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Versatile Desilylative Cross-Coupling of Silyl Enol Ethers and Allylic Silanes via Oxovanadium-Induced Chemoselective One-Electron Oxidation

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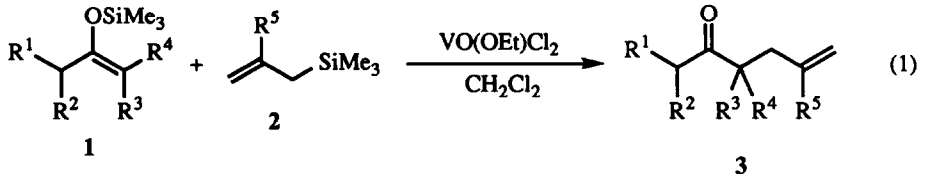
Abstract: The chemoselective cross-coupling of silyl enol ethers and allylic silanes to γ,δ-unsaturated ketones is achieved by the oxovanadium(V)-induced oxidative desilylation of the more readily oxidizable organosilicon compounds.

Desilylation via one-electron oxidation of organosilicon compounds is useful to generate radicals or cationic species through further one-electron oxidation, providing a versatile route to electrophilic synthetic equivalents.[1] In our previous paper,[2] an efficient method for oxidative desilylation of silyl enol ethers and allylic silanes has been developed by use of $VO(OR)Cl_2$ as a one-electron oxidant to produce 1,4-diketones and 1,5-dienes, respectively. Oxidation susceptibility, which is an important factor to control the chemoselective desilylation, appears to depend on redox potential. We herein describe a novel intermolecular chemoselective carbon-carbon bond formation between silyl enol ethers and allylic silanes.

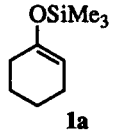
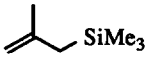
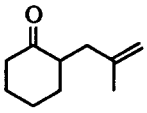
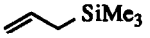
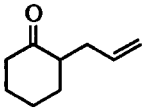
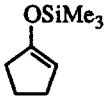
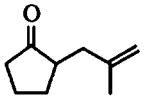
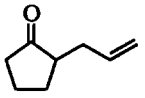
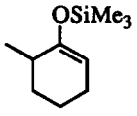
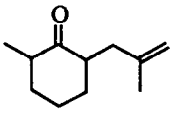
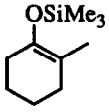
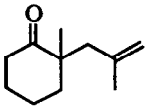
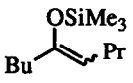
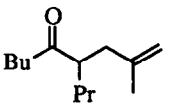
Oxidation of the silyl enol ether **1** with $VO(OEt)Cl_2$ in the presence of the allylic silane **2** in dichloromethane resulted in allylation to afford the γ,δ-unsaturated ketone **3** (eq. 1). Such an intermolecular cross coupling is of synthetic potential, but has been less accessible so far.



(1)

This method permits the selective cross-coupling of **1** with **2**. Some results with the readily oxidizable silyl enol ethers **1** are listed in Table 1. Only trace or small amounts of the homo-coupled 1,4-diketones and 1,5-hexadienes were produced under the conditions employed here. Use of three molar equivalents of $VO(OEt)Cl_2$ was required for the better conversion. The allylic silane **2a** was found to be the better acceptor rather than **2b**, suggesting that the yields depend on the addition step. The regioisomer **3** was not obtained in the oxidative allylation of **1e** and **1f** with **2a** to support the regioselective radical generation and carbon-carbon bond formation. It should be also noted that the coupling reaction occurred at the tertiary carbon of **1f**.

