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The Rate Enhancement Effect of Protodesilylation of Arylsilane Derivatives

Kiitiro Utimoto, Yasuyuki Otake, Hideaki Yoshino, Eiko Kuwahara, Koichiro Oshima, and Seijiro Matsubara*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-8501

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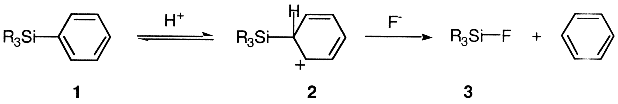
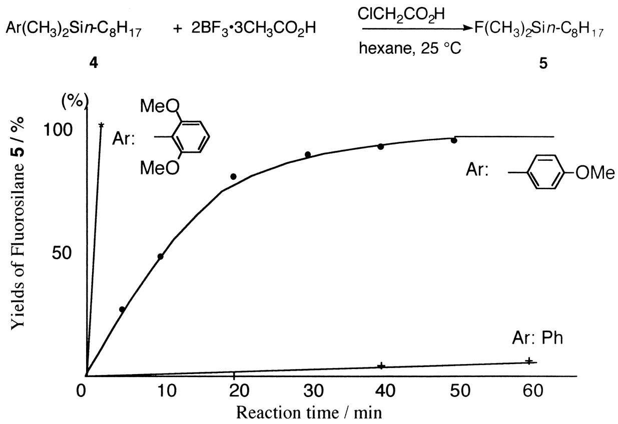
Protodesilylation of the aryl moiety in (*p*-methoxyphenyl)dimethylsilyl and (2,6-dimethoxyphenyl)dimethylsilyl groups proceeds much faster than that in a phenyldimethylsilyl group under acidic conditions; these aryl groups can be substituted with an F atom to give organosilyl fluoride even in the presence of an acid-sensitive group such as an alkenyl group.

Oxidation of a C–Si bond to a C–O bond developed by Tamao, Kumada,[1a] and Fleming[1b] created the concept of using a silyl group as a masked hydroxy group.[1] A silyl group as a masked hydroxy group has been widely used for organic transformations, as it is stable over a wide range of reaction conditions. Especially, Fleming used a stable dimethyl(phenyl)silyl group which is planned to be oxidized in two steps:[1b] protodesilylation and oxidation. The first step, protodesilylation is performed with protic acid and a fluoride ion to afford a fluorodimethylsilyl group which is easily oxidized with alkaline hydrogen peroxide or perbenzoic acid. This first step, protodesilylation, sometimes becomes a crucial reaction, as a protic reaction condition often causes a decomposition of the substrate. For example, alkenyldimethyl(phenyl)silane cannot be converted into alkenyldimethylsilyl fluoride under protic conditions, as the alkenyl group is protodesilylated faster than the phenyl group. A booster on the phenyl group should be introduced to achieve effective protodesilylation of the aryl moiety.

Considering the mechanism of protodesilylation in a dimethyl(phenyl)silyl group proposed by Eaborn,[2] the crucial step is the equilibrium between **1** and **2** (Scheme 1). For the effective protonation, introduction of an electron rich methoxy substituent on the phenyl group might be favored. As shown in Scheme 2, aryldimethyl(octyl)silane was treated with boron trifluoride–acetic acid complex (2/3) and chloroacetic acid. As an aryl group, phenyl, *p*-methoxyphenyl, and 2,6-dimethoxyphenyl were examined. As shown in Scheme 2, a methoxy group on the benzene ring accelerated the substitution reaction; 90% of dimethyl(octyl)phenylsilane was recovered unchanged even after 60 min, whereas (*p*-methoxyphenyl)dimethyl(octyl)silane was converted into **5** in 95% yield after 50 min. In the case of the reaction of (2,6-dimethoxyphenyl)dimethyl(octyl)silane, it was converted into **5** quantitatively within 5 min.



Scheme 1.



Scheme 2.

The booster effect on protodesilylation by a methoxy group benefits the selective protodesilylation even in the presence of an acid-sensitive group. As shown in Scheme 3, allenyl (**6a**), allyl (**9a**), and 1-alkynyl (**13a**) groups were intact during the reaction. Protodesilylation of the 1-alkenyl group competed with that of the *p*-methoxyphenyl group (**10a**); use of a 2,6-dimethoxyphenyl group improved this situation (**11a**, **12a**).

