Cathodic Coupling of Ketones with Ethoxyvinylsilanes. Useful Method for the Synthesis of 1,3-Diols[1]

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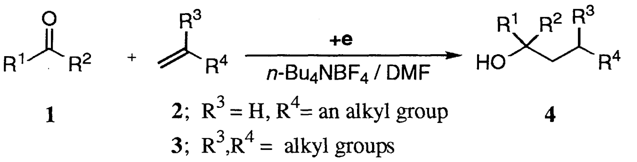
Cathodic coupling of ketones with ethoxydimethylvinylsilanes takes place regioselectively at the position β to ethoxydimethylsilyl group and affords 1-oxa-2-silacyclopentane derivatives as products which are easily transformed to 1,3-diols by oxidative desilylation.

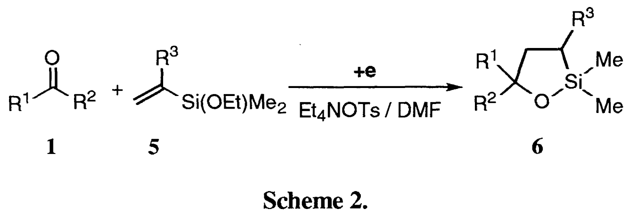
Cathodic intermolecular coupling reaction of a variety of ketones **1** with olefinic systems has already been reported in our previous studies,[2-4] in which it is clarified that this intermolecular coupling is greatly influenced by the structure of olefin. Namely, the coupling of **1** with terminal olefin **2** (R^3 = H, R^4 = an alkyl group) gave the corresponding coupling product **4** with good yield (~80%), whereas the presence of an alkyl group (R^3) on the carbon-carbon double bond remarkably obstructed the coupling reaction. Hence, the electroreduction of a mixture of **1** and 2-substituted 1-alkene **3** (R^3, R^4 = alkyl groups) gave the corresponding coupling product **4** with very low yield (~20%) (Scheme 1).



2; R^3 = H, R^4= an alkyl group
3; R^3,R^4 = alkyl groups

Scheme 1.

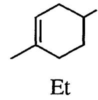
We have recently found a new type of the coupling reaction as reported in this paper. Namely, when a ethoxydimethylsilyl group is located on the double bond, its reactivity is remarkably modified. Thus, the coupling of **1** with ethoxydimethylsilyl substituted olefin **5** (R^3 = H or an alkyl group, R^4 = Si(OEt)Me_2 in **3**) afforded oxasilacyclopentanes **6** with excellent yield (Scheme 2).



Scheme 2.

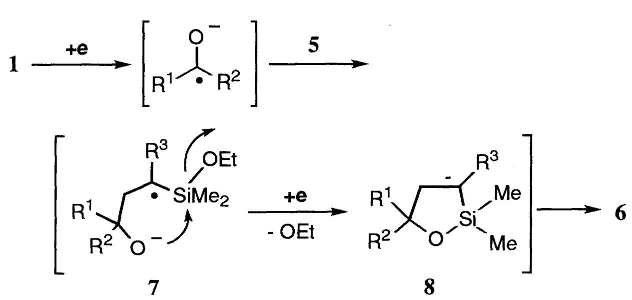
The cathodic coupling of **1** with **5** was carried out in a divided electrolysis cell (100 mL) equipped with a carbon fiber cathode, a platinum anode (2 x 2 cm), and a glass filter diaphragm (No.5). A solution of **1** (5 mmol) and **5** (10 mmol) in dry DMF (20 mL) containing Et_4NOTs (10 mmol) as a supporting electrolyte was put into a cathodic chamber of the cell. The anodic solution was 15 mL of dry DMF containing Et_4NOTs (5 mmol). After 3F/mol of electricity based on **1** (constant current condition of 0.2 A) was passed through the cell, the product was isolated by distillation under reduced pressure (bulb to bulb distillation). All products gave satisfactory spectroscopic values for the assigned structures.[5] Typical results are summarized in Table 1.

Table 1. Cathodic coupling of **1** with **5**[a]

Run	Ketone 1			Vinylsilane 5		Product 6	
	R^1	R^2		R^3		Yield / %[b,c]	
1	-(CH_2)$_5$-		**1a**	H	**5a**	70	**6a**
2	n-C_5H_{11}	n-C_5H_{11}	**1b**	H	**5a**	75	**6b**
3	Me	n-C_6H_{13}	**1c**	H	**5a**	75	**6c**
4	Me	n-Pr	**1d**	H	**5a**	79	**6d**
5	Me		**1e**	H	**5a**	79	**6e**
6	Me	Et	**1f**	n-Pr	**5b**[d]	62	**6f**[e]

[a] 3F/mol of electricity based on **1** was passed. [b] Isolated yield based on **1**. [c] The spectroscopic values of the products are shown in Ref. 5. [d] See Ref. 10. [e] The products were mixture of diastereomers (1 : 1).

