1-Nitro-2-(*tert*-butylamino)cyclohexene (5). The following experiment is typical of the procedure employed in the preparation of 1-nitro-2-(*tert*-butylamino)cycloalkenes. A stirred suspension of potassium amide was prepared by adding 7.82 g (0.20 g-atom) of freshly cut potassium metal and a crystal of ferric nitrate decahydrate to 150 mL of liquid ammonia. After the suspension was cooled to -40 °C, 15.33 g (0.10 mol) of *N*-cyclohexylidene-*tert*-butylamine (**2**) was added in one portion. After the suspension was stirred for 30 min, the temperature was lowered to -60 °C and 15.76 g (0.15 mol) of *n*-propyl nitrate added (**Caution**: cooling must be maintained during the addition of the nitrating agent as long as the high exotherm persists) over a period of 3 min while the reaction temperature was kept below -40 °C. After the suspension was stirred for 30 min at -33 °C, 11.77 g (0.22 mol) of ammonium chloride was added at -45 °C.

The ammonia was replaced with absolute ether, the inorganic salts were filtered off, and the ether was removed in vacuo. Trituration of the residue with hexane gave 9.54 g of crude **5**. Recrystallization from hexane using decolorizing carbon gave 8.77 g (44%) of **5** (mp 120–122 °C). Further recrystallization gave analytically pure **5**: mp 122–123 °C; UV max (95% C_2H_5OH) 246 nm (sh). 370 (log ϵ 4.31); IR (CCl_4) 1602 (C=N), 1219 and 1122 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.50 (s, 9, CH_3), 1.74 (m, 4, C_4H and C_5H), 2.70 (m, 4, C_3H and C_6H), 12.0 (br, 1, ^+NH); mass spectrum (70eV), *m/e* (rel intensity) 198 (59), 125 (100). Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.59; H, 9.15; N, 14.13. Found: C, 60.70; H, 8.91; N, 14.40.

1-Nitro-2-(*tert*-butylamino)cyclopentene (4). From 7.82 g (0.20 g-atom) of potassium, 13.9 g (0.10 mol) of *N*-cyclopentylidene-*tert*-butylamine, 15.75 g (0.15 mol) of *n*-propyl nitrate, and 12.77 g (0.24 mol) of ammonium chloride was obtained 6.40 g (35%) of **4**: mp 111–112 °C (hexane); UV max (95% C_2H_5OH) 241 nm (sh), 366 (log ϵ 4.39); IR (CCl_4) 1615 (C=N), 1205 and 1180 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.44 (s, 9, CH_3), 1.98 (m, 2, C_4H), 2.84 (m, 4, C_3H and C_5H), 10.2 (br, 1, ^+NH); mass spectrum (75 eV), *m/e* (rel intensity) 184 (50), 57 (100). Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.20. Found: C, 58.58; H, 8.71; N, 15.32.

1-Nitro-2-(*tert*-butylamino)cycloheptene (6). From 7.82 g (0.20 g-atom) of potassium, 16.7 g (0.10 mol) of *N*-cycloheptylidene-*tert*-butylamine, 15.75 g (0.15 mol) of *n*-propyl nitrate, and 12.30 g (0.23 mol) of ammonium chloride was obtained 10.72 g (50%) of **6**: mp 116–119 °C (hexane); UV max (95% C_2H_5OH) 245 nm (sh), 370 (log ϵ 4.19); IR (CCl_4) 1595 (C=N), 1212 and 1122 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.48 (s, 9, CH_3), 1.72 (m, 6, C_4H, C_5H, and C_6H), 2.88 (m, 4, C_3H and C_7H), 12.2 (br, 1, ^+NH); mass spectrum (75 eV), *m/e* (rel intensity) 212 (55), 57 (100). Anal. Calcd for $C_{11}H_{20}N_2O_2$: C, 62.23; H, 9.50; N, 13.19. Found: C, 61.97; H, 9.33; N, 13.14.

