Regioselective Synthesis of Allyltrimethylsilanes from Allylic Halides and Allylic Sulfonates. Application to the Synthesis of 2,3-Bis(trimethylsilyl)alk-1-enes

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The preparation of allyltrimethylsilanes by regioselective pathways is described. Treatment of (E)-1chloro-2-alkenes with a reagent prepared from 1 equiv each of trimethylsilyllithium and copper(I) iodide in hexamethylphosphoramide to presumably form a (trimethylsilyl)copper reagent affords 3-(trimethylsilyl)-1-alkenes in good to excellent yields with high regioselectivity. Treatment of these same 1-chloro-2-alkenes with (trimethylsilyl)lithium alone without added copper(I) iodide yields only (E)-1-(trimethylsilyl)-2-alkenes. A single allylic halide thus yields two regioisomeric allyltrimethylsilanes by proper choice of reaction conditions. The reaction of a variety of allylic sulfonates with (trimethylsilyl)copper has also been investigated. The mesylates of 2° and 3° allylic alcohols yield mixtures of isomeric allyltrimethylsilanes in which the 1-(trimethylsilyl)-2-alkenes predominate. With geraniol, the mesylate was prepared in situ and allowed to react with (trimethylsilyl)copper to afford two isomeric allyltrimethylsilanes in which the 3-(trimethylsilyl)-1-alkene predominates. Finally, these reactions have also been used to prepare a variety of 2,3-bis(trimethylsilyl)alk-1-enes, a class of unsaturated organosilanes which has received little attention in the literature.

In the past ten years, allylsilanes have seen increasing use in organic synthesis.¹ The reactivity of allylsilanes with a variety of electrophiles by regiospecific pathways is now well-documented, and more recently allylsilanes have been utilized as intermediates in the synthesis of a variety of natural products.² Although a number of methods now exist for introducing this functionality into a complex molecule,³ the problem of regio- and stereocontrol in the synthesis of allylsilanes has remained largely unsolved.⁴ It is obvious that in order to take full advantage of the predictable regiospecificity of the chemical reactions of allylsilanes, a storehouse of mild and controlled methods for the synthesis of this functional group is needed.

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We have recently reported a new method for synthesizing allyltrimethylsilanes from allylic halides using (trimethylsilyl)metal reagents⁵ and have used this method in the regioselective synthesis of two isomeric allylic trimethylsilanes from a single allylic halide by appropriate choice of reaction conditions.⁶ Herein, we report on the full scope of the reaction of allylic halides and allylic sulfonates with (trimethylsilyl)lithium in the presence (and absence) of 1 equiv of copper(I) iodide, as well as the application of this reaction to the synthesis of various 2,3-bis(trimethylsilyl)alk-1-enes, a relatively unexplored class of unsaturated organosilanes.^{7,8}

The preparation and reaction of (trialkylsilyl)metal reagents has only recently been explored. Various alkali metal reagents [(trimethylsilyl)lithium,⁹ (trimethylsilyl)sodium,^{10,11} and (trimethylsilyl)potassium¹⁰] have now been prepared. The reaction of a few substrates with a reagent prepared from chlorotrimethylsilane and magnesium in hexamethylphosphoramide has also been reported.¹² Two silyl aluminum reagents (tris(trimethylsilyl)aluminum etherate^{3d} and a reagent prepared from diethylaluminum chloride and phenyl(dimethylsilyl)lithium^{3f}) are known, and several reports of silylcopper reagents have appeared in the literature.^{3h,5,6,13} Less is known about the reactions of these metal reagents with allylic halides or other allyl derivatives to afford allylsilanes. A few isolated examples

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 Table I. Reaction of Simple Allylic Halides with (Trimethylsilyl)metal Reagents

entry	halide	reagent used ^a	product	yield, ^b %
1	1a	TMSLi	2a	3
2	1b	TMSLi	2b	.0
3	1 d	TMSLi	2a	7
4	1a	TMSCu	2a	64
5	1 b	TMSCu	2b	90°
6	1c	TMSCu	2c	68°
7	1 d	TMSCu	2a	45

^aTMSLi was prepared from hexamethyldisilane and commercially available methyllithium (dissolved in ether) in HMPA as solvent. The details for the preparation of TMSCu are described in general procedure A of the Experimental Section. ^b Yields were determined by gas chromatographic analysis using internal standards. ^c Yield refers to isolated products, purified by distillation. TMS = trimethylsilyl.

of the reaction of allylic halides with (trimethylsilyl)metal reagents have appeared.^{3c,e,10a,13a} Fleming has reported that lithium bis(phenyldimethylsilyl)cuprate reacts with tertiary allylic acetates to form allylsilanes in good yield.^{3h} The reaction of allylic acetates with tris(trimethylsilyl)aluminum etherate in the presence of a palladium or molybdenum catalyst is also known.^{3d} Allylic phosphates are known to afford allylsilanes upon treatment with a silylaluminum reagent.^{3f} In most cases the yields of products are good but mixtures of isomeric allylsilanes often result.

Results and Discussion

Initial Studies. Although allylsilanes have most commonly been synthesized via the reaction of a nucleophilic allylmetal reagent with an electrophilic trialkylsilyl halide, we explored the possibility of preparing allylic trimethylsilanes by the reverse strategy, namely, the reaction of a nucleophilic trimethylsilyl metal reagent with an electrophilic allyl moiety. Our initial investigation centered on finding a simple, easily prepared nucleophilic trimethylsilyl anion (TMS⁻M⁺) which would react with commercially available allylic halides to yield the desired allyltrimethylsilanes (eq 1). Since the reaction of allylic



halides with either (trimethylsilyl)sodium or (trimethylsilyl)potassium in hexamethylphosphoramide was known to give products arising predominantly from single electron transfer processes,^{10a} we concentrated on examining the reaction of these same allylic halides with other (trimethylsilyl)metal reagents such as (trimethylsilyl)lithium (TMSLi) and (trimethylsilyl)lithium in the presence of copper(I) iodide.

Our initial studies using four commercially available allylic halides (1a-d) are summarized in Table I. Treatment of allylic halides 1a, 1b, and 1d with (trimethylsilyl)lithium prepared from hexamethyldisilane and methyllithium (commercially available methyllithiumlithium bromide complex dissolved in ether) in hexamethylphosphoramide at 0-25 °C as previously described⁹ afforded little or none of the desired allyltrimethylsilane (entries 1-3). In contrast, treatment of allylic halides 1a-dwith (trimethylsilyl)lithium in the presence of 1 equiv of copper(I) iodide in hexamethylphosphoramide at 0-25 °C afforded the desired allyltrimethylsilane in good to ex-



cellent yield (entries 4-7). Because it was also found that the use of 2 equiv of (trimethylsilyl)lithium per copper iodide gave lower yields of 2b with 1b as starting material, the 1:1 ratio of (trimethylsilyl)lithium to copper iodide to presumably form a (trimethylsilyl)copper reagent was used for the remainder of this study. The solid copper iodide was most conveniently introduced into the reaction mixture as a solution in dimethyl sulfide. The role of the dimethyl sulfide in the reaction has not been determined, but once again yields using copper iodide dissolved in dimethyl sulfide were enhanced over reactions in which no dimethyl sulfide was present. Although the synthesis of commercially available allyltrimethylsilane¹⁴ (2a) by this methodology is not especially noteworthy, these simple examples demonstrate that functionalized allyltrimethylsilanes such as 2b and 2c are now readily available in good yield. For example, (2-bromoallyl)trimethylsilane 2b, which has in fact been prepared by at least two other groups, has already been shown to be a useful synthetic reagent.13a,15

Stereochemistry and Regiochemistry. Since the preparation of allyltrimethylsilanes from some simple allylic halides was successful, the reaction of (E)-1-halo-2-alkenes with (trimethylsilyl)lithium in the presence of copper iodide was investigated in an attempt to define the regio- and stereochemistry of the reaction. The needed allylic halides 5, 6, and 7 were prepared from carbonyl precursors 3 by the standard synthetic operations illustrated in Scheme I.

