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A CONVENIENT SYNTHESIS OF TERTIARY CARBINAMINES VIA N-ALUMINUM KETIMINES

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Abstract : Reaction of N-unsubstituted ketimines with organoaluminum reagents prepared from allylic and propargylic halides, allows to prepare, in good yields, tertiary carbinamines with three different groups (phenyl, alkyl and α-unsaturated group) on the tertiary carbon center.

The synthesis of secondary carbinamines $(R^1)(R^2)CH\text{-}NH_2$ has been described, by use of organolithium or organomagnesium reagents and "masked" imine derivatives of ammonia : these reactions involve arylsulfenylimines,[1] sulfonylimines,[2] sulfonyliminoethers [3,4] and N-trimethylsilylimines.[5] Recently N-metalloimines such as $R^1\text{-}CH{=}N\text{-}Al(iBu)_2$ and $R^1\text{-}CH{=}N\text{-}B(R)_2$ are used.[6, 7]

Tertiary carbinamines $(R^1)(R^2)(R^3)C\text{-}NH_2$ would can be obtained according to a similar scheme, but few cases are reported in literature ; we have noted the

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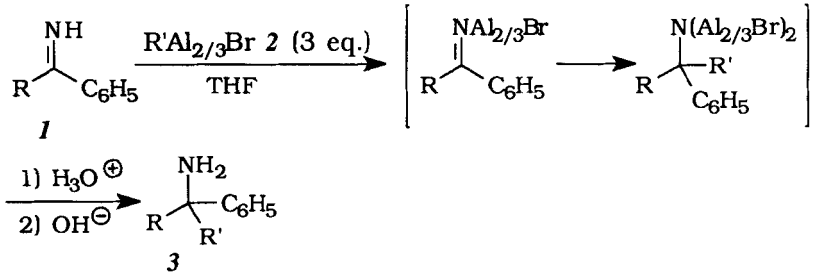
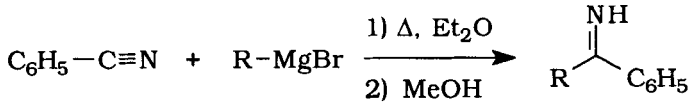
reaction of alkyl- or aryllithium reagents with some sulfenylketimines,[1] the reaction of allylic organometallic compounds with a N-tosyliminoether [4] and recently, the reaction of alkyl- or arylcerium reagents (prepared from organolithium derivatives) with nitriles or N-unsubstituted ketimines.[8]

We wish to report a convenient "one-step"synthesis of amines ***3*** from N-unsubstituted ketimines ***1*** and organoaluminum compounds ***2*** prepared from allylic and propargylic bromides, according to the sequence :



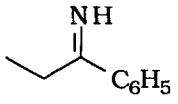
N-unsubstituted ketimines ***1*** are obtained by the reaction :[9]



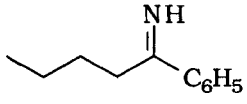
Yields : 51-80%

and the organoaluminum derivatives are prepared according to .[10-14]

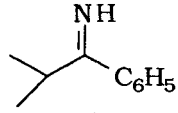
In this study, we consider three ketimines ***1a-c***



1a



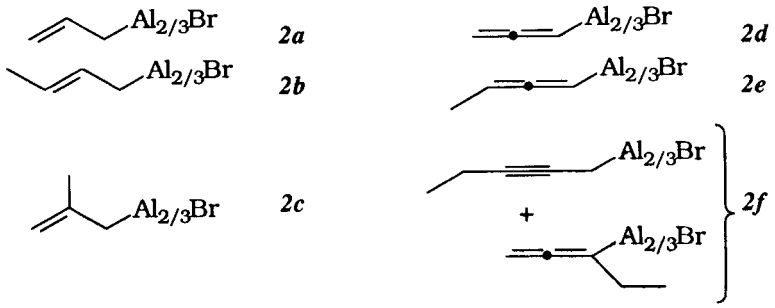
1b



1c

and six organoaluminum compounds ***2a-f*** ,which have the mentioned structures :[13,14]

Our results are shown in the table. In all cases, we obtained the amines ***3*** in good yields. Enolization of ketimines does not take place with the reactive



organoaluminum derivatives used in these experiences, as it appears with saturated Grignard reagents.[15]

At last, the reaction of N-unsubstituted ketimine ***1a*** with other CH_2=CH-CH_2M has been tried : the reaction is observed, but the yields in ***3aa*** are lower (61 and 70% respectively) by use of CH_2=CH-CH_2ZnBr/THF and CH_2=CH-CH_2MgBr/ether.

In summary, our method is very efficient to prepare tertiary carbinamines (R^1)(R^2)(R^3)C-NH_2 which possess one α–unsaturated group. Indeed, the Ritter reaction (addition of carbocations to nitriles),[16] which requires strongly acidic conditions, is not favourable for the preparation of these amines ***3*** because it may cause rearrangements ; in the same way, the reduction of tertiary nitro-compounds [17] may not be compatible with the ethylenic or propargylic group.

