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Synthesis of 3-Alkenylamines, 4-Alkenylamines and 3-Allenylamines via a Transamination Procedure

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Dedicated to the memory of Professor Gerrit L'abbé

Abstract : 3-Alkenylamines, 4-alkenylamines and 3-allenylamines were synthesized conveniently by potassium t-butoxide induced transamination of α-vinylaldimines, α-allylaldimines or α-allenylaldimines followed by hydrolysis with aqueous oxalic acid. © 1997 Elsevier Science Ltd.

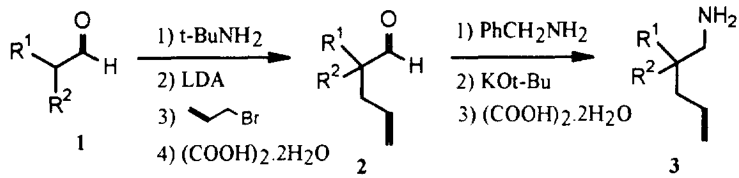
INTRODUCTION

Primary amines carrying a remote olefinic double bond in the side chain are valuable substrates for a variety of transformations. Their use, especially as source for the synthesis of azaheterocycles, has been underlined in recent years. The literature has seen a steady growth in development of syntheses of these alkenylamines. For a long time, primary allylamines were accessible with difficulty,[1] but recently, several useful procedures for the synthesis of these unsaturated amines have been published.[2] A similar evolution is seen for homoallylamines and bishomoallylamines, the synthesis of which has been published in scattered reports.[3] The continued interest in this area of unsaturated amines underlines their synthetic potential. Recent reports[4-6] on the synthesis of primary amines from carbonyl compounds urged us to unravel our own results in this area. These reports deal with the intramolecular reduction-oxidation process of carbonyl compounds to amines via a base-catalyzed [1,3]-proton shift in the azaallylic system of imines. Either N-benzhydryl,[4] N-benzyl[5] or N-(α-methyl)benzyl imines[6] were used for the transamination process leading to aliphatic amines,[4] 3-aminoazetidine-2-ones[4] and fluorinated aliphatic amines.[5,6] In our efforts to synthesize azaheterocycles with agrochemical interest, we required a suitable access to primary homoallylamines, bishomoallylamines and 3-allenylamines. To this end, we developed an entry towards these unsaturated amines via a mild transamination of unsaturated imines.

RESULTS AND DISCUSSION

The principle of the synthesis of unsaturated amines **3** and **11** entails (a) an imination process, (b) α-alkenylation or α-allenylation of the imine, (c) hydrolysis to the unsaturated aldehyde, (d) N-benzylimine formation, (e) transamination and (f) acidic hydrolysis. (Scheme 1; the process shows the synthesis of 4-alkenylamines **3**). Not all intermediates have to be isolated in pure state, making it an attractive and facile route to the target substrates (vide infra).

The direct allylation of aldehydes **1** to α-allylaldehydes **2** is not a selective process and leads to intractable reaction mixtures.[7] Therefore, a detour via N-t-butyl imines **4** (96-98% yield) and N-t-butyl α-allylimines **5** (82-97% yield) offers a suitable and flexible way for the synthesis of 4-alkenals **2** (80-89% yield),



Scheme 1

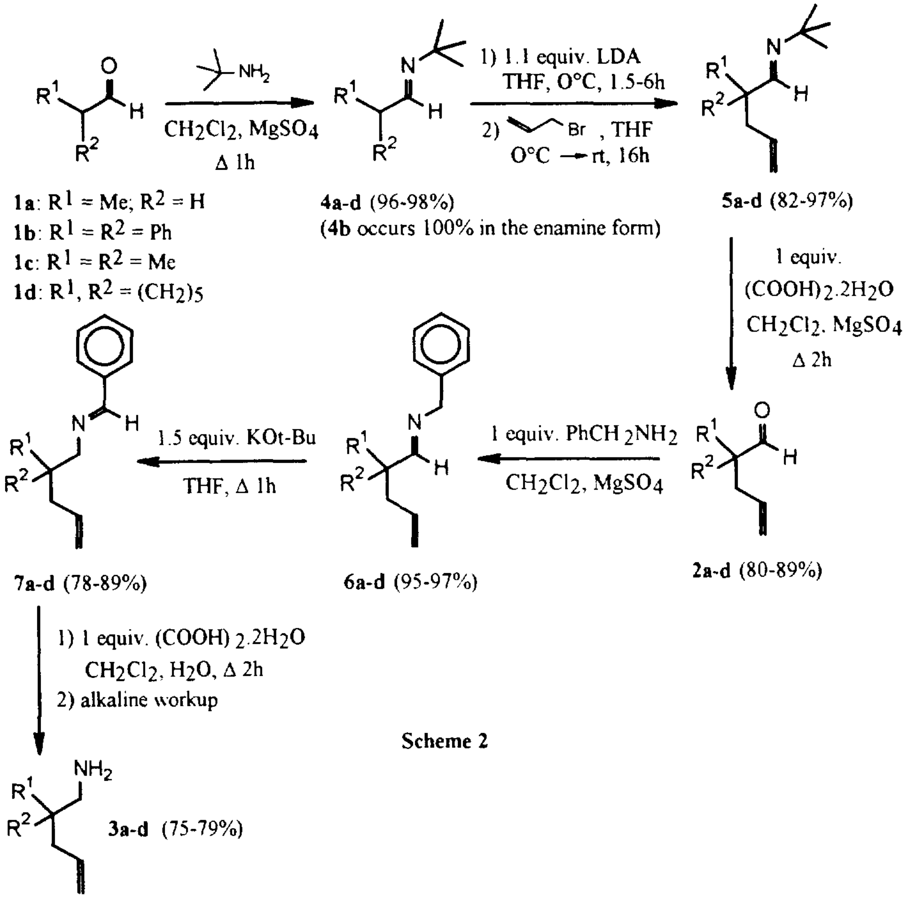
because virtually all substitution patterns in the aldehyde **1** or the allylbromide are tolerated and because of the high yields of the reactions. N-t-butylimines are most conveniently used for this purpose. The hydrolysis of α-allylaldimines **5** was performed under mild conditions, i.e. reflux with aqueous oxalic acid in a two phase system with dichloromethane. It is obvious that any 4-alkenal or γ,δ-unsaturated aldehyde from whatever source can be used in the further steps of this process towards 4-alkenylamines. In this respect, 2,2-dimethyl-4-pentenal **2c** was also prepared by a Claisen rearrangement utilizing isobutyraldehyde **1c** and 2-propen-1-ol.[8] Another example of this type concerns the commercially available 3-cyclohexene-1-carbaldehyde **8**.

The process of transamination of imines requires an activating substituent at the 1-position of the amine part. The N-benzyl substituent is very suitable for this purpose and there is no need to use the much more expensive benzhydrylamine. Imination of aldehydes **2** with benzylamine in dichloromethane in the presence of magnesium sulfate gave N-benzyl aldimines **6** in nearly quantitative yield. The transamination of N-benzyl imines **6** was performed with potassium t-butoxide (1.5 equiv.) in tetrahydrofuran under reflux for 1h. No side reactions were observed and again clean reactions to give N-(benzylidene)-4-alkenylamines **7** were observed.

