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A CONVENIENT ONE-POT SYNTHESIS OF CYCLOHEXENIC PRIMARY AMINES

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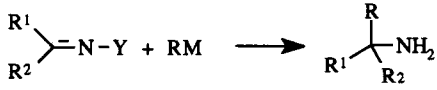
Abstract : The reaction between Grignard reagents prepared from allylic or propargylic halides and the N-phenylsulfenimine derived from the heptane-2,6-dione affords primary 1-alkenyl (or alkynyl)-3-methylcyclohex-2-enamines in good yields.

The synthesis of tertiary carbinamines $(R)(R^1)(R^2)C\text{-}NH_2$ may be obtained by use of organometallics and ketimines having a protective group Y on the imine function :



Among the varied protective groups ,[1,2] the phenylsulfenyl group seems very useful, at first because the transformation of a ketone in a N-phenylsulfenimine is easy ,[3,4] then because some recent publications describe the preparation of tertiary carbinamines from such "masked" ketimines and allylmagnesium bromide,[5] allylic organozinc derivatives [6] or alkyl(or phenyl)lithium reagents.[7,8]

Numerous applications of this reaction may be developed and, specially, this

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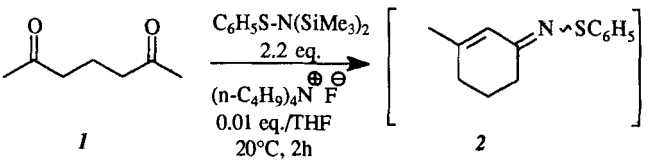
pathway would must be able to be extended to the preparation of primary diamines from diketones R-CO-$(CH_2)_n$-CO-R.

In this work, we describe the particular behaviour of the diketone CH_3-CO-$(CH_2)_3$-CO-CH_3 ***1*** which leads only to a cyclohexenic N-phenylsulfenimine ***2*** ; then, we show that the reaction between ***2*** and Grignard reagents derived from allylic or propargylic halides is a very convenient method to prepare cyclohexenic primary amines ***3***.

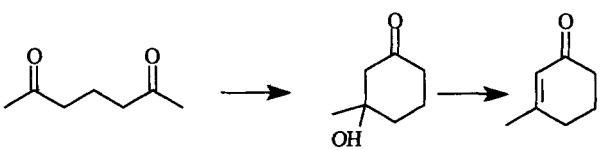
Preparation in situ of the N-phenylsulfenimine 2

When the diketone ***1*** is treated by 2.2 equivalents of N,N-bis(trimethylsilyl)phenylsulfenamide in the presence of tetrabutylammonium fluoride catalyst, according to,[3,4] it appears that only the monosulfenimine ***2*** is formed :



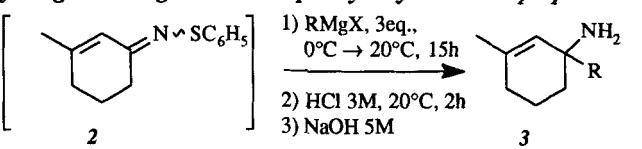
1 ***2***

This fact may be explained by the previous transformation in the medium, catalysed by ions F^-, of the diketone ***1*** in the cyclohexenic ketone resulting from intramolecular aldolisation reaction, followed by a crotonisation reaction :



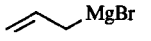
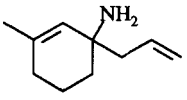
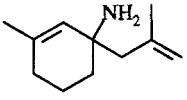
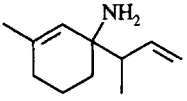
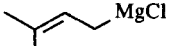
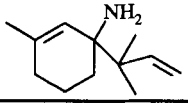
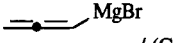
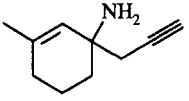
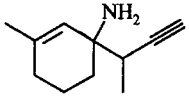
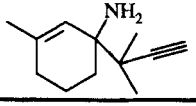
Such a transformation of the heptane-2,6-dione has been already observed, in the presence of a little quantity of alkali [9-11] and in its reaction with hydrazine.[12,13]

Reaction of Grignard reagents with N-phenylsulfenimine 2 prepared in situ :



2 ***3***

Table : Preparation of cyclohexenic primary amines

Organomagnesium derivative/ solvent	Product		Yield* (%)
 / THF		*3a*	63
 / THF		*3b*	55
 / THF		*3c*	64
 / THF		*3d*	57
 / $(C_2H_5)_2O$		*3e*	56
 / $(C_2H_5)_2O$		*3f*	40**
 / $(C_2H_5)_2O$		*3g*	25**

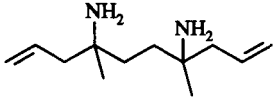
* Isolated yield.
** In these cases, a large quantity of 3-methylcyclohex-2-enone is recovered.

