Supporting Information

Novel One-Pot Vicinal Double C-Acylation of Styrenes and Methacrylates by Electroreduction

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Experimental Section

Styrene (**1a**), α -methylstyrene (**1g**), 1,1-diphenylethylene (**1i**), acid anhydrides (**2**), alkyl methacrylates (**5a**)~(**5c**), methacrylonitrile (**5d**), ethyl cinnamate (**5e**), ethyl crotonate (**5f**) and tetra-*n*-butylammonium bromide were purchased from Aldrich Chemical Co. Ltd, Tokyo Kasei Kogyo Co. Ltd and Nacalai Tesque Ltd, and were used without further purification. Styrene derivatives, **1d**~**1f**, **1h**, were prepared by Wittig reaction, and **1b** and **1c** were prepared by the reported method. *N,N*-Dimethylformamide (DMF) was dried over CaH₂ and then was distilled under reduced pressure.

¹H- and ¹³C-NMR spectra were measured by a JEOL JNM-EX-400 (400 and 100MHz) spectrometer or a JEOL JNM-GX-270 (270 and 67.8MHz) spectrometer, respectively, with TMS as an internal standard. IR spectra were measured by a JASCO IR-810 spectrometer. Mass spectra were obtained using a Shimadzu GC-MS QP-2000A or a JEOL JMS-600H. Gas chromatographic analysis was conducted through a Shimadzu GC-14B with FID using a capillary column packed with DB-17. The apparatus of cyclic voltammetry was ALS MODEL 600. The apparatus of elemental analysis was Yanaco CHN CORDER MT-6. Melting point was measured by a Yanaco MP-J3.

Typical Procedure for Electroreductive Double C-Acylation of Styrene and Alkyl methacrylate Derivatives.

In a 100mL of a beaker-type undivided cell equipped with Zn plates (40 × 70 × 0.5mm, nacalai tesque, 99%) as the cathode and the anode were introduced 60mL of anhydrous DMF as a solvent, *n*-Bu₄NBr (16.6mmol) as a supporting electrolyte, acid anhydrides or *N*-acylimidazoles (100mmol) and styrenes or alkyl methacrylates (10mmol). The electrolysis was carried out under constant current conditions (current density: 7mA/cm²) at -5~5°C with magnetic stirring until 6F/mol of electricity was passed. After the electrolysis, the reaction mixture was poured into saturated NaHCO₃ solution when acid anhydrides were used as the acylating agents. When *N*-acylimidazoles were used, the reaction mixture was poured into 1% HCl solution after the electrolysis. Organic materials were extracted with three 100 mL portions of ether. The combined ethereal solution was washed with saturated NaCl solution and dried over anhydrous MgSO₄. After removal of MgSO₄ by filtration and evaporation of the solvent, the isolation by column chromatography gave a diacylated compounds in satisfactory yields.

3-Phenyl-2,5-hexanedione (4a) ^[a]

¹H-NMR(270MHz, CDCl₃) δ 2.11(s, 3H), 2.15(s, 3H), 2.57(dd, J=3.8Hz, J=17.9Hz, 1H), 3.44(dd, J=10.3Hz, J=17.9Hz, 1H), 4.21(dd, J=3.8Hz, J=10.3Hz, 1H) and 7.18-7.36(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 28.84, 29.82, 46.30, 53.80, 127.30, 127.94(× 2), 128.85(× 2), 137.58, 206.25 and 206.59 ppm. IR(neat): 3030, 2970, 1710, 1600, 1500 and 1360cm⁻¹. EI-MS: m/z 190(M⁺).

4-Phenyl-3,6-octanedione (4b) ^[a]

¹H-NMR(400MHz, CDCl₃) δ 0.95(t, J=7.2Hz, 3H), 1.03(t, J=7.4Hz, 3H), 2.36-2.58(m, 5H), 3.44(dd, J=10.4Hz, J=18.0Hz, 1H), 4.24(dd, J=4.0Hz, 10.4Hz, 1H) and 7.19-7.33(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 7.49, 7.62, 34.63, 35.69, 45.31, 52.79, 127.26, 127.99(× 2), 128.86(× 2), 138.06, 209.48 and 209.82 ppm. IR(neat): 3030, 2980, 1720, 1600, 1500 and 1460cm⁻¹. EI-MS: m/z 218(M⁺).

