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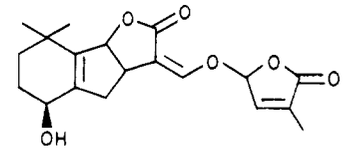
Strigol, a potent natural seed germination stimulant for parasitic crop pests of the genera *Striga* (witchweed) and *Orabanche* (broomrape), has been synthesized by Sih[1] and



strigol

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

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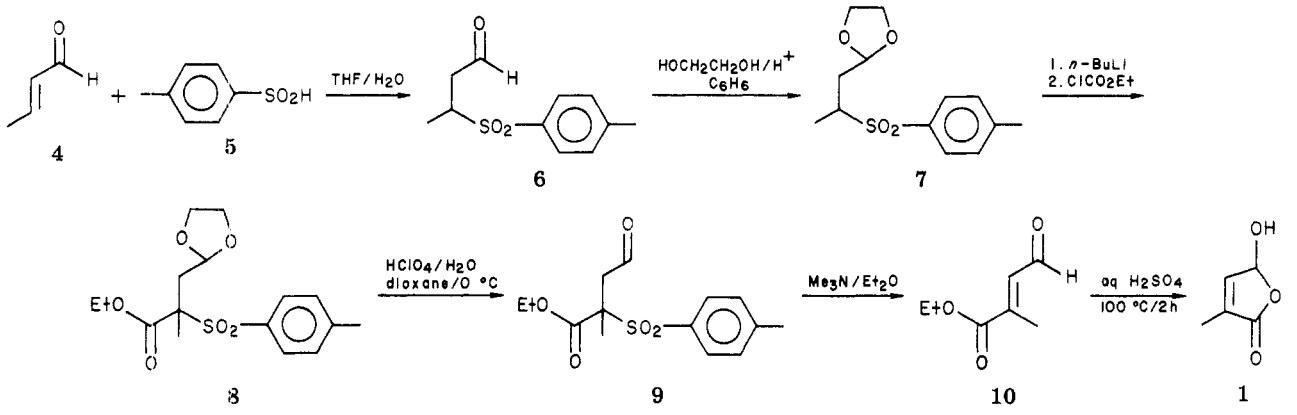
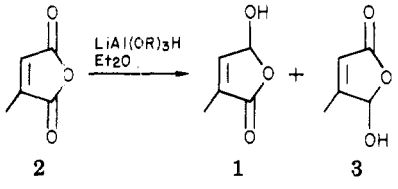
Scheme I



large-scale preparation. As part of a research project[3] directed toward an improved synthesis of strigol and a wide range of analogues, we wished to devise a short and convenient route to the hydroxy lactone moiety (2-methyl-4-hydroxybut-2-enolide) 1 in good yield without chromatography. Available reactions yielding compounds related to 1 involve free radical or photochemical processes. The addition of singlet oxygen to 3-methyl-2-furanoic acid[4,5] involves a potentially hazardous molozonide-like intermediate, and is probably ill suited to scale-up. *N*-Bromosuccinimide bromination[6] of 2-methylbutenolide, followed by silver acetate treatment, also gives a mixture of isomers. Although the unsubstituted hydroxybutenolide[7] has been known since 1905, the problem of regioselectivity has precluded simple reduction of citraconic anhydride 2.

We had hoped that use of one of the hindered hydridoaluminates, such as lithium tri-*tert*-butoxyaluminum hydride, which are reported to show great steric selectivity,[8] would give smooth reduction of the less hindered carbonyl of citraconic anhydride to yield 1. However, it was observed that the major product was the isomeric hydroxy lactone resulting from reduction of the more hindered carbonyl, the unwanted isomer 3 being obtained in an 8:1 mixture with the desired hydroxybutenolide 1.



The preferential reaction of the more hindered carbonyl may result from deactivation of the less hindered carbonyl by interaction with the electron-releasing methyl group, or could involve prior complexation of the less hindered carbonyl by the hydridoaluminate, followed by hydride transfer, as has previously been reported[9] for other systems. Use of other reducing agents gave over-reduction (to the diol) and loss of regioselectivity.

It occurred to us that the desired hydroxy lactone could be obtained by a similar method to that previously used in the cases of some 4-hydroxycyclopent-2-enones[10] in which the adduct of an arylsulfinic acid and conjugated enone (a γ-oxo sulfone) served as a conjugate acyl anion equivalent. Thus, crotonal was condensed with *p*-toluenesulfinic acid, prepared in situ from the sodium salt. The resulting γ-oxo sulfone was acetalized with ethylene glycol to give the stable, crystalline sulfone acetal 7 in excellent yield (Scheme I). This sulfone was treated with strong base, then ethyl chloroformate, to give 8. Acetal hydrolysis, followed by elimination of sulfinate with trimethylamine, gave the unsaturated ester–aldehyde **10**, which was allowed to react with aqueous acid to yield the desired hydroxy lactone in good yield, as reported[11] for the isomeric system. The known compound 1 agreed in all particulars with reported[5] values.

