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Oxidation of 2,3- and 2,5-Dihydro-1*H*-1-Benzazepines by Hydride Transfer to an Iminium Ion: Synthesis of 3*H*-1-Benzazepines

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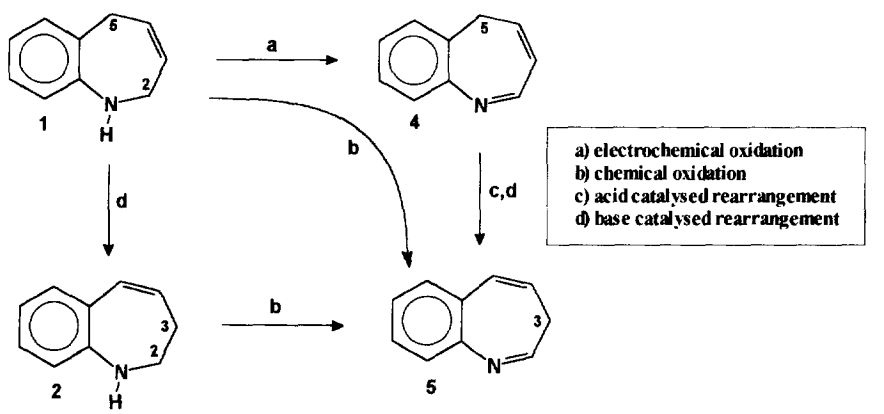
Key Words : 1-Benzazepines ; Oxidation ; HydrideTranfer ; Iminium Ion

Abstract Some 3*H*-1-benzazepines were prepared by dehydrogenation of secondary 2,3- and 2,5-dihydro-1*H*-1-benzazepines involving a hydride transfer to an iminium ion generated from a heterocyclic enamine and BF_3. With 2,5-dihydro-1*H*-1-benzazepines the initial formation of 5*H*-1-benzazepines was observed, whose treatment in the presence of BF_3 led to 3*H*-1-benzazepines. The same rearrangement could be performed with t-BuOK. The hydride transfer was demonstrated using a deuterium labelled substrate. Tertiary dihydro-1-benzazepines were also oxidized but underwent rearrangement to naphthylamine derivatives.

INTRODUCTION

In a previous article[1], we reported the synthesis of 5*H*-1-benzazepines **4** by electrochemical oxidation of 2,5-dihydro-1*H*-1-benzazepines **1**. In this paper we describe the preparation of 3*H*-1-benzazepines **5**, isomers of **4** , by two synthetic pathways. The first is the chemical oxidation of the 2,5- and 2,3-dihydro-1*H*-1-benzazepines **1** and **2**, the second the rearrangement of 5*H*-1-benzazepines **4**.

The use of classical oxidation reagents[2] such as MnO_2 or DDQ has not been successful. Therefore we employed the strategy previously described by Cook[3], involving a hydride transfer from secondary amines (in our case dihydro-1*H*-1-benzazepines **1** and **2**) to an iminium ion, acting as an hydride acceptor. The rearrangement of 5*H*-1-benzazepines **4** into 3*H*-1-benzazepines **5** was achieved either by a Lewis acid (BF_3) or a strong base (t-BuOK).

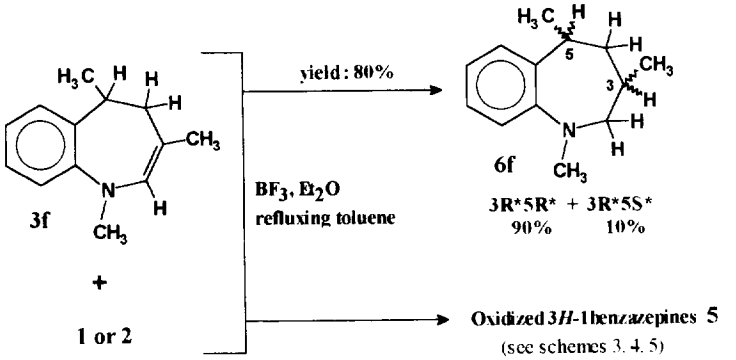


Scheme 1

RESULTS

Oxidations

The benzazepines **1**[4] or **2** [5] were allowed to react in refluxing toluene with the enamine **3f**[6] in the presence of BF_3-Et_2O (*scheme 2*). In every case **3f** led by reduction to **6f**, whose the thermodynamically favoured 3R*5R* diastereomer was obtained as the major product (90%). Depending on the starting material, three oxidation behaviours were observed.