It is important to note that N-benzyl α-allylaldimine **6c** ($R^1=R^2=Me$) did not undergo transamination into **7c** neither with sodium methoxide in methanol (1N, 1 equiv.) nor in THF (1 equiv.) under reflux for 0.5-2 h. Also potassium trimethylsilanolate (2 equiv.) in THF under reflux overnight did not induce a transamination. Catalytic amounts of potassium t-butoxide (0.1-0.3 equiv.) in THF under reflux for 0.5 h did not result in an isomerization of **6c** to **7c**. The latter base (1.1 equiv.) in THF for 2 h at room temperature partially converted **6c** into **7c** (about 50% conversion). The use of 1.1-3 equiv. of potassium t-butoxide in THF under reflux for 1 h is recommended as it completely converts aldimines **6** into the isomeric aldimines **7**.

The transamination of N-benzyl α-allylaldimines **6** to give N-(benzylidene)-4-alkenylamines **7** proceeds via an intermediate 2-azaallylic anion[9] which is protonated at the original site of the aldimine proton affording the conjugated N-(benzylidene)amines **7**. This transamination is a key step in the enzyme-catalyzed interconversion of α-amino acids and α-keto carboxylic acids. It can be expected that this transamination process is applicable to a whole variety of alkenylimines. However, α,β-unsaturated imines or β,γ-unsaturated imines having an α-hydrogen cannot be converted into the corresponding allylamines or homoallylamines because of competitive deprotonation in these substrates leading to conjugated 2-azadienes,[10] the hydrolysis of which leads to saturated aldehydes and benzaldehyde (see also further for a β,γ-unsaturated imine having no α-hydrogens; Scheme 5).

In this respect it has to be stressed that N-benzyl aldimines derived from aldehydes **1** cannot be used in the α-allylation procedure towards N-benzyl α-allylaldimines **6** because LDA (or any other base) gives a competitive deprotonation at the N-benzylic position and the α-position, giving rise to mixtures of allylation products.[11]

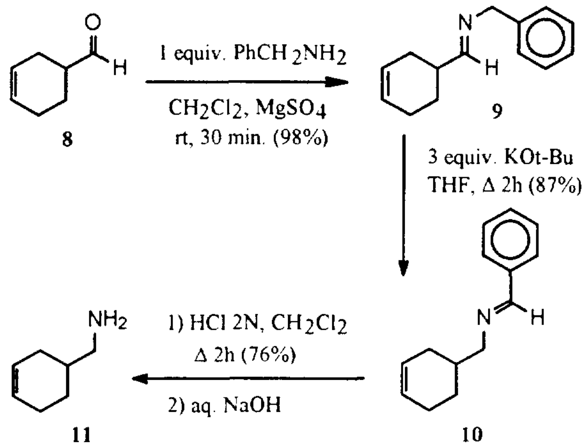


Scheme 2

The final step in the synthesis of 4-alkenylamines **3** concerns the hydrolysis of N-(benzylidene)-4-alkenylamines **7** with aqueous oxalic acid in a two phase system with dichloromethane. Alternatively, 2N hydrogen chloride can be used for the hydrolysis step. In both cases, high yields of the crude salts of 4-alkenylamines were obtained (75-89%). However, the generation of the free bases is accompanied by substantial losses of material if aqueous sodium hydroxide was used as the base (yields : 60-79%). It is recommended to use the crude salts as such or to generate the free bases in dry ether in the presence of triethylamine.

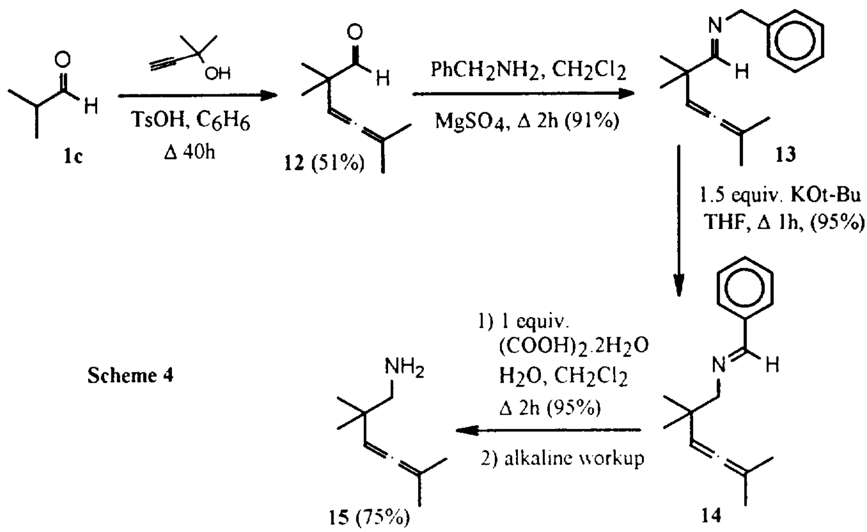
Alternatively, N-acetylation of the free alkenylamine to give the corresponding acetamide is a suitable procedure. In this way, N-(benzylidene)-2-methyl-4-pentenylamine **7a** was hydrolyzed with oxalic acid (1 molar equiv.) in a biphase system water/diethyl ether (reflux 2h) to give corresponding ammonium oxalate, which was basified in aqueous medium and subsequently reacted with acetic anhydride (5 equiv., 4h, rt) to afford N-(2-methyl-4-pentenyl)acetamide in 92% yield.

The suitability of the present method for the synthesis of alkenylamines was also demonstrated by the synthesis of (3-cyclohexen-1-yl)methylamine **11**. 3-Cyclohexene-1-carbaldehyde **8** was converted into the corresponding N-benzylaldimine **9** (98%), which underwent transamination with potassium t-butoxide in THF under reflux for 2h to afford N-(benzylidene)-3-cyclohexen-1-ylmethylamine **10** (87%). The latter rearranged aldimine **10** was hydrolyzed with 2N hydrogen chloride with dichloromethane as second phase to give pure 3-cyclohexen-1-ylmethylamine hydrochloride in 76% yield (Scheme 3).



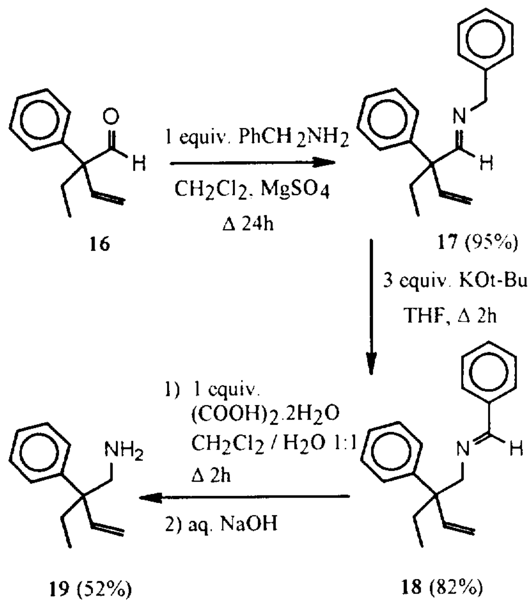
Scheme 3

Also 3-allenylamines are easily accessible according to the protocol outlined above, as exemplified for the synthesis of 2,5,5-trimethyl-3,4-hexadienylamine **15**. α-Allenylaldehyde **12** was prepared by acid-catalyzed reaction of isobutyraldehyde with 2-methyl-3-butyn-2-ol.[12] Conversion of the α-allenylaldehyde **12** into the N-benzylimine **13**, subsequent transamination with potassium t-butoxide in THF into N-(benzylidene)-2,2,5-trimethyl-3,4-hexadienylamine **14** and subsequent hydrolysis with aqueous oxalic acid provided a facile access to 2,2,5-trimethyl-3,4-hexadienylamine **15** (Scheme 4).



