are uncorrected. ^{1}H NMR spectra were recorded at 60 or 90 MHz. Chemical shifts are reported in parts per million (δ) relative to Me_4Si as an internal standard, with conventional nomenclature for splitting and coupling constants. Analytical gas chromatography (GLC) separations were performed on a Varian 2800 gas chromatograph. High-performance liquid chromatography (HPLC) separations were performed on a Waters Prep LC/System 500-A, with PrepPAK-500 silica cartridges (5.7 × 30 cm).

2,6,6-Trimethyl-2-hydroxy-4,4-(ethylenedioxy)cyclohexanone (10). To a well-stirred mixture of compound 8[8] (910 mg, 5.0 mmol), water (500 mL), and magnesium sulfate (2.4 g), previously cooled to 4 °C, was added dropwise a solution of potassium permanganate (1.02 g, 6.6 mmol) in water (240 mL), maintaining the temperature of the reaction mixture below 6 °C. After the mixture was stirred for an additional 30 min, enough sodium sulfite was added to decolorize the solution, and the reaction mixture was filtered through Celite. The clear solution was extracted with ethyl ether in a liquid–liquid extractor. The resultant ethereal solution was dried (K_2CO_3) and evaporated to yield 870 mg (72.5%) of **10** as an oil after purification by Kugelrohr distillation: bp 80 °C (0.5 mm); IR (film) 3480, 1710, 1085 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.96 (m, 4 H), 2.18 (m, 2 H), 1.98 (m, 2 H), 1.42 (s, 3 H), 1.23 and 1.20 (2 s, 6 H); ^{13}C NMR ($CDCl_3$) δ 216.4 (s), 106.7 (s), 74.4 (s), 64.3 (t), 63.8 (t), 46.6 (t), 46.4 (t), 42.6 (s), 28.0 (q), 27.3 (q), 27.2 (q). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.58; H, 8.88.

2,6,6-Trimethyl-4,4-(ethylenedioxy)cyclohex-2-en-1-one (2). A solution of compound **10** (15.2 g, 71 mmol) in pyridine (100 mL) was added slowly to a solution of methanesulfonyl chloride (9.75 g, 85 mmol) in pyridine (180 mL) cooled to 4 °C. After being stirred overnight at room temperature, the reaction mixture was heated under reflux for 4 h. After cooling slightly the dark solution was treated with water (120 mL) and allowed to cool to room temperature with stirring. Water was added, and the reaction mixture was extracted with ethyl ether. The organic layer was washed with water, a 20% copper sulfate solution, water, and saturated brine and dried ($MgSO_4$). Evaporation of the solvent and subsequent purification by Kugelrohr distillation yielded 8.8 g (63%) of **2**: bp 65 °C (0.025 mm) [lit.[6] bp 76–80 °C (0.5 mm)]; ^{13}C NMR ($CDCl_3$) δ 203.3 (s), 139.3 (d), 134.8 (s), 103.3 (s), 64.1 (t), 45.7 (t), 41.4 (s), 25.9 (q), 15.6 (q).

Methyl (*Z*)-3-Methyl-2-penten-4-ynoate (3). To a mixture containing methanol (650 mL), activated manganese dioxide[11] (62 g), sodium cyanide (9 g), and glacial acetic acid (3.2 g) was added a solution of the aldehyde **5**[3] (5.1 g, 54 mmol) in methanol (100 mL). The reaction mixture was stirred overnight at room temperature and then filtered at reduced pressure. The solid cake was washed with a 1:1 mixture of methanol and water. The filtrate was diluted with water and extracted with ethyl ether in a continuous liquid–liquid extractor for 12 h. The ethereal solution thus obtained was washed with saturated brine, dried ($MgSO_4$), and evaporated. The residue was distilled under reduced pressure to yield 5.4 g (80%) of **3**: bp 92–93 °C (30 mm); IR (film) 3270, 2950, 2080, 1730, 1630, 1215, 1145, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.07 (m, 1 H), 3.77 (s, 3 H), 3.63 (s, 1 H), 2.08 (d, 3 H, J = 2 Hz); ^{13}C NMR ($CDCl_3$) δ 165.0 (s), 134.0 (s), 126.0 (d), 88.7 (d), 82.0 (s), 51.2 (q), 25.1 (q).

