1-(Phenylsulfonyl)-2-(trimethylsilyl)ethane: A Valuable Intermediate for Synthesis of Olefins, Allyltrimethylsilanes, β-Trimethylsilyl Ketones, Vinyl Sulfones, 2-(Phenylsulfonyl)allyl Alcohols, and Varied Trimethylsilyl Derivatives

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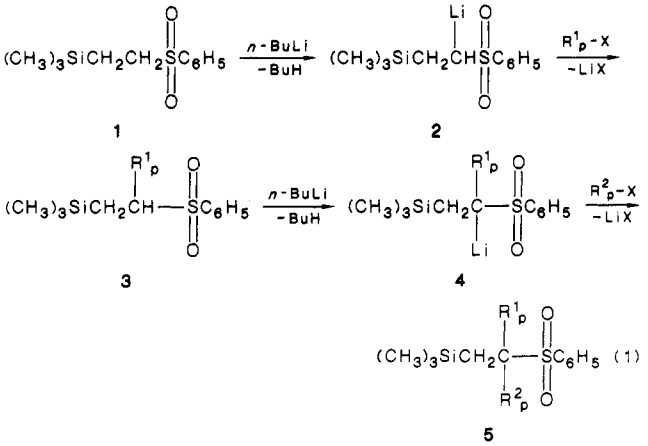
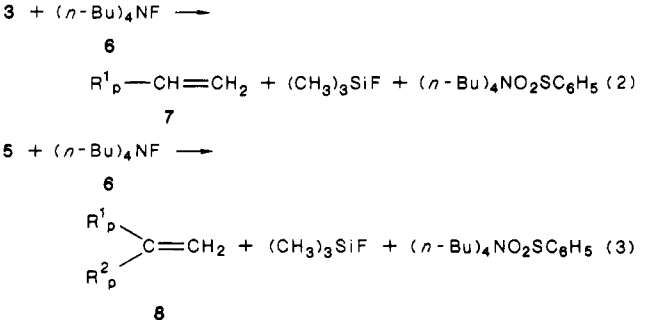
1-(Phenylsulfonyl)-2-(trimethylsilyl)ethane (1), prepared from 1-(trimethylsilyl)-2-(thiophenoxy)ethane and hydrogen peroxide, is converted by *n*-butyllithium to 1-(phenylsulfonyl)-1-lithio-2-(trimethylsilyl)ethane (2). Primary halides effect alkylation of 2 to 2-(phenylsulfonyl)-1-(trimethylsilyl)alkanes (3), reactions of which with *n*-butyllithium and then primary halides give higher 2-(phenylsulfonyl)-1-(trimethylsilyl)alkanes (5). Debenzenesulfonyltrimethylsilylation of 3 and 5 occurs efficiently with tetra-*n*-butylammonium fluoride (6) to yield mono- and disubstituted terminal olefins (7 and 8, respectively). 2-(Phenylsulfonyl)-3-(trimethylsilyl)-1-alkanols (14) result from reactions of 2 with aldehydes and ketones and then acidification. Allyltrimethylsilanes (18) are obtained by reductive elimination of mesylates (17) of 14 with sodium amalgam in methanolic disodium hydrogen phosphate. 2-(Phenylsulfonyl)-3-(trimethylsilyl)-1-propene (23), a 1-cationic-2-anionic equivalent (33), is preparable by (1) condensation of 1 and formaldehyde to 2-(phenylsulfonyl)-3-(trimethylsilyl)-1-propanol (24), (2) conversion of 24 by triphenylphosphine/carbon tetrachloride to 1-chloro-2-(phenylsulfonyl)-3-(trimethylsilyl)propane (25), and (3) elimination of 25 with triethylamine. β-Trimethylsilyl ketones (35) are produced by sodium amalgam reduction of α-phenylsulfonyl β-trimethylsilyl ketones (34) obtained by oxidation of 2-(phenylsulfonyl)-3-(trimethylsilyl)-1-propanols (14, R^2 = H) with chromic acid/sulfuric acid in acetone. Acidification of the adducts from 2 and epoxides yields 3-(phenylsulfonyl)-4-(trimethylsilyl)-1-butanols (38). Primary and secondary alcohols 38 are converted by chromic acid/sulfuric acid to 3-phenylsulfonyl 4-trimethylsilyl aldehydes and ketones (39). *n*-Butyllithium effects cyclization of methanesulfonates (40) of 37 to 1-(phenylsulfonyl)-1-[(trimethylsilyl)methyl]cyclopropanes (42) with displacement of lithium methanesulfonate. 1-(Phenylsulfonyl)-2-*n*-hexyl-1-[(trimethylsilyl)methyl]cyclopropane (46a) and 1-(phenylsulfonyl)-2-phenyl-1-[(trimethylsilyl)methyl]cyclopropane (46b) are eliminated by 6 to 1-*n*-hexyl-2-methylenecyclopropane (47a) and 1-methylene-2-phenylcyclopropane (47b), respectively. 2-(Phenylsulfonyl)-1-alkenes (49) are prepared by reactions of 6 with 2-(phenylsulfonyl)-2-chloro-1-(trimethylsilyl)alkanes (48) obtained (1) from *tert*-butyl hypochlorite and 2-(phenylsulfonyl)-2-lithio-1-(trimethylsilyl)alkanes (4) and/or (2) by reaction of 1-(phenylsulfonyl)-1-chloro-2-(trimethylsilyl)ethane (50) with *n*-butyllithium and alkylations of the resulting 1-(phenylsulfonyl)-1-chloro-1-lithio-2-(trimethylsilyl)ethane (51). Synthesis of 50 is best effected by base-catalyzed cleavage of 3-(phenylsulfonyl)-3-chloro-4-(trimethylsilyl)-2-butanone (54) prepared from 1-acetyl-1-(phenylsulfonyl)-2-(trimethylsilyl)ethane (53) and sodium hypochlorite. Chlorination of homologous α-phenylsulfonyl β-trimethylsilyl ketones (34) with *tert*-butyl hypochlorite is a general method for preparing alkyl 1-(phenylsulfonyl)-1-chloro-2-(trimethylsilyl)ethyl ketones (56). Dehydrochlorination of 50 to *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethene (55) is effected by 1,8-diazabicyclo[5.4.0]undec-7-ene. 2-(Phenylsulfonyl)-2-chloro-3-(trimethylsilyl)-1-alkanols (59) result from addition of 51 to aldehydes and ketones and then neutralization. Elimination of varied 59 by 6 yields 2-(phenylsulfonyl)allyl alcohols (60).

1-(Phenylsulfonyl)-2-(trimethylsilyl)ethane (1, eq 1) is converted by *n*-butyllithium to 1-(phenylsulfonyl)-1-lithio-2-(trimethylsilyl)ethane (2), reaction of which with 1-bromooctane yields 2-(phenylsulfonyl)-1-trimethylsilyl)decane (3, $R^1_p = CH_3(CH_2)_7$).[1] Deprotonation of 3



($R^1_p = CH_3(CH_2)_7$) by *n*-butyllithium in tetrahydrofuran and subsequent displacement of allyl bromide give 4-(phenylsulfonyl)-3-[(trimethylsilyl)methyl]-1-tridecane (5, $R^1_p = CH_3(CH_2)_7$, $R^2_p = CH_2{=}CHCH_2$).[1] Of special interest is that β-silyl sulfones 3 ($R^1_p = CH_3(CH_2)_7$) and 5 ($R^1_p = CH_3(CH_2)_7$ and $R^2_p = CH_2{=}CHCH_2$) undergo efficient debenzenesulfonyltrimethylsilylation by tetra-*n*-butylammonium fluoride (6) in refluxing tetrahydrofuran to yield 1-decene (7, $R^1_p = CH_3(CH_2)_7$; eq 2) and 2-*n*-octyl-1,4-pentadiene (8, $R^1_p = CH_3(CH_2)_7$, $R^2_p = CH_2{=}C\text{-}HCH_2$; eq 3).[1] The present paper describes the further



utility of 1 in synthesis.[2] As will be illustrated, 1 via 2 is

(1) (a) Kocienski, P. J. *Tetrahedron Lett.* **1979**, 2649. (b) Kocienski, P. J. *J. Org. Chem.* **1980**, *45*, 2037. Also see: (c) Kocienski, P.; Todd, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1777. (d) Kocienski, P.; Todd, M. *Ibid.* **1983**, 1783. (e) Kocienski, P. *Phosphorus Sulfur* **1985**, *24*, 97.

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a versatile intermediate for preparing mono- and disubstituted terminal olefins,[2a] allyltrimethylsilanes,[2b,3] β-trimethylsilyl ketones, vinyl sulfones,[2b,3] 2-(phenylsulfonyl)allyl alcohols[2b,3,4] and many other types of novel trimethylsilyl derivatives.[2b,3,4] It appears that **2**, its homologues, and its derivatives will be of considerable value in preparative organic chemistry.

In the present work, **1** was obtained conveniently in quantity[2b,3,4] (eq 4) by (1) reaction of vinylmagnesium bromide and chlorotrimethylsilane in tetrahydrofuran to give vinyltrimethylsilane (**9**),[5] (2) homolytic addition (99%) of thiophenol to **9** at 90 °C in the presence of azoisobutyronitrile (AIBN), and (3) oxidation (99%) of the resulting 1-(trimethylsilyl)-2-(thiophenoxy)ethane (**10**) with 30% hydrogen peroxide in warm acetic acid. Deprotonation of **1** in ethyl ether at −70 °C with 1 equiv of *n*-butyllithium in hexane occurs essentially quantitatively to give **2**. The behavior of **2** with various electrophiles and the chemistry of the resulting products are now summarized.

$$(CH_3)_3SiCl + BrMgCH{=}CH_2 \xrightarrow{THF} \underset{\mathbf{9}}{(CH_3)_3SiCH{=}CH_2} \xrightarrow[AIBN]{C_6H_5SH} \underset{\mathbf{10}}{(CH_3)_3SiCH_2CH_2SC_6H_5} \xrightarrow[HOAc]{H_2O_2} \mathbf{1} \xrightarrow[Et_2O]{n\text{-BuLi}} \mathbf{2} \quad (4)$$

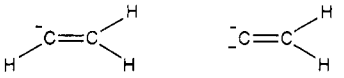
Alkylation reactions of **2** with varied halides were first studied.[2a] Primary bromides and iodides such as 1-bromobutane, 1-iodohexane, allyl bromide, and benzyl bromide are displaced (89%–92%) by **2** in ethyl ether at room temperature to give 2-(phenylsulfonyl)-1-(trimethylsilyl)alkanes (**3**, eq 1). With hindered primary halides, addition of hexamethylphosphoric triamide (HMPA) greatly accelerates alkylation. For example, in reaction of 1-bromo-3,3-dimethylbutane with **2** in ethyl ether for 24 h at room temperature, 95% of the alkyl halide is recovered. In HMPA (20%–25% by volume)/ethyl ether, however, displacement is complete within 2 h. Further, chlorotrimethylsilane reacts efficiently (93%) with **2** at 25 °C to give 1-(phenylsulfonyl)-1,2-bis(trimethylsilyl)ethane (**3**, $R^1_p = (CH_3)_3Si$). Conditions could not be found however for effective alkylation of **2** with secondary halides such as 2-bromopropane and bromocyclohexane.

2-(Phenylsulfonyl)-1-(trimethylsilyl)alkanes (**3**, monoalkylated derivatives of **2**) are readily converted to 2-(phenylsulfonyl)-2-lithio-1-(trimethylsilyl)alkanes (**4**, eq 1) by 1 equiv of *n*-butyllithium at −70 °C in ethyl ether. Lithio anions **4** are stable at room temperature for at least 24 h as indicated by quantitative recovery of **3** after quenching with water. Although hindered, **4** are efficiently alkylated to **5** (eq 1) by primary halides (1-bromobutane, benzyl bromide, and 3,3-dimethyl-1-bromobutane) in ethyl ether containing HMPA. Without HMPA, displacements do not occur even after 24 h.

Reactions of **3** (eq 2) and **5** (eq 3) with **6** (2.5–3.0 equiv) in tetrahydrofuran at 65 °C result in fluoride-induced desulfonylsilylation to give the corresponding mono- and disubstituted terminal olefins (**7** and **8**, respectively). The products (**7** and **8**) and yields in the present study are summarized in Table I. Alkylation of **3** and **5** and subsequent elimination is a superior synthesis of terminal olefins, and thus, **3** and **5** function as efficient equivalents for vinyl anion **11** and geminal vinyl dianion **12**.[1,2]

Table I. Synthesis of (a) 3 by Alkylation of 2 (Eq 1), (b) 7 by Elimination of 3 (Eq 2), (c) 5 by Alkylation of 4 As Derived from 3 (Eq 1), and (d) 8 by Elimination of 5 (Eq 3)

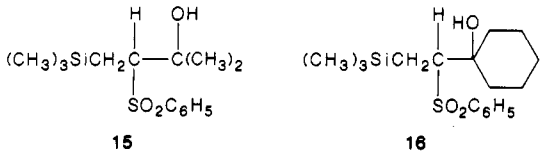
halide	3, %	7, %	halide	5, %	8, %
CH_3CH_2Br	95		$C_6H_5CH_2Br$	90	83
$CH_3(CH_2)_3Br$	93		$CH_3(CH_2)_3Br$	91	80
$CH_3(CH_2)_5I$	97	92			
$(CH_3)_3C(CH_2)_2Br$	89	84	$CH_2{=}CHCH_2Br$	90	76
$CH_2{=}CHCH_2Br$	96				
$C_6H_5CH_2Br$	90	85			



11 12

The reactions of **2** with aldehydes and ketones were then investigated. Aldehydes such as benzaldehyde, isobutyraldehyde, and 3-methyl-2-butenal (and others described later) and ketones such as acetone, 3-pentanone, C_4–C_6 cycloalkanones, and benzophenone react excellently with **2** in ethyl ether at −70 °C by carbonyl addition to give **14** upon acidification as in eq 5. When acetone and cyclohexanone are used and the adducts are neutralized with aqueous ammonium chloride, 3-(phenylsulfonyl)-2-methyl-4-(trimethylsilyl)-2-butanol (**15**) and 1-(phenylsulfonyl)-1-(1-hydroxy-1-cyclohexyl)-2-(trimethylsilyl)ethane (**16**) are obtained pure in >95% yields.

$$R^1R^2C{=}O + \mathbf{2} \longrightarrow \underset{\mathbf{13}}{(CH_3)_3SiCH_2CR^1R^2OLi} \xrightarrow{H^+} \underset{\mathbf{14}}{(CH_3)_3SiCH_2CR^1R^2OH} \quad (5)$$



15 16

Aldehyde and ketone adducts **13** (eq 5) react in situ with methanesulfonyl chloride (1 equiv) to give the corresponding mesylates (**17**) essentially quantitatively. Mesylates **17** are unstable oils at room temperature, but on dissolution in methanolic disodium hydrogen phosphate (4 equiv) at 0–5 °C and then reaction with sodium amalgam (6%)[6] they give the corresponding allyltrimethylsilanes (**18**, eq 6).[7] Allylsilanes **19** have become of intense interest in synthesis.[8] Of particular value are reactions

(2) (a) The present research on alkylation of **2** to **3** and **5** and then elimination to **7** and **8** was accomplished independent of that of ref **1a,b**.[3] It is clear that the accomplishments of ref **1a,b** predate those of this laboratory. Subsequent communications from this laboratory on the further development of **1** as a versatile synthesis intermediate are: (b) Hsiao, C.-N.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 1963. (c) Hsiao, C.-N.; Shechter, H. *Ibid.* **1982**, *23*, 3455.

(3) Much of the present research has been abstracted from the Ph.D. dissertation of Hsiao, C.-N., The Ohio State University, Columbus, Ohio, 1982.

(4) (a) Boeckman, R. K., Jr.; Blum, D. M.; Ganem, B.; Halvey, N. *Org. Synth.* **1978**, *58*, 152. (b) Vinyltrimethylsilane is purchasable from Aldrich Chemical Co., Inc.

(5) Griesbaum, G. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 273.