The reaction of an (E)-1-halo-2-alkene with a nucleophilic (trimethylsilyl)metal reagent could in theory yield a mixture of isomeric allyltrimethylsilanes, namely, a 3-(trimethylsilyl)-1-alkene 8, an (E)-1-(trimethylsilyl)-2-alkene 9, and a (Z)-1-(trimethylsilyl)-2-alkene 10 (eq 2). In



fact, treatment of (E)-1-chloro-2-nonene (5a) with (trimethylsilyl)copper prepared under our previously developed reaction conditions (HMPA as solvent, 0-25 °C) afforded a mixture consisting largely of the less stable isomer 8a (Table II, entry 1, ratio of 8a:9a, 87:13). After much experimentation which included varying the reaction

⁽¹⁴⁾ Aldrich Chemical Company presently sells 10 g of allyltrimethylsilane for \$14.60.

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Table II. Conversion of (E)-1-Halo-2-nonene to Isomeric Allyltrimethylsilanes

entry	compd	reagent	solvent	temp, °C	product ratio ^a 8a:9a:10a	yield, ^b %
1	5a	TMSCu	HMPA ^c	0-25	87:13:0	80
2	6 a	TMSCu	HMPA ^c	0-25	60:13:27	80
3	7 a	TMSCu	HMPA ^c	0-25	57:33:10	75
4	5a	TMSCu	$HMPA-ether^{d}$	-60	98:2:0	87
5	6a	TMSCu	$HMPA-ether^{d}$	-60	77:5:18	79
6	5 a	TMSLi	$HMPA-ether^{d}$	-60	9a only	78
7	6 a	TMSLi	$HMPA-ether^{d}$	-60	9a only	76

^a Ratios were determined by gas chromatography using an OV-17 column at 110 °C. ^b Yields refer to isolated products purified by column chromatography. ^c HMPA is the major solvent in the reaction. A small amount of ether from the commercially available methyllithium-ether solution is also present. Since the copper(I) iodide was dissolved in dimethyl sulfide before addition to the reaction mixture, dimethyl sulfide is also present. ^d The solution was approximately 25% HMPA in ether. TMS = trimethylsilyl.

Table 111. Conversion of Allync mandes to isomeric Allynchmethylsing	Table III.	Conversion of	Allvlic Allvlic	Halides to) Isomeric .	Allvltrimethvlsilan
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		E allylic halides				
entry	starting material	R	reagent	product ratio ^a 8:9:10	yield, ^b %	
1		C_6H_{13}	TMSCu	98:2:0	87	
2	5 a	C_6H_{13}	TMSLi	9a only	78	
3	5b	C_6H_5	TMSCu	94:6:0	80	
4	6 b °	C_6H_5	TMSLi	30:68:2	38	
5	5c	$C_{11}H_{23}$	TMSCu	86:8:6	78	
6	5c	$C_{11}H_{23}$	TMSLi	2:98:0	61	
7	5d	$c-C_6H_{11}$	TMSCu	92:8:0	86	
8	5d	$c-C_6H_{11}$	TMSLi	9d only	59	
9	5e	$C_{9}H_{19}$	TMSCu	88:7:5	75	
10	5e	$C_{9}H_{19}$	TMSLi	9e only	76	
				other allylic halides		
entry	starting material	reagent		product ratio ^a		yield, ^b %

entery	starting material	reagent	product ratio	yleiu, 76
11	(CH ₃) ₂ C=CHCH ₂ CH ₂ C(CH ₃)=CHCH ₂ Cl (11) ^d	TMSCu	(CH ₃) ₂ C=CHCH ₂ CH ₂ (CH ₃)C(TMS)CH=CH ₂ (12a) (95%)	69
			$(CH_3)_2C = CHCH_2CH_2C(CH_3) = CHCH_2TMS (12b) (5\%)$	
12	11	TMSLi	12a:12b, 9:91	74
13	$(C_6H_5)_2C = CHCH_2Cl (13)^e$	TMSCu	$(C_6H_5)_2C = CHCH_2TMS$ (14)	44
14	13	TMSLi	14 only	40
15	$CH_3(CH_2)_8CH(Cl)CH=CH_2 (15)^f$	TMSCu	8e:9e:10e, 20:37:43	82
16	15	TMSLi	8e:9e:10e, 19:81:0	75

^a The ratio of products was determined by gas chromatography using an OV 17 column at various temperatures. ^b Yields refer to isolated products purified by column chromatography. ^c In this case reaction of **6a** with TMSLi afforded a low yield of the desired allyltrimethylsilanes. ^d Prepared from geraniol as previously described (ref 16). ^e Prepared by the methodology indicated in Scheme I with benzophenone used as starting material. ^f Prepared from 1-nonen-3-ol as previously described (ref 17). The starting material was usually contaminated with varying amounts (ca. 25%) of the rearranged allylic chloride **5e**.

time, solvent system, temperature, and the number of equivalents of (trimethylsilyl)copper per substrate, it was discovered that the ratio of 8a:9a was improved to 98:2 by adding ether as a cosolvent with the HMPA and cooling the reaction to -60 °C (Table II, entry 4). Treatment of (E)-1-bromo-2-nonene (6a) with (trimethylsilyl)copper gave mixtures of 8a, 9a, and 10a under a variety of experimental conditions, but once again the yield of 8a at the expense of isomers 9a and 10a increased at lower temperature and with ether as a cosolvent (Table II, entries 2 and 5). Treatment of (E)-1-iodo-2-nonene (7a) with (trimethylsilyl)copper in HMPA at 0-25 °C likewise afforded a mixture of products and was thus not investigated further. It is noteworthy that under similar reaction conditions, as the halide was varied from chloride to bromide to iodide, the percentage of the less stable isomer 8a decreased relative to the amount of 9a and 10a formed.

From these studies it was concluded that the formation of 3-(trimethylsilyl)-1-alkenes from (E)-1-halo-2-alkenes and (trimethylsilyl)copper was favored by the use of chlorides as the allylic halide, low temperature, and a mixture of ether-HMPA as solvent.

Since 1-(trimethylsilyl)-2-alkenes 9a and 10a were never predominant products under any reaction conditions with (trimethylsilyl)copper as reagent, the reaction of 1-halo-2-alkenes 5a and 6a with other (trimethylsilyl)metal species was investigated in an attempt to find a complementary method which would generate either of these products. Although the reaction of (trimethylsilyl)lithium with allyl chloride in HMPA at 0-25 °C had afforded essentially none of the desired allyltrimethylsilane (Table I, entry 3), treatment of either 5a or 6a with (trimethylsilyl)lithium alone (without added copper iodide) under much milder reaction conditions (a mixture of ether-HMPA at low temperature) resulted in exclusive formation of the E isomer 9a in 78% and 76% yield, respectively. Thus, under these new milder reaction conditions, (trimethylsilyl)lithium was effective in forming allyltrimethylsilanes, but the regiochemistry was completely different from that observed with (trimethylsilyl)copper. From these studies it was concluded that the formation of 9a was favored by the use of (trimethylsilyl)lithium as the silylmetal reagent at low temperature in a mixture of ether-HMPA. Both allylic chloride 5a and allylic bromide 6a appeared to be equally effective in this reaction.

