A Highly Stereoselective Synthesis of Vinyl Bromides and Chlorides via Disubstituted Vinylsilanes

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A detailed study of the utility of vinylsilanes as intermediates in a stereoselective synthesis of vinyl halides is described. The requisite vinylsilanes are readily available from alkynes by hydroalumination–protonolysis or hydrosilation. Various methods of desilicohalogenation of intermediate dihalides from vinylsilanes **2a** and **3a** are compared. The effect of the alkyl substituent on the vinylsilane upon yield and stereoselectivity of the overall halogenation–desilicohalogenation sequence is studied. When the substituent is a primary or secondary alkyl group, the vinylsilanes are converted in good yields with high stereoselectivity to the vinyl chlorides and bromides; the overall reaction involves replacement of the trimethylsilyl group by halogen with inversion of stereochemistry about the double bond. When the substituent is a phenyl group the stereochemical outcome is retention about the double bond. When the alkyl substituent is *tert*-butyl, both isomeric vinylsilanes give *cis*-1-halo-3,3-dimethyl-1-butene as the product.

In an earlier communication[1] from this laboratory the feasibility of utilizing a vinylsilane as an intermediate in the stereoselective synthesis of vinyl halides was demonstrated. A detailed study of this general approach in terms of the effect of substituents and mode of desilicohalogenation on yields and stereoselectivity is the subject of this paper. The sequence leading to the vinyl halides is shown in Scheme I. An appropriate vinylsilane of defined stereochemistry can undergo trans addition of halogen (bromine or chlorine) to give an intermediate dihalo compound which upon desilicohalogenation via trans elimination will give the desired vinyl halide. The overall transformation involves replacement of the trimethylsilyl group by halogen with inversion of stereochemistry about the double bond.

Preparation of Vinylsilanes.[2] The requisite vinylsilanes can be easily prepared from the corresponding acetylenes. Thus the *cis*-vinylsilanes are made by lithiation of the appropriate acetylene with methyllithium followed by alkylation with chlorotrimethylsilane to give the 1-trimethylsilylacetylenes in high yields. These compounds can be reduced to the *cis*-vinylsilanes by a variety of methods as indicated in Scheme II. In terms of ease of reaction and overall yield the method of choice is hydralumination-protonolysis.[3] The yields for the preparation of the four *cis*-vinylsilanes used in these studies are given in Table I.

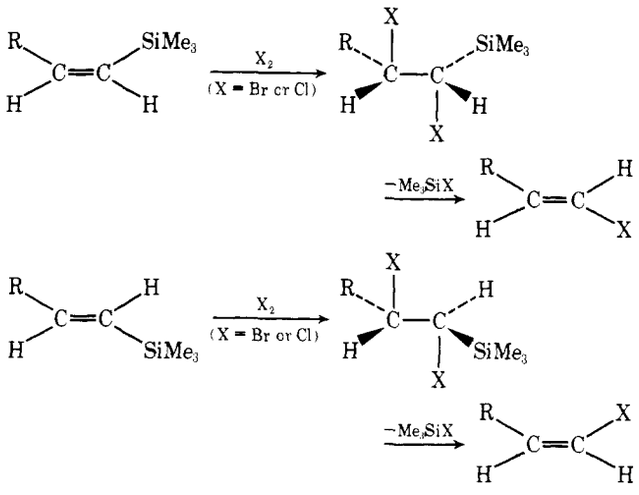
The *trans*-vinylsilanes were prepared by hydrosilation of the appropriate acetylenes with dimethylchlorosilane catalyzed by chloroplatinic acid.[4,5] Without isolation, the resulting *trans*-dimethylchlorosilylalkenes were subjected to treatment with methylmagnesium bromide to give the desired *trans*-trimethylsilylalkenes in good yields. The stereoselectivity in these reactions was very high, giving only the trans product. However, the regioselectivity was exclusively in the desired direction only for *tert*-butyl- and phenylacetylene. In the case of a primary substituent (*n*-butyl) 12% of the product was the 2-trimethylsilyl-1-alkene. For the more sterically demanding cyclohexyl group, 5% of the product had the silyl group at the internal position. The yields, regioselectivity, and stereoselectivity for the preparation of the four *trans*-vinylsilanes used in these studies are given in Table II.

Effect of Elimination Method on Yield and Stereoselectivity. With vinylsilanes of defined sterochemistry now readily available, an investigation into the effect of elimination methods on yield and stereoselectivity of vinyl halides via Scheme I was carried out. The two isomers of 1-trimethylsilyl-1-hexene were used for the study in this area.

It was found that the halogenation of these compounds proceeded in a straightforward manner with chlorine and bromine. However, iodination presented complications resulting in low overall yields and problems with reproducibility[1,6] and thus will not be considered further. Typically, a solution of bromine or chlorine in methylene chloride was added to the vinylsilane at −78 °C until the color of unreacted halide persisted. In spite of the retarding effect silicon exerts on the double bond toward electrophilic reagents,[7] these additions took place very rapidly at low temperatures to afford spectrally different dihalides from the *cis*- and *trans*-vinylsilanes (**2a** and **3a**). These dihalides were obtained in virtually quantitative yield and, if desired, could be purified by distillation.

With the 1-trimethylsilyl-1-hexenes, the halogenations were found to be quite insensitive to the reaction conditions employed. These reactions were run at a variety of temperatures, in the absence and presence of light, and even with a considerable excess of the halogen with little or no effect on the yield

Scheme I



Scheme II

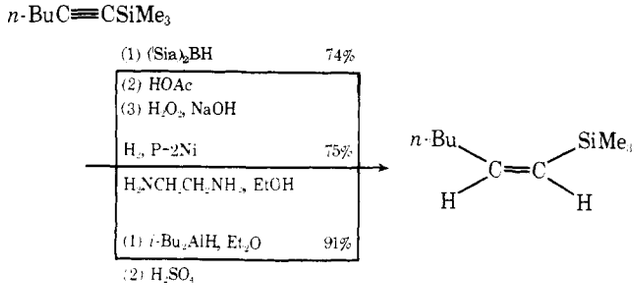


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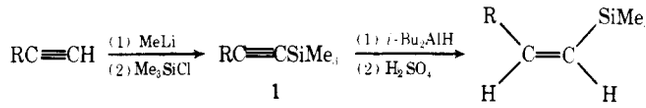
Table I. Preparation of *cis*-Vinylsilanes from Acetylenes



R	compd	registry no.	% yield of 1[a]	compd	registry no.	% yield of 2[a]	cis–trans[b]
n-Bu	**1a**	3844-94-8	94	**2a**	52835-06-0	91	99:1
cyclohexyl	**1b**	66270-60-8	91	**2b**	66270-75-5	96	99:1
t-Bu	**1c**	14630-42-3	92	**2c**	26567-95-3	87	99:1
Ph	**1d**	2170-06-1	96	**2d**	19319-11-0	97	98:2

[a] Distilled yield. [b] Determined by GLC.

or product purity. (It should be noted, however, that this is not always the case, as will be seen with the *tert*-butylvinylsilanes.) Finally, these dihalides were found to undergo slow decomposition upon standing, particularly in the presence of light at room temperature. Therefore, the crude dihalides were usually utilized after spectral analysis without further purification.

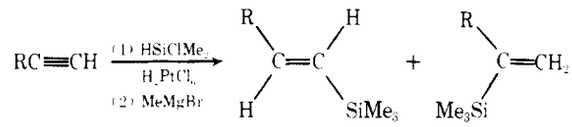
The purified dihalides from *cis*- and *trans*-1-trimethylsilyl-1-hexene were subjected to desilicohalogenation under three sets of conditions:[8] (1) sodium methoxide in methanol,[1,9] (2) potassium fluoride dihydrate in dimethyl sulfoxide,[1,6,10] and (3) alumina in pentane.[9] The results of this study are given in Table III. Sodium methoxide in methanol resulted in facile elimination of the dihalides to stereochemically pure *cis*- and *trans*-vinyl chlorides and bromides. These results lend support to the postulate that the stereochemical course of the reaction sequence (Scheme I) involves trans addition of halogen followed by trans desilicohalogenation. Recent work by Brook and co-workers[11] has given evidence that the halogenation of alkyl-substituted vinylsilanes does proceed in a trans manner, thereby indirectly confirming that the elimination was also trans.

