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Selective reduction and dehydrogenation of 6-benzylidene-octahydropyrrolo[1,2-*a*]pyrimidines and 5-benzylidene-hexahydropyrrolo[1,2-*a*]imidazoles as new approaches to *N*-(ω-aminoalkyl)pyrrolidines and bicyclic amidines

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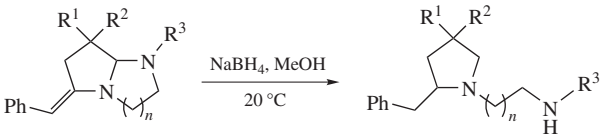
Sodium borohydride reduction of 6-benzylideneoctahydropyrrolo[1,2-*a*]pyrimidines and 5-benzylidenehexahydropyrrolo[1,2-*a*]imidazoles affords *N*-(ω-aminoalkyl)pyrrolidines, whereas these substrates react with H_2 or cyclohexene in the presence of catalytic amounts of Pd/C to give benzyl- or benzylidene-substituted bicyclic amidines, respectively.

Previously we have reported that treatment of 1-alkynyl-1-chlorocyclopropanes with lithium derivatives of 1,2-diaminoethane and 1,3-diaminopropane afforded hitherto unknown promising bicyclic ene aminals **1**, *viz.*, 5-benzylidenehexahydropyrrolo[1,2-*a*]imidazoles and 6-benzylideneoctahydropyrrolo[1,2-*a*]pyrimidines[1,2] containing highly reactive 2-methylidenepyrrolidine and bicyclic aminal moieties with a common nitrogen atom. 2-Alkylidenepyrrolidines are most liable to catalytic[3–7] and ionic[8] hydrogenation, reduction on treatment with sodium borohydrides,[3,9,10] bromine addition followed by ring expansion[11] as well as cyclization involving additional functional groups[12] and cycloaddition to activated acetylenes.[13] The bicyclic systems of hexahydropyrrolo[1,2-*a*]imidazole and octahydropyrrolo[1,2-*a*]pyrimidine can undergo alkylation at the nitrogen atom,[14,15] selective reduction with cleavage of one C–N bond,[16–23] oxidation to the corresponding amidines,[24] as well as hydrolysis on treatment with strong mineral acids.[16]

It could be expected that compounds **1** obtained would have reactivity characteristic of both 2-benzylidenepyrrolidines and bicyclic aminals and thus would undergo reactions involving both retention and transformation of the bicyclic system. This communication deals with studies on reduction of these compounds with complex metal hydrides and reactions that occur on contact with Pd catalysts in the presence and in the absence of dihydrogen.

We have herein discovered that treatment of substrates **1a–f** with a fivefold excess of $NaBH_4$ in methanol results in selective reduction of the enamine double bond with simultaneous cleavage of the aminal moiety to give the corresponding *N*-(ω-aminoalkyl)-pyrrolidines† **2a–f** in 72–88% yields (Scheme 1). In all cases, the products were obtained pure after aqueous workup, extraction and evaporation of the solvent. The alternative possible side products



1a–f **2a–f**

	R^1	R^2	R^3	*n*	Yield of **2** (%)
a	Me	Me	H	1	78
b	Me	Me	H	2	72
c	Me	Me	Me	2	83
d	$(CH_2)_5$		Me	2	88
e	H	H	H	2	80
f	H	H	Me	2	85

Scheme 1

† GLC analysis was carried out using a Hewlett-Packard 5890 Series II instrument with an HP-1 capillary column (30 m × 0.153 mm) and a Hewlett-Packard 3396A automatic integrator. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200p spectrometer in $CDCl_3$, $SiMe_4$ as the internal standard. Mass spectra were recorded on a Finningan DSQ II chromato-mass spectrometer.