Scheme 4

A final example concerns the synthesis of the homoallylamine **19** from 3-propenal derivative **16** (Scheme 5). Imination of aldehyde **16** with benzylamine gave the imine **17**, which was subsequently isomerized into N-(benzylidene)homoallylamine **18**. Final hydrolysis of imine **18** with aqueous oxalic acid and basification provided pure 2-ethyl-2-phenyl-3-butenylamine **19** in good overall yield.



Scheme 5

In conclusion, a facile procedure for the synthesis of unsaturated amines carrying the olefinic double bond at the 3- or 4-position or the allenic functionality at the 3-position is disclosed. It is obvious that this methodology is also applicable to substrates having the unsaturation at a more remote position.

EXPERIMENTAL SECTION

^{1}H NMR spectra (270 MHz or 60 MHz) and ^{13}C NMR spectra (68 MHz or 20 MHz) were run with a Jeol JNM-EX 270 NMR spectrometer or a Jeol PMX60 si NMR spectrometer or a Varian FT80 NMR spectrometer. Peak assignments were performed with the aid of the DEPT technique, 2D-COSY spectra, HETCOR spectra and/or off-resonance decoupled spectra. IR spectra were obtained from a Perkin Elmer model 1310 spectrophotometer while mass spectra were measured with a Varian MAT 112 spectrometer (70 eV) using a GC-MS coupling. Gas chromatography was executed with an Intersmat IGL 120 ML gas chromatograph (glass column, SE-30, H_2 carrier gas).

Synthesis of N-t-butylaldimines **4**

A solution of 0.10 mol aldehyde **1** in 100 ml of dichloromethane was treated with 0.11 mol of t-butylamine and 20 g $MgSO_4$. The stirred mixture was refluxed for 1 h, filtered, evaporated under vacuo and distilled under vacuo to give the pure N-t-butylaldimines **4**. B.p. (% yield) : **4a**, 99-100°C/760 mmHg, Lit.[13] bp. 47-49°C/95 mmHg, (96%); **4b**, 105-106°C/0.05 mmHg; (mp. 88°C, Lit.[14] mp. 77-83°C) (96%); **4c**, 114-117°C/760 mmHg, Lit.[15], bp. 50°C/75 mmHg (98%); **4d**, 80-85°C/16 mmHg, Lit.[16] bp. 37°C/0.55 mmHg (97%).

Synthesis of N-(4-penten-1-ylidene)t-butylamines **5**

An icecold solution of 0.0575 mol of diisopropylamine in 60 ml dry tetrahydrofuran was treated with 0.055 mol of butyllithium (2.5 M in hexane) under a nitrogen atmosphere. After stirring for 10 min, a solution of 0.05 mol of N-t-butylaldimine **4** in 10 ml THF was added dropwise after which stirring was continued at 0°C for 1.5 h (R^1=Me, H) or 6 h (R^1=Ph). The 1-azaallylic anion thus formed was treated dropwise at 0°C with 0.0525 mol of allylbromide in 10 ml THF. The mixture was stirred further for 16 h during which the temperature rose to ambient temperature. Aqueous workup and extraction with ether gave an extract which was dried (K_2CO_3) and evaporated in vacuo. The residual oil consisted of pure (> 95%; GC) α-allylaldimines **5**. These aldimines **5** were used as such in the next hydrolysis step. α-Allylaldimines **5**:**5a**, yield : 82%. Bp. 47-51°C/12 mmHg. IR (NaCl) : 1665 cm^{-1} (C=N), 1640 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$) : δ 1.05 (3H, d, J=6.93 Hz, CHMe); 1.16 (9H, s, Me_3); 2.05-2.31 (2H, m, CH_2); 2.38 (1H, septet, J= ~6.5 Hz, CHMe); 4.98-5.05 (2H, m, CH_2=); 5.68-5.83 (1H, m, CH=); 7.39 (1H, d, J=6.26 Hz, CH=N). ^{13}C NMR ($CDCl_3$) : δ 17.29 (Me); 29.70 (Me_3); 38.78 (CH_2); 39.39 (MeCH); 56.42 (CMe_3); 116.28 (CH_2=); 136.17 (CH=); 162.80 (C=N). Mass spectrum m/z (%) : 153 (M^+; 2); 138(18); 111(11); 98(45); 97(7); 96(10); 82(35); 81(15); 70(13); 69(5); 68(6); 58(11); 57(100); 56(14); 55(11); 43(7); 42(14); 41(46). Elem. Anal. : $C_{10}H_{19}N$, Calcd. 78.37% C, 12.49% H, 9.14% N. Found : 78.15% C, 12.42% H, 9.44% N; **5b**, yield 97% (purity > 97%). IR (NaCl) : 1656 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) : δ 1.17 (9H, s, t-Bu), 3.15 (2H, dt, J=6.9 Hz, J=1.3 Hz, CH_2-C=), 4.81-4.90 (2H, m, CH_2=C), 5.62-5.75 (1H, m, CH=C), 7.14-7.37 (10H, m, 2xPh), 7.91 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) : 29.52 (Me_3), 41.47 (CH_2), 55.90 (CPh_2), 56.89 (Me_3C-N), 116.94 (CH_2=C), 126.23 (C_p arom.), 127.99 and 128.80 (C_o and C_m arom.), 135.65 (CH=C), 144.44 (C_q arom.), 160.59 (CH=N). Mass spectrum m/z (%) : 291 (M^+, 11), 290(6), 276(9), 208(25), 207(16), 200(17), 194(10), 193(15), 179(8), 178(9), 165(11), 144(10), 130(121), 129(65), 128(10), 115(8), 111(12), 91(56), 84(12), 58(8), 57(100), 41(23). Elem. Anal. : $C_{21}H_{25}N$, Calcd. 4.81% N. Found 5.03% N; **5c**, yield 96%. Bp. 55-58°C/20 mmHg. IR (NaCl) : 1669 cm^{-1} (C=N), 1640 cm^{-1} (C=C). ^1H NMR (CCl_4) : δ 0.9 (6H, s, Me_2); 1.08 (9H, s, Me_3); 2.10 (2H, d, J=7 Hz, CH_2); 4.6-6.0 (3H, m, CH=CH_2); 7.33 (1H, s, N=CH). ^{13}C NMR ($CDCl_3$) : δ 24.85 (q, Me_2); 29.0 (q, C$\underline{Me_3}$); 38.55 (s, $\underline{C}Me_2$); 45.05 (t, $\underline{C}H_2$); 56.06 (s, $\underline{C}Me_3$); 116.85 (t, CH=C$\underline{H}_2$); 135.14 (d, C$\underline{H}$=CH_2); 163.76 (d, N=C$\underline{H}$). Elem. anal. : $C_{11}H_{21}N$, Calcd. 78.98% C, 12.65% H, 8.37% N. Found 78.77% C, 12.72% H, 8.51% N; **5d** (94% yield; bp. 109-115°C/15 mmHg, Lit.[16] bp. 51-55°C/0.5 mmHg).