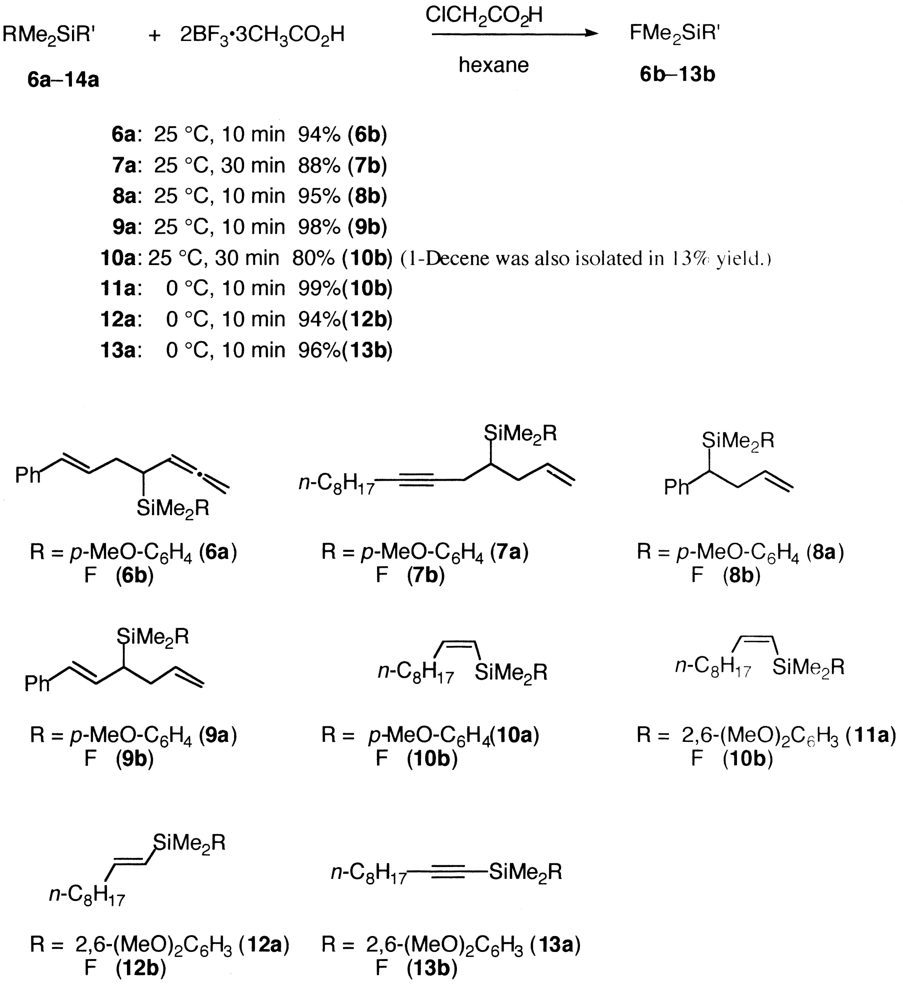
The fluorodimethylsilyl group is recognized as a hydroxy group precursor[1] and an important intermediate for the Hiyama coupling reaction via a hypercoordinated silicon intermediate.[3] The methoxy-substituted aryldimethylsilyl group will be a useful intermediate in the case of the selective preparation of 1-alkenyl-, allenyl-, 1-alkynyl-, or allyldimethylsilyl fluoride.

Experimental

All solvents and chemicals were used as obtained from commercial suppliers. Chromatographic purification of products was accomplished using forced-flow chromatography on Kanto Chemical Co., Inc. Silica gel 60 N (spherical, neutral). ^{1}H NMR spectra were recorded on Varian Gemini-2000 (300 MHz) instrument and are internally referenced to residual protic solvent signals.