1-Nitro-2-(*tert*-butylamino)-3-bromocyclohexene (7). (a) Using Compound 5. To a stirred solution of 5.94 g (0.030 mol) of **5** and 2.31 g (0.033 mol) of pyridine in 25 mL of chloroform was added dropwise, over a period of 25 min, 4.84 g (0.030 mol) of bromine dissolved in 25 mL of chloroform while the reaction temperature was kept at 3–5 °C. After continuing stirring for 30 min at ice bath temperature, the reaction mixture was washed with three 35-mL portions of water. The chloroform portion was dried ($MgSO_4$) and concentrated to give 9.53 g of solid residue. The residue was stirred successively in four 250-mL portions of ethyl ether, leaving 2.26 g of insoluble material which was pyridinium bromide.

Concentration of the combined ether extracts gave 7.00 g (84%) of crude **7**. Recrystallization gave 6.54 g (79%) of pure **7**: mp 131–135 °C dec (hexane); UV max (95% C_2H_5OH) 230 nm (log ϵ 3.66), 392 (4.21); IR (CCl_4) 1608 (C=N), 1215 and 1123 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.54 (s, 9, CH_3), 2.06 (m, 4, C_4H and C_5H), 2.80 (m, 2, C_3H), 5.30 (m, 1, C_6H), 11.3 (br, 1, ^+NH); mass spectrum (75eV), *m/e* (rel intensity) 278 (7.6), 276 (7.6), 57 (100). Anal. Calcd for $C_{10}H_{17}BrN_2O_2$: C, 43.34; H, 6.18; N, 10.11; Br, 28.84. Found: C, 43.61; H, 6.33; N, 10.36; Br, 29.00.

(b) Using Sodium 2-(*tert*-Butylamino)-2-cyclohexenenitronate (9). To a suspension of 1.82 g (8.2 mmol) of **9** in 40 mL of chloroform kept at 3–5 °C was added dropwise over a period of 10 min 1.31 g (8.2 mmol) of bromine dissolved in 10 mL of chloroform. After being stirred an additional 5 min at ice-bath temperature, the mixture was filtered and the filtrate dried ($MgSO_4$). Removal of the solvent gave 1.06 g (47%) of **7**, mp 129–130.5 °C dec (hexane). A mixture melting point determination with **7** obtained in (a) gave no depression. Also the IR and NMR spectra were identical with those of **7**.

Sodium 2-(*tert*-Butylamino)-2-cyclohexenenitronate (9). To a solution of 3.96 g (0.020 mol) of **5** in 250 mL of dry THF was added 0.929 g of sodium hydride suspended in mineral oil (52% sodium hydride by weight, 0.021 mol). After the mixture was stirred at 25 °C for 5 h, 480 mL (~0.020 mol) of hydrogen was collected. The reaction mixture was filtered and the residue washed with ethyl ether to give 4.50 g of air-dried crude **9**: IR (KBr) 3250 (NH_2) 1612 (C=N, C=C), 1231 and 1146 cm^{-1} (NO_2^-); NMR [$(CD_3)_2SO$] δ 1.16 (s, 9, CH_3), 1.52 (m, 2, C_4H), 2.00 (m, 2, C_5H), 2.50 (m, C_6H; this peak overlapped the residual proton peak of the solvent, and its integration was not obtained), 4.34 (t, 1, C_3H), 8.10 (s, 1, NH).

Conversion of Salt 9 to Compound 5. Crude **9** (0.83 g, 3.8 mmol) was suspended in 250 mL of ethyl ether, and glacial acetic acid (0.22 g, 3.8 mmol) was added dropwise while the reaction temperature was kept at 3–5 °C and the reaction mixture was kept under nitrogen. The reaction was continued 3 h at room temperature, the mixture filtered, and the filtrate dried ($MgSO_4$) and concentrated to give 0.51 g (68%) of **5**, mp 121–122 °C. The spectra were identical with those of authentic **5**.

