(*E*)- and (*Z*)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-2-butenes: Synthetic Equivalents for the 1-(1,3-Butadienyl) Anion and the 1,1-(1,3-Butadienyl) Dianion

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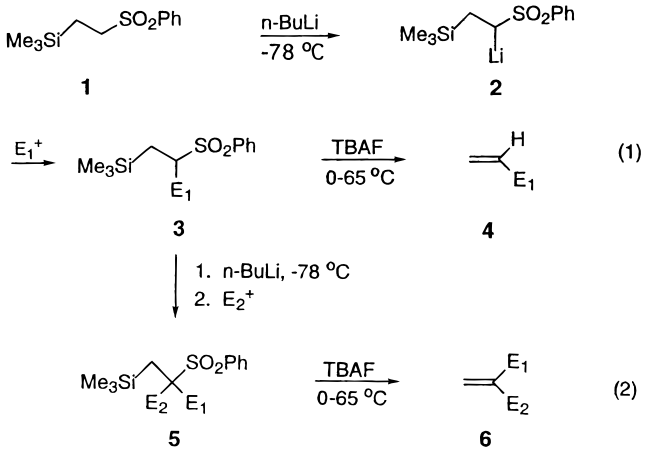
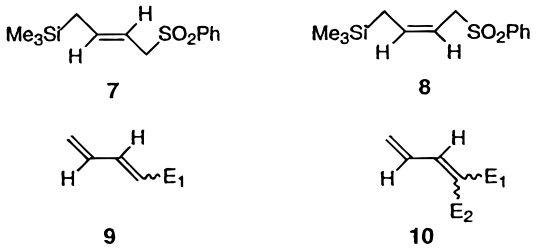
(*E*)- and (*Z*)-1-(phenylsulfonyl)-4-(trimethylsilyl)-2-butenes (**7** and **8**) are converted by *n*-BuLi to (*E*)- and (*Z*)-1-lithio-1-(phenylsulfonyl)-4-(trimethylsilyl)-2-butenes (**15** and **16**) with retention of initial stereochemistries. Reactions of **15** and **16** with electrophiles (protio and deuterio acids, primary, secondary, and benzyl halides, chloroformates, chlorothioformates, acid chlorides, epoxides, trialkylsilyl chlorides, and triethylgermanyl chloride) in THF or THF/HMPA give the corresponding (*E*)- and (*Z*)-1-(phenylsulfonyl)-1-substituted-4-(trimethylsilyl)-2-butenes (**32**) with stereochemical retention. That β,γ-unsaturated silyl sulfones **32** are formed instead of their α,β-unsaturated (conjugated) isomers are attributed to stabilizing multiple anionic and cationic hyperconjugation and to steric effects as in **29**−**31**. Of importance in synthesis is that **32** are eliminated by TBAF at −20 to 0 °C, thermally, or by column chromatography to (*E*)- (100 to > 93%) rather than (*Z*)-1-substituted-1,3-butadienes (**38**). Further, **32** undergo conversions by *n*-BuLi and various alkylating agents to (unconjugated) 1-(phenylsulfonyl)-1,1-disubstituted-4-(trimethylsilyl)-2-butenes (**46**) with retention of stereochemistry. Eliminations of **46** by fluoride ion, acid catalysis, or heat yield 1,1-disubstituted-1,3-butadienes (**53**). Silyl sulfones **7** and **8** are thus synthetic equivalents for the (*E*)-1-(1,3-butadienyl) anion (**44**) and the 1,1-(1,3-butadienyl) dianion (**57**). Silyl sulfones **7** and **8** also undergo efficient stereospecific intramolecular conversions by *n*-BuLi and α,ω-dihalides to 1,1-cycloalka-1-(phenylsulfonyl)-4-(trimethysilyl)-2-butenes (**62** and **71**) that are eliminated by fluoride ion, heat, or adsorption chromatography to 1,1-cycloalka-1,3-butadienes (**72**).

Introduction

Vicinal silylsulfonylethanes **3** and **5** (eqs 1 and 2), readily prepared from 1-(phenylsulfonyl)-2-(trimethylsilyl)ethane (**1**), *n*-BuLi, and electrophiles, are of value because fluoride ion effects their eliminations to 1-substituted and 1,1-disubstituted ethenes **4** and **6**, respectively, at 0−65 °C.[1] In further development of advantageous desulfonylsilylation methodology, syntheses and various substitution and elimination reactions of (*E*)- and (*Z*)-1-(phenylsulfonyl)-4-(trimethylsilyl)-2-butenes (**7** and **8**) to give 1-substituted and 1,1-disubstituted 1,3-butadienes **9** and **10** are now described.[2] The objective of this program is to develop advantageous methodology for preparing functionally substituted conjugated dienes.





Results and Discussion

Silylsulfonylbutenes **7** and **8** (eq 3) are prepared in 41−62% yields by (1) addition of [(trimethylsilyl)methyl]-magnesium chloride (**11**) to acrolein and acidification to give 4-(trimethylsilyl)-1-buten-3-ol (**12**, 68%),[3a] (2) deprotonation of **12** by *n*-BuLi and displacement of phenylsulfenyl chloride at −78 °C to produce (*E*)- and (*Z*)-(silylsulfinyl)-2-butenes **14** (70−85%)[3b] via 2,3-sigmatropic rearrangements of phenylsulfenate intermediate **13**, and (3) oxidation of sulfoxides **14** (77−85%) with MCPBA in

(1) (a) Kocienski, P. J. *Tetrahedron Lett.* **1979**, 2649. (b) Kocienski, P. J. J. *Org. Chem.* **1980**, *45*, 2037. (c) Hsiao, C.-N.; Shechter, H. *Tetrahedron. Lett.* **1982**, 3455. (d) Eisch, J. J.; Behrooz, M.; Dua, S. K. J. *Organomet. Chem.* **1985**, *285*, 121. (*E*) Hsaio, C.-N.; Shechter, H. *J. Org. Chem.* **1988**, *53*, 2688. (f) Kim, S. H.; Jin, Z.; Ma, S.; Fuchs, P. L. *Tetrahedron Lett.* **1995**, 4013 and references therein.

(2) (a) The initial results of the present study were communicated by the following: Hsiao, C.-N.; Shechter, H. *Tetrahedron Lett.* **1984**, *25*, 1219. (b) The possible utility of tetrabutylammonium triphenyldifluorosilicate [$Bu_4N(C_6H_5)_3SiF_2$] for elimination of **3**, **5**, **32**, and **6** has as yet not been determined.[2c,d] (c) Pilcher, A. S.; Ammon, H. J.; DeShong, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 5166. (d) Pelcher, A. S.; DeShong, P. J. *Org. Chem.* **1996**, *61*, 6901.

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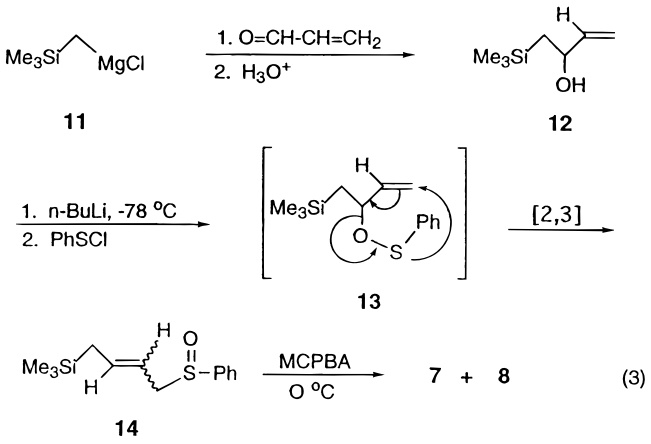
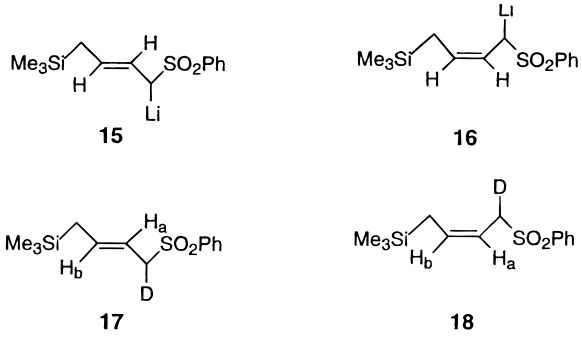
methylene chloride at 0 °C. The *E*:*Z* ratios of **7** and **8** usually range from 77:23 to 88:12. If needed, chromatography allows separation of pure **7** from mixtures of **7** and **8**.



n-BuLi (1 equiv) in THF converts **7** and **8** at −78 °C to lithio derivatives **15** and **16** which, when warmed to 20−25 °C for ∼30 min and quenched with D_2O (1 equiv), give deuterio derivatives **17** and **18** in 85% yield. If **15** and **16** in THF are kept at 25 °C for 3.3 h before deuteration, considerable decomposition occurs and the yields of deuterio products **17** and **18** are reduced to 47%. Lithio derivatives **15** and **16** are stable for only short periods at higher temperatures.

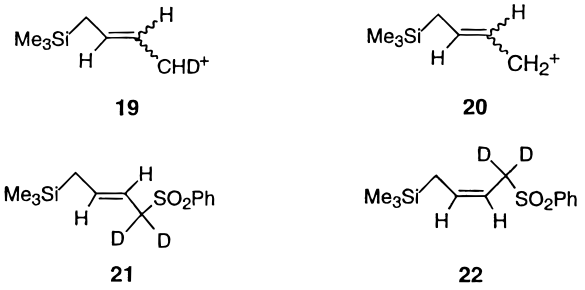


The structures, stereochemistries, and deuterium contents of **17** and **18** were determined by spectral methods. The proton-decoupled ^{13}C NMR of **17** and **18** has distinct sets of absorptions for each isomer. The ratios of the peak heights for comparable carbon atoms in the mixtures of **17** and **18** obtained from **7** (77%) and **8** (23%) range from 77:23 to 83:17. The ^1H NMR of **17** and **18** at 250 MHz reveals absorptions at δ 5.56 and 5.76, respectively, and couplings between H_b and H_a of 15.2 and 10.7 Hz, respectively. The *E*:*Z* ratio of **17** and **18** found by ^1H NMR is 79:21 and agrees with that determined by ^{13}C NMR. There is no significant change in the positions of and the stereochemistries about the carbon−carbon double bonds upon conversions of **7** and **8** to deuterio derivatives **17** and **18**.

(3) (a) Prepared initially by Sommer, L. H.; Goldberg, G. M.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 481. (b) The concentration of chloromethyltrimethylsilane in Et_2O or THF greatly affects the yield of **9** upon reaction with magnesium. When the (chloromethyl)trimethylsilane is ∼3.33 M, the yield of **9** is ∼95%. Under very dilute conditions, the yield of **9** is greatly lowered. (b) Phenylsulfenyl chloride should be added slowly so as to maintain the reaction temperature below −60 °C. At higher temperatures side products are formed which reduce the yield and make purification of **12** difficult.

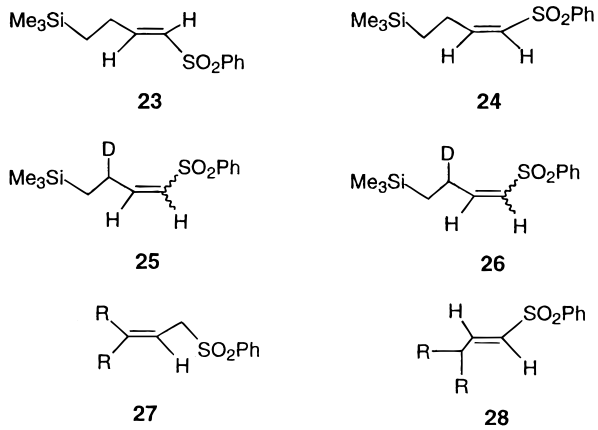
Incorporation of a single deuterium atom into the α-positions of **7** and **8** was determined to be ∼87% by comparing the area of the deuterium-coupled ^1H NMR doublet in the δ 3.75 region with that for trimethylsilyl ($\delta = 0.00$). High-resolution mass spectral analyses of **19** and **20** resulting from loss of phenylsulfinate ions in **17** and **18** reveal that the cations are formed in a ratio of 84:16 which agrees closely with the 87:13 deuterium value obtained from the ^1H NMR peak area integrations.

(*E*)- and (*Z*)-silyl sulfones **7** and **8** were then dideuterated with D_2O as follows. First, **7** and **8** were deprotonated with *n*-BuLi in THF at −78 °C. The solution was warmed slowly to room temperature, quenched with excess D_2O, and then worked up after 12.5 h. The only products detected are 1,1-dideuterio-2-butenes **21** and **22** in 89% yield. Dideuteration of the α-positions in **7** and



8 is apparent from inspection of the δ 3.7 regions of the ^1H NMR spectra of **21** and **22** which show only small (<5%) residual H absorptions. Dideuteration obviously arises after deprotonation of **17** and **18** by the lithium deuteroxide generated in quenching of **15** and **16**. Further illustration of rapid protium−deuterium exchange in which carbon−carbon double bonds do not move into conjugation with phenylsulfonyl groups is that dideuteriosilyl sulfones **21** and **22** are converted by H_2O/LiOH/THF to silyl sulfones **7** and **8** of natural deuterium abundances within 16 h.

