, 100 °C. GC peak integrals were recorded by using a Shimadzu Chromatopac C-E1B integrator.

1-Octyne and 5-decyne were purchased from Farchan Laboratories, Inc., OH. 3,3-Dimethyl-1-butyne was prepared by the literature procedure.[24] (*E*)-1-Octenyltrimethylsilane (**1**), -trifluorosilane (**2**), -pentafluorosilicate(2–) (**3**), and -triethoxysilane (**4**) were prepared from (*E*)-1-octenyltrichlorosilane,[12] respectively, by methylation with the methyl-Grignard reagent, by fluorination with $CuF_2{\cdot}2H_2O$,[25] by reaction with KF in water,[12] and by usual ethanolysis in the presence of triethylamine.

Reactions of 1, 2, and 3 with Halogenating Agents: General Procedures and Notes on the Results Listed in Table I. A mixture of an alkenylsilane (1 mmol) and a given dry solvent (5 mL) was placed in a one-necked flask equipped with a magnetic stirring bar and wrapped with aluminum foil. Under cooling with an ice bath, bromine or iodine chloride (ca. 1.1 mmol) was added dropwise via a microsyringe; crystalline NBS was added in one portion at 0 °C. After the given period of time, decane or dodecane was added as an internal standard for GLC analysis. In the case of the halogenolysis of **2** in CCl_4, the mixture was treated with DMF (1 mL) at 0 °C for 1 h and then subjected to GLC analysis. In the case of bromine and iodine chloride cleavage reactions of **1**, the mixture was treated with basic alumina (1 g) at room temperature for 15 min prior to GLC analysis.

^{13}C NMR Data of 1 and 2 Pertinent to Figure 1. **1** ($CDCl_3$): δ −1.19 (q), 14.01 (q), 22.62 (t), 28.74 (t), 28.90 (t), 31.79 (t), 36.78 (t), 129.51 (d, α to Si), and 147.31 (d, β to Si). **2** ($CDCl_3$): δ 13.74 (q), 22.48 (t), 27.54 (t), 28.68 (t), 31.59 (t), 36.69 (t), 109.23 (d of q, α to Si, ^2J(C–F) = 25.8 Hz), and 161.42 (d of q, β to Si, ^3J(C–F) = 2.3 Hz). **2** ($CDCl_3$ with 1 equiv of HMPA): δ 13.07 (q), 21.85 (t), 27.58 (t), 28.06 (t), 30.99 (t), 35.94 (t), 109.82 (d, α to Si, ^2J(C–F) = 0 Hz), and 160.37 (d, β to Si, ^3J(C–F) = 0 Hz).

^{1}H NMR Detection of Adducts in the Reaction of 2 with Iodine Chloride or Bromine Pertinent to Figure 3. To an NMR tube were added successively **2** (91 mg, 0.46 mmol), CCl_4 (300 μL, containing Me_4Si as an internal standard), and ICl (30 μL, ca. 0.5 mmol) in the dark. After 3 h of standing, the starting material disappeared and new signals due to adducts appeared. The δ 3–4 region is reproduced in Figure 3. The coupling constant, 8 Hz, between two methine protons, δ 3.45 (dq, J = 8 Hz and J(H–F) = 2 Hz) and 3.92 (br t, J = 8 Hz), is consistent with the erythro isomer, arising from trans addition. Upon addition of DMF (30 μL), the signals of the adduct were displaced by those of (*E*)-1-octenyl iodide (*E*/*Z* = 98/2 by GLC).

A similar reaction of **2** with bromine showed signals due to adducts (Figure 3). These signals wer assignable to a mixture of erythro and threo isomers in the ratio of ca. 3:1. Methine protons of erythro isomer: δ 3.12 (dq, J = 9 Hz and J(H–F) = 2 Hz) and 4.14 (dt, J = 9 and 4 Hz); methine protons of the threo isomer were tentatively assigned to δ 3.81 and around 4.1. Addition of DMF caused the appearance of signals due to 1-octenyl bromide (*E*/*Z* = 81/19 by GLC).

