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Registry No. **1a**, 15874-80-3; **1b**, 84602-85-7; **1c**, 5897-46-1; **1d**, 49639-05-6; **1e**, 3112-87-6; **2a**, 84602-86-8; **2b**, 74866-54-9; **2c**, 50464-16-9; **2d**, 50465-67-3; **2e**, 84602-87-9; **2f**, 84602-88-0; **2g**, 84602-89-1; **2h**, 84602-90-4; **3a**, 84602-91-5; **3b**, 84602-92-6; **3c**, 84602-93-7; **4a**, 84602-94-8; **4b**, 84602-95-9; **5**, 84602-96-0; **6a**, 84602-97-1; **7b**, 84602-98-2; **8b**, 84602-99-3; **9a**, 84603-00-9; **9b**, 84603-01-0; **10**, 84603-03-2; **11a**, 84603-02-1; **11b**, 84603-04-3; TBABr, 1643-19-2; C_2Cl_6, 67-72-1; CCl_4, 56-23-5; EtBr, 74-96-4; $CH_2{=}CHCH_2Br$, 106-95-6; $CH_2{=}CHCN$, 107-13-1; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_4Br$, 110-52-1.

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Generation of Metal-Free Silyl Anions from Disilanes and Fluoride Catalyst. Synthetic Reactions with Aldehydes and 1,3-Dienes

Summary: The Si–Si bond of disilanes is found to be cleaved by tetrabutylammonium fluoride (TBAF) in hexamethylphosphoric triamide to produce metal-free silyl anion and triorganosilyl fluoride. The disilane/TBAF reagent was studied spectrometrically. Synthetic application of the reagent with a catalytic amount of TBAF is illustrated by the reaction with aldehydes and 1,3-dienes.

Sir: Triorganosilyl anions have recently emerged as synthetic tools for introduction of silyl group into organic compounds.[1] Generation of the anionic species hitherto reported includes reduction of Si–X or Si–Si bond with alkaline metal or magnesium[1c] or nucleophilic substitution of one of the disilane silicon atoms with metal alkoxide or methyllithium at the sacrifice of half the molecule.[1] The chemical behavior of the silyl anions thus produced should be understood in association with the metal gegenion. Herewith we report that the disilane Si–Si bond is cleaved by tetrabutylammonium fluoride (TBAF) to give metal-free triorganosilyl anion and also that both silicon elements of disilanes are incorporated into aldehyde carbonyl and 1,3-diene units effectively.

We first studied the spectrometric behavior of disilane/TBAF reagent. Hexamethyldisilane (1.1 mmol) and anhydrous TBAF[2] (1.0 mmol) were dissolved in hexamethylphosphoric triamide (HMPA) (1.5 mL) to give a yellow solution, which showed ^{19}F NMR absorptions (CF_3COOH, standard) at δ 15.0 and 72.8 in ca. 2:1 intensity ratio in place of the absorption of TBAF δ 34.5. These new absorptions may be attributed to 5-coordinate silicon intermediate **1**[3] and trimethylsilyl fluoride,[4] respectively, on the basis of the reported values. ^1H NMR analysis (C_6H_6 as a standard)[5] gave a broad singlet at δ 0.0. Evaporation of all the volatile material gave a singlet peak at δ −0.17 (9 H intensity per 4 Bu)[6] consistent with structure **2**, which gave tetramethylsilane (δ 0.00) on treatment with excess methyl iodide. Thus, it seems reasonable to conclude that the following equilibrium exists in HMPA solution. It should be emphasized that trimethylsilyl anion in **2** is completely metal-free and will exhibit unique reactivity compared with the conventional R_3SiM reagents.[1c,7]

$$\mathrm{Me_3SiSiMe_3 + Bu_4N^+F^- \rightleftarrows \underset{\mathbf{1}}{Bu_4N^+[Me_3SiSiMe_3F]^-} \rightleftarrows \underset{\mathbf{2}}{Bu_4N^+SiMe_3^-} + Me_3SiF}$$

