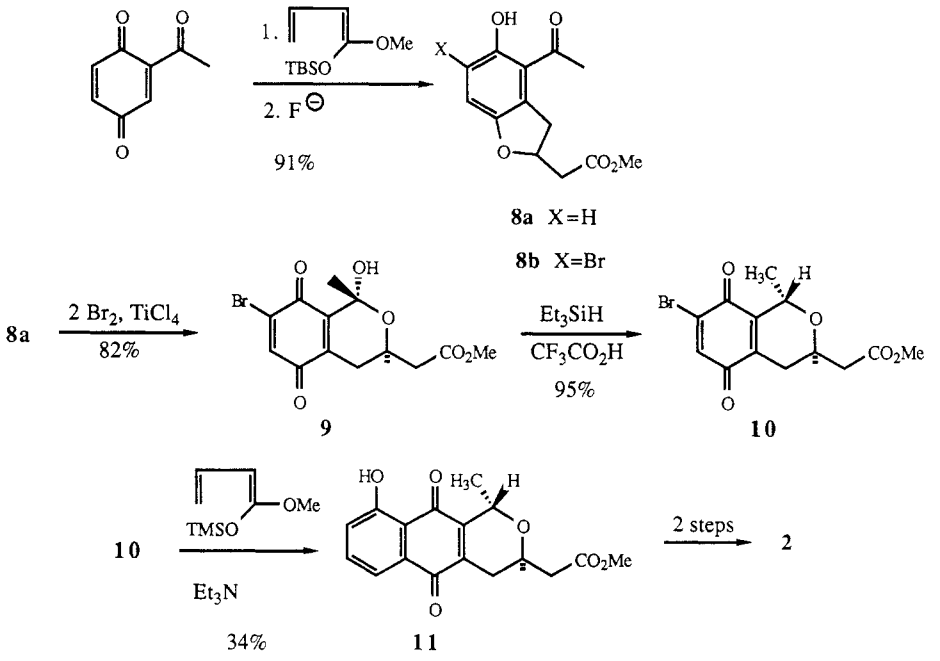
Scheme I



was cooled to 0 °C, and 40 mL of acetonitrile, 20 mL of pH 7.2 phosphate buffer, and 35 mL of tetra-*n*-butylammonium fluoride (1 M in THF) was added. The solution was allowed to warm to ambient temperature and acidified with 3 N HCl. The aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were dried, concentrated, and then purified by flash chromatography using 3:1 hexanes–ethyl acetate to provide 3.49 g (91% yield) of phenol **8a**. Phenol **8a** was a clear liquid: HRMS calcd for $C_{13}H_{14}O_5$ 250.08413, found 250.08439; IR (film) 3020, 1736, 1580, 1474, 1215, 827 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.58 (s, 3 H), 2.72 (dd, J = 16.2, 6.6 Hz, 1 H), 2.91 (dd, J = 16.2 and 6.3 Hz, 1 H), 3.23 (dd, J = 16.2, 7.2 Hz, 1 H), 3.71 (dd, J = 16.5, 8.7 Hz, 1 H), 3.74 (s, 3 H), 5.17 (m, 1 H), 6.79 (d, J = 9 Hz, 1 H), 6.95 (d, J = 9 Hz, 1 H), 12.16 (s, 1 H); TLC (3:1 H:EA) R_f = 0.30.

***trans*-Methyl (7-Bromo-3,4-dihydro-5,8-dioxo-1-methyl-1*H*-2-benzopyran-3-yl)acetate (10).** To a solution of phenol **8a** (0.75 g, 3.0 mmol) in 15 mL of CH_2Cl_2 at 25 °C was added 10.5 mL of a 1 M solution of $TiCl_4$ in CH_2Cl_2, followed by bromine (0.948 g, 6.0 mmol). The solution was stirred for 1.5 h. Water (10 mL) was carefully added, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with saturated $NaHCO_3$ solution and then with brine. The organic layer was dried and concentrated. The crude product was purified by flash chromatography using 3:1 hexanes–ethyl acetate to provide 0.85 g (82% yield) of **9**.

