extraction (hexane), drying (Na_2SO_4), and concentration of the resulting solution in vacuo, the residue was distilled to provide 2-hydroxy-2-methyl-4-nonanone (92%); Kugelrohr bp 80 °C (0.01 torr); IR (neat) 3450, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7 Hz, 3 H), 1.25 (s, 6 H), 1.0–1.8 (m, 6 H), 2.43 (t, J = 7 Hz, 2 H), 2.60 (s, 2 H); MS m/e (relative intensity) 172 (0.5), 157 (22), 154 (9), 116 (5), 114 (8), 101 (6), 99 (100), 71 (39); calcd for $C_{10}H_{20}O_2$ 172.1487, found 172.1475.

5 (R′ = CH_3, R″ = C_2H_5): Kugelrohr bp 80–85 °C (0.01 torr); IR (neat) 1710, 1260, 1040, 840 cm^{-1}; ^1H NMR (CCl_4) δ −0.15 (s, 9 H), 0.5–0.8 (m, 6 H), 1.03 (s, 3 H), 0.8–1.5 (m, 8 H), 2.0–2.4 (m, 4 H); MS, m/e (relative intensity) 243 (19), 229 (75), 171 (33), 145 (44), 129 (17), 99 (100), 75 (74), 73 (60), 71 (30); calcd for $C_{13}H_{27}SiO_2$ (M − CH_3) 243.1779, found 243.1772.

5 (R′ = CH_3, R″ = H): Kugelrohr bp 75–80 °C (0.01 torr); IR (neat) 1710, 1250, 1040, 840 cm^{-1}; ^1H NMR (CCl_4) δ 0.03 (s, 9 H), 0.87 (t, J = 7 Hz, 3 H), 1.10 (d, J = 6 Hz, 3 H), 0.9–1.8 (m, 6 H), 2.1–2.6 (m, 4 H), 4.0–4.1 (m, 1 H); MS, m/e (relative intensity) 230 (1), 215 (100), 171 (99), 159 (43), 143 (14), 117 (77), 101 (15), 99 (28), 75 (86), 73 (86); calcd for $C_{12}H_{28}SiO_2$ 230.1700, found 230.1681.

5 (R′ = C_6H_{11}, R″ = H): Kugelrohr bp 105–110 °C (0.01 torr); IR (neat) 1715, 1250, 1044, 840 cm^{-1}; ^1H NMR (CCl_4) δ 0.05 (s, 9 H), 0.8–1.0 (m, 20 H), 2.1–2.5 (m, 4 H), 3.9–4.2 (m, 1 H); MS, m/e (relative intensity) 298 (0.6), 283 (58), 227 (15), 215 (71), 185 (13), 171 (19), 152 (31), 137 (42), 99 (100), 72 (25), 73 (23), 71 (21).

5 (R′ = C_6H_5, R″ = H): microdistillation [Kugelrohr bp 90–95 °C (0.01 torr)] provided a solid, which upon recrystallization (pentane) had mp 48–49 °C and identical spectroscopic properties with those reported in the literature.[15b]

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Synthesis of High-Specific Activity Hydroprene: Use of an Iron Carbonyl Adduct To Protect an (*E*,*E*)-Dienoate during Homogeneous Tritiation