Scheme 2

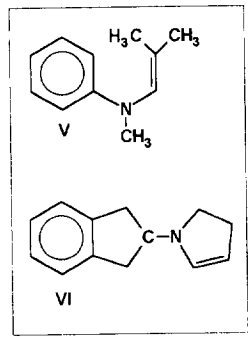
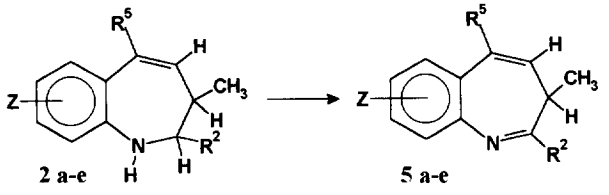


Fig 1

The high stability of **3f** , prepared by transposition of the 1,3,5-trimethyl-2,3-dihydro-1*H*-1-benzazepine **2f** in refluxing 2M aqueous HCl, seems to be fundamental. Indeed, substitution of **3f** by another enamines such as **V**[7] or **VI**[8] (*fig 1*) remained unsuccessful.

2,3-dihydro-1H-1-benzazepines 2a-e (*scheme3*)

The oxidized 3*H*-1-benzazepines **5a-c** were obtained after separation from polymers by column chromatography. For the products **5a-c** the best yields (30-35%) were observed for a reaction time of 4-5h. However yield was reduced to10% in the case of **5d** (R^5=H). With the benzazepine **2e**, bearing two hydrogen atoms at C-2, oxidation only led to polymers.



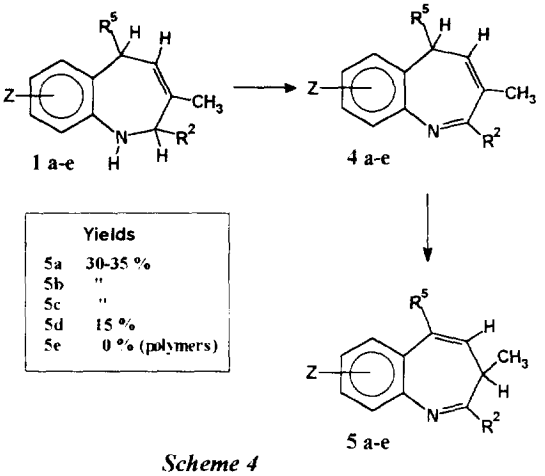
	Yields
R^2 = CH_3, R^5 = CH_3, Z = H : 5a	30-35 %
R^2 = CH_3, R^5 = CH_3, Z = CH_3(8) : 5b	"
R^2 = CH_3, R^5 = CH_3, Z = CH_3(9) : 5c	"
R^2 = CH_3, R^5 = H, Z = H : 5d	10%
R^2 = H, R^5 = H, Z = H : 5e	0% (polymers)

Scheme 3

2,5-dihydro-1H-1-benzazepines 1a-e (*scheme 4, fig 2*)

The oxidation of derivatives **1a-d** led first to the benzazepines **4a-d,** whose BF_3 catalysed isomerisation gave benzazepines **5a-d** . With **1a** and **1b**, the intermediates **4a** and **4b** were difficult to isolate because of their rapid rearrangement into the final products **5a** and **5b** . Compound **1c** led to the

accumulation of **4c** because the transformation of **4c** into **5c** was slow.In the case of **1d** (R^5 = H), as well as **2d** the yields were low (15%). The reaction had to be stopped after two hours to obtain a 20:80 mixture of **4d** + **5d** .Compound **1e** (R^2 = H) resulted exclusively in polymer formation.



Scheme 4

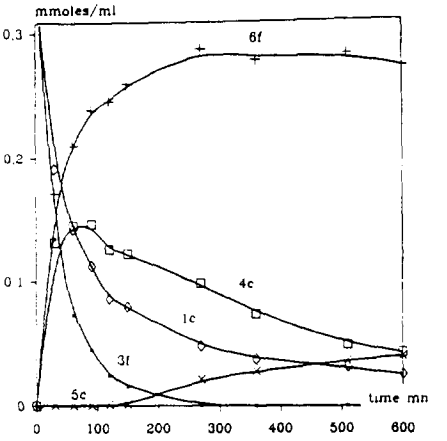
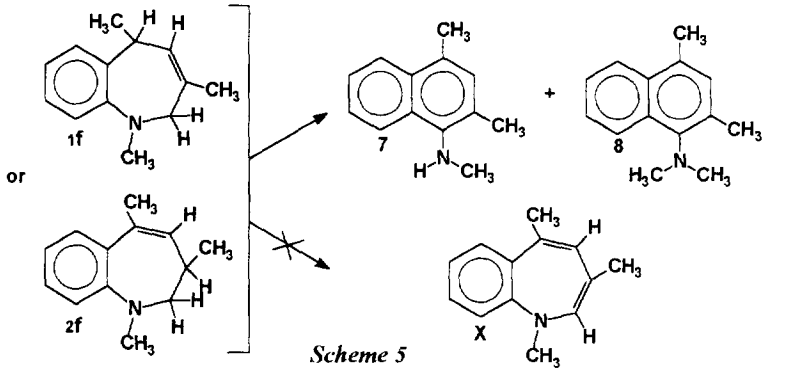