Experimental Section

All reactions were run with reagent quality chemicals, and drying of organic solutions in workups used anhydrous $MgSO_4$. Proton magnetic resonance (NMR) spectra were taken on a Varian XL-100 in continuous wave or Fourier transform mode, or on a Varian HA-100 in CW mode with D lock. NMR spectra were taken in $CDCl_3$ with internal Me_4Si standard, and are reported as δ (H, mult, *J*). Abbreviations used are: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, H = integral value of one resonating proton, *J* = coupling constants. High-resolution mass spectra were obtained by Dr. R. Wielesek of the University of Oregon Microanalytical Laboratory.

Lithium Tri-*tert*-butoxyaluminum Hydride Reduction of Citraconic Anhydride. Citraconic anhydride (112 mg, 1 mmol) was added to a suspension of lithium tri-*tert*-butoxyaluminum hydride (254 mg, 1 mmol) in dry ether (5 mL) at −55 °C under nitrogen. The reaction mixture was stirred vigorously and allowed to warm to room temperature over a period of 3 h. A 1-M solution of HCl in saturated aqueous NaCl was added, the solution was extracted with ether, and the organic phases was dried and stripped. NMR analysis of the total crude revealed a 1:8 mixture of the two isomeric hydroxy lactones 1 and 3, respectively: NMR (3) δ 5.97 (1 H, m), 5.89 (1 H, q, *J* = 1 Hz), 3.7 (1 H, s br), 2.14 (3 H, d, *J* = 1 Hz); (1) δ 6.90 (1 H, m), 6.08 (1 H, q, *J* = 1 Hz), 5.08 (1 H, s br), 1.88 (3 H, d, *J* = 1 Hz).

Lithium Trimethoxyaluminum Hydride Reduction of Citraconic Anhydride. Lithium aluminum hydride (38 mg, 1 mmol) in dry ether (5 mL) was stirred at 0 °C under nitrogen as dry methanol (96 mg, 0.112 mL, 3 mmol) was added dropwise. After 15 min, citraconic anhydride (112 mg, 0.090 mL, 1 mmol) was added. The reaction mixture was stirred for 2.5 h, and was worked up as before. NMR analysis showed the unwanted isomer 3 present in a ratio of about 3:1 over compound 1.

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3-(*p*-Toluenesulfonyl)butanal (6). Glacial acetic acid (6.0 g, 5.8 mL, 0.10 mol) was added dropwise to a solution of sodium *p*-toluenesulfinate monohydrate (21.4 g, 0.1 mol) in water (100 mL) plus tetrahydrofuran (50 mL) stirred at 0 °C under nitrogen. Freshly distilled crotonal (6.0 g, 8.25 mL, 0.1 mol) in THF (25 mL) was added, and the mixture was stirred for 21 h at room temperature. Water (250 mL) was then added, and the mixture was extracted with methylene chloride, which was dried and stripped to yield an oil. NMR analysis showed the material to be pure sulfone aldehyde **6**, which was used directly in the next step: NMR δ 9.78 (1 H, s), 7.78 (2 H, d, J = 8 Hz), 7.38 (2 H, d, J = 8 Hz), 3.64 (1 H, m), 3.17 (1 H, d of d, J = 19, 4 Hz), 2.60 (1 H, d of d, J = 19, 8 Hz), 2.44 (3 H, s), 1.28 (3 H, d, J = 8 Hz).

2-[2-(*p*-Toluenesulfonyl)propyl]-1,3-dioxolane (7). Crude aldehyde **6** (0.10 mol) was dissolved in dry benzene (200 mL) plus ethylene glycol (6.2 g, 5.6 mL, 0.10 mol) and *p*-toluenesulfonic acid (100 mg) was added as a catalyst. The mixture was refluxed under nitrogen through a Dean–Stark trap for 5 h, then the solution was cooled and washed with aqueous $NaHCO_3$, and the organic phase was dried and stripped. The oil was crystallized by taking it up in hexane/ethyl acetate, cooling in a dry ice/ethanol bath, and scratching briskly with a glass rod. The resulting white crystals were filtered and dried to yield 22.8 g (84%): mp 31–33 °C; NMR δ 7.74 (2 H, d, J = 8 Hz), 7.32 (2 H, d, J = 8 Hz), 4.96 (1 H, t, J = 5 Hz), 3.85 (4 H, m), 3.3 (1 H, m), 2.45 (3 H, s), 2.2 (1 H, m), 1.8 (1 H, m), 1.32 (3 H, d, J = 8 Hz).

2-[(*p*-Toluenesulfonyl)-2-(carboxyethyl)propyl]-1,3-dioxolane (8). Sulfone acetal **7** (19.8 g, 73 mmol) was dissolved in dry THF (200 mL) under nitrogen, to which triphenylmethane (100 mg) had been added as an indicator. Then, a solution of *n*-butyllithium in hexane (43 mL of 1.7 M solution, 73 mmol) was added dropwise and the mixture was stirred for 15 min at room temperature. The temperature was maintained with a water bath as ethyl chloroformate (11.9 g, 9.6 mL, 110 mol) was added over the period of 5 min. The solution was stirred for 21 h, then water was added and the product was extracted with methylene chloride, which was dried and stripped to yield **8** (25 g, 99%) as an oil: NMR δ 7.72 (2 H, d, J = 8 Hz), 7.34 (2 H, d, J = 8 Hz), 5.00 (1 H, d of d, J = 6, 4 Hz), 4.16 (2 H, q, J = 7 Hz), 3.8 (4 H, m), 2.58 (1 H, d of d, J = 14, 6 Hz), 2.45 (3 H, s), 2.20 (1 H, d of d, J = 14, 4 Hz), 1.67 (3 H, s), 1.21 (3 H, t, J = 7 Hz).

