Stereoselective Trisubstituted Olefin Synthesis via Vinylsilanes[1]

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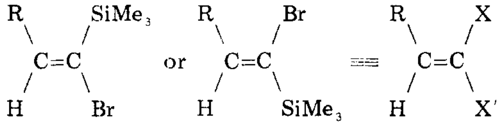
Received March 23, 1979

The utility of 1-bromo-1-(trimethylsilyl)-1-alkenes of defined stereochemistry in a stereoselective trisubstituted olefin synthesis is demonstrated. These α-bromosilanes are synthons of 1,1-dihaloalkenes in which each halogen group can be functionalized independently and stereoselectively. A study of the effect of alkyllithium reagent on alkylation of **1** and **2** shows that *sec*-butyllithium is more efficient than either *n*- or *tert*-butyllithium. Coupling of **1** and **2** via organocuprates is more effective with (PhS)(R)CuLi reagents than with the corresponding R_2CuLi species. Coupling of alkyllithium reagents with vinyl bromides can be carried out efficiently by using 20 mol % of cuprous iodide as long as the alkyllithium reagent does not undergo extensive halogen–metal exchange with the vinyl bromide. The alkylated vinylsilanes are converted to vinyl bromides by a bromination–desilicobromination technique developed earlier with minor experimental modifications. Finally both (*E*)- and (*Z*)-3-methyl-3-octene are prepared stereoselectively by a variety of methods from the appropriate vinyl bromide **8**, **9**, **11**, or **12**.

In the course of our studies[2] on the utility of vinylsilanes in organic synthesis[3] we have developed a highly stereospecific trisubstituted olefin synthesis[4] which is the subject of this paper. The basis of the synthetic scheme involves a 1-bromo-1-(trimethylsilyl)-1-alkene of defined stereochemistry as a synthon of a 1,1-dihaloalkene in which each halogen group can be functionalized independently and stereoselectively.

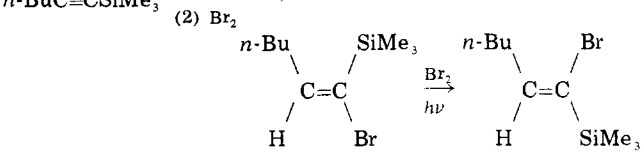


We chose to investigate alkylation and cuprate coupling reactions as our method of functionalization. The general route of our synthetic sequence is shown in Scheme I.

Scheme I

$$\mathrm{RCH{=}CBrSiMe_3} \xrightarrow[\text{or coupling}]{\text{alkylation}} \mathrm{RCH{=}CR'SiMe_3} \xrightarrow[\text{(2) NaOMe}]{\text{(1) Br}_2} \mathrm{RCH{=}CR'Br} \xrightarrow[\text{or coupling}]{\text{alkylation}} \mathrm{RCH{=}CR'R''}$$

The route recently developed by Zweifel[5] provided the 1-bromo-1-(trimethylsilyl)-1-alkenes of defined stereochemistry. Thus, hydralumination of 1-(trimethylsilyl)-1-hexyne with diisobutylaluminum hydride followed by cleavage of the intermediate vinylalane with bromine gave, in our hands, cleanly the *E* isomer **1** in 91% yield. The *Z* isomer **2** could be obtained (94% yield, 98% *Z* isomer) by subjecting **1** to less than an equivalent amount of bromine in the presence of a light source.



1 **2**

Alkylation of 1-Bromo-1-(trimethylsilyl)-1-alkenes.[6] With both isomers of the desired starting material in hand, we turned our attention to the manipulation of the vinyl bromide functionality. While there exist a large number of methods with this capability, we decided first to investigate the alkylation of the corresponding vinyllithium derivatives.[7] As such, conversion of 1-bromo-1-(trimethylsilyl)-1-alkenes **1** and **2** to their vinyllithium derivatives became our objective.

There are two commonly employed methods of lithiating halides: (1) direct metalation with lithium metal and (2) halogen–metal exchange with alkyllithium reagents. Both in our hands and by other workers[8] lithiation of bromovinylsilanes with lithium metal has proven to be unsatisfactory for synthetic purposes. This result dictated that we approach this problem by the second method, halogen–metal exchange with alkyllithium reagents which in this case is favored not only by formation of a vinyllithium species but also by the presence of silicon α to the carbanionic center to give further stabilization.[9]

It was found that virtually complete lithiation could be achieved by treatment with *n*-butyllithium. Two aspects of this exchange deserve special comment. First, whereas the exchange took place quite rapidly in tetrahydrofuran, little or no reaction was observed when diethyl ether was used as solvent. In addition, it was observed that complete exchange for the *Z* isomer **2** could be attained in 1–2 h at −78 °C. However, application of these conditions to the *E* isomer **1** resulted in substantial alkylation of the vinyllithium compound with the *n*-butyl bromide formed upon exchange.[10] A solution to this latter problem was found by running the exchange at −100 °C in the Trapp

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(1) Presented in part at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 13, 1978.

(2) (a) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424. (b) Miller, R. B.; McGarvey, G. *Synth. Commun.* **1977**, *7*, 475; **1978**, *8*, 291. Miller, R. B.; Reichenbach, T. *Tetrahedron Lett.* **1974**, 543.

(3) For recent reviews on organosilicon compounds in organic synthesis, see: Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15. Hudrlik, P. F. In "New Applications of Organometallic Reagents in Organic Synthesis"; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976; pp 127–59. Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442.

(4) For some other stereoselective synthesis of trisubstituted olefins via vinylsilanes, see: Westmijze, H.; Meijer, J.; Verneer, P. *Tetrahedron Lett.* **1977**, 1823. Chan, T. H.; Lau, P. W. K.; Mychajlowskij, W. *Ibid.* **1977**, 3317.

(5) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2739.

(6) (a) Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785. (b) *Tetrahedron Lett.* **1976**, 4839.

(7) For related alkylations, see: Uchida, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1977**, *33*, 2987.

(8) Husk, G. R.; Velitchko, A. M. *J. Organomet. Chem.* **1973**, *49*, 85.

(9) Cook, M. A.; Eaborn, C.; Jukes, A. E.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 529 and references cited therein.

(10) Millon, J.; Lorne, R.; Linstrumelle, G. *Synthesis* **1975**, 434.

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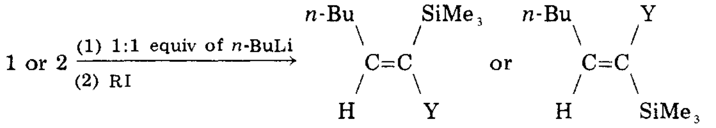
Table I. Alkylation of (*E*)- and (*Z*)-Bromovinylsilanes Using *n*-BuLi



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starting material	exchange cond		R	% Y in 3[a]					% Y in 4[a]		
	solvent	T, °C		Y = H	Y = Me	Y = Et	Y = *n*-Bu	Y = Br	Y = H	Y = Me	Y = Et
1	Trapp	-100	Me		60						
1	THF	-78	Et	(5)		(70)	(16)				
1	Trapp	-100	Et	(4)		75 (89)	(2)	(3)			
1	THF	-78	*n*-Bu	(3)			92 (97)				
2	THF	-78	Me							74	
2	THF	-78	Et						(4)		73 (86)

[a] Isolated yield (GLC yield).

solvent mixture[11] for 0.5 h. Thus, the conditions employed for bromine–lithium exchange illustrate the considerable difference in reactivity enjoyed by these two isomers.

We next endeavored to alkylate these vinyllithium compounds with various alkyl iodides. The results of this line of investigation are given in Table I. The problem of the undesirable alkylation with the *n*-butyl bromide formed during exchange is illustrated by the second and third entries. While the GLC results of running the reaction at -100 °C in the Trapp solvent mixture seem to indicate that this is an attractive solution to the problem, it was observed that substantial amounts of butylated material were obtained when the reaction was run on preparatively useful scales. This is reflected in the modest isolated yields of methylated (**3**, Y = Me) and ethylated (**3**, Y = Et) material (first and third entries, Table I). On the other hand, as would be predicted, butylation of the vinyllithium compound derived from **1** proceeded unhindered by this complication to give the alkylated product (**3**, Y = *n*-Bu) in excellent isolated yield (fourth entry, Table I). Indeed, if the exchange with **1** is effected with ethyllithium in tetrahydrofuran at -78 °C followed by alkylation with ethyl iodide, the ethylated product (**3**, Y = Et) could also be obtained in high yield (85% distilled yield, 88% GLPC yield; contrast this with the second entry of Table I).

The alkylation of the vinyllithium compound derived from (*Z*)-bromovinylsilane **2** also gave modest isolated yields resulting from methylation (**4**, Y = Me) and ethylation (**4**, Y = Et). The reason for the decreased yield when using methyl iodide was the formation of significant amounts of vinyl iodide by halogen–metal exchange of the vinyllithium compound with the methyl iodide.[6a] In fact, if the reaction was run at -100 °C, the vinyl iodide became almost the exclusive product.

Since side reactions leading to decreased yields and possible purification problems precluded the use of *n*-butyllithium as a general reagent for alkylating compounds such as **1** and **2**, we looked at the use of other alkyllithium reagents. Encouraged by reports that 2 equiv of *tert*-butyllithium effectively converted vinyl halides to their vinyllithium derivatives,[6,12] we examined its application to our compounds. Our observations are summarized in Table II. Under the conditions we employed, the use of *tert*-butyllithium was marred by the formation of substantial amounts of protonated material (**3** or **4**, Y = H). Neither the mode of addition nor the use of diethyl ether instead of tetrahydrofuran as solvent had any effect.

Table II. Alkylation of (*E*)- and (*Z*)-Bromovinylsilanes Using *t*-BuLi

$$1 \text{ or } 2 \xrightarrow[(2)\ \text{EtI}]{(1)\ t\text{-BuLi, solvent, } -78\ ^\circ\text{C}} 3 \text{ or } 4$$

starting material	equiv of *t*-BuLi	solvent	% Y in 3[a]		% Y in 4[a]	
			Y = H	Y = Et	Y = H	Y = Et
1	2.1	THF	23	77		
1	2.1	Et_2O	29	70		
2	2.1	THF			19	70
1	1.1	THF	21	79		
2	1.1	THF			18[b]	55[b]

[a] GLC yield. [b] Also 21% starting material (2).

It is of interest to note that we, as well as others,[13] observed that virtually identical results were obtained when only 1 equiv of *tert*-butyllithium was used instead of 2 equiv in the case of *E* isomer **1** (fourth entry, Table II). This result is unexpected in the face of reports which indicate that *tert*-butyl bromide, formed upon exchange, is rapidly converted to isobutylene in the presence of *tert*-butyllithium even at -120 °C.[6b] On the other hand, the recovery of significant amounts of starting material when *Z* isomer **2** is alkylated under these conditions (fifth entry, Table II) is consistent with *tert*-butyllithium being consumed in dehydrohalogenating *tert*-butyl bromide. These conflicting results with the two isomers probably reflect the ease with which **1** undergoes exchange relative to **2**.

Having found both *n*-butyllithium and *tert*-butyllithium to be unsatisfactory general reagents for effecting alkylation of our bromovinylsilanes, we turned to *sec*-butyllithium. This reagent offered the advantage of forming *sec*-butyl bromide upon exchange which would be less susceptible to alkylation than *n*-butyl bromide and should not undergo dehydrohalogenation as readily as *tert*-butyl bromide. Although we initially employed 2 equiv of *sec*-butyllithium, we found that treatment of either isomer of the bromovinylsilane with 1 equiv of this alkyllithium reagent in tetrahydrofuran at -78 °C for 0.5 h effected complete exchange. Table III gives the results obtained when alkylation was performed on the vinyllithium compounds formed under these conditions.

As can be seen, the alkylations proceeded in a stereospecific manner to afford the desired products (**3** and **4**,

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(11) Köbrich, G.; Trapp, H. *Chem. Ber.* **1966**, *99*, 680. See also: Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 41; **1972**, *11*, 473.