In practice, **9** was reduced directly to afford **10**. To a solution of **9** (0.280 g, 0.81 mmol) at −78 °C in 8 mL of CH_2Cl_2 was added triethylsilane (0.174 g, 1.5 mmol) followed by BF_3Et_2O (0.1 mL). After 30 min, the reaction was warmed to 25 °C and the solvent was removed. The crude product was immediately purified by flash chromatography using 3:1 hexanes–ethyl acetate to afford a 95% yield of **10**. Quinone **10** was an oil: HRMS calcd for $C_{13}H_{13}BrO_5$ 327.99463, found 327.99502; IR (film) 3061, 2982, 1738, 1668, 1655, 1595, 1259 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (d, J = 6.6 Hz, 3 H), 2.24 (ddd, J = 18.3, 10.4, 4.0 Hz, 1 H), 2.58 (dd, J = 15.8, 5.7 Hz, 1 H), 2.66–2.75 (m, 2 H), 3.73 (s, 3 H), 3.85–3.94 (m, 1 H), 4.69–4.78 (m, 1 H), 7.26 (s, 1 H); TLC (3:1 H:EA) R_f = 0.17.

***trans*-Methyl (3,4-Dihydro-5,10-dioxo-9-hydroxy-1-methyl-1*H*-naphtho[2,3-*c*]pyran-3-yl)acetate (11).** To a solution of **10** (0.098 g, 0.3 mmol) in 5 mL of CH_2Cl_2 was added dropwise 1-(trimethylsiloxy)-1-methoxy-1,3-butadiene (0.103 g, 0.6 mmol). The solution was stirred at −78 °C for 1 h and then allowed to warm to ambient temperature. Triethylamine (0.070 g, 0.7 mmol) was added, and the solution was stirred for 5 min. The solvent was removed in vacuo, and the residue was dissolved in acetonitrile. A 5% solution of HF in acetonitrile was added, and the solution was stirred for 5 min (TLC). The solvent was removed in vacuo, and the residue was partitioned between water and CH_2Cl_2. The crude product was purified by silica gel chromatography using 5:1 hexanes–ethyl acetate to provide 0.032 g (34%) of **11**. This compound was identical with that produced in our previous synthesis:[2] HRMS calcd for $C_{17}H_{16}O_5$ 300.0998, found 300.0993; IR (film) 3018, 2990, 1742, 1663, 1624, 1595, 1296, 1215 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54 (d, J = 6.6, Hz, 3 H), 2.34 (ddd, J = 18.5, 10.5, 4.0 Hz, 1 H), 2.63 (dd, J = 16.5, 5.4 Hz, 1 H), 2.75 (dd, J = 15.6, 7.5 Hz, 1 H), 2.88 (dt, J = 18.3, 2.7 Hz, 1 H), 3.74 (s, 3 H), 3.91–3.99 (m, 1 H), 4.86–4.90 (m, 1 H), 7.71–7.79 (m, 1 H), 8.04–8.10 (m, 1 H); TLC (3:1 H:EA) R_f = 0.47.

Acknowledgment. We thank the ISU Biotechnology Council for support of this work.

Registry No. **2**, 52934-83-5; **8a**, 124287-42-9; **8b**, 124287-45-2; **9**, 124287-43-0; **10**, 124287-44-1; **11**, 124438-93-3; CH_2=CHCH=C(OMe)TBSO, 119582-47-7; CH_2=CHCH=C(OMe)-TMS, 124287-46-3; acetylbenzoquinone, 1125-55-9.

