

Supplementary Information

Pd•Et₃B-Catalyzed Alkylation of Amines with Allylic Alcohols

Masanari Kimura, Makoto Futamata, Kazufumi Shibata, and Yoshinao Tamaru

Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, 1-14
Bunkyo-machi, Nagasaki 852-8521, Japan
masanari@net.nagasaki-u.ac.jp

General: Pd salts [Pd(PPh₃)₄, Pd(OAc)₂] and triethylborane (1.0 M solution in hexanes), were purchased and used without further purification. Tetrahydrofuran was distilled from a blue solution of sodium benzophenone ketyl under N₂ immediately prior to use. *cis*-5-Methoxycarbonylcyclohexen-3-ol (**2**) was prepared according to the literature.¹

Standard Experimental Procedure (run 2, Table 1): Into a N₂ purged flask containing Pd(PPh₃)₄ (0.05 mmol), were added successively THF (5 mL), allyl alcohol (1.2 mmol), *N*-methylaniline (1.0 mmol), and Et₃B (0.3 mmol, 1 M in hexane) via syringe. The reaction mixture was stirred at ambient temperature for 30 h, during which the reaction was monitored by means of TLC. After dilution with ethyl acetate (30 mL), the

mixture was washed with aq. NaHCO₃ and brine. The organic layer was dried (MgSO₄) and concentrated *in vacuo*, and the residue is purified by column chromatography over silica gel (FUJI SILYSIA NH; hexane) to provide **1a** in 96% yield.

***N*-2-Propenyl-*N*-methylaniline (1a)**

IR (neat film) ν 3060 (w), 2980 (w), 2870 (w), 1643 (w), 1448 (w), 1425 (w), 1352 (s), 1250 (s), 1211 (s), 748 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.91 (s, 3 H), 3.90 (dt, J = 5.1, 1.7 Hz, 2 H), 5.13 (ddd, J = 1.7, 3.3, 10.3 Hz, 1 H), 5.15 (ddd, J = 1.7, 3.3, 17.2 Hz, 1 H), 5.83 (ddt, J = 10.3, 17.2, 5.1 Hz, 1 H), 6.66 – 6.74 (m, 3 H), 7.18 – 7.24 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 38.0, 55.3, 112.6, 116.2, 116.5, 129.1, 129.4, 133.9, 149.60. Anal. Calcd for C₁₀H₁₃N: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.59; H, 8.94; N, 9.49.

Dibenzyl-2-propenylamine (1b)

IR (neat film) ν 3063 (w), 2922 (w), 2795 (m), 1641 (w), 1603 (w), 1495 (m), 1256 (w), 1121 (m), 745 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.06 (dt, J = 6.2, 1.8 Hz, 2 H), 3.57 (s, 4 H), 5.14 (ddd, J = 1.8, 3.3, 10.3 Hz, 1 H), 5.20 (ddd, J = 1.8, 3.3, 17.2 Hz, 1 H), 5.91 (ddt, J = 10.3, 17.2, 6.2 Hz, 1 H), 7.19 – 7.24 (m, 2 H), 7.27 – 7.32 (m, 4 H), 7.34 – 7.38 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 56.4, 57.8, 117.3, 126.8, 128.2, 128.7, 136.0, 139.7. Anal. Calcd for C₁₇H₁₉N: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.07; H, 8.24; N, 5.86.

Dicyclohexyl-2-propenylamine (1c)

IR (neat film) ν 2927 (s), 2852 (s), 1639 (w), 1448 (m), 1257 (w), 1103 (m), 912 (m)

cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.14 - 1.30 (m, 10 H), 1.67 - 1.76 (m, 10 H), 2.50 - 2.59 (m, 2 H), 3.20 (dt, *J* = 6.1, 1.8 Hz, 2 H), 4.97 (ddd, *J* = 1.8, 3.7, 10.3 Hz, 1 H), 5.10 (ddd, *J* = 1.8, 3.7, 17.2 Hz, 1 H), 5.85 (ddt, *J* = 10.3, 17.2, 6.1 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 25.3, 26.5, 31.9, 34.4, 49.3, 53.1, 114.2, 140.7. Anal. Calcd for C₁₅H₂₇N: C, 81.38; H, 12.29; N, 6.33. Found: C, 81.04; H, 12.20; N, 6.29.