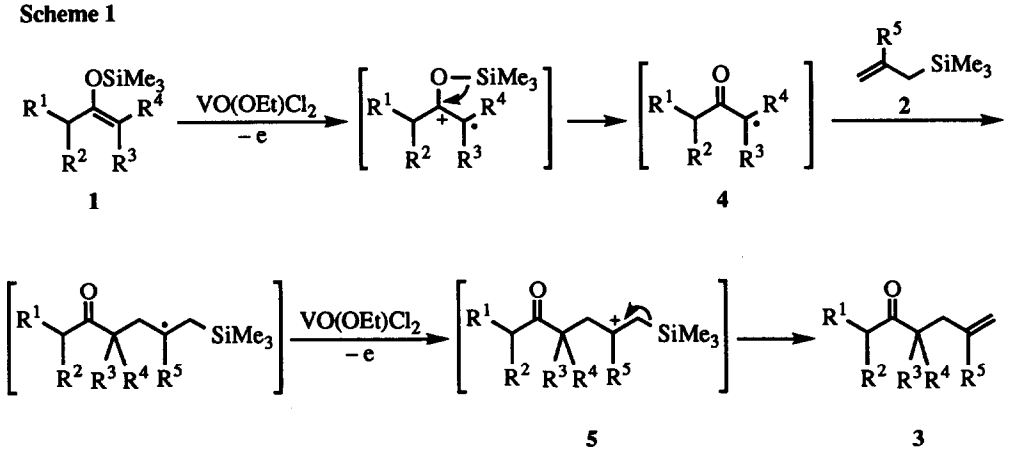
Table 1. $VO(OEt)Cl_2$-Induced Oxidative Coupling of **1** with **2**[a]

1	**2** (2 equiv.)	Product, %[b]
 **1a**	 **2a**	 **3a** 65 56[c]
1a	 **2b**	 **3b** 36[d]
 **1c**	**2a**	 **3c** 66
1c	**2b**	 **3d** 47[e]
 **1e**	**2a**	 **3e** 54[f]
 **1f**	**2a**	 **3f** 66
 **1g**	**2a**	 **3g** 32

[a] $VO(OEt)Cl_2$ (3 equiv.) was used unless otherwise stated. [b] Determined by GLC. The 1,4-diketone derived from **1** was produced in a trace amount unless otherwise stated. [c] $VO(OEt)Cl_2$ (2 equiv.). [d] The 1,4-diketone, 17%. [e] The 1,4-diketone, 5%. [f] *trans* : *cis* = 2 : 1.

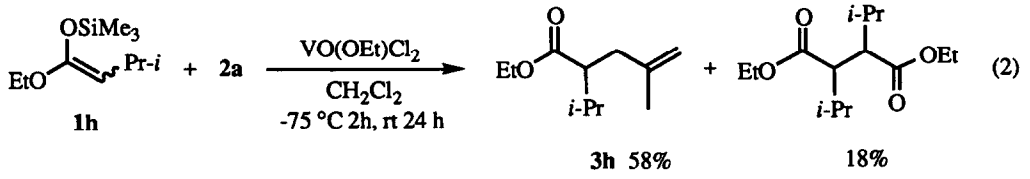
The silyl enol ether **1** is formally considered to be a cation equivalent according to the reaction path shown in Scheme 1. The chemoselective one-electron oxidation of **1** with $VO(OEt)Cl_2$ followed by desilylation generates the oxo radical **4**. The radical **4** regioselectively adds to **2** in a way to form the radical β to the trimethylsilyl group. Desilylation of the further oxidized cation **5**, which is likely to be stabilized by the β-effect of the trimethylsilyl group, leads to the formation of **3**.

Scheme 1



1 **4** **5** **3**

The silyl ketene acetal **1h** similarly underwent the coupling with **2a** to give the corresponding methallylated ester **3h** as shown in eq. 2.



1h **3h** 58% 18%

The readily oxidizable allylic silanes based on their redox potentials are expected to undergo the reverse addition for oxidative allylation. Treatment of cinnamyltrimethylsilane (**6a**) with $VO(OEt)Cl_2$ in the presence of the silyl enol ether **7a**, which is not oxidized with $VO(OEt)Cl_2$ under the present conditions, afforded the γ,δ-unsaturated ketones **8a** and **9a** via selective cleavage of a carbon-silicon bond of **6a**. The homo-coupled 1,5-hexadiene **10a** was obtained as a minor product (eq. 3 and Table 2). The more facile oxidative coupling was performed by utilization of the oxidant consisting of $VO(OEt)Cl_2$ and Me_3SiOTf as reported in the dehydrogenative aromatization.[3] The allylic silane **6a** also coupled with **7b**. Prenyltrimethylsilane (**6c**) worked as a radical precursor for the highly regioselective carbon-carbon bond formation at the α-position.