(12) Boeckman, R. K., Jr.; Bruza, K. J. *Tetrahedron Lett.* **1974**, 3365.

(13) Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Organomet. Chem.* **1976**, *107*, Cl.

Table III. Alkylation of (*E*)- and (*Z*)-Bromovinylsilanes Using *sec*-BuLi

$$1 \text{ or } 2 \xrightarrow[\text{(2) RX}]{\text{(1) 1.1 equiv of } sec\text{-BuLi, THF, } -78\ ^\circ\text{C}} 3 \text{ or } 4$$

starting material	RX	% Y in 3[a,b]		% Y in 4[a,b]	
		Y = H	Y = R	Y = H	Y = R
1	MeI		88		
1	EtI	(4)	90 (95)		
1	*n*-BuI	(2)	95 (97)		
1	*sec*-BuI	(93)[c]			
2	MeI				68
2	Me_2SO_4				90
2	EtI			(6)	93 (94)
2	*n*-BuI			(12)	76 (85)
2	*sec*-BuI			(87)	

[a] Isolated yield (GLC yield). [b] Isomeric purity at least 98% and in most cases >99%. [c] 2.2 equiv of *sec*-BuLi employed.

Table IV. Coupling of (*E*)- and (*Z*)-Bromovinylsilanes with R_2CuLi

$$1 \text{ or } 2 \xrightarrow{R_2CuLi \text{ (5 equiv)}} 3 \text{ or } 4$$

starting material	solvent	R	% Y in 3[a]		% Y in 4[a]	
			Y = H	Y = R	Y = H	Y = R
1	Et_2O	Et	61	37		
1	THF	Et	86	10		
2	Et_2O	Et			34	54
1	Et_2O	Et[b]	55	32		
1	Et_2O	*n*-Bu	47	53		

[a] GLC yield. [b] EtI added.

Y = R) in excellent yields. The alkylation of the vinyllithium compound derived from **2** with methyl iodide was again complicated by the formation of appreciable amounts of iodovinylsilane, resulting in the modest yield of methylated product (**4**, Y = R = Me; fifth entry, Table III). This problem was overcome by using an alkylating agent with a leaving group that was not susceptible to the exchange reaction. Thus alkylation with dimethyl sulfate gave a 90% isolated yield of methylated material (sixth entry, Table III).[14] Attempts at extending this alkylation procedure to the use of secondary alkylating agents were uniformly met with failure since dehydrohalogenation became the dominant pathway (fourth and ninth entries, Table III).

To briefly summarize our alkylation study, we have found that *sec*-butyllithium is an efficient (only 1 equiv necessary) and general reagent for effecting the halogen–metal exchange reaction with α-bromovinylsilyl compounds such as **1** and **2**. This is in contrast to the use of *n*-butyllithium and *tert*-butyllithium which is hindered by a variety of side reactions. Furthermore, alkylation of the vinyllithium compounds generated by the *sec*-butyl reagent generally proceeds in a stereospecific manner in excellent yields, being limited only by the nature of the alkylating agent.

Coupling Reactions of 1-Bromo-1-(trimethylsilyl)-1-alkenes with Organocopper Reagents. Having determined conditions for efficiently alkylating 1-bromo-1-(trimethylsilyl)-1-alkenes **1** and **2**, we thought it of interest to study the behavior of these compounds toward organocopper reagents. We began our investigation by utilizing the lithium dialkylcuprates, now enjoying widespread use in organic synthesis.[15] The results of this study are given in Table IV.

Table V. Coupling of (*E*)- and (*Z*)-Bromovinylsilanes with (PhS)(R)CuLi

$$1 \text{ or } 2 \xrightarrow[\text{THF}]{\text{(PhS)(R)CuLi}} 3 \text{ or } 4$$

starting material	R	equiv of (PhS)-(R)-CuLi	% Y in 3[a]		% Y in 4[a]	
			Y = H	Y = R	Y = H	Y = R
1	Et	2	(30)	(66)		
1	Et[b]	2	(17)	(81)		
1	*n*-Bu	4	(34)	(64)		
1	*sec*-Bu	2		73[c]		
1	*t*-Bu	4		69[c]		
2	Et	4			(16)	(68)
2	Et[b]	4			(12)	(84)
2	*n*-Bu	4			(19)[d]	(55)[d]
2	*sec*-Bu	4				33[c]
2	*t*-Bu	4				53[c]

[a] Isolated yield (GLC yield). [b] Added EtI. [c] Isomeric purity at least 97%. [d] Also 20% starting material (**2**).

The most prominent feature of this data is the large percentage of protonated material obtained in all cases. This product (**3** or **4**, Y = H) is thought to be derived by halogen–metal exchange giving a vinylcopper derivative which was protonated upon workup.[15b] This explanation is consistent with the observation that changing the solvent from diethyl ether to tetrahydrofuran (second entry, Table IV) was accompanied by a considerable increase in the protonated material. That **2** afforded a somewhat better yield of coupled products (**4**, Y = R = Et; third entry, Table IV) than **1** may be attributable to the relative reluctance to undergo halogen–metal exchange observed previously. A solution to this problem has been to trap the metalated species, prior to workup, with the alkyl iodide corresponding to the alkylcopper reagent.[15b] When this procedure was attempted with our system (fourth entry, Table IV), however, no significant change in products was observed. This may be due to the vinylcopper species derived from **1** being very sluggish toward alkylation, particularly in diethyl ether solvent.

The results depicted in Table IV are deserving of some general comments. First, **1** and **2** display marked differences in reactivity toward these reagents. Whereas the *E* isomer **1** is converted to products within 1 h at 0 °C, the *Z* isomer **2** requires 24 h at 0–10 °C for similar conversion. Secondly, the major problem with the lithium dialkylcuprate reagents in this sequence is that the temperature at which coupling proceeds at a reasonable rate is the temperature at which the reagent decomposes. This thermal instability is particularly bothersome when the R group on copper can undergo β-hydride elimination.[16] This problem has been circumvented by using a large excess of the copper reagent (in our case 5 equiv) which means an even larger excess of a potentially valuable lithium reagent may be required, clearly an inefficient process.

In an attempt to overcome the thermal instability problem, we considered the mixed-cuprate reagents which are reported to be more stable. The (PhS)(R)CuLi reag-

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[14] For another solution to this problem, see ref 6a.

[15] (a) Corey, E. J.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 3911. (b) *Ibid.* **1968**, *90*, 5615. (c) Whitesides, G. M.; Fischer, W. F.; San Filippo, J., Jr.; Bashe, R. W.; House, H. O. *Ibid.* **1969**, *91*, 4871.

[16] Whitesides, G. M.; Stedronsky, E. R.; Casey, C. P.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 1426. House, H. O.; DuBose, J. C. *J. Org. Chem.* **1975**, *40*, 788.

ents appeared to be the most attractive on the basis of their stability, the relatively small excess of reagent required, and the ease with which their reactions could be worked up.[17] Furthermore, considerable success had been realized when using these reagents with secondary and tertiary alkyl R groups. Application of these reagents to our bromovinylsilanes 1 and 2 gave the results depicted in Table V.

Ethylation using this sulfur-stabilized organocopper reagent (R = Et) proceeded in yields (first and sixth entry, Table V) that are very competitive with the examples given in the literature.[15b] As expected, considerable differences in reactivity were observed between the *E* isomer 1 and the *Z* isomer 2. It was found that complete conversion of the *E* isomer 1 could be effected by reaction of 2 equiv of (PhS)(Et)CuLi for 1 h at −78 °C followed by warming to room temperature. The *Z* isomer, on the other hand, required 4 equiv of reagent for 12 h at −30 °C, followed by several hours at room temperature. Despite the increased thermal stability of these reagents, decomposition was sufficiently competitive with coupling in the case of 2 that larger excesses of reagent were required. In the manner previously described, we attempted to increase the yields of desired product by trapping the metalated material with ethyl iodide and were successful in obtaining higher yields of ethylated products (second and seventh entries, Table V). That this procedure was successful in these cases and not in the earlier one is probably a solvent effect since we have observed that other alkylations proceed rapidly in tetrahydrofuran while being sluggish in diethyl ether.

Extension of this coupling procedure to other R groups proved to be equally encouraging. While reacting much more reluctantly than ethyl, the *n*-butyl reagent couples in respectable yield (third and eighth entries, Table V) which could, in theory, be increased through subsequent addition of *n*-butyl iodide. However, we were particularly interested by the results obtained when coupling was effected with secondary and tertiary R groups, especially with the *E* isomer 1. The isolated yields obtained with 1 (fourth and fifth entries, Table V) are very good considering the manipulation taking place. This was quite gratifying in view of the fact that alkylations with secondary and tertiary halides failed due to exclusive dehydrohalogenation.

During our search for other ways of improving upon the problems evident in our original coupling study, our attention was attracted to the unusual copper reagents being utilized by MacDonald and Still[18] and Ashby.[19,20] These new copper reagents ($Li_wCu_yR_z$) have been found to undergo much the same kind of reactions as $LiCuR_2$ but are more reactive. Since at the time of our work there were no reports of the application of reagents of this type to coupling reactions,[20] a study of the reaction of less than stoichiometric amounts of cuprous iodide with alkyllithiums toward our bromovinylsilanes seemed reasonable. The results of such a study are shown in Table VI.

The general procedure used was to treat 1 equiv of the bromovinylsilane (1 or 2) with 2 equiv of alkyllithium reagent and 0.4 equiv of cuprous iodide. Once again, the *Z* isomer 2 demanded considerably more vigorous reaction conditions than the *E* isomer 1. For example, whereas methylation of 1 was accomplished within 0.5 h at 0 °C, compound 2 required 48 h at room temperature to effect a similar transformation. In spite of this difference in reactivity, both isomers were methylated in excellent isolated yield by this procedure (first and second entries, Table VI). The diminished stereoselectivity observed when starting with the *Z* isomer 2 no doubt reflects the more vigorous conditions its reaction required.

Table VI. Coupling of (*E*)- and (*Z*)-Bromovinylsilanes with Alkyllithium Reagents Using 20 mol % of Cuprous Iodide

$$1 \text{ or } 2 \xrightarrow[0.4 \text{ equiv of CuI}]{2 \text{ equiv of RLi}} 3 \text{ or } 4$$

starting material	R	solvent	% Y in 3[a]		% Y in 4[a]	
			Y = H	Y = R	Y = H	Y = R
1	Me	Et_2O		95[b]		
2	Me	Et_2O				90[c]
1	Et	Et_2O	41	37		
2	Et	Et_2O			3	47
1	Et	THF	71	15		
1	Et	hexane	28[d]	17[d]		
1	*n*-Bu	Et_2O	44	35		

[a] GLC yield. [b] Isolated yield, [*Z*]:[*E*] = 99:1. [c] Isolated yield, [E]:[Z] = 95:5. [d] Also 37% starting material (1).

Encouraged by the success observed in methylation, we sought to extend this procedure to other alkyllithium reagents. As indicated in Table VI, attempted coupling with ethyllithium and *n*-butyllithium resulted in substantial amounts of protonated material. Since these alkyllithium reagents are strong enough bases to undergo the halogen–metal exchange reaction with 1 and 2 while methyllithium is not, it seems clear that lithiation is taking place followed by protonation upon workup. This view is lent further support by the fifth entry in Table VI which, in agreement with our earlier observations, suggests that the use of tetrahydrofuran as solvent facilitates the halogen–metal exchange reaction. Finally, we have found that the best solvent for this coupling procedure is diethyl ether. In view of the excellent results obtained for methylation, it seems that this method offers considerable promise as long as the limitation that the vinyl halide not undergo significant halogen–metal exchange with the lithium reagent is observed.