Reduction of bicyclic aminals **1a–f** *with* $NaBH_4$ *(general procedure).* $NaBH_4$ (380 mg, 10 mmol) was added to a solution of starting compound **1** (1 mmol) in methanol (5 ml) and the resulting mixture was stirred for 4 h. After that, water (15 ml) and diethyl ether (15 ml) were added to the reaction mixture, the organic layer was separated, and the aqueous layer was additionally extracted with diethyl ether (3×10 ml). The combined organic layers were dried with anhydrous K_2CO_3 and the solvent was evaporated to give the corresponding products **2a–f** as oils with >95% purity according to NMR data and elemental analyses.

[2-(2-Benzyl-4,4-dimethylpyrrolidin-1-yl)ethyl]amine **2a** was obtained from aminal **1a** in 78% yield. ^{1}H NMR, δ: 0.91 (s, 3H, Me), 1.04 (s, 3H, Me), 1.33 (dd, 1H, CHCH*H*CMe$_2$, ^2J 12.7 Hz, ^3J 8.3 Hz), 1.45 (dd, 1H, CHC*H*HCMe$_2$, ^2J 12.7 Hz, ^3J 7.4 Hz), 1.95 (d, 1H, NC*H*HCMe$_2$, *J* 9 Hz), 2.11 (br. s, 2H, NH$_2$), 2.20 (m, 1H, NCH$_2$C*H*HN), 2.40 (dd, 1H, PhC*H*H, ^2J 12.8 Hz, ^3J 9.4 Hz), 2.57–2.92 (m, 4H, PhCH$_2$C*H*, NCH_2C*H*HN), 2.84 (d, 1H, NC*H*HCMe$_2$, *J* 9 Hz), 2.99 (dd, 1H, PhC*H*H, *J* 12.8 Hz, *J* 3.9 Hz), 7.05–7.30 (m, 5H, Ph). ^{13}C NMR, δ: 28.7 (Me), 30.0 (Me), 35.6 (*C*Me$_2$), 40.4 (CH$_2$NH$_2$), 41.1 (*C*H$_2$Ph), 45.9 (C-3, *cyclo*-C$_4$N), 57.0 (NCH$_2$), 65.9 (C-5, *cyclo*-C$_4$N), 67.8 (C-2, *cyclo*-C$_4$N), 125.6, 127.9, 128.9 (Ph), 139.6 (C-1, Ph). Found (%): C, 77.32; H, 10.33; N, 11.92. Calc. for $C_{15}H_{24}N_2$ (%): C, 77.53; H, 10.41; N, 12.06.

[3-(2-Benzyl-4,4-dimethylpyrrolidin-1-yl)propyl]amine **2b** was obtained from aminal **1b** in 72% yield. ^{1}H NMR, δ: 0.92 (s, 3H, Me), 1.05 (s, 3H, Me), 1.34 (dd, 1H, CHCH*H*CMe$_2$, ^2J 12.6 Hz, ^3J 8.3 Hz), 1.46 (dd, 1H, CHC*H*HCMe$_2$, ^2J 12.6 Hz, ^3J 7.2 Hz), 1.43 (br. s, 2H, NH$_2$), 1.52–1.67 (m, 2H, NCH$_2$CH_2CH$_2$NH$_2$), 1.94 (d, 1H, NC*H*HCMe$_2$, *J* 9 Hz), 2.14 [ddd, 1H, NCH*H*(CH$_2$)$_2$NH$_2$, ^2J 11.6 Hz, ^3J 6.9 Hz, ^3J 5.4 Hz], 2.41 (dd, 1H, PhC*H*H, ^2J 12.5 Hz, ^3J 9.4 Hz), 2.47–2.61 (m, 1H, PhCH$_2$C*H*), 2.74 (t, 2H, CH_2NH$_2$, *J* 6.7 Hz), 2.83–2.98 [m, 1H, NCH*H*(CH$_2$)$_2$NH$_2$], 2.91 (d, 1H, NC*H*HCMe$_2$, *J* 9 Hz), 3.02 (dd, 1H, PhC*H*H, *J* 12.5 Hz, *J* 3.6 Hz), 7.05–7.30 (m, 5H, Ph). ^{13}C NMR, δ: 29.0 (Me), 30.3 (Me), 32.2 (NCH$_2$CH_2CH$_2$N), 35.5 (*C*Me$_2$), 40.9 (CH$_2$NH$_2$), 41.1 (*C*H$_2$Ph), 46.2 (C-3, *cyclo*-C$_4$N), 52.5 (NCH$_2$), 66.8 (C-2, *cyclo*-C$_4$N), 68.3 (C-5, *cyclo*-C$_4$N), 125.7, 128.0, 129.0 (Ph), 140.0 (C-1, Ph). MS, *m*/*z* (%): 155 ([M–CH$_2$Ph]$^+$, 44), 112 ([M–CH$_2$Ph–C$_3$H$_7$N]$^+$, 100). Found (%): C, 78.23; H, 10.38; N, 11.25. Calc. for $C_{16}H_{26}N_2$ (%): C, 77.99; H, 10.64; N, 11.37.