***N*-2-Propenylaniline (1d)**

IR (neat film) ν 3414 (s), 3051 (s), 2841 (m), 1645 (m), 1504 (s), 1433 (s), 1418 (m), 1315 (s), 1254 (s), 1180 (s), 746 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.78 (dt, *J* = 5.1, 1.5 Hz, 2 H), 5.16 (ddd, *J* = 1.5, 2.9, 10.3 Hz, 1 H), 5.28 (ddd, *J* = 1.5, 2.9, 17.2 Hz, 1 H), 5.96 (ddt, *J* = 10.3, 17.2, 5.1 Hz, 1 H), 6.63 (br t, *J* = 7.5 Hz, 2 H), 6.70 (br d, *J* = 7.5 Hz, 1 H), 7.14 - 7.20 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 46.6, 113.0, 116.2, 117.6, 129.3, 135.5, 148.1. Anal. Calcd for C₉H₁₁N: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.01; H, 8.40; N, 10.16.

***N,N*-Di-2-propenylaniline (1e)**

IR (neat film) ν 3061 (w), 2910 (w), 2860 (w), 1643 (w), 1599 (s), 1504 (s), 1352 (m), 746 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.92 (dt, *J* = 5.1, 1.8 Hz, 2 H), 5.14 (ddd, *J* = 1.8, 3.7, 10.3 Hz, 1 H), 5.17 (ddd, *J* = 1.8, 3.7, 17.2 Hz, 1 H), 5.86 (ddt, *J* = 10.3, 17.2, 5.1 Hz, 1 H), 6.64 - 6.73 (m, 3 H), 7.16 - 7.22 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 52.8, 112.4, 116.0, 116.4, 129.1, 134.1, 148.7. Anal. Calcd for C₁₂H₁₅N: C, 83.19; H, 8.73; N, 7.94. Found: C, 82.90; H, 8.70; N, 8.08.

***N,N*-Di-2-propenylbenzylamine (1f)**

IR (neat film) ν 3076 (m), 2795 (s), 1643 (m), 1448 (m), 1495 (m), 1452 (m), 1259 (m),

918 (vs), 739 (s), 698 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.07 (dt, $J = 6.2, 1.3$ Hz, 4 H), 3.57 (s, 2 H), 5.14 (ddd, $J = 1.3, 2.2, 10.3$ Hz, 2 H), 5.19 (ddd, $J = 1.3, 3.7, 17.2$ Hz, 2 H), 5.88 (ddt, $J = 10.3, 17.2, 6.2$ Hz, 2 H), 7.21 – 7.35 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 25.3, 26.5, 31.9, 34.4, 49.3, 53.1, 114.2, 140.7; HRMS, Calcd for $\text{C}_{13}\text{H}_{17}\text{N}$: 187.1361. Found m/z (relative intensity): 187.1335 (M^+ , 46), 160 (47), 91 (100).

***N, N*-Di-2-propenylcyclohexylamine (1g)**

IR (neat film) ν 3076 (s), 3007 (m), 2930 (vs), 2855 (s), 1641 (s), 1450 (s), 1418 (s), 1346 (m), 1261 (s), 914 (s), 806 (m); ^1H NMR (400 MHz, CDCl_3) δ 1.16 - 1.27 (m, 4 H), 1.57 - 1.68 (m, 2 H), 1.73 – 1.82 (m, 4 H), 2.53 (m, 1 H), 3.12 (brd d, $J = 6.4$ Hz, 4 H), 5.06 (ddd, $J = 1.8, 3.3, 10.3$ Hz, 2 H), 5.14 (ddd, $J = 1.8, 3.3, 16.9$ Hz, 2 H), 5.83 (ddt, $J = 10.3, 16.9, 6.4$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 26.2, 26.5, 29.2, 53.0, 59.2, 116.1, 137.7; HRMS, Calcd for $\text{C}_{12}\text{H}_{21}\text{N}$: 179.1674. Found m/z (relative intensity): 179.1680 (M^+ , 100), 138 (30), 96 (29), 83 (14).

***N*-2-Butenyl-*N*-methylaniline (1h)**

IR (neat film) ν 3026 (w), 2736 (m), 1599 (s), 1504 (s), 1450 (m), 1371 (s), 1204 (m), 1187 (w), 991 (s), 748 (vs), 691 (s); ^1H NMR (400 MHz, CDCl_3) δ 1.68 (br dd, $J = 1.3, 6.2$ Hz, 3 H), 2.89 (s, 3 H), 3.82 (br d, $J = 5.5$ Hz, 2 H), 5.47 (dtq, $J = 15.2, 5.5, 1.3$ Hz, 1 H), 5.60 (br dq, $J = 15.2, 6.2$ Hz, 1 H), 6.66 – 6.74 (m, 3 H), 7.18 – 7.25 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.6, 37.8, 54.5, 112.6, 116.3, 126.5, 127.4, 129.1, 149.7; HRMS, Calcd for $\text{C}_{11}\text{H}_{15}\text{N}$: 161.1204. Found m/z (relative intensity): 161.1204 (M^+ , 100), 146 (37), 120 (49), 106 (19).