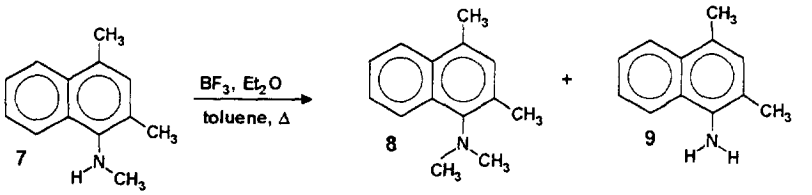
Fig 2: Evolution of 3f + 1c

N-methyl derivatives 1f and 2f (*scheme 5*)

Oxidation of the N-methyl benzazepines resulted in the formation of the naphthyl-1-amine derivatives **7** and **8**. The expected 1*H*-1-benzazepines **X** were not detected. The presence of CH_3 at C-2 induced the formation of polymers. The formation of small amounts of **8** could be explained by a BF_3 catalysed transformation of **7**. Indeed, in our experimental conditions **7** gave a 30:1 mixture of **8** and **9** (*scheme 6*).



Scheme 5



Scheme 6

Rearrangements

The electochemically prepared[1] 5*H*-1-benzazepines **4** underwent rearrangement into 3*H*-1-benzazepines **5** by either a strong base in an aprotic medium (t-BuOK, DME) or a Lewis acid (BF_3) in toluene. With t-BuOK benzazepines **5** were obtained in 80% yield. This method was employed to prepare pure samples of **5d, 5d'** (Et-2 analog of **5d**) and **5c** for the structural study. In contrast BF_3 induced significant formation of polymers.

STRUCTURAL ELUCIDATIONS

Detailled spectroscopic data are reported in the Experimental Section but the major observations are described in the following.

3H-1-benzazepines **5**: The m/z value of the molecular ion confirmed the dehydrogenation of **1** or **2**. The formation of the azomethine was attested by the presence of the C =N streching vibrations at 1640 cm^{-1} and by the δC-2 at 164-168 ppm. The complete attribution of the NMR signals was achieved using 2D NMR (^{13}C-^{1}H correlation) in addition to selective decoupling and NOE experiments The X-ray crystallographic study of **5a** established unambigously the structure shown in *fig 3*.

Naphthylamines **7,8,9**[9]: Hydrogen signals were attributed by selective decoupling and NOE experiments (*fig 4*). Carbons were assigned on the basis of ^{13}C-^{1}H correlations.

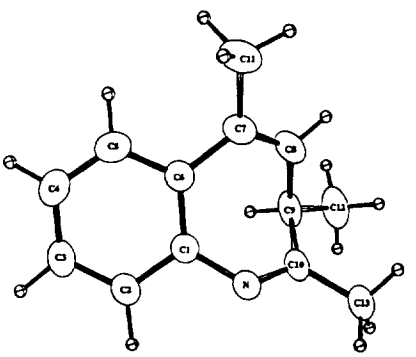


Fig 3

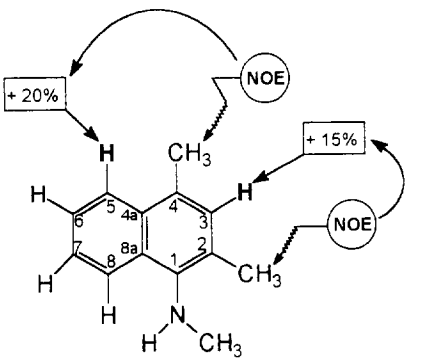
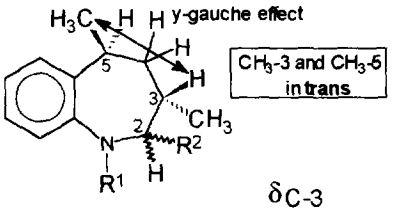


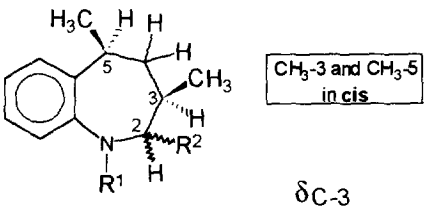
Fig 4

2,3,4,5-tetrahydro-1H-1-benzazepines **6**

Reduction of **3** was confirmed by MS. The relative configuration of the diasteromers was established by comparison of their ^{1}H NMR data with those of the previously described compound **IX**[6]. In ^{13}C NMR, the shifting of the CH-3 signal of the 3R*5S* isomer confirmed the *cis* relationship between H-3 and CH_3-5 (*fig 5*).



