(*E*)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-1-butene: An Advantageous Synthetic Equivalent for the 1-(1,3-Butadienyl) Anion and the 1,1-(1,3-Butadienyl) Dianion

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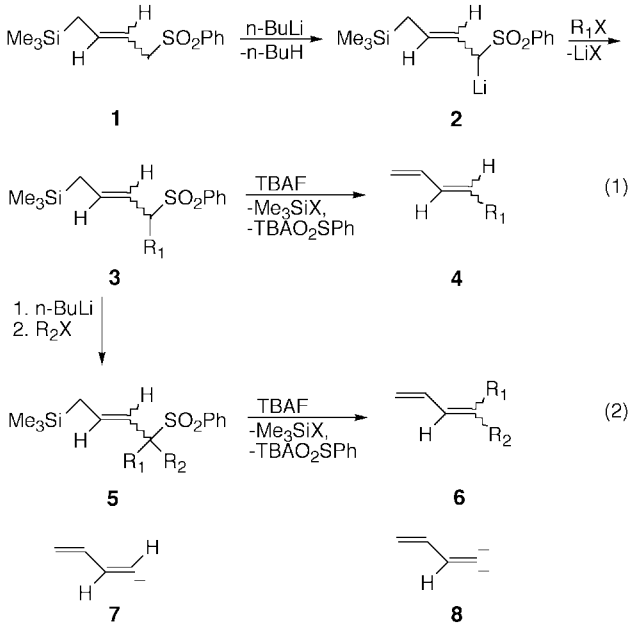
The (*E*)-1-(arylsulfonyl)-4-(trimethylsilyl)-1-butenes **9**, **25**, and **26** are prepared by $CuCl_2$-promoted and by photolytic additions of their precursor 1-arylsulfonyl chlorides and bromides to 4-(trimethylsilyl)-1-butene (**14**) and then dehydrohalogenation of the resulting 1-(arylsulfonyl)-2-halo-4-(trimethylsilyl)butanes **15a**, **15b**, **23a**, and **23b** with KOH, LDA, or *n*-BuLi. Silylbutene **14** is obtained from reaction of [(trimethylsilyl)methyl]magnesium chloride (**16**, X = Cl) and allyl bromide (**17**) and better by protiodesilylations of (*E*)- and (*Z*)-1,4-bis(trimethylsilyl)-2-butenes (**20**) with sulfuric or trifluoroacetic acids. (Arylsulfonyl)(trimethylsilyl)-1-butenes **9**, **25**, and **26** are converted efficiently by LDA or *n*-BuLi at −78 °C to 1-(arylsulfonyl)-1-lithio-4-(trimethylsilyl)-1-butenes **10**, **27a**, and **27b**, respectively. Reactions of **27a** and **27b** with deuterium oxide yield (*E*)-1-(4-chlorophenylsulfonyl)-1-deuterio-4-(trimethylsilyl)-1-butene (**28a**, 83%) and (*E*)-1-deuterio-1-(4-methylphenylsulfonyl)-4-(trimethylsilyl)-1-butene (**28b**, 89%), respectively. 1-Lithio derivatives **10**, **27a**, and **27b** undergo benzylations by benzyl bromide in THF/HMPA with retention of the positions of their olefinic double bonds to give the (*E*)-2-(arylsulfonyl)-1-phenyl-5-(trimethylsilyl)-2-pentenes **29a**, **29b**, and **29c**, respectively, in 84−90% yields. Of particular interest is that **29a**−**c** are isomerized to their corresponding 2-(arylsulfonyl)-1-phenyl-5-(trimethylsilyl)-3-pentenes **30a**−**c**, respectively, which then undergo conjugative eliminations of their arylsulfonyl and their trimethylsilyl groups to give (*E*)-5-phenyl-1,3-pentadiene (**33**) in 56−63% yields upon reactions with TBAF in THF at 25 °C. Further, **27b** reacts with 1,3-dichloropropane to form 1-chloro-4-(4-methylphenylsulfonyl)-7-(trimethylsilyl)-4-heptene (**35**) which is cyclized by *n*-BuLi to 1-(4-methylphenylsulfonyl)-1-(3-(trimethylsilyl)-1-propenyl)cyclobutane (**37**, 67%). Elimination of **37** by TBAF then gives allylenecyclobutane (**34**, *n* = 3, 84%) simply. This study thus reveals that **9**, **25**, and **26** have outstanding potential as 1-(1,3-butadienyl) anion (**7**) and 1,1-(1,3-butadienyl) dianion (**8**) synthons.

Introduction

(*E*)- and (*Z*)-1-(phenylsulfonyl)-4-(trimethylsilyl)-2-butenes (**1**) are converted by lithiation and alkylation to 1-substituted-2-butenes **3** (eq 1) and 1,1-disubstituted-2-butenes **5** (eq 2) which are eliminated efficiently by TBAF at −20 to 0 °C to their respective 1-substituted-1,3-butadienes **4** and 1,1-disubstituted-1,3-butadienes **6**.[1a,b,2] In these sequences **1** functions as an excellent synthon for the 1-(1,3-butadienyl) anion (**7**) and the 1,1-(1,3-butadienyl) dianion (**8**) and dienes **4** and **6** are essentially totally (100−96%) of (*E*) stereochemistry.[1a,b,2]

Results and Discussion

Now reported is that (*E*)-1-(phenylsulfonyl)-4-(trimethylsilyl)-1-butene (**9**) is also an excellent synthon for **7** (eq 3) and **8** (eq 4), respectively. The new methodologies involve (1) lithiation of **9** with *n*-BuLi or LDA, alkylation of **10**, isomerization of **11** by TBAF to (*E*)- and



(*Z*)-2-butenes **12**, and spontaneous elimination of **12** to **4** by the fluoride ion present and (2) allylic deprotonation of **11** by *n*-BuLi, alkylation of **13**, and reaction of 2-butenes **5** with TBAF to yield **6**. As will be demonstrated, using **9** is as efficient and less expensive than **1**.