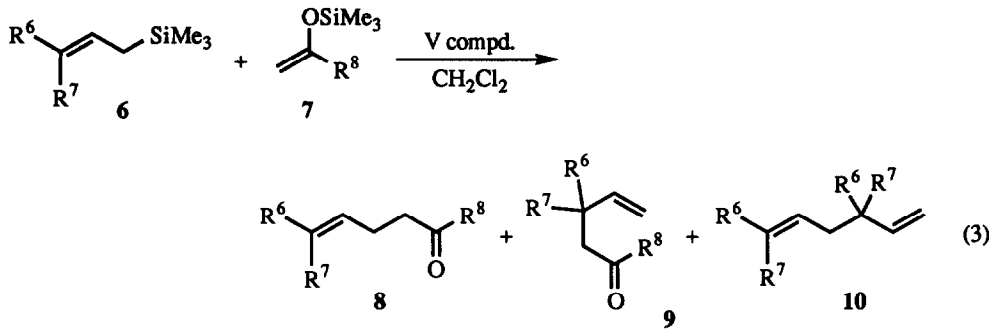
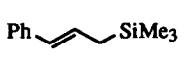
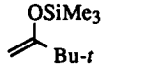
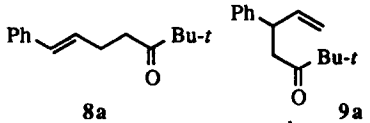
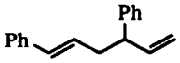
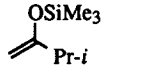
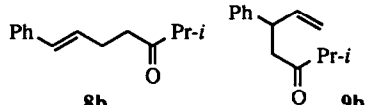
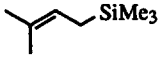
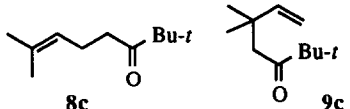
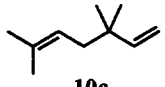


Table 2. Oxovanadium-Induced Oxidative Coupling of **6** with **7**

6	**7** (3 equiv.)	Products, %[a] **8** + **9** (**8** : **9**)	**10**
 **6a**	 **7a**	 **8a** **9a** 45 (5.9 : 1)[b] 60 (4.3 : 1)[c]	 **10a** 10 9
6a	 **7b**	 **8b** **9b** 46 (2.0 : 1)[c]	**10a** 12
 **6c**	**7a**	 **8c** **9c** 34 (> 19 : 1)[c]	 **10c** 13[d]

[a]Determined by GLC. [b]$VO(OEt)Cl_2$ (2 equiv.). [c]$VO(OEt)Cl_2$ (2 equiv.)-Me_3SiOTf (1 equiv.). [d]Determined by ^1H NMR.

The allylic radical generated by one-electron oxidation and subsequent desilylation is considered to be involved as an intermediate. The intermolecular addition of the radical species or further oxidized cation to the less readily oxidizable silyl enol ether **7** seems to give **8** and **9**.

Silyl enol ethers and allylic silanes serve as precursors or acceptors for radicals depending on their redox potentials, which are anticipated by MOPAC[4] calculated ionization potentials (Table 3). Oxovanadium(V) compounds are revealed to be versatile oxidants to induce such a chemoselective coupling reaction via oxidative desilylation under the controlled conditions.

Table 3. Calculated Ionization Potential[a]

Allylic Silanes and Silyl Enol Ethers	Ionization Potential, eV AM1	PM3
2b	9.516	9.292
2a	9.311	9.081
6c	8.898	8.807
7a	8.955	8.780
1a	8.613	8.492
1c	8.556	8.420

[a]MOPAC ver. 6.1.

Experimental

Representative Procedure for Oxidative Coupling of Silyl Enol Ether 1 with Allylic Silane 2. To a solution of $VO(OEt)Cl_2$ (549 mg, 3.0 mmol) in dichloromethane (5 mL) was added the allylic silane **2a** (257 mg, 2.0 mmol) at -75 °C under nitrogen, followed by dropwise addition of **1a** (170 mg, 1.0 mmol) over 20 min. The mixture was stirred for 2 h at -75 °C. Ether (15 mL) and 1.5 M aqueous HCl (0.5 mL) were added to the reaction mixture, which was extracted with ether (4 x 20 mL). The combined ethereal solution was washed with saturated $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated. GLC analysis (10% PEG 20 M 2.1 m column and 10% OV-17 2.1 m column, 180 °C) of the residue showed the formation of the ketone **3a** and the ketone derived by hydrolysis of **1a**.