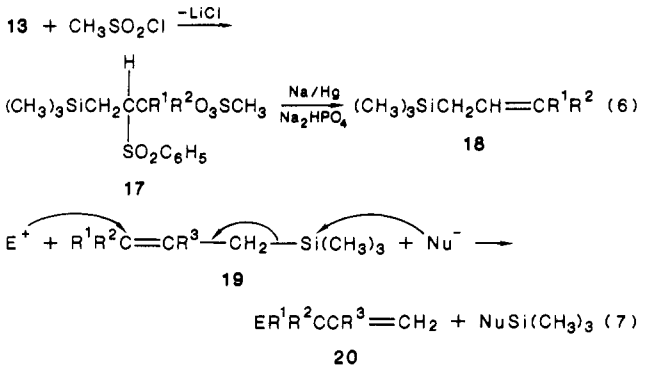
(6) The elimination method is that of Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477 and references therein.

(7) Carbonyl compounds have been converted to allylsilanes by Wittig reactions.[7b,c] The method is adequate for reactive aldehydes and ketones, but mildly hindered acyclic ketones and cyclopentanone give poor yields. (b) Seyferth, D.; Wursthorn, K. R.; Mammarella, R. E. *J. Org. Chem.* **1977**, *42*, 3104. (c) Fleming, I.; Paterson, I. *Synthesis* **1979**, 445. (d) For other methods of synthesis of allylsilanes, see: Biran, C.; Dunogues, J.; Calas, R.; Gerval, J.; Tskhovrebachville, T. *Synthesis* **1981**, 220 and references therein.

Table II. Conversions of 2 with Aldehydes and Ketones to 14 (Eq 5), 17 (Eq 5), and Then 18 (Eq 6)

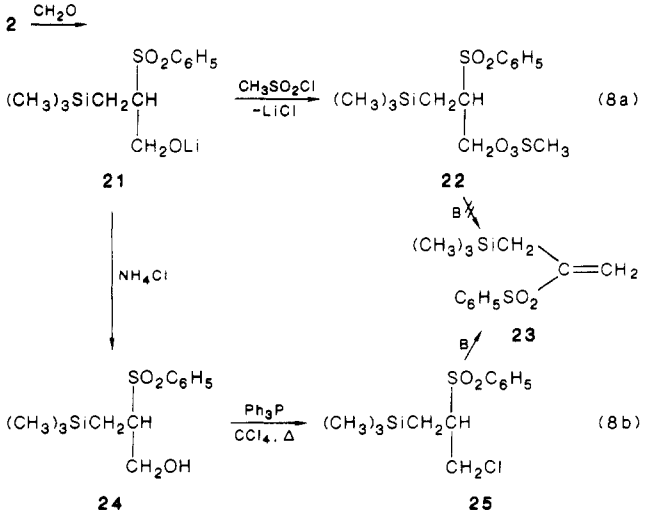
carbonyl	allylsilane (18)	yield, %	carbonyl	allylsilane (18)	yield, %
C_6H_5CHO	$C_6H_5CH{=}CHCH_2Si(CH_3)_3$ (*E* + *Z*)	92	$(CH_3)_2C{=}CHCHO$	$(CH_3)_2C{=}CHCH{=}CHCH_2Si(CH_3)_3$ (*E* + *Z*)	85
$CH_3C(O)CH_3$	$(CH_3)_2C{=}CHCH_2Si(CH_3)_3$	92	$C_2H_5C(O)C_2H_5$	$(C_2H_5)_2C{=}CHCH_2Si(CH_3)_3$	92
$C_6H_5C(O)C_6H_5$	$(C_6H_5)_2C{=}CHCH_2Si(CH_3)_3$	95	c-C_4H_6(=O)	c-C_4H_6=$CHCH_2Si(CH_3)_3$	95
c-C_5H_8(=O)	c-C_5H_8=$CHCH_2Si(CH_3)_3$	94	c-C_6H_{10}(=O)	c-C_6H_{10}=$CHCH_2Si(CH_3)_3$	94

of **19** with electrophiles to yield allyl derivatives (**20**) as in eq 7.[8]



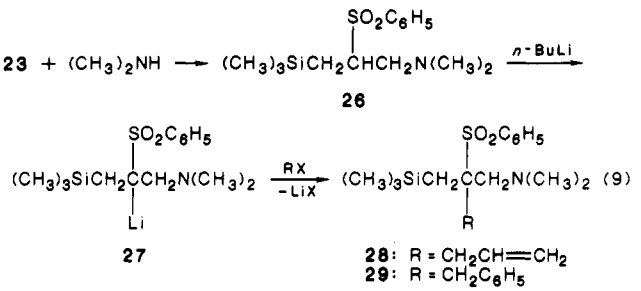
The overall results of conversion of **1** to **18** are summarized in Table II. Successful addition of **2** to benzophenone indicates that steric hindrance and conjugative stabilization in carbonyl groups do not seriously jeopardize reactions with **2**. Further, **2** is a good carbonyl-attacking nucleophile rather than a proton-abstracting base since enolizations of the cyclic and the dialkyl ketones do not occur. It is emphasized that reductive elimination of **17** is complete in less than 2 h,[6] workup is convenient, and the allylsilanes (**18**) are obtained efficiently and in analytical purity. Formation of [2-(trimethylsilyl)-ethylidene]cyclobutane in good yield reveals that reductive elimination of **17** occurs effectively to give strained allylsilanes. The present method is of further advantage in that cheap, readily available starting materials are used, the scope for synthesis is enormous, and the procedures are practical and adaptable to large-scale operation.

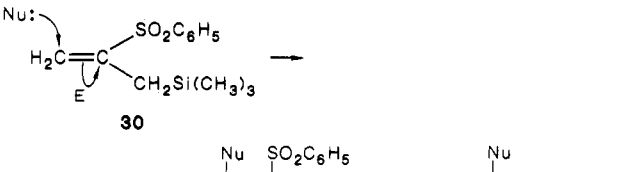
Synthesis of 2-(phenylsulfonyl)-3-(trimethylsilyl)-1-propane (**23**), a possible extremely valuable synthon, was then attempted as in eq 8a,b. Indeed, **2** condenses effectively with formaldehyde at 0 °C. The lithium 2-(phenylsulfonyl)-3-(trimethylsilyl)-1-propoxide (**21**) produced is efficiently trapped by 1 equiv of methanesulfonyl chloride to give 2-(phenylsulfonyl)-3-(trimethylsilyl)-1-propyl mesylate (**22**). All attempts, however, to eliminate **22** to 2-(phenylsulfonyl)-3-(trimethylsilyl)propene (**23**) under the following conditions were unsatisfactory: boiling triethylamine, potassium *tert*-butoxide/tetrahydrofuran at −70 to 25 °C, potassium *tert*-butoxide/dimethyl sulfoxide at 0 °C, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene or tetrahydrofuran at 25 °C.



Preparation of **23** was accomplished by the alternate sequence in eq 8b. 2-(Phenylsulfonyl)-3-(trimethylsilyl)-1-propanol (**24**) was obtained by quenching **21** with aqueous ammonium chloride. Reaction of **24** with triphenylphosphine in refluxing carbon tetrachloride affords 2-(phenylsulfonyl)-1-chloro-3-(trimethylsilyl)propane (**25**), an easily isolable solid, which is dehydrochlorinated by boiling triethylamine to **23** (93%).

Vinyl sulfone **23** is of interest as a Michael acceptor of nucleophiles to give adducts that then react with various electrophiles. Dimethylamine has thus been found to add to **23** (eq 9) to form 2-(phenylsulfonyl)-1-(*N*,*N*-dimethyl-amino)-3-(trimethylsilyl)propane (**26**, 100%). Deprotonation of **26** with *n*-butyllithium (eq 9) in tetrahydrofuran at −70 °C and then reactions of **27** with allyl bromide and benzyl bromide (eq 9) yield 4-(phenylsulfonyl)-5-(*N*,*N*-dimethylamino)-4-[(trimethylsilyl)methyl]-1-pentene (**28**, 95%) and 2-(phenylsulfonyl)-2-benzyl-1-(*N*,*N*-dimethylamino)-3-(trimethylsilyl)propane, (**29**, >94%). The overall transformations of **23** to **28** and **29** can be represented in general as via **30** to **31** (eq 10) and with the potential for





subsequent debenzenesulfonyltrimethylsilylation of **31** to **32** (eq 10) reveals the possible use of **23** as a 1-cationic-2-anionic allenic equivalent, **33**.

$$^{+}CH_2\text{–}C^{-}{=}CH_2$$

33

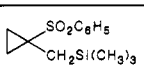
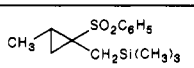
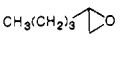
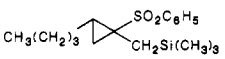
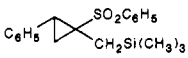
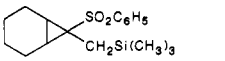
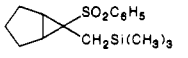
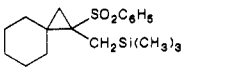
Little is known about β-trimethylsilyl ketones and their applications in synthesis.[9] In extension of earlier work

(8) For major reviews, see: (a) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: New York, 1979. (b) Utimoto, K.; Mukaiyama, T.; Saigo, K. *Kagaku no Ryoiki, Zokan* **1979**, *117*, 114; *Chem. Abstr.* **1979**, *90*, 6434. (c) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (d) Magnus, P. *Aldrichimica Acta* **1980**, *13*, 43.

Table III. Condensation of 2 with Aldehydes (Eq 5), Oxidation of 14 (R^2 = H) to 34 (Eq 11), and Debenzenesulfonylation of 34 to 35 (Eq 11)

aldehyde	34	yield, %	35	yield, %
CH_3CHO	$CH_3C(O)CH(SO_2C_6H_5)CH_2Si(CH_3)_3$	97	$CH_3C(O)(CH_2)_2Si(CH_3)_3$	90
$(CH_3)_2CHCHO$	$(CH_3)_2CHC(O)CH(SO_2C_6H_5)CH_2Si(CH_3)_3$	87	$(CH_3)_2CHC(O)(CH_2)_2Si(CH_3)_3$	88
$CH_3(CH_2)_2CHO$	$CH_3(CH_2)_2C(O)CH(SO_2C_6H_5)CH_2Si(CH_3)_3$	90	$CH_3(CH_2)_2C(O)(CH_2)_2Si(CH_3)_3$	70
$(CH_3)_2CHCH_2CHO$	$(CH_3)_2CHCH_2C(O)CH(SO_2C_6H_5)CH_2Si(CH_3)_3$	85	$(CH_3)_2CHCH_2C(O)(CH_2)_2Si(CH_3)_3$	92
c-$C_6H_{11}CHO$	c-$C_6H_{11}C(O)CH(SO_2C_6H_5)CH_2Si(CH_3)_3$	81		
C_6H_5CHO	$C_6H_5C(O)CH(SO_2C_6H_5)CH_2Si(CH_3)_3$	92		

Table IV. Conversions of 2 with Epoxides to 36 (Eq 12), Mesylates 40 (Eq 13), and Then 42 (Eq 13)

epoxides	42	yield, %	epoxides	42	yield, %
		55			75[a]
		57[a]			54[a]
		65[a]			51[a]
		45			

[a] Stereochemistry is unknown.

of this report, various aldehydes were efficiently condensed with **2** to give, after acidification, the corresponding 2-(phenylsulfonyl)-3-(trimethylsilyl)-1-propanols (**14**, R^2 = H). The secondary alcohols (**14**, R^2 = H) were then oxidized in situ by chromic oxide/sulfuric acid in acetone (Jones reagent)[10] to the corresponding α-phenylsulfonyl β-trimethylsilyl ketones (**34**) in high yields (eq 11, Table III). The α-phenylsulfonyl groups in **34** are readily removable. Thus treatment of **34** with excess sodium amalgam (6%) buffered with disodium hydrogen phosphate (4 equiv) at 0–5 °C (eq 11) results in β-trimethylsilyl ketones (**35**) in quantity and excellent purity. The results of four examples of preparation of **35** are summarized in Table III.

14, R^2 = H $\xrightarrow[H_2SO_4]{CrO_3}$ $(CH_3)_3SiCH_2C(H)(SO_2C_6H_5)C(O)CR^1$ **34** $\xrightarrow[Na_2HPO_4]{Na/Hg}$ $(CH_3)_3SiCH_2CH_2C(O)R^1$ **35** (11)

The present research then turned to further development of **2**. Addition of **2** to various epoxides takes place smoothly in ethyl ether at 20–30 °C to give adducts **36** (eq 12), acidification of which with aqueous ammonium chloride yields the corresponding 3-(phenylsulfonyl)-4-(trimethylsilyl)-1-butanols (**37**) efficiently. Reactions of **2** with unsymmetrical epoxides such as propylene oxide and styrene oxide occur regiospecifically at their (relatively unhindered) methylene positions to give, after hydrolysis, 4-(phenylsulfonyl)-5-(trimethylsilyl)-2-pentanol (**38a**, 95%) and 3-(phenylsulfonyl)-1-phenyl-4-(trimethylsilyl)-1-butanol (**38b**, 95%), respectively. Oxidation of **38a** and **38b**

2 $\xrightarrow{R_2C(O)CR_2}$ $(CH_3)_3SiCH_2CH(SO_2C_6H_5)CR_2CR_2OLi$ **36** $\xrightarrow{NH_4Cl}$ $(CH_3)_3SiCH_2CH(SO_2C_6H_5)CR_2CR_2OH$ **37** (12)

$(CH_3)_3SiCH_2CH(SO_2C_6H_5)CH(R^1)CR^2OH$ **38a**: $R^1 = CH_3$; R^2 = H; **b**: $R^1 = C_6H_5$; R^2 = H

$(CH_3)_3SiCH_2CH(SO_2C_6H_5)CH_2C(O)R^1$ **39a**: $R^1 = CH_3$; **b**: $R^1 = C_6H_5$

with Jones reagent then results in 4-(phenylsulfonyl)-5-(trimethylsilyl)-2-pentanone (**39a**, 94%) and 3-(phenylsulfonyl)-1-phenyl-4-(trimethylsilyl)-1-butanone (**39b**, 91%), respectively.

Of particular note is that adducts **36** (eq 12) are converted in situ by 1 equiv of methanesulfonyl chloride to 3-(phenylsulfonyl)-4-(trimethylsilyl)-1-butyl mesylates (**40**, eq 13). Upon addition of *n*-butyllithium (1 equiv), cyclization of **41** occurs with displacement of lithium methanesulfonate to give the corresponding 1-(phenylsulfonyl)-1-[(trimethylsilyl)methyl]cyclopropanes (**42**) in 45%–75% overall yields. Cyclopropanes **42** are easily purified, handleable, and assignable with confidence from their IR, NMR, and mass spectral and elemental analyses.

36 $\xrightarrow[-LiCl]{CH_3SO_2Cl}$ $(CH_3)_3SiCH_2CH(SO_2C_6H_5)CHR_2CR_2O_3SCH_3$ **40** $\xrightarrow[-BuH]{n\text{-}BuLi}$ $(CH_3)_3SiCH_2C(Li)(SO_2C_6H_5)CR_2CR_2O_3SCH_3$ **41** $\xrightarrow{-LiO_3SCH_3}$ **42** (13)

The scope and the success in the transformations of **2** and epoxides to **42** are summarized in Table IV. The mechanisms of ring closures of **41** to **42**, however, are as yet speculative.[11] Presumably ring closures of **41** involving displacement on primary and secondary centers are of the S_N2 type whereas that on a tertiary center involves S_N1-like processes with dipolar capture. The fact that 3-(phenylsulfonyl)-1,1-diphenyl-4-(trimethylsilyl)-1-propylmethanesulfonate is converted by *n*-butyllithium to 3-

(9) (a) Fleming, I.; Goldhill, J. *J. Chem. Soc., Chem. Commun.* **1978**, 176. (b) Fleming, I.; Goldhill, J. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1943.

