

Triphenylphosphine-Mediated Reduction of Electron-Deficient Propargyl Ethers to the Allylic Ethers

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Semihydrogenation of α,β -unsaturated ynoates and -ynones bearing a γ -alkoxy group can be performed using triphenylphosphine and water. α,β -Unsaturated ynoates were reduced to a mixture of *cis* and *trans* α,β -unsaturated enoates, whereas, ynones were reduced to *trans* α,β -unsaturated enones as the only products.

INTRODUCTION

Of the many methods available for reduction of alkynes, catalytic hydrogenation is one of the most convenient. The complete reduction of alkynes to the alkanes is easily accomplished with hydrogen over catalytic platinum, palladium or Raney nickel.¹ However, most useful from a synthetic point of view is the semihydrogenation² of alkynes to the *Z*-alkenes using Lindlar's catalyst³ or to the *E*-alkenes using sodium and liquid ammonia.⁴ Moreover, the reduction of propargyl alcohols to the *trans* allylic alcohols can also be performed using lithium aluminum hydride.⁵ The above known methods have fallen almost exclusively into the domain of metals or metal hydrides and often encountered severe reaction conditions. Therefore, an inexpensive reagent, which may exhibit a simple reaction condition for the semihydrogenation of alkynes, will attract much attention. It was previously reported that conjugated ynones isomerized to the dienones in the presence of a catalytic amount of triphenylphosphine;⁶ however, the less electron-deficient ynoates, required the more nucleophilic tributylphosphine⁶ or higher temperatures.⁷ The use of triphenylphosphine for the simple functional groups transformation as described above encourages us to further investigate this reagent. Herein, we wish to report a new type of reaction mediated by triphenylphosphine that provides a convenient reduction of α,β -unsaturated propargyl ethers to the corresponding allylic ethers.

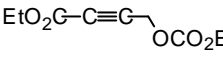
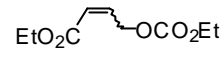
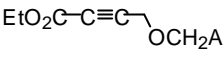

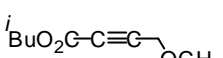

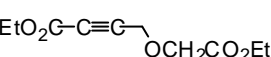
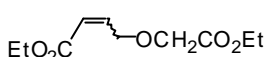
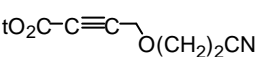
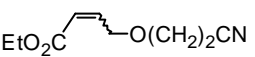
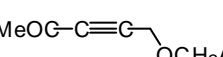
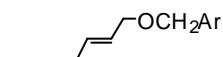
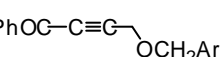
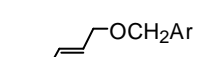
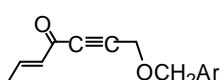
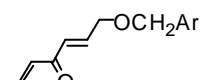
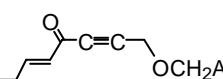
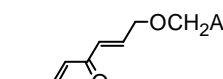
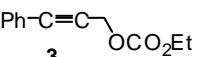
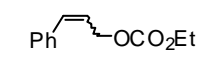
RESULTS AND DISCUSSION

The α,β -unsaturated ynoates and -ynones bearing a γ -alkoxy group were easily prepared starting from propargyl alcohol (see experimental section). Reaction of the ynoate **1a** and triphenylphosphine (1.1 equiv) in toluene at 5 °C afforded within 6 h a mixture of *cis* and *trans* allylic alcohols **2a**

(*cis*-**2a**/*trans*-**2a** = 2.8/1) in 79% yield after aqueous quenching and flash column chromatography on silica gel (entry 1, Table 1). In an effort to accelerate this process, we considered the use of a 2.0 molar equiv of triphenylphosphine. Thus, the reaction of **1a** with triphenylphosphine (2.0 equiv) in toluene at 5 °C generated within 2 h the *cis*-**2a** and *trans*-**2a** with the similar *cis/trans* ratio and isolated yield. Various α,β -unsaturated ynoates **1b-e** were reduced to *cis*- and *trans* α,β -unsaturated enoates **2b-e** using triphenylphosphine (2.0 equiv) under the same reaction conditions and the results are listed in Table 1 (entries 2-5). Whereas, α,β -unsaturated ynones **1f-i** underwent a smooth reduction even at -78 °C. The strong electron-withdrawing acyl substituent facilitates the reduction and the ynones **1f-i** are reduced at -78 °C to enones **2f-i** within 2 h in 47-79% yield (entries 6-9, Table 1). Only the *trans* α,β -unsaturated enone is isolated in each case. The compatibility of a phenyl (entry 7), an olefin (entry 8) and a diene (entry 9) moiety, which may not survive in sodium/ammonia or transition metal catalyzed reduction reactions, highlights the virtues of this semihydrogenation reaction. It must be mentioned that an electron-withdrawing group such as an ester or a keto attached to the triple bond is required for the semihydrogenation using triphenylphosphine and water. Phenylacetylene derivative **3** is recovered quantitatively after treatment with triphenylphosphine in refluxing toluene for 12 h (entry 10, Table 1).