The optimum conditions devised for the formation of either 3-(trimethylsilyl)-1-nonene (8a) or (E)-1-(trimethylsilyl)-2-nonene (9a) from a single starting material have been used to synthesize a variety of isomeric allyltrimethylsilanes. The results are summarized in Table III. The identity and composition of the product mixtures was assigned on the basis of spectral and gas chromatographic analysis. Satisfactory ¹H NMR, IR, GC-MS, and highresolution mass spectral data were obtained for new compounds. In some cases, 500-MHz NMR spectra were obtained on the various isomers. Isomer mixtures were in

Table IV. Reaction of Allylic Sulfonates with (Trimethylsilyl)copper

entry	alcohol	sulfonate (yield, ^a %)	allylsilane (yield, b %)	ratio ^c
1	4a	17a (87)	8a:9a:10a (52)	6.5:32:61.5
2	4e	17b (87)	8e:9e:10e (56)	3:36:61
3	4c	17c (67)	8c:9c:10c (33)	5:47.5:47.5
4	4d	17d (80)	8d:9d:10d (68)	9:91:0
5	4e	17e (92)	8e:9e:10e (87)	5:27:68
6	OH	OSO,CH,	TMS	
7	$18 \\ (CH_3)_2C = CHCH_2CH_2C(CH_3) = CHCH_2OH$	19 (80)	20 (49) 1 2a :1 2b (50) ^e	20 only 70:30

^aYield refers to isolated crude material. ^bYields refer to isolated products purified by column chromatography. ^cDetermined by gas chromatography using an OV-17 column at various temperatures. ^dThe mesylate could not be isolated without decomposition. ^eOverall yield from geraniol.

general readily separable by gas chromatography using an OV 17 column at various temperatures. Authentic samples of 1-(trimethylsilyl)-2-alkenes 9 and 10 were prepared from carbonyl precursors by methodology reported by Fleming^{3g} and Seyferth^{3a} and illustrated in eq 3. Reaction of an

$$\begin{array}{ccc} \textbf{RCHO} & \bullet & (\textbf{C}_{6}\textbf{H}_{3})\textbf{P} = \textbf{CHCHJMS} & & & \underline{9} & \bullet & \underline{10} & (3) \\ \underline{3} & & & \underline{16} & & & \\ \end{array}$$

aldehyde 3 with a trimethylsilyl-substituted Wittig reagent 16 afforded mixtures of 9 and 10 in which the Z isomer 10 usually predominated. All 3-(trimethylsilyl)-1-alkenes 8 gave typical vinyl absorption patterns in their NMR spectra and had lower GC retention times than those of isomers 9 and 10. All (E)-1-(trimethylsilyl)-2-alkenes 9 exhibited a medium-strong absorption in their IR spectra at about 960 cm⁻¹, as previously noted.^{3a,18} High-field ¹H NMR data showed that the -CH₂- bonded to the trimethylsilyl group was typically at higher field for the Eisomer 9 than for the Z isomer 10.

Certain trends are evident. The reaction of (trimethylsilyl)copper with most 1° allylic halides (5a-e, 11) produced a mixture of isomeric allyltrimethylsilanes in which the 3-(trimethylsilyl)-1-alkene 8 or 12a greatly predominated. The lone exception to this phenomenon was the case of 13, in which a 1-(trimethylsilyl)-2-alkene (14) was formed as the exclusive product. The reaction of (trimethylsilyl)lithium with all 1° allylic halides produced largely, or in many cases exclusively, 1-(trimethylsilyl)-2-alkenes 9, 12b, or 14 as products. These results continue the trends observed in the initial studies on the regiochemistry of this reaction. The formation of 3-(trimethylsilyl)-1-alkenes from 1-halo-2-alkenes is favored by the use of (trimethylsilyl)copper, whereas the formation of (E)-1-(trimethylsilyl)-2-alkenes from these same substrates is favored by the use of (trimethylsilyl)lithium as the silvlmetal reagent. This chemistry not only provides regioselective routes to isomeric allyltrimethylsilanes from a single starting material but also provides access to the thermodynamically less stable 3-(trimethylsilyl)-1-alkenes which have usually been difficult to prepare.

The case of the 2° allylic halide 15 was more complicated. With (trimethylsilyl)lithium, reaction afforded a mixture of products in which the thermodynamically preferred (E)-olefin 9e once again predominated. In contrast, the reaction of this same substrate with (trimethylsilyl)copper afforded a complex mixture of 8e, 9e, and 10e. The predictable regioselective formation of isomers 8 or 9 may thus be limited to the use of 1° allylic halides as substrates.

As yet the mechanisms of these reactions have not been established with surety. The reaction of (trimethylsilyl)sodium and (trimethylsilyl)potassium with halides in a polar aprotic solvent is known to give products derived from single electron transfer reactions.^{10a} By comparison.



Fleming has reported that the reaction of a silyl cuprate with 3° allylic acetates proceeds stereospecifically in an anti fashion,¹⁹ and so an electron transfer mechanism was not proposed. The fact that yields of the desired allyltrimethylsilanes are usually high with both silylmetal reagents and that no side products derived from radical intermediates have been isolated in this reaction would argue against electron transfer mechanisms in both cases. Products derived from radical pathways may in fact be present in small amounts and lost in the isolation and purification procedure. Moreover, the fact that the isomeric halides 5e and 15 give different product ratios when treated under similar reaction conditions with both reagents also argues against mechanisms which would generate a common intermediate from these two substrates, as might be expected if the reactions proceeded by electron transfer. That the observed products arise by a combination of S_N^2 and S_N^2 pathways is a likely possibility. Obviously more work is needed to clarify the reaction mechanism.

Allylic Sulfonates. In an effort to prepare allylsilanes from other readily available substrates, we examined the reaction of (trimethylsilyl)lithium and (trimethylsilyl)copper with 1°, 2°, and 3° allylic sulfonates. The results are summarized in Table IV. As a representative example, treatment of 1-nonen-3-ol (4a) with methanesulfonyl chloride and triethylamine afforded mesylate 17a which was not purified but treated directly with (trimethylsilyl)lithium or (trimethylsilyl)copper (Scheme II). Although the reaction of this mesylate with (trimethylsilyl)lithium gave almost none of the possible allyltrimethylsilanes 8a, 9a, or 10a, reaction of this same mesylate 17a with (trimethylsilyl)copper gave a 52% yield of a mixture in which the (E)- and (Z)-1-(trimethylsilyl)-2nonenes 9a and 10a were the major products (Table IV, entry 1). Reaction of the crude tosylate 17b derived from 1-dodecen-3-ol with (trimethylsilyl)copper gave comparable

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⁽¹⁹⁾ Fleming, I. Tetrahedron Lett. 1983, 24, 4151.

results (entry 2). The mesylates of 2° and 3° allylic alcohols could be isolated but were usually used immediately thereafter to avoid decomposition. The mesulate of geraniol decomposed on attempted isolation, but it could be prepared at low temperature with methyllithium and methanesulfonyl chloride in THF and then treated without isolation with (trimethylsilyl)copper to afford a mixture of allylsilanes 12a and 12b (entry 7). In all cases good vields of allyltrimethylsilanes were formed, and with the exception of geraniol, 1-(trimethylsilyl)-2-alkenes were by far the major products. The advantage of using allylic sulfonates as precursors to allylsilanes is their ease of preparation, coupled with the possibility that they may be formed in situ and reacted immediately with the silvl copper reagent. Moreover, an enolizable ketone such as cyclohexanone can be cleanly converted to allylsilane 20 in good overall yield by the sequence (1) addition of vinylmagnesium bromide; (2) treatment of the resulting alcohol 4 with methanesulfonyl chloride and triethylamine; and (3) reaction with (trimethylsilyl)copper. We have been unable to prepare 20 from cyclohexanone in good yield via an easily prepared allylic halide. The disadvantage of using allylic sulfonates as starting materials is that the reactions are less regioselective and the stereochemistry of the products is less predictable. Mixtures of 1-(trimethylsilyl)-2-alkenes often result, but the ratio of E:Z isomers is quite variable.

