

SUPPORTING INFORMATION

Title: The Formation of Cyclopropane Derivatives Bearing 1,2-Dicarbonyl Groups through Tandem Michael–Favorskii-Type Reactions with (*E*)- β -Styrylselenonium Triflate

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General. Melting points were obtained with a Yanagimoto micro-melting-point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO FT/IR-230 spectrophotometer. ¹H NMR spectra were recorded on a JEOL EX-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. ¹³C NMR spectra were obtained on a JEOL EX-400 (100 MHz) spectrometer with chloroform as an internal standard. The *J* values are given in Hz. Mass spectra (MS and HRMS) were recorded on a JEOL JMS-SX102A spectrometer with an electron impact (EI, 70 eV) or fast atom bombardment (FAB, glycerol or 3-nitrobenzylalcohol) techniques. Elemental analyses of new compounds were performed by a Yanaco CHN Corder MT-5. All chromatographic isolations were accomplished with Kieselgel 60 PF₂₅₄ containing gypsum (Merck) for preparative TLC. Organic solvents used were dried by standard methods. All active methylene compounds were purchased from commercial sources and were used without further purification.

1-[(1*R, 2*S**, 3*R**)-2-Benzoyl-3-phenylcyclopropyl]ethanone (2a) ¹:**

Pale yellow crystals, mp 98-99°C; IR (NaCl)/cm⁻¹ 1704, 1680; ¹H NMR (CDCl₃) δ: 2.32 (s, 3 H, CH₃), 2.8 (dd, *J* = 6.0, 9.3, 1 H, CH), 3.2 (dd, *J* = 6.0, 9.3, 1 H, CH), 3.36 (t, *J* = 6.0, 1 H, CH), 7.22 (d, *J* = 8.0, 2 H, ArH), 7.27 (t, *J* = 8.0, 1 H, ArH), 7.36 (d, *J* = 8.0, 2 H, ArH), 7.46 (d, *J* = 8.0, 2 H, ArH), 7.56 (t, *J* = 8.0, 1 H, ArH), 7.98 (d, *J* = 8.0, 2 H, ArH); ¹³C NMR (CDCl₃) δ: 30.8, 31.0, 37.1, 39.5, 126.4, 127.1, 128.1, 128.6, 133.3, 136.9, 138.2, 194.1, 202.9; MS (FAB) *m/z* 265 (M+H)⁺; Anal. Calcd for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.74; H, 6.21.

1-[(1*R, 2*R**, 3*S**)-2-Benzoyl-3-phenylcyclopropyl]ethanone (3a) ¹:**

Pale yellow crystals, mp 98-100°C; IR (NaCl)/cm⁻¹ 1705, 1670; ¹H NMR (CDCl₃) δ: 2.19(s, 3 H, CH₃), 3.17(dd, *J* = 6, 9, 1 H, CH), 3.36 (dd, *J* = 6, 9, 1 H, CH), 4.00 (t, *J* = 6, 1 H, CH), 7.20 - 7.4

(m, 5 H, ArH), 7.52 (t, $J = 7$, 2 H, ArH), 7.63 (t, $J = 7$, 1 H, ArH), 8.1 (d, $J = 7$, 2 H, ArH); MS (FAB) m/z 265 (M+H)⁺; HRMS (FAB) Calcd for C₁₈H₁₇O₂ (M+H)⁺ 265.1235. Found: 265.1235.

1-[(1R*, 2S*, 3s*)-2-Acetyl-3-phenylcyclopropyl]ethanone (2b):

Orange crystals, mp 44.5-45°C; IR (NaCl)/cm⁻¹ 1715; ¹H NMR (CDCl₃) δ: 2.31 (s, 6 H, CH₃), 2.60, (d, $J = 6$, 2 H, CH), 3.18 (t, $J = 6$, 1 H, CH), 7.13 (d, $J = 6.8$, 2 H, ArH), 7.23 - 7.34 (m, 3 H, ArH); ¹³C NMR (CDCl₃) δ: 31.0, 31.8, 40.1, 126.5, 127.4, 129, 138.4, 203.4; MS (FAB) m/z 203 (M+H)⁺; HRMS (FAB) Calcd for C₁₈H₁₇O₂ ([M+H]⁺) 203.1072. Found: 203.1079.