Scheme I outlines a potential mechanism for the reduction of the 4-alkoxy ynoates and -ynones in which the role of triphenylphosphine is proposed as a nucleophile. Conjugated addition of triphenylphosphine to the triple bond produced the zwitterionic intermediate **4**. Although allene intermediates were proposed in the isomerization of triple bonds to the dienes using triphenylphosphine,^{6,7} allene **5** was not isolated. This may indicate that the proton exchange between the vinyl carbanion and the allylic hydrogen (to give **6**) was not favorable. It is assumed that the electron repulsion imposed by the

Table 1. Triphenylphosphine-Mediated Reduction of Electron-Deficient Propargyl Ethers to the Allylic Ethers

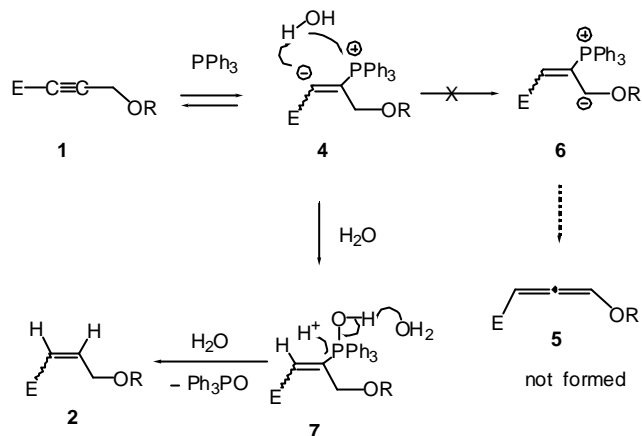
Entry	Substrate	Product	Isolated Yield	<i>Cis/Trans</i> ratio
1	 1a	 2a	79%	2.8 : 1
2 ^a	 1b	 2b	75%	2.0 : 1
3 ^a	 1c	 2c	76%	1.9 : 1
4	 1d	 2d	45%	1 : 1.2
5	 1e	 2e	52%	1 : 3.3
6 ^a	 1f	 2f	47%	trans only
7 ^a	 1g	 2g	79%	trans only
8 ^a	 1h	 2h	48%	trans only
9 ^a	 1i	 2i	54%	trans only
10	 3	 2	0%	

^a Ar = 4-methoxyphenyl

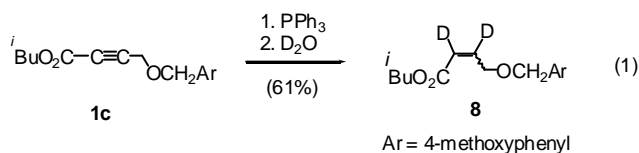
adjacent lone pair electrons of the oxygen atom impeded the formation of the allylic carbanion. Addition of water to **4** generated the intermediate **7**. Reaction of **7** with water afforded the α,β -unsaturated enoate or enone **2** after elimination of

triphenylphosphine oxide. A deuterium study further proved the proposed reaction path. Thus, quenching the reaction mixture obtained from addition of triphenylphosphine to **1c** with D_2O generated the dideuterated compound **8** in 61%

Scheme I

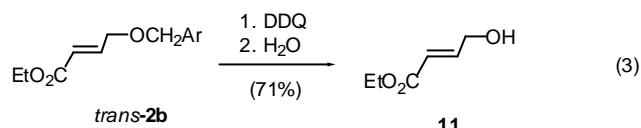
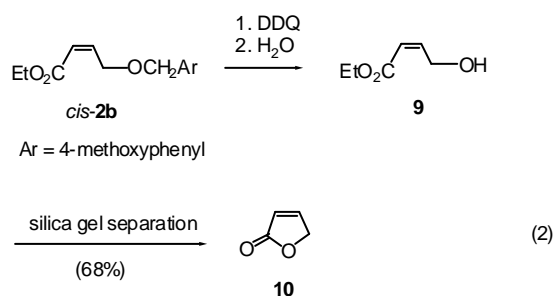


yield. The NMR study of **8** showed the deuterium incorporation (greater than 97%) at both vinyl carbons and less than 3% of the deuterium labeling at the allylic carbon (eq. 1).



Based upon the reaction path suggested in Scheme I, both *cis* and *trans* 4-alkoxyenoates and -enones are formed under the reaction conditions. However, the α,β -unsaturated *cis*-enones readily convert to the α,β -unsaturated *trans*-enones upon aqueous workup.² Thus, only the *trans*-enones are isolated from reduction of α,β -unsaturated ynones with triphenylphosphine (entries 6-9, Table 1).

The resulting α,β -unsaturated enoates *cis*-**2b** and *trans*-**2b** can further be manipulated as follows. Treatment of *cis*-**2b** with DDQ (2.0 equiv) in CH_2Cl_2 at 30 °C afforded within 4 h ethyl *cis*-4-hydroxy-2-butenate (**9**),⁸ which underwent lactonization upon purification on silica gel to afford 2(5*H*)-furanone (**10**)⁹ in 68% overall yield (eq. 2). Under the same



reaction conditions, *trans*-**2b** produced ethyl *trans*-4-hydroxy-2-butenate (**11**)¹⁰ in 71% yield (eq. 3).

In summary, we have described a novel, practical method for semihydrogenation of α,β -unsaturated enoates and -ynones bearing a γ -alkoxy group to the corresponding α,β -unsaturated enoates and -enones. The fact that the semihydrogenation of the carbon-carbon triple bonds proceeds under mild reaction conditions using triphenylphosphine and water offers a new synthetic method for this important organic transformation.