Conversion of Alkylated Vinylsilanes to Vinyl Bromides. Now that several methods for effecting substitution of alkyl groups for the bromine in 1 and 2 had been demonstrated, the next step in our general synthetic sequence (Scheme I) was the conversion of these resulting vinylsilanes into isomerically pure disubstituted vinyl halides. We chose to form the vinyl bromides by a method developed earlier in our laboratories[2] involving bromination of the vinylsilane followed by desilicohalogenation with sodium methoxide since this procedure was shown to proceed in high yields with excellent stereoselectivity. The results of this approach are given in Table VII. The procedure developed earlier had to undergo several modifications before it could be satisfactorily applied to 5 and 6. The first problem encountered was during bromination. If the vinylsilane was simply titrated with bromine until the first sign of unreacted halogen, considerable amounts of starting material were recovered. On the other hand, if too large an excess of halogen was used, side reactions took place leading to a mixture of olefinic compounds. After examining a variety of solvents, temperatures, and

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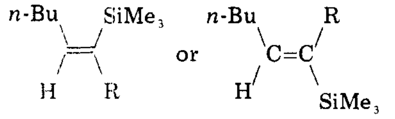
[17] Posner, G. H.; Whitten, C. E.; Sterling, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 7788.

[18] MacDonald, T. L.; Still, W. C. *J. Am. Chem. Soc.* **1975**, *97*, 5280. Still, W. C.; MacDonald, T. L. *Tetrahedron Lett.* **1976**, 2659.

[19] Ashby, E. C.; Lin, J. J.; Watkins, J. J. *J. Org. Chem.* **1977**, *42*, 1099. Ashby, E. C.; Watkins, J. J. *J. Chem. Soc., Chem. Commun.* **1976**, 784.

[20] Ashby, E. C.; Lin, J. J. *J. Org. Chem.* **1977**, *42*, 2805.

Table VII. Conversion of Alkylated Vinylsilanes to Vinyl Bromides



5 6

$$\xrightarrow[\text{(2) NaOMe, MeOH}]{\text{(1) Br}_2\text{, CH}_2\text{Cl}_2} n\text{-BuCH=C(Br)R}$$

7

starting material	R	% yield 7[a]	[E]:[Z] in 7[b]
5	Me	91	99:1
6	Me	87	<1:99
5	Et	93	97:3
6	Et	84	2:98
5	*n*-Bu	92	99:1
6	*n*-Bu	91	3:97
5	*sec*-Bu	75	98:2

[a] Isolated yields. [b] Determined by GLC analysis.

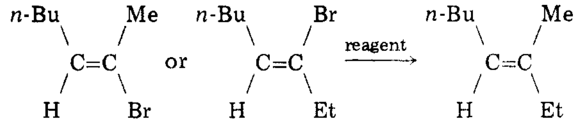
stoichiometries, we found that the dibromide could be cleanly obtained by slow addition of 1.25 equiv of bromine in methylene chloride at −78 °C followed by immediate workup (see Experimental Section). Since these dibromides were very sensitive compounds, they were taken on immediately without purification to the methoxide elimination step.

As the data indicate, vinylsilanes 5 and 6 could be converted to the corresponding vinyl bromides in excellent isolated yields and with high stereoselectivity. It may be that these isomeric purities are a lower limit since we have observed that substantial isomerization can occur during isolation if certain precautions are not taken. These compounds are very sensitive to heat so that temperatures during distillation should be kept at a minimum and the distillation should be carried out in the presence of a weak base, such as sodium carbonate. These vinyl halides formally represent the completion of our stereoselective trisubstituted olefin synthesis since the vinyl bromine group is interconvertible with other groups by methodology presently available. However, in order to make rigorous stereochemical assignments and to further demonstrate the synthetic utility of our approach, we carried out subsequent modifications on these vinyl bromides.

Preparation of (*E*)- and (*Z*)-3-Methyl-3-octene. As the final step of our general synthetic sequence, we looked into the conversion of vinyl bromides **8**, **9**, **11**, and **12** to the isomeric 3-methyl-3-octenes under a variety of conditions as indicated in Tables VIII and IX. Applications of the alkylation procedure using *sec*-butyllithium (first and fourth entries in Table VIII, first and third entries in Table IX) resulted in good yields of products having high isomeric purity. Not surprisingly, methylation with excess methyl iodide resulted predominantly in exchange to give the vinyl iodide. This problem was again circumvented by using dimethyl sulfate as the alkylating agent. An added benefit of these conversions was that the stereochemistry of the starting vinyl bromides was rigorously assigned since the (*E*)- and (*Z*)-3-methyl-3-octenes have been previously reported.[21]

We also tried the coupling methods with which we had been successful in our studies on the α-bromovinylsilanes. As shown in Tables VIII and IX, the coupling of methyl- and ethyllithium with 20 mol % of cuprous iodide with the (*E*)-vinyl bromides (second entry in both tables) proceeded quite well. It is of interest to contrast the reactivity of vinyl bromide **11** with the α-bromovinylsilane **1** under these conditions. Whereas the silyl compound **1** was completely methylated in less than 0.5 h at 0 °C, **11** required 24 h at room temperature. This again points out the useful activating effect of the trimethylsilyl group. The additional observation should be made that ethylation of **8** by this method proceeded quite well because ethyllithium does not undergo halogen–metal exchange in this case. This is in contrast to the behavior seen with the α-bromovinylsilanes and again illustrates that good results can be obtained if the limiting condition is met that the alkyllithium reagent not undergo exchange with the vinyl halide. As expected, application of this method to the (*Z*)-vinylbromides **9** and **12** proved considerably more difficult with poor yields of products being obtained. Finally, we examined ethylation with the (PhS)(Et)CuLi reagent (third entry, Table VIII; fifth entry, Table IX) and obtained modest yields at best, although no attempt was made to optimize the reaction conditions.

Table VIII. Preparations of (*E*)-3-Methyl-3-octene

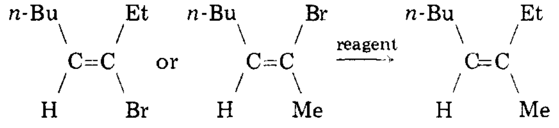


8 9 10

starting material	reagent	% yield[a]	[E]:[Z][b]
8	(1) *sec*-BuLi, (2) EtI	80 (87)	97:3
8	2 of equiv EtLi, 0.4 equiv of CuI	(74)	
8	2 equiv of (PhS)(Et)CuLi	(67)[c]	
9	(1) *sec*-BuLi, (2) Me_2SO_4	83	96:4
9	2 equiv of MeLi, 0.4 equiv of CuI	(5)[d]	

[a] Isolated yield (GLC yield). [b] Determined by GLC analysis. [c] Also 23% starting material (9). [d] Also 81% starting material (9).

Table IX. Preparations of (*Z*)-3-Methyl-3-octene



11 12 13

starting material	reagent	% yield[a]	[Z]:[E][b]
11	(1) *sec*-BuLi, (2) Me_2SO_4	80	>99:1
11	2 equiv of MeLi, 0.4 equiv of CuI	81 (89)	98:2
12	(1) *sec*-BuLi, (2) EtI	74 (77)	98:2
12	2 equiv of EtLi, 0.4 equiv of CuI	(49)	
12	4 equiv of (PhS)(Et)CuLi	(58)	

[a] Isolated yield (GLC yield) [b] Determined by GLC analysis.

Summary

The utility of 1-bromo-1-(trimethylsilyl)-1-alkenes of defined stereochemistry in a stereoselective trisubstituted

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[21] Bhalerao, U. T.; Rapoport, H. *J. Am. Chem. Soc.* 1971, *93*, 4835.

olefin synthesis has been demonstrated. These α-bromovinylsilanes are synthons of 1,1-dihaloalkenes in which each halogen group can be functionalized independently and stereoselectively. Alkylation of these compounds via intermediate vinyllithium species is best done by using *sec*-butyllithium as the exchange reagent, while coupling is best done by using the sulfur-stabilized cuprates. Coupling of alkyllithium reagents with vinyl bromides can be carried out efficiently with 20 mol % of cuprous iodide as long as the alkyllithium reagent does not undergo extensive halogen–metal exchange with the vinyl bromide. Finally the bromination–desilicobromination technique developed earlier for converting vinylsilanes into vinyl bromides works very well with minor experimental modifications.

Experimental Section

Boiling points were recorded at gauge pressure and are reported uncorrected. Infrared spectra were obtained on a Beckman IR-8 spectrometer with only selected absorptions being reported. Nuclear magnetic resonance (^{1}H) spectra were obtained on either a Varian EM 360 or Varian A-60A instrument. Chemical shifts are reported in δ values downfield relative to either the trimethylsilyl absorption of silicon-containing compounds or internal tetramethylsilane (where indicated). Low-resolution mass spectra were determined by Mr. Paul Bruins on a Consolidated Electrodynamics Corp. instrument. High-resolution mass spectra were determined by Mr. Kei Miyano on a Du Pont 21-492B mass spectrometer. Analytical GLC was performed on a Varian Aerograph Model 600-D instrument with 20% SF-96 on Chromosorb Q in a $^1/_8$ in. × 5 ft stainless steel column. GLC yields were obtained on the latter instrument by comparing the integrations of the product peak(s) against an internal standard peak by applying appropriate corrections for flame factors.

All alkyllithium reagents were obtained from commercial sources (Ventron or Aldrich). Methyllithium was standardized by the Gilman double-titration procedure with 1,2-dibromoethane.[22] All other alkyllithium reagents were standardized by titration with a standard solution of 2-butanol in xylene, using 1,10-phenanthroline as an indicator.[23] Bromine (Mallinckrodt) and anhydrous diethyl ether (Mallinckrodt) were used as received. Tetrahydrofuran (Mallinckrodt) was distilled from lithium aluminum hydride and stored under nitrogen over Linde 4-Å molecular sieves. Alkyl iodides were purified by passage down a column of neutral alumina (Baker, Brockman activity grade 1) after distillation. Cuprous iodide was recrystallized by the method of Kauffman and Teter.[24] Sodium methoxide in methanol (1 M) was prepared by placing the appropriate quantity of sodium metal in a known volume of methanol and filtering the resulting solution. All reactions were stirred magnetically and carried out under an atmosphere of nitrogen in oven-dried (150 °C) glassware.

General Alkylation Procedure Using *n*-Butyllithium in Trapp Solvent Mixture (Table I). To a three-necked, round-bottomed flask equipped with an addition funnel, a septum, and a low-temperature thermometer was added 7.06 g (30 mmol) of 1[5] and 60 mL of the Trapp solvent mixture (1:4:1, hexane–THF–Et_2O)[11]. After the mixture was cooled to –100 °C (liquid N_2/MeOH bath), 25.9 mL of 1.33 M *n*-butyllithium (34.5 mmol, 1.15 equiv) was added at a rate such that the temperature was maintained below –95 °C. The resulting mixture was stirred for 0.5 h at –100 °C, and then the alkyl iodide was added such that the temperature was again kept below –95 °C. After 0.5 h of stirring at –100 °C, the solution was allowed to warm to room temperature and then stirred an additional hour. At this time the reaction mixture was poured into saturated ammonium chloride solution, shaken, and separated. The aqueous layer was thoroughly washed with pentane, and the organic extracts were combined and dried over anhydrous sodium sulfate. After removal of the solvent by distillation at atmospheric pressure through a 25-cm column packed with glass helices, the residue was vacuum distilled to give the colorless product.

(a) Alkylation of 1 with Methyl Iodide (First Entry, Table I). Following the general procedure, 1 was alkylated with methyl iodide (39 mmol, 1.3 equiv) to give ((*Z*)-2-hepten-2-yl)trimethylsilane (3, Y = Me) in a 60% isolated yield: bp 52–54 °C (1.1 torr); IR (neat) 2970 (s), 1614 (m), 1440 (m), 1250 (s), 835 (s), 758 (s), 689 (m), 650 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.80 (br t, 3 H, J = 5.5 Hz, CH_2CH_3), 1.17 (m, 4 H, $(CH_2)_2$), 1.60 (broadened s, 3 H, $C{=}CCH_3$), 1.91 (m, 2 H, $C{=}CCH_2$), 5.82 (t of q, 1 H, J = 8 Hz, 2 Hz, $C{=}CH$); high-resolution mass spectrum[25] calcd (m/e) for $C_9H_{19}Si$ (M – CH_3), 155.1257; found, 155.1240.

