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One-Pot Synthesis of Secondary and Tertiary Naphthylpropylamines by Rhodium(I)-Catalysed Carbonylative Hydroaminomethylation

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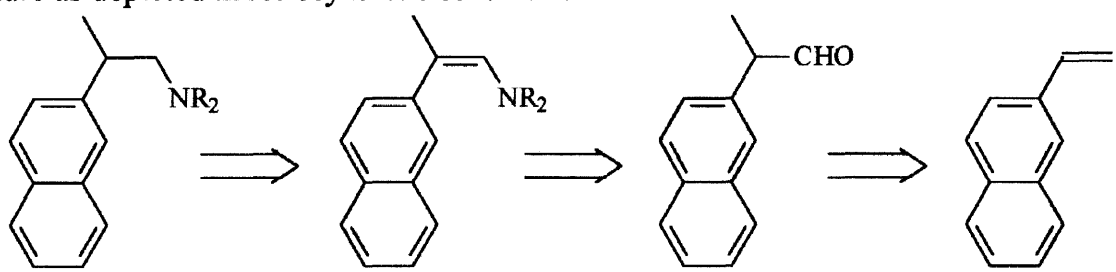
Abstract

Secondary and tertiary naphthylpropylamines are prepared in high yields by the reaction of 2-vinylnaphthalene, primary or secondary amines, carbon monoxide and hydrogen in presence of $[Rh(cod)Cl]_2$ as catalyst via a one-pot hydroformylation - amine condensation - reduction sequence.

Keywords: Hydroaminomethylation, Rhodium catalysis, Amines, Naphthylpropylamines, Carbonylation

Similar to the corresponding phenyl derivatives numerous naphthylpropylamines possess pharmacological activity.[1-9] So for example they are of importantance as antiacetylcholines [1], antihistamines [1], tranquillisers [2], and analgesics [2,3]. Furthermore they are known to show atropine and papaverine like activities.[1] In analogy to the homologous phenylpropylamines [10-12] they are usually prepared via a conventional two or three step procedures not involving transition metal catalysis.[1-9] We here report a simple one-pot procedure as depicted in retrosynthetic scheme 1.



1 2 3 4

Scheme 1. Retrosynthetic analysis of the hydroaminomethylation of 2-vinylnaphthalene **(4)**

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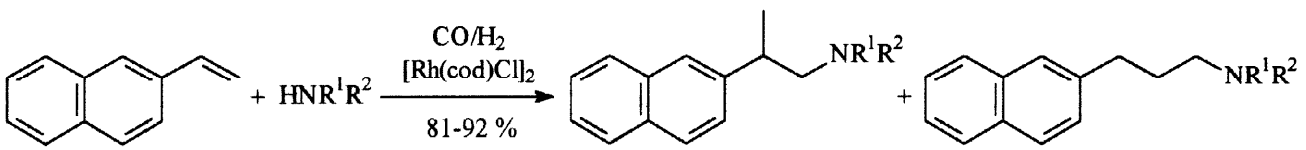
Following our interests in tandem hydroformylations [13] we recently reported the one-pot hydroaminomethylation as an efficient and convenient method to transform styrenes into the corresponding phenylpropylamines in high yields and selectivities.[13a] Here we now present use of this hydroformylation - amine condensation - reduction sequence starting from commercially available 2-vinylnaphthalene **(4)** (scheme 1).

Hydroaminomethylation of 2-vinylnaphthalene **(4)** with primary or secondary amines **5a-f**, carbon monoxide and hydrogen in presence of $[Rh(cod)Cl]_2$ as catalyst precursor proceeds in good up to excellent yields to the corresponding secondary or tertiary amine **6,7**, respectively. Due to electronic effects and in analogy to the hydroaminomethylation of styrene predominantly the *iso*-isomers **6a-f** are generated (scheme 2). The regioselectivity of the reaction can be controlled by phosphine or phosphite ligands.[13c]



4 **5a-f** **6a-f** **7a-e**

Scheme 2. Hydroaminomethylation of 2-vinylnaphthalene **(4)** with primary and secondary amines **5a-f**

As summarised in table 1 all conversions of 2-vinylnaphthalene **(4)** with various cyclic and acyclic, as well as aromatic amines **5** are nearly quantitative and highly chemoselective. Side products such as imines, enamines or aldehydes resulting from incomplete hydroaminomethylation are not observed.

