3-Acetoxy-1,7-octadiene (2). A mixture of $PdCl_2(PPh_3)_2$ (400 mg, 0.57 mmol), KOH (200 mg, 3.56 mmol), acetic acid (21.0 g, 0.35 mol), and triethylamine (35.4 g, 0.35 mol) was placed in a 100-mL autoclave and then butadiene (29 mL, 0.35 mol) was introduced. The autoclave was placed in an oil bath kept at 90 °C and stirred with a magnetic stirrer. After 10 h, ether (20 mL) was added to the resulting mixture and the solution was acidified with 3 N HCl and washed with brine. The organic layer was dried over magnesium sulfate and evaporated. The crude oil was distilled to give a mixture of 3-acetoxy-1,7-octadiene (2) and 1-acetoxy-2,7-octadiene (3) (1:2.7) (25 g, 85% based on butadiene). The fractional distillation of the mixture gave pure 3-acetoxyl-1,7-octadiene (2) (92 °C (24 Torr)): NMR (CCl_4) δ 1.52 (4 H, m), 1.80–2.27 (2 H, m), 2.00 (3 H, s), 4.78–6.13 (7 H, complex m); IR 1742, 1640, 1375, 1242 cm^{-1}.

1,3,8-Octanetriol (4). A solution of 3-acetoxy-1,7-octadiene (2) (3.36 g, 20.0 mmol) in dry tetrahydrofuran (15 mL) was placed in a flask under nitrogen atmosphere. Next the flask was placed in an ice bath and a 2.4 M solution of B_2H_6 in tetrahydrofuran (15 mL) was added slowly. The solution was stirred for 2 h at room temperature. A mixture of 5 N NaOH (15 mL) and 28% hydrogen peroxide (10 mL) was added dropwise to the flask at 0 °C and the mixture was stirred for 3 h at room temperature. The reaction mixture was poured into a cooled aqueous sodium thiosulfate solution to remove excess hydrogen peroxide. The solution was concentrated to 10 mL and continuous extraction with ethyl acetate was carried out. The extract was evaporated to give a crude triol 4 (2.59 g). The triol 4 was used in the next step without purification.

1-Hydroxy-5-(2-methyl-1,3-dioxan-4-yl)pentane (5). A mixture of the crude triol 4 (2.59 g), paraldehyde (5 mL), and a catalytic amount of *p*-toluenesulfonic acid dissolved in dry dichloromethane (10 mL) was placed in a flask under nitrogen atmosphere. The reaction was carried out for 2 h at room temperature. An aqueous sodium bicarbonate solution was added to the resulting mixture. The solution was extracted with dichloromethane and the extract was washed with brine. Dichloromethane and excess paraldehyde were removed under reduced pressure to give a crude oil. The oil was purified by column chromatography (silica gel, *n*-hexane/ether, 5:1) to afford alcohol 5 (2.40 g, 63.8% from 2): NMR (CCl_4) δ 1.24 (3 H, d, J = 5 Hz), 1.40 (10 H, broad), 3.31 (1 H, s), 3.40–4.23 (5 H, m), 4.65 (1 H, q, J = 5 Hz); IR 3450, 2945, 2870, 1135, 960 cm^{-1}.

Methyl 5-(2-Methyl-1,3-dioxan-4 yl)valerate (6b). The alcohol 5 (1.88 g, 10 mmol) dissolved in acetone (5 mL) was placed in a flask at 0 °C. Then Jones reagent (CrO_3–H_2SO_4) was added to the flask slowly. The color of a solution turned to green. The Jones reagent was added dropwise until its red-brown color remained. After water was added to the flask, the resulting mixture was extracted with ether. An aqueous sodium carbonate solution was added to the extract to remove neutral compounds. The aqueous layer was extracted with ether and acidified with 3 N HCl. The solution was extracted with dichloromethane and the extract was dried over magnesium sulfate. The solvent was removed to give the desired carboxylic acid **6a** (1.46 g, 72%): NMR (CCl_4) δ 1.22 (3 H, d, J = 5 Hz), 1.48 (8 H, broad), 2.32 (2 H, m), 3.20–4.22 (3 H, m), 4.60 (1 H, q, J = 5 Hz), 10.67 (1 H, s); IR 1720 cm^{-1}.