Further, varied γ-silyl-α,β-unsaturated sulfones should be preparable as above and the methods now described

(1) (a) Hsiao, C.-N.; Shechter, H. *Tetrahedron Lett.* **1984**, *25*, 1219. (b) Meagher, T.; Yet, L.; Hsiao, C.-N.; Shechter, H. *J. Org. Chem.* **1998**, *63*, 4181.

(2) For previous studies of eliminations of *vic*-trimethylsilyl(phenylsulfonyl) derivatives to olefins, see: (a) Kocienski, P. J. *Tetrahedron Lett.* **1979**, 2649. (b) Kocienski, P. J. *J. Org. Chem.* **1980**, *45*, 2037. (c) Hsaio, C.-N.; Shechter, H. *Tetrahedron Lett.* **1982**, 3455. (d) Eisch, J. J.; Behrooz, M.; Dua, S. K. *J. Organomet. Chem.* **1985**, *285*, 121. (e) Hsaio, C.-N.; Shechter, H. *J. Org. Chem.* **1988**, *53*, 2688. (f) Kim, S. H.; Jin, Z.; Ma, S.; Fuchs, P. L. *Tetrahedron Lett.* **1995**, 4013 and references therein.

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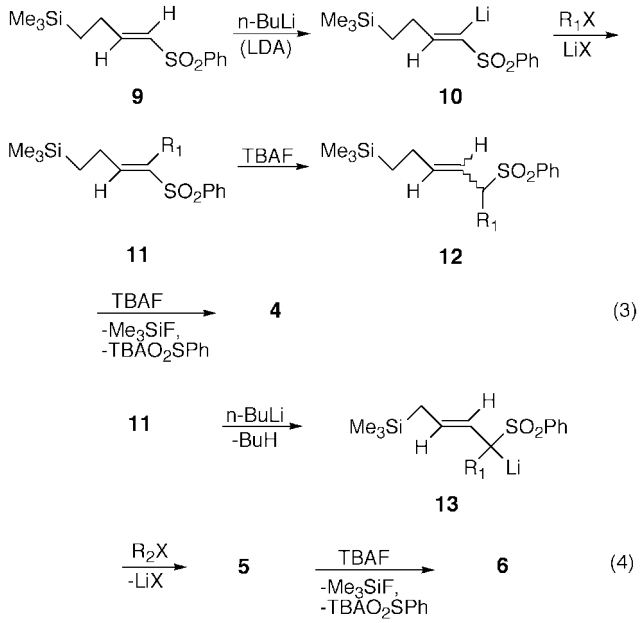
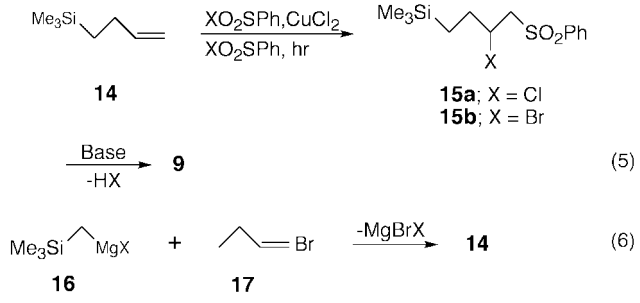


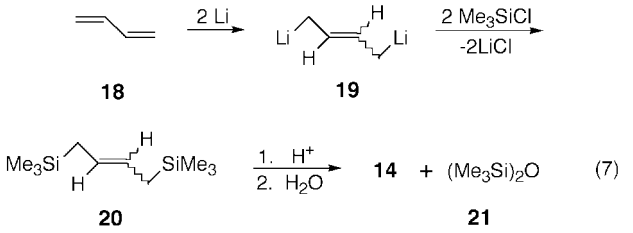
should be extendable to preparation of various conjugated diene derivatives.

Synthesis of **9** from 4-(trimethylsilyl)-1-butene (**14**) as summarized in eq 5 has now been developed as follows. Reaction of [(trimethylsilyl)methyl]magnesium bromide (**16**, X = Br) and allyl bromide (**17**) is reported to yield **14** (25%, eq 6).[3]. In the present work coupling of **17** with [(trimethylsilyl)methyl]magnesium chloride (**16**, X = Cl),[4] prepared from magnesium and commercially available (chloromethyl)trimethylsilane, also gives **14** in only 22−27% yields. A more satisfactory large-scale method for

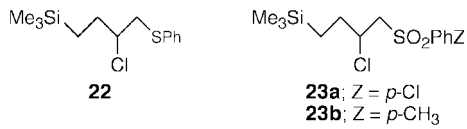


preparing **14** (eq 7) involves reductive-silylation of 1,3-butadiene (**18**) with lithium (2 equiv) and trimethylsilyl chloride (2 equiv, 40% conversion) to **20**.[5] Protiodesilylation of **20** with sulfuric acid in pentane or trifluoroacetic acid in CCl_4 occurs with rearrangment to give **14** (54−66%) and hexamethyldisiloxane (**21**).[6] Simple distillations yield large quantities of mixtures of **14** and **21** in ~2:1 ratio which are usable without further purification. If desired, rectification of mixtures of **14** and **21** allows preparation of pure **14**.

Halo(silyl)sulfonylbutanes such as **15a** and **15b** are presently prepared from **14** by addition of arylsulfonyl



chlorides as catalyzed by cupric chloride (eq 5)[7a−g] and by photolytic addition of arylsulfonyl bromides (eq 5).[7h] Of importance is that reaction of **14** with benzenesulfonyl chloride in acetonitrile/CH_2Cl_2 in the presence of cupric chloride and triethylamine hydrochloride at 105−115 °C for 17 h in a pressure container yields **15a** (69%). Addition of benzenesulfonyl chloride to **14** as above at temperatures above 100 °C is very slow. Use of the higher boiling solvent isobutyronitrile (bp 107−108 °C) instead of acetonitrile/CH_2Cl_2 allows satisfactory addition of benzenesulfonyl chloride to **14** without using pressure equipment. Increasing the solubility of cupric chloride in 2-ethoxyethyl ethyl ether using TDA-1 in place of triethylamine hydrochloride increases the rate of addition of benzenesulfonyl chloride to **14** to give **15a** (51%). The 2-chloro-1-(phenylsulfenyl)-4-(trimethylsilyl)butane (**22**, 8%) formed as a byproduct in the latter synthesis is oxidized efficiently by *m*-chloroperbenzoic acid (MCPBA) to **15a** (92%). Chlorosilyl sulfone **15a** is an oil that can be stored indefinitely without significant decomposition.