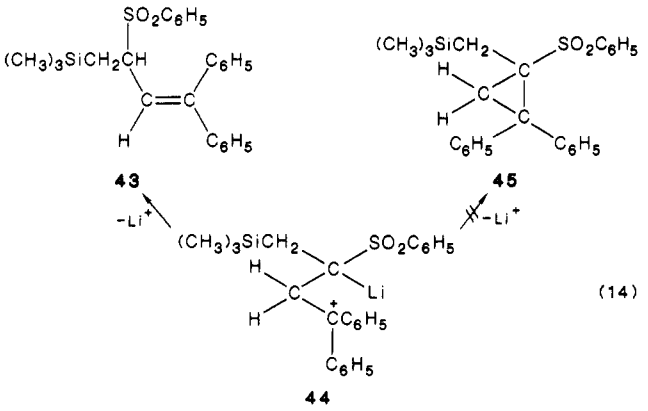
(10) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2555 and references therein.

(11) Similar cyclizations have been reported; see (a) Corbel, B.; Durst, T. *J. Org. Chem.* **1976**, *41*, 3648. (b) Gaoni, Y. *Tetrahedron Lett.* **1976**, 503; (c) Chang, Y.-H.; Pinnick, H. W. *J. Org. Chem.* **1978**, *43*, 373. (d) Gaoni, Y. *Tetrahedron Lett.* **1981**, *22*, 4339.

Table V. Chlorination of 3 via 4 to 48 (Eq 16) and Elimination of 48 to 49 (Eq 16)

3	48	yield, %	49	yield, %
$(CH_3)_3SiCH_2CH(SO_2C_6H_5)CH_2CH_3$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)CH_2CH_3$	95	$H_2C{=}C(SO_2C_6H_5)CH_2CH_3$	>99
$(CH_3)_3SiCH_2CH(SO_2C_6H_5)(CH_2)_3CH_3$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)(CH_2)_3CH_3$	93	$H_2C{=}C(SO_2C_6H_5)(CH_2)_3CH_3$	>99
$(CH_3)_3SiCH_2CH(SO_2C_6H_5)(CH_2)_5CH_3$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)(CH_2)_5CH_3$	92	$H_2C{=}C(SO_2C_6H_5)(CH_2)_5CH_3$	>99
$(CH_3)_3SiCH_2CH(SO_2C_6H_5)(CH_2)_2C(CH_3)_3$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)(CH_2)_2C(CH_3)_3$	89	$H_2C{=}C(SO_2C_6H_5)(CH_2)_2C(CH_3)_3$	>99
$(CH_3)_3SiCH_2CH(SO_2C_6H_5)CH_2CH{=}CH_2$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)CH_2CH{=}CH_2$	96	$H_2C{=}C(SO_2C_6H_5)CH_2CH{=}CH_2$	>99
$(CH_3)_3SiCH_2CH(SO_2C_6H_5)CH_2C_6H_5$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)CH_2C_6H_5$	90	$H_2C{=}C(SO_2C_6H_5)CH_2C_6H_5$	>99

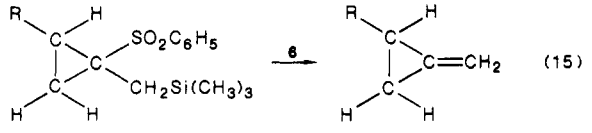
(phenylsulfonyl)-1,1-diphenyl-4-(trimethylsilyl)-1-butene (**43**, eq 14) rather than to 1-(phenylsulfonyl)-2,2-di-



43 **45** **44** (14)

phenyl-1-[(trimethylsilyl)methyl]cyclopropane (**45**) presumably means that loss of lithium ion from **44** and then rearrangement (eq 14) occur faster than does ring closure.

As has been previously summarized, elimination of varied α-phenylsulfonyl-β-trimethylsilyl derivatives is an excellent olefin synthesis. Analogously, reactions of 1-(phenylsulfonyl)-2-*n*-hexyl-1-[(trimethylsilyl)methyl]-cyclopropane (**46a**) and 1-(phenylsulfonyl)-2-phenyl-1-[(trimethylsilyl)methyl]cyclopropane (**46b**) with **6** (eq 15)

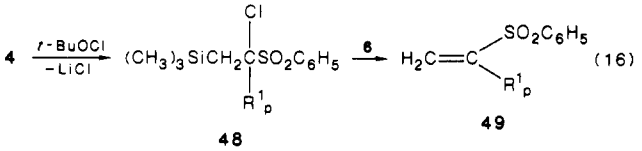


46 **47** (15)

46a: R = C_6H_{13} **47a**: R = C_6H_{13}, 96%
b: R = C_6H_5 **b**: R = C_6H_5, 95%

occur smoothly in tetrahydrofuran at 65 °C to give 1-*n*-hexyl-2-methylenecyclopropane (**47a**, 96%) and 1-methylene-2-phenylcyclopropane (**47b**, 95%). Unfortunately, elimination of **46** to **47** is not preparatively general. Complex mixtures are obtained from reactions of **6** with 6-(phenylsulfonyl)-6-[(trimethylsilyl)methyl]bicyclo-[3.1.0]hexane, 7-(phenylsulfonyl)-7-[(trimethylsilyl)-methyl]bicyclo[4.1.0]heptane, and 1-(phenylsulfonyl)-1-[(trimethylsilyl)methyl]spiro[2.5]octane, respectively, which have not been resolved.

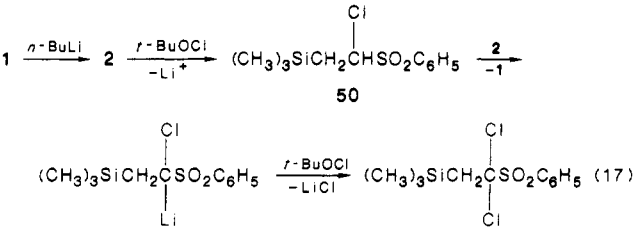
Preparation of 2-(phenylsulfonyl)-1-alkenes (1-alkylvinyl phenyl sulfones, **49**)[12] from the now readily available 2-(phenylsulfonyl)-1-(trimethylsilyl)alkanes (**3**) then became of interest.[13] An efficient synthesis of **49** was first developed (eq 16) that involved reaction of **3** with *tert*-butyl



48 **49** (16)

hypochlorite and elimination of chlorotrimethylsilane from the resulting 2-(phenylsulfonyl)-2-chloro-1-(trimethylsilyl)alkanes (**48**) with **6**. The preparative results are summarized in Table V.

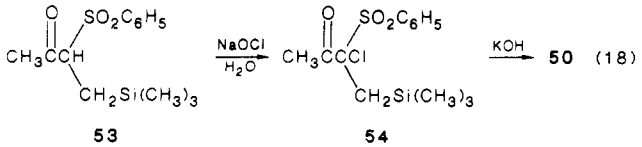
Because of its potential in synthesis, 1-(phenylsulfonyl)-1-chloro-2-trimethylsilane (**50**), the parent homologue of **48**, became a research objective. Deprotonation of **1** with *n*-butyllithium and then chlorination of **2** with *tert*-butyl hypochlorite under various conditions always gave mixtures of **50**, **1**, and 1-(phenylsulfonyl)-1,1-dichloro-2-trimethylsilane (**52**), however. Formation of **1** and **52** in the chlorination system has its origins in the acidity of **50**. Thus proton exchange between **2** and initially formed **50** lead to 1-(phenylsulfonyl)-1-chloro-1-lithio-2-(trimethylsilyl)ethane (**51**) with regeneration of **1** (eq 17).



50 **51** **52** (17)

Reaction of **51** with *tert*-butyl hypochlorite then yields **52** (eq 17). All efforts to alter chlorination of **2** so that **50** is formed advantageously for preparative purposes failed.

An effective synthesis of **50** was then developed (eq 18) involving conversion of 1-acetyl-1-(phenylsulfonyl)-2-(trimethylsilyl)ethane (**52**) with aqueous sodium hypochlorite (5.25%) to 3-(phenylsulfonyl)-3-chloro-4-(trimethylsilyl)-2-butanone (**54**) and then base-catalyzed cleavage of the **54** generated. Thus, treatment of **53** with



53 **54** (18)

(12) Vinyl sulfones (**49**) are of interest because of their addition reactions[12a-f] and the chemistry about their sulfone moieties:[12g-l] (a) Posner, G. H.; Brunelle, D. J. *J. Org. Chem.* **1973**, *38*, 2747. (b) Posner, G. H.; Brunelle, D. J. *Tetrahedron Lett.* **1973**, 935. (c) Fiandanese, V.; Marchese, G.; Naso, F. *Ibid.* **1978**, 5131. (d) Conrad, P. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 346. (e) Chirico, G. D.; Fiandanese, V.; Marchese, G.; Naso, F.; Sciacovelli, O. *J. Chem. Soc., Chem. Commun.* **1981**, 523. (f) Taber, D. F.; Saleh, S. A. *J. Org. Chem.* **1981**, *46*, 4819. (g) Field, L. *Synthesis* **1978**, 713. (h) Grobel, B.-T.; Seebach, D. *Ibid.* **1977**, 357. (i) Trost, B. M. *Acc. Chem. Res.* **1978**, *11*, 453. (j) Magnus, P. *Tetrahedron Lett.* **1977**, *33*, 2019. (k) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979. (l) Julia, M.; Launay, M.; Stacino, J. P.; Verpeaux, J. N. *Tetrahedron Lett.* **1982**, *23*, 2465. (m) Fabre, L. L.; Julia, M.; Verpeaux, J. N. *Ibid.* **1982**, *23*, 2469.

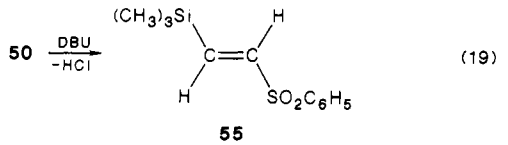
(13) (a) 1-Alkenyl aryl sulfones (RCH=CHSO$_2$Ar) and methyllithium give α-lithio derivatives (RCH=CLiSO$_2$Ar) at −95 °C, which react well with alkyl iodides, ketones, and chlorotrimethylsilane, etc. The method does not work, however, for vinyl sulfones (**49**) because of their rapid polymerization by alkyllithium reagents.[13b] (b) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3279. (c) Partial solutions reported for synthesis of **49** are: (1) lithiation and monoalkylation of 1-(phenylsulfonyl)-2-(dimethylamino)ethane (prepared from dimethylamine and phenyl vinyl sulfone), quaternization with methyl iodide, and Hofmann elimination with sodium hydroxide[13d] and (2) condensation of formaldehyde with salts of 1-benzoyl-1-alkyl phenyl sulfones, benzoyl transfer, and then benzoate elimination.[13e] (d) Kotake, H.; Inomata, K.; Sumita, M. *Chem. Lett.* **1978**, 717. (e) Ueno, Y.; Setoi, H.; Okawara, M. *Ibid.* **1979**, 47.

Table VI. Chlorinations of 34 to 56 (Eq 21)

56	yield, %	56	yield, %
$CH_3C(O)CCl(SO_2C_6H_5)CH_2Si(CH_3)_3$	82	$CH_3(CH_2)_2C(O)CCl(SO_2C_6H_5)CH_2Si(CH_3)_3$	88
$(CH_3)_2CHC(O)CCl(SO_2C_6H_5)CH_2Si(CH_3)_3$	84	$(CH_3)_2CHCH_2C(O)CCl(SO_2C_6H_5)CH_2Si(CH_3)_3$	87
$C_6H_5C(O)CCl(SO_2C_6H_5)CH_2Si(CH_3)_3$	92		

Chlorox and excess potassium hydroxide gives **50** in 85% yield. The sequence of **50** is rapid, usable on large scale, and highly recommended.

Chloro silyl sulfone **50** was then evaluated for synthesis. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was thus found to effect dehydrochlorination of **50** to *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethene (**55**, eq 19; ~100%) at



(19)

55

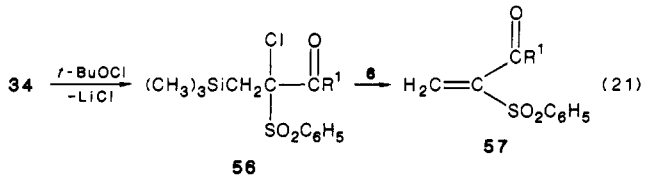
25–30 °C in tetrahydrofuran. Silylsulfonylethene **55** has been prepared previously[14] and used as an acetylene equivalent upon cycloaddition with 1,3-dienes and fluoride ion induced elimination of the trimethylsilyl and phenylsulfonyl groups in the cycloadducts.[14c] The present synthesis of **55** is practical.

Of further utility in synthesis is that deprotonation of **50** with *n*-butyllithium (1 equiv) occurs quantitatively in ethyl ether at −70 °C to give **51** (eq 17). Lithio reagent **51** can be stored for at least 5 h without change at −70 °C but decomposes on warming to room temperature. In the presence of added HMPA, **51** is alkylated elegantly by primary halides such as 1-bromobutane, 1-iodohexane, allyl bromide, benzyl bromide, and methyl chloromethyl ether to give **48** (eq 20). Displacements do not occur satisfac-

$$\mathbf{51} \xrightarrow{R_p\text{-}X} \mathbf{48} \qquad (20)$$

torily however with secondary halides. The sulfonylchloro(trimethylsilyl)alkanes (**48**) presently obtained are eliminated, as expected, to pure **49** by fluoride ion (**6**, eq 16) in impressive yields. The overall yields for conversions of **51** to **49** range from 90% to 95%. When synthesis of more than one **49** in a series is an objective, the methodology of eq 20 for preparing **48** is preferable to that of eq 16 because by use of **51** as a general reagent the number of different chlorinations is kept minimal.

Study was then extended to base-catalyzed chlorination of homologous α-phenylsulfonyl β-trimethylsilyl ketones (**34**) and elimination of the subsequent alkyl 1-(phenylsulfonyl)-1-chloro-2-(trimethylsilyl)ethyl ketones (**56**) to 2-(phenylsulfonyl)-1-alken-3-ones (**57**, eq 21). Indeed,

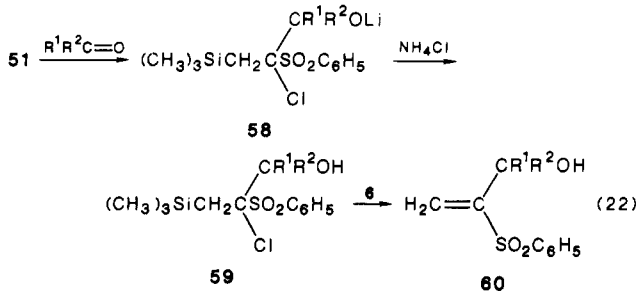


(21)

56 **57**

addition of catalytic quantities of Triton B (40% solution in methanol) to **34** and *tert*-butyl hypochlorite in methylene chloride yields the corresponding α-phenylsulfonyl α-chloro-β-trimethylsilyl ketones (**56**) preparatively as summarized in Table VI. Reaction of 2-(phenylsulfonyl)-2-chloro-1-(trimethylsilyl)-3-hexanone (**56**, R^1 = *n*-Pr) with **6** (eq 21), however, under a variety of conditions gives high molecular weight products. 2-(Phenylsulfonyl)-1-hexen-3-one (**57**, R^1 = *n*-Pr) was not isolated, apparently because of the rapidity of its Michael polymerization. Capture of **57** (R^1 = *n*-Pr) upon generation has not been investigated.

The utility of **51** in reactions other than alkylation and halogenation was then studied. Additions of **51** to the carbonyl groups of the aldehydes: butyraldehyde, isobutyraldehyde, cyclohexanecarboxaldehyde, benzaldehyde, and acrolein take place rapidly (eq 22) in ethyl ether



(22)

(HMPA is unnecessary) to give, after hydrolysis, the corresponding 2-(phenylsulfonyl)-2-chloro-3-(trimethylsilyl)-1-propanols (**59**, R^1 = H) in excellent yields and purities. Alcohols **59** (R^1 = H) are then eliminated efficiently by **6** to 2-(phenylsulfonyl)allyl alcohols (**60**, R^1 = H). Table VII reveals typical results for conversions of **51** to **60** as in eq 22. The present method is thus a valuable addition to previous routes for synthesis of **60**.[13,15]

Simple ketones such as acetone, 2-butanone, cyclohexanone, and cyclobutanone (eq 22) condense satisfactorily with **51**, albeit the rates of addition are slow as compared to aldehydes. Complete addition of **51** to acetone to give **58** (R^1 and R^2 = CH_3) occurs in 3 h. Quenching **58** (R^1 and R^2 = CH_3) with aqueous ammonium chloride at −70 °C gives 3-(phenylsulfonyl)-3-chloro-2-methyl-4-(trimethylsilyl)-2-butanol (**59**, R^1 and R^2 = CH_3) in 95% yield. Similar results are obtained with the other ketones studied (Table VII).

