phase was separated, washed with 5 mL of saturated aqueous NH_4Cl, dried with Na_2SO_4 or $CaCl_2$, and the evaporated. When yields were determined by GC, an internal standard (often benzylacetone) was added after the 5 mL of ether, and the organic phase was not evaporated. In those cases in which the temperature in Table II is cited as "−84 °C", the reaction mixture was cooled to −84 °C (N_2/ethyl acetate) prior to the addition of the α,β-unsaturated ketone. Thirty minutes after the addition, the reaction mixture, still at −84 °C, was poured into 5 mL of saturated aqueous NH_4Cl and worked up as described above. In those cases in which the temperature is cited as "−84 °C↑" in Table II, the cold bath was removed half way through the 30-min reaction time. At the end of the 30 min, the reaction mixture, now near room temperature, was worked up as described above.

Identification of Products. Except for entry 26 in Table II, the identity of each 1,4- and 1,2-addition product was confirmed by comparing the ^1H NMR spectrum and the GC retention time (coinjection) with that of authentic materials. The sources of the authentic materials are as follows: **7**, **9**, **11**, **13**, **15**, and **16** were obtained commercially; **1** was prepared by Isobe's method;[3a] **2**, **3**,[10] **4**,[10] **6**,[11] and **8**[10] were prepared by treating 2-cyclohexen-1-one with the corresponding Grignard reagent and were purified by preparative GC; **10**, **12**, and **14** were prepared by treating vinylmagnesium bromide (Aldrich) with the corresponding methyl ketone; **5** was prepared from lithium diphenylcuprate and 2-cyclohexen-1-one;[12] **17** was prepared from 2-cyclopenten-1-one and n-$Bu_2Cu(CN)Li_2$;[2] **18** was prepared from 2-cyclopenten-1-one and n-butyllithium.

3-Isopropylcyclopentanone (19). Following the general procedure and preparative GC, **19** was isolated as an oil: IR (neat) 1730 cm^{-1}; ^1H NMR (CCl_4) δ 0.93 (d, 6 H), 1.2–1.8 (m, 4 H), 1.8–2.3 (m, 4 H). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.32; H, 11.30.

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Registry No. **1**, 39178-69-3; **3**, 23396-36-3; **5**, 20795-53-3; **6**, 60174-90-5; **7**, 591-24-2; **8**, 23758-27-2; **9**, 111-13-7; **11**, 110-12-3; **13**, 2550-26-7; **15**, 107-87-9; **16**, 115-18-4; **17**, 57283-81-5; **19**, 10264-56-9; 2-cyclohexenone, 930-68-7; methyl vinyl ketone, 78-94-4; 2-cyclopentenone, 930-30-3; butylmagnesium chloride, 693-04-9; butylmagnesium bromide, 693-03-8; isopropylmagnesium chloride, 1068-55-9; isopropylmagnesium bromide, 920-39-8; phenylmagnesium chloride, 100-59-4; phenylmagnesium bromide, 100-58-3; methylmagnesium chloride, 676-58-4; methylmagnesium bromide, 75-16-1; methylmagnesium iodide, 917-64-6.

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Electrochemical Synthesis of Organosilicon Compounds

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Electrochemical reduction of allyl, aryl, and vinyl halides in the presence of a silylating agent (Me_3SiCl, HMe_2SiCl, and $PhMe_2SiCl$) in a solution of tetraethylammonium tosylate in dimethylformamide (DMF) gave the corresponding organosilicon compounds. The regioselectivity of the reaction of allylic halides depends on the nature of the silylating agent. Trimethylsilyl and dimethylphenylsilyl groups were introduced to the less substituted end of the allyl group, whereas the dimethylsilyl group was introduced to both ends of the allyl group. High chemoselectivity of the present approach was demonstrated by selective monosilylations of *p*-bromoiodobenzene and *p*-bromocinnamyl chloride to obtain (*p*-bromophenyl)trimethylsilane and (*p*-bromocinnamyl)trimethylsilane, respectively. A mechanism involving a carbanion intermediate is suggested.

