SUPPORTING INFORMATION

Title: Hydrolytic Deallylation of N-Allyl Amides Catalyzed by Pd$^{	ext{II}}$ Complexes
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General

$^1$H and $^{13}$C NMR spectra were recorded on a JEOL AL-400 spectrometer. GC analysis was carried out using an Agilent GC 6850 equipped with J & W INNOWax Column (length 30 m, 0.25 mm I.D.). GC-MS analysis was performed with a Thermo Fisher Scientific Polaris Q equipped with a Trace TR-5 Column (length 7 m, 0.32 mm I.D.). HPLC analysis was performed with a JASCO PU-1580 with UV-1575 chromatograph equipped with a DAICEL CHIRALCEL OD-H (eluent: hexane:2-propanol = 20:1). Optical rotations were measured with a Horiba SEPA-300 polarimeter. All compounds are known except for 12 and 19. Characterization of 12 and 19 is given in following part. Compound 20 was purchased from Wako Chemical. All amide products were commercially available and characterized by GC and GC-MS analysis except for following three compounds. β-Butyrolactam was synthesized by a literature procedure. ($S$)-N-(1-Phenylethyl)acetamide was synthesized from ($S$)-1-phenylethylamine and acetyl chloride. ($S$)-2-tert-Butoxycarbonylamino-3-phenylpropionic acid methyl ester was synthesized from L-phenylalanine methyl ester and Boc2O. H$_2$O was purchased from Taiyo Nippon Sanso ($^{18}$O: 99 atm%, lot: YEHO027A).

Syntheses of N-allyl amide substrates

Typical procedure for the synthesis of N-allyl amides (1, 5–13, 15–18): Under N$_2$ atmosphere, an amide was added to a suspension of sodium hydride (1.1–1.5 equiv.) in THF at 0 °C and stirred for 10–60 min at 0–60 °C. Then allyl bromide (1.1–2.0 equiv.) was added at 0 °C, and the mixture was stirred overnight at 20–85°C. Water was added, and the product was extracted with diethyl ether, then the extracts were dried over sodium sulfate. The solvents were removed and the residue was subjected to column chromatography on silica-gel to afford an N-allylamide.

N-allyl-N-methylbenzamide (1): prepared from N-methylbenzamide (4.05 g, 30 mmol), yield: 5.32 g (quant.). Existing as a 3:2 mixture of rotamers. $^1$H NMR (CDCl$_3$, 400 MHz) δ = 2.90 (bs, 3H, minor, C$_2$H$_3$), 3.05 (bs, 3H, major, C$_2$H$_3$), 3.83 (bs, 2H, major, NC$_2$H$_2$), 4.15 (bs, 2H, minor, NC$_2$H$_2$), 5.18–5.25 (m, 2H, CH=C$_2$H$_2$), 5.68–5.80 (m, 1H, major, C$_2$H=CH$_2$), 5.80–5.94 (m, 1H, minor, C$_2$H=CH$_2$), 7.34–7.44 (m, 5H, aromatic).

N-allyl-β-butyrolactam (5): prepared from β-butyrolactam (1.67 mL, 20 mmol), yield: 1.55 g (62%). $^1$H NMR (CDCl$_3$, 400 MHz) δ = 1.30–1.35 (m, 3H, CH$_3$), 2.48–2.55 (m, 1H, COC$_2$H$_2$), 3.04–3.12 (m, 1H, CHHCO), 3.60–3.69 (m, 1H, NCH$_2$), 3.69–3.72 (m, 1H, CH$_3$), 3.94–4.00 (m, 1H, NC$_2$H), 5.16–5.25 (m, 2H, CH=CH$_2$), 5.74–5.81 (m, 1H, CH=CH$_2$).

N-allyl-γ-butyrolactam (6): prepared from γ-butyrolactam (4.00 g, 47 mmol), yield: 6.11 g (quant.). $^1$H NMR (CDCl$_3$, 400 MHz) δ = 1.98–2.07 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.41 (t, J = 8.0 Hz, 2H, COCH$_2$), 3.35 (t, J = 7.2 Hz, 2H, NCH$_2$CH$_2$), 3.89 (d, J = 6.0 Hz, 2H, NCH$_2$CH=CH$_2$), 5.15–5.18 (m, 1H, CH=CHH), 5.19–5.21 (m, 1H, CH=CHH), 5.69–5.78 (ddt, J = 17.2, 10.0, 6.0 Hz, 1H, CH=CH$_2$).

