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1-Arylsulfonyl-4-trimethylsilyl-1-and-2-butenes, synthetic equivalents for 1-(1,3-butadienyl) anion and 1,1-(1,3-butadienyl) dianion

Meagher, Timothy Patrick, Ph.D.

The Ohio State University, 1988
1-ARYLSULFONYL-4-TRIMETHYLSILYL-1-AND-2-BUTENES, SYNTHETIC EQUIVALENTS FOR 1-(1,3-BUTADIENYL) ANION AND 1,1-(1,3-BUTADIENYL) DIANION

DISTRIBUTION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

By

Timothy Patrick Meagher

The Ohio State University

1988

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Dr. Matthew Platz
Dr. Anthony Czarnik
Dr. Robert Brueggemeier
Dr. Harold Shechter

Approved by
Harold Shechter
Adviser
Department of Chemistry
To my fiancee

Vicki Barnitz
ACKNOWLEDGMENTS

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PAPERS

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Major Field: Organic Chemistry
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CHAPTER I
INTRODUCTION

This thesis consists of two sections. The first section (Chapter 1) presents the chemistry of (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (1) and subsequent reactions which convert 1 to (E)-1-substituted-1,3-butadienes (2), 1,1-disubstituted-1,3-butadienes (3) and allylidene derivatives 4. The second section (Chapter 2) describes 1-arylsulfonyl-2-halo-4-trimethylsilylbutanes (5-9) and (E)-1-arylsulfonyl-4-trimethylsilyl-1-butenes (10-12) and their conversions to (E)-1-substituted-1,3-butadienes (3) and allylidenes (4).

\[
\begin{align*}
  &\text{(CH}_3\text{}_3\text{Si)}\text{C}_\text{H}_2\text{C}_\text{H}_3\text{SO}_2\text{Ar} \\
  &\text{5} \quad X = \text{Br, Ar = C}_6\text{H}_5 \\
  &\text{6} \quad X = \text{Cl, Ar = C}_6\text{H}_5 \\
  &\text{7} \quad X = \text{Br, Ar = C}_6\text{H}_4\text{-CH}_3\text{-p} \\
  &\text{8} \quad X = \text{Cl, Ar = C}_6\text{H}_4\text{-CH}_3\text{-p} \\
  &\text{9} \quad X = \text{Cl, Ar = C}_6\text{H}_4\text{-Cl}-p \\
  &\text{10} \quad \text{Ar = C}_6\text{H}_5 \\
  &\text{11} \quad \text{Ar = C}_6\text{H}_4\text{-CH}_3\text{-p} \\
  &\text{12} \quad \text{Ar = C}_6\text{H}_4\text{-Cl}-p
\end{align*}
\]

As will be demonstrated, 1, 5-9 and 10-12 have been found to be excellent synths for the 1-(1,3-butadienyl) anion (13) and 1,1-(1,3-butadienyl) dianion (14). Since the chemistry of 1, 5-9 and 10-12 is related
and since the objectives of this research are syntheses of substituted dienes, a common historical introduction will be given in this section.

The present research has its origins in the synthetic utility of 1-benzenesulfonyl-2-trimethylsilylethane (15). Anion 16 is generated quantitatively at -78 °C in THF or diethyl ether by deprotonation of 15 with n-butyl锂ium. Anion 16 as its lithio derivative is stable in THF solutions at room temperature for at least 24 h and reacts with a variety of electrophiles (primary halides, aldehydes, ketones, epoxides, acid halides, halogens, silyl halides, etc; Scheme 1). Further, sulfone 15 can be disubstituted. Of particular importance is that reactions of mono 17 and disubstituted 18 derivatives of 15 with fluoride ion result efficiently in debenzenesulfonyltrimethylsilylations to terminal alkenes 19 and 20. Sulfone 15 can thus be viewed as an effective synthon for vinyl anion 21 and vinyl dianion 22 (Scheme 2). Since routes to 21 and 22 are
limited, proper utilization of sulfone 15 represents an important addition to existing methods for synthesis of varied substituted alkenes.

**SCHEME 1**

1. n-BuLi, -78 °C
2. E' →

**SCHEME 2**

1. n-BuLi, -78 °C
2. E' →
Study of allyl sulfone 1 and its corresponding anion 23 was initiated in this laboratory by Hsiao. In a limited investigation, 23, as its lithio derivative, was alkylated with primary halides to give 24 as a mixture of E and Z isomers as illustrated in Equation 1. When 24 is treated with fluoride ion at 0 °C in THF elimination of the trimethylsilyl and the benzenesulfonyl groups occurs rapidly to give substituted 1,3-dienes (2, Equation 1) efficiently.

\[
\begin{align*}
23 & \xrightarrow{\text{E}} 24 \\
\text{(1)}
\end{align*}
\]

Sulfone 1 can therefore be considered to be a synthetic equivalent for 1-(1,3-butadienyl) anion 13. A reliable general method for generating of 13 is now highly desirable since in principle various substituted butadienes could be prepared by reactions of 13 with electrophiles (Equation 2).
In general, vinyl anions can be prepared using Grignard or lithiation methods. Thus, an obvious precursor for 13 is 1-bromo-1,3-butadiene (25, Equation 3). However, 25 and magnesium are reported to give poor yields of Grignard reagent 26.\(^3\)

\[
\begin{align*}
\text{25} & \overset{\text{Mg}}{\longrightarrow} \text{26} \\
\text{H} & \text{Br} & \text{H} & \text{MgBr}
\end{align*}
\]

A less direct method for preparing metallo analogs of 13 (Equation 4) involves transmetallation of 1-tributylstanny-1,3-butadiene (27) with n-butyllithium at -78 °C.\(^3\) Lithio derivative 28, though successfully condensed with cyclohexanones, has had little other study.\(^4\)
The difficulty in generating butadiene anion 13 directly has led to development of other butadiene anion synthons. For example, 3-sulfolene 29 can be converted into substituted butadienes via an alkylation-fragmentation sequence as in Equation 5.\(^5,6\) Deprotonation of 29 and alkylations of anion 30 yield substituted sulfolenes 31. 3-Sulfolenes 31 expell sulfur dioxide when heated and form terminal dienes 2. The retro-cycloadditions of sulfur dioxide from 31 are concerted and dienes are formed with high E stereochemistry. Complications, however, can arise in deprotonation of 29 and in reactions of anion 30 with electrophiles. Successful deprotonation of 29 usually occurs only when hindered lithium amides are used as bases in the presence of cation complexing co-solvents (HMPA) and at low temperatures. A further drawback is that the choice of electrophiles (E\(^+\)) is limited to those which are highly reactive (primary iodides and bromides and carbonyl compounds). A further complication is that at elevated temperatures 3-sulfolene anion 30 ring opens to 1-(1,3-butadienyl) sulfinate 32 (Equation 6).\(^7\)
A method circumventing the instabilities of 3-sulfolenes such as 30 has been developed (Scheme 3). Sulfone 33 is effectively deprotonated with n-butyllithium in THF at -78 °C. The resulting anion 34 alkylates well with a variety of electrophiles (primary halides, aldehydes, ketones, acyl halides, and esters) to sulfones 35. Retro-Diels-Alder reactions of 35 occur readily when heated to form cyclopentadiene and labile 3-sulfolenes 36 which then expell sulfur dioxide to give terminal dienes 2 which are electrophilically substituted.
With the previous discussion as background, the chemistry of 1-benzenesulfonyl-4-trimethylsilyl-2-butene (1) will now be described as has been developed in the present research. The studies of 1 have been directed toward deprotonation, anion stability, alkylations, ring cyclizations, and elimination of alkylated products. 1-Benzenesulfonyl-4-trimethylsilyl-2-butene (1) has thus been developed as an effective reagent in organic synthesis.
RESULTS AND DISCUSSION

PREPARATION OF 1- BENZENESULFONYL-4-TRIMETHYLSILYL-2-BUTENES (1)

The starting material, (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (1), as described was prepared by an efficient three step procedure developed by Hsiao (Scheme 4). Thus Grignard reagent 37 is prepared from commercially available chloromethyltrimethylsilane and condensed with acrolein to give 4-trimethylsilyl-1-buten-3-ol (38, 65%). Deprotonation of 38 with n-butyllithium and addition of phenylsulfonyl chloride yield (E)- and (Z)-1-phenylsulfinyl-4-trimethylsilyl-2-butenes (39, 70-95%) via spontaneous rearrangement of the initial 4-trimethylsilyl-1-buten-3-yl phenylsulfenate formed (40). Finally, oxidation of 39 with MCPBA gives (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (1, 87-95%). The E/Z ratio for 1 has now been determined to be 89:11 by high field $^1$H NMR techniques as follows. The resonance for protons H$_b$ in the E and Z isomers are cleanly separated at 300 MHz (Figure 1). H$_b$ absorptions in the Z- and E- isomers occur at δ 5.75 and 5.55, respectively. The assignments are based on the coupling between H$_a$ and H$_b$, $J_{ab} = 10.1$ Hz for the Z isomer and $J_{ab} = 15.4$ Hz for the E isomer. E and Z isomers of 1 can be partially resolved by routine column chromatography. Mixtures ranging from 68:18 E/Z to >99% E were obtained by chromatographic techniques.
Figure 1. 300-MHz $^1$H NMR spectra of the vinyl regions of (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-1-butenes (1) in CDCl$_3$. 
STUDIES OF THE STABILITY OF ALLYL ANION 23

It is important that anions be thermally stable if they react sluggishly with electrophiles.\(^{14,15}\) A study was thus made of the stability of allyl anion (23). First, (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes 1 (E/Z = 77:23) were deprotonated with one equivalent of n-butyllithium in THF at \(-78^\circ\text{C}\) (Equation 7). The deprotonation is accompanied by a bright yellow color that is characteristic of a solution of allyl anion 23. The mixture was allowed to warm slowly to room temperature (~ 10 min), stirred for 15 minutes at room temperature, quenched with deuterium oxide and worked up immediately. Column chromatography gave a mixture of (E)- and (Z)-1-benzenesulfonyl-1-deutero-4-trimethylsilyl-2-butenes (41) as a clear colorless viscous oil in 95% yield. However, when allyl anion 23 is kept at \(25^\circ\text{C}\) for 3.3 h, the yield of 41 is reduced to 45%. Allyl anion 23 is stable for only short periods at higher temperatures.

\[
\text{(CH}_3\text{)}_3\text{Si} \quad \text{(CH}_3\text{)}_3\text{Si} \quad \text{(CH}_3\text{)}_3\text{Si} \\
\quad \text{H} \quad \text{H} \quad \Theta \quad \text{H} \quad \text{H} \\
\quad \text{SO}_2\text{C}_6\text{H}_5 \quad \text{SO}_2\text{C}_6\text{H}_5 \quad \text{SO}_2\text{C}_6\text{H}_5 \\
\text{1} \quad \text{23} \quad \text{41} \\
\text{THF, } -78^\circ\text{C} \\
\text{n-BuLi} \\
\text{1. } -78^\circ\text{C} \text{ to } 25^\circ\text{C} \\
\text{2. } D_2O
\]

The structure of 41 is established from its spectral properties. The proton decoupled \(^{13}\text{C}\) NMR spectrum of 41 has two sets of peaks, one for each double bond isomer. The ratios of the peak heights for the two isomers range from
77:23 to 83:17. The absorption for a carbon (δ 60.01) is split into a triplet in accord with a carbon nucleus bonded to a single deuterium atom (spin number of 1).

The percent deuterium incorporation into 41 was determined by $^1$H NMR. Upon comparing the peak area of the δ 3.7 region, a doublet broadened by deuterium coupling to that for the trimethylsilyl region (δ 0.00), the percent deuterium incorporation at the α-position is found to be 87%. Also, the upfield component (H_a) of the vinyl region of 41 is simplified compared to 1 (Figure 2).

Figure 2. 250-MHz $^1$H NMR Spectra of the Vinyl Regions of 1-Benzencesulfonyl-1-deutero-4-trimethylsilyl-2-butene (41)

The E/Z ratio for (E)-and (Z)-1-benzenesulfonyl-1-deutero-4-trimethylsilyl-2-butenes (41) was determined by $^1$H NMR to be 79:21. At high field strength (250 MHz), H_b of the E and Z isomers of 41 are cleanly separated (Figure 2). H_b for the E and Z isomers occur at δ 5.56 and 5.76, respectively.
Stereochemical assignments are based on the coupling between $H_a$ and $H_b$; $H_b$ is coupled to $H_a$ by 15.2 Hz and 10.7 Hz for the E and Z isomers, respectively.

The ratio of (E)- and (Z)-1-benzenesulfonyl-1-deutero-4-trimethylsilyl-2-butenes (41) to (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (1) was also determined by high resolution mass spectral analysis. Two fragments, 1-deutero-4-trimethylsilylbutene cation 42 and 1-trimethylsilylbutene cation 43, resulting from loss of the benzenesulfonyl group were detected (Equation 8). The ratio of 42 to 43 is 84:16, which closely agrees with the $^1$H NMR peak area integration.

(E)- and -(Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes 1 (E/Z = 77:23) were converted to (E)- and (Z)-deuterobutenes 43 (E/Z = 79:21). Thus, the initial E/Z ratio was retained during the conversion. Assuming a small barrier for cis-trans isomerization between the two allyl anions 23 E and 23 Z, the ratio 79:21 could represent quenching the anion mixture at equilibrium. Assuming a large barrier for cis-trans isomerization, allyl anions 23 E and 23 Z retain the geometry of the initial (E) and (Z) isomers of 1 (Scheme 5).
In an attempt to isolate decomposition products of such allyl anions, (E)- and (Z)-4-benzenesulfonyl-5-phenyl-1-trimethylsilyl-2-pentenes (44) were deprotonated at -78 °C with n-butyllithium to give allyl anions 45 (Equation 9). Warming the solution to room temperature (25 °C), stirring for 2.5 h and quenching with water gave a complex mixture of compounds. GLC analysis revealed that 5-phenyl-1,3-pentadiene (46) was formed in trace quantity. TLC and $^1$H NMR analysis showed that 44 was recovered. TLC and GC-MS analyses showed that the decomposition processes were very complex and further separation and isolation of the products were not attempted.

It is interesting to compare the formation and stability of allyl anion 23 with that of 1-lithio-1-benzenesulfonyl-2-trimethylsilylethane 16. Both are easily formed by deprotonation with n-butyllithium at -78 °C. However, unlike 23, 16 is stable in THF at room temperature for at least 24 h as indicated by quantitative recovery of 15 after quenching with water.$^{2e}$
Deuterium and Protium Exchange Under Thermodynamic Conditions

(E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (1) were then converted to (E)- and (Z)-1-benzenesulfonyl-1,1-dideutero-4-trimethylsilyl-2-butenes (47) under thermodynamic conditions. First, 1 was deprotonated with one equivalent of n-butyllithium in THF at -78 °C. The solution was allowed to warm slowly to room temperature, stirred for 15 minutes at room temperature, quenched with deuterium oxide and worked up after 12.5 h. The only product isolated was 1,1-dideutero-2-butene 47 in 89% yield (Equation 10).
Identification of 47 was accomplished by spectral analysis. Diddeuteration of the α-position is apparent from inspection of the δ 3.7 region in the 1H NMR spectrum of 47 which showed only a small (< 5%) residual absorption.

\[
\text{[Diagram showing chemical reactions and structures]}
\]

Diddeuteration obviously arises upon deprotonation of initially formed 1-benzenesulfonyl-1-deutero-4-trimethylsilyl-2-butene (41) by lithium deuteroxide generated in the quenching of carbion 23. Evidence for rapid protium-deuterium exchange under these conditions is that 1-benzenesulfonyl-1,1-dideutero-4-trimethylsilyl-2-butene (47) exchanges its deuterium for hydrogen (THF/H₂O/LiOH) and returns to 1 of natural deuterium abundance within 19 h (vide infra). Protium exchange for deuterium at the α-position of 1-benzenesulfonyl-1,1-dideutero-4-trimethylsilyl-2-butene (47) giving 1 of natural abundance can be followed by 1H NMR. When 47 is treated with lithium hydroxide in a mixture of THF/H₂O, the percent hydrogen incorporation over time can be determined upon integration of the peak area of the δ 3.7 region (Table 1, Equation 11). These results along with those presented earlier in Equation 10 show that in aqueous alkali (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (1) exchange protium and deuterium readily.
Table 1. Protium-Deuterium Exchange of 47 to 1 in LiOH/THF/H$_2$O

<table>
<thead>
<tr>
<th>Reaction Time (h)</th>
<th>% Deuterium$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&gt;99</td>
</tr>
<tr>
<td>1.0</td>
<td>76</td>
</tr>
<tr>
<td>2.2</td>
<td>50</td>
</tr>
<tr>
<td>3.2</td>
<td>18</td>
</tr>
<tr>
<td>19.0</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

$^a$Determined by 90 MHz $^1$H NMR

Study of Deprotonation of 1

n-Butyllithium is an effective base for deprotonating (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butene (1) at -78 °C in THF.$^{2d}$ Study was then made of deprotonation of 1 with sodium amide and with sodium hydride under varied conditions (Equation 12). The insolubilities of these bases in THF, however, limit their deprotonation of 1 to temperatures of 0 °C and above.
Benzyl bromide and allyl bromide were used to trap anion 23 giving as isolated products 44 and 48, respectively.

\[
\begin{align*}
\text{1} & \quad \text{RBr} \quad \text{B} \\
1 & \quad \text{R} = \text{C}_6\text{H}_5\text{CH}_2^- \\
23 & \quad \text{R} = \text{H}_2\text{C} = \text{CHCH}_2^- \\
\end{align*}
\] (12)

The sluggishness of formation and the thermal instability\(^{16}\) of 1-benzenesulfonyl-4-trimethylsilylbutene allyl anion (23) lead to lower yields in its reactions with electrophiles at temperatures of 0 °C and higher (entries 1-3, Table 2). Changing the solvent system to dimethylformamide (DMF), an aprotic polar solvent, gave no improvement in yield (entry 4).
Table 2. Deprotonation of 1-Benzencesulfonyl-4-trimethylsilyl-2-butenes (1) and Alkylation of Allyl Anion 23.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>E</th>
<th>R</th>
<th>Product no.</th>
<th>yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-BuLi</td>
<td>THF</td>
<td>PhCH₂Br</td>
<td>PhCH₂⁻</td>
<td>44</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>NaNH₂</td>
<td>THF</td>
<td>PhCH₂Br</td>
<td>PhCH₂⁻</td>
<td>44</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>NaH</td>
<td>THF</td>
<td>H₂C=CHCH₂Br</td>
<td>H₂C=CHCH₂⁻</td>
<td>48</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>NaH</td>
<td>DMF</td>
<td>H₂C=CHCH₂Br</td>
<td>H₂C=CHCH₂⁻</td>
<td>48</td>
<td>52</td>
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ALKYLATION OF 1-BENZENESULFONYL-4-TRIMETHYLSILYL-2-BUTENES (1)

Having been satisfied that an effective base-solvent system had been found for generation of lithio 1-benzenesulfonyl-4-trimethylsilyl-2-butenes 23, study was initiated of their alkylation with various halides to give (E)- and (Z)- α-substituted-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (24) (Equation 13).
Table 3 shows that methyl iodide and primary bromides alkylate 23 efficiently in THF without the need of HMPA as a co-solvent. Of particular note is that benzyl bromide and methyl iodide react rapidly with 23 at -78 °C. The yellow color of the carbanion solution is discharged within a minute of addition of the halides and the yields of products are excellent.

HMPA is frequently added to a solvent to facilitate nucleophilic displacements. The HMPA is believed to solvate cations strongly leaving the counter anion "naked" and possibly more reactive. At -78 °C in THF n-butyl bromide alkylates 23 much slower than do methyl iodide and benzyl bromide and thus higher temperatures are needed. Addition of HMPA, however, greatly increases the alkylation rate (entry 4). At -78 °C alkylation with n-butyl bromide is complete within 40 min as evident from the fainter color of the solution and TLC analysis of the reaction mixture. The lower yield obtained in the absence of HMPA (entry 3) is explained by the instability of anion 23 at higher temperatures.
Table 3. Alkylation of 23 with Various Electrophiles.

<table>
<thead>
<tr>
<th>Entry</th>
<th>1, E/Z</th>
<th>Solvent</th>
<th>E</th>
<th>No.</th>
<th>Yield %</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>98:2</td>
<td>THF</td>
<td>CH$_3$I</td>
<td>49</td>
<td>97</td>
<td>98:2</td>
</tr>
<tr>
<td>2</td>
<td>80:20</td>
<td>THF</td>
<td>PhCH$_2$Br</td>
<td>44</td>
<td>99</td>
<td>79:21</td>
</tr>
<tr>
<td>3</td>
<td>98:2</td>
<td>THF</td>
<td>C$<em>5$H$</em>{11}$Br</td>
<td>50</td>
<td>89</td>
<td>96:4</td>
</tr>
<tr>
<td>4</td>
<td>98:2</td>
<td>THF/HMPA</td>
<td>C$<em>5$H$</em>{11}$Br</td>
<td>50</td>
<td>99</td>
<td>96:4</td>
</tr>
<tr>
<td>5</td>
<td>72:28</td>
<td>THF/HMPA</td>
<td>(CH$_3$)$_2$CHCH$_2$Br</td>
<td>51</td>
<td>83</td>
<td>75:25</td>
</tr>
<tr>
<td>6</td>
<td>85:15</td>
<td>THF/HMPA</td>
<td>(CH$_3$)$_2$CHCH$_2$Br</td>
<td>51</td>
<td>84</td>
<td>87:13</td>
</tr>
<tr>
<td>7</td>
<td>98:2</td>
<td>THF/HMPA</td>
<td>(CH$_3$)$_2$CHBr</td>
<td>52</td>
<td>97</td>
<td>98:2</td>
</tr>
<tr>
<td>8</td>
<td>85:15</td>
<td>THF/HMPA</td>
<td><img src="image" alt="image" />Br</td>
<td>53</td>
<td>35</td>
<td>85:15</td>
</tr>
<tr>
<td>9</td>
<td>-----</td>
<td>THF/HMPA</td>
<td><img src="image" alt="image" />OTs</td>
<td>53</td>
<td>27</td>
<td>-----</td>
</tr>
</tbody>
</table>
Figure 3. (E)- and (Z)-4-Benzenesulfonyl-1-trimethylsilyl-2-alkenes 49-53.

Alkylation of 23 by 1-bromo-2-methylpropane (a more hindered primary bromide, entry 5 and 6) and 2-bromopropane (a secondary bromide, entry 7) give no problems in THF/HMPA. However, bromocyclohexane (entry 8) substitutes poorly as does cyclohexyl tosylate (entry 9). In the reactions with relatively hindered halides, displacements are slowed and the thermal instability of 23 again becomes a problem.

GC-MS analysis of the reaction mixture of 23 and one equivalent of bromocyclohexane (54) detected cyclohexene (55) in trace amounts along with large quantities of recovered bromocyclohexane (54), 1-cyclohexyl-1,3-butadiene (56) (~13%) and initial 1 (>8-30%) (Equation 14). These facts rule out eliminations of cyclohexyl bromide or cyclohexyl tosylate as major paths in
reactions with 23. Attempts to encourage coupling by addition of cupric chloride and cuprous iodide, in catalytic and larger amounts, to a mixture of 23 and bromocyclohexane unfortunately gave complex products.

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Si} & \quad \text{SO}_2\text{C}_6\text{H}_5 \quad \text{H} \quad \text{54} \\
\text{THF, HMPA, 25 °C} \quad \rightarrow \\
\text{23} & \quad \text{56} + \\
\text{1} \quad \text{53} + \\
\text{55} &
\end{align*}
\]

The fact that 23 does not effect elimination of bromocyclohexane and cyclohexyl tosylate encouraged investigation of more highly \(\beta\)-substituted alkylating reagents. Addition of 2-bromo-1-phenylpropane (57) to a solution of 23 gives dl-(E)-and-(Z)-4-benzenesulfonyl-5-methyl-6-phenyl-1-trimethylsilyl-2-hexenes (58), a mixture of four diastereomers in 40% yield. Also isolated were (E)-1-phenyl-1-propene (59) and initial 1 in 26% and 33% yields, respectively (Equation 15).
Products 58, 59, and 1 have been identified by spectral analysis and/or comparison with authentic samples. Assignment of 59 was made from its spectral and GC retention properties. Its stereoisomer, (Z)-1-phenyl-1-propene (60), and regioisomer, allylbenzene, (61) could not be detected by GC methods. The $^1$H NMR of 58, a complex mixture of diastereomers, contains benzyl diastereotopic protons $H_a$ and $H_b$ and is quite complicated. However, the product mixture clearly shows trimethylsilyl, methyl, benzyl, vinyl and aromatic protons in a 9:3:2:2:10 ratio respectively, and its mass spectrum contains an exact mass for $M^+ - \text{PhSO}_2$. The mixture of compounds 58 possesses a sulfonyl group as evidenced from IR absorbances at 1300 and 1145 cm$^{-1}$. The IR absorption at 1250 cm$^{-1}$ also indicates a Si-Me stretch. GC-MS analysis using chemical ionization (CI) successfully separated three isomers whose peak area ratios are 54:42:4, and all contain the $(M^+ + 1)$ ion expected for 58.
The elimination reaction between allyl anion 23 and 2-bromo-1-phenylpropane (57) occurs regioselectively and stereoselectively giving (E)-3-phenyl-1-propene (59) as the only olefinic product. There are two paths possible for elimination: removal of the benzyl proton resulting in formation of (E)-1-phenyl-1-propene (59) or removal of a less hindered methyl proton to give allylbenzene (61). Benzyl hydrogens are approximately nine pKₐ units more acidic than methyl hydrogens. Therefore, allyl anion 23 appears reluctant to act as a base and effect eliminations of secondary bromides unless a β-hydrogen is activated by an electron accepting group such as phenyl. Also, it is significant that the material balance is high (99%). Thus, the lower yields of alkylation are not due to the instability of 23, but are caused by competing elimination since 1 is recovered in higher yields. Therefore, elimination occurs before complicated carbanion decomposition processes take place.

The high stereochemical selectivity is understandable upon considering the two conformations which can lead to elimination of 59 by an antiperiplanar E₂ process (Scheme 6). Elimination from conformer I is preferred since the phenyl and methyl groups are trans, leading to the E stereoisomer 59. Conformer II has steric interaction between its phenyl and methyl groups and its elimination would lead to a higher energy pathway and to the less stable Z isomer 60.
Increasing the reactivity of the electrophile was anticipated to obviate some of the problems of substitution of sterically hindered systems by 23. Cyclohexene oxide, seemed a likely choice (Equation 16). Carbanion 23 does indeed react smoothly with the epoxide in ethyl ether to give 62 as a mixture of four pairs of diastereomers in 83% yield.
Three pairs of diastereomers were detected by $^1$H NMR with $H_\alpha$ sulfone absorbances at $\delta$ 4.55, 4.18, and 3.55 downfield from tetramethylsilane (Figure 3). The ratio of diastereomeric pairs was 12:46:42 as determined by peak area integration at $\delta$ 4.55, 4.18 and 3.55. High field $^{13}$C NMR also detected four pairs of diastereomers as expected. Column chromatography of the mixture led to isolation of the most polar diastereomeric pair as a white crystalline solid which melts at 122-123 °C.

