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Facile synthesis of ketones from 1,1-disilylethenes *via* oxidation of *gem*-disilylalkanes

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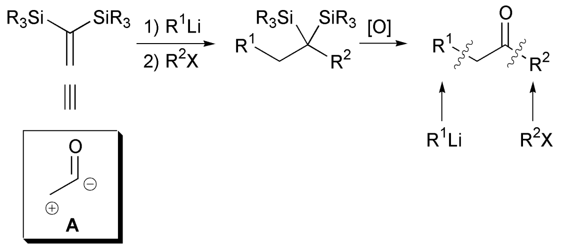
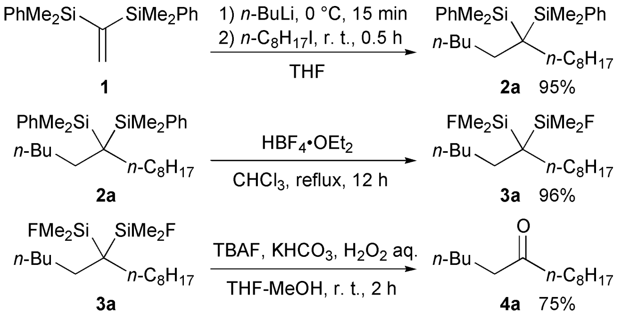
The oxidation of *gem*-disilylalkanes, which can be derived from 1,1-disilylethene, alkyllithiums and alkyl halides, affords the corresponding ketones.

The oxidation of a carbon–silicon bond is a highly important reaction to convert alkylsilanes to alcohols, and numerous applications utilizing the Kumada–Tamao–Fleming protocol have been published.[1] Although one can expect that the oxidation of *gem*-disilylalkanes with this procedure provides ketones, there have been no precedent reports on the use of this oxidation protocol for the synthesis of ketones to our best knowledge. Recently, we have reported the facile synthetic method to prepare 1,1-disilylethenes from dibromodisilylmethanes.[2] It then occurred to us that the addition of an alkyllithium to 1,1-disilylethenes[3] followed by the reaction of the resultant 1,1-disilylalkyllithium species with electrophiles such as alkyl halides would afford *gem*-disilylalkanes, which are promising precursors for the oxidative synthesis of ketones. Herein we wish to report the synthesis of ketones from 1,1-disilylethenes. In this reaction, 1,1-disilylethene acts as dipole **A** (Scheme 1).[3a] This is the first example of the oxidation of *gem*-disilylalkanes to provide ketones.

Butyllithium was added to a solution of 1,1-bis(dimethylphenylsilyl)ethene (**1**) at 0 °C and the resulting mixture was stirred for 15 min. Octyl iodide was then added and the mixture was stirred for 0.5 h at rt. Aqueous workup and purification by silica gel column chromatography gave 6,6-bis(dimethylphenylsilyl)teteradecane (**2a**)† in 95% yield. Treatment of **2a** with tetrafluoroboric acid etherate in refluxing chloroform for 12 h afforded 6,6-bis(fluorodimethylsilyl)tetradecane (**3a**)‡ in 96% yield.[4] The oxidation of **3a** with aqueous hydrogen peroxide in the presence of tetrabutylammonium fluoride (TBAF) and potassium hydrogencarbonate in tetrahydrofuran–methanol for 2 h at rt provided 6-tetradecanone in 75% yield (Scheme 2).



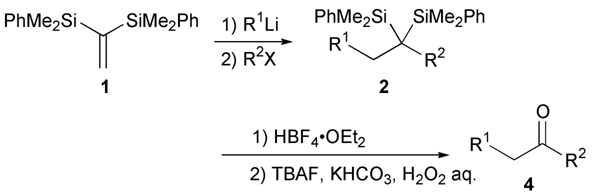
Scheme 1 Synthesis of ketones from 1,1-disilylethenes—our strategy.



Scheme 2 Three-step synthesis of ketones from 1,1-disilylethenes.

These three steps are carried out subsequently without an isolation of **2** or **3**. A variety of ketones can be synthesized by using the corresponding alkyllithiums and alkyl halides. The results are shown in Table 1.§ Not only alkyl iodides but also alkyl bromides or chlorides can be used as an electrophile. Secondary alkyl iodides failed to trap the intermediary 1,1-disilylalkyllithium species. A double bond is not tolerable in the fluorination step. For example, treatment of 4,4-bis(methyldiphenylsilyl)non-1-ene with HBF_4 afforded a complex mixture.

Table 1 Synthesis of ketones from 1,1-disilylethene



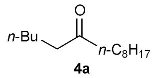
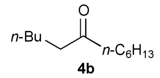
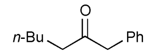
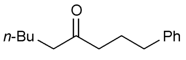
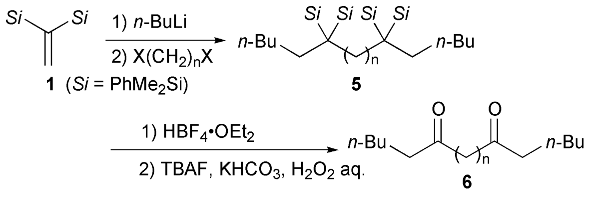
Entry	R^1Li	R^2X	Product	Yield (%)
1	*n*-BuLi	*n*-$C_8H_{17}I$	 **4a**	68
2	*n*-BuLi	*n*-$C_8H_{17}Br$	**4a**	73
3	*n*-BuLi	*n*-$C_6H_{13}Cl$	 **4b**	69
4	*n*-BuLi	$PhCH_2Br$	 **4c**	73
5	*n*-BuLi	$Ph(CH_2)_3Br$	 **4d**	71

Table 2 Synthesis of diketones[a]



Entry	*n*	X	Product	Yield (%)
1	4	I	**6a**	59
2	5	I	**6b**	63
3	6	I	**6c**	70
4	8	Br	**6d**	71
5	12	Br	**6e**	61

[a] Dihaloalkanes (0.5 eq.) were used.