The crude carboxylic acid was converted to the methyl ester **6b** with diazomethane. The product was purified by column chromatography (silica gel, *n*-hexane/ether, 10:1) to give the pure methyl ester **6b** (1.40 g, 65% from 5): NMR (CCl_4) δ 1.21 (3 H, d, J = 5 Hz), 1.42 (8 H, broad), 2.25 (2 H, m), 3.10–4.20 (3 H, m), 3.60 (3 H, s), 4.55 (1 H, q, J = 5 Hz); IR 2950, 1740 cm^{-1}.

Methyl 6,8-Dihydroxyoctanoate (7). A mixture of the protected product **6b** (1.00 g, 4.63 mmol) and dry methanol (50 mL) was refluxed in the presence of a catalytic amount of concentrated sulfuric acid. After 24 h, the solution was concentrated to 10 mL and the residue was diluted with water. The solution was extracted with ether. From the extract, unchanged ester (258 mg) was recovered. The aqueous solution was neutralized with sodium hydrogen carbonate solution and concentrated under reduced pressure. The residue was extracted with boiling ethyl acetate. The extract was dried over magnesium sulfate and evaporated to give methyl 6,8-dihydroxyoctanoate (7) (605 mg, 92.8% based on the consumed ester **6b**): NMR (CCl_4) δ 1.46 (8 H, m), 2.28 (2 H, t), 3.49–4.15 (5 H, m), 3.60 (3 H, s); IR 3370, 2925, 1740 cm^{-1}.

6,8-Dimercaptooctanoic Acid (8). A mixture of methyl 6,8-dihydroxyoctanoate (7) (500 mg, 2.63 mmol), thiourea (1.8 g, 23.6 mmol), and 57% HI (4 g) was heated under reflux for 24 h. After cooling, KOH (4 g) in water (10 mL) was added and the mixture was refluxed for 12 h under nitrogen. The mixture was then extracted with ether, acidified with 3 N HCl, and extracted with dichloromethane. The extract was washed with water, dried over magnesium sulfate, and evaporated to give a yellow oil (522 mg). The oil was distilled under reduced pressure (170–175 °C bath temperature (8.3×10^{-2} Torr)) to give 6,8-dimercapotooctanoic acid (8) (438 mg, 80%): NMR δ 3.08 (2 H, t, J = 6 Hz), 3.49 (1 H, m), 11.31 (1 H, s); IR 2925, 1710, 1410, 1285 cm^{-1}.

dl-α-Lipoic Acid (1). A mixture of dithiol acid 8 (190 mg, 0.913 mmol) and water (6 mL) containing NaOH (31 mg, 0.775 mmol) and ferric chloride (2 mg) was placed in a flask. The color of the solution turned to dark red. A stream of oxygen was bubbled through the solution until the reddish color changed to pale yellow. After 9 h, the resulting pale yellow solution was washed with dichloromethane. The aqueous layer was acidified with 3 N HCl and extracted with dichloromethane. The extract was dried over magnesium sulfate and evaporated to give a yellow oil, which solidified upon trituration with pentane. Crystallization from hexane gave *dl*-α-lipoic acid (1) (132 mg, 70%) as yellow needles: mp 60–61 °C (lit. mp 60 °C,[4] 60–60.5 °C,[5] 61 °C,[3] 61–62 °C[6,8]); NMR (CCl_4) δ 1.60 (8 H, broad), 2.37 (2 H, m), 3.08 (2 H, t, J = 6 Hz), 3.50 (1 H, m), 12.00 (1 H, s); IR 3300–2400, 1690, 1250, 945 cm^{-1}.

Acknowledgment. This work was supported financially by the Grant-in-aid administered by the Ministry of Education, Japanese Government (203510).