Synthesis of 2,3-Bis(trimethylsilyl)alk-1-enes. We have extended this chemistry to the synthesis of 2,3-bis-(trimethylsilyl)alk-1-enes 21-23, a class of unsaturated



organosilanes which has received little attention in the literature. These compounds are potentially interesting because they are simultaneously both an allyl- and a vinylsilane, and the proximity of these functional groups may provide useful information or reactions which may be added to the tremendous library of silicon chemistry already known.

Though the reaction of allyl- and vinylsilanes with various electrophiles is well-documented, much less is known about the reactions of compounds which contain both of these functionalities. It is generally agreed that allylsilanes are more reactive toward electrophiles than vinylsilanes are, but few examples of this phenomenon with substrates which are simultaneously allyl- and vinylsilanes have actually been reported.²⁰ There is in fact one example of the reaction of a 2,3-bis(trimethylsilyl)alk-1-ene with an electrophile, and the allylsilane does react preferentially to form an electrophilic substitution product.^{7a} It is likewise known that the reaction of allenylsilanes with electrophiles yields products derived from electrophilic attack at the double bond allyl and not vinyl to the trimethylsilyl group.²¹

The synthesis of 2,3-bis(trimethylsilyl)alk-1-enes from allenes has been reported by two groups.⁷ We examined the preparation of these unsaturated organosilanes 21-23 by the three-step reaction sequence illustrated in Scheme III. With use of methodology previously reported by Chan,²² the treatment of an aldehyde with (α -lithio-



Table V. Preparation of 2,3-Bis(trimethylsilyl)alk-1-enes

	-			
entry	starting material	method ^a	products (yield, ^b %)	ratio ^c
1	25a	I	21a:23a (98)	91:9
2	25a	II	22a only (72)	
3	24a	III	23a:22a (54)	2:1
4	26a	I	23a:22a (57)	65:35
5	25b	I	21b:23b (85)	87:13
6	25b	п	22b:23b (98)	85:15
7	24b	III	23b:22b (43)	82:18
8	25c	I	21c only (77)	
9	24c	III	23c only (47)	

^aMethod I: The chloride 25 or mesylate 26 was added to a solution of TMSCu in HMPA-ether at -60 °C. Method II: The chloride 25 was added to a solution of TMSLi in HMPA-ether at -60 °C. Method III: The mesylate 26 was formed in situ by reaction of alcohol 24 with methyllithium and methanesulfonyl chloride, and then 26 was treated with TMSCu in HMPA-ether at -60 °C. ^b Yields refer to isolated products purified by column chromatography. ^c Ratios were determined using an OV-17 column at various temperatures.

vinyl)trimethylsilane followed by quenching with water afforded trimethylsilyl-substituted allylic alcohols 24 in good yield. Conversion of these alcohols to trimethylsilyl-substituted allylic chlorides 25 was carried out with thionyl chloride in ether. Chan has reported that Z allylic chlorides 25 are formed as predominant or exclusive products with most substrates.²³ Reaction of 25 with either (trimethylsilyl)lithium or (trimethylsilyl)copper was carried out under conditions previously devised for the simple allylic halides 5. In addition we examined the treatment of allylic mesylates 26 with (trimethylsilyl)copper. The results are summarized in Table V.

Treatment of a trimethylsilyl-substituted allylic halide 25 or mesylate 26 with a (trimethylsilyl)metal reagent could in theory yield a mixture of three products 21-23 (eq 4). In fact, conditions have been devised to afford each

$$\frac{25}{\sigma_{\Gamma}} \xrightarrow{TMS^{+}M^{+}} R \xrightarrow{TMS} R \xrightarrow{TMS} R \xrightarrow{TMS} (4)$$

$$\frac{26}{21} \qquad 22 \qquad 23$$

of these products as the major or exclusive product under controlled conditions in good to excellent yield. For example, treatment of (Z)-1-chloro-2-(trimethylsilyl)-2-

^{(20) (}a) Grignon-Dubois, M.; Pillot, J.-P.; Dunogues, J.; Duffaut, N.; Calas, R.; Henner, B. J. Organomet. Chem. 1977, 127, 135. (b) Bourgeois, P.; Calas, R.; Merault, G. Ibid. 1977, 141, 23.

⁽²¹⁾ Bourgeois, P.; Calas, R.; Merault, G. J. Organomet. Chem. 1977, 141, 23.

⁽²²⁾ Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. J. Org. Chem. 1978, 43, 1526.

⁽²³⁾ For example, with a 1° R group such as $R = C_{10}H_{21}$, the Z isomer is formed exclusively; with a 2° R group such as R = cyclohexyl, the Z:E ratio was 90:10.

Regioselective Synthesis of Allyltrimethylsilanes

nonene (25a) with (trimethylsilyl)copper in ether-HMPA at -60 °C afforded a mixture of products consisting largely of 2,3-bis(trimethylsilyl)non-1-ene (21a) (Table V, entry 1, ratio of 21a:23a was 91:9). Conversely, treatment of this same halide with (trimethylsilyl)lithium afforded (Z)-1,2bis(trimethylsilyl)non-2-ene as the sole product. Finally, treatment of alcohol 24a with methyllithium and methanesulfonyl chloride in THF formed a mesylate in situ which was allowed to react with (trimethylsilyl)copper as previously described to afford a 2:1 mixture of 22a and 23a in which the major product was the (E)-olefin 23a. Mesylate 26a could also be isolated in quantitative yield and was used without purification in reaction with (trimethylsilyl)copper. In this case, the yield of products was 57% (Table V, entry 4, ratio of 23a:22a, 65:35).

The identity and composition of the product mixtures was assigned on the basis of spectral and gas chromatographic analysis. Satisfactory IR, 500-MHz NMR, and high-resolution mass spectral data were obtained for all new compounds. The identity of the E and Z isomeric alkenes 22 and 23 was established by a comparison of the chemical shift of their vinylic protons with the known chemical shift of vinylic protons of trisubstituted (E)- and (Z)-vinylsilanes 27 and 28.²⁴ The vinyl proton of the



(E)-vinylsilane 27 is typically $\delta 0.2-0.3$ further upfield than this same proton in the Z isomer 28. Comparable chemical shift differences were noted in the E and Z isomers 22 and 23. For example, the vinyl proton of 22a appears as a triplet at $\delta 5.82$ whereas the vinylic proton of 23a is a clean triplet at $\delta 5.60$. It should be noted that in the case of 25c, the reaction with (trimethylsilyl)lithium produced a complex mixture of products from which none of the desired product 22c could be isolated. The assignment of the E stereochemistry to the double bond of 23c is therefore made solely by analogy with products obtained under similar reaction conditions (Table V, entries 3 and 6) and cannot be absolutely inferred by comparison with its stereoisomer 22c.

