Silicon-Containing Carbanions. III. Synthesis of Vinyl Sulfoxides *via* 1-Trimethylsilyl-1-(phenylsulfinyl)methyllithium

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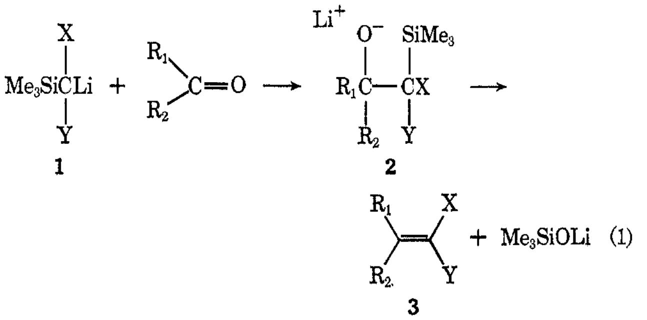
As part of a continuing study of trimethylsilyl-substituted organolithium reagents 1-trimethylsilyl-1-(phenylsulfinyl)methyllithium (**1d**) was prepared by metalation of trimethylsilylmethyl phenyl sulfoxide. Vinyl sulfoxides were formed in good yield by condensation of **1d** with the following carbonyl compounds: acrolein, adamantanone, benzaldehyde, benzophenone, cinnamaldehyde, cyclohexanone, cyclohexenone, and isobutyraldehyde. It was demonstrated that **1d** and related reagents can be prepared *in situ* by trimethylsilylation of, *e.g.*, (phenylsulfinyl)methyllithium and used for vinyl sulfoxide synthesis directly without ever isolating the thermally and hydrolytically sensitive trimethylsilylmethyl sulfoxide. Organolithium reagent **1d** reacted with ethyl benzoate to yield (phenylsulfinyl)acetophenone and with methyl iodide to yield 1-trimethylsilyl-1-(phenylsulfinyl)ethane as a single diastereomer which rearranged on heating in benzene at reflux to $Me_3SiOCH(SPh)CH_3$.

Elimination reactions proceeding through intramolecular attack on silicon by oxygen in a four-center process are common and provide the basis for a number of useful olefin syntheses.[1] Thus, 1-trimethylsilyl-1-alkyllithiums (**1**) add to aldehydes and ketones to give intermediates (**2**) which fragment to olefins and Me_3SiOLi under extremely mild conditions. The sequence depicted in eq 1 has been found to be broadly applicable to the synthesis of vinyl phenyl thioethers (**3a**),[2] diethyl vinylphosphonates (**3b**),[2] and ketene thioacetals (**3c**).[3]



a, X = H; Y = SPh
b, X = H; Y = $P(O)(OEt)_2$
c, X + Y = $-S(CH_2)_3S-$
d, X = H; Y = S(O)Ph
e, X = H; Y = H

It was considered of interest to investigate the possibility of vinyl sulfoxide (**3d**) formation by the analogous process in which metalation of trimethylsilylmethyl phenyl sulfoxide (**4**) would serve to produce the required 1-trimethylsilyl-1-(phenylsulfinyl)methyllithium (**1d**). The reasons for this interest include the obvious one of extending the scope of what presently appears to be a general olefination reaction by providing a simple synthetic route to vinyl sulfoxides,[4] as well as the fact that silylmethyl sulfoxides themselves represent a potentially interesting class of compounds.

Brook[5] has described the synthesis of **4** by reaction of trimethylsilylmethylmagnesium chloride with methyl benzenesulfinate and found it to be both hydrolytically and thermally unstable. Hydrolytic instability with respect to silicon–carbon bond cleavage is a common feature of compounds of the type R_3SiCH_2X where X is a highly electronegative substituent.[6] The thermal instability results from a four-center elimination of Me_3SiO^- involving the sulfoxide oxygen and is conceptually related to the conversion of **2** to **3**. Recombination of the fragments produces the observed product, trimethylsiloxymethyl phenyl sulfide (eq 2).

$$\underset{\mathbf{4}}{\mathrm{Me_3SiCH_2S(O)Ph}} \xrightarrow{60°} \mathrm{Me_3SiO^-} + \mathrm{CH_2{=}\overset{+}{S}Ph} \longrightarrow \mathrm{Me_3SiOCH_2SPh} \quad (2)$$

We have found that **4**, prepared by Brook's method, is sufficiently stable for study of its metalation provided care is taken in its preparation and it is stored at temperatures below 0°. The reactions of **1d**, resulting from metalation of **4**, are the subject of this report.

Results and Discussion

Metalation of **4** was accomplished at −70° in tetrahydrofuran using either *n*-butyllithium or *tert*-butyllithium to afford **1d**. The alternative mode of reaction, cleavage of the carbon–silicon bond to form butyltrimethylsilane and (phenylsulfinyl)methyllithium (**5**), did not occur to any measurable extent, as evidenced by the reaction of the resulting solution with benzophenone to afford 1-(phenylsulfinyl)-2,2-diphenylethylene (**6b**) as the exclusive product of carbonyl addition in 81–87% yield. Formation of the vinyl sulfoxide parallels the behavior of the other 1-trimethylsilylalkyllithium reagents depicted in eq 1. Had **5** rather than **1d** been formed from **4** the product would have been 1,1-diphenyl-2-(phenylsulfinyl)ethanol (**7**).[7] Independent generation of **5** from methyl phenyl sulfoxide and phenyllithium verified this and demonstrated

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[1] (a) D. J. Peterson, *Organometal. Chem. Rev. A*, **7**, 295 (1972); (b) D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968); (c) T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970).

[2] F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 939 (1972).