Table 1. Hydroaminomethylation of 2-vinylnaphthalene **(4)** with primary and secondary amines **5**

entry	olefin	amine	product	yield [%]	*iso*/*n*-ratio
1	4	diethylamine **(5a)**	**6a/7a**	81	2.2/1
2	4	piperidine **(5b)**	**6b/7b**	86	9.4/1
3	4	hexamethylenimine **(5c)**	**6c/7c**	89	3.8/1
4	4	morpholine **(5d)**	**6d/7d**	91	2.5/1
5	4	*N*-methylaniline **(5e)**	**6e/7e**	89	9.1/1
6	4	benzylamine **(5f)**	**6f**	92	-

In conclusion we have shown that the hydroaminomethylation with $[Rh(cod)Cl]_2$ as catalyst is an efficient method to transform 2-vinylnaphthalene directly into the corresponding secondary or tertiary amines. All primary and secondary amines employed in the reaction undergo selective one-pot hydroaminomethylation in high yields. In comparison to the conventional literature

known two or three step syntheses the amines are more easily accessible in even higher yields. Further investigations towards an extension of the synthetic potential of this reaction are in current progress.

EXPERIMENTAL

NMR spectra were recorded on Bruker spectrometers DPX 300 and DRX 400 using TMS as internal standard. IR spectra were obtained with a Nicolet Impact 400D, mass spectra on a Finnigan CA 5 and elementary analysis with a Leco CHNS-932. Column chromatography was carried out with aluminium oxide N (act. I) from ICN Biomedicals, Eschwege, by using MTBE (methyl *tert*-butyl ether)/PE (petroleum ether, bp 30-60 °C) mixtures as eluent. Gas chromatography was carried out on a Carlo Erba GC-4160 with 25 m or on a Fisons GC-8130 with 30 m CP sil-5 capillaries. GC-MS and GC-IR spectra were obtained by using comparable capillaries and a Finnigan MAT 8320 (MS) or a Bruker IFS 48 (IR), respectively. The $[Rh(cod)Cl]_2$ catalyst was prepared according to literature procedures.[14] Pressure reactions have been carried out in autoclaves (type A, 250 ml, PTFE-insert) from Berghof, Eningen, Germany.

General procedure for the hydroaminomethylation of 2-vinylnaphthalene (4)

A mixture of the 2-vinylnaphthalene **(4)** (1.8 mmol), the corresponding primary or secondary amine (1.8 mmol) and $[Rh(cod)Cl]_2$ (1 mol % Rh) in 10 ml anhydrous dioxane was heated for 2 d, at 120°C in an autoclave under 50 bar carbon monoxide and 50 bar hydrogen (p_{total} = 100 bar) pressure. The residue was dissolved in Et_2O and filtered through neutral alumina. Product mixtures were separated by column chromatography on neutral alumina using a mixture of MTBE/PE as eluent.

N,N-Diethyl-N-[2-(2-naphthyl)propyl]amine (6a). Obtained from 2-vinylnaphthalene **(4)** and diethylamine **(5a)** as a colourless oil in 56 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.98 (t, ^{3}J = 7.1 Hz, 6 H, 2 x CH_3), 1.35 (d, ^{3}J = 6.9 Hz, 3 H, CH_3), 2.52 (m, 5 H, 2 x NCH_2, NC<u>H</u>H-CHR_2), 2.65 (dd, ^{2}J = 12.9 Hz, ^{3}J = 6.2 Hz, 1 H, NCH<u>H</u>-CHR_2), 7.49 (m, 3 H, 3 x PhH), 7.77 (m, 4 H, 4 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 11.8 (2 x CH_3), 20.1 (CH_3), 38.7 (CH), 47.5 (2 x NCH_2), 60.9 (NCH_2), 125.0 (PhH), 125.3 (PhH), 125.7 (PhH), 126.1 (PhH), 127.5 (2 x PhH), 127.7 (PhH), 132.2 (Cq), 133.6 (Cq), 144.2 (Cq). GC-MS (EI, 70 eV): m/z (%) = 242 (M^++1, 13), 86 (100), 58 (4). IR (NaCl/film) $\tilde{\nu}$ = 3054 w, 2966 s, 2930 m, 2870 m, 2801 m, 1505 m, 1488 m, 1454 m, 1380 m, 1219 m, 1205 m, 745 cm^{-1} m.