Figure 4. 250-MHz $^1$H NMR spectra of the sinyl, $H_\alpha$ sulfonyl, and $H'_\alpha$ alcohol regions of 62: a) mixture of diastereomers, and b) most polar diastereomer
The stereochemistries of 44, 49 and 50-53 were determined by high field proton NMR. The coupling between protons $H_a$ and $H_b$ was obtained from inspection of absorbances in the vinyl region (Figure 5). $H_b$ absorbance of the $Z$ isomers, the furthest downfield component, are doublet of triplets and coupled to $H_a$ by 10 Hz (Figure 5). $H_b$ at δ 5.5 for the E isomer of 49, 50, and 51 is a doublet of triplets coupled to $H_a$ by 15 Hz. The stereochemistry of the major isomer in 44, 52, and 53 can not be assigned from inspection of the complex absorptions of their vinyl regions and is assumed to be trans.

Note is taken of the retentions of the E/Z ratios in the alkylation reactions of 1-benzenesulfonyl-4-trimethylsilyl-2-butenes (1) Such retention of double bond geometry has been observed previously in alkylation of (Z) and (E)-3-alkenonate esters and of (E)-1-benzenesulfonyl-2-pentenes.18

\[
\begin{align*}
44 & \quad R = \text{C}_6\text{H}_5CH_2^- \\
49 & \quad = \text{CH}_3 \\
50 & \quad = n-C_9H_{19}^- \\
51 & \quad = (\text{CH}_3)_2\text{CHCH}_2^- \\
52 & \quad = (\text{CH}_3)_2\text{CH}^- \\
53 & \quad = \text{Cyclohexyl} \\
\end{align*}
\]
Figure 5. $^1$H NMR spectra of the vinyl regions of (a) 49 (500-MHz), (b) 52 (500 MHz), (c) 51 (200-MHz), (d) 50 (500-MHz), (e) 53 (500-MHz), and (f) 44 (200-MHz)
ELIMINATION OF MONOALKYLATED PRODUCTS

Fluoride ion induced eliminations of $\beta$-functional silicon compounds are known to occur under relatively mild conditions.\textsuperscript{18,19} Tetrabutylammonium fluoride (TBAF)\textsuperscript{20} was found by Hsiao and Kocienski to effect debenzenesulfonyltrimethylsilylation of (E)- and (Z)-4-benzenesulfonyl-1-trimethylsilyl-2-alkenes \textsuperscript{18} via a 1,2 elimination in refluxing THF (Equation \textsuperscript{17} ).\textsuperscript{21a}

\begin{equation}
\begin{align*}
\text{(CH}_3)\text{3Si} & \quad \text{R} \quad \text{R'} \\
\text{SO}_2\text{C}_6\text{H}_5 & \\
\text{18} & \\
\text{+} & \text{TBAF} \\
\text{= (CH}_3)\text{3SiF} \\
\text{- C}_6\text{H}_5\text{SO}_2 & \\
\text{- TBA} & \\
\text{= R} \quad \text{R'}
\end{align*}
\end{equation}

Hsiao later discovered that 1-benzenesulfonyl-4-trimethylsilyl-2-alkenes (24) undergo elimination at lower temperatures very rapidly.\textsuperscript{21b} Elimination was complete within 20 minutes at 0 °C. The equation below illustrates the conversions of (E)- and (Z)-4-benzenesulfonyl-1-trimethylsilyl-2-alkenes (24) to (E)-alkyl-1,3-dienes (2). High field $^1$H NMR shows the stereochemistry of the dienes to be predominantly trans; however, the exact stereochemical purities of the alkyl-1,3-dienes were not determined.
In the present work fluoride-induced eliminations of (E)- and (Z)-1-trimethylsilyl-4-benzenesulfonyl-2-alkenes 44, 51, 53, 58, and 62 were studied. The results are summarized in Table 4 (entries 1-5).

TBAF (1.5 to 2.0 molar equivalents) was added to stirred solutions of (E)- and (Z)-1-trimethylsilyl-4-benzenesulfonyl-2-alkenes 44, 51, 53, 58, and 62. TLC analyses showed the reactions to be essentially instantaneous at 0 °C. If the elimination is done at -20 °C, the reaction time increases to approximately 1 h. If less than 1.5 equivalents of TBAF are employed, the diene along with starting material are detected by TLC. After stirring for 5 minutes, the reaction mixture was washed with water, dried, passed through silica gel and evaporated to give (E)- and (Z)-6-phenyl-1,3-pentadienes (64), (E)- and (Z)-5-methyl-1,3-heptadienes (65),
(E)- and (Z)-5-methyl-6-phenyl-1,3-hexadienes (66), and (E)-1-(1,3-butadienyl)cyclohexan-2-ol (67) as clear, colorless volatile oils in 52-85% yields. The yields reported for the 1,3-dienes are lower than actual yields because of unavoidable coevaporation of dienes with the solvent (pentane).

Table 4. Elimination of (E)- and (Z)-1-Benzensulfonyl-4-trimethylsilyl-2-butenes 44, 51, 53, 58, and 62 Using TBAF.

<table>
<thead>
<tr>
<th>Substrate Product</th>
<th>E/Z</th>
<th>Entry No.</th>
<th>Yield %</th>
<th>E/Z</th>
</tr>
</thead>
</table>
|                   |     | 1         | 53      | 85:15 | 63   | 57 | >99:1 
|                   |     | 2         | 44      | 80:20 | 64   | 52 | >99:1 
|                   |     | 3         | 51      | 98:2  | 65   | 63 | >99:1 
|                   |     | 4         | 58      | d     | 66   | 78 | 91:1 
|                   |     |           |         |       |      |    | 96:4 
|                   |     |           |         |       |      |    | >9:1 
|                   |     | 5         | 62      | d     | 67   | 83 | >99:1 

a) ratio determined by $^1$H NMR; b) ratio determined by GC-MS; c) ratio determined by $^{13}$C NMR; d) a mixture of 4 diastereomers.
Identifications of 63-67 were accomplished by spectral analyses and/or comparison to literature values. The $^1$H NMR spectrum of 66 contained methyl, vinyl, benzyl, allyl, and aromatic protons in a 3:3:5:5 ratio. The IR spectrum of 66 indicated the presence of a conjugated double bond since absorbances at 1600 and 1650 cm$^{-1}$ were detected. High resolution mass spectral analysis gave the correct molecular ion ($M^+$) for 66.

The stereochemical purities of the diene products were determined by $^1$H NMR, GC-MS, and $^{13}$C NMR methods. Elimination of 58, a mixture of four pairs of diastereomers, with TBAF is very stereoselective giving terminal diene 81 with nearly exclusive trans stereochemistry. The $^1$H NMR (250 MHz) of the vinyl region of 5-methyl-6-phenyl-1,3-butadiene (66) showed clean separation of all vinyl protons (Figure 6). The major isomer is assigned E stereochemistry on the basis of the coupling between vinyl protons H$_c$ at 5.67 ppm and H$_d$ at 5.99 ppm downfield from tetramethylsilane. The coupling constant $J_{cd}$ is 15.3 Hz which is a typical value for trans double bonds. Furthermore, GC-MS detected two isomers with nearly identical mass spectra both having molecular ion peaks corresponding to 66. The peak area ratio for the two isomers is 96:4. $^{13}$C NMR also indicated the presence of two isomers in a ratio greater than 9:1.

The GC-MS analysis of the reaction mixture from elimination of 53 detected only one isomer of diene 63, and its high field $^1$H NMR (200 MHz) showed only one isomer present in the vinyl region. Elimination of 62, a mixture of four pairs of diastereomers, also led to extremely pure trans diene 67 as determined by inspection of the vinyl region in the high field $^1$H NMR of 67 (Figure 6). Further, its $^{13}$C NMR (63 MHz) spectrum contained a single set of peaks corresponding to one stereoisomer.
The lower molecular weight dienes 68 and 69 were prepared by treating their precursors with TBAF in DMSO (Equation 19). The volatile products were isolated by flash distillation and trapping at -78 °C. Hexamethyldisiloxane is the only contaminant and was used as an internal reference for $^1$H NMR.

\[
\begin{align*}
\text{(CH}_3)_3\text{Si} & \quad \text{SO}_2\text{C}_6\text{H}_5 \\
\text{R} & \quad \text{H} \\
49 & \quad \text{R} = -\text{CH}_3 \\
52 & \quad \text{R} = -\text{CH(}\text{CH}_3)\text{)}_3 \\
68 & \quad \text{R} = -\text{CH}_3 \\
69 & \quad \text{R} = -\text{CH(}\text{CH}_3)\text{)}_3
\end{align*}
\]

**ELIMINATION OF 44 AND 53 UNDER PHASE TRANSFER CONDITIONS**

The extremely facile manner in which (E)- and (Z)-4-benzenesulfonyl-1-trimethylsilyl-2-alkenes 49-53, 58 and 62 eliminate when treated with TBAF encouraged study of other means to eliminate the trimethylsilyl and benzenesulfonyl groups. Investigation of other fluoride catalyzed conditions was initiated.\(^{22}\) Potassium fluoride, a convenient source of fluoride ion, was examined. No reaction occurs when (E)- and (Z)-4-benzenesulfonyl-1-trimethylsilyl-2-alkenes 53 and 44 are treated with potassium fluoride in refluxing acetonitrile for 24 h. The low reactivity of the fluoride ion under these conditions is attributed to the insolubility of potassium fluoride in acetonitrile. However, addition of a phase transfer reagent, cetyltrimethylammonium bromide (70), to a mixture of (E)- and (Z)-4-benzenesulfonyl-1-trimethylsilyl-2-alkenes 44 (E/Z =
Figure 6. $^1$H NMR spectra of the vinyl regions of (a) (E)- and (Z)-5-methyl-6-phenyl-1,3-hexadienes (66), 250-MHz; (b) (E)-1-(1,3-butadienyl)cyclohexan-2-ol (67), 250-MHz; and (c) (E)- and (Z)-1-cyclohexyl-1,3-butadienes (63), 200-MHz.
80/20) and potassium fluoride in acetonitrile gave, after refluxing for 16 h, \((E)\)-5-phenyl-1,3-pentadiene (64) in 63% yield (Equation 20).

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Si} & \quad \text{H} & \quad \text{C}_6\text{H}_5 \\
\text{SO}_2\text{C}_6\text{H}_5 & \quad \text{H} & \quad \text{C}_6\text{H}_5 \\
\text{4 4} & \quad \text{KF, CH}_3\text{CN} & \quad \text{7 0} \\
\text{CH}_3(\text{CH}_2)_1\text{N(CH}_3\text{)}_3\text{Br} & \quad \text{6 4}
\end{align*}
\]

Similarly, tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1)\textsuperscript{23} (71), an acyclic cryptand which solubilizes potassium fluoride, effected elimination of \((E)\)- and \((Z)\)-4-benzenesulfonyl-1-trimethylsilyl-2-alkenes 53 (\(E/Z = 85/15\)). When TDA-1 (71) is added to a mixture of 53 and potassium fluoride in refluxing acetonitrile, 1-cyclohexyl-1,3-butadiene (63) is obtained in 65% yield (Equation 21).

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Si} & \quad \text{H} & \quad \text{C}_6\text{H}_5 \\
\text{SO}_2\text{C}_6\text{H}_5 & \quad \text{H} & \quad \text{C}_6\text{H}_5 \\
\text{5 3} & \quad \text{KF, CH}_3\text{CN} & \quad \text{7 1} \\
\text{N(CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3\text{)}_3 & \quad \text{6 3}
\end{align*}
\]

Dienes 64 and 63 were identified by spectral and G.C. analyses and comparison to authentic samples. The yields were determined by GC analyses using allylbenzene as an internal standard. The stereochemistries of 63 and 64 were determined from the vinyl coupling constants in their \(^1\text{H}\) NMR spectra to be \(E/Z > 9/1\).
Potassium fluoride in combination with cetyltrimethylammonium bromide or TDA-1 are attractive alternates to commercially available TBAF since the former methods are considerably more cost effective. However, the phase transfer conditions require higher temperatures and longer reaction times. TBAF, a very reactive source of fluoride, is much milder and more expedient. This method is strongly recommended when starting materials and/or elimination products are sensitive to temperature or shorter reaction times are desired.

**ACID-INDUCED ELIMINATIONS**

An investigation of acid-induced elimination of benzenesulfonyl and trimethylsilyl groups was undertaken. Recently, it has been reported compounds containing sulfone groups are labile under strong Lewis acid conditions. Trost has published recently that allyl and tertiary sulfones when treated with aluminum chloride undergo ring cyclization (Scheme 7). Presumably this reaction is initiated by complexation of aluminum chloride with the oxygen on sulfone 72. Loss of the sulfone group from 73 generates carbocation 74 which leads to intramolecular ring closure via electrophilic aromatic substitution.

Based on the above knowledge it was felt that (E)- and (Z)-4-benzenesulfonyl-5-phenyl-1-trimethylsilyl-2-pentenes (44) could be induced to lose both the sulfone and silyl groups. When 44 (E/Z = 80:20) is treated with aluminum chloride, as illustrated in Equation 22, it does indeed give 5-phenyl-1,3-pentadiene (64) in 29% yield. Diene 64 was identified by spectral data and by comparison to an authentic sample. The stereochemistry of 64 is highly trans as determined by $^1$H NMR (E/Z > 9/1). The low yield of 64 is probably due
to the diene's sensitivity to acidic conditions.\textsuperscript{25} Replacing aluminium chloride with boron trifluoride as the Lewis acid unfortunately gave complicated products. Silylsulfone 44 was found unreactive HCl (12M) in THF even at refluxing conditions for 48 h.

\begin{center}
\textbf{SCHEME 7}
\end{center}

Scheme 8 illustrates a possible mechanism for the acid-induced elimination of 44. Aluminum chloride complexes with sulfone oxygen leading to the loss of the benzenesulfonyl group. The resulting allyl carbocation, 77, is assumed to be the intermediate. Carbocation 75 is a reasonable intermediate since the
positive charge is stabilized by allylic resonance and by hyperconjugation with the gamma-trimethylsilyl group. The now labile Si-C bond cleaves giving 5-phenyl-1,3-pentadiene 64.

\[ \text{SCHEME 8} \]

\[ (\text{CH}_3)_3\text{Si} \quad \overset{\text{C}_6\text{H}_5}{\text{CH}} \quad \overset{\text{SO}_2\text{C}_6\text{H}_5}{\text{CH}} \quad \overset{\text{AlCl}_3}{\text{CH}_2\text{Cl}_2} \quad \overset{\text{H}}{\text{C}} \quad \overset{\text{C}_6\text{H}_5}{\text{C}} \quad \overset{\text{AlCl}_3}{\text{O}} \quad \text{64} \]

\[ \overset{\text{CH}_3\text{Si}}{\text{AlCl}_3} \]

\[ (\text{CH}_3)_3\text{Si} \quad \overset{\text{C}_6\text{H}_5}{\text{CH}} \quad \overset{\text{SO}_2\text{C}_6\text{H}_5}{\text{CH}} \quad \overset{\text{AlCl}_3}{\text{CH}_2\text{Cl}_2} \quad \overset{\text{H}}{\text{C}} \quad \overset{\text{C}_6\text{H}_5}{\text{C}} \quad \overset{\text{AlCl}_3}{\text{O}} \quad \text{75} \]
Studies of Dialkylation of 1-Benzencesulfonyl-4-trimethylsilyl-2-butenes (1)

Attention next turned to dialkylation of 1-benzenesulfonyl-4-trimethylsilyl-2-butenes (1). A one pot method developed for dialkylation of 1 with methyl iodide is illustrated in Equation 23. The method consists of (1) reaction of allyl anion 23 in THF with methyl iodide at -30 °C to form 4-benzenesulfonyl-1-trimethylsilyl-2-pentene (49), (2) cooling the solution and addition of another equivalent of n-butyllithium to yield allyl anion 76, (3) addition of more methyl iodide and reaction at room temperature to give a chromatographically clean (E) and (Z) mixture of 4-benzenesulfonyl-4-methyl-1-trimethyl-2-pentenes (77) in 98% yield. The structures of 77 are established from their spectral properties. Since the absorbances of the vinyl protons (δ 5.2-5.7) are overlapping, the E/Z ratio of 77 could not be obtained by 1H NMR. The dimethylated product is assumed to be highly trans.

![Chemical Structures](image)

Products 78 and 79 resulting from gamma-alkylation of allyl anion 76 were not detected. The fact that the 1H NMR clearly reveals two protons in the vinyl
region for 77 rules out 78 and 79 as possible structures since the latter products have only one vinyl proton.

\[
\begin{align*}
(\text{CH}_3)_3\text{Si} &\quad (\text{CH}_3)_3\text{Si} \\
\text{CH}_3 &\quad \text{CH}_3 \\
\text{CH}_3 &\quad \text{CH}_3 \\
\text{SO}_2\text{C}_6\text{H}_5 &\quad \text{SO}_2\text{C}_6\text{H}_5
\end{align*}
\]

78

79

Dialkylation was further investigated using more sterically hindered substrates, (E)- and (Z)-4-benzenesulfonyl-5-phenyl-1-trimethylsilyl-2-butenes (44, Equation 24). Deprotonation of 44 (E/Z = 79:21) with n-butyllithium yielded a carbanion solution of allyl anion 80 which when treated with methyl iodide gave, after work up and silica gel chromatography, (E)- and (Z)-4-benzenesulfonyl-4-methyl-5-phenyl-1-trimethylsilyl-2-butenes (81) as a clear viscous oil in 97% yield.

\[
(\text{CH}_3)_3\text{Si} \quad (\text{CH}_3)_3\text{Si} \quad (\text{CH}_3)_3\text{Si} \quad (\text{CH}_3)_3\text{Si}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5 &\quad \text{C}_6\text{H}_5 \\
\text{SO}_2\text{C}_6\text{H}_5 &\quad \text{SO}_2\text{C}_6\text{H}_5 \\
\text{H} &\quad \text{H} \\
\text{H} &\quad \text{H}
\end{align*}
\]

44

80

81

(24)
The structural assignments of 81 were made by $^1$H NMR analysis. The resonance for the vinyl protons $H_a$ for the trans isomer ($\delta$ 5.53, $J_{ab} = 15.6$ Hz) is downfield from that of the cis isomer ($\delta$ 5.41, $J_{ab} = 11.2$ Hz). The E/Z ratio of 81 by $^1$H NMR is 80:20. Thus, the alkylation reaction proceeds with retention of stereochemistry.

![Structure 81](image)

Alkylations of (E)- and (Z)-4-benzenesulfonyl-5-phenyl-1-trimethylsilyl-2-butenes (44) were then extended to benzyl bromide. Reaction of allyl anion 80 with benzyl bromide affords, after crystallization of the product from hexane, (E)-4-benzenesulfonyl-4-benzyl-5-phenyl-1-trimethylsilyl-2-pentene (82) as a white solid (Equation 25). Benzyl derivative 82 is identified spectrally. The stereochemical assignment of 82 as E is based on the coupling ($J_{ab} = 17$ Hz) between the vinyl protons $H_a$ ($\delta$ 5.28) and $H_b$ ($\delta$ 5.78).
Alkylation of (E)- and (Z)-4-benzenesulfonyl-5-phenyl-1-trimethylsilyl-2-butene (44, E/Z = 80:20) were then extended to more sluggish electrophiles. Reaction of allyl anion 80 with 1-bromopentane requires HMPA as a co-solvent with THF. Upon quenching allyl anion 80 with 1-bromopentane (Equation 26) followed by aqueous workup and column chromatography, the following products were isolated: (E)- and (Z)-4-benzenesulfonyl-4-benzyl-1-trimethylsilyl-2-nonen (83) and (E)- and (Z)-5-phenyl-4-(1-pentyl)-1,3-pentadienes (84) in 61% and 30% yields respectively.
Products 83 and 84 have been identified from their spectral properties. Nonenes 83 are a clear colorless viscous oil which crystallizes to a white solid. After recrystallization in hexane, the $^1$H NMR of the product reveals the presence of two isomers, trans and cis, in a 79:21 ratio. Absorptions for two vinyl protons $H_a$ and $H_b$ are observed at $\delta$ 5.27 ($J_{ab} = 15.8$ Hz) and 5.42, respectively, for the trans isomer, while the cis isomer's $H_a$ and $H_b$ vinyl protons resonate at $\delta$ 5.12 ($J_{ab} = 12.4$ Hz) and 5.67, respectively. Disubstitution at the $\alpha$-position is confirmed since $H_a$ is coupled only to vinyl $H_b$. The two quaternary carbons as detected by $^{13}$C NMR at $\delta$ 71.77 (E isomer) and 73.37 (Z isomer) correspond to the $\alpha$-sulfone carbons.

Product 84, isolated by chromatographic techniques, is a mobile clear oil. Its $^1$H NMR and $^{13}$C NMR indicate the presence of two isomers in a 53:47 ratio (Table 5 and 6). GC-MS analysis results in separation of two isomers with nearly identical mass spectra; the peak area ratio is 54:46. Since trisubstitution about the double bond makes isomer identification difficult, certainty as to which isomer is cis and trans is obtained by NOE experiments (Figure 7). Fortunately, the most diagnostic vinyl protons, $H_c$ for both isomers, cleanly separate at $\delta$ 5.88 and 6.05, respectively. Irradiation at $\delta$ 5.88 enhances absorption at $\delta$ 3.39 (the benzyl protons). Thus the set of absorbances correspond to E isomer, 84 E.
Irradiation at δ 6.05 enhances δ 1.99 (the allyl protons) and thus this set of absorbances is assigned to Z isomer, 84 Z.

Having assigned allyl, benzyl, and vinyl proton absorbances by NOE methods made possible assignments of the $^{13}$C absorbances for allyl (4 E and 4 Z), benzyl (6 E and 6 Z), and vinyl (7 E, 9 E, 12 E, 7 Z, 9 Z, and 12 Z) carbons in E- and Z- 84 by $^1$H-$^{13}$C correlation (Table 6, Figure 8). The largest differences in chemical shifts for carbons in isomer pairs are seen for allyl (4 E and 4 Z) and benzyl (6 E and 6 Z) absorbances. Carbon 4 E is cis to the vinyl moiety and its absorbances (δ 30.29) are upfield from that for carbon 4 Z (δ 36.71) by 6.42 ppm. Similarly, carbon 6 Z is cis to the vinyl group and its absorbance (δ 36.52) is upfield from that for carbon 6 E (δ 43.74) by 7.22 ppm. The vinyl group causes an upfield shift by 6-7 ppm for allylic carbon nuclei located cis to it in butadienes. This shielding effect has been reported in monosubstituted 1,3-butadienes.26

Formation of diene 84 must have occurred during chromatographic separation of the products since TLC analysis did not result in detection of the diene in the alkylation mixture. That 84 is formed during chromatography is
confirmed by absorption of nonene 83 on Kieselgel, elution with pentane and evaporation to give 84 (42%, E/Z ratio = 54/46) as in Equation 27.

\[
\begin{align*}
\text{Silica Gel} & \\
83 & \rightarrow 84
\end{align*}
\]

Anion 80 is a nucleophile which might be expected to alkylate ambidently to give \( \alpha \)- and \( \gamma \)-regioisomers. However, products 85 resulting from \( \gamma \)-alkylation of 80 were not detected (Scheme 9). Surprisingly, \( \alpha \)-alkylation of 80 is highly favored even when a bulky substituent such as benzyl is present at the \( \alpha \)-position.

**SCHEME 9**
Figure 7. (X) 500-MHz $^1$H NMR spectra of: allyl, benzyl, and vinyl regions of 84 E and 84 Z; (Y) NOE difference spectra irradiation at δ 5.88; (Z) NOE difference spectra irradiation at δ 6.05.
Figure 8. 500-MHz $^1$H-$^{13}$C NMR correlation spectra of 84 E and 84 Z.
Table 5. $^1$H NMR (500 MHz) Chemical Shift Assignments$^a$ and Multiplicities for (E)- and (Z)-4-benzyl-1,3-nonadienes (84).

<table>
<thead>
<tr>
<th>Proton</th>
<th>E</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>0.88 (t, J = 7.5 Hz, 3 H)$^b$</td>
<td>0.87 (t, J = 7.5 Hz, 3 H)$^b$</td>
</tr>
<tr>
<td>-(CH$_2$)$_3$-</td>
<td>1.2-1.5 (m, 6 H)</td>
<td></td>
</tr>
<tr>
<td>Allyl</td>
<td>2.11 (t, J = 7.8 Hz, 2 H)</td>
<td>1.99 (t, J = 7.6 Hz, 2 H)</td>
</tr>
<tr>
<td>-CH$_2$Ph</td>
<td>3.39 (s, 2 H)</td>
<td>3.53 (s, 2 H)</td>
</tr>
<tr>
<td>H$_a$</td>
<td>5.02 (dd, J = 10.2, 1.7 Hz, 1 H)</td>
<td>5.07 (dd, J = 10.1, 1.7 Hz, 1 H)</td>
</tr>
<tr>
<td>H$_b$</td>
<td>5.13 (dd, J = 16.8, 1.8 Hz, 1 H)</td>
<td>5.21 (dd, J = 16.7, 1.8 Hz, 1 H)</td>
</tr>
<tr>
<td>H$_c$</td>
<td>5.88 (d, J = 10.9 Hz, 1 H)</td>
<td>6.05 (d, J = 10.9 Hz, 1 H)</td>
</tr>
<tr>
<td>H$_d$</td>
<td>6.61 (ddd, J = 16.9, 10.5, 10.5 Hz, 1 H)</td>
<td>6.74 (ddd, J = 16.8, 10.5, 10.5 Hz, 1 H)</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>7.1-7.4 (m, 5 H)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Assignments relative to tetramethylsilane. $^b$Assignments of these groups may be interchanged.
Table 6. $^{13}$C NMR (500 MHz) Chemical Shifts Assignments (δ)$^a$, Multiplicities$^b$ and $^1$H-$^{13}$C NMR Correlations for (E)- and (Z)-4-benzyl-1,3-nonadienes (84).