[3] F. A. Carey and A. S. Court, *ibid.*, **37**, 1926 (1972); D. Seebach, B. T. Grobel, A. K. Beck, M. Braun, and K. H. Geiss, *Angew. Chem., Int. Ed., Engl.*, **11**, 443 (1972); P. F. Jones and M. F. Lappert, *Chem. Commun.*, 526 (1972).

[4] For recent alternative syntheses of vinyl sulfoxides see (a) E. Block, *J. Amer. Chem. Soc.*, **94**, 642 (1972); (b) D. A. Evans, C. A. Bryan, and C. L. Sims, *ibid.*, **94**, 2891 (1972); (c) D. J. Abbott, S. Collona, and C. J. M. Stirling, *Chem. Commun.*, 471 (1971); (d) G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **35**, 2106 (1970).

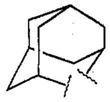
[5] A. G. Brook and D. G. Anderson, *Can. J. Chem.*, **46**, 2115 (1968).

[6] C. Eaborn and R. W. Bott in "Organometallic Compounds of the Group IV Elements," Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, pp 367–378.

[7] For reactions of methylsulfinyl carbanion with benzophenone see E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

TABLE I

REACTION OF 1-TRIMETHYLSILYL-1-PHENYLSULFINYLMETHYLLITHIUM WITH CARBONYL COMPOUNDS

Aldehyde or ketone	Product	R_1	R_2	Metalating agent	Yield, %[a]
Benzaldehyde	**6a**	H	Ph	*n*-BuLi	87[b]
				t-BuLi	81[c]
Benzophenone	**6b**	Ph	Ph	*n*-BuLi	72
				t-BuLi	75
Cyclohexanone	**6c**		$-(CH_2)_4-$	*n*-BuLi	66
				t-BuLi	67
Isobutyraldehyde	**6d**	H	$(CH_3)_2CH$	*n*-BuLi	30[d]
				t-BuLi	66[e]
Acrolein	**6e**	H	$CH_2{=}CH-$	*n*-BuLi	67[f]
				t-BuLi	72[f]
trans-Cinnamaldehyde	**6f**	H	$PhCH{=}CH$	*n*-BuLi	70
Cyclohexenone	**6g**		$-CH{=}CH(CH_2)_3-$	*t*-BuLi	24
Adamantanone	**6h**			*t*-BuLi	82

[a] Isolated yield of purified product. [b] Cis/trans = 1. [c] Cis/trans = 0.5. [d] Cis/trans = 2. [e] Cis/trans = 0.8. [f] Cis/trans = 1.

that the product was stable under the reaction conditions.

$$\underset{\textbf{1d}}{PhS(O)CH(Li)SiMe_3} + R_1R_2CO \longrightarrow \underset{\textbf{6}}{R_1R_2C{=}CHS(O)Ph}$$

$$\underset{\textbf{5}}{PhS(O)CH_2Li} + R_1R_2CO \longrightarrow R_1R_2C(OH)CH_2S(O)Ph$$

$$\textbf{7},\ R_1 = R_2 = Ph$$

$$\textbf{8},\ R_1 + R_2 = -(CH_2)_5-$$

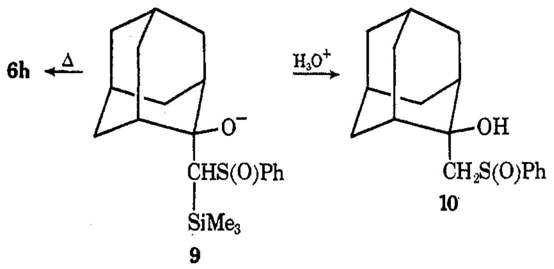
Similar results were found with cyclohexanone; vinyl sulfoxide **6c** was formed when **1d** was used while **8** was obtained on reaction with **5**.

A number of representative aldehydes and ketones reacted with **1d** to product vinyl sulfoxides in all cases and in generally good yields. These results are summarized in Table I. The structures of the products were established by the usual spectroscopic techniques and in certain instances (**6a** and **6e**) by comparison of physical properties with those previously reported (see Experimental Section for details). Most characteristic of the structures with respect to their nmr spectra was the signal for the vinyl proton on the carbon atom bearing the phenylsulfinyl group, which appeared at 1.1–1.5 ppm lower field than for the unsubstituted analog $R_2C{=}CH_2$.

As can be seen from Table I, vinyl sulfoxide formation is not stereoselective, mixtures of cis and trans isomers being formed from aldehydes. This has been previously observed in reaction of **1a** and **1b** and it is not yet clear as to the extent to which this reflects the stereoselectivity of addition of the unsymmetrical reagent to the carbonyl group *vs.* nonstereospecific elimination of Me_3SiOLi from the diastereomeric intermediate.

Conjugate addition did not occur when acrolein, cinnamaldehyde, or cyclohexenone was used, there being observed exclusively 1,2 addition to the carbonyl to afford dienyl phenyl sulfoxides **6e**, **6f**, and **6g**, respectively, as mixtures of cis and trans isomers in each case.

Addition of **1d** to 2-adamantanone has provided the only instance thus far in reactions of **1a–d** in which elimination of Me_3SiOLi is not spontaneous under the reaction conditions. When the experiment was performed in the normal way the isolated product was a mixture of **6h** and 2-(phenylsulfinyl)methyl-2-adamantanol (**10**). Since it seemed more likely that the formation of **10** resulted from **9** which hydrolyzed



during work-up rather than by addition of **5** (not observed in any other reactions of **4**) and that a reasonable explanation was that decomposition of the intermediate **9** was slow because of increased crowding in the transition state, the reaction was modified to the extent that the reaction mixture was refluxed for 0.5 hr prior to work-up. Under these conditions the vinyl sulfoxide **6h** was the sole product.

