num chloride had dissolved, (−)-β-pinene (13.6 g, 0.10 mol) was added. The solution was stirred for 48 hr at 25°, 25 ml of saturated sodium bicarbonate solution was added, and the solution was filtered by suction from the precipitated alumina. The organic layer was removed and the aqueous layer was extracted with 3 × 30 ml of ether. The combined organic extracts were dried over sodium sulfate and evaporated, giving 17 g of colorless liquid. Fractional distillation gave 15.38 g (70%) of **1**, bp 90° (0.5 mm). A gc retention time of 4.82 min (6 ft, 5% SE-30, 151°) showed the product to be greater than 98% pure: nmr ($CDCl_3$) δ 5.19 (1 H, br, CH=), 3.76 (3 H, s, OCH_3), 1.5–2.5 (12 H, m), 1.27 (3 H, s, CH_3), and 0.83 (3 H, s, CH_3); ir (neat) 2920, 1740, 1430, 1360, 1200, and 1160 cm^{-1}.

Anal. Calcd for $C_{14}H_{22}O_2$: mol wt, 222.1620. Found: mol wt, 222.1616.

Reaction of Methylenecyclohexane with Methyl Acrylate. To a solution of methyl acrylate (1.3 g, 15 mmol) in 5 ml of benzene were added aluminum chloride (0.14 g, 1 mmol) and methylenecyclohexane (1.25 g, 13 mmol). The solution was stirred for 48 hr at 25° and worked up as described above, giving 1.66 g (70%) of **5**. A gc retention time of 3.15 min (6 ft, 5% SE-30, 143°) indicated that the material was *ca.* 97% pure: nmr ($CDCl_3$) δ 5.4 (1 H, m, CH=), 3.67 (3 H, s, OCH_3), 2.26 (2 H, t, J = 6.5 Hz, CH_2CO_2), and 1.3–2.1 (12 H, m, CH_2); ir (neat) 2940, 2850, 1745, 1440, 1250, and 1160 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O_2$: mol wt, 182.1307. Found: mol wt, 182.1311.

Reaction of 2-Ethyl-1-butene with Methyl Acrylate. To a solution of methyl acrylate (10.3 g, 0.12 mol) in 50 ml of benzene was added aluminum chloride (1.4 g, 0.01 mol). After the aluminum chloride had dissolved, 2-ethyl-1-butene (8.4 g, 0.10 mol) was added. The solution was stirred for 72 hr at 25° and worked up as described for **1**, giving 14.2 g (83%) of yellow oil. Gc (6 ft, 5% SE-30, 115–190°) indicated this to be a mixture consisting of 83% of **7**, 13% of **8** and **9**, and 4% of two unidentified minor products. A 10-g portion of this was distilled, giving 7 g (58%) of methyl 5-ethyl-5-heptenoate (**7**), bp 78° (6 mm). Gc indicated the distillate to be greater than 95% pure. Gc indicated that the residue (1.3 g, 9%) consisted of 92% of a mixture of diadducts (**8** and **9**) and 8% of **7**.

The spectral data for **7** are ir (neat) 2960, 2870, 1740, 1435, 1245, 1200, and 1150 cm^{-1}; nmr ($CDCl_3$) δ 5.2 (1 H, q, J = 6 Hz, CH=), 3.66 (3 H, s, OCH_3), 1.7–2.5 (8 H, m), 1.58 (3 H, d, J = 6 Hz, CH_3), and 0.96 (3 H, t, J = 7 Hz, CH_3); gc retention time 3.8 min (6 ft, 5% SE-30, 112°).

Anal. Calcd for $C_{10}H_{18}O_2$: mol wt, 170.1303. Found: mol wt, 170.1307.

The spectral data for **8** and **9** are ir (neat) 2900, 2870, 1740, 1435, 1245, 1200, and 1168 cm^{-1}; nmr ($CDCl_3$) δ 4.9–5.5 (1 H, m, CH=), 3.63 (6 H, s, OCH_3), 1.3–2.5 (11 or 14 H, m), 0.98 (3 H, d, J = 6.5 Hz, $CHCH_3$), and 0.95 (0 or 3 H, t, J = 6 Hz, CH_3); gc retention time 3.2 min (6 ft, 5% SE-30, 185°).