Preparation of (*E*)-1-Octenyl Iodide. To a solution of **2** (600 mg, 3.04 mmol) in dry DMF (15 mL) was added dropwise ICl (200 μL, ca. 3.8 mmol) at 0 °C in the dard with stirring. After being stirred at 0 °C for 20 min and at room temperature for 2 h, the mixture was poured into water and extracted with pentane three times. The combined reddish extract was decolorized by washing with $Na_2S_2O_3$ solution and water and the drying over Na_2SO_4. Bulb-to-bulb distillation gave 608 mg (74% yield) of (*E*)-1-octenyl iodide[19c] (*E*/*Z* = 95/5 by GLC); bp 120 °C/3 mmHg (bath temperature); ^{1}H NMR (CCl_4) δ 0.92 (m, 3 H), 1.1–1.6 (m, 8 H), 1.95–2.25 (m, 2 H), 5.95 (dt, J = 14 and 1.5 Hz, 1 H), and 6.48 (dt, J = 14 and 7 Hz, 1 H); IR 945 cm^{-1}; MS, *m*/*e* (relative intensity) 238 (M^+, 23), 69 (100).

Preparation of (*Z*)-1-Octenyl Iodide. To a solution of **2** (797 mg, 4.04 mmol) in dry CCl_4 was added dropwise ICl (240 μL, ca. 4.5 mmol) at 0 °C in the dark with stirring and the mixture was stirred at room temperature for 2 h. After cooling down to 0 °C again, DMF (2 mL) was added dropwise to the mixture, resulting in the formation of precipitates. The mixture was stirred at room temperature for 1 h and worked up as above to give 674 mg (65% yield) of (*Z*)-1-octenyl iodide[26] (*Z* > 99% by GLC): bp 120–140 °C/5 mmHg (bath temperature); ^{1}H NMR (CCl_4) δ 0.92 (m, 3 H), 1.15–1.65 (m, 8 H), 1.95–2.30 (m, 2 H), and 5.95–6.30 (m, 2 H); MS, *m*/*e* (relative intensity) 238 (M^+, 9), 69 (100).

Preparation of (*E*)-1-Octenyl Bromide. A mixture of **4** (830 mg, 3.02 mmol), KHF_2 (709 mg, 9.07 mmol), and methanol (10 mL) was stirred at room temperature overnight. To the resulting white creamy mixture, containing organopentafluorosilicate(2–),[12] was added NBS (647 mg, 3.63 mmol), and the whole was stirred at room temperature overnight. After filtration the filtrate was poured into water (ca. 50 mL) and extracted with ether three times. The combined extract was washed successively with water, 6 N HCl, saturated $NaHCO_3$, and water and dried over Na_2SO_4. Bulb-to-bulb distillation gave 439 mg (76% yield) of (*E*)-1-octenyl bromide[21f] (*E*/*Z* = 93/7 by GLC): bp 52–60 °C/8 mmHg (bath temperature); ^{1}H NMR (CCl_4) δ 0.92 (m, 3 H), 1.1–1.7 (m, 8 H), 1.90–2.34 (m, 2 H), and 5.85–6.30 (m, 2 H); IR 933 cm^{-1}.

Preparation of (*Z*)-1-Octenyl Bromide. To a solution of **4** (826 mg, 3.0 mmol) in CCl_4 (10 mL) was added dropwise bromine (0.12 mL) at 0 °C. Care must be taken not to add an excess amount of bromine: the color of the reaction mixture should not become reddish, but yellowish, otherwise much lower stereoselectivity would result. After stirring at 0 °C to room temperature for 4 h, to the resulting clear yellow solution were added KHF_2 (706 mg, 9.04 mmol) and methanol (10 mL), and the mixture was stirred at room temperature overnight. The white precipitates were filtered and the filtrate was mixed with a dilute solution of $Na_2S_2O_3$ and then extracted with ether. Workup as above afforded 303 mg (53% yield) of (*Z*)-1-octenyl bromide[21d] (*Z*/*E* = 95/5 by GLC): bp 64–70 °C/17 mmHg (bath temperature); ^{1}H NMR (CCl_4) δ 0.92 (m, 3 H), 1.1–1.7 (m, 8 H), 2.0–2.35 (m, 2 H), 5.9–6.2 (m, 2 H).

