

Electronic Supplementary Information

One-pot β -substitution of enones with alkyl groups to β -alkyl enones

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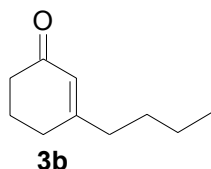
General. Infrared (IR) spectra were recorded on a Jasco FT300 FT/IR-420. ^1H NMR spectra were recorded on a JEOL JNM ECP500 (500 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL JNM ECP500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 ; δ 77.0 ppm). GC-Mass spectra were recorded on a Shimadzu GC-MS QP5050A by chemical ionization method using isobutane. Mass spectra (EI) were recorded on a JEOL JMS-AX505HA in Kitasato University. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer in Kitasato University. Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC-18A instrument equipped with a flame ionizing detector and a capillary column of TC-WAX (0.25 mm I.D. x 30 m, $df = 0.25\mu\text{m}$, GL Sciences Inc.) using naphthalene as an internal standard. Analytical TLC was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Silica-gel column chromatography was carried out on silica gel 60N (Kanto Kagaku Co., Ltd., spherical, neutral, 63–210 μm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. Diethyl ether was

distilled under argon from sodium/benzophenone ketyl. All β -alkyl substitution of enones was carried out under argon in dried glassware with magnetic stirring.

N-*tert*-Butylbenzenesufinimidoyl chloride (**1**)¹ was prepared according to the literature procedure. 2-Cyclohexen-1-one (**2**), 2-cyclopenten-1-one (**6**), and 2-cyclohepten-1-one (**8**) were purchased and purified by distillation. 4-Phenyl-2-cyclohexen-1-one (**4**)² was prepared by the reaction of trimethylsilyl enol ether of 4-phenylcyclohexanone and palladium acetate (1.2 equiv.) in acetonitrile (86% yield).³ β -Alkyl enones such as 3-methyl-2-cyclohexen-1-one (**3a**) and 3-methyl-2-cyclopenten-1-one (**7a**) were purchased and used after distillation as an authentic sample for GC-analysis.

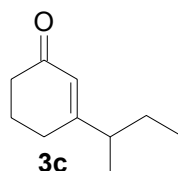
3-Butyl-2-cyclohexen-1-one (**3b**), 3-*sec*-butyl-2-cyclohexen-1-one (**3c**), 3-*tert*-butyl-2-cyclohexen-1-one (**3d**), and 3-butyl-2-cyclopenten-1-one (**7b**) were prepared according to the literature procedure⁴ by using the corresponding alkyl lithium. Spectrum data were shown below.

3-Butyl-2-cyclohexen-1-one (**3b**)⁵



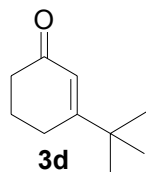
¹H NMR: δ 5.79 (s, 1H), 2.28 (t, J = 6.7 Hz, 2H), 2.22 (t, J = 6.0 Hz), 2.14 (t, J = 7.8 Hz, 2H), 1.94-1.89 (m, 2H), 1.44-1.38 (m, 2H), 1.30-1.23 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H). ¹³C NMR: δ 199.7, 166.6, 125.4, 37.6, 37.2, 29.5, 28.9, 22.6, 22.2, 13.6.

3-*sec*-Butyl-2-cyclohexen-1-one (**3c**)⁶



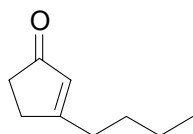
¹H NMR: δ 5.78 (s, 1H), 2.30-2.10 (5H, m), 1.95-1.85 (m, 2H), 1.50-1.30 (m, 2H), 1.05 (d, J = 6.9 Hz, 3H), 0.78 (t, J = 7.8 Hz, 3H). ¹³C NMR: δ 199.9, 170.7, 124.9, 43.1, 37.5, 27.3, 26.8, 22.7, 18.3, 11.6.

3-*tert*-Butyl-2-cyclohexen-1-one (**3d**)⁷



¹H NMR: δ 5.88 (s, 1H), 2.30-2.28 (m, 4H), 1.95-1.89 (m, 2H), 1.06 (s, 9H). ¹³C NMR: δ 200.0, 173.2, 122.3, 36.8, 36.1, 27.6, 25.2, 22.6.