Anal. Calcd for $C_{14}H_{24}O_4$: mol wt, 256.1674. Found: mol wt, 256.1668.

Reaction of 2-Methyl-1-pentene with Methyl Acrylate. To a solution of methyl acrylate (1.03 g, 12 mmol) in 5 ml of benzene was added aluminum chloride (0.28 g, 2 mmol). After dissolution of the aluminum chloride, 2-methyl-1-pentene (0.82 g, 10 mmol) was added and the solution was stirred for 96 hr at 25°. Work-up as for **1** gave 1.2 g (71%) of colorless oil. Gc (6 ft, 5% SE-30, 115–190°) indicated that a complx mixture of the various 1:1 and 2:1 adducts with methyl acrylate were present. These were not separated: ir (neat) 2960, 2870, 1745, 1440, and 1150 cm^{-1}; nmr ($CDCl_3$) δ 5.1 (t, J = 7 Hz, CH=), 4.7 (s, CH_2=), 3.65 (s, OCH_3), 1.58 (s, CH_3C=), and 0.89 (t, J = 6 Hz, CH_3). The gc characteristics follow: **10**, retention time 3.55 min (6 ft, 5% SE-30, 112°); **11** and **12**, retention times 3.40 and 3.80 min (6 ft, 5% SE-30, 185°).

Anal. Calcd for $C_{10}H_{18}O_2$: mol wt, 170.1307. Found: mol wt, 170.1309.

Reaction of (−)-β-Pinene with Methyl Vinyl Ketone. To a solution of anhydrous zinc bromide (4.0 g, 0.02 mol) in 100 ml of ether were added methyl vinyl ketone (10.5 g, 0.150 mol) and (−)-β-pinene (13.6 g, 0.10 mol). The solution was stirred for 7 days at 25°. It was then poured into water and filtered by suction to remove zinc salts. The ether layer was separated and the aqueous layer was extracted with 2 × 50 ml of ether. The combined ether layers were dried and evaporated. Fractional distillation of the residue gave the ketone **2**, bp 92° (0.5 mm) (13.04 g, 0.062 mol, 62%), which was 95% pure by gc: ir (neat) 2920, 1720, 1450, 1365, and 1165 cm^{-1}; nmr ($CDCl_3$) δ 5.20 (1 H, br, CH=), 1.4–2.6 (12 H, m, CH_2), 2.11 (3 H, s, $COCH_3$), 1.28 (3 H, s, CH_3), and 0.82 (3 H, s, CH_3); gc retention time 4.4 min (6 ft, 5% SE-30, 151°).

Anal. Calcd for $C_{14}H_{22}O$: mol wt, 206.1671. Found: mol wt, 206.1663.

Reaction of (−)-β-Pinene with Acrolein. To a solution of anhydrous zinc bromide (4.0 g, 0.02 mol) in 100 ml of ether were added acrolein (8.4 g, 0.15 mol) and (−)-β-pinene (13.6 g, 0.10 mol). The solution was stirred for 30 hr at 25° and worked up as for **2**. Fractional distillation of the residue gave the aldehyde **3**, bp 86° (0.45 mm) (6.05 g, 0.032 mol, 32%), which was 95% pure by gc: ir (neat) 2920, 2830, 2710, and 1725 cm^{-1}; nmr ($CDCl_3$) δ 9.78 (1 H, t, J = 1.9 Hz, CHO), 5.20 (1 H, m, CH=), 1.35–2.7 (12 H, m, CH_2), 1.23 (3 H, s, CH_3), and 0.83 (3 H, s, CH_3); gc retention time 3.25 min (6 ft, 5% SE-30, 145°).

Anal. Calcd for $C_{13}H_{20}O$: mol wt, 192.1514. Found: mol wt, 192.1513.

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Registry No. **1**, 42913-51-9; **2**, 42913-52-0; **3**, 22553-58-8; **5**, 42908-43-0; **7**, 42908-44-1; **8**, 42908-45-2; **9**, 42908-46-3; (−)-β-pinene, 18172-67-3; methyl acrylate, 96-33-3; methylenecyclohexane, 1192-37-6; 2-ethylene-1-butene, 760-21-4; 2-methyl-1-pentene, 763-29-1; methyl vinyl ketone, 78-94-4; acrolein, 107-02-8.