The usefulness of organosilicon compounds as synthetic intermediates[2] opens the question of their methods of preparation. Although several methods, including the direct method,[3] transmetalation,[4] hydrosilylation,[5] reductive silylation,[6] and methods using silyl anions[7] and disilanes,[8] have been developed so far, simple and versatile methods are still required especially from a view point of chemoselectivity. Recently we have reported an electro-

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Table I. Electrochemical Reduction of Cinnamyl Derivatives in the Presence of Various Silylating Agents[a]

cinnamyl derivative	silylating agent	electricity, F/mol	product	yield,[b] %
$PhCH{=}CHCH_2Cl$	Me_3SiCl	2.40	$PhCH{=}CHCH_2SiMe_3$ (1)	70
		2.85	1	(98)
	$MeC(OSiMe_3){=}NSiMe_3$	2.85		0
	Me_3SiOMe	2.87		0
	HMe_2SiCl	2.43	$PhCH{=}CHCH_2SiMe_2H$ (2a)	(84)
			$PhCH(SiMe_2H)CH{=}CH_2$ (2b)	(1:1)
	$PhMe_2SiCl$	2.45	$PhCH{=}CHCH_2SiMe_2Ph$ (3)	(66)
$PhCH{=}CHCH_2OAc$	Me_3SiCl	2.74	1	50
$PhCH{=}CHCH_2OCO_2Me$	Me_3SiCl	3.47	1	25
$PhCH{=}CHCH_2SO_2Ph$	Me_3SiCl	2.22	1	(30)
$PhCH{=}CHCH_2OPO(OEt)_2$	Me_3SiCl	9.60	1	trace

[a] Reactions were normally carried out with a cinnamyl derivative (1.0 mmol) and a silylating agent (5.0 mmol) in a solution of Et_4NOTs in DMF at room temperature. [b] Isolated yields. Yields in parentheses were determined by VPC.

chemical access to organosilicon compounds which involves cathodic reduction of organic halides in the presence of a silylating agent (eq 1).[9] We report herein the full details of this study.

$$R\text{–}X + R'_3SiCl \xrightarrow[Et_4NOTs/DMF]{+e} R\text{–}SiR'_3 \qquad (1)$$

Electrochemical reduction of organic halides has been studied extensively, and the general mechanism has been postulated as shown in Scheme I.[10] The initial electron

Scheme I

$$R\text{–}X \xrightarrow[slow]{+e} R\cdot \xrightarrow[very\ fast]{+e} R^- \xrightarrow{E^+} R\text{–}E$$

transfer produces an organic radical intermediate, but generally the second electron transfer is faster. Thus the generated carbanion intermediate is then free to enter into a reaction with an electrophile which may be present in the reaction medium. Various electrophiles such as proton,[11] carbon dioxide,[12] acyl halides,[13] and olefins[14] are reported to serve as trapping agents of this electrogenerated carbanion intermediate. We envisioned that the trapping of this metal-free carbanion intermediate by a suitable silylating agent would give the corresponding organosilicon compounds.

The origin of the concept has already been reported. Metal reduction of allylic ether in the presence of chlorotrimethylsilane is reported to yield allylic silanes.[15] Reduction of benzyl chloride by sodium naphthalene is reported to give the benzyl anion intermediate which is trapped by chlorotrimethylsilane.[16] It is also reported that electrochemical reduction of benzyl chlorides in the presence of chlorotrimethylsilane affords benzyltrimethylsilanes.[17] However, the generality of the concept had been still uncertain.[18] Thus we examined the electrochemical reduction of various types of organic halides in the presence of several silylating agents.