Synthesis of α-Allylaldehydes **2**

A solution of 0.05 mol of α-allylaldimine **5** in 100 ml dichloromethane was treated with 0.05 mol of oxalic acid dihydrate, dissolved in 60 ml water. The biphase system was vigorously stirred under reflux for 2 h after which the organic phase was isolated. The aqueous phase was extracted twice with 20 ml of dichloromethane and the combined organic phases were dried ($MgSO_4$). After evaporation of the solvent the remaining liquid consisted of pure (> 95%, GC) 4-alkenals **2**, which were used as such in the next imination step. The spectral data are exemplified for 2,2-diphenyl-4-pentenal **2b**. Compound **2b** was purified by flash chromatography (silica gel, hexane/EtOAc 95/5) to give the pure aldehyde in 86% yield (Rf 0.32). IR (NaCl) : 1722 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) : δ 3.09 (2H, dd, J=6.93 Hz and 1.32 Hz, CH_2-C=), 4.91-5.01 (2H, m, CH_2=C), 5.50-5.65 (1H, m, CH=C), 7.17-7.39 (10H, m, 2xC_6H_5), 9.82 (1H, s, CH=O). ^{13}C NMR ($CDCl_3$) : δ 38.76 (CH_2), 63.36 ($\underline{C}Ph_2$), 118.37 ($\underline{C}H_2$=C), 127.31 (C_p-arom.), 128.57 and 129.09 (C_o- and C_m-arom.), 133.50 ($\underline{C}$H=C), 139.64 (C_q-arom.), 198.33 (C=O). Mass spectrum m/z (%) : 237 (M^+; 12), 218(5), 208(14), 207(46), 206(6), 195(16), 192(6), 178(8), 167(21), 166(10), 165(25), 152(11), 130(22), 129(100), 128(22), 127(10), 115(11), 103(9), 92(12), 91(85), 77(13), 51(8). Elem. Anal. : Calcd. $C_{17}H_{16}O$, 86.41% C, 6.82% H. Found 86.29% C, 6.93% H. Other aldehydes **2**, **2a**, 89%; **2c**, 88% (bp. 125-127°C/760 mmHg, Lit.[8b] bp. 120-126°C); **2d**, 80% (bp. 78-81°C/13 mmHg, Lit.[8a] bp. 105-107°C/32 mmHg).

Synthesis of N-Benzyl Imines **6**, **9** and **13**

A solution of α-allylaldehydes **2** or aldehydes **8** or **12** (0.05 mol) in 50 ml dichloromethane was treated with benzylamine (0.05 mol) and magnesium sulfate (10 g). After stirring at room temperature (for aldehydes **2** and **8**) or at reflux (for aldehyde **12**) for a given time (see schemes 2, 3 and 4), the reaction mixture was filtered and the solvent was evaporated in vacuo to give pure N-benzyl imines **6**, **9** or **13** (purity > 97%) in 91-98% yield. Consequently, these aldimines were not distilled in vacuo but used further in the next transamination step.

Analytical samples of compounds **6c** and **6d** were obtained by vacuum distillation.

N-(2-Methyl-4-penten-1-ylidene)benzylamine **6a**

Yield : 95%. IR (NaCl) : 1664 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) : δ 1.11 (3H, d, J=6.6 Hz, Me), 2.09-2.40 (2H, m, CH_2), 2.44-2.51 (1H, m, CH-C=N), 4.56 (2H, d, J=0.99 Hz, C$\underline{H}_2$Ph), 5.00-5.09 (2H, m, CH_2=C), 5.71-5.84 (1H, m, CH=C), 7.20-7.34 (5H, m, C_6H_5), 7.66 (1H, dt, J=5.28, J=0.99 Hz, CH=N). ^{13}C NMR ($CDCl_3$) : δ 16.87 (CH_3), 38.33 (CH_2), 38.98 (C$\underline{H}$-Me), 64.80 ($\underline{C}H_2C_6H_5$), 116.53 ($\underline{C}H_2$=C), 126.83 (C_p-arom.), 127.78 and 128.37 (C_o- and C_m-arom.), 136.03 ($\underline{C}$H=C), 139.30 (C_q-arom.), 169.88 (C=N). Mass spectrum m/z (%) : 187 (M^+; 17), 186(23), 173(5), 172(21), 146(7), 145(15), 144(8), 96(10), 92(16), 91(100), 69(10), 65(17), 41(17).

N-(2,2-Diphenyl-4-penten-1-ylidene)benzylamine **6b**

Yield : 97%. IR (NaCl) : 1655 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) : δ 3.22 (2H, d, J=6.93 Hz, $C\underline{H}_2$-C=), 4.67 (2H, d, J=1.16 Hz, CH_2N), 4.84-4.91 (2H, m, CH_2=C), 5.61-5.76 (1H, m, CH=C), 7.16-7.37 (15H, m, 3xC_6H_5), 8.13 (1H, t, J=1.16 Hz, CH=N). ^{13}C NMR ($CDCl_3$) : δ 41.37 ($\underline{C}H_2$-C=), 56.55 ($\underline{C}Ph_2$), 64.55 (NCH_2), 117.39 (CH_2=), 126.52, 126.74, 127.56, 128.14, 128.34 and 128.84 (arom. $\underline{C}$H=), 134.98 (CH=), 139.42 and 143.72 (2xC_q arom.), 168.44 (C=N). Mass spectrum m/z (%) : 325 (M^+, 12), 324(8), 234(18), 193(6), 167(6), 165(7), 132(14), 130(6), 129(27), 128(7), 92(10), 91(100), 65(9).

N-(2,2-Dimethyl-4-penten-1-ylidene)benzylamine **6c**

Yield : 97%. Bp. 77-79°C/0.15 mmHg. IR (NaCl) : 1660 cm^{-1} (C=N). ^{1}H NMR (CCl_4) : δ 0.95 (6H, s, Me_2), 2.16 (2H, d, J=6.8 Hz, CH_2), 4.48 (2H, d, J=1.4 Hz, NCH_2), 4.7-6.1 (3H, m, CH=CH_2), 7.18 (5H, s, Ph), 7.54 (1H, t, J=1.4 Hz, CH=N). ^{13}C NMR ($CDCl_3$) : 24.77 (q, Me_2), 39.24 (s, $\underline{C}Me_2$), 44.88 (t, CH_2), 64.72 (t, NCH_2), 117.37 (t, $\underline{C}H_2$=C), 126.73 (d, =CH), 127.70 (d, =CH), 128.34 (d, =CH), 134.71 (d, =CH), 139.91 (s, $C_{quat.}$ arom.), 171.94 (d, CH=N). Elem. Anal. : $C_{14}H_{19}N$, Calcd. 83.53% C, 9.51% H, 6.96% N. Found 83.40% C, 9.59% H, 6.81% N.

N-[(1-Allyl-1-cyclohexyl)methylene]benzylamine **6d**

Yield : 97%. Bp. 84-88°C/0.04 mmHg. IR (NaCl) : 1660 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) : δ 1.2-1.9 (10H, m, $(CH_2)_5$), 2.19 (2H, d, J=7.6 Hz, CH_2-C=), 4.61 (2H, s, NCH_2), 4.9-6.0 (3H, m, CH=CH_2), 7.30 (5H, s, Ph), 7.57 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) : δ 22.35, 26.07 and 33.75 ($(CH_2)_5$), 42.50 ($\underline{C}(CH_2)_5$), 43.93 ($\underline{C}H_2C$=), 65.12 (NCH_2), 117.30 (CH=$\underline{C}H_2$), 126.28 (p. CH=), 127.67 (CH), 128.32 (o. CH='s), 134.19 (m. CH='s), 139.67 ($NCH_2\underline{C}$=), 172.31 (CH=N). Mass spectrum m/z (%) : 241 (M^+, 5), 240(3), 226(6), 186(8), 133(22), 91(100), 81(9), 67(7), 65(14), 41(15). Elem. Anal. $C_{17}H_{23}N$, Calcd. 84.59% C, 9.60% H, 5.80% N. Found : 84.51% C, 9.72% H, 5.94% N.