(b) Alkylation of 1 with Ethyl Iodide (Third Entry, Table I). Following the general procedure, 1 was alkylated with ethyl iodide (60 mmol, 2.0 equiv) to give ((*Z*)-3-octen-3-yl)trimethylsilane (3, Y = Et) in a 75% isolated yield: bp 59–63 °C (3 torr); IR (neat) 2975 (s), 1611 (m), 1450 (m), 1250 (s), 838 (s), 747 (s), 688 (m), 650 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.85 (overlapping t, 6 H, J = 5.5 Hz, 7.5 Hz, 2 CH_2CH_3), 1.18 (m, 4 H, $(CH_2)_2$), 1.95 (broadened q, 4 H, J = 7.5 Hz, 2 $CH_2C{=}C$), 5.79 (broadened t, 1 H, J = 7.5 Hz, $C{=}CH$); high-resolution mass spectrum[25] calcd (m/e) for $C_{11}H_{24}Si$ (M), 184.1648; found, 184.1664 (calcd for $C_{10}H_{21}Si$ (M – CH_3), 169.1413; found, 169.1401).

In a separate experiment using 5 mmol of 1, GLC analysis (*n*-decane as the internal standard) revealed that the product yields consisted of 4% ((*Z*)-1-hexen-1-yl)trimethylsilane (3, Y = H)[2], 2% ((*Z*)-5-decen-5-yl)trimethylsilane (3, Y = *n*-Bu), 3% starting material (1), and 89% of the desired ((*Z*)-3-octen-3-yl)trimethylsilane (3, Y = Et).

General Alkylation Procedure Using *n*-Butyllithium in Tetrahydrofuran (Table I). To a solution of α-bromovinylsilane 1 or 2[5] in tetrahydrofuran (~5 mL/mmol) which had been cooled to –78 °C (dry ice/acetone bath), 1.1 equiv of 2.30 M *n*-butyllithium was added while the temperature was maintained below –65 °C. After the resulting mixture was stirred at –78 °C (0.5 h for 1 and 2 h for 2), the alkyl iodide was added, again keeping the temperature below –65 °C. The solution was stirred 0.5 h at –78 °C, allowed to warm to room temperature, and then stirred an additional hour. At the end of this time, the reaction mixture was poured into a saturated ammonium chloride solution, shaken, and separated. The aqueous layer was extracted with pentane, and the organic extracts were combined and dried over anhydrous sodium sulfate. The mixture was either directly analyzed by GLC or distilled at atmospheric pressure to remove the solvent in the case of preparative runs. The residue from this latter procedure was distilled at reduced pressure to give the colorless product.

(a) Alkylation of 1 with Ethyl Iodide (Second Entry, Table I). Following the general procedure, 2 mmol of 1 was alkylated with ethyl iodide (4 mmol, 2 equiv) to give a product which by GLC analysis (*n*-decane as the internal standard) consisted of 5% (1-hexen-1-yl)trimethylsilane (3, Y = H), 16% ((*Z*)-5-decen-5-yl)trimethylsilane (3, Y = *n*-Bu), and 70% of the desired ((*Z*)-3-octen-3-yl)trimethylsilane (3, Y = Et).

(b) Alkylation of 1 with *n*-Butyl Iodide (Forth Entry, Table I). Following the general procedure, 20 mmol of 1 was alkylated with *n*-butyl iodide (20 mmol, 1 equiv) to give ((*Z*)-5-decen-5-yl)trimethylsilane (3, Y = *n*-Bu) in 92% isolated yield: bp 45–47 °C (0.1 torr); IR (neat) 2985 (s), 2940 (s), 2875 (s), 1610 (m), 1460 (m), 1250 (s), 848 (s), 759 (m), 689 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.80 (unsymmetrical t, 6 H, 2 $CH_2\mathbf{CH_3}$), 1.18 (m, 8 H, 2 $(CH_2)_2$), 1.97 (broadened q, 4 H, J = 7 Hz, 2 $CH_2C{=}C$), 5.78 (broadened t, 1 H, J = 7 Hz, $C{=}CH$); high-resolution mass spectrum[25] calcd (m/e) for $C_{12}H_{25}Si$ (M – CH_3), 197.1726; found, 197.1706.

In a separate experiment using 2 mmol of 1, GLC analysis (*n*-decane as the internal standard) revealed that the product yields consisted of 3% (1-hexen-1-yl)trimethylsilane (3, Y = H) and 97% of the desired product (3, Y = *n*-Bu).

(c) Alkylation of 2 with Methyl Iodide (Fifth Entry, Table I). Following the general procedure, 20 mmol of 2 was alkylated

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[22] Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1974**, *93*, 1379.

[23] Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

[24] Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 9.

[25] All samples on which high-resolution mass spectral data were obtained were purified by preparative GLC on a Varian Aerograph Model 90-P gas chromatograph with 10% SE-30 on Chromosorb W in a $^1/_4$ in. × 10 ft stainless steel column and shown to be homogeneous (one peak) on a 50-m SE-30 glass capillary column.

with methyl iodide (26 mmol, 1.3 equiv) to give ((*E*)-2-hepten-2-yl)trimethylsilane (**4**, Y = Me) in a 74% isolated yield: bp 66–68 °C (7 torr); IR (neat) 2980 (s), 2880 (s), 1616 (m), 1450 (m), 1250 (s), 948 (m), 837 (s), 752 (s), 691 (s) cm^{-1}; NMR (CCl$_4$) δ 0.00 (s, 9 H, (CH$_3$)$_3$Si), 0.88 (br t, 3 H, *J* = 5.5 Hz, CH$_2$CH$_3$), 1.30 (m, 4 H, (CH$_2$)$_2$), 1.61 (d, 3 H, *J* = 2 Hz, C=CCH$_3$), 2.03 (br q, 2 H, *J* = 6.5 Hz, CH$_2$C=C), 5.66 (t of q, 1 H, *J* = 7 Hz, 2 Hz, C=CH); high-resolution mass spectrum[25] calcd (*m*/*e*) for $C_{10}H_{22}Si$, 170.1492; found, 170.1507 (calcd for $C_9H_{19}Si$ (M − CH$_3$), 155.1257; found, 155.1257).

(d) Alkylation of 2 with Ethyl Iodide (Sixth Entry, Table I). Following the general procedure, 30 mmol of **2** was alkylated with ethyl iodide (39 mmol, 1.3 equiv) to give ((*E*)-3-octen-3-yl)trimethylsilane[2] (**4**, Y = Et) in a 73% isolated yield: bp 68–72 °C (8 torr); IR (neat) 2975 (s), 2880 (s), 1611 (m), 1450 (m), 1250 (s), 917 (m), 848 (s), 756 (s), 690 (m) cm^{-1}; NMR (CCl$_4$) δ 0.00 (s, 9 H, (CH$_3$)$_3$Si), 0.87 (overlapping t, 6 H, *J* = 8 Hz, 5.5 Hz, 2 CH$_2$CH$_3$), 1.31 (m, 4 H, (CH$_2$)$_2$), 2.03 (overlapping q, 4 H, *J* = 8 Hz, 7 Hz, 2 CH$_2$C=C), 5.60 (broadened t, 1 H, *J* = 7 Hz, C=CH); high-resolution mass spectrum[25] calcd (*m*/*e*) for $C_{11}H_{24}Si$ (M), 184.1648; found, 184.1640 (calcd for $C_{10}H_{21}Si$ (M − CH$_3$), 169.1413; found, 169.1409).

In a separate experiment using 1 mmol of **2**, GLC analysis (*n*-decane as the internal standard) revealed that the product yields consisted of 4% ((*E*)-1-hexen-1-yl)trimethylsilane[2] (**4**, Y = H) and 86% of the desired product (**4**, Y = Et).

General Alkylation Procedure Using *tert*-Butyllithium (Table II). To a solution of 3.36 M *tert*-butyllithium in dry solvent (~5 mL/mmol) cooled to −78 °C (dry ice/acetone bath) was added the α-bromovinylsilane **1** or **2** at a rate such that the temperature was maintained below −65 °C. (In the use of 1.1 equiv of *tert*-butyllithium the alkyllithium reagent was added to **1** or **2**.) After 0.5 h of stirring at −78 °C, ethyl iodide was added while again the temperature was kept below −65 °C. The resulting mixture was stirred at −78 °C for 15 min, allowed to warm to room temperature, and then stirred an additional hour. The reaction mixture was poured into saturated ammonium chloride solution, shaken, and separated. The aqueous layer was extracted with several portions of pentane. The combined organic extracts were dried over anhydrous sodium sulfate and analyzed by GLC using *n*-decane as an internal standard.

(a) Alkylation of 1 with 2.1 Equiv of *tert*-Butyllithium (First Entry, Table II). Following the general procedure, 2 mmol of **1** was subjected to 4.2 mmol (2.1 equiv) of *tert*-butyllithium in 10 mL of tetrahydrofuran and then alkylated with 4 mmol (2.0 equiv) of ethyl iodide. GLC analysis revealed the product yields to consist of 23% ((*Z*)-1-hexen-1-yl)trimethylsilane (**3**, Y = H) and 77% of the desired ((*Z*)-3-octen-3-yl)trimethylsilane (**3**, Y = Et).

(b) Alkylation of 1 with 2.1 Equiv of *tert*-Butyllithium (Second Entry, Table II). Following the general procedure, 2 mmol of **1** was subjected to 4.2 mmol (2.1 equiv) of *tert*-butyllithium in 10 mL of diethyl ether and then alkylated with 4 mmol (2.0 equiv) of ethyl iodide. GLC analysis revealed the product yields to consist of 29% **3**, Y = H, and 70% of the desired **3**, Y = Et.

(c) Alkylation of 2 with 2.1 Equiv of *tert*-Butyllithium (Third Entry, Table II). Following the general procedure, 1 mmol of **2** was subjected to 2.1 mmol (2.1 equiv) of *tert*-butyllithium in 10 mL of tetrahydrofuran and then alkylated with 2 mmol (2.0 equiv) of ethyl iodide. GLC analysis revealed the product yields to consist of 19% ((*E*)-1-hexen-1-yl)trimethylsilane (**4**, Y = H) and 70% of the desired ((*E*)-3-octen-3-yl)trimethylsilane (**4**, Y = Et).

(d) Alkylation of 1 with 1.1 Equiv of *tert*-Butyllithium (Fourth Entry, Table II). Following the general procedure, 1 mmol of **1** in 10 mL of tetrahydrofuran was treated with 1.1 mmol (1.1 equiv) of *tert*-butyllithium and then alkylated with 2 mmol (2.0 equiv) of ethyl iodide. GLC analysis revealed the product yields to consist of 21% **3**, Y = H, and 79% of the desired **3**, Y = Et.

(e) Alkylation of 2 with 1.1 Equiv of *tert*-Butyllithium (Fifth Entry, Table II). Following the general procedure, 1 mmol of **2** in 10 mL of tetrahydrofuran was treated with 1.1 mmol (1.1 equiv) of *tert*-butyllithium and then alkylated with 2 mmol (2.0 equiv) of ethyl iodide. GLC analysis revealed the product yields to consist of 18% **4**, Y = H, 21% of the starting material **2**, and 55% of the desired **4**, Y = Et.

General Alkylation Procedure Using *sec*-Butyllithium (Table III). To a solution of **1** or **2** in dry tetrahydrofuran (~2 mL/mmol) cooled to −78 °C (dry ice/acetone bath) was added 1.14 M *sec*-butyllithium (1.1 equiv) at a rate such that the temperature was maintained below −65 °C. After the mixture was stirred at −78 °C for 0.5 h, the alkylating agent was added while the temperature was again kept below −65 °C. The resulting mixture was stirred at −78 °C for 15 min, allowed to warm to room temperature, and then stirred an additional hour. At the end of this time, the reaction mixture was poured into a saturated ammonium chloride solution, shaken, and separated. The aqueous layer was thoroughly extracted with pentane and the combined organic extracts were dried over anhydrous sodium sulfate. The mixture was either directly analyzed by GLC, using *n*-decane as an internal standard, or distilled at atmospheric pressure to remove the solvent in the case of preparative runs. The residue from this latter procedure was distilled at reduced pressure to give the colorless product.

