Highly Efficient, Reversible Addition of Activated Methylene Compounds to Styrene Derivatives Catalyzed by Silver Catalysts

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Table of Contents

General Experimental Methods	S2
Characterization for compounds 5c , 5d , 5f , 6c , 6d , 7a and 7b	S2 to S5
Reference	S5
¹ H NMR spectra compounds 5c , 5d , 5f , 6c , 6d , 7a and 7b	S6 to S13

Experimental Section

All experiments were carried out under an inert atmosphere of nitrogen. Nitromethane and DCE were dried by 4Å molecular sieves. Flash column chromatography was performed over silica gel 30-60µm. ¹H NMR and ¹³C NMR spectra were acquired by 400 MHz and 100 MHz, or 300 MHz and 75 MHz, respectively, and referenced to the internal solvent signals. Compounds **3a-3o** and **4** have been reported.^{1,2} Compounds **5a-5f** were prepared following the reported method.^{3,4} Compound **5a-5b**, **5e** and **6a-6b** have also been reported.^{3,4} The data for new compounds **5c**, **5d**, **5f**, **6c**, **6d**, **7a** and **7b** were described here.

Typical procedure (entry 1, Table 2): AgOTf (25.6mg, 0.1mmol) were added into 2 mL of nitromethane under N₂. 2,4-Pentanedione (103µL, 1mmol) and styrene (172µL, 1.5mmol) were introduced into the solution. The mixture was stirred and heated to 100°C overnight and removed solvent under reduced pressure. The residue was isolated by flash chromatography with silica to give diketone alkylation product with 76% yield.

2-(5-Phenyl-pent-4-enoyl)-cyclopentanone (1:1 mixture of enol and diketone) (5c). IR (liquid film): $\nu_{\max}$ 3084, 3023, 2963, 2919, 2854, 1741, 1708, 1653, 1612, 1446, 1372, 1230, 1152, 963cm⁻¹; ¹H NMR (CDCl₃, 400MHz, ppm) δ 7.33-7.28(m, 4H), 7.22-7.17(m, 1H), 6.45-6.39(two d peaks overlap, 1H), 6.25-6.16(two td peaks overlap, 1H), 3.99(t, J = 8.0Hz, 0.5H, from diketone), 3.06(dt, J = 17.6, 7.2Hz, 0.5H, from enol), 2.67(dt, J = 17.6, 7.2Hz, 0.5H, from enol), 2.59-2.04(m, 6H), 2.31-2.25(m, 1H), 2.07(m, 1H), 2.07(m, 1H), 1.95-1.84(m, 2H); ¹³C NMR (CDCl₃, 100MHz, ppm) δ 213.1, 204.9, 203.8, 178.4, 137.6, 137.5, 131.2, 130.9, 129.0, 128.8, 128.7, 128.7, 127.4, 127.3, 126.2, 126.2, 110.0, 62.4, 42.9, 39.2, 37.2, 34.8, 29.2, 27.1, 26.1, 25.7, 21.8, 20.8; MS (EI) m/z (%) 242(M⁺), 224, 151, 130, 117(100), 91; HRMS calcd for C₁₆H₁₈O₂: 242.1307; found: 242.1304.

1,7-Diphenyl-hept-6-ene-1,3-dione (5d). IR (liquid film): $\nu_{\max}$ 3063, 3025, 2914, 1720, 1673, 1602, 1571, 1494, 1267, 1142, 963 cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 7.89(d, J = 8Hz, 2H), 7.53-7.21(m, 8H), 6.48(d, J = 16Hz, 1H), 6.28-6.22(m, 2H), 2.64-2.63(m, 4H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 196.1, 183.3, 137.5, 135.0, 132.5, 131.2, 128.9, 128.8, 127.4, 127.2, 126.3, 96.6, 39.4, 29.4; MS (EI) m/z (%) 278(M^+), 260, 187, 173, 147, 130, 105(100), 91, 77; HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$: 278.1307; found: 278.1302.

1-Phenyl-non-6-ene-1,3-dione (5f). IR (liquid film): $\nu_{\max}$ 3065, 2967, 2931, 2875, 1621, 1575, 1491, 1459, 1301, 1269, 1181, 1075, 966 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz, ppm) δ 7.90-7.86(m, 2H), 7.54-7.41(m, 3H), 6.17(s, 1H), 5.49(m, 2H), 2.53-2.35(m, 4H), 2.02(m, 2H), 0.98(t, J = 6.9Hz, 3H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 196.4, 183.4, 135.2, 133.6, 132.4, 128.8, 127.3, 127.2, 96.5, 39.7, 29.0, 26.0, 14.3; MS (EI) m/z (%) 230(M^+), 201, 162, 147, 120, 105(100), 69; HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: 230.1307 ; found: 230.1300.