The results (*Table*) show that the reaction with organomagnesium reagents prepared from allylic or propargylic halides leads only to primary cyclohexenic amines ***3***. The yields are good (55-64%) in the allylic series and we observe the allylic rearrangement with crotyl- and prenylmagnesium halides.

With Grignard reagents prepared from propargylic halides, the yields are lower, but we must note that the primary cyclohexenic amines possess a substituent with a propargylic structure only.

Remark : We have studied also the preparation of N-phenylsulfenimines derived from diketones CH_3-CO-$(CH_2)_n$-CO-CH_3 (n = 2, ***4***; n = 4, ***5***), then their reactivity towards Grignard reagents.

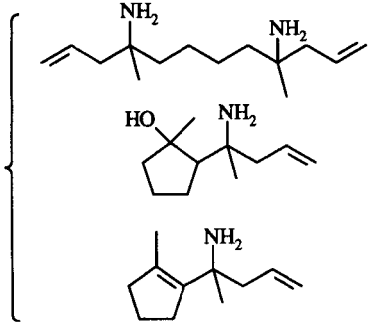
The diketone ***4*** leads to a normal bis-N-phenylsulfenimine, since we have obtained with allylmagnesium bromide only the primary diamine :



6a , yield = 63%

In our experimental conditions, aldolisation-crotonisation in situ of the diketone does not produce ; such a reaction is possible[14-18] but requests very drastic conditions.

The diketone ***5*** leads to more complex results. Then, by reaction with an excess of allylmagnesium bromide after formation in situ of N-phenylsulfenimine derivatives, we have obtained the mixture of three aminated products (yield = 70%) :



7a (42%)

8a (37%)

9a (21%)

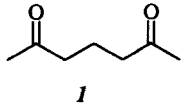
The formation of ***8a*** and ***9a*** may be explained by a limited aldolisation,[19] followed (or not) by a crotonisation of the diketone ***5***, before its transformation into a sulfenimine. Isolated ***8a*** may be deshydrated according to [20] producing ***9a*** with a good yield (75%).

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

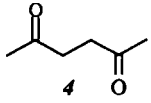
JNM JEOL EX 90 spectrometer, at 89.5MHz and 22.5MHz respectively, in $CDCl_3$ using TMS (^1H, $\delta = 0.00$ ppm) or $CDCl_3$ (^{13}C, $\delta = 77.0$ ppm) as internal standards ; chemical shifts are given in δ units. Mass spectra (MS, m/z, rel.%) were obtained on a Fisons Trio 1000 spectrometer (GC/MS, IC^+, CH_4) at 70eV.

*Preparation of diketones **1, 4 and 5***



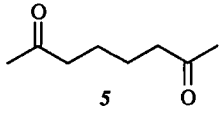
1

prepared according to ;[21] Eb. 60-62°C/0.5 torr, yield = 70%. Litt.[21] : 96-97°C/11 torr.



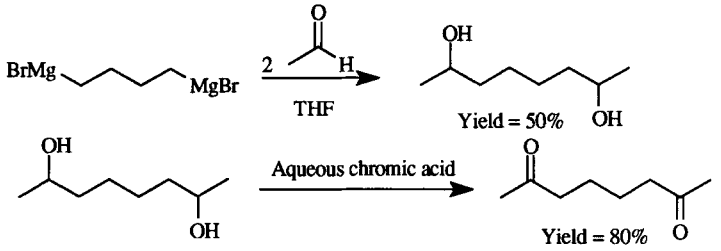
4

commercial product, distilled before use (69°C/11 torr).



5

This diketone was prepared in two steps, according to the scheme : [22,23]



Mp. 40°C ; Litt. [24] : 41°C.