3,3-Dibromo-2-amino-1-nitrocyclohexene (10). To a stirred solution of 2.00 g (7.2 mmol) of **7** in 20 mL of chloroform kept at 3–5 °C was added dropwise over a period of 10 min 1.15 g (7.2 mmol) of bromine dissolved in 10 mL of chloroform. Stirring was continued for 30 min. Then the reaction mixture was concentrated and the residue triturated with hexane to give 2.18 g of yellow solid, mp 121–125 °C. The solid was taken up in ethyl ether, the mixture filtered, and the filtrate concentrated to give a solid residue. Trituration with hexane afforded 1.14 g (53%) of crude **10**. Two recrystallizations, the first from cyclohexane and the second from hexane, gave 0.22 g (10%) of analytically pure **10**: mp 122.5–123 °C; UV max (95% C_2H_5OH) 230 nm (log ϵ 3.64), 371 (4.13); IR (CCl_4) 3470 and 3300 (NH_2), 1623 (C=C, C=N), 1382 and 1249 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.95 (m, 2, C_5H), 2.82 (m, 4, C_4H and C_6H), 7.65 (br, 2, NH_2); mass spectrum (15 eV), *m/e* (rel intensity) 302 (22), 300 (43), 298 (22), 221 (97), 219 (100). Anal. Calcd for $C_6H_8Br_2N_2O_2$: C, 24.03; H, 2.69; N, 9.34; Br, 53.28. Found: C, 24.00; H, 2.73; N, 9.09; Br, 53.60.

Acknowledgment. The support of this investigation by a grant from the IMC Chemical Group, Inc., is greatly appreciated.

Registry No. **1**, 25115-61-1; **2**, 37810-16-5; **3**, 71041-39-9; **4**, 71041-40-2; **5**, 71041-41-3; **6**, 71041-42-4; **7**, 71041-43-5; **9**, 71060-33-8; **10**, 71041-44-6; cyclohexanone, 108-94-1; *tert*-butylamine, 75-64-9; cycloheptanone, 502-42-1; cyclopentanone, 120-92-3; potassium amide, 17242-52-3.

A Convenient Preparation of β-Damascenone from Dimedone

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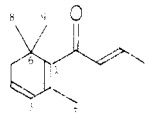
Received March 5, 1979

In contrast to synthetic studies of cyclocitryl homologues,[1] a different route from 3-ethoxy-6-[(*E*)-1-hydroxy-2-butenyl]-5,5-dimethyl-2-cyclohexen-1-one (**2a**),[2] prepared from the condensation of a kinetic enolate anion[3]

(1) Torii, S.; Uneyama, K.; Ichimura, H. *J. Org. Chem.* **1979**, *44*, 2229.
(2) The compound **2a** has been prepared from dimedone smoothly and used for the preparation of megastigma-4,6,8-trien-3-ones (**4**), a characteristic flavoring component of Burley tobacco: Torii, S.; Inokuchi, T.; Ogawa, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1233 and references cited therein.

0022-3263/79/1944-3412$01.00/0

of 3-ethoxy-5,5-dimethyl-2-cyclohexen-1-one with (*E*)-2-butenal, to β-damascenone (**1**), a characteristic odorous



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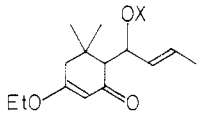
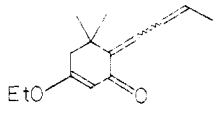


2a, X = H
b, X = CH(Me)OEt
c, X = THP



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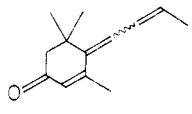
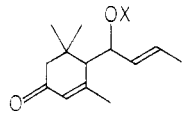


4

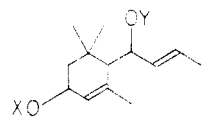
component of Bulgarian rose oil, *Rosa damascena* Mill.,[4,5] was investigated. As a procedure for the introduction of a C_4 unit to the cyclohexenyl moiety, the condensation of 2,6,6-trimethyl-2-cyclohexenone with 1-butyn-3-ol[6] and/or 2-butyn-1-ol[7] has been recorded in the literature. We present here a straightforward C_4 plus C_9 procedure for β-damascenone synthesis, indicating that the simplest approach to prepare the cyclohexadiene system of **1** is to use base-catalyzed elimination reaction of the good leaving group (AcO) on the key precursor **8**, prepared from dimedone.

When methylation of **2b** and/or **2c**, provided by etherification[8] of **2a**, was attempted using methylmagnesium iodide, the reagent caused 1,2-elimination of alkoxyl groups, resulting in the formation of **3** in 72–75% yields. But, methyllithium in ether led to the desired methylation, giving **5** in 49–50% yields. The yield of **5** was increased to 61% together with 7% of **3** and 20% of **4** when run in hexane solvent.