Scheme II

$$RCH_2{=}CH\text{–}CH_2\text{–}X \xrightarrow[-X^-]{+2e} RCH_2\text{–}\overset{\cdot\cdot}{C}\text{–}H\text{–}\overset{\cdot\cdot}{C}H_2 \xrightarrow{R'_3SiX} RCH_2{=}CHCH_2SiR'_3$$

Results and Discussion

First we chose cinnamyl chloride as a substrate for examination of various silylating agents. A mixture of cinnamyl chloride and an excess silylating agent in a solution of tetraethylammonium tosylate (Et_4NOTs) in dimethylformamide (DMF) was electrolyzed in a cathodic chamber of an H-type cell equipped with platinum electrodes. A constant current was passed at room temperature, and the current density was 10–20 mA/cm^2. Table I summarizes the results. The use of chlorotrimethylsilane as a silylating agent gave rise to the smooth formation of cinnamyltrimethylsilane (1) in high yields. Current yields were 60–70%. However, *O,N*-bis(trimethylsilylacetamide) and methoxytrimethylsilane turned out to be ineffective. Silicon–oxygen bonds seem to be inactive under these conditions. Chlorodimethylsilane and chlorodimethylphenylsilane were effective silylating agents and gave the corresponding silanes in good yields. Especially facile formation of the allylhydrosilane derivatives seems to be attractive from a view point of silicon synthesis. Thus the present method provides a general method for introduction of various silyl groups into allylic halides.

Regioselectivity of the present reaction depends on the nature of the silylating agent. Trimethylsilyl and dimethylphenylsilyl groups were introduced to the less substituted end of the allyl group exclusively. In contrast, the dimethylsilyl group was introduced to both ends of the allyl group in essentially equal amounts. Steric factors best account for the observations, since the less bulky dimethylsilyl group entered the more hindered end as well as the less hindered one, whereas the more bulky trimethylsilyl and dimethylphenylsilyl groups entered only the less hindered end.[19]

In addition to the halides, the acetoxyl group also served as a leaving group for the present reaction.[20] Cathodic

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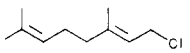
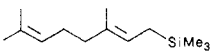
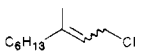
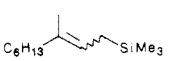
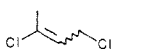
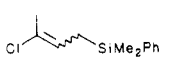
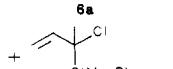
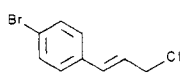
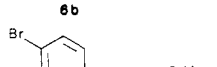
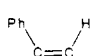
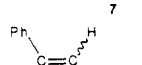
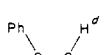
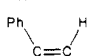
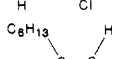
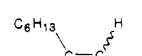
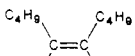
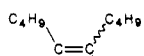
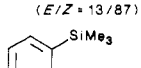
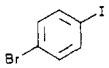
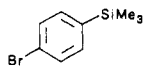
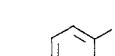
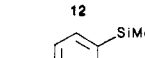
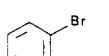
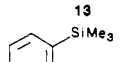
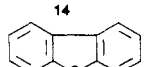
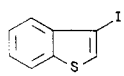
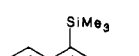
Table II. Electrochemical Silylation of Organic Halides[a]

organic halide	electricity, F/mol	product	yield,[b] %
$PhCH{=}CHCH_2Cl$	2.40	$PhCH{=}CHCH_2SiMe_3$ (1)	70
	2.85	1	(98)
	2.81	 (4)	59
	2.40	 (5)	63
	3.63	 (6a)	74[c]
		 (6b)	(7:3)
	2.39	 (7)	49
	2.95	 (8) (E/Z = 57/43)	(51)
	2.62	8 (E/Z = 68/32)	(23)
	2.93	8 (E/Z = 78/22)	(11)
	3.32	 (9) (E/Z = 57/43)	47
	7.37	 (10) (E/Z = 13/87)	(15)
	2.29	 (11)	(70)
	2.62	 (12)	60
	3.64	 (13)	(53)
	3.64	 (14)	(55)
	3.01	 (15)	(89)
	3.45	 (16)	(62)
	2.82	 (17)	(50)