Determination of (*E*)- and (*Z*)-1-Octenyl Chloride as Byproducts in Runs 1 and 5 in Table I. Isolation by preparative GLC. *E* isomer:[22c] ^{1}H NMR δ 0.8–1.1 (m, 3 H), 1.2–1.6 (m, 8 H), 1.9–2.2 (m, 2 H), and 5.8–6.1 (m, 2 H); IR 934 cm^{-1}; MS, *m*/*e* 146 and 148 (M^+). *Z* isomer:[22c] ^{1}H NMR δ 0.8–1.1 (m, 3 H), 1.2–1.7 (m, 8 H), 2.1–2.4 (m, 2 H), 5.73 (dt, J = 7 and 7 Hz, 1 H), and 6.02 (br d, J = 7 Hz, 1 H); MS, *m*/*e* 146 and 148 (M^+).

One-Pot Preparation of Alkenyl Halides from Acetylenes. (a) (*E*)-5-Bromo-5-decene. A mixture of 5-decyne (418 mg, 3.02 mmol) and triethoxysilane (721 mg, 4.39 mmol) was prepared. To an aliquot (ca. 1/10) were added two drops of $H_2PtCl_6{\cdot}6H_2O$ solution in 2-propanol (0.1 M solution). After being heated at 60 °C briefly to cause the hydrosilation, the remaining mixture was added to the warm reaction mixture dropwise to maintain the exothermic reaction. The complete disappearance of the acetylene was confirmed by GLC analysis. To the hydrosilation mixture were added KHF_2 (1371 mg, 17.56 mmol) and methanol (10 mL). After stirring at room temperature overnight, NBS (753 mg, 4.23 mmol) was added, and the mixture was stirred at room temperature for 4 h. Essentially the same workup as described for (*E*)-1-octenyl bromide gave 511 g (77% yield) of the product[12] (*E*/*Z* = 95/5 by GLC): bp 88–98 °C/19 mmHg (bath temperature); ^{1}H NMR (CCl_4) δ 0.8–1.1 (m, 6 H), 1.1–1.7 (m, 8 H), 1.8–2.3

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(m, 2 H), 2.40 (t, J = 7 Hz, 2 H), and 5.77 (t, J = 7 Hz, 1 H). If the hydrosilation product was isolated by distillation and subjected to the same transformation, isomerically pure ($E > 99\%$) bromide was obtained in 80% yield. The only impurity (ca. 5%) was tentatively assigned to 5-methoxy-5-decene (MS, m/e 170). The use of bromine (do not use in excess amounts) instead of NBS in the one-pot procedure afforded the bromide (E/Z = 95/5) in 76% yield, which contained more impurities. NBS is the reagent of choice.

(b) (*E*)-5-Iodo-5-decene. The use of iodine (1.0 molar equiv to the acetylene) at room temperature for 4 h, instead of NBS or bromine in (a), gave the (*E*)-iodide[22a] ($E > 99\%$) in 86% yield: bp 96 °C/18 mmHg; ^{1}H NMR (CCl_4) δ 0.8–1.15 (m, 6 H), 1.15–1.7 (m, 8 H), 2.06 (dt, J = 7 and 7 Hz, 2 H), 2.37 (t, J = 7 Hz, 2 H), 6.13 (t, J = 7 Hz, 1 H). Anal. Calcd for $C_{10}H_{19}I$: 266.0529. Found: 266.0536.

(c) (*Z*)-5-Bromo-5-decene. To the hydrosilation product obtained as above from 5-decyne (414 mg, 2.99 mmol) were added CCl_4 (10 mL) and bromine (0.135 mL; do not use in excess) dropwise at 0 °C. After stirring at 0 °C for 2 h, methanol (10 mL) and KHF_2 (1312 mg, 16.79 mmol) were added, and the mixture was stirred at room temperature overnight. Usual workup gave 544 mg (83% yield) of the Z isomer[12] ($Z > 98\%$): bp 88 °C/19 mmHg; ^{1}H NMR (CCl_4) δ 0.8–1.1 (m, 6 H), 1.1–1.7 (m, 8 H), 2.0–2.3 (m, 2 H), 2.40 (t, J = 7 Hz, 2 H), and 5.57 (t, J = 7 Hz, 1 H); MS, m/e (relative intensity) 218, 220 (M^+, 11), 83 (100).