Of further note is that, if the adduct (**59**, R^1 and R^2 = CH_3) from **51** and acetone is warmed to 0 °C and the mixture then neutralized, **50** and acetone are obtained in quantity. Further, warming the reaction product to 0 °C, recooling the mixture to −80 °C, and then neutralization with ammonium chloride lead totally to **50** and acetone. Thus, addition of **51** to acetone takes place slowly but completely at −70 °C. At 0 °C, however, the initial adduct (**59**, R_1 and R_2 = CH_3) collapses essentially completely, and **50** and acetone are the products of neutralization. Consistent with the above interpretation is that condensation of **51** with 2-butanone is only 85% complete at −70 °C (15% of 2-butanone was recovered), and 3-pentanone does not react with **51** to give a detectable adduct. The efficiencies of reactions of other metallo analogues of **51** with ketones have not yet been investigated.

Eliminations of tertiary alcohols **59** (eq 22) by fluoride ion (**6**) to their 2-(phenylsulfonyl)-*tert*-allylic alcohols (**60**) were then attempted. 3-Chloro-3-(phenylsulfonyl)-2-

(14) (a) Pillot, J. P.; Dunogues, J.; Calas, R. *Synthesis* **1977**, 469. (b) Bhattacharya, S. N.; Josiah, B. M.; Walton, D. R. M. *Organomet. Chem. Synth.* **1970/71**, *1*, 145. (c) Paquette, L. A.; William, R. V. *Tetrahedron Lett.* **1981**, *22*, 4643.

(15) The reactions of various nucleophiles with mesylates of **60** are being studied.

Table VII. Conversions of 51 with Aldehydes and Ketones to 59 (Eq 22) and Elimination of 59 to 60 (Eq 22)

$R_2C{=}O$	59	yield, %	60	yield, %
$CH_3(CH_2)_2CHO$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)CH(OH)(CH_2)_2CH_3$		$H_2C{=}C(SO_2C_6H_5)CH(OH)(CH_2)_2CH_3$	95
$(CH_3)_2CHCHO$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)CH(OH)CH(CH_3)_2$		$H_2C{=}C(SO_2C_6H_5)CH(OH)CH(CH_3)_2$	92
c-$C_6H_{11}CHO$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)CH(OH)C_6H_{11}$-c		$H_2C{=}C(SO_2C_6H_5)CH(OH)C_6H_{11}$-c	95
$H_2C{=}CHCHO$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)CH(OH)CH{=}CH_2$		$H_2C{=}C(SO_2C_6H_5)CH(OH)CH{=}CH_2$	94
C_6H_5CHO	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)CH(OH)C_6H_5$		$H_2C{=}C(SO_2C_6H_5)CH(OH)C_6H_5$	90
$CH_3C(O)CH_3$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)C(OH)(CH_3)_2$	95	$H_2C{=}C(SO_2C_6H_5)C(OH)(CH_3)_2$	91
$CH_3C(O)C_2H_5$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)C(OH)(CH_3)C_2H_5$	85		
$C_2H_5C(O)C_2H_5$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)C(OH)(C_2H_5)_2$	90		
c-$C_6H_{10}(=O)$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)$-c-$C_6H_{10}$(1-OH)	93		
c-$C_4H_6(=O)$	$(CH_3)_3SiCH_2CCl(SO_2C_6H_5)$-c-$C_4H_6$(1-OH)	93		

methyl-4-(trimethylsilyl)-2-butanol (**59**; R^1 and $R^2 = CH_3$) is converted efficiently (91%) by **6** to 3-(phenylsulfonyl)-2-methyl-3-buten-2-ol (**60**; R^1 and $R^2 = CH_3$). The elimination method does not work well with other tertiary alcohols (Table VII) available from condensation of **51** with ketones. Complex mixtures are obtained, and the problem deserves further investigation.

Further study of **1** and **10** and their homologues, analogues, and derivatives is in progress.

Experimental Section[16]

Typical Procedure A for Alkylation of 1-(Phenylsulfonyl)-2-(trimethylsilyl)ethane (1, Eq 1). (a) 4-(Phenylsulfonyl)-5-(trimethylsilyl)-1-pentene.[16] *n*-Butyllithium (27 mL, 1.7 M in hexane, 45.9 mmol) was syringed into a suspension of **1** (10 g, 41.3 mmol)[2b] in anhydrous ethyl ether (70 ml) at −70 °C. The white suspension changed immediately to a light yellow solution. After the mixture had been stirred 25 min, allyl bromide (6.0 g, 49.6 mmol) was added. The mixture was warmed to room temperature and stirred overnight while lithium bromide precipitated. The suspension was diluted with ethyl ether, washed with aqueous sodium chloride, dried ($MgSO_4$), filtered, and evaporated. The pale yellow residue was passed through a silica gel column and eluted with hexane and then with methylene chloride. After evaporation, 4-(phenylsulfonyl)-5-(trimethylsilyl)-1-pentene (11.2 g, 96%) was obtained as a colorless oil, which crystallized completely on standing: mp 41 °C; ^{1}H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 0.55–1.25 (m, 2 H, $(CH_3)_3SiCH_2$), 2.10–2.45 (m, 2 H, allylic), 2.70–3.10 (m, 5 H, aromatic). Anal. Calcd for $C_{14}H_{22}SO_2Si$: C, 59.57; H, 7.80. Found: C, 59.61; H, 7.78.

(b) 2-(Phenylsulfonyl)-1-(trimethylsilyl)butane. From **2** and bromoethane: a colorless oil (95%); ^{1}H NMR (CCl_4) δ −0.05 (s, 9 H, $Si(CH_3)_3$), 0.85 (t, 3 H, J = 6 Hz, CH_3), 0.50–1.50 (m, 4 H, two methylene), 2.70 (m, 1 H, methine), 7.45 (m, 3 H, aromatic), and 7.70 (m, 2 H, aromatic); exact mass calcd for $C_{13}H_{22}SO_2Si$ (M^+) 270.0477, found 270.0484.

(c) 2-(Phenylsulfonyl)-1-(trimethylsilyl)hexane. From **2** and 1-bromobutane: a colorless oil (93%); ^{1}H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.65–1.80 (m, 11 H, aliphatic chain and $(CH_3)_3SiCH_2$), 2.85 (m, 1 H, methine), 7.55 (m, 3 H, aromatic), and 7.85 (m, 2 H, aromatic); exact mass calcd for $C_{15}H_{26}SO_2Si$ 298.0148, found 298.01490. Anal. Calcd for $C_{15}H_{26}SO_2Si$: C, 60.39; H, 8.72; S, 10.73. Found: C, 60.28; H, 8.82; S, 10.62.

(d) 2-(Phenylsulfonyl)-1-(trimethylsilyl)octane. From **2** and 1-iodohexane: a colorless oil (97%); ^{1}H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.50–1.85 (m, 15 H, $(CH_3)_3SiCH_2$ and chain), 2.90 (m, 1 H, methine), 7.60 (m, 3 H, aromatic), and 7.90 (m, 2 H, aromatic); exact mass calcd for $C_{16}H_{27}SO_2Si$ ($M^+ - CH_3$) 311.0477, found 311.0484.

(e) 2-(Phenylsulfonyl)-5,5-dimethyl-1-(trimethylsilyl)-hexane. From **2** and 1-bromo-3,3-dimethylbutane in the presence of HMPA: white crystals (89%); mp 38 °C; ^{1}H NMR (CCl_4) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 0.90 (s, 9 H, *tert*-butyl), 0.6–1.75 (m, 6 H, three methylenes), 2.85 (m, 1 H, methine), 7.60 (m, 3 H, aromatic), and 7.85 (m, 2 H, aromatic). Anal. Calcd for $C_{17}H_{30}SO_2Si$: C, 62.57; H, 9.20; S, 9.81. Found: C, 62.83; H, 9.44; S, 9.69.

(f) 2-(Phenylsulfonyl)-1-phenyl-3-(trimethylsilyl)propane. From **2** and benzyl bromide: white crystals (90%); mp 62–63 °C; ^{1}H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 0.60–1.60 (m, 2 H, $(CH_3)_3SiCH_2$), 2.35–3.50 (m, 3 H, benzylic and methine), 7.15 (m, 5 H, aromatic), 7.60 (m, 3 H, aromatic), and 7.95 (m, 2 H, aromatic). Anal. Calcd for $C_{18}H_{24}SO_2Si$: C, 65.06; H, 7.23. Found: C, 64.85; H, 7.23.

(g) 1-(Phenylsulfonyl)-1,2-bis(trimethylsilyl)ethane. From **2** and chlorotrimethylsilane: mp 82 °C (from petroleum ether, 35–60 °C); ^{1}H NMR (CCl_4) δ −0.20 (s, 9 H, $Si(CH_3)_3$, 0.30 (s, 9 H, $Si(CH_3)_3$), 1.05 (m, 2 H, CH_2), 2.65 (t, 1 H, J = 6 Hz, methine), and 7.45–8.05 (m, 5 H, aromatic); exact mass calcd for $C_{13}H_{23}O_2Si_2S(M^+ - CH_3)$ 299.0957, found 299.0971.

General Procedure B for Fluoride-Induced Elimination of Monoalkylated 1-(Phenylsulfonyl)-2-(trimethylsilyl)-ethanes (3, Eq 1 and 2). (a) 1-Octene. Tetra-*n*-butylammonium fluoride (**6**, 6.0 mL, 1 M solution in THF, 6.0 mmol) was added to 2-(phenylsulfonyl)-1-(trimethylsilyl)octane (1.0 g, 3.0 mmol) in dry tetrahydrofuran (10 mL). The mixture was refluxed for 40 min, cooled, diluted with pentane, washed with water and saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and passed through silica gel. After evaporation of the solvent, 1-octene (0.32 g, 92%) was obtained as a colorless oil whose IR and ^{1}H NMR spectra are identical with those of an authentic sample.

(b) 5,5-Dimethyl-1-hexene. From 2-(phenylsulfonyl)-5,5-dimethyl-1-(trimethylsilyl)hexane: a colorless oil (84%); ^{1}H NMR (CCl_4) δ 0.85 (s, 9 H, *tert*-butyl), 1.05–2.10 (m, 4 H, CH_2CH_2), 4.80–6.10 (m, 3 H, allyl); exact mass calcd for C_8H_{16} (M^+) 112.0147, found 112.0141.[17]

(c) Allylbenzene. From 2-(phenylsulfonyl)-1-phenyl-3-(trimethylsilyl)propane, a colorless liquid (85%), identical with an authentic sample.

General Procedure C for Alkylation of 2-(Phenylsulfonyl)-1-(trimethylsilyl)alkanes (3) and Subsequent Fluoride-Induced Elimination of 5 (Eq 1 and 3). (a) 2-(1-Butyl)-1-hexene. *n*-Butyllithium (2.6 mL, 1.614 M solution in hexane, 4.16 mmol) was syringed into 2-(phenylsulfonyl)-1-(trimethylsilyl)hexane (1.0 g, 3.35 mmol) in anhydrous ethyl ether (10 mL) at −70 °C. The colorless solution turned yellow immediately and was stirred at −70 °C for 25 min. *n*-Butyl bromide (1.0 g, 7.3 mmol) was then added followed by HMPA (2.5 mL). The mixture was warmed to room temperature, stirred overnight, diluted with ethyl ether, and washed with water. The ether extract was dried ($MgSO_4$), filtered, evaporated, and then passed through a silica gel column while eluted with hexane and then with methylene chloride. Evaporation yielded 5-(phenylsulfonyl)-5-[(trimethylsilyl)methyl]nonane (1.08 g, 91%), a colorless oil, which was dissolved in anhydrous tetrahydrofuran (10 mL), refluxed (1 h) with **6** (10 mL, 1 M solution in THF, 10 mmol), cooled, diluted with pentane, and washed with water. The pentane extract was passed through silica gel (10 cm). Evaporation gave 2-(1-butyl)-1-hexene (0.34 g, 80%),[17] a colorless liquid: ^{1}H NMR (CCl_4) δ 0.70–1.60 (m, 14 H, chains), 1.95 (m, 4 H, allylic), and 4.60 (br s, 2 H, vinylic); exact mass calcd for $C_{10}H_{20}$ (M^+) 140.1154, found 140.1158.

(b) 2-(3,3-Dimethyl-1-butyl)-1,4-pentadiene. From 4-(phenylsulfonyl)-7,7-dimethyl-4-[(trimethylsilyl)methyl]-1-octene

(16) All new compounds presently reported are satisfactorily pure as evidenced by thin-layer, column, high-pressure liquid, or gas chromatography, respectively, and give proper exact masses and IR and NMR spectra. Essentially, all products that are crystalline and stable to shipment were subjected to elemental analysis. The IR spectra of all compounds prepared are recorded in the dissertation of C.-N. Hsiao.[3]

(17) ASTM Special Technical Publication No. 109A, *Physical Constants of Hydrocarbons C_1 to C_{10}*; American Society for Testing and Materials: Philadelphia, PA, 1963.

(76%), as prepared by alkylation of 4-(phenylsulfonyl)-5,5-dimethyl-1-(trimethylsilyl)hexane: a colorless liquid; ^{1}H NMR (CCl_4) δ 0.90 (s, 9 H, *tert*-butyl), 1.05–2.15 (m, 4 H, CH_2CH_2), 2.75 (br d, 2 H, C=CCH_2C=C), 4.70 (br s, 2 H, vinylic), 4.75–6.05 (m, 3 H, allyl group); exact mass calcd for $C_{11}H_{20}$ (M^+) 152.0016, found 152.0017.

(c) 2-Ethyl-3-phenylpropene. From 2-(phenylsulfonyl)-1-phenyl-2-[(trimethylsilyl)methyl]butane (93%), as prepared by alkylation of 2-(phenylsulfonyl)-1-(trimethylsilyl)butane with benzyl bromide: a colorless oil; ^{1}H NMR (CCl_4) δ 1.05 (t, 3 H, J = 6 Hz, CH_3), 2.00 (br q, 2 H, J = 6 Hz, CH_3CH_2), 3.35 (br s, 2 H, benzylic), 4.75 (m, 2 H, vinylic), and 7.10 (br s, 5 H, aromatic); exact mass calcd for $C_{11}H_{14}$ (M^+) 146.1185, found 146.1177.

General Procedure D for Synthesis of Allylsilanes (18; Eq 5 and 6). (a) [2-(Trimethylsilyl)ethylidene]cyclopentane. General procedure D used for synthesis of allylsilanes **18** is described in detail for preparation of [2-(trimethylsilyl)-ethylidene]cyclopentane in reference 2b: ^{1}H NMR (CCl_4) δ –0.06 (s, 9 H, $Si(CH_3)_3$), 1.29 (br d, 2 H, $(CH_3)_3SiCH_2$), 1.59 (m, 4 H, ring), 2.09 (m, 4 H, ring allylic), and 5.19 (br, 1 H, vinylic); exact mass calcd for $C_{10}H_{20}Si$ (M^+) 168.1334, found 168.1338.

(b) (*E*)- and (*Z*)-5-Methyl-1-(trimethylsilyl)-2,4-pentadienes. From β,β-dimethylacrolein and **2** via procedure D: a colorless liquid (85%); ^{1}H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$, 1.69 (m, 8 H, allylic), and 5.70 (m, 3 H, vinylic); exact mass calcd for $C_{10}H_{20}Si$ (M^+) 168.1334, found 168.1338.

(c) (*E*)- and (*Z*)-1-Phenyl-3-(trimethylsilyl)-1-propenes. From benzaldehyde and **2** via procedure D: a colorless liquid (92%); ^{1}H NMR (CCl_4) δ 0.20 (s, 9 H, $Si(CH_3)_3$), 1.90 (m, 2 H, allylic), 6.27 (m, 2 H, vinylic), 7.30 (m, 5 H, aromatic); exact mass calcd for $C_{12}H_{18}Si$ (M^+) 190.1177, found 190.1183.