The reactions of other silyl enol ethers or allylic silanes were carried out similarly. The results are shown in Table 1. The products were identified by spectral comparison of the authentic samples.[5]

2-(2-Methyl-2-propenyl)cyclohexanone (3a). IR (neat) 3076, 2940, 2864, 1714, 1650 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.2-1.4 (m, 2H), 1.6-1.9 (m, 2H), 1.69 (s, 3H), 1.91 (dd, 1H, *J* = 13.9, 8.3 Hz), 2.0-2.2 (m, 2H), 2.3-2.5 (m, 3H), 2.57 (dd, 1H, *J* = 13.9, 5.0 Hz), 4.65 (brs, 1H), 4.76 (brs, 1H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 22.3, 24.8, 28.0, 33.3, 37.4, 42.0, 48.4, 111.8, 143.3, 212.8; EIMS *m/z* 152 (M^+, 27), 137 (57), 123 (23), 109 (57), 97 (17), 95 (52), 81 (61), 67 (97), 55 (100).

2-(2-Propenyl)cyclohexanone (3b). IR (neat) 3080, 2944, 2868, 1714, 1644 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.2-1.4 (m, 1H), 1.6-1.8 (m, 2H), 1.8-2.2 (m, 4H), 2.2-2.5 (m, 3H), 2.5-2.6 (m, 1H), 4.99 (dq, 1H, *J* = 17.2, 1.3 Hz), 5.02 (dq, 1H, *J* = 10.6, 0.9 Hz), 5.75 (ddt, 1H, *J* = 17.2, 10.6, 6.3 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 25.8, 28.7, 34.2, 34.6, 42.8, 51.1, 117.0, 137.3, 213.3; EIMS *m/z* 138 (M^+, 32), 123 (18), 109 (48), 97 (17), 95 (57), 79 (75), 67 (100), 55 (62).

2-(2-Methyl-2-propenyl)cyclopentanone (3c). IR (neat) 3080, 2948, 2884, 1744, 1652 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.4-1.6 (m, 1H), 1.70 (t, 3H, *J* = 0.7 Hz), 1.7-1.8 (m, 1H), 1.91 (dd, 1H, *J* = 14.2, 5.0 Hz), 1.9-2.4 (m, 5H), 2.51 (dd, 1H, *J* = 14.2, 3.6 Hz), 4.69 (brs, 1H), 4.75 (brs, 1H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 20.5, 22.1, 29.4, 38.0 x 2, 47.3, 111.6, 143.5, 220.9; EIMS *m/z* 138 (M^+, 27), 110 (18), 95 (28), 83 (24), 82 (97), 79 (23), 70 (13), 67 (100), 55 (66).

2-(2-Propenyl)cyclopentanone (3d). IR (neat) 3080, 2972, 2884, 1740, 1644 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.5-1.7 (m, 1H), 1.7-1.9 (m, 1H), 1.9-2.4 (m, 6H), 2.4-2.6 (m, 1H), 5.01 (dq, 1H, *J* = 9.9, 1.0 Hz), 5.06 (dq, 1H, *J* = 17.2, 1.7 Hz), 5.76 (ddt, 1H, *J* = 17.2, 9.9, 6.9 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 21.5, 29.9, 34.8, 39.1, 49.5, 117.3, 136.8, 221.5; EIMS *m/z* 124 (M^+, 25), 96 (45), 81 (24), 67 (100), 55 (52).

2-Methyl-6-(2-methyl-2-propenyl)cyclohexanone (3e). ***cis*-Isomer:** IR (neat) 3080, 2972, 2940, 2864, 1716, 1650 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.95 (d, 3H, *J* = 6.6 Hz), 1.0-1.3 (m, 2H), 1.62 (s, 3H), 1.6-1.8 (m, 2H), 1.80 (dd, 1H, *J* = 14.3, 8.8 Hz), 1.9-2.2 (m, 2H), 2.3-2.5 (2m, 2H), 2.51 (dd, 1H, *J* = 14.3, 5.0 Hz), 4.57 (q, 1H, *J* = 0.7 Hz), 4.68 (s, 1H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 15.1, 22.9, 26.0, 35.2, 37.7, 37.9, 46.2, 48.9, 111.9, 144.2, 214.2; EIMS *m/z* 166 (M^+, 42), 151 (59), 123 (42), 111 (14), 108 (67), 95 (88), 93 (54), 82 (75), 67 (100), 55 (86). ***trans*-Isomer:** IR (neat) 3080, 2972, 2940, 2860, 1714, 1652 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.00 (d, 3H, *J* = 6.6 Hz), 1.4-1.5 (m, 1H), 1.5-1.8 (m, 4H), 1.63 (s, 3H), 1.8-2.0 (m, 1H), 2.07 (dd, 1H, *J* = 14.2, 8.9 Hz), 2.37 (dd, 1H, *J* = 14.2, 6.9 Hz), 2.4-2.7 (m, 2H), 4.61 (t, 1H, *J* = 1.0 Hz), 4.68 (t, 1H, *J* = 1.3 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 15.4, 20.9, 21.9, 31.6, 35.4, 38.9, 42.6, 46.8, 112.3, 142.9, 216.1; EIMS *m/z* 166 (M^+, 36), 151 (61), 123 (41), 111 (22), 109 (35), 95 (63), 93 (50), 82 (68), 67 (100), 55 (86).