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$^{13}$C-NMR</th>
<th>$^1$H-NMR</th>
<th>$^{13}$C-NMR</th>
<th>$^1$H-NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(e)</td>
<td>(CH$_2$)</td>
<td>(e)</td>
<td>(CH$_2$)</td>
</tr>
<tr>
<td>1</td>
<td>13.98 (o)</td>
<td>0.87-0.88 (CH$_3$)</td>
<td>13.98 (o)</td>
<td>0.87-0.88 (CH$_3$)</td>
</tr>
<tr>
<td>2</td>
<td>22.50 (e)</td>
<td>(CH$_2$)</td>
<td>22.50 (e)</td>
<td>(CH$_2$)</td>
</tr>
<tr>
<td>3</td>
<td>28.24 (e)$^c$</td>
<td>(CH$_2$)</td>
<td>27.56 (e)$^c$</td>
<td>(CH$_2$)</td>
</tr>
<tr>
<td>4</td>
<td>30.29 (e)</td>
<td>2.11 (allyl)</td>
<td>36.71 (e)</td>
<td>1.99 (allyl)</td>
</tr>
<tr>
<td>5</td>
<td>31.77 (e)$^d$</td>
<td>(CH$_2$)</td>
<td>31.56 (e)$^d$</td>
<td>(CH$_2$)</td>
</tr>
<tr>
<td>6</td>
<td>43.74 (e)</td>
<td>3.39 (CH$_2$Ph)</td>
<td>36.52 (e)</td>
<td>3.53 (CH$_2$Ph)</td>
</tr>
<tr>
<td>7</td>
<td>115.54 (e)</td>
<td>5.02 ($H_a$), 5.13 ($H_b$)</td>
<td>115.78 (e)</td>
<td>5.07 ($H_a$), 5.21 ($H_b$)</td>
</tr>
<tr>
<td>8</td>
<td>126.06 (o)</td>
<td>(Ar)</td>
<td>125.97 (o)</td>
<td>(Ar)</td>
</tr>
<tr>
<td>9</td>
<td>127.38 (o)</td>
<td>5.88 ($H_c$)</td>
<td>126.82 (o)</td>
<td>6.05 ($H_c$)</td>
</tr>
<tr>
<td>10</td>
<td>128.25 (o)$^g$</td>
<td>(Ar)</td>
<td>128.32 (o)$^g$</td>
<td>(Ar)</td>
</tr>
<tr>
<td>11</td>
<td>129.08 (o)$^f$</td>
<td>(Ar)</td>
<td>128.55 (o)$^f$</td>
<td>(Ar)</td>
</tr>
<tr>
<td>12</td>
<td>133.08 (o)</td>
<td>6.60 ($H_d$)</td>
<td>133.22 (o)</td>
<td>6.74 ($H_d$)</td>
</tr>
<tr>
<td>13</td>
<td>139.82 (u)$^g$</td>
<td></td>
<td>139.90 (u)$^g$</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>143.14 (u)$^h$</td>
<td></td>
<td>142.09 (u)$^h$</td>
<td></td>
</tr>
</tbody>
</table>

a) Relative to the triplet of deuterochloroform, center line at 77.00 ppm; b) (o) denotes a carbon with three or one hydrogens attached; (e) denotes a carbon with two hydrogens attached; (u) denotes a quaternary carbon; c-h) assignments of these groups may be interchanged.
ELIMINATION OF DIALKYLATED PRODUCTS
FLUORIDE INDUCED ELIMINATIONS

Eliminations of dialkylated products 77 and 81-83 were effected using TBAF. Silylsulfone 77 eliminated rapidly with TBAF in DMSO and flash vacuum distillation led to the volatile products: 4-methyl-1,3-pentadiene (86) in 72% yield and hexamethyldisiloxane (Equation 28). Diene 86 was identified by its spectral properties and by comparison with the literature.

\[
\text{(CH}_3\text{)}_3\text{SiCH}_3\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5 \xrightarrow{\text{TBAF}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3, DMSO, 25^\circ\text{C} \quad \text{(28)}
\]

As illustrated in Equation 29, when (E)- and (Z)-4-benzenesulfonyl-4-methyl-5-phenyl-1-trimethylsilyl-2-butenes (81) are treated with TBAF in THF at 0 \(^\circ\)C, (E)- and (Z)-4-methyl-5-phenyl-1,3-pentadienes (87, 75%) are formed. No 81 was detected immediately after addition of TBAF. The rapidities of the elimination reactions are impressive.

\[
\text{(CH}_3\text{)}_3\text{SiCH}_3\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5 \xrightarrow{\text{TBAF}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3, \text{THF, 0}^\circ\text{C} \quad \text{(29)}
\]
Dienes 87 are identified from their spectral properties. The dienes 87 are conjugated as evidenced from IR olefinic bond stretching (1650 and 1600 cm\(^{-1}\)). Two isomers are detected by \(^1\)H NMR and \(^{13}\)C NMR analyses (Table 7 and 8). Two benzyl protons corresponding to two geometric isomers of 87 resonate at δ 3.35 and 3.50; their relative peak areas are 80 and 20, respectively. NOE experiments allow stereochemical assignments of the benzyl, methyl, and vinyl (H\(_c\)) proton absorbances of the E and Z isomers. Irradiation of the vinyl proton (H\(_c\)) absorbance at δ 5.93 caused enhancement of δ 3.35 (benzyl protons) in the NOE difference spectrum of 87. Thus, the major isomer is assigned E stereochemistry since NOE showed that vinyl proton H\(_c\) and the benzyl protons have a cis relationship. GC-MS analysis of the diene mixture separated two isomers for which peak area integration revealed to be present in a 80:20 ratio. The mass spectra of the geometric isomers 87 were nearly identical and gave proper molecular ion peaks.

\[ \text{87} \]

\(^1\)H-\(^{13}\)C correlation spectral data allowed assignment of carbon and proton shifts for 87 (Table 8, Figure 9). The largest differences in chemical shifts for carbons in isomer pairs are seen for allyl and benzyl absorbances. The vinyl
group causes an upfield shift by 6-8 ppm for allylic carbon nuclei located cis to it. This effect is also seen in diene 84 as discussed earlier.

(E)- and (Z)-4-benzenesulfonyl-4-benzyl-5-phenyl-1-trimethylsilyl-2-pentenes (82) are also eliminated rapidly by TBAF in THF (Equation 30). 5-Phenyl-4-methylphenyl-1,3-pentadiene (88) is formed in 83% yield. The IR spectrum of 88 indicates the presence of a conjugated double bond (1640 and 1600 cm⁻¹). The proton NMR shows benzyl, vinyl and aromatic absorptions in a 2:2:5 ratio. Diene 88 thus is identified completely by spectral analysis.

As for the previous dialkylated reactants 83 eliminates smoothly when treated with TBAF. Dienes 84 are produced in 65% yield (Equation 31); two stereoisomers, E and Z are present in a 54:46 ratio. The identifications, stereochemical assignments and isomer ratios for diene 84 were determined in the same manner as previously described when 83 was converted to 84 using silica gel.
Figure 9. 500-MHz $^1$H-$^{13}$C NMR correlation spectra of 87 E and 87 Z.
Table 7. $^1$H NMR (500 MHz) Chemical Shift Assignments ($\delta$)\textsuperscript{a} and Multiplicities for (E)- and (Z)-4-Methyl-5-phenyl-1,3-pentadienes (87).

<table>
<thead>
<tr>
<th>Hydrogen</th>
<th>E</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>1.70 (s, 3 H)</td>
<td>1.53 (s, 3 H)</td>
</tr>
<tr>
<td>Benzyl</td>
<td>3.35 (s, 2 H)</td>
<td>3.50 (s, 2 H)</td>
</tr>
<tr>
<td>$H_a$</td>
<td>5.01-5.06 (two overlapping dd, $J = 10.2$, 1.7 Hz, 1 H)</td>
<td></td>
</tr>
<tr>
<td>$H_b$</td>
<td>5.13 (dd, $J = 16.8$, 1.9 Hz, 1 H)</td>
<td>5.18 (d, $J = 16.7$ Hz, 1 H)</td>
</tr>
<tr>
<td>$H_c$</td>
<td>5.93 (d, $J = 10.5$ Hz, 1 H)</td>
<td>6.01 (d, $J = 10.6$ Hz, 1 H)</td>
</tr>
<tr>
<td>$H_d$</td>
<td>6.57 (ddd, $J = 16.8$, 10.5, 10.5 Hz, 1 H)</td>
<td>6.72 (ddd, $J = 16.8$, 10.5, 10.5 Hz, 1 H)</td>
</tr>
<tr>
<td>$C_6H_5$</td>
<td>7.1-7.4 (m, 5H)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Assignments relative to tetramethylsilane.
Table 8. $^{13}$C NMR (500 MHz) Chemical Shift Assignments ($\delta$)$^a$ and Multiplicities$^b$ for (E)- and (Z)-4-Methyl-5-phenyl-1,3-pentadienes (87).

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>E $^{13}$C-NMR</th>
<th>E $^1$H-NMR</th>
<th>Z $^{13}$C-NMR</th>
<th>Z $^1$H-NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.47 (o)</td>
<td>1.70 (CH$_3$)</td>
<td>23.50 (o)</td>
<td>1.53 (CH$_3$)</td>
</tr>
<tr>
<td>2</td>
<td>46.24 (e)</td>
<td>3.35 (CH$_2$Ph)</td>
<td>38.28 (e)</td>
<td>3.50 (CH$_2$Ph)</td>
</tr>
<tr>
<td>3</td>
<td>115.52 (e)</td>
<td>5.01-5.06 (H$_a$, H$_b$)</td>
<td>115.64 (e)</td>
<td>5.01-5.06 (H$_a$, H$_b$)</td>
</tr>
<tr>
<td>4</td>
<td>126.13 (o)</td>
<td>(Ar)</td>
<td>126.06 (o)</td>
<td>(Ar)</td>
</tr>
<tr>
<td>5</td>
<td>127.12 (o)</td>
<td>5.93 (H$_c$)</td>
<td>127.47 (o)</td>
<td>6.01 (H$_c$)</td>
</tr>
<tr>
<td>6</td>
<td>128.30 (o)</td>
<td>(Ar)</td>
<td>128.38 (o)</td>
<td>(Ar)</td>
</tr>
<tr>
<td>7</td>
<td>128.96 (o)</td>
<td>(Ar)</td>
<td>128.57 (o)</td>
<td>(Ar)</td>
</tr>
<tr>
<td>8</td>
<td>133.24 (o)</td>
<td>6.57 (H$_d$)</td>
<td>133.05 (o)</td>
<td>6.72 (H$_d$)</td>
</tr>
<tr>
<td>9</td>
<td>138.42 (u)</td>
<td></td>
<td>137.98 (u)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>139.62 (u)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Relative to the triplet of deuterchloroform, center line at 77.00 ppm; b) (o) denotes a carbon with three or one hydrogen atom attached; (e) denotes a carbon with two hydrogens attached; (u) denotes a quaternary carbon.
Elimination of Disubstituted Products under Acidic Conditions

The behaviors of 44 and 81-83 were investigated under acidic conditions. When 44, 81 and 83 are refluxed in hydrochloric acid (12 M)-THF mixtures for 24 h, they are recovered quantitatively. However, 82 decomposes rapidly to a complex mixture when treated at 25 °C with aqueous hydrochloric acid (12 M). One of the products identified is diene 88 (Equation 32) as detected in the crude mixtures by ¹H NMR and isolated by GC techniques. The reaction products were too complicated to determine the yields of 88 accurately. Further, 82 decomposes in deuterochloroform to 88 in a few hours.²⁷

![Chemical structures and reaction scheme]

\[\text{44} \quad R = \text{CH}_2\text{C}_6\text{H}_5 \quad 82 \quad R = \text{CH}_2\text{C}_6\text{H}_5 \quad R' = \text{H} \quad R' \quad \text{H} \]

\[\text{81} \quad R = \text{CH}_2\text{C}_6\text{H}_5 \quad 83 \quad R = \text{CH}_2\text{C}_6\text{H}_5 \quad R' = \text{CH}_3 \quad R' \quad \text{(CH}_2\text{)}_4\text{CH}_3\]

\[\text{82} \quad \text{HCl} \quad \text{THF/H}_2\text{O} \quad \text{88} \quad (32)\]
Conversion of 82 to diene 88 might proceed as illustrated in Scheme 10. Protonation of the oxygen of the sulfonyle group leads to intermediate 89 which collapses to phenylsulfinic acid and carbocation 90. Carbocation 90 is tertiary, allylic and possesses a trimethylsilyl group at the gamma-position which can stabilize positive charge through silyl hyperconjugation.

Elimination of arylsulfonyl groups under Lewis acid conditions\(^{24}\) and on silica gel\(^{1b}\) has precedent. However, the sensitivity of 82 to hydrochloric acid is striking because of the relative inertness of 44, 81, and 83. Sulfone 82 is substituted at its sulfonyle position by two benzyl groups and loss of its benzenesulfonyl group would result in relief of strain. Further, loss of the benzenesulfonyl group creates 90, a relatively stable carbocation which is tertiary, allylic, and gamma to a trimethylsilyl group. However, upon considering the possible stabilities of 81 and 83, both of which might be capable of forming
stable carbocations, it appears that steric factors play a major role in collapse of 82. Models of 44, 81, 82, and 83 suggest that 82 is the most congested substrate and its two benzyl and its sulfonyl groups cannot adopt a comfortable conformation. Sulfone 83 is unstable to silica gel, as was previously discussed, for probably one or more of the reasons just mentioned.

**Elimination by G.C. Thermolysis**

The reactivity of 82 under acidic conditions encouraged study of 44 and 81-83 under higher temperatures. When 44 and 81 are injected into a gas chromatograph (injector temperature = 375 °C) products eluting from the column were not obtained. On the other hand, 82 and 83 debenzenesulfonylsilylated when injected into a GC (injector temperature = 375 °C, Equation 33) to product dienes 84 (45%) and 88 (52%).

\[
\begin{align*}
\text{83} & \quad R = (\text{CH}_2)_4\text{CH}_3 \\
\text{82} & \quad R = \text{CH}_2\text{C}_6\text{H}_5
\end{align*}
\]

\[
\begin{align*}
\text{84} & \quad R = (\text{CH}_2)_4\text{CH}_3 \\
\text{88} & \quad R = \text{CH}_2\text{C}_6\text{H}_5
\end{align*}
\]
Cyclization Reactions of (E)- and (Z)-1-Benzene sulfonyl-4-trimethylsilyl-2-butene s (1)

Having demonstrated that (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butene s (1) can undergo dialkylation in a one-pot procedure, it became of interest to investigate ring cyclization of 1. Scheme 11 illustrates the conversions of carbanion 23 to (E)- and (Z)-1-benzenesulfonyl-1-(trimethylsilyl-1-propenyl)cycloalkanes 91. Carbanion 23 is first alkylated with an α,ω-dihaloalkane to generate monoalkylated compound 92. Deprotonation of 92 with n-butyllithium gives carbanion 93 which upon α-alkylation (ring closure) results in formation of 91.

**SCHEME 11**
α-Alkylation followed by α-ring closure does indeed occur with a variety of α,Ω-dihalides. Ring cyclization of 23 [derived from 1 (E:Z = 85:15)] with 1,2-dibromoethane occurs smoothly in THF/HMPA mixtures between -78 °C and room temperature to give (E)- and (Z)-6-bromo-4-benzenesulfonyl-1-trimethylsilyl-2-hexenes (94, Equation 34). Hexenes 94 are readily deprotonated by addition of n-butyllithium to give allyl anion 95. Of interest then is that 95 undergoes cyclization with displacement of lithium bromide to yield the corresponding (E)- and (Z)-1-benzenesulfonyl-1-(3-trimethylsilyl-1-propenyl)cyclopropanes (96, 95%). Recrystallization of 96 in pentane leads to isolation of one geometric isomer. Table 9 contains further examples of ring cyclization of 23 to four-membered (97), five-membered (98), and six-membered ring (99) derivatives (Equation 35). Note should be taken that the cyclized derivatives 97-99 retain the stereochemistries of 1.
Table 9. Cyclizations of (E)-and (Z)-1-Benzene sulfonfyl-4-trimethylsilyl-2-
butenes (1, E/Z = 85:15)

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Y</th>
<th>n+1</th>
<th>X(CH₂)ₙY</th>
<th>Product</th>
<th>no.</th>
<th>% yield</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br</td>
<td>Br</td>
<td>4</td>
<td>97</td>
<td>87</td>
<td>86:14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td>Br</td>
<td>5</td>
<td>98</td>
<td>89</td>
<td>85:15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Br</td>
<td>Br</td>
<td>6</td>
<td>99</td>
<td>78</td>
<td>84:16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cyclic derivatives 96-99 are identified by spectral analysis. Cyclopropane 96 was isolated after recrystallization as a single isomer as evidenced by a single set of ¹³C NMR peaks. The vinyl region of the ¹H NMR spectrum of 96 contains a complex pattern which integrates for two protons. Since the coupling constant Jₐₙ could not be determined, the stereochemistry of 96 could not be confidently assigned. Product 96 is assumed, however, to be the E stereoisomer. Products 97-99 are oils and are mixtures of E and Z isomers as evidenced by their ¹³C NMR for which each contains two sets of peaks. The ¹H
NMR of 97-99 exhibit well separated vinyl proton absorbances from which isomer identifications and ratios were obtained (Table 10).

Table 10. 250-MHz $^1$H NMR Chemical Shift Assignments of H$_a$ for Ring Cyclization Products 97, 98, and 99.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H$_a$, E isomer</th>
<th>H$_a$, Z isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td>δ 5.29 (J$_{ab}$, 15.4 Hz)</td>
<td>δ 5.09 (J$_{ab}$, 11.9 Hz)</td>
</tr>
<tr>
<td>98</td>
<td>δ 5.21 (J$_{ab}$, 15.6 Hz)</td>
<td>δ 5.05 (J$_{ab}$, 11.6 Hz)</td>
</tr>
<tr>
<td>99</td>
<td>δ 4.92 (J$_{ab}$, 15.9 Hz)</td>
<td>δ 4.70 (J$_{ab}$, 11.5 Hz)</td>
</tr>
</tbody>
</table>

The regiochemistry of ring cyclization heavily favors formation of α, α-dialkylated ring products 91 over α, γ-dialkylated isomers 100 (Scheme 12). It is unclear however whether the stereospecificity stems from regiochemical control exerted by the sulfonyl group or whether stereoelectronic effects preclude gamma-alkylation. The strong tendencies of the conjugated sulfonyl anions to alkylate at their α-positions have been demonstrated in this work and by others.$^{28}$ Little attention has been directed however to the stereoelectronic requirements for allyl anion ring cyclization.$^{29}$ Allyl anions have demonstrated
conformational stability which suggests that the \( \pi \)-orbitals of the allyl systems prefer to be coplanar, thus insuring maximum orbital overlap. With this being the case, ring closure at an \( \alpha \)-position would be difficult for shorter chain lengths since backside attack is precluded. This point is illustrated by allyl anions I and II in which the \( \pi \)-orbitals are coplanar (Scheme 13). In structure I the carbon chain is trans to the gamma-carbon whereas in II the carbon chain is cis to the gamma-carbon. Alkylation of I or II at their gamma-positions is unfavored for shorter carbon chains \((n < 6)\). Further valuable information could be obtained by studying the effects of anion stabilizing groups (carbonyl, nitrile, trialkylsilyl, etc) at \( \alpha \)-positions on the directions of ring cyclization.

**SCHEME 12**

![Scheme 12](image-url)
Addition of two equivalents of base to 1 before addition of the α-Ω dihalide would simplify the cyclization method. Thus, ring cyclization of anion 23 was attempted in the presence of excess n-butyllithium (2 equivalents) (Equation 36). The only products, however, were (E)- and (Z)-4-benzenesulfonyl-1-trimethylsilyl-2-octenes (101) in 90% yield. Apparently excess n-butyllithium reacts with 1,3-dibromopropane (102) rapidly to give 1-bromobutane via a transmetallation process. 1-Bromobutane then aiylates anion 23 to give 101 (Equation 37).
Cyclizations were attempted under thermodynamic conditions. Treatment of (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes 1 with sodium hydride in DMF followed by 1,3-dibromopropane (102) yields (E)- and (Z)-4-benzenesulfonyl-1-trimethylsilyl-2,6-heptadienes (48, 49%, Equation 38). Products 48 is derived by alkylation of 23 by allyl bromide which is formed by dehydrohalogenation of 102 (Equation 39). Products 48 were identified spectrally. The $^1$H NMR and IR spectra of 48 are identical with that of samples prepared by reaction of anion 23 and allyl bromide.
Cyclizations via Epoxides

 Allyl anion 23 alkylates well with cyclohexene oxide as discussed earlier and ring cyclization of 1-benzenesulfonyl-1-lithio-2-trimethylsilylethane (15) using epoxides has been studied by Hsiao. It was thus of interest to explore cyclopropylation of 23 via ethylene oxide. Scheme 14 illustrates synthesis of cyclopropyl derivatives 96 from 23. Addition of 23 to ethylene oxide in ethyl ether gives alkoxides 103 which are converted in situ by methanesulfonyl chloride to mesylates 104. Addition of one equivalent of n-butyllithium causes formation of anions 105 which undergo cyclization to 1-benzenesulfonyl-1-(3-trimethylsilyl-1-propenyl) cyclopropane 96.

 Indeed, allyl anion 23 generated in ethyl ether at -78 °C, when treated with ethylene oxide followed by methanesulfonyl chloride and refluxing, gives mesylate 104. Another portion of n-butyllithium when added to 104, results in formation of anion 105 which cyclizes to (E)- and (Z)-benzenesulfonyl-1-(trimethylsilyl-1-propenyl)cyclopropane (96, 28%) along with 1-benzenesulfonyl-1-(3-trimethylsilyl-1-propenyl)tetrahydropyran (106, 8%; Equation 40).
SCHEME 14

\[ \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \rightarrow \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \]  
\[ \text{OMs} \rightarrow \text{CH}_3\text{SO}_2\text{Cl} \]

\[ \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \rightarrow \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \]  
\[ \text{OMs} \rightarrow \text{n-BuLi} \]

\[ \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \rightarrow \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \]  
\[ \text{OMs} \rightarrow \text{n-BuLi} \]

\[ \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \rightarrow \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \]  
\[ \text{OMs} \rightarrow \text{n-BuLi} \]

\[ \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \rightarrow \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \]  
\[ \text{OMs} \rightarrow \text{n-BuLi} \]

\[ \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \rightarrow \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \]  
\[ \text{OMs} \rightarrow \text{n-BuLi} \]

\[ \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \rightarrow \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \]  
\[ \text{OMs} \rightarrow \text{n-BuLi} \]

\[ \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \rightarrow \text{(CH}_3\text{)}_3\text{Si} - \text{SO}_2\text{C}_6\text{H}_5 \]  
\[ \text{OMs} \rightarrow \text{n-BuLi} \]
Formation of 106 is detailed in Scheme 15. Intermediate 103, formed as before by nucleophilic attack of anion 23 on ethylene oxide, is further deprotonated by n-butyllithium giving allyl dianion 107 which reacts with ethylene oxide to yield dianion 108. Addition of methanesulfonyl chloride generates mesylate 109 which cyclizes to 106. Products 96 and 106 were assigned spectrally. Tetrahydropyran 106 contains a quaternary sulfanyl-substituted carbon as evidenced by uncoupled absorption at δ 65.96 in its off resonance $^{13}$C NMR spectrum. The absorbances for the ring protons Hₐ-Hₐ are well separated in the $^1$H NMR spectra of 106 and their assignments are based on their chemical shift and coupling patterns. The absorption for axial proton H₃ (δ 3.42) is upfield from its geminal equatorial neighbor (H₄, δ 3.85) and that for axial proton H₅ (δ 2.27) is downfield from its geminal equatorial neighbor (H₆, δ 1.76). Protons H₅ and H₃ are coupled to each other by approximately 12 Hz which are typical for trans diaxial ring protons. The stereochemistry of the double bond is trans since vinyl protons H₇ (δ 5.02) and H₈ (δ 5.60) are coupled by approximately 16 Hz. Further, when the H₇ region is irradiated in a NOE difference experiment, the allyl protons (δ 1.57) are enhanced (5.17%) and the vinyl proton (δ 5.60) is not. These results reveal a cis relationship for H₇ and the allyl protons whereas H₆ and H₈ are trans.
Since the absorptions of the ring protons in 106 are well separated, a study of the conformations of the cyclohexane system was initiated using high field NMR techniques. Two relatively stable conformations of 106 are chair forms I and II. NOE difference experiments give evidence that the more stable conformation is chair I. Irradiation of the axial proton $H_c$ region enhances the absorptions of both vinyl protons $H_e$ (2.26%) and $H_f$ (2.46%) whereas there is none in the aromatic region. These results are consistent with structure I since $H_c$, $H_e$, and $H_f$ are close spatially. Since irradiation of $H_d$ did not enhance
absorption in the vinyl or aromatic regions the results are also consistent with structure I and inconsistent with structure II.

Having successfully prepared various 1-benzenesulfonyl-1-(trimethylsilyl-1-propenyl) cycloalkanes, it became of interest to study their elimination reactions. 1-Benzencesulfonyl-1-(3-trimethylsilyl-1-propenyl)cyclopropane 96 reacts with TBAF in DMSO to afford allylidencyclopropane (110, 90%; Equation 41) which was isolated along with hexamethyldisiloxane by flash vacuum techniques.

**ELIMINATION OF CYCLOADUCTS**

Having successfully prepared various 1-benzenesulfonyl-1-(trimethylsilyl-1-propenyl) cycloalkanes, it became of interest to study their elimination reactions. 1-Benzencesulfonyl-1-(3-trimethylsilyl-1-propenyl)cyclopropane 96 reacts with TBAF in DMSO to afford allylidencyclopropane (110, 90%; Equation 41) which was isolated along with hexamethyldisiloxane by flash vacuum techniques.
Allylidene 110 was identified spectrally and by comparison with literature properties. Cyclopropane 110 is stable for prolonged periods at -78 °C. Upon warming 110 to room temperature, however, the clear colorless oil turns cloudy and presumably polymerizes. Solutions of 110 in deuterochloroform remain stable for several days. Allylidencyclopropane (110) has recently been of synthetic and theoretical interest. In particular 110 undergoes Diels-Alder reactions under mild conditions. Thus, diene 110 reacts at room temperature with a variety of dieneophiles possessing two or more activating groups to give spiro compounds (Equation 42).

\[
\begin{align*}
\text{110} & \quad + \quad \text{N-phenyltriazolinedione (111)} \\
\text{Benzene} & \quad 20 ^\circ C, 16 \text{ h} \\
\text{112} &
\end{align*}
\]

To confirm preparation of 110, its Diels-Alder reaction with N-phenyltriazolinedione (111) was investigated. Cycloaddition of 110 and 111 occurs essentially instantly upon admixture at -78 °C to form triazolodione 112 (81%, Equation 43), a stable white solid. Cycloadduct 112 was identified spectrally and by elemental analyses. The IR spectrum of 112 contains absorption at 1680 cm\(^{-1}\) consistent with an amide carbonyl stretch. The \(^{13}\)C NMR of 112 reveals two carbonyls as evidenced by absorptions at \(\delta 150.68\) and 152.36. The exact mass of 112 is proper.
Fluoride-induced debenzenesulfonyltrimethylsilylations were further investigated. Cyclobutanes 113 and cyclopentanes 114 (Equation 44; Table 11, entries 1 and 2) were prepared by treating DMSO solutions of 97 and 98 with TBAF in DMSO. Dienes 113 and 114 were isolated by flash vacuum distillation and trapping at -78 °C. Cyclohexylidene derivative 115 was prepared by treating THF solutions of 99 with TBAF in THF. Product 115 was isolated by chromatography techniques and evaporation of the solvent.