Upon addition to unsaturated functional group A=B, trimethylsilyl anion gives $\equiv$SiAB$^-$, which is subsequently silylated by Me_3SiF to regenerate the fluoride catalyst. Thus, catalytic amount of TBAF should be enough for the $\equiv$SiABSi$\equiv$ production. This concept is visualized by the reaction with alkanals.[8]

To the pale yellow reagent solution prepared by treatment of hexamethyldisilane (0.31 mL, 1.5 mmol) with TBAF (0.1 mmol or 0.5 M THF solution, 0.2 mL) in HMPA (2 mL) (room temperature, 5 min) was added undecanal (0.21 mL, 1.0 mmol), and the mixture was stirred for 4.5 h. The color ascribed to the trimethylsilyl anion vanished at this moment. GLC analysis of the reaction mixture revealed the presence of 1-(trimethylsilyl)-1-((trimethylsilyl)oxy)undecane and undecyl trimethylsilyl ether only. Workup effected by treatment with concentrated HCl/MeOH (1:10) (1 mL), extraction with ether, washing with aqueous NH_4Cl solution and then with brine, concentration, followed by purification by silica gel column chromatography (hexane/ethyl acetate, 10:1), gave 1-(trimethylsilyl)-1-undecanol[9] (0.163 g, 67% yield) along with 1-undecanol (44 mg, 26%).

$$\mathrm{RCHO + Me_3SiSiR'_3 \xrightarrow[HMPA]{TBAF\ (5\ mol\ \%)} RCH(OSiMe_3)SiR'_3 \xrightarrow{H_3O^+} RCH(OH)SiR'_3}$$

The procedure is applied to various aldehydes and disilanes, and the results are given in the order of aldehyde,

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(1) (a) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520. Fleming, I.; Newton, T. W.; Roessier, F. *Ibid.* **1981**, 2527. (b) Tamao, K.; Akita, M.; Kanatani, R.; Ishida, N.; Kumada, M. *J. Organomet. Chem.* **1982**, 226, C9. (c) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981; pp 134–140 and references cited therein.

(2) Kuwajima, I.; Nakamura, E. *J. Am. Chem. Soc.* **1975**, *97*, 3257.

(3) ^{19}F NMR (MeCN, CF_3COOH standard, room temperature) of $Ph_3SiF_2^-NPr_4^+$ is reported to give an absorption at δ 18.8 [Kuroda, K.; Ishikawa, N. *Nippon Kagaku Zasshi* **1970**, *91*, 77], while the spectra (CH_2Cl_2 solution, $CFCl_3$ standard) of $Ph_2SiF_3^-NEt_4^+$ at low temperatures exhibit two peaks at δ 98.0 (axial) and 134.0 (equatorial) in a ratio of 2:1 [Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155]. According to Muetterties and his co-worker, the peaks coalesce into a single one at δ 110 on warming to room temperature, in agreement with the observation of Ishikawa and Kuroda (δ 38.9, CF_3COOH). Since organic ligands prefer the equatorial position of five-coordinate trigonal-bipyramidal silicon species (loc. cit.), the absorption at δ 15.0 from CF_3COOH (δ 93 calculated on the basis of $CFCl_3$) in our experiment can be ascribed to the axial fluorine. This assignment is supported by the data in: Farnham, W. B.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4608.

(4) Hunter, B. K., Reeves, L. W. *Can. J. Chem.* **1968**, *46*, 1399.

(5) The chemical shift of benzene in HMPA was found to be δ 7.40 (tetramethylsilane, standard).

