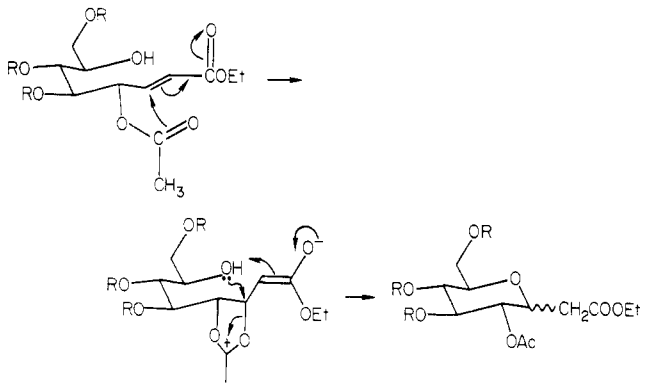
Scheme III



tained more easily, and the Michael-type ring closure can occur by treatment with sodium methoxide. In the case of the tetra-*O*-acetyl derivative **2**, the direct cyclization to the *C*-glucopyranosyl derivative **3** may rely on the "participation" of the acyloxy substituent at C-4 (Scheme III), as happens in the glycosidation reaction. In agreement with this last hypothesis, 2-*O*-benzyl-3,4,6-tri-*O*-acetyl-D-glucopyranose (**9**), which differs from **1** by the presence of a "nonparticipating" benzyl-protecting group at the required position, when submitted to the Wittig reaction with (carbethoxymethylene)triphenylphosphorane, yielded the enoate **10** but no *C*-glucopyranosyl derivative.

It is noteworthy that the acetyl protecting group, which was considered unsuitable for the synthesis of *C*-glycosides via the described procedure, owing to the basic condition employed for the cyclization of the Wittig reaction product, could become the protecting group of choice, if present at C-2 in the starting aldehydo sugar, because of its capability to induce the spontaneous formation of the *C*-glucopyranosides.

Experimental Section

General Methods. Column chromatography was performed using 230–400 mesh Merck silica gel. Thin-layer chromatography (TLC) was done on Merck silica gel HF-254 plates, using hexane–ethyl acetate, 2:1 (a) or 1:1 (b), as eluant. The spots were detected with UV light and/or by spraying with 50% aqueous sulfuric acid and heating at 110 °C. NMR spectra were obtained on a Varian XL-100 spectrometer. IR spectra were obtained on a Perkin-Elmer 681 instrument. Melting points are uncorrected. Usual workup refers to diluting with an organic solvent, washing with water to neutrality, drying over Na_2SO_4, and evaporating under reduced pressure.

Reaction of 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose (7) with (Carbethoxymethylene)triphenylphosphorane. 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose[7] (5.4 g, 10 mmol) in CH_3CN (50 mL) was refluxed with (carbethoxymethylene)triphenylphosphorane (6.7 g, 20 mmol). After 16 h the solvent was removed under reduced pressure, and the residue, submitted to chromatography (hexane–ethyl acetate 2:1), afforded **8** (5.2 g, oil): IR (Nujol) ν_{max} 3450, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7 Hz, CH_3), 3.87 (m, H-7), 4.26 (q, J = 7 Hz, OCH_2CH_3), 3.52, 4.48, 4.66, and 4.76 (OCH_2Ph), 4.1–4.6 (H-5, H-6, H-8, H-8'), 5.53 (d, J = 9 Hz, H-4), 6.20 (d, J = 16 Hz, H-2), 7.20 (d, J = 16 Hz, H-3), 7.3 (Ar H); ^{13}C NMR ($CDCl_3$) 119.71 (=CHCOO), 139.56 (CH=), 166.32 (COO) ppm.

Attempted Cyclization of 8. (a) Compound **8** (100 mg) was treated with sodium ethoxide (0.1 M, 0.5 mL); after 30 min at room temparature, TLC analysis (eluant a) showed the presence of only unreacted **8**; the same result was obtained after 15 min under reflux.