N-[(3-Cyclohexen-1-yl)methylidene]benzylamine **9**

Yield : 98%. IR (NaCl) : 1667 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) : δ 1.5-2.6 (7H, m, CH_2-CH-CH_2CH_2), 46 (2H, s, NCH_2), 5.7 (2H, broad s, CH=CH), 7.2-7.4 (5H, m, C_6H_5), 7.73 (1H, d, J=4.6 Hz, CH=H). ^{13}C NMR ($CDCl_3$) : δ 24.22 (CH_2), 25.66 (CH_2), 27.98 (CH_2), 39.32 (CH), 64.92 (NCH_2), 125.42 and 126.81 ($\underline{C}$H=$\underline{C}$H), 127.01 (C_p arom.), 127.73 and 128.37 (C_o and C_m arom.), 139.40 (C_q arom.), 169.31 (CH=N). Mass spectrum m/z (%) : 199 (M^+, 17), 170(5), 133(15), 132(8), 108(16), 106(6), 92(13), 91(100), 81(11), 79(8), 77(5), 65(15), 41(7).

N-(2,2,5-Trimethyl-3,4-hexadien-1-ylidene)benzylamine **13**

Yield : 91%. IR (NaCl) : 1659 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) : δ 1.20 (6H, s, Me_2), 1.69 (6H, d, J=2.7 Hz, Me_2C=C), 4.59 (2H, d, J=1.15 Hz, CH_2N), 5.02 (1H, septet, J=2.7 Hz, CH=C), 7.20-7.35 (5H, m, C_6H_5), 7.61 (1H, t, J=1.15 Hz, CH=N). ^{13}C NMR ($CDCl_3$) : 20.70 (Me_2), 25.30 ($\underline{Me_2}C$=), 40.66 ($Me_2\underline{C}$-C=N), 64.44 (CH_2N), 96.37 ($\underline{C}$H=C), 97.14 ($Me_2\underline{C}$=C), 126.72 (C_p-arom.), 127.64 and 128.30 (C_o- and C_m-arom.), 139.57 (C_q-arom.), 171.52 ($\underline{C}$H=N), 200.71 (=$\underline{C}$=). Mass spectrum m/z (%) : 227 (M^+, 6), 226(3), 213(13), 212(40), 185(8), 136(13), 121(7), 120(6), 110(18), 109(7), 96(6), 95(23), 92(15), 91(100), 81(6), 79(7), 77(7), 67(15), 65(16), 55(10), 43(8), 41(15).

Isomerization of N-Benzyl α-Allylimines **6**, **9** and **13** into N-(Benzylidene)homoallylamines **7**, **10** and **14** respectively

A solution of N-benzyl α-allylimines **6**, **9** or **13** (0.05 mol) in 50 ml of dry THF (distilled from benzophenone ketyl) was treated with potassium t-butoxide (0.075 mol). The mixture was stirred under reflux for 1 h, then cooled to room temperature and poured in 100 ml of water. Extraction twice with diethyl ether, washing the combined organic layers with brine, drying of the combined extracts ($MgSO_4$) and evaporation of the solvent afforded an oily residue which consisted of N-(benzylidene)amines **7**, **10** or **14** respectively in high purity (> 95%). The reaction products can be distilled in vacuo or can be used as such in the next hydrolysis step. Compounds **7a-c** were prepared in 78-89% yield, while N-(benzylidene)amines **10** and **14** were obtained in 87% and 95% yield, respectively.

N-(Benzylidene)-2-methyl-4-pentenylamine **7a**

Yield : 78%. Bp. 55-65°C/0.01 mmHg. IR (NaCl) : 1640 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) : δ 0.95 (3H, d, J=6.27 Hz, Me), 1.91-2.02 (1H, m, MeC<u>H</u>), 1.91-2.02 and 2.15-2.24 (elk 1H, elk m, C<u>H</u>$_2$CH=), 3.40 (1H, dxdxd, J_1=11.46 Hz, J_2=6.52 Hz, J_3=0.99 Hz, N<u>H</u>CH), 3.58 (1H, dxdxd, J_1=11.46 Hz, J_2=5.53 Hz, J_3=1.32 Hz, NHC<u>H</u>), 4.99-5.06 (2H, m, =CH_2), 5.75-5.91 (1H, m, CH=), 7.38-7.41 (3H, m, m- and p-CH='s), 7.71-7.75 (2H, m, o-CH='s), 8.24 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) : δ 17.95 (Me), 34.23 (Me<u>C</u>H), 39.28 (<u>C</u>H$_2$CH=); 67.58 (CH_2N), 115.99 (CH_2=), 128.05 and 128.55 (C_o- and C_m-arom.), 130.46 (C_p-arom.), 136.35 (C_q-arom.), 137.12 (<u>C</u>H=CH_2); 161.09 (CH=N). Mass spectrum m/z (%) : 187 (M^+, 27), 186(100), 172(6), 144(10), 119(19), 118(61), 117(11), 104(23), 91(60), 90(11), 77(11), 65(10), 41(24). Elem. Anal. : $C_{13}H_{17}N$, Calcd. 83.37% C, 9.15% H, 7.48% N. Found 83.49% C, 9.15% H, 7.48% N.

N-(Benzylidene)-2,2-diphenyl-4-pentenylamine **7b**

Yield : 82%. Flash chromatography, silica gel, hexane/EtOAc 99/1, Rf=0.20. IR (NaCl) : 1641 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) : δ 3.08 (2H, d, J=6.92 Hz, C<u>H</u>$_2$CH=), 4.23 (2H, d, J=0.99 Hz, NCH_2), 4.96-5.10 (2H, m, CH_2=), 5.43-5.58 (1H, m, C<u>H</u>=CH_2), 7.12-7.59 (15H, m, arom. =CH's), 7.88 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) : δ 41.81 (<u>C</u>H$_2$CH=), 51.01 ((C_6H_5)$_2$<u>C</u>), 67.71 (CH_2N), 117.91 (CH_2=), 125.82, 127.71, 127.96, 128.01, 128.26, 128.34 (arom. =CH's), 134.77 (CH_2=<u>C</u>H), 136.42, 146.84 (arom. C_{quat}), 161.78 (C=N). Mass spectrum m/z (%) : 325 (M^+, 16), 324(13), 284(8), 208(9), 207(23), 182(10), 181(44), 180(11), 178(11), 165(13), 130(13), 129(62), 128(14), 119(17), 118(88), 103(10), 92(12), 91(100), 90(9), 77(11), 65(9). Elem. Anal. $C_{24}H_{23}N$, Calcd. 88.57% C, 7.12% H, 4.30% N. Found 88.67% C, 7.20% H, 4.39% N.