Transformation of α- and β-Ionones into α- and β-Damascone and β-Damascenone Using Allylsilane Chemistry

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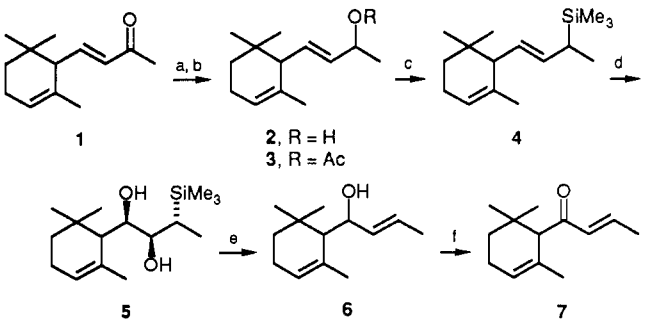
The damascones and damascenones are flavor components present in *Rosa damascena* and in several varieties of fruits, grapes, and wines.[1] Their importance as essences for perfumes, cosmetics, and foods has justified the large number of syntheses reported recently in the literature.[2]

(1) See for example: Weeks, W. W. In *Biogeneration of Aromas*; Parlamient, T. H., Croteau, R., Eds.; ACS Symposium Series 317; American Chemical Society: Washington, DC, 1986; p 157.

(2) For the more recent syntheses, see: Fehr, C.; Galindo, J. *J. Am. Chem. Soc.* **1988**, *110*, 6909. Snowden, R. L.; Linder, S. M.; Muller, B. L.; Shulte-elte, K. H. *Helv. Chim. Acta* **1987**, *70*, 1868. Zaidlewicz, M. *Tetrahedron Lett.* **1986**, *27*, 5135. Noef, F.; Decarzant, R. *Tetrahedron* **1986**, *42*, 3245. Uneyama, K.; Fujibayashi, S.; Torii, S.; *Tetrahedron Lett.* **1985**, *27*, 4637.

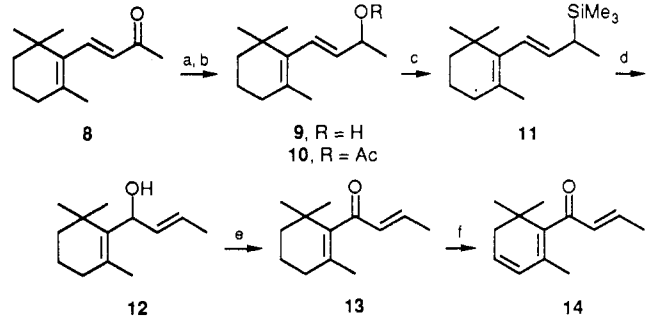
0022-3263/90/1955-1106$02.50/0

Scheme I[a]



[a] (a) $NaBH_4$/MeOH; (b) Ac_2O/Et_3N/DMAP; (c) $(Me_3Si)_2$-CuLi·LiCN; (d) $OsO_4/Me_3NO{\cdot}3H_2O$; (e) KH/THF; (f) MnO_2/acetone.

Scheme II[a]



[a] (a) $NaBH_4$/MeOH; (b) Ac_2O/EtN/DMAP; (c) $(Me_3Si)_2$-CuLi·LiCN; (d) MCPBA, TBAF·$3H_2O$; (e) PDC/DMF; (f) NBS, DABCO/DMAP, 80 °C/25 mmHg.

We report here a new preparation of α-damascone (**7**), β-damascone (**13**), and β-damascenone (**14**), employing, as key reagents, allylsilanes derived from α- and β-ionone (**1** and **8**).

By reduction of α-ionone (**1**) with $NaBH_4$, ionol (**2**) was obtained in a purity sufficient for direct transformation with acetic anhydride into acetate **3**. This allylic acetate reacted with (trimethylsilyl)cuprate (prepared from (trimethylsilyl)lithium and copper cyanide)[3] regiospecifically at C-3, giving the (*E*)-allylsilane **4** (Scheme I).

Osmylation of **4** using OsO_4/Me_3NO,[4] gave diol **5**, which underwent Peterson elimination with KH in THF to give exclusively the (*E*)-α-damascol (**6**). Assuming this elimination to be a syn process,[5] we presumed that OsO_4 approached the allylsilane double bond from the opposite side of the trimethylsilyl group.