2-Methyl-2-(2-methyl-2-propenyl)cyclohexanone (3f). IR (neat) 3080, 2944, 2872, 1710, 1646 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.08 (s, 3H), 1.5-2.0 (m, 6H), 1.67 (brs, 3H), 2.26 (d, 1H, *J* = 13.9 Hz), 2.3-2.4 (m, 1H), 2.49 (d, 1H, *J* = 13.9 Hz), 2.5-2.6 (m, 1H), 4.65 (brs, 1H), 4.83 (brs, 1H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 21.1, 23.3, 24.3, 27.6, 38.9, 40.0, 45.5, 48.7, 114.7, 142.2, 215.8; EIMS *m/z* 166 (M^+, 20), 151 (42), 123 (26), 111 (15), 108 (35), 95 (60), 82 (51), 67 (91), 55 (100).

2-Methyl-4-propyl-1-nonen-5-one (3g). IR (neat) 3084, 2968, 2944, 2880, 1716, 1652 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.89 (t, 3H, *J* = 7.3 Hz), 0.90 (t, 3H, *J* = 7.3 Hz), 1.2-1.4 (m, 5H), 1.5-1.7 (m, 3H), 1.71 (s, 3H), 2.05 (dd, 1H, *J* = 14.2, 6.3 Hz), 2.29 (dd, 1H, *J* = 14.2, 8.2 Hz), 2.40 (t, 2H, *J* = 13.9 Hz), 2.68 (ddt, 1H, *J* = 8.2, 6.3, 4.9 Hz), 4.66 (brs, 1H), 4.74 (brs, 1H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 13.9, 14.1, 20.6, 22.4x2, 25.5, 33.9, 40.0, 42.0, 50.1, 112.2, 143.2, 214.3; EIMS *m/z* 196 (M^+, 1), 167 (9), 153 (10), 139 (9), 111 (36), 97 (11), 85 (87), 69 (97), 57 (100), 55 (70); HRMS calcd for $C_{13}H_{24}O$ 196.1828, found 196.1829.

Ethyl 4-Methyl-2-isopropyl-4-pentenoate (3h). IR (neat) 3080, 2972, 2884, 1736, 1652, 1470, 1268 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.93, 0.97 (2d, 6H, *J* = 6.9 Hz), 1.24 (t, 3H, *J* = 6.9 Hz), 1.72 (brs, 3H), 1.85 (dsept, 1H, *J* = 6.9, 6.6 Hz), 2.1-2.3 (m, 1H), 2.2-2.4 (m, 2H), 4.11 (q, 2H, *J* = 6.9 Hz), 4.69 (brs, 1H), 4.72 (brs, 1H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 14.3, 20.2, 20.3, 22.3, 30.6, 38.0, 51.0, 59.8, 111.5, 143.5, 175.1; EIMS *m/z* 184 (M^+, 1), 141 (52), 129 (26), 113 (41), 111 (45), 101 (21), 95 (43), 83 (17), 69 (100), 55 (71); HRMS calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1462

Diethyl 2,3-diisopropylsuccinate (a mixture of diastereomers, The stereochemistry was not determined, but the molar ratio was 2.4 : 1 by ^1H NMR.). IR (neat) 2972, 2884, 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) the major isomer: δ 0.88 (d, 6H, *J* = 6.9 Hz), 1.06 (d, 6H, *J* = 6.9 Hz), 1.25 (t, 6H, *J* = 7.3 Hz), 1.9-2.1 (m, 2H), 2.67 (dd, 2H, *J* = 3.3, 1.7 Hz), 4.12 (q, 4H, *J* = 7.3 Hz); the minor isomer: δ 0.94, 0.95 (2d, 12H, *J* = 7.3 Hz), 1.27 (t, 6H, *J* = 7.3 Hz), 1.7-1.9 (m, 2H), 2.80 (dd, 2H, *J* = 2.6, 1.7 Hz), 4.15 (q, 4H, *J* = 7.3 Hz); EIMS *m/z* 213 (M^+-EtO, 19), 173 (17), 129 (100), 115 (53), 101 (42), 99 (26), 87 (18), 83 (34), 73 (11), 69 (66), 55 (52).