Methyl (*Z*)-3-Methyl-5-[1-hydroxy-2,6,6-trimethyl-4,4-(ethylenedioxy)-2-cyclohexenyl]-2-penten-4-ynoate (11). A solution of the ester **3** (3.7 g, 30 mmol) in tetrahydrofuran (50 mL) was added to a solution of lithium diisopropylamide (30 mmol) in tetrahydrofuran (500 mL) at −78 °C and stirred for 10 min. A solution of compound **2** (5.5 g, 28 mmol) in tetrahydrofuran (100 mL) was added. The temperature of the reaction mixture was allowed to rise slowly to −30 °C (about 45 min) and then maintained for another 45 min. The reaction mixture was quenched by addition of a saturated aqueous solution of ammonium chloride and the product was extracted with ethyl ether. The ethereal layer was washed with water and saturated brine, dried ($MgSO_4$), and evaporated to afford 9.5 g (100%) of crude **11**. Compound **11** was used in the next step without further purification. An analytical sample was prepared by purification through preparative HPLC using as an eluent a mixture of *n*-hexane and ethyl acetate (6:4): IR (film) 3400, 2200, 1710, 1615, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.95 (m, 1 H), 5.35 (br s, 1 H), 3.90 (s, 4 H), 3.75 (s, 3 H), 2.00 (d, 3 H, J = 1 Hz), 1.95 (d, 3 H, J = 1 Hz), 1.15 (s, 3 H), 1.10 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.0 (s), 140.1 (s), 134.4 (s), 125.6 (d), 123.1 (d), 104.6 (s), 101.4 (s), 85.3 (d), 74.5 (s), 63.9 (t), 63.7 (t), 51.0 (q), 43.3 (t), 39.0 (s), 25.2 (q), 24.7 (q), 22.3 (q), 18.6 (q).

Methyl (2*Z*,4*E*)-3-Methyl-5-(1-hydroxy-2,6,6-trimethyl-4-oxo-2-cyclohexenyl)-2,4-pentadienoate (12). To a solution of **11** (1.0 g, ≃3.1 mmol) in a 2:1 mixture of dimethylformamide and water (375 mL), maintained under an oxygen-free nitrogen atmosphere, was added dropwise an aqueous solution of chromium (II) sulfate[10] until the blue color was no longer discharged. The reaction mixture was stirred at room temperature for 24 h. Water and solid ammonium sulfate were then added, and after being stirred for 30 min, the reaction mixture was extracted with ethyl ether. The organic layer was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by preparative HPLC, eluting with *n*-hexane/ethyl acetate (4:6) and then with *n*-hexane/ethyl acetate (9:1) to yield 301 mg (35%) of **12**: IR (CCl_4) 3620, 2960, 1715, 1670, 1630, 1600 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.81 (d, 1 H, J = 16 Hz), 6.15 (d, 1 H, J = 16 Hz), 5.83 (br s, 1 H), 5.67 (br s, 1 H), 3.68 (s, 3 H), 2.35 (d, 1 H, J = 17 Hz), 2.20 (d, 1 H, J = 17 Hz), 2.01 (d, 3 H, J = 1 Hz), 1.90 (d, 3 H, J = 1 Hz), 1.10 (s, 3 H), 1.00 (s, 3 H); mass spectrum, m/e (relative intensity) 278 (M^+, 1), 245 (2), 190 (100), 134 (50), 91 (40), 41 (20).