(b) **8** (200 mg) in CH_2Cl_2 (5 mL) was treated with *p*-toluenesulfonic acid (50 mg). After 30 min at room temperature TLC analysis (eluant a) showed the formation of a single product, which was recovered by usual workup (91 mg) and crystallized from hexane (mp 61 °C). Structure **11** was assigned to this product: ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7 Hz, CH_3), 4.25 (q, J = 7 Hz, OCH_2CH_3), 4.49 (s, OCH_2C=), 4.56 (s, OCH_2C=), 6.33 (d, J = 15 Hz, H-3), 6.40 (d, J = 4 Hz, H-5 or H-6), 6.56 (d, J = 4 Hz, H-5 or H-6), 7.41 (d, J = 15 Hz, H-2); mass spectrum, m/e 286, 179, 151, 91. Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.36; H, 6.25.

(c) To a solution of **8** (100 mg) in CH_2Cl_2 (10 mL), a saturated solution of $NaHCO_3$ (5.5 mL) was added. The mixture was stirred at room temperature, and a solution of iodine (81 mg) in CH_2Cl_2 (5 mL) was added dropwise. After 2 h, TLC analysis (eluant a) showed the quantitative formation of the furano derivative **11** as in method b.

Reaction of 2,3,4,6-Tetra-*O*-acetyl-D-glucopyranose (1) with (Carbethoxymethylene)triphenylphosphorane. 2,3,4,6-Tetra-*O*-acetyl-D-glucopyranose[8] (1 g, 2.9 mmol) in CH_3CN (25 mL) was refluxed with (carbethoxymethylene)triphenylphosphorane (2 g, 5.8 mmol). After 20 h, TLC analysis (eluant b) showed the formation of two predominant products. The solvent was then removed under reduced pressure, and the residue was chromatographed (hexane–ethyl acetate, 2:1). To the higher R_f (0.40) predominant product (305 mg, oil) was assigned the structure of the *C*-glucopyranoside **3** (ca. 1:1 mixture of α and β isomers): ^1H NMR ($CDCl_3$) δ 2.47 (0.5-H, d, H-2), 2.6 (0.5-H, m, H-2 of the other isomer), 3.6–5.2 (9-H); ^{13}C NMR ($CDCl_3$) 37.27 and 33.20 (C-2 of the two isomers) ppm.

To the lower R_f (0.25) product (117 mg, oil) was assigned the structure **2**: ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7 Hz, CH_3), 2.0–2.1 (12-H, OAc), 3.65 (m, H-7), 4.1–4.5 (4-H, CH_2O), 5.1–5.5 (H-5 and H-6), 5.98 (dd, $J_{3,4}$ = 5 Hz, $J_{4,5}$ = 7 Hz, H-4), 6.29 (d, J = 5 Hz, H-2), 7.37 (d, J = 5 Hz, H-3).

Reaction of 2-*O*-Benzyl-3,4,6-tri-*O*-acetyl-D-glucopyranose (9) with (Carbethoxymethylene)triphenylphosphorane. 2-*O*-Benzyl-3,4.6-tri-*O*-acetyl-D-glucopyranose[9] (**9**; 120 mg, 0.3 mmol) in CH_3CN (5 mL) was refluxed with (carbethoxymethylene)triphenylphosphorane (209 mg, 0.6 mmol). After 20 h, the solvent was removed under reduced pressure, and the residue was purified by chromatography. The only detectable product was the enoate **10** (35 mg, oil): ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7 Hz, CH_3), 2.00, 2.05, and 2.05 (s, OAc), 3.65 (m, H-7), 4.0–4.2 (H-4, H-8, H-8'), 4.25 (q, J = 7 Hz, OCH_2CH_3), 4.83 (s, OCH_2Ph), 5.47 (d, J = 10 Hz, H-6), 5.83 (dd, $J_{5,6}$ = 10 Hz, $J_{4,5}$ = 5 Hz, H-5), 6.20 (d, J = 16 Hz, H-2), 7.10 (d, J = 16 Hz, H-3).

Registry No. **1**, 40437-08-9; **2**, 83232-14-8; α-**3**, 83232-12-6; β-**3**, 83232-13-7; **7**, 38768-81-9; **8**, 82933-07-1; **9**, 83232-15-9; **10**, 83232-16-0; **11**, 83232-11-5; (carboethoxymethylene)triphenylphosphorane, 1099-45-2.