IR : 1730F (C=O).

^1H NMR : 2.45 (t, 4H, CH_2CO, ^3J 6.5Hz) ; 2.13 (s, 6H, CH_3) ; 1.56 (t, 4H, CH_2, ^3J 6.5Hz).

^{13}C NMR : 208.1 (CO) ; 43.0 ($\underline{C}H_2CO$) ; 29.5 (CH_3) ; 22.9 (CH_2).

Preparation of allylic Grignard reagents

The allyl-, methallyl- and crotylmagnesium bromides were prepared at 0-5°C in THF medium and the 3-methylbut-2-enylmagnesium chloride was formed also in THF at -15°C.[25]

Preparation of Grignard reagents from propargylic bromides

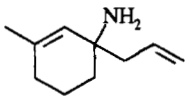
They were prepared at 18-20°C in ether medium according to. [26,27]

General procedure

A solution 1M in THF of tetrabutylammonium fluoride (2mL) was added

slowly at room temperature to a solution of diketone (0.02mol) and of N,N-bis(trimethylsilyl)phenylsulfenamide (0.044mol, 11.8g) in THF (43mL). During the addition, the temperature of the medium was increased until 40-45°C. The reaction mixture was then maintained under stirring at room temperature for 2h. After cooling at 0°C, the Grignard reagent prepared from 0.1mol of allylic or propargylic halide was added slowly. The mixture was stirred for 15h at room temperature and then treated with saturated ammonium chloride solution (100mL). The aqueous layer was separated and extracted with ether (4 x 60mL). The combined organic extracts were treated under stirring for 2h with a solution of 3M hydrochloric acid. The aqueous layer was then cooled at 0°C and treated by 5M sodium hydroxide solution until pH = 10. After extraction with ether (4 x 60mL), drying of the organic phase ($MgSO_4$) and removal of solvent under reduced pressure, the primary amine was bulb to bulb distilled.

Products from 1



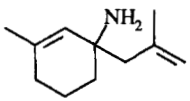
3-methyl-1-(prop-2-enyl)cyclohex-2-enamine *3a*

IR : 3360w, 3280w, 1590br w (NH_2) ; 3080m, 1640m, 1000m, 915s (CH_2=CH) ; 1665w (C=CH).

^{1}H NMR : 6.10-5.55 (m, 1H, C<u>H</u>=CH_2) ; 5.22 (app. s, 1H, C=CH) ; 5.20-4.85 (m, 2H, CH_2=) ; 2.14 (d, 2H, CH_2C=, ^3J 7.3Hz) ; 2.00-1.40 (m, 6H, $(CH_2)_3$) ; 1.63 (app. s, 3H, CH_3) ; 1.42 (br s, 2H, NH_2).

^{13}C NMR : 133.8 (C=, <u>C</u>H=CH_2) ; 129.0 (<u>C</u>H=C) ; 117.4 (CH_2=) ; 50.1 (C-N) ; 47.2 (<u>C</u>H_2CH=) ; 35.9 (<u>C</u>H_2C-N) ; 29.5 (<u>C</u>H_2C=) ; 23.1 (CH_3) ; 18.9 (C<u>C</u>H_2C).

MS : 192 [$(M+C_3H_5)^+$, 0.5] ; 180 [$(M+C_2H_5)^+$, 2] ; 152 [$(M+H)^+$, 12] ; 150 [$(M+H)^+ - H_2$, 14] ; 135 [$(M+H)^+ - NH_3$, 100] ; 110 [$(M+H)^+ - C_3H_6$, 56].



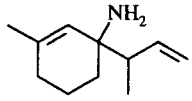
3-methyl-1-(2-methylprop-2-enyl)cyclohex-2-enamine *3b*

IR : 3360w, 3280w, 1590br m (NH_2) ; 3080m, 1640m, 890s ($C=CH_2$) ; 1665w (sh) (C=CH).

^{1}H NMR : 5.14 (app. s, 1H, CH=) ; 4.77 and 4.65 (2 app. s, 2H, CH_2=) ; 2.05 (s, 2H, CH_2C=) ; 1.69 (app. s, 6H, CH_3) ; 1.54 (br s, 2H, NH_2) ; 1.90-1.20 (m, 6H, $(CH_2)_3$).