Oxidation of **6** with activated MnO_2 in acetone gave α-damascone (**7**) in 53% yield. Several attempts to improve the yield by changing the reaction conditions or changing the oxidizing agent (we tried PDC/DMF, DMSO/$(COCl)_2/Et_3N$, or CrO_3/pyridine) did not give better results.

The transformation of α-ionone (**1**) into α-damascone (**7**) was achieved in 22% overall yield[6] and did not affect the chiral center present in the starting material,[7] giving **7** in optically pure form ($[\alpha]^{20}_D$ = +330° (*c* = 10 in $CHCl_3$) [lit.[7b] $[\alpha]^{20}_D$ = +324° (*c* = 10 in $CHCl_3$)].

β-Damascone (**13**) and β-damascenone (**14**) were analogously prepared from β-ionone (**8**) via allylsilane **11**. Treatment of **11** with MCPBA followed by TBAF gave β-damascol **12** in 55% yield (see Scheme II).

Compound **12** was oxidized with PDC in DMF at 0 °C to give β-damascone (**13**). β-Damascone (**13**) was transformed into β-damascenone (**14**) by a modification of a previously described procedure.[8] Bromination was performed with NBS at 40 °C, and dehydrohalogenation carried out in a Kughelrohr apparatus, under vacuum at 80 °C in presence of DABCO/DMAP, gave β-damascenone (**14**) in good yield (86%).

The use of allylsilanes **4** and **11** in synthesis of terpenes and carotenoids is currently under way in our laboratories.

Experimental Section

(*Z*)-1-(2,6,6-Trimethylcyclohex-2-en-1-yl)but-1-en-3-ol (α-Ionol, 2). Sodium borohydride (1.09 g, 29 mmol) was dispersed in dry methanol (50 mL) and cooled to 0 °C, and then (+)-α-ionone (**1**) ($[\alpha]^{25}_D$ = +385° (*c* = 5, hexane), (2,4-dinitrophenyl)hydrazone, mp = 126–128 °C, lit.[7c] mp 129 °C, 5 g, 26.0 mmol) in dry methanol (10 mL) was added slowly. After 1 h at 0 °C, the mixture was warmed to room temperature and stirred for 3 h. The flask was cooled again at 0 °C, and a saturated solution of NH_4Cl (25 mL) was cautiously added. The mixture was extracted three times with Et_2O; the organic fractions were collected and dried over Na_2SO_4. Evaporation of the solvent gave **2** (4.7 g, 93%) as an oil, which was used without further purification. A small sample was submitted to spectroscopic analysis after PTLC: IR (neat) 3340, 2927, 1650, 1455, 870 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.750 and 0.772 (2 s, 3 H), 0.831 and 0.835 (2 s, 3 H), 1.13 (m, 2 H), 1.210 and 1.217 (2 d, *J* = 7 Hz, 3 H), 1.31 (m, 2 H), 1.55 (m, 3 H), 1.93 (m, 1 H), 2.045 (br d, 1 H, OH), 4.252 (m, 1 H, H(2)), 5.32 (m, 1 H, H(2)-cycle), 5.40 (m, 1 H, H(3)), 5.45 (m, 1 H, H(4)); MS *m/e* (%) 194 (M^+, 1), 138 (33), 123 (18), 95 (95), 43 (100).

(*E*)-1-(2,6,6-Trimethylcyclohex-1-en-1-yl)but-1-en-3-ol (β-Ionol, 9). β-Ionol **9** (4.5 g, 90%) was prepared as previously described for **2**: IR (neat) 3360, 2930, 1450, 875 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.934 (s, 6 H), 1.613 (s, 3 H), 1.92 (m, 2 H), 4.33 (m, 1 H, H(3)), 5.445 (dd, J_1 = 17 Hz, J_2 = 7 Hz, 1 H, H(2)), 6.000 (d, *J* = 17 Hz, 1 H, H(1)); MS *m/e* (%) 194 (M^+, 7), 161 (65), 136 (26), 121 (93), 119 (54), 93 (43), 91 (42), 43 (100).