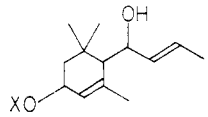
Treatment of **5a** with $LiAlH_4$ in ether, giving **6a** (96%), followed with acetic anhydride in pyridine provided the acetate **6b** (95%). Hydrolysis of the ether bond of **6b** with



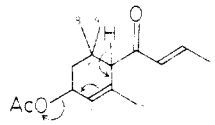
5a, X = CH(Me)OEt
b, X = THP



6a, X = H ; Y = CH(Me)OEt
b, X = Ac ; Y = CH(Me)OEt
c, X = Ac ; Y = THP



7a, X = Ac
b, X = Et



8

pyridinium *p*-toluenesulfonate (PPTS) in ethanol at 40 °C for 3 h afforded the alcohol **7a** (94%), but hydrolysis of **6b** at 55 °C gave a 1:1 mixture of **7a** and **7b** in 43% yield. Tetrahydropyranyl ether **6c** was found to be less reactive than **6b** in PPTS-ethanol and could be hydrolyzed at 55 °C for 3 h, giving 29% of a 1:1 mixture of **7a** and **7b**.

Oxidation of **7a** with activated manganese dioxide[9] in dichloromethane afforded the enone **8** in 87% yield. In contrast, treatment of **7a** with pyridinium chlorochromate–dichloromethane[10] gave less than 40% yield of **8** and *N*-chlorosuccinimide–dimethyl sulfide[11] caused elimination of the hydroxyl group of **7a**. Thermal decomposition of **8** in 1,5-diazabicyclo[5.4.0]undec-5-ene under reflux for 20 s gave the desired **1** in 79% yield as the result of 1,4-elimination of acetic acid.

Experimental Section

The boiling points and melting points are uncorrected. IR spectra were determined with a JASCO IRA-1 grating spectrometer. ^1H NMR (100 MHz) and ^{13}C NMR (25.05 MHz) spectra were determined with a JEOL FX-100 spectrometer. Samples were dissolved in $CDCl_3$ and the chemical shift values are expressed in δ values (ppm) relative to Me_4Si as an internal standard. Elemental analyses were performed in our laboratory.

3-Ethoxy-6-[(*E*)-1-(1-ethoxy)ethoxy-2-butenyl]-5,5-dimethyl-2-cyclohexen-1-one (2b). A solution of **2a** (244 mg, 1.02 mmol), ethoxyethylene (147 mg, 2.05 mmol), and PPTS (10 mg, 0.04 mmol) in CH_2Cl_2 (7 mL) was stirred at room temperature for 7 h. The mixture was quenched with cold aqueous saturated $NaHCO_3$ and extracted with ether–benzene. The extracts were washed with brine, dried (Na_2SO_4), and concentrated to give 301 mg (95%) of **2b** as an oil: bp 72.0–74.0 °C (0.015 mm, Kugelrohr); IR (neat) 1651 (C=O), 1612 (C=C), 1217, 1197, 1148, 1135, 1086, 1032, 967 cm^{-1}; ^1H NMR δ 1.07, 1.20 (s, 6, CH_3), 1.13–1.30 (m, 6, CH_3), 1.35 (t, 3, J = 7 Hz, CH_3), 1.67 (d, 3, J = 6 Hz, CH_3), 2.01, 2.63 (d, 2, J = 17 Hz, CH_2O), 4.35 (m, 1, C=CCHO), 4.67 (q, 1, J = 6 Hz, OCHO), 5.32 (d, 1, J = 2 Hz, HC=C), 5.40–5.80 (m, 2, HC=C). Anal. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: C, 69.70; H, 9.45.

3-Ethoxy-5,5-dimethyl-6-[(*E*)-1-(2-tetrahydropyranyloxy)-2-butenyl]-2-cyclohexen-1-one (2c). In a manner similar to **2b**, **2c** was prepared in 93% yield by the reaction of **2a** and dihydropyran: mp 79.0–80.0 °C; IR (Nujol) 3060, 3030, 1644 (C=O), 1614 cm^{-1} (C=C); ^1H NMR δ 1.08, 1.23 (s, 6, CH_3), 1.66 (d, 3, J = 8 Hz, CH_3), 1.10–2.81 (m, 12, CH_2, CH), 3.25–4.04 (m, 4, CH_2O), 4.17–4.71 (m, 2, CHO), 5.22–5.84 (m, 3, HC=C). Anal.