The isomeric purity of the vinyl halides are essentially the same as the starting vinylsilanes (see Tables I and II) which indicates that the halogenation and elimination steps take place stereospecifically under these conditions. Not only are the vinyl halides obtained in excellent isomeric purities but also in high yields. In the case at hand, the GLC yield probably reflects a more accurate picture of the efficiency of this process than the isolated yield since the vinyl halides, particularly the vinyl chlorides, were quite volatile and were separated only with difficulty from hexamethyldisiloxane which was formed as a side product. This contention was borne out when higher boiling vinyl halides were prepared and isolated in excellent yields.

The second set of elimination conditions was potassium fluoride dihydrate in dimethyl sulfoxide. Once again, the vinyl halide formed readily and generally in higher isolated yields than with sodium methoxide–methanol due to less hexamethyldisiloxane formation which simplified purification of the vinyl halide by distillation. Unfortunately this method resulted in relatively poor stereoselectivity. This problem may be attributable to the use of dimethyl sulfoxide, a highly ionizing solvent, which may promote substantial amounts of E-1 type elimination in a manner similar to that proposed by Jarvie.[12]

The third and final set of elimination conditions was a slurry of neutral alumina (Brockman activity grade 1) in pentane.[9] This method was discovered in an attempt to purify several grams of a recalcitrant dibromide by column chromatography. Unpredictably, the only compound that eluted was the elimination product, the vinyl bromide. Subsequent experimentation showed that reproducible results could be obtained by simply stirring the dihalide in a slurry of alumina in pentane,

Table II. Preparation of *trans*-Vinylsilanes from Acetylenes



R	compd	% yield[a]	3–4[b]	3 trans–cis[b]
n-Bu	**a**	79	88[c]:12[d]	>99:1
cyclohexyl	**b**	93	95[e]:5[f]	>99:1
t-Bu	**c**	93	100[g]:0	>99:1
Ph	**d**	80	100[h]:0	>99:1

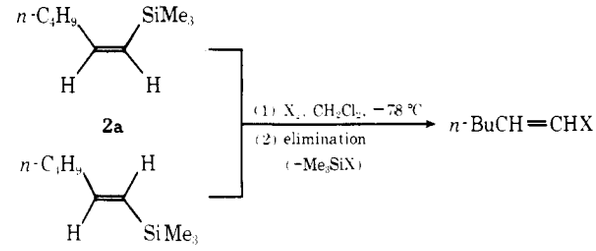
[a] Distilled yield of **3** + **4**. [b] Determined by GLC. [c] Registry no. 54731-98-7. [d] Registry no. 59549-81-4. [e] Registry no. 66270-74-4. [f] Registry no. 67478-58-4. [g] Registry no. 20107-37-3. [h] Registry no. 19372-00-0.

then filtering off the alumina to afford the pure vinyl halide in pentane. This remarkably mild method of effecting elimination emphasizes the facility with which β-functionalized silanes react. Examination of Table III shows that the yields obtained by this procedure are very competitive with those obtained using sodium methoxide. However, the data regarding the stereoselectivity are presently quite puzzling. While the dihalides derived from the *trans*-vinylsilane go very cleanly to the expected *cis*-vinyl halides, the elimination of the dihalides from the *cis*-vinylsilane takes place with much less stereoselectivity.

Effect of Variation of R Group Upon Yield and Stereoselectivity. Having shown Scheme I to be a viable approach to isomerically pure vinyl halides under a variety of conditions, a study of the effect of the R group in the vinylsilane upon yield and stereoselectivity of the vinyl halides was carried out. This consisted of subjecting *cis*- and *trans*-vinylsilanes containing primary, secondary, tertiary, and phenyl R groups to a standard set of reaction conditions. We selected methanolic sodium methoxide as our standard elimination conditions on the basis of the high yields and stereoselectivity obtained previously. The results of this study are given in Table IV.

As with the example of R as a primary group (*n*-butyl) discussed in the previous section, the halogenation of both *cis*- and *trans*-cyclohexylvinylsilanes (R = secondary group) proceeded smoothly with chlorine and bromine to yield stable dihalides. In this instance, and in all instances subsequent to this, the dihalides were characterized spectrally, then used without further purification. Exposure of these compounds to methoxide elimination conditions afforded the expected vinyl halides in excellent overall yields and isomeric purities. These high isolated yields probably reflect, to some extent, the higher boiling points of these vinyl halides relative to R being *n*-butyl, thus facilitating their separation from the ubiquitous hexamethyldisiloxane.

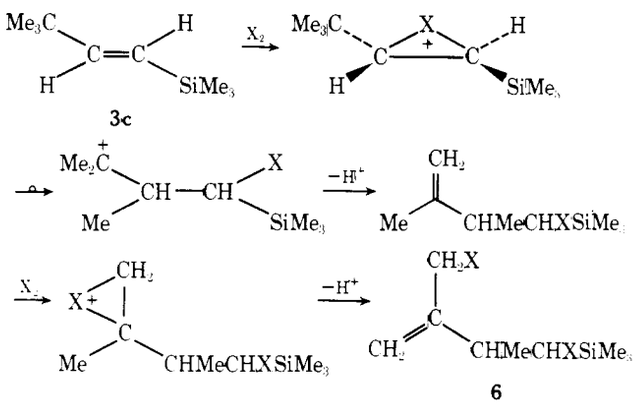
Table III. Effect of Elimination Method on Yield and Stereoselectivity



starting material	X	method of elimination	% isolated yield (% GLC yield)	cis–trans	ref
2a	Cl	NaOMe/MeOH	68 (85)	2:98	9
		$KF{\cdot}2H_2O/Me_2SO$	85	2:98	*a*
		alumina/n-C_5H_{12}	65 (84)	23:77	9
3a	Cl	NaOMe/MeOH	66 (85)	>99:1	9
		$KF{\cdot}2H_2O/Me_2SO$	66	86:14	*a*
		alumina/n-C_5H_{12}	62 (85)	99:1	9
2a	Br	NaOMe/MeOH	84 (96)	5:95	9
		$KF{\cdot}2H_2O/Me_2SO$	94	32:68	*a*
		alumina/n-C_5H_{12}	79 (85)	15:85	9
3a	Br	NaOMe/MeOH	86 (100)	98:2	9
		$KF{\cdot}2H_2O/Me_2SO$	73	93:7	*a*
		alumina/n-C_5H_{12}	68 (93)	99:1	9

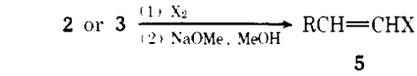
[a] This paper.

Scheme III



While the results obtained using primary and secondary alkyl groups certainly met our expectations and justified our faith in this reaction sequence, the use of a tertiary R group (*tert*-butyl) proved considerably less straightforward. The different behavior of these compounds first became apparent during the halogenation reaction. Halogenation of the *cis-tert*-butylvinylsilane (**2c**) readily took place under the usual conditions of the addition of the halogen in methylene chloride at −78 °C to afford pure, stable dihalides in virtually quantitative yields. However, application of these conditions to the *trans-tert*-butylvinylsilane (**3c**) gave two products. The major product was the desired dihalide but a substantial portion was a rearranged product that showed spectral properties (NMR, IR, and mass spectra) consistent with compound **6**. There is ample precedent for the migration of a methyl group during the halogenation of *tert*-butylvinyl species[13] and compound **6** can be imagined as arriving through a route outlined in Scheme III. At present it is unclear as to why the trans isomer undergoes rearrangement while the corresponding cis isomer does not. The problem of rearrangement in the halogenation of the trans isomer was overcome by variation of solvent. Thus halogenation in carbon tetrachloride at 0 °C gave the desired dihalide with only very small amounts of rearranged product.