1-[(1R*, 2R*, 3r*)-2-Acetyl-3-phenylcyclopropyl]ethanone (3b) ²:

Pale yellow oil; IR (NaCl)/cm⁻¹ 1697; ¹H NMR (CDCl₃) δ: 2.1(s, 3 H, CH₃), 2.2(s, 3 H, CH₃), 2.96, (dd, $J = 5$, 10, 1 H, CH), 3.12 (dd, $J = 5$, 10, 1 H, CH), 3.28 (t, $J = 5$, 1 H, CH), 7.14 - 7.34 (m, 5 H, ArH); ¹³C NMR (CDCl₃) δ: 31.2, 31.3, 33.1, 36.8, 39.9, 127.3, 128.3, 128.6, 133.9, 201.4, 205.3; MS (FAB) m/z 203 (M+H)⁺; HRMS (FAB) Calcd for C₁₈H₁₇O₂ ([M+H]⁺) 203.1072. Found: 203.1078.

[(1R*, 2S*, 3s*)-2-Benzoyl-3-phenylcyclopropyl](phenyl)methanone (2c) ³:

Pale yellow crystals, mp 141.5-142.0°C; IR (NaCl)/cm⁻¹ 1683; ¹H NMR (CDCl₃) δ: 3.39 (d, 2 H), 3.55 (t, 1 H), 7.3 - 7.46 (m, 9 H), 7.53 (t, 2 H), 7.99 (d, 4 H); ¹³C NMR (CDCl₃) δ: 31.2, 36.9, 126.5, 127.2, 128.3, 128.6, 128.8, 133.1, 137.1, 138.5, 194.3; MS (EI) m/z 326 (M)⁺; HRMS (EI) Calcd for C₂₃H₁₈O₂ (M⁺) 326.1307. Found: 326.1303.

[(1R*, 2R*, 3r*)-2-Benzoyl-3-phenylcyclopropyl](phenyl)methanone (3c):

Pale yellow crystals, mp 102.5-103°C; IR (NaCl)/cm⁻¹ 1664; ¹H NMR (CDCl₃) δ: 3.57 (dd, $J = 5$, 10, 1 H, CH), 3.80 (dd, $J = 5$, 10, 1 H, CH), 4.24 (t, $J = 5$, 1 H, CH), 7.1 - 7.3 (m, 6 H, ArH), 7.4 - 7.6 (m, 6 H, ArH), 7.62 (t, 1 H, ArH), 7.9 (d, 2 H, ArH), 8.16 (d, 2 H, ArH); ¹³C NMR (CDCl₃) δ: 29.8, 37.4, 38.0, 127.3, 128.26, 128.31, 128.4, 128.6, 128.7, 128.8, 133.2, 133.5, 134.3, 137.1, 137.5, 188.0, 193.7, 197.4; MS (EI) m/z 326 (M)⁺; HRMS (EI) Calcd for C₂₃H₁₈O₂ (M⁺) 326.1307. Found: 326.1310.

(1R*, 2S*, 3R*)-2-benzoyl-3-phenylcyclopropanecarbonitrile (2d) ⁴:

Pale yellow crystals, mp 125-126°C; IR (NaCl)/cm⁻¹ 1672, 2236; ¹H NMR (CDCl₃) δ: 2.35 (dd, $J = 6.35$, 8.3, 1 H, CH), 3.40 (m, 2 H, CH), 7.19 (d, $J = 6.83$, 2 H, ArH), 7.34 (m, 3 H, ArH), 7.52 (t, J

= 7, 2 H, ArH), 7.63 (t, $J = 7$, 1 H, ArH), 8.06 (d, $J = 7$, 2 H, ArH); ^{13}C NMR (CDCl_3) δ : 15.8, 30.9, 32.2, 116., 126.5, 128.8, 129, 133.9, 135.8, 136.5, 192.7; MS (FAB) m/z 248 ($\text{M}+\text{H}$) $^+$; Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{NO}$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.52; H, 5.31; N, 5.61.