10-Phenyl-spiro[4.5]decane-1,6-dione (6c). IR (liquid film): $\nu_{\max}$ 3060, 3030, 2985, 2880, 1748, 1694, 1493, 1449, 1316, 1251, 1155, 1130, 1098, 980, 962 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz, ppm) δ 7.29-7.10(m, 5H), 3.57(dd, J = 9.9, 4.2Hz, 1H), 2.60-2.56(m, 2H), 2.27-2.19(m, 3H), 2.08-1.68(m, 6H), 1.45-1.40(m, 1H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 216.7, 210.3, 140.5, 129.2, 128.5, 127.1, 68.8, 48.1, 39.5, 39.7, 30.5, 27.9, 23.8, 19.5; MS (EI) m/z (%) 242(M^+ , 100), 224, 196, 185, 171, 137, 129, 115, 104, 91, 81; HRMS calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$: 242.1307; found: 242.1310.

another diastereomer: IR (liquid film): $\nu_{\max}$ 3062, 3030, 2956, 2921, 2864, 1729, 1699, 1494, 1453, 1444, 1319, 1136, 1118, 1013, 927, 906, 896 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz, ppm) δ 7.29-7.14(m, 5H), 3.11(td, J = 13.5, 6.3Hz, 1H), 2.95-2.89(m, 1H), 2.82-2.73(m, 2H), 2.51-2.45(m, 1H), 2.26-2.04(m, 2H), 1.86-1.42(m, 5H), 1.44-1.07(m, 1H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 216.3, 205.6, 141.3, 128.9, 128.6, 70.2, 55.7, 41.6, 39.3, 30.1, 28.5,

26.2, 19.8; MS (EI) m/z (%) 242(M^+ , 100), 224, 196, 185, 171, 137, 129, 115, 104, 91, 81; HRMS calcd for $C_{16}H_{18}O_2$: 242.1307; found: 242.1309.

2-Benzoyl-3-phenyl-cyclohexanone (6d). IR (liquid film): $\nu_{\max}$ 3061, 3030, 2951, 2941, 2920, 2862, 1706, 1675, 1596, 1446, 1351, 1241, 1170, 1103, 1015, 916cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz, ppm) δ 7.71(d, $J = 7.2\text{Hz}$, 2H), 7.48(m, 1H), 7.36(m, 2H), 7.25-7.21(m, 4H), 7.17-7.11(m, 1H), 4.72(d, $J = 10.8\text{Hz}$, 1H), 3.72(ddd, $J = 10.8, 10.8, 3.6\text{Hz}$, 1H), 2.64-2.59(m, 2H), 2.21-2.15(m, 2H), 2.08-1.91(m, 2H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 207.9, 197.3, 143.0, 137.8, 133.2, 128.9, 128.7, 128.3, 127.3, 127.0, 64.1, 47.4, 42.3, 33.4, 25.4; MS (EI) m/z (%) 278(M^+), 260, 221, 204, 173(100), 105, 91, 77; HRMS calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1303.

2-(5-Methyl-dihydro-furan-2-ylidene)-1-phenyl-ethanone (7a). IR (liquid film): $\nu_{\max}$ 3059, 2976, 2932, 1656, 1598, 1584, 1570, 1440, 1386, 1187, 1160, 1040, 910, 893cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 7.90-7.88(m, 2H), 7.48-7.40(m, 3H), 6.50(d, $J = 1.6\text{Hz}$, 1H), 4.62(ddq, $J = 8.0, 6.4, 6.4\text{Hz}$, 1H), 3.51(dddd, $J = 19.2, 8.8, 4, 1.6\text{Hz}$, 1H), 3.16(dddd, $J = 19.2, 9.6, 9.6, 2\text{Hz}$, 1H), 2.30(m, 1H), 1.78-1.69(m, 2H), 1.42(d, $J = 6.4\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 75MHz, ppm) δ 207.1, 179.1, 145.8, 131.9, 128.5, 127.8, 95.1, 80.9, 32.5, 31.4, 20.9; MS (EI) m/z (%) 202(M^+ , 100), 173, 145, 125, 105, 69; HRMS calcd for $C_{13}H_{14}O_2$: 202.0994; found: 202.0992.

The configuration of the double bond was determined by 1D NOESY (the proton on 6.50ppm was selected).

1-Phenyl-2-(5-propyl-dihydro-furan-2-ylidene)-ethanone (7b). IR (liquid film): $\nu_{\max}$ 3060, 2958, 2931, 2873, 1655, 1599, 1585, 1571, 1445, 1380, 1164, 903cm^{-1} ; ^1H NMR (CDCl_3 , 400MHz, ppm) δ 7.91-7.89(m, 2H), 7.48-7.40(m, 3H), 6.50(s, 1H), 4.48(dddd, $J = 7.2, 7.2, 7.2, 7.2\text{Hz}$, 1H), 3.49(dddd, $J = 19.2, 9.6, 4, 1.2\text{Hz}$, 1H), 3.14(dddd, $J = 19.2, 9.6, 9.6, 2\text{Hz}$, 1H), 2.28(m, 1H), 1.80-1.70(m, 2H), 1.60-1.41(m, 4H), 1.00(t, $J = 7.2, 3\text{Hz}$); ^{13}C NMR

(CDCl₃, 75MHz, ppm) δ 190.5, 179.3, 140.1, 131.8, 128.5, 127.8, 95.0, 84.7, 37.5, 32.3, 29.7, 19.4, 14.4; MS (EI) m/z (%) 230(M⁺), 201, 173, 161, 147, 105(100), 77; HRMS calcd for C₁₅H₁₈O₂: 230.1307; found: 230.1301.

The five member ring and the configuration of the double bond were determined by H-H COSY and 1D NOESY (the proton on 6.50ppm was selected).

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yxq-2-1204

Data Collected on: m300-mercury300
Archive directory: /export/home/xyao/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1
Solvent: CDCl3

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.0595500 MHz
DATA PROCESSING
FT size 32768
Total time 0 min

5f

STANDARD 1H OBSERVE

Data Collected on: m400-mercury400
 Archive directory: /export/home/xyao/vnmrsys/data
 Sample directory:
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.998 sec
 Width 6410.3 Hz
 8 repetitions
 OBSERVE H1, 400.1245662 MHz
 DATA PROCESSING
 FT size 32768
 Total time 9 min