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Preparation of an Optically Active Intermediate for the Synthesis of Prostaglandins

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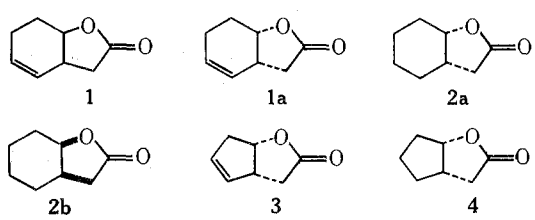
This paper describes the resolution of the (±)-cis-fused lactone **1** and unambiguous demonstration that the levo form possesses the absolute configuration shown in **1a**, which corresponds to the natural prostanoic acid stereochemistry. Since (±)-**1** has been utilized previously for the synthesis of (±)-11-deoxyprostaglandins[1] and also racemic primary prostaglandins,[2] a new route is thus established to these prostanoids in the optically active natural series.



The (±)-lactone **1** was hydrolyzed to the hydroxy acid and treated with (−)-1-(1-naphthyl)ethylamine[3] in ethyl acetate. Three recrystallizations of the resulting salt from ethyl acetate–methanol afforded a product of constant rotation, $[\alpha]^{27}D$ +63°. Conversion of this salt to the dextro

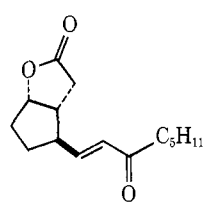
lactone **1**, $[\alpha]^{27}D$ +28°, was effected by acidification with hydrochloric acid and isolation. Use of (+)-1-(1-naphthyl)-ethylamine[3] in the resolution led to the levo lactone **1**, $[\alpha]^{27}D$ −28°.

The lactone sector rule allows the use of optical rotatory dispersion (ORD) data to assign absolute configuration to optically active bicyclic lactones.[4] Based on this rule the lactone **2a** should have either a plain negative curve or a negative Cotton effect near 225 nm. Hydrogenation of (+)-**1** over palladium on carbon in ethyl acetate gave a dextro lactone which showed a plain positive curve indicating the absolute configuration **2b**.

Additional evidence for the validity of the lactone sector method in these systems was obtained with a lower homolog of **1**. The (−) lactone **3** had earlier been obtained by resolution and converted to natural prostaglandins,[5] thereby demonstrating absolute configuration. Hydrogenation of levo **3** afforded the dihydro derivative **4**, which was found to exhibit a negative Cotton effect as predicted by the lactone sector rule.

Definitive proof for the assignment of **1a** for levo **1** was obtained by chemical correlation with the enone **5**, which was prepared from the (−) iodohydrin **6** of known absolute configuration. Treatment of levo **1** (**1a**) with thallic nitrate gave the (−) aldehyde **7**.[1] This was converted to the (+) enone **5**, $[\alpha]^{27}D$ +38.7°, by treatment with the sodio derivative of dimethyl 2-oxoheptylphosphonate.[1]

The racemic iodohydrin **6** has earlier been converted to the enone **5**.[6] The (−) iodohydrin **6**, which has the natural prostanoic acid stereochemistry,[7] was transformed to the (+) enone **5** by the following route. The (+) benzyl ether lactone **10** was prepared in quantitative yield from (−)-**6** by treatment with methanesulfonyl chloride and pyridine.[8] Treatment of (+)-**10** with acetic anhydride and boron trifluoride etherate afforded in 94% yield the (+) acetoxy lactone **11**,[8] which was hydrogenated over rhodium on alumina in tetrahydrofuran to provide the (−) saturated lactone **8** in 96% yield. Saponification of (−)-**8** with potassium carbonate in methanol gave the (−) alcohol **9** in 97% yield. Oxidation of (−)-**9** with Collins reagent[9] provided in 83% yield the (−) aldehyde **7**, which was converted to the enone **5**, $[\alpha]^{27}D$ +39.6°, in 65% yield. It can be concluded, therefore, that the levo lactone **1**, $[\alpha]^{27}D$ −28°, is fully resolved and has the absolute configuration of natural prostaglandins.