The facts that the unconjugated silylsulfonyl-2-butenes **7** and **8** do not rearrange significantly to their conjugated sulfone isomers, (*E*)- and (*Z*)-1-butenes **23** and **24**, or undergo deuterium incorporation to form (*E*)- and (*Z*)-3-deuterio-1-butenes **25** and (*E*)- and (*Z*)-3,3-dideuterio-1-butenes **26** raise significant points. β,γ-Unsaturated



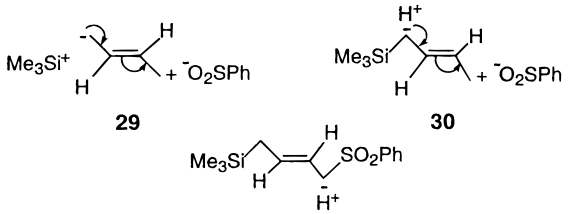
(nonconjugated) sulfones **27** are more stable than their α,β-unsaturated (conjugated) isomers **28**.[4] Hine et al. have suggested that **28** are not highly stabilized because sulfonyl groups are weak conjugaters.[4] Now emphasized,

Table 1. Reactions of 1-Lithio Derivatives 15 and 16 of (*E*)- and (*Z*)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-2-butenes (7 and 8) with Electrophiles (eq 4)

Entry	7 and 8, E/Z Ratio[a]	Electrophile	Product, Eq 4 E_1=	Yield(%)[b]	E/Z Ratio[a]
1	98:2	CH_3I	**32a**, CH_3	97	98:2
2	80:20	$C_6H_5CH_2Br$	**32b**, $CH_2C_6H_5$	99	79:21
3	98:2	*n*-$C_5H_{11}Br$	**32c**, *n*-C_5H_{11}	99	96:4
4	72:28	$(CH_3)_2CHCH_2Br$[c]	**32d**, $CH_2CH(CH_3)_2$	83	75:25
5	98:2	$(CH_3)_2CHBr$[c]	**32e**, $CH(CH_3)_2$	97	98:2
6	77:23	C_2H_5OCOCl	**32f**, $CO_2C_2H_5$	67	83:17
7	86:14	C_2H_5SCOCl	**32g**, $COSC_2H_5$	45	79:21
8	77:23	$(CH_3)_3CCOCl$	**32h**, $COC(CH_3)_3$	75	72:28
9	80:20	C_6H_5COCl	**32i**, COC_6H_5	64	∞
10	70:30		**32j**, 	83	*d*
11	70:30		**32k**, $CH_2CH(OH)CH_3$	59	*d*
12	70:30		**32l**, $CH_2CH(OH)C_2H_5$	52	*d*
13	70:30		**32m**, $CH_2CH(OH)C_6H_5$	54	*d*
14	77:23	$(C_2H_5)_3GeCl$	**32n**, $Ge(C_2H_5)_3$	35	82:18
15	55:45	$(CH_3)_3SiCl$	**32o**, $Si(CH_3)_3$	51	52:48
16	77:23	$[(CH_3)_2CH]_3SiCl$	**32p**, $Si[CH(CH_3)_2]_3$	33	∞

[a] The *E*/*Z* ratios were calculated from ^{1}H NMR as described in the text. [b] Yields of isolated products. [c] Reactions were conducted in THF/HMPA. [d] The stereochemistries of the products are unknown.

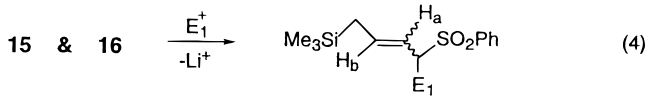
in addition to steric effects, are that important factors in the greater thermodynamic stabilities of **7** and **8** over **23** and **24** are multiple anionic and cationic hyperconjugation as illustrated in part in **29**−**31**.[5] Similar significant hyperconjugative effects may be operational in **17**, **18**, **21**, **22**, and **27** and in other β,γ-unsaturated systems.[5]



29 **30**

31

Study was then made of reactions of lithio derivatives **15** and **16** with electrophiles to give (*E*)- and (*Z*)-1-substituted-2-butenes **32** (eq 4). Methyl iodide and benzyl bromide (Table 1, entries 1 and 2) alkylate **15** and **16** efficiently at C-1 at −78 °C in THF to give (*E*)- and (*Z*)-2-pentenes **32a** and (*E*)- and (*Z*)-5-phenyl-2-pentenes **32b**, respectively. The yellow colors of solutions of lithio



32 (4)

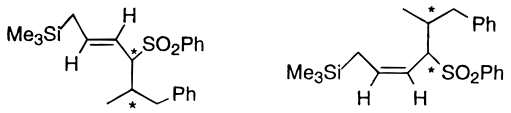
reagents **15** and **16** are discharged within 1 min after addition of the alkyl halides, and the yields of **32a** and **32b** are excellent. 1-Bromopentane (Table 1, entry 3) reacts much slower than the previous halides at −78 °C in THF to yield (*E*)- and (*Z*)-2-nonenes **32c**. HMPA accelerates alkylation of 1-bromopentane at −78 °C. Increases in the reaction temperatures (−20 to 23 °C) result however in significant decomposition of **15** and **16** and lower yields of alkylation products **32c**. Reactions of **15** and **16** with 1-bromo-2-methylpropane (Table 2, entry 4), a slightly hindered halide, occur satisfactorily in THF/HMPA at −78 °C to produce (*E*)- and (*Z*)-2-heptenes **32d**. Synthesis of 1-substituted 2-butenes **32** (E_1 = alkyl) from sodio analogues of **15** and **16** prepared from reactions of **7** and **8** with sodium hydride or sodium amide in THF is unsatisfactory. The insolubilities of these bases in THF limit deprotonations of **7** and **8** to temperatures of 0 °C and above, and under such conditions, thermal decompositions of sodio analogues of **15** and **16** become excessive.

Table 2. Fluoride Ion Eliminations (eq 5) of (*E*)- and (*Z*)-1-(Phenylsulfonyl)-1-substituted-4-(trimethylsilyl)-2-alkenes (32−35)

Entry	Substrate, E=	E/Z Ratio[a]	Product, Eq 5 E_1=	Yield(%)[b]	E/Z Ratio[c]
1	**32a**, CH_3	98:2	**38a**, CH_3	76	>98:2
2	**32b**, $CH_2C_6H_5$	79:21	**38b**, $CH_2C_6H_5$	52	>99:1
3	**32d**, $CH_2CH(CH_3)_2$	75:25	**38d**, $CH_2CH(CH_3)_2$	63	>93:7
4	**32e**, $CH(CH_3)_2$	98:2	**38e**, $CH(CH_3)_2$	85	>98:2
5	**32f**, $CO_2C_2H_5$	83:17	**38f**, $CO_2C_2H_5$	51	∞
6	**32h**, $COC(CH_3)_3$	72:28	**38h**, $COC(CH_3)_3$	74	∞
7	**32i**, COC_6H_5	100:0	**38i**, COC_6H_5	66	∞
8	**32j**, 	*d*	**38j**, 	83	>99:1
9	**32k**, $CH_2CH(OH)CH_3$	*d*	**38k**, $CH_2CH(OH)CH_3$	76	∞
10	**32l**, $CH_2CH(OH)C_2H_5$	*d*	**38l**, $CH_2CH(OH)C_2H_5$	88	∞
11	**32m**, $CH_2CH(OH)C_6H_5$	*d*	**38m**, $CH_2CH(OH)C_6H_5$	57	∞
12	**32p**, $Si[CH(CH_3)_2]_3$	100:0	**38p**, $Si[CH(CH_3)_2]_3$	61	∞
13	**33,34**, $CH(CH_3)CH_2C_6H_5$	*d*	**38q**, $CH(CH_3)CH_2C_6H_5$	78	>96:4
14	**35**, c-C_6H_{11}	85:15	**36**, c-C_6H_{11}	57	>99:1

[a] The *E*/*Z* ratios were determined from ^{1}H NMR as described in the text. [b] Yields of isolated products. [c] The *E*/*Z* ratios were determined by high-field ^{1}H and ^{13}C NMR methods. [d] The stereochemistries of **32j**−**m**, **33**, and **34** are unknown.

Alkylations of **15** and **16** by 2-bromopropane, a secondary halide (Table 1, entry 5), in THF/HMPA yield (*E*)- and (*Z*)-2-hexenes **32e** (97%). The more hindered secondary bromide, 2-bromo-1-phenylpropane, behaves as expected in that diastereomeric substitution products (*E*)- and (*Z*)-2-hexenes **33** and **34** (40%) are formed along with



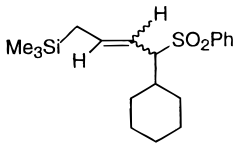
33 **34**

(*E*)-1-phenyl-1-propene (26%) and **7** and **8** (33%). Further, bromocyclohexane and cyclohexyl tosylate are displaced by **15** and **16** to give (*E*)- and (*Z*)-1-cyclohexyl-2-butenes **35** slowly and inefficiently (35−27%). During reactions of bromocyclohexane with **15** and **16**, **35** is converted in part to (*E*)-1-cyclohexyl-1,3-butadiene (**36**,

(4) (a) Hine, J.; Linden, S.-M.; Wang, A.; Thiagarajan, V. *J. Org. Chem.* **1980**, *45*, 2821. (b) Hine, J.; Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 4766. The equilibrium constant, K_1, for *trans*-*n*-butyl 2-butenyl sulfone/*trans*-*n*-butyl 1-butenyl sulfone in *t*-BuOH at 25 °C is 40 ± 15; $-\Delta G$ = 2.2 ± 0.3 kcal/mol.

(5) (a) Only a portion of the cationic hyperconjugative forms involving Me_3Si^+ and H^+ and anionic hyperconjugative forms involving $^-O_2S-Ph$ has been illustrated. This concept will be developed further in publications from this laboratory. (b) Baker, J. W. *Hyperconjugation*; Oxford University Press: London E.C., 1952; Vol. 4, p 58. (c) Shechter, H.; Shepherd, J. W. *J. Am. Chem. Soc.* **1954**, *76*, 2716.

13%), **7** and **8** (7−30%), and cyclohexene and much of the bromocyclohexane is recovered. Attempts to improve coupling of secondary halides with **15** and **16** by addition of cupric chloride or cuprous iodide give complex product mixtures.



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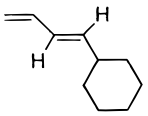

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The *E*:*Z* ratios of **32a**, **32c**, and **32d** (eq 4, Table 1) have been determined by high-field ^{1}H NMR methods. The H_b absorptions of the *Z*-isomers of the above product pairs are doublets of triplets at δ 5.0−5.2 and couple to H_a by ∼9 Hz. For the corresponding *E*-isomers, the resonances of H_b are doublets at δ 5.55 which are coupled by ∼13 Hz to H_a. The stereochemistries of **32b**, **32e**, and **35** cannot be designated directly because their olefinic ^{1}H NMR absorptions are not adequately resolved. The structures are assignable however by ^{13}C NMR on the premise that the *E*-isomer of a product pair obtained from **7** and **8** is always major. Of further importance in alkylations and cycloalkylations of **15** and **16** (Table 1) is that the stereochemistries of the products are essentially identical with those of initial **7** and **8**. Such retentions in the geometries of highly conjugated allylic anionic systems have been previously observed in base-catalyzed α-alkylations of (*E*)- and (*Z*)-3-alkenoate esters[6] and of (*E*)-1-phenylsulfonyl-2-pentene.[6]

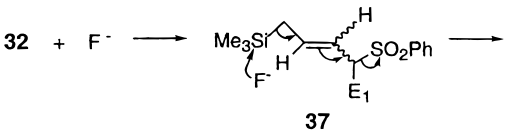
Reactions of acid chlorides with lithio derivatives **15** and **16** are satisfactory. Additions of ethyl chloroformate, ethyl chlorothioformate, and trimethylacetyl chloride (Table 1, entries 6−8) to **15** and **16** in THF at −78 °C result in rapid displacements to give 1-carbalkoxy-, 1-carbothioalkoxy-, and 1-acyl-2-butenes **32f**, **32g**, and **32h**, respectively, in 45−75% yields. Each product pair exhibits two sets of ^{13}C NMR (63 MHz) absorptions, one set for each geometrical isomer. The *E*:*Z* ratio of **32f** (Table 1) is determined after integration of the $(CH_3)_3Si$ ^{1}H NMR singlets at δ 0.06 (*Z*) and −0.01 (*E*) or the α-silylmethylene hydrogen doublets at δ 1.48 (J = 7.0 Hz, *Z*) and 1.55 (J = 7.4 Hz, *E*). Similarly, the *E*:*Z* ratio of **32g** (Table 1) is obtained upon integration of the doublets at δ 4.56 (J = 8.5 Hz, *E*) and 4.80 (J = 8.5 Hz, *Z*). Of value is that **32h** separates cleanly on column chromatography to give its (*E*)- and (*Z*)-isomers in 59 and 16% yields, respectively. Further, the *E*:*Z* ratios (Table 1) of **32g**−**h** are similar to those of the **7** and **8** used in the preparations and thus there are no significant stereochemical changes in the above transformations of lithio derivatives **15** and **16** (eq 4). The silylsulfonyl-3-penten-1-one **32i** (Table 1, entry 9) obtained from **15** and **16** (80:20) and benzoyl chloride is a single isomer however and is presumed to be of *E*-stereochemistry. The reason **32i** is the exclusive product of benzoylation of **15** and **16** has not been established.[7]

Reactions of lithio reagents **15** and **16** with epoxides were then developed. Cyclohexene oxide (Table 1, entry 10) is ring-opened by **15** and **16** in Et_2O at −78 °C to give cyclohexanols **32j** in 83% yield after neutralization. Three pairs of diastereomers in a ratio of 12:46:42 are indicated for **32j** by the ^{1}H NMR H_a sulfone absorbances at δ 4.55, 4.15, and 3.55 downfield from that of tetramethylsilane. High-field ^{13}C NMR reveals however that **32j** consists of four pairs of diastereomers, one pair in small amounts. Column chromatography results in isolation of the most polar diastereomeric pair from **32j** as a white crystalline solid. The structures of the diastereomers of **32j** cannot be designated further as yet.

Propylene oxide (Table 1, entry 11), an unsymmetrical epoxide, undergoes regiospecific alkylation at its methylene group upon reaction with **15** and **16** at 23 °C in THF to give, after acidification, 5-hepten-2-ols **32k** (59%). Similarly, **15** and **16** effect sterically directed ring openings of 1,2-epoxybutane (Table 1, entry 12) and styrene oxide (Table 1, entry 13) to yield 6-octen-3-ols **32l** (52%) and 4-hexen-1-ols **32m** (54%), respectively, upon neutralization. The stereochemistries of **32k**, **32l**, and **32m** could not be established by ^{1}H and ^{13}C NMR methods. The products were used directly in elimination experiments as will be described later.

Reactions of lithio derivatives **15** and **16** with trialkylgermanyl and trialkylsilyl chlorides have been studied. Triethylgermanyl chloride (Table 1, entry 14) reacts at 23 °C in THF/HMPA with **15** and **16** to give (*E*)- and (*Z*)-1-(triethylgermanyl)-2-butenes **32n** (35%). Similarly, trimethylsilyl chloride (Table 1, entry 15) is displaced by **15** and **16** at 23 °C in THF to yield (*E*)- and (*Z*)-1,4-bis-(trimethylsilyl)-2-butenes **32o** (51%). Although the reaction yields have not been maximized, the *E*:*Z* ratios of **32n** and **32o** as found from ^{1}H NMR and ^{13}C NMR correspond (Table 1) to that of the **7** and **8** used in the syntheses. Tri(2-propyl)silyl chloride (Table 1, entry 16), a sterically hindered reactant, is essentially inert to **15** and **16** in a 77:21 ratio in THF at 23 °C for 4 h. Addition of HMPA (5 molar equiv) however results in greatly accelerated silylations of **15** and **16** to give 1-(tri(2-propyl)silyl)-2-butene **32p** (33%) which ^{1}H and ^{13}C NMR reveal to be a single and presumably the *E*-isomer. Exclusive formation of (*E*)-**32p** presumably arises because reaction of tri(2-propyl)silyl chloride occurs much more rapidly with **15** than with **16**.