Marcus F. Boehm and Glenn D. Prestwich*

Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400

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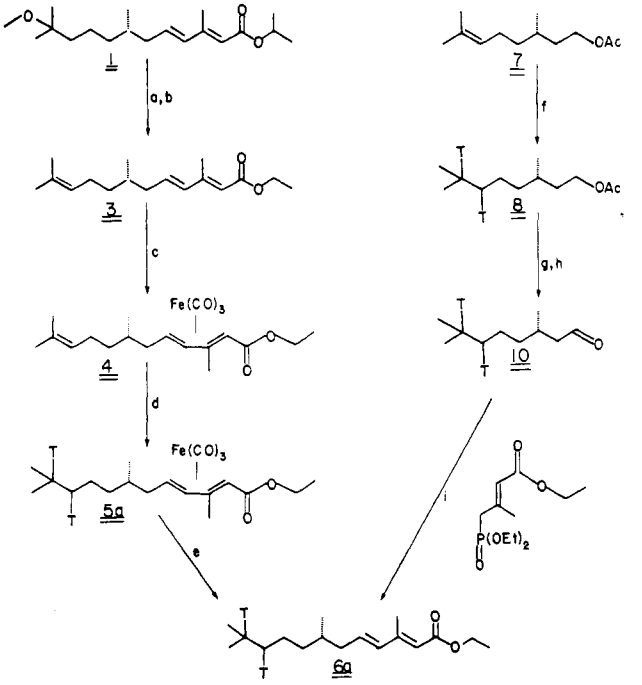
The dodecadienoates, e.g., methoprene (1) and hydroprene (6), are important commercial insect growth regulators related to insect juvenile hormones (JH).[1] Despite the abundant literature on the preparation and testing of over 5000 JH analogues (JHA),[1,2] little is known of the molecular action of these analogues. In order to study macromolecular binding components, synthetic methods are needed for preparing high specific activity radiolabeled juvenile hormones (JH) and juvenile hormone analogues (JHA).[3-5] Following the preparation of the chiral JH homologues[6] and an iodinated (7*S*)-methoprene analogue[7] we turned our attention to the synthesis of high specific activity tritium-labeled (7*S*)-hydroprene, a potent insect growth regulator currently being developed for domestic cockroach control.[8]

Scheme I. Synthesis for (7*S*)-[$^3H_2$]Hydroprene[a]



[a] Reagents: (a) NaOEt, EtOH, 20 °C, 15 h (87%); (b) concentrated H_2SO_4, hexane, 20 °C, 18 h (89%); (c) $Fe_3(CO)_{12}$, benzene, 85 °C, 6.5 h, (85%); (d) $Rh[(C_6H_5)_3P]_3Cl$, $^3H_2$, benzene, 20 °C, 15 h, (93%); (e) $(NH_4)_2Ce(NO_3)_6$, CH_3CN, 0 °C, 4 h; (f) 10% Pd/C, EtOAc, $^3H_2$, 20 °C, 1 h; (g) 3 N NaOH, MeOH, 20 °C, 4 h; (h) PDC CH_2Cl_2, 20 °C, 4 h; (i) $EtOC(O)CH{=}C(CH_3)CH_2P(O)(OEt)_2$, NaOEt, DMF, 20 °C, 1.5 h.

Selective hydrogenation of one double bond in a polyene is crucial for preparing stoichiometrically and specifically tritium-(or deuterium-)labeled substances. When trienoates containing the (2*E*,4*E*)-dienoate unit and a third olefinic bond in the terminal 10,11- or the internal 8,9-position were hydrogenated with tris(triphenylphosphine)rhodium chloride, 5% Pt/C, or 10% Pd/C catalysts, however, hydrogenation of the Δ^4 bond of the dienoate was competitive with reduction of the nonconjugated olefinic bond.[17] In order to hydrogenate (or tritiate) an isolated olefinic bond selectively in the presence of a dienoate, a protecting group for the dienoate was needed that could be easily attached and removed without alteration of the 2*E*,4*E* stereochemistry of the dienoate. Iron tricarbonyl is one such protecting group and has been used previously to protect a B ring $\Delta^{5,7}$ diene during the hydrogenation of a side chain Δ^{22} double bond in a steroid.[9] We report the application of this methodology to protect a (2*E*,4*E*)-dienoate during a remote hydrogenation or tritiation using a homogeneous catalyst. The iron tricarbonyl complex also prevented isomerization of the dienoate. We also report that a more traditional route to the tritiated dienoate is inferior in yield and stereochemical purity to the dienoate protection procedure.