	δC-3
$R^1 = CH_3$, $R^2 = H$: **3f** (3R*5R*)	30.24
$R^1 = H$, $R^2 = CH_3$: **IXa** (2R*3R*5R*)	33.80
$R^1 = H$, $R^2 = CH_3$: **IXb** (2R*3S*5S*)	39.00

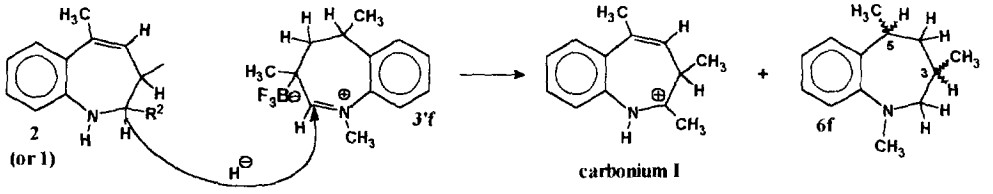


	δC-3
$R^1 = CH_3$, $R^2 = H$: **3f** (3R*5R*)	35.16
$R^1 = H$, $R^2 = CH_3$: **IXc** (2R*3R*5R*)	36.30
$R^1 = H$, $R^2 = CH_3$: **IXd** (2R*3S*5S*)	42.10

Fig 5

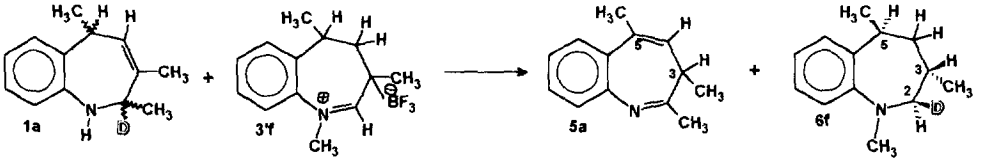
DISCUSSION

In agreement with the study of Cook[3] the following mechanism (*scheme 7*) can explain the oxidation of **1** and **2**