^{13}C NMR : 142.5 (<u>C</u>=CH_2) ; 133.6 (C=) ; 129.9 (CH=) ; 114.4 (CH_2=) ; 50.8 (<u>C</u>H_2C=CH_2) ; 50.7 (C-N) ; 36.5 (<u>C</u>H_2C-N) ; 29.8 (<u>C</u>H_2C=) ; 24.9 and 23.5 (CH_3) ; 19.4 (C<u>C</u>H_2C).

MS : 194 [$(M+C_2H_5)^+$, 1] ; 166 [$(M+H)^+$, 4] ; 164 [$(M+H)^+ - H_2$, 8] ; 149 [$(M+H)^+ - NH_3$, 100] ; 110 [$(M+H)^+ - C_4H_8$, 49].



3-methyl-1-(1-methylprop-2-enyl)cyclohex-2-enamine *3c*

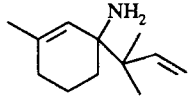
Two diastereoisomers : 50/50.

IR : 3360w, 3290w, 1600br w (NH_2) ; 3080m, 1640m, 1000m, 910s (CH_2=CH) ; 1665w (C=CH).

^{1}H NMR : 6.10-5.55 (m, 1H, C<u>H</u>=CH_2) ; 5.40-4.85 (m, 3H, CH_2=, C=CH) ; 2.35-1.30 (m, 7H, CHC-N, $(CH_2)_3$) ; 1.65 (app. s, 3H, CH_3C=) ; 1.26 (br s, 2H, NH_2) ; 1.01 and 0.96 (2d, 3H, CH_3, $^3J_1$ 6.9Hz, $^3J_2$ 6.9Hz).

^{13}C NMR : 140.2 and 140.1 (<u>C</u>H=CH_2) ; 134.6 and 134.1 (C=) ; 128.2 and 128.1 (<u>C</u>H=C) ; 115.2 and 114.4 (CH_2=) ; 52.2 and 52.1 (C-N) ; 48.5 and 47.2 (<u>C</u>HC=) ; 33.3 and 31.9 (<u>C</u>H_2C-N) ; 29.6 (<u>C</u>H_2C=) ; 23.3 (<u>C</u>H_3C=) ; 18.7 and 18.5 (C<u>C</u>H_2C) ; 14.7 and 13.3 (CH_3).

MS : 206 [(M+C_3H_5)$^+$, 0.4] ; 194 [(M+C_2H_5)$^+$, 1] ; 166 [(M+H)$^+$, 10] ; 164 [(M+H)$^+$– H_2, 9] ; 149 [(M+H)$^+$– NH_3, 100] ; 110 [(M+H)$^+$– C_4H_8, 33].



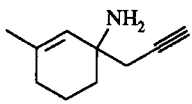
3-methyl-1-(1,1-dimethylprop-2-enyl)cyclohex-2-enamine *3d*

IR : 3370w, 3310w, 1600br w (NH_2) ; 3080m, 1640m, 1005m, 910s (CH_2=CH) ; 1665w (C=CH).

^{1}H NMR : 6.25 -5.85 (m, 1H, C<u>H</u>=CH_2) ; 5.39 (app. s 1H, C=CH) ; 5.15-4.80 (m, 2H, CH_2=) ; 1.95-1.25 (m, 6H, $(CH_2)_3$) ; 1.66 (app. s, 3H, CH_3C=) ; 1.19 (br s, 2H, NH_2) ; 1.01 (s, 6H, $(CH_3)_2$C).

^{13}C NMR : 145.4 (<u>C</u>H=CH_2) ; 135.1 (C=) ; 126.1 (C=<u>C</u>H) ; 112.3 (CH_2=) ; 54.6 (C-N) ; 43.0 (<u>C</u>C=) ; 31.3 (<u>C</u>H_2C-N) ; 29.7 (<u>C</u>H_2C=) ; 23.9 (<u>C</u>H_3C=) ; 21.9 and 21.2 ((<u>C</u>H_3)$_2$C, diastereotopy) ; 19.3 (C<u>C</u>H_2C).