(6) (Trimethylsilyl)sodium in HMPA prepared according to the procedure by Sakurai et al. [Sakurai, H.; Okada, A.; Kira, M.; Yonezawa, K. *Tetrahedron Lett.* **1971**, 1511] showed singlet peaks at δ −0.18 and −0.12. (Trimethylsilyl)lithium exhibits an absorption at δ 1.73 (in dimethoxyethane) or δ 1.33 (in cyclopentane) higher field than that of cyclopentane (generally δ 1.51): Schaaf, T. F.; Oliver, J. P. *J. Am. Chem. Soc.* **1969**, *91*, 4327.

(7) Davis, D. D.; Gray, C. E. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 283.

(8) Addition of trimethylsilyl anion to carbonyl compounds: (a) Jutzi, P.; Schröder, F.-W. *J. Organomet. Chem.* **1970**, *24*, C43. (b) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063.

(9) ^1H NMR (CCl_4) δ 0.00 (s, 9 H), 0.88 (t, J = 6 Hz, 3 H), 1.0–1.7 (m, 19 H), 3.20 (t, J = 6 Hz, 1 H); IR (neat) 3400, 1245, 835 cm^{-1}; MS; *m/e* (rel %) 229 (M^+ − 15, 2), 91 (34), 75 (80), 73 (100), 57 (20), 43 (26).

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Table I. Reaction of Disilanes (3) with 1,3-Dienes (4) To Give 1,4-Disilyl-2-butenes (5)

entry	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	yield of 5,[a] %	E/Z ratio[n]
1	Me	Me	Me	Me	Me	Me	H	H	78	100:0
2	Et	Et	Et	Et	Et	Et	H	H	78[b]	98:2
3	Me	Me	Me	Ph	Ph	Ph	H	H	56[c]	64:36
4	Me	Me	Me	Me	Me	Me	H	Me	68[d]	95:5
5	Et	Et	Et	Et	Et	Et	H	Me	81[e]	96:4
6	Me	Me	Me	Me	Me	Me	Me	Me	81[f]	99:1
7	Et	Et	Et	Et	Et	Et	Me	Me	62[g]	>99:1
8	Me	Me	Me	Ph	Ph	Ph	Me	Me	48[h]	93:7
9	Me	Me	Me	Me	Me	Me	H	$Me_2C{=}CHCH_2CH_2$	77[i]	84:16
10	Me	Me	Ph	Me	Me	Ph	H	H	73[j]	>99:1
11	Me	Me	Ph	Me	Me	Ph	H	Me	69[k]	89:11
12	Me	Me	Ph	Me	Me	Ph	Me	Me	71[l]	>99:1
13	Me	Me	$CH{=}CH_2$	Me	Me	$CH{=}CH_2$	Me	Me	15[m]	o