It is interesting to compare the relative ease of decomposition of various species having the structure represented by **2**. When X or Y is a substituent capable of stabilizing a carbanionic center, decomposition of **2** is spontaneous under the conditions of condensation of **1** and carbonyl compounds.[1-3] On the other hand, when X and Y are hydrogen, decomposition is rapid only at elevated temperatures.[1b,c] Such a dependence on carbanion-stabilizing power suggests an intermediate or transition state for the conversion of **2** to **3** in which considerable electron density is built up at the carbon atom from which the trimethylsilyl group is lost. This point is discussed in greater detail in the accompanying paper.[8]

The ready conversion of **2d** to **3d** not only is consistent with this description but also provides strong evidence against the alternative explanation that the effect of substituents is to stabilize a developing double bond in the transition state. It has been conclusively established that the conjugative effect of a sulfinyl group with a carbon–carbon double bond is negligible by observing that equilibration of α,β-unsaturated

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[8] C. Trindle, J.-T. Hwang, and F. A. Carey, *J. Org. Chem.*, **38**, 2664 (1973).

sulfoxides leads to preferential formation of the β,γ isomer.[9] If stabilization of the developing double bond were important it reasonably follows that **2d** would be converted to **3d** less readily than **2e** to **3e**, in contrast to what is actually observed.

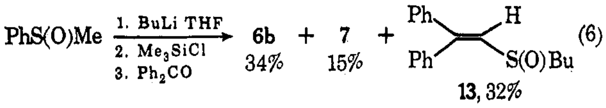
In situ generation of trimethylsilylmethyl sulfoxides was examined because, if successful, it would offer great advantages in convenience for synthetic purposes. When a solution containing 2 equiv of methylsulfinylmethyllithium (**11**) in tetrahydrofuran was treated with 1 equiv of trimethylchlorosilane followed by 1 equiv of benzophenone, 1-(methylsulfinyl)-2,2-diphenylethylene (**12**)[4d] was isolated in 50% yield. The reaction sequence described by eq 3–5 is proposed.

$$\underset{\mathbf{11}}{CH_3S(O)CH_2Li} + Me_3SiCl \longrightarrow CH_3S(O)CH_2SiMe_3 \quad (3)$$

$$CH_3S(O)CH_2Li + CH_3S(O)CH_2SiMe_3 \longrightarrow CH_3S(O)CH_3 + CH_3S(O)CH(Li)SiMe_3 \quad (4)$$

$$CH_3S(O)CH(Li)SiMe_3 + Ph_2CO \longrightarrow \underset{\mathbf{12}}{Ph_2C{=}CHS(O)CH_3} + Me_3SiOLi \quad (5)$$

Attempted *in situ* formation of **1d** by a similar process in which methyl phenyl sulfoxide was metalated with *n*-butyllithium, then allowed to react with trimethylchlorosilane and benzophenone, gave the mixture of products summarized in eq 6.



(6)

13, 32%

Compounds **6** and **7** are presumably derived from **1d** and **5**, respectively, while the formation of 1-(*n*-butylsulfinyl)-2,2-diphenylethylene (**13**) suggests 1-trimethylsilyl-1-(*n*-butylsulfinyl)methyllithium (**14**) as its precursor. Since no **13** was observed when preformed **4** was metalated and treated with benzophenone, it follows that **14** results from reaction of trimethylchlorosilane with (*n*-butylsulfinyl)methyllithium formed in a prior step. The most plausible explanation involves the exchange process represented by eq 7–9.

$$PhS(O)Me + n\text{-}BuLi \longrightarrow \underset{\mathbf{5}}{PhS(O)CH_2Li} + BuH \quad (7)$$

$$\underset{\mathbf{5}}{PhS(O)CH_2Li} \longrightarrow CH_2{=}S{=}O + PhLi \quad (8)$$

$$CH_2{=}S{=}O + n\text{-}BuLi \longrightarrow n\text{-}BuS(O)CH_2Li \quad (9)$$

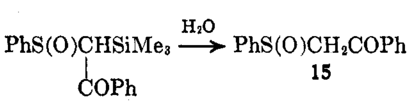
$$n\text{-}BuS(O)CH_2Li + Me_3SiCl \longrightarrow \underset{\mathbf{14}}{n\text{-}BuS(O)CH_2SiMe_3} \quad (10)$$

Such an exchange of ligands on sulfur by way of a sulfine intermediate has been suggested previously to rationalize the methyllithium-induced racemization of aryl methyl sulfoxides as well as a number of other reactions of sulfoxides.[10] It is of interest that the corresponding process (eq 11) does not occur with **1d**.

$$\mathbf{1d} \not\longrightarrow PhLi + Me_3SiCH{=}S{=}O \quad (11)$$

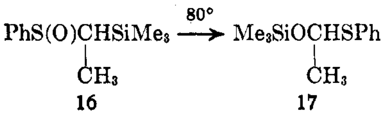
Simple steric considerations would predict a greater tendency for **1d** to fragment than for **5**. The decreased tendency of **1d** toward fragmentation can be most readily understood in terms of an enhanced stabilization of **1d** relative to **5**. Stabilization of carbanionic centers by adjacent silicon has been shown to be important in a number of cases, the most thorough studies being those of Schmidbaur,[11] who has observed appreciable stabilization of sulfur and phosphorus ylides by silicon and ascribes the stabilizing effect to either a "d-orbital π interaction or an altered charge distribution in the σ skeleton."

