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Silylamines in Organic Synthesis. Facile Synthetic Routes to Unsaturated Protected Primary Amines.

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Abstract - The reactions of lithium N,N-bis(trimethylsilyl)aminomethyl acetylide with electrophilic reagents offered a short preparation of substituted and functional propargyl amines. These are shown to be useful precursors of various unsaturated protected primary amines. Addition reactions to the carbon-carbon triple bond or isomerisation reactions gave rise to allylic, dienic and α-allenic amines.

Introduction

Among the great many protections available for a primary amino group[1], the use of aminosilanes as protected primary amines was early recognised[2-4]. The silicon-nitrogen bond especially in the case of bis(silyl)amines can withstand a variety of reaction conditions, and deprotection to the free amine can be obtained under very mild acidic or nucleophilic conditions[2-5]. The use of chelating bis(silyl)derivatives as protective group[6-9] or the use of a bulky substituent at the silicon atom, have also been reported to provide an enhanced stability. Nevertheless the simple protection of primary amino groups with two trimethylsilyl substituents proved to be efficient. The alkylation reactions of protected amino-acids were for example easily achieved[4].

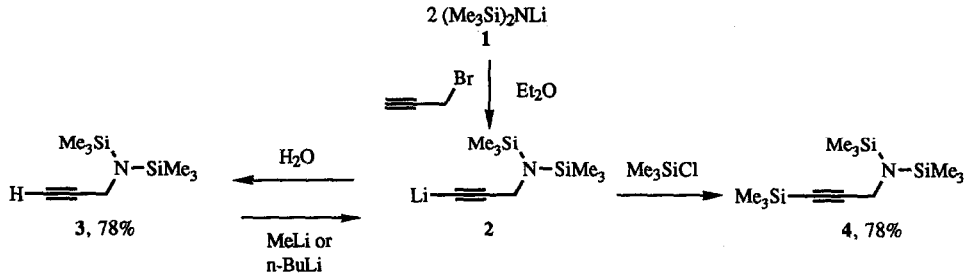
As part of our effort to develop the use of amino silanes for the synthesis of organic nitrogen compounds and heterocycles, we investigated some uses of hexamethyldisilazane for the synthesis of functional protected amines. Lithium bis(trimethylsilyl)amide : $(Me_3Si)_2NLi$, widely used as a strong base in organic synthesis[11], has, only in a few cases, been used to propose new direct aminolysis reactions of organic halides[12-14]. We found that the reaction of $(Me_3Si)_2NLi$ with propargyl bromide afforded a straightforward route to a γ-amino lithium acetylide[15]. Such a reagent is of potential interest for amino alkylation reactions[14,16-18]. The reactions of this γ-amino three-carbon nucleophile can not only offer a short access to substituted or functional propargylic amines, but can also provide facile routes to a variety of unsaturated amines upon subsequent addition or isomerisation reactions of the carbon-carbon triple bond. Unsaturated amines are of interest and continiung efforts have been directed towards the synthesis of allylic, propargylic or allenic amines[19-20], for their importance in organic synthesis, and also because of their physiological properties[19-21].

We wish to report here a detailed account of the reactivity of 1-lithio-3-bis(trimethylsilyl)aminoprop-1-yne towards electrophilic reagents. We show that the trimethylsilylation at nitrogen offers an efficient protection in the condensation reactions of the lithium acetylide and that one can take advantage of the reactivity of the triple bond to obtain easy and short syntheses of ethylenic, dienic or allenic amines. A portion of this study has been communicated[15].

Results and discussion

By analogy with the reaction of metal amides and propargyl halides[22], we investigated the reaction of lithium bis(trimethylsilyl)amide **1** in the case of propargyl bromide. The known alkylation of a metal silylamide[12] was found to proceed under very mild reaction conditions in ether. The reaction of two moles of the lithium amide **1** (scheme 1) gave ether solutions of 1-lithio-3-bis(trimethylsilyl)aminoprop-1-yne **2**. The ethereal solution of **2** contained one equivalent of hexamethyldisilazane (HMDS). The formation of **2** in high yield was established upon quenching with water or chlorotrimethylsilane leading to a 78% yield of propargylic amines **3** and **4** respectively. HMDS free solutions of the lithium acetylide **2** can be prepared from **3** which underwent

Scheme 1: Reaction of Lithium Bis(trimethylsilyl)amide with Propargyl Bromide.