(±)-Abscisic Acid (1). Compound **12** (301 mg, 1.1 mmol) was treated with a solution of sodium hydroxide (12.0 g) in a 2:1 mixture of methanol and water (30 mL). The reaction mixture was stirred at room temperature for 1 h and then diluted with water and acidified with 0.1 N sulfuric acid. The product was extracted with ethyl ether, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was recrystallized from ethyl acetate and petroleum ether to afford 232 mg (80%) of **1** as a white crystalline solid: mp 183–184 °C (lit.[2a] mp 188–190 °C); IR (KBr) 3400, 3200–2300, 1680, 1645, 1625, 1600, 985 cm^{-1}; ^{1}H NMR ($CDCl_3/CD_3OD$) δ 7.73 (d, 1 H, J = 16 Hz), 6.11 (d, 1 H, J = 16 Hz), 5.91 (br s, 1 H), 5.74 (br s, 1 H), 2.41 (d, 1 H, J = 17 Hz), 2.25 (d, 1 H, J = 17 Hz), 1.99 (d, 3 H, J = 1.5 Hz), 1.89 (d, 3 H, J = 1.5 Hz), 1.07 (s, 3 H), 1.00 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 199.3 (s), 167.9 (s), 164.6 (s), 149.3 (s), 136.0 (d), 127.7 (d), 126.0 (d), 118.1 (d), 78.9 (s), 49.2 (t), 41.2 (s), 23.6 (q), 22.5 (q), 20.6 (q), 18.6 (q); mass spectrum, m/e (relative intensity) 264 (M^+, 2), 246 (5), 190 (83), 162 (60), 134 (74), 91 (100).

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Registry No. (±)-1, 14375-45-2; **2**, 14203-64-6; **3**, 99708-52-8; **4**, 6153-05-5; **5**, 52421-93-9; **6**, 78-59-1; **8**, 65339-06-2; **9**, 65339-07-3; (±)-**10**, 99708-51-7; (±)-**11**, 99708-53-9; (±)-**12**, 6901-96-8.

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Synthesis of (3*R*,4*R*)-3-(Benzyloxy)-4-(formyloxy)-1-nitro-1-cyclopentene, a Chiral Synthon for Prostaglandin Syntheses, from D-Glucose

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The conjugate addition of organometallic reagents to activated cyclopentenes has proven to be a potential strategy in the total synthesis of biologically active cyclopentanoid natural products, notably in the prostaglan-

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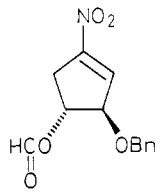
din series.[1] In spite of extensive use of 4-hydroxy-2-cyclopenten-1-one and its derivatives as Michael acceptors, little attention has been paid to the preparation and utilization of functionalized 1-nitro-1-cyclopentenes.[2,3] We report here the synthesis of a chiral prostaglandin synthon, nitrocyclopentene **1**, from an inexpensive carbohydrate, D-glucose.[4]



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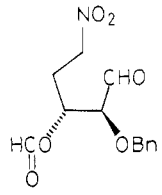
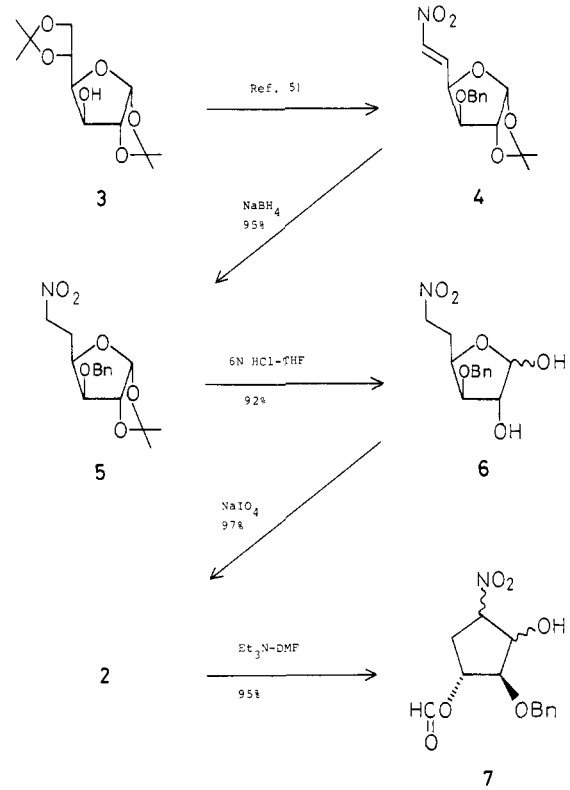


2

Synthesis of **1** utilizes the C(3) and C(4) carbons of glucose diacetonide **3** as a chiral source for the requisite C(3) and C(4) positions of the target. The cyclopentene ring is formed by intramolecular aldolization–dehydration of the acyclic 5-nitroaldehyde **2** which results from oxidative cleavage at the C(1)–C(2) bond of the 6-nitrofuranoside **6**.