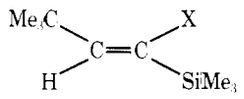
Table IV. Effect of R Group Upon Yield and Stereoselectivity



starting material	R	X	% isolated yield (% GLC yield)	**5** cis–trans
2a	n-Bu	Cl	68 (85)[b]	2:98
		Br	84 (96)[b]	5:95
2b	cyclohexyl	Cl	97	1:99
		Br	98	1:99
2c	t-Bu	Cl	(91)[a]	92:8
		Br	70 (96)[a]	99:1
2d	Ph	Cl	58	90:10
		Br	94	96:4
3a	n-Bu	Cl	66 (85)[b]	99:1
		Br	86 (100)[b]	98:2
3b	cyclohexyl	Cl	88	95:5
		Br	93	99:1
3c	t-Bu	Cl	(82)	99:1
		Br	31 (58)	87:13
3d	Ph	Cl	66	8:92
		Br	99	1:99

[a] $KF{\cdot}2H_2O/Me_2SO$ was used as the method of elimination. [b] Reference 9.

Now that both the *tert*-butyl dichlorides and dibromides could be prepared quite cleanly, we turned to their elimination to vinyl chlorides and bromides. Unfortunately, this process also exhibited complications. While treatment of the dihalides derived from the *trans*-vinylsilane (**3c**) with the usual conditions of methanolic sodium methoxide at 0 °C resulted in normal elimination products (*cis*-vinyl chloride and bromide), similar treatment of the dihalides from the cis isomer (**2c**) gave little or no reaction. Elimination could be forced if the reaction was run at reflux for several hours, but the product of dehydrohalogenation (**7**) predominates. This result is explainable if one examines the conformers necessary for trans elimination. Conformer **8** expected to lead to the desired *trans*-vinyl halide via desilicohalogenation should experience severe in-



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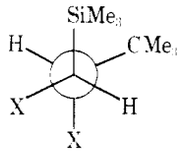
teractions between the *tert*-butyl and trimethylsilyl groups. Arrangement of these two groups to minimize their interaction results in conformer **9** which is ideally set up for dehydrohal-



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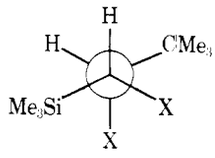

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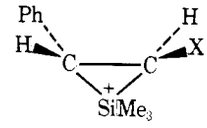
ogenation by a basic reagent such as sodium methoxide. Based upon the α-anion stabilizing property of silicon,[14] the direction of dehydrohalogenation would be expected to give silylvinyl halide **7.** This has been confirmed in the case where X is bromine by comparison with an authentic sample.[15] In the dihalide derived from the *trans*-vinylsilane (**3c**) the conformer leading to dehydrohalogenation is even more sterically congested than the conformer leading to the desilicohalogenation.

In an attempt to suppress dehydrohalogenation in the dihalides derived from *cis*-vinylsilane **2c,** potassium fluoride dihydrate was used as the eliminating reagent. The products, although ones of exclusive desilicohalogenation, turn out to be *cis*-1-halo-3,3-dimethyl-1-butenes, the same products derived from the dihalides of the *trans*-vinylsilane **3c.** The stereochemistry of these vinyl halides was shown not to be trans by comparison with authentic samples synthesized by an independent route (see Scheme IV). The above results indicate that in the dihalides derived from *cis*-vinylsilane **2c** cis elimination or gauche elimination[16] is favored with fluoride ion over trans elimination which requires the steric interactions contained in conformer **8.**

Finally, the last R group to be examined was that of phenyl. Our initial halogenations of these compounds resulted in a mixture of olefinic products. As this seemed to be due to thermal instability of the product under our reaction workup conditions, halogenation was carried at −78 °C followed by removal of the solvent and excess halogen via vacuum pump at −78 °C and then addition of methanolic sodium methoxide at that temperature. As can be seen in Table IV, we obtained fair yields with good stereoselectivity for the β-chlorostyrenes and excellent yields and stereoselectivity for the corresponding bromo compounds. However, the stereochemistry was clearly the opposite of what would be predicted by trans halogenation followed by trans elimination (see Scheme I). In all cases a small amount of the α-halostyrene was also obtained.

This anomalous behavior has been previously observed by Koenig and Weber in the treatment of β-trimethylsilylstyrenes with deuterium chloride[17] and bromine in polar media.[18] That deuteration takes place six to seven times more rapidly when the phenyl group is replaced by a *p*-tolyl group indicates a buildup of positive charge at the benzylic center which these workers postulate could be stabilized by a bridging silicon species.[19] This line of reasoning offers a most economical explanation for our observations. Halogenation of *trans*-β-trimethylstyrene (**3d**) could proceed via a silicon-stabilized cationic species **10** which upon attack by halide ion



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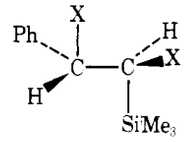

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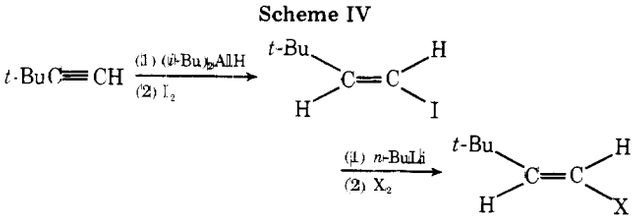
would afford dihalide **11,** formally the product of cis halogenation.[20] Trans elimination of this dihalide would then give the *trans*-β-halostyrenes observed, an effective replacement of silicon by halide with retention of stereochemistry about the double bond. In a completely analogous manner, the *cis*-β-trimethylsilylstyrene (**2d**) would undergo cis halogenation followed by trans elimination to afford the *cis*-β-halostyrenes. Evidence for such a stereochemical sequence was recently obtained by Brook[21] when X-ray analysis of the dibromide derived from *trans*-β-triphenylsilylstyrene showed that halogenation had, indeed, proceeded in a cis manner.

Summary. A detailed study of the utility of vinylsilanes as intermediates in a stereoselective synthesis of vinyl halides is described. The requisite vinylsilanes are readily available by hydroalumination-protonolysis or hydrosilation of alkynes. Halogenation of an appropriate vinylsilane of defined stereochemistry followed by desilicohalogenation with methanolic sodium methoxide gives good yields of vinyl chlorides and bromides with high stereoselectivity. When the vinylsilane has a primary or secondary alkyl substituent the overall reaction involves replacement of the trimethylsilyl group by halogen with inversion of stereochemistry about the double bond. However, when the substituent is a phenyl group the stereochemical outcome is retention about the double bond. When the alkyl substituent is *tert*-butyl both isomeric vinylsilanes give *cis*-1-halo-3,3-dimethyl-1-butene as the product.

