Catalytic Ethenylation Reaction of Phenol Using $SnCl_4$

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^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Varian Mercury (400 MHz). Chemical shift values are given in ppm relative to internal Me_4Si. IR spectra were recorded on a JASCO FT/IR-410. MS spectra were taken with a JEOL JMS-DX303.

Ethenylation of Phenol. Under an argon atmosphere, to phenol (376 mg, 4.0 mmol) in chlorobenzene (12 mL) were added 1.6 M butyllithium in hexane (1.25 mL, 2.0 mmol) and $SnCl_4$ (0.12 mL, 1.0 mmol) at 0 °C, successively. The mixture was stirred for 10 min at room temperature, when trimethylsilylethyne (0.71 mL, 5.0 mmol) was added. Then, the mixture was heated at 105 °C for 3 h. Methanol (10 mL), THF (10 mL), and potassium fluoride (232 mg, 4.0 mmol) were added, and the organic materials were extracted with ethyl acetate, dried over $MgSO_4$, filtered, and concentrated to a small volume under reduced pressure (concentration to dryness caused the decomposition of the product). Flash chromatography (hexane:ethyl acetate = 50:1) over silica gel separated the product from a small amount of unreacted starting material. To the product was added pyridine (1.62 mL) and acetic anhydride (0.96 mL), and the mixture was stirred at room temperature for 12 h. The mixture was then poured into water, and the organic materials were extracted with ethyl acetate, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (hexane: ethyl acetate = 10:1) over silica gel gave 2-ethenylphenyl acetate (583 mg, 90%).

2-Ethenyl-6-ethylphenyl acetate. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.20 (3H, t, J = 3.6 Hz), 2.35 (3H, s), 2.52 (2H, q, J = 3.6 Hz), 5.31 (1H, dd, J = 10.8, 1.2 Hz), 5.73 (1H, dd, J = 17.2, 1.2 Hz), 6.68 (1H, dd, J = 17.2, 10.8 Hz), 7.17 (2H, m), 7.41 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.0, 20.4, 23.2, 116.0, 123.8, 125.9, 128.4, 130.2, 130.5, 136.0, 146.1, 168.5. IR (neat) 2970, 1763, 1209, 799, 752 cm^{-1}. MS (EI) m/z 190 (M^+, 15%), 148 (M^+-C_2H_3O, 100%). HRMS. Calc for $C_{12}H_{14}O_2$: 190.0994. Found: 190.0989.

2-Ethenyl-6-(isopropyl)phenyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (6H, d, J = 6.8 Hz), 2.36 (3H,s), 2.96 (1H, septet, J = 6.8 Hz), 5.31 (1H, dd, J = 11.2, 1.2 Hz), 5.72 (1H, dd, J = 17.6, 1.2 Hz), 6.67 (1H, dd, J = 17.6, 11.2 Hz), 7.22 (2H, m), 7.40 (1H, m). ^{13}C NMR (100 MHz, CDCl3): δ 20.8, 23.3, 27.6, 116.4, 123.9, 126.0, 126.3, 130.5, 130.9, 140.7, 145.5, 169.1. IR (neat) 2965, 1764, 1208, 797, 751 cm^{-1}. MS (EI) m/z 204 (M^+, 15%), 164 (M^+-C_2H_3O, 95%), 147 (M^+-C_2H_3O-CH_3, 100%). HRMS. Calc for $C_{13}H_{16}O_2$: 204.1150. Anal. Found: 204.1145.

2-Ethenyl-4-iodo-6-methylphenyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (3H, s), 2.34 (3H, s), 5.34 (1H, dd, J = 11.2, 1.2 Hz), 5.72 (1H, dd, J = 17.6, 1.2 Hz), 6.58 (1H, dd, J = 17.6, 11.2 Hz), 7.47 (1H, d, J = 1.2 Hz), 7.70 (1H, d, J = 1.2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.2, 20.6, 90.7, 117.6, 129.3, 132.6. 133.0, 133.1, 138.8, 146.7, 168.3. IR (neat) 2925, 1762, 1208, 837, 780 cm^{-1}. MS (EI) m/z 302 (M^+, 15%), 260 (M^+-C_2H_3O, 100%). HRMS. Calc for $C_{11}H_{11}O_2I$: 301.9804. Anal. Found: 301.9813.

2-Ethenyl-4-chloro-6-methylphenyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14 (3H, s), 2.44 (3H, s), 5.36 (1H, dd, J = 11.2, 0.8 Hz), 5.73 (1H, dd, J = 17.6, 0.8 Hz), 6.62 (1H, dd,

J = 17.6, 11.2 Hz), 7.13 (1H, d, *J* = 1.6 Hz), 7.36 (1H, d, *J* = 1.6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.4, 20.6, 117.6, 123.8, 129.5, 129.9, 131.3, 131.9, 132.5, 145.2, 168.4. IR (neat) 2928, 1763, 1209, 869, 796 cm^{-1}. MS (EI) m/z 210 (M^+, 9%), 168 (M^+-C_2H_3O, 100%). HRMS. Calc for $C_{11}H_{11}O_2Cl$: 210.1448. Anal. Found: 210.1442.

Spectra data of 2-ethenylphenyl acetate, 2-etheny-6-methylphenyl acetate, 2-ethenyl-6-(*t*-butyl)phenyl acetate, 2-etheny-4-methylphenyl acetate, 2-ethenyl-4-(*t*-butyl)phenyl acetate, 2-etheny-4-methoxyphenyl acetate, 2-etheny-4-chlorophenyl acetate, 3-(*t*-butyl)-2-ethenylphenyl acetate, 3-(*t*-butyl)-6-ethenylphenyl acetate, 2-ethenyl-3-(*t*-butyldimethylsiloxy)phenyl acetate, 6-ethenyl-3-(*t*-butyldimethylsiloxy)phenyl acetate, and 2-ethenyl-1-naphtyl acetate coincided with those described in the reference 1.