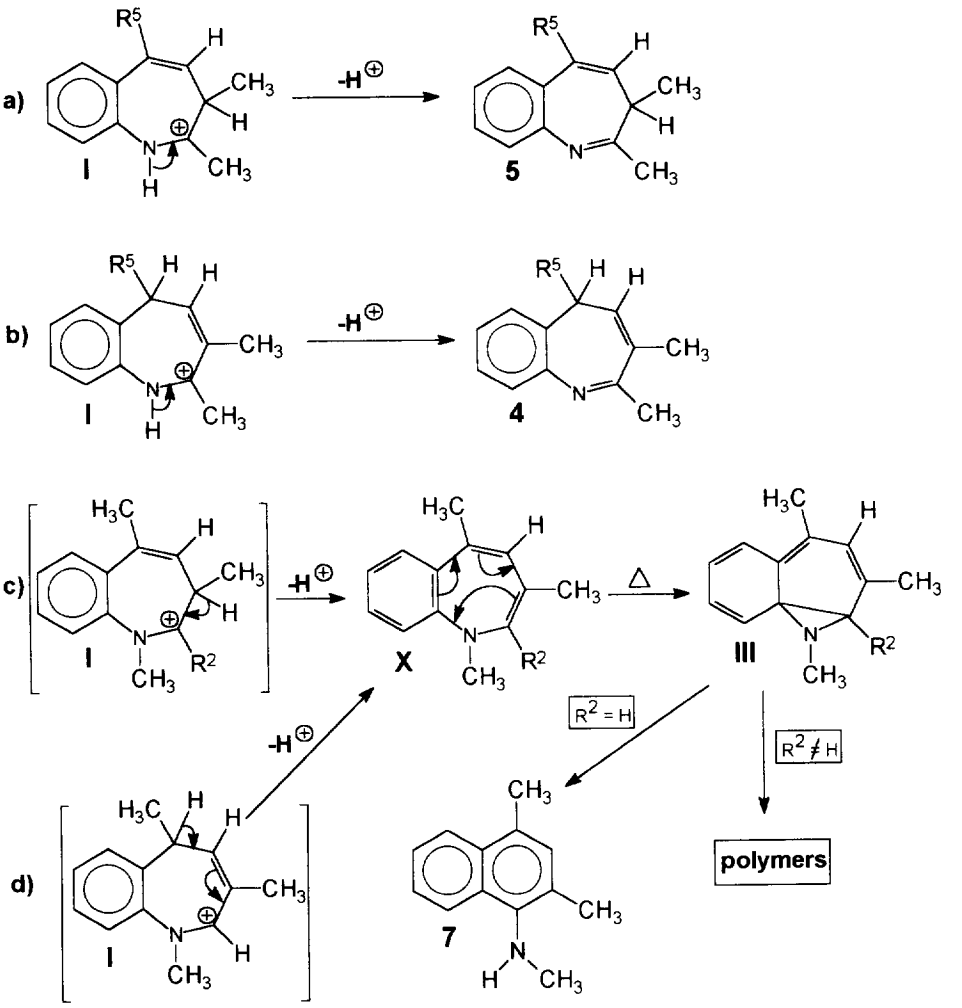
scheme 7

The iminium ion **3'f** , acting as an hydride acceptor in our experiments , is formed by the β-attack of BF_3 on the heterocyclic enamine **3**[10]. The abstraction of a hydride ion from the α-carbon of benzazepines **1** or **2** and its nucleophilic attack on the α-carbon of the iminium **3'f** resulted in the formation of the reduced benzazepine **6f** and of the carbonium ion **I**. This hydrid tranfer from our heterocyclic amines to **3'f** has been demonstrated using the deuterium labelled compound **1a** as starting material , which was obtained as a 20/80 mixture of the 2R*5R* and 2R*5S*isomers, by $LiAlD_4$ reduction of **4a**. The deuterium incorporation at C-2 of the major isomer of **6f** (≃ 60%) was controlled by ^1H and ^2H NMR. (*scheme 8*).



scheme 8

As shown on *scheme 9*, the transformation of the carbonium **I** depended on the nature of the amino group.

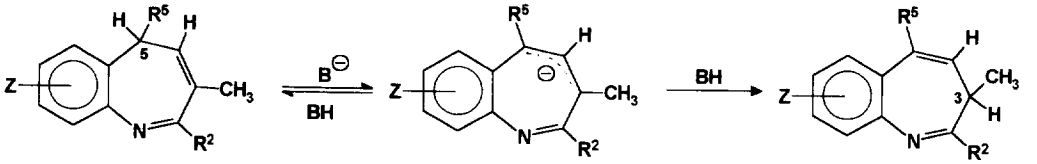


Scheme 9

-If the starting benzazepines were secondary (R^1 = H), deprotonation occured at N-1 and the 3*H*-1-benzazepines **5** were formed either directly (a) or after rearrangement (b).

-If **1** or **2** were tertiary ($R^1 = CH_3$), the elimination of the proton from C-3 (c) or C-5 (d) is presumed to result in formation of the 1*H*-1-benzazepine **X**; however this was not isolated. As reported in the literature[11], this antiaromatic heterocycle **X** underwent the aromatic naphthyl-1-amine derivative **7** by electrocyclisation into the aziridino derivative **III**. This aromatisation was impossible if $R^2 \neq H$ and then polymers were obtained.

The base catalysed rearrangement of benzazepines **5** into **4** involved an allylic carbanion **II**. In a previous paper[5], concerning the preparation of 2,3-dihydro-1*H*-1-benzazepines from 2,5-dihydro-1*H*-1-benzazepines, such an intermediate was postulated.



scheme 10

CONCLUSION

Use of hydride acceptors such as iminium ions is an interesting alternative for the preparation of imines from secondary amines. Application of this strategy to 2,5 or 2,3-dihydro- 1*H*-benzazepines led to the synthesis of the rarely described 3*H*-1-benzazepines[12] which may also be obtained by base catalysed rearangements of 5*H*-1-benzazepines. However, in order to develop this synthetic methodology, the use of others iminium ions or carbonium ions[13] , more easily available, is under investigation.

EXPERIMENTAL SECTION

General

Melting points were determined on a Kofler apparatus and were not corrected. Elemental analyses were carried out at the Faculté de Pharmacie (Université de Paris XI). Purification by column chromatography were done on 70-230 mesh silica gel (Merck). GC were done on a glass capillary column(SE 52) with a Carlo Erba Fractovap 4160 instrument. TLC analyses were performed on pre-coated aluminium sheets of silica gel 60 F_{254} (layer thickness : 0.22 mm)(Merck). Indicated R_f values were determined using as eluent (50-50 petroleum ether-ether). IR spectra were recorded on a Perkin-Elmer 16 PC. NMR spectra were recorded on a Brucker AM 300 FT spectrometer at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO) at 300 MHz (^{1}H) or 75 Mhz (^{13}C). Chemical shifts were expressed in ppm downfield from TMS and coupling constants (J) in Hertz. The solvant was $CDCl_3$. ^{1}H NMR : AB systems were presented in the following order: H-α (δ : centered) the more deshielded, H-β (δ centered) the more shielded, JH-α H-β. Long-range coupling constants were indicated using Jlr. ^{13}C NMR : broad band and gated decoupling spectra were recorded. The assignments were made using chemical shifts and coupling constants (^{1}J and long-range coupling). Values with an asterisk * could be interverted. 2D NMR : the sequences were indicated in the text. The high resolution mass spectra were determined on a Varian MAT 311 double-focusing instrument at the CRMPO with a source temperature of 140°C, an ion accelerating potential of 3 kV, and ionizing electrons of 70 eV and 300 mA. A direct Insertion Probe was used.