(a) Alkylation of 1 with Methyl Iodide (First Entry, Table III). Following the general procedure, 25 mmol of **1** was alkylated with 50 mmol (2.0 equiv) of methyl iodide to give 88% isolated yield of ((*Z*)-2-hepten-2-yl)trimethylsilane (**3**, Y = Me). GLC analysis (50-m SE-30 glass capillary column) of this product indicated that the silylheptene was >99% the *Z* isomer.

(b) Alkylation of 1 with Ethyl Iodide (Second Entry, Table III). Following the general procedure, 20 mmol of **1** was alkylated with 40 mmol (2.0 equiv) of ethyl iodide to give a 90% isolated yield of ((*Z*)-2-octen-2-yl)trimethylsilane (**3**, Y = Et). GLC analysis (50-m SE-30 glass capillary column) of this product indicated that the silyloctene was in a 99:1 [*Z*]:[*E*] ratio.

In a separate experiment using 2 mmol of **1**, GLC analysis revealed that the product yields consisted of 4% **3**, Y = H, and 95% of the desired **3**, Y = Et.

(c) Alkylation of 1 with *n*-Butyl Iodide (Third Entry, Table III). Following the general procedure, 20 mmol of **1** was alkylated with 40 mmol (2.0 equiv) of *n*-butyl iodide to give a 95% isolated yield of ((*Z*)-5-decen-5-yl)trimethylsilane (**3**, Y = *n*-Bu). GLC analysis (50-m SE-30 glass capillary column) of this product indicated that the silyldecene was >99% the *Z* isomer.

In a separate experiment using 2 mmol of **1**, GLC analysis revealed that the product yields consisted of 2% **3**, Y = H, and 97% of the desired **3**, Y = *n*-Bu.

(d) Attempted Alkylation of 1 with *sec*-Butyl Iodide (Fourth Entry, Table III). Following the general procedure except employing 2.1 equiv of *sec*-butyllithium, an attempt to alkylate 2 mmol of **1** with 4 mmol (2.0 equiv) of *sec*-butyl iodide was carried out. GLC analysis revealed the only product to be **3**, Y = H, obtained in 93% yield.

(e) Alkylation of 2 with Methyl Iodide (Fifth Entry, Table III). Following the general procedure, 40 mmol of **2** was alkylated with 80 mmol (2.0 equiv) of methyl iodide to give a 68% isolated yield of ((*E*)-2-hepten-2-yl)trimethylsilane (**4**, Y = Me). GLC analysis (50-m SE-30 glass capillary column) of this product indicated the silylheptene was in a 99:1 [*E*]:[*Z*] ratio. In addition a 13% isolated yield of ((*Z*)-1-iodo-1-hexen-1-yl)trimethylsilane[5] was obtained.

(f) Alkylation of 2 with Dimethyl Sulfate (Sixth Entry, Table III). Following the general procedure, 30 mmol of **2** was alkylated with 60 mmol (2.0 equiv) of dimethyl sulfate to give a 90% isolated yield of the desired ((*E*)-2-hepten-2-yl)trimethylsilane (**4**, Y = Me). GLC analysis (50-m SE-30 glass capillary column) of this product indicated the silylheptene was in a 99:1 [*E*]:[*Z*] ratio.

(g) Alkylation of 2 with Ethyl Iodide (Seventh Entry, Table III). Following the general procedure, 50 mmol of **2** was alkylated with 100 mmol (2.0 equiv) of ethyl iodide to give a 93% isolated yield of ((*E*)-2-octen-2-yl)trimethylsilane (**4**, Y = Et). GLC analysis (50-m SE-30 glass capillary column) of this product indicated the silyloctene was in a 99:1 [*E*]:[*Z*] ratio.

In a separate experiment using 1 mmol of **2**, GLPC analysis revealed that the product yields consisted of 6% **4**, Y = H, and 94% of the desired **4**, Y = Et.

(h) Alkylation of 2 with *n*-Butyl Iodide (Eighth Entry, Table III). Following the general procedure, 30 mmol of **2** was alkylated with 60 mmol (2.0 equiv) of *n*-butyl iodide to give a 76% isolated yield[26] of ((*E*)-5-decen-5-yl)trimethylsilane (4, Y = *n*-Bu). GLC analysis (50-m SE-30 glass capillary column) of this product indicated the silyldecene was in a 98:2 [*E*]:[*Z*] ratio. The compound had the following properties: bp 51–54 °C (0.1 torr); IR (neat) 2970 (s), 2890 (s), 1614 (m), 1466 (m), 1252 (s), 838 (s), 758 (m), 694 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.89 (br t, 6 H, *J* = 5.5 Hz, 2 CH_2CH_3), 1.25 (m, 8 H, 2 $(CH_2)_2$), 2.02 (m, 4 H, 2 CH_2CC), 5.64 (t, 1 H, *J* = 6.5 Hz, C=CH); high-resolution mass spectrum[25] calcd (*m/e*) for $C_{13}H_{28}Si$ (M), 212.1961; found, 212.1963 (calcd for $C_{12}H_{25}Si$ (M − CH_3), 197.1726; found, 197.1728).

In a separate experiment using 1 mmol of **2**, GLC analysis revealed that the product yields consisted of 12% **4**, Y = H, and 85% of the desired **4**, Y = *n*-Bu.

(i) Attempted Alkylation of 2 with *sec*-Butyl Iodide (Ninth Entry, Table III). Following the general procedure, an attempt to alkylate 1 mmol of **2** with 2 mmol (2.0 equiv) of *sec*-butyl iodide was carried out. GLC analysis revealed the only product to be **4**, Y = H, obtained in 87% yield.

General Coupling Procedure Using R_2CuLi (Table IV). A flask containing 5 mmol (5 equiv) of cuprous iodide was thoroughly purged of air, and 20 mL of dry solvent was added. The resulting slurry was cooled in a salted ice bath and 10 mmol (10 equiv) of alkyllithium reagent was slowly added and the mixture stirred for 15 min to form the black dialkylcuprate. After the mixture was cooled to −78 °C (dry ice/acetone bath), 1 mmol of **1** or **2** in a few milliliters of solvent was added at a rate such that the temperature was maintained below −65 °C. The solution was then warmed to 0 °C where it was stirred for 5 h. After allowing the mixture to warm to room temperature, it was poured into a separatory funnel containing concentrated ammonium hydroxide and was shaken, with frequent venting, until all the solids had dissolved. The intensely blue aqueous layer was separated and thoroughly extracted with pentane. The combined organic extracts were dried over anhydrous sodium sulfate and analyzed by GLC using *n*-decane as an internal standard.

(a) Coupling of 1 with Et_2CuLi (First Entry, Table IV). Following the general procedure, **1** was reacted with Et_2CuLi in diethyl ether solvent. GLC analysis revealed the product yields consisted of 61% ((*Z*)-1-hexen-1-yl)trimethylsilane (**3**, Y = H) and 37% of the desired ((*Z*)-3-octen-3-yl)trimethylsilane (**3**, Y = Et).

(b) Coupling of 1 with Et_2CuLi (Second Entry, Table IV). Following the general procedure, **1** was reacted with Et_2CuLi in tetrahydrofuran solvent. GLC analysis revealed the product yields consisted of 86% **3**, Y = H, and only 10% of the desired **3**, Y = Et.

(c) Coupling of 2 with Et_2CuLi (Third Entry, Table IV). Following the general procedure except that the mixture was stirred 24 h at 0–10 °C instead of 5 h at 0 °C, **2** was reacted with Et_2CuLi in diethyl ether solvent. GLC analysis revealed the product yields consisted of 34% ((*E*)-1-hexen-1-yl)trimethylsilane (**4**, Y = H) and 54% of the desired ((*E*)-3-octen-3-yl)trimethylsilane (**4**, Y = Et).

(d) Coupling of 1 with Et_2CuLi Followed by Ethyl Iodide (Fourth Entry, Table IV). Following the general procedure, except that after the 5 h of stirring at 0 °C, 1 mmol (1 equiv) of ethyl iodide was added and the mixture stirred 1 h at 0 °C before warming to room temperature, **1** was reacted with Et_2CuLi in diethyl ether solvent. GLC analysis revealed the product yields consisted of 55% **3**, Y = H, and 32% of the desired **3**, Y = Et.

(e) Coupling of 1 with *n*-Bu_2CuLi (Fifth Entry, Table IV). Following the general procedure, **1** was reacted with *n*-Bu_2CuLi in diethyl ether solvent. GLC analysis revealed the product yields consisted of 47% **3**, Y = H, and 53% of the desired ((*Z*)-5-decen-5-yl)trimethylsilane (**3**, Y = *n*-Bu).

General Coupling Procedure Using (PhS)(R)CuLi (Table V). The organocuprate reagent was prepared by a modification of the literature procedure.[17] The appropriate amount of thiophenol (1 equiv/equiv of RLi) in dry tetrahydrofuran was cooled to 0 °C in an ice bath. An approximately 1 M solution of lithium thiophenoxide was obtained upon careful addition of an equimolar amount of 2.17 M *n*-butyllithium. This solution was transferred by syringe to a slurry of an equimolar amount of cuprous iodide in tetrahydrofuran to afford a clear, yellow solution of the thiocopper species. The temperature during the addition was maintained at 20 °C by moderating with an ice bath. The resulting mixture was cooled to −78 °C (dry ice/acetone bath) to yield a yellow-white suspension, and an equimolar amount of the appropriate alkyllithium reagent was introduced at a rate such that the temperature was maintained below −65 °C. After the resulting suspension was stirred for a few minutes, the α-bromovinylsilane **1** or **2** was added while again the temperature was maintained below −65 °C. This mixture was stirred at −78 °C for an appropriate amount of time and then reacted further as indicated. At the end of the reaction time, the mixture was poured into a saturated ammonium chloride solution and vigorously shaken until all the dark solids were replaced by light yellow solids. After removal of the organic phase and most of the solids, the aqueous layer was thoroughly extracted with fresh pentane. The combined organic extracts were washed with two portions of 3 N sodium hydroxide solution and once with saturated sodium chloride solution, filtered away from the remaining light yellow solids, and dried over anhydrous sodium sulfate. The resulting mixture was either directly analyzed by GLC using *n*-decane as an internal standard or distilled at atmospheric pressure to remove the solvent in the case of preparative runs. The residue from this latter procedure was distilled at reduced pressure to give the colorless product.

(a) Coupling of 1 with (PhS)(Et)CuLi (First Entry, Table V). Following the general procedure, 2 mmol of **1** was reacted with 4 mmol (2.0 equiv) of (PhS)(Et)CuLi for 0.5 h at −78 °C, and the mixture was allowed to warm to room temperature and then stirred an additional hour. GLC analysis revealed the product yields consisted of 30% ((*Z*)-1-hexen-1-yl)trimethylsilane (**3**, Y = H) and 66% of the desired ((*Z*)-3-octen-3-yl)trimethylsilane (**3**, Y = Et).

(b) Coupling of 1 with (PhS)(Et)CuLi Followed by Ethyl Iodide (Second Entry, Table V). Following the general procedure, 2 mmol of **1** was reacted with 4 mmol (2.0 equiv) of (PhS)(Et)CuLi for 0.5 h at −78 °C and then 4 mmol (2.0 equiv) of ethyl iodide was added. This mixture was stirred 15 min at −78 °C, allowed to warm to room temperature, and then stirred an additional 3 h. GLC analysis revealed the product yields consisted of 17% **3**, Y = H, and 81% of the desired **3**, Y = Et.