N-allyl-δ-valerolactam (7): prepared from δ-valerolactam (4.66 g, 47 mmol), yield: 6.51 g (99%). $^1$H NMR (CDCl$_3$, 400 MHz) δ = 1.77–1.83 (m, 4H, CH$_2$(CH$_2$)$_2$CH$_2$), 2.38–2.42 (m, 2H, COCH$_2$), 3.23–3.25 (m, 2H, NCH$_2$CH$_2$), 3.97–4.01 (m, 2H, NCH$_2$CH=CH$_2$), 5.15 (dd, J = 16.8, 1.6 Hz, 1H, CH=CHH), 5.17 (dd, J = 10.4, 1.6 Hz, 1H, CH=CHH), 5.76 (ddt, J = 16.8, 10.4, 6.0 Hz, 1H, CH=CH$_2$).
N- Allyl-ε-caprolactam (8): prepared from ε-caprolactam (10.62 g, 94 mmol), yield: 6.51 g (99%). ¹H NMR (CDCl₃, 400 MHz) δ = 1.60–1.74 (m, 6H, CH₂(C₂H₅)₂CH₂), 2.53–2.56 (m, 2H, COCH₂), 3.29–3.31 (m, 2H, NCH₂CH=C=CH₂), 4.01 (ddd, J = 6.0, 1.4, 1.4 Hz, 2H, NCH₂CH=C=CH₂), 5.12–5.14 (m, 1H, CH=CHH), 5.15–5.19 (m, 1H, CH=C=CHH), 5.76 (ddt, J = 16.8, 10.4, 6.0 Hz, 1H, CH=CH₂).

N- Allyl-ω-heptanolactam (9): prepared from ω-heptanolactam (3.82 g, 30 mmol), yield: 6.09 g (99%). ¹H NMR (CDCl₃, 400 MHz) δ = 1.45–1.85 (m, 8H, CH₂(C₂H₅)₄CH₂), 2.48–2.54 (m, 2H, COCH₂), 3.45–3.48 (m, 2H, NC₂H₂CH₂), 3.99 (d, J = 6.0 Hz, 2H, NC₂H₂CH=CH₂), 5.13–5.19 (m, 2H, CH=C₂H₂), 5.76–5.84 (ddt, J = 17.2, 10.4, 6.0 Hz, 1H, CH=CH₂).

Ethyl N-allyl-N-ethylcarbamate (10): prepared from ethyl N-ethylcarbamate (4.78 g, 30 mmol), yield: 4.23 g (67%). ¹H NMR (CDCl₃, 400 MHz) δ = 1.10 (t, J = 7.2 Hz, 3H, NCH₂C₂H₃), 1.25 (t, J = 7.2 Hz, 3H, OCH₂C₂H₃), 3.27 (bs, 2H, NC₂H₂CH₃), 3.86 (bs, 2H, NC₂H₂CH=CH₂), 4.14 (q, J = 7.2 Hz, 2H, OC₂H₂CH₃), 5.09–5.18 (m, 2H, CH=C₂H₂), 5.73–5.84 (m, 1H, C₂H=CH₂).

N- Allyloxazolidinone (11): prepared from oxazolidinone (3.48 g, 40 mmol), yield: 2.75 g (54%). ¹H NMR (CDCl₃, 400 MHz) δ = 3.54 (dt, J = 1.6, 8.0 Hz, 2H, NC₂H₂CH₂), 3.87 (d, J = 6.0 Hz, 2H, NC₂H₂CH=CH₂), 4.34 (dt, J = 1.2, 8.0 Hz, 2H, OC₂H₂), 5.24–5.32 (m, 2H, CH=C₂H₂), 5.75–5.80 (m, 1H, C₂H=CH₂).