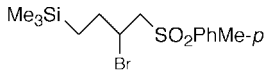
2-Chloro-1-(4-chlorophenylsulfonyl)-4-(trimethylsilyl)butane (**23a**) and 2-chloro-(4-methylphenylsulfonyl)-4-(trimethylsilyl)butane (**23b**), prepared by addition of 4-chlorophenylsulfonyl chloride and of 4-methylphenylsulfonyl chloride to **14** as above, are stable crystalline solids that also can be used satisfactorily in the present synthesis methodology.

Arylsulfonyl bromides add to olefins photolytically to give vicinal arylsulfonyl(bromo)alkanes.[7h−j] In a present method irradiation of benzenesulfonyl bromide in **14** in THF with an ordinary 500 W light bulb yields **15b** (eq 5, 48%).[8] Similarly, *p*-toluenesulfonyl bromide and **14** in benzene give **24** (62%). The photochemical addition reactions can be monitored conveniently by GC methods, and the unreacted bromides are separated easily from the reaction products by column chromatography. During chromatography of **24** minor dehydrobromination

(3) Hauser, C. R.; Hance, C. R. *J. Am. Chem. Soc.* **1952**, *74*, 5091.
(4) Sommer, L. H.; Goldberg, G. M.; Gold, J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1947**, *69*, 980.
(5) Weyenberg, D. R.; Toporder, L. H.; Nelson, L. E. *J. Org. Chem.* **1968**, *33*, 1975.
(6) (a) Sommer, L. H.; Tyler, L. G.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 2872. (b) Salimareeva, I. M.; Zhebarov, O. Z.; Bogatova, N. G.; Yurev, V. P. *Zh. Obskch. Khim.* **1981**, *51*, 420.

(7) For previous examples of such additions, see: (a) Cristol, S. J.; Reeder, J. A. *J. Org. Chem.* **1961**, *26*, 2182. (b) Vasil'eva, M. A.; Bychkova, T. I.; Kushnarev, D. F.; Rozova, T. I.; Kalabina, A. V. *Zh. Org. Khim.* **1977**, *13*, 283. (c) Asscher, M.; Vofsi, D. *J. Chem Soc.* **1964**, 4962. (d) Amiel, Y. *Tetrahedron Lett.* **1971**, 661. (e) Yoshiaki, K.; Muria, S.; Sonoda, N.; Tsutsumi, S. *Organomet. Chem. Synth.* **1972**, *1*, 465. (f) Dunoques, J.; Pillot, J.-P.; Duffaut, N.; Calas, R. *C. R. Acad. Sci. Ser. C* **1974**, *278*, 467. (g) Pillot, J. P.; Dunoques, J.; Calas, R. *Synthesis* **1977**, 469. (h) Zakharkin, L. I.; Zhigareva, G. C. *Zh. Org. Khim.* **1973**, *9*, 891. Boll, W. *Liebigs Ann. Chim.* **1979**, 1655. (i) Kalabina, A. V.; Vasil'eva, M. A.; Bychkova, T. I. *Zh. Org. Khim.* **1979**, *15*, 268. (j) Doomes, E.; Clarke, U.; Neitzel, J. *J. Org. Chem.* **1987**, *52*, 1540.
(8) An alternate method for preparing **11**, **22**, and **23** which has not been evaluated in this work is addition of arylsulfenyl chlorides to **10** followed by oxidation with percarboxylic acids: Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208.

occurs to give **25** (5%). Elimination product **25** exhibits a single set of ^{13}C NMR absorptions and is assigned (*E*) stereochemistry from its ^{1}H NMR because its olefinic protons exhibit coupling of 15.0 Hz.



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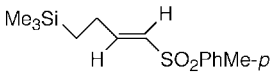

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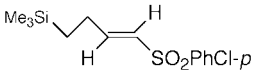

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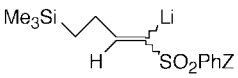
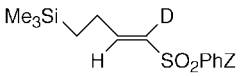
Halosulfones **15a**, **15b**, **23a**, and **23b** are eliminated efficiently by various bases.[9] Reaction of **15a** with potassium hydroxide in THF−water at room temperature gives **9** (91%). Additionally, **23a** is converted by *n*-BuLi in THF at −78 °C to **26** (98%). Further, treatment of **23b** with LDA at −78 °C and then aqueous ammonium chloride yields **25** (93%). Also, photoaddition of an arylsulfonyl bromide to **14** (eq 5) followed by dehydrobromination of the photoproduct can be combined into a one-pot procedure. Thus, irradiation of **14**, **21**, and *p*-toluenesulfonyl bromide in THF followed by addition of aqueous potassium hydroxide results in elimination of **15b** to yield **25** (42%). As for **25**, **9** and **26** are assigned (*E*) stereochemistries because they each have ^{13}C NMR absorptions for a single isomer and ^{1}H NMR couplings of 15.0 Hz for their olefinic hydrogens.

Generation and determination of the behavior of vinyl sulfone α-anions similar to **10** have had limited study.[10] Sulfonyl-1-butenes **9**, **26**, and **25** are presently found to be readily converted to **10**, **27a**, and **27b**, respectively, with LDA or *n*-BuLi in THF at −78 °C. The deprotonations with LDA are essentially complete within seconds; *n*-BuLi requires from 1 to 15 min. Deuterations of **27a** and **27b** with D_2O then yield (*E*)-1-deuterio-1-butenes **28a** (83%) and **28b** (89%), respectively, assigned spectrally and intuitively as follows. Deuteriobutene **28a** has a single set of ^{13}C NMR absorbances, and its ^{1}H NMR reveals 79% deuterium at its α-position as determined from its vinyl proton resonance at δ 6.30. Since the remaining vinyl proton absorbances (δ 6.9−7.1) are complex, the stereochemistry of **28a** was not rigorously assigned. From the above spectral information and subsequent chemistry, the stereochemistry of **28a** is presumed to be (*E*). Similar information leads to the provisional (*E*) stereochemical assignment of **28b**.