Other electrophilic substrates also reacted with **1d**. (Phenylsulfinyl)acetophenone was isolated in 76% yield from reaction with ethyl benzoate. Because cleavage of trimethylsilyl groups from β-ketosilanes occurs with extreme ease,[12] it is reasonable to believe that this results from hydrolysis of a benzoylated intermediate.



$$\underset{\text{COPh}}{PhS(O)CHSiMe_3} \xrightarrow{H_2O} \underset{\mathbf{15}}{PhS(O)CH_2COPh}$$

Alkylation of **1d** with methyl iodide produced 1-trimethylsilyl-1-(phenylsulfinyl)ethane (**16**) in 92%



$$\underset{\mathbf{16}}{\underset{CH_3}{PhS(O)CHSiMe_3}} \xrightarrow{80°} \underset{\mathbf{17}}{\underset{CH_3}{Me_3SiOCHSPh}}$$

yield apparently as a single diastereomer judging from the clean nmr spectrum and sharp melting point of the product.[13]

This compound was more thermally stable than trimethylsilylmethyl phenyl sulfoxide but did rearrange in refluxing benzene (2 hr) to afford the *O*-trimethylsilyl *S*-phenyl thioacetal **17**. Such a rearrangement suggests a possible aldehyde synthesis in which **1d** functions as a latent or masked carbonyl equivalent.[14,15] This avenue has not been explored in detail but is not practical at present because **1d** did not prove sufficiently reactive toward other alkyl halides (butyl iodide, 1,5-dibromopentane) to justify further investigation.

Experimental Section

Nmr spectra were recorded on a Hitachi Perkin-Elmer R-20 spectrometer in $CDCl_3$ and chemical shifts are reported in parts per million (δ) from internal tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 337 grating instrument as KBr disks for solids and pressed films for liquids. Melting points are corrected and were determined on a Thomas-Hoover apparatus. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E spectrometer at an ionizing potential of 70 eV.

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[9] (a) D. E. O'Connor and W. I. Lyness, *J. Amer. Chem. Soc.*, **85**, 3044 (1963); (b) D. E. O'Connor and C. D. Broaddus, *ibid.*, **86**, 2267 (1964); (c) D. E. O'Connor and W. I. Lyness, *ibid.*, **86**, 3840 (1964).

[10] J. Jacobus and K. Mislow, *ibid.*, **89**, 5228 (1967), and references cited therein.

[11] H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, **11**, 944 (1972).

[12] P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, 1785 (1972), and references cited therein.

[13] Stereoselective reactions of sulfinyl carbanions with electrophiles have been previously observed: (a) T. Durst, *J. Amer. Chem. Soc.*, **91**, 1034 (1969); (b) T. Durst, R. Viau, and M. R. McClory, *ibid.*, **93**, 1077 (1971); (c) R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *ibid.*, **94**, 8795 (1972); (d) T. Durst, R. R. Fraser, M. R. McClory, R. B. Swingle, R. Viau, and Y. Y. Wigfield, *Can. J. Chem.*, **48**, 2148 (1970); (e) K. Nishihata and M. Nishio, *Chem. Commun.*, 958 (1971); (f) S. Bory, R. Lett, B. Moreau, and A. Marquet, *Tetrahedron Lett.*, 4921 (1972).

[14] (a) D. Lednicer, *Advan. Org. Chem., Methods Results*, **8**, 179 (1972); (b) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969).

[15] Hydrolysis of *O*-alkyl *S*-phenyl thioacetals to aldehydes occurs readily; see T. H. Fife and E. Anderson, *J. Amer. Chem. Soc.*, **92**, 5464 (1970).

Microanalyses were performed by Alfred Bernhardt, Engelskirchen, West Germany.

All reactions were carried out in an atmosphere of dry nitrogen. Tetrahydrofuran was distilled from lithium aluminum hydride. *n*-Butyllithium in *n*-hexane, *tert*-butyllithium in pentane, and phenyllithium in benzene-ether were purchased from Alfa Inorganics.

General Procedure for Synthesis of Vinyl Sulfoxides.—Trimethylsilylmethyl phenyl sulfoxide (**4**, 500 mg, 2.35 mmol) was dissolved in 10 ml of purified tetrahydrofuran under a nitrogen atmosphere and cooled to −70°. A solution of *tert*-butyllithium in pentane (1.7 ml, 3.06 mmol) was added to form a clear yellow solution of **1d**. A solution of 2.35 mmol of the carbonyl compound in ~2 ml of tetrahydrofuran was added and the reaction mixture was stirred at −70° for 10 min and then allowed to warm to room temperature. After 2 hr at room temperature, 20 ml of saturated aqueous ammonium chloride solution was added, the tetrahydrofuran layer was separated, and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried ($MgSO_4$ or Na_2SO_4) and evaporated to afford the crude product.

An identical procedure was used for reactions in which *n*-butyllithium was the base. Yield data for these reactions can be found in Table I.

1-(Phenylsulfinyl)-2,2-diphenylethylene (6b).—The crude product crystallized on being washed with ether, yielding 535 mg (75%) of **6b**, mp 104.5–108.5°. After recrystallization from dichloromethane–ether the compound had mp 110–112°; ir (KBr) 1440, 1035, 1025, 805, 770, 750, 728, 710, 700, 690 cm^{-1}; nmr ($CDCl_3$) δ 7.2–7.9 (m, 15, aromatic) and 6.78 ppm (s, 1, C=CH); mass spectrum (70 eV) *m/e* (rel intensity) 304 (1), 288 (21), 257 (25), 256 (100), 195 (46), 179 (35), 178 (83), 167 (71), 165 (44), 152 (28), 77 (33).

The analytical sample was obtained from a previous preparation as a clear syrup by preparative tlc.

Anal. Calcd for $C_{20}H_{16}OS$: C, 78.91; H, 5.30; S, 10.53. Found: C, 78.73; H, 5.39; S, 10.38.

Phenyl Styryl Sulfoxide (6a).—A mixture of *cis*- and *trans*-phenyl styryl sulfoxides was obtained in 81% yield by preparative tlc of the crude product on silica gel using benzene–ether as the solvent. The product composition was determined by nmr at 100 MHz to be cis/trans = 0.5.[16]

Anal. Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30; S, 14.04. Found: C, 73.46; H, 5.29; S, 13.91.