Registry No.—**1,** 1077-28-7; **2,** 66859-02-7; **3,** 3491-27-8; **4,** 66859-03-8; **5,** 66859-04-9; **6a,** 66859-05-0; **6b,** 66859-06-1; **7,** 66859-07-2; **8,** 7516-48-5; butadiene, 106-99-0; acetic acid, 64-19-7.

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Stereoselective Synthesis of 1-Substituted (*E,E*)- and (*E,Z*)-2,4-Decadienyl Derivatives

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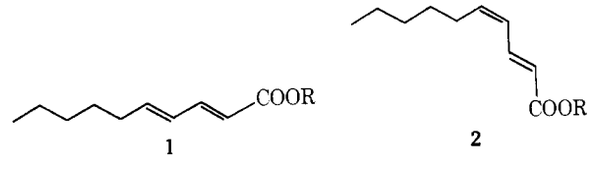
Recently we required the ethyl esters of (*E,E*)-2,4-decadienoic acid (1, R = H) and the corresponding (*E,Z*)-2,4-decadienoic acid (2, R = H). Since these compounds were to serve as starting materials in a synthesis of the prostaglandin nucleus, it was imperative that our syntheses be stereoselec-



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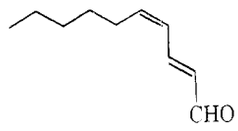
tive. The *N*-isobutylamide of **1** (pellitorine) is an insecticidal compound from *Anacyclus pyrethrum*. A number of syntheses of pellitorine have proceeded via acid **1** or its esters,[2-6] which in turn were prepared by a number of different routes. However, the ready availability of (*E,E*)-2,4-decadienal[7] led us to consider it as a precursor of acid **1** (R = H). Following the suggestion of Ohloff and Pawlak,[4] we oxidized (*E,E*)-2,4-decadienal to the ethyl ester **1** (R = Et) in 80% yield using MnO_2–NaCN in ethanol–acetic acid.[8] VPC analysis of this product indicated that the ratio of the *E,E* ester **1** (R = Et) to the *E,Z* ester **2** (R = Et) was 93:7 which was the same as the ratio of isomers in the starting aldehyde.[7] Thus it would appear that the oxidation is stereoselective.

Next we turned to the preparation of the *E,Z* compounds **2**, **3**, and **4**. The ethyl ester **2** (R = Et) is one of the flavor



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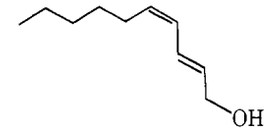

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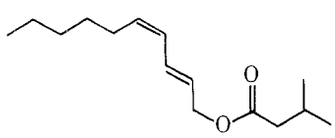
constituents of Bartlett pears.[9] This ester has also been synthesized by a number of different routes.[4,5,10] The methyl ester **2** (R = Me, methyl stillingate)[11] has also been synthesized.[2] Unfortunately these syntheses proceed with either low yield or low stereoselectivity. Our route to ester **2** (R = Et) is shown in Scheme I.

The dianion of propargyl alcohol[12] was alkylated with 1-bromopentane in liquid NH_3 to give 2-octyn-1-ol in 50% yield. This alcohol was oxidized to 2-octynal in 83% with MnO_2[13] in CH_2Cl_2. Condensation of the 2-octynal with the anion of triethyl phosphonoacetate[14] produced ethyl (*E*)-2-decen-4-ynoate[2] in 97% yield. The acetylene was reduced with hydrogen and Lindlar's catalyst[15] to give the desired ethyl (*E,Z*)-2,4-decadienoate (**2**, R = Et) in 94% yield. This was contaminated with 4% starting material and <2% of the *E,E* isomer. The spectral data of the above ester **2** (R = Et) were identical with those reported from previous syntheses of this ester and for the product isolated from Bartlett pears.[4,5] The ester **2** (R = Et) was reduced with diisobutylaluminum hydride in hexane to produce (*E,Z*)-2,4-decadien-1-ol (**4**) in 90% yield. This can be oxidized with MnO_2 to the corresponding aldehyde **3** which is one of the flavor constituents of black tea.[16] Finally the (*E,Z*)-2,4-decadien-1-ol was acylated with isovaleryl chloride and triethylamine to give, in 98% yield, (*E,Z*)-2,4-decadienyl isovalerate (**5**) which has recently been isolated from cypress oil.[18] The spectral data of our synthetic material were identical to those reported for the natural product.[18]