N,N-Diethyl-N-[3-(2-naphthyl)propyl]amine (7a). Obtained from 2-vinylnaphthalene **(4)** and diethylamine **(5a)** as a colourless oil in 25 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.01 (t, ^{3}J = 7.2 Hz, 6 H, 2 x CH_3), 1.87 (m, 2 H, CH_2), 2.49 (t, ^{3}J = 7.8 Hz, 2 H, NCH_2), 2.53 (q, ^{3}J =

7.2 Hz, 4 H, 2xNCH$_2$), 2.77 (t, ^{3}J = 7.8 Hz, 2 H, NCH$_2$), 7.38 (m, 3 H, 3 x PhH), 7.62 (s, 1 H, PhH), 7.76 (m, 3 H, 3 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 11.6 (2 x CH$_3$), 28.5 (CH$_2$), 34.0 (CH$_2$), 46.8 (2 x NCH$_2$), 52.4 (NCH$_2$), 125.0 (PhH), 125.8 (PhH), 126.3 (PhH), 127.3 (PhH), 127.4 (PhH), 127.5 (PhH), 127.7 (PhH), 131.9 (Cq), 133.6 (Cq), 139.9 (Cq). GC-MS (EI, 70 eV): m/z (%) = 242 (M$^+$+1, 34), 141 (5), 115 (7), 86 (100), 72 (13), 58 (7). IR (NaCl/film) $\tilde{\nu}$ = 3050 m, 2966 s, 2929 s, 2853 m, 1507 m, 1464 m, 1447 m, 1382 m, 699 cm^{-1} m.

1-[2-(2-Naphthyl)propyl]piperidine (6b). Obtained from 2-vinylnaphthalene **(4)** and piperidine **(5b)** as a colourless oil in 86 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 1.34 (d, ^{3}J = 6.9 Hz, 3 H, CH$_3$), 1.39 (m, 2 H, CH$_2$), 1.54 (m, 4 H, 2 x CH$_2$), 2.40 (m, 6 H, 3 x NCH$_2$), 3.10 (m, 1 H, CH), 7.39 (m, 3 H, 3 x PhH), 7.62 (s, 1 H, 1 x PhH), 7.76 (m, 3 H, 3 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 20.1 (CH$_3$), 24.5 (CH$_2$), 26.0 (2 x CH$_2$), 37.6 (CH), 55.0 (2 x NCH$_2$), 66.9 (NCH$_2$), 125.0 (PhH), 125.2 (PhH), 125.7 (PhH), 126.1 (PhH), 127.5 (2 x PhH), 127.7 (PhH), 132.1 (Cq), 133.6 (Cq), 144.1 (Cq). GC-MS (EI, 70 eV): m/z (%) = 254 (M$^+$+1, 9), 207 (4), 253 (4), 115 (7), 98 (100), 73 (16), 55 (11). IR (NaCl/film) $\tilde{\nu}$ = 3053 s, 2930 vs, 2852 s, 2799 s, 2771 s, 1600 m, 1507 m, 1466 m, 1454 s, 1442 s, 1377 m, 1347 m, 1269 m, 1156 s, 1122 s, 853 s, 816 s, 745 cm^{-1} s.

1-[3-(2-Naphthyl)propylpiperidine (7b) was only observed as a side product in small amounts and has not been isolated. **7b** was characterised in the crude product mixture by GC-MS. GC-MS (EI, 70 eV): m/z (%) = 255 (M$^+$+2), 141 (7), 115 (11), 100 (100), 70 (14), 56 (11).

1-[2-(2-Naphthyl)propyl]azepane (6c). Obtained from 2-vinylnaphthalene **(4)** and hexamethylenimine **(5c)** as a colourless oil in 70 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 1.34 (d, ^{3}J = 6.9 Hz, 3 H, CH$_3$), 1.52 (m, 8 H, 4 x CH$_2$), 2.60 (dd, ^{2}J = 12.6 Hz, ^{3}J = 8.4 Hz, 1 H, NCHH-CHR$_2$), 2.66 (m, 4 H, 2 x NCH$_2$), 2.77 (dd, ^{2}J = 12.6 Hz, ^{3}J = 6.3 Hz, 1 H, NCHH-CHR$_2$), 3.03 (m, 1 H, CH), 7.48 (m, 3 H, 3 x PhH), 7.62 (s, 1 H, PhH), 7.76 (m, 3 H, 3 x PhH). ^{13}C NMR (100 MHz, CDCl$_3$, 20 °C): δ = 19.9 (CH$_3$), 27.2 (2 x CH$_2$), 28.3 (2x CH$_2$), 38.8 (CH), 55.6 (2 x NCH$_2$), 65.5 (NCH$_2$), 125.0 (PhH), 125.3 (PhH), 125.7 (PhH), 126.2 (PhH), 127.5 (2 x PhH), 127.6 (PhH), 132.2 (Cq), 133.6 (Cq), 144.2 (Cq). GC-MS (EI, 70 eV): m/z (%) = 268 (M$^+$+1, 12), 112 (100), 58 (33). IR (NaCl/film) $\tilde{\nu}$ = 3053 w, 2942 vs, 2851 s, 2809 s, 1453 m, 1375 m, 1354 m, 1126 m, 1082 m, 852 m, 816 s, 745 cm^{-1} s. $C_{19}H_{25}N$ (267.4): Calc. C, 85.3; H, 9.4; N, 5.2. Found C, 85.3; H, 9.5; N, 5.2.