The iron carbonyl complex was synthesized in two steps from (7*S*)-methoprene. Methoprene was converted to the ethyl ester 2 (87%) with sodium ethoxide in ethanol, and sulfuric acid mediated elimination of methanol in a bi-

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phasic hexane mixture[7] gave the ethyl dodecatrienoate **3** (89%) (Scheme I). Reaction of the dodecatrienoate **3** with triiron dodecacarbonyl in benzene under reflux resulted in the iron tricarbonyl–dienoate complex **4** (85%).[10,11] Homogeneous tritiation using a threefold molar excess of Wilkinson's catalyst at room temperature for 16 h afforded the tritiated complex **5a** (93%). Oxidative removal of the iron carbonyl with ceric ammonium nitrate in acetonitrile gave only the 2*E*,4*E* isomer of (7*S*)-hydroprene **6a** (66%).

High-resolution mass spectra of the iron carbonyl complexes showed parent ions at m/z 404.1290 for **4** and m/z 406.1424 for **5**. The ^{1}H NMR data of the complexes indicated the disappearance of the C-3 methyl doublet at 2.26 ppm (J = 1 Hz) to give a singlet at 2.46 ppm as a result of the iron complex; ^{13}C NMR data showed a broad peak between 207 and 212 ppm corresponding to the iron carbonyls. The broadening can be attributed to nonequivalence of the iron carbonyls on the NMR time scale.[12]

For comparison, we also synthesized ^{3}H-labeled hydroprene from the 3*S* enantiomer of citronellyl acetate (**7**). Catalytic tritiation with carrier-free $^3H_2$ in EtOAc in the presence of 10% palladium on charcoal gave the tritium-labeled dihydrocitronellyl acetate **8** (74%). Hydrolysis (3 N NaOH–MeOH) and oxidation of the alcohol (PDC) gave [6,7-$^3H_2$]dihydrocitronellal (**10**) (60%). Condensation of the aldehyde **10** with the anion of diethyl [3-(ethoxycarbonyl)-2-methyl-2-propenyl]phosphonate in DMF gave a mixture of 2*E*,4*E* and 2*Z*,4*E* isomers,[13] which could be separated by HPLC to give [$^3H_2$]-(7*S*)-hydroprene **6a** (38%).

The synthetic scheme utilizing the iron tricarbonyl complex as a protecting group was chosen to minimize the number of synthetic steps involving radioactive compounds and to increase the yield of the final tritiated product. [$^3H_2$]- or [$^1H_2$]hydroprene synthesized via the iron tricarbonyl adduct showed only the 2*E*,4*E* isomer and was therefore easier to purify than (7*S*)-hydroprene synthesized via the phosphonate condensation, which gave a 2:1 mixture of 2*E*,4*E*/2*Z*,4*E* isomers.[13]

The specific activities differed as a result of the two catalysts employed in the tritiation. Use of palladium on charcoal resulted in much higher specific activity (114 Ci/mmol) due to tritium–hydrogen exchange with the allylic[14,15] and vinylic[16] protons, while both allylic and vinylic exchange are essentially absent during transfer of tritide from rhodium to carbon using Wilkinson's catalyst. Since it was impractical to conduct the tritiation above 1 atm, above 20 °C, or for longer than 24 h, it was empirically determined that a large excess of tris(triphenylphosphine)rhodium chloride could be employed at ambient conditions to achieve complete hydrogenation (and subsequent tritiation) of the Δ^{10} olefinic bond. Catalytic reduction of the iron carbonyl complex was unsuccessful using palladium on charcoal and platinum on charcoal catalysts. Similar problems were encountered by Barton et al. in their attempts to hydrogenate a steroidal iron carbonyl complex;[9] they resorted to addition of benzyldimethylsilane to promote hydride transfer.

To our knowledge, this is the first example of the use of an iron tricarbonyl adduct to protect an acyclic diene or a dienoate system during selective reduction of an alkene. We expect that this method will be valuable for the selective introduction of isotopic labels in other complex polyenes.