N-(Benzylidene)-2,2-dimethyl-4-pentenylamine **7c**

Yield : 88%. Bp. 148-152°C/15 mmHg. IR (NaCl) : 1645 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) : δ 0.95 (6H, s, Me_2), 2.09 (2H, d, J=7 Hz, CH_2), 3.32 (2H, s, broadened, NCH_2), 4.7-6.2 (3H, m, CH=CH_2), 7.2-7.5 (3H, m, CH= m. and p. arom.), 7.5-7.8 (2H, m, CH= ortho arom.), 8.16 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) : δ 25.67 (q, Me_2), 35.25 (s, <u>C</u>Me$_2$), 45.10 (t, CH=), 72.03 (t, NCH_2), 116.95 (t, CH_2=), 128.11 (d, CH=), 128.47 (d, CH=), 130.28 (d, CH=), 135.42 (d, <u>C</u>H=CH_2), 136.74 (s, C_{quat} arom.), 160.62 (d, CH=N). Mass spectrum m/z (%) : 201 (M^+, 26), 200(90), 186(10), 145(12), 144(13), 119(26), 118(100), 104(13), 91(84), 77(13), 55(32), 41(29). Elem. Anal. $C_{14}H_{19}N$, Calcd. 83.53% C, 9.51% H, 6.96% N. Found 83.42% C, 9.55% H, 7.02% N.

1-[N-(Benzylidene)aminomethyl]-1-allylcyclohexane **7d**

Yield : 89%. IR (NaCl) : 1647 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) : δ 1.4-1.5 (10H, m, ($C\underline{H}_2)_5$), 2.16 (2H, d, J=7.3 Hz, $C\underline{H}_2$CH=), 3.41 (2H, s, CH_2N), 5.0-5.1 (2H, m, $C\underline{H}_2$=CH), 5.8-6.0 (1H, m, CH_2=C$\underline{H}$), 7.31-7.34 (3H, m, m- and p- CH='s), 7.68-7.73 (2H, m, o- CH='s), 8.18 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) : δ 21.58, 26.31 and 33.89 (($\underline{C}H_2)_5$), 37.39 (($CH_2)_5\underline{C}$), 40.63 ($\underline{C}H_2$CH=), 68.23 (N$\underline{C}H_2$), 116.93 ($\underline{C}H_2$=CH), 127.98, 128.41 and 130.19 (arom. =CH's), 135.06 ($\underline{C}$H=CH_2), 136.58 (C_q-arom.), 160.48 (CH=N). Mass spectrum m/z (%) : 241 (M^+, 100), 226(17), 201(12), 199(10), 120(35), 119(88), 106(19), 104(14), 91(47), 81(25), 67(19), 55(14).

N-(Benzylidene)-(3-cyclohexen-1-yl)-methylamine **10**

Yield : 87%. IR (NaCl) : 1644 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) : δ 1.2-2.2 (7H, m, CH_2-CH-CH_2-CH_2), 3.55 (2H, ~d, J=6.6 Hz, NCH_2), 5.68 (2H, s, broadened, CH=CH), 7.25-7.40 (3H, m, CH_m and CH_p arom.), 7.7-7.8 (2H, m, CH_o arom.), 8.26 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) : δ 24.83 (CH_2), 26.81 (CH_2), 29.91 (CH_2), 34.82 (CH), 67.56 (CH_2N), 126.16 and 127.06 (HC=CH), 128.05 and 128.53 (C_o and C_m arom.), 130.44 (C_p arom.), 136.30 (C_q arom.), 160.98 (CH=N). Mass spectrum m/z (%) : 199 (M^+, 8), 198(8), 156(3), 120(28), 119(68), 118(100), 104(6), 92(6), 91(57), 90(5), 79(13), 77(11), 65(8), 41(13).

N-(Benzylidene)-2,2,5-trimethyl-3,4-hexadienylamine **14**

Yield : 95%. IR (NaCl) : 1642 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$) : δ 1.07 (6H, s, Me_2), 1.66 (6H, d, J=2.9 Hz, Me_2C=), 3.46 (2H, d, J=0.7 Hz, NCH_2), 4.99 (1H, septet, J=2.9 Hz, CH=C), 7.38-7.42 (3H, m, m- and p-CH='s), 7.73-7.76 (2H, O-CH='s), 8.22 (1H, t, J=0.7 Hz, CH=N). ^{13}C NMR ($CDCl_3$) : δ 20.81 (Me_2), 26.45 (Me_2C=), 36.91 ($Me_2\underline{C}$=CH_2), 72.83 (CH_2N), 96.71 ($Me_2\underline{C}$), 98.26 ($\underline{C}$H=C), 128.10 and 128.46 (C_o- and C_m-arom.), 130.35 (C_p-arom.), 136.51 (C_q-arom.), 161.17 (CH=N), 199.96 (=C=). Mass spectrum m/z (%) : 227 (M^+, 42), 226(68), 213(24), 212(51), 211(18), 197(20), 196(29), 131(27), 119(41), 118(93), 117(24), 109(51), 107(25), 106(19), 98(19), 92(24), 91(100), 90(22), 89(18), 81(26), 77(26), 69(18), 67(60), 65(27), 55(35), 53(20), 43(31), 41(46).

Synthesis of 4-Alkenylamines **3**, cycloalkenylamine **11** and 3-allenylamine **15**

A solution of N-(benzylidene)-4-alkenylamines **7** (0.05 mol) in 50 ml of dichloromethane was treated with 50 ml of water and oxalic acid (0.05 mol). The biphase system was refluxed under vigorous stirring for 2 h. Afterwards, the organic phase was isolated and the aqueous phase was extracted once more with 15 ml of dichloromethane. Evaporation of water in vacuo from the aqueous phase affords a solid material which mainly contains the 4-alkenylamine **3** under oxalate form. It can be used as such for future experiments. The free amines were generated by addition of 12 ml of water and slow addition of aqueous NaOH (12N) at 0°C. The alkaline solution (pH ≈ 14) was extracted three times with dichloromethane. After drying ($MgSO_4$), the solvent was evaporated carefully in vacuo or at atmospheric pressure utilizing a short Vigreux column. Alternatively, the free amines can be dissolved again in dry diethyl ether and treated with gaseous hydrogen chloride in order to obtain precipitated hydrochlorides of amines **3**.

2-Methyl-4-pentenylamine **3a**

Yield : 60%. Mp. of the hydrochloride : 89°C. Lit.[17] bp. 59°C/70 mmHg, Lit.[18] bp. 115-116°C/760 mmHg. IR (NaCl) : 1640 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$) : δ 0.91 (3H, d, J=6.60 Hz, CH_3), 1.38 (2H, broad s, NH_2), 1.43-1.61 (1H, m, C$\underline{H}$Me), 1.85-1.96 and 2.08-2.19 (each 1H, each m, $C\underline{H}_2$-C=), 2.51 and 2.63 (each 1H, each dd, J=10.37 Hz, J=6.93 Hz, J=5.77 Hz, $C\underline{H}_2$N), 4.95-5.08 (2H, m, CH_2=), 5.72-

5.87 (1H, m, CH=). ^{13}C NMR ($CDCl_3$) : δ 17.30 (CH_3), 36.28 (<u>C</u>H-Me), 38.83 (<u>C</u>H_2-C=), 48.01 (CH_2N), 115.87 (CH_2=), 137.16 (CH=). Mass spectrum m/z (%) : no M^+, 84 (M^+-Me, 35), 82(62), 81(10), 70(26), 68(14), 77(68), 58(21), 57(96), 56(100), 44(27), 43(22), 42(19), 41(87).