(d) 3-Methyl-1-(trimethylsilyl)-2-butene. By condensation of **2** with acetone, methanesulfonylation, and reductive elimination: a colorless liquid; bp 133–134 °C (760 mmHg) [lit.[7c] bp 135 °C (753 mmHg)]; ^{1}H NMR (CCl_4) δ 0.03 (s, 9 H, $Si(CH_3)_3$), 1.39 (br d, 2 H, $(CH_3)_3SiCH_2$), 1.55 (br s, 3 H, CH_3), 1.72 (br s, 3 H, CH_3), and 5.09 (br t, 1 H, vinylic); exact mass calcd for $C_8H_{18}Si$ (M^+) 142.1177, found 142.1182.

(e) 3-Ethyl-1-(trimethylsilyl)-2-pentene. Upon condensation of diethyl ketone with **2** (procedure D): a colorless liquid (92%, purity over 98% by GC); ^{1}H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.97 (m, 6 H, two allylic CH_3), 1.50 (m, 2 H, $(CH_3)_3SiCH_2$), 2.01 (br q, 4 H, allylic), and 5.05 (br t, 1 H, vinylic); exact mass calcd for $C_{10}H_{22}Si$ (M^+) 170.1490, found 170.1496.

(f) [2-(Trimethylsilyl)ethylidene]cyclohexane. By extension of procedure D to the product of condensation of cyclohexanone with **2**: a colorless liquid (94%, purity over 98% by GC); ^{1}H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.38 (d, 2 H, $(CH_3)_3SiCH_2$), 1.53 (m, 6 H, ring), 2.04 (m, 4 H, ring allylic), and 5.04 (br t, 1 H, vinylic); the NMR spectrum is identical with literature data;[7b] exact mass calcd for $C_{11}H_{22}Si$ (M^+) 182.1490, found 182.1496.

(g) [2-(Trimethylsilyl)ethylidene]cyclobutane. From **2** and cyclobutanone (procedure D): a colorless liquid (95%) of >98% purity by GC (SE-30, 15%, 10 ft, 125 °C); ^{1}H NMR (CCl_4) δ –0.06 (s, 9 H, $Si(CH_3)_3$), 1.14 (br d, 2 H, $(CH_3)_3SiCH_2$), 1.84 (m, 2 H, ring), 2.54 (br q, 4 H, ring allylic), and 4.94 (br t, 1 H, vinylic); exact mass calcd for $C_9H_{18}Si$ (M^+) 154.1177, found 154.1181.

(h) 1,1-Diphenyl-3-(trimethylsilyl)-1-propene. From benzophenone and **2** (procedure D): a colorless oil (95%); ^{1}H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.65 (d, 2 H, J = 6 Hz, $(CH_3)_3SiCH_2$), 6.10 (t, 1 H, J = 6 Hz, vinylic), and 7.25 (m, 10 H, aromatic); exact mass calcd for $C_{18}H_{22}Si$ (M^+) 266.0798, found 266.0807.

2-(Phenylsulfonyl)-3-(trimethylsilyl)-1-propanol (24; Eq 8a,b). Gaseous formaldehyde was passed at –10 °C into a solution prepared from **2** (10 g, 41.3 mmol) and *n*-butyllithium (27 mL, 1.55 M solution in hexane, 42 mmol) in ethyl ether (100 mL). After the mixture had been warmed to 0 °C, stirred for 15 min, and diluted with ethyl ether, aqueous ammonium chloride was added. Workup yielded **24** (11.0 g, 98%) as a colorless oil: ^{1}H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.90 (m, 2 H, $(CH_3)_3SiCH_2$), 2.95 (m, 2 H, methine and alcoholic), 4.75 (m, 2 H, $HOCH_2$), and 7.55–8.05 (m, 5 H, aromatic); exact mass calcd for $C_{11}H_{17}O_3SiS$ ($M^+ - CH_3$) 257.0667, found 257.0674.

2-(Phenylsulfonyl)-1-chloro-3-(trimethylsilyl)propane (25; Eq 8b). A solution of **24** (9.10 g, 33.4 mmol) and triphenylphosphine (11.4 g, 43.5 mmol) in carbon tetrachloride (100 mL) was refluxed overnight, cooled, and vacuum evaporated. The residue was suspended with a mixture of ethyl ether and hexane (2:1) and filtered through silica gel. Evaporation yielded **25** (7.29 g, 75%) as a colorless oil which crystallized completely on standing: mp 89–90 °C (from ethyl ether); ^{1}H NMR (CCl_4) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 0.65–1.55 (m, 2 H, $(CH_3)_3SiCH_2$), 3.15 (center of a symmetrical multiplet of 8 peaks, 1 H, methine), 3.70 (d, 2 H, J = 6 Hz, $ClCH_2$), and 7.40–8.00 (m, 5 H, aromatic). Anal. Calcd for $C_{12}H_{19}SO_2SiCl$: C, 49.57; H, 6.54. Found: C, 49.94; H, 6.66.

2-(Phenylsulfonyl)-3-(trimethylsilyl)-1-propene (23, Eq 8b). A solution of **25** (7.08 g, 24.1 mmol) in triethylamine (100 mL) was refluxed overnight and then vacuum evaporated. The residue was suspended in ethyl ether, filtered, extracted with 5% hydrochloric acid and with saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and then filtered through neutral alumina. Evaporation yielded **23** (5.7 g, 93%) as a colorless oil: ^{1}H NMR (CCl_4) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 1.70 (d, 2 H, J = 1.5 Hz, allylic), 5.50 (t, 1 H, J = 1.5 Hz, vinylic), 6.10 (s, 1 H, vinylic), and 7.40–8.00 (m, 5 H, aromatic). Anal. Calcd for $C_{12}H_{18}SO_2Si$: C, 56.69; H, 7.08; S, 12.60. Found: C, 56.82; H, 7.25; S, 12.53.

2-(Phenylsulfonyl)-1-(*N*,*N*-dimethylamino)-3-(trimethylsilyl)propane (26; Eq 9). Dimethylamine (15 mL) was added to **23** (3.0 g, 11.8 mmol) in anhydrous ethyl ether (10 mL). The mixture was stirred overnight and concentrated under vacuum. The residue was diluted with methylene chloride and ethyl acetate, passed through silica gel, and evaporated to **26** (3.54 g, 100%): a light yellow oil; ^{1}H NMR (CCl_4) δ 0.15 (s, 9 H, $Si(CH_3)_3$), 0.60–1.55 [m, 2 H, $(CH_3)_3SiCH_2$], 2.05 (s, 6 H, $(CH_3)_2N$), 2.05–2.75 (m, 2 H, $(CH_3)_2NCH_2$), 3.05 (m, 1 H, methine), and 7.60–7.95 (m, 5 H, aromatic); exact mass calcd for $C_{14}H_{25}SO_2NSi$ (M^+) 299.1375, found 299.1383.

4-(Phenylsulfonyl)-5-(*N*,*N*-dimethylamino)-4-[(trimethylsilyl)methyl]-1-pentene (28; Eq 9). *n*-Butyllithium (2.5 mL, 1.7 M in hexane, 4.25 mmol) was syringed into **26** (1.0 g, 3.34 mmol) in dry tetrahydrofuran (20 mL) at –70 °C. After having been stirred 20 min, the orange solution changed to a yellow suspension. Allyl bromide (1.0 g, 8.26 mmol) was added followed by HMPA (2.5 mL). The mixture was warmed to 0 °C (15 min), quenched with water, diluted with ethyl ether, and worked up to give **28** (1.07 g, 95%) as a light yellow oil: ^{1}H NMR (CCl_4) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 1.15 (m, 2 H, $(CH_3)_3SiCH_2$), 2.15 (s, 6 H, $(CH_3)_2N$), 2.40 (d, 2 H, J = 6 Hz, allylic), 2.60 (s, 2 H, $(CH_3)_2NCH_2$), 4.80–6.05 (m, 3 H, vinylic), and 7.40–7.95 (m, 5 H, aromatic); exact mass calcd for $C_{17}H_{29}SO_2NSi$ (M^+) 339.0677, found 339.0671.

2-(Phenylsulfonyl)-2-benzyl-1-(*N*,*N*-dimethylamino)-3-(trimethylsilyl)propane (29; Eq 9). Benzyl bromide (0.44 g, 2.60 mmol) and then HMPA (1.0 mL) were added to a mixture of *n*-butyllithium (0.8 mL, 1.66 M in hexane, 1.32 mmol) and **26** (0.311 g, 1.04 mmol) in dry THF (5 mL) at –78 °C. After the mixture had been worked up as for **28**, column chromatography of the crude product on silica gel yielded **29** (0.37 mg, 92%), a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9 H, $Si(CH_3)_3$), 1.05 (d, 2 H, J = 2 Hz, $(CH_3)_3SiCH_2$), 2.25 (s, 6 H, $(CH_3)_2N$), 2.60 (s, 2 H, CH_2Ph), 3.15 (d, 2 H, J = 5 Hz, $(CH_3)_2NCH_2$), and 7.10–8.00 (m, 10 H, aromatic); exact mass calcd for $C_{21}H_{31}SiO_2SN$ (M^+) 389.6367, found 389.6357.

Standard Procedure E for Synthesis of α-Phenylsulfonyl β-Trimethylsilyl Ketones (34; Eq 11). (a) 1-Acetyl-1-(phenylsulfonyl)-2-(trimethylsilyl)ethane. Standard procedure E is described in detail in reference 2c for synthesis of 1-acetyl-1-(phenylsulfonyl)-2-(trimethylsilyl)ethane (97%): white crystals (mp 67 °C, from petroleum ether); ^{1}H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.10 (d, 2 H, J = 6 Hz, $(CH_3)_3SiCH_2$), 2.40 (s, 3 H, CH_3C=O), 4.00 (t, 1 H, active methine), and 7.45–7.85 (m, 5 H, aromatic); exact mass calcd for $C_{12}H_{17}SO_3Si$ ($M^+ - CH_3$) 269.0667, found 269.0675. Anal. Calcd for $C_{13}H_{20}SO_3Si$: C, 54.93, H, 7.04; S, 11.27. Found: C, 54.65; H, 6.98; S, 11.33.

(b) 2-(Phenylsulfonyl)-1-(trimethylsilyl)-3-hexanone. From butyraldehyde and **2** as in procedure E: white crystals (90%); mp 54–55 °C from petroleum ether (35–60 °C); ^{1}H NMR (CCl_4) δ –0.05 (s, 9 H, $Si(CH_3)_3$), 1.00 (m, 5 H, CH_2CH_3), 1.60 (sextet, 2 H, J = 6 Hz, $EtCH_2$), 2.30–3.25 (symmetric multiplet

of 12 peaks, centered at 2.75, 2 H, $(CH_3)_3SiCH_2$), 4.05 (dd, 1 H, J = 6 Hz, methine), and 7.60 (m, 5 H, aromatic); exact mass calcd for $C_{14}H_{21}SO_3Si$ ($M^+ - CH_3$) 297.0980, found 297.0987. Anal. Calcd for $C_{15}H_{24}SO_3Si$: C, 57.69; H, 7.69. Found: C, 57.84; H, 7.67.

(c) 2-(Phenylsulfonyl)-4-methyl-1-(trimethylsilyl)-3-pentanone. From isobutyraldehyde and **2** as in procedure E: white crystals (87%); mp 69–70 °C (from petroleum ether (35–60 °C)/ethyl acetate, 10:1); ^1H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.05 (br d, 2 H, J = 6 Hz, $(CH_3)_3SiCH_2$), 1.20 (d, 6 H, J = 6 Hz, $(CH_3)_2CH$), 3.25 (heptet, 1 H, J = 6 Hz, $(CH_3)_3CH$), 4.20 (br t, 1 H, J = 6 Hz, methine), and 7.60 (m, 5 H, aromatic); exact mass calcd for $C_{15}H_{24}SO_3Si$ (M^+) 312.1215, found 312.1222. Anal. Calcd for $C_{15}H_{24}SO_3Si$: C, 57.69; H, 7.69. Found: C, 57.62; H, 7.35.

(d) 2-(Phenylsulfonyl)-5-methyl-1-(trimethylsilyl)-3-hexanone. From 3-methylbutyraldehyde as in procedure E: white crystals (85%); mp 54–55 °C (from petroleum ether, 35–60 °C); ^1H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 0.90–1.30 (m, 8 H, $(CH_3)_2CH$ and $(CH_3)_3SiCH_2$), 2.10 (m, 1 H, $(CH_3)_2CH$), 2.20–3.20 (symmetrical multiplet of 8 peaks, centered at 2.70, 2 H, $(CH_3)_2CHCH_2$), 4.05 (dd, 1 H, J = 6 Hz, methine), and 7.65 (m, 5 H, aromatic). Anal. Calcd for $C_{16}H_{22}SO_3Si$: C, 58.89; H, 7.97. Found: C, 58.90; H, 8.08.

(e) Cyclohexyl 1-(Phenylsulfonyl)-2-(trimethylsilyl)ethyl Ketone. From cyclohexanecarboxaldehyde and **2** as in procedure E: white crystals (84%); mp 76–77 °C (from petroleum ether and ethyl acetate, 10:1); ^1H NMR (CCl_4) δ −0.05 (s, 9 H, $Si(CH_3)_3$), 0.95 (br d, 2 H, J = 7 Hz, $(CH_3)_3SiCH_2$), 0.75–2.05 (m, 10 H, ring), 2.95 (m, 1 H, ring methine), 4.15 (br t, 1 H, J = 7 Hz, methine), and 7.50 (m, 5 H, aromatic). Anal. Calcd for $C_{18}H_{28}SO_3Si$: C, 61.36; H, 7.95. Found: C, 61.60; H, 7.87.

(f) 1-(Phenylsulfonyl)-1-benzoyl-2-(trimethylsilyl)ethane. By Jones oxidation of the adduct from benzaldehyde and **2** via procedure E: white crystals (92%); mp 95–96 °C (from petroleum ether and ethyl acetate, 10:1); ^1H NMR (CCl_4) δ −0.10 (s, 9 H, $Si(CH_3)_3$), 1.20 (br d, 2 H, J = 7 Hz, $(CH_3)_3SiCH_2$), 4.95 (br t, 1 H, J = 7 Hz, methine), and 7.35–8.05 (m, 10 H, aromatic); exact mass calcd for $C_{17}H_{19}SO_3Si$ ($M^+ - CH_3$) 331.0824, found 331.0831. Anal. Calcd for $C_{18}H_{22}SO_3Si$: C, 62.42; H, 6.35. Found: C, 62.57; H, 6.31.

General Procedure F for Reductive Debenzenesulfonylation of α-Phenylsulfonyl β-Trimethylsilyl Ketones (34; Eq 11). (a) 4-(Trimethylsilyl)-2-butanone. Sodium amalgam (6%; 15 g) was added in small portions at 0 °C to 1-acetyl-1-(phenylsulfonyl)-2-(trimethylsilyl)ethane (3 g, 10.6 mmol) dissolved in a mixture of methanol (20 mL) and disodium hydrogen phosphate (6.0 g, 42.2 mmol). Reductive desulfonation was complete in 2 h. The suspension was diluted with pentane, decanted, and washed with a saturated aqueous solution of sodium bicarbonate. The organic extract was dried ($MgSO_4$), filtered, evaporated, and distilled to give 4-(trimethylsilyl)-2-butanone (1.37 g, 90%): a colorless liquid; bp 48 °C (9 mmHg); ^1H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 0.75 (t, 2 H, J = 10 Hz, $(CH_3)_3SiCH_2$), 2.10 (s, 3 H, CH_3), and 2.35 (t, 2 H, J = 10 Hz, active methylene); exact mass calcd for $C_7H_{16}OSi$ (M^+) 144.1048, found 144.1062.