EXPERIMENTAL

All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Toluene was distilled from calcium hydride under nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from a deep blue sodium benzophenone ketyl solution. Flash column chromatography, following the method of Still,¹¹ was carried out with E. Merck 230-400 mesh silica gel using the indicated solvents. Analytical thin-layer chromatography was performed with silica gel 60 F₂₅₄ plastic plates of 0.2-mm thickness. The term "concentration" refers to the removal of solvent with an aspirator pump. The term "under nitrogen" implies that the apparatus was evacuated (oil pump) and then filled with nitrogen three times. Nuclear magnetic resonance (NMR) spectra were recorded at 200 and 400 MHz for ¹H NMR and 50.2 and 100.4 MHz for ¹³C NMR, and Varian G-200 (200 MHz) spectrometers. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (*m/z*) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Hsin-Chu, Taiwan. Elemental analyses were obtained with a Perkin-Elmer CHN-2400 elemental analyzer at the Microanalytical Service Laboratory of National Taiwan University.

Starting Materials

The following starting materials were prepared according to literature procedures: ethyl 4-carbomethoxy methoxybut-2-ynoate (**1d**),¹² ethyl 4-(2-cyanoethoxy)but-2-ynoate (**1e**)¹² and 5-(4-methoxybenzyloxy)pent-3-yn-2-one (**1f**).¹³

Ethyl 4-ethoxycarbonyloxybut-2-ynoate (**1a**)

A mixture of propargyl alcohol (0.48 g, 8.50 mmol) and *n*-BuLi (12.5 mL, 18.70 mmol) in 20 mL of THF was stirred at -78 °C for 0.5 h under nitrogen. The reaction mixture was quenched with 1.77 mL (18.70 mmol) of ethyl chloroformate at -78 °C. The reaction mixture was stirred at -78 °C for 30 min and 5 °C for 2 h before being diluted with a mixture of ethyl acetate and hexanes (1/5, 50 mL). The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate, and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **1a** (1.32 g, 6.53 mmol, 77%) as a colorless oil: IR (CH₂Cl₂) 2991, 2982, 2251, 1712, 1620 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.85 (s, 2H), 4.27 (m, 4H), 1.33 (t, *J* = 7.3 Hz, 3H), 1.32 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100.4 MHz, CDCl₃) δ 154.1, 152.6, 80.0, 78.4, 64.7, 62.1, 54.2, 14.0, 13.8; MS (EI) *m/z* (rel intensity) 201 (M⁺+1, 1), 155 (100), 127 (16), 111 (16), 108 (27), 101 (14), 84 (30), 67 (10); HRMS (EI) *m/z* calcd for C₉H₁₃O₅ (M⁺+1) 201.0764, found 201.0762.

Ethyl 4-(4-methoxybenzyloxy)but-2-ynoate (**1b**)

A mixture of propargyl alcohol (5.0 g, 89.28 mmol) and sodium hydride (3.9 g, 60% in mineral oil, 97.50 mmol) in 30 mL of THF was stirred at 5 °C for 0.5 h under nitrogen. The reaction mixture was quenched with 4-methoxybenzyl bromide (17.95 g, 89.28 mmol) and stirred at 25 °C for 8 h. The reaction mixture was diluted with hexane followed by the usual workup to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give 3-(4-Methoxybenzyloxy)propyne (12.60 g, 71.59 mmol, 80%). To a mixture of 3-(4-Methoxybenzyloxy)propyne (5.0 g, 28.41 mmol) and *n*-BuLi (1.6 M in hexanes, 18.7 mL, 29.92 mmol) in 25 mL of THF at -78 °C under nitrogen was added ethyl chloroformate (3.24 g, 29.83 mmol). The reaction mixture was stirred at -78 °C for 30 min and 5 °C for 2 h and was diluted with a mixture of ethyl acetate and hexanes (1/1, 100 mL). The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate, and concentrated to give the crude mixture. Flash column chromatography (silica gel, 8% ethyl acetate/hexanes) to give **1b** (5.04 g,

20.32 mmol, 72%) as a colorless oil: IR (CH₂Cl₂) 3047, 2994, 2984, 2236, 1711, 1613, 1586, 1512, 1466, 1367 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.28 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.55 (s, 2H), 4.20-4.30 (m, 4H), 3.81 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (50.2 MHz, CDCl₃) δ 159.51, 153.04, 129.74, 128.69, 113.78, 83.16, 78.02, 71.49, 61.92, 56.15, 55.03, 13.73; MS (EI) *m/z* (rel intensity) 248 (M⁺, 78), 201 (18), 175 (26), 147 (27), 137 (43), 136 (42), 135 (78), 121 (100), 120 (65); HRMS (EI) *m/z* calcd for C₁₄H₁₆O₄ 248.1049, found 248.1051.

iso-Butyl 4-(4-methoxybenzyloxy)but-2-ynoate (**1c**)

A mixture of 3-(4-Methoxybenzyloxy)propyne (1.5 g, 8.52 mmol) and *n*-BuLi (1.6 M in hexanes, 5.9 mL, 9.44 mmol) in 20.0 mL of THF at -78 °C under nitrogen was quenched with *t*-butyl chloroformate (1.29 g, 9.44 mmol) to give **1c** (2.25 g, 8.18 mmol, 96%) as a colorless oil: IR (CH₂Cl₂) 3060, 2966, 2876, 2239, 1698, 1613, 1586, 1513, 1469, 1419 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.51 (s, 2H), 4.21 (s, 2H), 3.95 (d, *J* = 6.6 Hz, 2H), 3.75 (s, 3H), 2.01-1.82 (m, 1H), 0.96 (s, 3H), 0.92 (s, 3H); ¹³C NMR (50.2 MHz, CDCl₃) δ 159.37, 152.97, 129.57, 128.58, 113.61, 83.13, 76.34, 71.63, 71.36, 56.02, 54.80, 27.21, 18.56; MS (EI) *m/z* (rel intensity) 276 (M⁺, 25), 219 (14), 190 (18), 175 (41), 146 (28), 137 (30), 136 (41), 135 (82), 121 (100), 120 (58). Anal. Calcd for C₁₆H₂₀O₄: C, 69.54; H, 7.30. Found: C, 69.50; H, 7.03.