EXPERIMENTAL

IR spectra were recorded on a IR 4240 Beckman spectrometer ; ν frequencies are given in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded on a Jeol JNM EX 90 spectrometer, at 89.5MHz and 22.5MHz respectively, in $CDCl_3$ using TMS (^1H, δ = 0.00 ppm) or $CDCl_3$ (^{13}C, δ = 77.00 ppm) as internal standards ; chemical shifts are given in δ units. Mass spectra were obtained on a Fisons Trio 1000 spectrometer at 70 eV.

Table : Synthesis of primary amines from N-aluminum ketimines

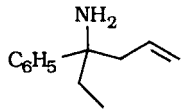
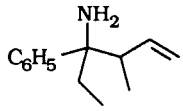
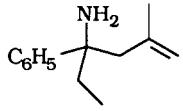
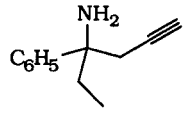
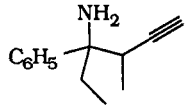
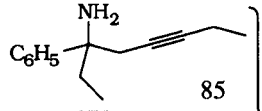
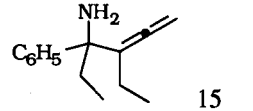
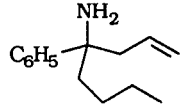
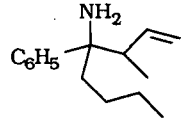
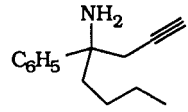
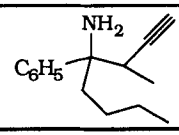
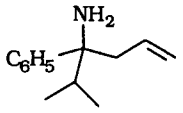
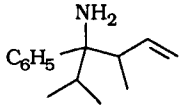
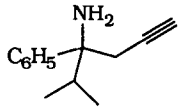
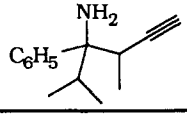
Ketimine	$R'Al_{2/3}Br$	Product		Yield % [a]
1a	***2a***		***3aa***	94 [b]
1a	***2b***		***3ab***	80
1a	***2c***		***3ac***	70
1a	***2d***		***3ad***	70
1a	***2e***		***3ae***	54
1a	***2f***	 85  15	***3af*** ***3af'***	50
1b	***2a***		***3ba***	63
1b	***2b***		***3bb***	54
1b	***2d***		***3bd***	60

Table (continued)

Ketimine	$R'Al_{2/3}Br$	Product	Yield % [a]
1b	***2e***	 ***3be***	53
1c	***2a***	 ***3ca***	84
1c	***2b***	 ***3cb***	50
1c	***2d***	 ***3cd***	52
1c	***2e***	 ***3ce***	46

[a] Isolated yields
[b] 86% yield, when ether was used as solvent.

*Preparation of ketimines **1a-c** according to* [9]

To a solution of Grignard reagent prepared from alkylbromide (0.3 mol), magnesium (0.3 mol, 7.3 g) in dry ether (180 mL), a solution of benzonitrile (0.2 mol, 20.6 g) in dry ether (100 mL) was added dropwise at such a rate that to maintain a slight reflux. After 15 h at reflux, the mixture was cooled at -15 , - 10°C and anhydrous methanol (1.87 mol, 60.0g) was added dropwise cautiously under a vigourous stirring. After complete addition, the white precipitate was filtered, the ether was evaporated and the ketimine was isolated by trap-to-trap.

1-phenylpropan-1-imine *1a*

Yield : 80% ; Litt.[18] 101-102°C/15 Torr.

IR : 3350br w (=NH) ; 1620s (C=N) ; 3060m, 3030w, 1575m, 1450s, 740s, 690vs (C_6H_5).

^{1}H NMR : 9.11 (br s, 1H, NH) ; 7.90-7.10 (m, 5H, C_6H_5) ; 2.66 (q, 2H, CH_2, ^3J 7.3Hz) ; 1.05 (t, 3H, CH_3, ^3J 7.3Hz).

^{13}C NMR : 178.4 (C=N) ; 138.3 (C_1) ; 129.5 (C_4) ; 127.7 (C_2, C_6) ; 125.7 (C_3, C_5) ; 29.3 (CH_2) ; 9.4 (CH_3).

1-phenylpentan-1-imine *1b*

Yield : 51% ; Litt.[19] 144°C/10 Torr.

IR : 3350br w (=NH) ; 1615s (C=N) ; 3060m, 3030w, 1575m, 1460s, 760s, 690vs (C_6H_5).