[a] Yield was estimated after purification by distillation or chromatography. [b] Bp 130-140 °C (0.9 torr); ^{1}H NMR ($CDCl_3$ for all spectra shown here) δ 0.3-0.7 (m, 12 H), 0.8-1.1 (m, 18 H), 1.3-1.5 (m, 4 H), 5.1-5.3 (m, 2 H). [c] R_f (SiO_2 TLC for all data here, hexane) 0.3; ^{1}H NMR δ -0.16 (s, 5.8 H), 0.05 (s, 3.2 H), 1.32 (d, J = 6 Hz, 1.3 H), 1.37 (d, J = 6 Hz, 0.7 H), 2.25 (d, J = 6 Hz, 1.3 H), 2.26 (d, J = 6 Hz, 0.7 H), 5.2-5.4 (m, 1.3 H), 5.3-5.5 (m, 0.7 H), 7.2-7.6 (m, 15 H). [d] Bp 95-108 °C (13 torr); ^{1}H NMR δ 0.03 (s, 18 H), 1.42 (d, J = 8 Hz, 2 H), 1.49 (s, 2 H), 1.54 (s, 3 H), 4.99 (t, J = 8 Hz, 1 H). [e] Bp 140-150 °C (1 torr); ^{1}H NMR δ 0.3-0.7 (m, 12 H), 0.8-1.1 (m, 18 H), 1.35 (d, J = 9 Hz, 2 H), 1.43 (s, 2 H), 1.53 (s, 3 H), 4.89 (t, J = 9 Hz, 1 H). [f] Bp 115-125 °C (13 torr); ^{1}H NMR δ 0.00 (s, 18 H), 1.46 (s, 4 H), 1.51 (s, 6 H). [g] Bp 140-150 °C (1.5 torr); ^{1}H NMR δ 0.3-0.7 (m, 12 H), 0.8-1.1 (m, 18 H), 1.47 (s, 4 H), 1.56 (s, 6 H). [h] R_f 0.3 (hexane); ^{1}H NMR δ -0.05 (s, 9 H), 1.29 (s, 2 H), 1.42 (s, 6 H), 2.34 (s, 2 H), 7.2-7.7 (m, 15 H). [i] Bp 165-175 °C (15 torr); ^{1}H NMR δ 0.00 (s, 18 H), 1.41 (d, J = 8 Hz, 2 H), 1.46 (s, 2 H), 1.62 (s, 3 H), 1.69 (s, 3 H), 1.9-2.1 (m, 4 H), 4.93 (t, J = 8 Hz, 1 H), 5.0-5.2 (m, 1 H). [j] R_f 0.4 (hexane); ^{1}H NMR δ 0.20 (s, 12 H), 1.57-1.70 (m, 4 H), 5.1-5.3 (m, 2 H), 7.2-7.5 (m, 10 H). [k] R_f 0.4 (hexane); ^{1}H NMR δ 0.20 (s, 6 H), 0.22 (s, 6 H), 1.40 (s, 3 H), 1.58 (d, J = 7 Hz, 2 H), 1.67 (s, 2 H), 4.93 (t, J = 7 Hz, 1 H), 7.2-7.5 (m, 10 H). [l] R_f 0.4 (hexane); ^{1}H NMR δ 0.25 (s, 12 H), 1.40 (s, 6 H), 1.70 (s, 4 H), 7.2-7.5 (m, 10 H). [m] Bp 100-110 °C (13 torr); ^{1}H NMR δ 0.10 (s, 12 H), 1.57 (s, 6 H), 5.5-6.4 (m, 6 H). [n] Estimated by GLC or HPLC. [o] Not determined.

disilane, product,[10] % yield: *n*-$C_{10}H_{21}CHO$, $Me_3SiSiMe_3$, *n*-$C_{10}H_{21}CH(OH)SiMe_3$, 67; *n*-$C_{10}H_{21}CHO$, $Me_3SiSiPh_3$, *n*-$C_{10}H_{21}CH(OH)SiPh_3$, 64; *n*-C_3H_7CHO, $Me_3SiSiPh_3$, *n*-$C_3H_7CH(OH)SiPh_3$, 60; *i*-C_3H_7CHO, $Me_3SiSiPh_3$, *i*-$C_3H_7CH(OH)SiPh_3$, 61; *t*-C_4H_9CHO, $Me_3SiSiMe_3$, *t*-$C_4H_9CH(OH)SiMe_3$, 30; *t*-C_4H_9CHO, $Me_3SiSiPh_3$, *t*-$C_4H_9CH(OH)SiPh_3$, 33; $CH_2{=}O$, $Me_3SiSiPh_3$, $HOCH_2SiPh_3$, 38. Noteworthy is that fluoride anion attacks selectively the less hindered silicon atom of an unsymmetrical disilane to give electronically favored silyl anion, as exemplified by the reaction with 1,1,1-trimethyl-2,2,2-triphenyldisilane, which invariably gave triphenylsilyl adducts only.