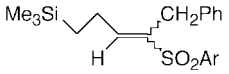


27a; Z = *p*-Cl
27b; Z = *p*-CH_3



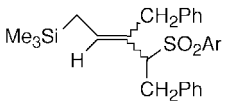
28a; Z = *p*-Cl
28b; Z = *p*-CH_3

The behaviors of α-lithio vinyl sulfones **10**, **27a**, and **27b** with benzyl bromide were then investigated. The lithiates, prepared in situ from **15a**, **23a**, and **23b**, respectively, with 2 equiv of LDA or *n*-BuLi at −78 °C, were stirred for various times and then benzyl bromide was added followed by HMPA (2.1 equiv). Stirring **10**, **27a**, and **27b** for 0.2 h at −78 °C and then adding benzyl bromide followed by HMPA gives benzylated products **29a**, **29b**, and **29c** in 89, 84, and 90% yields, respectively.



29a; Ar = Ph
29b; Ar =PhMe-*p*
29c; Ar = PhCl-*p*

The benzylations are accelerated by HMPA. Keeping **10**, **27a**, and **27b** at −78 °C for 1.5 h before adding benzyl bromide and then HMPA leads to **29a** (67%), **29b** (63%), and **29c** (45%) in significantly lower yields. Further, warming **27a** from −78 to 25 °C in 1 h and then adding benzyl bromide and HMPA give only a 30% yield of **29c**. Lithio derivatives **10**, **27a**, and **27b** decompose at −78 °C and should be derivatized shortly after generation. The products of thermal decomposition of **10**, **27a**, and **27b** are as yet unknown. Of further interest is that lithio allyl derivative **2** reacts much more rapidly than **10**, **27a**, or **27b** with benzyl bromide. The relative unreactivities of **10**, **27a**, and **27b** are interpretable on the basis that their lithium vinyl bonds are tighter than that for the lithium allyl moiety in **2**.

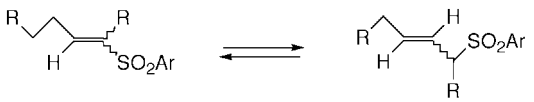


30a; Ar = C_6H_5
30b; Ar =$C_6H_4CH_3$-*p*
30c; Ar = C_6H_4Cl-*p*

Benzyl derivatives **29a**−**c** are assigned by spectral methods. Each product gives a single set of ^{13}C NMR absorbances, thus indicating that only single isomers are present. (*E*) stereochemistries are assigned to **29a** and **29c** because proton NOE differences reveal that the hydrogens at C-1 (benzyl) and C-4 (allyl) are on *cis* carbon atoms. Irradiation of the allyl (C-4) protons (δ 2.15) of **29a** results in enhancement of the NMR of its benzyl (C-1) hydrogen (δ 3.68, 5.71%). Similarly, irradiation of the hydrogen at C-4 in the allyl group of **29c** (δ 2.1−2.2) gives an increase in the NMR absorption of its benzyl (C-1) hydrogen of 5.66% (δ 3.69). On the basis of the results with **29a** and **29c**, the stereochemistry of **29b** is presumed to be (*E*).

Attention next turned to isomerizations of **29a**, **29b**, and **29c** to **30a**, **30b**, and **30c**, respectively, followed by elimination of their trimethylsilyl and their arylsulfonyl groups.

α-Alkenyl (**31**) and allyl (**32**) sulfones generally interconvert under basic conditions (eq 8), and the equilibria usually favor the allyl (unconjugated) isomers **32** heavily when R′ is aryl or alkyl.[11]

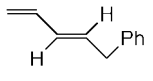


31 **32** (8)

Desirable methodology for **29a**−**c** will be to combine deconjugation to **30a**−**c** by fluoride ion functioning as a base followed by rapid elimination of **30a**−**c** to (*E*)-5-phenyl-1,3-pentadiene (**33**). These conditions are met

(9) (a) β-Halo sulfones are readily dehydrohalogenated by hydroxide bases[7c] or tertiary amines.[9b] (b) Skell, P. S.; McNamara, J. H. *J. Am. Chem. Soc.* **1957**, *79*, 85.

(10) (a) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3277. (b) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3279.



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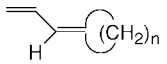
simply at present by treatment of **29a**−**c** with 1 equiv of TBAF at room temperature to give **33** in 56, 63, and 59% yields, respectively. The above method of synthesis of **33** in quantity is cheaper and just as convenient as synthesis of **1** and its conversion by *n*-BuLi and benzyl bromide to **30a** (R = $CH_2C_6H_5$) followed by detrimethylsilylphenylsulfonylation by TBAF as previously described.[1b]

1,1-Cycloalka-1,3-butadienes (**34**, $n = 2-5$) have been prepared previously from **1**.[1b] Preparation of **34** ($n = 3$) from **25** (eq 9) then became of interest. The lithio derivative **27b** of **25** has now been found to be monoalkyl-



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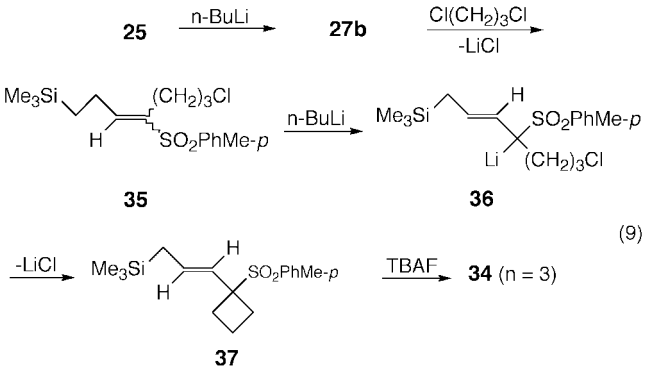

25 **27b** **35** **36** **37**

(9)

ated by 1,3-dichloropropane to give (3-chloropropyl) derivative **35**. Reaction of **35** with *n*-BuLi results in removal of an allyl proton at C-6 and generation of lithio allyl intermediate **36**. Ring closure with displacement of chloride ion from **36** then gives 1-(1-propenyl)cyclobutane **37** in 67% yield. Conjugative elimination of the trimethylsilyl and the 4-methylbenzenesulfonyl groups in **37** by TBAF at 0 °C in THF then yields allylenecyclobutane (**34**, $n = 3$, 84%). The overall sequence from **25** to **34**, $n = 3$, is satisfactory and at least the equal to that found previously for **1**, *n*-BuLi, 1,3-dichloropropane, *n*-BuLi, and TBAF.[1b] Further, the present methodology has excellent potential for preparing cycloalkadienes such as **34** ($n = 2$, 4, and 5) as well as varied 1,1-disubstituted-1,3-butadienes (**6**).