Eliminations of (*E*)- and (*Z*)-1-substituted 2-butenes **32** (eq 5) to 1-substituted 1,3-butadienes **38** have been studied. Additions of commercial TBAF (1.5−2.0 molar equiv) to **32** (Table 2) in THF or Et_2O at 0 °C result in near-instantaneous formations of conjugated dienes **38** (eq 5) in 52−75% yield along with trimethylsilyl fluoride (**39**) and phenylsulfinate ion (**40**). At −20 °C reaction



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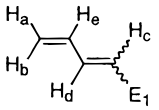


38

+ Me_3SiF + ^-O_2SPh (5)

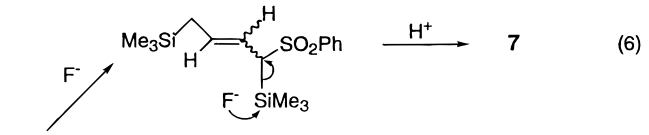
39 **40**

times increase to ∼1 h. If less than 1.5 equiv of TBAF is used, initial **32** remains. The elimination method (eq 5, Table 2) usually works well with commercial TBAF which contains much water and with silyl sulfones that contain

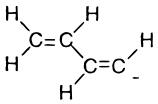
(6) Cunico, R. F.; Han, Y.-K. J. *Organomet. Chem.* **1976**, *105*, C29.
(7) Among the many possibilities are that (*E*)-**32i** had been produced in better yield and/or undergoes elimination faster than (*Z*)-**32i**.

alkyl, arylalkyl, cycloalkyl, ester, ketone, or hydroxyl groups (see Experimental Section). For **32** which eliminate to highly volatile, conjugated dienes that cannot be separated easily from THF or Et_2O, the reactions can be accomplished efficiently in DMSO at 23 °C. Thus, **32a** and **32e** are converted by TBAF (Table 2) in DMSO and flash distillations to (*E*)-1,3-pentadiene (**38a**, 76%) and (*E*)-5-methyl-1,3-hexadiene (**38e**, 85%), respectively.

The behavior of fluoride ion with (*E*)- and (*Z*)-1,4-bis-(trimethylsilyl)-2-butenes (**32o**) is different than that with **32a**−**m**, **33**, **34**, and **35** (Table 2). Reaction of **32o** with TBAF (2 equiv) at 0 °C gives (*E*)-1-(phenylsulfonyl)-4-(trimethylsilyl)-2-butene (**7**, eq 6, 70%) by attack of fluoride ion on the trimethylsilyl groups at the 1-positions and then aqueous workup. (*E*)-1-(Trimethylsilyl)-1,3-butadiene (**43**, eq 7), the conjugative elimination product, is not produced. (*E*)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-



1-[tri(2-propyl)silyl]-2-butene (**32p**) however has its silicon at C-1 highly encumbered and is not attacked by fluoride ion as is **32o** (eq 6). Satisfactory 1,4-elimination of **32p** thus does occur with TBAF (2 equiv) at 20−23 °C in <15 min to yield the single geometric isomer, (*E*)-1-[(tri-2-propyl)silyl]-1,3-butadiene (**38p**, eq 5, Table 2, 61%). Generally, conjugative desulfonylsilylation of **32** (Table 2) is an excellent low-temperature method for preparing 1-substituted-1,3-butadiene derivatives **38** (eq 5), and thus **7** and **8** are effective synthetic equivalents for the 1-(1,3-butadienyl) anion (**44**).

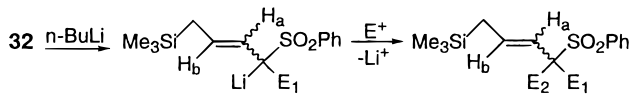


44

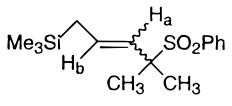
High-field ^{1}H and ^{13}C NMR methods reveal that almost all of the elimination products (Table 2) are totally (100%) or near totally (98 to >99%) single geometric isomers. ^{13}C NMR evidence does indicate that **38d** and **38q** contain second isomers (Table 2) in 7% and 4% amounts. Of note are that the ^{1}H NMR absorptions (250 MHz) of the olefinic hydrogens in **38a**−**q** and **36** (Table 2) are cleanly separated and the single or the major dienes are assigned *E*-stereochemistries on the basis of coupling constants (J_{cd}) of 14.8−16.3 Hz for protons H_c and H_d as represented in **38** in eq 5. Elimination of silyl sulfones **32** by fluoride ion is therefore clearly an excellent method for preparing (*E*)-1-substituted-1,3-dienes (**38**), and thus **7** and **8** can be described more completely as practical synthetic equivalents for the (*E*)-1-(1,3-butadienyl) anion (**44**). What is not yet clear, however, are the detailed mechanisms of conversions of **32** by fluoride ion to **38** (eq 5) other than that the reactions are rapid. Although conjugative 1,4-elimination reactions usually occur more rapidly by cis than trans processes,[8] cis- and/or trans-desulfonylsilylations of **32** with steric control by the substituent at C-1 can give products (*E*)-**38** essentially exclusively. Further studies of the stereochemistries of eliminations of (silylsulfonyl)alkenes are in progress.

Investigation has also been made of other fluorides and other reagents which effect conjugative eliminations of **32**. Potassium fluoride does not eliminate **32b** (Table 2) or **35** in refluxing acetonitrile (bp 81.6 °C) in 24 h. The lack of reaction in these experiments is due to the insolubility of the fluoride reagent. Potassium fluoride and **32b** (Table 2) in refluxing acetonitrile for 16 h in the presence of the phase-transfer reagent, cetyltrimethylammonium bromide, give **38b** however in 63% yield. Similarly, addition of tris[2-(2-methoxyethoxy)-ethyl]amine (TDA-1, an acyclic cryptand) to **35** and potassium fluoride in refluxing acetonitrile yields **36** (Table 2, 65%).[9] The (*E*) and (*Z*) ratios of the **38b** and the **36** produced, as determined from their olefinic ^{1}H NMR coupling constants, are >99:1, respectively. Potassium fluoride in combination with phase-transfer reagents therefore is a satisfactory alternate to TBAF for eliminations of **32** if the higher reaction temperatures and the longer reaction times are unimportant. Aluminum chloride, when used in molar excess quantities (3 equiv) in methylene chloride at −78 °C, eliminates **32b** to **38b** (Table 2; *E*:*Z* ratio of >9:1) in 29% yield. The aluminum chloride methodology suffers in that the **38b** formed reacts extensively with the Lewis acid present.[10] Further, the eliminative behavior of **32b** in the presence of boron trifluoride is unsatisfactory.

Attention next turned to practical alkylative conversions of various 1-substituted-2-butenes **32** to 1,1-disubstituted derivatives **46** (eq 8). 2-Butenes **7** and **8** are



found to be converted in a one-pot procedure to (*E*)- and (*Z*)-2-pentenes **47** in 98% yield from (1) lithio intermediates **15** and **16** in THF with methyl iodide (1 equiv) at −30 °C, (2) addition of *n*-BuLi (1 equiv) at −78 °C, and (3) reaction with methyl iodide (1.5 equiv) at 20−25 °C. The stereochemistries of (*E*,*Z*)-**47** could not be assigned by ^{1}H NMR because the absorptions of their olefinic protons (δ 5.2−5.7) overlap.



47

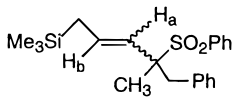
Alkylation was then extended to **32b** ($E_1 = CH_2C_6H_5$, Table 1). Deprotonation of **32b** (*E*:*Z* = 79:21) with *n*-BuLi, reaction with methyl iodide, workup, and chro-

(8) Hill, R. K.; Bock, M. G. *J. Am. Chem. Soc.* **1978**, *100*, 637.

(9) (a) Soula, G. *J. Org. Chem.* **1985**, *50*, 3717. (b) TDA-1 was obtained from the Aldrich Chemical Co., Milwaukee, WI.

(10) Reaction was effected by adding $AlCl_3$ (769 mg, 5.76 mmol) to **32b** (806 mg, 2.25 mmol) in CH_2Cl_2 (10 mL) at −78 °C, stirring (0.5 h), and then adding pentane (20 mL) and water.

matography give (*E*)- and (*Z*)-2-pentenes **48** in an 80:20 ratio in 97% yield. The geometric assignments of the products are based on ^{1}H NMR in that the absorption for H_a in (*E*)-**48** (δ 5.53, J_{ab} = 15.6 Hz) is downfield from that in (*Z*)-**48** (δ 5.41, J_{ab} = 11.2 Hz). Methylation thus proceeds with retention of olefinic stereochemistry. Further, benzylations of the 1-lithio derivatives of **32b** (E_1 = $CH_2C_6H_5$, Table 1) give (*E*)- and (*Z*)-dibenzyl derivatives **49** from which (*E*)-**49** can be crystallized in 71% overall yield from hexane. The stereochemistry of (*E*)-**49** is assigned from the olefinic ^{1}H NMR coupling (J_{ab} = 17 Hz) between H_a (δ 5.28) and H_b (δ 5.78).



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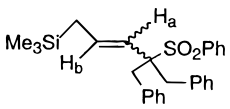
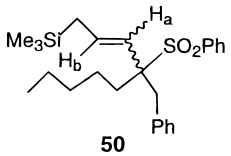


49

1-Bromopentane is of interest because it reacts slowly with 1-lithio derivatives of **32b** (E_1 = $CH_2C_6H_5$, *E*:*Z* = 80:20, Table 1) in HMPA/THF at ~15 °C to give, after aqueous workup and column chromatography on silica gel, the substitution products, (*E*)- and (*Z*)-2-nonenes **50**, and elimination products, (*E*)- and (*Z*)-1,3-nonadienes **51**, in 61 and 30% yields, respectively.



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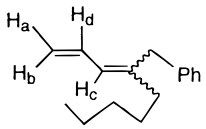
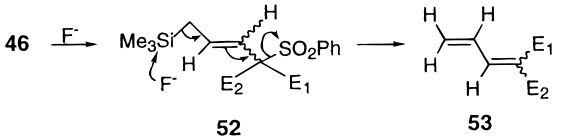


51

Dialkylates **50** are white solids which display ^{1}H NMR absorptions for olefinic protons H_a and H_b at δ 5.27 (J_{ab} = 15.8 Hz) and 5.42 for the *E*-isomer and at δ 5.12 (J_{ab} = 12.4 Hz) and 5.67 for the *Z*-isomer. Disubstitutions at the C-1 positions in (*E*,*Z*)-**50** are confirmed since H_a couple only to H_b. ^{13}C NMR reveals the presence of two quaternary carbons by absorptions at δ 71.77 (*E*-isomer) and 73.37 (*Z*-isomer). The *E*:*Z* ratio of **50** is 79:21 and therefore essentially identical to that of its **32b** precursors.

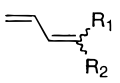
Dienes **51** are formed simply by conjugative eliminations of (*E*,*Z*)-**50** during column chromatography.[11] ^{1}H NMR, ^{13}C NMR, and GC-MS all indicate that **51** consists of *E*- and *Z*- isomers in a 53−54:47−46 ratio. NOE experiments reveal cleanly separated absorptions in (*E*,*Z*)-**51** at δ 5.88 and 6.05, respectively. Irradiation at δ 5.88 enhances magnetic resonance of the benzyl protons at δ 3.39 and thus allows assignment of (*E*)-**51**. Irradiation at δ 6.05 amplifies absorption of the allyl protons at δ 1.99 and therefore the absorbances arise from (*Z*)-**51**.

Conjugative eliminations of 1,1-disubstituted-2-butenes **46** to 1,1-disubstituted-1,3-butadienes **53** by fluoride ion (eq 9), acid catalysis, or heat were then studied as follows.

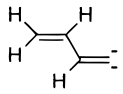


52 **53** (9)

Dimethyl(silyl)sulfones (*E*,*Z*)-**47** are converted to **54** (R_1 and R_2 = CH_3; 72%) by TBAF in DMSO at 25 °C and then flash vacuum distillation. Pentadienes **55** (R_1 and R_2 = CH_2Ph) result from eliminations of (*E*,*Z*)-**49** by either TBAF in THF at 0 °C (83%), aqueous hydrochloric acid (12 M) at 25 °C, or gas chromatography (>52%). Further, dienes (*E*,*Z*)-**51** are obtained from (*E*,*Z*)-**50** with TBAF/THF at 0 °C (65%) or by heating. Of note are reactions of (*E*,*Z*)-**48** with TBAF in THF at 0 °C to yield (*E*)- and (*Z*)-1,3-pentadienes **56** (75%) for which GC-MS analysis and NOE reveal that the *E*:*Z* ratio is 80:20. The latter eliminations are emphasized because neither (*E*)-**48** nor (*Z*)-**48** could be detected immediately after addition of the TBAF. The rapidities and the efficiencies of the above elimination reactions at 0 °C are impressive. Silyl sulfones **7** and **8** therefore are excellent synthetic equivalents for the 1,1-(1,3-butadienyl) dianion **57** as well as for **44**.

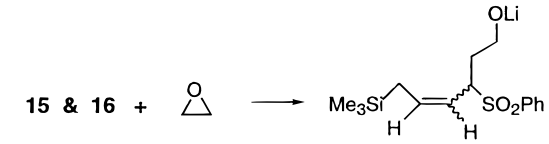


54 : R_1 and R_2 = CH_3
55 : R_1 and R_2 = CH_2-Ph
56 : R_1 = CH_3; R_2 = CH_2-Ph

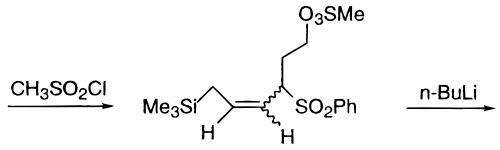


57

Synthesis of (*E*)- and (*Z*)-1-(3-(trimethylsilyl)-1-propenyl)cyclopropanes **62**, possibly as in eq 10, then became a major objective. Indeed, **15** and **16**, when treated with ethylene oxide (**58**) at −78 °C followed by methanesulfonyl chloride and refluxing, give mesylates **60**. Addition of *n*-BuLi then results in lithio derivatives (*E*,*Z*)-**61** which ring close to cyclopropanes (*E*,*Z*)-**62** (28% overall yield from **15** and **16**).