When aldehydes of ArCHO type were allowed to react with hexamethyldisilane and TBAF catalyst, an ca. 1:1 mixture of *dl* and meso 1,2-diarylethanediols was produced after hydrolytic workup.[11] Cesium fluoride also was an

$$\mathrm{ArCHO} \xrightarrow[\mathrm{TBAF\ or\ CsF}]{\mathrm{Me_3SiSiMe_3}} \mathrm{ArCH(OH)CH(OH)Ar}$$

effective catalyst, but potassium fluoride was completely inactive. Aldehydes having electron-donating substituents give good yields of the pinacols, whereas *p*-nitrobenzaldehyde or pyridine-4-carbaldehyde proved to be sluggish. The results are presented in the order ArCHO, catalyst, % yield of pinacol:[10] C_6H_5CHO, TBAF, 94; C_6H_5CHO, CsF, 100; C_6H_5CHO, TBAF ($Me_3SiSiPh_3$ employed), 84; C_6H_5CHO, TBAF ($Me_2(EtO)SiSi(OEt)Me_2$ employed), 73; *p*-$BuOC_6H_4CHO$, TBAF, 95; *p*-$MeOC_6H_4CHO$, TBAF, 87; *p*-$Me_2NC_6H_4CHO$, CsF, 26;[12a] *p*-$Me_2NC_6H_4CHO$, TBAF, 61;[12b] *p*-ClC_6H_4CHO, CsF, 90; 1-naphthyl-CHO, CsF, 48.[12c]

Extention of the reaction to other carbonyl compounds and oxiranes turned out to be futile: recovery of 4-*tert*-butylcyclohexanone, dimerization of 2-cyclohexenone,[13] recovery of styrene oxide and 4-octene oxide, and polymerization of acrolein were observed in sharp contrast to the reaction of R_3SiM (M = Li or K).[1c,8,14]

The characteristic feature of the disilane/TBAF reagent system is observed in the transformation of 1,3-dienes into 1,4-disilyl-2-butenes.[15] A tetrahydrofuran (THF) solution of TBAF (0.5 M solution, 1.0 mL, 0.5 mmol) was added to hexamethyldisilane (1.46 g, 10 mmol) dissolved in HMPA (10 mL) at room temperature under an argon atmosphere, and the reagent solution was stirred for 5 min. 1,3-Butadiene (0.27 L, 12 mmol) was injected with the aid of a syringe, and the reaction mixture was stirred for 24 h at room temperature. Workup followed by distillation gave (*E*)-1,4-bis(trimethylsilyl)-2-butene[16] (1.57 g, 75% yield). GLC analysis showed a single peak. On the basis of the IR and ^{1}H NMR spectra the configuration of the

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[10] Products were isolated by column chromatography and/or distillation. All the products are characterized spectrometrically and analytically.

[11] This behavior parallels the reactivity of (triphenylsilyl)lithium: (a) Wittenberg, D.; Wu, T. C.; Gilman, H. *J. Org. Chem.* **1959**, *24*, 1349. Gilman, H.; Lichtenwalter, G. D. *J. Am. Chem. Soc.* **1958**, *80*, 607. The addition of trimethylsilyl anion to carbonyl compounds may be initiated by electron transfer, as the blue color ascribed to ketyl is observed in the reaction of benzophenone with hexamethyldisilane/TBAF reagent, though the adduct was not obtained to any extent. Thus, the pinacol dimerization of ArCHO may be ascribed to $Ar\dot{C}HOM$ (M = $SiMe_3$ or $^-$). However, another reaction path for the dimerization is also possible, which involves the Brook rearrangement of $ArCH(SiMe_3)O^-$ to $ArCH^-OSiMe_3$ followed by addition to the second molecule of ArCHO.

[12] (a) The starting aldehyde was recovered (54%). (b) *p*-(Dimethylamino)-α-(trimethylsilyl)benzyl alcohol was produced in 8% yield. (c) The starting aldehyde (23%) was recovered. 1-Naphthylmethanol was the byproduct (13%).

[13] The major product was tentatively assigned as 2,2′-bis(3-(trimethylsilyl)cyclohexanone).