(1R*, 2R*, 3R*)-2-benzoyl-3-phenylcyclopropanecarbonitrile (3d) ⁵:

Pale yellow crystals, mp 101-102°C; IR (NaCl)/ cm^{-1} 1672, 2242; ^1H NMR (CDCl_3) δ : 2.73 (dd, $J = 5, 9$, 1 H, CH), 3.07 (dd, $J = 5, 9$, 1 H, CH), 3.63 (t, $J = 5$, 1 H, CH), 7.4 (m, 5 H, ArH), 7.55 (t, $J = 7$, 2 H, ArH), 7.65 (t, $J = 7$, 1 H, ArH), 8.03 (d, $J = 7$, 2 H, ArH); MS (FAB) m/z 248 ($\text{M}+\text{H}$) $^+$; HRMS (FAB) Calcd for $\text{C}_{17}\text{H}_{14}\text{NO}$ ($[\text{M}+\text{H}]^+$) 248.1075. Found: 248.1078.

Benzyl (1R*, 2S*, 3S*)-2-acetyl-3-phenylcyclopropanecarboxylate (2e):

White crystals, mp 45-45.5°C; IR (NaCl)/ cm^{-1} 1604, 1715; ^1H NMR (CDCl_3) δ : 2.28 (s, 3 H, CH_3), 2.47 - 2.58 (m, 2 H, CH), 3.22 (t, $J = 6$, 1 H, CH), 5.15 (s, 2 H, PhCH_2), 7.11 (d, $J = 7.3$, 2 H, CH), 7.23 - 7.37 (m, 8 H, ArH); ^{13}C NMR (CDCl_3) δ : 30.2, 30.8, 31.8, 37.8, 67.1, 126.4, 127.1, 128.3, 128.4, 128.5, 128.6, 135.6, 137.7, 168.8, 202.4; MS (EI) m/z 294 (M) $^+$; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3$ (M^+) 294.1256. Found: 294.1254.

Ethyl (1R*, 2S*, 3S*)-2-benzoyl-3-phenylcyclopropanecarboxylate (2f) ⁵:

Pale yellow crystals, mp 98.5-100.5°C; IR (NaCl)/ cm^{-1} 1682, 1731; ^1H NMR (CDCl_3) δ : 1.14 (t, $J = 7.2$, 3 H, CH_3), 2.64 (dd, $J = 6.3, 10$, 1 H, CH), 3.09 (dd, $J = 6.3, 10$, 1 H, CH), 3.37 (t, $J = 6.3$, 1 H, CH), 4.09 (q, $J = 7.2$, 2 H, CH_2), 7.2 - 7.28 (m, 3 H, ArH), 7.34 (t, $J = 7$, 2 H, ArH), 7.46 (t, $J = 7$, 2 H, ArH), 7.55 (d, $J = 7$, 1 H, ArH), 8.02 (d, $J = 7$, 2 H, ArH); ^{13}C NMR (CDCl_3) δ : 14.0, 29.7, 31.6, 35.1, 61.1, 126.6, 127.1, 128.6, 128.7, 133.3, 136.9, 138.1, 169.1, 193.7; MS (EI) m/z 294 (M) $^+$; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3$ (M) $^+$ 294.1256. Found: 294.1248.

Diethyl 2-phenylcyclopropane-1,1-dicarboxylate (4a) ⁶:

Yellow oil; IR (NaCl)/ cm^{-1} 1280, 1325, 1720, 1731; ^1H NMR (CDCl_3) δ : 0.86 (t, $J = 7$, 3 H, CH_3), 1.29 (t, $J = 7$, 3 H, CH_3), 1.70 (dd, $J = 5, 8$, 1 H, CH), 2.17 (dd, $J = 5, 8$, 1 H, CH), 3.21 (t, $J = 8$, 1 H, CH), 3.84 (dd, $J = 7, 14$, 2 H, CH_2), 4.16 - 4.32 (m, 2 H, CH_2), 7.1 (m, 5 H, ArH); ^{13}C NMR (CDCl_3) δ : 13.6, 14.1, 18.7, 32.1, 37.4, 61.1, 61.6, 127.3, 128.1, 128.5, 134.6, 166.6, 169.8; MS (EI) m/z 262 (M) $^+$; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4$ (M^+) 262.1205. Found: 262.1216.