<u>2,2-Diphenyl-4-pentenylamine **3b**</u>

Yield : 75%. Lit.[19] mp. of the hydrobromide : 223-225°C. IR (NaCl) : 3390 cm^{-1} (NH_2), 1639 cm^{-1} (C=C). ^1H NMR ($CDCl_3$) : δ 1.01 (2H, s, broad, NH_2), 2.91 (2H, d, J=6.93 Hz, C<u>H</u>$_2$-C=), 3.30 (2H, s, CH_2N), 4.92-5.06 (2H, m, CH_2=), 5.31-5.46 (1H, m, CH=), 7.13-7.27 (10H, m, 2xC_6H_5). ^{13}C NMR ($CDCl_3$) : δ 41.06 (<u>C</u>H_2-C=), 48.48 (CH_2N), 51.27 (<u>C</u>Ph_2), 117.64 (CH_2=), 126.00 (C_p-arom.), 128.01 and 128.14 (C_o- and C_m-arom.), 134.57 (CH=), 146.20 (C_q-arom.). Mass spectrum m/z (%) : 237 (M^+, 11), 236(6), 208(8), 207(16), 206(26), 180(9), 179(8), 178(12), 165(18), 146(17), 130(16), 129(89), 128(21), 127(10), 120(18), 115(12), 103(9), 92(10), 91(100), 77(14).

<u>2,2-Dimethyl-4-pentenylamine **3c**</u>

Yield : 72%. Bp. 67°C/68 mmHg. IR (NaCl) : 3325 cm^{-1} (C=C). ^1H NMR ($CDCl_3$) : δ 0.85 (6H, s, Me_2), 1.16 (2H, s, broad, NH_2), 1.97 (2H, d, J=7.59 Hz, C<u>H</u>$_2$CH=), 2.45 (2H, s, NCH_2), 4.99-5.05 (2H, m, CH_2=), 5.73-5.87 (1H, m, CH_2=C<u>H</u>). ^{13}C NMR ($CDCl_3$) : δ 24.60 (Me_2), 34.91 (Me_2<u>C</u>), 44.02 (<u>C</u>H_2CH=), 52.69 (CH_2N), 116.89 (<u>C</u>H_2=CH), 135.34 (CH_2=<u>C</u>H). Mass spectrum m/z (%) : 112 (M^+-1, 3), 99(6), 98(45), 96(20), 82(21), 81(24), 78(32), 67(29), 57(40), 56(38), 55(100), 41(47). Elem. Anal. $C_7H_{15}N$. Calcd. 74.27% C, 13.36% H, 12.37% N. Found 74.35% C, 13.28% H, 12.22% N.

<u>1-(Aminomethyl)-1-allylcyclohexane **3d**[20]</u>

Yield : 79%. Bp. 74-76°C/8 mmHg. Lit.[20b] bp. 112-114°C/25 mmHg. IR (NaCl) : 3310 cm^{-1} (NH_2), 1638 cm^{-1} (C=C). ^1H NMR ($CDCl_3$) : δ 1.07 (2H, s, broad, NH_2), 1.25-1.46 (10H, m, $(CH_2)_5$), 2.07 (2H, dt, J_1=7.58 Hz, J_2=0.99 Hz, C<u>H</u>$_2$CH=), 2.52 (2H, s, NCH_2), 5.01-5.08 (2H, m, C<u>H</u>$_2$=CH), 5.73-5.88 (1H, m, CH_2=C<u>H</u>). ^{13}C NMR ($CDCl_3$) : δ 21.53 and 33.28 ((<u>C</u>H_2)$_2$$CH_2$(<u>C</u>$H_2$)$_2$), 26.45 (($CH_2$)$_2$<u>C</u>$H_2$($CH_2$)$_2$), 37.05 ($CH_2$<u>C</u>=$CH_2$), 39.89 (<u>C</u>$H_2$CH=$CH_2$), 48.84 ($NCH_2$), 116.80 (<u>C</u>$H_2$=CH), 135.06 ($CH_2$=<u>C</u>H). Mass spectrum m/z (%) : 153 (M^+, 1), 152(1), 151(1), 138(26), 107(17), 95(21), 81(100), 79(36), 69(20), 67(54), 57(32), 56(21), 55(36), 53(18), 44(27), 41(71). Elem. Anal. $C_{10}H_{19}N$. Calcd. 78.37% C, 12.50% H, 9.14% N. Found 78.44% C, 12.62% H, 9.03% N.

<u>(3-Cyclohexen-1-yl)methylamine **11**</u>

Bp. 67-61°C/22 mmHg (yield 76%, as hydrochloride, mp 203-207°C). IR (NaCl) : 3300 cm^{-1} (NH_2, broad). ^1H NMR ($CDCl_3$) : δ 1.2-2.2 (7H, m, CH_2-CH-CH_2-CH_2), 1.29 (2H, s, NH_2), 2.61 (2H, d, J=6.3 Hz, C<u>H</u>$_2$$NH_2$), 5.6-5.7 (2H, m, CH=CH). ^{13}C NMR ($CDCl_3$) : δ 24.94 (CH_2), 26.38 (CH_2), 29.45 (CH_2), 37.16 (CH), 48.10 (NCH_2), 126.13 and 127.17 (CH=CH). Mass spectrum m/z (%) : 111 (M^+, 10), 95(8), 94(86), 80(17), 79(100), 77(15), 66(11), 56(23), 53(12), 43(11), 41(17). Elem. Anal. $C_7H_{13}N$, Calcd. 75.62% C, 11.78% H, 12.60% N. Found 75.65% C, 11.88% H, 12.49% N.

<u>2,2,5-Trimethyl-3,4-hexadienylamine **15**</u>

Yield : 75% (yield : 95%, as oxalate). Bp. 77-79°C/27 mmHg. IR (NaCl) : 1462-1368-1197-1023 cm^{-1}. ^1H NMR ($CDCl_3$) : δ 0.96 (6H, s, Me_2), 1.27 (2H, s, broad, NH_2), 1.70 (6H, d, J=2.90 Hz, Me_2C=), 2.47 (2H, s, CH_2N), 4.80 (1H, septet, J=2.90 Hz, CH=C). ^{13}C NMR ($CDCl_3$) : δ 20.79 (Me_2), 25.39 (<u>Me</u>$_2$C=), 37.13 (<u>C</u>Me_2), 53.39 (NCH_2), 96.48 (Me_2<u>C</u>=), 97.05 (CH=), 200.47 (=C=). Mass spectrum m/z (%) :

139 (M^+, 44), 125(13), 124(66), 110(83), 109(31), 108(20), 107(74), 95(100), 93(19), 91(29), 81(34), 79(37), 77(22), 69(20), 68(22), 67(95), 56(21), 55(65), 53(23), 43(42), 41(67). Elem. Anal. $C_9H_{17}N$, Calcd. 77.63% C, 12.31% H, 10.06% N. Found 77.50% C, 12.18% H, 10.09% N.

Synthesis of N-(2-methyl-4-pentenyl)acetamide

The hydrolysis of N-(benzylidene)-2-methyl-4-pentenylamine **7a** was performed with 1 molar equiv. oxalic acid dihydrate in water/diethyl ether under reflux for 2 h. The ether layer was discarded and the aqueous phase was extracted once more with diethyl ether. The aqueous phase was evaporated in vacuo and the residue was made alkaline with 6N NaOH. To this mixture was added acetic anhydride (5 equiv.) and stirring was continued for 4 h at room temperature. Extraction twice with dichloromethane, drying of the organic extracts ($MgSO_4$) and evaporation of the solvent gave the crude amide, which was purified by flash chromatography (silica gel, EtOAc/MeOH 9/1, Rf=0.61) to afford pure N-(2-methyl-4-pentenyl)acetamide in 92% yield.