Compounds 113-115 were identified by spectral analysis and/or by comparison with the literature. The IR spectra of 113-115 contain absorptions at 1650-1670 cm\(^{-1}\) and 1600 cm\(^{-1}\) characteristic of conjugated dienes. The \(^1\)H NMR spectra of 113-115 contain absorptions for protons H\(_a\)-H\(_d\) in the vinyl regions.
Table 11. Fluoride Induced Eliminations of (E) and (Z)-1-benzenesulfonyl-1-(trimethylsilyl-1-propenyl) cyclobutanes (97), (E) and (Z)-1-benzenesulfonyl-1-(3-trimethylsilyl-1-propenyl) cyclopentanes (98), and (E)- and(Z)-benzenesulfonyl-1-(3-trimethylsilyl-1-propenyl) cyclohexanes (99).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>n+1</th>
<th>Conditions</th>
<th>Product</th>
<th>%Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>97</td>
<td>4</td>
<td>TBAF, DMSO, 25 °C</td>
<td>113</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td>5</td>
<td>TBAF, DMSO, 25 °C</td>
<td>114</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>99</td>
<td>6</td>
<td>TBAF, THF, 0 °C</td>
<td>115</td>
<td>78</td>
</tr>
</tbody>
</table>

Treatment of tetrahydropyran 106 with TBAF in THF at 0 °C results in 4-allylidenetetrahydropyran (116, 87%; Equation 45). Identification of 116 was achieved by spectral analysis. The IR spectrum of 116 contains two absorptions at 1650 cm⁻¹ and 1600 cm⁻¹ characteristic for conjugated dienes. The ¹H NMR spectrum of 116 has absorptions in vinyl regions corresponding to protons Hₐ-Hₜ. GC resolution (GC-HR-MS) successfully separated 116 from deuterochloroform NMR solutions, and the mass spectrum of 116 contains a molecular ion peak corresponding to the exact mass of 116.
Conclusions

The present investigation has explored the synthetic utility of (E)- and (Z)-1-benzenesulfonyl-4-trimethylsilyl-2-butenes (1) for preparing various 1-substituted -1,3-butadienes (2), 1,1-disubstituted-1,3-butadienes (3), and allylidene cycloalkanes (4). Silylsulfone (1) is prepared via an efficient three step reaction sequence starting from commercially available chloromethyltrimethylsilane. Addition of n-butyllithium to (1) generates allyl anion (23).

The present research has shown that 23 is stable for short periods of time (10 min) at room temperature. However, when 23 is kept at room temperature for a prolonged time (3 hr) it decomposes significantly. The instability of 23 at room temperature contrasts with its analog, anion 16, which is generated by deprotonation of 1-benzenesulfonyl-2-trimethylsilylthane (15) with n-butyllithium. The pathway for anion 23 decomposition could not be determined since complex products were obtained.

Anion 23 is successfully substituted with deuterium when it is quenched with deuterium oxide. The α-position of silylsulfone 1 is readily exchanged for
deuterium when 1 is treated with deuterium oxide under basic conditions. Anion 23 substitutes various alkyl halides and cyclohexyl-4-methylphenylsulfonate, and cyclohexene oxide. The substituted derivatives of 1 debenzenesulfonyltrimethylsilylate rapidly when treated with tetrabutylammonium fluoride in THF at 0 °C giving 1-substituted-1,3-butadienes (2). The stereochemistries of 2 are highly trans as determined by high field ¹H NMR. Aluminium chloride also causes 2 to debenzenesulfonyletrimethylsilylate yielding dienes as products.

Disubstitution of 1 is achieved by deprotonation of mono-substituted 2 then treating the resulting carbanion solution with an alkylhalide. When disubstituted derivatives of 1 are treated with TBAF in THF at 0 °C, they debenzenesulfonyletsilylate to give 1,1-disubstituted-1,3-butadienes (3). The dibenzyl substituted compound (82) is particularly sensitive too silica gel and hydrochloric acid. Silylsulfone (82) debenzenesulfonyletsilylates when absorbed on silica gel or when treated with hydrochloric acid in THF solutions. The stereochemistries of 3 were determined by NOE techniques.

Ring cyclization of carbanion 23 is efficiently obtained by treating 23 with an αω-dihalide followed by an equivalent of n-butyllithium. The ring cyclized products when treated with TBAF are easily converted into allylidene cycloalkanes (4). The dephenylsulfonysilylation of ring cyclized products occurs under extremely mild conditions which is ideal for generating sensitive dienes such as allylidene cyclopropane (110).
CHAPTER II

INTRODUCTION

This chapter describes the preparation and chemistry of 1-arylsulfonyl-1-halo-4-trimethylsilylbutanes 5-9 and (E)-1-arylsulfonyl-4-trimethylsilyl-1-butanes 10-12. As will be demonstrated 5-9 and 10-12 are excellent reagents for synthesizing 1-substituted-1,3-butenes 2 and allylidene cycloalkanes 4 and are therefore related to 1 which was discussed in Chapter 1.

\[
\begin{align*}
5 & \quad X = \text{Br}, \ Ar = \text{C}_6\text{H}_5 \\
6 & \quad X = \text{Cl}, \ Ar = \text{C}_6\text{H}_5 \\
7 & \quad X = \text{Br}, \ Ar = \text{C}_6\text{H}_4\text{-CH}_3\text{-p} \\
8 & \quad X = \text{Cl}, \ Ar = \text{C}_6\text{H}_4\text{-CH}_3\text{-p} \\
9 & \quad X = \text{Cl}, \ Ar = \text{C}_6\text{H}_4\text{-Cl-p} \\
10 & \quad Ar = \text{C}_6\text{H}_5 \\
11 & \quad Ar = \text{C}_6\text{H}_4\text{-CH}_3\text{-p} \\
12 & \quad Ar = \text{C}_6\text{H}_4\text{-Cl-p} \\
117 & \quad Ar = \text{C}_6\text{H}_5 \\
118 & \quad Ar = \text{C}_6\text{H}_4\text{-CH}_3\text{-p} \\
119 & \quad Ar = \text{C}_6\text{H}_4\text{-Cl-p}
\end{align*}
\]

\[
\begin{align*}
2 & \quad \text{R} \\
4 & \quad (\text{CH}_2)_n
\end{align*}
\]
Reagents 5-9 and 10-12 are of interest because their preparations are more general, expedient and cost effective compared to 1. Another important difference between allyl sulfones 1 and vinyl sulfones 10-12 is that deprotonation of 1 generates allyl anions 23 (Equation 46) whereas deprotonation of 10-12 gives α-vinyl anions 117-119 (Equation 47) for which little is known. This study therefore compares the stabilities and the reactivities of α-vinylsulfonyl anions 117-119 to allylsulfonyl anions 23.

\[
\begin{align*}
\text{CH}_3\text{Si} & \begin{array}{c} \text{H} \\ \text{H} \end{array} \begin{array}{c} \text{SO}_2\text{Ar} \\ \text{SO}_2\text{Ar} \end{array} & \text{+ Base} & \text{CH}_3\text{Si} & \begin{array}{c} \text{H} \\ \text{H} \end{array} \begin{array}{c} \text{SO}_2\text{Ar} \\ \text{SO}_2\text{Ar} \end{array} \\
\text{1} & & \text{23} \\
\text{CH}_3\text{Si} & \begin{array}{c} \text{H} \\ \text{H} \end{array} \begin{array}{c} \text{SO}_2\text{Ar} \\ \text{SO}_2\text{Ar} \end{array} & \text{+ Base} & \text{CH}_3\text{Si} & \begin{array}{c} \text{H} \\ \text{H} \end{array} \begin{array}{c} \text{SO}_2\text{Ar} \\ \text{SO}_2\text{Ar} \end{array} \\
\text{10-12} & & \text{117-119} \\
\end{align*}
\]

RESULTS AND DISCUSSION

Preparation of 1-Arylsulfonyl-1-halo-4-trimethylsilylbutanes 5-9 and (E)-1-Arylsulfonyl-4-trimethylsilyl-1-butenes 10-12

4-Trimethylsilyl-1-butene (120) is of interest as a practical precursor to 1-arylsulfonyl-1-halo-4-trimethylsilylbutanes 5-9 and (E)-1-arylsulfonyl-4-trimethylsilyl-1-butenes 10-12. As will be demonstrated, varied 1-arylsulfonyl-1-halo-4-trimethylsilylbutanes can be prepared from 120 by copper-catalyzed
additions of arylsulfonyl chlorides\textsuperscript{34-37} (Equation 48) or by photolytic additions of arylsulfonyl bromides\textsuperscript{38,39} (Equation 49).\textsuperscript{38}

\[
\begin{align*}
&\begin{array}{c}
(CH_3)_3SiCH=CH_2 \\
120
\end{array} \xrightarrow{\text{ClSO}_2C_6H_4-Y_p} \begin{array}{c}
(CH_3)_3SiCH=CH_2SO_2C_6H_4-Y_p \\
\text{Cl}
\end{array} \quad \text{(48)} \\
&\begin{array}{c}
(CH_3)_3SiCH=CH_2 \\
120
\end{array} \xrightarrow{\text{BrSO}_2C_6H_4-Y_p} \begin{array}{c}
(CH_3)_3SiCH=CH_2SO_2C_6H_4-Y_p \\
\text{Br}
\end{array} \quad \text{(49)}
\end{align*}
\]

Previous to the present research the availability of 120 has been limited. Study was initiated of advantageous methods for preparing 120. Reaction of trimethylsilylmethylmagnesium bromide (121) and allyl bromide to 120 has been reported (Equation 50).\textsuperscript{41} In the present work coupling of allyl bromide with trimethylsilylmethylmagnesium chloride (37)\textsuperscript{42}, derived from commercially available chloromethyltrimethylsilane and magnesium, has been investigated. Under varied conditions reaction of 37 with allyl bromide gave 120 in only 22-27\% yields. Since the yields of 120 are unsatisfactory a more effective preparative method is needed.

A satisfactory method developed for preparing 120 from 1,3-butadiene is illustrated in Equation 51. Thus, 1,3-butadiene when treated with lithium in the presence of trimethylsilyl chloride gives 1,4-bis(trimethylsilyl)-2-butene (122) via reductive silylation.\textsuperscript{43} Protomonodesilylation of 122 with sulfuric acid\textsuperscript{44} in
pentane or trifluoroacetic acid\textsuperscript{45} in carbon tetrachloride yields 120 and hexamethyldisiloxane (123). Fractional distillation affords a mixture of 120 and 123 (2:1 ratio) which is usable without further purification. If desired spinning band distillations of mixtures of 120/123 yield pure 120. Large quantities of 120 are readily obtained by the method developed. Compounds 120 and 123 were identified by spectral analysis and by literature comparison. The yields and ratios of mixtures of 120 and 123 were determined by GC and \textsuperscript{1}H NMR methods

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{SiCH}_2\text{MgX} & + \text{Br} & \rightarrow & \text{(CH}_3\text{)}_3\text{Si} & \rightarrow
\end{align*}
\]

\text{120}

\text{121} \quad X = \text{Br}

\text{37} \quad X = \text{Cl}

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{SiCl} & \rightarrow \text{Li, THF} & \rightarrow & \text{(CH}_3\text{)}_3\text{Si} & \rightarrow \quad & \text{1. H} \oplus & \rightarrow \quad & \text{2. H}_2\text{O}
\end{align*}
\]

\text{122}

\text{120} \quad \text{123}

\text{Preparation of 1-Arylsulfonyl-2-chloro-4-trimethylsilylbutanes}

1-Arylsulfonyl-2-chloro-4-trimethylsilylbutanes 6, 8 and 9 are readily prepared by homolytic addition of arylsulfonyl chlorides to 4-trimethylsilyl-1-butene (120, Equation 52, Table 11). For example, 4-chlorobenzenesulfonyl chloride and 120 in the presence of cupric chloride and triethylamine hydrochloride in acetonitrile-methylene chloride mixtures gives 2-chloro-1-(4-chlorobenzenesulfonyl)-4-trimethylsilylbutane (9, 69%, entry 1; Table 11).
The additions proceed very slowly at temperatures below 100 °C and therefore in low boiling solvents such as acetonitrile and methylene chloride the reactions must be carried out in sealed tubes or closed containers. Changing to isobutyronitrile, a higher boiling solvent (bp = 107-108 °C), allows addition of the sulfonyl chloride to take place under reflux. Under such conditions p-toluenesulfonyl chloride adds to 120 to form 2-chloro-1-(4-methylbenzenesulfonyl)-4-trimethylsilylbutane (8, 53%; entry 2, Table 12).

Table 12. Preparation of 1-Arylsulfonyl-2-chloro-4-trimethylsilylbutanes

<table>
<thead>
<tr>
<th>entry</th>
<th>Ar</th>
<th>conditions</th>
<th>product</th>
<th>yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₄-Clp</td>
<td>CH₃CN, CH₂Cl₂, (C₂H₅)₃NHCl</td>
<td>9</td>
<td>69</td>
</tr>
<tr>
<td>2</td>
<td>C₆H₄-Clp</td>
<td>(CH₃)₂CHCN, (C₂H₅)₃NHCl</td>
<td>8</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>C₆H₅</td>
<td>C₂H₅O(CH₂)₂OC₂H₅, N(CH₂CH₂OCH₂CH₂OCH₃)₃</td>
<td>6</td>
<td>51</td>
</tr>
</tbody>
</table>
Increasing the solubility of cupric chloride in the organic phase of the reaction mixtures increases effectiveness of the catalyst. Triethylamine hydrochloride has generally been used as a solubilizing agent for these reactions. TDA-1 is known to solubilize mono and divalent cations of various sizes. Replacing triethylamine hydrochloride with TDA-1 greatly increases the solubility of cupric chloride in 2-ethoxyethyl ether. Thus, benzenesulfonyl chloride in the presence of TDA-1 and cupric chloride adds to 120 in 2-ethoxyethyl ether to form 1-benzenesulfonyl-2-chloro-4-trimethylsilylbutane (6, 51%, entry 3, Table 11) and minor amounts of 1-phenylsulphenyl-2-chloro-4-trimethylsilylbutane (124, 8%). Oxidation of 124 with MCPBA yields 6 (92%, Equation 53).

\[
\begin{align*}
\text{MCPBA} & \quad \text{CH}_2\text{Cl}_2, 0 ^\circ \text{C} \\
\text{124} & \quad \text{6}
\end{align*}
\]

\beta\text{-chlorosilylsulfonyl}butanes 8 and 9 are crystalline materials and 6 is an oil that can be stored indefinitely without significant decomposition. Assignments of 6, 8, 9 and 124 were made spectrally and/or by elemental analyses. The IR spectra of 6, 8, and 9 exhibit absorptions for sulfonyl groups as evidenced by IR bands at approximately 1300 cm\(^{-1}\) and 1150 cm\(^{-1}\). The mass spectra of 6, 8, and 9 indicate the presence of chlorine since fragments containing \(^{35}\text{Cl}\) and \(^{37}\text{Cl}\) are produced.
Preparation of 1-Arylsulfonfonyl-2-bromo-4-trimethylsilylbutanes

Arylsulfonfonyl bromides add to olefins under mild photolytic conditions.\textsuperscript{38,39} This method was extended to preparation of 1-arylsulfonfonyl-2-bromo-4-trimethylsilylbutanes 5 and 7 (Equation 54).

\[ \text{BrSO}_2\text{Ar} + (\text{CH}_3)_3\text{SiCH}_2\text{C}_6\text{H}_5 + \text{Br} \rightarrow (\text{CH}_3)_3\text{SiCH}_2\text{C}_6\text{H}_5 \text{SO}_2\text{Ar} \]

Benzenesulfonfonyl bromide (125) adds to 4-trimethylsilyl-1-butene (120) in THF when irradiated with a 500 watt light bulb to yield 1-benzenesulfonfonyl-2-bromo-4-trimethylsilylbutane (5, 62%). Similarly, \( \text{p} \)-toluenesulfonfonyl bromide (126) and 120 give 2-bromo-(4-methylbenzenesulfonfonyl)-4-trimethylsilylbutane (7, 48%). The addition reactions are monitored conveniently by GC methods and unreacted sulfonfonyl bromides 125 and 126 can be recovered chromatographically. During chromatography of 7, minor dehydrohalogenation occurs to give (E)-1-(4-methylbenzenesulfonfonyl)-4-trimethylsilyl-1-butene (11, 5%) after chromatography (Equation 55).
Spectral and/or elemental analyses were used to assign 5, 7, and 11. The sulfonyl groups in 5, 7, and 11 give IR absorbances at 1300 and 1500 cm\(^{-1}\). Product 11 is a single stereoisomer since its \(^{13}\)C NMR contains only one set of peaks. The stereochemistry of 11 is assigned as trans by \(^1\)H NMR in that the vinyl protons are coupled to each other by 15.0 Hz, a typical trans coupling constant.

### Dehydrohalogenation of 1-Arylsulfonyl-2-halo-4-trimethylsilylbutanes

β-halosulfones are usually dehydrohalogenated using hydroxide ion or tertiary amines.\(^{34,46}\). 1-Benzene sulfonyl-2-chloro-4-trimethylsilylbutanes 6, when treated with potassium hydroxide in THF-water, dehydrohalogenate efficiently to give (E)-1-benzene sulfonyl-4-trimethylsilyl-1-butene (10, 91%, Equation 56).

\[
\begin{align*}
\text{(CH}_3)_3\text{Si} & \quad \text{Cl} & \quad \text{SO}_2\text{C}_6\text{H}_5 & \quad \text{KOH} & \quad \text{THF/H}_2\text{O} & \quad \text{(CH}_3)_3\text{Si} \\
\text{6} & & & & & \quad \text{H} & \quad \text{SO}_2\text{C}_6\text{H}_5 \\
\end{align*}
\]

Addition of the sulfonyl bromide to 4-trimethylsilyl-1-butene (120) and dehydrobromination to 11 can be combined into a one pot procedure. As illustrated in Equation 57, a mixture of 120 (2 parts) hexamethyldisiloxane (1 part), 4-methylbenzenesulfonyl bromide (126) in THF are irradiated. The
conversion to 7 is monitored by GC techniques. When 120 is no longer detected, irradiation is terminated. Addition of aqueous potassium hydroxide (0.6 M) and rapid stirring dehydrobrominates 7 to (E)-1-(4-methylbenzenesulfonyl)-4-trimethylsilyl-1-butene (11) containing initial 126. Further stirring eventually results in conversion of 126 to potassium p-toluenesulfonate (127) which is removed by washing the reaction product with aqueous sodium bicarbonate.

![Chemical Structure](image)

Upon developing satisfactory conditions for dehydrohalogenating β-halosulfones 6 and 8 under thermodynamic conditions, attention was turned to dehydrohalogenations of β-halosulfones 8 and 9 under kinetic conditions. When 2-chloro-1-(4-methylbenzenesulfonyl)-4-trimethylsilylbutane (8) is treated with lithium diisopropylamide at -78 °C in THF and the reaction mixture is quenched with aqueous ammonium hydrochloride, (E)-1-(4-methylbenzenesulfonyl) 4-trimethylsilyl-1-butene (11, 93%; Equation 58) is obtained. Similarly, 2-chloro-(4-chlorobenzenesulfonyl)-4-trimethylsilylbutane (9) is converted by n-butyllithium to (E)-1-(4-chlorobenzenesulfonyl) 4-trimethylsilyl-1-butene (12, 98%; Equation 59). Butenes 11 and 12 are
assigned spectrally. The $^{13}$C NMR of 12 contains one set of peaks showing it to be a single geometric isomer. The stereochemistry of 12 as trans is assigned from its $^1$H NMR vinyl coupling constants (15 Hz).

\[
\begin{align*}
\text{8} &\xrightarrow{\text{LDA}} \text{11} \\
\text{9} &\xrightarrow{\text{n-BuLi}} \text{12}
\end{align*}
\]

**Generation of Vinyl Anions 117, 118, and 119**

Generation and determination of the reactivities of vinylsulfone anions have been little studied. α-Sulfonylvinylolithium reagents have been reported by Eisch.\textsuperscript{47} For example, when (E)-1-benzenesulfonyl-1-propene (128) reacts with methylolithium in THF at -95°C, a carbanion solution of 129 as its lithio derivative is created. In a limited study 129 was shown to react with primary halides to form substituted vinyl sulfones (Equation 60).
Since 10-12 are readily available in the present research it became of interest to develop good methods for generating vinyl anions 117-119. As will be demonstrated n-butyllithium and lithium diisopropylamide are effective bases for preparing vinylsulfonyl anions 117-119. Thus, (E)-1-(4-chlorobenzenesulfonyl)-4-trimethylsilyl-1-butene (12) is rapidly converted to the lithio derivative of 119 upon reaction with lithium diisopropylamide in THF at -78 °C. The solution of anion 119 is deep yellow. Deuteration of 119 with deuterium oxide then yields (E)-1-deutero-1-(4-chlorophenylsulfonyl)-4-trimethylsilyl-1-butene (130, 83 %, Equation 61) assigned spectrally as follows. The \(^{13}\)C-NMR spectrum of 130 reveals a single set of absorbances for only one geometric isomer. The \(^1\)H NMR NMR shows that 130 contains 79% deuterium at its \(\alpha\)-position as determined by peak area integration of the vinyl region (\(\delta\) 6.30). The remaining vinyl proton absorbances (\(\delta\) 6.9-7.1) are complex. Therefore the stereochemistry of 130 can not be assigned with confidence and is assumed to be \text{trans}. 
Since dehydrohalogenations of $\beta$-halosulfones 5-9 can be performed under kinetic conditions, it seemed possible that the dehydrohalogenation and anion formation steps could be combined into a one pot process. Generation of vinyl anions 117-119 directly from $\beta$-halosulfones 5-9 would be advantageous since it makes the preparation and isolation of vinyl sulfones unnecessary. Another advantage is that halosulfones 5-9 can be stored for prolonged periods without significant decomposition, whereas, vinyl sulfones 10-12 and allyl sulfones 1 decompose after several weeks of storage at room temperature.

As illustrated in Equation 62, addition of 8 to LDA in THF generates a deep yellow solution of vinyl anion 118. When deuterium oxide is added to the carbanion solution, (E)-1-deutero-(4-methylbenzenesulfonyl)-4-trimethylsilyl-1-butene (131, 89%) is formed.
n-Butyllithium is also an effective base for generating carbanion solutions of 117-119 in THF. Lithium diisopropylamide however deprotonates vinyl sulfones 10-12 more rapidly than n-butyllithium as is indicated by the rapid intense yellow color formed when LDA is added to 10-12, whereas, under comparable conditions, n-butyllithium requires 10-15 minutes for completion of deprotonation of 10-12.

Thus, dehydrohalogenation and deprotonation of 5-9 can be performed in one pot at low temperatures with either n-butyllithium or lithium diisopropylamide. Therefore, carbanions 117-118 are obtainable directly from silylsulfonyl halides 5-9. Inverse addition of either base to the β-halosulfone is also successful in generating carbanion solutions of 117-118. Delivery of slightly more than one equivalent of base to solutions of 5-9 is signaled by the changes in color caused by formation of anions 117-118. Therefore, the change from clear colorless to slightly yellow was routinely used as a method to titrate the alkyllithium or lithium amide used as a base. Addition of another equivalent of base completes the deprotonation process giving a yellow carbanion solution.
Study of the Stabilities of Vinyl Sulfone Anions

Little attention has been paid to α-vinylsulfone anions and an important aspect which has not been addressed are their thermal stabilities. The stabilities of such anions are important if high temperatures and/or long times are required for reaction with varied electrophiles.

Vinylsulfone anions 117-119 are generated by treating 5, 7, 8, and 9, respectively, with two equivalents of LDA or n-butyllithium in THF. The yellow carbanion solutions were allowed to stir for periods of time and then benzyl bromide was added followed by HMPA (Equation 63). The times the anions were allowed to stir, the temperatures at which they were kept, and the yields of benzylated products isolated are contained in Table 13.
### Table 13. Study of the Stability of Vinyl Anions 117-119

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time (h)</th>
<th>Temp (°C)</th>
<th>Product</th>
<th>Yield,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>1.5</td>
<td>-78</td>
<td>132</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.2</td>
<td>-78</td>
<td>132</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.2</td>
<td>-78</td>
<td>133</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>1.7</td>
<td>-78</td>
<td>133</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>1.0</td>
<td>-78 to 25</td>
<td>134</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>1.5</td>
<td>-78</td>
<td>134</td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>0.2</td>
<td>-78</td>
<td>134</td>
<td>90</td>
</tr>
</tbody>
</table>

Vinyl anions 117-119 are not stable for prolonged periods even at -78 °C. The dramatic decreases in yields of alkylated products with increase in time are indicative of the instabilities of 117-119. The anion derived from 9 is highly sensitive. Alkylations of anions 117-119 with benzyl bromide are sluggish in the absence of HMPA. Such behavior is in contrast to that of allyl anion 23 which alkylates benzyl bromide essentially instantaneously at -78 °C in THF in the absence of HMPA. Allyl anions 23 as their lithio derivatives are therefore more reactive than their vinyl anion counterparts 117-119.
Table 14 contains the results of alkylations of $\alpha$-arylsulfonyl-$\alpha$-vinyl anions 117-119 as derived from $\beta$-halosilylsulfonylbutanes 5-9 (Equation 66). Anions 117-119 were generated by addition of the indicated base (2 equivalents) to $\beta$-halosilylsulfonylbutanes 5-9 at -78°C and, after stirring for 10 min, benzyl bromide was introduced and the mixtures were allowed to warm to room temperature. The products (132-134, 71-79%) were isolated by chromatographic techniques. The yields of products were generally improved when HMPA is used as a co-solvent (entries 2, 5, and 9).