(c) Coupling of 1 with (PhS)(*n*-Bu)CuLi (Third Entry, Table V). Following the general procedure, 1 mmol of **1** was reacted with 4 mmol (4.0 equiv) of (PhS)(*n*-Bu)CuLi for 0.5 h at −78 °C and 12 h at −20 ± 10 °C, and the mixture was allowed to warm to room temperature and stirred overnight. GLC analysis revealed the product yields consisted of 34% **3**, Y = H, and 64% of the desired ((*Z*)-5-decen-5-yl)trimethylsilane (**3**, Y = *n*-Bu).

(d) Coupling of 1 with (PhS)(*sec*-Bu)CuLi (Fourth Entry, Table V). Following the general procedure, 15 mmol of **1** was reacted with 30 mmol (2.0 equiv) of (PhS)(*sec*-Bu)CuLi for 1 h at −78 °C, and the mixture was allowed to warm to room temperature and then stirred an additional hour. Distillation at reduced pressure gave a 73% isolated yield of ((*Z*)-3-methyl-4-nonen-4-yl)trimethylsilane (**3**, Y = *sec*-Bu). GLC analysis (50-m SE-30 glass capillary column) indicated this product was in a 99:1 [*Z*]:[*E*] ratio. The compound had the following properties: bp 76–80 °C (5 torr); IR (neat) 2975 (s), 2890 (s), 1606 (m), 1455 (m), 1374 (m), 1250 (s), 839 (s), 758 (s), 686 (s) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.78 (broadened t, 6 H, *J* = 5.5 Hz, 2 CH_2CH_3), 0.83 (d, 3 H, *J* = 5.5 Hz, $CHCH_3$), 1.17 (m, 6 H, 3 CH_2), 2.00 (broadened q, 3 H, *J* = 7 Hz, CH_2C=C and CHC=C), 5.81 (t, 1 H, *J* = 7.5 Hz, C=CH); high-resolution mass spectrum[25] calcd (*m/e*) for $C_{12}H_{25}Si$ (M − CH_3), 197.1726; found, 197.1728.

(e) Coupling of 1 with (PhS)(*t*-Bu)CuLi (Fifth Entry, Table V). Following the general procedure, 20 mmol of **1** was reacted with 80 mmol (4 equiv) of (PhS)(*t*-Bu)CuLi at −30 °C (dry ice/carbon tetrachloride bath) and then 12 h at −20 ± 10 °C, and the mixture was allowed to warm to room temperature and stirred overnight. Distillation at reduced pressure gave a 69% isolated yield of ((*Z*)-2,2-dimethyl-3-octen-3-yl)trimethylsilane (**3**, Y = *t*-Bu). GLC analysis (50-m SE-30 glass capillary column) indicated this product was in a 98:2 [*Z*]:[*E*] ratio. The compound had the

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[26] This yield was lowered relative to the other alkylations in Table III because small amounts of ((*Z*)-1-iodo-1-hexen-1-yl)trimethylsilane[5] were present which were removed by lithiation with *sec*-butyllithium followed by quenching with methanol and then redistillation of the product.

following properties: bp 51–54 °C (0.2 torr); IR (neat) 2960 (s), 2890 (s), 1593 (m), 1463 (m), 1363 (m), 1262 (s), 1252 (s), 839 (s), 726 (m), 693 (m), 680 (m), 655 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.71 (br t, 3 H, J = 5 Hz, CH_2CH_3), 0.85 (s, 9 H, $(CH_3)_3C$), 1.06 (m, 4 H, $(CH_2)_2$), 1.88 (m, 2 H, $CH_2C{=}C$), 5.72 (t, 1 H, J = 8 Hz, $C{=}CH$); high-resolution mass spectrum[25] calcd (m/e) for $C_{13}H_{28}Si$ (M), 212.1961; found, 212.1943 (calcd for $C_{12}H_{25}Si$ (M − CH_3), 197.1726; found, 197.1706).

(f) Coupling of 2 with (PhS)(Et)CuLi (Sixth Entry, Table V). Following the general procedure, 1 mmol of **2** was reacted with 4 mmol (4.0 equiv) of (PhS)(Et)CuLi for 0.5 h at −78 °C and 12 h at −20 ± 10 °C, and the mixture was allowed to warm to room temperature and stirred overnight. GLC analysis revealed the product yields consisted of 16% ((*E*)-1-hexen-1-yl)trimethylsilane (**4**, Y = H) and 68% of the desired ((*E*)-3-octen-3-yl)trimethylsilane (**4**, Y = Et).

(g) Coupling of 2 with (PhS)(Et)CuLi Followed by Ethyl Iodide (Seventh Entry, Table V). Following the general procedure, 1 mmol of **2** was reacted with 4 mmol (4.0 equiv) of (PhS)(Et)CuLi for 0.5 h at −78 °C and 12 h at −20 ± 10 °C after which time 4 mmol (4 equiv) of ethyl iodide was added. The resulting mixture was stirred 1 h at −20 ± 10 °C, allowed to warm to room temperature, and stirred overnight. GLC analysis revealed the product yields consisted of 12% **4**, Y = H, and 84% of the desired **4**, Y = Et.

(h) Coupling of 2 with (PhS)(*n*-Bu)CuLi (Eighth Entry, Table V). Following the general procedure, 1 mmol of **2** was reacted wtih 4 mmol (4.0 equiv) of (PhS)(*n*-Bu)CuLi for 0.5 h at −78 °C and 12 h at −20 ± 10 °C, and the mixture was allowed to warm to room temperature and stirred overnight. GLC analysis revealed the product yields consisted of 19% **4**, Y = H, 20% starting material (**2**), and 55% of the desired ((*E*)-5-decen-5-yl)trimethylsilane (**4**, Y = *n*-Bu).

(i) Coupling of 2 with (PhS)(*sec*-Bu)CuLi (Ninth Entry, Table V). Following the general procedure, 20 mmol of **2** was reacted with 80 mmol (4.0 equiv) of (PhS)(*sec*-Bu)CuLi at −30 °C and 12 h at −20 ± 10 °C, and the mixture was allowed to warm to room temperature and stirred overnight. Distillation at reduced pressure gave a 33% yield of ((*E*)-3-methyl-4-nonen-4-yl)trimethylsilane (**4**, Y = *sec*-Bu). GLC analysis (50-m SE-30 glass capillary column) indicated this product was in a 97:3 [*E*]:[*Z*] ratio. The compound had the following properties: bp 65–70 °C (4 torr); IR (neat) 2980 (s), 2890 (s), 1595 (m), 1455 (s), 1378 (m), 1250 (s), 926 (m), 835 (s), 757 (s), 689 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.84 (m, 6 H, 2 CH_2CH_3), 0.95 (d, 3 H, J = 8 Hz, $CHCH_3$), 1.22 (m, 6 H, 3 CH_2), 2.00 (m, 2 H, $CH_2C{=}C$), 2.40 (pentet, 1 H, J = 8 Hz, CHCC), 5.59 (t, 1 H, J = 6 Hz, $C{=}CH$); high-resolution mass spectrum[25] calcd (m/e) for $C_{13}H_{28}Si$ (M), 212.1961; found, 212.1936 (calcd for $C_{12}H_{25}Si$ (M − CH_3), 197.1726; found, 197.1717).

(j) Coupling of 2 with (PhS)(*t*-Bu)CuLi (Tenth Entry, Table V). Following the general procedure, 20 mmol of **2** was reacted with 80 mmol (4.0 equiv) of (PhS)(*t*-Bu)CuLi at −30 °C and 12 h at −20 ± 10 °C, and the mixture was allowed to warm up to room temperature and stirred overnight. Distillation at reduced pressure gave a 53% isolated yield of ((*E*)-2,2-dimethyl-3-octen-3-yl)trimethylsilane (**4**, Y = *t*-Bu). GLC analysis (50-m SE-30 glass capillary column) indicated this product was >99% *E*. The compound had the following properties: bp 50–52 °C (0.1 torr); IR (neat) 2975 (s), 2880 (s), 1583 (m), 1460 (m), 1361 (m), 1250 (s), 930 (m), 835 (s), 756 (m), 683 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.80 (m, 3 H, CH_2CH_3), 1.05 (s, 9 H, $(CH_3)_3C$), 1.12 (m, 4 H, $(CH_2)_2$), 2.11 (m, 2 H, $CH_2C{=}C$), 5.51 (t, 1 H, J = 7.5 Hz, $C{=}CH$); high-resolution mass spectrum[25] calcd (m/e) for $C_{13}H_{28}Si$ (M), 212.1961; found, 212.1976 (calcd for $C_{12}H_{25}Si$ (M − CH_3), 197.1726; found, 197.1712).

General Coupling Procedure Using Alkyllithium Reagents and 20 mol % of Cuprous Iodide (Table VI). To a flask, thoroughly purged of air, containing 0.4 equiv of cuprous iodide (20 mol % relative to alkyllithium reagent) was added dry solvent. The resulting slurry was cooled to 0 °C (ice bath) and treated with 2 equiv of alkyllithium reagent. The resulting clear solution was stirred a few minutes at 0 °C and 1 equiv of the α-bromovinylsilane **1** or **2** was added in a few milliliters of solvent. After the appropriate reaction time, the mixture was poured into a separatory funnel containing concentrated ammonium hydroxide and shaken, with frequent venting, until all solids had dissolved. The layers were separated and the blue aqueous layer was thoroughly extracted with pentane. The combined organic extracts were dried over anhydrous sodium sulfate. The resulting mixture was either directly analyzed by GLC, using *n*-decane as an internal standard, or distilled at atmospheric pressure to remove the solvent in the case of preparative runs. The residue from this latter procedure was distilled at reduced pressure to give the colorless product.

(a) Coupling of 1 with Methyllithium and 20 mol % of Cuprous Iodide (First Entry, Table VI). Following the general procedure, 30 mmol of **1** was reacted with a methyllithium–cuprous iodide mixture in diethyl ether solvent for 0.5 h at 0 °C. The reaction was worked up after warming to room temperature. Distillation at reduced pressure gave a 95% isolated yield of ((*Z*)-2-hepten-2-yl)trimethylsilane (**3**, Y = Me). GLC analysis (50-m SE-30 glass capillary column) showed this product was in a 99:1 [*Z*]:[*E*] ratio.

(b) Coupling of 2 with Methyllithium and 20 mol % of Cuprous Iodide (Second Entry, Table VI). Following the general procedure, 20 mmol of **2** was reacted with a methyllithium–cuprous iodide mixture in diethyl ether solvent for 48 h at room temperature. Distillation at reduced pressure gave a 90% isolated yield of ((*E*)-2-hepten-2-yl)trimethylsilane (**4**, Y = Me). GLC analysis (50-m SE-30 glass capillary column) showed this product was in a 95:5 [*E*]:[*Z*] ratio.

(c) Coupling of 1 with Ethyllithium and 20 mol % of Cuprous Iodide (Third Entry, Table VI). Following the general procedure, 1 mmol of **1** was reacted with an ethyllithium–cuprous iodide mixture in diethyl ether solvent for 0.5 h at 0 °C. The reaction was worked up after warming to room temperature. GLC analysis revealed the product yields consisted of 41% ((*Z*)-1-hexen-1-yl)trimethylsilane (**3**, Y = H) and 37% of the desired ((*Z*)-2-octen-2-yl)trimethylsilane (**3**, Y = Et).

(d) Coupling of 2 with Ethyllithium and 20 mol % of Cuprous Iodide (Fourth Entry, Table VI). Following the general procedure, 1 mmol of **2** was reacted with an ethyllithium–cuprous iodide mixture in diethyl ether solvent for 24 h at 0–10 °C. GLC analysis revealed the product yields consisted of 3% ((*E*)-1-hexen-1-yl)trimethylsilane (**4**, Y = H) and 47% of the desired ((*E*)-2-octen-2-yl)trimethylsilane (**4**, Y = Et).

(e) Coupling of 1 with Ethyllithium and 20 mol % of Cuprous Iodide in Tetrahydrofuran (Fifth Entry, Table VI). Following the general procedure, 1 mmol of **1** was reacted with an ethyllithium–cuprous iodide mixture in tetrahydrofuran solvent for 0.5 h at 0 °C. The reaction was worked up after warming to room temperature. GLC analysis revealed the product yields consisted of 71% **3**, Y = H, and 15% of the desired **3**, Y = Et.