Scheme IV



Experimental Section

Melting points are reported uncorrected. Boiling points were recorded at gauge pressure and are reported uncorrected. Infrared spectra were obtained on a Beckman IR-8 spectrometer with only selected peaks being reported. Nuclear magnetic resonance (^{1}H) spectra were obtained on either a Varian EM 360 or a Varian A-60A instrument. Chemical shifts are reported in δ values (ppm) 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 Corporation instrument. High-resolution mass spectra were determined by Mr. Kei Miyano on a Varian M-60 mass spectrometer. Samples for mass spectral analysis were purified by preparative GLC on a Varian Aerograph Model 90-P gas chromatograph with 10% SE-30 on Chromosorb W in a 0.25 in. × 10 ft stainless steel column. Analytical GLC was performed on a Varian Aerograph Series 1400 gas chromatograph with glass capillary columns (as indicated) or a Varian Aerograph Model 600-D instrument with 20% SF-96 on Chromosorb Q in a $\frac{1}{8}$ in. × 5 ft stainless steel column. GLC yields were obtained on the latter instrument by comparing the integrations of the product peak against an internal standard peak 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 using 1,2-dibromoethane.[22] *n*-Butyllithium was standardized by titration with a standard solution of 2-butanol in xylene using 1,10-phenanthroline as an indicator.[23] Methylmagnesium bromide, prepared from methyl bromide, was standardized for total base by quenching an aliquot with water and titrating with standard hydrochloric acid solution using phenolphthalein indicator. Borane–tetrahydrofuran solution was standardized by measuring hydrogen gas evolution.[24] Diisobutylaluminum hydride (Texas Alkyls) was transferred from the lecture bottle into a storage flask which was maintained under a N_2 atmosphere. The

neat reagent (5.4 M) was transferred by means of a syringe. All alkynes were obtained from Farchan Division, Story Chemical Co. and were used without purification except phenylacetylene which was distilled prior to use. Chlorine (Matheson), 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. 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.

General Preparation of 1-Alkynyl(trimethyl)silanes. A magnetically stirred solution of alkyne (0.20 mol) in anhydrous ether (100 mL) cooled to −78 °C was treated with 1.8 M methyllithium (122 mL, 0.22 mol, 1.1 equiv) at a rate such that the temperature was maintained below −60 °C. After stirring the milky solution for 90 min at −78 °C, chlorotrimethylsilane (26.1 g, 0.24 mol, 1.2 equiv) was added again taking care to maintain the temperature below −60 °C. The resulting mixture was stirred at −78 °C for 2 h, allowed to warm to room temperature, and stirred an additional 5 h. After cooling with an ice bath, water (200 mL) was carefully added. The layers were separated and the aqueous layer was extracted with fresh ether. The combined organic layers were washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. Solvent was removed by distillation at atmospheric pressure through a 25-cm column packed with glass helices. Vacuum distillation of the residue yielded the colorless product.

(a) 1-Hexynyl(trimethyl)silane (1a). Following the general procedure, 1-hexyne was converted into **1a** in 94% yield: bp 73–76 °C (30 Torr) [lit.[4] bp 155 °C; lit.[3] bp 71–73 °C (36 Torr)].

(b) 2-Cyclohexylethynyl(trimethyl)silane (1b). Following the general procedure, cyclohexylacetylene was converted to **1b** in 91% yield: bp 70–72 °C (5 Torr) [lit.[3] bp 82–83 °C (7 Torr)]; high-resolution mass spectrum, calcd (*m/e* of P − CH_3) for $C_{11}H_{20}Si(P)$ 165.1100, found 165.1100.

(c) 3,3-Dimethyl-1-butynyl(trimethyl)silane (1c). Following the general procedure, *tert*-butylacetylene was converted to **1c** in 92% yield: bp 62–67 °C (100 Torr) [lit.[5] bp 57 °C (60 Torr), lit.[3] bp 80–81 °C (150 Torr)]; high-resolution mass spectrum, calcd (*m/e*) for $C_9H_{11}Si$ 154.1178, found 154.1190.

(d) 2-Phenylethynyl(trimethyl)silane (1d). Following the general procedure, phenylacetylene was converted to **1d** in 96% yield: bp 64–67 °C (0.7 Torr) [lit.[25] bp 59–60 °C (1.0 Torr)].

Preparation of *cis*-1-Hexenyl(trimethyl)silane (2a). (a) Hydroboration Protonolysis. Disiamylborane was prepared[26] by careful addition of 2-methyl-2-butene (21.0 g, 0.30 mol) in dry tetrahydrofuran (60 mL) to a magnetically stirred solution of 1.35 M borane (110 mL, 0.149 mol) in tetrahydrofuran which had been cooled in a dry ice/CCl_4 bath. Addition was at a rate such that the temperature was maintained below −10 °C. After stirring for 2 h at 0 °C, the mixture was cooled to −10 °C and **1a** (23.0 g, 0.149 mol) in tetrahydrofuran (30 mL) was added without allowing the temperature to reach 0 °C. After stirring at room temperature for 2 h the tetrahydrofuran was removed in vacuo leaving a viscous residue which was cooled in an ice bath. Then glacial acetic acid (75 mL) was added and the mixture was refluxed for 2 h. After being carefully poured into ice water, the mixture was treated with 3 N sodium hydroxide (50 mL) and 30% hydrogen peroxide (32.7 mL) and stirred 1.5 h at room temperature. Ether was added and the layers separated. The aqueous layer was extracted with fresh ether and the combined organic layers were washed sequentially with 20% sodium hydroxide, 5% hydrochloric acid, saturated sodium bicarbonate solution, and saturated sodium chloride solution. Following drying over anhydrous sodium sulfate, the solvent was removed at atmospheric pressure and the residue was vacuum distilled to give **2a** (17.27 g, 74% yield) as a colorless liquid: bp 76–78 °C (35 Torr) [lit.[4] bp 60 °C (20 Torr)].

(b) Catalytic Hydrogenation. The P-2Ni catalyst was prepared by Brown's procedure[27] from nickel acetate tetrahydrate (1.88 g, 7.5 mmol, 0.005 equiv) in a low-pressure hydrogenation apparatus. The apparatus was purged and filled with hydrogen and **1a** (23.2 g, 0.150 mol) was introduced into the reaction vessel via syringe. The mixture was stirred until hydrogen uptake ceased and then filtered through activated charcoal into a separatory funnel. The light purple solution was partitioned between water and pentane and shaken and the layers separated. After thorough extraction of the aqueous layer with fresh pentane, the combined organic fractions were dried over anhydrous sodium sulfate. Solvent was removed by atmospheric distillation through a 25-cm glass helices packed column and the residue was vacuum distilled to give **2a** (17.6 g, 75% yield). GLC analysis (50 m SE-30 glass capillary column) showed the product to be 3% **1a** with the remaining 97% as **2a** with a 96:4 ratio of cis–trans isomers.

(c) Hydroalumination Protonation.[26] To a magnetically stirred solution of **1a** (24.34 g, 0.158 mol) in anhydrous ether (80 mL) was slowly added 5.4 M diisobutylaluminum hydride (33.6 mL, 0.181 mol, 1.15 equiv). After stirring for an additional 7 h at room temperature,[28] the reaction mixture was syringed into a separatory funnel containing cold 10% H_2SO_4 (500 mL) and ice. As quickly as possible this mixture was shaken and the layers separated. After extraction of the aqueous layer with fresh ether, the organic layers were combined and washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. Removal of the solvent by atmospheric distillation was followed by vacuum distillation of the residue to give **2a** (22.3 g, 91% yield). GLC analysis as before indicates less than 2% of **1a** with the remaining 98% as **2a** with a 99:1 cis–trans ratio

***cis*-2-Cyclohexylethenyl(trimethyl)silane (2b).** Following the procedure for preparation of **2a** via hydroalumination-protonation, **1b** was converted to **2b** in 96% yield [GLC analysis (50 m OV-101 glass capillary column) shows the product to be 99% of the cis isomer and no **1b** remaining]: bp 71–73 °C (5 Torr); IR (neat) 1605, 1250, 860, and 767 cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.80–2.38 (m, 11 H), 5.18 (d, 1 H, J = 14 Hz, C=C**H**Si), and 5.77–6.15 (d of d, 1 H, J = 14 and 9 Hz, **CH**=CSi); high-resolution mass spectrum, calcd (*m/e*) for $C_{11}H_{22}Si$ 182.1492, found 182.1482.

***cis*-3,3-Dimethyl-1-butenyl(trimethyl)silane (2c).** Following the procedure for preparation of **2a** via hydroalumination-protonation, **1c** was converted to **2c** in 87% yield [GLC analysis (50 m OV-101 glass capillary column) shows the product to be 99% of the cis isomer and no **1c** remaining]: bp 80–84 °C (97 Torr), [lit.[29] 109–110 °C]; high-resolution mass spectrum, calcd (*m/e* of P − CH_3) for $C_9H_{20}Si$-(P) 141.1100, found 141.1132.