(1-Phenylsulfinyl)methylenecyclohexane (6c).—Preparative tlc of the crude product from 231 mg (2.35 mmol) of cyclohexanone on silica gel using benzene–ether (1:1) as the solvent gave 351 mg (67%) of **6c** as a colorless oil: nmr ($CDCl_3$) δ 7.5 (m, 5, aromatic), 5.95 (s, 1, C=CH), 2.7 and 2.2 (br m, 4, $C{=}CCH_2$), and 1.6 ppm (br, 6, CH_2); ir (neat) 1630, 1440, 1080, 1040, 1020, 800, 740, 690 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 220 (16), 204 (27), 203 (100), 110 (33), 93 (60), 91 (33), 77 (46), 67 (31), 55 (31), 41 (48).

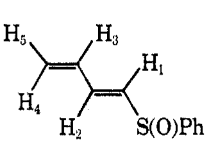
Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32; S, 14.55. Found: C, 70.87; H, 7.25; S, 14.67.

***cis*- and *trans*-2-Isopropylvinyl Phenyl Sulfoxide (6d).**—This reaction was carried out on a 4.7-mmol scale using *n*-butyllithium as the base at −70°. The crude product (563 mg) was chromatographed (preparative tlc) on silica gel using chloroform–ether (8:2) as the eluent to give two fractions. The less polar fraction (170 mg) consisted mainly of diphenyl disulfide and was discarded. The more polar fraction (287 mg, 30%) was a mixture of cis and trans vinyl sulfoxides. The analytical sample was prepared by rechromatography under the same conditions: ir (neat) 3060, 2980, 2940, 1630, 1480, 1450, 1085, 1040, 1000, 750, 730, 690 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 194 (11), 178 (27), 177 (100), 110 (24), 78 (33), 51 (24), 43 (30).

Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; S, 16.50. Found: C, 67.84; H, 7.08; S, 16.65.

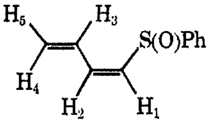
Analysis of the nmr spectrum at 100 MHz ($CDCl_3$) permitted the determination of the cis/trans ratio as 2:1. The spectrum showed, in addition to the aromatic multiplet at δ 7.4–7.8 and the methyl protons as a multiplet at δ 1, a doublet of doublets, *J* = 7, 15 Hz, centered at δ 6.7 which integrated for ~0.25 H and is assigned to *i*-PrC=CH of the trans isomer. The remaining vinyl protons appeared as a multiplet containing at least seven lines from δ 5.8 to 6.3 and integrated for ~1.75 H. Since the total area for vinyl protons is equivalent to 2 H, it follows that the trans isomer is only one-half as abundant as the cis isomer. This receives confirmation from consideration of the signals for $(CH_3)CH{=}C$, which appeared as two multiplets centered at δ 3.2 and 2.4 with areas in the relative ratio 2:1, respectively. The peak at lower field may be assigned to the $(CH_3)_2CH$ which is cis to the sulfoxide on the basis of the anisotropic effect of the sulfoxide group expected to be highly deshielding.[17]

Butadienyl Phenyl Sulfoxide (6e).—The crude product obtained from 0.17 ml (2.5 mmol) of freshly distilled acrolein was purified by preparative tlc on silica gel using benzene–ether (1:1) as the solvent to give 343 mg (82%) of **6e** as a pale yellow oil. The nmr spectrum of the product both at 60 and 100 MHz was extremely complex, as anticipated for a strongly coupled five-spin system. By comparing the 60 MHz spectrum (in CCl_4) with that of authentic *trans*-**6e** it could be ascertained that this compound was present.[18] Measuring the spectrum at 100 MHz of 60 mg of the product in 0.4 ml of $CDCl_3$ containing 50 mg of $Eu(fod)_3$ simplified the spectrum sufficiently so that it was possible to assign certain signals and not only verify that *cis*-**6e** was present but to determine that *cis*-**6e** and *trans*-**6e** were present in approximately equal amounts. The peak positions and assignments in the presence of the shift reagent are given below and are consistent with expectation. (δ values represent centers of multiplets.)



trans-**6e**

H_1: 7.2, d, J_{12} = 15 Hz
H_2: 8.2, dd, J_{12} = 15, J_{23} = 10Hz
H_3: 6.4–6.9, dt, J_{23} = J_{35} = 10, J_{34} = 17 Hz



cis-**6e**

H_1: overlaps with meta and para aromatic protons (7.3–7.5)
H_2: 6.7 (t) J_{12} = J_{23} = 10 Hz

These nmr experiments were actually run on a sample obtained from a reaction in which *n*-butyllithium was used as the metalating agent, but there was no difference in the composition of the product obtained for the reaction when *tert*-butyllithium was the base, as evidenced from the appearance of the 60-MHz spectrum.

***cis*- and *trans*-1-(Phenylsulfinyl)-*trans*-4-phenylbutadiene (6f).**—Using *n*-butyllithium as the metalating agent, a solution of **1d** was prepared in tetrahydrofuran at −70° and treated with 310 mg (2.35 mmol) of *trans*-cinnamaldehyde. After hydrolysis and extraction 695 mg of product was obtained which was subjected to preparative tlc on silica gel using 1:1 benzene–ether as the eluent. The middle band was isolated as a yellow liquid (504 mg) and found to be mainly a mixture of *cis*- and *trans*-**6f** from its nmr spectrum. Rechromatography using 1:1 ethyl acetate–cyclohexane as the solvent gave a pure mixture of isomers (415 mg, 70%), ir (neat) 1630, 1580, 1440, 1090, 1040, 1000, 750, 730, 700 cm^{-1}. The nmr spectrum in $CDCl_3$ at 100 MHz revealed the presence of two doublets centered at δ 6.40 and 6.15 in the ratio 2:1, respectively. The low-field doublet had a coupling constant of 14 Hz and the one at higher field had a coupling constant of 10 Hz, leading to the assignment of *trans*-**6f** to the major product and *cis*-**6f** to the minor product. Together these two signals integrated for 1 proton out of a total area equivalent to 14 protons.

Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55; S, 12.61. Found: C, 75.32; H, 5.39; S, 12.48.

3-(1-Phenylsulfinyl)methylenecyclohexene (6g).—Addition of **1d** to cyclohexenone was carried out in the usual manner at −70° to yield 614 mg of an oil which purified with difficulty. Four separate preparative tlc steps were employed to afford, ultimately, 123 mg (24%) of **6g** as a colorless liquid: ir (neat) 3060, 3040, 2950 (CH), 1720, 1640, 1450, 1085, 1040 (S=O), 1000, 945, 870, 750, 740, 690 cm^{-1}; nmr ($CDCl_3$) δ 7.7–7.2 (m, 5, aromatic),

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[16] The nmr spectra of the cis and trans isomers are sufficiently different in the region δ 6–7 to permit determination of composition; see T. H. Kinstle and W. R. Oliver, *Org. Mass Spectrom.*, **6**, 699 (1972).

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[18] This spectrum was kindly provided by Professor David A. Evans of UCLA. We acknowledge his assistance with thanks.

7.05–6.85 and 6.4–5.8 (m, 3, vinyl H), and 3–1.5 ppm (m, 6, ring CH_2).

Anal. Calcd for $C_{13}H_{14}OS$: C, 71.52; H, 6.46; S, 14.69. Found: C, 71.27; H, 6.54; S, 14.49.

2-(1-Phenylsulfinyl)methyleneadamantane (6h).—The general procedure was modified to the extent that the reaction mixture was refluxed for 0.5 hr prior to work-up. The crude product was recrystallized from ether–pentane to yield 521 mg (82%) of **6h**, mp 81.5–85°. Recrystallization from the same solvent mixture gave the analytical sample: mp 88–89°; ir (KBr) 3050, 2900, 2850, 1620, 1440, 1080, 1038, 1030, 800, 745, 720, 700, 690 cm^{-1}; nmr ($CDCl_3$) δ 7.5 (m, 5, aromatic), 5.92 (s, 1, C=CH), 3.6 and 2.5 (br, 2, C=CCH), and 2.0 ppm (br, 12); mass spectrum (70 eV) *m/e* (rel intensity) 272 (100), 256 (26), 255 (24), 224 (46), 223 (32), 167 (20), 105 (32), 93 (26), 91 (74), 79 (43), 77 (37), 67 (32), 41 (40).

Anal. Calcd for $C_{17}H_{20}OS$: C, 74.96; H, 7.40; S, 11.77. Found: C, 74.97; H, 7.26; S, 11.64.

In a previous experiment using *n*-butyllithium as the base and omitting the 0.5-hr reflux step, *i.e.*, standard conditions, the crude product was a yellow syrup (742 mg) from which was obtained by a combination of preparative tlc on silica gel and fractional recrystallization 97 mg of pure **6h** (mp 88.5–91.5°) and 47 mg of **10** (mp 142–143°): nmr ($CDCl_3$) δ 7.5 (m, s, aromatic), 4.18 (s, 1, OH), 3.1 [q, 2, J = 14 Hz, $CH_2S(O)$], 2.6–2.0 (br m, 3), and 2.0–1.5 ppm (br m, 11). The analytical sample had mp 143.5–144°.

Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.63; S, 11.04. Found: C, 70.14; H, 7.42; S, 10.90.

***In Situ* Generation of 1-Trimethylsilyl-1-(methylsulfinyl)-methyllithium. Reaction with Benzophenone.**—To a solution of 785 mg (10 mmol) of dimethyl sulfoxide (distilled from calcium hydride) in 30 ml of tetrahydrofuran was added 4.5 ml of 2.3 *M* *n*-butyllithium in *n*-hexane at 25°. After the addition was complete the resulting suspension was cooled to −15° and 0.7 ml (5.5 mmol) of trimethylchlorosilane was added to form a yellow solution. After 1 hr a solution of 910 mg (5 mmol) of benzophenone in 3 ml of tetrahydrofuran was added and the solution was stirred at −15° for 0.5 hr and then at 25° for 1.5 hr. Work-up in the usual way afforded 1.18 g of a thick yellow oil which was taken up in ether–dichloromethane and *n*-hexane was added until the hot solution was turbid. On cooling, 610 mg (50%) of 1-(methylsulfinyl)-2,2-diphenylethylene (**12**), mp 86–92°, was deposited. Recrystallization gave material of mp 98–100° (lit. mp 106°),[4d] the nmr spectrum of which was identical with that reported.

***In Situ* Generation of 1d. Reaction with Benzophenone.**—To a solution of 2.1 g (15 mmol) of methyl phenyl sulfoxide in 30 ml of purified tetrahydrofuran at −70° was added 16 mmol of *n*-butyllithium (6.83 ml of a 2.34 *M* solution in *n*-hexane). A yellow solution formed to which was added 0.96 ml (815 mg, 7.5 mmol) of trimethylchlorosilane and the solution was stirred for 50 min. Benzophenone (910 mg, 5 mmol) in 3 ml of tetrahydrofuran was added rapidly and after 15 min at −70° the cooling bath was removed and the now deep red solution was allowed to warm to room temperature. Hydrolysis with saturated aqueous ammonium chloride and extraction with dichloromethane gave 2.74 g of crude product which was chromatographed on 100 g of silica gel. Elution with 400 ml of ether gave 364 mg of a yellow liquid which was a complex mixture as estimated by nmr and was not further characterized. A further 100 ml of ether removed 567 mg of solid which on recrystallization from ether gave 246 mg (15%) of phenyl (2,2-diphenyl-2-hydroxy)ethyl sulfoxide (**7**), mp 128.5–131°, identified by comparison of its nmr spectrum with that of authentic material (see below). Recrystallization from dichloromethane–ether gave material of mp 122–123°; ir (KBr) 1450, 1200, 1180, 1060, 1025, 1000, 780, 760, 700 cm^{-1}; nmr ($CDCl_3$) δ 7.7–7.0 (m, 15, aromatic), 5.69 (s, 1, OH), and 3.58 ppm (s, 2, CH_2).