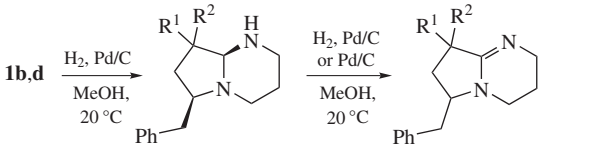
resulting from cleavage of the bridging C–N bond were not observed, which points to a high chemoselectivity of this process.

Note that the application of a stronger reductant such as $LiAlH_4$ instead of $NaBH_4$ did not cause any transformation of these substrates. For instance, prolonged (6 h) refluxing of compound **1c** with a three-fold excess of $LiAlH_4$ in THF gave only the recovered compound in 69% yield with no traces of any reduction products.

Unfortunately, attempted reduction of the bridging C–N bond by treatment with diisobutylaluminium hydride (DIBAL-H), which was previously[22,23] used for similar transformations of unsaturated octahydropyrido[1,2-*a*]pyrimidines and octahydropyrrolo[1,2-*a*]pyrimidines, failed. Prolonged (24 h) refluxing of compound **1b** with excess DIBAL-H in toluene yielded only a hardly-separable mixture of several components, with pyrrolidine **2b** being the major (~40%) one.

Considering the known data[3–7] on double bond hydrogenation in substituted 2-benzylidenepyrrolidines with dihydrogen in the presence of Pd/C, we subjected compounds **1** onto such reactions. Hydrogenation of aminals **1b**,**d** in methanol at ~20 °C in the presence of a catalytic amount of 10% Pd/C in an H_2 atmosphere (excessive pressure 0.1–0.2 bar) resulted not only in fast hydrogenation of the C=C bond but also in relatively slow dehydrogenation of the C–NH bond to furnish benzyl-substituted bicyclic amidines **4a**,**b** in 69–76% yields as final products (Scheme 2).‡

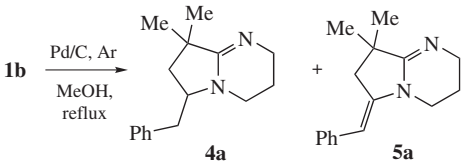
Formation of intermediate aminals **3** was proved experimentally by detecting them in the mixture after 1.5 h processing. After this time, the reaction mixture contained ~85% of aminal **3a** as one stereoisomer according to ^{1}H and ^{13}C NMR data. Based on spectral and literature data[3,7] on selectivity of double bond hydrogenation in substituted 2-benzylidenepyrrolidines, the *cis*-arrangement of the benzyl and amine substituents in the pyrrolidine moiety was assigned. Further keeping of the reaction mixture with a catalytic amount of Pd/C in methanol at 20 °C, either in the presence of hydrogen or in an argon atmosphere, resulted in the formation of amidine **4a** that was completed in approximately 10 days. The discovered catalytic dehydrogenation provides the first example of such reactions in the series of alicyclic aminals and opens a new approach to alicyclic amidines. Previously, such processes in the presence of Pd catalysts were only observed in cases where the C=N bond being formed was conjugated with an aromatic moiety.[25–29]