***cis*-β-Styryl(trimethyl)silane (2d).** Following the procedure for preparation of **2a** via hydroalumination-protonation, **1d** was converted to **2d** in 97% yield [GLC analysis (50 m OV-101 glass capillary column) indicates a 98:2 cis–trans ratio and no **1d** remaining]: bp 75–77 °C (5 Torr) [lit.[4] bp 85 °C (7 Torr)].

General Preparation of *trans*-1-Alkenyl(trimethyl)silanes. To freshly distilled chlorodimethylsilane (17.11 g, 0.177 mol, 1.1 equiv) was added 2 drops of 10% chloroplatinic acid and the mixture was stirred until homogeneous. Then anhydrous ether (25 mL) was added and the alkyne (0.160 mol) was added in anhydrous ether (10 mL) at a rate such that a steady reflux was maintained. After cooling the mixture to 0 °C, 1.78 M methylmagnesium bromide (117 mL, 0.208 mol, 1.3 equiv) was dripped into the vessel, allowed to warm to room temperature, and stirred an additional 6 h. Saturated ammonium chloride solution (250 mL) was added to the cooled mixture and the layers were separated. After the aqueous layer was extracted with pentane, the combined organic layers were dried over anhydrous sodium sulfate and the solvent was removed by atmospheric distillation through a 25-cm glass helices packed column. The residue was vacuum distilled to give colorless product which was analyzed by GLC to determine regioisomeric and stereoisomeric ratios.

(a) *trans*-1-Hexenyl(trimethyl)silane (3a). Following the general procedure, 1-hexyne was converted in 79% yield to a product that was 88% **3a** (less than 1% cis isomer) with the remaining 12% attributed to **4a** (GLC analysis on a 50 m SE-30 glass capillary column): bp 72–76 °C (30 Torr) [lit.[4] bp 60 °C (20 Torr)]; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.85 (broad t, 3 H, J = 6 Hz, CH_2CH_3), 1.27 (m, 4 H, $(-CH_2-)_2$), 2.00 (m, 2 H, CH_2C=C), 5.47 (d, 1 H, J = 18.5 Hz, C=C**H**Si), and 5.72 to 6.20 (d of t, 1 H, J = 18.5 and 5.2 Hz, **CH**=CSi), the impurity **4a** appears as two multiplets at 5.02 and 5.45 (Si-C=C**H**$_2$); high-resolution mass spectrum, calcd (*m/e*) for $C_9H_{20}Si$ 156.1335, found 156.1316.

(b) *trans*-2-Cyclohexylethenyl(trimethyl)silane (3b). Following the general procedure, cyclohexylacetylene was converted in 93% yield to a product that was 95% **3b** (less than 1% cis isomer) with the remaining 5% being attributed to **4b** (GLC analysis on a 50 m OV-101 glass capillary column): bp 71–74 °C (4 Torr); IR (neat) 1610, 1250, 865, and 840 cm^{-1}; NMR (CCl_4) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.80–2.33 (m, 11 H), 5.46 (d, 1 H, J = 19 Hz, C=C**H**Si), and 5.76–6.17 (d of d, 1 H, J = 19 and 5 Hz, **CH**=CSi); high-resolution mass spectrum, calcd (*m/e*) for $C_{11}H_{22}Si$ 182.1492, found 182.1472.

(c) *trans*-3,3-Dimethyl-1-butenyl(trimethyl)silane (3c). Following the general procedure, *tert*-butylacetylene was converted in 93% yield to **3c** (GLC analysis on a 50 m OV-101 glass capillary column shows less than 1% cis isomer and no detectable **4c**): bp 75–78 °C (98 Torr) [lit.[29] bp 128–130 °C]; high-resolution mass spectrum, calcd (*m/e* of P − CH_3) for $C_9H_{20}Si(P)$ 141.1100, found 141.1094.

(d) *trans*-β-Styryl(trimethyl)silane (3d). Following the general procedure, phenylacetylene was converted in 80% yield to **3d** (GLC analysis on a 50 m OV-101 glass capillary column shows less than 1% cis isomer and no detectable **4d**): bp 64–67 °C (0.7 Torr) [lit.[4] bp 81 °C (5 Torr)].

General Elimination Procedure Using Potassium Fluoride Dihydrate–Dimethyl Sulfoxide (Table III). To a solution of the dihalide (0.020 mol) derived from either *cis*- or *trans*-vinylsilanes (**2** and **3**, respectively) in dimethyl sulfoxide (10 mL) was added potassium fluoride dihydrate (2.82 g, 0.030 mol, 1.5 equiv) and the suspension was stirred at room temperature for 9 h. The mixture was taken up in enough water to dissolved all solids and thoroughly extracted with pentane. After drying the combined pentane extracts over anhydrous sodium sulfate, the solvent was removed by atmospheric distillation through a 25-cm glass helices packed column. The residue was distilled at reduced pressure to afford the product as a colorless liquid.

(a) *trans*-1-Chloro-1-hexene (Table III). Following the general procedure, the dichloride[9] of **2a** was converted in 85% yield to 1-chloro-1-hexene [bp 60–70 °C (90 Torr)] which by GLC analysis (5 ft 20% SF-96 on Chromosorb Q) has an isomeric ratio of 98% trans–2% cis. The products were identical by comparison with authentic samples.[15]

(b) *cis*-1-Chloro-1-hexene (Table III). Following the general procedure, the dichloride[9] of **3a** was converted in 66% yield to 1-chloro-1-hexene which by GLC analysis (5 ft 20% SF-96 on Chromosorb Q) has an isomeric ratio of 86% cis–14% trans. The products were identical by comparison with authentic samples.[15]

(c) *trans*-1-Bromo-1-hexene (Table III). Following the general procedure, the dibromide[9] of **2a** was converted in 94% yield to 1-bromo-1-hexene which by GLC analysis (5 ft 20% SF-96 on Chromosorb Q) has an isomeric ratio of 68% trans–32% cis. The products were identical by comparison with authentic samples.[15]

(d) *cis*-1-Bromo-1-hexene (Table III). Following the general procedure, the dibromide[9] of **3a** was converted in 73% yield to 1-bromo-1-hexene which by GLC analysis (5 ft 20% SF-96 on Chromosorb Q) has an isomeric ratio of 93% cis–7% trans. The products were identical by comparison with authentic samples.[15]

General Halogenation–Elimination Procedures Used in Table IV. Halogenation. To a magnetically stirred solution of vinylsilane (**2** or **3**, 0.020 mol) in methylene chloride (40 mL) which had been cooled to −78 °C was added dropwise a solution of halogen in methylene chloride (3 M for bromine and saturated for chlorine) until the first persistence of halogen color. The solution was then shaken with 10% sodium sulfite solution and the layers separated. After thoroughly extracting the aqueous layer with fresh methylene chloride, the combined organic layers were washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. Removal of the solvent by rotory evaporation gave the dihalide product in virtually quantitative yield. After spectral analysis the dihalide was used without further purification in the following elimination procedure.

Elimination. The crude dihalide (0.020 mol) in methylene chloride (10 mL) was cooled to 0 °C in an ice bath and treated with 1 M sodium methoxide in methanol (30 mL, 0.030 mol, 1.5 equiv). The resulting mixture was magnetically stirred for 1 h at 0 °C, allowed to warm to room temperature, then stirred an additional 2 h. The mixture was next partitioned between water and pentane and the layers separated. After thorough extraction of the aqueous layer with fresh pentane, the organic layers were combined, washed with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Removal of the solvent by atmospheric distillation through a 25-cm glass helices packed column yielded a residue which was vacuum distilled to give the colorless product which was analyzed by GLC to determine stereoisomeric ratios.