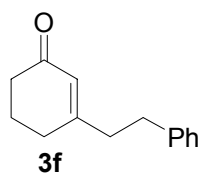
3-Butyl-2-cyclopenten-1-one (**7b**)⁵



¹H NMR: δ 5.90-5.88 (m, 1H), 2.55-2.51 (m, 2H), 2.40-2.32 (m, 4H), 1.57-1.48 (m, 2H), 1.37-1.20 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ¹³C NMR: δ 209.7, 182.8, 128.8, 34.7, 32.7, 31.0, 28.6, 21.9, 13.22.

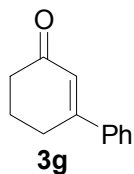
Following compounds were isolated after the β-substitution of enones with an alkyl group by using **1**.

3-(2-phenylethyl)-2-cyclohexen-1-one (**3f**)⁸



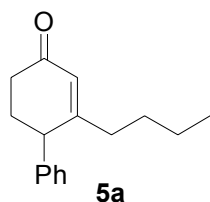
¹H NMR: δ 7.31-7.16 (m, 5H), 5.89 (s, 1H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 2.35 (t, *J* = 6.7 Hz, 2H), 2.29 (t, *J* = 5.7 Hz), 1.98 (tt, *J* = 6.7, 5.7 Hz, 2H). ¹³C NMR: δ 199.7, 166.4, 140.6, 128.7, 128.1, 127.1, 126.9, 45.1, 36.0, 33.7, 31.5, 29.1, 22.2, 13.7.

3-Phenyl-2-cyclohexen-1-one (**3g**)



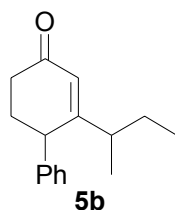
¹H NMR: δ 7.55-7.52 (m, 2H), 7.42-7.40 (m, 3H), 6.41 (s, 1H), 2.76 (t, *J* = 6.0 Hz, 2H), 2.47 (t, *J* = 6.9 Hz, 2H), 2.17-2.12 (m, 2H). ¹³C NMR: δ 199.7, 159.6, 138.6, 129.8, 128.6, 125.9, 125.2, 37.1, 27.9, 22.6.

3-Butyl-4-phenyl-2-cyclohexen-1-one (**5a**)



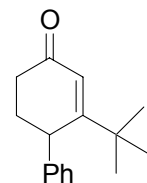
^1H NMR: δ 7.35-7.15 (m, 5H), 6.11 (s, 1H), 3.64 (t, $J = 4.1$ Hz), 2.40-2.20 (m, 3H), 2.10-2.00 (m, 3H), 1.50-1.35 (m, 2H), 1.30-1.15 (m, 2H), 0.83 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR: 199.7, 166.4, 140.6, 128.7, 128.1, 127.1, 126.9, 45.1, 36.0, 33.7, 31.5, 29.1, 22.2, 13.73. IR(KBr, cm^{-1}) 2930, 1673, 1626, 703; MS(EI) m/z 228 (M⁺). HRMS(EI) Found: m/z 228.1527. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: 228.1514.

3-*sec*-Butyl-4-phenyl-2-cyclohexen-1-one (**5b**)



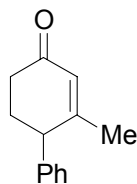
^1H NMR (as a mixture of diastereomers): δ 7.32-7.17 (m, 5H), 6.13 (s, 0.57H), 6.10 (s, 0.43H), 3.73-3.71 (m, 1H), 2.40-2.20 (m, 3H), 2.05-1.95 (m, 2H), 1.56-1.44 (m, 1H), 1.41-1.30 (m, 1H), 1.02 (d, $J = 6.9$ Hz, 1.71H), 0.97 (d, $J = 7.3$ Hz, 1.29H), 0.83 (t, $J = 7.4$ Hz, 1.71H), 0.79 (t, $J = 7.4$ Hz, 1.29H). ^{13}C NMR (as a mixture of diastereomers): 200.1, 200.0, 171.1, 170.7, 140.3, 140.3, 128.7, 128.6, 128.3, 128.2, 127.0, 126.9, 125.9, 125.8, 45.3, 43.8, 41.5, 40.1, 33.4, 33.2, 31.8, 31.5, 29.2, 27.2, 20.2, 17.9, 12.0, 11.3. IR(KBr, cm^{-1}) 2963, 1671, 1452, 1248, 884, 704; MS(EI) m/z 228 (M⁺). HRMS(EI) Found: m/z 228.1517. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: 228.1514.