(S)-N- Allyl- N-(1-phenylethyl)acetamide (12): prepared from (S)-N-(1-phenylethyl)acetamide (4.8 g, 30 mmol), yield: 0.98 g (16%). Existing as a 3:1 mixture of rotamers. ¹H NMR (CDCl₃, 400 MHz) δ = 1.49 (d, J = 7.2 Hz, 3H, major, CHC₂H₃), 1.62 (d, J = 7.2 Hz, 3H, minor, CHC₂H₃), 2.12 (s, 3H, major, CH₃CO), 2.22 (s, 3H, minor, CH₃CO), 3.44 (dd, J = 6.4, 15.6 Hz, 1H, minor, NCH₂CH=CH₂), 3.54–3.74 (m, 2H, major and minor, CH₂(C₂H₅)₃), 4.12 (dd, J = 4.8, 15.6 Hz, 1H, minor, NCH₂HCH=CH₂), 4.96–5.13 (m, 2H, major and minor, CH=CH₂, and 1H, minor, CHC₂H₃), 5.56 (ddt, J = 17.2, 10.4, 5.2 Hz, 1H, major, CH=CH₂), 5.77 (ddt, J = 16.4, 10.4, 6.0 Hz, 1H, minor, CH=CH₂), 6.11 (q, J = 7.2 Hz, 1H, major, CH₂(C₂H₅)₃), 7.22–7.38 (m, 5H, aromatic), ¹³C NMR (CDCl₃, 150 MHz) δ = 16.5 (major), 18.6 (minor), 21.9, 45.1 (minor), 46.5 (major), 50.7 (major), 56.2 (minor) 115.7 (minor), 116.1(major), 126.4 (minor), 127.1 (major), 127.3 (minor), 128.0 (major), 128.2 (major), 128.5 (minor), 134.9, 140.5 (minor), 140.8 (major), 170.1(major), 171.0 (major); elemental analysis: calcd (%) for C₁₃H₁₇NO: C 76.81, H 8.43, N 6.89; found: C 76.86, H 8.51, N 6.92; [α]D²⁵ = –25.0 (c = 1.00, CHCl₃).

(S)-2-(Allyl-tert-butoxycarbonylamino)-3-phenylpropionic acid methyl ester (13): prepared from (S)-2-tert-butoxycarbonylamino-3-phenylpropionic acid methyl ester (8.3 g, 30 mmol), using potassium carbonate instead of sodium hydride, yield: 2.14 g (22%). Existing as a 2:1 mixture of rotamers. ¹H NMR (CDCl₃, 400 MHz) δ = 1.39–1.50 (bs, 9H, major and minor, C(CH₃)₃), 3.10–3.40, 3.73–4.12 (m, 2H, major and minor, PHCH₂), 2H major and minor, NCH₂CH=CH₂, and 1H major, NCH₂, 3.70–3.72 (bs, 3H, major and minor, OCH₃), 4.37–4.43(m, 1H, minor, NCH₂), 4.96–5.03 (m, 2H, major and minor, CH=CH₂), 5.45–5.58 (m, 1H, major and minor, CH=CH₂), 7.13–7.31 (m, 5H, aromatic); [α]D²⁵ = 50.5 (c = 1.00, CHCl₃).
**N-Allyldiacetamide (15):** obtained as a byproduct of 14, see synthesis of 14 (4.05 g, 30 mmol), yield: 3.74 g (6%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 2.42$ (s, 6H, COCH$_3$), 4.34–4.35 (m, 2H, NCH$_2$CH=CH$_2$), 5.12 (ddd, $J = 17.2, 0.8, 0.8$ Hz, 1H, CH=CHH), 5.20 (ddd, $J = 10.4, 0.8, 0.8$ Hz, 1H, CH=CHH) 5.84 (ddt, $J = 17.2, 10.4, 5.6$ Hz, 1H, CH=CH$_2$).

**N,N-Diallylacetamide (16):** prepared from N-allylacetamide 14 (4.5 mL, 40 mmol), yield: 1.77 g (31%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 2.10$ (s, 3H, COCH$_3$), 3.87 (d, $J = 4.8$ Hz, 2H, NC$_2$H$_4$CH=CH$_2$), 3.99 (d, $J = 6.4$ Hz, 2H, NC$_2$H$_4$CH=CH$_2$), 5.10–5.23 (m, 4H, CH=C$_2$H$_2$), 5.70–5.83 (m, 2H, CH=CH$_2$).