(a) *trans*-1-Chloro-2-cyclohexylethylene (Table IV). By the general halogenation procedure, **2b** was chlorinated to give the dichloride in 100% yield as a white, crystalline solid: mp 70–73 °C; NMR (CCl_4) δ 0.00 (s, 9 H, $\mathbf{CH_3}_3Si$), 0.50–2.22 (m, 11 H), 3.38 (d, 1 H, J = 2.5 Hz, **CH**ClSi), and 3.58 (d of d, 1 H, J = 2.5 and 8.5 Hz, **CH**ClCClSi).

Elimination of the crude dichloride by the general sodium methoxide–methanol procedure gave in 97% yield 1-chloro-2-cyclohexylethylene which by GLC analysis (5 ft 20% SF-96 on Chromosorb Q) has an isomeric ratio of 99% trans–1% cis: bp 61–64 °C (6 Torr); IR (neat) 1620, 942, 823, and 780 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 0.65–2.35 (m, 11 H) and 5.76 (m, 2 H, **CH=CH**); high-resolution mass spectrum, calcd (m/e) for $C_8H_{13}{}^{35}Cl$ 144.0707, found 144.0686.

(b) *trans*-1-Bromo-2-cyclohexylethylene (Table IV). By the general halogenation procedure, **2b** was brominated to give the dibromide in 100% yield as a white, crystalline solid: mp 96–97.5 °C; NMR (CCl_4) δ 0.00 (s, 9 H, $\mathbf{CH_3}_3Si$), 0.50–2.38 (m, 11 H), 3.48 (d, 1 H, J = 3 Hz, **CH**BrSi), and 3.66 (d of d, 1 H, J = 3 and 9 Hz, **CH**BrCBrSi).

Elimination of the crude dibromide by the general sodium methoxide–methanol procedure gave in 98% yield 1-bromo-2-cyclohexylethylene which by GLC analysis (5 ft 20% SF-96 on Chromosorb Q) has an isomeric ratio of 99% trans–1% cis: bp 70–74 °C (4.8 Torr); IR (neat) 1615, 940, and 713 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 0.66–2.50 (m, 11 H) and 6.02 (m, 2 H, CH=CH). The products were identical by comparison with authentic samples.[15]

(c) *cis*-1-Chloro-2-cyclohexylethylene (Table IV). By the general halogenation procedure, **3b** was chlorinated to give the dichloride in 100% yield as a slightly yellow oil: NMR (CCl_4) δ 0.00 (s, 9 H, $\mathbf{CH_3}_3Si$), 0.50–2.50 (m, 11 H), 3.24 (d, 1 H, J = 11 Hz, **CH**ClSi), and 3.74 (d of d, 1 H, J = 11 and 2.5 Hz, **CH**ClCClSi).

Elimination of the crude dichloride by the general sodium methoxide–methanol procedure gave in 88% yield 1-chloro-2-cyclohexylethylene which by GLC analysis (5 ft 20% SF-96 on Chromosorb Q) has an isomeric ratio of 95% cis–5% trans: bp 63–67 °C (12 Torr); IR (neat) 1625, 960, 890, 805, 743, and 715 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 0.50–3.00 (m, 11 H) and 5.38–5.92 (unsymmetrical pentet, 2 H, **CH=CH**); high-resolution mass spectrum, calcd (m/e) for $C_8H_{13}{}^{35}Cl$ 144.0707, found 144.0681.

(d) *cis*-1-Bromo-2-cyclohexylethylene (Table IV). By the general halogenation procedure, **3b** was brominated to give the dibromide in 99% yield as a slightly discolored solid: mp 45–50 °C; NMR (CCl_4) δ 0.00 (s, 9 H, $\mathbf{CH_3}_3Si$), 0.50–2.50 (m, 11 H), 3.40 (d, 1 H, J = 12 Hz, **CH**BrSi), and 3.90 (d of d, 1 H, J = 12 and 2.5 Hz, **CH**BrCBrSi).

Elimination of the crude dibromide by the general sodium methoxide–methanol procedure gave in 93% yield 1-bromo-2-cyclohexylethylene which by GLC analysis (5 ft 20% SF-96 on Chromosorb Q) has an isomeric ratio of 99% cis–1% trans: bp 61–65 °C (4.8 Torr); IR (neat) 1620, 1320, 1285, 960, 890, 710, and 670 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 0.50–2.80 (m, 1 H) and 5.80 (m, 2 H, **CH=CH**). The products were identical by comparison with authentic samples.[15]

(e) *cis*-1-Chloro-3,3-dimethyl-1-butene (Table IV). From 2c. By the general halogenation procedure, **2c** was chlorinated to give the dichloride in 100% yield as a slightly yellow liquid: NMR (CCl_4) δ 0.00 (s, 9 H, $\mathbf{CH_3}_3Si$), 0.92 (s, 9 H, $\mathbf{CH_3}_3C$), 3.47 (d, 1 H, J = 1.5 Hz, **CH**ClSi), and 3.68 (d, 1 H, J = 1.5 Hz, **CH**ClCClSi).

Elimination of the crude dichloride by the general potassium fluoride dihydrate–dimethyl sulfoxide procedure described earlier gave in 91% GLC yield (*n*-octane as internal standard) 1-chloro-3,3-dimethyl-1-butene with an isomeric ratio of 92% cis–8% trans (GLC analysis on 5 ft 20% SF-96 on Chromosorb Q): IR (neat) 1620, 1210, 904, 792, and 700 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 1.11 (s, 9 H, $\mathbf{CH_3}_3C$), 5.55 (d, 1 H, J = 8 Hz, **CH**=CCl), and 5.78 (d, 1 H, J = 8 Hz, C=**CH**Cl); low-resolution mass spectrum, (m/e) parent peak 118 ($C_6H_{11}{}^{35}Cl$).

From 3c. Chlorination of **3c** was carried out by the general halogenation procedure except that carbon tetrachloride was used as the solvent and the temperature was maintained at 0 °C. Normal workup gave the crude dichloride as a slightly yellow liquid: NMR (CCl_4) δ 0.00 (s, 9 H, $\mathbf{CH_3}_3Si$), 0.90 (s, 9 H, $\mathbf{CH_3}_3C$), 3.29 (d, 1 H, J = 6.5 Hz, **CH**ClSi), and 4.00 (d, 1 H, J = 6.5 Hz, **CH**ClCClSi).

Elimination of the crude dichloride by the general sodium methoxide–methanol procedure gave in 82% GLC yield (*n*-octane as internal standard) 1-chloro-3,3-dimethyl-1-butene with an isomeric ratio of 99% cis–1% trans. The GLC and spectral characteristics of this product were identical to those of the vinyl chloride obtained from **2c**.

(f) *cis*-1-Bromo-3,3-dimethyl-1-butene (Table IV). From 2c. By the general halogenation procedure, **2c** was brominated to give the dibromide in 96% yield as a slightly yellow solid: mp 45–56 °C; NMR (CCl_4) δ 0.00 (s, 9 H, $\mathbf{CH_3}_3Si$), 0.92 (s, 9 H, $\mathbf{CH_3}_3C$), 3.51 (d, 1 H, J = 2 Hz, **CH**BrSi), and 3.83 (d, 1 H, J = 2 Hz, **CHBr**CBrSi).

Elimination of the crude dibromide by the general potassium fluoride dihydrate–dimethyl sulfoxide procedure described earlier gave in 70% yield (96% GLC yield using *n*-nonane as internal standard) 1-bromo-3,3-dimethyl-1-butene with an isomeric ratio of 99% cis–1% trans (GLC analysis on 5 ft 20% SF-96 on Chromosorb Q): bp 60–64 °C (119 Torr); IR (neat) 1614, 1220, 900, 843, 770, 700, and 694 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 1.11 (s, 9 H, $\mathbf{CH_3}_3C$), 5.88 (d, 1 H, J = 8.5 Hz), and 6.07 (d, 1 H, J = 8.5 Hz); high-resolution mass spectrum, calcd (m/e for P − CH_3) for $C_6H_{11}{}^{79}Br(P)$ 146.9810, found 146.9810.