In conclusion, **9**, **25**, and **26** serve as excellent synthons for the 1-(1,3-butadienyl) anion (**7**) and the 1,1-(1,3-butadienyl) dianion (**8**).

Experimental Section

General Considerations. Product separations, spectroscopic determinations, analyses, purification of solvents, and typical procedures in various experiments have been handled as previously detailed.[1b]

(*E*)-1,4-Bis(trimethylsilyl)-2-butene (20). 1,3-Butadiene (**18**, 62.0 g, 1.26 mol) condensed at −78 °C was added in 4 h to a mixture of trimethylsilyl chloride (259.0 g, 2.38 mol), lithium (17.3 g, 2.50 mol), and THF (350 mL) at 0−10 °C under argon. The mixture was then stirred for 24 h, filtered, washed with H_2O and brine, and concentrated to a clear colorless liquid. Fractional distillation yielded **20** (94.50 g, 40%): bp 90−95 °C (38 mmHg), whose IR and ^{1}H NMR spectra agree with the literature.[12]

4-(Trimethylsilyl)-1-butene (14). Method A. Sulfuric acid (36.8 g, 0.38 mol, 98%) was added in 0.5 h to **20** (75.8 g, 0.38 mol) in pentane (300 mL) at 0 °C. The mixture was stirred further for 0.5 h. The pentane layer was washed with H_2SO_4 until hexamethyldisiloxane (**21**) was no longer detected by GC, washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and fractionally distilled in a packed column (glass helices; 20 × 1 cm) to give **14** (26.4 g, 54%): bp 112−115 °C. The IR and ^{1}H NMR spectra of **14** agree with literature data.[6b]

Method B. Trifluoroacetic acid (2.8 g, 24.9 mmol) was slowly added to **20** (5.0 g, 24.9 mmol) in CCl_4 under argon at 3 °C. The mixture was stirred for 1.5 h and poured into saturated aqueous $NaHCO_3$/ice. The organic phase was washed with H_2O and brine, dried ($MgSO_4$), and fractionally distilled (Fenske glass ring, Hempel column; 10 × 1 cm) to yield **14** (2.10 g, 66%) of satisfactory spectral properties: bp 112−115 °C.[6b]

Method C. [(Trimethylsilyl)methyl]magnesium chloride (**16**, X = Cl)[13] was prepared from (chloromethyl)trimethylsilane (20 g, 0.16 mol) and magnesium (3.97 g, 0.16 mol) in Et_2O (50 mL). The solution was cooled to 0 °C, and allyl bromide (**17**, 28 g, 0.23 mol) was added. The resulting mixture was refluxed for 5 h, cooled, and poured into saturated aqueous NH_4Cl/ice. The organic layer was washed with H_2O and brine, dried ($MgSO_4$), and distilled to give **14** (6.0 g, 29%): bp 112−115 °C.[6b]

2-Chloro-1-(4-chlorophenylsulfonyl)-4-(trimethylsilyl)butane (23a). 4-Chlorobenzenesulfonyl chloride (6.5 g, 30.7 mmol), **14** (4.0 g, 31.1 mmol), acetonitrile (2 mL), CH_2Cl_2 (10 mL), cupric chloride (0.41 g, 3.0 mmol), and triethylamine hydrochloride (0.64 g, 4.6 mmol) were placed in a threaded glass pressure tube and deoxygenated for 1.5 h. The tube was sealed and heated to 105−115 °C for 17 h, cooled, and then opened. The mixture was taken up in Et_2O, washed with H_2O, 10% HCl, and 10% aqueous Na_2CO_3, dried ($MgSO_4$), and concentrated to a white semisolid (9.46 g). Column chromatography (silica gel; ethyl acetate−hexane, 0−5%) gave **23a** (7.28 g, 69% yield) as a white solid and 4-chlorobenzenesulfonyl chloride (1.71 g, 26% recovery). Recrystallization of the product from hexane yielded pure **23a**, a white solid: mp 82−84 °C; ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 9 H), 0.4−0.7 (m, 2 H), 1.6−1.9 (m, 2 H), 3.4−3.6 (m, 2 H), 4.26 (quin, $J = 6.0$ Hz, 1 H), 7.53 (d, $J = 8.7$ Hz, 2 H), 7.86 (d, $J = 8.7$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.9 (q), 12.4 (t), 32.9 (t), 56.9 (d), 62.9 (t), 129.6 (d), 129.7 (d), 138.1 (s), 140.8 (s); mass spectrum, *m/e* calcd for $C_{12}H_{17}Cl_2O_2SSi$ ($M^+ - CH_3$, ^{35}Cl) 323.0096, found 323.0110. Anal. Calcd for $C_{13}H_{20}Cl_2O_2SSi$: C, 46.01; H, 5.94. Found: C, 46.38; H, 5.86.

2-Chloro-1-(4-methylphenylsulfonyl)-4-(trimethylsilyl)butane (23b). A stirred solution of **14** (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 mixture was refluxed under argon. After 24 h, **14** was not detected by GC. Saturated aqueous $NaHCO_3$ was added to the reaction mixture which was then refluxed for 3.5 h. After cooling, the reaction product was worked up as in the synthesis of **23a** and concentrated to a light brown solid (18.05 g). Column chromatography (silica gel, ethyl acetate−hexane, 0−1%) gave **23b** (13.14 g, 53%) as a white crystalline solid: mp 79−80 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H),

(11) (a) Hine, J.; Linden, S.-M.; Wang, A.; Thiagarajan, V. *J. Org. Chem.* **1980**, *45*, 2821. (b) Hine, J.; Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 476. (c) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965; pp 32−65. (d) For recent discussion of the origins of such differences, see ref 1b.