The known nitroalkene **4** was prepared, with some improvement, in five steps (75% overall yield), starting with diacetone glucose (**3**).[5] Since catalytic hydrogenation of conjugated nitroalkenes is reported to be a complex reaction,[6] we investigated the reduction of α,β-unsaturated



nitroolefin **4**, utilizing sodium borohydride.[7] Thus, the reduction of **4** took place smoothly on treatment with sodium borohydride in methanol to give **5** in 95% yield. Deprotection of **5** to the hemiacetal **6** was carried out by stirring in a mixed solution of 6 M hydrochloric acid and tetrahydrofuran (92% yield). Oxidation of **6** with sodium metaperiodate[8] in methanol resulted in cleavage of the carbon–carbon bond at C(1)–C(2) to give the desired aldehyde **2** in 97% yield.

Treatment of **2** with a catalytic amount of triethylamine in dimethylformamide at room temperature gave the desired nitrocyclopentanol **7** in 95% yield. Alkaline bases such as sodium methoxide and sodium carbonate[9] were unsatisfactory due to their strong basicity and uncompatibility with the functional groups of **7**. The dehydration of **7** to **1** was first attempted by using acetic anhydride in pyridine, giving the desired **1** in poor yields (10–15%). However, the yield of **1** was improved to 86–92% by using either methanesulfonyl chloride in ether at 0–40 °C or 1,3-dicyclohexylcarbodiimide (DCC)[10] and a catalytic amount of $CuCl_2 \cdot 2H_2O$ in ether.

Experimental Section

Boiling points are indicated by an air-bath temperature without correction. IR spectra were obtained with a JASCO IRA-1 grating spectrometer. ^1H NMR spectra were recorded on either a Hitachi R-24 (60-MHz), a JEOL FX-100 (100-MHz), or a JEOL GX-400 (400-MHz)[11] spectrometer. ^{13}C NMR spectra were obtained with a JEOL FX-100 (25.05-MHz) spectrometer. Samples were dissolved in $CDCl_3$, and the chemical shifts are expressed in δ values (ppm) relative to Me_4Si as an internal standard. Optical rotations were taken on a JASCO DIP-140 digital polarimeter in $CHCl_3$.

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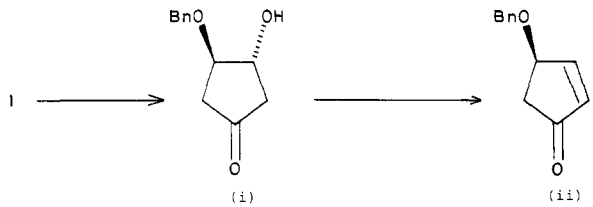
(2) Use of the nitro group assembled into a cyclopropane ring as a latent carbonyl function in prostaglandin syntheses: Corey, E. J.; Vlattas, I.; Harding, K. *J. Am. Chem. Soc.* **1969**, *91*, 535. The nitrocyclopentene **1** thus obtained is convertible into (4*R*)-4-(benzyloxy)-2-cyclopentenone (ii) via i. Experimental details are as follows: Preparation of i: A lead foil (3 cm^2) was polished with sandpaper and activated by washing with concentrated HNO_3. This plate was immersed into a two-phase solution of CH_2Cl_2 (0.5 mL)–20% $HClO_4$ (2.5 mL)–dioxane(0.2 mL)[12] and to this mixture was added the nitrocyclopentene **1** (44 mg, 0.168 mmol). After being stirred at room temperature for 1 h, the mixture was treated with 37% HCHO (1 mL) and stirred for an additional 2 h. Extractive workup followed by column chromatography (SiO_2, hexane/AcOEt, 3:1) gave hydroxy ketone **i** as an oil: IR (neat) 3400 (OH), 3040, 3015, 1741 (C=O), 1627, 1495, 1453, 1386, 1155, 1072, 1027, 735, 695 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.75 (br, 1, OH), 2.10–2.84 (m, 4, CH_2CO), 4.08 (m, 1, CHO), 4.50 (m, 1, CHOBn), 4.58 (s, 2, CH_2Ph), 7.29 (s, 5, PhH). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.76; H, 6.96. Preparation of ii: To a cooled (0 °C) solution of **i** (10 mg, 0.048 mmol) and Et_3N (0.027 mL, 0.19 mmol) was added dropwise $MeSO_2Cl$ (0.0075 mL, 0.097 mmol). After being stirred at 0 °C for 30 min and at room temperature for 1 h, the mixture was poured into cold 5% HCl and extracted with toluene/AcOEt (1:1). Usual workup followed by column chromatography (SiO_2, hexane/AcOEt, 5:1) gave **ii** (8 mg, 89%) as an oil: $[\alpha]^{16}_D$ + 42° (*c* 0.9 in $CHCl_3$); IR (neat) 3040, 3010, 1712 (C=O), 1652 (C=C), 1492, 1447, 1346, 1179, 1105, 1066, 787, 731, 692 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 2.38 (d,d, J = 18.3, 2.0 Hz, 1, CHC=O), 2.74 (d,d, J = 18.3, 5.8 Hz, 1, CHC=O), 4.67 (s, 2, CH_2Ph), 4.82 (m, 1, CHOBn), 6.33 (d,d, J = 5.8, 1.5 Hz, 1, C=CHCO), 7.44 (s, 5, PhH), 7.69 (d, d, J = 5.8, 2.3 Hz, 1, CH=CC=O).