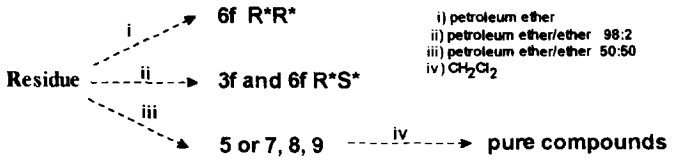
Starting material

The starting benzazepines were prepared according to references[4,5,6] . The deuterium labelled compound **1a** was prepared from the imine **4a**[1] by D_4LiAl reduction in the THF (yield : 50%).

Synthesis procedures

- Method A :*Oxidations*: The BF_3-Et_2O (0,2 ml) was added to a refluxing solution of the starting benzazepines **1** or **2** (5 mmol) and of the enamine **3f** (5 mmol) in 15 ml of toluene . The reaction end was determined by GC or TLC (6-8h). The organic layer was separated after treatment with an alkaline solution and the aqueous phase was extracted with ether. The combined organic layers were dried (K_2CO_3) and

concentrated. The residue was purified by column chromatography and, depending of the eluent **3f**, **6f R*S***, **6f R*R*** and **5** or **7**, **8**, **9** could be separated and purified:



The purity (= 98%) was checked by GC, TLC and MS. The 3*H*-1-benzazepines **5** have to be stored at -5°C; at RT or in $CDCl_3$ degradation occured in the course of days. Compounds **5** showed a characteristic smell.

For the study of the reaction evolution by GC the tetrahydronaphthalene was used as internal standard.

- Method B: *Rearrangement*: The DME solution of the 5*H*-1-benzazepines (1mmol/2ml) **4d, 4d'**and **4c** were stirred 1h at RT in the presence of an excess of t-BuOK. After usual treatement the 3*H*-1-benzazepines were purified by column chromatography.

2,3,5-trimethyl-3*H*-1-benzazepine : 5a

m.p: 50-51. I.R ν(cm^{-1}) C=N : (1632)

^{1}H NMR: CH_3-2(s:2.24) ; CH_3-3(d:1.39) , H-3(m 1.86) ; H-4(dd:5.36), JH-4 H-3 (5.8), Jld(1) ; CH_3-5(sm:2.16) ; H-6(d:7.55) ; H-7(t.7.13) , H-8(t 7.32) ; H-9(d.7.30) ;

NOE: Irradiation of CH_3-5: H-4 (+ 12%), H-6 (+ 20%) and of CH_3-3: H-4 (+ 14%)

^{13}C NMR: CH_3-2(22.68); C-2(166.82); CH_3-3(15.62); C-3(38.04); C-4 (127.70); CH_3-5(20.87), ^{3}J(6) ; C-5(133.36); C-5a(131.26); C-6(126,45); C-7(123.11); C-8(126.67); C-9(126.34); C-9a(146.18).

2D NMR: ^{13}C ^{1}H correlation

M.S. m/e, rel.intensity % : M$^+$ 185, 79 ; 184, 29 ; 170, 100 ; 129, 27 ; 128, 38 ; 127,15 ; 115, 15 ; 77, 15.

Exact mass : m/e = 185.1208 (calc. for $C_{13}H_{15}N$ m/e = 185.12044)

2,3,5,8-tetramethyl-3*H*-1-benzazepine : 5b

I.R ν(cm^{-1}):C=N : (1644)

^{1}H NMR: CH_3-2(s:2.23); CH_3-3(d:1.39); H-3(m:1.87); JH-3 H-4 (5.7); H-4(dd: 5.30); Jld(1.2) ; CH_3-5(sm:2.14); H-6(d:7.44); H-7(dd:6.97); CH_3-8(s:2,38); H-9(sm:7.15).

NOE: irradiation of CH_3-5: H-4 (+9%), H-6 (+14%) .

^{13}C NMR: CH_3-2(22.66); C-2(166.52); CH_3-3(15.65); C-3(38.11); C-4(126.70) ;CH_3-5(20.88)^{3}J(6) ; C-5(133.31) ; C-5a(128.66) ; C-6(126.21) ; C-7(124.42) ;CH_3-8(21.13) ; C-8(136.48) ; C-9(126.59) ; C-9a(146.35). 2D NMR: ^{13}C ^{1}H correlation

M.S. m/e, rel.intensity %: M$^+$ 199, 88; 198, 18; 184, 100; 143, 9; 128, 21; 115, 9.

Exact mass : m/e = 199.1376 (calc. for $C_{14}H_{17}N$ m/e = 199.13609)

2,3,5,9-tetramethyl-3*H*-1-benzazepine : 5c

Method A: after 7h obtention of a mixture of **5c** (65%) and **4c** (35%). Method B: obtention of **5c** pure.

I.R ν(cm^{-1}):C=N (1634)

^{1}H NMR: CH_3-2(s:2.23); CH_3-3(d:1.41); H-3(m:1.77); H-4(dd:3.9), JH-3 H-4(5.6), Jld(1);CH_3-5(sm:2.15) ; H-6(d:7.42); H-7(dd:7.04); H-8(dm:7.16); CH_3-9(s:2.39).