(12) Weyenberg, D. R.; Toporder, L. H.; Nelson, L. E. *J. Org. Chem.* **1968**, *33*, 1975.

(13) Sommer, L. H.; Goldberg, G. M.; Gold, J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 481.

0.4−0.7 (m, 2 H), 1.6−2.0 (m, 2 H), 2.47 (s, 3 H), 3.52 (d, J = 6.3 Hz, 2 H), 4.2 (m, 1 H), 7.37 (d, J = 7.9 Hz, 2 H), 7.81 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.9 (q), 12.4 (t), 21.6 (q), 32.8 (t), 57.1 (d), 62.9 (t), 128.2 (d), 130.0 (d), 136.8 (s), 145.1 (s); mass spectrum, *m/e* calcd for $C_{13}H_{20}ClO_2SSi$ ($M^+ - CH_3$, ^{35}Cl) 303.0642, found 303.0663. Anal. Calcd for $C_{14}H_{23}ClO_2SSi$: C, 52.71; H, 7.27. Found: C, 52.60; H, 7.20.

2-Chloro-1-(phenylsulfonyl)-4-(trimethylsilyl)butane (15a) and 2-Chloro-1-(phenylsulfenyl)-4-(trimethylsilyl)butane (22). 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 and then heated to 130 °C. A solution of **14** (12.1 g, 9.43 mmol) and **21** (6.3 mL) was added via syringe pump (2.5 mL/h for 4.0 h, then 13.3 mL/h for 11.0 h) to the red-brown reactant solution. The mixture was then heated for 11 h at 120−124 °C. The brown solution was worked up as described for **23a** and concentrated to a dark oil (31.45 g). Column chromatography (silica gel; ethyl acetate−hexane, 0−3%) yielded **22** (1.97 g, 8%) as a clear colorless oil [^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.5−0.8 (m, 2 H), 1.6−2.0 (m, 2 H), 3.3 (AB q, J = 13.8 Hz), 3.9−4.0 (m, 1 H), 7.1−7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −1.9 (q), 12.5 (t), 31.1 (t), 41.4 (t), 63.9 (d), 126.6 (d), 129.0 (d), 130.1 (d), 135.4 (s); mass spectrum, *m/e* calcd for $C_{13}H_{21}ClSSi$ (M^+, ^{35}Cl) 272.0822, found 272.0863] and **15a** (14.82 g, 51%): ^{1}H NMR ($CDCl_3$) δ −0.05 (s, 9 H), 0.4−0.7 (m, 2 H), 1.6−1.9 (m, 2 H), 3.4−3.5 (m, 2 H), 4.2−4.3 (m, 1 H), 7.4−7.9 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −2.0, 12.2, 32.6, 56.9, 62.6, 128.0, 129.2, 133.9, 139.4; mass spectrum, *m/e* calcd for $C_{21}H_{18}ClO_2SSi$ ($M^+ - CH_3$, ^{35}Cl) 289.0485, found 289.0482.

Synthesis of 15a by Oxidation of 22. MCPBA (0.25 g, 1.23 mmol, 85%) was added to a solution of **22** (0.12 g, 0.43 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The white suspension was warmed to room temperature and then stirred for 1.5 h. The mixture was dissolved in Et_2O, washed with saturated aqueous sodium metabisulfite, saturated aqueous $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated to **15a** (0.12 g, 92%). The ^{1}H NMR and IR of **15a** are identical to those of a previous sample.

2-Bromo-1-(phenylsulfonyl)-4-(trimethylsilyl)butane (15b). Procedure A. A stirred solution of **14** (5.80 g, 45.2 mmol), **21** (2.99 g), benzenesulfonyl bromide (10.0 g, 45.2 mmol), and THF (30 mL) in Pyrex was deoxygenated with argon for 20 min and then irradiated with a 500 W clear incandescent bulb. After 3.5 h, the mixture was concentrated to a clear colorless viscous oil (15.26 g). Column chromatography (silica gel; ethyl acetate−hexane, 0−5%) yielded benzenesulfonyl bromide (4.98 g, 50% recovery) and then **15b** (7.51 g, 48%), a clear, colorless oil: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 9 H), 0.5−0.7 (m, 2 H), 1.7−2.0 (m, 2 H,), 3.5−3.7 (m, 2 H), 4.3−4.4 (m, 1H), 7.5−7.9 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −1.9, 13.5, 33.1, 48.5, 63.1, 128.0, 129.4, 134.0, 139.5; mass spectrum, *m/e* calcd for $C_{12}H_{18}BrO_2SSi$ ($M^+ - CH_3$, ^{79}Br) 332.9980, found 332.9988, ($M^+ - CH_3$, ^{81}Br) 336.0038, found 336.0006.

2-Bromo-(4-methylphenylsulfonyl)-4-(trimethylsilyl)butane (24). Procedure A with *p*-toluenesulfonyl bromide using benzene as the reaction solvent gave after 29 h parent bromide (26% recovery) as the first eluent followed by **24** (62%), a white crystalline solid: mp 72 °C from hexane; ^{1}H NMR ($CDCl_3$) δ 0.0 (s, 9 H), 0.5−0.7 (m, 2 H), 1.7−2.0 (m, 2 H), 2.45 (s, 3 H), 3.65 (m, 2 H), 4.2−4.4 (m, 1 H), 7.37 (d, J = 8.2 Hz, 2 H), 7.80 (d, J = 8.2 Hz, 2 H); irradiation of the multiplet at δ 4.2−4.4 simplified δ 3.65 to a singlet and simplified δ 1.7−2.0 somewhat; ^{13}C NMR ($CDCl_3$) δ −1.9 (q), 13.5 (t), 21.6 (q), 33.1 (t), 48.7 (d), 63.2 (t), 128.1 (d), 130.0 (d), 136.6 (s), 145.1 (s); mass spectrum, *m/e* calcd for $C_{13}H_{20}BrO_2SSi$ ($M^+ - CH_3$, ^{79}Br) 347.0136, found 347.0136, ($M^+ - CH_3$, ^{81}Br) 349.0116, found *m/e* 349.0128. Anal. Calcd for $C_{14}H_{23}BrO_2SSi$: C, 46.27; H, 6.38. Found: C, 46.52; H, 6.22. The last eluent, **25** (5%), was identified by comparison with an authentic sample.