^1H NMR : 8.97 (br s, 1H, NH) ; 7.95-7.10 (m, 5H, C_6H_5) ; 2.71 (t, 2H, CH_2C=, ^3J 7.2Hz) ; 1.85-1.05 (m, 4H, CH_2CH_2) ; 0.92 (t, 3H, CH_3, ^3J 6.9Hz).

^{13}C NMR : 178.6 (C=N) ; 138.8 (C_1) ; 129.8 (C_4) ; 128.2 (C_2, C_6) ; 126.1 (C_3, C_5) ; 37.1 ($\underline{C}H_2C$=) ; 28.1 ($\underline{C}H_2CC$=) ; 22.1 ($\underline{C}H_2CH_3$) ; 13.6 (CH_3).

2-methyl-1-phenylpropan-1-imine *1c*

Yield : 52% ; Litt.[18] 98-99°C/14 Torr.

IR : 3350br w (=NH) ; 1615s (C=N) ; 3060m, 3030w, 1580m, 1465s, 770s, 695vs (C_6H_5).

^1H NMR : 9.05 (br s, 1H, NH) ; 7.95-7.15 (m, 5H, C_6H_5) ; 3.16 (hept., 1H, CH, ^3J 6.7Hz) ; 1.17 (d, 6H, CH_3, ^3J 6.7Hz).[20]

^{13}C NMR : 184.2 (C=N) ; 139.5 (C_1) ; 129.7 (C_4) ; 128.3 (C_2, C_6) ; 126.3 (C_3, C_5) ; 33.7 (CH) ; 20.1 (CH_3).

Organometallics

The aluminum derivatives were prepared from allylic or propargylic bromides in tetrahydrofuran, according to.[10-14] Allylmagnesium bromide was made in ether medium [21] and allylzinc bromide was obtained in tetrahydrofuran. [22]

*Reaction of organoaluminum compounds with ketimines **1a**, **1b** and **1c***

A solution of ketimine (0.025 mol) in dry THF (10 mL) was added at 20°C to the organoaluminic prepared in THF from an allylic or propargylic bromide (0.1 mol). The mixture was heated at 65°C for 1 h and then maintained under stirring at room temperature for 15 h. The reaction mixture was poured on 2M hydrochloric acid (150 mL) and stirred for 30 min. The aqueous layer was separated and extracted with ether (2 x 60 mL). The aqueous layer was then cooled at 0°C and treated by 10M sodium hydroxide until pH = 10. After extraction with ether (4 x 60 mL), drying of the organic phase (magnesium sulfate) and removal of the solvent, the primary amine was distilled under reduced pressure.

Products

3-Phenylhex-5-en-3-amine *3aa*

Eb 69°C/0.05 Torr.

IR : 3380w, 3320vw, 1605br m (NH_2) ; 3080m, 3010vw, 1640m, 1000m, 920s (CH_2=CH) ; 3060m, 3030w, 1580m, 1495s, 760s, 700vs (C_6H_5).

^{1}H NMR : 7.65-7.05 (m, 5H, C_6H_5) ; 5.90-5.30 (m, 1H, CH_X=) ; 5.25-4.85 (m, 2H, CH_2=) ; 2.60 and 2.37 (A and B of ABX, 2H, CH_2C=, $^2J_{AB}$ 13.6Hz, $^3J_{AX}$ 7.9Hz, $^3J_{BX}$ 6.1Hz) ; 1.77 (q, 2H, CH_2, ^3J 7.5Hz) ; 1.47 (s, 2H, NH_2) ; 0.70 (t, 3H, CH_3, ^3J 7.5Hz).

^{13}C NMR : 146.5 (C_1) ; 134.0 (CH=) ; 127.7 (C_3, C_5) ; 125.7 (C_4) ; 125.6 (C_2, C_6) ; 118.1 (CH_2=) ; 57.2 (C-N) ; 48.1 ($\underline{C}H_2C$=); 35.8 (CH_2) ; 7.8 (CH_3).

MS (IC$^+$, CH_4) m/z : 216 [$(M+C_3H_5)^+$, 0.4%] ; 204 [$(M+C_2H_5)^+$, 2] ; 176 [$(M+H)^+$, 26] ; 159 [$(M+H)^+ - NH_3$, 77] ; 146 [$(M+H)^+ - C_2H_6$, 11] ; 134 [$(M+H)^+ - C_3H_6$, 100] ; 98 [$(M+H)^+ - C_6H_6$, 33].

4-methyl-3-phenylhex-5-en-3-amine *3ab*

Eb 70°C/0.05 Torr.

Two diastereoisomers : 30/70.

IR : 3390w, 3330vw, 1605br m (NH_2) ; 3085m, 3010vw, 1635m, 1005m, 915s (CH_2=CH) ; 3070m, 3030w, 1585m, 1495s, 760s, 705vs (C_6H_5).

