

(s), 850 (s), 825 (s), 810 (s), 730 (s), 690 (s)  $\text{cm}^{-1}$ ; 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  $\text{C}_{17}\text{H}_{20}\text{Si}$  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;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -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)  $\text{cm}^{-1}$ .

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).<sup>7h</sup>

**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;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -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)  $\text{cm}^{-1}$ .

Spectral data were identical with those of an authentic sample.<sup>7h</sup>

**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:**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  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:**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  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)  $\text{cm}^{-1}$ ; mass spectrum, calcd for  $\text{C}_{12}\text{H}_{17}\text{ClSi}$  224.0786, found 224.0775.

**1-(4-Bromophenyl)-3-(trimethylsilyl)propene (7):**  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  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)  $\text{cm}^{-1}$ ; mass spectrum, calcd for  $\text{C}_{12}\text{H}_{17}\text{BrSi}$  268.0283, found 268.0285.

**1-Bromo-4-(trimethylsilyl)benzene (12):** VPC (150 °C)  $R_t$  2.6 min;  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ )  $\delta$  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)  $\text{cm}^{-1}$ ; mass spectrum, calcd for  $\text{C}_9\text{H}_{13}\text{BrSi}$  227.9969, found 227.9942.

**4-(Trimethylsilyl)dibenzofuran (15):** VPC (230 °C)  $R_t$  3.4 min;  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ )  $\delta$  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)  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  242 (P+2, 1.7), 241 (P+1, 6.8), 240 (P, 30.2), 227 (5.5), 226 (20.2), 225 (100), 195 (20.4), 165 (18.8), 113 (14.5); mass spectrum, calcd for  $\text{C}_{15}\text{H}_{16}\text{OSi}$  240.0969, found 240.0970. Anal. Calcd for  $\text{C}_{15}\text{H}_{16}\text{OSi}$ : 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;  $^1\text{H}$  NMR (60 MHz,  $\text{CCl}_4$ )  $\delta$  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)  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  (%) 197 (2.1), 196 (5.6), 194 (35.3), 177 (16.8), 173 (100); mass spectrum, calcd for  $\text{C}_{11}\text{H}_{14}\text{SSi}$  206.0585, found 206.0587. Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{SSi}$ : 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

Kenso Soai\* and Atsuhiko Ookawa

Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

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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  $\text{LiBH}_4$ -MeOH (1 equiv added at the beginning)-ether than with  $\text{LiBH}_4$ -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  $\text{LiBH}_4$ -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.<sup>1</sup> 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:<sup>1c,2</sup> (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 sol-

vents, has not been fully studied.

This article reports the use of  $\text{LiBH}_4$  and MeOH in ether solvents as selective reducing agents with significant synthetic potential.<sup>3</sup>

Lithium borohydride ( $\text{LiBH}_4$ ) is commercially available and also easily prepared from sodium borohydride ( $\text{NaBH}_4$ )<sup>4</sup> and has been reported to be a selective reducing agent for esters,<sup>2,5</sup> although such reductions are relatively slow.

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