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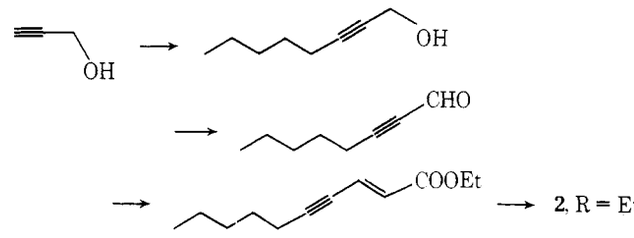
Experimental Section

All IR spectra were taken in chloroform solution on a Perkin-Elmer Model 700 spectrophotometer and were calibrated with the 1601 cm^{-1} band of polystyrene. The ^1H-NMR spectra were taken in deuteriochloroform on Varian Model T-60 or Model XL-100 spectrometers. Tetramethylsilane was used as an internal standard. Chemical shifts are reported on the δ scale. Coupling constants are quoted in hertz and the multiplicity of the signal is designed as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The mass spectra were recorded with either an Atlas CH-4b or, for high resolution, on AEI-MS-50 mass spectrometer. In both cases, the spectra were obtained at 70 eV. Gas chromatography was carried out on a Hewlett Packard

Scheme I. Synthesis of Ethyl (*E,Z*)-2,4-Decadienoate (2, R = Et)



Model 5830A using helium as the carrier gas, 6 ft × 1/8 in. OV-1 and OV-17 as the columns and flame ionization detector.

Ethyl (*E,E*)-2,4-Decadienoate (1, R = Et). To 25 mL of ethanol was added 0.164 g (1.08 mM) of (*E,E*)-2,4-decadienal, 1.952 g of MnO_2,[13] 0.277 g (12 mM) of sodium cyanide, and 0.098 mL of acetic acid. This mixture was allowed to stir at room temperature overnight. The MnO_2 was then filtered off and the ethanol was removed under reduced pressure. The resulting solid was dissolved in 25 mL of water and this solution was extracted with 3 × 25 mL of ethyl ether. The organic layer was dried and the solvent removed under reduced pressure giving 0.143 g (80%) of ester **1** (R = Et). GC analysis showed this ester to be 95% pure with no trace of starting aldehyde. A small quantity was isolated by gas chromatography: IR 1710, 1640, and 1620 cm^{-1}; NMR 6.9–7.4 (m, 1 H), 5.5–6.2 (m, 3 H), 4.13 (q, J = 7, 2 H), 2.0–2.4 (m, 1 H), 0.7–1.6 (m, 9 H); MS *m/e* 197 (8), 196 (43), 151 (28), 128 (11), 127 (15), 126 (13), 125 (100), 123 (13), 122 (13), 121 (8), 114 (8), 112 (6), 111 (10), 109 (6), 108 (10), 107 (8), 99 (18), 98 (30), 97 (53), 96 (13), 95 (13), 94 (10), 93 (10), 84 (6), 83 (10), 82 (10), 81 (50). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.29; H, 10.29.

2-Octyn-1-ol. In a 2-L flask was condensed 1 L of ammonia and a catalytic amount of $Fe(NO_3)_3$ was added. To the solution was slowly added 12.55 g (1.8 mol) of lithium. After the blue color had disappeared, 54.6 mL (.92 mol) of propargyl alcohol in 200 mL of tetrahydrofuran was added over 15 min. The mixture was left for 1 h and then 124 mL (1.0 mol) of 1-bromopentane dissolved in 100 mL of dry tetrahydrofuran was added. After 45 min the reaction was quenched with solid ammonium chloride. The ammonia was evaporated and the resulting solution was washed with brine and dried and the solvent removed under reduced pressure. The 2-octyn-1-ol distilled at 90 °C (8 mm) yielding 57.2 g (50%) of product: IR 3700, 3500, 2330, and 2250 cm^{-1}; NMR 4.16 (m, 2 H), 3.67 (s, 1 H), 2.0–2.36 (m, 2 H), 1.0–1.8 (m, 6 H), 0.7–1.0 (m, 3 H); MS *m/e* 126 (1), 95 (39), 93 (44), 91 (13), 83 (52), 82 (17), 81 (30), 79 (39), 77 (22), 70 (74), 69 (48), 68 (22), 67 (83), 66 (13), 65 (17), 57 (26), 55 (91), 54 (22), 53 (35), 52 (30), 51 (22), 43 (44), 42 (39), 41 (100), 40 (22), 39 (78), 31 (13), 29 (74), 38 (44), 27 (52). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.33; H, 11.10.