General Procedure. To a solution of aryldimethylsilyl substituted compound (**4**, **6a**–**13a**, 1.0 mmol) in hexane (2.0 mL), $2BF_3•3AcOH$ (0.18 g, 0.5 mmol) and $ClCH_2CO_2H$ (0.085 g, 1.0 mmol) were added at the indicated temperature in Scheme 3. The resulting mixture was stirred for 10–30 min. The reaction was quenched by an addition of sat. $NaHCO_3$ aq (20 ml). The mixture was extracted with hexane, dried over Na_2SO_4, and concentrated in vacuo. The obtained residue was characterized by ^{1}H NMR analysis.[4]

(*E*)-4-Fluorodimethylsilyl-7-phenyl-1,2,6-heptatriene (6b). ^{1}H NMR ($CDCl_3$, 20 °C) δ 0.30 (d, J = 7.5 Hz, 3H), 0.31 (d, J = 7.5 Hz, 3H), 1.70–1.82 (m, 1H), 2.30–2.60 (m, 2H), 4.79 (dd , J =



Scheme 3.

6.3, 2.7 Hz, 2H), 5.15 (dt, J = 8.4, 6.3 Hz, 1H), 6.28 (dt, 15.9, 6.9 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 7.16–7.40 (m, 5H).

4-Fluorodimethylsilyl-1-pentadecen-6-yne (7b). ^{1}H NMR ($CDCl_3$, 20 °C) δ 0.27 (d, J = 7.8 Hz, 3H), 0.28 (d, J = 7.8 Hz, 3H), 0,88 (t, J = 6.6 Hz, 3H), 1.02–1.13 (m, 1H), 1.20–1.38 (m, 12H), 2.06–2.40 (m, 6H), 5.00–5.11 (m, 2H), 5.70–5.84 (m, 1H).

4-Fluorodimethylsilyl-4-phenyl-1-butene (8b). ^{1}H NMR ($CDCl_3$, 20 °C) δ 0.15 (d, J = 7.5 Hz, 3H), 0.16 (d, J = 7.5 Hz, 3H), 2.26–2.34 (m, 1H), 2.58–2.65 (m, 2H), 4.88–5.04 (m, 2H), 5.66–5.80 (m, 1H), 7.05–7.32 (m, 5H).

***(E)*-4-Fluorodimethylsilyl-6-phenyl-1,5-hexadiene (9b).** ^{1}H NMR ($CDCl_3$, 20 °C) δ 0.29 (d, J = 7.5 Hz, 3H), 0.30 (d, J = 7.5 Hz, 3H), 1.98–2.10 (m, 1H), 2.30–2.52 (m, 2H), 5.00–5.18 (m, 2H), 5.81–5.94 (m, 1H), 6.13 (dd, J = 15.9, 9.3 Hz, 1H), 6.36 (d, J = 15.9 Hz, 1H), 7.18–7.40 (m, 5H).

***(Z)*-1-Fluorodimethylsilyl-1-decene (10b).** ^{1}HNMR($CDCl_3$, 20 °C) δ 0.31 (d, J = 7.5 Hz, 6H), 0.94 (t, J = 6.6 Hz, 3H), 1.20–1.45 (m, 12H), 2.10–2.22 (t, J = 7.2 Hz, 2H), 5.44 (dd, J = 14.1, 7.8 Hz, 1H), 6.43 (dt, J = 14.1, 7.5 Hz, 1H).

***(E)*-1-Fluorodimethylsilyl-1-decene (12b).** ^{1}HNMR($CDCl_3$, 20 °C) δ 0.27 (d, J = 7.5 Hz, 6H), 0.84 (t, J = 6.6 Hz, 3H), 1.20–1.42 (m, 8H), 2.10–2.17 (t, J = 7.2 Hz, 2H), 5.61–5.69 (m, 1H), 6.27 (ddt, J = 18.9, 6.3, 1.2 Hz, 1H).

1-Fluorodimethylsilyl-1-decyne (13b). ^{1}H NMR ($CDCl_3$, 20 °C) δ 0.34 (d, J = 6.9 Hz, 6H), 0.95 (t, J = 6.6 Hz, 3H), 1.22–1.42 (m, 10H), 1.48–1.60 (m, 2H), 2.24 (td, J = 7.2, 2.4 Hz, 1H).

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