MS : 220 [(M+C_3H_5)$^+$, 0.7] ; 208 [(M+C_2H_5)$^+$, 2] ; 180 [(M+H)$^+$, 14] ; 178 [(M+H)$^+$– H_2, 11] ; 163 [(M+H)$^+$– NH_3, 100] ; 110 [(M+H)$^+$– C_5H_{10}, 70].



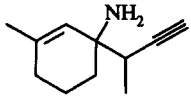
3-methyl-1-(prop-2-ynyl)cyclohex-2-enamine *3e*

IR : 3360w, 3240w (sh), 1590br m (NH_2) ; 3310s, 2130w, 635br s (HC≡C) ; 1670m (C=CH).

^{1}H NMR : 5.33 (app. s, 1H, CH=) ; 2.27 (d, 2H, CH_2C≡, ^4J 2.5Hz) ; 2.05 (t, 1H, HC≡, ^4J 2.5Hz) ; 2.00-1.40 (m, 6H, $(CH_2)_3$) ; 1.64 (app. s, 3H, CH_3) ; 1.56 (br s, 2H, NH_2).

^{13}C NMR : 134.6 (C=) ; 127.6 (CH=) ; 80.6 (C≡) ; 70.1 (HC≡) ; 49.8 (C-N) ; 35.6 (<u>C</u>H_2C-N) ; 32.7 (<u>C</u>H_2C≡) ; 29.4 (<u>C</u>H_2C=) ; 23.0 (CH_3) ; 19.0 (C<u>C</u>H_2C).

MS : 178 [(M+C_2H_5)$^+$, 2] ; 150 [(M+H)$^+$, 11] ; 148 [(M+H)$^+$– H_2, 19] ; 133 [(M+H)$^+$– NH_3, 100] ; 110 [(M+H)$^+$– C_3H_4, 90].



3-methyl-1-(1-methylprop-2-ynyl)cyclohex-2-enamine *3f*

After bulb to bulb distillation, the amine ***3f*** was purified by preparative gas chromatography from the mixture of ***3f*** and recovered ketone.

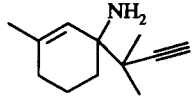
Two diastereoisomers : 70/30.

IR : 3350m, 3220m (sh), 1585br m (NH_2) ; 3300s, 2110w, 630br s (HC≡C) ; 1670w (C=CH).

^{1}H NMR : 5.31 (app. s, 1H, CH=) ; 2.45 (qd, 1H, CHC≡, ^3J 7.0Hz, ^4J 2.1Hz) ; 2.06 (d, 1H, HC≡, ^4J 2.1Hz) ; 2.00-1.35 (m, 6H, $(CH_2)_3$) ; 1.66 (app. s, 3H, CH_3C=) ; 1.38 (br s, 2H, NH_2) ; 1.16 and 1.12 (2d, 3H, $C\underline{H}_3CH$, $^3J_1$ 7.0Hz, $^3J_2$ 7.0Hz).

^{13}C NMR : 135.6 and 135.5 (C=); 127.4 and 125.9 (HC=) ; 86.2 and 86.0 (C≡) ; 69.9 (HC≡) ; 52.1 (C-N) ; 37.4 and 36.7 ($\underline{C}HC$≡) ; 34.1 and 31.6 ($\underline{C}H_2C$-N) ; 29.7 and 29.6 ($\underline{C}H_2C$=) ; 23.4 ($\underline{C}H_3C$=) ; 19.0 and 18.6 ($C\underline{C}H_2C$) ; 15.2 and 14.9 (CH_3).

MS : 204 [$(M+C_3H_5)^+$, 0.8] ; 192 [$(M+C_2H_5)^+$, 2] ; 164 [$(M+H)^+$, 11] ; 162 [$(M+H)^+ - H_2$, 8] ; 147 [$(M+H)^+ - NH_3$, 100] ; 110 [$(M+H)^+ - C_4H_6$, 46].



3-methyl-1-(1,1-dimethylprop-2-ynyl)cyclohex-2-enamine *3g*

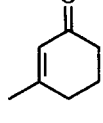
After bulb to bulb distillation, the amine ***3g*** is obtained by preparative gas chromatography from the mixture of ***3g*** and recovered ketone.

IR : 3350m, 3220m (sh), 1590br m (NH_2) ; 3300s, 2110w, 630br s (HC≡C) ; 1665m (C=CH).