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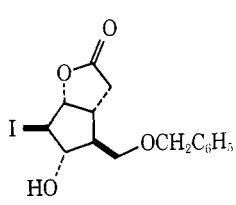

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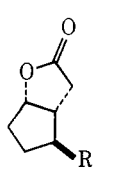
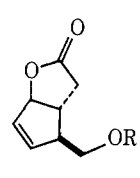


7, R = CHO
8, R = CH_2OCOCH_3
9, R = CH_2OH



10, R = $CH_2C_6H_5$
11, R = $COCH_3$

Experimental Section

Resolution of Lactone 1. The lactone **1**[1] (1.10 g, 8 mmol) was added to a solution of lithium hydroxide (250 mg, 10 mmol) in 5 ml of water and 2 ml of dimethoxyethane. The solution was stirred for 10 hr at 25° and then evaporated to dryness. The white, crystalline residue was taken up in 2 ml of water and 5 ml of ethyl acetate and cooled to 0°. Oxalic acid solution (10% in water) was added at 0° until pH 3.5 was reached. Saturated sodium chloride solution (10 ml) was added, and the reaction mixture was extracted with four portions of ethyl acetate which were dried and evaporated at 10°. The residual hydroxy acid was taken up in 10 ml of ethyl acetate, and (−)-1-(1-naphthyl)ethylamine[3] (1.54 g, 9.0 mmol) was added. After standing for 24 hr at 25° and 12 hr at 0°, white crystals had formed. The crystals were filtered, dried, and recrystallized from ethyl acetate–methanol, giving a salt with $[\alpha]^{27}D$ +59° (*c* 1.4, CH_3OH). An additional recrystallization gave a product with $[\alpha]^{27}D$ +62° (*c* 0.8, CH_3OH). A final recrystallization gave 700 mg (53%) of a salt with $[\alpha]^{27}D$ +63° (*c* 1.2, CH_3OH), indicating completion of the resolution.

Relactonization of the resolved (−)-1-(1-naphthyl)ethylammonium salt was effected by standard procedures. The salt (700 mg, 2.14 mmol) was dissolved in 1.2 equiv of aqueous sodium hydroxide solution. This solution was extracted with two portions of ether to remove the amine. The aqueous layer was acidified with 10 *N* hydrochloric acid and was extracted with five portions of methylene chloride. Tlc analysis of this solution indicated that relactonization had occurred spontaneously. The combined organic extracts were dried and evaporated, giving the lactone **1** (250 mg, 1.82 mmol, 85%) with $[\alpha]^{27}D$ +28° (*c* 0.6, CH_3OH).

Preparation of (−) Lactone 1. Use of (+)-1-(1-naphthyl)ethylamine instead of the (−) isomer gave after three recrystallizations from ethyl acetate–methanol the white, crystalline salt (730 mg, 2.23 mmol, 56%) with $[\alpha]^{27}D$ −63° (*c* 0.65, CH_3OH). Relactonization as described above gave the (−) lactone **1** (270 mg, 1.95 mmol, 87%) with $[\alpha]^{27}D$ −28° (*c* 0.83, CH_3OH).

Reduction of (+) Lactone 1. (+) Lactone **1** (35 mg) and 5% palladium on carbon (35 mg) were placed in 5 ml of ethyl acetate and stirred for 24 hr under hydrogen (1 atm). The solution was filtered and the residue was washed with several portions of ethyl acetate. The combined filtrates were evaporated, giving 33 mg of lactone **2b** as a colorless oil: nmr ($CDCl_3$) δ 4.4–5.0 (1 H, m, CHOCO), 0.8–2.8 (11 H, m); ir (neat) 2930, 2855, 1775, and 1170 cm^{-1}; $[\alpha]^{27}D$ +45.5° (*c* 0.43, CH_3OH); ORD (*c* 0.033, CH_3OH) 27°; $[\phi]_{350}$ +378°, $[\phi]_{300}$ +588°, $[\phi]_{250}$ +966°, $[\phi]_{220}$ +1680°, $[\phi]_{200}$ +4620°.