α-Ionol Acetate (3). α-Ionol (**2**) (4.7 g, 24.2 mmol) was dissolved in CH_2Cl_2 (55 mL), and the solution cooled at 0 °C. Acetic anhydride (3.6 g, 35.5 mmol) was added, followed by dry Et_3N (5.5 g, 55 mmol) and 4-(dimethylamino)pyridine (0.4 g). The mixture was warmed to room temperature and stirred overnight. The flask was transferred to a Rotavap and concentrated at 40 °C/5 mmHg. The residue was passed through a short path silica gel column (40 g ca. of silica gel Merck 60 H), using hexane (300 mL) as eluant. Evaporation of the solvent gave **3** as a gas chromatographically pure oil (5.4 g, 95% yield): IR (neat) 3010, 2950, 1710, 1675, 1450, 990 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.82 (s, 3 H), 0.89 (s, 3 H), 1.20 (m, 2 H), 1.31 (d, *J* = 7 Hz, 2 H), 1.40 (m, 2 H), 1.60 (s, 3 H), 2.0 (m, 4 H), 5.4 (m, 3 H); MS *m/e* (%) 236 (M^+, 3), 176 (40), 161 (100), 119 (42), 105 (51), 43 (86).

β-Ionol Acetate (10). Product **10** was prepared and purified (5.4 g, 98% yield) as previously described for **3**: IR (neat) 3010, 2940, 1710, 1670, 1440, 990 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.95 (s, 6 H), 1.35 (d, *J* = 6 Hz, 3 H), 1.4 (m, 2 H), 1.6 (m, 2 H), 1.67 (s, 2 H), 1.6 (m, 2 H), 1.67 (s, 3 H), 1.90 (m, 2 H), 2.05 (s, 3 H), 5.4 (m, 2 H), 6.12 (d, *J* = 18 Hz, 1 H); MS *m/e* (%) 236 (M^+, 3), 176 (20), 161 (68), 133 (28), 119 (36), 105 (45), 91 (30), 43 (100).

(*E*)-1-(2,6,6-Trimethylcyclohex-2-en-1-yl)-3-(trimethylsilyl)but-1-ene (4). To a solution of (trimethylsilyl)cuprate[3] (1.50 mmol) in THF (5 mL), cooled at −78 °C, was added acetate **3** (650 mg, 2.75 mmol) in THF (1 mL). The mixture was allowed to warm to room temperature overnight and transferred into a separatory funnel, and diethyl ether (25 mL) was added followed by

(3) Capella, L.; Degl'Innocenti, A.; Reginato, G.; Ricci, A.; Taddei, M.; Seconi, G. *J. Org. Chem.* **1989**, *54*, 1473.
(4) Vedejs, E.; McClure, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 1094.
(5) Fleming, I.; Terret, N. K. *J. Organomet. Chem.* **1984**, *264*, 99.
(6) The last oxidative step was dramatic for the overall yields which dropped from 41% (α-damascol, **6**) to 22% (α-damascone, **7**).
(7) (+)-α-Ionone (**1**) was obtained resolving the commercially available material. (a) Woodward, R. B.; Kohmann, T. P.; Harris, G. C. *J. Am. Chem. Soc.* **1941**, *63*, 120. (b) Sobotka, H.; Bloch, E.; Cahnmann, H.; Feldbau, E.; Rosen, E. *J. Am. Chem. Soc.* **1943**, *65*, 2061. (c) Ohloff, Uhde, G. *Helv. Chim. Acta* **1970**, *53*, 531.
(8) Demole, E.; Enggist, P.; Sauberl, U.; Stall, M.; Kovats, E. sz. *Helv. Chim. Acta* **1970**, *53*, 541.