***N*-(3-Phenyl-2-propenyl)-*N*-methylaniline (1i)**

IR (neat film) ν 3059 (w), 3026 (m), 2872 (w), 1599 (vs), 1506 (vs), 1448 (m), 1354 (s), 1209 (m), 1119 (m), 964 (s), 748 (s), 691 (s); ^1H NMR (400 MHz, CDCl_3) δ 2.97 (s, 3 H), 4.07 (dd, $J = 1.5, 5.5$ Hz, 2 H), 6.24 (br dt, $J = 15.9, 5.5$ Hz, 1 H), 6.51 (br d, $J = 15.9$ Hz, 1 H), 6.71 (m, 1 H), 6.76 – 6.80 (m, 2 H), 7.18 – 7.36 (m, 7 H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.0, 55.0, 112.7, 116.6, 125.8, 126.3, 127.4, 128.5, 129.2, 131.4, 137.0, 149.7; HRMS, Calcd for $\text{C}_{16}\text{H}_{17}\text{N}$: 223.1361. Found m/z (relative intensity): 223.1334 (M^+ , 70), 120 (8), 117 (100), 106 (8), 77 (16).

***N*-(2-Methyl-2-propenyl)-*N*-methylaniline (1j)**

IR (neat film) ν 3065 (m), 2909 (m), 1601 (vs), 1504 (vs), 1447 (s), 1371 (s), 1213 (s), 993 (m), 748 (vs), 691 (s); ^1H NMR (400 MHz, CDCl_3) δ 1.72 (br d s, 3 H), 2.94 (s, 3 H), 3.79 (br d s, 2 H), 4.80 (br s, 1 H), 4.84 (br s, 1 H), 6.65 – 6.71 (m, 3 H), 7.18 – 7.23 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.0, 38.2, 58.9, 110.8, 116.3, 129.1, 141.6, 149.7; HRMS, Calcd for $\text{C}_{11}\text{H}_{15}\text{N}$: 161.1204. Found m/z (relative intensity): 161.1213 (M^+ , 63), 120 (100), 106 (4), 91 (3), 77 (17).

5-(Methylphenylamino)-cyclohex-3-enecarboxylic acid methyl ester (3):

(Stereoisomeric mixture; *cis:trans* = 2.6:1) IR (nea) ν 3024 (w), 2949 (w), 1736 (s), 1599 (vs), 1504 (vs), 1435 (w), 1310 (m), 1202 (m), 1171 (m), 991 (w), 750 (s), 692 (m); (*cis*-isomer) ^1H NMR (400 MHz, CDCl_3) δ 1.67 (dt, $J = 11.0, 12.8$ Hz, 1 H), 2.17 (dm, $J = 12.8$ Hz, 1 H), 2.26 – 2.39 (m, 2 H), 2.69 – 2.80 (m, 2 H), 2.74 (s, 3 H), 3.67 (s, 3 H), 4.55 (m, 1 H), 5.65 (dm, $J = 10.6$ Hz, 1 H), 5.88 (dddd, $J = 2.6, 5.1, 7.3, 10.0$ Hz, 1 H), 6.58 – 6.82 (m, 2 H), 7.16 – 7.26 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.5, 27.6, 32.1, 39.4, 51.8, 55.8, 113.3, 117.0, 128.3, 129.3, 130.3, 149.4, 175.3. *trans*-

isomer: ^1H NMR (400 MHz, CDCl_3) δ 1.94 (ddd, $J = 4.0, 6.2, 13.6$ Hz, 1 H), 2.08 (ddd, $J = 5.9, 8.4, 13.6$ Hz, 1 H), 2.26 – 2.39 (m, 2 H), 2.69 – 2.80 (m, 2 H), 2.83 (s, 3 H), 3.70 (s, 3 H), 4.55 (m, 1 H), 5.70 (dm, $J = 10.6$ Hz, 1 H), 5.96 (dddd, $J = 2.2, 3.7, 6.2, 10.0$ Hz, 1 H), 6.58 – 6.82 (m, 2 H), 7.16 – 7.26 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.0, 28.0, 33.2, 37.0, 51.5, 55.9, 112.5, 112.8, 116.6, 117.3, 128.7, 129.3, 130.3, 149.3, 175.6; HRMS, Calcd for: 245.1416. Found m/z (relative intensity): 245.1414 (M^+ , 100), 230 (12), 214 (5), 186 (14), 139 (5), 106 (16).

Reference

1) B. M. Trost, J. M. Timko, J. L. Stanton, *J. C. S. Chem. Comm.*, 1978, 436.