From these studies we have shown that it is possible to synthesize a variety of 2,3-bis(trimethylsilyl)alk-1-enes from an appropriate precursor in high yield and, in most cases, with high regio- and stereoselectivity. In some cases, the observed stereochemistry follows the trends noted in the preparation of allyltrimethylsilanes. Formation of compounds having the general structure 21 possessing a trimethylsilyl group substituted at the 3-position and a terminal carbon-carbon double bond is favored by the use of a halide 25 as the reacting substrate and (trimethylsilyl)copper as the silylmetal reagent. The formation of 22 in which the position and stereochemistry of the double bond of the starting halide 25 has been retained in the product is favored by the use of (trimethylsilyl)lithium as the silvlmetal reagent. The predominant formation of the E isomer 23 from mesulates 26 is without precedent in the formation of the simple allyltrimethylsilanes 8-10. It is similar to the stereochemistry observed by Chan in the reaction of acetates of 2-(trimethylsilyl)-1-alkene-3-ols with organocuprate reagents.²⁵ In the present case, reaction of (trimethylsilyl)copper with the 2° allylic mesylate must occur via a conformation which minimizes the steric in-



teraction of the bulky trimethylsilyl group and the R group of the starting material, as in 29. This leads to formation



of the *E* isomer 23 where R and trimethylsilyl are trans to each other. This rationale also explains why the stereoselectivity of the reaction is higher with a bulkier 2° R group (26b, R = cyclohexyl), compared with a 1° R group (26a, R = n-C₆H₁₃). This methodology thus provides easy access to a variety of potentially interesting unsaturated organosilanes.

Conclusions

We have devised a new method to prepare allyltrimethylsilanes from allylic halides and allylic sulfonates using (trimethylsilyl)metal reagents. It is now possible to convert an (E)-1-halo-2-alkene into either a 3-(trimethylsilyl)-1-alkene or an (E)-1-(trimethylsilyl)-2-alkene by proper choice of reaction conditions. Since these allylic halides are readily available from carbonyl precursors by known reactions, this method allows a carbonyl compound to be regioselectively converted to either of two isomeric allyltrimethylsilanes by a high-yield stepwise procedure (Scheme IV). This complements existing methodology since Wittig reaction of an aldehyde with a trimethylsilyl-substituted phosphorane produces a mixture of allyltrimethylsilanes in which the Z isomer is usually the predominant product.

The reaction of (trimethylsilyl)copper with 2° allylic sulfonates produces a mixture of isomeric allyltrimethylsilanes in which 1-(trimethylsilyl)-2-alkenes predominate. The use of allylic sulfonates as precursors to allylsilanes is especially attractive for preparing 1-(trimethylsilyl)-2alkenes having a trisubstituted carbon-carbon double bond such as **20**. In this case only one product, a 1-(trimethylsilyl)-2-alkene, is formed.

Finally, it has been possible to use this methodology to prepare 2,3-bis(trimethylsilyl)alk-1-enes. Treatment of a trimethylsilyl-substituted allylic halide such as 25 or a trimethylsilyl-substituted allylic mesylate 26 with a (trimethylsilyl)metal reagent affords either 21, 22, or 23 by proper choice of reaction conditions.

Experimental Section

General Methods. All reactions involving oxygen- or moisture-sensitive compounds were performed in flame-dried apparatus under an argon atmosphere introduced by alternately evacuating and filling the reaction vessel at least 3 times with argon. During the reaction, a positive inert atmosphere was maintained by opening the system to an argon-filled balloon. Most

⁽²⁴⁾ Chan, T. H.; Michajlowskij, W.; Amoroux, R.; Tetrahedron Lett. 1977, 1605.

⁽²⁵⁾ Michajlowskij, W.; Chan, T. H. Tetrahedron Lett. 1976, 4439.

proton magnetic resonance spectra (¹H NMR) were determined in chloroform-*d* by using a Varian T-60 or WM 500 MHz spectrometer. Chemical shifts are recorded in δ (parts per million) downfield from tetramethylsilane. Infrared (IR) spectra were recorded on either a Perkin-Elmer Model 298 or 457 spectrometer and are reported in wavenumbers. Analytical gas chromatography was performed on a Hewlett-Packard Model 5710A gas chromatograph with a flame ionization detector. All analyses were performed by using a 6 ft × $^{1}/_{8}$ in. diameter OV-17 column. Column chromatography was carried out with Merck 70–230-mesh silica gel 60.

Materials. Ultrapure copper(I) iodide (Alfa) and purified copper(I) iodide (Fisher, further purified by soxhlet extraction with tetrahydrofuran) were used with equal success in the preparation of (trimethylsilyl)copper. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride at reduced pressure prior to use. Ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl under argon.

Starting Materials. Commercially available allyl chloride, allyl bromide, 2,3-dichloropropene, and 2,3-dibromopropene were distilled under an argon atmosphere prior to use. Cinnamyl chloride (5b) was distilled at reduced pressure, and cinnamyl bromide (6b) was purified by silica gel column chromatography. Allylic chlorides 5a, 5c, 5d, 5e, and 13 were prepared in good yield from carbonyl precursors 3 by the standard two-step sequence: (1) addition of 1-2 equiv of vinylmagnesium bromide in ether at 0-25 °C; and (2) treatment of the resulting alcohol 4 with excess thionyl chloride at 0-25 °C in ether. These materials were purified by column chromatography using petroleum ether as eluent. Allylic bromide 6a was prepared from 4a in 34% yield by treatment with excess phosphorus tribromide in ether at 0 °C and purified by column chromatography. Allylic iodide 7a was prepared from 5a in 48% yield by using sodium iodide in acetone. Geranyl chloride (11) was prepared from geraniol in 76% yield as previously described.¹⁶ The 2° allylic chloride 15 was prepared from 1-dodecen-3-ol in 67% yield by using known methodology¹⁷ but was contaminated with varying amounts of the isomeric halide 5e. Allylic mesylates 17a, 17c, 17d, 17e, and 19 were prepared in 67-92% crude yield by standard procedures: treatment of the alcohol 4 with 1.8 equiv of methanesulfonyl chloride and 2.0 equiv of triethylamine for 1 h at -10 °C in methylene chloride. These mesylates were used immediately without purification. Storage even for a few days at low temperatures resulted in extensive decomposition. Tosylate 17b was prepared in 87% crude yield from alcohol 4e by treatment with 1.0 equiv of methyllithium and 1.05 equiv of p-toluenesulfonyl chloride for 0.5 h at 0 °C in 3:1 ether-HMPA. (α -Bromovinyl)trimethylsilane was prepared as previously described.²⁶ The synthesis of all other compounds is detailed below.

General Procedure A: Reaction of Volatile Allylic Halides 1a-d with (Trimethylsilyl)copper. To a solution of hexamethyldisilane (2.5 mmol) in HMPA (3 mL) at 0-5 °C under argon was added methyllithium (2.5 mol of Aldrich methyllithiumlithium bromide complex in ether) dropwise. After being stirred for 3 min, the resulting red solution was treated with copper(I) iodide (2.5 mmol) in dimethyl sulfide (1 mL). The resulting black solution was stirred for 3 min, and allylic halide **1a-d** (1 mmol) was added rapidly via syringe. The reaction mixture was warmed to room temperature and stirred for 1.5 h. It was then poured into 25 mL of pentane and 25 mL of saturated ammonium chloride solution (buffered to pH 8 by addition of ammonium hydroxide), and the mixture was vigorously stirred for 1 h. The aqueous phase was extracted with two 25-mL portions of pentane, and the combined organic extracts were washed with water and dried over magnesium sulfate. The pentane was removed by distillation at atmospheric pressure and the allyltrimethylsilane 2 was isolated by distillation. The yields of 2a-c are summarized in Table I.