NH_4Cl/NH_4OH solution (5 mL). The organic layer was separated, washed with brine, and dried (Na_2SO_4). Removal of the solvent and purification by column chromatography on silica gel (eluant: hexane) gave 520 mg of **4** (76% yield): ^1H NMR ($CDCl_3$, 300 Mhz) δ -0.079 (s, 9 H), 0.758 (s, 3 H), 0.823 (s, 3 H), 0.991 (d, 3 H, J = 7 Hz), 1.12 (m, 1 H), 1.34 (m, 1 H), 1.50 (m, 1 H), 1.536 (s, 3 H), 1.94 (m, 2 H), 2.013 (d, 1 H, J = 9 Hz), 4.946 (ddd, 1 H, J_1 = 16 Hz, J_2 = 9 Hz, J_3 = 1 Hz), 5.31 (m, 1 H), 5.356 (ddd, J_1 = 16 Hz, J_2 = 10 Hz, J_3 = 1 Hz); MS m/e (%) 250 (M^+, 5), 73 (100). Anal. Calcd for $C_{16}H_{30}Si$: C, 76.77, H, 12.07. Found: C, 76.07; H, 12.10.

(*E*)-1-(2,6,6-Trimethylcyclohex-1-en-1-yl)-3-(trimethylsilyl)but-1-ene (11). Product **11** was prepared and purified (580 mg, 84% yield) as previously described for **4**: ^1H NMR ($CDCl_3$, 300 MHz) δ -0.050 (s, 9 H), 0.926 (s, 3 H), 0.931 (s, 3 H), 1.044 (d, 1 H, J = 7 Hz), 1.39 (m, 2 H), 1.42 (m, 2 H), 1.53 (m, 3 H), 1.620 (s, 3 H), 1.91 (m, 2 H), 5.326 (dd, 1 H, J_1 = 17 Hz, J_2 = 10 Hz), 5.593 (d, 1 H, J = 17 Hz); MS m/e (%) 250 (M^+), 73 (100). Anal. Calcd for $C_{16}H_{30}Si$: C, 76.77; H, 12.07. Found: C, 76.32; H, 12.11.

1-(2,6,6-Trimethylcyclohex-2-en-1-yl)-3-(trimethylsilyl)-butane-1,2-diol (5). Osmium tetraoxide (2.5 mL of a 2.5 wt % solution in 2-methyl-2-propanol, 0.25 mmol) was added to a solution of trimethylamine *N*-oxide dihydrate (225 mg, 2 mmol in THF/water, 10/1 (2.5 mL)). Allylsilane **4** (500 mg, 2 mmol) dissolved in THF/water 8/1 (1 mL) was added slowly at 0 °C, and the mixture was stirred at room temperature overnight. Methyl sulfide (0.5 mL) was added, the mixture was filtered, and the clear solution was extracted with diethyl ether and washed with a saturated solution of HCl and brine. After drying (Na_2SO_4), the solution was evaporated, and the crude product was purified by column chromatography on silica gel (eluant ethyl acetate), yielding 430 mg (75%); IR (neat) 3450, 2940, 1460, 1250, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ -0.020 (s, 9 H), 0.790 (s, 3 H), 0.801 (s, 3 H), 0.830 (d, J = 5 Hz, 3 H), 1.40 (m, 2 H), 1.75 (m, 1 H), 1.556 (s, 3 H), 1.65 (m, 1 H), 1.89 (m, 2 H), 2.10 (m, 2 H, OH), 4.10 (m, 2 H), 5.26 (m, 1 H); MS m/e (%) 266 ($M^+ - H_2O$), 43 (100).