[a] Reactions were normally carried out with an organic halide (1.0 mmol) and trimethylchlorosilane (5.0 mmol) in a 0.2 M solution of Et_4NOTs in DMF at room temperature. [b] Isolated yields. Yields in parentheses were determined by VPC. [c] $PhMe_2SiCl$ was used as a silylating agent. [d] E/Z = 89/11.

reduction of cinnamyl acetate in the presence of chlorotrimethylsilane gave cinnamyltrimethylsilane in 50% yield (Table I). Cinnamyl carbonate and cinnamyl sulfone also afforded the same product, but the yields were low. Cinnamyl phosphate was inactive under these conditions.

Results obtained for several allylic substrates are summarized in Table II. Reaction of geranyl chloride with chlorotrimethylsilane gave geranyltrimethylsilane. However, geranyl acetate and linaloyl acetate did not afford the allylsilane derivatives. In these cases the acetoxyl group was ineffective as a leaving group. Presumably the reduction potentials of these allylic acetates are in a low cathodic range. In the case of 1,3-dichloro-2-butene a mixture of regioisomeric products (**6a** and **6b**) was obtained, although a rather bulky silylating agent, chlorodimethylphenylsilane, was employed. The electronic factor of the allylic moiety also seems to play some role in the regiochemical control.

Inspection of the reduction potentials of reactants is important for the elucidation of the reaction mechanism. It is reported that the reduction potentials of allyl chlorides are $-1.8 \sim -1.9$ V vs. SCE in DMF.[21] On the other hand, Corriu reported that electrochemical reduction of halosilanes takes place at $-2 \sim -2.5$ V vs. SCE.[22] Thus it is reasonable to consider that allyl chloride is reduced first at the cathode to produce the allyl anion intermediate which is trapped by a chlorosilane (Scheme II). A mechanism involving the allyl radical intermediate seems to be less likely based upon the result obtained with chlorodimethylsilane. Generally the organic radical is known to abstract the hydrogen atom bound to silicon rather than to replace chlorine,[23] but this is not the case. As described in the previous part of this paper, the reaction of cinnamyl chloride with chlorodimethylsilane gave cinnamyldimethylsilane rather than cinnamylchlorodimethylsilane.

Although attempts to use alkyl halides as the substrate were unsuccessful, the present concept can be applied to vinylic and aromatic halides. The results are summarized in Table II. The reactivities of vinyl chlorides and bromides were low under the conditions, but the vinyl iodides reacted smoothly to give the corresponding vinylsilanes.

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(22) (a) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Chem. Soc., Chem. Commun.* **1977**, 649. (b) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *Ibid.* **1979**, 457. (c) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Organomet. Chem.* **1980**, *186*, 19. (d) Corriu, R. J. P.; Dabosi, G., Martineau, M. *Ibid.* **1980**, *188*, 63.

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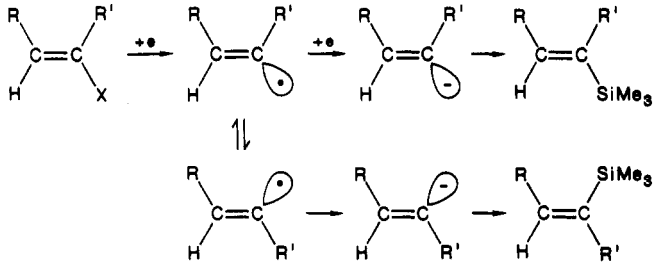
Scheme III