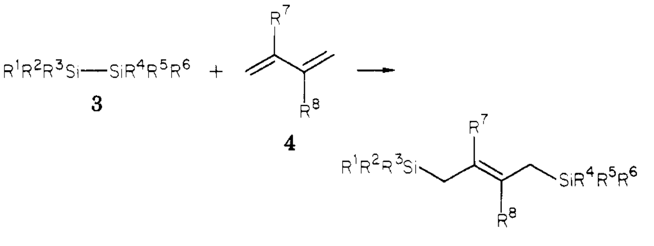
[14] (a) Reetz, M. T.; Plachky, M. *Synthesis* **1976**, 199. (b) Dervan, P. B.; Shippey, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 1265.

[15] Other synthetic methods for disilylation of 1,3-dienes: (a) Dunogues, J.; Calas, R.; Dedier, J.; Pisciotti, F. *J. Organomet. Chem.* **1970**, *25*, 51. (b) Dunogues, J.; Arreguy, B.; Biran, C.; Calas, R.; Pisciotti, F. *Ibid.* **1973**, *63*, 119. (c) Weyenberg, D. R.; Toporcer, L. H.; Nelson, L. E. *J. Org. Chem.* **1968**, *33*, 1975. (d) U.S. Patent 3187032.

[16] Transition-metal catalysts are able to achieve the similar disilylation of 1,3-dienes with disilanes having H or F as the substituents: (a) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87. (b) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (c) Sakurai, H.; Kamiyama, H.; Nakadaira, Y. *Chem. Lett.* **1975**, 887. (d) Matsumoto, H.; Shono, K.; Wada, A.; Matsubara, I.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 185.

product was established.[17] Formation of dimeric product (i.e., 1,3-butadiene/disilane, 2:1) was less than 3% as revealed by GLC assay of the crude products.

The reaction was applied to various disilanes (**3**) and 1,3-butadienes (**4**) to produce 1,4-disilyl-2-butenes (**5**) (Table I). Salient features of the reaction are summarized as follows.



5

(1) Reaction conditions are extremely mild (neutral reagent, room temperature, atmospheric pressure) compared with the reductive disilylation[15] or the transition-metal-catalyzed disilylation[16] of 1,3-dienes.

(2) Oligomerization of 1,3-dienes is suppressed compared with the reductive disilylation.[15] These oligomers are easily separated by simple distillation or chromatography.

(3) *E* Isomers of **5** are produced with high selectivity. 1,2-Disilylation products were not produced to any measurable extent.

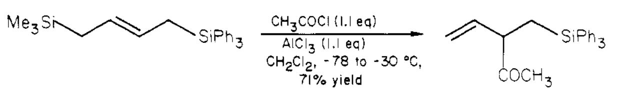
(4) Scrambling of silyl group does not take place. For example, unsymmetric disilanes such as 1,1,1-trimethyl-2,2,2-triphenyldisilane (entries 3 and 8 of Table I) give **5** having a silyl group at each end. In view of the selective attack of fluoride ion to the less hindered silicon atom, the reaction seems to be initiated here by triphenylsilyl anion.

(5) Use of equimolar amounts of 1,3-dienes and disilanes is essential for effective *E* olefin formation. When a 7:1 mole ratio of isoprene and disilane with 7 mol % of TBAF in HMPA was employed for the reaction of run 4 in Table I, the yield of 2:1 product increased only 30% at the slight expense of *E* selectivity. Reaction in concentrated solutions decreased the total yield of products with somewhat increased formation of the 2:1 product.

(6) Aprotic polar solvent such as HMPA or 1,3-dimethyl-2-imidazolidinone (DMI) is particularly essential for the reaction (cf. run 4, Table I; in DMI 47% yield with 89% *E*). Dimethylformamide or THF turned out to be ineffective.

(7) The disilylation is sensitive to the substitution pattern, as 1,3-dienes having substituents on the 1 and/or 4 carbon(s) were recovered unchanged. The olefinic bond remains intact as shown by the reaction of myrcene (entry 9).