3a $R^1 = R^2 = Me$ **4a** $R^1 = R^2 = Me$, 76%
3b $R^1 + R^2 = (CH_2)_5$ **4b** $R^1 + R^2 = (CH_2)_5$, 69%

Scheme 2

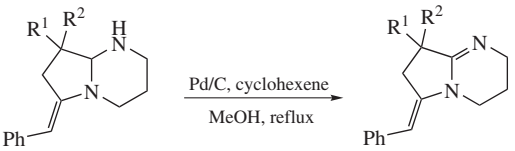
In the absence of dihydrogen, the process was not selective. Refluxing of compound **1b** in methanol in the presence of Pd/C (10%) for 2 h gave a mixture of compounds **4a** and **5a** in 1.5 : 1 ratio, apparently due to parallel dehydrogenation of the C–N bond in the original molecule and partial hydrogenation of the C=C bonds in aminals **1b** and **5a** with dihydrogen evolving.



4a : **5a** = 1.5 : 1

Scheme 3

We succeeded to direct the process towards benzylidene amidines **5** by using cyclohexene as the hydrogen scavenger (Scheme 4). Refluxing aminals **1b** and **1d** in methanol in the presence of Pd/C for 2–4 h under these conditions led to their selective conversion to hitherto unknown benzylidene-substituted amidines§ **5a**, **5b** in 62 and 40% yields, respectively.



1b $R^1 = R^2 = Me$ **5a** $R^1 = R^2 = Me$
1d $R^1 + R^2 = (CH_2)_5$ **5b** $R^1 + R^2 = (CH_2)_5$

Scheme 4

N-*[3-(3-Benzyl-2-azaspiro[4.5]dec-1-yl)propyl]*-N-*methylamine* **2d** was obtained from aminal **1f** in 85% yield. ^{1}H NMR, δ: 1.19–1.45 (m, 11 H, 5 CH_2, CHCH*H*C), 1.51 (dd, 1H, CHC*H*HC, ^2J 12.7 Hz, ^3J 6.9 Hz), 1.60–1.80 (m, 2 H, $NCH_2CH_2CH_2NH_2$), 1.89 (d, 1H, NC*H*HC, J 9.3 Hz), 1.92 (br. s, 1H, NH), 2.14 [ddd, 1H, NCH*H*$(CH_2)_2$NHMe, ^2J 11.7 Hz, ^3J 7.2 Hz, ^3J 5.3 Hz], 2.41 (dd, 1H, PhC*H*H, ^2J 12.2 Hz, ^3J 9.4 Hz), 2.43 (s, 3 H, NH*Me*), 2.43–2.57 (m, 1H, $PhCH_2CH$), 2.64 (t, 2 H, CH_2NHMe, J 6.7 Hz), 2.95 [ddd, 1H, NCH*H*$(CH_2)_2$NHMe, ^2J 11.7 Hz, ^3J 8.0 Hz, ^3J 8.0 Hz], 3.03 (dd, 1H, PhC*H*H, J 12.2 Hz, J 3.2 Hz), 3.07 (d, 1H, NC*H*HCMe$_2$, J 9.3 Hz), 7.05–7.30 (m, 5 H, Ph). ^{13}C NMR, δ: 23.5, 23.6, 25.9 (3 CH_2, *cyclo*-C_6H_{10}), 28.4 ($NCH_2CH_2CH_2N$), 36.5 (NMe), 38.4, 39.0 (2 CH_2, *cyclo*-C_6H_{10}), 39.4 (C-4, *cyclo*-C_4N), 40.9 (CH_2Ph), 44.2 (C-3, *cyclo*-C_4N), 51.1 (CH_2NMe), 53.2 (NCH_2), 66.0 (C-2, *cyclo*-C_4N), 66.5 (C-5, *cyclo*-C_4N), 125.8, 128.1, 129.2 (Ph), 140.0 (C-1, Ph). MS, *m/z* (%): 209 ([M – CH_2Ph]$^+$, 19), 152 ([M – CH_2Ph – C_3H_7N]$^+$, 100), 44 ([C_2H_6N]$^+$, 40). Found (%): C, 79.56; H, 10.51; N, 9.01. Calc. for $C_{20}H_{32}N_2$ (%): C, 79.94; H, 10.73; N, 9.32.