(i) (ii)

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Elemental analyses were performed in our laboratory.

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose (4). Dehydration of the nitro alcohol was improved as follows. To a cooled (0 °C) solution of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-L-idofuranose (4.0 g, 11.8 mmol) and Et_3N (4.93 mL, 35.4 mmol) in ether (30 mL) was added dropwise $MeSO_2Cl$ (1.46 mL, 18.9 mmol). After being stirred at 0 °C for 30 min and at room temperature for 5 h, the mixture was poured into cold 5% HCl and extracted with AcOEt. The extracts were washed with brine and dried (Na_2SO_4). Evaporation of the solvents followed by column chromatography (SiO_2, hexane/AcOEt, 3:1) of the residue afforded the nitroolefin 4 (3.71 g, 98%) as an oil: bp 135–140 °C (0.04 mm); $[\alpha]^{23}_D$ −30.46° (*c* 1.50) (lit.[5] −29.1°); IR (neat) 3090, 3040, 3021, 1655 (C=C), 1527 (NO_2), 1449, 1350 (NO_2), 1327, 1157, 1075, 1025, 785, 760, 692 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.31, 1.47 (s, 6, CH_3), 3.99 (d, *J* = 3.6 Hz, 1, CHO), 4.40–4.90 (m, 5, CH_2Ph, C=$CHNO_2$, CHO), 5.93 (d, *J* = 3.6 Hz, 1, CHO), 7.10–7.35 (m, 6, PhH, CH=CNO_2); ^{13}C NMR ($CDCl_3$) δ 26.1 (q), 26.8 (q), 72.2 (t), 77.0 (d), 82.4 (d, 2C), 105.1 (d), 112.3 (s), 127.8 (d), 128.3 (d), 128.6 (d), 136.0 (d), 136.7 (s), 140.9 (d).

3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hexanofuranose (5). To a cooled (0 °C) solution of nitroolefin 4 (3.5 g, 10.9 mmol) in MeOH (30 mL) was added dropwise a solution of $NaBH_4$ (0.62 g, 16.4 mmol) in H_2O (6 mL) over a period of 30 min. The mixture was stirred at room temperature for 5 h and then treated with cold 5% HCl. The products were taken up in benzene/AcOEt (1:1), and extracts were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 3:1) to give **5** (3.35 g, 95%) as an oil: bp 130–135 °C (0.02 mm); $[\alpha]^{22}_D$ −44.28° (*c* 1.57); IR (neat) 3042, 3017, 1554 (NO_2), 1490, 1448, 1426, 1372 (NO_2), 1347, 1252, 1210, 1160, 1072, 1071, 885, 852, 785, 757, 732, 692 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.32, 1.48 (s, 6, CH_3), 2.36 (m, 2, CH_2), 3.86 (d, *J* = 4 Hz, 1, CHO), 4.18–4.80 (m, 6, CH_2Ph, CH_2NO_2, CHO), 5.94 (d, *J* = 4 Hz, 1, OCHO), 7.40 (s, 5, PhH); ^{13}C NMR ($CDCl_3$) δ 26.1, 26.3, 71.7, 72.4, 76.6, 82.0, 82.1, 104.7, 111.7, 127.8, 128.1, 128.6, 137.1. Anal. Calcd for $C_{16}H_{21}NO_6$: C, 59.43; H, 6.55. Found: C, 59.34; H, 6.63.