^{1}H NMR : 5.53 (app. s, 1H, CH=) ; 2.14 (s, 1H, HC≡) ; 2.00-1.35 (m, 11H, $(CH_2)_3$, CH_3C= and NH_2) ; 1.24 and 1.20 (2s, 6H, $(CH_3)_2C$, diastereotopy).

^{13}C NMR : 136.0 (C=) ; 126.1 (CH=) ; 90.8 (C≡) ; 69.5 (HC≡) ; 55.0 (C-N) ;39.9 ($\underline{C}C$≡) ; 30.3 and 30.0 ($\underline{C}H_2C$= , $\underline{C}H_2C$-N) ; 24.7 ($\underline{C}H_3C$=) ; 23.9 and 23.8 (($\underline{C}H_3)_2C$, diastereotopy) ; 19.5 ($C\underline{C}H_2C$)

MS : 218 [$(M+C_3H_5)^+$, 1] ; 206 [$(M+C_2H_5)^+$, 2] ; 178 [$(M+H)^+$, 15] ; 176 [$(M+H)^+ - H_2$, 12] ; 161 [$(M+H)^+ - NH_3$, 100] ; 110 [$(M+H)^+ - C_5H_8$, 85].



3-methylcyclohex-2-enone (recovered product)

Eb. 90-91°C/17 torr ; Litt.[12] : 48-50°C/2.3 torr , Yield = 63%.

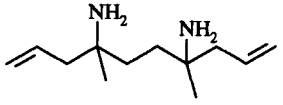
IR : 1670vs (C=O) ; 1630s (C=CH).

^{1}H NMR : 5.83 (app. s, 1H, CH=) ; 2.50-2.15 (m, 4H, CH_2C=, CH_2C=O) ; 2.15-1.75 (m, 2H, CH_2) ; 1.97 (app. s, 3H, CH_3).

^{13}C NMR : 198.4 (C=O) ; 161.9 (C=) ; 125.8 (CH=) ; 36.3 ($\underline{C}H_2C$=O) ; 30.2 ($\underline{C}H_2C$=) ; 23.7 (CH_3) ; 21.9 (C$\underline{C}H_2$C).

MS : 151 [(M+C_3H_5)$^+$, 6] ; 139 [(M+C_2H_5)$^+$, 10] ; 111 [(M+H)$^+$, 100] ; 93 [(M+H)$^+$– H_2O, 1].

Product from 4



4,7-dimethyldeca-1,9-diene-4,7-diamine *6a*

IR : 3350m, 3280m, 1595br m (NH_2) ; 3080m, 1640m, 1000m, 915s (CH_2=CH).

^{1}H NMR : 6.12-5.55 (m, 2H, CH=) ; 5.28-4.86 (m, 4H, CH_2=) ; 2.10 (d, 4H, CH_2C=, ^3J 7.3Hz) ; 1.51 and 1.37 (2 app. s, 8H, NH_2, CH_2) ; 1.04 (s, 6H, CH_3).

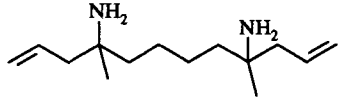
^{13}C NMR : 133.8 (CH=) ; 117.5 (CH_2=) ; 50.6 (C-N) ; 46.7 ($\underline{C}H_2C$=) ; 35.8 (CH_2) ; 27.2 (CH_3).

MS : 237 [(M+C_3H_5)$^+$, 2] ; 197 [(M+H)$^+$, 50] ; 181 [(M+H)$^+$– CH_4, 12] ; 180 [(M+H)$^+$– NH_3, 63] ; 155 [(M+H)$^+$– C_3H_6, 96] ; 138 [(M+H)$^+$– NH_3, – C_3H_6, 100] ; 96 [(M+H)$^+$– NH_3, – 2 C_3H_6, 9].

Products from 5

The mixture of ***7a***, ***8a*** and ***9a*** is distilled on a Kugelrohr apparatus and three fractions were obtained :

- the first fraction gives mainly ***9a*** and this amine was purified by chromatography on silica gel (40-63µm) by eluting with AcOEt/MeOH (90/10) ;
- the second fraction is merely constituted of ***8a*** (purity > 95%) ;
- ***7a*** is the major product of the third fraction and this diamine is purified by chromatography on silica gel (40-63µm) by eluting with MeOH.