IR (NaCl, cm^{-1}) : 3280 cm^{-1} (NH), 1634 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) : δ 0.91 (3H, d, J=6.60 Hz, $C\underline{H}_3CH$), 1.67-1.80 (1H, m, $C\underline{H}CH_3$), 1.86-2.03 and 2.07-2.17 (each 1H, each m, $C\underline{H}_2CH=$), 1.98 (3H, s, $C\underline{H}_3C$), 3.02-3.23 (2H, m, CH_2N), 5.00-5.07 (2H, m, $CH_2=$), 5.7-5.80 (1H, m, CH=), 5.83 (1H, broad s, NH). ^{13}C NMR ($CDCl_3$) : δ 17.45 ($\underline{C}H_3CH$), 23.09 ($\underline{C}H_3C$), 33.15 ($\underline{C}HCH_3$), 38.90 ($\underline{C}H_2CH=$), 45.21 (CH_2N), 116.30 ($CH_2=$), 136.53 (CH=), 170.71 (C=O). Mass spectrum m/z (%) : 141 (M^+, 6), 126(6), 100(13), 99(62), 98(14), 82(50), 74(8), 73(64), 72(91), 67(44), 60(60), 58(64), 57(22), 56(18), 43(100), 41(53). Elem. Anal. $C_8H_{15}NO$, Calcd. 68.05% C, 10.71% H, 9.92% N. Found 68.12% C, 10.84% H, 9.82% N.

Synthesis of 2-Ethyl-2-phenyl-3-butenylamine **19**

As described above, imination of 2-ethyl-2-phenyl-3-butenal **16** with benzylamine (1 equiv.) in dichloromethane in the presence of $MgSO_4$ under reflux for 24 h gave imine **17** in 95% yield. The isomerization of the latter imine **17** into the N-(benzylidene)homoallylamine **18** was accomplished with potassium t-butoxide (3 equiv.) in THF under reflux for 2 h, essentially as described above (yield 82%). The final hydrolysis of compound **18** to give homoallylamine **19** was performed with aqueous oxalic acid (1 equiv.) in the presence of dichloromethane as a second phase (reflux 2 h; see procedure above). After removal of the organic phase, the aqueous phase was basified with solid sodium hydroxide and the aqueous phase was extracted three times with dichloromethane. The extracts were dried ($MgSO_4$) and evaporated in vacuo to give homoallylamine **19** in 82% yield.

N-(2-Ethyl-2-phenyl-3-buten-1-ylidene)benzylamine **17**

Yield : 95%. IR (NaCl) : 1660 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) : δ 0.83 (3H, t, J=7.26 Hz, Me), 2.06-2.19 (2H, m, $C\underline{H}_2Me$), 4.67 (2H, s, NCH_2), 4.99 (1H, dd, J=17.32, J=0.99 Hz, $\underline{H}CH=CH$), 5.29 (1H, dd, J=10.9 Hz, J=0.99 Hz, $HC\underline{H}=CH$), 6.30 (1H, dd, J=17.32 Hz, J=10.9 Hz, $C\underline{H}=CH_2$), 7.20-7.41 (10H, m, 2xPh), 7.80 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) : δ 9.06 (Me), 29.27 (CH_2), 54.46 ($C_{quat.}$), 64.72 (NCH_2), 115.70 ($\underline{C}H_2=CH$), 126.56 and 126.77 (p. CH='s), 127.67, 127.94, 128.30 and 128.33 (o. and m. CH='s), 141.08 ($\underline{C}H=CH_2$), 139.37 and 142.37 (each $=C_{quat.}$), 168.42 (C=N). Mass spectrum m/z (%) : 263 (M^+, 6), 248(4), 235(5), 234(8), 172(6), 146(18), 145(23), 117(19), 92(11), 91(100), 65(15), 41(8). Elem. Anal. $C_{19}H_{21}N$, Calcd. 86.65% C, 8.04% H, 5.32% N. Found 86.43% C, 8.12% H, 5.46% N.

N-(Benzylidene)-2-ethyl-2-phenyl-3-butenylamine **18**

IR (NaCl) : 1645 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) : δ 0.83 (3H, t, J=7.42 Hz, CH_3) : 1.94-2.03 (2H, m, $C\underline{H}_2CH_3$), 3.90 and 3.99 (each 1H, each dd, J=11.54 Hz, J=1.32 Hz, CH_2N), 5.12 (1H, dd, J=17.81 Hz, J=1.32 Hz, $\underline{H}CH$=CH), 5.26 (1H, dd, J=10.88 Hz, J=1.32 Hz, $HC\underline{H}$=CH), 6.06 (1H, dd, J=17.81 Hz, J=10.88 Hz, CH_2=C$\underline{H}$), 7.15-7.38 (8H, m, $C_6\underline{H}_5C$ and m- and o- =CH's), 7.64-7.67 (2H, m- and o- =CH's), 8.07 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) : δ 8.48 (Me), 28.52 ($\underline{C}H_2CH_3$), 49.58 ($CH_2\underline{C}$), 67.66 (CH_2N), 113.82 ($\underline{C}H_2$=CH), 125.86, 127.78, 128.01, 128.37 and 130.31 (arom. =CH's), 136.37 and 144.22, (each C_q-arom.), 144.22 ($\underline{C}H=CH_2$), 161.53 (CH=N). Mass spectrum m/z (%) : no M^+, 235 (M^+-28, 3), 234(4), 158(3), 145(10), 119(17), 118(100), 117(10), 115(8), 92(8), 91(64), 65(8).

2-Ethyl-2-phenyl-3-butenylamine **19**

Yield : 82% (purity > 95%). Decomposition upon attempted vacuum distillation. IR (NaCl) : 3385 cm^{-1} (NH_2). ^1H NMR ($CDCl_3$) : δ 0.75 (3H, t, J=7.43 Hz, Me), 1.53 (2H, s, NH_2), 1.82 (2H, q, J=7.48 Hz, $C\underline{H}_2CH_3$), 2.97 and 3.03 (each 1H, each d, J=13.20 Hz, CH_2N), 5.13 (1H, dd, J_1=17.82 Hz, J=0.99 Hz, $\underline{H}CH$=CH), 5.33 (1H, dd, J=10.89 Hz, J=0.99 Hz, $HC\underline{H}$=CH), 5.97 (1H, dd, J=17.82 Hz, J=10.89 Hz, H_cC=C$\underline{H}$), 7.22-7.36 (5H, m, C_6H_5). ^{13}C NMR ($CDCl_3$) : δ 7.51 (Me), 27.50 ($\underline{C}H_2Me$), 47.35 (CH_2N), 49.29 ($\underline{C}$Ar), 113.46 (CH_2=), 125.09 (C_p-arom.), 126.63 and 127.21 (C_o- and C_m-arom.), 142.39 ($\underline{C}H=CH_2$), 143.09 (C_q-arom.). Mass spectrum m/z (%) : 175 (M^+, 2), 174(0.6), 159(1), 158(5), 147(13), 146(100), 145(99), 144(13), 131(14), 130(17), 129(38), 128(26), 118(11), 117(83), 116(13), 115(45), 105(12), 103(11), 91(52), 77(21), 65(17), 63(11), 51(20), 43(33), 41(23).

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