From 3c. Bromination of **3c** was carried out by the general halogenation procedure except that carbon tetrachloride was used as the solvent and the temperature was maintained at 0 °C. Normal workup gave the crude dibromide as a slightly yellow liquid: NMR (CCl_4) δ 0.00 (s, 9 H, $\mathbf{CH_3}_3Si$), 0.87 (s, 9 H, $\mathbf{CH_3}_3C$), 3.37 (d, 1 H, J = 4.5 Hz, **CHBr**Si), and 4.38 (d, 1 H, J = 4.5 Hz, **CHBr**CBrSi).

Elimination of the crude dibromide by the general sodium methoxide–methanol procedure gave in 31% yield (58% GLC yield using *n*-nonane as internal standard) 1-bromo-3,3-dimethyl-1-butene with an isomeric ratio of 87% cis–13% trans. Spectral and GLC character-

istics were identical to those of the vinyl bromide obtained from **2c**.

General Procedure for Preparation of β-Halostyrenes (Table IV). To a magnetically stirred solution of the β-styryl(trimethyl)silane (**2d** or **3d**, 0.020 mol) in methylene chloride (10 mL) which had been cooled to −78 °C was added dropwise a solution of halogen in methylene chloride (3 M for bromine and saturated for chlorine) until the first persistence of halogen color. The mixture was then pumped on under vacuum (0.5–1.5 Torr) while maintaining the temperature at −78 °C until the halogen color disappeared and a viscous residue remained. To this residue still at −78 °C was added 1 M sodium methoxide in methanol (30 mL, 0.030 mol, 1.5 equiv) and the solution was allowed to warm up to room temperature. After an additional 3 h of stirring, the mixture was partitioned between 10% sodium sulfite solution and pentane and the layers separated. The aqueous layer was extracted with fresh pentane and the combined organic fractions were dried over anhydrous sodium sulfate. Removal of the solvent in vacuo afforded a yellow residue which was distilled at reduced pressure to yield the β-halostyrene.

(a) *cis*-β-Chlorostyrene (Table IV). By the general procedure described above, **2d** was chlorinated and eliminated in 58% yield to β-chlorostyrene with an isomeric ratio of 90% cis–10% trans (GLC analysis on 5 ft 20% SF-96 on Chromosorb Q): bp 44–45 °C (1 Torr) [lit.[30] bp 59 °C (3.5 Torr)]; IR (neat) 1613, 850, 778, 728, and 695 cm^{-1}; NMR[31] (CCl_4, internal Me_4Si) δ 6.15 (d, 1 H, J = 9 Hz, C=**CH**Cl), 6.53 (d, 1 H, J = 9 Hz, **CH**=CCl), and 7.00–7.93 (m, 5 H, aromatic H); high-resolution mass spectrum, calcd (m/e) for $C_8H_7{}^{35}Cl$ 138.0237, found 138.0214. The GLC analysis also indicated a 10% impurity attributed to α-chlorostyrene.

(b) *cis*-β-Bromostyrene (Table IV). By the general procedure described above, **2d** was brominated and eliminated in 94% yield to β-bromostyrene with an isomeric ratio of 96% cis–4% trans (GLC analysis on 5 ft 20% SF-96 on Chromosorb Q): bp 49–52 °C (1 Torr); IR (neat) 1610, 940, 735, and 694 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 6.25 (d, 1 H, J = 8.5 Hz, C=**CH**Br), 6.89 (d, 1 H, J = 8.5 Hz, **CH**=CBr), and 7.06–7.92 (m, 5 H, aromatic H). The products were identical by comparison with authentic samples.[15] The GLC also indicated a 5% impurity attributed to α-bromostyrene.

(c) *trans*-β-Chlorostyrene (Table IV). By the general procedure described above, **3d** was converted in 66% yield to β-chlorostyrene with an isomeric ratio of 92% trans–8% cis (GLC analysis on 5 ft 20% SF-96 on Chromosorb Q): bp 48–52 °C (1.5 Torr) [lit.[32] bp 83–86 °C (19 Torr)]; IR (neat) 1610, 940, 860, 815, 745, and 698 cm^{-1}; NMR[31] (CCl_4, internal Me_4Si) δ 6.53 (d, 1 H, J = 14 Hz, C=**CH**Cl), 6.80 (d, 1 H, J = 14 Hz, **CH**=CCl), and 7.21 (s, 5 H, aromatic H); high-resolution mass spectrum, calcd (m/e) for $C_8H_7{}^{35}Cl$ 138.0237, found 138.0211. The GLC analysis also indicated a 4% impurity attributed to α-chlorostyrene.

(d) *trans*-β-Bromostyrene (Table IV). By the general procedure described above, **3d** was converted in 99% yield to β-bromostyrene with an isomeric ratio of 99% trans–1% cis (GLC analysis on 5 ft 20% SF-96 on Chromosorb Q): bp 87–90 °C (5.5 Torr); IR (neat) 1610, 945, 740, and 698 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 6.52 (d, 1 H, J = 14 Hz, C=**CH**Br), 6.94 (d, 1 H, J = 14 Hz, **CH**=CBr), and 7.13 (s, 5 H, aromatic H). The products were identical by comparison with authentic samples.[13] The GLC analysis also indicated a 5% impurity attributed to α-bromostyrene.

***trans*-3,3-Dimethyl-1-iodo-1-butene (Scheme IV).**[26] To a solution of *tert*-butylacetylene (4.12 g, 0.050 mol) in *n*-hexane (20 mL) at 0 °C was added over a 20 min period 5.4 M diisobutylaluminum hydride (9.25 mL, 0.050 mol). After maintaining the temperature at 0 °C for 1 h, the mixture was allowed to warm to room temperature and stirred an additional 4 h. Solvent was removed in vacuo (1.5 Torr), tetrahydrofuran (35 mL) was added, and the mixture was cooled to −78 °C. A solution of iodine (12.7 g, 0.050 mol) in tetrahydrofuran (25 mL) was added dropwise at a rate such that the temperature remained below −60 °C. Then the mixture was warmed to 0 °C and poured into an efficiently stirred slurry of 20% sulfuric acid (100 mL) which had been precooled to ca. −40 °C. After warming to room temperature, sodium thiosulfate was added until the solution was decolorized. The layers were separated and the aqueous layer thoroughly washed with 1 N sodium hydroxide solution and saturated sodium chloride and dried over anhydrous sodium sulfate. After removal of solvent by atmospheric distillation, the residue was vacuum distilled to give colorless product (6.25 g, 60% yield): bp 70–72 °C (59 Torr); IR (neat) 1598, 955, 765, and 685 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 1.00 (s, 9 H, $(\mathbf{CH_3})_3C$), 5.90 (d, 1 H, J = 14 Hz), and 6.50 (d, 1 H, J = 14 Hz); high-resolution mass spectrum calcd (m/e) for $C_6H_{11}I$ 209.9906, found 209.9891.

***trans*-1-Chloro-3,3-dimethyl-1-butene (Scheme IV).** To a solution of the *trans*-vinyl iodide (1.62 g, 0.0077 mol) prepared above in ether (15 mL) at −78 °C was added 1.67 M *n*-butyllithium (5.09 mL, 0.0085 mol, 1.1 equiv) at such a rate that the temperature remained below −60 °C and the mixture was stirred for 1 h. While still at −78 °C, chlorine gas was bubbled directly into the mixture, first becoming cloudy then quickly turning bright yellow-green. The mixture was shaken with 10% sodium sulfite solution and separated, and the aqueous layer was extracted with fresh ether. The combined organic extracts were washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. The solvent was removed by careful atmospheric distillation through a 25-cm glass helices packed column and the crude vinyl chloride was purified by preparative GLC (10% SF-96 on Chromosorb Q): IR (neat) 1610, 945, 825, and 760 cm^{-1}; NMR (CCl_4, internal Me_4Si) δ 1.05 (s, 9 H, $(\mathbf{CH_3})_3C$) and 5.88 (s, 2 H, **CH**=**CH**); low-resolution mass spectrum, (m/e) parent 118 ($C_6H_{11}{}^{35}Cl$).