58 **59**



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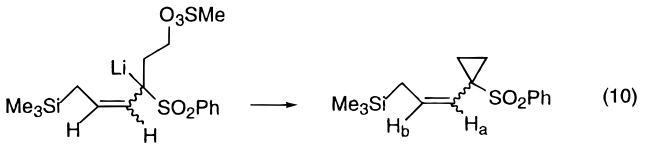
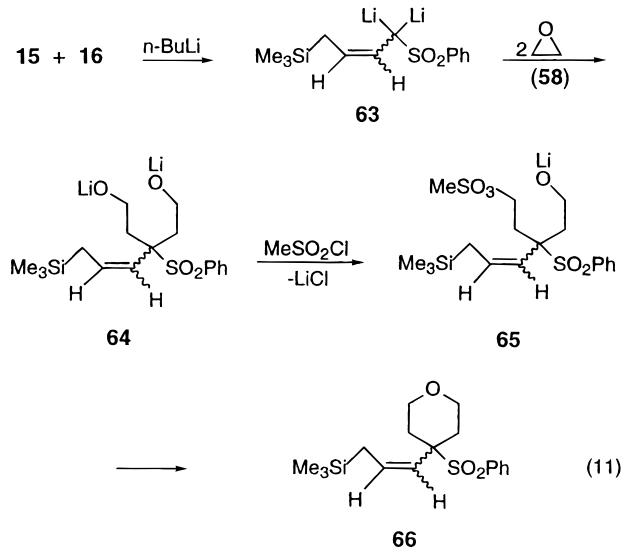


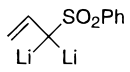
61 **62** (10)

Tetrahydropyrans (*E*,*Z*)-**66** are also obtained (8%) from the above experiment. Formation of **66** presumably occurs (eq 11) by dilithiation of **15** and **16** by *n*-BuLi (1.1 equiv), addition of ethylene oxide (**58**) to **63**, reactions of **64** with methanesulfonyl chloride, and then ring closures of **65** by displacement. Sulfones are known to be dilithiated in their α-positions by *n*-BuLi.[12]

(11) (a) The leaving group abilities of sulfones are increased by Lewis acids. (b) Trost, B. M.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 7260. (c) Kocienski and Todd [Kocienski, P.; Todd, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1777] report that certain sulfones eliminate upon chromatography on silica gel.

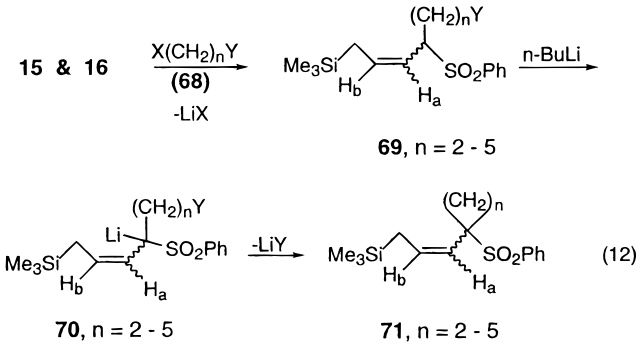


Of particular relevance to the present proposal for formation of **66** is that allyl phenyl sulfone is converted by *n*-BuLi (>2 equiv) to 1,1-dilithioallyl phenyl sulfone (**67**).[12]



Cyclopropanes (*E*,*Z*)-**62** were identified spectroscopically and from their chemistry as will be described. Crystallization of the cyclopropanes from hexane gives a single isomer as evidenced by its single set of ^{13}C NMR peaks. The ^{1}H NMR of the crystallized product is complex but integrates for two olefinic protons. Although the coupling constant, J_{ab}, for the olefinic hydrogens could not be determined, the pure cyclopropane isolated is assumed to be (*E*)-**62**.

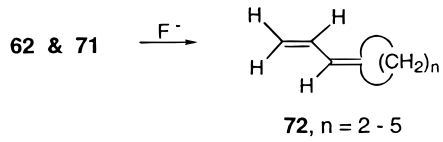
Searches were then made of a better synthesis of cyclopropanes (*E*,*Z*)-**62** and a general method for preparing their higher cycloalkane homologues. Reactions of 1,2-dibromoethane [eq 12; **68** = $Br(CH_2)_2Br$] in THF/HMPA with **15** and **16**, as prepared from **7** and **8** of 85:15 ratio,



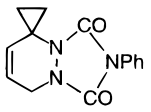
occur smoothly at −78 to 20 °C to give (*E*)- and (*Z*)-6-bromo-2-hexenes **69** [$Y(CH_2)_n$ = $Br(CH_2)_2$] which are lithiated by *n*-BuLi with displacement of lithium bromide to yield (95%) cyclopropyl derivatives (*E*,*Z*)-**62** (**71**; *n* = 2). Recrystallization of the ring-closure products from pentane gives the single cyclopropane assigned previously as (*E*)-**62**. The overall synthesis of (*E*)-**62** is excellent.

Reactions of **15** and **16** in an 85:15 ratio with **68** were extended as in eq 12 to 1,3-dibromopropane, 1-bromo-4-chlorobutane, and 1,5-dibromopentane. The monoalkylated products formed, **69** [$(CH_2)_nY$ = $Br(CH_2)_3$, $Br(CH_2)_4$, and $Br(CH_2)_5$], are converted by *n*-BuLi and ring closure (eq 12) to the corresponding four-, five-, and six-membered ring (*E*)- and (*Z*)-1-(3-(trimethylsilyl)-1-propenyl)cycloalkanes **71** (*n* = 3, 4, and 5) in 87, 89, and 78% yields, respectively. Each of the products exhibits ^{13}C NMR absorptions for *E*- and *Z*-isomers. The ^{1}H NMR of the olefinic hydrogens, H_a and H_b, in each product are well-separated and their chemical shifts (δ 5.29−4.92, J_{ab} = 15.4−15.9 Hz; δ 5.09−4.70, J_{ab} = 11.9−11.5 Hz) allow assignments of the *E*- and *Z*-isomers of each pair. The *E*:*Z* ratios for the cyclobutane, cyclopentane, and cyclohexane derivatives **71** (*n* = 3, 4, and 5) prepared range only from 84:16 to 86:14, and thus there is essentially total retention in the stereochemistries in the above cycloalkylations of **15** and **16**.

Silylsulfonyl eliminations of (*E*,*Z*)-**62**, its four-, five-, and six-membered ring homologues (*E*,*Z*)-**71** [$(CH_2)_n$, *n* = 3, 4, and 5], and tetrahydropyrans (*E*,*Z*)-**67** were then investigated. Reactions of (*E*,*Z*)-**62** with TBAF in DMSO at 0 °C (eq 13) and flash vacuum distillation yield



allylenecyclopropane (**72**, *n* = 2; 90%), a diene of considerable synthetic and theoretical interest.[13] Allylene **72** (*n* = 2), a polymerizable conjugated diene, is stable for prolonged periods at −78 °C, and its structure is confirmed by comparison with literature properties.[13] The conjugated dienic behavior of **72** (*n* = 2) is further elaborated by effecting its near instantaneous cycloaddition to 4-phenyl-1,2,4-triazoline-3,5-dione at −78 °C to give triazolodione **73** (81%).

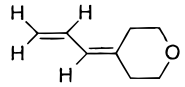


In extensions of the above methodology, allylenecyclobutane (**72**, *n* = 3; 87%) and allylenecyclopentane (**72**, *n* = 4; 89%) are obtained simply by rapid distillations of solutions of cyclobutanes (*E*,*Z*)-**71** (*n* = 3) and cyclopentanes (*E*,*Z*)-**71** (*n* = 4) from DMSO containing TBAF. Further, treatment of cyclohexanes (*E*,*Z*)-**71** (*n* = 5) and tetrahydropyrans (*E*,*Z*)-**69** with fluoride ion in THF at 0 °C and chromatography on silica gel result in efficient production of allylenecyclohexane (**72**, *n* = 5; 78%) and 4-allylenetetrahydropyran (**74**, 87%), respectively. The

(12) (a) Kaiser, E. M.; Solter, L. E.; Schwarz, R. A.; Beard, R. D.; Hauser, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 4238. (b) Evans, J. B.; Marr, G. J. *J. Chem. Soc., Perkins Trans. 1* **1972**, 2502. (c) Eisch, J. J.; Behrooz, M.; Dua, S. K. J. *Organomet. Chem.* **1985**, *285*, 121. (d) Gais, H.-J.; Volhardt, J.; Lukas, K. L. *Angew. Chem.* **1985**, *97*, 695 and references therein. (f) Yet, L. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1995. (g) The suggestions of J. J. Eisch concerning the mechanism of formation of **67** are appreciated.

(13) (a) Blome, H. Dissertation, Bochum, West Germany, 1973. (b) Brinker, V. H.; Konig, L. *J. Am. Chem. Soc.* **1979**, *101*, 4783. (c) Binger, P.; Germer, A. *Chem. Ber.* **1981**, *114*, 3325. (d) Zutterman, F.; Krief, A. *J. Org. Chem.* **1983**, *48*, 1135.

structures of **72** (n = 3, 4, and 5) and **74** are established by spectral methods and by comparison with literature data.[13]



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In conclusion, silyl sulfones **7** and **8** undergo efficient and stereospecific electrophilic conversions to their corresponding 1-substituted (**32**, eq 4), 1,1-disubstituted (**46**, eq 8), and 1,1-cycloalka (**71**, eq 12) silyl sulfones. Such substituted silyl sulfones are eliminated by fluoride ion, thermally, or adsorption chromatography to 1-substituted (**38**, eq 5), 1,1-disubstituted (**53**, eq 9), and 1,1-cycloalka (**72**, eq 13) 1,3-dienes, respectively. Silyl sulfones **7** and **8** are therefore of value as synthetic equivalents for **44** and **57**. The use of silyl sulfones for preparing *o*-quinodimethanes and other unusual dienes advantageously are described in detail in separate publications from this laboratory.[14]

Experimental Section

General Considerations. Proton nuclear magnetic resonance spectra are reported in parts per million on the δ scale when $CDCl_3$ is denoted as the solvent with residual $CHCl_3$ at δ 7.26 as an internal reference. The ^{1}H NMR spectra are reported as follows: chemical shifts [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in hertz, integration, and interpretation]. ^{13}C NMR chemical shifts are reported in parts per million relative to the center line of the $CDCl_3$ triplet (77.0 ppm) and are denoted as "e" (none or two protons attached), "o" (one or three protons attached), and "u" (quaternary carbon) as determined from the APT pulse sequence and as "C" (no protons attached), "CH" (one proton attached), "CH_2" (two protons attached), or "CH_3" (three protons attached) as determined from the DEPT pulse sequence. Mass spectra were recorded at an ionization energy of 70 eV. THF was predried over potassium hydroxide and distilled from lithium aluminum hydride, Et_2O was distilled from sodium benzophenone ketyl, and CH_2Cl_2 was distilled from calcium hydride. All reactions were conducted under argon. EM Laboratories 0.25 mm thick precoated silica gel 60F-254 plates were used for analytical chromatography. Elemental analyses were performed by MicroAnalyses, Inc., Wilmington, DE, or Atlantic Microlab, Inc., Norcross, GA.

4-(Trimethylsilyl)-1-buten-3-ol (10). (Chloromethyl)trimethylsilane (20.0 g, 0.163 mol) in anhydrous THF (30 mL) was added in 2 h to a suspension of magnesium turnings (4.50 g, 0.205 mol) in anhydrous THF (120 mL). The mixture was stirred at room temperature for 1 h and cooled to 0 °C. Acrolein (9.50 g, 0.170 mol) in anhydrous THF (30 mL) was then added (15 min), and the mixture was stirred for 45 min. The solution was diluted with Et_2O, quenched with hydrochloric acid, washed with water and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The yellow liquid residue (26.0 g) was distilled at 54−56 °C at 1.7 mmHg to give colorless **10** (16.2 g, 69%): ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9 H), 0.83−1.30 (m, 2 H), 2.05 (bs, 1 H), 4.25 (bq, J = 7.2 Hz, 1 H), 5.01 (dd, J = 7.8, 1.0 Hz, 1 H), 5.15 (dd, J = 14.5, 1.3 Hz, 1 H), 5.82−5.92 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.8, 26.3, 71.5, 113.4, 143.4; exact mass calcd for $C_7H_{16}SiO$ *m/e* 144.0970, found *m/e* 144.0970.

(*E*)- and (*Z*)-1-(Phenylsulfinyl)-4-(trimethylsilyl)-2-butenes (12). Phenylsulfenyl chloride (6.80 g, 47.1 mmol) was added slowly to **10** (6.80 g, 47.1 mmol) and *n*-BuLi (30.6 mL, 49.0 mmol, 1.60 M in hexane) in anhydrous THF (50 mL) at −78 °C.[3b] The red color of the phenylsulfenyl chloride disappeared immediately on addition. The resulting light yellow solution was then stirred at room temperature for 2 h, diluted with Et_2O, washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to a yellow oil (10.9 g). Flash chromatography (silica gel; ethyl acetate:hexanes, 1:2) yielded **12** (7.86 g, 66%), a light yellow liquid: ^{1}H NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −0.03 (s, 9 H), 1.41 (d, J = 7.8 Hz, 2 H), 1.49 (d, J = 8.2 Hz, 2 H), 3.50 (d, J = 7.5 Hz, 2 H), 5.05−5.15 (m, 1 H), 5.56−5.65 (m, 1 H), 7.47−7.65 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −2.1, −1.9, 19.3, 23.7, 55.5, 60.8, 113.2, 114.4, 124.3, 127.4, 128.9, 130.8, 130.9, 135.1, 137.4, 143.4; exact mass calcd for $C_7H_{15}Si$ (M^+ − SOPh) *m/e* 127.0943, found *m/e* 127.0935.

(*E*,7)- and (*Z*,8)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-2-butenes. To **12** (15.24 g, 60.5 mmol) in CH_2Cl_2 (300 mL) was slowly added MCPBA (12.7 g, 58.9−62.5 mmol, 80−85% assay) at 0 °C. The white suspension was stirred at 0 °C for 2 h, diluted with Et_2O, washed with aqueous $NaHCO_3$, 25% aqueous sodium metabisulfite, and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting light yellow liquid (16.2 g) on chromatography (silica gel; ethyl acetate: hexanes, 1:5) gave **7** and **8** (15.87 g, 98%) as a viscous colorless oil: IR (neat film) 1310, 1250, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −0.08 (s, 9 H), 1.24 (d, J = 8.1 Hz, 2 H), 1.45 (d, J = 8.1 Hz, 2 H), 3.74 (d, J = 7.4 Hz, 2 H), 3.80 (d, J = 7.4 Hz, 2 H), 5.10−5.35 (m, 1 H), 5.51−5.80 (m, 1 H), 7.52−7.86 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −2.1, −2.0, 20.8, 23.6, 54.9, 60.1, 112.5, 113.4, 128.2, 128.3, 128.9, 129.3, 133.4, 133.5, 135.6, 138.5; exact mass calcd for $C_7H_{15}Si$ (M^+ − SO_2Ph) *m/e* 127.0943, found *m/e* 127.0936.