(*E*)-1-(2,6,6-Trimethylcyclohex-2-en-1-yl)but-2-en-1-ol (α-Damascol, 6). Potassium hydride (228 mg of a 35% dispersion in mineral oil, 2 mmol) was washed with pentane under nitrogen atmosphere; THF (5 mL) was added, followed by diol **5** (400 mg, 1.4 mmol). The mixture was stirred at room temperature for 30 min, water was cautiously added, and the product was extracted into ether. The ether was dried over Na_2SO_4 and evaporated in vacuum to give product **6** as an oil. Column chromatography on silica gel (eluant hexane/ethyl acetate 10/1) gave 220 mg, 81% yield: IR (neat) 3450, 2960, 1620, 1450, 980 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), δ 0.968 (s, 3 H), 1.014 (s, 3 H), 1.42 (m, 2 H), 1.506 (s, 3 H), 1.70 (m, 3 H), 1.92 (m, 2 H), 2.10 (d, J = 8 Hz, 1 H), 2.70 (d, 1 H, OH), 4.12 (m, 1 H), 5.36 (m, 1 H), 5.56 (m, 1 H), 5.81 (m, 1 H); MS m/e (%) 194 (M^+, 11), 43 (100). Anal. Calcd for $C_{13}H_{22}O$: C, 80.30; H, 11.41. Found: C, 80.20; H, 11.36.

(*E*)-1-(2,6,6-Trimethylcyclohex-2-en-1-yl)but-2-en-1-one (α-Damascone, 7). To a dispersion of MnO_2 (activated form, purchased from Aldrich) (1 g) in acetone, alcohol **6** (194 mg, 1 mmol) was added, and the mixture was stirred until TLC showed disappearance of the starting material. The liquid was decanted, and the residue was washed several times with Et_2O. The organic layers collected were washed with a saturated solution of NH_4Cl and brine and dried over Na_2SO_4. After evaporation of the solvent, α-damascone (**7**) was purified by PTLC (eluant hexane/ethyl acetate (20/1) to yield 103 mg, 54%: IR (neat) 2980, 1690, 1660, 825 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.835 (s, 3 H), 0.960 (s, 3 H), 1.34 (m, 1 H), 1.40 (m, 1 H), 1.550 (s, 3 H), 1.886 (d, J = 6 Hz, 3 H), 2.796 (s, 1 H), 5.421 (m, 1 H), 6.196 (dq, J_1 = 16 Hz, J_2 = 1 Hz, 1 H), 6.779 (dq, J_1 = 16 Hz, J_2 = 6 Hz, 1 H); $[\alpha]^{20}_D$ = +330° (c = 10, $CHCl_3$) [lit.[7c] $[\alpha]^{20}_D$ = +324° (c = 10, $CHCl_3$)].

(*E*)-1-(2,6,6-Trimethylcyclohex-1-en-1-yl)but-2-en-1-ol (β-Damascol, 12). To a dispersion of MCPBA (431 mg of 80% MCPBA, 2 mmol) in CH_2Cl_2 (5 mL) cooled at -78 °C was added allylsilane **11** (500 mg, 2 mmol) in CH_2Cl_2 (1 mL). The mixture was warmed to room temperature, and then methyl sulfide (1 mL) was added. The mixture was diluted with diethyl ether (20 mL) and washed subsequently with a saturated solution of NH_4Cl and brine. After drying over Na_2SO_4 the solvent was evaporated and the crude product was dissolved in THF (2 mL) and added to a solution of TBAF·$3H_2O$ (540 mg, 2 mmol) in THF (5 mL). The mixture was stirred overnight and then diethyl ether (10 mL) was added; the organic layer was washed with a saturated solution of NH_4Cl and dried over Na_2SO_4. After evaporation of the solvent, **12** was purified by column chromatography on silica gel (eluant hexane/ethyl acetate, 8/1), affording 216 mg, 55%: IR (neat) 3470, 2930, 1655, 1630, 1460, 877 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.968 (s, 3 H), 1.014 (s, 3 H), 1.32 (m, 2 H), 1.406 (s, 3 H), 1.715 (d, J = 5 Hz, 3 H), 1.78 (m, 2 H), 2.783 (br, 1 H, OH), 4.445 (d, J = 7 Hz, 1 H), 5.531 (dq, J_1 = 15 Hz, J_2 = 5 Hz, 1 H), 5.780 (dq, J_1 = 15 Hz, J_2 = 2 Hz, 1 H); MS m/e (%) 194 (M^+, 11), 123 (29), 109 (37), 91 (21), 55 (22), 43 (100). Anal. Calcd for $C_{13}H_{22}O$; C, 80.30; H, 11.41. Found: C, 80.46; H, 11.46.