Unfortunately stereochemical integrity was lost during the reaction. In the case of monosubstituted vinyl halides, a mixture of (*E*)- and (*Z*)-vinylsilanes were obtained from isomerically pure (*E*)-vinyl halides. However, in the case of disubstituted vinyl halides, (*Z*)-vinylsilanes were produced predominantly from (*E*)-vinyl halides. Presumably equilibration took place at the stage of the vinyl radical intermediate (Scheme III).[24] In the former case, equilibration of vinyl radical gives a mixture of *E* and *Z* radicals, and thus further reduction followed by trapping by chlorotrimethylsilane gave a mixture of (*E*)- and (*Z*)-vinylsilane. In the latter case, however, the (*E*)-vinyl radical is much more stable than the (*Z*)-vinylradical, and the (*E*)-vinyl radical is reduced to the (*E*)-vinyl anion which is subsequently trapped by chlorotrimethylsilane to give the (*Z*)-vinylsilane (Scheme III). Different stereoselectivities exhibited by chloro-, bromo-, and iodostyrenes are consistent with this scheme. One-electron reduction of iodostyrene to the radical intermediate is the easiest among the three, while reduction of chlorostyrene to the radical is the most difficult. However, the reduction potential of the styryl radical to the carbanion does not depend on the origin of the radical. Thus, in the case of iodostyrene, the radical intermediate seems to be accumulated most extensively, and such a radical can undergo facile cis/trans isomerization.[24] On the other hand, in the case of chlorostyrene, the radical intermediate seems to be readily reduced to the carbanion as soon as it forms. Therefore, use of chlorostyrene exhibited limited stereochemical scrambling.

Aromatic halides were also examined as a substrate for the present reaction, as shown in Table II. Chlorobenzene did not afford the corresponding phenyltrimethylsilane at all. Bromobenzene gave the desired product, but the yield was low. Switching to iodobenzene resulted in smooth formation of phenyltrimethylsilane (**11**) in 70% yield. These observations are consistent with reduction potentials of aryl halides.[25] Heteroaromatic halides such as 3-bromopyridine and 3-iodobenzothiophene also reacted without any difficulty to afford the corresponding heteroaromatic silanes.

One of the intriguing advantages of electrochemical processes is that one can tune up the reaction precisely by simply controlling the reaction potential.[11a] This advantage would also merit the present approach. High chemoselectivity of the present electrochemical silylation reaction is demonstrated by the following simple example. Bromobenzene and iodobenzene can be distinguished quite easily even in constant current conditions, because difference in their reduction potentials is relatively large (~0.6 V). Therefore the selective monosilylation of *p*-bromoiodobenzene was accomplished to obtain (*p*-bromophenyl)trimethylsilane (**12**) in 60% yield. The amount of disilylated product was negligible. Selective monosilylation of *p*-bromocinnamyl chloride also afforded (*p*-bromocinnamyl)trimethylsilane (**7**). Thus the present electrochemical reaction offers a simple, versatile, and chemoselective approach for the introduction of a silyl group into organic molecules.

Experimental Section

General Methods. Tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) was prepared according to the literature,[26] and its solution in dimethylformamide (DMF) was dried over 4-Å molecular sieves overnight before use. Chlorotrimethylsilane was distilled from tributylamine before use. Other chlorosilanes were used as obtained commercially.

Plastic-support precoated (Merck Silica Gel 60 F_{254}, 0.2 mm) plates were employed for analytical TLC. Vapor-phase chromatography (VPC) was performed on a Shimadzu GC-4B or GC-4C gas chromatograph equipped with a 1 m × 3 mm column packed with Silicone DC-550 (20%) on Celite 545. Flow rate was normally 20 mL/min. Proton NMR spectra were determined on a Varian T-60A (60 MHz) instrument or a Varian XL-200 (200 MHz) spectrometer. Infrared (IR) spectra were determined on a Hitachi 215 grating spectrometer. Mass spectra were obtained on a JEOL JMS-D300 mass spectrometer connected with a JEOL JGC-20K gas chromatograph and a JMA-200 data processing system, or a Hitachi M-80A mass spectrometer connected with a Hitachi M-003 data processing system. The ionization potential was 70 eV. 4-Iododibenzofuran[27] and 3-iodobenzothiophene[28] were prepared according to the literature procedures.