Experimental Section

(7*S*)-Methoprene (90% pure, GC) was obtained from Zoecon Research Institute. Tritiations were performed with carrier-free tritium gas at the National Tritium Labeling Facility (NTLF) at the Lawrence Berkeley Laboratory. All solvents were distilled before use. Flash chromatographic purifications were carried out on Woelm Silica 32–63 μm. HPLC purifications were conducted on a Waters M-45 HPLC equipped with a Whatman Partisil M9 10/25 column and a Shoeffel UV Monochromator GM 770 detector. TLC was performed with MN Polygram Sil G/UV 254 (4 × 8 cm) TLC plates. All products were homogeneous by TLC (R_f's are reported for 20% EtOAc/hexane). ^{1}H NMR and ^{13}C NMR spectra were determined on an NT-300 spectrometer. Only diagnostic resonances are reported, and integrated intensities are consistent with the assignments indicated. Multiplicity of carbon signals was verified by the attached proton test (APT). Mass spectra (HRMS) were obtained at 70-eV ionization potential on a Spectros MS 30 spectrometer with a DS 50 data system. UV spectra were measured in hexane on an LKB Ultraspec II. IR spectra were measured neat on a Perkin-Elmer 727 infrared spectrophotometer. Autoradiography was performed on Kodak XAR-5 film. Radio TLC scanning (RTLCS) was performed on a Bioscan System 500 imaging scanner. Radioactive samples were counted in an LKB 1218 Rackbeta liquid scintillation counter using a PPO–POPOP–toluene scintillation cocktail.

Ethyl (2*E*,4*E*)-11-Methoxy-3,7,11-trimethyl-2,4-dodecadienoate (2). To a solution of 1.5 g (4.84 mmol) of (7*S*)-methoprene (isopropyl (2*E*,4*E*)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate) in 200 mL of ethyl alcohol was added 0.167 g (7.26 mmol) of sodium metal. The reaction mixture was stirred for 15 h at room temperature and then concentrated in vacuo. The residue was dissolved in 100 mL of 20% EtOAc–hexane, washed (1:1 H_2O–brine), dried ($MgSO_4$), concentrated, and chromatographed (5% EtOAc–hexane on silica gel) to give 1.25 g (4.22 mmol) of the pure ethyl ester **2** (87% yield): TLC, R_f 0.52; ^{1}H NMR ($CDCl_3$) δ 0.83 (d, J = 6.6 Hz, C-7 CH_3), 1.14 (br s, H-12, C-11 CH_3), 1.26 (t, J = 7.1 Hz, OCH_2CH_3), 2.26 (d, J = 1.1 Hz, C-3 CH_3), 3.15 (s, C-11 OCH_3), 4.15 (q, J = 7.1 Hz, OCH_2CH_3), 5.67 (m, H-2), 6.07 (m, H-4, H-5).

Ethyl (2*E*,4*E*)-3,7,11-Trimethyl-2,4,10-dodecatrienoate (3). To 700 mg (2.36 mmol) of ethyl ester **2** in 200 mL of hexane was added 6 drops of concentrated H_2SO_4 and the reaction mixture stirred for 18 h at ambient temperature.[7] The reaction mixture was filtered through a pad of silica gel and concentrated to give a mixture of starting material and a 9:1 mixture of 2*E*,4*E*/2*Z*,4*E* trienoate **3**. Purification by MPLC (0.5% ether–hexane on silica gel) gave 250 mg (0.84 mmol) of starting material **2** and 360 mg (1.36 mmol) of pure (2*E*,4*E*)-trienoate **3** (93% combined yield): TLC, R_f 0.65; ^{1}H NMR ($CDCl_3$) δ 0.83 (d, J = 6.6 Hz, C-7 CH_3), 1.26 (t, J = 7.1 Hz, OCH_2CH_3), 1.59 (d, J = 0.5 Hz, C-11 CH_3), 1.67 (d, J = 0.8 Hz, H-12), 2.26 (d, J = 1.1 Hz, C-3 CH_3), 4.15 (q, J = 7.1 Hz, OCH_2CH_3), 5.07 (m, H-10), 5.67 (m, H-2), 6.07 (m, H-4, H-5).