(f) Coupling of 1 with Ethyllithium and 20 mol % of Cuprous Iodide in Hexane (Sixth Entry, Table VI). Following the general procedure, 1 mmol of **1** was reacted with an ethyllithium–cuprous iodide mixture in hexane solvent for 0.5 h at 0 °C. The reaction was worked up after warming to room temperature. GLC analysis revealed the product yields consisted of 28% **3**, Y = H, 47% starting material (**1**), and 17% of the desired **3**, Y = Et.

(g) Coupling of 1 with *n*-Butyllithium and 20 mol % of Cuprous Iodide (Seventh Entry, Table VI). Following the general procedure, 1 mmol of **1** was reacted with an *n*-butyllithium–cuprous iodide mixture (made at −78 °C) in diethyl ether solvent for 0.5 h at 0 °C. The reaction was worked up after warming to room temperature. GLC analysis revealed the product yields consisted of 44% **3**, Y = H, and 35% of the desired ((*Z*)-3-octen-3-yl)trimethylsilane (**3**, Y = *n*-Bu).

General Procedure for Conversion of Alkylated Vinylsilanes to Vinyl Bromides (Table VII). (1) Bromination. To a solution of 1 equiv of alkylated vinylsilane **5** or **6** in methylene chloride (~1 mL of CH_2Cl_2/mmol of **5** or **6**), cooled to −78 °C (dry ice/acetone bath), was slowly added a solution of 1.25 equiv of bromine in methylene chloride (~2 mmol of Br_2/mL of CH_2Cl_2). To the red-orange solution was added 25 mL of methanol and 0.50 g of sodium sulfite and the resulting mixture was vigorously stirred until the mixture became light yellow. While still cold (−78 °C), the reaction mixture was quickly poured into a separatory funnel containing 10% sodium sulfite solution and shaken until all of the color had disappeared. After separation, the aqueous layer was thoroughly extracted with pentane, and the combined organic extracts were dried over anhydrous sodium sulfate. In the absence of light, the solvent was removed by rotary evaporation at room temperature to afford the crude dibromide which was used in the next step without further purification.

(2) Desilicobromination. The crude dibromide was quickly dissolved in about 10 mL of precooled (0 °C, ice bath) methanol and treated with 1.5 equiv of freshly prepared 1 M sodium methoxide in methanol while at 0 °C. The resulting mixture was stirred for 1 h at 0 °C, allowed to warm to room temperature, and then stirred an additional 2 h. Then the reaction mixture was partitioned between pentane and water and separated. The aqueous layer was thoroughly extracted with fresh pentane, and the combined organic extracts were dried over anhydrous sodium sulfate. The solvent was removed by distillation at atmospheric pressure in the presence of solid sodium carbonate to afford a residue which was vacuum distilled, once again in the presence of solid sodium carbonate, to give the product as a colorless liquid.

(a) Conversion of 5 (R = Me) to (*E*)-2-Bromo-2-heptene (First Entry, Table VII). Following the general procedure, 25.2 mmol of ((*Z*)-2-hepten-2-yl)trimethylsilane (**5**, R = Me) was brominated to give a 98% yield of the crude dibromide: IR (neat) 2975 (s), 2875 (m), 1450 (m), 1375 (m), 1253 (s), 1230 (m), 1020 (m), 926 (m), 846 (s), 762 (m), 692 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.41–2.15 (m, 9 H, $CH_3(CH_2)_3$), 1.53 (s, 3 H, CH_3CBrSi), 3.89 and 4.06 (two d, 1 H, J = 2 Hz, CHBrCBrSi). The crude dibromide was immediately eliminated with sodium methoxide in methanol following the general procedure. Distillation at reduced pressure afforded a 91% isolated yield of the desired (*E*)-2-bromo-2-heptene (GLC analysis revealed the product to be in a 99:1 [*E*]:[*Z*] ratio): bp 63–66 °C (16 torr); IR (neat) 2975 (s), 2940 (s), 2875 (s), 1646 (m), 1455 (m), 1428 (m), 1379 (m), 1140 (m), 1057 (m), 840 (m), 637 (m) cm^{-1}; NMR (CCl_4, internal Me_4Si standard) δ 0.91 (br t, 3 H, J = 6 Hz, CH_2CH_3), 1.33 (m, 4 H, $(CH_2)_2$), 2.00 (br q, 2 H, J = 7.5 Hz, $CH_2C{=}C$), 2.18 (d, 3 H, J = 1.5 Hz, $C{=}CCH_3$), 5.80 (t of q, 1 H, J = 7.5, 1.5 Hz, $CH{=}C$); high-resolution mass spectrum[25] calcd (*m*/*e*) for $C_7H_{13}{}^{79}Br$, 176.0201; found, 176.0191 (calcd (*m*/*e*) for $C_7H_{13}{}^{81}Br$, 178.0181; found, 178.0175).

(b) Conversion of 6 (R = Me) to (*Z*)-2-Bromo-2-heptene (Second Entry, Table VII). Following the general procedure, 49.5 mmol of ((*E*)-2-hepten-2-yl)trimethylsilane (**6**, R = Me) was brominated to give a 100% yield of the crude dibromide: IR (neat) 2980 (s), 2890 (s), 1456 (m), 1375 (m), 1254 (s), 1015 (m), 845 (s), 761 (m), 693 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.71 (m, 3 H, CH_2CH_3), 0.91–2.40 (m, 6 H, $(CH_2)_3$), 1.52 (s, 3 H, CH_3CBrSi), 3.90 and 4.06 (two d, 1 H, J = 2 Hz, CHBrCBrSi). The crude dibromide was immediately eliminated with sodium methoxide in methanol following the general procedure. Distillation at reduced pressure afforded an 87% isolated yield of the desired (*Z*)-2-bromo-2-heptene (GLC analysis revealed the product to be >99% *Z*): bp 50–54 °C (7 torr); IR (neat) 2980 (s), 2945 (s), 2880 (s), 1663 (m), 1450 (m), 1380 (m), 1282 (m), 1148 (m), 1055 (m), 824 (m) cm^{-1}; NMR (CCl_4, internal Me_4Si standard) δ 0.88 (br t, 3 H, J = 5.5 Hz, CH_2CH_3), 1.31 (m, 4 H, $(CH_2)_2$), 2.12 (br q, 2 H, J = 6 Hz, $CH_2C{=}C$), 2.33 (d, 3 H, J = 1.5 Hz, $C{=}CCH_3$), 5.57 (t of q, 1 H, J = 6.5, 1.5 Hz, $CH{=}C$); high-resolution mass spectrum[25] calcd (*m*/*e*) for $C_7H_{13}{}^{79}Br$, 176.0201; found, 176.0188 (calcd (*m*/*e*) for $C_7H_{13}{}^{81}Br$, 178.0181; found, 178.0159).

(c) Conversion of 5 (R = Et) to (*E*)-3-Bromo-3-octene (Third Entry, Table VII). Following the general procedure, 28.2 mmol of ((*Z*)-3-octen-3-yl)trimethylsilane (**5**, R = Et) was brominated to give a 100% yield of the crude dibromide: IR (neat) 2960 (s), 2890 (s), 1460 (m), 1379 (m), 1252 (s), 1225 (m), 840 (s), 800 (m), 760 (m), 694 (m), 630 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.50–2.50 (m, 14 H, $CH_3(CH_2)_3$ and CH_3CH_2), 3.92 and 4.08 (two br s, 1 H, CHBrCBrSi). The crude dibromide was immediately eliminated with sodium methoxide in methanol following the general procedure. Distillation at reduced pressure afforded a 93% isolated yield of the desired (*E*)-3-bromo-3-octene (GLC analysis revealed the product to be in a 97:3 [*E*]:[*Z*] ratio): bp 55–57 °C (1.8 torr); IR (neat) 2980 (s), 2945 (s), 2878 (s), 1643 (m), 1459 (s), 1378 (m), 1260 (m), 1142 (m), 1092 (m), 1070 (m), 890 (m), 844 (m) cm^{-1}; NMR (CCl_4, internal Me_4Si standard) δ 0.92 (br t, 3 H, J = 5.5 Hz, CH_2CH_3), 1.10 (t, 3 H, J = 7.5 Hz, $C{=}CCH_2CH_3$), 1.35 (m, 4 H, $(CH_2)_2$), 2.02 (br q, 2 H, J = 6.5 Hz, *n*-$PrCH_2C{=}C$), 2.43 (q, 2 H, J = 7.5 Hz, $C{=}CCH_2CH_3$), 5.76 (t, 1 H, J = 7.5 Hz, $CH{=}C$); high-resolution mass spectrum[25] calcd (*m*/*e*) for $C_8H_{15}{}^{79}Br$, 190.0357; found, 190.0347 (calcd (*m*/*e*) for $C_8H_{15}{}^{81}Br$, 192.0338; found, 192.0339).

(d) Conversion of 6 (R = Et) to (*Z*)-3-Bromo-3-octene (Fourth Entry, Table VII). Following the general procedure, 44.4 mmol of ((*E*)-3-octen-3-yl)trimethylsilane (**6**, R = Et) was brominated to give a 100% yield of the crude dibromide: IR (neat) 2970 (s), 2885 (m), 1457 (m), 1380 (m), 1252 (s), 888 (m), 845 (s), 800 (m), 759 (m), 690 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.40–2.50 (m, 14 H, $CH_3(CH_2)_3$ and CH_2CH_3), 3.88 and 4.04 (two d, 1 H, J = 2 Hz, CHBrCBrSi). The crude dibromide was immediately eliminated with sodium methoxide in methanol following the general procedure. Distillation at reduced pressure afforded an 84% isolated yield of the desired (*Z*)-3-bromo-3-octene (GLC analysis revealed the product to be in a 98:2 [*Z*]:[*E*] ratio): bp 52–56 °C (4.5 torr); IR (neat) 2940 (s), 2880 (s), 1652 (m), 1454 (s), 1376 (m), 1136 (m), 900 (m), 830 (m) cm^{-1}; NMR (CCl_4, internal Me_4Si standard) δ 0.90 (br t, 3 H, J = 5 Hz, CH_2CH_3), 1.10 (t, 3 H, J = 7.5 Hz, $C{=}CCH_2CH_3$), 1.30 (m, 4 H, $(CH_2)_2$), 2.11 (br t, 2 H, J = 6.5 Hz, *n*-$PrCH_2C{=}C$), 2.42 (q of t, 1 H, J = 6.5 Hz, 1.0 Hz, $CH{=}C$); high-resolution mass spectrum[25] calcd (*m*/*e*) for $C_8H_{15}{}^{79}Br$, 190.0357; found, 190.0354 (calcd (*m*/*e*) for $C_8H_{15}{}^{81}Br$, 192.0338; found, 192.0351).

(e) Conversion of 5 (R = *n*-Bu) to (*E*)-5-Bromo-5-decene (Fifth Entry, Table VII). Following the general procedure, 17.4 mmol of ((*Z*)-5-decen-5-yl)trimethylsilane (**5**, Y = *n*-Bu) was brominated to give a 98% yield of the crude dibromide: IR (neat) 2970 (s), 2880 (s), 1459 (m), 1380 (m), 1254 (s), 1222 (m), 928 (m), 845 (s), 760 (m), 734 (m), 691 (m), 630 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.47–2.40 (m, 18 H, 2 $CH_3(CH_2)_3$), 3.95 and 4.13 (two d, 1 H, J = 1.5 Hz, CHBrCBrSi). The crude dibromide was immediately eliminated with sodium methoxide in methanol following the general procedure. Distillation at reduced pressure afforded a 92% isolated yield of the desired (*E*)-5-bromo-5-decene (GLC analysis revealed the product to be in a 99:1 [*E*]:[*Z*] ratio): bp 54–56 °C (0.5 torr); IR (neat) 2955 (s), 2875 (s), 1638 (m), 1458 (s), 1376 (m), 1210 (m), 1137 (m), 946 (m), 840 (m), 731 (m) cm^{-1}; NMR (CCl_4, internal Me_4Si standard) δ 0.94 (m, 6 H, 2 CH_2CH_3), 1.35 (m, 8 H, 2 $(CH_2)_2$), 2.02 (br q, 2 H, J = 6.5 Hz, $CH_2C{=}CBr$), 2.33 (br q, 2 H, J = 7 Hz, $C{=}CBrCH_2$), 5.81 (t, 1 H, J = 6.5 Hz, $CH{=}C$); high-resolution mass spectrum[25] calcd (*m*/*e*) for $C_{10}H_{19}{}^{79}Br$, 218.0671; found, 218.0678 (calcd (*m*/*e*) for $C_{10}H_{19}{}^{81}Br$, 220.0651; found, 220.0648.