Electrochemical Silylation of Organic Halides (General Procedure). An organic halide (1 mmol), a chlorosilane (5 mmol), and a 0.2 M solution of tetraethylammonium tosylate in DMF (3 mL) was placed in the cathodic chamber of an H-type cell equipped with a platinum cathode and anode (10 × 10 mm). A 0.2 M solution of tetraethylammonium tosylate in DMF (4 mL) was placed in the anodic chamber. Constant electric current (normally 10 mA) was passed by using a Kikusui Model PAB-32-0.5 regulated DC power supply with stirring at room temperature. After the reaction (monitored by VPC or TLC), the reaction mixture in the cathodic chamber was poured into crushed ice. Organic materials were extracted with hexane or ether and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by flash chromatography, bulb-to-bulb distillation, or preparative VPC.

Spectral data of some organosilicon compounds prepared by the present method are given below. Other organosilicon compounds were identified by comparison of their spectral data with those of authentic samples.

3-(Dimethylsilyl)-1-phenylpropene (2a) and 3-(Dimethylsilyl)-3-phenylpropene (2b). Allylsilanes **2a** and **2b** were characterized as a mixture. The spectral assignments were based on relative intensity. VPC (160 °C): **2a**, R_t 1.5 min; **2b**, R_t 2.5 min.

2a: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.16 (d, J = 3.7 Hz, 6 H), 1.78 (dd, J = 6.6 and 3.2 Hz, 2 H), 3.9–4.05 (m, 1 H), 6.2–6.4 (m, 2 H), 7.1–7.5 (m, 5 H).

2b: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.04 (d, J = 3.6 Hz, 3 H), 0.10 (d, J = 3.6 Hz, 3 H), 3.05–3.15 (m, 1 H), 3.9–4.05 (m, 1 H), 4.95–5.15 (m, 2 H), 6.1–6.4 (m, 1 H), 7.1–7.5 (m, 5 H).

2a + 2b: TLC R_f 0.39 (hexane); IR (liquid film) 3090 (w), 3060 (w), 3025 (m), 2960 (m), 2910 (w), 2120 (s), 1640 (w), 1630 (m), 1600 (m), 1500 (m), 1250 (s), 960 (s), 890 (s), 740 (s), 700 (s) cm^{-1}; mass spectrum, *m/e* (%) 177 (P+1, 0.2), 176 (P, 1.2), 148 (34.5), 117 (10.4), 115 (15.5), 91 (8.7), 72 (19.4), 59 (100); mass spectrum, calcd for $C_{11}H_{16}Si$ 176.1020, found 176.1000.

3-(Dimethylphenylsilyl)-1-phenylpropene (3). TLC R_f 0.58 (9:1 hexane/ethyl acetate); VPC (230 °C) R_t 4.6 min.; ^{1}H NMR (60 MHz, CCl_4) δ 0.34 (s, 6 H), 1.8–1.95 (m, 2 H), 6.0–6.2 (m, 2 H), 7.0–7.6 (m, 10 H); IR (liquid film) 3050 (m), 3010 (m), 2950 (m), 1640 (m), 1600 (m), 1495 (m), 1425 (s), 1250 (s), 1110 (s), 960

(24) See ref 11a. See also: Singer, L. A.; Kong, N. P. *J. Am. Chem. Soc.* **1966**, *88*, 5213.
(25) Sease, J. W.; Burton, F. G.; Nickol, S. L. *J. Am. Chem. Soc.* **1968**, *90*, 2595.
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(28) Gaertner, R. *J. Am. Chem. Soc.* **1952**, *74*, 4950.

(s), 850 (s), 825 (s), 810 (s), 730 (s), 690 (s) cm^{-1}; mass spectrum, m/e (%) 252 (P, 3.4), 137 (4.3), 136 (13.9), 135 (100), 107 (6.9), 105 (7.7), 91 (5.1); mass spectrum, calcd for $C_{17}H_{20}Si$ 252.1334, found 252.1335.