Anal. Calcd for $C_{20}H_{18}O_2S$: C, 74.50; H, 5.63; S, 9.94. Found: C, 74.42; H, 5.53; S, 10.06.

Concentration of the ether solution which remained after **7** had crystallized caused 146 mg (10%) of **6b** to be deposited, mp 100–104°.

Elution of the chromatographic column with 100 ml more of ether removed a further 360 mg (24%) of **6b** (identified by nmr) which on being washed with ether gave 280 mg of material, mp 111–112°.

Continued elution with 400 ml of 1:1 ethyl acetate–ether removed 71 mg of an oil, which was discarded. The solvent was changed to pure ethyl acetate (250 ml) to elute 462 mg (32%) of a white, crystalline solid, mp 85–89°, identified as 1-(*n*-butylsulfinyl)-2,2-diphenylethylene (**13**). Recrystallization from dichloromethane–ether gave the analytical sample: mp 94–95°; ir (KBr) 3070, 3050, 2970, 2940, 2880, 1500, 1480, 1450, 1410, 1340, 1100, 1080, 1035 (sh), 1015 (vs), 1000, 825, 805, 762, 730, 700 cm^{-1}; nmr ($CDCl_3$) δ 7.30 (10, aromatic), 6.72 (s, 1, vinyl), 2.7 [m, 2, $CH_2S(O)$], 2–1.1 (m, 4, CH_2CH_2), and 0.9 ppm (skewed t, 3, CH_3).

Anal. Calcd for $C_{18}H_{20}OS$: C, 76.01; H, 7.09; S, 11.27. Found: C, 75.90; H, 7.19; S, 11.08.

1,1-Diphenyl-2-(phenylsulfinyl)ethanol (7).—Methyl phenyl sulfoxide (1.05 g, 7.5 mmol) in 15 ml of tetrahydrofuran was metalated with phenyllithium (3.5 ml of a 2.3 *M* solution in 7:3 benzene–ether) at −70°. A solution of 1.365 g (7.5 mmol) of benzophenone in 3 ml of tetrahydrofuran was added. After 0.5 hr at −70° the solution was warmed to room temperature and worked up as usual to afford 2.40 g (100%) of **7** as a white, crystalline solid, mp 134–136°. Repeated recrystallization from methylene chloride–ether gave material of mp 127–128° (lit.[19] mp 152). The nmr spectrum was identical with that of the product formed in the preceding experiment.

1-(Phenylsulfinyl)methylcyclohexanol (8).—To a solution of (phenylsulfinyl)methyllithium prepared in a manner identical with that above was added 784 mg (8.0 mmol) of cyclohexanone. After recrystallization of the crude product from methylene chloride–ether, 1.63 g (91%) of **8** was obtained as white flakes, mp 97–99° (lit.[19] mp 98°).

Reaction of 1-Trimethylsilyl-1-(phenylsulfinyl)methyllithium with Ethyl Benzoate.—To a solution of **1d** prepared from 4.7 mmol of **4** in 25 ml of tetrahydrofuran (*tert*-butyllithium was the metalating agent) at −72° was added 705 mg (4.7 mmol) of ethyl benzoate. After 10 min at −72° the cooling bath was removed and the solution was allowed to stir for 3 hr and then refluxed for 30 min. Saturated ammonium chloride solution was added and the reaction mixture was extracted with dichloromethane. The organic extracts were dried ($MgSO_4$) and the solvent was evaporated to yield 1.14 g of a yellow oil which was chromatographed (preparative tlc) on silica gel (1:1 ethyl acetate–benzene). The major component of the mixture (435 mg, 76%) crystallized and was determined to be (phenylsulfinyl)acetophenone (**15**) by comparison of its nmr[20] and ir[20,21] spectra with those reported.

Because the melting point of repeatedly recrystallized product (70.5–71.5°) was at variance with that recorded in the literature (mp 76–77°,[21] 79–80°,[20] 81°[22]) it was submitted for analysis.

Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95; S, 13.12. Found: C, 68.75; H, 4.92; S, 13.02.

1-Trimethylsilyl-1-(phenylsulfinyl)ethane (16).—To a solution of **1d** prepared from 2.35 mmol of **4** and *n*-butyllithium in 15 ml of tetrahydrofuran was added 0.16 ml (355 mg, 2.5 mmol) of methyl iodide. After 0.5 hr at −70° the solution was kept at −40° for 0.5 hr and then warmed to 25° and worked up in the usual manner to give 489 mg (92%) of **16** as an oil which crystallized on standing. The nmr of the crude product was identical with that of the analytical sample, mp 66–67.5°, obtained by preparative tlc (silica gel with methylene chloride–ether) and recrystallization from ether–cyclohexane: nmr ($CDCl_3$) δ 7.47 (s, 5, aromatic), 1.91 (q, 1, J = 7 Hz, SCHSi), 1.0 (d, 3, J = 7 Hz, CH_3C), and 0.25 ppm (s, 9, $SiMe_3$).

Anal. Calcd for $C_{11}H_{18}OSSi$: C, 58.36; H, 8.01; S, 14.16; Si, 12.39. Found: C, 58.48; H, 8.05; S, 14.00; Si, 12.18.