**N-Allylphthalimide (17):** prepared from phthalimide (5.89 g, 40 mmol), yield: 2.14 g (45%) $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 4.28–4.32$ (m, 2H, NC$_2$H$_4$CH=CH$_2$), 5.18–5.22 (m, 1H, CH=CH$_2$), 5.22–5.29 (m, 1H, CH=C$_2$H$_2$), 5.85–5.95 (m, 1H, CH=CH$_2$), 7.72–7.74 (m, 2H, aromatic), 7.85–7.87 (m, 2H, aromatic).

**N-Allylformanilide (18):** prepared from formanilide (4.85 g, 40 mmol), yield: 5.32 g (quant.) $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 4.42$ (dd, $J = 5.6, 0.8$ Hz, 2H, NCH$_2$CH=CH$_2$), 5.14–5.23 (m, 2H, CH=C$_2$H$_2$), 5.80–5.90 (m, 1H, CH=CH$_2$), 7.18–7.41 (m, 5H, aromatic), 8.48 (s, 1H, CHO).

**N-Allyl-N-methylacetamide (2):** N-Allylacetamide 14 (2.3 mL, 20 mmol) was added to a suspension of sodium hydride (1.8 g, 45 mmol) in THF at 0 °C and stirred for 1 h, and then methyl iodide (25.0 mL, 400 mmol) was added to this solution at 0 °C. Then, the mixture was refluxed overnight. Water was added, and the product was extracted with ethyl acetate. The extracts were dried over sodium sulfate, the solvents were removed, and the residue was subjected to column chromatography on silica-gel. The elution with ethylacetate-hexane mixture (10:1) afforded 2 (3.58 g, 99%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 2.01–2.11$ (m, 3H, COCH$_3$), 2.85–2.96 (m, 3H, NC$_2$H$_3$), 3.83–4.00 (m, 2H, NC$_2$H$_4$CH=CH$_2$), 5.05–5.24 (m, 2H, CH=C$_2$H$_2$), 5.65–5.84 (m, 1H, CH=CH$_2$).

**N-Allyl-N-ethylacetamide (3):** N-Allylacetamide 14 (4.5 mL, 40 mmol) was added to a suspension of sodium hydride (1.8 g, 48 mmol) in THF at 0 °C and stirred for 1 h, and then ethyl iodide (6.4 mL, 80 mmol) was added to this solution at 0 °C. Then the mixture was refluxed overnight at 80 °C. Water was added, and the product was extracted with diethyl ether. The extracts were dried over sodium sulfate, the solvents were removed, and the residue was subjected to column chromatography on silica-gel. The elution with diethylether-hexane mixture (10:1) afforded 3 (1.60 g, 31%). Existing as a 1:1 mixture of rotamers. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 1.11, 1.17$ (two sets of t, $J = 7.2$ Hz, 3H, NCH$_2$CH$_2$), 2.06, 2.12 (two sets of s, 3H, COCH$_3$), 3.31, 3.39 (two sets of q, $J = 7.2$ Hz, 2H, NCH$_2$CH$_2$), 3.88, 3.98 (two sets of d, $J = 6.0$ Hz, 2H, NCH$_2$CH=CH$_2$), 5.12–5.23 (m, 2H, CH=CH$_2$), 5.72–5.84 (m, 1H, CH=CH$_2$).
**N-Allyl-N-benzylacetamide (4):** N-Allylacetamide 14 (4.5 mL, 40 mmol) was added to a suspension of sodium hydride (1.8 g, 45 mmol) in THF at 0 °C and stirred for 1 h, and then benzyl bromide (6.5 mL, 55 mmol) was added to this solution at 0 °C. Then the mixture was refluxed overnight at 75 °C. Water was added, and the product was extracted with ethyl acetate. The extracts were dried over sodium sulfate, the solvents were removed, and the residue was subjected to column chromatography on silica-gel. The elution with diethylether-hexane mixture (2:1) afforded 4 (6.63 g, 78 %). Existing as a 3:2 mixture of rotamers. 1H NMR (CDCl3, 400 MHz), δ = 2.14 (s, 3H, minor, COC\(\text{CH}_3\)), 2.15 (s, 3H, major, COC\(\text{CH}_3\)), 3.81 (d, \(J = 4.4 \text{ Hz}\), 2H, major, \(\text{NC}\text{H}_2\text{CH=CH}_2\)), 4.01 (d, \(J = 6.0 \text{ Hz}\), 2H, minor, \(\text{NC}\text{H}_2\text{CH=CH}_2\)), 4.50 (s, 1H, minor, PhC\(\text{H}_2\)), 4.59 (s, 1H, major, PhC\(\text{H}_2\)), 5.07–5.23 (m, 2H, major and minor, CH=CH\(\text{H}_2\)), 5.67–5.83 (m, 1H, major and minor, CH=CH\(\text{H}_2\)), 7.15–7.38 (m, 5H, aromatic).