(*E*,17)- and (*Z*,18)-1-Deuterio-1-(phenylsulfonyl)-4-(trimethylsilyl)-2-butenes. *n*-BuLi (0.21 mL, 0.56 mmol, 2.65 M) in hexane was added to a solution of **7** and **8** (80:20 ratio; 150 mg, 0.56 mmol) in THF (10 mL) at 0 °C. After being stirred at 25 °C for 3.3 h, the mixture was quenched with D_2O (1 mL). The solution was immediately neutralized with aqueous ammonium chloride, washed with H_2O, dried ($MgSO_4$), filtered, and concentrated to a yellow clear oil (0.12 g). Column filtration (silica gel; ethyl acetate 5%) yielded (*E*)-**17** and (*Z*)-**18** (71 mg, 47%): ^{1}H NMR ($CDCl_3$, *E*/*Z* isomer 79:21, 87% monodeuterium incorporation) δ −0.08 (s, 9 H), 1.25 (dd, J = 7.5, 1.4 Hz, 2 H), 1.46 (dd, J = 8.2, 1.1 Hz, 2 H), 3.72 (bd, J = 7.2 Hz, 1 H), 5.18−5.26 (m, 1 H, H_a), 5.56 (dt, J = 15.2, 8.2 Hz, 1 H, H_b), 5.76 (dt, J = 10.7, 9.0 Hz, 1 H, H_b), 7.49−7.91 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*/*Z* ratio 77:23 to 83:17) δ −2.1, 18.9, 23.7, 60.0, 112.5, 129.0, 128.3, 128.4, 129.0, 133.4, 133.5, 135.8, 138.6, 138.8; mass spectrum, *m/e* calcd for $C_{13}H_{19}DO_2SSi$ (M^+) 269.1016, found 269.1005; $C_7H_{14}DSi/C_7H_{15}Si$ (M^+ − O_2SPh) isotope ratio 84/16.

(*E*)- and (*Z*)-1,1-Dideuterio-1-(phenylsulfonyl)-4-(trimethylsilyl)-2-butenes (21 and 22). Products **21** and **22**, yield 89%, a light yellow liquid: ^{1}H NMR (CCl_4, >95% deuterium incorporation) δ −0.00 (s, 9 H), 1.2−1.6 (m, 2 H), 5.18 (bd, J = 15 Hz, 1 H), 5.32−5.97 (m with a dt at 5.62, J = 15.7 Hz, 1 H), 7.50−8.14 (m, 5 H); mass spectrum *m/e* calcd for $C_7H_{12}D_2Si$ (M^+ − O_2SPh) 128.0990, found 128.1001.

Procedure A for Monosubstitution Reactions of (*E*)- and (*Z*)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-2-butenes with Electrophiles (7 and 8). (*E*)- and (*Z*)-4-(Phenylsulfonyl)-1-(trimethylsilyl)-2-pentenes (32a). *n*-BuLi (3.51 mL, 7.38 mmol, 2.10 M in hexane) was syringed slowly into a solution of **7** and **8** (1.80 g, 6.71 mmol) in anhydrous THF (10 mL) at −78 °C. The stirred mixture turned bright yellow. After 20 min, methyl iodide (1.26 g, 8.88 mmol) was added. The mixture was stirred for 1 h at room temperature, worked up, and concentrated in vacuo to a yellow oil (1.39 g). Column chromatography (silica gel; ethyl acetate:hexanes, 1:10) afforded **32a** (1.84 g, 97%) as a colorless viscous liquid: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ 0.00 (s, 9 H), 1.35 (d, J = 6.0 Hz, 3 H), 1.48 (m, 2 H), 3.59 (m, 1 H), 5.13 (dd, J = 15.0, 7.0 Hz, 1 H), 5.58 (dt, J = 15.0, 8.0 Hz, 1 H), 7.3−8.0 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −2.0, 14.1, 23.6, 64.0, 120.8, 128.8, 129.1, 133.4, 135.6, 137.8; exact mass calcd for $C_8H_{17}Si$ (M^+ − SO_2-

(14) (a) Lenihan, B. D.; Shechter, H. *J. Org. Chem.* **1998**, *63*, 2072. (b) Lenihan, B. D.; Shechter, H. *J. Org. Chem.* **1998**, *63*, 2086.

Ph) *m/e* 141.1099, found *m/e* 141.1092. Anal. Calcd for $C_{14}H_{22}O_2SSi$: C, 59.52; H, 7.85. Found: C, 59.64; H, 7.55.

(*E*)- and (*Z*)-5-Phenyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-pentenes (32b). Procedure A, yield 99%, a clear viscous oil: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ 0.09 (s, 9 H), 1.66 (m, 2 H), 3.16 (H_a, dd, J_{ab} = 13.6 Hz, J = 11.6 Hz, 1 H), 3.85 (H_b, dd, J_{ab} = 13.5 Hz, J = 3.0 Hz, 1 H), 4.06 (H_c, m, 1 H), 5.3−5.7 (m, 2 H), 7.4−8.3 (m, 10H); irradiation at δ 1.66 simplified the vinyl absorption region to 5.3−5.4 (m, 1 H) and 5.58 (d, J = 14.9 Hz, 1 H); irradiation at δ 4.06 simplified the vinyl and benzyl magnetic resonance regions to 5.38 (dd, J = 15.2, 4.3 Hz, 1 H) and 5.4−5.7 (m, 1 H) and 3.85 (d, J = 15.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −2.1, 23.7, 34.0, 71.0, 118.8, 126.7, 128.5, 128.9, 129.2, 133.5, 137.1, 138.0, 138.3; exact mass calcd for $C_{14}H_{21}Si$ ($M^+ - SO_2Ph$) *m/e* 217.1412, found *m/e* 217.1407. Anal. Calcd for $C_{20}H_{26}O_2SSi$: C, 66.99; H, 7.31. Found: C, 67.03; H, 6.94.

Procedure B for Monosubstitution Reactions of 7 and 8 with Electrophiles. (*E*)- and (*Z*)-4-(Phenylsulfonyl)-1-(trimethylsilyl)-2-nonenes (32c). *n*-BuLi (1.97 mL, 2.95 mmol, 1.50 M in hexane) was syringed into a solution of **7** and **8** (726 mg, 2.70 mmol) in anhydrous THF (20 mL). After 20 min, 1-bromopentane (429 mg, 2.84 mmol) followed by HMPA (2.57 mL, 14.00 mmol) was added. After being warmed to room temperature, the mixture was stirred for 1 h, worked up, and concentrated to a yellow viscous oil (1.13 g). Column chromatography (silica gel; ethyl acetate 0−5%) gave **32c** (875 mg, 99%) as a light yellow oil: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ 0.00 (s, 9 H), 0.7−2.2 (m with a δ, J = 8.0 Hz at δ 1.46, 13 H), 3.30 (bt, J = 9.0 Hz, 1 H), 4.95 (dd, J = 15.0, 9.0 Hz, 1 H), 5.40 (dt, J = 15.0, 8.0 Hz, 1 H), 7.3−8.0 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −2.0, 13.9, 22.4, 23.7, 26.3, 27.4, 31.2, 69.6, 119.8, 128.8, 129.1, 133.3, 137.2, 138.3; exact mass calcd for $C_{12}H_{25}Si$ ($M^+ - SO_2Ph$) *m/e* 197.1726, found *m/e* 197.1729.

(*E*)- and (*Z*)-6-Methyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-heptenes (32d). Procedure B, yield 83%, a colorless viscous oil: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ 0.00 (s, 9 H), 0.79 (d, J = 6.5 Hz, 3 H), 0.94 (d, J = 6.5 Hz, 3 H), 1.2−1.8 (m, 5 H), 3.53 (bt, J = 9.3 Hz, 1 H), 4.99 (dd, J = 15.2, 9.4 Hz, 1 H), 5.47 (dt, J = 15.2, 9.1 Hz, 1 H), 7.5−7.9 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −2.0, 20.5, 23.5, 25.2, 35.9, 68.1, 119.7, 128.7, 129.0, 133.2, 137.1, 138.1; exact mass calcd for $C_{11}H_{23}Si$ ($M^+ - SO_2Ph$) *m/e* 183.1569, found *m/e* 183.1592.

(*E*)- and (*Z*)-5-Methyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-hexenes (32e). Procedure B, yield 97%, a colorless oil: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ −0.07 (s, 9 H), 0.95 (d, J = 7.0 Hz, 3 H), 1.08 (d, J = 7.0 Hz, 3 H), 1.35−1.52 (m, 2 H), 2.65 (m, 1 H), 3.30 (m, 1 H), 5.27 (m, 2 H), 7.4−7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −2.0, 18.0, 22.0, 23.7, 26.9, 74.9, 116.5, 128.7 (2 coincidental peaks), 133.1, 138.1, 139.3; exact mass calcd for $C_{10}H_{21}Si$ ($M^+ - SO_2Ph$) *m/e* 169.1413, found *m/e* 169.1392. Anal. Calcd for $C_{16}H_{26}O_2SSi$: C, 61.89; H, 8.44. Found: C, 61.39; H, 8.23.

(*E*)- and (*Z*)-5-Methyl-6-phenyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-hexenes (33 and 34). Procedure B: column chromatography gives as the first eluent (*E*)-1-phenyl-1-propene (25%) and initial bromide as assigned by ^{1}H NMR and GLC analyses (column QF-1, 15%, Chromosorb W). The second eluent is (*E*)-**33** and (*Z*)-**34** (40%), an unresolved mixture of diastereomers as a colorless oil. The ^{1}H NMR of the mixture could not be assigned because of the ambiguous coupling patterns; mass spectrum, *m/e* calcd for $C_{16}H_{25}Si$ ($M^+ - O_2SPh$) 245.1725, found 245.172. GC-Cl-MS (isobutane) of the product revealed three isomers, A,B, and C, in a ratio of 54:42:4: isomer A, *m/e* (relative intensity) 387 (0.4, $M^+ + H$), 287 (5), 245 (31), 215 (100), 173 (8), 143 (38), 126 (11), 105 (6), 91 (6), 73 (5); isomer B, 387 (0.4 $M^+ + H$), 287 (19), 245 (24), 215 (100), 173 (7), 143 (33), 126 (7), 105 (5), 91 (4), 73 (5); isomer C, 387 (1, $M^+ + H$), 287 (100), 245 (5), 215 (22), 173 (1), 143 (1). Last, **7** and **8** (33% recovery) were eluted from the column.

Ethyl (*E*)- and (*Z*)-2-(Phenylsulfonyl)-5-(trimethylsilyl)-3-pentenoates (32f). Procedure A, yield 67%, liquid: ^{1}H NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −0.01 (s, 9 H), 1.20 (t, J = 7.1 Hz, 3 H), 1.46 (d, J = 8.0 Hz, 2 H), 1.55 (d, J = 7.4 Hz, 2 H), 4.13 (q, J = 7.1 Hz, 2 H), 4.47 (d, J = 9.5 Hz, 1 H), 5.27−5.37 (m, 1 H), 5.74−5.86 (m, 1 H), 7.50−7.56 (m, 2 H), 7.59−7.68 (m, 1 H), 7.84−7.87 (m, 2 H); ^{13}C NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −2.1, −2.0, 13.8, 23.7, 24.1, 60.3, 62.1, 74.6, 113.4, 114.3,128.3, 128.8, 129.0, 129.5, 133.4, 134.0, 137.4, 138.6, 142.8, 165.1; exact mass calcd for $C_{10}H_{19}O_2Si$ ($M^+ - SO_2Ph$) *m/e* 199.1154, found *m/e* 199.1201. Anal. Calcd for $C_{16}H_{24}O_4SSi$: C, 56.44; H, 7.10. Found: C, 56.79; H, 6.72.

Ethyl (*E*)- and (*Z*)-2-(Phenylsulfonyl)-5-(trimethylsilyl)-3-pentenethioates (32 g). Procedure A, yield 45%, a viscous liquid: ^{1}H NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −0.08 (s, 9 H), −0.02 (s, 9 H), 1.17 (t, J = 7.4 Hz, 3 H), 1.56 (d, J = 9.5 Hz, 2 H), 2.85 (q, J = 7.4 Hz, 2 H), 4.56 (d, J = 9.5 Hz, 1 H), 4.90 (d, J = 9.5 Hz, 1 H), 5.27−5.40 (m, 1 H), 5.74−5.90 (m, 1 H), 7.47−7.68 (m, 3 H), 7.81−7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −2.0, −1.9, 14.2, 18.9, 19.7, 24.1, 24.2, 80.3, 112.5, 114.2, 128.3, 128.4, 128.7, 128.9, 129.6, 134.0, 135.7,140.6, 190.8; exact mass calcd for $C_8H_{14}OSi$ ($M^+ - SO_2Ph$, SCH_2CH_3) *m/e* 154.0814, found *m/e* 154.0813. Anal. Calcd for $C_{16}H_{24}O_3S_2Si$: C, 54.90; H, 6.78. Found: C, 54.69; H, 6.95.

(*E*)- and (*Z*)-2,2-Dimethyl-4-(phenylsulfonyl)-7-(trimethylsilyl)-5-hepten-3- ones (32h). Procedure A: (1) (*E*)-**32h** (59%), a white solid [mp 99−100 °C; ^{1}H NMR ($CDCl_3$, *E*-isomer) δ −0.03 (s, 9 H), 1.13 (s, 9 H), 1.50 (d, J = 8.0 Hz, 2 H), 5.04−5.15 (m, 2 H), 5.73−5.85 (m, 1 H), 7.49−7.87 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −1.9, 24.0, 25.9, 45.8, 73.6, 117.0, 128.5, 130.2, 133.8, 137.6, 142.3, 206.2; exact mass calcd for $C_{12}H_{23}OSi$ ($M^+ - SO_2Ph$) *m/e* 211.1520, found *m/e* 211.1545. Anal. Calcd for $C_{20}H_{28}O_3SSi$: C, 61.32; H, 8.01. Found: C, 61.63; H, 8.01] and (2) (*Z*)-**32h** (16%), a colorless oil [^{1}H NMR ($CDCl_3$, *Z*-isomer) δ 0.06 (s, 9 H), 1.16 (s, 9 H), 1.46−1.66 (m, 2 H), 5.02−5.07 (m, 1 H), 5.52 (d, J = 10.1 Hz, 1 H), 5.77−5.81 (m, 1 H), 7.48−7.84 (m, 5 H); ^{13}C NMR ($CDCl_3$, *Z*-isomer) δ −1.5, 19.3, 26.0, 45.5, 68.5, 117.3, 128.4, 130.3, 133.8, 136.3, 137.5, 206.6; exact mass calcd for $C_{12}H_{23}OSi$ ($M^+ - SO_2Ph$) *m/e* 211.1520, found *m/e* 211.1541].