(b) 2-Methyl-5-(trimethylsilyl)-3-pentanone. By reductive debenzenesulfonylation of 2-(phenylsulfonyl)-4-methyl-1-(trimethylsilyl)-3-pentanone: a colorless liquid (70%); bp 188 °C (760 mmHg); ^1H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$, 0.75 (t, 2 H, J = 7 Hz, $(CH_3)_3SiCH_2$), 1.10 (d, 6 h, J = 6 Hz, $(CH_3)_2CH$), and 2.25–2.75 (m, overlap of a heptet, 1 H, J = 6 Hz, $(CH_3)_3CH$, and a triplet, 2 H, J = 7 Hz, active methylene); exact mass calcd for $C_8H_{17}OSi$ ($M^+ - CH_3$) 157.1048, found 157.1052.

(c) 1-(Trimethylsilyl)-3-hexanone. From 2-(phenylsulfonyl)-1-(trimethylsilyl)-3-hexanone: a colorless liquid (70%); bp 188 °C (760 mmHg); ^1H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 0.75 (t, 2 H, J = 7 Hz, $(CH_3)_3SiCH_2$), 0.95 (t, 3 H, J = 6 Hz, CH_3), 1.60 (sextet, 2 H, J = 6 Hz, CH_3CH_2), and 2.20–2.50 (m, 4 H, a triplet, 2 H, J = 6 Hz, $C_2H_5CH_2$, and a second triplet, 2 H, J = 7 Hz, $(CH_3)_3SiCH_2CH_2$); exact mass calcd for $C_9H_{20}OSi$ (M^+) 172.1283, found 172.1289.

(d) 5-Methyl-1-(trimethylsilyl)-3-hexanone. By Debenzenesulfonylation of 2-(phenylsulfonyl)-5-methyl-1-(trimethylsilyl)-3-hexanone: a colorless oil (92%); bp 65 °C (2.5 mmHg); ^1H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 0.55 (t, 2 H, J = 7 Hz, $(CH_3)_3SiCH_2$), 0.90 (br d, 7 H, a doublet, 6 H, J = 6 Hz, $(CH_3)_2CH$, and a multiplet, 1 H, methine), and 2.05–2.35 (m, 4 H, a triplet, 2 H, J = 7 Hz, $(CH_3)_3SiCH_2CH_2$, and a doublet, 6 H, J = 6 Hz, $(CH_3)_2CH$, and a multiplet, 1 H, methine), and 2.05–2.35 (m, 4 H, a triplet, 2 H, J = 7 Hz, $(CH_3)_3SiCH_2CH_2$, and a doublet, 2 H, J = 6 Hz, $(CH_3)_2CHCH_2$); exact mass calcd for $C_{10}H_{22}OSi$ (M^+) 186.1339, found 186.1445.

4-(Phenylsulfonyl)-5-(trimethylsilyl)-2-pentanone (39a). Propylene oxide (10 mL) was added to **2** as prepared from *n*-butyllithium (8 mL, 1.7 M in hexane, 13.6 mmol) and **1** (3.0 g, 12.4 mmol) in ethyl ether (50 mL) at −70 °C. The mixture was stirred for 40 min at −70 °C and quenched with saturated ammonium chloride. Usual workup gave 4-(phenylsulfonyl)-5-(trimethylsilyl)-2-pentanol (**38a**, 95%) which was dissolved in acetone (50 mL). Jones reagent (65 mL, 1.86 N) was added to the cooled solution (~0 °C). After 1 h, the suspension was diluted with ethyl ether, washed with aqueous sodium bicarbonate, dried ($MgSO_4$), and filtered. Evaporation yielded **39a** (3.5 g, 94%): white crystals; mp 63 °C, from petroleum ether 35–60 °C; ^1H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 0.55–1.20 (m, 2 H, $(CH_3)_3SiCH_2$), 2.10 (s, 3 H, CH_3CO), 2.15–3.15 (m, 2 H, CH_3COCH_2), 3.55–3.90 (m, 1 H, methine), and 7.50–7.95 (m, 5 H, aromatic). Anal. Calcd for $C_{14}H_{22}SO_3Si$: C, 56.37; H, 7.38. Found: C, 56.02; H, 7.35.

3-(Phenylsulfonyl)-1-phenyl-4-(trimethylsilyl)-1-butanone (39b). As in the preparation of **38a** and **38b**, styrene oxide and **2** were converted to 3-(phenylsulfonyl)-1-phenyl-4-(trimethylsilyl)-1-butanol (**38b**, 95%), oxidation of which yielded **39b** (91%): white crystals; mp 83 °C, from petroleum ether and ethyl acetate, 10:1); ^1H NMR (CCl_4) δ 0.02 (s, 9 H, $Si(CH_3)_3$), 0.60–1.40 (m, 2 H, $(CH_3)_3SiCH_2$, 2.70–3.85 (m, 2 H, $C_6H_5COCH_2$), 3.95 (m, 1 H, methine), and 7.25–7.95 (m, 10 H, aromatic). Anal. Calcd for $C_{19}H_{24}SO_3Si$: C, 63.33; H, 6.66; S, 8.88. Found: C, 63.08; H, 6.48; S, 9.15.

General Procedure G for Synthesis of 1-(Phenylsulfonyl)-1-[(trimethylsilyl)methyl]cyclopropanes (42; Eq 13). (a) 1-(Phenylsulfonyl)-1-[(trimethylsilyl)methyl]-cyclopropane. *n*-Butyllithium (13 mL, 1.6 M in hexane, 20.8 mmol) was syringed into **1** (5.0 g, 20.6 mmol) stirred in ethyl ether (100 mL) at −70 °C. After 25 min, ethylene oxide (15 mL) was added. The solution was refluxed for 90 min and cooled to −10 °C, and methanesulfonyl chloride (2.37 g, 20.6 mmol) in anhydrous ethyl ether (5 mL) was added. Lithium chloride precipitated instantly. The suspension was refluxed for 25 min and cooled to −70 °C, and additional *n*-butyllithium (15 mL, 1.6 M in hexane, 24.0 mmol) was added. The pale yellow suspension was warmed to room temperature, stirred for 45 min, diluted with ethyl ether, washed with water, dried ($MgSO_4$), filtered, and evaporated under vacuum. The residue was chromatographed on silica gel and eluted first with hexane and then with benzene. Evaporation yielded 1-(phenylsulfonyl)-1-[(trimethylsilyl)methyl]cyclopropane (3.04 g, 55%) as a colorless oil: ^1H NMR (CCl_4) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 1.10 (s, 2 H $(CH_3)_3SiCH_2$), 1.25 (center of a symmetrical multiplet of 8 peaks, AB system, 4 H, ring), and 7.45–7.90 (m, 5 H, aromatic); exact mass calcd for $C_{12}H_{17}SO_2Si$ ($M^+ - CH_3$) 253.0718, found 253.0724.

(b) 1-(Phenylsulfonyl)-2-methyl-1-[(trimethylsilyl)-methyl]cyclopropane. From propylene oxide: colorless oil (75%); ^1H NMR (CCl_4) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 0.90–1.90 (m, 8 H, CH_3, $(CH_3)_3SiCH_2$ and ring), and 7.45–7.90 (m, 5 H, aromatic); exact mass calcd for $C_{13}H_{19}O_2SiS$ ($M^+ - CH_3$) 267.0874, found 267.0884.

(c) 6-(Phenylsulfonyl)-6-[(trimethylsilyl)methyl]bicyclo[3.1.0]hexane. From cyclopentene oxide: white crystals (51%); mp 87–88 °C; ^1H NMR (CCl_4) δ 0.25 (s, 9 H, $Si(CH_3)_3$), 0.65 (s, 2 H, $(CH_3)_3SiCH_2$), 1.30–2.40 (m, 8 H, ring), and 7.40–7.90 (m, 5 H, aromatic); exact mass calcd for $C_{15}H_{21}O_2SiS$ ($M^+ - CH_3$) 293.1031, found 293.1038. Anal. Calcd for $C_{16}H_{24}SO_2Si$: C, 62.33; H, 7.79; S, 10.38. Found: C, 62.86; H, 8.18; S, 10.00.

(d) 7-(Phenylsulfonyl)-7-[(trimethylsilyl)methyl]bicyclo[4.1.0]heptane. From cyclohexene oxide: white crystals (65%); mp 121–122 °C; ^1H NMR (CCl_4) δ 0.25 (s, 9 H, $Si(CH_3)_3$), 1.75 (s, 2 H, $(CH_3)_3SiCH_2$), 1.25 (m, 6 H, protons trans to $PhSO_2$ C-3, C-6, and C-7 trans to $C_6H_5SO_2$), 1.95 (m, 4 H, protons cis to $PhSO_2$), and 7.40–7.90 (m, 5 H, aromatic); exact mass calcd for $C_{13}H_{23}O_2SiS$ ($M^+ - CH_3$) 307.1187, found 307.1196. Anal. Calcd for $C_{17}H_{26}SO_2Si$: C, 63.35; H, 8.07; S, 9.93. Found: C, 63.10; H, 8.29; S, 9.81.

(e) 1-(Phenylsulfonyl)-1-[(trimethylsilyl)methyl]spiro-[2.5]octane. From methylenecyclohexane oxide: colorless oil (45%); ^{1}H NMR (CCl_4) δ 0.10 (s, 9 H, $Si(CH_3)_3$, 0.05–2.40 (m, 14 H, rings + $SiCH_2$), and 7.35–7.95 (m, 5 H, aromatic); exact mass calcd for $C_{17}H_{25}SO_2Si$ ($M^+ - CH_3$) 321.1175, found 321.1190.

(f) 3-(Phenylsulfonyl)-1,1-diphenyl-4-(trimethylsilyl)-1-butene (43). From 1,1-diphenylethylene oxide: white crystals (71%); mp 117 °C; ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.05–1.55 (m, 2 H, $(CH_3)_3SiCH_2$), 3.65–4.00 (m, 1 H, allylic), 5.85 (d, 1 H, J = 10 Hz, vinylic), and 6.70–7.85 (m, 15 H, aromatic); exact mass calcd for $C_{24}H_{25}SO_2Si$ ($M^+ - CH_3$) 405.2267, found 405.2275.

1-*n*-Hexyl-2-methylenecyclopropane (47a; Eq 12, 13, and 15). 1-Octene oxide (1.6 g, 12.4 mmol) in ethyl ether (3 mL) was added to a solution derived from **1** (3.0 g, 12.4 mmol) and *n*-butyllithium (7.4 mL, 1.7 M in hexane, 12.6 mmol) in ethyl ether (40 mL) at −70 °C. After the mixture had been warmed to room temperature, stirred overnight, and cooled to −10 °C, methanesulfonyl chloride (1.43 g, 12.5 mmol) was added. The suspension that formed was refluxed 25 min and cooled to −70 °C, and another portion of *n*-butyllithium (9 mL, 1.7 M in hexane, 15.3 mmol) was added. After 45 min, the pale yellow suspension was diluted with ethyl ether and washed with water. The organic extract was dried ($MgSO_4$), filtered, evaporated, and chromatographed on silica gel with hexane and then benzene as elutants. Evaporation of the solvents gave 1-(phenylsulfonyl)-2-*n*-hexyl-1-[(trimethylsilyl)methyl]cyclopropane (**46a**, 2.48 g, 57%) as a colorless oil: ^{1}H NMR (CCl_4) δ 0.15 (s, 9 H, $Si(CH_3)_3$), 0.35–1.95 (m, 18 H, $SiCH_2$, chain and ring), and 7.45–8.00 (m, 5 H, aromatic).

A mixture of **46a** (1.0 g, 2.84 mmol), anhydrous tetrahydrofuran (5 mL), and **6** (7 mL, 1.0 M solution in THF, 7 mmol) was refluxed for 90 min, cooled, diluted with petroleum ether (35–60 °C), washed with water, and then passed through silica gel. Evaporation yielded **47a** (0.37 g, 96%): a colorless oil; IR (cm^{-1}, neat) 2960, 2920, 2845, 1745 (c-C_3H_4=), 1465, and 880; ^{1}H NMR (CCl_4) δ 0.45–1.40 (m, 16 H, chain and ring) and 5.15 (m, 2 H, vinylic); exact mass calcd for $C_{10}H_{18}$ (M^+) 138.1408, found 138.1415.

1-Methylene-2-phenylcyclopropane (47b). Styrene oxide was converted by **2**, methanesulfonyl chloride, and then *n*-butyllithium (by the procedure for **46a**) to 1-(phenylsulfonyl)-2-phenyl-1-[(trimethylsilyl)methyl]cyclopropane (**46b**, 54%). Reaction of **46b** with **6** yielded (95%): a faint yellow liquid; IR (cm^{-1}, neat) 3050, 3020, 2980, 1740 (c-C_3H_4=), 1600, 1490, 1450, 890, 740, and 690; ^{1}H NMR (CCl_4) δ 1.05–1.90 (m, 2 H, ring methylene), 2.55 (m, 1 H, ring methine), 5.55 (m, 2 H, vinylic), and 7.00–7.40 (m, 5 H, aromatic); exact mass calcd for $C_{10}H_{10}$ (M^+) 130.0782, found 130.0784.

General Procedure H for Chlorination of 1-Alkyl-1-(phenylsulfonyl)-2-(trimethylsilyl)ethanes (7; Eq 16). (a) 4-(Phenylsulfonyl)-4-chloro-5-(trimethylsilyl)-1-pentene. To 4-(phenylsulfonyl)-5-(trimethylsilyl)-1-pentene (1.0 g, 3.55 mmol) stirred in ethyl ether (15 mL) was added *n*-butyllithium in hexane (2.3 mL, 1.7 M, 3.90 mmol) under nitrogen at −70 °C. After the above mixture was stirred for 45 min, *tert*-butyl hypochlorite (0.65 g, 5.99 mmol) in ethyl ether (5 mL) was added quickly. The faint yellow solution became colorless instantaneously, and saturated aqueous ammonium chloride was added. Usual workup followed by filtration and chromatography (silica gel, benzene/hexane, 1:1) gave 4-(phenylsulfonyl)-4-chloro-5-(trimethylsilyl)-1-pentene (1.03 g, 92%) as a colorless oil: ^{1}H NMR (CCl_4) δ 0.15 (s, 9 H, $Si(CH_3)_3$), 1.65 (s, 2 H, $(CH_3)_3SiCH_2$), 2.55–3.10 (m, 2 H, allylic), 5.00–6.20 (m, 3 H, vinylic), and 7.50–8.10 (m, 5 H, aromatic); exact mass calcd for $C_{13}H_{18}O_2SiSCl$ ($M^+ - CH_3$) 301.0485, found 301.0474.

(b) 2-(Phenylsulfonyl)-2-chloro-1-(trimethylsilyl)butane. From 2-(phenylsulfonyl)-1-(trimethylsilyl)butane: colorless oil (92%); ^{1}H NMR (CCl_4) δ 0.25 (s, 9 H, $Si(CH_3)_3$), 1.25 (t, 3 H, J = 6 Hz, CH_3), 1.75 and 1.80 (2 s, 2 H, $(CH_3)_3SiCH_2$), 1.85–2.60 (m, 2 H, CH_3CH_2), 7.65 (m, 3 H, aromatic), and 8.05 (m, 2 H, aromatic); exact mass calcd for $C_{12}H_{18}SiO_2SCl$ ($M^+ - CH_3$) 289.0112, found 289.0119.

(c) 2-(Phenylsulfonyl)-2-chloro-1-(trimethylsilyl)hexane. From 2-(phenylsulfonyl)-1-(trimethylsilyl)hexane: colorless oil (95%); ^{1}H NMR (CCl_4) δ 0.25 (s, 9 H, $Si(CH_3)_3$), 0.80–2.50 (m, 9 H, chain), 1.70 and 1.75 (2 s, 2 H, $(CH_3)_3SiCH_2$), 7.60 (m, 3 H, aromatic), and 8.00 (m, 2 H, aromatic); exact mass calcd for $C_{14}H_{22}O_2SiSCl$ ($M^+ - CH_3$) 317.0798, found 317.0807.

(d) 2-(Phenylsulfonyl)-2-chloro-1-(trimethylsilyl)octane. From 2-(phenylsulfonyl)-1-(trimethylsilyl)octane: colorless oil (92%); ^{1}H NMR (CCl_4) δ 0.25 (s, 9 H, $Si(CH_3)_3$), 0.85–2.45 (m, 13 H, chain), 1.70 and 1.85 (2 s, 2 H, $(CH_3)_3SiCH_2$), 7.65 (m, 3 H, aromatic), and 8.05 (m, 2 H, aromatic); exact mass calcd for $C_{16}H_{26}O_2SiSCl$ ($M^+ - CH_3$) 345.1111, found 345.1119.