(*E*)-1-(Phenylsulfonyl)-4-(trimethylsilyl)-1-butene (9). Potassium hydroxide (1.0 g, 17.8 mmol) in water (5 mL) was added to **15a** (0.5 g, 1.64 mmol) in THF (5 mL). The heterogeneous mixture was stirred vigorously for 2 h and diluted with Et_2O. The organic layer was washed with H_2O and brine, dried ($MgSO_4$), and concentrated to **9** (0.40 g, 91%), a clear colorless oil: ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 9 H), 0.5−0.6 (m, 2 H), 2.1−2.2 (m, 2 H), 6.30 (dt, J = 15.0, 1.6 Hz, 1 H), 7.03 (dt, J = 15.0, 6.3 Hz, 1 H), 7.4−7.6 (m, 3 H), 7.8−7.9 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.9 (q), 14.4 (t), 26.1 (t), 127.5 (d), 129.1 (d), 129.3 (d), 133.1 (d), 140.8 (s), 149.5 (d). The ^{1}H NMR and IR of **9** are consistent with literature values.[1a,b,14]

(*E*)-1-(4-Methylphenylsulfonyl)-4-(trimethylsilyl)-1-butene (25). Procedure B. A stirred solution of **14** (5.0 g, 38.9 mmol), **21** (2.6 g), and *p*-toluenesulfonyl bromide (9.2 g, 39.1 mmol) in THF was deoxygenated 30 min with argon and photolyzed for 14 h with a 500 W incandescent bulb. Aqueous potassium hydroxide (30 mL, 0.6 M, 18 mmol) was added, and the resulting mixture was stirred for 1 h. The organic phase was worked up as for **14** (method B) and concentrated to a cloudy yellow oil (6.98 g) which solidified. Recrystallization from methanol gave **25** (4.37 g, 42%) as a white solid: mp 48.5−49.5 °C (from pentane); ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 9 H), 0.5−0.6 (m, 2 H), 2.1−2.2 (m, 2 H), 2.41 (s, 3 H), 6.28 (dt, J = 15.0, 1.6 Hz, 1 H), 6.99 (dt, J = 15.0, 6.3 Hz, 1 H), 7.30 (d, J = 7.9 Hz, 2 H), 7.74 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.9, 14.4, 21.5, 26.0, 127.5, 129.6, 129.7, 137.9, 144.0, 148.8; mass spectrum *m/e* calcd for $C_{14}H_{22}O_2SSi$ (M^+) 282.1110, found 282.1117. Anal. Calcd for $C_{14}H_{22}O_2SSi$: C, 59.52; H, 7.85. Found: C, 59.34; H, 7.93.

Procedure C. *n*-BuLi (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 20 min, **23b** (0.96 g, 3.01) in THF (4 mL) was added (2 min). After being stirred at −78 °C for 10 min, the mixture was quenched with aqueous saturated NH_4Cl and allowed to warm to room temperature, and CH_2Cl_2 was added. The organic phase was washed with H_2O and brine, dried, ($MgSO_4$), and concentrated to a viscous oil which solidified on standing. Column chromatography (Florisil; ethyl acetate, 5%) yielded **25** (0.79 g, 93%) as a clear colorless oil which crystallized to a white solid with properties identical to that prepared previously.

(*E*)-1-(4-Chlorophenylsulfonyl)-4-(trimethylsilyl)-1-butene (26). Procedure C with *n*-BuLi and **23a** followed by workup yielded **26** (0.44 g, 98%), a fluffy white solid: mp 73−74 °C; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.5−0.7 (m, 2 H), 2.1−2.3 (m, 2 H), 6.28 (dt, J = 15.0, 1.6 Hz), 7.05 (dt, J = 15.0, 6.3 Hz), 7.49 (d, J = 8.8 Hz, 2 H), 7.80 (d, J = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.9 (q), 14.5 (t), 26.2 (t), 129.0 (d, coincident peaks), 129.5 (d), 139.4 (s), 139.9 (s), 150.3 (d); mass spectrum *m/e* calcd for $C_{13}H_{18}ClSSiO_2$ ($M^+ - H$) 301.0485, found 301.0476. Anal. Calcd for $C_{13}H_{18}ClSSiO_2$: C, 51.55; H, 6.32. Found: C, 51.36; H, 6.34.

(*E*)-1-(4-Chlorophenylsulfonyl)-1-deuterio-4-(trimethylsilyl)-1-butene (28a). Procedure C involving addition of D_2O to a solution from **26**, *n*-BuLi, diisopropylamine, and THF, workup as for **9**, and column chromatography (Florisil; ethyl acetate−hexane, 1−2%) gave **28a** (83%), a white solid: mp 72−73 °C; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.5−0.6 (m, 2 H), 2.1−2.3 (m, 2 H), 6.30 (dt, J = 15.0, 1.6 Hz, 79% deuterium incorporation), 6.9−7.1 (m, 2 H), 7.50 (dt, J = 8.8 Hz, 2 H), 7.80 (d, J = 8.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.9 (q), 14.5 (t), 26.2 (t), 129.1 (d), 129.5 (d), 139.5 (s), 139.9 (s), 150.2 (d); mass spectrum *m/e* calcd for $C_{12}H_{15}DClO_2SSi$ ($M^+ - CH_3$, ^{37}Cl) 290.0362, found 290.0398.

(*E*)-1-Deuterio-1-(4-methylphenylsulfonyl)-4-(trimethylsilyl)-1-butene (28b). Procedure C with **27b** gave **28b** (89%), a colorless oil which solidified: mp 48−49 °C (from pentane); ^{1}H NMR (CCl_4) δ 0.00 (s, 9 H), 0.5−0.6 (m, 2 H), 2.1−2.5 (m, 2 H), 2.45 (s, 3 H), 6.24 (J = 15 Hz, >90% deuterium incorporated), 6.95 (bt, J = 7 Hz, 1 H), 7.32 (d, J = 8 Hz, 2 H), 7.74 (d, J = 8 Hz, 2 H); mass spectrum *m/e* calcd for $C_{14}H_{21}DO_2SSi$ (M^+) 283.1173, found 283.1158.