1-[3-(2-Naphthyl)propyl]azepane (7c). Obtained from 2-vinylnaphthalene **(4)** and hexamethylenimine **(5c)** as a colourless oil in 19 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): δ = 1.61 (m, 8 H, 4 x CH$_2$), 1.88 (m, 2 H, CH$_2$), 2.52 (t, ^{3}J = 7.6 Hz, 2 H, NCH$_2$), 2.62 (m, 4 H, 2 x NCH$_2$), 2.78 (t, ^{3}J = 7.6 Hz, 2 H, NCH$_2$), 7.41 (m, 3 H, 3 x PhH), 7.61 (s, 1 H, PhH), 7.77 (m,

3 H, 3 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 27.0 (2 x CH_2), 28.1 (2 x CH_2), 29.2 (CH_2), 33.8 (CH_2), 55.5 (2 x NCH_2), 57.6 (NCH_2), 125.0 (PhH), 125.8 (PhH), 126.3 (PhH), 127.36 (PhH), 127.37 (PhH), 127.5 (PhH), 127.7 (PhH), 131.9 (Cq), 133.6 (Cq), 140.0 (Cq). GC-MS (EI, 70 eV): m/z (%) = 268 (M^++1, 12), 112 (100), 58 (33). IR (NaCl/film) $\tilde{\nu}$ = 3053 w, 2924 s, 2852 m, 2809 m, 1468 m, 1453 m, 1360 m, 816 m, 746 cm^{-1} m. $C_{19}H_{25}N$ (267.4): Calc. C, 85.3; H, 9.4; N, 5.2. Found C, 85.2; H, 9.4; N, 5.2.

4-[2-(2-Naphthyl)propyl]morpholine (6d). Obtained from 2-vinylnaphthalene **(4)** and morpholine **(5d)** as a colourless oil in 65 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.35 (d, ^{3}J = 6.6 Hz, 3 H, CH_3), 2.55 (m, 6 H, 3 x NCH_2), 3.09 (m, 1 H, CH), 3.65 (br s, 4 H, 2 x OCH_2), 7.39 (m, 3 H, 3 x PhH), 7.62 (s, 1 H, 1 x PhH), 7.77 (d, J = 7.6 Hz, 3 H, 3 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 20.0 (CH_3), 37.2 (CH), 54.0 (2 x NCH_2), 66.3 (NCH_2), 66.9 (2 x OCH_2), 125.1 (PhH), 125.2 (PhH), 125.8 (PhH), 125.9 (PhH), 127.48 (PhH), 127.51 (PhH), 127.8 (PhH), 132.2 (Cq), 133.5 (Cq), 143.4 (Cq). GC-MS (EI, 70 eV): m/z (%) = 256 (M^++1, 3), 153 (7), 100 (100), 70 (30), 56 (27). IR (NaCl/film) $\tilde{\nu}$ = 3053 m, 2959 vs, 2931 s, 2892 s, 2867 s, 2853 s, 2806 s, 1507 m, 1455 s, 1272 s, 1143 s, 1118 vs, 1012 s, 866 s, 819 s, 747 cm^{-1} s. $C_{17}H_{21}NO$ (255.4): Calc. C, 80.0; H, 8.3; N, 5.5. Found C, 80.4; H, 8.1; N, 5.3.