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The use of a dihaloalkane as an electrophile provided the corresponding diketone in moderate yield (Table 2).

In summary, we have achieved the oxidation of *gem*-disilylalkanes into the corresponding ketones. *gem*-Disilylalkanes are easily synthesized from 1,1-bis(dimethylphenylsilyl)-ethene. Two alkyl groups are introduced from alkyllithiums and alkyl halides respectively.

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Notes and references

† 6,6-Bis(dimethylphenylsilyl)tetradecane (**2a**): R_f = 0.53 (hexane); IR (neat) 2930, 2855, 1466, 1427, 1250, 1107, 808, 772, 735, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 12H), 0.88 (t, J = 6.9 Hz, 3H), 0.89 (t, J = 6.6 Hz, 3H), 1.14–1.37 (m, 18 H), 1.64–1.74 (m, 4 H), 7.23–7.35 (m, 6 H), 0.89 (dd, J = 1.8, 7.5 Hz, 4H); ^{13}C NMR (75.3 MHz, $CDCl_3$) δ −1.37, 14.01, 14.04, 17.90, 22.50, 22.59, 26.00, 26.29, 29.24, 29.41, 30.83, 31.43, 31.47, 31.78, 33.09; Found: C, 77.38; H, 10.96%. Calcd for $C_{30}H_{50}Si_2$: C, 77.18; H, 10.79%.

‡ 6,6-Bis(fluorodimethylsilyl)tetradecane (**3a**): R_f = 0.40 (hexane); IR (neat) 2930, 2856, 1468, 1379, 1258, 870, 827, 795, 762 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (d, J = 8.4 Hz, 12H), 0.88 (t, J = 6.9 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H), 1.20–1.38 (m, 18 H), 1.54–1.63 (m, 4 H); ^{13}C NMR (75.3 MHz, $CDCl_3$) δ −0.87 (d, J = 15.4 Hz), 13.98 (2C), 22.33, 22.57 (d, J = 22.3 Hz), 26.14, 26.47, 29.03, 29.05, 29.24, 29.28, 30.73, 31.76, 32.93; Found: C, 61.91; H, 11.78%. Calcd for $C_{18}H_{40}F_2Si_2$: C, 61.65; H, 11.50%.

§ *Experimental procedure*: Butyllithium (1.2 mmol, hexane solution) was added to a solution of **1** (1.0 mmol) in THF (2 mL) at 0 °C and the mixture was stirred for 15 min. Alkyl halide (1.3 mmol for monohalide, 0.25 mmol for dihalide) was added and the mixture was stirred for 0.5 h at rt. Aqueous workup gave the crude product **2** or **5**. A solution of **2** or **5** and $HBF_4 \cdot OEt_2$ (6 mmol, Et_2O solution) in chloroform (5 mL) was refluxed for 12 h. The mixture was passed through a short column of Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in THF (1 mL) and MeOH (3 mL). TBAF (8 mmol, THF solution), $KHCO_3$ (8 mmol) and H_2O_2 (40 mmol, 30% aqueous solution) were successively added and the mixture was stirred for 2 h at rt. The reaction mixture was poured into saturated aqueous $NaHSO_3$ carefully and extracted with hexane. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica gel column chromatography provided **4** or **6**.

1 For reviews, see: (*a*) E. W. Colvin, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 7, p. 641; (*b*) I. Fleming, *Chemtracts Org. Chem.*, 1996, **9**, 1–64; (*c*) K. Tamao, in *Organosilicon and Bioorganosilicon Chemistry: Structure, Bonding, Reactivity and Synthetic Application*, ed. H. Sakurai, Halsted Press, New York, 1985, p. 231; (*d*) K. Tamao, *J. Synth. Org. Chem. Jpn.*, 1988, **41**, 861.

2 A. Inoue, J. Kondo, H. Shinokubo and K. Oshima, *Chem. Lett.*, 2001, 956.

3 (*a*) D. Seebach, R. Bürstinghaus, B.-Th. Gröbel and M. Kolb, *Liebigs Ann. Chem.*, 1977, 830–845; (*b*) A. Hirai, M. Nakamura and E. Nakamura, *J. Am. Chem. Soc.*, 2000, **122**, 11791–11798; (*c*) P. Knochel, M. C. P. Yeh and C. Xiao, *Organometallics*, 1989, **8**, 2831–2835; (*d*) K. Itami, K. Mitsudo and J. Yoshida, *Angew. Chem.*, 2001, **113**, 2399–2401; *Angew. Chem., Int. Ed.*, 2001, **40**, 2337–2339; (*e*) M. P. Cooke Jr. and R. K. Widener, *J. Am. Chem. Soc.*, 1987, **109**, 931–933.

4 (*a*) I. Fleming, R. Henning and H. Plaut, *J. Chem. Soc., Chem. Commun.*, 1984, 29–31; (*b*) S. H. Bergens, P. Noheda, J. Whelan and B. Bosnich, *J. Am. Chem. Soc.*, 1992, **114**, 2121–2128.