3-*tert*-Butyl-4-phenyl-2-cyclohexen-1-one (**5c**)



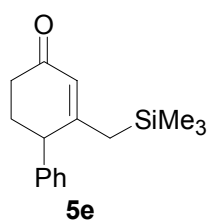
^1H NMR: δ 7.30-7.15 (m, 5H), 6.26 (s, 1H), 3.95 (t, $J = 4.1$ Hz, 1H), 2.35-2.15 (m, 3H), 2.05-2.00 (m, 1H), 1.03 (9H, s). ^{13}C NMR: δ 200.9, 172.7, 140.2, 128.5, 127.9, 126.7, 125.6, 41.5, 37.3, 32.6, 32.1, 29.19. IR(KBr, cm^{-1}) 2966, 1671, 1245, 760, 704; MS(EI) m/z 228 (M⁺). HRMS(EI) Found: m/z 228.1520. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: 228.1514.

3-Methyl-4-phenyl-2-cyclohexen-1-one (**5d**)⁹



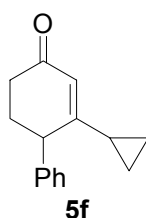
¹H NMR: δ 7.35-7.15 (m, 5H), 6.09 (s, 1H), 3.57 (t, $J = 4.6$ Hz, 1H), 2.40-2.25 (m, 3H), 2.10-2.00 (m, 1H), 1.81 (3H, s). ¹³C NMR: δ 199.4, 162.5, 140.5, 128.7, 128.4, 128.0, 127.0, 46.4, 33.9, 31.4, 23.4. IR(KBr, cm⁻¹) 1670, 1248, 703.

4-Phenyl-3-trimethylsilylmethyl-2-cyclohexen-1-one (**5e**)



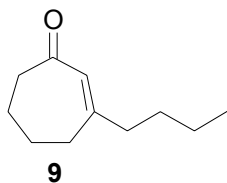
¹H NMR: δ 7.33-7.19 (m, 5H), 6.00 (s, 1H), 3.53 (t, $J = 4.6$ Hz, 1H), 2.40-2.20 (m, 3H), 2.05-2.00 (m, 1H), 1.85 (d, $J = 12$ Hz, 1H), 1.54 (d, $J = 12$ Hz, 1H), 0.06 (s, 9H). ¹³C NMR: δ 198.9, 166.7, 140.3, 128.7, 128.3, 127.0, 126.0, 46.6, 32.9, 31.2, 29.4, -1.3. IR(KBr, cm⁻¹) 1663, 1249, 847; MS(EI) m/z 258 (M⁺). HRMS(EI) Found: m/z 258.1434. Calcd for C₁₆H₂₂OSi: 258.1440.

3-Cyclopropyl-4-phenyl-2-cyclohexen-1-one (**5f**)



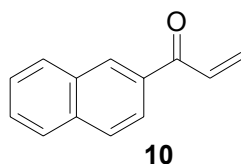
¹H NMR: δ 7.34-7.21 (m, 5H), 5.89 (s, 1H), 3.67 (t, $J = 5.0$ Hz, 1H), 2.40-2.22 (m, 3H), 2.07-2.02 (m, 1H), 1.30-1.25 (m, 1H), 0.86-0.75 (m, 3H), 0.62-0.59 (m, 1H). ¹³C NMR: δ 199.2, 169.2, 140.6, 128.7, 128.2, 126.9, 122.6, 45.0, 33.6, 31.6, 16.7, 10.4, 10.1. IR(KBr, cm⁻¹) 3025, 2943, 1655, 1618, 1251, 703; MS(CI) m/z 213 (M⁺); MS(EI) m/z 212 (M⁺). HRMS(EI) Found: m/z 212.1191. Calcd for C₁₅H₁₆O: 212.1201.