Ethyl (2*E*,4*E*)-3,7,11-Trimethyl-2,4,10-dodecatrienoate–Fe(CO_3) (4). To 80 mg (0.30 mmol) of trienoate **3** in 10 mL of benzene was added 120 mg (0.24 mmol) of triiron dodecacarbonyl and the reaction refluxed for 6.5 h at 85 °C. Since the R_f values on silica TLC of starting and iron tricarbonyl adduct were identical, the reaction was monitored by observing the disappearance of the 1625-cm^{-1} (C=C) IR absorption band from the uncomplexed diene. The solvent was removed, and the product was purified by chromatography (elution first with hexane to remove excess triiron dodecacarbonyl and then with 2% EtOAc–hexane) to give 103 mg (0.25 mmol) of the iron carbonyl complex **4** (85% yield): TLC, R_f 0.65; ^{1}H NMR ($CDCl_3$) δ 0.83 (d, J = 6.6 Hz, C-7 CH_3), 0.75 (m, H-2, H-5, H-6), 1.26 (t, J =

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7.1 Hz, OCH_2CH_3), 1.59 (d, J = 0.5 Hz, C-11 CH_3), 1.67 (d, J = 0.5 Hz, H-12), 2.46 (s, C-3 CH_3), 4.08 (q, J = 7.1 Hz, OCH_2CH_3), 4.95–5.04 (d overlapping t, H-4, H-10); ^{13}C NMR ($CDCl_3$) δ 14.17 (OCH_2CH_3), 17.61 (C-11 CH_3), 18.65 (C-7 CH_3), 19.57 (C-3 CH_3), 25.41 (C-6), 25.87 (C-12), 35.20 (C-7), 35.88 (C-9), 37.21 (C-8), 47.64 (C-5), 59.95 (OCH_2CH_3), 60.36 (C-2), 89.75 (C-4), 99.75 (C-3), 124.39 (C-10), 131.31 (C-11), 207–212 (br, $Fe(CO)_3$); HRMS (70 eV), m/z (relative intensity) 404.1290 (2, $C_{20}H_{28}O_5Fe$), 320.1462 (11), 210.0362 (5), 139.0761 (3), 68.9941 (100), calcd for $C_{20}H_{28}O_5Fe$ 404.1278, found 404.1290.

Ethyl (2*E*,4*E*)-3,7,11-Trimethyl-2,4-dodecadienoate–Fe(CO_3) (5). A solution of tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst; 115 mg, 0.12 mmol) in 1 mL of dry benzene was degassed four times and flushed with hydrogen gas. The catalyst was vigorously stirred under a hydrogen atmosphere for 4 h until the solution turned from red-brown to yellow-orange. The iron carbonyl complex 4 (15 mg, 0.037 mmol) in 0.5 mL of benzene was added to the charged catalyst, and the reaction was stirred under hydrogen for 15 h. The reaction mixture was concentrated to a paste and the residue was suspended in 5 mL of 2% EtOAc–hexane and filtered (florisil–silica gel) to give 14 mg (0.034 mmol) of the 10,11-dihydro iron carbonyl complex 5 (93% yield): TLC, R_f 0.65; ^1H NMR ($CDCl_3$) δ 0.82 (d, J = 6.6 Hz, C-7 CH_3), 0.85 (d, J = 6.6 Hz, H-12, C-11 CH_3), 1.24 (t, J = 7.1 Hz, OCH_2CH_3), 2.46 (s, C-3 CH_3), 4.08 (q, J = 7.01 Hz, OCH_2CH_3), 4.98 (d, J = 7.8 Hz, H-4); HRMS (70 eV), m/z (relative intensity) 406.1424 (1), $C_{20}H_{30}O_5Fe$), 322.1596 (27), 210.0317 (52), 139.0740 (100), 68.9952 (91), calcd for $C_{20}H_{30}O_5Fe$ 406.1434, found 406.1424.