Reduction of (−) Lactone 3. (−) Lactone **3** (33 mg) was reduced over 5% palladium on carbon (33 mg) as described above for lactone **1**, giving 29 mg of **4** as a colorless oil: nmr ($CDCl_3$) δ 5.0 (1 H, m, CHOOCO), 1.4–2.8 (9 H, m); ir (neat) 2960, 2870, 1775, and 1175 cm^{-1}; $[\alpha]^{27}D$ −36° (*c* 0.48, CH_3OH); ORD (*c* 0.145, CH_3OH) 27°; $[\phi]_{350}$ −74°, $[\phi]_{300}$ −139°, $[\phi]_{250}$ −435°, $[\phi]_{225}$ −1164°, $[\phi]_{210}$ −365°.

Oxidation of Lactone 1.[1] To a solution of (−) lactone **1** (236 mg, 1.7 mmol) in 1.5 ml of aqueous 4 *M* sodium perchlorate and 0.5 *M* perchloric acid solution was added thallic nitrate (0.8 g, 1.2 equiv). Stirring was continued for 1 hr at 27° and the mixture was neutralized to pH 7 with solid sodium bicarbonate and then saturated with sodium chloride. The solution was extracted with three 10-ml portions of methylene chloride which were dried and evaporated giving the crude aldehyde **7**, which was converted directly to enone **5**: nmr ($CDCl_3$) δ 9.71 (1 H, s, CHO), 5.05 (1 H, m, CHOOC), 1.4–3.6 (8 H, m); ir (neat) 2720, 1765, 1715, and 1165 cm^{-1}; tlc R_f 0.55 (17:3 benzene–methanol); mass spectrum 154 (M), 126 (M − CO), and 110 (M − CO_2).

Preparation of Enone 5.[1] Sodium hydride (80 mg, 1.6 mmol) was placed under argon in a three-necked flask equipped with an overhead stirrer. Dimethoxyethane (12 ml) was added and the solution was stirred at 25°. Dimethyl 2-oxoheptylphosphonate (378 mg, 1.7 mmol) in dimethoxyethane (8 ml) was then added. After stirring for 1 hr at 25° the reaction was cooled to 0° and the aldehyde **7** (from previous reaction) in dimethoxyethane (6 ml) was added dropwise at 0°. After stirring for 1.5 hr at 0° and for 1.0 hr at 25°, the solution was neutralized with acetic acid. The solvent was evaporated and the residue was chromatographed on 15 g of silica gel (Woelm, activity III) with 97:3 methylene chloride–ethyl acetate to give enone **5** (220 mg, 0.88 mmol, 52% from lactone **1**): nmr ($CDCl_3$) δ 6.80 (1 H, d of d, *J* = 16, 7 Hz, =CH), 6.16 (1 H, d, *J* = 16 Hz, =CHCO), 5.06 (1 H, m, CHOCO), 0.65–3.40 (19 H, m); ir (neat) 1770, 1670, 1655, 1630, 1160, and 980 cm^{-1}; uv λ_{max} (methanol) 225 nm (ε 14,400); tlc R_f 0.60 (9:1 methylene chloride–ethyl acetate); $[\alpha]^{27}D$ +38.7° (*c* 3.58, $CHCl_3$).

Anal. Calcd for $C_{15}H_{22}O_3$: mol wt, 250.1569. Found: mol wt, 250.1563.

Preparation of Benzyl Ether Lactone 10.[8] A homogeneous solution of the (−) iodohydrin **6** (800 mg, 2.05 mmol) and dry pyridine (4.0 ml) was treated with methanesulfonyl chloride (0.27

ml). The reaction mixture was stirred for 2 hr at −20° and then for 2 hr at 0°. The reaction was quenched at 0° by addition of a saturated sodium thiosulfate solution (20 ml) followed by extraction of the product with three 20-ml portions of ether. The combined ether extracts were washed with water (2 × 30 ml) and 5% hydrochloric acid (2 × 25 ml). The organic layer was then dried over magnesium sulfate and evaporated, giving the (+) olefin **10** (515 mg, 2.05 mmol, 100%) as a yellow oil which was homogeneous by tlc: nmr ($CDCl_3$) δ 7.33 (5 H, s, aromatic H), 5.80–6.15 (2 H, m, =CH), 5.40–5.60 (1 H, m, HCOCO), 4.52 (2 H, s, CH_2 phenyl), 3.40 (2 H, d of d, J = 6, 3 Hz, CH_2O), and 2.2–3.0 (4 H, m); ir (neat) 1770, 1165, 1100, 1020, 740, and 690 cm^{-1}; tlc R_f 0.48 (1:1 benzene–ether); $[\alpha]^{27}D$ +205.7° (*c* 0.7, $CHCl_3$).