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Reductive Cyclization Caused by Cobaloxime I. A New Method for the Synthesis of β-Methylene-γ-butyrolactones

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A β-methylene-γ-butyrolactone structural unit is present in some furanoid terpenes.[1] A few methods of synthesizing the unit have been reported. One method involves the reaction of an enol ether with the carbene derived from diazomalonate as a key step,[2] and the second method

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0022-3263/82/1947-5382$01.25/0

Scheme I

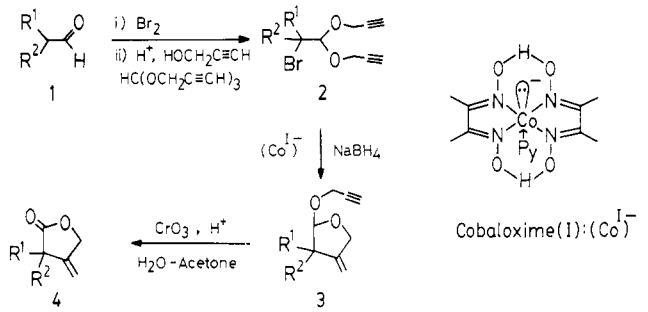

Table I. Isolated Yields[a] of 2-Bromoalkanal Diprop-2-ynyl Acetals (2), 4-Methylene-2-[(2-propynyl)oxy]oxolanes (3), and β-Methylene-γ-butyrolactones (4)

			% yield		
aldehyde 1	R^1	R^2	2	3	4
1a	Me	Pr	88	73	72
1b	Et	Et	92	73	78
1c	Et	Bu	91	75	79
1d	$(CH_2)_5$		92	64	67

[a] Figures in the table are yields of each step.

utilizes the thermally induced cyclization of a β,γ-epoxy ester.[3] The total synthesis of (±)-bakkenolide, a β-methylene-γ-butyrolactone sesquiterpene, uses a third method which involves the stereoselective [2,3] sigmatropic rearrangement of the carbazate derivative.[4] Here an additional method which involves the reductive cyclization of 2-bromoalkanal acetals caused by cobaloxime I is described.

We have reported a method for the synthesis of α-methylene-γ-butyrolactones by the reductive cyclization of 2-[(2-propynyl)oxy]ethyl bromides caused by cobaloxime I followed by the allylic oxidation of the resulting 3-methyleneoxolanes.[5] In a similar manner, the reductive cyclization of 2-bromoalkanal diprop-2-ynyl acetals (**2**) and the oxidation of the resulting 4-methylene-2-[(2-propynyl)oxy]oxolanes (**3**) gives β-methylene-γ-butyrolactones (**4**). This sequential reaction is illustrated in Scheme I.

In the first step aldehyde **1** is brominated followed by acetalization with 2-propynol and tris[(2-propynyl)oxy]-methane to give 2-bromoalkanal diprop-2-ynyl acetal (**2**). Reductive cyclization of **2** effected by 10–15 mol % of cobaloxime I (see Experimental Section) affords the oxolane **3** (see Table I). A cyclization process of this type has been discussed in our earlier paper,[6] and we have proposed an electron-transfer mechanism involving the cyclization of a 2,2-bis[(2-propynyl)oxy]ethyl radical.

In the last step the CrO_3 oxidation of oxolane **3** under acidic conditions gave a β-methylene-γ-butyrolactone (**4**). The lactones were obtained in 39–54% yields from the aldehydes. The chlorocobaloxime III[7] was used as the starting material to prepare the cobaloxime I; the former complex is easily obtained from cobalt chloride, dimethylglyoxime, and pyridine and is very stable to air, water, heat, and light. This synthetic method should be generally applicable to α,α-disubstituted β-methylene-γ-butyrolactones.

Experimental Section

Preparaton of Tris[(2-propynyl)oxy]methane. Triethoxymethane (14.8 g, 100 mmol), 2-propynol (40 mL), dry benzene (300 mL), and conc sulfuric acid (6 drops) were placed in a flask equipped with a rectifying column. The mixture was heated for 6 h to remove ethanol azeotropically (bp ca. 68 °C). The distillation was continued for another 2 h (bp ca. 78 °C). The mixture was treated with anhydrous potassium carbonate (1 g), cooled to room temperature, treated with saturated aqueous $NaHCO_3$ (100 mL), and extracted with ether (2 × 100 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ and dried over anhydrous potassium carbonate. The distillation gave 12.72 g (71%) of tris[(2-propynyl)oxy]methane: bp 103–110 °C (9 mm); IR (CCl_4) 3305, 2130 cm^{-1}; ^1H NMR (CCl_4) δ 2.31 (t, 3 H, J = 2 Hz), 4.27 (d, 6 H, J = 2 Hz), 5.59 (s, 1 H). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.72; H, 5.50.