Ethyl (2*E*,4*E*)-3,7,11-Trimethyldodecadienoate (6). To 14 mg (0.034 mmol) of the 10,11-dihydro iron carbonyl complex in 10 mL of CH_3CN at 0 °C was added 102 mg (0.202 mmol) of ceric ammonium nitrate. The reaction mixture was stirred at 0 °C for 4 h and diluted with 100 mL of 20% EtOAc–hexane. The organics were washed (H_2O–brine), concentrated, and chromatographed (2% EtOAc–hexane) to give 8.4 mg (0.031 mmol) of (7*S*)-hydroprene 6 (93% yield): TLC, R_f 0.65; UV λ_{max} 261 nm (ϵ 32 700); ^1H NMR ($CDCl_3$) δ 0.87 (br d, J = 6.6 Hz, C-7 CH_3, C-11 CH_3, H-12), 1.24 (t, J = 7.1 Hz, OCH_2CH_3), 2.24 (d, J = 1.1 Hz, C-3 CH_3), 4.14 (q, J = 7.1 Hz, OCH_2CH_3), 5.64 (m, H-2), 6.06 (m, H-4, H-5).

Ethyl [10,11-$^3H_2$]-(2*E*,4*E*)-3,7,11-Trimethyl-2,4-dodecadienoate–Fe(CO_3 (5a). The same procedure and quantities were used as for compound 5 above, except that the reaction was conducted with carrier-free tritium gas and the product purified by chromatography (2.5% EtOAc–hexane on silica gel). The radiolabeled iron complex was stored in heptane–toluene below −20 °C after HPLC.

Ethyl [10,11-$^3H_2$]-(2*E*,4*E*)-3,7,11-Trimethyldodecadienoate (6a). To 3 mg (0.0074 mmol) of the 10,11-ditritio iron carbonyl complex 5a in a 2 mL CH_3CN at 0 °C was added 22 mg (0.044 mmol) of ceric ammonium nitrate. The reaction mixture was stirred at 0 °C for 4 h and diluted with 5 mL of 20% EtOAc–hexane. The organics were washed with H_2O–brine, dried with $MgSO_4$, and purified by HPLC (0.5% ether–hexane) to give 1.3 mg (0.0049 mmol) of [$^3H_2$]hydroprene 6a (66% yield). The total radioactivity was 321 mCi giving a specific activity of 65.5 Ci/mmol: TLC, R_f 0.65; λ_{max} 261 nm (ϵ 32 500); ^1H NMR ($CDCl_3$) δ 0.87 (br d, J = 6.6 Hz, C-7 CH_3, C-11 CH_3, H-12), 1.29 (t, J = 7.2 Hz, OCH_2CH_3), 2.28 (d, J = 1.1 Hz, C-3 CH_3), 4.18 (q, J = 7.2 Hz, OCH_2CH_3), 5.70 (br s, H-12), 6.09 (m, H-4, H-5).

(*S*)-(−)-[6,7-$^3H_2$]Dihydrocitronellyl Acetate (8). To 60 mg (0.303 mmol) of citronellyl acetate (7) in 20 mL of EtOAc was added 20 mg of 10% Pd/C catalyst. The mixture was degassed three times, flushed with tritium gas, and stirred under a tritium atmosphere for 1 h. The mixture was filtered (Florisil), concentrated, and chromatographed (5% EtOAc–hexane) to give 45 mg (0.225 mmol) of the radiolabeled acetate 8, specific activity >60 Ci/mmol (74% yield). Autoradiography of TLC plates indicated that the radioactivity comigrated with radioinert dihydrocitronellyl acetate: TLC; R_f 0.72.