(*E*)-1-Phenyl-2-(phenylsulfonyl)-5-(trimethylsilyl)-3-penten-1-one (32i). Procedure A, yield 64%, a viscous yellow liquid: ^{1}H NMR ($CDCl_3$) δ −0.05 (s, 9 H), 1.54 (d, J = 6.9 Hz, 2 H), 5.34−5.44 (m, 1 H), 5.56 (d, J = 9.2 Hz, 1 H), 5.82−5.95 (m, 1 H), 7.29−7.66 (m, 6 H), 7.83−7.98 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −1.9, 24.2, 74.4, 115.8, 117.3, 127.6, 128.5, 128.6, 128.7, 128.9, 129.1, 130.0, 133.9, 133.9, 136.1, 137.2 142.9, 191.3; exact mass calcd for $C_{14}H_{19}OSi$ ($M^+ - SO_2Ph$) *m/e* 231.1206, found *m/e* 231.1214. Anal. Calcd for $C_{20}H_{24}O_3SSi$: C, 64.48; H, 6.49. Found: C, 64.65; H, 6.25.

(*E*)- and (*Z*)-2-(1-(Phenylsulfonyl)-4-(trimethylsilyl)-2-buten-1-yl)cyclohexanols (32j). Procedure A, column chromatography of the reaction product gave **32j** (83%), a partially resolved mixture of diastereomers (two by TLC). The more polar isomer was obtained as a colorless oil which crystallized to a white solid: mp 122−123 °C; ^{1}H NMR ($CDCl_3$, polar isomer) δ −0.13 (s, 9 H), 1.21−2.33 (m, 11 H), 3.17 (m, 1 H), 4.17 (dd, J = 9.4, 2.1 Hz, 1 H), 5.3−5.4 (m, 2 H), 7.34−7.95 (m, 5 H); ^{13}C NMR ($CDCl_3$, polar isomer) δ −2.0, 23.7, 24.9, 25.2, 26.4, 36.4, 44.2, 68.5, 70.6, 116.4, 128.6, 128.7, 133.1, 138.2, 139.0; mass spectrum (polar isomer), *m/e* calcd for $C_{13}H_{26}OSi$ ($M^+ - O_2SPh$) 226.1753, found 226.1720.

(*E*)- and (*Z*)-4-(Phenylsulfonyl)-7-(trimethylsilyl)-5-hepten-2-ols (32k). Procedure A, yield 59%, a yellow oil: ^{1}H NMR ($CDCl_3$) δ -0.11 (s, 9 H), 1.14, 1.21 (d, J = 6.2 Hz, 3 H), 1.32−1.50 (m, 2 H), 1.6−1.9 (m, 1 H), 2.02−2.20 (m, 2 H), 3.6−4.1 (m, 1 H), 4.9−5.1 (m, 1 H), 5.40−5.58 (m, 1 H), 7.40−7.85 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ -2.0, 22.7, 23.6, 24.3, 64.5, 65.5, 66.5, 66.7, 119.0, 119.9, 128.8, 128.8, 129.0, 133.3, 133.4, 137.3, 137.5, 137.8; exact mass calcd for $C_{10}H_{21}OSi$ ($M^+ - SO_2Ph$) *m/e* 205.1362, found *m/e* 205.1349. Anal. Calcd for $C_{16}H_{26}O_3SSi$: C, 58.85; H, 8.03. Found: C, 58.57; H, 7.63.

(*E*)- and (*Z*)-5-(Phenylsulfonyl)-8-(trimethylsilyl)-6-octen-3-ols (32l). Procedure A, yield 52%, a yellow viscous oil: ^{1}H NMR ($CDCl_3$) δ −0.12 (s, 9 H), 0.88 (t, J = 7.4 Hz, 3 H), 1.32−1.55 (m, 4 H), 1.64−1.82 (m, 1 H), 2.0−2.3 (m, 2 H), 3.38−3.50 (m), 3.68−3.94 (m, 1 H), 4.95−5.12 (m, 1 H), 5.38−5.55 (m, 1 H), 7.40−7.85 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −2.0, −1.9, 9.5, 9.8, 23.5, 23.6, 29.4, 31.0, 34.4, 35.6, 66.4, 66.5, 69.7,

70.5, 119.1, 120.2, 128.7, 128.8, 129.0, 129.1, 133.3, 133.4, 137.1, 137.8; exact mass calcd for $C_{11}H_{23}OSi$ ($M^+ - SO_2Ph$) *m/e* 199.1520, found *m/e* 199.1528. Anal. Calcd for $C_{17}H_{28}O_3SSi$: C, 59.96; H, 8.29. Found: C, 59.52; H, 8.08.

(*E*)- and (*Z*)-1-Phenyl-3-(phenylsulfonyl)-6-(trimethylsilyl)-4-hexen-1-ols (32m). Procedure A, yield 54%, a viscous yellow liquid: ^{1}H NMR ($CDCl_3$) δ −0.05 (s, 9 H), 1.42−1.52 (m, 2 H), 2.15 (s, 1 H), 2.40−2.51 (m, 2 H), 3.40−3.49 (m, 1 H), 4.81 (t, J = 7.1 Hz, 1 H), 5.02−5.16 (m, 1 H), 5.36−5.70 (m, 1 H), 7.23−7.94 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −2.2, −1.9, 23.7, 37.2, 66.1, 66.6, 70.7, 71.8, 119.4, 120.8, 125.6, 126.0, 127.9, 128.1, 128.4, 128.6, 128.7, 128.8, 129.0, 133.4, 137.4, 137.7, 138.3, 142.5; exact mass calcd for $C_{15}H_{23}OSi$ ($M^+ - SO_2Ph$) *m/e* 247.1520, found *m/e* 47.1503.

(*E*)- and (*Z*)-1-(Phenylsulfonyl)-1-(triethylgermanyl)-4-(trimethylsilyl)-2-butenes (32n). Procedure B, yield 35%, a colorless oil: ^{1}H NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −0.28 (s, 9 H), −0.17 (s, 9 H), 1.09−1.14 (m, 15 H), 1.31−1.37 (m, 2 H), 3.51 (d, J = 10.8 Hz, 1 H), 3.84 (d, J = 11.0 Hz, 1 H), 5.01−5.10 (m, 1 H), 5.22−5.34 (m, 1 H), 5.35−5.46 (m, 1 H), 7.42−7.55 (m, 3 H), 7.75−7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −2.0, 5.2, 5.3, 8.8, 8.9, 17.9, 23.1, 56.1, 60.9, 119.2, 127.8, 128.0, 128.5, 128.6, 129.2, 132.4, 132.4, 132.5, 140.1, 141.0; exact mass calcd for $C_{19}H_{34}SO_2SiGe$ *m/e* 428.1261, found *m/e* 428.1241. Anal. Calcd for $C_{19}H_{34}SO_2SiGe$: C, 54.42; H, 8.02. Found: C, 54.61; H, 8.03.

(*E*)- and (*Z*)-1-(Phenylsulfonyl)-1,4-bis(trimethylsilyl)-2-butenes (32o). Procedure A, yield 51%, a yellow viscous oil: ^{1}H NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −0.27 (s, 9 H), −0.19 (s, 9 H), 0.28 (s, 9 H), 1.31 (m, 2 H), 3.32 (bd, J = 10.3 Hz, 1 H), 3.68 (bd, J = 10.7 Hz, 1 H), 5.02−5.42 (m, 2 H), 7.45−7.80 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E* and *Z*-isomers) δ −2.1, −2.0, −1.3, −1.1, 20.0, 23.2, 57.8, 63.0, 120.3, 127.8, 128.1, 128.5, 128.9, 130.6, 130.8, 132.5, 132.6, 133.8, 140.7, 140.8; exact mass calcd for $C_{16}H_{28}O_2SSi_2$ *m/e* 340.1349, found *m/e* 340.1303. Anal. Calcd for $C_{16}H_{28}O_2SSi_2$: C, 56.42; H, 8.29. Found: C, 56.57; H, 7.89.

(*E*)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-1-[tri(2-propyl)-silyl]-2-butene (32p). Procedure A, yield 33%, an off-white solid: mp 101−102 °C: ^{1}H NMR ($CDCl_3$) δ −0.15 (s, 9 H), 1.19 (dd, J = 15.6, 7.4 Hz, 18 H), 1.26−1.54 (m, 5 H), 3.61 (d, J = 11.0 Hz, 1 H), 4.82−4.95 (m, 1 H), 5.35−5.46 (m, 1 H), 7.43−7.57 (m, 3 H), 7.75−7.83 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.9, 12.2, 20.9, 23.3, 60.2, 119.5, 128.0, 128.5, 132.4, 134.3, 140.8; exact mass calcd for $C_{22}H_{40}O_2SSi_2$ *m/e* 424.2287, found *m/e* 424.2251. Anal. Calcd for $C_{22}H_{40}O_2SSi_2$: C, 62.21; H, 9.49. Found: C, 61.87; H, 9.51.

(*E*)- and (*Z*)-4-Cyclohexyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-butenes (35). Procedure B, yield 35%, a clear oil: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ −0.08 (s, 9 H), 1.03−1.76 (m, 11 H), 2.12 (bd, J = 12.7 Hz, 1 H), 2.35 (m, 1 H), 3.31 (dd, J = 9.8, 3.2 Hz, 1 H), 5.19−5.32 (m, 2 H), 7.31−7.81 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −1.9, 23.6, 26.0, 26.4, 28.6, 32.1, 36.7, 74.9, 117.4, 128.7, 133.0, 137.4, 139.1; exact mass calcd for $C_{13}H_{25}Si$ ($M^+ - SO_2Ph$) *m/e* 209.1726, found *m/e* 209.1720. Reactants **7** and **8** (30%) were also recovered.

Procedure B with cyclohexyl *p*-toluenesulfonate at room temperature led to **35** (27% conversion).

General Procedure C for Fluoride-Induced Eliminations of Silyl Sulfones in DMSO. (*E*)- and (*Z*)-1,3-Pentadienes (38a). DMSO (7 mL) was added to TBAF (7.08 mL, 7.08 mmol, 1.0 M in THF), and the mixture was concentrated (0.1 mmHg/25 °C). The TBAF/DMSO reagent was then added to **32a** (1.08 g, 3.82 mmol) in DMSO (5 mL) at 25 °C. After being stirred for 20 min, the mixture was flash distilled (15 °C/30−100 mmHg). The volatile components were trapped at −78 °C to give a mixture of **38a** (197 mg, 76%) and hexamethyldisiloxane (213 mg). The IR and ^{1}H NMR of **38a** are essentially identical to that of an authentic sample.

General Procedure D for Fluoride-Induced Eliminations of 1-(Phenylsulfonyl)-1-substituted-4-(trimethylsilyl)-2-butenes (32). (*E*)-5-Phenyl-1,3-pentadiene (38b). TBAF (1.74 mL, 1.74 mmol, 1.0 M in THF) was added to **32b** (313 mg, 0.870 mmol) in anhydrous THF (10 mL) at 0 °C. The dark mixture was stirred for 30 min, worked up, and concentrated in vacuo to a brown oil (140 mg). Column chromatography (silica gel; ethyl acetate:hexanes, 1:5) afforded **38b** (65 mg, 52%): ^{1}H NMR ($CDCl_3$) δ 3.42 (d, J = 6.9 Hz, 2 H), 4.99 (H_a, dd, J = 9.4, 1.2 Hz, 1 H), 5.12 (H_b, dd, J = 16.5, 1.5 Hz, 1 H), 5.84 (H_c, dt, J = 15.1, 7.0 Hz, 1 H), 6.10 (H_d, dd, J = 15.1, 10.2 Hz, 1 H), 6.33 (H_e, ddd, J = 16.8, 10.1 Hz, 1 H). The IR and ^{1}H NMR spectra of **38b** agree with literature values.[15a]

KF/Cetyltrimethylammonium Bromide Methodology for Eliminating 32b to (*E*)-5-Phenyl-1,3-pentadiene (38b). A solution of **32b** (272 mg, 0.76 mmol), potassium fluoride (170 mg, 3.0 mmol), and cetyltrimethylammonium bromide (40 mg, 0.11 mmol) in acetonitrile (10 mL) was refluxed for 16 h. VPLC analysis using (*E*)-propenylbenzene as an internal standard showed **38b** to be produced in 63% yield.

(*E*)- and (*Z*)-6-Methyl-1,3-heptadienes (38d). Procedure D, yield 63%, a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.83 (d, J = 6.6 Hz, 6 H), 1.59 (m, 1 H), 1.90 (dd, J = 6.9 Hz, 2 H), 4.89 (H_a, dd, J = 10.0, 0.50 Hz, 1 H), 5.00 (H_b, dd, J = 16.7, 0.5 Hz, 1 H), 5.58 (H_c, dt, J = 15.1, 7.4 Hz, 1 H), 5.95 (H_d, dd, J = 15.0, 10.3 Hz, 1 H), 6.23 (H_e, ddd, J = 16.9, 10.2, 10.1 Hz, 1 H). Irradiation at δ 1.50 caused δ 5.58 to collapse to a doublet, J = 15.0 Hz; GC-MS detected two isomers in a 93:7 ratio [major isomer *m/e* (relative intensity 110 (38, M^+), 95 (21), 81 (10), 67 (89) 56 (61), 54 (65), 43 (99), 41 (100), 39 (50); minor isomer *m/e* (relative intensity) 110 (37), 95 (38), 81 (7), 67 (93), 56 (57), 54 (59), 43 (89), 41 (100), 39 (59)].

(*E*)-1-Cyclohexyl-1,3-butadiene (36). Procedure D, yield 57%: ^{1}H NMR ($CDCl_3$) δ 1.10−2.11 (m, 11 H, ring), 5.03 (H_a, dd, J = 15.3, 6.8 Hz, 1 H), 5.18 (H_b, dd, J = 16.8, 0.6 Hz, 1 H), 5.75 (H_c, dd, J = 15.3, 6.8 Hz, 1 H), 6.11 (H_d, dd, J = 15.3, 10.2 Hz, 1 H), 6.40 (H_e, ddd, J = 16.9, 10.2, 10.1 Hz, 1 H). The IR and ^{1}H NMR spectra of **36** correspond to the literature.[15b]

KF/TDA-1 Methodology for Elimination. (*E*)-1-Cyclohexyl-1,3-butadiene (36). A solution of **35** (270 mg, 0.77 mmol), anhydrous KF (134 mg, 2.31 mmol), and TDA-1 (30 mg, 0.09 mmol) in acetonitrile (10 mL) was refluxed for 20 h. VPLC analysis revealed that **36** is formed in 65% yield.