4-(4-Methoxybenzyloxy)-1-phenylbut-2-yn-1-one (**1g**)

A mixture of 3-(4-Methoxybenzyloxy)propyne (1.00 g, 5.68 mmol) and *n*-BuLi (1.6 M in hexanes, 4.3 mL, 6.82 mmol) in 20.0 mL of THF at -78 °C under nitrogen was quenched with benzoyl chloride (0.88 g, 6.25 mmol) to give **1g** (1.30 g, 4.81 mmol, 82%) as a colorless oil: IR (CH₂Cl₂) 3060, 3008, 2988, 2959, 2912, 2866, 2228, 2060, 1723, 1582, 1465, 1422, 1349, 1275, 1268, 1243, 1001 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 8.14 (d, *J* = 7.0 Hz, 2H), 7.63-7.46 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.64 (s, 2H), 4.43 (s, 2H), 3.81 (s, 3H); ¹³C NMR (50.2 MHz, CDCl₃) δ 177.50, 159.69, 136.46, 134.29, 129.89, 129.63, 128.86, 128.65, 113.99, 90.29, 84.13, 71.86, 56.72, 55.18; MS (EI) *m/z* (rel intensity) 280 (M⁺, 8), 250 (3), 222 (2), 175 (2), 144 (81), 137 (48), 121 (100), 105 (59), 77 (66), 54 (18). Anal. Calcd for C₁₈H₁₆O₃: C, 77.12; H, 5.75. Found: C, 76.71; H, 5.57.

(*E*)-1-(4-Methoxybenzyloxy)hept-5-en-2-yn-4-one (**1h**)

A mixture of 3-(4-Methoxybenzyloxy)propyne (1.00 g, 5.68 mmol) and *n*-BuLi (1.6 M in hexanes, 4.30 mL, 6.82

mmol) in 15.0 mL of THF at $-78\text{ }^{\circ}\text{C}$ under nitrogen was quenched with *trans*-crotonyl chloride (0.65 g, 6.25 mmol) to give **1h** (0.95 g, 3.89 mmol, 69%) as a colorless oil: IR (CH_2Cl_2) 3068, 2988, 2866, 2216, 1646, 1628, 1586, 1465, 1441, 1376, 1350, 1303, 1270, 1252, 1034 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.28 (d, $J = 8.4$ Hz, 2H), 7.24–7.09 (m, 1H), 6.89 (d, $J = 8.2$ Hz, 2H), 6.19 (d, $J = 15.6$ Hz, 1H), 4.56 (s, 2H), 4.31 (s, 2H), 3.79 (s, 3H), 1.97 (dd, $J = 7.0, 1.6$ Hz, 3H); ^{13}C NMR (50.2 MHz, CDCl_3) δ 177.81, 159.61, 150.18, 133.56, 129.80, 128.84, 113.92, 88.08, 83.46, 71.72, 56.58, 55.17, 18.30; MS (EI) m/z (relintensity) 244 (M^+ , 5), 213 (1), 186 (5), 171 (5), 145 (10), 137 (59), 121 (100), 108 (84), 91 (12), 77 (30), 69 (23), 66 (5). Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3$: C, 73.75; H, 6.60. Found: C, 73.45; H, 6.80.

(5E,7E)-1-(4-Methoxybenzyloxy)nona-5,7-dien-2-yn-4-one (1i)

A mixture of 3-(4-Methoxybenzyloxy)propyne (2.32 g, 13.19 mmol) and *n*-BuLi (1.6 M in hexanes, 9.90 mL, 15.83 mmol) in 20.0 mL of THF at $-78\text{ }^{\circ}\text{C}$ under nitrogen was quenched with *trans*-sorbic acid chloride (2.07 g, 15.83 mmol) to give **1i** (2.15 g, 7.95 mmol, 61%) as a colorless oil: IR (CH_2Cl_2) 3069, 3047, 2989, 2840, 2211, 1624, 1587, 1514, 1420, 1300, 1243, 1082 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.41 (ddd, $J = 15.4, 10.0, 2.8$ Hz, 1H), 7.30 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 6.30 (m, 2H), 6.14 (d, $J = 14.8$ Hz, 1H), 4.58 (s, 2H), 4.34 (s, 2H), 3.80 (s, 3H), 1.90 (d, $J = 5.0$ Hz, 3H); ^{13}C NMR (50.2 MHz, CDCl_3) δ 178.00, 159.64, 149.24, 142.71, 130.09, 129.85, 129.51, 128.91, 113.95, 87.93, 83.83, 71.69, 56.67, 55.20, 18.86; MS (EI) m/z (relintensity) 269 (M^+ , 1), 258 (11), 227 (5), 213 (4), 199 (12), 175 (5), 145 (18), 137 (34), 135 (42), 121 (100), 109 (9), 77 (8), 66 (3); HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$ 270.1256, found 270.1254.