Compounds 132-134 were identified by spectral methods. Single sets of absorbances are present in the $^{13}$C NMR of 132-134 indicating that only single isomers are present. Trans-stereochemistry was assigned with confidence for 132 and 134 since proton NOE difference experiments show that the allyl and the benzyl protons are cis*. Irradiation of the allyl region ($\delta$ 2.15) of 132 leads to enhancement of its benzyl region ($\delta$ 3.68, 5.71%). Similarly irradiation of the allyl region ($\delta$ 2.1-2.2) of 134 enhances its benzyl region ($\delta$ 3.69, 5.66%).
Table 14. Alkylation Study of Vinyl Anions 117-119 with Benzyl Bromide

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Base</th>
<th>Solvent</th>
<th>Product</th>
<th>%Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>n-BuLi</td>
<td>THF</td>
<td>132</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>n-BuLi</td>
<td>THF/HMPA</td>
<td>132</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>n-BuLi</td>
<td>THF</td>
<td>132</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>n-BuLi</td>
<td>THF</td>
<td>133</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>LDA</td>
<td>THF/HMPA</td>
<td>133</td>
<td>84</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>LDA</td>
<td>THF</td>
<td>133</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>n-BuLi</td>
<td>THF</td>
<td>133</td>
<td>76</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>n-BuLi</td>
<td>THF</td>
<td>134</td>
<td>79</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>LDA</td>
<td>THF/HMPA</td>
<td>134</td>
<td>90</td>
</tr>
</tbody>
</table>

Desilylsulfonfylataion of 132-134 to Diene 64

Attention next turned to elimination of the arylsulfonfyl and the trimethylsilyl groups in 132-134. In order for 1,4-eliminations to take place, vinyl sulfones 132-134 have to be isomerized to allyl sulfones (Equation 64).
Allyl (135) and vinyl (136) sulfones generally interconvert under basic conditions and the equilibria heavily favor the allyl isomers (when \( R \) equals aryl or alkyl, Equation 65). It was felt therefore that methods to deconjugate 132-134 could be found.

A desirable methodology would be to combine deconjugation and elimination in a one pot procedure, thus transforming vinyl sulfones 132-133 directly to substituted-1,3-butadienes. This condition is met when 132-134 is treated with an equivalent of tetrabutylammonium fluoride (TBAF) at room temperature (Equations 66). Sulfones 132, 133, and 134 are cleanly converted to 5-phenyl-1,3-pentadiene (64) in 56, 63 and 59% yields, respectively, when stirred with TBAF in THF.
Ring Cyclization of β-halosulfone 7

The direction of this research then turned to cyclizations of β-halosulfone 7. A carbanion solution of 118, generated from 7, when treated with 1,3-dichloropropane undergoes monoalkylation to 137. Deprotonation of 137 with n-butyllithium then leads to removal of an allyl proton and generation of allyl anion 138. Cyclization of 138 then gives 1-(4-methylbenzenesulfonyl)-1-(3-trimethylsilyl)-1-propenylcyclobutane (139, 67%, Equation 67). Cyclobutane 139 was confidently assigned spectrally.

Cyclobutane 139, having its double bond isomerized to the allylic position, when treated with TBAF it is rapidly converted to allyldienecyclobutane (113, 84%, Equation 68). Thus cyclization of vinylsulfones 10-12 via this methodology has enormous potential for preparing 1-arylsulfonyl-4-trialkylsilyl-2-butenes which have already been demonstrated in this work to eliminate to varied cycloalkylallylenes.
The present research has studied 1-arylsulfonyl-1-halo-4-trimethylsilyl-
butanes 5-9 and (E)-1-arylsufonyl-1-trimethylsilyl-4-butenes 10-12 with respect
to their abilities to be converted into 1-substituted-1,3-butadienes (2) and
allylidene cycloalkanes (4). Reagents 5-9 are preparable by free radical
addition of arylsulfonyl halides to 4-trimethylsilyl-1-butene (120) as obtained by
protomonodesilation of 1,4-bis(trimethylsilyl)-2-butene (122). Silylsulfones 10-12 can obtained by dehydrohalogenation of 5-9 with varied bases. Bases studied were potassium hydroxide, lithium diisopropylamide, and n-butyllithium.

Vinyl anions 117-119 as derived from 5-9 or 10-12 and n-butyllithium or lithium diisopropylamide alkylate benzyl bromide in THF/HMPA mixtures to yield trans-alkylated products (132-134). Vinyl anions 117-119 decompose rapidly when warmed to room temperature and therefore are not as stable as allyl anion 23. Further, anions 117-119 are not as reactive as allyl anion 23 toward benzyl bromide. Fluoride induced dearylsulfonylsilylation of 132-134 results in formation of 5-phenyl-1,3-pentadiene (64). Ring cyclization of vinyl anion 118, as obtained from 7, with 1,3-dichloropropane gives cycloadduct 139. Dearylsulfonylsilylation of 139 with TBAF results in formation of allylidencyclobutane (113).
EXPERIMENTAL

All melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected as are boiling points. $^1$H nuclear magnetic resonance spectra were recorded on Varian Associates EM-90 and Bruker 200, 250, 300 or 500 MHz spectrometers. Proton shift values are reported in parts per million (ppm) from internal tetramethylsilane on the $\delta$ scale when CDCl$_3$ is denoted as the solvent with residual CHCl$_3$ at $\delta$ 7.26 as an internal reference. Spectra reported with CCl$_4$ as the solvent have no internal standard; the proton shifts are reported relative to the (CH$_3$)$_3$Si functionality at $\delta$ 0.00 or hexamethyldisiloxane (HMDS). Multiplicities are denoted as follows: s (singlet), d (doublet), t (triplet), q (quartet), and quin (quintet). $^{13}$C nuclear magnetic resonance spectra were recorded on Bruker 80, 250 or 500 MHz spectrometers. Carbon chemical shifts are reported in ppm relative to the center line of the CDCl$_3$ triplet (77.0 ppm) and are denoted as "e" (none or two protons attached) or "o" (one or three protons attached) 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. Infrared spectra were taken on a Perkin-Elmer 457 instrument. Mass spectra were recorded on a Kratos MS-30 instrument at an ionization energy of 70 ev. Gas chromatography - mass spectra (GC-MS) were recorded on a Finnigen 4021 Quadrupole instrument using electron impact and chemical ionization (CI) with the molecular ion designated as M$^+$. All reactions were conducted under a positive atmosphere of nitrogen or argon. Solvents and reagents were dried and purified prior to use.
for reactions and chromatography when deemed necessary. Analytical thin-layer chromatography was performed with EM Laboratories 0.25 mm thick precoated silica gel 60F-254 plates. Column chromatography was effected on Macherey Nagel-Kieselgel (60/70-270 mesh). The chromatography solvent is denoted as the volume percent of ethyl acetate in hexane or petroleum ether (60-90 °C).

(E)- and (Z)-Benzensulfonyl-4-trimethylsilyl-2-butenes (1)\textsuperscript{2d}

MCBA (12.7 g, 58.9-62.5 mmol, 80-85% assay) was added in small portions to a stirred solution of (E)- and (Z)-1-phenylsulfinyl-4-trimethylsilyl-2-butenes (39), (15.24 g, 60.5 mmol) in dichloromethane (300 mL) at 0 °C. After 0.5 h the reaction mixture was taken up in diethyl ether (100 mL), washed with saturated sodium bicarbonate (3 x 100 mL), 25% aqueous sodium metabisulfite (100 mL) and brine (50 mL), dried (MgSO\textsubscript{4}), filtered and concentrated to give a viscous yellow oil (16.2 g). Column chromatography (silica gel, 880 g; ethyl acetate 10 %) yields 1 as a clear colorless viscous oil (15.87 g, 98%): IR (neat film) 3060, 3030, 2950, 1645, 1490, 1445, 1305, 1250, 1145, 1085, 850, 690 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) δ -0.10 (s, 9 H, (CH\textsubscript{3})\textsubscript{3}Si), 1.45 (bd, J= 6 Hz, 2 H, SiCH\textsubscript{2}), 3.70 (bd, J = 6 Hz, 2 H, SO\textsubscript{2}CH\textsubscript{2}), 5.10-5.80 (m, 2 H, vinyl), 7.45-7.90 (m, 5 H, aromatic); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, E and Z isomers) δ -2.13 (CH\textsubscript{3}), 18.79 (CH\textsubscript{2}, Z), 23.57 (CH\textsubscript{2}, E), 54.82 (CH\textsubscript{2}, Z), 60.20 (CH\textsubscript{2}, E), 112.42 (CH, Z), 113.30 (CH, E), 128.19 (CH, E), 128.92 (CH,E)\textsuperscript{49}, 133.38 (CH, E), 133.47 (CH, Z), 135.67 (CH, Z), 138.51 (CH, E); mass spectrum, m/e calcd for C\textsubscript{7}H\textsubscript{15}Si (M\textsuperscript{-}, - C\textsubscript{6}H\textsubscript{5}SO\textsubscript{2}) 127.0943, found 127.0968.
Study of the Stability of Anion 23

(E)- and (Z)-1-Benzencesulfonyl-1-deutero-4-trimethylsilyl-2-
butenes (41)

n-Butyllithium (0.21 mL, 0.56 mmol, 2.65 M) in hexane was added to a
stirred solution of 1 (150 mg, 0.56 mmol) in THF (10 mL). The ice bath was
removed, and after stirring at 25 °C for 3.3 h, the mixture was quenched with
deuterium oxide (1 mL). The solution was immediately neutralized with
saturated ammonium chloride solution (3 mL), washed with water, dried
(MgSO₄), filtered and concentrated to a yellow clear oil (0.12 g). Column
filtration (silica gel, 3 g, ethyl acetate 5%) yielded 41 (71 mg, 47%); IR (CDCl₃)
3060, 3020, 2960, 1650, 1310, 1250, 1150, 1090, 970, 850, 690 cm⁻¹; ¹H
NMR (CDCl₃, E/Z ratio 79:21, 87% mono deuterium incorporation) δ -0.08 (s, 9
H, (CH₃)₃Si), 1.25 (dd, J = 7.5, 1.4 Hz, SiCH₂, Z isomer), 1.46 (dd, J = 8.2, 1.1
Hz, 2 H, SiCH₂, E isomer), 3.72 (bd, J = 7.2 Hz, 1 H, SO₂CHD), 5.18-5.26 (m, 1
H, Hₐ, E and Z isomers), 5.56 (dt, J = 15.2, 8.2 Hz, 1 H, Hₖ, E isomer), 5.76 (dt, J
= 10.7, 9.0 Hz, 1 H, Hₖ, Z isomer), 7.49-7.91 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃,
E/Z ratio 77:23 to 83:17) δ -2.06 (CH₃), 18.90 (CH₂, Z isomer), 23.68 (CH₂, E
isomer), 60.01 (triplet), 112.46 (CH, Z isomer), 113.32 (CH, E isomer), 128.28
(CH, E isomer), 128.39 (CH, Z isomer), 128.97 (CH, E isomer), 133.41 (CH, E
isomer), 133.49 (CH, Z isomer), 135.76 (CH, Z isomer), 138.56 (CH, E isomer)
138.81 (C, E isomer); mass spectrum, m/e calcd for C₁₃H₁₉DO₂SSi (M⁺) 269.1016, found 269.1005; C₇H₁₄DSi/C₇H₁₅Si (M⁺ - C₆H₅SO₂) isotope ratio
84/16.
(E)-and (Z)-1-Benzencesulfonyl-1,1-dideutero-4-trimethylsilyl-2-butene (47)

n-Butyllithium (1.38 mL, 3.73 mmol, 2.70 M) in hexane was syringed into a stirred solution of 1 (1.00 g, 3.73 mmol) and THF (60 mL) at -78 °C. After 15 min, HMPA (3.4 g, 18.7 mmol) was added and the ice bath was removed. The temperature rose slowly (~1 h) from -78 to 25 °C. The solution was stirred an additional 15 min and then quenched with deuterium oxide (2 mL). After stirring for 12.5 h, the mixture was diluted with ether (50 mL), washed with saturated ammonium chloride solution (20 mL), 10% HCl (5 x 20 mL), saturated sodium bicarbonate solution (20 mL) and brine (20 mL, dried (MgSO₄), filtered and concentrated to give 47 (0.89 g, 89%) as a viscous light yellow oil; IR (neat film) 3060, 3030, 2950, 1645, 1490, 1445, 1305, 1250, 1145, 1080, 965, 850, 690 cm⁻¹, ¹H NMR (CCI₄, >95% deuterium incorporation) δ 0.00 (s, 9 H, (CH₃)₃Si), 1.2-1.6 (m, 2 H, SiCH₂), 5.18 (bd, J = 15 Hz, 1 H, vinyl, E isomer), 5.32-5.97 (m with a dt at 5.62, J = 15, 7 Hz, 1 H, vinyl), 7.50-8.14 (m, 5 H, C₆H₅); mass spectrum, m/e calcd for C₇H₁₂D₂Si (M⁺ - C₆H₅S₀₂) 128.0990, found 128.1001.

General Procedure A. Deprotonation of 1 with n-Butyllithium in THF

(E)- and (Z)-4-Benzencesulfonyl-5-phenyl-1-trimethylsilyl-2-pentenes (44)²d

Method A

n-Butyllithium (1.54 mL, 3.23 mmol, 2.10 M in hexane) was slowly syringed into a stirred solution of 1 (791 mg, 2.95 mmol) in anhydrous THF (10 mL) at -78 °C. The clear colorless mixture turned clear bright yellow. After the solution had been stirred 20 min, benzyl bromide (552 mg, 3.23 mmol) was added, and
the ice bath was removed. The mixture was stirred for 1 h at room temperature. The solution was taken up with ethyl ether (20 mL), washed with water (2 x 10 mL) and brine (10 mL), dried (MgSO₄), filtered and evaporated to give a yellow viscous oil (1.39 g). Column chromatography (silica gel, 30 g; ethyl acetate 0-5%) yielded 44 (1.05 g, 99%) as a clear colorless viscous oil: IR (neat film) 3060, 3030, 2950, 1645, 1445, 1305, 1250, 1145, 965, 850, 690 cm⁻¹; ¹H NMR (CDCl₃, E isomer) δ 0.09 (s, 9 H, (CH₃)₃Si), 1.66 (m, 2H, SiCH₂), 3.16 (Hₐ, dd, Jₐb = 13.6 Hz, J = 11.6 Hz, 1 H, C₆H₅CH), 3.85 (Hₖ, dd, J₂ = 13.5 Hz, J = 3.0 Hz, 1 H, C₆H₅CH), 4.06 (Hₙ, m, 1 H, SO₂CH), 5.3 - 5.7 (m, 2H, vinyl), 7.4-8.3 (m, 10 H, C₆H₅); irradiation at δ 1.66 simplified the vinyl region to 5.3-5.4 (m, 1 H, vinyl) and 5.58 (d, J = 14.9 Hz, 1 H, vinyl); irradiation at δ 4.06 simplified the vinyl and benzyl 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 H, 1 H); ¹³C NMR (CDCl₃, E isomer) δ -2.13 (q), 23.67 (t), 33.95 (t), 70.96 (d), 118.80, 126.68, 128.53, 128.86, 129.19, 133.45, 137.11, 137.99, 138.26; mass spectrum, m/e calcld for C₁₄H₂₁Si (M⁺ - C₆H₅SO₂) 217.1412, found 217.1407. Anal. Calcd for C₂₀H₂₆O₂SSi: C, 66.99; H, 7.31. Found: C, 67.03; H, 6.94.

Deprotonation with Sodium Amide in THF

Method B

Sodium amide (60 mg, 1.53 mmol) was added to a stirred solution of 1 (140 mg, 0.52 mmol) and benzyl bromide (100 mg, 0.59 mmol) in THF (10 mL) at 0 °C. The slurry was stirred at room temperature for 2 h. The mixture was dissolved in ethyl ether (20 mL), washed with water (2 x 10 mL) and brine (10 mL), dried (MgSO₄), filtered and concentrated to give a yellow viscous oil (190
mg). Column chromatography (silica gel, ethyl acetate, 0-5%) yielded 44 (75 mg, 40%).

**Deprotonation of 1 with Sodium Hydride in THF**

**Method A**

Freshly washed (benzene) sodium hydride (0.30 g, 6.25 mmol, 50% dispersion in oil) and then allyl bromide (1.35 g, 11.16 mmol) were added to a stirred solution of 1 (1.00 g, 3.72 mmol) in THF (10 mL) at 0 °C and the mixture was refluxed for 4 h. After allowing the mixture to cool, the suspension was diluted with ethyl ether (20 mL), washed with water (2 x 10 mL) and brine (10 mL), dried (MgSO₄), filtered and concentrated to a yellow viscous oil (1.23 g).

Column chromatography (silica gel, 20 g, ethyl acetate 0-3%) yielded a partially resolved mixture of two isomers of 48 (0.65 g, 57%) as a clear colorless viscous oil: IR (neat film) 3065, 3010, 2960, 1640, 1580, 1480, 1445, 1400, 1300, 1250, 1210, 1140, 1080, 1020, 1000, 970, 920, 820, 850, 755, 715, 690 cm⁻¹; ¹H NMR (CCl₄, major isomer) δ 0.00 (s, 9H, (CH₃)₃Si), 1.50 (d, J = 7 Hz, 2 H, SiCH₂), 2.85 (Hₐₕ, m, 2H, allyl), 3.45 (Hₗ, m, 1H, SO₂CH), 4.9-6.3 (m, 5 H, vinyl), 7.5-8.2 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃, major isomer) δ -2.03 (CH₃), 23.57 (CH₂), 32.05 (CH₂), 68.81 (CH), 118.02 (CH₂), 118.82 (CH), 128.98 (CH), 129.26 (CH), 133.29 (CH), 133.39 (CH), 137.55 (C), 137.65 (CH); mass spectrum, m/e calcd for C₁₆H₂₃O₂SSi (M⁺ - H) 307.1188, found 307.1130.
Deprotonation of 1 with Sodium Hydride in DMF

Method B

Freshly washed (benzene) sodium hydride (207 mg, 4.31 mmol, 50% dispersion in oil) and then allyl bromide (1.20 g, 5.9 mmol) were added to a stirred solution of 1 (532 mg, 1.98 mmol) in DMF (10 mL) and the mixture was stirred at room temperature for 10 h. Standard workup gave 48 (318 mg, 52%).

(E)- and (Z)-4-Benzene sulfonyl-1-trimethylsilyl-2-pentenes (49)

General procedure A was followed in which methyl iodide (1.26 g, 8.88 mmol) was used as the alkylating agent to convert 1 (1.80 g, 6.71 mmol) to 49 (1.84 g, 97%) as a clear colorless viscous oil: IR (CCl₄) 3060, 3030, 2945, 2890, 1650, 1445, 1400, 1320, 1310, 1250, 1150, 1090, 1070, 1025, 965, 850, 690, 600 cm⁻¹;¹H NMR (CCl₄, E isomer) δ 0.00 (s, 9 H, (CH₃)₃Si), 1.35 (d, J = 6 Hz, 3 H, CH₃), 3.59 (m, 1 H, SO₂CH), 5.13 (dd, J = 15, 7 Hz, 1 H, vinyl), 5.58 (dt, J = 15, 8 Hz, 1 H, vinyl), 7.3-8.0 (m, 5 H, C₆H₅);¹³C NMR (CDCl₃) δ -1.95 (q), 14.06 (q), 23.57 (t), 64.04 (d), 120.78 (d), 128.82 (d), 129.14 (d), 133.35 (d), 135.60 (d), 137.78 (s); mass spectrum, m/e calcd for C₈H₁₇Si (M+ - C₆H₅SO₂) 141.1099, found 141.1092. Anal. Calcd for C₁₄H₂₂O₂SSi: C, 59.52; H, 7.85; Found: C, 59.64; H, 7.55.

(E)- and (Z)-4-Benzene sulfonyl-1-trimethylsilyl-2-nonenes (50)²d

Method A

Following standard procedure A, 1 (741 mg, 2.76 mmol) was alkylated with 1-bromopentane (453 mg, 3.00 mmol) to give 50 (835 mg, 89%), as a light
yellow oil: IR (neat film) 3060, 3020, 2960, 2860, 1650, 1585, 1450, 1410, 1310, 1250, 1210, 1150, 1085, 1025, 1000, 760, 740, 690 cm⁻¹; ¹H NMR (CCl₄, E isomer) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.7-2.2 (m with a d, J = 8 Hz at δ 1.46, 13 H, (CH₂)₄CH₃, SiCH₂), 3.30 (bt, J = 9 Hz, 1 H, SO₂CH), 4.95 (dd, J = 15.0, 9.0 Hz, 1 H, vinyl), 5.40 (dt, J = 15.0, 8.0 Hz, 1 H, vinyl), 7.3-8.0 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃, E isomer) δ -1.95 (q), 13.84 (q), 22.37, 23.68, 26.31, 27.35, 31.23, 69.61 (d), 119.80 (d), 128.76 (d), 129.09 (d), 133.25 (d), 137.24 (d), 138.28 (s); mass spectrum, m/e calcld for C₁₂H₂₅O₂SSi (M⁺ - C₆H₅SO₂) 197.1726, found 197.1729.

**General Procedure B. Alkylation of 1 in THF/HMPA**

**Method B**

n-Butyllithium (1.97 mL, 2.95 mmol, 1.50 M in hexane) was syringed slowly into a stirred solution of 1 (726 mg, 2.70 mmol) in anhydrous THF (10 mL). After stirring the mixture for 20 min, 1-bromopentane (429 mg, 2.84 mmol) followed by HMPA (2.57 mL, 14.00 mmol) were added. After warming to room temperature the mixture was stirred for 1 h, taken up in ethyl ether (20 mL), washed with water (5 x 10 mL) and brine (10 mL), dried (MgSO₄), filtered and concentrated to a yellow viscous oil (1.13 g). Column chromatography (silica gel, 30 g, ethyl acetate 0-5%) gave 50 (875 mg, 99%).

**(E)- and (Z)-4-Benzencesulfonyl-6-methyl-1-trimethylsilyl-2-heptenes (51)**

General procedure B was followed in which isobutyl bromide (411 mg, 3.00 mmol), used as the alkylation agent in the presence of HMPA (1.03 mL, 5.58
mmol), converted 1 (720 mg, 2.68 mmol) to 51 (729 mg, 83%) as a clear colorless viscous oil: IR (neat film) 3060, 3020, 2960, 1650, 1470, 1450, 1300, 1250, 1150, 1085, 850, 690 cm⁻¹; ¹H NMR (CDCl₃, E isomer) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.79 (d, J = 6.5 Hz, 3 H, CH₃), 0.94 (d, 6.5 Hz, 3 H, CH₃), 1.2-1.8 (m, 5 H, SiCH₂, CH₂CH(CH₃)₂), 3.53 (bt, J = 9.3 Hz, 1 H, SO₂CH), 4.99 (dd, J = 15.2, 9.4 Hz, 1 H, vinyl), 5.47 (dt, J = 15.2, 9.1 Hz, 1H, vinyl), 7.5-7.9 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃, E isomer) δ -2.00 (q), 20.46, 23.52, 25.16, 35.88 (t), 68.14 (d), 119.74 (d), 128.71(d), 129.04 (d), 133.19 (d), 137.13 (d), 138.11 (s); mass spectrum, m/e calc'd for C₁₁H₂₀Si (M⁺ - C₆H₅SO₂) 183.1569, found 183.1592.

(E)- and (Z)-4-Benzencesufonyl-5-methyl-1-trimethylsilyl-2-hexenes (52)

Following general procedure B, 1 (733 mg, 2.73 mmol), HMPA (2.43 mL, 13.9 mmol) and 2-bromopropane (354 mg, 2.90 mmol) were converted to 52 (852 mg, 97%), a clear colorless viscous oil: IR (neat film) 3060, 3030, 2960, 1645, 1465, 1390, 1370, 1300, 1250, 1140, 1080, 970, 850, 690 cm⁻¹; ¹H NMR (CDCl₃, E isomer) δ -0.07 (s, 9 H, (CH₃)₃Si), 0.95 (d, J = 7.0 Hz, 3H, CH₃), 1.08 (d, J = 7.0 Hz, 3H, CH₃), 1.35-1.52 (m, 2H, SiCH₂), 2.65 (m, 1 H, (CH₃)₂CH), 3.30 (m, 1 H, SO₂CH), 5.27 (m, 2 H, vinyl), 7.4-7.8 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃, major isomer) δ -1.95 (q), 17.94 (q), 21.99 (q), 23.74 (t), 26.91 (d), 74.91 (d), 116.52 (d), 128.71 (d, two coincident peaks), 133.08 (d), 138.06 (d), 139.31 (s); mass spectrum, m/e calc'd for C₁₀H₂₁Si (M⁺ - C₆H₅SO₂) 169.1413, found 169.1392. Anal. Calcd for C₁₆H₂₆O₂SSi: C, 61.89; H, 8.44. Found: C, 61.39; H, 8.23.
(E)- and (Z)-4-Benzencesulfonyl-4-cyclohexyl-1-trimethylsilyl-2-butenes (53)

**Method A**

Following general procedure B, 1 (672 mg, 2.50 mmol) was reacted in the presence of HMPA (1.74 mL, 10.00 mmol) with bromocyclohexane (2.00 g, 12.26 mmol) to give 53 (305 mg, 35%), a mixture of E/Z isomers, as a clear colorless viscous oil: IR (CCl₄) 3060, 3020, 2930, 2850, 1640, 1445, 1400, 1310, 1250, 1140, 1080, 690 cm⁻¹; ¹H NMR (CDCl₃, E isomer) δ -0.08 (s, 9 H, (CH₃)₃Si), 1.03-1.76 (m, 11 H, SiCH₂ and ring), 2.12 (bd, J = 12.7 Hz, 1 H, ring), 2.35 (m, 1 H, ring), 3.31 (dd, J = 9.8, 3.2 Hz, 1 H, SO₂CH), 5.19-5.32 (m, 2 H, vinyl), 7.31-7.81 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃) δ -1.92, 23.59, 26.03, 26.40, 28.62, 32.13, 36.68 (CH), 74.91 (CH), 117.48 (CH), 128.66 (CH)⁴⁹, 133.04 (CH), 137.43 (CH), 139.13; mass spectrum, m/e calcd for C₁₃H₂₅Si (M⁺ - C₆H₅SO₂) 209.1726, found 209.1710, and 1 (202 mg, 30% recovery).

**Method B**

Standard procedure B was followed using 1 (505 mg, 1.88 mmol) and cyclohexyl p-toluenesulfonate (2.36 g, 9.28 mmol) as reagents in the presence of HMPA (1.29 mL, 7.42 mmol). After stirring at room temperature for 19 h, the mixture was worked up as usual to give 53 (173 mg, 27%).