(*E*)-1-Phenyl-2-(phenylsulfonyl)-5-(trimethylsilyl)-2-pentene (29a). Procedure D. *n*-BuLi (1.13 mL, 2.93 mmol,

(14) Kinney, W. A.; Crouse, G. D.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4986.

2.60 M in hexane) was slowly added to **9** (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 mixture was warmed to room temperature and quenched with saturated aqueous NH_4Cl. The organic layer was washed with 10% HCl and brine, dried ($MgSO_4$), filtered, and concentrated to a light yellow mobile oil (0.57 g). Column chromatography (silica gel, ethyl acetate, 0−5%) yielded **29a** (0.45 g, 89%), a colorless oil: ^{1}H NMR ($CDCl_3$) δ −0.05 (s, 9 H), 0.5−0.6 (m, 2 H), 2.0−2.2 (m, 2 H), 3.68 (s, 2 H), 6.9−7.7 (m, 11 H); 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%); ^{13}C NMR ($CDCl_3$) δ −1.9, 15.2, 23.4, 31.9, 126.3, 128.0, 128.1, 128.3, 128.8, 132.8, 136.9, 138.4, 140.1, 146.5; mass spectrum *m/e* calcd for $C_{20}H_{26}O_2SSi$ (M^+) 358.1423, found 358.1413.

(*E*)-2-(4-Methylphenylsulfonyl)-1-phenyl-5-(trimethylsilyl)-2-pentene (29b). Using **25** in procedure D yielded **29b** (0.43 g, 84%), a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.5−0.6 (m, 2 H), 2.1−2.2 (m, 2 H), 2.44 (s, 3 H), 3.73 (s, 2 H), 7.0−7.3 (m, 8 H), 7.69 (d, J = 8.3 Hz, 2 H); 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; ^{13}C NMR ($CDCl_3$) δ −1.9 (q), 15.2 (t), 21.5 (q), 23.4 (t), 32.0 (t), 126.2 (d), 128.1 (d), 128.2 (d), 128.3 (d), 129.5 (d), 137.1 (s), 137.2 (s), 138.7 (s), 143.7 (s), 146.0 (d); mass spectra, *m/e* calcd for $C_{21}H_{28}O_2SSi$ (M^+) 372.1580, found 372.1569.

(*E*)-2-(4-Chlorophenylsulfonyl)-1-phenyl-5-(trimethylsilyl)-2-pentene (29c). Procedure D with benzyl bromide and **23b** gave **29c** as a viscous oil which crystallized to a pink-white solid, 90% yield: mp 75−76 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ −0.04 (s, 9 H), 0.5−0.6 (m, 2 H), 2.1−2.2 (m, 2 H), 3.69 (s, 2 H), 6.9−7.2 (m, 6 Hz), 7.28 (d, J = 8.7 Hz, 2 H), 7.59 (d, J = 8.7 Hz, 2 H); 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%); ^{13}C NMR ($CHCl_3$) δ −1.9, 15.3, 23.5, 31.9, 126.4, 128.1, 128.3, 129.0, 129.4, 136.6, 138.3, 138.8, 139.4, 147.0; mass spectrum *m/e* calcd for $C_{20}H_{25}ClO_2SSi$ (M^+, ^{35}Cl) 392.1033, found 392.1030. Anal. Calcd for $C_{20}H_{25}ClO_2SSi$: C, 61.12; H, 6.41. Found: C, 60.84; H, 6.21.

(*E*)-5-Phenyl-1,3-pentadiene (33). TBAF (2.50 mL, 1 m in THF) was added to a stirred solution of **30a** (493 mg, 1.25 mmol) in THF (18 mL) under argon at 25 °C. After 26 h, the reaction mixture was taken up in pentane, washed with H_2O and brine, and passed through a short column of neutral alumina in pentane. Evaporation of the solution under argon gave **33** (101 mg, 56%). The ^{1}H NMR and GC analyses of **33** agree with those of an authentic sample.

By the above procedure **30b** (510 mg, 1.37 mmol) was converted to **33** (124 mg, 63%). Similarly, **30c** (497 mg, 1.39 mmol) yielded **33** (118 mg, 59%). The IR, ^{1}H NMR, MS, and GC properties of **33** obtained from **30b** and **30c** correspond to those of a sample prepared previously.

Allylenecyclobutane (34, *n* = 3). *n*-BuLi (1.00 mL, 2.70 M, 2.75 mmol) was added to **25** (0.50 g, 1.38 mmol) in anhydrous THF (10 mL) at −78 °C under argon. Upon addition of HMPA (2.0 g, 11.0 mmol) and 1,3-dichloropropane (0.19 g, 1.67 mmol), the cooling bath was removed, and the mixture was stirred for 1 h and then cooled (−78 °C). Additional *n*-BuLi (0.50 mL, 1.38 mmol) was added, and the clear yellow solution was allowed to warm to room temperature. After 1 h, the mixture was worked up as for **33** and concentrated to a yellow clear oil. Column chromatography (silica gel; ethyl acetate 0−6%) yielded **37** (0.28 g, 67%) as a colorless oil: ^{1}H NMR (CCl_4) δ 0.00 (s, 9 H), 1.50 (d, J = 7 Hz, 2 H), 1.6−2.1 (m, 2 H), 2.41 (s, 3 H), 2.6−3.0 (m, 2 H), 5.0−5.8 (m, 2 H), 7.25 (d, J = 9 Hz, 2 H), 7.62 (d, J = 9 Hz, 2 H); mass spectrum, *m/e* calcd for $C_{10}H_{19}Si$ (M^+ − *p*-$CH_3C_6H_4SO_2$) 167.1256, found 167.1274.

Following the procedure used for preparing **33** from **30a**, **37** (0.28 g, 0.87 mmol) was converted to **34**, *n* = 3 (69 mg, 84%), identical with a prior sample.[12]

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Supporting Information Available: NMR spectra (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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