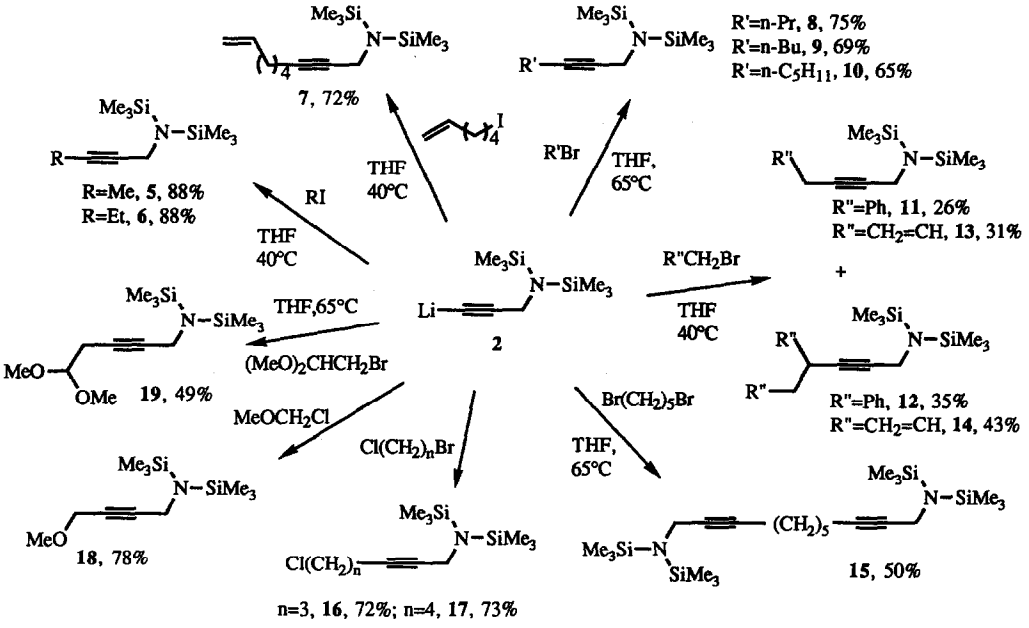
a quantitative metallation upon treatment with MeLi or n-BuLi. The intermediate **2** represents a readily accessible propargyl amine synthon. The reactions of this protected γ-amino lithium acetylide with electrophiles are of interest for the preparation of various unsaturated primary amines.We therefore examined the reactivity of **2** with the aim of showing that a wide variety of unsaturated protected primary amines are readily accessible from this versatile nucleophilic γ-amino three-carbon reagent.

1 - Preparation of substituted propargyl amines

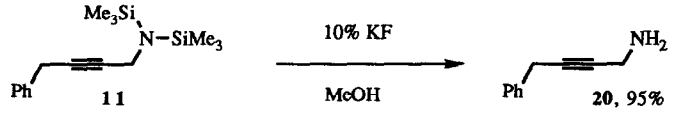
We first studied the simple alkylation reactions of reagent **2** with alkyl halides. As shown in scheme 2, the reactions of alkyl iodides in THF gave high yields of the expected substituted alkynes **5** and **6**. The reactions of alkyl bromides proceeded similarly in refluxing THF to yield alkynes **8-10**. Alkylation with benzyl or allyl bromides led to a mixture of mono and dialkylated products. The latter arose probably from a competitive metallation of the initially formed mono alkylated compounds **11** and **13** owing to a basic character of the acetylide reagent **2**. The resulting stabilized carbanion then rapidly alkylated to **12** and **14**. No reaction of **2** was observed with alkyl chloride. The reactions of dihalo alkanes thus led to the diamino derivative **15** when 1,5-

dibromopentane was used and to α, ω-chloroamino derivatives **16,17** when reacting chlorobromopropane or butane. The alkylation was also successful in the case of a functional bromide. Chloromethyl methyl ether gave good yield of the expected amino ether **18**. The reaction of bromoacetaldehyde dimethylacetal afforded the protected acetylenic amino aldehyde **19** although in a moderate yield. The alkylation reactions of **2** therefore easily lead to various protected propargyl amines. Deprotection to the free amines proceeded smoothly upon

Scheme 2: Alkylation Reactions of γ-Amino Acetylide **2** (prepared by metallation of propargylamine **3**).

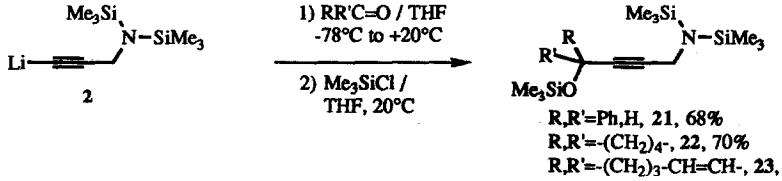


treatment with methanol in the presence of catalytic amount of potassium fluoride. For example the bis(silyl)amine **11** underwent a quantitative desilylation upon stirring in MeOH at 20°C for a few hours (eq - 1).