3-Butyl-2-cyclohepten-1-one (**9**)¹⁰



¹H NMR: δ 5.90 (s, 1H), 2.56 (t, J = 6.4 Hz, 2H), 2.40 (t, J = 6.0 Hz, 2H), 2.18 (t, J = 7.8 Hz, 2H), 1.80-1.75 (m, 4H), 1.50-1.30 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H). ¹³C NMR: δ 204.1, 162.4, 129.1, 42.1, 40.7, 32.5, 29.7, 25.1, 22.3, 21.2, 13.8. IR(KBr, cm⁻¹) 1660; MS(EI) m/z 166 (M⁺). HRMS (EI) Found: m/z 166.1348. Calcd for C₁₁H₁₈O: 166.1358.

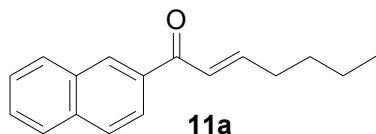
2-Naphthyl vinyl ketone (**10**) was prepared by the following procedure.



To a stirred suspension of *N,O*-dimethylhydroxylamine hydrochloride (0.57 g, 5.84 mmol) in CH₂Cl₂ (20 mL) was added triethylamine (1.33 g, 13.1 mmol) and 2-naphthoyl chloride (1.00 g, 5.25 mmol) at 0 °C, and the mixture was stirred overnight at room temperature. The mixture was washed with 1N HCl solution and saturated NaHCO₃, dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was purified by silica gel chromatography (hexane/ethyl acetate = 2/1) to give *N*-methoxy-*N*-methyl-2-naphthalenecarboxamide (1.11 g, 5.18 mmol, 99%).

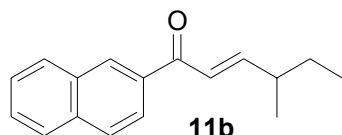
To a stirred solution of *N*-methoxy-*N*-methyl-2-naphthalenecarboxamide (1.00 g, 4.65 mmol) in dry ether (47 mL) was added a solution of vinylmagnesium bromide in THF (1 N, 9.3 mL) at -78 °C, and the mixture was stirred at 0 °C for 10 min. The reaction was quenched by adding saturated NH₄Cl solution, and the resulting mixture was extracted with ethyl acetate. The extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 20/1) to give **10**¹¹ (350 mg, 1.92 mmol, 41%) as a colorless solid: mp 39-40 °C. ¹H NMR: δ 8.47 (s, 1H), 8.04 (dd, J = 1.4, 8.3 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.61 (ddd, J = 1.4, 6.7, 8.0 Hz, 1H), 7.57 (ddd, J = 1.4, 6.9, 7.6 Hz, 1H), 7.33 (dd, J = 11, 17 Hz, 1H), 6.51 (dd, J = 1.4, 17 Hz, 1H), 5.99 (dd, J = 11 Hz, 1H). ¹³C NMR: δ 190.8, 135.5, 134.6, 132.5, 132.3, 130.4, 130.0, 129.5, 128.6, 128.5, 127.8, 126.8, 124.4.

(*E*)-2-(2-Heptenoyl)naphthalene (**11a**)



^1H NMR: δ 8.44 (s, 1H), 8.03 (dd, $J = 1.9, 8.7$ Hz, 1H), 7.97 (d, $J = 7.8$ Hz, 1H), 7.91 (d, $J = 8.7$ Hz, 1H), 7.88 (d, $J = 8.3$ Hz, 1H), 7.61-7.53 (m, 2H), 7.14 (dt, $J = 15, 6.9$ Hz, 1H), 7.04 (d, $J = 15$ Hz), 2.37 (q, $J = 6.9$ Hz, 2H), 1.58-1.52 (m, 2H), 1.45-1.38 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR: δ 190.7, 150.0, 135.4, 135.3, 132.5, 129.9, 129.4, 128.4, 128.2, 127.8, 126.7, 125.8, 124.5, 32.6, 30.3, 22.3, 13.9. IR(KBr, cm^{-1}) 1666, 1618, 1293, 750; MS(EI) m/z 238 (M⁺). HRMS(EI) Found: m/z 238.1355. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$: 238.1358.