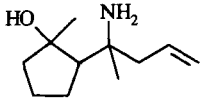
4,9-dimethyldodeca-1,11-diene-4,9-diamine *7a*.

IR : 3360m, 3280m, 1595br m (NH_2) ; 3080m, 1640m, 1000m, 915s (CH_2=CH).

^{1}H NMR : 6.00-5.35 (m, 2H, CH=) ; 5.25-4.55 (m, 4H, CH_2=) ; 1.96 (d, 4H, CH_2C=, ^3J 7.2Hz) ; 1.90-0.85 (m, 8H, $(CH_2)_4$) ; 1.20 (br s, 4H, NH_2) ; 0.91 (s, 6H, CH_3).

^{13}C NMR : 134.3 (CH=) ; 117.7 (CH_2=) ; 51.1 (C-N) ; 47.1 ($\underline{C}H_2C$=) ; 42.6 ($\underline{C}H_2C$-N) ; 27.5 (CH_3) ; 24.3 (CH_2).

MS : 265 [(M+C_3H_5)$^+$, 2] ; 253 [(M+C_2H_5)$^+$, 1] ; 225 [(M+H)$^+$, 27] ; 223 [(M+H)$^+$– H_2, 6] ; 209 [(M+H)$^+$– CH_4, 14] ; 208 [(M+H)$^+$– NH_3, 49] ; 183 [(M+H)$^+$– C_3H_6, 100].



2-(1-amino-1-methylbut-3-enyl)-1-methylcyclopentanol *8a*.

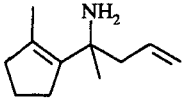
Two diastereoisomers (^{13}C NMR).

IR : 3440br m (OH) ; 3360m, 3280m, 1595br m (NH_2) ; 3080m, 1640m, 1000m, 915s (CH_2=CH).

^1H NMR : 6.05-5.40 (m, 1H, CH=) ; 5.25-4.70 (m, 2H, CH_2=) ; 2.40-1.90 (m, 4H, CH_2C=, CH, OH) ; 1.85-0.90 (m, 14H, $(CH_2)_3$, NH_2, CH_3).

^{13}C NMR : 133.7 and 133.4 (CH=) ; 118.9 and 118.4 (CH_2=) ; 79.6 (C-OH) ; 57.9 and 55.3 (CH) ; 54.0 and 51.1 (C-N) ; 50.6 and 47.1 ($\underline{C}H_2C$-N) ; 42.6 and 41.6 ($\underline{C}H_2C$-O) ; 24.0, 23.8, 18.1 and 17.9 (CH_2CH_2) ; 27.6, 25.2, 25.0 and 23.6 (CH_3).

MS : 184 [$(M+H)^+$, 16] ; 182 [$(M+H)^+ - H_2$, 4] ; 168 [$(M+H)^+ - CH_4$, 10] ; 167 [$(M+H)^+ - NH_3$, 21] ; 166 [$(M+H)^+ - H_2O$, 67] ; 149 [$(M+H)^+ - H_2O, - NH_3$, 100] ; 142 [$(M+H)^+ - C_3H_6$, 33].



2-[1-(2-methylcyclopent-1-enyl)]pent-4-en-2-amine *9a*.

IR : 3360m, 3280m, 1590br m (NH_2) ; 3080m, 1640m, 1000m, 915s (CH_2=CH).

^1H NMR : 6.05-5.35 (m, 1H, CH=) ; 5.25-4.70 (m, 2H, CH_2=) ; 2.65-1.90 (m, 6H, CH_2C=) ; 1.85-1.35 (m, 7H, CH_2, NH_2, CH_3C=) ; 1.24 (s, 3H, CH_3).

^{13}C NMR : 138.9 and 131.7 (C=) ; 134.7 (CH=) ; 117.8 (CH_2=) ; 54.4 (C-N) ; 47.5 (=C$\underline{C}H_2C$-N) ; 41.3 and 35.7 ($\underline{C}H_2C$=) ; 28.8 ($\underline{C}H_3C$-N) ; 21.4 (CH_2) ; 15.9 (=C$\underline{C}H_3$).