Ethyl (*E*)-2,4-Pentadienoate (38f). Procedure D, yield 51%, a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.29 (t, J = 7.3 Hz, 3 H), 4.24 (q, J = 7.2 Hz, 2 H), 5.48 (H_a, dd, J = 10.5, 0.6 Hz, 1 H), 5.60 (H_b, dd, J = 16.9, 0.6 Hz, 1 H), 5.91 (H_c, d, J = 15.4 Hz, 1 H), 6.45 (H_d, ddd, J = 17.5, 10.3 Hz, 1 H), 7.26 (H_e, dd, J = 15.5, 4.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 60.4, 122.3, 125.4, 134.8, 144.6, 166.8; exact mass calcd for $C_7H_{10}O_2$ *m/e* 126.0681, found *m/e* 126.0717. The spectra of **38f** correspond to reported values.[15c]

(*E*)-2,2-Dimethyl-4,6-heptadien-3-one (38h). Procedure D, yield 74%, a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 9 H), 5.51 (H_a, dd, J = 9.4, 0.6 Hz, 1 H), 5.64 (H_b, dd, J = 15.5, 0.7 Hz, 1 H), 6.46 (H_c, ddd, J = 17.6, 9.2, 7.7 Hz, 1 H), 6.57 (H_d, d, J = 14.3 Hz, 1 H), 7.26 (H_e, dd, J = 15.8, 11.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.2, 43.0, 124.9, 125.9, 135.3, 142.8, 204.4; exact mass calcd for $C_9H_{14}O$ *m/e* 138.1045, found *m/e* 138.1048. The above spectra agree with that reported.[15d]

(*E*)-1-(1,3-Butadienyl)cyclohexan-2-ol (38j).[15e] Procedure D, yield 83%, a clear colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.14−1.34 (m, 4 H), 1.64−2.05 (m, 5 H), 3.20−3.30 (m, 1 H), 5.02 (H_a, dd, J = 9.8, 1.4 Hz, 1 H), 5.14 (H_b, dd, J = 17.0, 1.1 Hz, 1 H), 5.57 (H_c, dd, J = 15.1, 8.6 Hz, 1 H), 6.17 (H_d, dd, J = 15.0, 10.3 Hz, 1 H), 6.32 (H_e, ddd, J = 16.5, 10.5, 9.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.7, 25.1, 31.2, 34.0, 49.9, 73.2, 116.1, 132.7, 136.5, 136.8; exact mass calcd for $C_{10}H_{16}O$ *m/e* 152.1201, found *m/e* 152.1188. The spectral data for **38j** are similar to that recorded.

(*E*)-4,6-Heptadien-2-ol (38k).[15f] Procedure D, yield 76%, a viscous yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.20 (d, J = 6.2 Hz, 3

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H), 1.88 (bs, 1 H), 2.12−2.21 (m, 2 H), 3.76−3.86 (m, 1 H), 4.99 (H_a, dd, J = 10.2, 1.7 Hz, 1 H), 5.11 (H_b, dd, J = 16.3, 1.7 Hz, 1 H), 5.61−5.73 (H_c, m, 1 H), 6.11 (H_d, dd, J = 15.1, 10.6 Hz, 1 H), 6.29 (H_e, ddd, J = 16.8, 10.2, 10.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.8, 42.4, 67.3, 116.0, 130.5, 134.1, 136.8; exact mass calcd for $C_7H_{12}O$ *m/e* 112.0888, found *m/e* 112.0911.

(*E*)-1-Phenyl-3,5-hexadien-1-ol (38m). Procedure D, yield 57%, a liquid: ^{1}H NMR ($CDCl_3$) δ 2.09 (bs, 1 H), 2.54 (t, J = 7.1 Hz, 2 H), 4.74 (t, J = 6.6 Hz, 1 H), 5.03 (H_a, dd, J = 8.6, 1.7 Hz, 1 H), 5.15 (H_b, dd, J = 15.8, 1.7 Hz, 1 H), 5.62−5.74 (H_c, m, 1 H), 6.15 (H_d, dd, J = 14.8, 10.5 Hz, 1 H), 6.32 (H_e, ddd, J = 16.7, 10.2, 10.2 Hz, 1 H), 7.28−7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 42.6, 73.6, 116.2, 125.8, 127.6, 128.4, 130.1, 134.4, 136.7, 143.8; exact mass calcd for $C_{12}H_{14}O$ *m/e* 174.1045, found *m/e* 174.1091. The spectra agree with published data.[15h]

(*E*)-1-[Tri(2-propyl)silyl]-1,3-butadiene (38p). Procedure D, yield 61%, a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.01−1.11 (m, 21 H), 5.10 (H_a, dd, J = 9.8, 1.6 Hz, 1 H), 5.21 (H_b, dd, J = 16.8, 1.6 Hz, 1 H), 5.79 (H_c, d, J = 20.5 Hz, 1 H), 6.36 (H_d, ddd, J = 16.6, 9.6, 9.4 Hz, 1 H), 6.58 (H_e, dd, J = 20.5, 9.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 20.6, 117.0, 129.3, 140.3, 146.7; exact mass calcd for $C_{13}H_{26}Si$ *m/e* 210.2004, found *m/e* 210.1780.

(*E*)- and (*Z*)-5-Methyl-6-phenyl-1,3-hexadienes (38q). Procedure D, yield 78%, a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.01 (d, J = 4.5 Hz, 3 H), 2.43−2.75 (m, 3 H), 4.95 (H_a, dd, J = 10.0, 1.7 Hz, 1 H), 5.07 (H_b, dd, J = 16.9, 1.7 Hz, 1 H), 5.67 (H_c, dd, J = 15.3, 6.4 Hz, 1 H), 5.99 (H_d, dd, J = 15.4, 10.4 Hz, 1 H), 6.28 (H_e, ddd, J = 17.1, 10.2, 10.1 Hz, 1 H), 7.10−7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.5, 38.3, 43.4, 115.1, 125.9, 128.1, 128.2, 129.3, 137.4, 140.2, 140.5; mass spectrum, *m/e* calcd for $C_{13}H_{16}(M^+)$ 172.1259; GC-MS detected two isomers in a ratio of 96:4 [major isomer *m/e* (relative intensity) 172 (8), 143 (5), 91 (44), 81 (100), 65 (15), 53 (15), 41 (18), 39 (15); minor isomer *m/e* (relative intensity) 172 (15), 143 (100), 128 (86), 115 (38), 91 (30), 77 (10), 65 (13), 51 (11), 39 (23)].

Single-Pot Dialkylations of (*E*)- and (*Z*)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-2-butenes. (*E*)- and (*Z*)-4-Methyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-pentenes (47). *n*-BuLi (0.22 mL, 0.35 mmol, 1.60 M in hexane) was added to **7** and **8** (83 mg, 0.31 mmol) at −78 °C in THF (10 mL). After 20 min, methyl iodide (91 mg, 0.64 mmol) was added. The mixture was warmed to −30 °C and recooled to −78 °C, and additional *n*-BuLi (0.30 mL, 0.48 mmol, 1.60 M) was added. The solution was stirred for 15 min, and more methyl iodide (68 mg, 0.48 mmol) was added. The mixture was warmed to ∼20 °C, stirred for 1 h, taken up in Et_2O, worked up, and concentrated. Column chromatography (silica gel; ethyl acetate 0−5%) of the concentrate gave (*E*,*Z*)-**47** (93 mg, 98%), a colorless viscous oil: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 1.2−1.7 (m with a singlet at δ 1.33; 8 H), 5.2−5.7 (m, 2 H), 7.3−8.0 (m, 5 H); mass spectrum, *m/e* calcd for $C_9H_{19}Si$ ($M^+ - O_2SPh$) 155.1256, found 155.1244.

Procedure E for Monoalkylation of (*E*)- and (*Z*)-1-(Phenylsulfonyl)-1-substituted-4-(trimethylsilyl)-2-butenes (32); (*E*)- and (*Z*)-4-Methyl-5-phenyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-pentenes (48). *n*-BuLi (0.23 mL, 0.53 mmol, 2.30 M) was added to a solution of **32b** (170 mg, 0.48 mmol) in THF (10 mL) at −78 °C. Methyl iodide (136 mg, 0.96 mmol) was added after 20 min. The solution was then stirred 1 h at room temperature, diluted with Et_2O, worked up, and concentrated to a yellow mobile oil, 211 mg. Column chromatography (silica gel; ethyl acetate 0−3%) yielded (*E*,*Z*)-**48** (170 mg, 97%): ^{1}H NMR ($CDCl_3$, *E*-isomer) δ −0.12 (s, 9 H), 1.21 (s, 3 H), 1.46 (m, 2 H), 3.17 (H_a, d, J = 12.9 Hz, 1 H), 3.29 (H_b, d, J = 13.0 Hz, 1 H), 5.19 (dt, J = 15.6, 7.5 Hz, 1 H), 5.53 (dt, J = 15.6 Hz, 1.2 Hz, 1 H), 7.0−7.3 (m, 5 H), 7.4−7.9 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −1.8 (q), 17.1 (e), 23.7 (t), 39.5 (t), 69.0 (s), 124.3 (d), 126.7 (d), 127.9 (d), 128.3 (d), 130.7 (d), 130.8 (d), 133.3 (d), 134.6 (d), 135.2 (s), 135.7 (s); mass spectrum, *m/e* calcd for $C_{15}H_{23}Si$ ($M^+ - O_2$-SPh) 231.1569, found 231.1590.

(*E*)- and (*Z*)-4-Benzyl-5-phenyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-pentenes (49). Procedure E, yield 71%, white crystals: mp 100−101 °C (from hexane): ^{1}H NMR (CCl_4, *E*-isomer) δ 0.00 (s, 9 H), 1.52 (d, J = 8 Hz, 2 H), 3.25 (s, 4 H), 5.28 (d, J = 17 Hz, 1 H), 5.78 (dt, J = 17.8 Hz, 1 H), 7.1−8.0 (m, 15 H); mass spectrum, *m/e* calcd for $C_{20}H_{25}O_2SSi$ ($M^+ - C_7H_7$) 357.1344, found 357.1304.

(*E*)- and (*Z*)-4-Benzyl-5-phenyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-nonenes (50) and (*E*)- and (*Z*)-4-Benzyl-1,3-nonadienes (51). Procedure E, (*E*,*Z*)-**50**, yield 61%, a clear oil [^{1}H NMR (CCl_4, *E*-isomer) δ 0.07 (s, 9 H), 0.81−1.86 (m, 13 H), 3.18 (H_a, d, J = 13.8 Hz, 1 H) 3.44 (H_b, J = 13.9 Hz, 1 H), 5.27 (d, J = 15.8 Hz, 1 H), 5.42 (dt, J = 15.8, 7.8 Hz, 1 H), 7.1−7.9 (m, 10 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ 1.8 (o), 13.9 (o), 22.3 (e), 23.6 (e), 23.9 (e), 31.0 (e), 32.5 (e), 36.6 (e), 71.8 (u), 125.3 (o), 135.6 (u), 136.6 (o), 128.2 (o), 130.6 (o), 130.6 (o), 133.2 (o), 134.0 (o), 135.7 (u), 136.6 (u), mass spectrum, *m/e* calcd for $C_{19}H_{31}Si$ ($M^+ - O_2SPh$) 287.2195, found 287.2200] and (*E*,*Z*)-**51** (yield 30%, *E*/*Z* = 54:46) as a clear colorless oil [IR (neat film) 1600 cm^{-1}; NOE differences with irradiation at δ 5.88 gave enhancements at δ 3.39 (4.85%), 5.13 (5.18%), 6.61 (1.82%), and 7.1−7.2 (2.24%); NOE differences with irradiation at δ 6.05 resulted in enhancements at δ 1.99 (4.32%), 5.21 (5.55%), and 6.74 (1.54%); mass spectrum, *m/e* calcd for $C_{16}H_{22}$ (M^+) 214.1722, found 214.1744; GC-MS detected two isomers in a 54:46 ratio [major isomer *m/e* (relative intensity) 214 (30, M^+), 171 (1), 157 (17), 143 (100), 129 (40), 128 (28), 115 (18), 91 (67), 81 (16), 79 (10), 77 (9), 67 (18), 65 (14); minor isomer *m/e* (relative intensity) 214 (29, M^+), 171 (1), 157 (18), 143 (100), 129 (39), 128 (28), 115 (18), 91 (62), 81 (14), 79 (9), 67 (17), 65 (13)]].

Elimination of (*E*)- and (*Z*)-4-Benzyl-4-(phenylsulfonyl)-1-(trimethylsilyl)-2-nonenes (50) on Silica Gel. Debenzenesulfonyltrimethylsilylation of (*E*,*Z*)-**50** (127 mg, 0.30 mmol) was effected on silica gel (pentane). After 0.5 h, the column was eluted with pentane and evaporated to yield (*E*,*Z*)-**51** (27 mg, 42%).

(*E*)- and (*Z*)-4-Methyl-5-phenyl-1,3-pentadienes (56). Procedure D, yield 75%, an oil: ^{1}H NMR ($CDCl_3$, *E*- and *Z*-isomers) δ 1.53 (s, 3 H, *Z*), 1.70 (s, 3 H, *E*), 3.35 (s, 2 H, *E*), 3.50 (s, 2 H, *Z*), 5.01−5.06 (H_a, two overlapping dd, J_E = 10.2, 1.7 Hz, *E* and *Z*), 5.13 (H_b, dd, J = 16.8, 1.9 Hz, 1 H, *E*), 5.18 (H_b, d, J = 16.7, Hz, 1 H, *Z*), 5.93 (H_c, d, J = 10.5 Hz, 1 H, *E*), 6.01 (H_c, d, J = 10.6 Hz, 1 H, *Z*), 6.57 (H_d, ddd, J = 16.8, 10.5 Hz, 1 H, *E*), 6.72 (H_d, ddd, J = 16.8, 10.5, 10.5 Hz, 1 H, *Z*), 7.1−7.4 (m, 5 H); NOE differences with irradiation at δ 5.93 gave enhancements at 3.35 (2.93%) and 5.13 (2.53%); ^{13}C NMR ($CDCl_3$, *E* and *Z*-isomers) δ 16.5 (o, *Z*), 23.5 (o, *Z*), 38.3 (e, *Z*), 46.2 (e, *E*), 115.5 (e, *E*), 115.6 (e, *Z*), 126.1 (o, *Z*), 126.1 (o, *E*), 127.1 (o, *E*), 127.5 (o, *Z*), 128.3 (o, *E*), 128.4 (o, *Z*), 128.6 (o, *Z*), 129.0 (o, *E*), 133.1 (o, *Z*), 133.4 (o, *E*), 138.0 (u, *Z*), 138.4 (u, *E*), 139.6 (u, *E*); mass spectrum, *m/e* calcd for $C_{12}H_{14}$ (M^+) 158.1095, found 158.1095. GC-MS detected two isomers in a 80:20 ratio [major isomer *m/e* (relative intensity) 158 (46), 143 (100), 129 (56), 128 (75), 115 (38), 103 (5), 91 (53), 80 (12), 79 (15), 77 (18), 65 (39), 63 (16), 51 (24).