General procedure for semihydrogenation of 4-alkoxyenoates and -ynones using triphenylphosphine and water

A mixture of 4-alkoxyenoates or -ynones, triphenylphosphine (2.0 molar equiv) in 20 mL of toluene was stirred at $5\text{ }^{\circ}\text{C}$ ($-78\text{ }^{\circ}\text{C}$ for ynones) for 2 h under nitrogen. The reaction mixture was then quenched with 5 mL of water at $5\text{ }^{\circ}\text{C}$ and was diluted with a mixture of ethyl acetate and hexanes (1/5, 50 mL). The resulting solution was washed with water (100 mL \times 3) and brine (100 mL \times 3), dried over anhydrous magnesium sulfate, and concentrated to give the crude mixture.

Ethyl 4-ethoxycarbonyloxybut-2-enoate (2a)

The crude mixture obtained from addition of triphenylphosphine (2.1 g, 8.0 mmol) to **1a** (0.8 g, 4.0 mmol) at $5\text{ }^{\circ}\text{C}$ was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give *cis*-**2a** (0.47 g, 2.33 mmol, 58%) and *trans*-**2a** (0.17 g, 0.84 mmol, 21%) as colorless oils.

Cis-isomer

IR (CH_2Cl_2) 3052, 3047, 2992, 2982, 1747, 1715, 1656, 1390, 1373, 1342 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.25 (dt, $J = 11.8, 5.0$ Hz, 1H), 5.83 (dt, $J = 11.8, 2.4$ Hz, 1H), 5.19 (dd, $J = 2.2$ Hz, 2H), 4.23–4.09 (m, 4H), 1.31–1.15 (m, 6H); ^{13}C NMR (50.2 MHz, CDCl_3) δ 165.59, 154.91, 144.12, 120.69, 65.67, 64.06, 60.33, 14.04, 13.98; MS (EI) m/z (relintensity) 202 (M^+ , 41), 200 (17), 199 (100), 198 (44), 183 (30), 149 (32). Anal. Calcd for $\text{C}_9\text{H}_{14}\text{O}_5$: C, 53.46; H, 6.98. Found: C, 53.63; H, 6.81.

Trans-isomer

IR (CH_2Cl_2) 3054, 2990, 2985, 1748, 1715, 1635, 1446, 1425, 1372, 1340, 1288 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.93 (dt, $J = 15.8, 4.6$ Hz, 1H), 6.06 (dt, $J = 15.8, 1.8$ Hz, 1H), 4.78 (dd, $J = 2.0$ Hz, 2H), 4.28–4.15 (m, 4H), 1.42–1.25 (m, 6H); ^{13}C NMR (50.2 MHz, CDCl_3) δ 154.76, 140.50, 122.59, 65.59, 64.41, 60.58, 14.13, 14.10; MS (EI) m/z (relintensity) 202 (M^+ , 5), 200 (12), 189 (24), 157 (63), 129 (61), 128 (37), 127 (100), 101 (82), 100 (36), 99 (96), 86 (58), 73 (48). Anal. Calcd for $\text{C}_9\text{H}_{14}\text{O}_5$: C, 53.46; H, 6.98. Found: C, 53.51; H, 7.05.

Ethyl 4-(4-methoxybenzyloxy)but-2-enoate (2b)

The crude mixture obtained from addition of triphenylphosphine (2.09 g, 8.00 mmol) to **1b** (1.00 g, 4.00 mmol) at $5\text{ }^{\circ}\text{C}$ was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give *cis*-**2b** (0.50 g, 2.00 mmol, 50%) and *trans*-**2b** (0.25 g, 1.00 mmol, 25%) as colorless oils.

Cis-isomer

IR (CH_2Cl_2) 3055, 2984, 2961, 1714, 1651, 1613, 1514, 1465, 1444, 1417, 1384 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.26 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 6.40 (dt, $J = 11.6, 4.8$ Hz, 1H), 5.79 (dt, $J = 11.8, 2.4$ Hz, 1H), 4.61 (q, $J = 2.4$ Hz, 2H), 4.45 (s, 2H), 4.13 (q, $J = 7.0$ Hz, 2H), 3.74 (s, 3H), 1.26 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (50.2 MHz, CDCl_3) δ 165.73, 159.14, 148.19, 129.86, 129.18, 119.21, 113.58,

72.21, 67.85, 59.80, 54.12, 13.84; MS (EI) m/z (rel intensity) 250 (M^+ , 1), 138 (39), 137 (68), 136 (100), 121 (92), 120 (57); HRMS (EI) m/z calcd for $C_{14}H_{19}O_4$ ($M^+ + 1$) 251.1205, found 251.1280.

Trans-isomer

IR (CH_2Cl_2) 3049, 2987, 2961, 2939, 1715, 1663, 1613, 1586, 1514, 1465, 1368, 1305 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 7.25 (d, $J = 8.2$ Hz, 2H), 6.97 (dd, $J = 15.6, 4.4$ Hz, 1H), 6.87 (d, $J = 8.2$ Hz, 2H), 6.11 (dt, $J = 15.6, 2.2$ Hz, 1H), 4.47 (s, 2H), 4.23–4.10 (m, 4H), 3.77 (s, 3H), 1.27 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 166.17, 159.29, 144.73, 129.71, 129.16, 121.24, 113.73, 72.24, 68.14, 60.10, 55.00, 13.98; MS (EI) m/z (rel intensity) 250 (M^+ , 25), 221 (15), 161 (26), 137 (22), 136 (50), 121 (98), 120 (97), 98 (62), 90 (81), 89 (100). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.85; H, 6.92.

iso-Butyl 4-(4-methoxybenzyloxy)but-2-enoate (2c)

The crude mixture obtained from addition of triphenylphosphine (2.85 g, 10.86 mmol) to **1c** (1.50 g, 5.43 mmol) at 5 °C was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give *cis*-**2c** (0.76 g, 2.73 mmol, 50%) and *trans*-**2c** (0.39 g, 1.41 mmol, 26%) as colorless oils.