(e) 2-(Phenylsulfonyl)-2-chloro-5,5-dimethyl-1-(trimethylsilyl)hexane. From 2-(phenylsulfonyl)-5,5-dimethyl-1-(trimethylsilyl)hexane: colorless oil (92%); ^{1}H NMR (CCl_4) δ 0.25 (s, 9 H, $Si(CH_3)_3$), 1.00 (s, 9 H, *tert*-butyl), 1.15–2.30 (m, 4 H, CH_2CH_2), 1.65 and 1.70 (2 s, 2 H, $(CH_3)_3SiCH_2$), 7.65 (m, 3 H, aromatic), and 8.05 (m, 2 H, aromatic); exact mass calcd for $C_{16}H_{26}O_2SiCl$ ($M^+ - CH_3$) 345.1111, found 345.1119.

(f) 2-(Phenylsulfonyl)-2-chloro-1-phenyl-3-(trimethylsilyl)propane. From 2-(phenylsulfonyl)-1-phenyl-3-(trimethylsilyl)propane: white crystals (65%); mp 105 °C; ^{1}H NMR (CCl_4) δ 0.3 (s, 9 H, $Si(CH_3)_3$), 1.55–2.10 (m, 2 H, $(CH_3)_3SiCH_2$), 3.10–4.05 (m, 2 H, benzylic), 7.45 (m, 5 H, aromatic), 7.75 (m, 3 H, aromatic), and 8.20 (m, 2 H, aromatic); exact mass calcd for $C_{17}H_{20}SiO_2SCl$ ($M^+ - CH_3$) 351.0557, found 351.0552.

General Procedure I for Fluoride-Induced Elimination of 1-Alkyl-1-(phenylsulfonyl)-1-chloro-2-(trimethylsilyl)-ethanes (48; Eq 16). (a) 2-(Phenylsulfonyl)-1-butene. Tetra-*n*-butylammonium fluoride (**6**, 1.0 mL, 1 M in THF, 1.0 mmol) was added to 2-(phenylsulfonyl)-2-chloro-1-(trimethylsilyl)butane (0.1 g, 0.33 mmol) in dry tetrahydrofuran (5 mL). The mixture was stirred at room temperature for 10 min, quenched with water, and extracted with ether. The ether extract was dried ($MgSO_4$), filtered, and evaporated. Elution of the resulting residue with benzene through a short silica gel column and evaporation of the solvent yielded 2-(phenylsulfonyl)-1-butene (64.4 mg, 100%): a light yellow oil; ^{1}H NMR (CCl_4) δ 1.10 (t, 3 H, J = 6 Hz, CH_3), 2.20 (br q, 2 H, J = 6 Hz, 1.5 Hz, allylic), 5.60 (t, 1 H, J = 1.5 Hz, vinylic), 6.25 (br s, 1 H, vinylic), 7.50 (m, 3 H, aromatic), and 7.80 (m, 2 H, aromatic); exact mass calcd for $C_{10}H_{12}SO_2$ (M^+) 196.0557, found 196.0564.

(b) 2-(Phenylsulfonyl)-5,5-dimethyl-1-hexene. From 2-(phenylsulfonyl)-2-chloro-5,5-dimethyl-1-(trimethylsilyl)hexane: a light yellow oil (100%); ^{1}H NMR (CCl_4) δ 0.80 (s, 9 H, *tert*-butyl), 1.20 (m, 2 H, $(CH_3)_3CCH_2$), 2.05 (m, 2 H, allylic), 5.50 (t, 1 H, J = 1.5 Hz, vinylic), 6.15 (s, 1 H, vinylic), 7.45 (m, 3 H, aromatic), and 7.75 (m, 2 H, aromatic); exact mass calcd for $C_{14}H_{20}SO_2$ (M^+) 252.1183, found 252.1190.

1-(Phenylsulfonyl)-1-chloro-2-(trimethylsilyl)ethane (50; Eq 18). Synthesis of **50** from **53** is described in detail in ref 2c: mp 53 °C (from hexane/ethyl acetate, 20:1); ^{1}H NMR (CCl_4) δ 0.18 (s, 9 H, $Si(CH_3)_3$), 0.78–1.88 (m, 2 H, $(CH_3)_3SiCH_2$), 4.38–4.68 (q, 1 H, $ClCHSO_2Ph$), and 7.43–7.98 (m, 5 H, aromatic). Anal. Calcd for $C_{11}H_{17}SO_2SiCl$: C, 47.75; H, 6.15; S, 11.75; Cl, 12.82. Found: C, 47.90; H, 6.09; S, 11.77; Cl, 12.72.

1-(Phenylsulfonyl)-1,1-dichloro-2-(trimethylsilyl)ethane (52; Eq 17). By addition of *tert*-butyl hypochlorite (0.5 g, 4.60 mmol) to a mixture of **50** (1.0 g, 3.62 mmol) and *n*-butyllithium (2.5 mL, 1.7 M in hexane, 4.25 mmol) at −70 °C and standard workup: white crystals (95%); mp 115–116 °C (from petroleum ether, 35–65 °C); ^{1}H NMR (CCl_4) δ 0.35 (s, 9 H, $Si(CH_3)_3$), 2.25 (s, 2 H, CH_2), and 7.45–8.20 (m, 5 H, aromatic); exact mass calcd for $C_{10}H_{13}O_2SiSCl_2$ ($M^+ - CH_3$) 294.9782, found 294.9791.

***trans*-1-(Phenylsulfonyl)-2-(trimethylsilyl)ethene (55; Eq 19).** A solution of **50** (2.3 g, 8.3 mmol) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU, 2.0 g, 13.1 mmol) in anhydrous tetrahydrofuran (25 mL) was stirred at room temperature under argon for 80 h. The resulting suspension was passed through a silica gel column and eluted with petroleum ether (35–60 °C) and then with benzene. Evaporation of the solution yielded **55** (1.90 g, 95%): mp 59–60 °C (from petroleum ether, lit.[14] mp 60 °C); ^{1}H NMR (CCl_4) δ 0.13 (s, 9 H, $Si(CH_3)_3$), 6.40, 6.70, 6.97, 7.27 (q, AB system, 2 H, vinylic), and 7.35–7.85 (m, 5 H, aromatic).

General Procedure J for Alkylation of 1-(Phenylsulfonyl)-1-chloro-2-(trimethylsilyl)ethane (50) and Fluoride-Induced Elimination of the Resulting 2-(Phenylsulfonyl)-2-chloro-1-(trimethylsilyl)alkanes (48; Eq 20 and 16). (a) 2-(Phenylsulfonyl)-3-phenyl-1-propene. General procedure J is described in detail in reference 2c for synthesis of 2-(phenylsulfonyl)-3-phenyl-1-propene (96%): a light yellow oil; ^{1}H NMR (CCl_4) δ 3.50 (r s, 2 H, benzylic) 5.30 (t, 1 H, J =

1.5 Hz, vinylic), 6.27 (r s, 1 H, vinylic), and 6.85–7.95 (m, 10 H, aromatic); exact mass calcd for $C_{15}H_{14}SO_2$ (M^+) 258.0874, found 258.0884.

(b) 2-(Phenylsulfonyl)-1-hexene. From 1-bromobutane and **51**: a light yellow oil (94%); ^1H NMR (CCl_4) δ 0.6–1.65 (m, 7 H, aliphatic), 2.20 (br t, 2 H, J = 6 Hz, 1.5 Hz, allylic), 5.60 (t, 1 H, J = 1.5 Hz, vinylic), 6.25 (s, 1 H, vinylic), 7.50 (m, 3 H, aromatic), and 7.80 (m, 2 H, aromatic); exact mass calcd for $C_{12}H_{16}SO_2$ (M^+) 224.0870, found 224.0879.

(c) 2-(Phenylsulfonyl)-1-octene. From 1-iodohexane and **51**: a light yellow oil (96%); ^1H NMR (CCl_4) δ 0.55–1.65 (m, 11 H, aliphatic), 2.20 (br t, 2 H, J = 6 Hz, 1.5 Hz, allylic), 5.60 (t, 1 H, J = 1.5 Hz, vinylic), 6.25 (s, 1 H, vinylic), 7.50 (m, 3 H, aromatic), and 7.85 (m, 2 H, aromatic); exact mass calcd for $C_{14}H_{20}SO_2$ (M^+) 252.1183, found 252.1188.

(d) 2-(Phenylsulfonyl)-3-methoxy-1-propene. From methyl chloromethyl ether and 1-(phenylsulfonyl)-1-chloro-1-lithio-2-(trimethylsilyl)ethane (**51**): a light yellow oil (97%); ^1H NMR (CCl_4) δ 3.15 (s, 3 H, CH_3), 4.00 (t, 2 H, J = 1.5 Hz, allylic), 5.95 (t, 1 H, J = 1.5 Hz, vinylic), 6.35 (t, 1 H, vinylic), 7.50 (m, 3 H, aromatic), and 7.80 (m, 2 H, aromatic); exact mass calcd for $C_{10}H_{12}SO_3$ (M^+) 212.1115, found 212.1120.

(e) 2-(Phenylsulfonyl)-1,4-pentadiene. From allyl bromide: a light yellow oil (94%); ^1H NMR (CCl_4) δ 2.90 (dd, 2 H, J = 6 Hz, 1.5 Hz, allylic), 4.80–6.55 (m, 3 H, allylic vinyl group), 5.55 (t, 1 H, J = 1.5 Hz, vinylic), 6.25 (s, 1 H, vinylic), and 7.30–7.90 (m, 5 H, aromatic); exact mass calcd for $C_{11}H_{12}SO_2$ (M^+) 208.0557, found 208.0553.

General Procedure K for Chlorination of α-Phenylsulfonyl β-Trimethylsilyl Ketones (34; Eq 21). (a) 3-(Phenylsulfonyl)-3-chloro-4-(trimethylsilyl)-2-butanone (54). To a solution of 1-acetyl-1-(phenylsulfonyl)-2-(trimethylsilyl)ethane (**53**, 0.5 g, 1.76 mmol) and *tert*-butyl hypochlorite (0.21 g, 1.93 mmol) in methylene chloride (20 mL) at 0 °C was added 1 drop of Triton B (40% benzyltrimethylammonium hydroxide in methanol). The mixture was stirred 1 min, diluted with ethyl ether, and washed in the water. The ether extract was dried ($MgSO_4$), filtered, evaporated, dissolved in hexane/ethyl acetate (10:1; 25 mL), and chilled to 0 °C to give **54** (0.46 g, 82%): white crystals, mp 64–65 °C; ^1H NMR (CCl_4) δ 0.02 (s, 9 H, $Si(CH_3)_3$), 1.65 (center of quartet, AB system, $(CH_3)_3SiCH_2$), 2.50 (s, 3 H, CH_3), and 7.45–7.95 (m, 5 H, aromatic); exact mass calcd for $C_{12}H_{16}O_3SiSCl$ ($M^+ - CH_3$) 303.0277, found 303.0289.

(b) 2-(Phenylsulfonyl)-2-chloro-1-(trimethylsilyl)-3-hexanone. From 2-(phenylsulfonyl)-1-(trimethylsilyl)-3-hexanone: white crystals (88%); mp 63–64 °C; ^1H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.05 (t, 3 H, J = 6 Hz, CH_3), 1.65 (sextet, 2 H, J = 6 Hz, CH_3CH_2), 1.70 (center of a quartet, AB system, 2 H, $(CH_3)_3SiCH_2$), 2.90 (t, 2 H, J = 6 Hz, active methylene), and 7.80 (m, 5 H, aromatic); exact mass calcd for $C_{14}H_{20}O_3SiSCl$ ($M^+ - CH_3$) 331.0590, found 331.0598.

(c) 2-(Phenylsulfonyl)-2-chloro-4-methyl-1-(trimethylsilyl)-3-pentanone. From 2-(phenylsulfonyl)-4-methyl-1-(trimethylsilyl)-3-pentanone: white crystals (84%); mp 78–79 °C; ^1H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.30 (d, 6 H, J = 6 Hz, $(CH_3)_2CH$), 1.50 (center of a quartet, AB system, 2 H, $(CH_3)_3SiCH_2$), 3.70 (heptet, 1 H, J = 6 Hz, methine), and 7.45–8.00 (m, 5 H, aromatic); exact mass calcd for $C_{15}H_{23}O_3SiSCl$ (M^+) 346.0825, found 346.0833.

(d) 2-(Phenylsulfonyl)-2-chloro-5-methyl-1-(trimethylsilyl)-3-hexanone. From 2-(phenylsulfonyl)-5-methyl-1-(trimethylsilyl)-3-hexanone: a colorless oil (87%); ^1H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.00 (d, 6 H, J = 6 Hz, $(CH_3)_2CH$), 1.65 (center of quartet, AB system, 2 H, $(CH_3)_3SiCH_2$), 2.00 (m, 1 H, methine), 2.80 (d, 2 H, J = 6 Hz, active methylene), and 7.45–7.95 (m, 5 H, aromatic); exact mass calcd for $C_{16}H_{25}O_3SiSCl$ (M^+) 360.0825, found 360.0833.

(e) 1-(Phenylsulfonyl)-1-benzoyl-1-chloro-2-(trimethylsilyl)ethane. From 1-(phenylsulfonyl)-1-benzoyl-2-(trimethylsilyl)ethane: white crystals (92%); mp 102–103 °C; ^1H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.90 (center of a quartet, AB system, 2 H, $(CH_3)_3SiCH_2$), and 7.25–8.25 (m, 10 H, aromatic); exact mass calcd for $C_{17}H_{18}O_3SiSCl$ ($M^+ - CH_3$) 365.0434, found 365.0442.

General Procedure L for Addition of 50 to Carbonyl Compounds and Subsequent Fluoride-Induced Elimination of 59 (Eq 22). (a) 2-(Phenylsulfonyl)-1-cyclohexyl-2-propen-1-ol. Synthesis of 2-(phenylsulfonyl)-1-cyclohexyl-2-propen-1-ol (95%) via general procedure L is described in detail in ref 2c: a white solid; mp 76 °C from petroleum ether (35–60 °C)/ethyl acetate (5:1); ^1H NMR (CCl_4) δ 0.70–1.80 (m, 11 H, ring), 2.25 (d, 1 H, J = 3 Hz, alcoholic), 4.05 (br t, 1 H, allylic), 5.95 (s, 1 H, vinylic), 6.35 (s, 1 H, vinylic), and 7.40–7.90 (m, 5 H, aromatic). Anal. Calcd for $C_{15}H_{20}SO_3$: C, 64.28; H, 7.14; S, 11.43. Found: C, 63.84; H, 7.04; S, 11.01.

(b) 2-(Phenylsulfonyl)-1-hexen-3-ol. From butyraldehyde as above: light yellow oil (95%); ^1H NMR (CCl_4) δ 0.60–1.60 (m, 7 H, aliphatic), 2.75 (d, 1 H, J = 6 Hz, alcoholic), 4.25 (br q, 1 H, J = 6 Hz, 1.5 Hz, allylic), 5.95 (s, 1 H, vinylic), 6.25 (s, 1 H, vinylic), 7.50 (m, 3 H, aromatic), and 7.85 (m, 2 H, aromatic); exact mass calcd for $C_{12}H_{16}SO_3$ (M^+) 240.1338, found 240.1344.

(c) 2-(Phenylsulfonyl)-4-methyl-1-penten-3-ol. From isobutyraldehyde and 1-(phenylsulfonyl)-1-chloro-1-lithio-2-(trimethylsilyl)ethane: a light yellow oil (92%); ^1H NMR (CCl_4) δ 0.80 (d, 6 H, J = 6 Hz, methyl groups), 1.80 (m, 1 H, $(CH_3)_3CH$), 2.65 (br d, 1 H, J = 6 Hz, alcoholic), 3.95 (br, 1 H, allylic), 5.95 (s, 1 H, vinylic), 6.25 (s, 1 H, vinylic), 7.50 (m, 3 H, aromatic), and 7.80 (m, 2 H, aromatic); exact mass calcd for $C_{12}H_{16}SO_3$ (M^+) 240.1338, found 240.1344.