(*E*)- and (*Z*)-1-(Phenylsulfonyl)-1-(3-(trimethylsilyl)-1-propenyl)cyclopropanes (62) and (*E*)- and (*Z*)-1-(Phenylsulfonyl)-1-(3-(trimethylsilyl)-1-propenyl)tetrahydropyrans (66). A solution was prepared from **7** and **8** (509 mg, 1.89 mmol) and *n*-BuLi (0.79 mL, 2.09 mmol, 2.65 M in hexane) in Et_2O (10 mL) at −78 °C. Excess ethylene oxide (**66**, 1.13 g, 25.67 mmol) was added. The mixture was refluxed for 1.3 h and then cooled to 0 °C. Methanesulfonyl chloride (0.22 g, 1.90 mmol) was added. The solution was refluxed for 1.5 h and then cooled to −78 °C. More *n*-BuLi (0.79 mL) was added, and the bright yellow suspension was warmed to room temperature. After 20 min, the mixture was diluted with Et_2O, worked up, and concentrated to a clear yellow liquid (0.75 g). Column chromatography (silica gel; ethyl acetate 0−10%) yielded (*E*)-**62** (160 mg, 28%), the first eluent, a white crystalline solid, mp 60−63 °C: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ −0.11 (s, 9 H), 1.02 (H_a, dd, J = 6.5, 4.2 Hz, 2 H), 1.40 (d, J = 7.1 Hz. 2 H), 1.69 (dd, J = 6.6, 4.2 Hz, 2 H), 5.5−5.6 (m, 2 H), 7.4−7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −2.0 (q), 12.8 (t), 23.1 (t), 44.0 (s), 120.6 (d), 128.6 (d), 128.7 (d), 133.0 (d), 135.9 (d), 139.0 (s); mass spectrum *m/e* calcd for $C_{15}H_{22}O_2SSi$ (M^+)

294.1110, found 294.1108. Anal. Calcd for $C_{15}H_{22}O_2SSi$: C, 61.18; H, 7.53. Found: C, 61.19; H, 7.50.

The second eluent, (*E*,*Z*)-**67** (50 mg, 8%), was a clear oil: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ 0.02 (s, 9 H), 1.57 (d, J = 8.2 Hz, 2 H), 1.76 (d, J = 12.7 Hz, 2 H, H_a), 2.27 (ddd, J = 12.7, 13.0, 4.7 Hz, 2 H, H_b), 3.42 (ddd, J = 12.5, 11.8, 1.3 Hz, 2 H, H_c), 3.85 (dd, J = 11.2, 4.1 Hz, 2 H, H_d), 5.02 (d, J = 15.9 Hz, 1 H, H_e), 5.60 (dt, J = 16.2, 8.0 Hz, 1 H, H_f), 7.4−7.9 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −1.7, 24.2, 29.4, 63.5, 66.0, 121.7, 128.4, 130.8, 133.5, 135.2, 137.5; NOE differences with irradiation at δ 3.42 gave enhancements at δ 1.76 (3.21%), δ 3.85 (29.63%), δ 5.02 (2.26%), and δ 5.60 (2.46%); NOE differences with irradiation at δ 3.42 resulted in enhancements at δ 1.76 (3.21%), δ 3.85 (29.63%), δ 5.02 (2.26%), δ 5.60 (2.46%), and δ 3.42 (25.74%); NOE differences with irradiation at δ 5.02 led to enhancements at δ 1.57 (5.17%), δ 1.76 (4.76%), δ 3.42 (2.24%), and δ 7.80 (1.97%); mass spectrum, *m*/*e* calcd for $C_{11}H_{21}OSi$ ($M^+ - O_2SPh$) 197.1362, found 197.1371; GC-CI-MS (CH_4) *m*/*e* (relative intensity) 339 (100, $M^+ + 1$), 323 (46), 251 (17), 215 (39), 125 (24), 123 (10), 111 (25), 107 (47), 95 (15).

Procedure F for Cycloalkylation of 1-(Phenylsulfonyl)-4-(trimethylsilyl)-2-butenes (7 and 8); (*E*)- and (*Z*)-1-(Phenylsulfonyl)-1-(3-(trimethylsilyl)-1-propenyl)cyclopropanes (62). *n*-BuLi (1.60 mL, 3.87 mmol, 2.42 M in hexane) was added to **7** and **8** (0.96 g, 3.57 mmol) at −78 °C in THF (10 mL). After 10 min, 1,2-dibromoethane (**68**, 812 mg, 4.32 mmol) was added. After 1 h, the solution was recooled to −78 °C and additional *n*-BuLi (2.20 mL, 5.32 mmol) was added. The mixture, after warming to room temperature, was stirred for 1 h, diluted with Et_2O, worked up, and concentrated to a yellow liquid oil (1.23 g). Column chromatography (silica gel; ethyl acetate 0−5%) yielded (*E*,*Z*)-**62** (1.01 g, 95%), a viscous oil which solidified upon standing; mp 63−65 °C (from pentane). The product was identical with that prepared from **15** and **16** with **58** and subsequent ring closure of **61** (eq 8).

(*E*)- and (*Z*)-1-(Phenylsulfonyl)-1-(3-(trimethylsilyl)-1-propenyl)cyclobutanes (71, *n* = 3). Procedure F, yield 87%, a colorless oil: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ −0.06 (s, 9 H), 1.46 (dd, J = 8.0, 1.0 Hz, 2 H), 1.6−2.3 (m, 4 H), 2.7−3.0 (m, 2 H), 5.29 (d, J = 15.4 Hz, 1 H), 5.49 (dt, J = 15.4, 7.9 Hz, 1 H), 7.4−7.9 (m, 5 H); irradiation at δ 1.6−2.3 collapses δ 2.7−3.0 to a bs; irradiation at δ 1.46 collapses δ 5.49 to a d; ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −1.9, 15.1, 23.2, 27.8, 66.9, 123.9, 128.4, 129.6, 133.2, 133.3, 136.3; mass spectrum, *m*/*e* calcd for $C_{10}H_{19}Si$ ($M^+ - O_2SC_6H_5$) 167.1256, found 167.1271; CI-MS (CH_4), *m*/*e* (relative intensity) 309 (2, $M^+ + H$), 287 (6), 269 (4), 243 (10), 214 (88), 199 (28), 167 (100), 95 (33), 73 (31).

(*E*)- and (*Z*)-1-(Phenylsulfonyl)-1-(3-(trimethylsilyl)-1-propenyl)cyclopentanes (71, *n* = 4). Procedure F, yield 89%, a liquid: ^{1}H NMR ($CDCl_3$, *E*- and *Z*-isomers) δ −0.03 (s, 9 H, *Z*), 0.08 (s, 9 H, *E*), 1.43 (dd, J = 8.00, 0.8 Hz, 2 H), 1.5−1.8 (m, 6 H), 2.2−2.4 (m, 2 H), 5.03 (dt, J = 11.6, 1.7 Hz, 2 H, *Z*), 5.21 (d, J = 15.6 Hz, 1 H, *E*), 5.43 (dt, J = 15.5, 8.0 Hz, 1 H, *E*), 5.59 (dt, J = 11.5, 9.2 Hz, 2 H, *Z*), 7.4−7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −2.0, 23.3, 23.9, 32.7, 74.4, 125.2, 128.2, 129.9, 132.8, 133.0, 137.2; mass spectrum, *m*/*e* calcd for $C_{11}H_{21}Si$ ($M^+ - O_2SPh$) 181.1412, found 181.1447.

(*E*)- and (*Z*)-1-(Phenylsulfonyl)-1-(3-(trimethylsilyl)-1-propenyl)cyclohexanes (71, *n* = 5). Procedure F, yield 78%, a colorless oil: ^{1}H NMR ($CDCl_3$, *E*-isomer) δ −0.02 (s, 9 H), 1.0−1.9, (m, 12 H), 4.92 (dd, J = 15.9, 1.1 Hz, 1 H), 5.49 (dt, J = 15.9, 8.2 Hz, 1 H), 7.4−7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$, *E*-isomer) δ −1.9, 21.5, 23.8, 25.1, 28.8, 68.4, 122.9, 128.0, 130.7, 133.0, 135.6, 136.0; mass spectrum, *m*/*e* calcd for $C_{12}H_{23}Si$ (M^+-O_2SPh) 195.1569, found 195.1557.

Allylenecyclopropane (72, *n* = 2). Procedure D gave **83** (*n* = 2, 90%) and hexamethyldisiloxane (HMDS) as a colorless oil stable at room temperature for several days. Diene **72** (*n* = 2) turned cloudy upon standing: ^{1}H NMR (CCl_4) δ 0.00 (s, HMDS), 1.05 (s, 4 H), 5.00−5.45 (m, 2 H), 6.32−6.88 (m, 2 H). The IR and ^{1}H NMR spectra of **72** (*n* = 2) are identical with the literature.[15c]

***N*-Phenyl-4,5-diazaspiro[2.5]oct-7-ene-4,5-dicarboximide (73).** TBAF (7.13 mL, 7.13 mmol, 1.0 M solution in THF) was added to **83** (*n* = 2; 1.40 g, 4.75 mmol) in THF (15 mL) at 0 °C. After 5 min, the mixture was diluted with Et_2O, worked up, and cooled (−78 °C). 4-Phenyl-1,2,4-triazoline-3,5-dione[15g] (0.83 g, 4.75 mmol) was then added in 1 h. The temperature of the reaction mixture was not allowed to rise above 60 °C. The mixture was filtered, concentrated to a brown solid (1.10 g), and chromatographed (silica gel; ethyl acetate 25%) to give **73** (0.98 g, 81%) as a white crystalline solid: mp 130−131 °C (from hexane): ^{1}H NMR ($CDCl_3$) δ −0.92 (dd, J = 7.6 Hz, 2 H), 2.10 (dd, J = 7.6 Hz, 2 H), 4.17 (dd, J = 3.2 Hz, 2 H), 5.22 (dt, J = 11.2 Hz, 1 H), 5.82 (dt, J = 11.3 Hz, 1 H), 7.2−7.7 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 12.0 (t), 40.9 (s), 43.8 (t), 118.3 (d), 125.6 (d), 128.1 (d), 129.1 (d), 130.5 (d), 150.7 (s), 152.4 (s); mass spectrum, *m*/*e* calcd for $C_{14}H_{13}N_3O_2$ (M^+) 255.1007, found 255.1004. Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13. Found: C, 65.47; H, 4.99.

Allylenecyclobutane (72, *n* = 3). Procedure E, yield 61%; HMDS 22%: ^{1}H NMR ($CDCl_3$) δ 0.08 (s, HMDS), 2.01 (quin, J = 7.9 Hz, 2 H), 2.7−2.8 (m, 4 H), 4.91 (H_a, dd, J = 10.2, 0.9 Hz, 1 H), 4.99 (H_b, dd, J = 17.0, 0.9 Hz, 1 H), 5.78 (H_c, dt, J = 10.8, 2.2 Hz, 1 H), 6.27 (H_d, ddd, J = 7.0, 10.8, 10.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 1.9 (q, HMDS), 17.1 (t), 29.9 (t), 31.3 (t), 113.0 (t), 121.7 (d), 133.1 (d), 146.0 (s); mass spectrum, *m*/*e* calcd for C_7H_{10} (M^+) 94.0782, found 94.0789.

Allylenecyclopentane (72, *n* = 4). Procedure C, yield 51%; HMDS 11%: ^{1}H NMR ($CDCl_3$) δ 0.12 (s, HMDS), 1.6−1.8 (m, 4 H), 2.3−2.4 (m, 4 H), 4.95 (H_a, dd, J = 9.2, 1.0 Hz, 1 H), 5.04 (H_b, dd, J = 16.1, 0.8 Hz, 1 H), 5.99 (H_c, d, J = 10.9, 1 H), 6.46 (H_d, dd, J = 17.0, 10.6, 10.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 1.8 (q, HMDS), 26.1 (t), 26.3 (t), 29.2 (t), 33.8 (t), 113.2 (t), 121.3 (d), 134.7 (d), 147.6 (s); mass spectrum, *m*/*e* calcd for C_8H_{12} (M^+) 108.0939, found 108.0955.

Allylenecyclohexane (72, *n* = 5).[15g,h] Procedure D, yield 67%: ^{1}H NMR ($CDCl_3$) δ 1.5−1.6 (m, 6 H), 2.15 (bs, 2 H), 2.29 (bs, 2 H), 4.97 (H_a, dd, J = 10.2, 2.0 Hz, 1 H), 5.10 (H_b, dd, J = 16.8, 2.0 Hz, 1 H), 5.80 (H_c, d, J = 10.9 Hz, 1 H), 6.63 (H_d, ddd, J = 16.8, 10.8, 10.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.8, 27.7, 28.5, 29.2, 37.2, 114.4, 122.7, 132.7, 144.1; mass spectrum *m*/*e* calcd for C_9H_{14} 122.1096, found 122.1094. The spectra of **72** (*n* = 5) are identical with that in the literature.[15g,h]

4-Allylenetetrahydropyran (74). Procedure C, yield 87%: ^{1}H NMR ($CDCl_3$) δ 2.27 (t, J = 5.2 Hz, 2 H), 2.42 (t, J = 5.0 Hz, 2 H), 3.69 (quin, J = 5.6 Hz, 4 H), 5.02 (H_a, dd, J = 10.2, 1.6 Hz), 5.16 (H_b, dd, J = 16.8, 1.7 Hz), 5.88 (H_c, d, J = 11.0 Hz), 6.57 (H_d, ddd, J = 16.7, 10.6, 10.5 Hz); ^{13}C NMR ($CDCl_3$) δ 30.2, 37.0, 68.5, 69.3, 115.8, 124.3, 131.9, 138.0; GC-HR-MS, *m*/*e* calcd for $C_8H_{12}O$ 124.0856, found 124.0872.

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Supporting Information Available: Experimental summaries and analytical data for **38e**, **38I**, **38l**, **54**, and **55** and NMR spectra (80 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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