(E)- and (Z)-4-Benzencesulfonyl-5-methyl-6-phenyl-1-trimethylsilyl-2-hexenes (58)

Standard procedure B was followed using 1 (3.00 g, 11.18 mmol) and 2-bromo-1-phenylpropane (6.67 g, 33.50 mmol) as the alkylating agent in the
presence of HMPA (7.78 mL, 44.64 mmol). After stirring at room temperature for 19 h, the mixture was worked up as usual and column chromatographed (silica gel, 120 g; ethyl acetate 2%) to give as the first eluent a mixture of (E)-1-phenyl-1-propene (59) (3.40 g, 26%) and 2-bromo-1-phenylpropane (57) by \(^1\)H NMR and GLC analysis (column QF-1, 15%, 10" x 1/4", chromosorb W). The second eluent was 58 (1.74 g, 40%), an unresolved mixture of diastereomers, as a clear colorless viscous oil: IR (CDCl\(_3\)) 3060, 3030, 2960, 1640, 1445, 1300, 1250, 1145, 1080, 840, 600 cm\(^{-1}\); \(^1\)H NMR could not be assigned due to ambiguous coupling patterns; mass spectrum, \(m/e\) calcd for C\(_{16}\)H\(_{25}\)Si (M\(^+\) - C\(_6\)H\(_5\)SO\(_2\)) 245.1725, found 245.1723; GC-Cl-MS (isobutane) detected three isomers A:B: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). Lastly, 1 (0.99 g, 33% recovery) was eluted from the column.

\((E)-\) and \((Z)-2-(1-Benzenesulfonyl-4-trimethylsilyl-2-buten-1-yl)-cyclohexanols (62)\)

Cyclohexene oxide (562 mg, 5.72 mmol) was added to a cold (-78 °C) carbanion solution prepared from 1 (509 mg, 1.90 mmol) in diethyl ether (10 mL). After warming to room temperature and stirring for 1 h, the mixture was taken up with ether (20 mL), washed with water (2 x 10 mL) and brine (20 mL), dried (MgSO\(_4\)), filtered and concentrated to give a faint yellow oil (0.78 g). Column chromatography (silica gel, 13 g, ethyl acetate 2-20 %) yielded 62
(575 mg, 83%), a partially resolved mixture of diastereomers (two by TLC). The more polar isomer was obtained pure as a clear colorless oil which crystallized to a white solid: mp 122-123 °C; IR (neat film) 3495, 3060, 3025, 2940, 2860, 2860, 1640, 1585, 1480, 1450, 1400, 1300, 1250, 1140, 1085, 1070, 1025, 1000, 970, 910, 850, 760, 720, 690, 650 cm⁻¹; ¹H NMR (CDCl₃, polar isomer) δ -0.13 (s, 9 H, (CH₃)₃Si), 1.21-2.33 (m, 11 H, ring, SiCH₂, OH), 3.17 (m, 1 H, CHO), 4.17 (dd, J = 9.4, 2.1 Hz, SO₂CH), 5.3-5.4 (m, 2 H, vinyl), 7.34-7.95 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃, polar isomer) δ -1.96 (CH₃), 23.65 (CH₂), 24.86 (CH₂), 25.23 (CH₂), 26.36 (CH₂), 36.36 (CH₂), 44.22 (CH), 68.47 (CH), 70.57 (CH), 116.44 (CH), 128.57 (CH), 128.68 (CH), 133.06 (CH) 138.22 (CH), 139.00 (C); mass spectrum (polar isomer), m/e calcd for C₁₃H₂₆O Si (M⁺ - C₆H₅SO₂) 226.1753, found 226.1720.

**General Procedure C**

Fluoride-Induced Elimination of 1-Substituted-1-benzenesulfonyl-4-trimethyl-2-butenes

(E)-1-Cyclohexyl-1,3-butadiene (63)

**Method A**

Tetra-n-butyrammonium fluoride (4.56 mL, 4.56 mmol, 1.0 M in THF) was added to a stirred solution of 53 (808 mg, 2.28 mmol) in anhydrous THF (5 mL) at 0 °C. The mixture was stirred for 20 min, diluted with pentane (20 mL), washed with water (3 x 10 mL) and brine (10 mL) and dried (MgSO₄). The diene solution was passed through silica gel (5 g, pentane) and then evaporated to give 63 (143 mg, 57%), a clear colorless mobile oil: IR (neat film)
3100, 3070, 3040, 2980, 2880, 1650, 1600, 1460, 995, 960, 900 cm⁻¹; ¹H NMR (CDCl₃) δ 1.10-2.11 (m, 11 H, ring), 5.03 (Hₐ, dd, J = 10.9, 0.6 Hz, 1 H), 5.18 (Hₐ, dd, J = 16.8, 0.6 Hz, 1 H), 5.75 (Hₐ, dd, J = 15.3, 6.8 Hz, 1H), 6.11 (Hₐ, dd, J = 15.3, 10.2 Hz, 1 H), 6.40 (Hₐ, ddd, J = 16.9, 10.2, 10.1 Hz, 1 H); GC-MS detected one isomer, m/e (relative intensity) 136 (68, M⁺), 121 (15), 107 (33), 93 (24), 79 (72), 67 (100), 54 (49). The IR and ¹H NMR spectra are in agreement with the literature.⁵⁰

Method B

A stirred solution containing 53 (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 showed 63 to be formed in 65% yield (using E-propenylbenzene as an internal standard).

(E) and (Z) -5-Phenyl-1,3-pentadienes (64)²ᵈ

Method A

Standard procedure C was followed in which 44 (313 mg, 0.87 mmol) was converted into 64 (65 mg, 52%) as a clear colorless oil: IR (CDCl₃) 3080, 3060, 3040, 2960, 1650, 1600 cm⁻¹; ¹H NMR (CDCl₃, E and Z isomers) δ 0.00 (s, HMDS), 3.42 (d, J = 6.9 Hz, 2 H, benzyl, E isomer), 3.54 (d, J = 6.9 Hz, 2 H, benzyl, Z isomer), 4.99 (Hₐ, dd, J = 9.4, 1.2 Hz, 1 H), 5.12 (Hₐ, dd, J = 16.5, 1.5 Hz, 1 H), 5.84 (Hₐ, dt, J = 15.1, 7.0 Hz, 1 H), 6.10 (Hₐ, dd, J = 15.1, 10.2 Hz, 1 H), 6.33 (Hₐ, ddd, J = 16.8, 10.1, 10.1 Hz, 1 H); irradiation at 3.42 collapses 5.84 to a doublet, J = 15.1 Hz; mass spectrum, m/e calcld for C₆H₁₂ 144.0939, found 144.0930.
Method B

A stirred solution containing 44 (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 showed 64 to be formed in 63% yield (using E-propenylbenzene as an internal standard).

Method C

Aluminum chloride (769 mg, 5.76 mmol) was added to a stirred solution of 44 (806 mg, 2.25 mmol) in methylene chloride (10 mL) at -78 °C. After stirring for 0.5 h, the mixture was taken up with pentane (20 mL), washed with water (3 x 10 mL) and brine (10 mL) and dried (MgSO₄). The diene solution was passed through silica gel (5 g, pentane) to give after evaporation 64 (94 mg, 29%).

(E)- and (Z)-6-Methyl-1,3-heptadienes (65)

Following general procedure C, 51 (1.21 g, 3.73 mmol) was converted into 65 (259 mg, 63%): IR (neat film) 3100, 3070, 2960, 2870, 1650, 1600, 1450, 1380, 1372, 990, 915 cm⁻¹; ¹H NMR (CDCl₃, E isomer) δ 0.83 (d, J = 6.6 Hz, 6 H, CH₃), 1.59 (m, J = 6.6 Hz, 1 H, (CH₃)₂CH), 1.90 (dd, J = 6.9 Hz, 2 H, CH₂), 4.89(Hₐ, dd, J = 10.0, 0.5 Hz 1 H), 5.00 (H₇, dd, J = 16.7, 0.5 Hz, 1H), 5.58 (Hc, dt, J = 15.1, 7.4 Hz, 1 H), 5.95 (He, dd, J = 15.0, 10.3 Hz, 1 H), 6.23 (Ha, ddd, J = 16.9, 10.2, 10.1 Hz, 1 H); irradiation at δ 1.90 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), 93 (67), 56 (57), 54 (59), 43 (89), 41 (100), 39 (59).

(E)- and (Z)-5-Methyl-6-phenyl-1,3-hexadienes (66)

Following standard procedure C, 0.58 (0.93 g, 2.40 mmol) was eliminated to 66 (322 mg, 78%), as a clear colorless oil: IR (neat film) 3100, 3070, 3040, 2980, 2930, 2880, 1650, 1600, 1455, 1380, 1010, 955, 900, 750, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 1.01 (d, J = 4.5 Hz, 3 H, CH₃), 2.43-2.75 (m, 3 H, CHCH₂), 4.95 (Hα dd, J = 10.0, 1.7 Hz, 1 H), 5.07 (Hβ dd, J = 16.9, 1.7 Hz, 1 H), 5.67 (Hc dd, J = 15.3, 6.4 Hz, 1 H), 5.99 (Hd dd, J = 15.4, 10.4 Hz, 1 H), 6.28 (He ddd, J = 17.1, 10.2, 10.1 Hz, 1H), 7.10-7.35 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃) δ 19.52 (CH₃), 38.25 (CH), 43.43 (CH₂), 115.09 (CH₂), 125.85 (CH), 128.13 (CH), 129.22 (CH), 129.32 (CH), 137.35 (CH), 140.24 (CH), 140.53 (C); mass spectrum, m/e calcd for C₁₃H₁₆ (M⁺) 172.1252, found 172.1259; GC-MS detected two isomers in the following ratio 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)].

(E)-1-(1,3-Butadienyl)cyclohexan-2-ol (67)

General procedure C was followed in which 62 (372 mg, 1.01 mmol) was converted into 67 (128 mg, 83%), a clear colorless oil: IR (neat film) 3380, 3080, 3040, 3000, 2930, 2860, 1645, 1600, 1450, 1050, 1000, 950, 930, 900, 870 cm⁻¹; ¹H NMR (CDCl₃) δ 1.14-1.34 (m, 4 H, ring), 1.64-2.05 (m, 5 H, ring), 3.20-3.30 (m, 1H, CHOH), 5.02 (Hα dd, J = 9.8, 1.4 Hz, 1 H), 5.14 (Hβ dd, J = 17.0, 1.1 Hz,
1H), 5.57 (Hc, dd, J = 15.1, 8.6 Hz, 1H), 6.17 (Hd, dd, J = 15.0, 10.3 Hz, 1H),
6.32 (He, ddd, J = 16.5, 10.5, 9.8 Hz, 1H); 13C NMR (CDCl3) δ 24.72 (CH2),
25.10 (CH2), 31.22 (CH2), 33.95 (CH2), 49.87 (CH), 73.21 (CH), 116.07 (CH2),
132.67 (CH), 136.50 (CH), 136.78 (CH); mass spectrum, m/e cacld for C10H16O
152.1201, found 152.1188. The IR and 'H NMR spectra are in agreement with
the literature.3a

General Procedure D
(E)- and (Z)-1,3-Pentadiene (68)

DMSO (7 mL) was added to tetra-n-butylammonium fluoride (7.08 mL, 7.08
mmol, 1.0 M in THF) and, the mixture was concentrated (0.1 mm Hg /25 °C).
The TBAF/DMSO reagent was then added to a stirred solution of 49 (1.08 g,
3.82 mmol) in DMSO (5 mL) at 25 °C. After stirring for 20 min, the mixture was
flash distilled (25 °C / 30-100 mm Hg). The volatile components were trapped
at -78 °C to give a mixture of 68 (197 mg, 76%) and hexamethyldisiloxane (213
mg). The IR and 'H NMR of 68 are in agreement with an authentic sample.

(E)- and (Z)-5-Methyl-1,3-hexadiene (69)

Standard procedure D was followed in which 52 (0.95 g, 3.06 mmol) was
converted into 69 (250 mg, 85%) whose IR and 'H NMR spectra are in
agreement with the literature.51,52
Studies of Dialkylation of (E)- and (Z)-1-Benzencesulfonyl-4-trimethylsilyl-2-butenes (2)

**Standard Procedure (E)**

(E)- and (Z)-4-Benzencesulfonyl-4-methyl-1-trimethylsilyl-2-pentenes (77)

n-Butyllithium (0.22 mL, 0.35 mmol, 1.60 M in hexane) was added to a stirred solution of 1 (83 mg, 0.31 mmol) at -78 °C in THF (10 mL). After stirring the clear yellow mixture for 20 min, methyl iodide (91 mg, 0.64 mmol) was added. The cold bath was removed, and the mixture warmed to -30 °C. The now clear colorless solution was recooled to -78 °C and additional n-butyllithium (0.30 mL, 0.48 mmol, 1.60 M) was added. The mixture was stirred for 15 min, and then more methyl iodide (68 mg, 0.48 mmol) was added. After warming to room temperature and being stirred for 1h, the mixture was taken up in ethyl ether (10 mL), washed with water (2 x 10 mL) and brine (10 mL), dried (MgSO₄), filtered and concentrated to a faint yellow oil, 150 mg. Column chromatography (silica gel, 15 g, ethyl acetate 0-5%) gave 77 (93 mg, 98%) as a clear colorless viscous oil: IR (CCl₄) 3060, 3030, 2960, 1650, 1450, 1400, 1370, 1300, 1250, 1150, 690 cm⁻¹; ¹H NMR (CCl₄) δ 0.00 (s, 9 H, (CH₃)₃Si), 1.2-1.7 (m with a singlet at δ 1.33; 8 H, CH₃ and SiCH₂), 5.2-5.7 (m, 2 H, vinyl), 7.3-8.0 (m, 5 H, C₆H₅); mass spectrum, m/e calcld for C₉H₁₉Si (M⁺ - C₆H₅SO₂) 155.1256, found 155.1244.
Standard Procedure F

(E) and (Z)-4-Benzanesulfonyl-4-methyl-5-phenyl-1-trimethylsilyl-2-butenes (81)

n-Butyllithium (0.23 mL, 0.53 mmol, 2.30 M) was added to a cold (-78 °C) solution of 44 (170 mg, 0.48 mmol) in THF (10 mL). After stirring the mixture for 20 min, methyl iodide (136 mg, 0.96 mmol) was added. The cooling bath was removed and the solution was stirred 1 h at room temperature. The mixture was taken up in ethyl ether (10 mL), washed with water (10 mL) and brine (10 mL), dried (MgSO₄), filtered and concentrated to a faint yellow clear mobile oil, 211 mg. Column chromatography (silica gel, 6 g, ethyl acetate 0-3%) yielded 81 (170 mg, 97%): IR (CCl₄) 3060, 3030, 2960, 1650, 1450, 1400, 1300, 1250, 1150, 1060, 1030, 970, 690, 600 cm⁻¹; ¹H NMR (CDCl₃, E isomer) δ -0.12 (s, 9 H, (CH₃)₃Si), 1.21 (s, 3 H, CH₃), 1.46 (m, 2 H, SiCH₂), 3.17 (Hₐ, d, J= 12.9 Hz, 1 H, C₆H₅CH), 3.29 (Hₐ, d, J = 13.0 Hz, 1 H, C₆H₅CH), 5.19 (dt, J = 15.6, 7.5 Hz, 1 H, vinyl), 5.53 (dt, J = 15.6 Hz, 1.2 Hz, 1 H, vinyllic), 7.0-7.3 (m, 5 H, C₆H₅), 7.4-7.9 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃, E isomer) δ -1.79 (q), 17.11 (q), 23.71 (t), 39.48 (t), 69.03 (s), 124.32 (d), 126.69 (d), 127.87 (d), 128.28 (d), 130.72 (d), 130.76 (d), 133.34 (d), 134.61 (d), 135.23 (s), 135.73 (s); mass spectrum, m/e calcd for C₁₅H₂₃Si (M⁺ - C₆H₅SO₂) 231.1569, found 231.1590.

(E) and (Z)-4-Benzanesulfonyl-4-benzyl-5-phenyl-1-trimethylsilyl-2-pentenes (82)

Standard procedure F was followed in which benzyl bromide (180 mg, 1.05 mmol) was used as the alkylating agent to convert 44 (112 mg, 0.31 mmol) to 82 (99 mg, 71%) as a white crystalline solid; mp 100-101 °C (from hexane); IR
(CCI₄) 3060, 3020, 2940, 1640, 1490, 1440, 1300, 1245, 1080, 690 cm⁻¹; ¹H NMR (CCI₄, E isomer) δ 0.00 (s, 9 H, (CH₃)₃Si), 1.52 (d, J = 8 Hz, 2 H, SiCH₂), 3.25 (s, 4 H, C₆H₅CH₂), 5.28 (d, J = 17 Hz, 1 H, vinyl), 5.78 (dt, J = 17, 8 Hz, 1 H vinyl), 7.1-8.0 (m, 15 H, C₆H₅); mass spectrum, m/e calcd for C₂₀H₂₅O₂SSi (M⁺ - C₇H₇) 357.1344, found 357.1304.

(E)- and (Z)-4-Benzenesulfonyl-4-benzyl-1-trimethylsilyl-2-nolones (83)

1-Bromopentane (2.50 g, 16.5 mmol) and 80 (1.50 g, 4.1 mmol) were reacted in the presence of HMPA (3.0 g, 16.7 mmol) according to standard procedure F to give 83 (1.10 g, 61%), a clear colorless viscous oil; 3060, 2860, 1450, 1310, 1250, 1150, 1090, 850, 690 cm⁻¹; ¹H NMR (CDCl₃, E isomer), δ -0.07 (s, 9 H, (CH₃)₃Si), 0.81-1.86 (m, 13 H, (CH₂)₄CH₃, SiCH₂), 3.18 (Hₐ, d, J = 13.8 Hz, 1 H, C₆H₅CH), 3.44 (Hₐ, J = 13.9 Hz, 1 H, C₆H₅CH), 5.27 (d, J = 15.8 Hz, 1 H, vinyl), 5.42 (dt, J = 15.8, 7.8 Hz, 1 H, vinyl), 7.1-7.9 (m, 10 H, C₆H₅); ¹³C NMR (CDCl₃, E isomer) δ -1.79 (o), 13.92 (o), 22.30 (e), 23.55 (e), 23.94 (e), 30.95 (e), 32.47 (e), 36.63 (e), 71.78 (u), 125.32 (o), 126.68 (o), 127.92 (o), 128.15 (o), 130.59 (o), 130.63 (o), 133.20 (o), 133.96 (o), 135.66 (u), 136.55 (u); mass spectrum, m/e calcd for C₁₉H₃₁Si (M⁺ - C₆H₅SO₂) 287.2195, found 287.2200; and 84 (270 mg, 30%, E/Z = 54:46) as a clear colorless oil; IR (neat film) 3080, 3060, 3020, 2960, 2920, 2850, 1640, 1600, 1490, 1450, 990, 900, 700 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 C₁₆H₂₂ (M⁺)
214.1722, found 214.1744; GC-MS detected two isomers in the following ratio 54:46 [major isomer m/e (relative intensity) 214 (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 (M+), 171 (1), 157 (18), 143 (100), 129 (39), 128 (28), 115 (18), 91 (62), 81 (14), 79 (9), 77 (9), 67 (17), 65 (13)].

Elimination of 83 on Silica Gel

Debenzenesulfonfyltrimethylsilylation of 83 (127 mg, 0.30 mmol) was achieved by absorption on silica gel (3 g, pentane). After 0.5 h, the column was eluted with pentane to give after evaporation, 84 (27 mg, 42%).

(E)-4-Methyl-1,3-pentadienes (86)

Standard procedure D was followed in which 77 (324 mg, 1.09 mmol) was debenzenesulfonfyltrimethylsilylated to give 86 (65 mg, 72%); IR (CCl₄) 3080, 3060, 3020, 2960, 2850, 1650, 1600, 1450, 1375, 1000, 970, 900 cm⁻¹; ¹H NMR (CCl₄) δ 1.8 (bs, 6H, CH₃), 4.80 (Hₐ, J = 10 Hz, 1 H), 5.10 (Hₐ, d, J = 15 Hz, 1 H), 5.85 (H₉, d, J = 10 Hz, 1 H), 6.55 (H₉, ddd, J = 16, 10, 10 Hz, 1 H). The IR and ¹H NMR spectra are in agreement with the literature.⁵²,⁵³

(E)- and (Z)-4-Methyl-5-phenyl-1,3-pentadienes (87)

As described in general procedure C, 81 (137 mg, 0.37 mmol) was treated with TBAF (0.73 mL, 0.73 mmol, 1.0 M in THF) to yield 87 (44 mg, 75%) as a clear colorless oil; IR (CCl₄) 3080, 3060, 3020, 2960, 2920, 2850, 1650, 1600, 1450, 1375, 1000, 970, 900 cm⁻¹; ¹H NMR (CDCl₃, E and Z isomers) δ 1.53 (s, 3
H, CH₃, Z isomer), 1.70 (s, 3 H, CH₃, E isomer), 3.35 (s, 2 H, C₆H₅CH₂, E isomer), 3.50 (s, 2 H, C₆H₅CH₂, Z isomer) 5.01-5.06 (Hₐ, two overlapping dd, Jₑ = 10.2, 1.7 Hz, E and Z isomer), 5.13 (Hₑ, dd, J = 16.8, 1.9 Hz, 1H, E isomer), 5.18 (Hₑ, d, J = 16.7 Hz, 1 H, Z isomer), 5.93 (Hₓ, d, J = 10.5 Hz , 1 H, E isomer), 6.01 (Hₓ, d, J = 10.6 Hz, 1 H, Z isomer), 6.57 (Hₓ, ddd, J = 16.8, 10.5, 10.5 Hz, 1 H, E isomer), 6.72 (Hₓ, ddd, J = 16.8, 10.5, 10.5 Hz, 1 H, Z isomer), 7.1-7.4 (m, 5 H, C₆H₅); NOE differences with irradiation at 5.93 gave enhancements at 3.35 (2.93%), 5.13 (2.53%); ¹³C NMR (CDCl₃, E and Z isomers) δ 16.47 (o, E), 23.50 (o, Z), 38.28 (e, Z), 46.23 (e, E), 115.52 (e, E), 115.64 (e, Z), 126.06 (o, Z), 126.13 (o, E), 127.12 (o, E), 127.47 (o, Z), 128.30 (o, E), 128.38 (o, Z), 128.57 (o, Z), 128.96 (o, E), 133.05 (o, Z), 133.24 (o, E), 137.98 (u, Z), 137.42 (u, E), 139.62 (u, E); mass spectrum, m/e calcd for C₁₂H₁₄ (M⁺) 158.1095, found 158.1095. GC-MS detected two isomers in the following ratio 80:20 [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); minor isomer m/e (relative intensity) 158 (39), 143 (100), 129 (49), 128 (75), 115 (34), 103 (3), 91 (47), 80 (10), 79 (13), 77 (17), 65 (35), 63 (14), 51 (24).

5-Phenyl-4-methylphenyl-1,3-pentadiene (88)

Treatment of 82 (73 mg, 0.16 mmol) with TBAF (0.32 mL, 0.32 mmol, 1M in THF) as in procedure C gave 88 (31 mg, 83%) as a clear colorless oil; IR (CCl₄) 3080, 3060, 3020, 2950, 1640, 1600, 1450, 980, 900, 690 cm⁻¹; ¹H NMR (CDCl₃) δ 3.40 (s, 2 H, C₆H₅CH₂), 3.57 (s, 2H, C₆H₅CH₂), 5.24 (Hₐ, d, J = 10.1 Hz, 1 H), 5.36 (Hₑ, d, J = 16.7 Hz, 1 H), 6.19 (Hₓ, d, J = 10.8 Hz, 1 H), 6.88 (Hₓ, ddd, J = 16.3, 10.8, 10.8 Hz); ¹³C NMR (CDCl₃) δ 35.82 (e), 42.97 (e), 116.94
(E), 126.10 (o), 128.28 (o), 128.38 (o), 128.65 (o), 129.14 (o), 132.88 (o), 139.38 (o), 139.43 (u), 140.90 (u); mass spectrum, $m/e$ calcd for $C_{18}H_{18}$ 234.1409, found 234.1400.

**(E)- and (Z)-5-phenyl-4-(1-pentyl)-1,3-pentadienes (84)**

Following general procedure C, 83 (153 mg, 0.36 mmol) and TBAF (0.71 mmol, 1.0M in THF) yielded 84 (50 mg, 65%).

**Thermolysis of 83.**

Decomposition of 83 (93 mg, 0.22 mmol) by preparative GC (SE 30, 10%, Chromosorb P, 6' x 0.25", flow rate 60 mL/min, injection temperature 375 °C, oven temperature 180 °C) yielded 84 (21 mg, 45%).

**Thermolysis of 82.**

Thermolysis of 82 (120 mg, 0.27 mmol) by preparative GC (SE 30, 10%, Chromosorb P, 6' x 0.25", flow rate 60 mL/min, injection temperature 375 °C, oven temperature 180 °C) gave 88 (33 mg, 52%).

**Cyclizations of 1-Benzenesulfonyl-4-trimethylsilyl-2-butenes (1)**

**General Procedure (H)**

**(E)- and (Z)-1-Benzenesulfonyl-1-(trimethylsilyl-1-propenyl) cyclopropanes (96)**

**Method A**

n-Butyllithium (1.60 mL, 3.87 mmol, 2.42 M in hexane) was slowly added to a stirred solution of 1 (0.96 g, 3.57 mmol) at -78 °C in THF (10 mL).
solution was stirred at -78 °C for 10 min. 1,2-Dibromoethane (812 mg, 4.32 mmol) was added to the cold solution, and the cold bath was removed. After stirring at room temperature for 1 h, the solution was recooled to -78 °C, and another portion of n-butyllithium (2.20 mL, 5.32 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 1 h. The solution was taken up with ether (20 mL), washed with water (10 mL) and brine (10 mL), dried (MgSO₄) and concentrated to give a light yellow viscoius oil (1.23 g). Column chromatography (silica gel, 30 g; ethyl acetate 0-5%) yielded 96 (1.01 g, 95%) as a clear colorless viscoius oil which solidified upon standing; mp 63-65 °C (from pentane); IR (CDCl₃) 3070, 3020, 2960, 1690, 1445, 1415, 1300, 1250, 1200, 1140, 1080, 1030, 1000, 970, 840 cm⁻¹; ¹H NMR (CDCl₃, E isomer) δ -0.11 (s, 9H, (CH₃)₃Si), 1.02 (H₆, dd, J = 6.5, 4.2 Hz, 2H, ring), 1.40 (d, J = 7.1 Hz, 2H, SiCH₂), 1.69 (dd, J = 6.6, 4.2 Hz, 2H, ring), 5.5-5.6 (m, 2H, vinyl), 7.4-7.8 (m, 5H, C₆H₅); ¹³C NMR (CDCl₃) δ -2.02 (q), 12.74 (t), 23.06 (t), 43.92 (s), 120.54 (d), 128.59 (d), 128.65 (d), 132.96 (d), 135.90 (d), 138.99 (s); mass spectrum, m/e calcd for C₁₅H₂₂O₂SSi (M⁺) 294.1110, found 294.1108. Anal. Calcd for C₁₅H₂₂O₂SSi: C, 61.18; H, 7.53. Found: C, 61.19; H, 7.50.