Rearrangement of 16.—A solution of **16** (57 mg, 0.25 mmol) in 10 ml of dry benzene was refluxed under nitrogen for 2 hr. Tlc analysis of the reaction mixture at this point indicated the absence of starting material, so the solution was evaporated to leave 38.7 mg (68%) of **17** as a colorless oil: ir (neat) 3090, 2970, 1600, 1480, 1450, 1250, 1110, 1030, 950, 750, and 700 cm^{-1}; nmr ($CDCl_3$) δ 7.5–7.2 (m, 5, aromatic), 5.25 (q, 1, J = 7 Hz, SCHO), 1.55 (d, 3, J = 7 Hz, CH_3CH), and 0.05 ppm (s, 9, $SiMe_3$); mass spectrum (70 eV) *m/e* (rel intensity) 226 (4), 117 (62), 75 (22), 73 (100).

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Anal. Calcd for $C_{11}H_{18}OSSi$: C, 58.36; H, 8.01; S, 14.16. Found: C, 58.52; H, 7.79; S, 14.31.

Registry No.—**1d**, 40110-24-5; **4**, 18789-72-5; *cis*-**6a**, 40110-65-4; *trans*-**6a**, 40110-66-5; **6b**, 40110-26-7; **6c**, 40110-27-8; *cis*-**6d**, 40110-67-6; *trans*-**6d**, 40110-68-7; *trans*-**6e**, 40110-69-8; *cis*-**6e**, 40110-70-1; *cis*-**6f**, 40110-71-2; *trans*-**6f**, 40110-72-3; **6g**, 40110-28-9; **6h**, 40110-29-0; **7**, 23975-23-7; **8**, 23975-27-1; **10**, 40110-32-5; **12**, 21147-11-5; **13**, 40110-34-7; **15**, 6099-23-6; **16**, 40110-36-9; **17**, 40110-37-0; benzaldehyde, 100-52-7; adamantanone, 700-58-3; cyclohexanone, 108-94-1; acrolein, 107-02-8; *trans*-cinnamaldehyde, 14371-10-9; cyclohexenone, 930-68-7; 1-trimethylsilyl-1-(methylsulfinyl)methyllithium, 40110-38-1; benzophenone, 119-61-9; dimethyl sulfoxide 67-68-5; trimethylchlorosilane, 75-77-4; methyl phenyl sulfoxide, 1193-82-4; ethyl benzoate, 93-89-0.

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Silane Reductions in Acidic Media. II. Reductions of Aryl Aldehydes and Ketones by Trialkylsilanes in Trifluoroacetic Acid. A Selective Method for Converting the Carbonyl Group to Methylene[1a,b]

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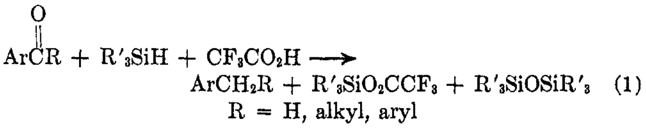
Trialkylsilanes in trifluoroacetic acid media selectively reduce the carbonyl group of arylcarbonyl compounds to methylene. Aryl alkyl ketones and diaryl ketones that can be synthesized by Friedel–Crafts acylation procedures are quantitatively reduced to the corresponding arenes. Benzaldehydes substituted with activating groups form the corresponding toluenes; however, substituted toluene formation is competitive with Friedel–Crafts alkylation. Specific γ-lactone formation occurs in the reduction of 3-benzoylpropanoic and *o*-benzoylbenzoic acids. The requirements and limitations of trialkylsilane reductions have been examined and procedures for the isolation of arene products determined.

The reduction of the carbonyl group of aldehydes and ketones to methylene has enjoyed wide application in organic syntheses. Of the reductive methods that have been employed, the Clemmensen[2] and Wolff–Kishner[3] reactions have exhibited the most general utility. Other methods, including catalytic hydrogenation,[4] reductions using Raney nickel in hydroxide media,[5] and trichlorosilane–trialkylamine[6] and metal hydride reductions,[7] have been successfully applied more specifically to aryl aldehydes and ketones.

Kursanov, Parnes, and coworkers have recently reported the reduction of the carbonyl group of benzophenone, Michler's ketone, acetophenone, and 2,4,6-trimethylbenzaldehyde to methylene using triethylsilane in trifluoroacetic acid media.[8] Because of the good yields reported for these silane reductions and the reported ability of silanes to undergo hydride transfer to relatively stable carbenium ions,[9,10] we expected that silane reductions of aldehydes and ketones would represent a convenient and synthetically useful method for transforming a carbonyl group to methylene. In this paper we report the application of trialkylsilanes to reductions of aryl aldehydes and ketones in acidic media.

Results

The yields of arylhydrocarbon products from trialkylsilane reductions of the corresponding carbonyl compounds are given in Table I. In general, 2 equiv of silane are required for the reduction of 1 equiv of carbonyl compound to the methylene product in trifluoroacetic acid (eq 1); silane products are the trial-



$$\mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R} + \mathrm{R'_3SiH} + \mathrm{CF_3CO_2H} \longrightarrow \mathrm{ArCH_2R} + \mathrm{R'_3SiO_2CCF_3} + \mathrm{R'_3SiOSiR'_3} \quad (1)$$

$\mathrm{R} = \mathrm{H}$, alkyl, aryl

kylsilyl trifluoroacetate and hexaalkyldisiloxane in amounts that vary with the reaction conditions. Reductions were observed to occur readily at room temperature and for phenyl alkyl ketones and diaryl ketones generally required less than 15 min for complete reduction. Reductions of aliphatic aldehydes and ketones, such as octanal and cyclohexanone, did not give the corresponding methylene products.

Trifluoroacetic acid was chosen as the solvent for these reactions because of its acidity and good solvat-

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