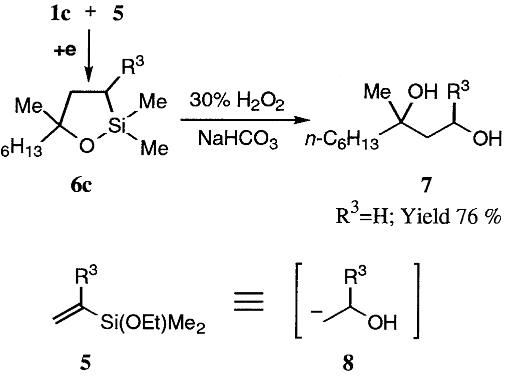
The role of ethoxydimethylsilyl group in this coupling is remarkable in mechanistic aspect. One of the important driving forces on this type of coupling is the stabilization of the radical and anionic intermediates **7**[6] and **8** by the neighboring silyl group as it has already been reported in our previous papers.[7-9] In the coupling of **5**, however, the irreversible formation of a siloxane ring in the intermediates (from **7** to **8**) is a unique and the most important factor to promote this coupling (Scheme 3).



Scheme 3.

The unique and important role of the ethoxydimethylsilyl group in this coupling is most clearly seen in the reaction shown in run 6 (Table 1). Namely, the cathodic coupling of **1f** and **5b** (corresponding to the 2-substituted 1-alkene **3**) gave **6f** with 62% yield, whereas the combination of **1f** and **3** (R^3 = Me, R^4 = *n*-Pr, Scheme 1) afforded **4** only in 22% yield.[2]

This coupling is also valuable as a synthetic reaction since the product **6** is a useful key intermediate for the transformation of **1** to 1,3-diol. For example, the oxidative desilylation of **6c** with 30% H_2O_2 afforded 1,3-diol **7**[13] in 76% yield (Scheme 4).[14] The fact that **7** is formed by the cathodic coupling of **1** and **5** followed by the oxidative desilylation indicates that the reaction shown in Scheme 4 is the equivalent of the reaction of **1** and the anion **8** which is unstable and difficult to prepare by the conventional method.



6c **7**

R^3=H; Yield 76 %

5 **8**

Scheme 4.

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References and Notes

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5 **6a:** IR (neat) 2940, 2870, 1455, 1255, 980, 900, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.76 (t, *J* = 7.8 Hz, 2H), 1.28-1.60 (m, 10H), 1.71 (t, *J* = 7.8 Hz, 2H); HRMS Found: 184.12988. Calcd for $C_{10}H_{20}SiO$: 184.1284.

6b: IR (neat) 2950, 1255, 1010, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 6H), 0.76 (t, *J* = 7.7 Hz, 2H), 0.86 (t, *J* = 6.3 Hz, 6H), 1.18-1.48 (m, 16H), 1.70 (t, *J* = 7.7 Hz, 2H); Anal. Found: C, 69.96; H, 12.74%. Calcd for $C_{15}H_{32}SiO$: C, 70.24; H, 12.57%.

6c: IR (neat) 2960, 2930, 2860, 1255, 955, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 3H), 0.18 (s, 3H), 0.79 (t, *J* = 7.9 Hz, 2H), 0.86 (t, *J* = 5.7 Hz, 3H), 1.14 (s, 3H), 1.20-1.45 (m, 10H), 1.60-1.82 (m, 2H); Anal. Found: C, 67.32; H, 12.46%. Calcd for $C_{12}H_{26}SiO$: C, 67.22; H, 12.22%.

6d: IR (neat) 2970, 2880, 1255, 1090, 1010, 960, 935, 840, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (s, 3H), 0.17 (s, 3H), 0.79 (t, *J* = 7.9 Hz, 2H), 0.88 (t, *J* = 6.5 Hz, 3H), 1.13 (s, 3H), 1.20-1.50 (m, 4H), 1.56-1.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.12, 0.44, 10.34, 14.64, 17.54, 27.41, 35.49, 45.05, 81.82; HRMS Found: 172.1288. Calcd for $C_9H_{20}SiO$: 172.1284.

6e: IR (neat) 2960, 1255, 940, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (s, 3H), 0.20 (s, 3H), 0.78 (t, *J* = 7.5 Hz, 2H), 1.08, 1.10 (s, 3H), 1.50-2.05 (m, 9H), 5.39 (m, 1H); HRMS Found: 224.15767. Calcd for $C_{13}H_{24}SiO$: 224.15972.

6f: IR (neat) 2960, 2850, 1460, 1250, 1000, 945, 830, 780 cm^{-1}; ^1H NMR 0.07 (s, 3H), 0.19, 0.21 (s, 3H), 0.70-0.95 (m, 6H), 1.11, 1.20 (s, 3H), 1.15-1.60 (m, 8H), 1.89-1.90, 2.00-2.10 (m, 1H); Anal. Found: C, 65.89; H, 12.19%. Calcd for $C_{11}H_{24}SiO$: C, 65.93; H, 12.07%.

6 The coupling reaction seems to be initiated by the electroreduction of **1** since ethoxyvinylsilanes were not reduced under anhydrous conditions of electroreduction.

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10 2-Trimethylsilyl-1-penten **5b** was prepared by the known procedure.[11,12]

5b: IR (neat) 2970, 1250, 1105, 1080, 825, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.89 (t, *J* = 7.3 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.35-1.54 (m, 2H), 5.60-5.63 (m, 1H); MS *m/e* (relative intensity) 157 (100, M^+-Me), 103 (65), 89 (18), 75 (41); Anal. Found: C, 62.55; H, 11.90%. Calcd for $C_9H_{20}SiO$: C, 62.72; H, 11.70%.

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