General Procedure B: Reaction of Allylic Halides 5a-e, 11, 13, and 15 and Allylic Sulfonates 17a-e and 19 with (Trimethylsilyl)copper. To a solution of hexamethyldisilane (2.5 mmol) in HMPA (3 mL) at 0-5 °C under argon was added methyllithium (2.5 mmol of Aldrich methyllithium-lithium bromide complex in ether) dropwise. After being stirred for 3

min, the resulting red solution was treated with copper(I) iodide (2.5 mmol) in dimethyl sulfide (1 mL), and the black reaction mixture was stirred for 3 min. Ether (6 mL) was added and the reaction mixture was cooled to -60 °C and stirred for 5 min. A solution of the allylic halide or allylic sulfonate (1 mmol) in ether (1 mL) was added dropwise, and the reaction mixture was stirred for 1 h at -60 to -50 °C. The cold solution was poured into 50 mL of petroleum ether and 50 mL of saturated ammonium chloride solution (buffered to pH 8 by addition of ammonium hydroxide), and the mixture was vigorously stirred for 1 h. The aqueous phase was extracted with three 25-mL portions of petroleum ether, and the combined organic extracts were dried over magnesium sulfate, filtered, and concentrated. The crude product was purified by silica gel column chromatography using petroleum ether as eluent to afford the desired allyltrimethylsilane. The specific yields and product ratios are summarized in Tables III and IV.

General Procedure C: Reaction of Allylic Halides 5a-e, 11, 13, and 15 with (Trimethylsilyl)lithium. To a solution of hexamethyldisilane (2.5 mmol) in HMPA (3 mL) at 0-5 °C under argon was added methyllithium (2.5 mmol of Aldrich methyllithium-lithium bromide complex in ether) dropwise. After being stirred for 3 min, the resulting red solution was diluted with ether (6 mL), and the reaction mixture was cooled to -60 °C and stirred for 5 min. The color of the reaction mixture changed from orange to yellow during this time. A solution of the allylic halide (1 mmol) in ether (1 mL) was added dropwise, and the reaction mixture was stirred for 1 h at -60 to -50 °C. The cold solution was poured into 50 mL of petroleum ether and 50 mL of saturated ammonium chloride solution, and the aqueous phase was extracted with three 25-mL portions of petroleum ether. The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated. The crude product was purified by silica gel column chromatography using petroleum ether as eluent to afford the desired allyltrimethylsilane. Specific yields and product ratios are summarized in Table III.

General Procedure D: Wittig Reaction of Aldehydes 3 with Wittig Reagent 16. The procedure of Fleming was employed.^{3g} To a slurry of methyl triphenylphosphonium bromide (1.125 mmol) in THF (3 mL) at 0 °C under argon was added *n*-butyllithium (1.25 mmol of a solution in hexane) dropwise over 15 min. The orange solution was warmed to room temperature, stirred for 45 min, and cooled to 0 °C, and iodomethyltrimethylsilane (1.125 mmol) was added over 10 min. The reaction mixture was stirred for 1.25 h at room temperature and cooled to -78 °C, and n-butyllithium (1.25 mmol) was added to afford a homogeneous red solution. The reaction was warmed to room temperature, stirred 1.5 h, and cooled to -78 °C, and the carbonyl compound 3 (1 mmol) was added in 1 mL of THF. The reaction mixture was stirred 0.5 h at -78 °C, warmed to room temperature, and stirred 20 h. The reaction mixture was partitioned between ether and saturated ammonium chloride solution, and the aqueous phase was extracted with ether. The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated. The crude product was purified via silica gel column chromatography using petroleum ether as eluent to afford the desired allyltrimethylsilanes. In most cases, when mixtures of isomeric E and Z products could be formed, the Z isomer 10 was, by far, the major product in this reaction mixture. This was true with $R = C_{11}H_{23}$ (E:Z ratio, 11:89), $R = C_9H_{19}$ (E:Z ratio, 28:72), $R = c \cdot C_6H_{11}$ (E:Z ratio, 0:100), and $R = C_6H_{13}$ (8:92).

Reaction of (Trimethylsilyl)copper with the Methanesulfonate Ester of Geraniol, Prepared in Situ. To a solution of geraniol (1 mmol) in 2 mL of THF at -78 °C under argon was added halide-free methyllithium (1.1 mmol, 0.73 mL of a 1.5 M solution in ether). The reaction mixture was stirred 5 min, and methanesulfonyl chloride (1.1 mmol) was added via syringe. The reaction mixture was stirred 40 min at -78 °C. It was then transferred via syringe to a stirred solution of (trimethylsilyl)copper (2.5 mmol, prepared from hexamethyldisilane, methyllithium, and copper(I) iodide in dimethyl sulfide as detailed above in general procedure B) in HMPA (3 mL) and ether (7.8 mL) at -60 °C. The reaction mixture was stirred for 1 h at -60 to -50°C. It was then partitioned between 50 mL of petroleum ether and 50 mL of saturated ammonium chloride solution buffered to pH 8 by addition of ammonium hydroxide. Workup and

⁽²⁶⁾ Boeckman, R. K. Org. Synth. 1979, 58, 152.

product purification proceeded as in general procedure B to afford a 50% yield of a mixture of isomeric allylsilanes 12a and 12b (ratio 70:30).

Spectral Data on Allyltrimethylsilanes. All new compounds gave satisfactory NMR, IR, and mass spectral data. Allyltrimethylsilane (2a) prepared by the present methodology was identical in all respects with a sample of 2a purchased from Aldrich. (E)-Cinnamyltrimethylsilane (9b), (Z)-cinnamyltrimethylsilane (10b), and 20 were identical with material prepared by known chemistry.^{3g} The NMR spectral data of these compounds has previously been reported and will therefore not be detailed herein.^{3a,b,g} Although some spectral characteristics of 9a and 10a,^{3g} 8b,^{4a} 12b,^{3m} and 2b^{15b} have also been mentioned in the literature, complete spectral data on these compounds have been obtained. Detailed spectral data on some representative allyltrimethylsilanes (2b, 2c, 8a, 9a, 10a, 12a and 12b) and 2,3bis(trimethylsilyl)alk-1-enes (21a, 22a, 23a) is presented in this Experimental Section. The reader is referred to the supplementary material available which contains full spectroscopic data on all allyltrimethylsilanes and 2,3-bis(trimethylsilyl)alk-1-enes which are not presented below.

Spectroscopic Data on Allyltrimethylsilanes. (2-Bromoallyl)trimethylsilane (2b):^{15b} NMR (CDCl₃, 80 MHz) δ 0.1 (s, 9 H, Si(CH₃)₃), 2.06 (s, 2 H, CH₂), 5.18 (bs, 1 H, =-CH₂), 5.25 (bs, 1 H, =-CH₂); IR (CHCl₃) λ_{max} at 2960, 2890, 1615, 1410, 1225, 1195, 1160, 1060, 855, 700 cm⁻¹; mass spectrum, m/e 192 and 194 (M⁺), 177 and 179, 137 and 139, 73.

(2-Chloroallyl)trimethylsilane (2c): NMR (CDCl₃, 60 MHz) δ 0.08 (s, 9 H, Si(CH₃)₃), 1.92 (bs, 2 H, CH₂), 4.88 (bs, 1 H, =CH₂), and 4.98 (bs, 1 H, =CH₂); IR (CHCl₃) λ_{max} at 2960, 2900, 1620, 1410, 1250, 1195, 1160, 1080, 930, 805, 690 cm⁻¹; mass spectrum, m/e 148 and 150 (M⁺), 133, 93 and 95, 74, 73.