3-*O*-Benzyl-5,6-dideoxy-6-*C*-nitro-α-D-*xylo*-hexanofuranose (6). A solution of **5** (668 mg, 2.07 mmol) in THF (1 mL) and 6 M HCl (4 mL) was stirred at room temperature for 10 h. The mixture was extracted with AcOEt, and the extracts were washed with brine and dried (Na_2SO_4). Evaporation of the solvents followed by column chromatography (SiO_2, hexane/AcOEt, 1:1) gave **6** (539 mg, 92%) as an oil: $[\alpha]^{16}_D$ +11.23° (*c* 4.12); IR (neat) 3380 (OH), 3068, 3035, 1555 (NO_2), 1500, 1455, 1432, 1380 (NO_2), 1350, 1209, 1116, 1062, 739, 700 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.24 (m, 2, CH_2), 3.49–4.67 (m, 8, CH_2Ph, CHO, OH), 4.93 (d, *J* = 16.1 Hz, 1, CHO), 5.34 (d, *J* = 3.8 Hz, 1, OCHO), 7.27 (s, 5, PhH). Anal. Calcd for $C_{13}H_{17}NO_6$: C, 55.12; H, 6.05. Found: C, 55.05; H, 6.16.

(2*S*,3*R*)-2-(Benzyloxy)-3-(formyloxy)-5-nitropentanal (2). To a cooled (0 °C) solution of diol **6** (500 mg, 1.77 mmol) in MeOH (1 mL) was added a solution of $NaIO_4$ (492 mg, 2.30 mmol) in H_2O (6 mL). The mixture was stirred at room temperature for 5 h and then partitioned with saturated $NaHCO_3$ and toluene/AcOEt (1:1). The organic layer was washed with brine, dried (Na_2SO_4), and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt, 1:1) to afford **2** (482 mg, 97% as an oil: bp 140–145 °C (0.02 mm); $[\alpha]^{17}_D$ −24.91° (*c* 5.00); IR (neat) 3041, 3020, 2710 (CHO), 1725 (CHO), 1555 (NO_2), 1495, 1452, 1431, 1376 (NO_2), 1156, 1068, 916, 878, 751, 699 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 2.38 (m, 2, CH_2), 3.92 (d, *J* = 3.6 Hz, 1, CHO), 4.35 (t, *J* = 6.4 Hz, 2, CH_2NO_2), 4.67 (AB_q, *J* = 11 Hz, 2, CH_2Ph), 5.38 (m, 1, CHOCO), 7.33 (s, 5, PhH), 7.97 (s, 1, OCHO), 9.61 (s, 1, CHO); ^{13}C NMR ($CDCl_3$) δ 28.0 (t), 68.9 (d), 71.7 (t), 73.5 (t), 82.7 (d), 128.4 (d), 128.6 (d), 128.7 (d), 136.2 (s), 160.1 (d), 200.0 (d). Anal. Calcd for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38. Found: C, 55.63; H, 5.46.