(d) (*E*)-1-Bromo-3,3-dimethyl-1-butene was obtained in 49% yield by similar procedures to those described in (a) and by careful workup of the highly volatile product; E/Z = 98/2, bp 65 °C/122 mmHg (bath temperature). The rather low yield was attributable to the high volatility of the product, since the yield determined by GLC was 86%. ^{1}H NMR were superimposable on the literature data.[5]

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The Stereochemistry of S_N2' Addition to Macrocyclic α-Methylenecycloalkylidene Epoxides by Organocopper Reagents

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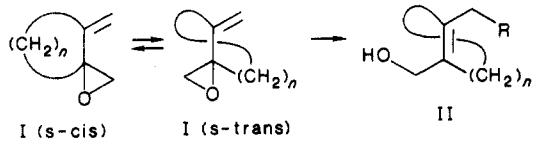
The addition of *n*-butylmagnesium bromide–copper(I) iodide in THF–dimethyl sulfide has been carried out with the 12-, 14-, and 16-membered optically active (*R*)-2-methylenecycloalkylidene epoxides **9a**, **9b**, and **9d**. In each case, the S_N2' substitution products **10** and **11** were formed with the trans predominating by 9:1 or better. The 12- and 14-membered cycloalkylidene epoxides **9a** and **9b** gave the (*R*)-cycloalkenylcarbinols **10a** and **10b** of over 90% optical purity. Accordingly, attack on the double bond must occur syn to the epoxide oxygen via the O-exo s-trans conformer of **9a** and **9b**. The 16-membered cycloalkylidene epoxide **9d** gave racemic cycloalkenylcarbinol **10d** upon treatment with the foregoing organocopper reagent. This result is attributable to racemization of **10d** rather than nonselective S_N2' addition.

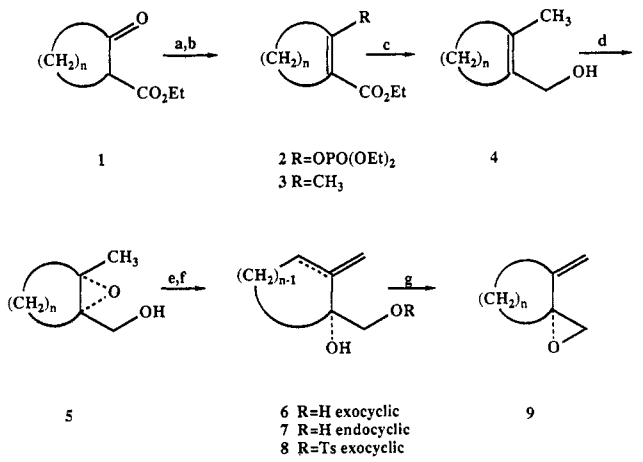
Additions of organocopper reagents to α-methylenecycloalkylidene epoxides (I) have been found to proceed via S_N2' displacement to afford predominantly (*Z*)-cycloalkenylcarbinols (II).[1] The regio- and stereochemical preferences of this addition are thought to arise from a



reactant-like transition state involving π complexation of the organocopper[2] to the lower energy s-trans conformer[3] of the cycloalkylidene epoxide.[1] The present investigation was undertaken to examine the stereoselectivity of the attack relative to the epoxide oxygen. Previous studies of this nature have employed rigid cycloalkene epoxides with fixed s-cis or, less commonly, s-trans geometries.[4] In these cases a general preference for anti S_N2' attack was noted.

For our approach we planned to use optically active α-methylenecycloalkylidene epoxides of known configuration (e.g., **9**; see Figure 1). Addition of the organocopper reagent as described previously would afford the *trans*-cycloalkenylcarbinols (e.g., **10**). These cycloalkenes are

Scheme I[a,b]



[a] **a** series, n = 10; **b** series, n = 12; **d** series, n = 14. [b] (a) NaH, Et_2O, 0 °C; $ClPO(OEt)_2$; (b) CH_3Li·LiBr, CuI, Et_2O, −78 to 0 °C; (c) DIBAH, hexane; (d) $Ti(O\text{-}i\text{-}Pr)_4$, (+)-DET, TBHP, CH_2Cl_2, −23 °C, 2–3 h; (e) Et_2AlNR_2, 0 °C–reflux; (f) *p*-TsCl, Et_3N, DMAP, CH_2Cl_2, 0 °C; (g) $PhCH_2NMe_3OH$, Et_2O, 20 °C.

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(3) Calculations were performed on the 12-membered system I (n = 10) by W. Clark Still using his programs Ringmaker–Bakmod–Model. We are indebted to Prof. Still for his valued assistance.

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