^{13}C NMR: CH_3-2(22.36); C-2(164.40); CH_3-3(15.64); C-3(38.43); C-4(127.80); *C-5(133.56); C-5a(130.48) CH_3-5(21.14)^{3}J (6); C-6(123.93); C-7(122.63); C-8(127.74); CH_3-9(19.03)^{3}J(5), *C-9(133.60) ; C-9a(145.13).

M.S. m/e, rel.intensity % : M$^+$ 199,100 ; 198,14 ; 184, 83 ; 171, 19 ; 170, 13 ; 169, 8 ; 143, 13 ; 141, 9 ; 128, 22 ; 115, 19. Exact mass : m/e = 199.1362 (calc. for $C_{14}H_{17}N$ m/e = 199.13609)

2,3-dimethyl-3*H*-1-benzazepine : 5d

IR : ν(cm^{-1}) : C=N: (1634)

^{1}H NMR : CH_3-2(sm:2.25); CH_3-3(d:1.45); H-3(m:1.92); H-4(dd:5.54); JH-4 H-5(9.5); JH-4 H-3(5.5) ; H-5(dd:6.68); JH-5 H-3(1.6); H-6(d:7.31); H-7(t:7.13); H-8(t:7.26); H-9(d:7.42)

^{13}C NMR: CH_3-2(23.14); C-2(164.37); CH_3-3(15.53); C-3(38.78); C-4(130.00); C-5(128.45); C-5a(128.81) ; C-6(129.35); C-7(123.25); *C-8(126.82); *C-9(126.87); C-9a(146.69).

M.S. m/e, rel.intensity %: M+ 171,100 ; 170, 29 , 156, 59 ; 144,14 ; 143, 17) ; 130, 17 ; 129, 35 ; 128, 22 ; 127,17 ; 115, 44 . Exact mass : m/e = 171.1041(calc. for $C_{12}H_{13}N$ m/e = 171.10479)

2-ethyl-3-methyl-3*H*-1-benzazepine : 5d'

IR: ν(cm^{-1}) C=N: (1664)

^{1}H NMR : CH_2-CH_3-2(m:2.60 and t:1.17); H-3(m:2.08); CH_3-3(d:1.39); H-4(dd:5.57), JH-4 H-3(6), JH4-H-5(9.4); H-5(dd:6.67), JH-5 H-3(1.1); H-6(d:7.34); H-7(t:7.13); H-8(t:7.30); H-9(d:7.41) .

^{13}C NMR:CH_3-CH_2-2(12.04-29.42), C-2(168.84); CH_3-3(14.69); C-3(38.88);C-4(130.18); C-5(128.16); C-5a(128.69); C-6(129.32); C-7(123.17); C-8(126.73); C-9(12.02); C-9a(146.72). For attribution of C-7 and C-9 irradiation at 7.13 ppm and for C-5 and C-6 at 6.678 ppm. 2D NMR:^{13}C ^{1}H correlation

M.S. m/e, rel.intensity % : M+ 199 ,88 , 198,18 ; 184,100 ; 143, 9 ; 128, 21 ; 115, 9.

Exact mass : m/e = 199.1376 (calc. for $C_{14}H_{17}N$ m/e = 199.13609)

***N*-methyl-2,4-dimethylnaphtyl-1-amine : 7**

m.p : 37-39. I.R ν(cm^{-1}):N-H (3372)

^{1}H NMR: NH(s:3.28); CH_3N-1(s:2.88); CH_3-2(s:2.41); H-3(s:7.13); CH_3-4 (s:2.60), H-5(d:7.92); H-6(t:7.43) ; H-7(t:7.47); H-8(d:8.12).

NOE: irradiation of CH_3-4:H-5 (+20%) and of CH_3-2: H-3 (+15%)

^{13}C NMR: CH_3N-1(37.09); C-1(142.17); CH_3-2(17.71); *C-2(128.93); C-3(130.12); CH_3-4(18.93) ; C-4(132.44); *C-4a(128.84); C-5(124.62); C-6(124.70); C-7(125.15); C-8(123.24); C-8a(125.42).

2D NMR: ^{13}C ^{1}H correlation

M.S. m/e, rel.intensity % :M+ 185,100 ; 184, 15 , 170, 72 , 169, 9 ; 168, 13 ; 154, 8 ; 143,13 ;141, 8 ;128, 19 ; 115,9 . Exact mass : m/e = 185.1208 (calc. for $C_{13}H_{15}N$ m/e = 185.12044)

2,4-dimethylnaphtyl-1-amine : 8

m.p : 60-61. I.R ν(cm^{-1}):N-H (3365)

^{1}H NMR: NH(s:3.85), CH_3-2(s:2.31); H-3(s:7.06); CH_3-4(s:2.57) ;H-5 H-8 (m:7.78-7.94) , H-6 and H-7(m:7.42-7.47).