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Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 70.72; H, 9.33.

6-[(*E*)-2-Butenylidene]-3-ethoxy-5,5-dimethyl-2-cyclohexen-1-one (3), 4-[(*E*)-2-Butenylidene]-3,5,5-trimethyl-2-cyclohexen-1-one (4), and 4-[(*E*)-1-(1-Ethoxy)ethoxy-2-butenyl]-3,5,5-trimethyl-2-cyclohexen-1-one (5a). To a vigorously stirred solution of **2b** (167 mg, 0.54 mmol) in hexane (9 mL) was added an ethereal solution of 1.5 M MeLi (0.7 mL, 1.05 mmol) at 3–4 °C. The mixture was stirred at 3–4 °C for 40 min, quenched with cold aqueous saturated $NaHCO_3$, and extracted with ether–benzene. The extracts were washed with aqueous saturated $NaHCO_3$, dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, hexane–AcOEt 3:1) to give 21 mg (20%) of **4**[2] (R_f 0.56, hexane–AcOEt 3:1), 8 mg (7%) of **3**[2] (R_f 0.53), and 92 mg (61%) of **5a** (R_f 0.48) as oils. **5a**: bp 55.0–56.0 °C (0.007 mm, Kugelrohr); IR (neat) 3025, 1665 (C=O), 1630 (C=C), 1136, 1125, 1087, 1056, 1005, 972, 935 cm^{-1}; ^1H NMR δ 1.03 (s, 3, CH_3), 1.15 (s, 3, CH_3), 1.16 (t, 3, J = 7 Hz, CH_3), 1.27 (d, 3, J = 5.5 Hz, CH_3), 1.66 (d, 3, J = 6 Hz, CH_3), 1.80–2.85 (m, 3, CH_2, CH), 2.10 (s, 3, CH_3), 3.20–3.67 (m, 2, CH_2O), 4.34 (d, d, 1, J = 9, 3 Hz, CHO), 4.68 (q, 1, J = 5.5 Hz, CHO), 5.10–5.82 (m, 2, HC=C), 5.97 (br s, 1, HC=C). Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.88; H, 10.10.

6-[(*E*)-2-Butenylidene]-5,5-dimethyl-3-ethoxy-2-cyclohexen-1-one (3). To a solution of **2c** (99 mg, 0.31 mmol) in ether (4 mL) was added a solution of MeMgI prepared from MeI (220 mg, 1.55 mmol) and magnesium (37 mg, 1.53 mmol) in ether (3 mL) at 0–5 °C. The mixture was stirred at 0–5 °C for 1 h, quenched with cold aqueous saturated NH_4Cl, and worked up in the usual manner to give 49 mg (72%) of **3**.

4-[(*E*)-1-(1-Ethoxy)ethoxy-2-butenyl]-3,5,5-trimethyl-2-cyclohexen-1-ol (6a). To a suspension of $LiAlH_4$ (30 mg, 0.79 mmol) in ether (1 mL) was added a solution of **5a** (81 mg, 0.29 mmol) in ether (2 mL) at 0–5 °C. The mixture was stirred at room temperature for 1 h and quenched with cold AcOEt (0.5 mL) and cold aqueous 5% $NaHCO_3$ (0.3 mL). The organic layer was decanted and the white precipitate in the flask was washed with ether–benzene. The combined extracts were dried (Na_2SO_4) and concentrated. The residue was chromatographed (SiO_2, hexane–AcOEt 3:1) to give 81 mg (96%) of **6a** as an oil: bp 60.5–61.8 °C (0.005 mm, Kugelrohr); IR (neat) 3360 (OH), 1664 (C=C), 1121, 1092, 1055, 1028, 1000, 967, 952, 929 cm^{-1}; ^1H NMR δ 0.91–1.07 (m, 6, CH_3), 1.23 (q, 3, J = 7 Hz, CH_3), 1.25 (d, 3, J = 6 Hz, CH_3), 1.50–2.20 (m, 3, CH_2, CH), 1.66 (d, 3, J = 3 Hz, CH_3), 1.84 (br s, 3, CH_3), 2.45 (br s, 1, OH), 3.28–3.80 (m, 2, CHO), 3.96–4.40 (m, 2, CHO), 4.58–4.76 (m, 1, OCHO), 5.15–5.97 (m, 3, HC=C). Anal. Calcd for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71. Found: C, 72.35; H, 10.52.