For characteristics of compounds **2c**,**e**,**f**, see Online Supplementary Materials.

‡ *Synthesis of bicyclic amidines* **4a**,**b** *from aminals* **1b**,**d** *(general procedure)*. Catalyst 10% Pd/C (10 mg) was added to a solution of starting compound **1** (1 mmol) in methanol (5 ml) and the mixture was stirred for 10 days at ~20 °C under hydrogen (excess pressure 0.1–0.2 bar). The reaction progress was monitored by NMR. After the process was complete, the catalyst was filtered off and additionally washed with methanol (10 ml). The resulting solution was passed through a thin silica gel layer and the solvent was evaporated to give an oily compound, which according to NMR data was one of the corresponding amidines **4a**,**b** with >95% purity.

*6-Benzyl-8,8-dimethyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine* **4a** was obtained from aminal **1b** in 76% yield. ^{1}H NMR, δ: 1.05 (s, 3 H, Me), 1.16 (s, 3 H, Me), 1.45 (dd, 1H, C*H*HCMe$_2$, ^2J 12.5 Hz, ^3J 8.4 Hz), 1.52–1.95 (m, 2 H, $NCH_2CH_2CH_2N$), 1.68 (dd, 1H, C*H*HCMe$_2$, ^2J 12.5 Hz, ^3J 6.4 Hz), 2.47 (dd, 1H, PhC*H*H, ^2J 13.1 Hz, ^3J 9.2 Hz), 2.99–3.58 (m, 5 H, $NCH_2CH_2CH_2N$, $PhCH_2CH$), 3.15 (dd, 1H, PhCH*H*, ^2J 13.1 Hz, ^3J 4.3 Hz), 7.10–7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 20.9 ($NCH_2CH_2CH_2N$), 26.6 (Me), 26.8 (Me), 40.4 (CMe_2), 40.5, 42.2, 42.6, 43.9 ($PhCH_2$, $NCH_2CH_2CH_2N$, $PhCH_2CHCH_2$), 60.6 ($PhCH_2CH$), 126.5, 128.5, 129.2 (Ph), 138.0 (C-1, Ph), 142.9 (*C*=CHPh), 166.9 (C=N). Found (%): C, 79.45; H, 8.96; N, 11.32. Calc. for $C_{16}H_{22}N_2$ (%): C, 79.29; H, 9.15; N, 11.56.

*6′-Benzyl-3′,4′,6′,7′-tehrahydro-2′*H*-spiro(cyclohexane-1,8′-pyrrolo-[1,2-*a*]pyrimidine)* **4b** was obtained from aminal **1d** in 69% yield. ^{1}H NMR, δ: 1.02–1.97 (m, 12 H, *cyclo*-C_6H_{10}, $NCH_2CH_2CH_2N$), 1.44 (dd, 1H, $PhCH_2CHCHH$, ^2J 13.2 Hz, ^3J 7.4 Hz), 1.94 (dd, 1H, $PhCH_2CHCHH$, ^2J 13.2 Hz, ^3J 7.2 Hz), 2.50 (dd, 1H, PhC*H*H, ^2J 13.2 Hz, ^3J 9.0 Hz), 3.10 (dd, 1H, PhCH*H*, ^2J 13.2 Hz, ^3J 4.5 Hz), 3.15–3.72 (m, 5 H, $NCH_2CH_2CH_2N$, $PhCH_2CH$), 7.10–7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 20.0 ($NCH_2CH_2CH_2N$); 22.2, 22.3, 24.9, 33.3, 34.8 (*cyclo*-C_6H_{10}), 36.3 (C-4, *cyclo*-C_4N), 40.1, 41.3, 41.8, 45.9 ($PhCH_2$, $NCH_2CH_2CH_2N$, $PhCH_2CHCH_2$), 62.0 ($PhCH_2CH$), 126.6, 128.5, 129.0 (Ph), 136.9 (C-1, Ph), 168.0 (C=N). Found (%): C, 80.99, H, 9.12; N, 9.68. Calc. for $C_{19}H_{26}N_2$ (%): C, 80.80; H, 9.28; N, 9.92.