(1*R*,2*R*)-2-(Benzyloxy)-3-hydroxy-4-nitrocyclopentan-1-ol Formate (7). To a cooled (0 °C) solution of nitro aldehyde **2** (290 mg, 1.03 mmol) in DMF (3 mL) Et_3N was added dropwise (0.03 mL, 0.21 mmol). The mixture was stirred at room temperature for 5 h, and the reaction was quenched with cold 5% HCl. The mixture was extracted with AcOEt, and the extracts were washed with brine, dried (Na_2SO_4), and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/AcOEt, 2:1) to give **7** (276 mg, 95%) as an oil: $[\alpha]^{18}_D$ −5.62° (*c* 2.75); IR (neat) 3400 (OH), 3045, 3020, 1722 (CHO), 1555 (NO_2), 1498, 1454, 1372 (NO_2), 1170, 1121, 782, 760, 697 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$), δ 2.00–3.50 (m, 4, CH_2, $CHNO_2$, OH), 3.70–4.25 (m, 1, CHO), 4.30–4.90 (m, 1, CHO), 4.67 (s, 2, CH_2Ph), 5.18 (m, 1, CHOCO), 7.32 (s, 5, PhH), 7.97 (br s, 1, OCHO). Anal. Calcd for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38. Found: C, 55.40; H, 5.29.

(3*R*,4*R*)-3-(Benzyloxy)-4-(formyloxy)-1-nitro-1-cyclopentene (1). To a cooled (0 °C) solution of nitro alcohol **7** (120 mg, 0.43 mmol) and Et_3N (0.24 mL, 1.72 mmol) in ether (8 mL) was added dropwise $MeSO_2Cl$ (0.053 mL, 0.69 mmol). The mixture was stirred at 0 °C for 30 min and at reflux for 5 h, and then the reaction was quenched with cold 5% HCl. The mixture was extracted with AcOEt, and the extracts were washed with brine and dried (Na_2SO_4). Evaporation of the solvent followed by column chromatography (SiO_2, hexane/AcOEt, 3:1) gave the cyclopentene **1** (103 mg, 92%) as an oil: $[\alpha]^{20}_D$ −118.79° (*c* 1.45); IR (neat) 3038, 3018, 1720 (C=O), 1643 (C=C), 1523 (NO_2), 1451, 1360 (NO_2), 1164, 1095, 1064, 739, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (d, *J* = 17.6 Hz, 1, $CHCNO_2$), 3.52 (dd, *J* = 17.6, 7.3 Hz, 1, $CHCNO_2$), 4.69 (AB_q, *J* = 17.6 Hz, Δ_{AB} = 27.6 Hz, 2, CH_2Ph), 4.71 (m, 1, CHOBn), 5.43 (dt, *J* = 7.3, 3.3 Hz, 1, CHOC=O), 6.85 (d, *J* = 1.8 Hz, 1, CH=CNO_2), 7.35 (m, 5, PhH), 8.05 (s, 1, CHO); ^{13}C NMR ($CDCl_3$) δ 35.3 (t), 72.4 (t), 76.5 (d), 85.1 (d), 128.0 (d), 128.3 (d), 128.7 (d), 132.3 (d), 136.9 (s), 151.9 (s), 159.9 (d). Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98. Found: C, 59.18; H, 4.81.

Dehydration of 7 with 1,3-Dicyclohexylcarbodiimide (DCC). A solution of **7** (150 mg, 0.535 mmol), DCC (221 mg, 1.07 mmol), and $CuCl_2 \cdot 2H_2O$ (5.0 mg, 0.03 mmol) in ether (5 mL) was heated at reflux for 24 h. Evaporation of the solvent followed by column chromatography (SiO_2, hexane/AcOEt, 5:1) of the residue afforded **1** (120 mg, 86%) as an oil.

Stereospecific Synthesis of the Important Retinoid Synthon Ethyl *trans*-3-Formyl-2-butenoate via Direct Two-Stage Oxidation of Ethyl 3-Methyl-2-butenoate

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all-trans-Retinoic acid is a metabolite of vitamin A (retinol) capable of supporting the functions of vitamin A in the maintenance of normal growth and epithelial cell differentiation.[1] Retinoic acid and some of its analogues (retinoids) have recently generated much interest as agents useful for the treatment of skin disorders[2] and as potential cancer chemopreventive or chemotherapeutic compounds.[3,4] At present, it remains unclear whether retinoic acid or further metabolites of retinoic acid represent biologically active forms of the vitamin.

Recently we have been engaged in programs directed toward the preparation of retinoic acid metabolites and their analogs.[5,6] Our present interests require the synthesis of quantities of the ethyl ester of *trans*-3-formyl-2-bute-

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