4-[(*E*)-1-(1-Ethoxy)ethyl-2-butenyl]-3,5,5-trimethyl-2-cyclohexen-1-ol Acetate (6b). A solution of **6a** (269 mg, 0.95 mmol) and Ac_2O (672 mg, 6.65 mmol) in pyridine (2.5 mL) was stirred at 0–5 °C for 30 min and at room temperature for 12 h. The mixture was poured into cold aqueous 5% tartaric acid and extracted with ether–benzene. The extract was worked up in the usual manner and the crude product was chromatographed (SiO_2, hexane–AcOEt 6:1) to give 294 mg (95%) of **6b** as an oil: bp 56.5–58.5 °C (0.007 mm, Kugelrohr); IR (neat) 1731 (ester C=O), 1665 cm^{-1} (C=C); ^1H NMR δ 0.95, 1.05 (s, 6, CH_3), 1.20 (t, 3, J = 7 Hz, CH_3), 1.24 (d, 3, J = 7 Hz, CH_3), 1.30–2.08 (m, 6, CH_3, CH_2, CH), 1.86 (complex, 3, CH_3), 2.01, 2.02 (s, 3, $COCH_3$), 3.51 (q, 2, J = 7 Hz, CH_2O), 4.06–4.39 (m, 1, CHO), 4.52–4.78 (m, 1, CHO), 5.03–5.79 (m, 4, HC=C, CHO). Anal. Calcd for $C_{19}H_{32}O_4$: C, 70.33; H, 9.94. Found: C, 70.55; H, 10.22.

4-[(*E*)-1-Hydroxy-2-butenyl]-3,5,5-trimethyl-2-cyclohexen-1-ol Acetate (7a). A solution of **6b** (105 mg, 0.32 mmol) and PPTS (6 mg, 0.023 mmol) in EtOH (5 mL) was stirred at 40 °C for 3 h. The mixture was concentrated and the residue was chromatographed (SiO_2, hexane–AcOEt 3:1) to give 77 mg (94%) of **7a** as an oil: bp 62.0–63.0 °C (0.02 mm, Kugelrohr); IR (neat) 3430 (OH), 3020, 1730 (ester C=O), 1667 cm^{-1} (C=C); ^1H NMR δ 0.96, 1.04 (s, 6, CH_3), 1.20–2.20 (m, 4, CH_2, CH, OH), 1.70 (d, 3, J = 5 Hz, CH_3), 1.88 (s, 3, CH_3), 2.03 (s, 3, $COCH_3$), 4.42 (m, 1, CHO), 5.52 (m, 1, CHOCO), 5.42–5.87 (m, 3, HC=C). Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.57. Found: C, 71.57; H, 9.48.

The reaction of **6b** (93 mg, 0.29 mmol) and PPTS (10 mg, 0.04 mmol) in EtOH (5 mL) at 55 °C afforded 31 mg (43%) of a 1:1 mixture of **7a** and **7b**: IR (neat) 3430 (OH), 3020, 1731, 1716, 1667 (C=C), 1241, 1082, 969 cm^{-1}; ^1H NMR δ 0.97, 1.05 (s, 6, CH_3), 1.20 (t, J = 7 Hz, CH_3), 1.38–2.19 (m, 6, CH_3, CH_2, CH), 1.89 (complex, 3, C=CCH_3), 2.04 (s, $COCH_3$), 2.23 (s, 1, OH), 3.53 (q, J = 7 Hz, OCH_2), 4.49 (br s, 1, C=CCHO), 5.32 (m, 1, CHO), 5.51–5.96 (m, 3, HC=C).