5-Phenyl-4,7-decanedione (4c)

¹H-NMR(400MHz, CDCl₃) δ 0.79(t, J=7.3Hz, 3H), 0.89(t, J=7.3Hz, 3H), 1.46-1.64(m, 4H), 2.31-2.56(m, 5H), 3.42(dd, J=10.5Hz, J=17.9Hz, 1H), 4.23(dd, J=3.7Hz, J=10.5Hz, 1H) and 7.18-7.34(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 13.41, 13.56, 16.96, 17.09, 43.42, 44.61, 45.69, 53.10, 127.33, 128.13(× 2), 128.92(× 2), 137.99, 209.20 and 209.28 ppm. IR(neat): 3030, 2960, 1710, 1490, 1450 and 1360cm⁻¹. EI-MS: m/z 246(M⁺). Anal.Calcld.for C₁₆H₂₂O₂: C, 78.01; H, 9.00. Found: C, 77.82; H, 9.03.

2,7-Dimethyl-4-phenyl-3,6-octanedione (4d)

¹H-NMR(400MHz, CDCl₃) δ 0.88(d, J=6.8Hz, 3H), 1.06(d, J=6.8Hz, 3H), 1.12(d, J=6.8Hz, 3H), 1.17(d, J=6.8H, 3H), 2.53-2.64(m, 2H), 2.71(sept, J=6.8Hz, 1H), 3.45(dd, J=10.0Hz, J=18.0Hz, 1H), 4.40(dd, J=4.0Hz, J=10.0Hz, 1H) and 7.18-7.33(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 18.02, 18.08(× 2), 19.07, 39.46, 40.70, 43.81, 51.56, 127.27, 128.19(× 2), 128.92(× 2), 138.17, 212.66 and 213.01 ppm. IR(neat): 3020, 2970, 2930, 1710, 1490, 1470 and 1380cm⁻¹. EI-MS: m/z 246(M⁺). Anal.Calcld.for C₂₂H₂₆N₄O₅ (mono-(2,4-dinitrophenylhydrazone)): C, 61.96; H, 6.15; N, 13.14. Found: C, 61.82; H, 5.96; N, 13.15.

Phenylbutanedioic acid dimethyl ester (4e) ^[b]

¹H-NMR(400MHz, CDCl₃) δ 2.67(dd, J=5.2Hz, J=17.0Hz, 1H), 3.21(dd, J=10.2Hz, 17.0Hz, 1H), 3.67(s, 6H), 4.09(dd, J=5.2Hz, J=10.2Hz, 1H) and 7.27-7.34(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 37.55, 47.03, 51.82, 52.31, 127.62, 127.68(× 2), 128.85(× 2), 137.61, 171.93 and 173.38 ppm. IR(neat): 3030, 2960, 1730, 1500 and 1440cm⁻¹. EI-MS: m/z 222(M⁺). mp: 56~58 °C

Phenylbutanedioic acid diethyl ester (4f) ^[c]

¹H-NMR(400MHz, CDCl₃) δ 1.19(t, J=7.2Hz, 3H), 1.22(t, J=7.0Hz, 3H), 2.66(dd, J=5.0Hz, J=17.2Hz, 1H), 3.19(dd, J=10.0Hz, J=17.2Hz, 1H), 4.05-4.21(m, 5H) and 7.24-7.34(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 13.96, 14.05, 37.83, 47.21, 60.63, 61.02, 127.47, 127.66(× 2), 128.72(× 2), 137.79, 171.43 and 172.86 ppm. IR(neat): 3030, 2980, 1740, 1500 and 1460cm⁻¹. EI-MS: m/z 250(M⁺).

3-(3-Fluorophenyl)- 2,5-hexanedione (4g)

¹H-NMR(400MHz, CDCl₃) δ 2.14(s, 3H), 2.17(s, 3H), 2.60(dd, J=4.0Hz, J=18.1Hz, 1H), 3.43(dd, J=10.1Hz, J=18.1Hz, 1H), 4.23(dd, J=4.0Hz, J=10.1Hz, 1H), 6.91-7.02(m, 3H) and 7.28-7.34(m, 1H) ppm. ¹³C-NMR(CDCl₃) δ 28.92, 29.75, 46.20, 53.34, 114.48(d, J=20.1Hz), 115.02(d, J=22.0Hz), 123.84, 130.55(d, J=7.3Hz), 140.06(d, J=7.4Hz), 162.92(d, J=246.9Hz), 206.29 and 206.39 ppm. IR(neat): 3000, 2900, 1720, 1620, 1590, 1490 and 1360cm⁻¹. EI-MS: m/z 208(M⁺). Anal.Calcld.for C₁₂H₁₃FO₂: C, 69.22; H, 6.29. Found: C, 68.92; H, 6.17.