(*S*)-(−)-[6,7-$^3H_2$]Dihydrocitronellol (9). To 3.0 mg (0.014 mmol) of 8 in 1 mL of MeOH was added 0.5 mL of a 3 N NaOH solution. The mixture was stirred at room temperature for 4 h or until hydrolysis was complete (TLC). The reaction mixture was poured into 10 mL of a 1:1 ether–water solution, washed (water–brine), dried ($MgSO_4$), concentrated, and chromatographed (10% EtOAc–hexane) to give 1.3 mg (0.008 mmol) of the labeled alcohol 9 (60% yield). RTLCS indicated that the radioactivity comigrated with radioinert dihydrocitronellol (>90% ^3H radiochemical purity): TLC, R_f 0.27.

(*S*)-(−)-[6,7-$^3H_2$]Dihydrocitronellal (10). To 1.3 mg (0.008 mmol) of 5 in 1 mL of CH_2Cl_2 at ambient temperature was added 6 mg (0.016 mmol) of pyridinium dichromate (PDC). The reaction was stirred for 4 h and diluted with 20 mL of ether. The organics were filtered through Florisil, concentrated and chromatographed (10% EtOAc–hexane) to give 0.72 mg (0.0046 mmol) of the labile labeled aldehyde 10 (55% yield). RTLCS indicated that the radioactivity comigrated with radioinert dihydrocitronellal (>90% ^3H radiochemical purity): TLC, R_f 0.42.

Ethyl [10,11-H_2]-(2*E*,4*E*)-3,7,11-Trimethyl-2,4-dodecadienoate (6a). To 0.18 mg (0.0012 mmol) of aldehyde 5 in 0.4 mL of dry DMF was added 0.5 mg (0.0019 mmol) of diethyl [3-(ethoxycarbonyl)-2-methyl-2-propenyl]phosphonate and 0.1 mL of a 0.065 M solution of NaOEt in EtOH of 0 °C under nitrogen. The reaction was stirred at room temperature for 1.5 h and then poured into brine. The organics were extracted with 1:1 ether–hexane, dried ($MgSO_4$), and chromatographed (1% ether–hexane) to give a 2:1 mixture of 2*E*,4*E*/2*Z*,4*E* isomers of [$^3H_2$]hydroprene. The two isomers were separated by HPLC (0.5% ether–hexane) to give 0.12 mg (0.000 45 mmol) of pure (2*E*,4*E*)-[$^3H_2$]hydroprene (38% yield) calculated by mass and by UV absorption. The total radioactivity was 51.4 mCi giving a specific activity of 114 Ci/mmol.

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Preparation of 5-Alkyl-2-*tert*-butyl-1,3-dioxolan-4-ones by Trimethylsilyl Triflate Catalyzed Reactions between Bis(trimethylsilyl) Derivatives of α-Hydroxy Carboxylic Acids and Pivaldehyde

Thomas R. Hoye,*† Brian H. Peterson, and Jeanne D. Miller

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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That 5-alkyl-2-*tert*-butyl-1,3-dioxolan-4-ones **1** are useful substrates[1] for self-reproduction of chirality[2] and other applications[3] has been effectively demonstrated. Having a need for some optically pure 2-alkylated derivatives of malic acid, having had some difficulty in preparing the dioxolanone **1a** by the direct acid-catalyzed condensation of malic acid with pivaldehyde,[1] and aware of the useful ketalization method of Noyori involving trimethylsilyl triflate catalyzed reactions of bis(trimethylsilyl) ethers of vicinal diols with ketones,[4] we have studied the analogous transformations of the trimethylsilyl α-[(trimethylsilyl)-oxy]acetate derivatives **2** with trimethylsilyl triflate (Me_3SiOTf) and pivaldehyde. Others have recently described preparations of 1,3-dioxan-4-one acetals[5] and 1,3-dioxolan-4-one ketals[3b,6] by Me_3SiOTf-catalyzed cycliza-

† Fellow of the Alfred P. Sloan Foundation.

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