Anal. Calcd for $C_{15}H_{16}O_3$: mol wt, 244.1100. Found: mol wt, 244.1106.

Preparation of the (+) Acetoxy Lactone 11.[8] The (+) benzyl ether lactone **10** (500 mg, 2.05 mmol) was dissolved in acetic anhydride (10 ml) and cooled to 0° under an argon atmosphere. Boron trifluoride etherate (0.05 ml) was added dropwise with stirring at 0°. After stirring for 15 min at 0° the reaction was quenched with water (1.5 ml). The solvent was then evaporated. The crude product was passed through a column of silica gel (Woelm, activity III, 25 g) to remove benzyl acetate. Elution was carried out with benzene (200 ml), 99:1 benzene–ether (200 ml), 97:3 benzene–ether (200 ml), and 95:5 benzene–ether (500 ml), giving the acetoxy lactone **11** 380 mg, 94%): nmr ($CDCl_3$) δ 6.03 (2 H, br s, =CH), 5.45–5.68 (1, H, m, HCOCO), 4.08 (2 H, d, J = 6 Hz, CH_2OAc), 2.1–3.2 (4 H, m), and 2.02 (3 H, s, CH_3CO_2); ir (neat) 1770, 1730, 1240, 1165, 1020, and 755 cm^{-1}; tlc R_f 0.30 (1:1 benzene–ether), 0.50 (17:3 benzene–methanol); $[\alpha]^{27}D$ +226.7° (*c* 1.73, $CHCl_3$).

Anal. Calcd for $C_{10}H_{12}O_4$: mol wt, 196.0736. Found: mol wt, 196.0723.

Preparation of the Acetoxy Lactone 8. The (+) acetoxy lactone **11** (210 mg, 1.07 mmol) and 5% rhodium on alumina (150 mg) were placed in 10 ml of tetrahydrofuran and stirred for 4 hr at 27° under hydrogen (1 atm). The solution was then filtered and the residue was washed with several portions of ether. The combined filtrates were evaporated, giving the saturated acetoxy lactone **8** (205 mg, 1.03 mmol, 96%): nmr ($CDCl_3$) δ 4.98 (1 H, m, CHOCO), 4.03 (2 H, d J = 6 Hz, CH_2OAc), 2.05 (3 H, s, CH_3CO_2), and 1.2–3.0 (8 H, m); ir (neat) 1770, 1740, 1230, 1165, and 1035 cm^{-1}; tlc R_f 0.30 (1:1 benzene–ether); $[\alpha]^{27}D$ −1.2° (*c* 0.81, $CHCl_3$); mass spectrum *m/e* 198 (M, w), 156 (M − CH_2CO, s), and 138 (M − CH_3CO_2H, vs).

Anal. Calcd for $C_{10}H_{14}O_4$: mol wt, 198.0892. Found: mol wt, 198.0890.

Preparation of Alcohol 9. The acetoxy lactone **8** (200 mg, 1.01 mmol) and freshly powdered potassium carbonate (138 mg, 1.0 mmol) were dissolved in methanol (4 ml) under argon. The solution was stirred for 30 min at 25° and neutralized with 10 *N* hydrochloric acid (0.2 ml). The solvent was evaporated and the resulting slurry was washed exhaustively with ethyl acetate. The combined organic extracts were dried over magnesium sulfate and concentrated to afford the alcohol **9** (154 mg, 0.98 mmol, 97%) which was homogeneous by tlc: nmr ($CDCl_3$) δ 5.00 (1 H, br, CHOOC), 3.92 (1 H, br, OH), 3.54 (2, H, d, J = 6 Hz, CH_2OH), 1.3–3.0 (8 H, m); ir (neat) 3400, 1770, 1170, 1035 cm^{-1}; tlc R_f 0.30 (17:3 benzene–methanol); $[\alpha]^{27}D$ −20.4° (*c* 0.66, $CHCl_3$); mass spectrum *m/e* 156 (M, s), 139 (M − OH, m), and 138 (M − H_2O, vs).

Anal. Calcd for $C_8H_{12}O_3$: mol wt, 156.0786. Found: mol wt, 156.0789.