3-(3-Chlorophenyl)- 2,5-hexanedione (4h)

¹H-NMR(400MHz, CDCl₃) δ 2.14(s, 3H), 2.17(s, 3H), 2.58(dd, J=4.0Hz, J=18.0Hz, 1H), 3.42(dd, J=10.2Hz, J=18.0Hz, 1H), 4.20(dd, J=4.0Hz, J=10.2Hz, 1H) and 7.09-7.29(m, 4H) ppm. ¹³C-NMR(CDCl₃) δ 29.01, 29.78, 46.24, 53.28, 126.32, 127.75, 128.21, 130.27, 134.79, 139.62, 206.24 and 206.35 ppm. IR(neat): 3050, 3000, 1720, 1600, 1570, 1480, 1430 and 1360cm⁻¹. EI-MS: m/z 226(M⁺, ³⁷Cl), 224(M⁺, ³⁵Cl). Anal.Calcld.for C₁₂H₁₃ClO₂: C, 64.15; H, 5.83. Found: C, 64.42; H, 5.90.

3-(3-Methoxyphenyl)- 2,5-hexanedione (4i)

¹H-NMR(400MHz, CDCl₃) δ 2.12(s, 3H), 2.16(s, 3H), 2.57(dd, J=4.0Hz, J=18.2Hz, 1H), 3.42(dd, J=10.0Hz, J=18.2Hz, 1H), 3.79(s, 3H), 4.19(dd, J=4.0Hz, J=10.0Hz, 1H), 6.73-6.83(m, 3H), 7.22-7.26(m, 1H) ppm. ¹³C-NMR(CDCl₃) δ 28.78, 29.78, 46.19, 53.76, 55.06, 112.72, 113.70, 120.38, 129.98, 139.16, 159.94, 206.59 and 206.79 ppm. IR(neat): 3000, 2950, 1720, 1600, 1580, 1490, 1360 and 1260cm⁻¹. EI-MS: m/z 220(M⁺). Anal.Calcd.for C₁₃H₁₆O₃: C, 70.89; H, 7.32. Found: C, 70.65; H, 7.24.

3-(4-Methylphenyl)- 2,5-hexanedione (4j)

¹H-NMR(400MHz, CDCl₃) δ 2.11(s, 3H), 2.16(s, 3H), 2.32(s, 3H), 2.54(dd, J=3.6Hz, J=18.2Hz, 1H), 3.41(dd, J=10.0Hz, J=18.2Hz, 1H), 4.18(dd, J=3.6Hz, J=10.0Hz, 1H), 7.08(d, J=7.8Hz, 2H) and 7.14(d, J=7.8Hz, 2H) ppm. ¹³C-NMR(CDCl₃) δ 20.93, 28.78, 29.89, 46.35, 53.45, 127.97(× 2), 129.71(× 2), 134.68, 137.20, 206.82 and 207.21 ppm. IR(neat): 3000, 2920, 1720, 1510 and 1350cm⁻¹. EI-MS: m/z 204(M⁺). Anal.Calcd.for C₂₅H₂₄N₈O₈ (di-(2,4-dinitrophenylhydrazine)): C, 53.19; H, 4.29; N, 19.85. Found: C, 53.33; H, 4.35; N, 19.53.

3-Methyl-3-phenyl- 2,5-hexanedione (4k)

¹H-NMR(400MHz, CDCl₃) δ 1.73(s, 3H), 1.99(s, 3H), 2.03(s, 3H), 2.87(d, J=17.2Hz, 1H), 3.22(d, J=17.2Hz, 1H) and 7.25-7.37(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 20.97, 25.56, 31.10, 52.07, 53.94, 126.01(× 2), 127.20, 128.79(× 2), 141.50, 206.66 and 209.13 ppm. IR(neat): 3050, 2980, 1710, 1600, 1500, 1450 and 1360cm⁻¹. EI-MS: m/z 204(M⁺-Ac). Anal.Calcd.for C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.42; H, 7.86. mp: 33~34°C