2-Octynal. In a 500-mL flask was placed 250 mL of methylene chloride, 25 g of active MnO_2, and 3.64 g (28.9 mM) of 2-octyn-1-ol. The mixture was left at room temperature for 4 h. The MnO_2 was filtered off and the solvent removed under reduced pressure yielding 2.963 g (83%) of 2-octynal which distilled at 49 °C (0.1 mm): IR 2250 and 1670 cm^{-1}; NMR 9.08 (s, 1 H), 2.38 (t, J = 6, 2 H), 1.2–1.8 (m, 6 H), 0.7–1.2 (m, 3 H); MS *m/e* 124 (1), 123 (9), 109 (33), 96 (10), 95 (100), 81 (38), 70 (19), 68 (43), 67 (48), 57 (19), 56 (14), 55 (52), 54 (14), 53 (24), 41 (86), 39 (57), 29 (90), 28 (29), 27 (43). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.45; H, 9.90.

Ethyl (*E*)-2-Decen-4-ynoate. A 0.957-g (19.9 mM) sample of NaH (50% mineral oil) was stirred in 50 mL of dry tetrahydrofuran. To this mixture was added 4.64 g (19.9 mM) of triethyl phosphonoacetate. When the evolution of H_2 stopped, the mixture was cooled to −20 °C (CCl_4 and dry ice) and 2.47 g (19.9 mM) of 2-octynal was added slowly and the reaction was left at −20 °C for 2 h. The mixture was then extracted with ethyl ether and the ether layer dried. The solvent was removed under reduced pressure yielding 3.77 g (97%) of the desired ester: IR 2250, 1705, 1620, and 960 cm^{-1}; NMR 6.67 (d t, J = 16 and 2, 1 H), 6.03 (d, J = 16, 1 H), 4.15 (q, J = 7, 2 H), 2.2–2.5 (m, 2 H), 1.0–1.6 (m, 9 H), 0.6–1.0 (m, 3 H); MS *m/e* 194 (2), 179 (17), 169 (5), 166 (12), 165 (48), 151 (21), 149 (55), 148 (17), 147 (21), 138 (5), 137 (21), 133 (21), 125 (7), 124 (10), 123 (41), 121 (48), 120 (36), 119 (59), 111 (10), 110 (43), 109 (55), 107 (17), 106 (17), 105 (45), 98 (19), 96 (26), 95 (21), 94 (69), 93 (38), 92 (35), 91 (62), 83 (17), 82 (35), 81 (52), 80 (14), 79 (71), 78 (19), 77 (50), 57 (17), 55 (83), 53 (27), 51 (28), 41 (78), 39 (58), 29 (100), 28 (55), 27 (50). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.10; H, 9.43.

Ethyl (*E,Z*)-2,4-Decadienoate (2, R = Et). In a 50-mL flask was placed 0.115 g of freshly prepared Lindlar's catalyst,[15] 2 drops of quinoline, 0.906 g (4.67 mM) of the above ester, and 25 mL of hexane.