Typical Procedure for the Preparation of 2-Bromoalkanal Diprop-2-ynyl Acetals (2). A solution of bromine (4.8 g, 30 mmol) in 1.5 mL of dichloromethane (methanol free) was added dropwise to a solution of 2-ethylbutanal (**1b**; 3.0 g, 30 mmol) in 3 mL of anhydrous ether over a period of 45 min under water cooling. After the mixture was stirred for 22 h at room temperature, 20 mL of benzene was added to the reaction mixture, and the mixture was cooled in an ice bath. After addition of anhydrous potassium carbonate (3.0 g) and anhydrous sodium thiosulfate (0.5 g), the mixture was stirred for 45 min at 0 °C and for 2 h at room temperature. The precipitated salts were filtered off and washed with benzene. Toluenesulfonic acid (0.25 g) and 2-propynol (9 mL) were added to the combined benzene solutions. The mixture was heated for 3 h to remove water azeotropically. The mixture was further treated with tris[(2-propynyl)oxy]-methane (1.78 g, 10 mmol) and refluxed for another 3 h. The mixture was cooled to room temperature. After addition of saturated aqueous $NaHCO_3$ (50 mL) the mixture was extracted with ether (3 × 30 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ and dried over anhydrous potassium carbonate. After the removal of the solvent, distillation (in the presence of a small amount of anhydrous potassium carbonate) gave 7.54 g of 2-bromo-2-ethylbutanal diprop-2-ynyl acetal (**2b**): bp 73–78 °C (0.3 mm); IR (CCl_4) 3310, 2130 cm^{-1}; ^1H NMR (CCl_4) δ 1.02 (t, 6 H, J = 8 Hz), 1.92 (q, 4 H, J = 8 Hz), 2.37 (t, 2 H, J = 2 Hz), 4.16–4.57 (m, 4 H), 4.87 (s, 1 H).

All other 2-bromoalkanal acetals were prepared in the same manner.

2a: bp 68–74 °C (0.2 mm); IR (CCl_4) 3310, 2130 cm^{-1}; ^1H NMR (CCl_4) δ 0.96 (t, 3 H, J = 8 Hz), 1.64 (s, 3 H), 1.43–1.92 (m, 4 H), 2.31–2.42 (m, 2 H), 4.32–4.45 (m, 4 H), 4.75 (s, 1 H).

2c: bp 85–90 °C (0.23 mm); IR (CCl_4) 3310, 2132 cm^{-1}; ^1H NMR (CCl_4) δ 0.85–1.05 (m, 3 H), 1.02 (t, 3 H, J = 8 Hz), 1.15–2.02 (m, 8 H), 2.38, (t, 2 H, J = 2 Hz), 4.15–4.56 (m, 4 H), 4.84 (s, 1 H).

2d: bp 92–97 °C (0.29 mm); IR (CCl_4) 3310, 2130 cm^{-1}; ^1H NMR (CCl_4) δ 1.10–2.03 (m, 10 H), 2.35 (t, 2 H, J = 2 Hz), 4.33–4.44 (m, 4 H), 4.71 (s, 1 H).

All of the bromides gradually turn yellow and are relatively unstable (satisfactory elemental analyses were not obtained). After distillation, therefore, they were converted directly to the oxolanes without further purification.

