Oxidative Cross-Coupling of Acrylates with Vinyl Carboxylates Catalyzed by Pd(OAc)₂/HPMoV/O₂ System

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Supporting Information

Table of contents

S1-S4: Experimental Procedures and spectral data for the products **3aa-3fd**

S5: Copies of ¹H and ¹³C NMR spectra for **3aa**

S6: Copies of ¹H and ¹³C NMR spectra for **3ba**

S7: Copies of ¹H and ¹³C NMR spectra for **3ca**

S8: Copies of ¹H and ¹³C NMR spectra for **3da**

S9: Copies of ¹H and ¹³C NMR spectra for **3fa**

S10: Copies of ¹H and ¹³C NMR spectra for **3fd**

Experimental Section

General Procedures. All starting materials were commercially available and used without further purification. GLC analysis was performed with a flame ionization detector using a 0.2 mm x 25 m capillary column (OV-1). ^1H - and ^{13}C -NMR were measured at 270 MHz and 67.5 MHz, respectively, in CDCl_3 with Me_4Si as the internal standard.

Procedure for Oxidative Cross-Coupling of *n*-Butyl Acrylate (**1c**) with Vinyl Acetate (**2a**).

A solution of $\text{Pd}(\text{OAc})_2$ (0.1 mmol), $\text{H}_4\text{PMo}_{11}\text{VO}_{40}\cdot n\text{H}_2\text{O}$ ($\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, $n = 30$) (46.7 mg, ca. 0.02 mmol), NaOAc (0.1 mmol), *n*-butyl acrylate (**1c**) (1 mmol), and vinyl acetate (**2a**) (5 mmol) in acetic acid (5 mL) was placed in a round-bottom flask (30 mL) equipped with a balloon filled with O_2 , and the mixture was allowed to react under stirring at 90 °C for 5 h. The reaction gave *n*-Butyl 5-(acetoxo)-2,4-pentadienoate (**3ca**) and *n*-butyl 3-acetoxo acrylate (**4c**) in 62% and 5% yields, respectively. The product was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane : ethyl acetate = 19:1). All yields were detected by GLC analysis with dimethyl adipate as internal standard. The products were characterized by ^1H and ^{13}C NMR, GC-MS, GC-IR and GC-HRMS, respectively.

Unfortunately, the products were difficult to be isolated in pure form, although these products were obtained in *E,E*-isomer rich form. The following spectral data showed the *E,E*-isomer of **3aa**, **3ba**, **3ca**, **3da**, and **3fa**. In order to show the purity, copies of ^1H and ^{13}C NMR spectra have been added on S5-S10. The purity was determined by the ^1H NMR and GC measurements.

***E,E*-Methyl 5-(acetoxo)-2,4-pentadienoate (3aa):** IR (neat, cm^{-1}) 892, 1111, 1205, 1655, 1743, 1791, 2960; ^1H NMR(270 MHz, CDCl_3) δ 2.20 (s, 3H), 3.74 (s, 3H), 5.90 (d, $J = 15.1$ Hz, 1H), 6.12 (d,d, $J = 11.8, 12.2$ Hz, 1H), 7.27 (d,d, $J = 11.8, 15.1$ Hz, 1H), 7.68 (d, $J = 12.2$ Hz,

1H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 20.7, 51.6, 113.0, 120.8, 140.3, 144.1, 166.5, 166.7; HRMS (EI) calcd for $\text{C}_8\text{H}_{10}\text{O}_4$ $[\text{M}]^+$ 170.0579, found 170.0574.

***E,E*-Ethyl 5-(acetox)-2,4-pentadienoate (3ba):** IR (neat, cm^{-1}) 896, 1110, 1206, 1654, 1737, 1789, 2986; ^1H NMR(270 MHz, CDCl_3) δ 1.30 (t, $J = 7.3$ Hz, 3H), 2.18 (s, 3H), 4.21 (q, $J = 7.3$ Hz, 3H), 5.90 (d, $J = 16.2$ Hz, 1H), 6.12 (d,d, $J = 11.6, 11.9$ Hz, 1H), 7.26 (d,d, $J = 11.9, 16.2$ Hz, 1H), 7.68 (d, $J = 11.6$ Hz, 1H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 14.3, 20.6, 60.3, 112.9, 121.3, 140.0, 143.9, 166.3, 166.8; HRMS (EI) calcd for $\text{C}_9\text{H}_{12}\text{O}_4$ $[\text{M}]^+$ 184.0736, found 184.0726.