3-(*p*-Toluenesulfonyl)-3-(carboxyethyl)butanal (9). Ester **8** (3.42 g, 10 mmol) was dissolved in dioxane (50 mL) and water (8 mL) and cooled to 0 °C under nitrogen as 60% aqueous perchloric acid (42 mL) was added dropwise over 15 min. The mixture stirred at 0 °C for 2 h, then water (200 mL) was added and the product was extracted with methylene chloride. The organic phase was washed with water, dried, and stripped to yield sulfone aldehyde **9**, which was used immediately in the next step: NMR δ 9.74 (1 H, s), 7.72 (2 H, d, J = 8 Hz), 7.32 (2 H, d, J = 8 Hz), 4.12 (2 H, q, J = 7 Hz), 3.54 (1 H, d, J = 18 Hz), 2.94 (1 H, d, J = 18 Hz), 2.45 (3 H, s), 1.84 (3 H, s), 1.17 (3 H, t, J = 7 Hz).

Ethyl β-Formylmethacrylate (10). Aldehyde **9** (10 mmol) was dissolved in ether (50 mL) and trimethylamine gas was bubbled through while cooling in a water bath. An oil formed and precipitated, and the ether solution was decanted. The precipitate was shown by NMR to be trimethylammonium *p*-toluenesulfinate. The ether solution was washed with brine, and the ether was carefully removed under a nitrogen stream. The crude yellow oil was purified by molecular distillation at 100 °C (0.2 mmHg), yielding pure unsaturated ester **10** of undetermined stereochemistry, but with greater than 90% selectivity (presumably the *E* isomer). The yield was 785 mg (56% from **8**): NMR δ 10.28 (1 H, d, J = 8 Hz), 6.84 (1 H, d of q, J = 8, 1 Hz), 4.30 (2 H, q, J = 7 Hz), 2.34 (3 H, d, J = 1 Hz), 1.34 (3 H, t, J = 7 Hz).

3-Methyl-5-hydroxy-2(5*H*)-furanone (2-Methyl-4-hydroxybut-2-enolide) (1). Unsaturated ester **10** (785 mg, 5.6 mmol) was heated at 100 °C for 2 h under nitrogen in 10% aqueous sulfuric acid (10 mL). The mixture was then cooled to room temperature, saturated with NaCl, and extracted three times with methylene chloride. The organic phase was dried and carefully stripped to yield the crystalline hydroxy lactone. The material could be purified by sublimation at 100 °C (0.25 mmHg), but was best purified by recrystallization from cyclohexane plus a few drops of ether to give a total of 420 mg (72%) from two crystal crops: mp 69–71 °C (lit.[5] 69–71 °C); NMR δ 6.90 (1 H, m), 6.10 (1 H, q, J = 1 Hz), 3.7 (1 H, s br), 1.90 (3 H, d, J = 1 Hz).

Registry No. 1, 931-23-7; **2**, 616-02-4; **3**, 40834-42-2; **4**, 4170-30-3; **5**, 824-79-3; **6**, 71041-35-5; **7**, 70451-38-6; **8**, 71041-36-6; **9**, 71041-37-7; **10**, 71041-38-8; ethyl chloroformate, 541-41-3.

3-Ethylidenecyclohexyl Acetates from Acetic Acid Treatment of 1-(1-Hydroxyethyl)bicyclo[3.1.0]hexanes

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In the course of studies directed toward the partial synthesis of vitamin D analogues, it became of interest to prepare 3-ethylidenecyclohexanols in which the geometry of the exocyclic double bond could be controlled by the choice of an appropriate synthetic method. Surprisingly, the parent system has not yet been reported, and a general, stereoselective synthesis of such a γ,δ-disubstituted homoallylic system apparently has not been studied.

Of the methods available for the preparation of homoallylic alcohols,[1] we chose to investigate the rearrangement of the cyclopropylcarbinyl system generated from 1-(1-hydroxyethyl)bicyclo[3.1.0]hexane (**1**). This system, which

1a R = H **1b**
c R = α-naphthNHCO **d**
e R = 3,5-$(NO_2)_2C_6H_3CO$ **f**
g R = CH_3CO **h**

2a **2b**

is present in the rigid framework of 6α- and 6β-hydroxy-3α,5α-cyclosteroids, has been found to rearrange selectively and in high yield on acid treatment to give the corresponding steroidal 5-en-3β-ol system.[2] Solvolysis of the closely related bicyclo[3.1.0]hex-1-ylmethyl *p*-nitrobenzoate affords >80% yield of 3-methylenecyclohexanol.[3] Recent studies on the solvolysis of 3,5-cyclovitamin D

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