(*E*)-1-(2,6,6-Trimethylcyclohex-1-en-1-yl)but-2-en-1-one (β-Damascone, 13). Pyridinium dichromate (376 mg, 1 mmol) was dissolved in dry DMF (2 mL), and alcohol **12** (194 mg, 1 mmol) was added. The mixture was stirred at room temperature for 2 h, then Et_2O (10 mL) was added, and the solution was washed with a HCl solution followed by brine. After drying over Na_2SO_4, the solvent was evaporated and **13** was purified by PTLC (eluant hexane/ethyl acetate, 20/1) to give 130 mg, 68% yield: IR (neat) 2940, 1675, 1640, 1615, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), δ 0.986 (s, 3 H), 1.016 (s, 3 H), 1.26 (m, 2 H), 1.41 (m, 2 H), 1.486 (s, 3 H), 1.58 (m, 2 H), 1.906 (dd, J_1 = 6 Hz, J_2 = 1 Hz, 1 H), 6.061 (dq, J_1 = 16 Hz, J_2 = 1 Hz, 1 H), 6.629 (dq, J_1 = 16 Hz, J_2 = 6 Hz, 1 H); MS m/e (%) 192 (M^+, 12), 136 (43), 43 (100). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.87; H, 10.56.

(*E*)-1-(2,6,6-Trimethylcyclohexa-1,3-dienyl)but-2-en-1-one (β-Damascenone, 14). *N*-Bromosuccinimide (196 mg, 1.1 mmol) was dissolved in dry CH_2Cl_2 (3 mL), ketone **13** (192 mg, 1 mmol) in CCl_4 (3 mL) was added, and the mixture was heated at 50 °C; DABCO (224 mg, 2 mmol) was added, followed by 4-(dimethylamino)pyridine (15 mg). After filtration the solution was poured in a round-bottomed flask, and the solvent was evaporated at a rotavap. The flask was transferred in a Kughelrohr apparatus and heated at 80 °C under vacuum (25 mmHg) for 1 h. The residue was treated with Et_2O (5 mL) and 10% HCl (2 mL). The organic layer was separated, washed with brine, and dried over Na_2SO_4. After evaporation of the solvent product **14** was purified by column chromatography on silica gel (eluant hexane/ethyl acetate, 20/1) to yield 168 mg, 86%: IR (neat) 2940, 1670, 1635, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.005 (s, 3 H), 1.010 (s, 3 H), 1.625 (s, 3 H), 1.930 (dd, J_1 = 7 Hz, J_2 = 1 Hz, 3 H), 2.109 (d, J = 2 Hz, 2 H), 5.79 (m, 2 H), 6.10 (dq, J_1 = 16 Hz, J_2 = 1 Hz, 1 H), 6.750 (dq, J_1 = 1 Hz, J_2 = 7 Hz, 1 H); MS m/e (%) 190 (1), 126 (36), 43 (100). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.46; H, 9.56.

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Registry No. 1, 24190-29-2; **2** (isomer 1), 124152-01-8; **2** (isomer 2), 120523-19-5; **3** (isomer 1), 124152-02-9; **3** (isomer 2), 124152-04-1; **4**, 124099-57-6; **5**, 124099-58-7; **6**, 28102-24-1; **7**, 28102-28-5; **8**, 79-77-6; (±)-**9**, 53078-25-4; (±)-**10**, 124152-03-0; (±)-**11**, 124099-59-8; (±)-**12**, 124099-60-1; **13**, 23726-91-2; **14**, 23726-93-4.

An Efficient Synthesis of α-Silylacetates Having Various Types of Functional Groups in the Molecules

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The synthetic utility of α-silyl esters has been shown in a variety of organic reactions.[1] One of the most practical

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