Cis-isomer

IR (CH_2Cl_2) 3065, 3057, 2964, 1712, 1613, 1514, 1469, 1443, 1424, 1417 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 7.25 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 12.1$ Hz, 2H), 6.41 (dt, $J = 11.8, 4.8$ Hz, 1H), 5.81 (dt, $J = 11.6, 2.6$ Hz, 1H), 4.60 (q, $J = 2.4$ Hz, 2H), 4.45 (s, 2H), 3.87 (d, $J = 6.6$ Hz, 2H), 3.74 (s, 3H), 1.95–1.85 (m, 1H), 0.94 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 165.76, 159.11, 148.13, 129.95, 129.80, 129.15, 119.15, 113.70, 113.53, 70.01, 67.87, 54.74, 27.33, 18.72; MS (EI) m/z (rel intensity) 278 (M^+ , 2), 227 (25), 217 (11), 162 (10), 137 (58), 136 (42), 121 (100), 120 (98). Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.07; H, 7.60.

Trans-isomer

IR (CH_2Cl_2) 3052, 3048, 2965, 1715, 1613, 1514, 1468, 1424, 1304, 1286 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 7.25 (d, $J = 8.8$ Hz, 2H), 6.96 (dt, $J = 15.8, 4.4$ Hz, 1H), 6.88 (d, $J = 11.8$ Hz, 2H), 6.12 (dt, $J = 15.8, 2.0$ Hz, 1H), 4.46 (s, 2H), 4.11 (q, $J = 2.0$ Hz, 2H), 3.92 (d, $J = 6.6$ Hz, 2H), 3.76 (s, 3H), 1.97–1.87 (m, 1H), 0.95 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 166.12, 159.22, 144.18, 129.60, 129.12, 121.07, 113.64, 72.21, 70.17, 68.08, 54.88, 27.46, 18.77; MS (EI) m/z (rel intensity) 278 (M^+ , 5), 221 (21), 137 (60), 136

(42), 35 (22), 121 (100), 120 (53); HRMS (EI) m/z calcd for $C_{16}H_{22}O_4$ 278.1518, found 278.1514.

Ethyl 4-ethoxycarbonylmethoxybut-2-enoate (2d)

The crude mixture obtained from addition of triphenylphosphine (2.46 g, 0.94 mmol) to **1d** (0.10 g, 0.47 mmol) at 5 °C was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give *cis*-**2d** (0.02 g, 0.09 mmol, 20%) and *trans*-**2d** (0.03 g, 0.12 mmol, 25%) as colorless oils.

Cis-isomer

IR (CH_2Cl_2) 2993, 2978, 1751, 1714, 1651 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.42 (dt, $J = 11.7, 5.6$ Hz, 1H), 5.85 (d, $J = 11.7$ Hz, 1H), 4.69 (d, $J = 5.6$ Hz, 2H), 4.22 (q, $J = 7.3$ Hz, 2H), 4.16 (q, $J = 7.3$ Hz, 2H), 4.11 (s, 2H), 1.30 (t, $J = 7.3$ Hz, 3H), 1.27 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 170.1, 165.9, 147.0, 119.9, 69.6, 60.2, 14.2; MS (EI) m/z (rel intensity) 217 ($M^+ + 1$, 8), 170 (100), 143 (36), 129 (16), 113 (24), 101 (8), 83 (18); HRMS (EI) m/z calcd for $C_{10}H_{16}O_5$ 216.1234, found 216.1000.

Trans-isomer

IR (CH_2Cl_2) 2989, 1751, 1718, 1664 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.95 (dt, $J = 15.6, 4.5$ Hz, 1H), 6.10 (d, $J = 16.1$ Hz, 1H), 4.27 (d, $J = 4.5$ Hz, 2H), 4.25 (q, $J = 7.3$ Hz, 2H), 4.21 (q, $J = 7.3$ Hz, 2H), 4.17 (s, 2H), 1.31 (t, $J = 7.3$ Hz, 3H), 1.27 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 169.9, 166.0, 142.0, 122.0, 69.9, 67.9, 61.0, 60.4, 14.2; MS (EI) m/z (rel intensity) 217 ($M^+ + 1$, 18), 170 (100), 143 (42), 129 (10), 113 (6), 101 (6), 83 (12); HRMS (EI) m/z calcd for $C_{10}H_{16}O_5$ 216.1234, found 216.0664.

Ethyl 4-(2-cyanoethoxy)but-2-enoate (2e)

The crude mixture obtained from addition of triphenylphosphine (0.38 g, 1.44 mmol) to **1e** (0.13 g, 0.72 mmol) at 5 °C was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give *cis*-**2e** (0.02 g, 0.11 mmol, 14%) and *trans*-**2e** (0.05 g, 0.28 mmol, 38%) as colorless oils.

Cis-isomer

IR (CH_2Cl_2) 2989, 2879, 2254, 1712, 1651, 1631 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.34 (dt, $J = 11.7, 5.9$ Hz, 1H), 5.86 (d, $J = 11.7$ Hz, 1H), 4.64 (d, $J = 5.9$ Hz, 2H), 4.16 (q, $J = 7.3$ Hz, 2H), 3.70 (t, $J = 5.9$ Hz, 2H), 2.63 (t, $J = 7.3$ Hz, 2H), 1.29 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 165.9, 146.8, 120.1, 117.6, 69.0, 65.1, 60.3, 18.8, 14.2; MS (EI) m/z (rel intensity) 183 (M^+ , 5), 154 (8), 137 (100), 129 (20), 110 (8), 83 (48); HRMS (EI) m/z calcd for $C_9H_{13}NO_3$

183.2066, found 183.0891.