(f) Conversion of 6 (R = *n*-Bu) to (*Z*)-5-Bromo-5-decene (Sixth Entry, Table VII). Following the general procedure, 19.8 mmol of ((*E*)-5-decen-5-yl)trimethylsilane (**6**, R = *n*-Bu) was brominated to give a 100% yield of the crude dibromide: IR (neat) 2980 (s), 2885 (s), 1460 (s), 1380 (m), 1253 (s), 1224 (m), 924 (m), 845 (s), 759 (m), 734 (m), 689 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.40–2.53 (m, 18 H, 2 $CH_3(CH_2)_3$), 3.91 and 4.05 (two d, 1 H, J = 2 Hz, CHBrCBrSi). The crude dibromide was immediately eliminated with sodium methoxide in methanol following the general procedure. Distillation at reduced pressure afforded a 91% isolated yield of the desired (*Z*)-5-bromo-5-decene (GLC analysis revealed the product to be in a 97:3 [*Z*]:[*E*] ratio): bp 55–57 °C (0.5 torr); IR (neat) 2975 (s), 2940 (s), 2875 (s), 1650 (m), 1455 (m) cm^{-1}; NMR (CCl_4, internal Me_4Si standard) δ 0.91 (unsymmetrical t, 6 H, J = 5.5 Hz, 2 CH_2CH_3), 1.37 (m, 8 H, 2 $(CH_2)_2$), 2.14 (br q, 2 H, J = 6 Hz, $CH_2C{=}CBr$), 2.35 (br q, 2 H, J = 6 Hz, $C{=}CBrCH_2$), 5.57 (t of t, 1 H, J = 6, 1 Hz, $CH{=}C$); high-resolution mass spectrum[25] calcd (*m*/*e*) for $C_{10}H_{19}{}^{79}Br$, 218.0671; found, 218.0681 (calcd (*m*/*e*) for $C_{10}H_{19}{}^{81}Br$, 220.0651; found, 220.0668).

(g) Conversion of 5 (R = *sec*-Bu) to (*E*)-4-Bromo-3-methyl-4-nonene (Seventh Entry, Table VII). Following the general procedure, 8.9 mmol of ((*Z*)-3-methyl-4-nonen-4-yl)trimethylsilane (**5**, R = *sec*-Bu) was brominated to give an 87% yield of the crude dibromide: IR (neat) 2980 (s), 2945 (s), 2890 (s), 1459 (s), 1310 (m), 1255 (s), 1096 (m), 845 (s), 760 (m), 694 (m) cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.30–2.50 (m, 18 H, $CH_3(CH_2)_3$ and $CH_2CH_2CH(CH_3)$), 3.95 (m, 1 H, CHBrCBrSi). The crude dibromide was immediately eliminated with sodium methoxide in methanol following the general procedure. Distillation at reduced pressure afforded a 75% overall isolated yield of the desired (*E*)-4-bromo-3-methyl-4-nonene (GLC analysis revealed the product to be in a 98:2 [*E*]:[*Z*] ratio): bp 74–78 °C

(3.5 torr); IR (neat) 2980 (s), 2940 (s), 2880 (s), 1634 (m), 1456 (s), 1379 (m), 1144 (m), 1090 (m), 908 (m), 835 (m), 780 (m), 739 (m) cm^{-1}; NMR (CCl_4, internal Me_4Si standard) δ 0.91 (m, 6 H, 2 CH_2CH_3), 1.01 (d, 3 H, J = 7 Hz, $CHCH_3$), 1.33 (m, 6 H, 3 CH_2), 2.06 (br q, 2 H, J = 7 Hz, $CH_2C{=}CBr$), 2.46 (symmetrical m, 1 H, $C{=}CBrCH$), 5.81 (t, 1 H, J = 7 Hz, $CH{=}C$); high-resolution mass spectrum[25] calcd (m/e) for $C_{10}H_{19}{}^{79}Br$, 218.0671; found, 218.0659 (calcd (m/e) for $C_{10}H_{19}{}^{81}Br$, 220.0651; found, 220.0663).

Preparation of (*E*)-3-Methyl-3-octene (10). (a) From 8 Using the *sec*-Butyllithium Alkylation Procedure (First Entry, Table VIII). Following the general procedure described for Table III, 13 mmol of **8** was alkylated with 26 mmol (2.0 equiv) of ethyl iodide to give an 80% isolated yield of (*E*)-3-methyl-3-octene (**10**) (GLC analysis on a 50-m SE-30 glass capillary column revealed the product to be in a 97:3 [*E*]:[*Z*] ratio): bp 63–67 °C (60 torr); low-resolution mass spectrum, parent peak at m/e 126; base peak at m/e 55. The spectra of this compound are in accord with its published spectra.[21]

In a separate experiment using 1 mmol of **8**, GLC analysis with *n*-decane as an internal standard revealed the product yield to be 87%.

(b) From 8 Using Ethyllithium and 20 mol % of Cuprous Iodide (Second Entry, Table VIII). Following the general procedure described for Table VI, 1 mmol of **8** was reacted with an ethyllithium–cuprous iodide mixture in diethyl ether solvent for 24 h at 0–10 °C. GLC analysis with *n*-decane as an internal standard revealed the yield to be 74% of the desired product **10**.

(c) From 8 Using (PhS)(Et)CuLi (Third Entry, Table VIII). Following the general procedure described for Table V, 1 mmol of **8** was reacted with 2 mmol (2.0 equiv) of (PhS)(Et)CuLi for 4 h at −78 °C, and the mixture was allowed to warm to room temperature and then stirred an additional 4 h. GLC analysis with *n*-decane as an internal standard revealed the product yields consisted of 23% starting material **8** and 67% of the desired compound **10**.

(d) From 9 Using the *sec*-Butyllithium Alkylation Procedure (Fourth Entry, Table VIII). Following the general procedure described for Table III, 20 mmol of **9** was alkylated with 40 mmol (2.0 equiv) of dimethyl sulfate to give an 83% isolated yield of the desired product **10** (GLC analysis on a 50 m SE-30 glass capillary column revealed the product to be in a 96:4 [*E*]:[*Z*] ratio).

(e) From 9 Using Methyllithium and 20 mol % of Cuprous Iodide (Fifth Entry, Table VIII). Following the general procedure described for Table VI, 1 mmol of **9** was reacted with a methyllithium–cuprous iodide mixture in diethyl ether solvent for 48 h at room temperature. GLC analysis with *n*-decane as an internal standard revealed the product yields to be 81% starting material (**8**) and 5% of the desired compound **10**.

Preparation of (*Z*)-3-Methyl-3-octene (13). (a) From 11 Using the *sec*-Butyllithium Alkylation Procedure (First Entry, Table IX). Following the general procedure described for Table III, 25.7 mmol of **11** was alkylated with 51.4 mmol (2.0 equiv) of dimethyl sulfate to give an 80% isolated yield of (*Z*)-3-methyl-3-octene (**13**) (GLC analysis on a 50 m SE-30 glass capillary column revealed the product to be >99% Z): bp 65–69 °C (60 torr); low-resolution mass spectrum, parent peak at m/e 126; base peak at m/e 55. The spectra of this compound are in accord with its published spectra.[21]

(b) From 11 Using Methyllithium and 20 mol % of Cuprous Iodide (Second Entry, Table IX). Following the general procedure described for Table VI, 18 mmol of **11** was reacted with a methyllithium–cuprous iodide mixture in diethyl ether solvent for 48 h at room temperature. Distillation of the crude mixture at reduced pressure gave an 81% isolated yield of the desired compound **13** (GLC analysis on a 50 m SE-30 glass capillary column revealed the product to be in a 98:2 [*Z*]:[*E*] ratio).

In a separate experiment using 1 mmol of **11**, GLC analysis with *n*-decane as an internal standard revealed the product yield to be 89%.

(c) From 12 Using the *sec*-Butyllithium Alkylation Procedure (Third Entry, Table IX). Following the general procedure described for Table III, 25 mmol of **12** was alkylated with 50 mmol (2.0 equiv) of ethyl iodide to give a 74% isolated yield of the desired product **13** (GLC analysis on a 50 m SE-30 glass capillary column revealed the product to be in a 98:2 [*Z*]:[*E*] ratio).

In a separate experiment using 1 mmol of **12**, GLC analysis with *n*-decane as an internal standard revealed the product yield to be 77%.

(d) From 12 Using Ethyllithium and 20 mol % of Cuprous Iodide (Fourth Entry, Table IX). Following the general procedure described for Table VI, 1 mmol of **12** was reacted with an ethyllithium–cuprous iodide mixture in diethyl ether solvent for 48 h at room temperature. GLC analysis with *n*-decane as an internal standard revealed the product yields to be 3% starting material (**12**) and 49% of the desired compound **13**.

(e) From 12 Using (PhS)(Et)CuLi (Fifth Entry, Table IX). Following the general procedure described for Table V, 1 mmol of **12** was reacted with 4 mmol (4.0 equiv) of (PhS)(Et)CuLi for 12 h at −20 ± 10 °C (dry ice/carbon tetrachloride bath), and the mixture was allowed to warm to room temperature and stirred overnight. GLC analysis with *n*-decane as an internal standard revealed the product yield to be 54% of the desired compound **13**.

Acknowledgment. The authors thank the Committee on Research, University of California, Davis, for partial support of this work and Professor George Zweifel for providing some authentic samples and the glass capillary columns used in this study.

Registry No. 1, 65425-93-6; **2**, 65425-94-7; **3** (Y = Me), 71720-11-1; **3** (Y = Et), 71720-12-2; **3** (Y = *n*-Bu), 71720-13-3; **3** (Y = H), 26567-95-3; **3** (Y = *sec*-Bu), 71720-14-4; **3** (Y = *t*-Bu), 71720-15-5; **4** (Y = Me), 71720-16-6; **4** (Y = H), 20107-37-3; **4** (Y = Et), 71720-17-7; **4** (Y = *n*-Bu), 71720-18-8; **4** (Y = *sec*-Bu), 71720-19-9; **4** (Y = *t*-Bu), 71720-20-2; (*E*)-**7** (R = Me), 66070-25-5; (*Z*)-**7** (R = Me), 66070-24-4; (*E*)-**7** (R = Et), 71720-21-3; (*Z*)-**7** (R = Et), 71720-22-4; (*E*)-**7** (R = *n*-Bu), 71720-23-5; (*Z*)-**7** (R = *n*-Bu), 71720-24-6; (*E*)-**7** (R = *sec*-Bu), 71720-25-7; (*Z*)-**7** (R = *sec*-Bu), 71720-26-8; (*E*)-**10**, 59643-72-0; (*Z*)-**10**, 59643-71-9; MeI, 74-88-4; EtI, 75-03-6; *n*-BuI, 542-69-8; *sec*-BuI, 513-48-4; Me_2SO_4, 77-78-1; Et_2CuLi, 38297-20-0; *n*-Bu_2CuLi, 24406-16-4; (PhS)(Et)CuLi, 71733-93-2; (PhS)(*n*-Bu)CuLi, 53128-68-0; (PhS)(*sec*-Bu)CuLi, 53972-31-9; (PhS)(*t*-Bu)CuLi, 50281-66-8; MeLi, 917-54-4; EtLi, 811-49-4; *n*-BuLi, 109-72-8.