A slight positive pressure of hydrogen was applied to the flask. When 1 equiv (103 mL) of H_2 was taken up the catalyst was filtered off. The solution was washed with mild acid and dried and the solvent was removed under reduced pressure yielding 0.900 g of product shown to be 94% pure by GC analysis. A small sample was isolated by gas chromatography: IR 1710, 1630, and 1605 cm^{-1}; NMR 7.55 (d, d, J = 16 and 10, 1 H), 5.80 (d, J = 16, 1 H), 5.5–6.3 (m, 2 H), 4.18 (q, J = 7, 2 H), 2.0–2.2 (m, 2 H), 1.0–1.7 (m, 9 H), 0.7–1.0 (m, 3 H); MS *m/e* 197 (9), 196 (61), 167 (6), 151 (42), 129 (48), 128 (26), 127 (29), 126 (16), 125 (100), 123 (19), 122 (32), 121 (16), 114 (10), 108 (19), 98 (26), 97 (29), 81 (61), 79 (32), 67 (68), 55 (29), 53 (23), 41 (42), 29 (90). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.45; H, 10.27. Found: C, 73.50; H, 10.20.

(*E,Z*)-2,4-Decadien-1-ol (4). To 4.66 mL (4.5 mM) of DIBAL (20% in hexane, Aldrich) was added 15 mL of hexane and this solution was cooled to 0 °C (N_2 atmosphere) with stirring. Then 0.378 g (1.92 mM) of ethyl (*E,Z*)-2,4-decadienoate (**2**, R = Et) dissolved in 5 mL of hexane was slowly added to the DIBAL solution. The reaction was left at 0 °C for 2 h. To the reaction was added 3 mL of methanol and after 10 min 10 mL of aqueous dilute HCl was added and the mixture was left for 1 h. The resulting solution was then extracted with ethyl ether and the organic layer was dried and the solvent removed yielding 0.266 g (90%) of the alcohol **4**. The spectral data of the crude alcohol 4 were identical to that reported by Tabacchi et al.[18] for (*E,Z*)-2,4-decadien-1-ol: IR 3400 and 980 cm^{-1}; NMR 5.2–6.7 (m, 4 H), 3.79 (d, J = 6, 2 H), 1.9–2.4 (m, 3 H, one exchanges on addition of D_2O), 1.0–1.8 (m, 9 H), 0.7–1.0 (m, 3 H).

(*E,Z*)-2,4-Decadien-1-yl Isovalerate (5). In a 25-mL flask was placed 0.235 g (1.53 mM) of (*E,Z*)-2,4-decadien-1-ol (**4**) dissolved in 10 mL of dry tetrahydrofuran. To this solution of the alcohol was added 0.22 mL (1.6 mM) of triethylamine and then 0.30 mL (2.5 mM) of isovaleryl chloride.[17] The solution was refluxed for 2 h and left at room temperature for 12 h. Then 25 mL of ethyl ether was added and the resulting solution was extracted with aqueous saturated $NaHCO_3$. The organic layer was dried and the solvent removed under reduced pressure yielding 0.364 g (98%) of the desired ester **5**: IR 1730 and 980 cm^{-1}; NMR 6.4–6.8 (d, d, J = 7.5 and 5.5, 1 H), 5.4–6.2 (m, 3 H), 4.57 (d, J = 6, 2 H), 1.8–2.4 (m, 4 H), 1.1–1.7 (m, 7 H), 0.7–1.0 (d, J = 3, 9 H); MS *m/e* 238 (6), 137 (5), 136 (5), 111 (4), 110 (8), 99 (4), 85 (100), 83 (7), 82 (8), 81 (12), 80 (14), 79 (20), 77 (7), 71 (8), 69 (13), 68 (10), 67 (22), 57 (79), 55 (18), 54 (104), 43 (29), 42 (7), 41 (40), 39 (12), 29 (26). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.53; H, 10.80.

Acknowledgments. We are grateful to Professor R. Tabacchi and Dr. F. Näf for copies of spectral data and to the National Research Council of Canada for financial support.

Registry No.—1 (R = Et), 7328-34-9; **2** (R = Et), 3025-30-7; **4**, 16195-71-4; **5**, 56699-32-2; 2-octyn-1-ol, 20739-58-6; 2-octynal, 1846-68-0; ethyl (*E*)-2-decene-4-ynoate, 66901-42-6; (*E,E*)-2,4-decadienal, 25152-84-5; propargyl alcohol, 107-19-7; 1-bromopentane, 110-53-2; triethyl phosphonoacetate, 867-13-0; isovaleryl chloride, 108-12-3.