3,7-Dimethyl-1-(trimethylsilyl)-2,6-octadiene (4). TLC R_f 0.70 (hexane); VPC (150 °C) R_t 2.8 min; ^1H NMR (200 MHz, $CDCl_3$) δ −0.03 (s, 9 H), 1.38 (d, J = 8.6 Hz, 2 H), 1.53 (s, 3 H), 1.59 (s, 3 H), 1.66 (s, 3 H), 1.9–2.1 (m, 4 H), 5.0–5.2 (m, 2 H); IR (liquid film) 2950 (s), 2920 (s), 1440 (m), 1380 (m), 1250 (s), 1155 (m), 850 (s) cm^{-1}.

Only the E isomer was obtained in this case, which was confirmed by comparison of NMR data of the product with those of an authentic sample (E/Z mixture).[7h]

3-Methyl-1-(trimethylsilyl)-2-nonene (5). E and Z isomers were characterized as a mixture: VPC (100 °C) Z isomer, R_t 8.8 min; E isomer, R_t 10.2 min; ^1H NMR (200 MHz, $CDCl_3$) δ −0.03 (s, 9 H), 0.75–0.95 (m, 3 H), 1.15–1.45 (m, 10 H), 1.52 (s, E isomer) and 1.65 (s, Z isomer) (65:35 total 3 H), 1.9–2.05 (m, 2 H), 5.0–5.2 (m, 1 H); IR (liquid film) 2950 (s), 2925 (s), 2850 (s), 1470 (m), 1380 (w), 1250 (s), 1155 (m), 850 (s) cm^{-1}.

Spectral data were identical with those of an authentic sample.[7h]

3-Chloro-1-(dimethylphenylsilyl)-2-butene (6a) and 3-Chloro-3-(dimethylphenylsilyl)-1-butene (6b). Allylsilanes **6a** (a mixture of E and Z isomers) and **6b** were characterized as a mixture. The spectral assignments were based on the relative intensity.

6a: ^1H NMR (200 MHz, $CDCl_3$) δ 0.33 and 0.36 (two s, total 6 H), 1.8–1.95 (m, 2 H), 2.10 (s with fine couplings, 3 H), 5.46 (t, J = 8.3 Hz with fine couplings) and 5.63 (t, J = 9.3 Hz with fine couplings) (total 2 H), 7.3–7.7 (m, 5 H).

6b: ^1H NMR (200 MHz, $CDCl_3$) δ 0.44 and 0.48 (two s, 6 H), 1.60 (s, 3 H), 5.0–5.2 (m, 2 H), 5.96 (dd, J = 10.6 and 16.9 Hz, 1 H), 7.3–7.7 (m, 5 H).

6a + 6b: IR (liquid film) 3060 (w), 3050 (w), 3000 (w), 2950 (m), 2920 (w), 1425 (s), 1250 (s), 1115 (s), 1060 (m), 830 (s), 695 (s) cm^{-1}; mass spectrum, calcd for $C_{12}H_{17}ClSi$ 224.0786, found 224.0775.

1-(4-Bromophenyl)-3-(trimethylsilyl)propene (7): ^1H NMR (60 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 1.6–1.75 (m, 2 H), 6.1–6.3 (m, 2 H), 7.10 (d, J = 9 Hz, 2 H), 7.25 (d, J = 9 Hz, 2 H); IR (liquid film) 2940 (m), 1635 (m), 1480 (s), 1245 (s), 1140 (m), 1065 (m), 1000 (m), 955 (m), 855 (s) cm^{-1}; mass spectrum, calcd for $C_{12}H_{17}BrSi$ 268.0283, found 268.0285.