***trans*-1-Bromo-3,3-dimethyl-1-butene (Scheme IV).** To a stirred solution of the *trans*-vinyl iodide (1.00 g, 0.0048 mol) in ether (10 mL) at −78 °C was added 1.45 M *n*-butyllithium (3.62 mL, 0.0053 mol, 1.1 equiv) at such a rate that the temperature remained below −60 °C and the mixture was stirred for 1 h. While still at −78 °C, bromine (1.14 g, 0.0072 mol, 1.5 equiv) was slowly added and the solution was stirred for an additional hour then allowed to warm to 0 °C. The reaction mixture was shaken with 10% sodium sulfite solution, the layers separated, and the aqueous layer extracted thoroughly with fresh ether. The combined organic extracts were washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. The solvent was removed by atmospheric distillation through a 25-cm glass helices packed column and the crude vinyl bromide was purified by preparative GLC (10% SF-96 on Chromosorb Q): NMR (CCl_4, internal Me_4Si) δ 1.07 (s, 9 H, $(\mathbf{CH_3})_3C$), 5.98 (d, 1 H, J = 14 Hz), and 6.24 (d, 1 H, J = 14 Hz).

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Registry No.—*trans*-1-chloro-1-hexene, 50586-19-1; *cis*-1-chloro-1-hexene, 50586-18-0; *trans*-1-bromo-1-hexene, 13154-13-7; *cis*-1-bromo-1-hexene, 13154-12-6; *trans*-1-chloro-2-cyclohexylethylene, 67404-71-1; *trans*-1-bromo-2-cylohexylethylene, 67478-59-5; *cis*-1-chloro-2-cyclohexylethylene, 67404-70-0; *cis*-1-bromo-2-cyclohexylethylene, 42843-50-5; *cis*-1-chloro-3,3-dimethyl-1-butene, 18314-61-9; *threo*-(1,2-dichloro-3,3-dimethylbutyl)trimethylsilane, 67478-60-8; *cis*-1-bromo-3,3-dimethyl-1-butene, 66070-32-4; *threo*-(1,2-dibromo-3,3-dimethylbutyl)trimethylsilyl, 67478-61-9; *cis*-β-chlorostyrene, 4604-28-8; *cis*-β-bromostyrene, 588-73-8; *trans*-β-chlorostyrene, 4110-77-4; *trans*-β-bromostyrene, 588-72-7; *trans*-3,3-dimethyl-1-iodo-1-butene, 61382-45-4; *trans*-1-chloro-3,3-dimethyl-1-butene, 18314-62-0; *trans*-1-bromo-3,3-dimethyl-1-butene, 38203-90-6; 1-hexyne, 693-02-7; cyclohexylacetylene, 931-48-6; *tert*-butylacetylene, 917-92-0; phenylacetylene, 536-74-3; chlorotrimethylsilane, 75-77-4; chlorodimethylsilane, 1066-35-9; *threo*-(1,2-dichloro-2-cyclohexylethyl)trimethylsilane, 67478-62-0; *threo*-(1,2-dibromo-2-cyclohexylethyl)trimethylsilane, 67478-63-1; *erythro*-(1,2-dichloro-2-cyclohexylethyl)trimethylsilane, 67478-64-2; *erythro*-(1,2-dibromo-2-cyclohexylethyl)trimethylsilane, 67478-65-3; *erythro*-(1,2-dichloro-3,3-dimethylbutyl)trimethylsilane, 67478-66-4; *erythro*-(1,2-dibromo-3,3-dimethylbutyl)trimethylsilane, 67478-67-5.

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2-Carbomethoxy-1,3-butadiene: A Convenient Synthesis of a Stable Precursor and a Survey of Its Diels–Alder Reactions[1]

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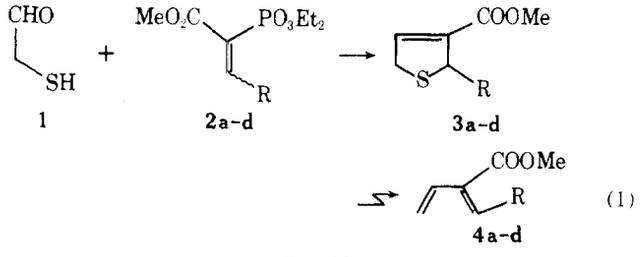
A facile synthesis of 3-carbomethoxy-2,5-dihydrothiophene sulfone (**3a**) and some 2-substituted derivatives is reported. The materials decompose thermally into sulfur dioxide and conjugated dienes. The Diels–Alder reactions of 2-carbomethoxy-1,3-butadiene appear to proceed well only with electron-deficient dienophiles, but ^{13}C NMR indicates that in most cases the products are a mixture of regioisomers.

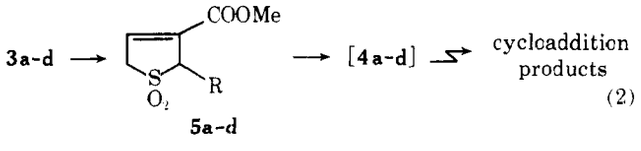
We have recently reported[2] a procedure which allows the rapid assembly of 3-carboxylated 2,5-dihydrothiophenes in high yield and have shown that these are excellent precursors to substituted 1,3-butadienes which carry an ester function at the interior position of the diene system. Notable omissions from the compounds described[2] were those derived from α-mercaptoacetaldehyde (1) and in particular the parent compound **3a** (eq 1). Using the previously described conditions



(1)

a, R = H
b, R = Ph
c, R = c-C_6H_{11}
d, R = *n*-C_4H_7

(refluxing pyridine, triethylamine solution), 1 consistently refused to provide dihydrothiophenes in acceptable yields. This omission was especially unfortunate as diene **4a** is reported[3] to be very unstable and the possibility of storing **4a** as the sulfone **5a** which would undergo chelatropic sulfur dioxide elimination (eq 2) under the conditions required for



(2)

Diels–Alder cycloaddition was a distinctly attractive possibility. Goldberg and Dreiding[4] have recently reported the synthesis of **4a** by another method, but we report here the simple solution to the synthesis of **3a** and the reaction of **4a** with some representative dienophiles.

Results and Discussion

A. Dihydrothiophene Synthesis and Oxidation. Prior work on the condensation of vinylphosphonates[2] and vinylphosphonium salts[5] with α-mercaptocarbonyl compounds had utilized pyridine as solvent to provide the required base and to facilitate dissolution of the reactants. Other related reactions have employed phase-transfer conditions.[6] Neither of these procedures produced acceptable amounts of products when **1** was employed. After extensive experimentation, it was found that the simple expedient of using dichloromethane containing triethyl amine as the reaction medium afforded excellent yields of **3**. The reaction mixture is initially heterogeneous but becomes homogeneous as the reaction proceeds. The same method works well for other α-mercaptoaldehydes, but not ketones. In some cases, using homologues of **1**, the yields using the present procedure were marginally lower than when pyridine was used, but the products required substantially less purification. The compounds prepared using **1** are shown in Table I.

The oxidation of **3** to sulfones **5** was carried out by the previously reported method.[7] Decomposition of these on a gas chromatograph afforded sulfur dioxide and diene as the only volatile products.

B. Diels–Alder Reactions of 2-Carbomethoxy-1,3-butadiene (4a). Sulfone **5a** is a stable crystalline compound. When it is heated in refluxing toluene, a moderately rapid evolution of sulfur dioxide occurs. In the absence of added dienophile a high yield of dimethyl 4-vinylcyclohexene-1,4-dioate (**6**)[8] is formed. No sign of isomeric materials could be

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