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Synthesis of Tetrasubstituted Cyclopropenes and Medium to Large Carbocyclic Alkenes by the Intramolecular Reductive Coupling of Diketones with Titanium Trichloride–Lithium Aluminum Hydride

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Low-valent titanium reagents offer a convenient method for the preparation of alkenes from ketones.[1] The intramolecular reductive coupling of dicarbonyls to cycloalkenes has been carried out.[2] Recently, McMurry and Kees have shown[2c] the potential of the method in medium- and large-ring carbocyclic synthesis by preparing cycloalkenes, ring size 4–16, with $TiCl_3$/Zn–Cu. There have been no reports of cyclopropene synthesis by low-valent titanium reagents. 1,2-Diphenylcyclobutene is the only strained-ring alkene to have been previously prepared by reductive coupling of a diketone.[2b,c] We wish to report the first synthesis of cyclopropenes in addition to the synthesis of medium to large carbocyclic alkenes[3] by the intramolecular reductive coupling of dibenzoylalkanes with $TiCl_3$–$LiAlH_4$.

Results and Discussion

Attempts to prepare 1,2-diphenylcyclopropene and 3-methyl-1,2-diphenylcyclopropene by the coupling of dibenzoylmethane and 1,1-dibenzoylethane were unsuccessful.[4] However, complete substitution of alkyl groups for the acidic hydrogens of the 1,3-diketone resulted in the successful preparation of tetrasubstituted cyclopropenes. 3,3-Dimethyl- and 3,3-diethyl-1,2-diphenylcyclopropene (**2** and **4**) were prepared in 40–46% yield by the coupling of dimethyl- and diethyldibenzoylmethane (**1** and **3**) with $TiCl_3$–$LiAlH_4$. A series of 1,2-diphenylcycloalkenes was also investigated. 1,2-Diphenylcycloalkenes of ring size 5, 8, 9, 10, and 12 were prepared in 50–60% yield by the coupling of a series of dibenzoylalkanes with $TiCl_3$–$LiAlH_4$. 1,2-Diphenylcyclobutene and 1,2-diphenylcyclohexene have previously been prepared by the $TiCl_3$–$LiAlH_4$ method.[2b] The results are summarized in Table I.

The yield (46%) of cyclopropene **2** by the $TiCl_3$–$LiAlH_4$ method compares favorably with that (20%) of the procedure of Closs[5] (alkyne, dichloroalkane, alkyllithium) as employed by Friedrich and Fiato[6] in the synthesis of **2**. The $TiCl_3$–$LiAlH_4$ method also has the advantage of producing only one isomer. The $TiCl_3$–$LiAlH_4$ method would appear to be a new general route to 3,3-disubstituted cyclopropenes.[7]

The yields of the large cycloalkenes ranged between 50 and 60%. Little or no drop in yield was noted for the synthesis of the medium rings in contrast to other methods of ring preparation.[8] The apparent lack of variation of yield with ring size is in complete agreement with the results[2c] of McMurry and Kees. McMurry and Kees report higher yields of cycloalkenes by the more elaborate $TiCl_3$/Zn–Cu method.[2c] Titanium reagents apparently overcome effects[8] encountered in the preparation of medium rings. Surprisingly, even rapid addition of the diketones as powders to the $TiCl_3$–$LiAlH_4$ reagent under nitrogen only lowered the isolated yields of 1,2-diphenylcycloalkenes to 35–40%. It is remarkable that large, medium, normal, and strained rings can be prepared by the $TiCl_3$–$LiAlH_4$ method in moderate yield without the need to alter the reaction conditions.

The mechanism of the intermolecular coupling of carbonyls was suggested[1c] to proceed via reduction of a carbonyl to a radical anion followed by coupling to form the pinacol dianion. Judging from the results of Corey,[9] *cis*-pinacol dianions are

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