Trans-isomer

IR (CH₂Cl₂) 2991, 2982, 2254, 1722, 1664, 1304 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.94 (dt, *J* = 15.6, 4.3 Hz, 1H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.21 (m, 4H), 3.71 (d, *J* = 8.9 Hz, 2H), 2.64 (t, *J* = 8.9 Hz, 2H), 1.29 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100.4 MHz, CDCl₃) δ 166.0, 142.8, 122.0, 117.5, 69.8, 65.4, 60.5, 18.9, 14.2; MS (EI) *m/z* (rel intensity) 183 (M⁺, 100), 153 (6), 138 (100), 129 (10), 110 (22); HRMS (EI) *m/z* calcd for C₉H₁₃NO₃ 183.2066, found 183.0890.

(E)-5-(4-Methoxybenzyloxy)pent-3-en-2-one (2f)

The crude mixture obtained from addition of triphenylphosphine (2.39 g, 9.16 mmol) to **1f** (1.00 g, 4.58 mmol) at -78 °C was purified via flash column chromatography (silica gel, 15% ethyl acetate/hexanes) to give **2f** (0.47 g, 2.14 mmol, 47%) as a colorless oil: IR (CH₂Cl₂) 3061, 2938, 1721, 1678, 1633, 1613, 1514, 1422, 1360 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.78 (dt, *J* = 16.0, 2.2 Hz, 1H), 6.31 (dt, *J* = 16.0, 1.8 Hz, 1H), 4.48 (s, 2H), 4.15 (dd, *J* = 1.8 Hz, 2H), 3.78 (s, 3H), 3.24 (s, 3H); ¹³C NMR (50.2 MHz, CDCl₃) δ 198.01, 159.28, 143.07, 130.13, 129.56, 129.19, 113.70, 72.34, 68.26, 54.97, 26.90; MS (EI) *m/z* (rel intensity) 220 (M⁺, 5), 152 (9), 138 (21), 137 (93), 136 (21), 121 (100), 109 (22), 84 (24). Anal. Calcd for C₁₃H₁₆O₃: C, 70.89; H, 7.32. Found: C, 70.52; H, 7.29.

(E)-4-(4-Methoxybenzyloxy)-1-phenylbut-2-en-1-one (2g)

The crude mixture obtained from addition of triphenylphosphine (5.20 g, 19.87 mmol) to **1g** (2.79 g, 9.94 mmol) at -78 °C was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2g** (2.22 g, 7.87 mmol, 79%): IR (CH₂Cl₂) 3070, 3047, 3007, 2986, 2959, 1674, 1613, 1580, 1448, 1360, 1327, 1271, 1252, 1209, 1114 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.95 (d, *J* = 7.0 Hz, 2H), 7.57-7.43 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.11 (dt, *J* = 14.0, 3.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.56 (s, 2H), 4.26 (dd, *J* = 3.8, 1.6 Hz, 2H), 3.82 (s, 3H); ¹³C NMR (50.2 MHz, CDCl₃) δ 190.43, 159.45, 144.62, 137.71, 132.82, 129.82, 129.38, 128.62, 128.56, 124.93, 113.90, 72.56, 68.81, 55.17; MS (EI) *m/z* (rel intensity) 282 (M⁺, 1), 276 (2), 253 (2), 223 (1), 199 (1), 174 (3), 160 (5), 146 (40), 135 (17), 121 (100), 105 (33), 91 (7), 77 (18), 51 (4); HRMS (EI) *m/z* calcd for C₁₈H₁₈O₃ 282.1256, found 282.1258.

(2E,5E)-1-(4-Methoxybenzyloxy)hepta-2,5-dien-4-one (2h)

The crude mixture obtained from addition of triphenyl-

phosphine (0.64 g, 2.46 mmol) to **1h** (0.30 g, 1.23 mmol) at -78 °C was purified via flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **2h** (0.15 g, 0.59 mmol, 48%) as a colorless oil: IR (CH₂Cl₂) 3069, 3060, 2988, 2938, 1669, 1642, 1615, 1514, 1465, 1360, 1262, 1253, 1245, 1035 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.03-6.83 (m, 4H), 6.61 (dt, *J* = 15.6, 1.8 Hz, 1H), 6.33 (dt, *J* = 15.6, 1.8 Hz, 1H), 4.50 (s, 2H), 4.17 (dd, *J* = 4.2, 0.8 Hz, 2H), 3.79 (s, 3H), 1.90 (dd, *J* = 6.8, 1.0 Hz, 3H); ¹³C NMR (50.2 MHz, CDCl₃) δ 189.05, 159.36, 143.59, 142.56, 130.56, 129.76, 129.28, 127.42, 113.79, 72.39, 68.63, 55.09, 18.18; MS (EI) *m/z* (rel intensity) 246 (M⁺, 1), 203 (5), 173 (1), 147 (2), 135 (11), 121 (100), 110 (58), 95 (26), 69 (5); HRMS (EI) *m/z* calcd for C₁₅H₁₈O₃ 246.1256, found 246.1255.