***E,E-n*-Butyl 5-(acetox)-2,4-pentadienoate (3ca):** IR (neat, cm^{-1}) 893, 1110, 1205, 1654, 1736, 1791, 2969; ^1H NMR(270 MHz, CDCl_3) δ 0.95 (t, $J = 7.0$ Hz, 3H), 1.36-1.48 (m, 2H), 1.60-1.74 (m, 2H), 2.17 (s, 3H), 4.14 (t, $J = 7.0$ Hz, 2H), 5.90 (d, $J = 15.1$ Hz, 1H), 6.12 (d,d, $J = 11.9, 12.2$ Hz, 1H), 7.29 (d,d, $J = 11.9, 15.1$ Hz, 1H), 7.68 (d, $J = 12.2$ Hz, 1H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 13.8, 19.2, 20.7, 30.8, 64.3, 113.0, 121.4, 140.0, 143.9, 166.5, 167.0; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4$ $[\text{M}]^+$ 212.1049, found 212.1037.

***E,E-i*-Butyl 5-(acetox)-2,4-pentadienoate (3da):** IR (neat, cm^{-1}) 889, 1110, 1205, 1654, 1736, 1791, 2969; ^1H NMR(270 MHz, CDCl_3) δ 0.95 (t, $J = 6.8$ Hz, 6H), 2.19 (s, 3H), 2.12-2.24 (m, 1H), 3.93 (d, $J = 6.8$ Hz, 2H), 5.92 (d, $J = 15.1$ Hz, 1H), 6.12 (d,d, $J = 11.3, 12.2$ Hz, 1H), 7.26 (d,d, $J = 11.3, 15.1$ Hz, 1H), 7.80 (d, $J = 12.2$ Hz, 1H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 19.2, 20.7, 27.8, 70.5, 113.0, 121.3, 140.0, 143.9, 166.5, 166.9; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4$ $[\text{M}]^+$ 212.1049, found 212.1062.

***E,E*-2-Ethylhexyl 5-(acetox)-2,4-pentadienoate (3fa):** IR (neat, cm^{-1}) 980, 1122, 1176, 1261, 1301, 1746, 1766, 2939, 2970; ^1H NMR(270 MHz, CDCl_3) δ 0.88-0.93 (m, 6H), 1.30-1.41 (m, 8H), 1.57-1.62 (m, 1H), 2.17-2.24 (m, 3H), 4.01 (d, $J = 5.9$ Hz, 2H), 5.91 (d, $J = 15.1$ Hz, 1H), 6.12 (d,d, $J = 11.6, 12.2$ Hz, 1H), 7.24 (d,d, $J = 11.6, 15.1$ Hz, 1H), 7.68 (d, $J = 12.2$ Hz, 1H); ^{13}C

NMR (67.5 MHz, CDCl_3) δ 11.1, 14.1, 20.7, 23.0, 23.9, 29.0, 30.5, 38.9, 66.8, 113.0, 121.4, 139.9, 143.9, 166.6, 167.0; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{24}\text{O}_4$ $[\text{M}]^+$ 268.1675, found 268.1685.

2-Ethylhexyl 5-(acetoxy)-5-(methyl)-2,4-pentadienoate (3fd); The information on stereochemistry of the product **3fd** has not been obtained. IR (neat, cm^{-1}) 1029, 1133, 1206, 1268, 1655, 1733, 1778, 2939, 2971; ^1H NMR (270 MHz, CDCl_3) δ 0.87-0.93 (m, 6H), 1.26-1.43 (m, 8H), 1.58-1.63 (m, 1H), 2.05-2.23 (m, 6H), 4.04-4.08 (m, 2H), 5.88 (d, $J = 15.4$ Hz, 1H), 5.96 (d, $J = 11.6$ Hz, 1H), 7.33 (d,d, $J = 11.6, 15.4$ Hz, 1H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 11.1, 14.1, 20.4, 20.9, 23.0, 23.9, 29.0, 30.5, 38.9, 66.8, 115.4, 120.5, 136.7, 153.1, 167.0, 168.1; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{26}\text{O}_4$ $[\text{M}]^+$ 282.1831, found 282.1839.

ca. 64% purity, *E,E*-rich on ^1H NMR

ca. 62% purity, *E,E*-rich on ^1H NMR

ca. 60% purity, *E,E*-rich on GC