^{1}H NMR : 7.45-7.00 (m, 5H, C_6H_5) ; 6.05-5.30 (m, 1H, CH=) ; 5.25-4.75 (m, 2H, CH_2=) ; 2.75-2.30 (m, 1H, CHC=) ; 2.15-1.35 (m, 2H, CH_2) ; 1.30 (br s, 2H, NH_2) ; 1.10-0.50 (m, 6H, CH_3).

^{13}C NMR : 145.6 (C_1) ; 140.3 (CH=) ; 127.7 and 127.6 (C_3 , C_5) ; 126.5, 126.2 and 125.7 (C_2, C_6, C_4) ; 115.7 and 115.1 (CH_2=) ; 59.9 (C-N) ; 48.5 and 48.0 (CH) ; 34.2 and 32.5 (CH_2) ; 14.8 and 13.4 ($\underline{C}H_3CH$) ; 8.0 and 7.9 (CH_3).

MS (IC$^+$, CH_4) m/z : 230 [$(M+C_3H_5)^+$, 1%] ; 218 [$(M+C_2H_5)^+$, 3] ; 190 [$(M+H)^+$, 31] ; 173 [$(M+H)^+ - NH_3$, 45] ; 160 [$(M+H)^+ - C_2H_6$, 7] ; 134 [$(M+H)^+ - C_4H_8$, 100] ; 112 [$(M+H)^+ - C_6H_6$, 19].

5-methyl-3-phenylhex-5-en-3-amine *3ac*

Eb 77°C/0.06 Torr.

IR : 3380w, 3320vw, 1610br m (NH_2) ; 3080m, 1645m, 895s (CH_2=C) ; 3065m, 3035w, 1585m, 1495s, 770s, 705vs (C_6H_5).

^{1}H NMR : 7.55-7.05 (m, 5H, C_6H_5) ; 4.90-4.55 (m, 2H, CH_2=) ; 2.56 and 2.40 (A and B of AB, 2H, CH_2C=, $^2J_{AB}$ 13.1Hz) ; 1.94 and 1.68 (A and B of ABX_3, 2H, CH_2, $^2J_{AB}$ 14.6Hz, $^3J_{AX}$ = $^3J_{BX}$ 7.5Hz) ; 1.56 (s, 2H, NH_2) ; 1.26 (s, 3H, CH_3C=) ; 0.69 (t, $3H_X$, CH_3, ^3J 7.5Hz).

^{13}C NMR : 146.6 (C_1) ; 142.3 (C=) ; 127.7 (C_3, C_5) ; 125.75 (C_2, C_6) ; 125.7 (C_4) ; 114.8 (CH_2=) ; 57.1 (C-N) ; 52.3 ($\underline{C}H_2C$=) ; 36.7 (CH_2) ; 24.3 ($\underline{C}H_3C$=) ; 7.8 (CH_3).

MS (IC$^+$, CH_4) m/z : 230 [(M+C_3H_5)$^+$, 0.6%] ; 218 [(M+C_2H_5)$^+$, 1] ; 190 [(M+H)$^+$, 19] ; 173 [(M+H)$^+$ – NH_3, 40] ; 160 [(M+H)$^+$ – C_2H_6, 6] ; 134 [(M+H)$^+$ – C_4H_8, 100] ; 112 [(M+H)$^+$ – C_6H_6, 12].

3-phenylhex-5-yn-3-amine *3ad*

Eb 77°C/0.05 Torr.

Product with ≤ 4% of allenic isomer.

IR : 3370w, 3320vw (sh), 1605br m (NH_2) ; 3300s, 2120vw, 685s (C≡CH) ; 3060w, 3030w, 1585m, 1495s, 760s, 700vs (C_6H_5).

^1H NMR : 7.65-7.05 (m, 5H, C_6H_5) ; 2.61 (d, 2H, CH_2C≡, ^4J 2.5Hz) ; 1.95 (t, 1H, HC≡, ^4J 2.5Hz) ; 1.84 (q, 2H, CH_2, ^3J 7.4Hz) ; 1.67 (s, 2H, NH_2) ; 0.70 (t, 3H, CH_3, ^3J 7.4Hz).

^{13}C NMR : 145.3 (C_1) ; 127.8 (C_3, C_5) ; 126.2 (C_4) ; 125.5 (C_2, C_6) ; 81.0 (C≡) ; 71.0 (HC≡) ; 57.1 (C-N) ; 34.8 (CH_2) ; 33.9 ($\underline{C}H_2C$≡).

MS (IC$^+$, CH_4) m/z : 214 [(M+C_3H_5)$^+$, 0.5%] ; 202 [(M+C_2H_5)$^+$, 1] ; 174 [(M+H)$^+$, 13] ; 157 [(M+H)$^+$ – NH_3, 70] ; 144 [(M+H)$^+$ – C_2H_6, 15] ; 134 [(M+H)$^+$ – C_3H_4, 100] ; 96 [(M+H)$^+$ – C_6H_6, 30].