Typical Procedure for the Preparation of 4-Methylene-2-[(2-propynyl)oxy]oxolanes (3). Sodium borohydride (1.9 g, 50 mmol) was added to 370 mL of ethanol containing 10 N aqueous NaOH (5 mL) and pyridine (25 mL). Chlorocobaloxime III[7] (2.0 g, 5 mmol) was added to this mixture under nitrogen. To the resulting black solution of cobaloxime I was added a solution of bromide **2b** (13.7 g, 50 mmol) in 50 mL of ether over a period of 2 h under water cooling, and the reaction mixture was stirred for an additional hour. After removal of the ethanol under reduced pressure, 150 mL of water was added, and the mixture was extracted with ether-hexane (1:4, 5 × 50 mL). The combined extracts were washed with water and dried over anhydrous sodium sulfate. After the removal of the solvent, distillation gave 7.05 g of 3,3-diethyl-4-methylene-2-[(2-propynyl)oxy]oxolane (**3b**): bp

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91–98 °C (17 mm); IR (CCl_4) 3313, 2130, 1672, 891 cm^{-1}; ^1H NMR (CCl_4) δ 0.79 (t, 3 H, J = 8 Hz), 0.86 (t, 3 H, J = 8 Hz), 1.15–1.64 (m, 4 H), 2.20 (t, 1 H, J = 2 Hz), 4.09–4.20 (m, 2 H), 4.30–4.39 (m, 2 H), 4.68 (t, 1 H, J = 2 Hz), 4.80–4.91 (m, 2 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.85; H, 9.28.

All other oxolanes **3** were prepared in the same manner.

3a: bp 52–57 °C (1.4 mm); IR (CCl_4) 3311, 2130, 1672, 888 cm^{-1}; ^1H NMR (CCl_4) δ 0.83–0.98 (m, 3 H), 1.04 (s, 3 H), 1.10–1.45 (m, 4 H), 2.22 (t, 1 H, J = 2 Hz), 4.02–4.18 (m, 2 H), 4.26–4.39 (m, 2 H), 4.69–4.83 (m, 3 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.23; H, 9.14.

3c: bp 58–64 °C (0.25 mm); IR (CCl_4) 3312, 2133, 1671, 891 cm^{-1}; ^1H NMR (CCl_4) δ 0.70–1.70 (m, 14 H), 2.23 (t, 1 H, J = 2 Hz), 4.06–4.18 (m, 2 H), 4.28–4.37 (m, 2 H), 4.68 (t, 1 H, J = 2 Hz), 4.80 (s, 1 H), 4.85 (t, 1 H, J = 2 Hz). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.35; H, 9.88.

3d: bp 69–72 °C (0.4 mm); IR (CCl_4) 3315, 2130, 1665, 884 cm^{-1}; ^1H NMR (CCl_4) δ 1.05–1.90 (m, 10 H), 2.24 (t, 1 H, J = 2 Hz), 4.07–4.18 (m, 2 H), 4.26–4.36 (m, 2 H), 4.70–4.81 (m, 2 H), 5.11 (s, 1 H). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.75; H, 8.70.

Typical Procedure for the Preparation of β-Methylene-γ-butyrolactones (4). To a solution of oxolane **6b** (1.94 g, 10 mmol) in 30 mL of acetone was added dropwise a solution of chromium trioxide (7.0 g, 70 mmol) in 40 mL of 10% aqueous H_2SO_4 over a period of 1 h under ice–water cooling. After the mixture was stirred for 2 h at 0 °C and overnight at room temperature, 100 mL of water was added, and the product was extracted with ether (4 × 20 mL). The combined ethereal extracts were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and dried over anhydrous sodium sulfate. After the removal of the solvent, the distillation gave 1.21 g of α,α-diethyl-β-methylene-γ-butyrolactone (**4b**); bp 105–109 °C (20 mm); IR (CCl_4) 1787, 1678, 900 cm^{-1}; ^1H NMR (CCl_4) δ 0.82 (t, 6 H, J = 8 Hz), 1.35–1.92 (m, 4 H), 4.65 (t, 2 H, J = 2 Hz), 4.94 (t, 1 H, J = 2 Hz), 5.19 (t, 1 H, J = 2 Hz). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.24; H, 9.45.

All other lactones **4** were obtained in the same manner.

4a: bp 97–103 °C (20 mm); IR (CCl_4) 1783, 1680, 900 cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (t, 3 H, J = 7 Hz), 1.25 (s, 3 H), 1.10–1.78 (m, 4 H), 4.71 (t, 2 H, J = 2 Hz), 4.99 (t, 1 H, J = 2 Hz), 5.10 (t, 1 H, J = 2 Hz). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.77; H, 9.13.