3-Ethyl-3-phenyl- 2,5-hexanedione (4l)

¹H-NMR(400MHz, CDCl₃) δ 0.79(t, J=7.2Hz, 3H), 1.91(s, 3H), 1.92(s, 3H), 2.09(dq, J=7.2Hz, J=15.0Hz, 1H), 2.42(dq, J=7.2Hz, J=15.0Hz, 1H), 3.10(d, J=16.4Hz, 1H), 3.18(d, J=16.4Hz, 1H) and 7.23-7.37(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 8.66, 24.94, 25.30, 31.46, 45.95, 57.91, 126.52(× 2), 127.18, 128.79(× 2), 140.57, 207.19 and 208.80 ppm. IR(neat): 3050, 2960, 1700, 1600, 1500, 1440 and 1350cm⁻¹. EI-MS: m/z 218(M⁺-Ac). Anal.Calcd.for C₁₄H₁₈O₂: C, 77.03; H, 8.31. Found: C, 76.61; H, 8.13. mp: 48~50°C

3,3-Diphenyl- 2,5-hexanedione (4m)

¹H-NMR(270MHz, CDCl₃) δ 1.97(s, 3H), 2.10(s, 3H), 3.59(s, 2H) and 7.20-7.33(m, 10H) ppm. ¹³C-NMR(CDCl₃) δ 27.54, 31.34, 52.26, 63.75, 126.94(× 2), 128.04(× 4), 128.91(× 4), 141.61(× 2), 205.65 and 206.16 ppm. IR(neat): 3050, 3000, 1700, 1600, 1500, 1440 and 1350cm⁻¹. EI-MS: m/z 266(M⁺). Anal.Calcd.for C₁₈H₁₈O₂: C, 81.17; H, 6.81. Found: C, 81.32; H, 6.99. mp: 111~113°C

2-Acetyl-2-methyl-4-oxo-pentanoic acid benzyl ester (6a)

¹H-NMR(400MHz, CDCl₃) δ 1.49(s, 3H), 2.12(s, 3H), 2.19(s, 3H), 3.03(d, J=18.0Hz, 1H), 3.11(d, J=18.0Hz, 1H), 5.12(d, J=12.0Hz, 1H), 5.17(d, J=12.0Hz, 1H) and 7.30-7.37(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 20.49, 26.34, 30.06, 48.82, 57.18, 67.25, 128.17, 128.33, 128.52, 135.23, 171.88, 205.09 and 205.47 ppm. IR(neat): 3030, 2950, 1750, 1710 and 1500 cm⁻¹. EI-MS: m/z 262(M⁺). Anal.Calcd.for C₁₅H₁₈O₄: C, 68.68; H, 6.92. Found: C, 68.24; H, 6.95.

2-Acetyl-2-methyl-4-oxo-pentanoic acid methyl ester (6b) [d]

¹H-NMR(400MHz, CDCl₃) δ 1.48(s, 3H), 2.16(s, 3H), 2.66(s, 3H), 3.04(d, J=18.2Hz, 1H), 3.11(d, J=18.2Hz, 1H) and 3.73(s, 3H) ppm. ¹³C-NMR(CDCl₃) δ 20.36, 26.22, 29.95, 48.71, 52.44, 56.90, 172.48, 205.12 and 205.44 ppm. IR(neat): 2990, 1730, 1710 and 1360 cm⁻¹. EI-MS: m/z 186(M⁺).

2-Acetyl-2-methyl-4-oxo-pentanoic acid ethyl ester (6c) [e]

¹H-NMR(400MHz, CDCl₃) δ 1.26(t, J=8.0Hz, 3H), 1.48(s, 3H), 2.16(s, 3H), 2.27(s, 3H), 3.04(d, J=18.0Hz, 1H), 3.10(d, J=18.0Hz, 1H) and 4.19(q, J=8.0Hz, 2H) ppm. ¹³C-NMR(CDCl₃) δ 13.78, 20.44, 26.29, 30.04, 48.75, 57.03, 61.42, 172.01, 205.36 and 205.53 ppm. IR(neat): 2980, 1730, 1710 and 1360 cm⁻¹. EI-MS: m/z 200(M⁺).