***N,N*-dimethyl-2,4-dimethylnaphtyl-1-amine : 9**

IR : absence of νNH

^{1}H NMR: 2N-CH_3-1(s:2.87); CH_3-2(s:2.31); H-3(s:6.98); CH_3-4(s:2.49); H-5 and H-8(m:7.70- 8.20); H-6 and H-7 (m:7.25-7.40).

M.S. m/e, rel.intensity %: M+ 17, 84 ; 174, 16 , 160, 25 ;146, 8 ; 144, 9 ; 13, 30 ; 132, 100 ; 118, 18 , 117, 21 ; 91, 14. Exact mass : m/e = 175.1358 (calc. for $C_{12}H_{17}N$ m/e = 175.13609)

(3R*5R*) 1,3,5-trimethyl-2,3,4,5-tetrahydro-1*H*-1-benzazepine : 6f

^{1}H NMR: CH_3-1(s:2.84); H-2(dd:2.83), JH-2 H-2(11.6), JH-2 H-3(1.5); H-2(dd:2.71), JH-2 H-3(3.2) , CH_3-3(d:0.85); H-3(m:.68); 2H-4(m:1.45); H-5(m:3.24); CH_3-5(d:1.30); Ar(m:6.85-7.18).

^{13}C NMR: CH_3-1(42.02); C-2(62.85); CH_3-3(19.72), C-3(30.24); C-4(41.58); CH_3-5(19.11); C-5(34.41) ; C-5a(138.25); C-6(126.04); C-7(120.83); C-8(126.40); C-9(116.32) ; C-9a(150.46).

For attribution of CH_3-3 irradiation at 0.98 and for C-5 at 3.37.

M.S. m/e, rel.intensity %: M+ 189, 100 ; 188, 7 ; 174, 37 ; 160, 19 ; 14, 17) ; 146, 18 ; 144, 9 ;132, 60 ;117, 13 ; 91, 8. Exact mass : m/e = 189.1509 (calc. for $C_{13}H_{19}N$ m/e = 189.15174)

Analysis: Calc.% C: 82,48 ; H: 10,12 ; N : 7,40

Found % C: 82,31 ; H: 10,23 ; N : 7,31

(3R*5S*) 1,3,5-trimethyl -2,3,4,5-tetrahydro-1*H*-1-benzazepine : 6f

^{1}H NMR: CH_3-1(s:2.89); H-2a (ddd:2.92), JH-2a H-3(3.8), JH-2a H-2b(12.7), JH-2a H-4(1.5) ; H-2b(dd:2.18), JH-2b H-3(11.1); H-3(m:2.01); CH_3-3(d:0.79); H-4(dm:1.74), JH4 H-3(4), JH-4 H-5(1.6), JH-4 H-4(13.26); H-4(dm:0.89), JH-4 H-3(11.4), JH-4 H-5(10.5); H-5(m:3.01); CH_3-5(d:1.35) ; Ar(m:6.97-7.23).

^{13}C NMR: CH_3-1(43.59); C-2(64.06); *C-3(35.16); CH_3-3(19.73); C-4(42.86); CH_3-5(21.54); *C-5(34.40); C-5a(140.24); C-6(125.44); C-7(121.92); C-8(126.19); C-9(116.34); C-9a(152.82).

(2R*3S*5S*) 1,3,5-trimethyl -2,3,4,5-tetrahydro-1*H*-1-benzazepine D labelled at C-2 : 6f

^{1}H NMR: intensity of H-2a(2.83) : 100%; intensity of H-2b(2.71) :35%

^{2}H NMR: (CCl_4) : $CDCl_3$ at 7,274 ppm ; D-2 at 2.78ppm.

X-ray data of 5a: $C_{13}H_{15}N$: Mr = 185.27, monoclinic, $P2_1/n$, a = 12.793(4), b = 9.474(4), c = 8.631(3) Å, β = 92.11(2)°, V = 1045.4(5) $Å^{-3}$, Z =4, D_X = 1.18 Mg m^{-3}, λ(MoKα) = 0.70926Å, μ = 0.64 cm^{-1}, F(000) = 400, T = 120 K, final R = 0.049 for 1067 observations. The sample (0.25*0.30*0.45 mm) is studied on an automatic diffractometer CAD4 ENRAF-NONIUS with graphite monochromatized MoKα radiation. Due to a low melting point, the study was made at low temperature (120 K). The cell parameters are obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max}$ = 50°, scan $\omega/2\theta$ = 1, t_{max} = 60s, range HKL : H 0.9 K 0.10 L -14.14, intensity controls without appreciable decay (0.3%) gives 1706 reflections from which 1067 were independent (R_{int} = 0.020) with I>3σ(I). Atomic scattering factors from International Tables for X-ray Crystallography[14]. All the calculations were performed on a Digital MicroVAX 3100 computer with the MOLEN package[15]

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