4-methyl-3-phenylhex-5-yn-3-amine *3ae*

Eb 82°C/0.04 Torr.

IR : 3380w, 3320vw (sh), 1600br m (NH_2) ; 3300s, 2110w, 680vs (C≡CH) ; 3060w, 3030w, 1580m, 1495s, 755s, 700vs (C_6H_5).

^1H NMR : 7.60-7.05 (m, 5H, C_6H_5) ; 2.91 (qd, 1H, CH, ^3J 7.0Hz, ^4J 2.5Hz,) ; 2.16 (d, 1H, HC≡, ^4J 2.5Hz) ; 2.04 and 1.92 (A and B of ABX_3, 2H, CH_2, $^2J_{AB}$ 12.1Hz, $^3J_{AX} = {}^3J_{BX}$ 7.4Hz) ; 1.50 (br s, 2H, NH_2); 0.88 (d, 3H, $C\underline{H}_3CH$, ^3J 7.0Hz) ; 0.65 (t, $3H_X$, CH_3, ^3J 7.4Hz).

^{13}C NMR : 143.4 (C_1) ; 127.9 (C_3, C_5) ; 126.1 (C_4) ; 126.0 (C_2, C_6) ; 86.4 (C≡) ; 71.0 (HC≡) ; 59.9 (C-N) ; 38.1 (CH) ; 35.1 (CH_2) ; 15.5 ($\underline{C}H_3CH$) ; 8.0 (CH_3).

MS (IC$^+$, CH_4) m/z : 228 [(M+C_3H_5)$^+$, 0.5%] ; 216 [(M+C_2H_5)$^+$, 1] ; 188 [(M+H)$^+$, 20] ; 171 [(M+H)$^+$ – NH_3, 48] ; 158 [(M+H)$^+$ – C_2H_6, 14] ; 134 [(M+H)$^+$ – C_4H_6, 100] ; 110 [(M+H)$^+$ – C_6H_6, 19].

3-phenyloct-5-yn-3-amine *3af*

Eb 91-92°C/0.01 Torr.

Product obtained in mixture 85/15 with ***3af'***.

IR : 3375w, 3315vw, 1605m (NH_2) ; 2140vw, (C≡C) ; 3060w, 3030w, 1585m, 1495s, 765s, 700vs (C_6H_5).

^1H NMR : 7.65-6.95 (m, 5H, C_6H_5) ; 2.57 (t, 2H, ≡CCH_2C-N, ^5J 2.4Hz) ; 2.00 (qt, 2H, $CH_3C\underline{H}_2C\equiv$, ^3J 7.5Hz, ^5J 2.4Hz) ; 1.84 (q, 2H, CH_2, ^3J 6.8Hz) ; 1.70 (s, 2H, NH_2) ; 1.05 (t, 3H, $CH_3CC\equiv$, ^3J 7.5Hz) ; 0.70 (t, 3H, CH_3, ^3J 6.8Hz).

^{13}C NMR : 145.6 (C_1) ; 127.5 (C_3, C_5) ; 125.8 (C_4) ; 125.4 (C_2, C_6) ; 84.2 and 75.7 (C≡C) ; 57.0 (C-N) ; 34.5 and 34.2 ($\underline{C}H_2$-$C(NH_2)$-$\underline{C}H_2$) ; 13.9 ($\underline{C}H_3CC\equiv$) ; 12.0 ($\underline{C}H_2C\equiv$) ; 8.0 (CH_3).

MS (IC$^+$, CH_4) m/z : 242 [$(M+C_3H_5)^+$, 1%] ; 230 [$(M+C_2H_5)^+$, 5] ; 202 [$(M+H)^+$, 32] ; 185 [$(M+H)^+ - NH_3$, 80] ; 172 [$(M+H)^+ - C_2H_6$, 9] ; 134 [$(M+H)^+ - C_5H_8$, 100] ; 124 [$(M+H)^+ - C_6H_6$, 22].

4-ethyl-3-phenylhex-4,5-dien-3-amine *3af'*

Product obtained in mixture 15/85 with ***3af***.

IR : 1960m (C=C=CH_2).

^1H NMR : 4.95 (t, 2H, CH_2=C, ^5J 3.6Hz).

^{13}C NMR : 204.8 (=C=) ; 145.9 (C_1) ; 127.9 (C_3, C_5) ; 125.9 (C_4) ; 125.4 (C_2, C_6) ; 113.1 (C=) ; 78.6 (CH_2=) ; 59.5 (C-N) ; 33.7 ($\underline{C}H_2$C-N) ; 20.0 ($\underline{C}H_2$C=) ; 12.1 ($\underline{C}H_3$CC=) ; 7.8 (CH_3).

3-phenyloct-7-en-3-amine *3ba*

Eb 92°C/0.01 Torr.