(d) 2-(Phenylsulfonyl)-1-phenyl-2-propen-1-ol. From benzaldehyde: white crystals (90%); mp 93 °C [from petroleum ether (35–60 °C)/ethyl acetate (5:1)]; ^1H NMR (CCl_4) δ 2.95 (br, 1 H, alcoholic), 5.50 (s, 1 H, benzylic), 5.85 (s, 1 H, vinylic), 6.45 (s, 1 H, vinylic), and 7.00–7.85 (m, 10 H, aromatic). Anal. Calcd for $C_{15}H_{14}SO_3$: C, 65.69; H, 5.11. Found: C, 65.73; H, 5.13.

(e) 2-(Phenylsulfonyl)-1,4-pentadien-3-ol. From acrolein: light yellow oil (95%); ^1H NMR (CCl_4) δ 2.95 (br s, 1 H, J = 6 Hz, alcoholic), 4.85 (br, 1 H, allylic), 5.00–5.90 (m, 3 H, allyl pattern), 6.00 (s, 1 H, vinylic), 6.35 (s, 1 H, vinylic), 7.55 (m, 3 H, aromatic), and 7.90 (m, 2 H, aromatic); exact mass calcd for $C_{11}H_{12}SO_3$ (M^+) 224.1226, found 224.1232.

Standard Procedure M for Synthesis of 1,1-Dialkyl-2-(phenylsulfonyl)-2-chloro-3-(trimethylsilyl)-1-propanols (59; Eq 22). (a) 3-(Phenylsulfonyl)-3-chloro-2-methyl-4-(trimethylsilyl)-2-butanol. *n*-Butyllithium (1.6 mL, 1.7 M in hexane, 2.72 mmol) was syringed under nitrogen into **50** (0.7 g, 2.53 mmol) in ethyl ether (10 mL) at −70 °C. The yellow solution was stirred for 15 min, and acetone (0.13 g, 2.72 mmol) was added. The mixture was stirred for 3 h at −70 °C, quenched with aqueous ammonium chloride, washed with water, dried ($MgSO_4$), and evaporated. 3-(Phenylsulfonyl)-3-chloro-2-methyl-4-(trimethylsilyl)-2-butanol (0.72 g, 95%) crystallized completely as a white solid on standing: mp 105 °C (from petroleum ether/ethyl acetate, 5:1); ^1H NMR (CCl_4) δ 0.05 (s, 9 H, $Si(CH_3)_3$), 1.40, 1.60 (br s, 6 H, dimethyl), 1.90, 2.10 (4 peaks, 2 H, AB system, $(CH_3)_3SiCH_2$), 2.95 (br s, 1 H, alcoholic), and 7.50–8.15 (m, 5 H, aromatic). Anal. Calcd for $C_{14}H_{23}SO_3SiCl$: C, 50.23; H, 6.87; S, 9.57; Cl, 10.60. Found: C, 50.19; H, 6.76; S, 9.41; Cl, 10.57.

(b) 1-[1-(Phenylsulfonyl)-1-chloro-2-(trimethylsilyl)-ethyl]cyclohexanol. From cyclohexanone: white crystals (93%); mp 128 °C (from petroleum ether and ethyl acetate, 5:1); ^1H NMR (CCl_4) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.25, 1.45, 1.90, 2.10 (4 peaks, 2 H, AB system, $(CH_3)_3SiCH_2$), 1.45–2.15 (m, 10 H, ring), 2.65 (s, 1 H, alcoholic), and 7.50–8.15 (m, 5 H, aromatic). Anal. Calcd for $C_{17}H_{27}SO_3SiCl$: C, 54.47; H, 7.21. Found: C, 54.65; H, 7.27.

(c) 1-[1-(Phenylsulfonyl)-1-chloro-2-(trimethylsilyl)-ethyl]cyclobutanol. From cyclobutanone: white crystals, mp 64 °C (from petroleum ether and ethyl acetate, 5:1): ^1H NMR (CCl_4) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 1.35, 1.50, 1.60, 1.75 (4 peaks, 2 H, AB system, $(CH_3)_3SiCH_2$), 1.60–2.10 (m, 4 H, 2 C-2, 2 C-4 of cyclobutanol), 2.20–2.75 (m, 2 H, 2 C-3 of cyclobutanol), 3.60 (2 peaks, 1 H, alcoholic), and 7.35–8.00 (m, 5 H, aromatic). Anal. Calcd for $C_{15}H_{23}SO_3SiCl$: C, 51.95; H, 6.64. Found: C, 51.99; H, 6.67.

3-(Phenylsulfonyl)-2-methyl-3-buten-2-ol (60, R_1 and R_2 = CH_3). Tetra-*n*-butylammonium fluoride (**6**, 2.0 mL, 1 M in THF, 2.0 mmol) was added to **59** (R_1 and R_2 = CH_3, 0.1 g, 0.30 mmol) in dry tetrahydrofuran (5 mL). The mixture was stirred at room temperature for 10 min, quenched with water, and extracted with ethyl ether. Standard workup yielded **60** (R_1 and R_2 = CH_3, 61.5 mg, 91%) as a colorless oil: ^1H NMR (CCl_4) δ 1.45 (s, 6 H, dimethyl), 3.00 (s, 1 H, alcoholic), 5.90 (s, 1 H, vinylic),

6.15 (s, 1 H, vinylic), and 7.45–7.90 (m, 5 H, aromatic); exact mass calcd for $C_{11}H_{14}SO_3$ (M^+) 226.1226, found 226.1231.

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Registry No. 1, 73476-18-3; 2, 111976-51-3; 3 (R'p = CH_2=$CHCH_2$), 84363-58-6; 3 (R'p = C_2H_5), 84363-54-2; 3 (R'p = $CH_3(CH_2)_3$), 84363-55-3; 3 (R'p = $CH_3(CH_2)_7$), 73476-19-4; 3 (R'p = $(CH_3)_3C(CH_2)_2$), 84363-57-5; 3 (R'p = $C_6H_5CH_2$), 84363-59-7; 3 (R'p = TMS), 111976-52-4; 5 (R'p = R^2p = $CH_3(CH_2)_3$), 111976-53-5; 5 (R'p = $(CH_3)_3C(CH_2)$ R^2p = CH_2=$CHCH_2$), 111976-54-6; 5 (R'p = C_2H_5, R^2p = $C_6H_5CH_2$), 111976-56-8; 8 (R'p = R^2p = $CH_3(CH_2)_3$), 6795-79-5; 8 (R'p = $(CH_3)_3C(CH_2)_2$, R^2p = CH_2=$CHCH_2$, 111976-55-7; 8 (R'p = C_2H_5, R^2p = $C_6H_5CH_2$), 3968-89-6; 15, 111976-57-9; 16, 111976-58-0; *E*-18 (R' = H, R^2 = C_6H_5), 40595-34-4; *Z*-18 (R' = C_6H_5, R^2 = H), 40595-35-5; 18 (R' = R^2 = CH_3), 18293-99-7; 18 (R' = R^2 = C_6H_5), 83438-57-7; 18 (R', R^2 = -$(CH_2)_4$), 83438-58-8; *E*-18 (R' = H, R^2 = $(CH_3)_2C$=CH), 83438-69-1; *Z*-18 (R' = H, R^2 = $(CH_3)_2C$=CH), 83438-60-2; 18 (R' = R^2 = C_2H_5), 63922-77-0; 18 (R', R^2 = -$(CH_2)_3$), 83438-59-9; 18 (R', R^2 = -$(CH_2)_5$), 63922-76-9; 23, 111976-61-5; 24, 111976-59-1; 25, 111976-60-4; 26, 111976-62-6; 28, 111976-63-7; 29, 111976-64-8; 34 (R' = CH_3), 84363-73-5; 34 (R' = $(CH_3)_2CH$), 111976-65-9; 34 (R' = $CH_3(CH_2)_2$), 111976-66-0; 34 (R' = $(CH_3)_2CHCH_2$), 111976-67-1; 34 (R' = c-C_6H_{11}), 111976-68-2; 34 (R' = C_6H_5), 111976-69-3; 35 (R' = CH_3), 13506-88-2; 35 (R' = $(CH_3)_2CH$), 17869-46-4; 35 (R' = $CH_3(CH_2)_2$), 15047-42-4; 35 (R' = $(CH_3)_2CHCH_2$), 13506-98-4; 38a, 111976-70-6; 38b, 111976-72-8; 39a, 111976-71-7; 39b, 111976-73-9; 42 (from ethylene oxide), 111976-74-0; 42 (from 1-butylethylene oxide), 111976-75-1; 42 (from cyclohexene oxide), 111976-76-2; 42 (from methylenecyclohexane oxide), 111976-77-3; 42 (from propylene oxide), 111976-78-4; 42 (from styrene oxide), 111976-79-5; 42 (from cyclopentene oxide), 111976-80-8; 43, 111976-81-9; 46a, 111976-82-0; 46b, 111976-79-5; 47a, 22628-88-2; 47b, 29817-09-2; 48 (R'p = C_2H_5), 84363-60-0; 48 (R'p = $CH_3(CH_2)_3$), 84363-61-1; 48 (R'p = $CH_3(CH_2)_5$), 84363-62-2; 48 (R'p = $(CH_3)_3C(CH_2)_2$), 84363-66-6; 48 (R'p = CH_2=$CHCH_2$), 84363-67-7; 48 (R'p = $C_6H_5CH_2$), 84363-68-8; 49 (R'p = C_2H_5), 84363-63-3; 49 (R'p = $CH_3(CH_2)_3$), 84363-64-4; 49 (R'p = $CH_3(CH_2)_5$), 84363-65-5; 49 (R'p = $(CH_3)_3C(CH_2)_2$), 84363-69-9; 49 (R'p = CH_2=$CHCH_2$), 84363-70-2; 49 (R'p = $C_6H_5CH_2$), 84363-71-3; 50, 84363-74-6; 51, 84363-75-7; 52, 111976-83-1; 53, 84363-73-5; 54, 111976-84-2; 55, 64489-06-1; 56 (R' = $CH_3(CH_2)_2$), 111976-85-3; 56 (R' = $(CH_3)_2CH$), 111976-86-4; 56 (R' = $(CH_3)_2CHCH_2$), 111976-87-5; 56 (R' = C_6H_5), 111976-88-6; 59 (R' = H, R^2 = $CH_3(CH_2)_2$), 84363-76-8; 59 (R' = H, R^2 = $(CH_3)_2CH$), 84391-09-3; 59 (R' = H, R^2 = c-C_6H_{11}), 84391-10-6; 59 (R' = H, R^2 = CH_2=CH), 84363-78-0; 59 (R' = H, R^2 = C_6H_5), 84363-77-9; 59 (R' = R^2 = CH_3), 111976-89-7; 59 (R' = CH_3, R^2 = C_2H_5), 111976-90-0; 59 (R', R^2 = -$(CH_2)_5$), 111976-91-1; 59 (R', R^2 = -$(CH_2)_3$), 111976-92-2; 60 (R' = H, R^2 = $CH_3(CH_2)_2$), 84363-80-4; 60 (R' = H, R^2 = $(CH_3)_2CH$), 84363-79-1; 60 (R' = H, R^2 = c-C_6H_{11}), 84363-81-5; 60 (R' = H, R^2 = CH_2=CH), 84363-83-7; 60 (R' = H, R^2 = C_6H_5), 84363-82-6; 60 (R' = R^2 = CH_3), 111976-93-3; CH_3CH_2Br, 74-96-4; $CH_3(CH_2)_3Br$, 109-65-9; $CH_3(CH_2)_5I$, 638-45-9; $(CH_3)_3C(CH_2)_2Br$, 1647-23-0; CH_2=$CHCH_2Br$, 106-95-6; $C_6H_5CH_2Br$, 100-39-0; $ClSi(CH_3)_3$, 75-77-4; CH_2=$CH(CH_2)_5CH_3$, 111-66-0; CH_2=$CH(CH_2)_2C(CH_3)_3$, 7116-86-1; CH_2=$CHCH_2C_6H_5$, 300-57-2; C_6H_5CHO, 100-52-7; $CH_3C(O)CH_3$, 67-64-1; $C_6H_5C(O)C_6H_5$, 119-61-9; c-C_5H_8(=O), 108-94-1; $(CH_3)_2C$=CHCHO, 107-86-8; $C_2H_5C(O)C_2H_5$, 96-22-0; c-C_4H_6(=O), 1191-95-3; c-C_6H_{10}(=O), 108-94-1; HCHO, 50-00-0; $(CH_3)_2NH$, 124-40-3; CH_3CHO, 75-07-0; $(CH_3)_2CHCHO$, 78-84-2; $CH_3(CH_2)_2CHO$, 123-72-8; $(CH_3)_2CHCH_2CHO$, 590-86-3; c-$C_6H_{11}CHO$, 2043-61-0; CH_3OCH_2Cl, 107-30-2; CH_2=CHCHO, 107-02-8; $CH_3C(O)C_2H_5$, 78-93-3; 1,1-diphenylethylene oxide, 882-59-7; ethylene oxide, 75-21-8; 1-butylethylene oxide, 1436-34-6; cyclohexene oxide, 286-20-4; methylenecyclohexane oxide, 185-70-6; propylene oxide, 75-56-9; styrene oxide, 96-09-3; cyclopentene oxide, 285-67-6; 2-(phenylsulfonyl)-3-methoxy-1-propene, 84363-84-8; 1-octene oxide, 2984-50-1.

Rhodium(II) Acetate Catalyzed Reactions of 2-Diazo-1,3-indandione and 2-Diazo-1-indanone with Various Substrates

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Decomposition of 2-diazo-1,3-indandione (3) by rhodium(II) acetate (1) in cyclohexane and in benzene results in overall carbon–hydrogen insertion to give 2-substituted 1,3-indandiones. Anisole, 1, and 3 yield 2-(4-methoxyphenyl)-1,3-indandione (74%); benzenes substituted by single methyl or halogen groups yield the corresponding ortho- and para-substitution products. Spirocyclopropanes are obtained by rhodium(II)-catalyzed additions of 3 to olefins; electron-deficient olefins do not give adducts. Substituted 4*H*-indeno[1,2-*b*]furan-4-ones and 2,3-disubstituted spiro[cyclopropene-1,2'-[2*H*]indene]-1',3'-diones are formed from rhodium(II)-catalyzed reactions of 3 with acetylenes. Reactions of 1 and 3 with cyclohexane, olefins, acetylenes, and arenes involve selective electrophilic carbenic or ylidic processes. 2-Diazo-1-indanone (4) is converted by 1 to 2,2'-bis[indan-1-one] (48). Thiophenol reacts with 4 and 1 to yield 2-(phenylthio)-1-indanone (49). Cyclopropanations of cyclohexene and styrene by 4 as catalyzed by 1 result in spiro[bicyclo[4.1.0]heptane-7,2'-[2*H*]indan]-1-one (50) and 2-phenylspiro[cyclopropane-1,2'-[2*H*]inden]-1'(3'*H*)-one (51), respectively.

Rhodium(II) acetate (1) is a dimer of $Rh(O_2CCH_3)_2$ containing a rhodium–rhodium single bond and four acetate ligands symmetrically attached to the two rhodium atoms as in 2.[1] Diazo compounds frequently react advantageously in the presence of 1 and related rhodium catalysts.[2] The behavior of 2-diazo-1,3-indandione (3) and 2-diazo-1-indanone (4) with 1 in varied substrates is now reported.

(1) (a) Christoph, G. G.; Yoh, Y.-B. *J. Am. Chem. Soc.* **1979**, *101*, 1422. (b) Adducts are formed from 1 with electron-donating basic ligands such as methanol, water, and tetrahydrofuran but not with olefins. These adducts are stable, crystalline compounds that decompose to 1 upon heating.[1c] (c) Johnson, S. A.; Hunt, H. R.; Neumann, H. M. *Inorg. Chem.* **1963**, *2*, 690.

(2) For summaries of the literature of the utility of 1 in synthesis, see: (a) Maas, G. *Top. Current Chem.* **1987**, *137*, 75. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (c) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. In *The Chemistry of the Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; Part 2, Chapter 18. (d) References in 2a–c.

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