3-(Trimethylsilyl)-1-nonene (8a): NMR (CDCl₃, 500 MHz) δ –0.02 (s, 9 H, Si(CH₃)₃), 0.89 (t, 3 H, CH₃), 1.16–1.60 (m, 10 H, CH₂), 1.94–2.02 (m, 1 H, CH), 4.82 (dd, 1 H, =CH₂, J = 10.5, 2 Hz, with additional poorly resolved allylic coupling), 4.89 (dd, 1 H, =CH₂, J = 17, 2 Hz, with additional poorly resolved allylic coupling), and 5.56–5.68 (m, 1 H, =CH); IR (film) λ_{max} 3070, 2960, 2920, 2850, 1635, 1460, 1245, 1100, 890, 830 cm⁻¹; mass spectrum, m/e 198 (M⁺), 183, 124, 99, 85, 74, 73 (base); exact mass calculated for C₁₂H₂₆Si 198.1804, observed 198.1798.

(*E*)-1-(Trimethylsilyl)-2-nonene (9a): NMR (CDCl₃, 500 MHz) δ -0.01 (s, 9 H, Si(CH₃)₃), 0.89 (t, 3 H, CH₃), 1.14–1.40 (m, 8 H, CH₂), 1.41 (dd, 2 H, CH₂TMS, J = 8, 1 Hz), 1.93–2.10 (m, 2 H, CH₂), 5.22–5.30 (m, 1 H, =CH), 5.32–5.48 (m, 1 H, =CH); IR (film) λ_{max} at 3000, 2950, 2920, 2850, 1630, 1460, 1240, 1150, 960 (*E* C=C), 830 cm⁻¹, mass spectrum, m/e 198 (M⁺), 99, 74, 73 (base); exact mass calculated for C₁₂H₂₆Si 198.1804, observed 198.1794.

(Z)-1-(Trimethylsilyl)-2-nonene (10a): NMR (CDCl₃, 500 MHz) δ 0.01 (s, 9 H, Si(CH₃)₃), 0.90 (t, 3 H, CH₃), 1.22–1.40 (m, 8 H, CH₂) 1.45 (d, 2 H, CH₂TMS, J = 8 Hz, some allylic coupling present but difficult to resolve), 1.95–2.04 (m, 2 H, CH₂), 5.24–5.35 (m, 1 H, =CH), 5.35–5.46 (m, 1 H, CH); IR (film) λ_{max} at 3000, 2960, 2920, 2850, 1640, 1460, 1240, 1140, 850 cm⁻¹; mass spectrum, m/e at 198 (M⁺), 74, 73 (base); exact mass calculated for C₁₂H₂₆Si 198.1804, observed 198.1794.

Allyltrimethylsilane (12a): NMR (CDCl₃, 500 MHz) δ -0.05 (s, 9 H, Si(CH₃)₃), 1.01 (s, 3 H, CH₃), 1.32–1.52 (m, 2 H, CH₂), 1.60 (s, 3 H, CH₃), 1.69 (s, 3 H, CH₃), 1.78–1.98 (m, 2 H, CH₂), 4.72 (dd, 1 H, —CH, J = 17, 2 Hz), 4.95 (dd, 1 H, —CH, J = 11, 1.5 Hz), 5.08–5.16 (m, 1 H, —CH), 5.82 (dd, 1 H, —CH, J = 11, 17 Hz); IR (film) λ_{max} at 3080, 2980, 2920, 2860, 1620, 1450, 1250, 900, 860, 840 cm⁻¹; mass spectrum, m/e at 210 (M⁺), 153, 141, 75, 74, 73 (base); exact mass calculated for C₁₃H₂₆Si 210.1804, observed 210.1794.

Geranyltrimethylsilane (12b): NMR (CDCl₃, 500 MHz) δ -0.01 (s, 9 H, Si(CH₃)₃), 1.40 (d, 2 H, CH₂TMS), 1.56 (s, 3 H, CH₃), 1.61 (s, 3 H, CH₃), 1.68 (s, 3 H, CH₃), 1.94-2.12 (m, 4 H, CH₂), 5.08-5.14 (m, 1 H, =CH), 5.14-5.22 (m, 1 H, =CH); IR (film) λ_{max} at 2960, 2920, 1660, 1440, 1370, 1250, 1150, 850, 830 cm⁻¹; mass spectrum, m/e at 210 (M⁺), 141, 86, 85, 74, 73 (base); exact mass calculated for C₁₃H₂₆Si, 210.1804, observed 210.1792.

Preparation of 2-(Trimethylsily!)-1-alken-3-ols 24. Alcohols **24a-c** were prepared from the corresponding carbonyl precursors **3a-c** and $(\alpha$ -lithiovinyl)trimethylsilane (prepared from $(\alpha$ -

bromovinyl)trimethylsilane²⁶ and 2 equiv of *tert*-butyllithium) exactly as described by Chan.²² Yields after purification by silica gel column chromatography were 63–81%. Spectral data was in agreement with that reported by Chan.

Preparation of 1-Chloro-2-(trimethylsilyl)-2-alkenes 25. Using the procedure detailed by Chan,²² **24a-c** were converted to halides **25a-c** by using thionyl chloride and ether. Yields after purification by column chromatography were 40–70%. Spectral data was in agreement with that reported by Chan.

Reaction of 1-Chloro-2-(trimethylsilyl)-2-alkenes 25 with (Trimethylsilyl)copper. Trimethylsilyl-substituted allylic chlorides 25a-c were treated with (trimethylsilyl)copper for 1 h at -60 °C in HMPA-ether solution exactly as described in general procedure B. The crude products were purified by silica gel column chromatography using petroleum ether as eluent to afford the desired 2,3-bis(trimethylsilyl)alk-1-ene 21-23. The specific yields and product ratios are summarized in Table V. In all cases 2,3-bis(trimethylsilyl)alk-1-enes 21 were the predominant products.

Reaction of 1-Chloro-2-(trimethylsilyl)-2-alkenes 25 with (**Trimethylsilyl)lithium.** Trimethylsilyl-substituted allylic chlorides 25a and 25b were treated with (trimethylsilyl)lithium for 1 h at -60 °C in HMPA-ether solution exactly as described in general procedure C. The crude products were purified by silica gel column chromatography using petroleum ether as eluent to afford the desired 2,3-bis(trimethylsilyl)alk-1-ene 21-23. The specific yields and product ratios are summarized in Table V. In both cases, (Z)-1,2-bis(trimethylsilyl)alk-2-enes 22 were the predominant products.

Reaction of (Trimethylsilyl)copper with Methanesulfonate Esters 26, Prepared in Situ. The methanesulfonate esters 26a-c of alcohols 24a-c were prepared at ~78 °C from methyllithium and methanesulfonyl chloride in THF, and without isolation, these mesylates were treated with (trimethylsilyl)copper exactly as described for geraniol above. The crude products were purified by silica gel column chromatography using petroleum ether as eluent to afford the desired 2,3-bis(trimethylsilyl)alk-1-ene 21-23. The specific yields and product ratios are summarized in Table V. In all cases, (E)-1,2-bis(trimethylsilyl)alk-2-enes 23 were the predominant products.