IR : 3370w, 3320vw, 1600 br m (NH_2) ; 3075m, 3010w, 1640m, 995m, 915s (CH_2=CH) ; 3060m, 3030m, 1580m, 1490s, 765s, 700vs (C_6H_5).

^1H NMR : 7.60-6.95 (m, 5H, C_6H_5) ; 5.85-5.25 (m, 1H, CH_X=) ; 5.20-4.75 (m, 2H, CH_2=) ; 2.60 and 2.36 (A and B of ABX, 2H, CH_2C=, $^2J_{AB}$ 13.6Hz, $^3J_{AX}$ 5.1Hz, $^3J_{BX}$ 8.0Hz) ; 1.90-0.90 (m, 6H, CH_2) ; 1.46 (s, 2H, NH_2) ; 0.81 (t, 3H, CH_3, ^3J 7.0Hz).

^{13}C NMR : 146.9 (C_1) ; 134.0 (CH=) ; 127.8 (C_3, C_5) ; 125.7 (C_4) ; 125.5 (C_2, C_6) ; 118.2 (CH_2=) ; 57.0 (C-N) ; 48.7 ($\underline{C}H_2$C=) ; 43.3 ($\underline{C}H_2$C-N) ; 25.7 ($\underline{C}H_2$CC-N) ; 23.0 ($CH_3\underline{C}H_2$) ; 13.8 (CH_3).

MS (IC$^+$, CH_4) m/z : 244 [$(M+C_3H_5)^+$, 1%] ; 232 [$(M+C_2H_5)^+$, 2] ; 204[$(M+H)^+$, 33] ; 187 [$(M+H)^+ - NH_3$, 52] ; 162 [$(M+H)^+ - C_3H_6$, 100] ; 146 [$(M+H)^+ - C_4H_{10}$, 27] ; 126 [$(M+H)^+ - C_6H_6$, 25].

6-methyl-3-phenyloct-7-en-3-amine *3bb*

Eb 96°C/0.01 Torr.

Two diastereoisomers : 40/60.

IR : 3390w, 3330vw, 1605br m (NH_2) ; 3080m, 3010w, 1635m, 1005m, 915s (CH_2=CH) ; 3060m, 3030w, 1585m, 1500s, 765s, 705vs (C_6H_5).

^{1}H NMR : 7.70-7.05 (m, 5H, C_6H_5) ; 6.10-5.30 (m, 1H, CH=) ; 5.25-4.75 (m, 2H, CH_2=) ; 2.53 (quint., 1H, CHC=, ^3J 7.0Hz) ; 2.15-0.60 (m, 12H, CH_2, CH_3) ; 1.39 (s, 2H, NH_2).

^{13}C NMR : 146.13 and 146.07 (C_1) ; 140.4 (CH=) ; 127.7 and 127.6 (C_3, C_5) ; 126.4, 126.1 and 125.7 (C_4, C_2, C_6) ; 115.8 and 115.2 (CH_2=) ; 59.7 and 59.6 (C-N) ; 48.8 and 48.2 (CHC=) ; 41.6 and 39.9 (CH_2C-N) ; 25.92 and 25.86 (CH_2CC-N) ; 23.24 and 23.18 (CH_3CH_2) ; 14.8, 14.0 and 13.4 (CH_3).

MS (IC$^+$, CH_4) m/z : 258 [(M+C_3H_5)$^+$, 1%] ; 246 [(M+C_2H_5)$^+$, 4] ; 218 [(M+H)$^+$, 41] ; 201 [(M+H)$^+$ – NH_3, 46] ; 162 [(M+H)$^+$ – C_4H_8, 100] ; 160 [(M+H)$^+$ – C_4H_{10}, 22] ; 140 [(M+H)$^+$ – C_6H_6, 20].

3-phenyloct-7-yn-3-amine *3bd*

Eb 88°C/0.01 Torr.

Product with ≤ 4% of allenic isomer.

IR : 3365w, 3330vw (sh), 1600br m (NH_2) ; 3300s, 2120w, 635s (C≡CH) ; 3060w, 3030w, 1580m, 1490s, 765s, 700vs (C_6H_5).

^{1}H NMR : 7.85-7.05 (m, 5H, C_6H_5) ; 2.64 (d, 2H, CH_2C≡, ^4J 2.7Hz) ; 1.98 (t, 1H, HC≡, ^4J 2.7Hz) ; 1.80 (br s, 2H, NH_2) ; 1.95-1.55 (m, 2H, CH_2C-N) ; 1.50-0.90 (m, 4H, $CH_3CH_2CH_2$) ; 0.83 (t, 3H, CH_3, ^3J 6.6Hz).

^{13}C NMR : 145.7 (C_1) ; 127.9 (C_3, C_5) ; 126.2 (C_4) ; 125.4 (C_2, C_6) ; 81.0 (C≡) ; 71.0 (HC≡) ; 56.9 (C-N) ; 42.1 (CH_2C-N) ; 34.3 (CH_2C≡) ; 25.9 (CH_3CCH_2) ; 22.8 (CH_3CH_2) ; 13.8 (CH_3).