4-[3-(2-Naphthyl)propyl]morpholine (7d). Obtained from 2-vinylnaphthalene **(4)** and morpholine **(5d)** as a colourless oil in 26 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.89 (m, 2 H, CH_2), 2.37 (t, ^{3}J = 7.6 Hz, 2 H, NCH_2), 2.41 (br s, 4 H, 2 x NCH_2), 2.79 (t, ^{3}J = 7.6 Hz, 2 H, NCH_2), 3.71 (t, ^{3}J = 4.7 Hz, 4 H, 2 x OCH_2), 7.32 (m, 1 H, PhH), 7.41 (m, 2 H, 2 x PhH), 7.60 (s, 1 H, PhH), 7.77 (m, 3 H, 3 x PhH).^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 28.0 (CH_2), 33.6 (CH_2), 53.6 (NCH_2), 58.2 (NCH_2), 66.9 (2 x OCH_2), 125.0 (PhH), 125.8 (PhH), 126.3 (PhH), 127.2 (PhH), 127.3 (PhH), 127.5 (PhH), 127.8 (PhH), 131.9 (Cq), 133.5 (Cq), 139.5 (Cq). GC-MS (EI, 70 eV): m/z (%) = 255 (M^++1, 16), 141 (10), 115 (12), 100 (100), 70 (16), 56 (18). IR (NaCl/film) $\tilde{\nu}$ = 3051 m, 2943 s, 2853 s, 2806 s, 1508 m, 1444 m, 1358 m, 1305 m, 1270 m, 1137 m, 1118 vs, 1008 m, 917 m, 860 m, 817 m, 746 cm^{-1} m. $C_{17}H_{21}NO$ (255.4): Calc. C, 80.0; H, 8.3; N, 5.5. Found C, 80.0; H, 8.1; N, 5.2.

N-Methyl-N-[2-(2-naphthyl)propyl]-N-phenylamine (6e). Obtained from 2-vinylnaphthalene **(4)** and *N*-methylaniline **(5e)** as an orange oil in 89 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.36 (d, ^{3}J = 7.0 Hz, 3 H, CH_3), 2.68 (s, 3 H, NCH_3), 3.35 (m, 1 H, CH), 3.44 (dd, ^{2}J = 14.6 Hz, ^{3}J = 7.3 Hz, 1 H, NCH<u>H</u>-CHR_2), 3.56 (dd, ^{2}J = 14.6 Hz, ^{3}J = 7.3 Hz, 1 H, NC<u>H</u>H-CHR_2), 6.68 (m, 2 H, 2 x PhH), 7.28 (m, 3 H, 3 x PhH), 7.41 (m, 3 H, 3 x PhH), 7.60 (s, 1 H, PhH), 7.76 (m, 3 H, 3 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 18.9 (CH_3), 38.4 (CH), 39.5 (NCH_3), 60.8 (NCH_2), 111.7 (2 x PhH), 115.8 (PhH), 125.3 (PhH), 125.6 (PhH), 125.8 (PhH), 125.9 (PhH), 127.5 (2 x PhH), 128.0 (PhH), 132.3 (Cq), 133.5 (Cq), 142.6 (Cq). GC-MS (EI, 70 eV):

m/z (%) = 276 (M^++1, 3), 153 (4), 120 (100), 104 (7), 91 (3), 77 (13), 51 (6). IR (NaCl/film) $\tilde{\nu}$ = 3054 s, 2961 s, 2930 s, 2904 s, 2872 s, 1599 vs, 1505 vs, 1450 m, 1372 vs, 1344 s, 1244 m, 1216 m, 1193 m, 992 m, 856 m, 818 s, 746 cm^{-1} vs.

N-Methyl-N-[3-(2-naphthyl)propyl]-N-phenylamine (7e) was only observed as a side product in small amounts and has not been isolated. **7e** was characterised in the crude product mixture by GC-MS. GC-MS (EI, 70 eV): m/z (%) = 276 (M^++1, 15), 223 (6), 169 (8), 120 (100), 105 (8), 73 (5).

N-Benzyl-N-[2-(2-naphthyl)propyl]amine (6f). Obtained from 2-vinylnaphthalene **(4)** and benzylamine **(5f)** as a yellow oil in 92 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.33 (d, ^3J = 6.9 Hz, 3 H, CH_3), 2.88 (m, 2 H, NCH_2), 3.13 (m, 1 H, CH), 3.81 (s, 2 H, NCH_2Ph), 7.33 (m, 6 H, 6 x PhH), 7.64 (s, 1 H, PhH), 7.77 (m, 5 H, 5 x PhH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 20.2 (CH_3), 40.2 (CH), 53.8 (NCH_2), 56.1 (NCH_2), 125.3 (PhH), 125.6 (PhH), 125.7 (PhH), 125.9 (PhH), 126.8 (PhH), 126.9 (PhH), 127.6 (PhH), 127.9 (PhH), 128.3 (2 x PhH), 128.4 (2 x PhH), 132.3 (Cq), 133.5 (Cq), 140.3 (Cq), 142.7 (Cq). GC-MS (EI, 70 eV): m/z (%) = 276 (M^++1, 100), 155 (9), 120 (33), 91 (45), 65 (6). IR (NaCl/film): $\tilde{\nu}$ = 3084 w, 3057 m, 3026 m, 2961 s, 2926 s, 2871 m, 1495 m, 1453 s, 1125 m, 908 vs, 818 s, 733 cm^{-1} vs.

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