Oxidation of Alcohol 9. Collins reagent (2.34 g, 9 mmol) and dry Celite (4.3 g) were dissolved in 23 ml of dry methylene chloride under argon and cooled to 0°. A solution of alcohol **9** (154 mg, 0.98 mmol) in 5 ml of methylene chloride was added. The solution was stirred for 1 hr at 0° and sodium bisulfate (5.0 g) was added. The solution was stirred for 10 min at 25° and filtered through a pad of anhydrous magnesium sulfate. The residue was washed with several portions of methylene chloride. The combined filtrate was evaporated, giving aldehyde **7** (125 mg, 0.81 mmol, 83%) which was homogeneous by tlc: nmr ($CDCl_3$) δ 9.71 (1 H, s, CHO), 5.05 (1 H, m, CHOCO), 1.4–3.6 (8 H, m); ir (neat) 2720, 1765, 1715, and 1165 cm^{-1}; tlc R_f 0.55 (17:3 benzene–methanol); $[\alpha]^{27}D$ − 41° (*c* 0.61, $CHCl_3$); mass spectrum *m/e* 154 (M), 126 (M − CO), and 110 (M − CO_2).

Preparation of Enone 5. The aldehyde **7** (105 mg, 0.68 mmol) was treated as described above giving the enone **5** (110 mg, 0.44 mmol, 65%) which was homogeneous by tlc. This material was identical with an authentic sample by tlc and ir and nmr spectral comparison, $[\alpha]^{27}D$ +39.6° (*c* 1.59, $CHCl_3$).

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Registry No. (±)-**1**, 43119-22-8; (−)-**1**, 43119-23-9; (−)-**1** (+)-1-(1-naphthyl)ethylamine salt, 43119-24-0; **1a**, 43119-25-1; **1a** (−)-1-(1-naphthyl)ethylamine salt, 43119-26-2; **2b**, 43119-27-3; **3**, 43119-28-4; **4**, 43119-29-5; **5**, 43119-30-8; **6**, 31767-37-0; **7**, 43119-32-0; **8**, 43119-33-1; **9**, 43119-34-2; **10**, 35761-79-6; **11**, 35761-78-5; (−)-1-(1-naphthyl)ethylamine, 10420-89-0; (+)-1-(1-naphthyl)-ethylamine, 3886-70-2.

References and Notes

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Reduction of Enedicarbonyl Compounds with Titanous Ion

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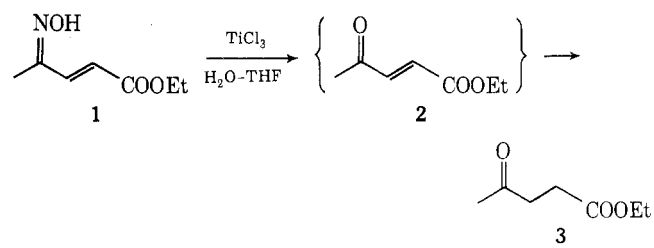
We recently had occasion to treat ethyl 4-oximino-2-pentenoate (**1**) (obtained from ethyl 3-bromolevulinate by Mattox–Kendall reaction with hydroxylamine[1]) with aqueous $TiCl_3$ according to the deoximation procedure of Timms and Wildsmith.[2] Although we expected that ethyl 4-oxo-2-pentenoate (**2**) would result, the sole product of the reaction was the saturated keto ester, ethyl levulinate (**3**).



1 2 3

The simplest rationalization of this result is to assume that **2** is in fact formed initially, and that $TiCl_3$ is capable of effecting rapid further reduction of enedicarbonyl compounds to their saturated analogs. This has indeed proved to be the case, and we have carried out a short study of the reaction which suggests that it is a gentle, effective, and remarkably simple method to use. Our results are given in Table I.

As can be seen from Table I, the reaction, which is usually complete within 15 min at room temperature, works quite well for diketones (examples **4**, **6**, **8**), for keto esters (example **2**), and for diacids (example **10**). The reaction fails completely for diesters, however, even when a prolonged reflux is employed. This presumably reflects the undoubted higher reduction potential of **12** *vs.* the other substrates.[3]

Similar methods of reduction of enedicarbonyl compounds have been reported using chromous ion,[4-6] al-