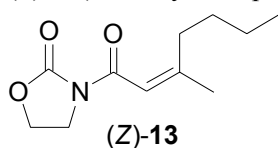
(*E*)-2-(4-Methyl-2-hexenoyl)naphthalene (**11b**)



^1H NMR: δ 8.44 (s, 1H), 8.03 (dd, $J = 1.4, 8.7$ Hz, 1H), 7.97 (d, $J = 8.3$ Hz, 1H), 7.91 (d, $J = 8.7$ Hz, 1H), 7.88 (d, $J = 8.3$ Hz, 1H), 7.62-7.53 (m, 2H), 7.04 (dd, $J = 6.6, 16$ Hz), 7.00 (d, $J = 16$ Hz, 1H), 2.43-2.35 (m, 1H), 1.65-1.46 (m, 2H), 1.16 (d, $J = 6.9$ Hz, 3H), 0.96 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR: δ 190.9, 155.1, 135.4, 135.4, 132.5, 129.9, 129.5, 128.4, 128.2, 127.8, 126.7, 124.6, 124.2, 38.8, 29.0, 19.1, 11.8. IR(KBr, cm^{-1}) 2962, 1667, 1616, 1459, 1360, 1296, 1187, 1124, 984, 822, 750; MS(EI) m/z 238 (M⁺). HRMS (EI) Found: m/z 238.1371. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$: 238.1358.

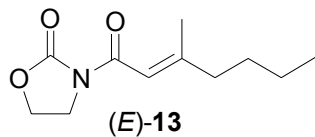
N-Crotonoyl-2-oxazolidone (**12**) was prepared by Evans' procedure.¹²

(*Z*)-*N*-(3-Methyl-2-heptenoyl)-2-oxazolidone ((*Z*)-**13**)



^1H NMR: δ 6.89 (s, 1H), 4.38 (t, $J = 8.0$ Hz, 2H), 4.04 (t, $J = 8.0$ Hz, 2H), 2.58 (t, $J = 7.8$ Hz, 2H), 1.97 (d, $J = 0.9$ Hz, 3H), 1.48-1.42 (m, 2H), 1.40-1.35 (m, 2H), 0.92 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR: δ 164.8, 163.8, 153.4, 115.0, 61.7, 42.7, 34.3, 30.3, 25.9, 22.9, 13.9. IR(KBr, cm^{-1}) 1773, 1678, 1627, 1387, 1269, 1217, 1043, 708; MS(EI) m/z 211 (M⁺). HRMS(EI) Found: m/z 211.1192. Calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_3$: 211.1208. NOE (1.28%) was observed between the vinylic proton and the 3-methyl group.

(*E*)-*N*-(3-Methyl-2-heptenoyl)-2-oxazolidone ((*E*)-**13**)



^1H NMR: δ 6.93 (s, 1H), 4.38 (t, $J = 8.1$ Hz, 2H), 4.04 (t, $J = 8.1$ Hz, 2H), 2.22 (t, $J = 7.6$ Hz, 2H), 2.16 (d, $J = 1.4$ Hz, 3H), 1.51-1.44 (m, 2H), 1.35-1.30 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR: δ 165.4, 163.3, 153.5, 114.7, 61.7, 42.6, 41.2, 29.6, 22.3, 19.9, 13.9. IR(KBr, cm^{-1}) 2929, 1775, 1678, 1627, 1386, 1269, 1222, 1185, 1042: MS(CI) 212 (M+1); MS(EI) m/z 211 (M+). HRMS(EI) Found: m/z 211.1208. Calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_3$: 211.1208.

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