Method B

1-Benzenesulfonyl-1-(3-trimethylsilyl-1-propenyl)tetrahydropyran (106)

A stirred carbanion solution was prepared from 1 (509 mg, 1.89 mmol) and n-butyllithium (0.79 mL, 2.09 mmol, 2.65 M in hexane) in ethyl ether (10 mL) at -78 °C. Excess ethylene oxide (1.13 g, 25.67 mmol) was added, and the bath was removed. The mixture was gently refluxed for 1.3 h, and then the mixture
was cooled to 0 °C. Methanesulfonyl chloride (0.22 g, 1.90 mmol) was added. The solution was brought to reflux for 1.5 h and then cooled to -78 °C. Another portion of n-butyllithium (0.79 mL) was added and the bright yellow suspension was allowed to warm to room temperature. After stirring for 20 min, the mixture was diluted with ethyl ether (30 mL), washed with water (20 mL) and brine (20 mL), dried (MgSO₄), filtered and concentrated to give a clear yellow viscous oil (0.75 g). Column chromatography (silica gel, 30 g; ethyl acetate 0-10%) yielded 96 (160 mg, 28%), the first eluent, as a white crystalline solid. The second eluent 106 (50 mg, 8%) was a clear colorless viscous oil; IR (neat film) 3060, 3020, 2960, 2860, 1640, 1445, 1300, 1250, 1140, 850, 690 cm⁻¹; ¹H NMR (CDCl₃, E isomer) δ 0.02 (s, 9 H, (CH₃)₃Si), 1.57 (d, J = 8.2 Hz, 2 H, SiCH₂), 1.76 (d, J = 12.7 Hz, 2 H, H₉), 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, 1H, H_e), 5.60 (dt, J= 16.2, 8.0 Hz, 1H, H_f), 7.4-7.9 (m, 5H, C₆H₅); ¹³C NMR (CDCl₃, E isomer) δ -1.71 (CH₃), 24.20 (CH₂), 29.43 (CH₂), 63.47 (CH₂), 65.96 (C), 121.66 (CH), 128.37 (CH), 130.78 (CH), 133.50 (CH), 135.20 (C), 137.49 (CH); NOE difference 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 difference 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 difference with irradiation at δ 3.85 gave enhancements at δ 2.22 (4.46%) and δ 3.42 (25.74%); NOE difference with irradiation at δ 5.02 gave 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 C₁₁H₂₁OSi (M⁺ - C₆H₅SO₂) 197.1362, found 197.1371; GC-CI-MS (CH₄)
(E)- and (Z)-1-Benzenesulfonyl-1-(3-trimethylsilyl-1-propenyl) cyclobutanes (97)

Method A

Standard procedure H was followed in which 1 (2.00 g, 7.45 mmol) and 1,3-dibromopropane (4.51 g, 22.34 mmol) was converted to 97 (1.99 g, 87%): a clear colorless viscous oil; IR (neat film) 3060, 2950, 1640, 1580, 1445, 1300, 1250, 1140, 1065, 1020, 995, 970, 850,750, 690 cm⁻¹;¹H NMR (CDCl₃, E isomer) δ -0.06 (s, 9 H, (CH₃)₃Si), 1.46 (dd, J = 8.0, 1.0 Hz, 2 H, SiCH₂), 1.6-2.3 (m, 4 H, ring), 2.7-3.0 (m, 2 H, ring), 5.29 (d, J = 15.4 Hz, 1 H, vinyl), 5.49 (dt, J = 15.4, 7.9 Hz, 1 H, vinyl) 7.4-7.9 (m, 5 H, C₆H₅); irradiation at δ 1.6-2.3 collapses δ 2.7-3.0 to a bs; irradiation at 1.46 collapses 5.49 to a d; ¹³C NMR (CDCl₃, E isomer) δ -1.94 (CH₃), 15.14 (CH₂), 23.17 (CH₂), 27.81 (CH₂), 66.86 (C), 123.86 (CH), 128.44 (CH), 129.58 (CH), 133.15 (CH), 133.25 (CH), 136.34 (C); mass spectrum, m/e calcd for C₁₀H₁₉Si (M+ - C₆H₅SO₂) 167.1256, found 167.1271; Cl-MS (CH₄), 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-Benzenesulfonyl-1-(3-trimethylsilyl-1-propenyl) cyclopentanes (98)

According to general procedure (P), 1-bromo-4-chlorobutane (2.91 g, 16.98 mmol) was converted to 98 (1.63 g, 89%) as a clear colorless oil; IR (neat film) 3060, 3020, 3000, 2950, 2890, 1650, 1585, 1450, 1300, 1250, 1150, 1070, 970,
920, 850, 730, 690 cm⁻¹; ¹H NMR (CDCl₃, E and Z isomer) δ -0.03 (s, 9 H, (CH₃)₃Si, Z isomer), 0.08 (s, 9H, (CH₃)₃Si, E isomer), 1.43 (dd, J = 8.0, 0.8 Hz, 2 H, SiCH₂), 1.5-1.8 (m, 6 H, ring), 2.2-2.4 (m, 2 H, ring), 5.03 (dt, J = 11.6, 1.7 Hz, 2 H, vinyl, Z isomer), 5.21 (d, J = 15.6 Hz, 1 H, vinyl, E isomer), 5.43 (dt, J = 15.5, 8.0 Hz, 1 H, vinyl, E isomer), 5.59 (dt, J = 11.5, 9.2 Hz, 2 H, vinyl, Z isomer), 7.4-7.8 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃, E isomer) δ -1.99 (CH₃), 23.26 (CH₂), 23.88 (CH₂), 74.39 (C), 125.21 (CH), 128.19 (CH), 129.92 (CH), 132.81 (CH), 133.03 (CH), 137.21 (C); mass spectrum, m/e calcd for C₁₁H₂₁Si (M⁺ - C₆H₅SO₂) 181.1412, found 181.1447.

(E)- and (Z)-1-Benzenesulfonyl-1-(3-trimethylsilyl-1-propenyl)cyclohexanes (99)

The carbanion solution prepared from 1 (1.53 g, 5.69 mmol) and n-butyllithium (2.40 mL, 6.25 mmol, 2.60 M in hexane) was treated with 1,5-dibromopentane (3.85 g, 16.73 mmol). Additional n-butyllithium (2.84 mL, 7.39 mmol) was added to the mixture. General procedure H was followed to give 99 (1.46 g, 78%) as a clear colorless oil; IR (neat film) 3070, 3030, 2950, 2860, 1640, 1580, 1445, 1400, 1300, 1290, 1250, 1140, 1085, 1050, 1020, 975, 860, 760, 710, 690, 600 cm⁻¹; ¹H NMR (CDCl₃, E isomer) δ -0.02 (s, 9 H, (CH₃)₃Si), 1.0-1.9 (m, 12 H, ring and SiCH₂), 4.92 (dd, J= 15.9, 1.1 Hz, 1 H, vinyl), 5.49 (dt, J = 15.9, 8.2 Hz, 1 H, vinyl), 7.4-7.8 (m, 5 H, C₆H₅); ¹³C NMR (CDCl₃, E isomer) δ -1.85 (CH₃), 21.52 (CH₂), 23.84 (CH₂), 25.13 (CH₂), 28.79 (CH₂), 68.41 (C), 122.93 (CH), 127.97 (CH), 130.67 (CH), 133.03 (CH), 135.64 (C), 135.95 (CH); mass spectrum, calcd m/e for C₁₂H₂₃Si (M⁺ - C₆H₅SO₂) 195.1569, found 195.1557.
(E)- and (Z)-4-Benzene sulfonyl-1-trimethylsilyl-2-octenes (101)

n-Butyllithium (3.70 mL, 8.51 mmol, 2.30 M in hexane) was slowly added to 1 (0.97 g, 3.61 mmol) in THF (10 mL) at -78 °C. The resulting clear yellow solution was stirred for 20 min. 1,2-Dibromoethane (930 mg, 4.95 mmol) was added followed by HMPA (3.0 mL, 17.24 mmol). The solution was allowed to warm to 0 °C. The solution was quenched with water (30 mL) and the organic phase was separated, diluted with ether (20 mL), washed with brine (30 mL), dried (MgSO₄), filtered and concentrated. Column chromatography (silica gel, 20 g; ethyl acetate 0-10%) gave 101 (1.05 g, 90%) as a faint yellow clear oil; negative Beilstein test for halide; IR (neat film) 3060, 3020, 2960, 2860, 1650, 1585, 1450, 1410, 1310, 1250, 1210, 1150, 1085, 1025, 1000, 970, 850, 760, 740, 690 cm⁻¹; ¹H NMR (CCl₄) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.7-1.6 (m with a doublet at δ 1.45, J = 8 Hz, 11 H, (CH₂)₃CH₃, SiCH₂), 3.32 (td, J = 8, 3 Hz, 1H, CHSO₂), 4.8-5.7 (m, 2 H, vinyl), 7.4-8.1 (m, 5 H, C₆H₅); mass spectrum, m/e calcd for C₁₁H₂₃Si (M⁺ - C₆H₅SO₂) 183.1569, found 183.1582.

4-Benzene sulfonyl-1-trimethylsilyl-2,6-heptadiene (48)

Freshly washed (benzene) sodium hydride (206 mg, 4.29 mmol, 50% dispersion in oil) was added to a stirred solution of 1 (533 mg, 2.71 mmol) in DMF (8 mL) at 0 °C. 1,3-Dibromopropane (1.20 g, 5.94 mmol) was added to the slurry, and the mixture was allowed to warm to room temperature. After stirring for 10 h, the slurry was diluted with ethyl ether (10 mL), washed with water (2 x 10 mL), and brine (10 mL), dried (MgSO₄), filtered and concentrated to a yellow
mobile oil (783 mg). Column chromatography (silica gel, 30 g; ethyl acetate 0-3%) gave 48 (298 mg, 49%) and 1 (255 mg, 48% recovery).

**Allylidene cyclopropane (110)**

Standard procedure D was followed in which 96 (1.00 g, 3.40 mmol) was debenzenesulfonyltrimethylsilylated to give a mixture of 110 (246 mg, 90%) and hexamethyldisiloxane (193 mg) as a clear colorless oil which was stable in solution at room temperature for several days; The neat material, however, turned cloudy white upon standing: IR (CCl₄) 1635, 1610 cm⁻¹; ¹H NMR (CCl₄) δ 0.00 (s, HMDS), 1.05 (s, 4 H, ring), 5.00-5.45 (m, 2 H, vinyl), 6.32-6.88 (m, 2 H, vinyl). The IR and ¹H NMR spectra are identical with the literature.

**Preparation of Triazolidione (112)**

TBAF (7.13 mL, 7.13 mL, 1.0 M solution in THF) was added to a stirred solution of 96 (1.40 g, 4.75 mmol) in THF (15 mL) at 0 °C. After stirring for 5 min, the solution was taken up in deoxygenated ethyl ether, washed with water (3 x 20 mL) and brine (20 mL), dried (Na₂SO₄), filtered and cooled (-78 °C). N-phenyltriadizolinedione (111)⁵³ (0.83 g, 4.75 mmol) was slowly (1 h) added to the cold solution of 110. The solution temperature was not allowed to rise above -60 °C. The red color of 111 disappeared upon solution. After the addition was complete, the pink solution was filtered and concentrated to a brown solid (1.10 g). Column chromatography (silica gel, 20 g; ethyl acetate 25%) gave 112 (0.98 g, 81%) as a white crystalline solid; mp 130-131 °C (from hexane); IR (CDCl₃) 3050, 3010, 2850, 1680 cm⁻¹; ¹H NMR (CDCl₃) δ 0.92 (dd, J = 7, 6 Hz, 2 H, cyclopropyl), 2.10 (dd, J = 7, 6 Hz, 2 H, cyclopropyl), 4.17 (dd, J = 3, 2 Hz, 2
 Allylidenecyclobutane (113)

Standard procedure D was followed in which 97 (662 mg, 2.14 mmol) was converted to a mixture of 113 (124 mg, 61%) and hexamethyldisiloxane (168 mg) a clear colorless oil; IR (neat film) 3080, 2960, 2920, 1670, 1600, 1415, 1250,990, 890 cm⁻¹; ¹H NMR (CDCl₃) δ 0.08 (s, HMDS), 2.01 (quin, J = 7.9 Hz, 2H, ring), 2.7-2.8 (m, 4 H, allyl), 4.91 (Hₐ, dd, J = 10.2, 0.9 Hz, 1 H), 4.99 (Hₐ, dd, J = 17.0, 0.9 Hz, 1 H), 5.78 (Hₐ, dt, J = 10.8, 2.2 Hz, 1 H), 6.27 (Hₐ, ddd, J = 17.0, 10.8, 10.2 Hz, 1 H); ¹³C NMR (CDCl₃) δ 1.76 (q, HMDS), 17.11 (t), 29.94 (t), 31.30 (t), 113.01 (t), 121.65 (d), 133.07 (d), 146.03 (s); mass spectrum, m/e calcd for C₇H₁₀ (M⁺) 94.0782, found 94.0789.

 Allylidenecyclopentane (114)

General procedure D was followed in which 98 (1.92 g, 2.85 mmol) was debenzenesulfonyltrimethylsilated to give a mixture of 114 (158 mg, 51%) and HMDS (53 mg, 11%) a clear colorless oil; IR (CDCl₃) 3080, 2960, 2870, 1650, 1600, 1460, 990, 890 cm⁻¹; ¹H NMR (CDCl₃) δ 0.12 (s, HMDS), 1.6-1.8 (m, 4 H, ring), 2.3-2.4 (m, 4H, allyl), 4.95 (Hₐ, dd, J = 9.2, 1.0 Hz, 1 H), 5.04 (Hₐ, dd, J = 16.1, 0.8 Hz, 1H), 5.99 (Hₐ, d, J = 10.9 Hz, 1 H), 6.46 (Hₐ, dd, J = 17.0, 10.6, 10.5 Hz, 1 H); ¹³C NMR (CDCl₃) δ 1.76 (q, HMDS), 26.10 (t), 26.31 (t), 29.18 (t), 33.83
Allylidene cyclohexane (115)

General procedure C was followed in which 99 (0.88 g, 2.61 mmol) was converted to 115 (215 mg, 67%) as a clear colorless oil; IR (neat film) 3080, 3040, 2920, 2860, 1650, 1600, 1450, 990, 890 cm⁻¹; ¹H NMR (CDCl₃) δ 1.5-1.6 (m, 6 H, ring), 2.15 (bs, 2 H, allyl), 2.29 (bs, 2 H, allyl), 4.97 (Hₐ, dd, J = 10.2, 2.0 Hz, 1 H), 5.10 (Hₐ, dd, J = 16.8, 2.0 Hz, 1 H), 5.80 (Hₖ, d, J = 10.9 Hz, 1 H), 6.63 (Hₖ, ddd, J = 16.8, 10.8, 10.3 Hz, 1 H); ¹³C NMR (CDCl₃) δ 26.78 (CH₂), 27.72 (CH₂), 28.48 (CH₂), 29.24 (CH₂), 37.23 (CH₂), 114.40 (CH₂), 122.73 (CH), 132.69 (CH), 144.05 (CH); mass spectrum, m/e calcd for C₉H₁₄ 122.1096, found 122.1094. The spectra of 115 are identical with that in the literature.⁵⁴,⁵⁵

4-Allylidenetetrahydropyran (116)

According to general procedure C, 106 (43 mg, 0.13 mmol) was converted to 116 (13 mg, 87%); IR (neat film) 3080, 2960, 2870, 1650, 1600, 1460, 1100, 990, 890 cm⁻¹; ¹H NMR (CDCl₃) δ 2.27 (t, J = 5.2 Hz, 2 H, allyl), 2.42 (t, J = 5.0 Hz, 2 H, allyl), 3.69 (quin, J = 5.6 Hz, 4 H, CH₂O), 5.02 (Hₐ, dd, J = 10.2, 1.6 Hz), 5.16 (Hₐ, dd, J = 16.8, 1.7 Hz), 5.88 (Hₖ, d, J = 11.0 Hz), 6.57 (Hₖ, ddd, J = 16.7, 10.6, 10.5 Hz); ¹³C NMR (CDCl₃) δ 30.20, 36.95, 68.51, 69.32, 115.75, 124.27, 131.85, 138.02; GC-HR-MS, m/e calcd for C₈H₁₂O 124.0856, found 124.0872.
Preparation of
(E)-1,4-bis(trimethylsilyl)-2-butene (122)$^{43}$

Butadiene (62.0 g, 1.26 mol) condensed in a Dry Ice bath was added dropwise in 4 h to a stirred mixture of trimethylsilyl chloride (259.0 g, 2.38 mol), lithium (17.3 g, 2.50 mol) and THF (350 mL) under argon at 0 °C. The temperature was maintained between 0-10 °C throughout the addition. After stirring for an additional 24 h at room temperature, the mixture was filtered, washed with water (2 x 20 mL) and brine (100 mL) and concentrated to a clear colorless liquid. Fractional distillation gave 122 (94.50 g, 40 %): bp 90-95 °C (38 mmHg) 92-94 °C (35 mm Hg); its IR and $^1$H NMR spectra are in agreement with the literature.

4-Trimethylsilyl-1-butene (120)

Method A

Sulfuric acid (36.8 g, 0.38 mol, 98%) was slowly added in 0.5 h to a stirred solution of 122 (75.8 g, 0.38 mol) and pentane (300 mL) at 0 °C. Since the reaction was exothermic careful addition was necessary to maintain the temperature below 10 °C. After the addition was complete, the mixture was stirred for 0.5 h. The pentane layer was decanted and washed with sulfuric acid until hexamethyldisiloxane could no longer be detected by GC analysis. The pentane layer was then washed with saturated aqueous sodium bicarbonate (100 mL, until neutral) and brine (20 mL), dried (MgSO$_4$) and fractionally
distilled (helices, 20 x 1 cm column) to give 120 (26.4 g, 54 %): bp 108-110 °C.
The IR and $^1$H NMR spectra of 120 agree with literature data.$^{45}$

**Method B**

Freshly distilled trifluoroacetic acid (2.8 g, 24.9 mmol) was slowly added to a stirred solution of 122 (5.0 g, 24.9 mmol) in CCl$_4$ under argon at 3 °C. After stirring for 1.5 h, the mixture was poured into saturated aqueous sodium bicarbonate/ice. The organic phase was separated, washed with water (2 x 20 mL) and brine (20 mL), dried (MgSO$_4$) and fractionally distilled (glass fenske ring, 10 x 1 cm hempel column) to yield 120 (2.10 g, 66%): bp 108-110 °C.

**Method C**

Trimethylsilylmethyl magnesium chloride$^9$ was prepared from chloromethyltrimethylsiline$^{10}$ (20 g, 0.16 mol) and magnesium (3.97 g, 0.16 mol) in ether (50 mL). The solution was cooled to 0 °C then allyl bromide (28 g, 0.23 mol) was added to the Grignard reagent. The resultant mixture was refluxed for 5 h, cooled, and poured on to saturated aqueous ammonium chloride/ice. The organic layer was separated, washed with water (2 x 30 mL) and brine (30 mL), dried (MgSO$_4$) and distilled to give 120 (6.0 g, 29%): bp 112-115 °C.
1-(4-Chlorobenzenesulfonyl)-2-chloro-4-trimethylsilylbutane (9)

4-Chlorobenzenesulfonyl chloride (6.5 g, 30.7 mmol), 120 (4.0 g, 31.1 mmol), acetonitrile (2 mL), dichloromethane (10 mL), cupric chloride (0.41 g, 3.0 mmol), and triethylamine hydrochloride (0.64 g, 4.6 mmol) were placed in an ace-thread pressure tube and deoxygenated for 1.5 h. The tube was sealed and heated to 105-115 °C for 17.0 h. After cooling, the pressure tube was opened. The mixture was taken up in ether (20 mL), washed with water (2 x 10 mL), 10% HCl (2 x 10 mL), 10% Na2HCO3 (4 x 10 mL), dried (MgSO4) and concentrated to give a white semisolid (9.46 g). Column chromatography (silica gel, 90 g, ethyl acetate 0-5%) gave 9 (7.28 g, 69% yield) as a white solid and recovered 4-chlorobenzenesulfonyl chloride (1.71 g, 26% recovery). Recrystallization from hexane gave 9 as a fine white crystalline solid: mp 82-84 °C; IR (KBr) 3100, 2960, 2920, 1580, 1480, 1440, 1400, 1330, 1300, 1280, 1250, 1180, 1160, 1140, 1090, 1010, 940, 870, 830, 785, 700, 580 cm⁻¹; ¹H NMR (CDCl₃) δ -0.01 (s, 9 H, (CH₃)₃Si), 0.4-0.7 (m, 2 H, SiCH₂), 1.6-1.9 (m, 2 H, CH₂), 3.4-3.6 (m, 2 H, SO₂CH₂), 4.26 (quin, J = 6.0 Hz, 1 H, ClCH), 7.53 (d, J = 8.7 Hz, 2 H, Ar), 7.86 (d, J = 8.7 Hz, 2 H, Ar); ¹³C NMR (CDCl₃) δ -1.94 (q), 12.43 (t), 32.87 (t), 56.92 (d), 62.89 (t), 129.62 (d), 129.71 (d), 138.06 (s), 140.79 (s); mass spectrum, m/e calcd for C₁₂H₁₇Cl₂O₂Si (M⁺ - CH₃, ¹³C) 323.0096, found 323.0110. Anal. Calcd for C₁₃H₂₆Cl₂O₂SSi: C, 46.01; H, 5.94. Found: C, 46.38; H, 5.86.
2-Chloro-1-(4-methylbenzenesulfonyl)-4-trimethylsilylbutane (8)

A stirred solution of 120 (10.0 g, 77.9 mmol), cupric chloride (1.0 g, 7.8 mmol), triethylammonium chloride (2.1 g, 15.6 mmol) and isobutyronitrile (30 mL) was deoxygenated with argon for 1 h. p-Toluenesulfonyl chloride (14.8 g) was then added to the clear dark red solution. The reaction mixture was refluxed (103-113 °C, solution temperature) under argon. After 24 h 120 could not be detected by GC analysis. Saturated aqueous sodium bicarbonate (30 mL) was added to the reaction mixture which was then refluxed for 3.5 h. After cooling, the mixture was taken up in ethyl ether (20 mL), washed with saturated aqueous sodium bicarbonate (5 x 60 mL), 10% HCl (20 mL), dried (MgSO₄) and concentrated to a light brown solid (18.05 g). Column chromatography (silica gel, 100 g, ethyl acetate 0-1%) gave 8 (13.14 g, 53%) as a white crystalline solid: mp 79-80 °C (from hexane); IR (neat film) 3060, 2960, 2920, 1595, 1285, 1250, 1140, 1090, 865, 840, 770 cm⁻¹; ¹H NMR (CDCl₃) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.4-0.7 (m, 2 H, SiCH₂), 1.6-2.0 (m, 2 H, CH₂), 2.47 (s, 3 H, CH₃), 3.52 (d, J = 6.3 Hz, 2 H, SO₂CH₂), 4.2-4.3 (m, 1 H, ClCH), 7.37 (d, J = 7.9 Hz, 2 H, Ar), 7.81 (d, J = 8.3 Hz, 2 H, Ar); ¹³C NMR (CDCl₃) δ -1.89 (q), 12.42 (t), 21.60 (q), 32.76 (t), 57.14 (d), 62.94 (t), 128.22 (d), 130.02 (d), 136.75 (s), 145.11 (s); mass spectrum, m/e calcd for C₁₃H₂₀ClO₂SSi (M⁺ - CH₃, ³⁵Cl) 303.0642, found 303.0663. Anal. Calcd for C₁₄H₂₃ClO₂SSi: C, 52.71; H, 7.27. Found: C, 52.60; H, 7.20.
1-Benzencesulfonyl-2-chloro-4-trimethylsilylbutane (6) and 1-
Benzencesulfenyl-2-chloro-4-trimethylsilylbutane (124)

A stirred mixture of benzenesulfonyl chloride (16.70 g, 94.6 mmol), cupric chloride (1.27 g, 9.44 mmol), and TDA-1 (6.90 g, 21.4 mmol) in 2-ethoxyethyl ether (30 mL), was deoxygenated for 1.25 h then heated to 130 °C. A solution of 120 (12.1 g, 9.43 mmol) and hexamethyldisiloxane (6.3 mL) was added via a syringe pump (2.5 mL/h for 4.0 h then 13.3 mL/h for 11.0 h) to the resultant reddish brown opaque solution. After the addition was complete, the mixture was heated for an additional 11 h between 120-124 °C. The brown solution was diluted with ether (equal volume) washed with 10% HCl (25 mL), saturated aqueous sodium bicarbonate (2 x 25 mL) and brine (25 mL), dried (MgSO₄), filtered and concentrated to give a dark oil (31.45 g). Column chromatography (silica gel, 512 g, ethyl acetate 0-3%) gave 124 (1.97 g, 8%), a clear colorless oil: IR (neat film) 3060, 2950, 1585, 1480, 1440, 1250, 1025, 865, 845, 740, 690 cm⁻¹; ¹H NMR (CDCl₃) δ 0.03 (s, 9 H, (CH₃)₃Si), 0.5-0.8 (m, 2 H, SiCH₂), 1.6-2.0 (m, 2 H, CH₂), 3.30 (AB q, J = 13.8 Hz, SCH₂), 3.9-4.0 (m, 1 H, ClCH), 7.1-7.5 (m, 5 H, Ar); ¹³C NMR (CDCl₃) δ -1.87 (q), 12.51 (t), 31.06 (t), 41.37 (t), 63.91 (d), 126.63 (d), 129.03 (d), 130.06 (d), 135.39 (s); mass spectrum, m/e calcd to C₁₃H₂₁ClSi (M⁺, 35Cl) 272.0822, found 272.0836 and 6 (14.82 g, 51%): IR (neat film) 3070, 2960, 1585, 1450, 1310, 1250, 1150, 1085, 865, 840, 750, 690 cm⁻¹; ¹H NMR (CDCl₃) δ -0.05 (s, 9 H, (CH₃)₃Si), 0.4-0.7 (m, 2 H, SiCH₂, 1.6-1.9 (m, 2 H, CH₂), 3.4-3.5 (m, 2 H, SO₂CH₂), 4.20-4.30 (m, 1 H, ClCH), 7.4-7.9 (m, 5 H, Ar); ¹³C NMR (CDCl₃) δ -2.03, 12.22, 32.59, 56.90,
62.58, 127.96 129.20, 133.86, 139.42; mass spectrum, m/e calcd for
C_{21}H_{18}ClO_{2}SSi (M^{+} - CH_{3}, ^{35}Cl) 289.0485, found 289.0482.