Dibenzyl 2-phenylcyclopropane-1,1-dicarboxylate (4b) :

Pale yellow crystals, mp 67-69°C; IR (NaCl)/cm⁻¹ 1275, 1323, 1730, 1740; ¹H NMR (CDCl₃) δ: 1.78 (dd, *J* = 5, 8.5, 1 H, CH), 2.25 (dd, *J* = 5, 8.5, 1 H, CH), 3.30 (t, *J* = 8.5, 1 H, CH), 4.78 (s, 2 H, PhCH₂), 5.17 (d, *J* = 12, 1 H, CH), 5.28 (d, *J* = 12, 1 H, CH), 6.95 (d, *J* = 7, 2 H, ArH), 7.18-7.28 (m, 8 H, ArH), 7.33 (s, 5 H, ArH); ¹³C NMR (CDCl₃) δ: 19.1, 32.6, 37.4, 67.1, 67.3, 127.4, 127.88, 127.94, 128.1, 128.16, 128.25, 128.47, 128.50, 134.4, 135.2, 135.4, 166.4, 169.5; MS (FAB) *m/z* 387 (M+H)⁺; Anal. Calcd for C₂₅H₂₂O₄: C, 77.70; H, 5.74. Found: C, 77.30; H, 5.78.

(1r*, 1aS*, 7aR*)-1-Phenyl-1a,7a-dihydro-1H-cyclopropa[b]naphthalene-2,7-dione (8a):

Pale yellow crystals, mp 149-150°C; IR (NaCl)/cm⁻¹ 1677; ¹H NMR (CDCl₃) δ: 3.0 - 3.1 (m, 3 H, CH), 7.13 (d, *J* = 7.33, 2 H, ArH), 7.2 - 7.4 (m, 3 H, ArH), 7.7 - 7.8 (m, 2 H, ArH), 8.0 - 8.1 (m, 2 H, ArH); ¹³C NMR (CDCl₃) δ: 37.0, 37.6, 126.3, 127.1, 127.8, 128.8, 132.6, 134.3, 136.5, 191.4; MS (EI) *m/z* 248 (M)⁺; HRMS (EI) Calcd for C₁₇H₁₂O₂ (M⁺) 248.0837. Found: 248.0833.

(1R*, 7S*, 8s*)-8-Phenylbicyclo[5.1.0]octane-2,6-dione (8b):

White crystals, mp 83-83.5°C; IR (NaCl)/cm⁻¹ 1680; ¹H NMR (CDCl₃) δ: 1.69 (q, *J* = 13.8, 1 H, CH), 2.03 (m, 1 H, CH), 2.59 (d, *J* = 6.84, 2 H, CH), 2.70 (m, 2 H, CH), 2.81 (m, 2 H, CH), 3.44 (t, *J* = 6.5, 1 H, CH), 7.14 (d, *J* = 6.84, 2 H, ArH), 7.27 - 7.35 (m, 3 H, ArH); ¹³C NMR (CDCl₃) δ: 22.1, 34.0, 39.7, 41.6, 126.5, 127.7, 128.9, 136.6, 205.9; MS (FAB) *m/z* 215 (M+H)⁺; HRMS (FAB) Calcd for C₁₄H₁₅O₂ ([M+H]⁺) 215.1072. Found: 215.1084.

(1R*, 7S*, 8s*)-4,4-Dimethyl-8-phenylbicyclo[5.1.0]octane-2,6-dione (8c):

Pale yellow crystals, mp 125-126.5°C; IR (NaCl)/cm⁻¹ 1666; ¹H NMR (CDCl₃) δ: 0.92 (s, 3 H, CH₃), 1.14 (s, 3 H, CH₃), 2.41 (d, *J* = 12.2, 2 H, CH), 2.61 (d, *J* = 6.35, 2 H, CH), 2.92 (d, *J* = 12.2, 2 H, CH), 3.46 (t, *J* = 6.35, 1 H, CH), 7.14 (d, *J* = 8.31, 2 H, ArH), 7.26 - 7.34 (m, 3 H, ArH); ¹³C NMR (CDCl₃) δ: 24.8, 33.0, 34.2, 34.6, 40.7, 54.6, 126.5, 127.7, 128.9, 136.6, 204.6; MS (EI) *m/z* 242 (M)⁺; HRMS (EI) Calcd for C₁₆H₁₈O₂ (M⁺) 242.1307. Found: 242.1297.

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