The products obtained herein should have wide applicability in view of synthetic reactions exploited by Calas and others.[18] Particular attention should be paid to unsymmetrically substituted 1,4-disilyl-2-butenes. For example, 1-(trimethylsilyl)-4-(triphenylsilyl)-2-butene was selectively transformed into 3-((triphenylsilyl)methyl)-4-penten-2-one (selectivity more than 95%). Further synthetic applications are in progress in our laboratories.[19]



Registry No. **1**, 84824-61-3; **2**, 84812-32-8; **3** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Et), 1633-09-6; **3** ($R^1 = R^2 = R^4 = R^5$ = Me; $R^3 = R^6$ = Ph), 1145-98-8; **3** ($R^1 = R^2 = R^4 = R^5$ = Me; $R^3 = R^6 = CH{=}CH_2$), 1450-29-9; **4** (R^7 = H; R^8 = Me), 78-79-5; **4** ($R^7 = R^8$ = Me), 513-81-5; **4** (R^7 = H; $R^8 = Me_2C{=}CHCH_2CH_2$), 123-35-3; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Me; $R^7 = R^8$ = H), 16054-35-6; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Et; $R^7 = R_8$ = H), 84812-44-2; (*E*)-**5** ($R^1 = R^2 = R^3$ = Me; $R^4 = R^5 = R^6$ = Ph; $R^7 = R^8$ = H), 84812-45-3; (*Z*)-**5** ($R^1 = R^2 = R^3$ = Me; $R^4 = R^5 = R^6$ = Ph; $R^7 = R^8$ = H), 84812-46-4; (*E*)-**5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^8$ = Me; R^7 = H), 16109-36-7; (*Z*)-**5** ($R^1 = R^2 = R^3 = R^4 = R^5$ = R6 = R^8 = Me; R^7 = H), 16054-36-7; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Et; R^7 = H; R^8 = Me), 84812-47-5; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8$ = Me), 16054-38-9; **5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Et; $R^7 = R^8$ = Me), 84812-48-6; (*E*)-**5** ($R^1 = R^2 = R^3 = R^7 = R^8$ = Me; $R^4 = R^5 = R^6$ = Ph), 84812-49-7; (*Z*)-**5** ($R^1 = R^2 = R^3 = R^7 = R^8$ = Me; $R^4 = R^5 = R^6$ = Ph), 84812-50-0; (*E*)-**5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Me; R^7 = H; $R^8 = Me_2C{=}CHCH_2CH_2$), 84812-51-1; (*Z*)-**5** ($R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = Me; R^7 = H; $R^8 = Me_2C{=}CHCH_2CH_2$), 84812-52-2; **5** ($R^1 = R^2 = R^4 = R^5$ = Me; $R^3 = R^6$ = Ph; $R^7 = R^8$ = H), 84812-53-3; (*E*)-**5** ($R^1 = R^2 = R^4 = R^5 = R^8$ = Me; $R^3 = R^6$ = Ph; R^7 = H), 84812-54-4; (*Z*)-**5** ($R^1 = R^2 = R^4 = R^5 = R^8$ = Me; $R^3 = R^6$ = Ph; R^7 = H), 84812-55-5; **5** ($R^1 = R^2 = R^4 = R^5 = R^7 = R^8$ = Me; $R^3 = R^6$ = Ph), 84812-56-6; **5** ($R^1 = R^2 = R^4 = R^5 = R^7 = R^8$ = Me; $R^3 = R^6 = CH{=}CH_2$), 84812-57-7; TBAF, 429-41-4; $Me_3SiSiMe_3$, 1450-14-2; $Me_3SiSiPh_3$, 1450-18-6; $Me_2(EtO)SiSi(OEt)Me_2$, 18419-84-6; *n*-C_3H_7CHO, 123-72-8; *i*-C_3H_7CHO, 78-84-2; *t*-C_4H_9CHO, 630-19-3; $CH_2{=}O$, 50-00-0; C_6H_5CHO, 100-52-7; *p*-$BuOC_6H_4CHO$, 5736-88-9; *p*-$MeOC_6H_4CHO$, 123-11-5; *p*-$Me_2NC_6H_4CHO$, 100-10-7; *p*-ClC_6H_4CHO, 104-88-1; 1-naphthyl-CHO, 66-77-3; *n*-$C_{10}H_{21}CH(OH)SiPh_3$, 84812-35-1; *n*-$C_3H_7CH(OH)SiPh_3$, 84812-36-2; *i*-$C_3H_7CH(OH)SiPh_3$, 84812-37-3; *t*-$C_4H_9CH(OH)SiMe_3$, 84812-38-4; *t*-$C_4H_9CH(OH)SiPh_3$, 20083-30-1; $HOCH_2SiPh_3$, 18670-80-9; $C_6H_5CH(OH)CH(OH)C_6H_5$, 492-70-6; *p*-$MeOC_6H_4CH(OH)CH(OH)C_6H_4$-*p*-OMe, 4464-76-0; *p*-$BuOC_6H_4CH(OH)CH(OH)C_6H_4$-*p*-OBu, 84812-39-5; *p*-$Me_2NC_6H_4CH(OH)CH(OH)C_6H_4$-*p*-$NMe_2$, 54322-62-2; *p*-$ClC_6H_4CH(OH)CH(OH)C_6H_4$-*p*-Cl, 38152-44-2; 1-naphthyl-CH(OH)CH(OH)-1-naphthyl, 84812-40-8; undecanal, 112-44-7; 1,3-butadiene, 106-99-0; trimethylsilyl fluoride, 420-56-4; 1-(trimethylsilyl)-1-((trimethylsilyl)oxy)undecane, 84812-33-9; undecyl trimethylsilyl ether, 17957-64-1; 1-(trimethylsilyl)-1-undecanol, 84812-34-0; 3-((triphenylsilyl)methyl)-4-penten-2-one, 84812-41-9; *p*-(dimethylamino)-α-(trimethylsilyl)benzyl alcohol, 84812-42-0; 1-naphthylmethanol, 4780-79-4; 2,2′-bis(3-(trimethylsilyl)cyclohexanone), 84812-43-1.