1-(4-Acetoxy-2,6,6-trimethyl-2-cyclohexen-1-yl)-2(*E*)-buten-1-one (8). To a suspension of activated MnO_2[9] (793 mg, 9.1 mmol) in CH_2Cl_2 (3 mL) was added a solution of **7a** (78 mg, 0.31 mmol) in CH_2Cl_2 (3 mL). The mixture was vigorously stirred at room temperature for 5 h and diluted with hot acetone. The insoluble materials were separated by centrifugation and the organic layer was concentrated. The crude product was chromatographed (SiO_2, hexane–AcOEt 5:1) to give 67 mg (87%) of 8 as white crystals: mp 82.0–83.5 °C; IR (Nujol) 3040, 1724 (ester C=O), 1684 (C=O), 1672 (C=C), 1622 (C=C), 1357, 1321, 1180, 1126, 1080, 1022, 973 cm^{-1}; ^1H NMR δ 0.90, 1.03 (s, 6, CH_3), 1.50–1.83 (m, 2, CH_2), 1.62 (complex, 3, CH_3), 1.92 (d, d, 3, J = 7, 2 Hz, CH_3), 2.07 (s, 3, $COCH_3$), 2.94 (br s, 1, COCH), 5.33 (m, 1, CHOCO), 5.61 (br s, 1, HC=C), 6.29 (d, q, 1, J = 16, 2 Hz, HC=C), 6.89 (d, q, 1, J = 16, 7 Hz, HC=C); ^{13}C NMR δ 18.4 (q, butenyl γ-CH_3), 21.5 (q, acetyl CH_3), 23.2 (q, C-7), 28.5 (q, C-8, C-9), 34.7 (s, C-6), 36.5 (t, C-5), 60.8 (d, C-1), 69.4 (d, C-4), 123.5 (d, C-3), 132.5 (d, butenyl α-CH), 135.8 (s, C-2), 143.5 (d, butenyl β-CH), 171.4 (s, acetyl C=O), 200.8 (s, butenyl C=O). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.98; H, 9.00.

1-(2,6,6-Trimethylcyclohexa-1,3-dienyl)-2(*E*)-buten-1-one (β-Damascenone) (1). A mixture of 8 (44 mg, 0.18 mmol) and 1,5-diazabicyclo[5.4.0]undec-5-ene (50 mg, 0.33 mmol) was heated at reflux for 20 s and chromatographed (SiO_2, hexane–AcOEt 10:1) to give 27 mg (79%) of **1** as an oil: bp 36.0–37.5 °C (0.01 mm, Kugelrohr) [lit.[4] 57 °C (0.001 mm)]; IR (neat) 3030, 2800, 1670 (shoulder), 1637 (C=O), 1615 (C=C), 1440, 1302, 1290, 1250, 1222, 971, 929 cm^{-1}; ^1H NMR δ 1.05 (s, 6, CH_3), 1.64 (s, 3, CH_3), 1.94 (d, d, 3, J = 7, 2 Hz, CH_3), 2.14 (d, 2, J = 3 Hz, CH_2), 5.77 (d, 1, J = 13 Hz, HC=C), 5.91 (d, d, 1, J = 13, 4 Hz, HC=C), 6.18 (d, q, 1, J = 16, 1.5 Hz, HC=C), 6.85 (d, q, 1, J = 16, 7 Hz, HC=C); ^{13}C NMR δ 18.4 (q, butenyl γ-CH_3), 19.5 (q, C-7), 26.4 (q, C-8, C-9), 33.9 (s, C-6), 39.5 (t, C-5), 127.5 (d, C-3), 128.2 (s, C-1), 128.2 (d, C-4), 134.8 (d, butenyl α-CH), 139.6 (s, C-2), 146.4 (d, butenyl β-CH), 201.4 (s, butenyl C=O).

Registry No. 1, 23726-93-4; **2a**, 70982-59-1; **2b**, 70941-42-3; **2c**, 70941-43-4; **3**, 70941-44-5; **4**, 70941-45-6; **5a**, 70941-46-7; **6a**, 70941-47-8; **6b**, 70941-48-9; **7a**, 70941-49-0; **7b**, 70941-50-3; **8**, 70941-51-4; ethoxyethylene, 109-92-2; dihydropyran, 110-87-2.

Convenient Synthesis of the 2-Methyl-4-hydroxybut-2-enolide Moiety of Strigol

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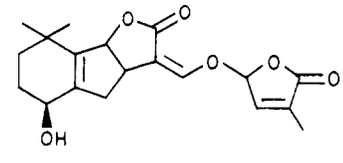
Received March 23, 1979

Strigol, a potent natural seed germination stimulant for parasitic crop pests of the genera *Striga* (witchweed) and *Orabanche* (broomrape), has been synthesized by Sih[1] and



strigol

MacAlpine,[2] but by methods not readily adaptable to

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