2-Acetyl-2-methyl-4-oxo-pentanenitrile (6d)

¹H-NMR(400MHz, CDCl₃) δ 1.48(s, 3H), 2.17(s, 3H), 2.58(s, 3H), 2.96(d, J=18.2Hz, 1H) and 3.29(d, J=18.2Hz, 1H) ppm. ¹³C-NMR(CDCl₃) δ 22.81, 27.33, 28.87, 40.01, 51.09, 121.20, 202.20 and 203.31 ppm. IR(neat): 2980, 2240 and 1720 cm⁻¹. EI-MS: m/z 153(M⁺). Anal.Calcd.for C₂₀H₁₉N₃O₈ (di-(2,4-dinitrophenylhydrazon)): C, 46.79; H, 3.73; N, 24.55. Found: C, 46.80; H, 3.91; N, 24.25.

2-Methyl-4-oxo-pentanoic acid benzyl ester (7a) [f]

¹H-NMR(400MHz, CDCl₃) δ 1.20(d, J=7.2Hz, 3H), 2.13(s,3H), 2.48(dd, J=4.8Hz, J=17.2Hz, 1H), 2.89-3.02(m, 2H), 5.10(d, J=13.4Hz, 1H), 5.13(d, J=13.4Hz, 1H) and 7.29-7.38(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 16.93, 29.95, 34.66, 46.46, 66.28, 127.91, 128.04, 128.44, 135.94, 175.42 and 206.40 ppm. IR(neat): 3030, 2970, 1740, 1720 and 1500 cm⁻¹. EI-MS: m/z 220(M⁺).

3-Phenyl-4-oxopentanoic acid ethyl ester (7e) [g]

¹H-NMR(400MHz, CDCl₃) δ 1.21(t, J=7.0Hz, 3H), 2.11(s, 3H), 2.52(dd, J=5.0Hz, J=17.1Hz, 1H), 3.20(dd, J=9.9Hz, 17.1Hz, 1H), 4.06-4.13(m, 2H), 4.19(dd, J=5.0Hz, 9.9Hz, 1H) and 7.21-7.35(m, 5H) ppm. ¹³C-NMR(CDCl₃) δ 14.04, 28.79, 36.95, 54.78, 60.54, 127.64, 128.15, 129.05, 137.37, 171.97 and 206.70 ppm. IR(neat): 3030, 2990, 1740, 1720, 1600, 1500 and 1460cm⁻¹. EI-MS: m/z 220(M⁺).

3-Methyl-4-oxopentanoic acid ethyl ester (7f) ^[h]

¹H-NMR(400MHz, CDCl₃) δ 1.16(d, J=7.2Hz, 3H), 1.25(t, J=7.2Hz, 3H), 2.23(s, 3H), 2.30(dd, J=5.4Hz, J=16.5Hz, 1H), 2.76(dd, J=8.8Hz, J=16.5Hz, 1H), 2.99-3.05(m, 1H) and 4.12(q, J=7.2Hz, 2H) ppm. ¹³C-NMR(CDCl₃) δ 14.04, 16.38, 28.28, 36.80, 42.60, 60.41, 172.17 and 210.72 ppm. IR(neat): 2980, 1740, 1720 and 1460cm⁻¹. EI-MS: m/z 158(M⁺).

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3-Phenyl-2,5-hexanedione [4a]

4-Phenyl-3,6-octanedione [4b]

5-Phenyl-4,7-decanedione [4c]

2,7-Dimethyl-4-phenyl-3,6-octanedione [4d]

Phenylbutanedioic acid dimethyl ester [4e]

Phenylbutanedioic acid diethyl ester [4f]

3-(3-Fluorophenyl)-2,5-hexanedione [4g]

3-(3-Chlorophenyl)-2,5-hexanedione [4h]

3-(3-Methoxyphenyl)-2,5-hexanedione [4i]

3-(4-Methylphenyl)-2,5-hexanedione [4j]

3-Methyl-3-phenyl-2,5-hexanedione [4k]

3-Ethyl-3-phenyl-2,5-hexanedione [4]

3,3-Diphenyl-2,5-hexanedione [4m]

2-Acetyl-2-methyl-4-oxopentanoic acid benzyl ester [6a]

2-Acetyl-2-methyl-4-oxopentanoic acid methyl ester [6b]

2-Acetyl-2-methyl-4-oxopentanoic acid ethyl ester [6c]

2-Acetyl-2-methyl-4-oxopentanenitrile [6d]

2-Methyl-4-oxopentanoic acid benzyl ester [7a]

3-Methyl-4-oxopentanoic acid ethyl ester [7f]