Representative Procedure for Oxidative Coupling of Allylic Silane 6 and Silyl Enol Ether 7 with $VO(OEt)Cl_2$-Me_3SiOTf. To a solution of $VO(OEt)Cl_2$ (366 mg, 2.0 mmol) in dichloromethane (10 mL) was

added Me_3SiOTf (222 mg, 1.0 mmol) at 0 °C under nitrogen. The reaction mixture was stirred for 1 h and cooled to -75 °C. The silyl enol ether **7a** (517 mg, 3.0 mmol) was added and then the allylic silane **6a** (190 mg, 1.0 mmol) was added dropwise over 30 min at -75 °C. The mixture was stirred for 2 h at the same temperature. After warming to room temperature, stirring was continued for 24 h. Ether (20 mL) and 5% aqueous $Na_2S_2O_3$ (0.5 mL) were added to the reaction mixture, which was extracted with ether (2 x 20 mL). conc. HCl (0.5 mL) was added to the aqueous solution, which was extracted with ether (3 x 20 mL). The combined ethereal solution was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated. GLC analysis (10% PEG 20 M 2.1 m column and 10% OV-17 2.1 m column, 200 °C) of the residue showed the formation of **8a**, **9a**, and **10a**.

The reactions shown in Table 2 were carried out similarly. The products were identified by spectral comparison of the authentic samples.[5]

2,2-Dimethyl-7-phenyl-6-heptene-3-one (8a). IR (neat) 3064, 3032, 2972, 2936, 2876, 1708, 1602 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.15 (s, 9H), 2.46 (dt, 2H, J = 7.6, 6.8 Hz), 2.66 (dt, 2H, J = 7.6, 1.0 Hz), 6.20 (dt, 1H, J = 15.9, 6.8 Hz), 6.40 (dt, 1H, J = 15.9, 1.0 Hz), 7.2-7.4 (m, 5H); EIMS *m/z* 216 (M^+, 22), 159 (33), 117 (72), 91 (19), 85 (12), 57 (100); HRMS calcd for $C_{15}H_{20}O$ 216.1515, found 216.1516.

2,2-Dimethyl-5-phenyl-6-heptene-3-one (9a). IR (neat) 3088, 3032, 2976, 2912, 2876, 1710, 1642, 1604 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.05 (s, 9H), 2.89 (dd, 1H, J = 6.9, 1.3 Hz), 2.90 (dd, 1H, J = 6.9, 1.3 Hz), 3.99 (t, 1H, J = 6.9 Hz), 5.01 (tt, 1H, J = 17.2, 1.3 Hz), 5.04 (tt, 1H, J = 10.6, 1.3 Hz), 5.98 (ddd, 1H, J = 17.2, 10.6, 6.9 Hz), 7.1-7.4 (m, 5H); EIMS *m/z* 216 (M^+, 1), 117 (69), 115 (17), 91 (12), 85 (16), 57 (100); HRMS calcd for $C_{15}H_{20}O$ 216.1515, found 216.1515.

2-Methyl-7-phenyl-6-heptene-3-one (8b). IR (neat) 3032, 2972, 2936, 1714, 1656, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.11 (d, 6H, J = 6.9 Hz), 2.48 (dt, 2H, J = 6.9, 6.6 Hz), 2.62 (sept, 1H, J = 6.9 Hz), 2.63 (t, 2H, J = 6.9 Hz), 6.20 (dt, 1H, J = 15.8, 6.6 Hz), 6.40 (d, 1H, J = 15.8 Hz), 7.2-7.4 (m, 5H); EIMS *m/z* 202 (M^+, 21), 159 (28), 131 (17), 129 (15), 117 (92), 115 (41), 91 (60), 77 (14), 71 (100), 65 (12), 51 (18); HRMS calcd for $C_{14}H_{18}O$ 202.1358, found 202.1356.