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Conjugate Addition of Moderately Soft Anions to a Vinyl Sulfone[1]

Summary: The potassium and, in part, lithium anions of ethyl acetate, dimethyl acetamide, acetonitrile, acetophenone, pinacalone, and (trimethylsilyl)acetylene undergo conjugate addition to 3-(*tert*-butyldimethylsiloxy)-1-cyclohexenyl *tert*-butyl sulfone. The resultant α-sulfonyl anions may be protonated or trapped with an electrophile (MeI) stereospecifically. The usefulness of these reactions

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[17] For the assignment of the configuration, see ref 15c.

[18] (a) Calas, R.; Dunogues, J.; Pillot, J.-P.; Biran, C,; Pisciotti, F.; Arreguy, B. *J. Organomet. Chem.* **1975**, *85*, 149. (b) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981; pp 97–124. (c) Kumada, M. et al. *J. Synth. Org. Chem., Jpn.* **1982**, *40*, 462–590.

[19] We are indebted to Dr. Kohei Tamao, Department of Synthetic Chemistry, Kyoto University, for helpful discussions and to Shin-etsu Chemical Co., Ltd., for the generous gift of disilanes.

† Graduate Research Associate. David Ross Fellow, 1981–1982. Texaco Fellow, 1982–1983.

(1) Syntheses via Vinyl Sulfones 10. For paper 9, see: S. G. Pyne, D. C. Spellmeyer, S. Chen, and P. L. Fuchs, *J. Am. Chem. Soc.*, 104, 5728 (1982).

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