Spectral Data on 2,3-Bis(trimethylsilyl)alk-1-enes 21–23. 2,3-Bis(trimethylsilyl)non-1-ene (21a): NMR (CDCl₃, 500 MHz) δ -0.02 (s, 9 H, Si(CH₃)₃), 0.07 (s, 9 H, Si(CH₃)₃), 0.89 (t, 3 H, CH₃), 1.07–1.45 (m), 1.50–1.58 (m), 1.61–1.67 (m), 5.40 (d, 1 H, =-CH₂, J = 2 Hz), 5.50 (d, 1 H, =-CH₂, J = 2 Hz); IR (film) λ_{max} at 3040, 2950, 2920, 2850, 1580, 1450, 1400, 1240, 905, 830, 745, 680 cm⁻¹; mass spectrum, m/e at 270 (M⁺), 255, 196, 182, 167, 154, 139, 125, 111, 97, 85, 74, 73; exact mass calculated for C₁₅H₃₄Si₂ 270.2199, observed 270.2195.

(Z)-1,2-Bis(trimethylsilyl)non-2-ene (22a): NMR (CDCl₃, 500 MHz) δ -0.01 (s, 9 H, Si(CH₃)₃), 0.13 (s, 9 H, Si(CH₃)₃), 0.90 (t, 3 H, CH₃), 1.24-1.38 (m, 8 H, CH₂), 1.55 (d, 2 H, CH₂TMS, J = 1 Hz), 2.06-2.13 (m, 2 H, CH₂), 5.82 (dt, 1 H, =CH, J = 6, 1 Hz); IR (film) λ_{max} at 2950, 2920, 2850, 1600, 1455, 1400, 1240, 830, 750, 680, 640 cm⁻¹; mass spectrum, m/e 270 (M⁺), 196, 182, 167, 139, 131, 126, 111, 97, 74, 73, 72; exact mass calculated for C₁₅H₃₄Si₂ 270.2199, observed 270.2192.

(E)-1,2-Bis(trimethylsilyl)non-2-ene (23a): NMR (CDCl₃, 500 MHz) δ 0.02 (s, 9 H, Si(CH₃)₃), 0.05 (s, 9 H, Si(CH₃)₃), 0.90 (t, 3 H, CH₃), 1.24–1.40 (m, 8 H, CH₂), 1.65 (s, 2 H, CH₂TMS), 1.96–2.06 (m, 2 H, CH₂), 5.60 (t, 1 H, =CH, J = 7 Hz); IR (film) λ_{max} at 2950, 2920, 2850, 1630, 1600, 1445, 1320, 1240, 1140, 830, 745, 710, 680 cm⁻¹; mass spectrum, m/e 270 (M⁺), 255, 196, 182, 167, 154, 139, 125, 112, 111, 97, 74, 73 (base); exact mass calculated for C₁₆H₃₄Si₂ 270.2199, observed 270.2194.

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Registry No. 1a, 106-95-6; 1b, 513-31-5; 1c, 78-88-6; 1d, 107-05-1; 2a, 762-72-1; 2b, 81790-10-5; 2c, 18187-38-7; 4a, 21964-44-3; 4c, 17642-48-7; 4d, 4352-44-7; 4e, 4048-42-4; 5a, 67242-74-4; 5b, 21087-29-6; 5c, 91899-45-5; 5d, 58649-21-1; 5e, 71518-12-2; 6a, 35329-43-2; 6b, 26146-77-0; 7a, 65689-00-1; 8a, 87976-83-8; 8b, 35802-50-7; 8c, 91899-29-5; 8d, 91899-32-0; 8e, 91899-34-2; 9a, 63922-74-7; 9b, 40595-34-4; 9c, 91899-30-8; 9d, 91899-33-1; 9e, 91899-35-3; 10a, 63922-75-8; 10c, 91899-31-9; 10e, 91899-36-4; 11, 5389-87-7; 12a, 85956-58-7; 12b, 78055-70-6; 13, 24626-27-5; 14, 83438-57-7; 15, 42886-46-4; 17a, 91899-47-7; 17c, 91899-48-8; 17d, 91899-49-9; 17e, 91899-50-2; 18, 1940-19-8; 19, 91899-51-3; 20, 63922-76-9; 21a, 91899-37-5; 21b, 91899-40-0; 21c, 91899-43-3; 22a, 91899-38-6; 22b, 91899-42-2; 23a, 91899-39-7; 23b, 91899-41-1; 23c, 91899-44-4; 24a, 91899-46-6; 24b, 58649-14-2; 24c, 51666-96-7; 25a, 91899-52-4; 25b, 58649-17-5; 25c, 58844-31-8; 26a, 91899-53-5; Me₃SiLi, 18000-27-6; Me₃SiCu, 91899-54-6; geraniol, 106-24-1.

Supplementary Material Available: Full spectroscopic data (¹H NMR, IR, low and high resolution mass spectra) for allyltrimethylsilanes 8b-e, 9c-e, 10c-e, and 14 and 2,3-bis(trimethylsilyl)alk-1-enes 21b,c, 22b, and 23b,c may be obtained (6 pages). Ordering information is given on any current masthead page.

Allenes and Acetylenes. 28.1 On the Mechanism of Reduction of **Propargylic Ethers and Acetates with Organocuprates**

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The amounts of substitution and reduction products from the reactions of two types of propargylic methyl ethers and acetates with organocuprates were determined. The methyl ethers give rise to more of the reduction products than the acetates. It is shown that "reduced" allenes are formed by hydrolysis of an organometallic intermediate whereas "reduced" acetylenes are formed mainly by another mechanistic pathway. The mechanisms of these reduction reactions are discussed in terms of stabilized, transient Cu(III)-intermediates and concerted β -hydride transfer in the formation of the acetylene.

In a number of cases, reductions of acetylenic compounds with various organocopper reagents have been reported. Thus, propargylic acetates,^{2,3} tosylates,⁴ chlorides,⁵ oxiranes,⁶ and methyl ethers^{7,8} have all been found to give varying amounts of allenes in which a hydrogen has been introduced instead of the expected alkyl group (eq 1). The reduction has found application in the synthesis

$$-\hat{c} - c \equiv c - \frac{H_{2}cu^{-}}{2H_{2}c(D_{2}O)} > c = c = c < H(D)$$
(1)

of, for example, allenic prostaglandins^{2a,3} and amines.⁸ A mechanistic interpretation of an analogous reaction of allylic ethers has been reported.9

The present study is an attempt to further elucidate the mechanism of the above reaction and the factors which affect the apparent competition between reduction and substitution in the reactions of organocuprates with propargylic compounds.

Results

The propargylic methyl ethers 1a and 1b and acetates 2a and 2b were allowed to react with an ethylcuprate,

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Table I. Reactions of Compounds 1 and 2 with EtMgBr-CuBr • Me₂S (4:1) in THF at -30 °C

compd	reacn time, h	redn prod, percent of total (%3; %4)	substn prod, percent of total (%5; %6)	total GC yield of 3–6 , %
1 a	22	79 ^a (23; 56)	21ª (17; 4)	>75
1 a	20	78 ^b (22; 56)	22^{b} (17; 5)	>95
1b	20	91 (71; 20)	9 (9; -)	>95
2a	1.5	30 (22; 8)	70 (58; 12)	75
2b	5	45 (42; 3)	55 (31; 24)	45
2b	2^{c}	37 (37; -)	63 (37; 26)	80

 a Mean of two runs giving reduction products 85% and 72% and substitution products 15% and 28%, respectively. ^bRun with 10% CuBr·Me₂S. ^cRun with 40% CuBr·Me₂S.

derived from EtMgBr and CuBr·Me₂S, in tetrahydrofuran (THF) at -30 °C. As is shown in Scheme I, the reactions give four products (3, 4, 5, and 6) in addition to butane and ethene, which are postulated to be formed in an amount equivalent to the sum of the reduction products.⁹ The relative amounts of reduction (3 and 4) and substitution products (5 and 6) are listed in Table I. In the case

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