2-Methyl-5-phenyl-6-heptene-3-one (9b). IR (neat) 3088, 3064, 2972, 2940, 1716, 1642, 1604 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.97, 1.04 (2d, 6H, J = 6.9 Hz), 2.50 (sept, 1H, J = 6.9 Hz), 2.85 (dd, 1H, J = 16.5, 7.3 Hz), 2.88 (dd, 1H, J = 16.5, 7.3 Hz), 3.95 (dt, 1H, J = 7.3, 6.9 Hz), 5.01 (dt, 1H, J = 17.2, 1.3 Hz), 5.05 (dt, 1H, J = 10.2, 1.3 Hz), 5.97 (ddd, 1H, J = 17.2, 10.2, 6.9 Hz), 7.1-7.4 (m, 5H); EIMS *m/z* 202 (M^+, 1), 159 (16), 117 (80), 115 (33), 91 (29), 77 (13), 71 (100), 53 (11); HRMS calcd for $C_{14}H_{18}O$ 202.1358, found 202.1357.

2,2,7-Trimethyl-6-octene-3-one (8c). IR (neat) 3060, 2972, 2936, 2876, 1710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.13 (s, 9H), 1.62 (s, 3H), 1.67 (d, 3H, J = 1.3 Hz), 2.24 (dt, 2H, J = 7.6, 6.9 Hz), 2.50 (t, 2H, J = 7.6 Hz), 5.07 (tq, 1H, J = 6.9, 1.3 Hz); EIMS *m/z* 168 (M^+, 5), 111 (32), 83 (19), 69 (100), 57 (59), 55 (23); HRMS calcd for $C_{11}H_{20}O$ 168.1515, found 168.1515.

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References

1. Chemical oxidation: Ochiai, M.; Arimoto, M.; Fujita, E. *Tetrahedron Lett.* **1981**, *22*, 4491; Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *Chem. Pharm. Bull.* **1985**, *33*, 989; Wilson, S. R.; Augelli-Szafran, C. E. *Tetrahedron* **1988**, *44*, 3983. Electrochemical oxidation: Yoshida, J.-i.; Murata, T.; Isoe, S. *Tetrahedron Lett.* **1986**, *27*, 3373; Takahaski, T.; Suda, K.; Ohmori, H.; Masui, M. *Chem. Lett.* **1987**, 1335; Koizumi, T.; Fuchigami, T.; Nonaka, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 219. Photochemical oxidation: Ohga, K.; Mariano, P.S. *J. Am. Chem. Soc.* **1982**, *104*, 617; Mizuno, K.; Terasaka, K.; Ikeda, M.; Otsuji, Y. *Tetrahedron Lett.* **1985**, *26*, 5819. Oxidative allylation of organostannanes with allylic silanes has been reported: Takeda, T.; Takagi, Y.; Takano, H.; Fujiwara, T. *Tetrahedron Lett.* **1992**, *33*, 5381; Narasaka, K.; Kohno, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3456; Yoshida, J.-i.; Itoh, M.; Isoe, S. *J. Chem. Soc., Chem. Commun.* **1993**, 547.
2. Fujii, T.; Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1992**, *33*, 5823; **1993**, *34*, 5601.
3. Hirao, T.; Mori, M.; Ohshiro, Y. *J. Org. Chem.* **1990**, *55*, 358; Hirao, T.; Mori, M.; Ohshiro, Y. *Chem. Lett.* **1991**, 783.
4. AM1 method: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. PM3 method: Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 209.
5. Brodsky, N. C.; Kalo, J. *J. Org. Chem.* **1978**, *43*, 2557; Tsuda, T.; Okada, M.; Nishi, S.-i.; Saegusa, T. *Ibid.* **1986**, *51*, 421; Molander, G. A.; Mckie, J. A. *Ibid.* **1992**, *57*, 3132; Semisch, C.; Margaretha, P. *J. Fluorine Chem.* **1986**, *34*, 105; Becker, D.; Baba, T.; Nakano, K.; Sawa, K.; Izumi, K.; Nishiyama, S.; Tsuruya, S.; Masai, M.; Yamada, H. *J. Mol. Catal.* **1991**, *64*, 201; Watanabe, Y.; Yoneda, T.; Okumura, T.; Ueno, Y.; Toru, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3030.

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