MS (IC$^+$, CH_4) m/z : 242 [(M+C_3H_5)$^+$, 1%] ; 230 [(M+C_2H_5)$^+$, 2] ; 202 [(M+H)$^+$, 20] ; 185 [(M+H)$^+$ – NH_3, 34] ; 162 [(M+H)$^+$ – C_3H_4, 100] ; 144 [(M+H)$^+$ – C_4H_{10}, 27] ; 124 [(M+H)$^+$ – C_6H_6, 26].

6-methyl-3-phenyloct-7-yn-3-amine *3be*

Eb 95°C/0.01 Torr.

IR : 3380w, 3330vw (sh), 1605br m (NH_2) ; 3300s, 2110vw, 630s (C≡CH) ; 3060w, 3030w, 1580m, 1490s, 760s, 700vs (C_6H_5).

^{1}H NMR : 7.65-7.05 (m, 5H, C_6H_5) ; 2.92 (qd, 1H, CHC≡, ^3J 7.0Hz, ^4J 2.4Hz) ; 2.18 (d, 1H, HC≡, ^4J 2.4Hz) ; 1.95 (t, 2H, CH_2C-N, ^3J 6.0Hz) ; 1.63 (br s, 2H, NH_2) ; 1.45-0.60 (m, 10H, $CH_3CH_2CH_2$, CH_3CH).

^{13}C NMR : 143.9 (C_1) ; 128.0 (C_3, C_5) ; 126.0 (C_4) ; 125.9 (C_2, C_6) ; 86.5 (C≡) ; 71.1 (HC≡) ; 59.6 (C-N) ; 42.4 (CH_2C-N) ; 38.4 (CH) ; 25.9 (CH_3CCH_2) ; 23.0

($CH_3\underline{C}H_2$) ; 15.5 ($\underline{C}H_3CH$) ; 13.9 (CH_3).

MS (IC$^+$, CH_4) m/z : 256 [$(M+C_3H_5)^+$, 1%] ; 244 [$(M+C_2H_5)^+$, 3] ; 216 [$(M+H)^+$, 30] ; 199 [$(M+H)^+ - NH_3$, 29] ; 162 [$(M+H)^+ - C_4H_6$, 100] ; 158 [$(M+H)^+ - C_4H_{10}$, 25] ; 138 [$(M+H)^+ - C_6H_6$, 19].

2-methyl-3-phenylhex-5-en-3-amine *3ca*

Eb 75°C/0.05 Torr.

IR : 3380w, 3320vw, 1610br m (NH_2) ; 3080m, 3010w, 1635m, 995m, 910s (CH_2=CH) ; 3060m, 3020w, 1585m, 1490s, 760s, 700vs (C_6H_5).

^{1}H NMR: 7.60-6.95 (m, 5H, C_6H_5) ; 5.80-4.75 (m, 3H, CH_2=CH_X) ; 2.69 and 2.40 (A and B of ABX, 2H, CH_2C=, $^2J_{AB}$ 13.9Hz, $^3J_{AX}$ 4.9Hz, $^3J_{BX}$ 8.0Hz) ; 2.01 (hept., 1H, CH, ^3J 6.9Hz) ; 1.43 (s, 2H, NH_2) ; 0.95 and 0.66 (2d, 6H, CH_3, ^3J 6.9Hz, diastereotopy).

^{13}C NMR : 146.2 (C_1) ; 134.6 (CH=) ; 127.6 (C_3, C_5) ; 126.2 (C_2, C_6) ; 125.7 (C_4) ; 117.9 (CH_2=) ; 59.7 (C-N) ; 45.5 (CH_2) ; 37.8 (CH) ; 17.4 and 16.7 [$(\underline{C}H_3)_2C$, diastereotopy].

MS (IC$^+$, CH_4) m/z : 230 [$(M+C_3H_5)^+$, 1%] ; 218 [$(M+C_2H_5)^+$, 3] ; 190 [$(M+H)^+$, 33] ; 173 [$(M+H)^+ - NH_3$, 20] ; 148 [$(M+H)^+ - C_3H_6$, 100] ; 146 [$(M+H)^+ - C_3H_8$, 30] ; 112 [$(M+H)^+ - C_6H_6$, 35].

2,4-dimethyl-3-phenylhex-5-en-3-amine *3cb*

Eb 79°C/0.01 Torr.

Two diastereoisomers : 30/70.

IR : 3390w, 3320vw, 1600br m (NH_2) ; 3080m, 3010w, 1635m, 1000m, 915s (CH_2=CH) ; 3060m, 3030w, 1590w, 1490m, 760s, 705vs (C_6H_5).