**N-Allylacetamide (14):** Allylamine (33 mL, 430 mmol) was added dropwise with stirring to acetic anhydride (70 mL, 735 mmol) at 0 °C. After the addition was completed (~1 h) the temperature was raised to 100 °C for 1.5 h. The solvents were removed, and the residue was subjected to column chromatography on silica-gel. The elution with dichloromethane-hexane mixture (10:1) afforded 14 (41.7 g, 98%). 1H NMR (CDCl3, 400 MHz) δ = 2.01 (s, 3H, COC\(\text{H}_3\)), 3.86–3.88 (m, 2H, \(\text{NC}\text{H}_2\text{CH=CH}_2\)), 5.13 (d, \(J = 10.4 \text{ Hz}\), 1H, \(\text{CH=CH}_2\)), 5.19 (d, \(J = 16.8 \text{ Hz}\), 1H, CH=CH\(\text{H}_2\)), 5.75 (bs, 1H, NH), 5.84 (ddt, \(J = 16.8, 10.4, 5.6 \text{ Hz}\), 1H, \(\text{CH=CH}_2\)).

**Ru-catalyzed isomerization of 9**

**N-((E)-1-Propenyl)-ω-heptanolactam (19):** N-Allyl-ω-heptanolactam 9 (1.8 mL, 10 mmol) and toluene (10 mL) were placed into a dry nitrogen filled 50 mL Schlenk tube, and the vessel was degassed by three freeze-thaw cycles. To this was added RuCl\(_2\)(PPh\(_3\))\(_3\) under N\(_2\) atmosphere. The mixture was refluxed for 20 h at 110 °C. The solvents were removed, and residue was subjected to column chromatography on silica-gel. The elution with diethylether-hexane mixture (1:1) afforded 19 (1.60 g, 96%). The olefin geometry was determined by coupling constants of 1H NMR. 1H NMR (CDCl3, 400 MHz) δ = 1.42–1.87 (m, 8H, \(\text{CH}_2(\text{CH}_2)_{4}\text{CH}_2\)), 1.73 (dd, \(J = 6.4, 1.6 \text{ Hz}\), 3H, \(\text{CH}_3\)), 2.55–2.60 (m, 2H, COC\(\text{H}_2\)), 3.74 (t, \(J = 6.0 \text{ Hz}\), 2H, \(\text{NC}\text{H}_2\)), 5.09 (dq, \(J = 14.4, 6.4 \text{ Hz}\), 1H, CHCH\(\text{H}_2\)), 7.19 (dd, \(J = 14.4, 1.6 \text{ Hz}\), 1H, NCH=CH); 13C NMR (CDCl3, 150 MHz) δ = 15.2, 23.8, 26.2, 27.7, 28.8, 34.3, 43.5, 105.9, 125.7, 172.8; elemental analysis: calcld (%) for C\(_{10}\)H\(_{17}\)NO: C 71.81, H 10.25, N 8.37; found: C 71.84, H 10.28, N 8.27.

**18O-labeled experiment**

Hydrolytic deallylation with H\(_2\)\(^{18}\)O was carried out with 8: propanal was analyzed by GC-MS: \(m/z\) calcld for C\(_3\)H\(_7\)\(^{18}\)O: 61.1 [M+H]; found 61.0; \(m/z\) calcld for C\(_3\)H\(_5\)\(^{18}\)O: 59.0 [M–H]; found 59.0. cf. the reaction with H\(_2\)O; GC-MS: \(m/z\) calcld for C\(_3\)H\(_5\)O: 59.0 [M+H]; found 59.0; \(m/z\) calcld for C\(_3\)H\(_5\)O: 57.0 [M–H]; found 57.0. In both cases, same fragments 42.3 (C\(_3\)H\(_6\)) and 40.1 (C\(_3\)H\(_4\)) was observed.

**Reference**