MS : 194 [$(M+C_2H_5)^+$, 1%] ; 166 [$(M+H)^+$, 16] ; 164 [$(M+H)^+ - H_2$, 35] ; 150 [$(M+H)^+ - CH_4$, 16] ; 149 [$(M+H)^+ - NH_3$, 100] ; 124 [$(M+H)^+ - C_3H_6$, 64].

REFERENCES

1. Mc Omie J.F.W., in *"Protective Groups in Organic Chemistry"*, Plenum Press Ed., London, **1973**, pp. 43-93.
2. Greene T.W. and Wuts P.G.M., in "*Protective Groups in Organic Synthesis*", Second Edition, Wiley J., New York, **1991**, pp. 362-372.
3. Morimoto T., Nezu Y., Achiwa K. and Sekiya M., *J.C.S. Chem. Commun.*, **1985**, pp. 1584-1585.
4. Boivin J., Fouquet E. and Zard S.Z., *Tetrahedron Lett.*, **1990**, *31*, 3545-3548.
5. Fuganti C., Grasselli P. and Pedrocchi-Fantoni G., *J. Org. Chem.*, **1983**,

48, 909-910 and ref. cited therein.

6. Aidene M., Barbot F. and Miginiac L., *J. Organomet. Chem.*, **1997**, *534*, 117-127.
7. Davis F.A. and Mancinelli P.A., *J. Org. Chem.*, **1978**, *43*, 1797-1800 and ref. cited therein.
8. Burnett D.A., Hart D.J. and Liu J., *J. Org. Chem.*, **1986**, *51*, 1929-1930.
9. Harries C., *Ber. Dtsch. Chem. Ges.*, **1914**, *47*, 784-791.
10. Harries C., *Ann.*, **1914**, *406*, 173-226.
11. Fargher R.G. and Perkin W.H., *J. Chem. Soc.*, **1914**, *105*, 1353-1367.
12. Overberger C.G. and Monagle J.J., *J. Am. Chem. Soc.*, **1956**, *78*, 4470-4473.
13. Stetter H., in *"Methoden der Organischen Chemie"*, Houben-Weyl, Georg Thieme Verlag, Stuttgart, **1976**, *Vol. 7/2b*, p. 1511 and ref. cited therein.
14. Stetter H., in *"Methoden der Organischen Chemie"*, Houben-Weyl, Georg Thieme Verlag, Stuttgart, **1976**, *Vol. 7/2b*, p. 1507 and ref. cited therein.
15. Acheson R.M. and Robinson Sir R., *J. Chem. Soc.*, **1952**, pp. 1127-1133.
16. Blaise E.E., *C. R. Acad. Sci.*, **1914**, *158*, 708-711.
17. Hunsdiecker H., *Ber. Dtsch. Chem. Ges.*, **1942**, *75*, 455-460.
18. Ellison R.A., *Synthesis*, **1973**, pp. 397-412 and ref. cited therein.
19. Kossanyi J., *Bull. Soc. Chim. Fr.*, **1965**, pp. 722-732 and ref. cited therein.
20. Posner G.H., Shulman-Roskes E.M., Oh C.H.,Carry J.C., Green J.V., Clark A.B., Dai H. and Anjeh T.E.N., *Tetrahedron Lett.*, **1991**, *32*, 6489-6492.
21. Overberger C.G., Gibb T.B., Chibnik S., Huang P.T. and Monagle J.J., *J. Am. Chem. Soc.*, **1952**, *74*, 3290-3292.
22. Denise B., Ducom J. and Fauvarque J.F., *Bull. Soc. Chim. Fr.*, **1972**, pp. 990-1000.
23. Brown H.C., Garg C.P. and Liu K.T., *J. Org. Chem.*, **1971**, *36*, 387-390.
24. Adkins H. and Scanley C., *J. Am. Chem. Soc.*, **1951**, *73*, 2854-2856.
25. Barbot F. and Miginiac Ph., *Bull. Soc. Chim. Fr.*, **1977**, pp. 113-116.
26. Gaudemar M., *Ann. Chim. Fr.*, **1956**, *1*, 161-220.
27. Barbot F. and Miginiac Ph., *J. Organomet. Chem.*, **1992**, *440*, 249-261.

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