(2E,5E,7E)-1-(4-Methoxybenzyloxy)nona-2,5,7-trien-4-one (2i)

The crude mixture obtained from addition of triphenylphosphine (2.52 g, 9.62 mmol) to **1i** (1.30 g, 4.81 mmol) at -78 °C was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2i** (0.71 g, 2.60 mmol, 54%) as a colorless oil: IR (CH₂Cl₂) 3066, 3060, 3047, 2986, 2960, 2840, 1664, 1640, 1614, 1514, 1465, 1444, 1378, 1288, 1275, 1174, 1034, 1001 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.25-7.18 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.90 (dt, *J* = 15.8, 4.2 Hz, 1H), 6.62 (dt, *J* = 15.8, 1.8 Hz, 1H), 6.33-6.18 (m, 3H), 4.51 (s, 2H), 4.19 (dd, *J* = 4.2, 2.0 Hz, 2H), 3.80 (s, 3H), 1.86 (d, *J* = 4.8 Hz, 3H); ¹³C NMR (50.2 MHz, CDCl₃) δ 189.31, 159.37, 143.93, 142.24, 140.66, 130.45, 129.79, 129.31, 127.98, 126.51, 113.82, 72.40, 68.67, 55.11, 18.63; MS (EI) *m/z* (rel intensity) 273 (M⁺-1, 2), 260 (1), 176 (2), 147 (2), 136 (62), 121 (100), 108 (10), 67 (2); HRMS (EI) *m/z* calcd for C₁₇H₂₀O₃ 272.1412, found 272.1411.

iso-Butyl 4-(4-methoxybenzyloxy)-2,3-dideuterobut-2-enoate (8)

The crude mixture obtained from addition of triphenylphosphine (0.26 g, 1.0 mmol) to **1c** (0.27 g, 1.0 mmol) followed by quenching the reaction mixture with 0.6 mL of D₂O was purified via flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give *cis*-**8** (0.11 g, 0.39 mmol, 39%) and *trans*-**8** (0.06 g, 0.21 mmol, 22%) as colorless oils.

Cis-isomer

¹H NMR (200 MHz, CDCl₃) δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.61 (s, 2H), 4.48 (s, 2H), 3.89 (d, *J* = 6.6 Hz, 2H), 3.80 (s, 3H), 1.94-1.83 (m, 1H), 0.93 (d, *J* = 6.8

Hz, 6H); ^{13}C NMR (50.2 MHz, CDCl_3) δ 166.05, 159.28, 148.05, 129.95, 129.37, 113.75, 72.42, 70.25, 67.96, 55.05, 27.51, 18.91.

Trans-isomer

^1H NMR (200 MHz, CDCl_3) δ 7.28 (d, $J = 8.6$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 4.49 (s, 2H), 4.17 (s, 2H), 3.93 (d, $J = 6.6$ Hz, 2H), 3.81 (s, 3H), 2.00–1.81 (m, 1H), 0.94 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (50.2 MHz, CDCl_3) δ 166.39, 159.40, 144.29, 129.78, 129.31, 121.36, 113.85, 72.42, 70.40, 68.18, 55.15, 27.65, 18.95.

2(5*H*)-Furanone (10)⁹

A mixture of *cis*-**2b** (0.3 g, 1.20 mmol), DDQ (0.54 g, 2.40 mmol), and water (1.0 mL) in 17.0 mL of dichloromethane was stirred at 25°C for 4 h under nitrogen. The reaction mixture was diluted with dichloromethane (50.0 mL) and filtered through celite. The resultant solution was washed with water (100 mL \times 3) and brine (100 mL \times 3), dried over anhydrous magnesium sulfate, and concentrated to give the crude mixture. The ^1H NMR spectral data of the crude mixture was identified as enonoate **9**.⁸ The crude mixture was purified via flash column chromatography (silica gel, 30% ethyl acetate/hexanes) to give **10** (68.0 mg, 0.81 mmol, 68%) as a colorless oil: ^1H NMR (200 MHz, D_2O) δ 7.78 (dt, $J = 5.4, 1.0$ Hz, 1H), 6.13–6.12 (m, 1H), 4.96–4.94 (m, 2H); ^{13}C NMR (50.2 MHz, CDCl_3) δ 173.90, 153.30, 121.11, 72.12.

Ethyl (*E*)-4-hydroxy-2-butenolate (11)¹⁰

The crude mixture obtained from reaction (as described above for **9**) of *trans*-**2b** (0.30 g, 1.20 mmol), DDQ (0.55 g, 2.42 mmol), and water (1.0 mL) was purified via flash column chromatography (silica gel, 20% ethyl acetate/hexanes) to give **11** (0.11 g, 0.85 mmol, 71%) as a colorless oil. ^1H NMR (200 MHz, CDCl_3) δ 7.03 (dt, $J = 15.8, 4.0$ Hz, 1H), 6.09 (dt, $J = 15.4, 2.0$ Hz, 1H), 4.35 (dd, $J = 4.0, 2.0$ Hz, 2H), 4.19 (q, $J = 7.2$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (50.2 MHz, CDCl_3) δ 166.80, 147.37, 119.83, 61.42, 60.39, 13.95.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the National Science Council of the Republic of China (NSC-89-2113-M-003-020) for financial support.

Received March 26, 2001.

Key Words

Triphenylphosphine; Propargyl ether;
Semihydrogenation; α,β -Unsaturated ynoate;
 α,β -Unsaturated ynone; α,β -Unsaturated enoate;
 α,β -Unsaturated enone.

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