1-Benzenesulfonfyl-2-chloro-4-trimethylsilylbutane (6) by Oxidation
of 124

MCPBA (0.25 g, 1.23 mmol, 85%) was added to a stirred solution of 124
(0.12 g, 0.43 mmol) in dichloromethane (3 mL) at 0 °C. The white suspension
was allowed to warm to room temperature and stirred for 1.5 h. The mixture
was dissolved in ethyl ether (20 mL), washed with saturated aqueous sodium
metabisulfite (20 mL), saturated aqueous sodium bicarbonate (2 x 10 mL) and
brine (10 mL), dried (MgSO_{4}) and concentrated to 6 (0.12 g, 92%): the ^1H NMR
and IR are identical to a previously prepared sample of 6.

1-Benzenesulfonfyl-2-bromo-4-trimethylsilylbutane (5)

A stirred solution of 120 (5.80 g, 45.2 mmol), hexamethyldisiloxane (2.99
g), benzenesulfonyl bromide (10.0 g, 45.2 mmol) and THF (30 mL) was
deoxygenated with argon for 20 min. A 500 watt clear incandescent bulb was
used to irradiate the solution in a Pyrex flask. After 3.5 h, the mixture was
concentrated to a clear colorless viscous oil (15.26 g). Column chromatography
(silica gel, 90 g, ethyl acetate 0-5%) yielded benzenesulfonyl bromide (4.98 g,
50 % recovery) and then 5 (7.51 g, 48 % yield) as a clear colorless mobile oil:
IR (neat film) 3060, 2960, 1585, 1450, 1340, 1310, 1250, 1150, 1090, 865, 840,
740, 690 cm^{-1}; ^1H NMR (CDCl_{3}) δ -0.01 (s, 9 H, (CH_{3})_{3}Si), 0.5-0.7 (m, 2 H,
SiCH_{2}), 1.7-2.0 (m, 2 H, CH_{2}), 3.5-3.7 (m, 2 H, SO_{2}CH_{2}), 4.3-4.4 (m, 1 H, BrCH),
7.5-7.9 (m, 5 H, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ -1.91 (CH$_3$), 13.52 (CH$_2$), 33.09 (CH$_2$),
48.49 (CH), 63.09 (CH$_2$), 128.03 (CH), 129.37 (CH), 134.01 (CH), 139.47 (C);
mass spectrum, m/e calcd for C$_{12}$H$_{18}$BrO$_2$SSi (M$^+$ - CH$_3$, $^{79}$Br) 332.9980, found
332.9988, (M$^+$ -CH$_3$, $^{81}$Br) 336.0038, found 336.0006.

2-Bromo-(4-methylbenzenesulfonyl)-4-trimethylsilylbutane (7)

A stirred solution of 120 (5.0 g, 38.9 mmol), p-toluenesulfonyl bromide (9.2
g, 39.1 mmol) and benzene (30 mL) was deoxygenated for 1 h with argon. The
mixture was irradiated with a 150 watt incandescent bulb for 29 h and
concentrated to a faint yellow viscous oil which crystallized. Column
chromatography (silica gel, ethyl acetate 0-2%) gave p-toluenesulfonyl bromide
(2.41 g, 26% recovery) as the first eluent and followed by 7 (10.45 g, 62%) as a
white crystalline solid: mp 72 °C from hexane; IR (CCl$_4$) 3040, 2960, 1590,
1410, 1330, 1250, 1150, 1090, 1020 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.00 (s, 9 H,
(CH$_3$)$_3$Si), 0.5-0.7 (m, 2 H, SiCH$_2$), 1.7-2.0 (m, 2 H, CH$_2$), 2.45 (s, 3 H, CH$_3$),
3.65 (m, 2 H, SO$_2$CH$_2$), 4.2-4.4 (m, 1 H, BrCH), 7.37 (d, J = 8.2 Hz, 2 H, Ar), 7.80
(d, J = 8.2 Hz, 2 H, Ar); irradiation of the multiplet at $\delta$ 4.2-4.4 simplified $\delta$ 3.65 to
a singlet and simplifies $\delta$ 1.7-2.0 somewhat; $^{13}$C NMR (CDCl$_3$) $\delta$ -1.89 (q), 13.54
(t), 21.60 (q), 33.07 (t), 48.74 (d), 63.23 (t), 128.09 (d), 130.02 (d), 136.55 (s),
145.14 (s); mass spectrum, m/e calcd for C$_{13}$H$_{20}$BrO$_2$SSi (M$^+$-CH$_3$, $^{79}$Br)
347.0136, found m/e 347.0136, (M$^+$-CH$_3$, $^{81}$Br) 349.0116, found m/e 349.0128.
Anal. Calcd for C$_{14}$H$_{23}$BrO$_2$SSi: C, 46.27; H, 6.38. Found: C, 46.52; H, 6.22.
The last eluent was (E)-1-(4-Methylbenzenesulfonyl)-4-trimethylsilyl-1-butene
(11) (0.56 g, 5%):
(E)-1-Benzenesulfonyl-4-trimethylsilyl-1-butene (10)

A solution of potassium hydroxide (1.0 g, 17.8 mmol) in water (5 mL) was added to 6 (0.5 g, 1.64 mmol) in THF (5 mL). The heterogeneous mixture was stirred vigorously for 2 h and then diluted with ethyl ether (20 mL). The organic layer was separated, washed with water (10 mL) and brine (10 mL), dried (MgSO₄) and concentrated to 10 (0.40 g, 91%), a clear colorless oil: IR (neat film) 3060, 2950, 2900, 1625, 1450, 1325, 1250, 1150, 1090, 980, 860, 845, 760, 690 cm⁻¹; ¹H NMR (CDCl₃) δ -0.03 (s, 9 H, (CH₃)₃Si), 0.5-0.6 (m, 2 H, SiCH₂), 2.1-2.2 (m, 2 H, allyl), 6.30 (dt, J = 15.0, 1.6 Hz, 1 H, vinyl), 7.03 (dt, J = 15.0, 6.3 Hz, 1 H, vinyl), 7.4-7.6 (m, 3 H, Ar), 7.8-7.9 (m, 2 H, Ar); ¹³C NMR (CDCl₃) δ -1.93 (q), 14.39 (t), 26.05 (t), 127.45 (d), 129.10 (d), 129.25 (d), 133.06 (d), 140.80 (s), 149.47 (¢). The ¹H NMR and IR of 10 are consistent with literature values.⁵⁶

(E)-1-(4-Methylbenzenesulfonyl)-4-trimethylsilyl-1-butene (11)

Method A

A stirred solution of 120 (5.0 g, 38.9 mmol), hexamethyldisiloxane (2.6 g), and p-toluenesulfonyl bromide (9.2 g, 39.1 mmol) in THF was deoxygenated for 30 min with argon. A 500 watt incandescent bulb was used to irradiate the solution for 14 h. Aqueous potassium hydroxide (30 mL, 0.6M, 18 mmol) was added and the resulting mixture was stirred for one hour. The organic phase was separated and washed with saturated sodium bicarbonate (3 x 10 mL) and brine (10 mL), dried (MgSO₄), filtered and concentrated to a cloudy yellow oil
(6.98 g) which solidified. Recrystallization in methanol gave 11 (4.37 g, 42%) as a white solid: mp 48.5-49.5 °C (from pentane); IR (neat film) 3050, 2950, 1620, 1595, 1320, 1305, 1290, 1250, 1150, 1090, 975, 870, 840, 660 cm⁻¹; ¹H NMR (CDCl₃) δ -0.03 (s, 9 H, (CH₃)₃Si), 0.5-0.6 (m, 2 H, Si(CH₂)₂), 2.1-2.2 (m, 2 H, CH₂), 2.41 (s, 3 H, CH₃), 6.28 (dt, J = 15.0, 1.6 Hz, 1 H, vinyl), 6.99 (dt, J = 15.0, 6.3 Hz, 1 H, vinyl), 7.30 (d, J = 7.9 Hz, 2 H, Ar), 7.74 (d, J = 8.3 Hz, 2 H, Ar); ¹³C NMR (CDCl₃) δ -1.92, 14.43, 21.47, 26.01, 127.52, 129.57, 129.74, 137.89, 143.98, 148.81; mass spectrum, m/e calcd for C₁₄H₂₂O₂Si (M⁺) 282.1110, found 282.1117. Anal. Calcd for C₁₄H₂₂O₂Si: C, 59.52; H, 7.85. Found: C, 59.34; H, 7.93.

Method B

n-Butyllithium (1.27 mL, 3.30 mmol, 2.60 M in hexane) was added to a stirred solution of diisopropylamine (0.35 g, 3.45 mmol) and THF (30 mL) under argon at -78 °C. After stirring the cold mixture for 20 min, 8 (0.96 g, 3.01) in THF (4 mL) was slowly added (2 min). The solution went from faint yellow to almost colorless. After stirring at -78 °C for 10 min, the mixture was quenched with aqueous saturated ammonium chloride (2 mL), and the ice bath was removed. The solution was allowed to warm to room temperature and taken up in methylene chloride (20 mL). The organic phase was washed with water (2 x 10 mL) and brine (30 mL), dried (MgSO₄) and concentrated to a clear faint yellow viscous oil which solidified upon standing. Column chromatography (forisil, 30 g; ethyl acetate, 5%) gave 11 (0.79 g, 93%) as a clear colorless oil which crystallized, after concentration to a white solid.
(E)-1-(4-Chlorobenzenesulfonyl)-4-trimethylsilyl-1-butene (12)

n-Butyllithium (0.58 mL, 1.48 mmol, 2.55 M in hexane) was slowly added to a stirred solution of 9 (0.50 g, 1.47 mmol) in anhydrous THF (20 mL) at -78 °C under argon. A faint yellow color was observed at the vortex which quickly disappeared. The clear colorless solution was stirred for 10 min, poured into water (20 mL), neutralized with saturated aqueous ammonium chloride (20 mL) and diluted with ethyl ether (20 mL). The organic phase was separated, washed with brine (10 mL), dried (MgSO₄), and concentrated to 12 (0.44 g, 98%) a fluffy white solid: mp 73-74 °C; IR (KBr) 3040, 2950, 1620, 1320, 1250, 1140, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.5-0.7 (m, 2 H, SiCH₂), 2.1-2.3 (m, 2 H, allyl), 6.28 (dt, J = 15.0, 1.6 Hz, vinyl), 7.05 (dt, J = 15.0, 6.3 Hz, vinyl), 7.49 (d, J = 8.8 Hz, 2 H, Ar), 7.80 (d, J = 8.8 Hz, 2 H, Ar); ¹³C NMR (CDCl₃) δ -1.87 (q), 14.47 (t), 26.21 (t), 129.02 (d), 129.06 (d), 129.52 (d), 139.43 (s), 139.85 (s), 150.28 (d); mass spectrum, m/e calcd for C₁₃H₁₈SSiO₂ (M⁺ - H) 301.0485, found 301.0476. Anal. Calcd for C₁₃H₁₈ClSSiO₂: C, 51.55; H, 6.32. Found: C, 51.36; H, 6.34.

(E)-1-Deutero-(4-chlorobenzenesulfonyl)-4-trimethyl-1-butene (130)

n-Butyllithium (0.13 mL, 2.60 M, 0.34 mmol) was added to stirred diisopropylamine (37 mg, 0.37 mmol) in THF (12 mL) at -78 °C under argon. The mixture was stirred 25 min and then 12 (94 mg, 0.31 mmol) in THF (2 mL) was added. The resulting deep yellow solution was stirred for 10 min at -78 °C
and then deuterium oxide was added. The reaction mixture was taken up in ethyl ether (20 mL), neutralized with saturated aqueous ammonium chloride (10 mL), washed with water (10 mL), brine (10 mL), dried (MgSO₄), and concentrated to a white solid (78 mg). Column chromatography (florisil, 3 g; ethyl acetate 1-2%) yielded 130 (78 mg, 83 %) as a white solid: mp 72-73 °C; IR (cm⁻¹, KBr pellet) 3040, 2950, 1620, 1320, 1250, 1140, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.5-0.6 (m, 2 H, SiCH₂), 2.1-2.3 (m, 2 H, allyl), 6.30 (dt, J = 15.0, 1.6 Hz, vinyl, 79% deuterium incorporation), 6.9-7.1 (m, 2 H, vinyl), 7.50 (d, J = 8.8 Hz, 2 H, Ar), 7.80 (d, J = 8.7 Hz, 2 H, Ar); ¹³C NMR (CDCl₃) δ -1.86 (q), 14.49 (t), 26.18 (t), 129.07 (d), 129.53 (d), 139.45 (s), 139.87 (s), 150.16 (d); mass spectrum, m/e calcd for C₁₂H₁₅CD₂O₂SiS (M+ - CH₃, ³⁷Cl) 290.0362, found 290.0398.

(E)-1-Deutero-(4-methylbenzenesulfonyl)-4-trimethyl-1-butene (131)

n-Butyllithium (1.23 mL, 3.20 mmol, 2.60 M in hexane) was added to a stirred solution of diisopropylamine (0.32 g, 32.0 mmol) in THF (20 mL) under argon at 0 °C. The mixture was cooled to -78 °C and 8 (0.50 g, 1.57 mmol) in THF (4 mL) was added (2 min). The solution was now a clear bright yellow. The cold mixture was stirred (10 min) and deuterium oxide (2 mL) was added. The yellow color discharged within 5 sec to give a clear colorless solution. After warming to room temperature, the mixture was taken up in dichloromethane (20 mL). The organic phase was washed with water (2 x 10 mL) and brine (40 mL), dried (MgSO₄) and concentrated to a viscous clear yellow oil (0.46 g). Column chromatography (florisil, 20 g; ethyl acetate 5%) gave 131 (0.40 g, 89%), a
clear colorless oil which solidified upon standing: mp 48-49 °C (from pentane);
IR (neat film) 3050, 2950, 1620, 1595, 1320, 1305, 1290, 1250, 1150, 1090, 975, 870, 840, 660 cm⁻¹; ¹H NMR (CCl₄) δ -0.00 (s, 9 H, (CH₃)₃Si), 0.5-0.6 (m, 2 H, SiCH₂), 2.1-2.5 (m, 2 H, CH₂), 2.45 (s, 3 H, CH₃), 6.24 (d, J = 15 Hz, vinyl, > 90% deuterium incorporated), 6.95 (bt, J = 7 Hz, 1 H, vinyl), 7.32 (d, J = 8 Hz, 2 H, Ar), 7.74 (d, J = 8 Hz, 2 H, Ar); mass spectrum, m/e calcd for C₁₄H₂₁D₂O₆Si (M⁺) 283.1173, found 283.1158.

(E)-2-Benzensulfonyl-1-phenyl-5-trimethylsilyl-2-pentene (132)

n-Butyllithium (1.13 mL, 2.93 mmol, 2.60 M in hexane) was slowly added to a stirred solution of 5 (0.50 g, 1.43 mmol) in THF (10 mL) at -78 °C. The clear yellow solution was stirred for 10 min and then benzyl bromide (0.49 g, 2.86 mmol) was added followed by HMPA (0.54 g, 3.02 mmol). The solution was allowed to warm to room temperature. The now clear colorless solution was quenched with saturated aqueous ammonium chloride (10 mL). The organic layer was separated, washed with 10% HCl (3 x 10 mL) and brine (10 mL), dried (MgSO₄), filtered and concentrated to a light yellow mobile oil (0.57 g). Column chromatography (silica gel, ethyl acetate 0-5%) gave 132 (0.45 g, 89%) as a clear colorless oil: IR (neat film) 3060, 3030, 2950, 1635, 1600, 1495, 1400, 1305, 1250, 1145, 1090, 860, 850, 750, 690 cm⁻¹; ¹H NMR (CDCl₃) δ -0.05 (s, 9 H, (CH₃)₃Si), 0.5-0.6 (m, 2 H, SiCH₂), 2.0-2.2 (m, 2 H, allyl), 3.68 (s, 2 H, benzyl), 6.9-7.7 (m, 11 H, Ar and vinyl); NOE experiments: irradiation of δ 2.15 enhances δ 0.5-0.6 (7.96%) and δ 3.68 (5.71%); irradiation of δ 3.68 enhances δ 2.0-2.2 (9.03%); ¹³C NMR (CDCl₃) δ -1.94 (CH₃), 15.21 (CH₂),
23.41 (CH₂), 31.91 (CH₂), 126.29 (CH), 128.01 (CH), 128.07 (CH), 128.27 (CH), 128.79 (CH), 132.76 (CH), 136.92 (CH), 138.44 (C), 140.12 (C), 146.53 (CH); mass spectrum, m/e calcd for C₂₀H₂₆O₂SSi (M⁺) 358.1423, found 358.1413.

(E)-2-(4-Methylbenzenesulfonoyl)-1-phenyl-5-trimethylsilyl-2-pentene (133)

A LDA solution was prepared by adding n-butyllithium (1.16 mL, 3.01 mmol, 2.60 M) to diisopropylamine (0.43 mL, 0.31 g, 3.04 mmol) in THF (20 mL) at -78 °C. After stirring the LDA solution for 30 min, 7 (0.50 g, 1.38 mmol) in THF (4 mL) was added. The resulting solution was a deep clear yellow. After stirring the mixture 10 min, HMPA (0.54 g, 3.01 mmol) was added. The ice bath was removed and the solution was stirred for 3.0 h. The mixture was dissolved in ethyl ether (20 mL), washed with water (3 x 30 mL), and brine (10 mL), dried (MgSO₄), and concentrated to a viscous yellow oil (0.63 g). Column chromatography (silica gel, 12 g, ethyl acetate 0-4%) resulted in 133 (0.43 g, 84%), a clear colorless oil: IR 3070, 3030, 2960, 1640, 1600, 1495, 1455, 1315, 1305, 1250, 1145, 1090, 865, 840, 760, 700, 670, 655 cm⁻¹; ¹H NMR (CDCl₃) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.5-0.6 (m, 2 H, SiCH₂), 2.1-2.2 (m, 2 H, CH₂), 2.44 (s, 3 H, CH₃), 3.73 (s, 2 H, benzyl), 7.0-7.3 (m, 8 H, Ar and vinyl), 7.69 (d, J = 8.3 Hz, 2 H, Ar); decoupling experiments: irradiation at δ 0.5-0.6 simplifies δ 2.1-2.2 to a doublet; irradiation of δ 2.1-2.2 simplifies δ 0.5-0.6 to a singlet; ¹³C NMR (CDCl₃) δ -1.92 (q), 15.24 (t), 21.45 (q), 23.39 (t), 31.95 (t), 126.20 (d), 128.14 (d), 128.16 (d), 128.28 (d), 129.49 (d), 137.05 (s), 137.17 (s), 138.66 (s), 143.70 (s), 146.02 (d); mass spectra, m/e calcd for C₂₁H₂₈O₂SSi (M⁺) 372.1580, found 372.1569.
(E)-2-(4-Chlorobenzenesulfonyl)-1-phenyl-5-trimethylsilyl-2-pentene (134)

n-Butyllithium (1.27 mL, 3.23 mmol, 2.55 M in hexane) was added dropwise to diisopropylamine (0.33 g, 3.23 mmol) stirred in anhydrous THF (20 mL) under argon at -78 °C. The resulting LDA solution was stirred for 0.5 h and then added dropwise to 9 (0.50 g, 1.47 mmol) in anhydrous THF (10 mL) under argon at -78 °C. The resulting clear deep yellow solution was stirred at -78 °C for 10 min and HMPA (0.58 g, 3.23 mmol) was added. Immediate addition of benzyl bromide (0.51 g, 3.00 mmol) was effected to the orange clear solution, and the mixture was allowed to warm to room temperature. After stirring for 20 min, the mixture was poured into aqueous saturated ammonium chloride (40 mL), washed with brine (10 mL), dried (MgSO₄), filtered and concentrated to a faint yellow clear viscous oil. Column chromatography (neutral alumina, 20 g; ethyl acetate 0-10%) gave 134 (0.52 g, 90%) as a viscous light pink oil which crystallized to a pinkish white solid: mp 75-76 °C (from hexane); IR (CCl₄) 3070, 3030, 2960, 1635, 1490, 1490, 1475, 1455, 1395, 1320, 1295, 1280, 1250, 1150, 1090, 1025, 860 cm⁻¹; ¹H NMR (CDCl₃) δ -0.04 (s, 9 H, (CH₃)₃Si), 0.5-0.6 (m, 2 H, SiCH₂), 2.1-2.2 (m, 2 H, allyl), 3.69 (s, 2 H, benzyl), 6.9-7.2 (m, 6 H, vinyl and Ar), 7.28 (d, J = 8.7 Hz, 2 H, Ar), 7.59 (d, J = 8.7 Hz, 2 H, Ar); decoupling experiments: irradiation of δ 0.6 simplifies δ 2.2 to a doublet and irradiation of δ 2.2 simplifies δ 0.6 to a singlet; NOE experiments: irradiation at δ 2.1-2.2 enhances δ 3.69 (5.66%) and δ 0.5-0.6 (7.07%); irradiation at δ 3.69 enhances δ 2.1-2.2 (9.59%); ¹³C NMR (CDCl₃) δ -1.94 (CH₃), 15.30 (CH₂), 23.48 (CH₂), 31.88 (CH₂), 126.37 (CH) 128.10 (CH), 128.34 (CH), 128.99 (CH), 129.43 (CH), 136.56 (C), 138.27 (C), 138.77 (C), 139.35 (C), 146.98 (CH); mass
spectrum, m/e calcd for C_{20}H_{25}ClO_{2}Si (M^+,^{35}Cl) 392.1033, found 392.1030. Anal. Calcd for C_{20}H_{25}ClO_{2}Si: C, 61.12; H, 6.41. Found: C, 60.84; H, 6.21.

Elimination of (E)-2-Arylsulfonyl-1-phenyl-5-trimethylsilyl-2-pentenes

General Procedure A

TBAF (2.50 mL, 1 m, in THF) was added to a stirred solution of 132 (493 mg, 1.25 mmol) in THF (18 mL) under argon at 25 °C. After 25.5 h, the reaction mixture was taken up in pentane (20 mL), washed with water (5 x 10 mL) and brine (10 mL) and passed through a short column (neutral alumina, 5 g, pentane). Evaporation of the solution under a stream of argon gave 64 (101 mg, 56%). The 1H NMR and GC analyses of 64 agrees with that of an authentic sample.

Following general procedure A, 133 (510 mg, 1.37 mmol) was converted to 64 (124 mg, 63%).

General procedure A was followed in which 134 (497 mg, 1.39 mmol) was converted to 64 (118 mg, 59%).

Ring Cyclization and Elimination of 7

n-Butyllithium (1.00 mL, 2.70 M, 2.75 mmol) was added to 7 (0.50 g, 1.38 mmol) stirred in anhydrous THF (10 mL) at -78 °C under argon. HMPA (2.0 g, 11.0 mmol) and then 1,3-dichloropropane (0.19 g, 1.67 mmol) were added to
the clear yellow solution. The ice bath was removed and, after stirring for 1 h, the mixture was cooled (-78 °C). Additional n-butyllithium (0.50 mL, 1.38 mmol) was added, and the solution was allowed to warm to room temperature. After 1 h, the mixture was quenched with aqueous ammonium chloride (10 mL), taken up in ether (20 mL), washed with water (3 x 10 mL) and brine (10 mL), dried (MgSO₄), filtered and concentrated to a yellow clear oil. Column chromatography (silica gel; ethyl acetate 0-6%) gave 139 (0.28 g, 67%) as a clear colorless oil: IR (film) 3040, 2950, 1620, 1320, 1250, 1140, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.00 (s, 9H, (CH₃)₃Si), 1.50 (d, J = 7, Hz, 2 H, SiCH₂), 1.6-2.1 (m, 2 H, ring), 2.41 (s, 3 H, benzyl), 2.6-3.0 (m, 2 H, ring), 5.0-5.8 (m, 2 H, vinyl)), 7.25 (d, J = 9 Hz, 2 H, Ar), 7.62 (d, J = 9 Hz, 2 H, Ar); mass spectrum, m/e calcd for C₁₀H₁₉Si (M⁺ - p-CH₃-C₆H₅SO₂) 167.1256, found 167.1274.

Following general procedure A, 139 (0.28 g, 0.87 mmol) was converted to 113 (69 mg, 84%).
REFERENCES


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\begin{align*}
\text{1} & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3 \\
\text{II} & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{I} & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3 & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3 \\
\text{II} & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3 & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3
\end{align*}
\]

\begin{align*}
\text{I} & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3 & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3 \\
\text{II} & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3 & \quad \text{CH}_3 \quad \text{Sn(} \text{CH}_3)_3 \quad \text{CH}_3
\end{align*}

(10) Chloromethyltrimethylsilane is commercially available from Petrarch Systems, Bartram Road, Bristol, PA 19007.
(11) Concentration greatly alters the success of generating Grignard reagent 39. If larger amounts of solvent (diethyl ether or THF) are used than reported by Sommer,9 the yield of 39 is greatly reduced. The concentration (3.33 M) of chloromethyltrimethylsilane used by Sommer for Grignard reagent 39 in 95%. Under more dilute conditions (0.4 M) the yield of 39 is so small that it can not be detected by Gilman's reagent and allyl alcohol 40 cannot be found after acrolein is added.
(13) It is crucial that the phenylsulfenyl chloride be added slowly so as to maintain the reaction temperature below -60 ºC. Rapid delivery of phenylsulfenyl chloride leads to an exothermic reaction. At temperatures greater than -60 ºC, complex mixtures of side products are formed which reduce the yield of 41 considerably and make purification more difficult.


(16) The 1-benzene-4-trimethylsilyl-2-alkenes formed in these reactions are also probably unstable to the conditions.


(20) Tetrabutylammonium fluoride is sold commercially as a 1.0 M solution in THF (Aldrich Chemical Company).


(22) For another report on fluoride induced silicon carbon cleavage under phase transfer conditions, see: Roser, J.; Eberbach, W. Synthetic Commun. 1986, 16, 983.

(23) TDA-1 is commercially available from Aldrich Chemical Company, see: Soula, G. J. Org. Chem. 1985, 50, 3717.


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\text{CH}_3\text{S} \quad \text{SO}_2\text{C}_6\text{H}_5\text{-CH}_3 \quad 1.\text{NaH, DMF} \rightarrow \quad \text{CH}_3\text{S} \quad \text{SO}_2\text{C}_6\text{H}_5\text{-CH}_3
\]


(37) Pillot, J. P.; Dunoques, J.; Calas, R. Synthesis 1977, 469.


(40) An alternate preparation of 5-9 not evaluated in this work is the addition of arylsulfenyl chlorides, generated in situ, to alkenes followed by oxidation giving β-halo sulfones Iv; Hopkins, P. B.; Fuchs, P.L. J. Org. Chem. 1976, 43, 1208.

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\begin{align*}
R\overset{C_6H_5SCl}{\rightarrow}R\overset{\text{RCO}_2H}{\rightarrow}R\overset{\text{Iv}}{\rightarrow}\end{align*}
\]


(49) It is believed another absorbance is buried under this region.