To conclude, different reductants applied to ene aminals of type **1** afford different products, which seem multipurpose promising, *e.g.*, for medicinal chemistry.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.01.011.

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§ *Synthesis of benzylidene-substituted bicyclic amidines* **5a**,**b** *from aminals* **1b**,**d** *(general procedure)*. Catalyst 10% Pd/C (10 mg) and cyclohexene (820 mg, 10 mmol) were added to a solution of starting compound **1** (1 mmol) in methanol (5 ml) and the reaction mixture was refluxed for 4 h with stirring under argon. After the process was complete, the catalyst was filtered off and additionally washed with methanol (10 ml). The filtrate was passed through a thin layer of silica gel and the solvent was evaporated. The target product was isolated from the residue by recrystallization or chromatography.

*(6*E*)-6-Benzylidene-8,8-dimethyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]-pyrimidine* **5a** was obtained from aminal **1b** in 62% yield. The compound was isolated by recrystallization from hexane. ^{1}H NMR, δ: 1.28 (s, 6H, 2Me), 1.85–1.98 (m, 2H, $NCH_2CH_2CH_2N$), 2.81 (d, 2H, $=CCH_2$, *J* 1.8 Hz), 3.45–3.53 (m, 4H, $NCH_2CH_2CH_2N$), 5.55 (t, 1H, =C*H*Ph, *J* 1.8 Hz), 7.10–7.40 (m, 5H, Ph). ^{13}C NMR, δ: 20.1 ($NCH_2CH_2CH_2N$), 27.1 (2Me), 39.5 (CMe_2), 40.3, 41.8, 44.1 ($=CCH_2$, $NCH_2CH_2CH_2N$), 97.9 (=*C*HPh); 124.6, 127.2, 128.4 (Ph), 138.0 (C-1, Ph), 142.9 (*C*=CHPh), 164.4 (C=N). MS, *m*/*z* (%): 240 (M^+, 100), 239 ($[M-H]^+$, 58), 225 ($[M-Me]^+$, 46).

*(6′*E*)-6′-Benzylidene-3′,4′,6′,7′-tehrahydro-2′*H*-spiro(cyclohexane-1,8′-pyrrolo[1,2-*a*]pyrimidine)* **5b** was obtained from aminal **1d** in 40% yield. The compound was isolated by chromatography on neutral Al_2O_3 (eluent: hexane–diethyl ether, 5:1). ^{1}H NMR, δ: 1.15–1.75 (m, 10H, *cyclo*-C_6H_{10}), 1.75–1.88 (m, 2H, $NCH_2CH_2CH_2N$), 2.75 (d, 2H, $=CCH_2$, *J* 1.9 Hz), 3.33–3.45 (m, 4H, $NCH_2CH_2CH_2N$), 5.42 (t, 1H, =C*H*Ph, *J* 1.9 Hz), 7.00–7.35 (m, 5H, Ph). ^{13}C NMR, δ: 20.2 ($NCH_2CH_2CH_2N$), 22.5, 25.2, 34.8 (*cyclo*-C_6H_{10}), 43.7 (C-1, *cyclo*-C_6H_{10}), 36.9, 40.1, 44.0 ($=CCH_2$, $NCH_2CH_2CH_2N$), 97.3 (=*C*HPh), 124.2, 127.0, 128.3 (Ph), 138.0 (C-1, Ph), 143.3 (*C*=CHPh), 164.2 (C=N). MS, *m*/*z* (%): 280 (M^+, 100), 279 ($[M-H]^+$, 52).

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