1-Bromo-4-(trimethylsilyl)benzene (12): VPC (150 °C) R_t 2.6 min; ^1H NMR (60 MHz, CCl_4) δ 0.27 (s, 9 H), 6.8–7.35 (m, 4 H); IR (liquid film) 3070 (w), 3035 (w), 3005 (w), 2950 (s), 2895 (w), 1575 (s), 1480 (s), 1380 (m), 1255 (s), 1105 (w), 1065 (s), 1010 (m), 1000 (m), 840 (s), 800 (s), 750 (s), 715 (s) cm^{-1}; mass spectrum, calcd for $C_9H_{13}BrSi$ 227.9969, found 227.9942.

4-(Trimethylsilyl)dibenzofuran (15): VPC (230 °C) R_t 3.4 min; ^1H NMR (60 MHz, CCl_4) δ 0.47 (s, 9 H), 7.05–7.6 (m, 5 H), 7.8–8.0 (m, 2 H); IR (liquid film) 3050 (w), 2950 (m), 2900 (w), 1580 (w), 1490 (w), 1470 (m), 1450 (s), 1390 (s), 1250 (s), 1180 (s), 880 (m), 830 (s), 750 (s) cm^{-1}; mass spectrum, m/e 242 (P+2, 1.7), 241 (P+1, 6.8), 2400 (P, 30.2), 227 (5.5), 226 (20.2), 225 (100), 195 (20.4), 165 (18.8), 113 (14.5); mass spectrum, calcd for $C_{15}H_{16}OSi$ 240.0969, found 240.0970. Anal. Calcd for $C_{15}H_{16}OSi$: C, 74.95; H, 6.71. Found: C, 75.22; H, 6.76.

3-(Trimethylsilyl)benzothiophene (16): VPC (200 °C) R_t 2.9 min; ^1H NMR (60 MHz, CCl_4) δ 0.41 (s, 9 H), 7.1–7.5 (m, 3 H), 7.7–7.95 (m, 2 H); IR (liquid film) 3050 (w), 2950 (m), 2880 (w), 1470 (m), 1450 (m), 1410 (s), 1250 (s), 1060 (m), 960 (s), 830 (s), 760 (s), 720 (s) cm^{-1}; mass spectrum, m/e (%) 197 (2.1), 196 (5.6), 194 (35.3), 177 (16.8), 173 (100); mass spectrum, calcd for $C_{11}H_{14}SSi$ 206.0585, found 206.0587. Anal. Calcd for $C_{11}H_{14}SSi$: C, 64.02; H, 6.84. Found: C, 64.17; H, 6.89.

Mixed Solvents Containing Methanol as Useful Reaction Media for Unique Chemoselective Reductions with Lithium Borohydride

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The reducing ability of lithium borohydride is greatly enhanced in mixed solvents containing methanol. Esters, lactones, and epoxides are reduced chemoselectively more rapidly with $LiBH_4$–MeOH(1 equiv added at the beginning)–ether than with $LiBH_4$–ether in the presence of other reducible groups such as carboxylic acid, chloro, nitro, and carbamoyl. On the other hand, nitro, nitrile, carboxyl, and primary and tertiary amide groups are reduced with $LiBH_4$–MeOH(4 equiv dropwise addition)–diglyme(or tetrahydrofuran). However, secondary amides derived from aliphatic amines and metal carboxylate are not reduced. Thus, unique chemoselective reductions of primary amide in the presence of secondary amide or metal carboxylate are achieved.

Metal hydrides and complex metal hydrides are widely used as reducing agents for organic compounds.[1] And much effort has been expended on developing a practical reducing system with novel functional group selectivities. In order to vary the reducing ability of complex metal borohydrides several methods have been applied:[1c,2] (1) varying the cation, (2) addition of metal salts, (3) varying the solvent, (4) use of catalysts. In spite of many efforts, the choice of solvent, especially the effects of mixed solvents, has not been fully studied.

This article reports the use of $LiBH_4$ and MeOH in ether solvents as selective reducing agents with significant synthetic potential.[3]

Lithium borohydride ($LiBH_4$) is commercially available and also easily prepared from sodium borohydride ($NaBH_4$)[4] and has been reported to be a selective reducing agent for esters,[2,5] although such reductions are relatively slow.

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