4c: bp 65–69 °C (0.37 mm); IR (CCl_4) 1781, 1673, 899 cm^{-1}; ^1H NMR (CCl_4) δ 0.82 (t, 3 H, J = 8 Hz), 0.90 (t, 3 H, J = 6 Hz), 1.00–1.95 (m, 8 H), 4.63 (t, 2 H, J = 2 Hz), 4.94 (t, 1 H, J = 2 Hz), 5.16 (t, 1 H, J = 2 Hz). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.29; H, 9.76.

4d:[2] bp 62–64 °C (0.32 mm); mp 42–43 °C; IR (CCl_4) 1785, 1672, 898 cm^{-1}; ^1H NMR (CCl_4) δ 1.20–2.10 (m, 10 H), 4.67 (t, 2 H, J = 2 Hz), 5.02 (t, 1 H, J = 2 Hz), 5.08 (t, 1 H, J = 2 Hz).

Registry No. **1a**, 123-15-9; **1b**, 97-96-1; **1c**, 123-05-7; **1d**, 2043-61-0; **2a**, 83561-19-7; **2b**, 83561-20-0; **2c**, 83561-21-1; **2d**, 83561-22-2; **3a**, 83561-23-3; **3b**, 83561-24-4; **3c**, 83561-25-5; **3d**, 83561-26-6; **4a**, 83561-27-7; **4b**, 83561-28-8; **4c**, 83561-29-9; **4d**, 63965-86-6; cobaloxime (I), 53790-02-6; triethoxymethane, 122-51-0; $HC(OCH_2C{\equiv}CH)_3$, 83561-30-2; $HOCH_2C{\equiv}CH$, 107-19-7.

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Facile Synthesis of the Enantiomers of *exo*-Brevicomin

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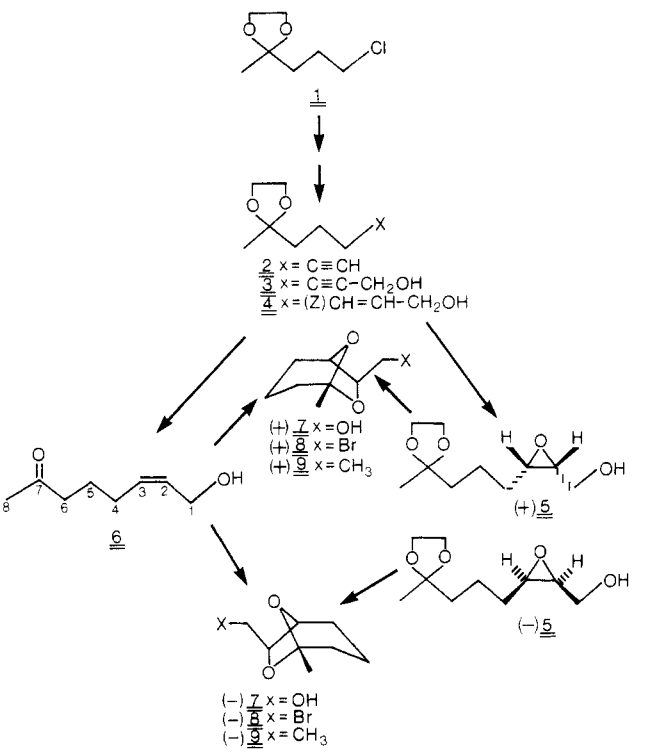
exo-Brevicomin (**9**) is produced by three species of *Dendroctonus* beetles as part of their pheromone complex.[1-3] Two of the species, *D. brevicomis* (western pine beetle) and *D. ponderosae* (mountain pine beetle), are of major economic importance in western North Amercia. Racemic *exo*-brevicomin is attractive in the field to *D. brevicomis* although it is known that the (1*R*,7*R*)-(+) isomer is naturally produced by these beetles. The effects of racemic *exo*-brevicomin on *D. ponderosae* vary from antiaggregation to attraction, apparently depending on the release rate of the pheromone, as well as on the host and location of the population being tested.[3] This variation raises the possibility that different populations of *D. ponderosae* discriminate between different chiral isomers of *exo*-brevicomin. In order to examine the field response of *D. ponderosae* to the enantiomers of *exo*-brevicomin and to determine the chirality of *exo*-brevicomin in *D. ponderosae*, we required efficient syntheses of both chiral forms of this bicyclic ketal.

Scheme I



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