^{1}H NMR : 7.60-7.05 (m, 5H, C_6H_5) ; 5.95-5.30 (m, 1H, CH=) ; 5.20-4.75 (m, 2H, CH_2=) ; 3.00-2.00 (m, 2H, CH) ; 1.42 (s, 2H, NH_2) ; 0.95-0.60 (m, 9H, CH_3).

^{13}C NMR : 143.7 and 143.5 (C_1) ; 140.7 (CH=) ; 127.8, 127.4, 127.2 and 125.9 (C_2, C_3, C_4, C_5, C_6) ; 115.5 and 115.1 (CH_2=) ; 62.0 and 61.9 (C-N) ; 44.7 and 43.8 ($\underline{C}$HC=) ; 34.0 and 33.7 [$(CH_3)_2\underline{C}H$] ; 17.6, 17.5, 16.7 and 16.6 [$(\underline{C}H_3)_2C$, diastereotopy] ; 15.1 and 13.7 (CH_3).

MS (IC$^+$, CH_4) m/z : 244 [$(M+C_3H_5)^+$, 2%] ; 232 [$(M+C_2H_5)^+$, 5] ; 204 [$(M+H)^+$, 54] ; 187 [$(M+H)^+ - NH_3$, 19] ; 160 [$(M+H)^+ - C_3H_8$, 20] ; 148 [$(M+H)^+ - C_4H_8$, 100] ; 126 [$(M+H)^+ - C_6H_6$, 27].

2-methyl-3-phenylhex-5-yn-3-amine *3cd*

Eb 80°C/0.01 Torr.

Product with ≤ 4% of allenic isomer.

IR : 3380w, 3330vw (sh), 1605br m (NH_2) ; 3305s, 2120w, 635s (HC≡C) ; 3060m, 3030w, 1580m, 1495w, 765s, 705vs (C_6H_5).

^{1}H NMR : 7.65-7.00 (m, 5H, C_6H_5) ; 2.70 (d, 2H, $CH_2C\equiv$, ^4J 2.6Hz) ; 2.1 (hept., 1H, CH, ^3J 6.8Hz) ; 1.87 (t, 1H, HC≡, ^4J 2.6Hz) ; 0.88 and 0.73 (2d, 6H, CH_3, ^3J 6.8Hz, diastereotopy).

^{13}C NMR : 145.0 (C_1) ; 127.6 (C_3, C_5) ; 126.2 (C_2, C_4, C_6) ; 81.4 (C≡) ; 70.9 (HC≡) ; 59.7 (C-N) ; 37.1 (CH) ; 31.4 (CH_2) ; 17.5 and 17.0 [($\underline{C}H_3)_2C$, diastereotopy].

MS (IC$^+$, CH_4) m/z : 228 [$(M+C_3H_5)^+$, 0.5%] ; 216 [$(M+C_2H_5)^+$, 1] ; 188 [$(M+H)^+$, 16] ; 171 [$(M+H)^+ - NH_3$, 49] ; 148 [$(M+H)^+ - C_3H_4$, 100] ; 144 [$(M+H)^+ - C_3H_8$, 36] ; 110 [$(M+H)^+ - C_6H_6$, 35].

2,4-dimethyl-3-phenylhex-5-yn-3-amine *3ce*

Eb 86°C/0.01 Torr.

Two diastereoisomers : 20/80.

IR : 3380w, 3320vw (sh), 1600br m (NH_2) ; 3300s, 2115w, 635s (HC≡C) ; 3060m, 3030w, 1580m, 1495s, 760s, 705vs (C_6H_5).

^{1}H NMR : 7.80-6.95 (m, 5H, C_6H_5) ; 3.75-3.15 (m, 1H, CHC≡) ; 2.70-1.95 (m, 2H, CH, HC≡) ; 1.57 (br s, 2H, NH_2) ; 1.35-0.50 (m, 9H, CH_3).

^{13}C NMR : 141.1 (C_1) ; 128.5, 128.2, 127.4, 127.3, 126.8 and 126.2 (C_2, C_3, C_4, C_5, C_6) ; 86.9 and 86.3 (C≡) ; 71.1 and 70.6 (HC≡) ; 62.1 (C-N) ; 36.2, 35.2, 34.4 and 34.0 (CH) ; 19.0, 17.7, 17.4, 16.6, 15.8 and 15.6 (CH_3).

MS (IC$^+$, CH_4) m/z : 242 [$(M+C_3H_5)^+$, 1%] ; 230 [$(M+C_2H_5)^+$, 1] ; 202 [$(M+H)^+$, 28] ; 185 [$(M+H)^+ - NH_3$, 33] ; 158 [$(M+H)^+ - C_3H_8$, 33] ; 148 [$(M+H)^+ - C_4H_6$, 100] ; 124 [$(M+H)^+ - C_6H_6$, 27].

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