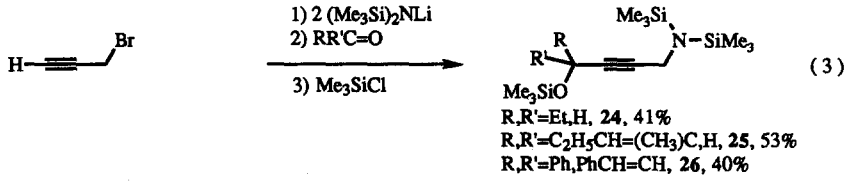
(1)

The reaction of **2** with ketones and aldehydes gave rise to α-acetylenic amino alcohols which were isolated as their trimethylsilyl derivatives (eq - 2). The reaction of unsaturated ketone led to the expected 1,2 - addition



(2)

product **23** in a high yield. These compounds can be obtained in a one-pot reaction starting from propargyl bromide(eq - 3).Moderate yields were obtained, although similar to the overall yields of the two steps synthesis implying the isolation of propargyl amine **3** (eq - 2). The protected amino alcohols **21,25,26** desilylated quantitatively upon stirring in MeOH in the presence of 10 mol.% of KF.



(3)

R,R'=Et,H, **24**, 41%
R,R'=$C_2H_5CH=(CH_3)C$,H, **25**, 53%
R,R'=Ph,PhCH=CH, **26**, 40%

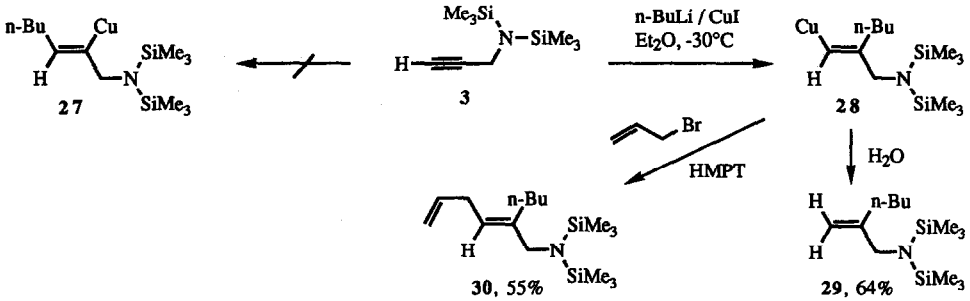
2 - Preparation of substituted allylic amines

The readily accessible propargyl amines **3** and **4** (scheme 1) are of interest for the preparation of allylic amines via selective addition reactions on the carbon-carbon triple bond. We examined some carbo- and hydrometallation reactions.

i) Addition of organocopper reagents :

Carbometallation generally offers a route to regio and stereodefined vinyl organometallics[23], variable regioselectivity may however be found in the case of functional alkynes. The regioselectivity of the addition of organocopper reagents to propargylic dialkylamines was reported to result in the formation of linear or branched adduct depending on the solvent used[24]. In contrast to the reaction with the dialkyl analogues, addition to N,N-bis(silyl)propargylamine **3** gave exclusively the branched adduct **28** (scheme 3). The regioselectivity of the addition of n-BuCu was unambiguously established upon quenching **28** with water to give the allyl amine **29**.

Scheme 3:Addition of Organocopper Reagent to Propargyl Amine **3**.

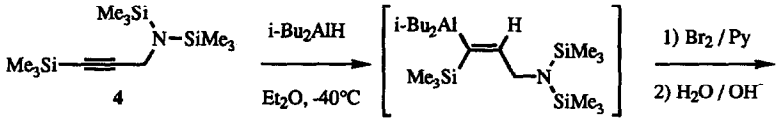


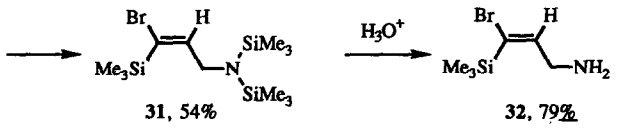
The ^{13}C NMR spectra of **29** showed two signals for the vinylic carbon : one singlet at 151.4 ppm and one triplet at 108.6 ppm (J^1_{C-H} = 155Hz) in full agreement with the proposed structure. A similar result was obtained in the reaction of n-Bu_2CuLi. It is noteworthy that the reversed stereoselectivity was recently reported in the silylcupration of **3** [20d]. In the case of N,N-dialkyl propargylamines under our reaction conditions only the linear adduct of the type **27** was observed. The formation of the branched adduct **28** (scheme 3) is consistent with the proposed interpretation[24] in which a lower nucleophilicity of the $(Me_3Si)_2N$ group account for a lack of intramolecular stabilisation of the linear adduct **27**. The observed selective carbocupration provides a route to

substituted allylamines which are of interest for the synthesis of natural and biologically active products[19,21]. The alkylation of intermediates **28** was achieved with allyl bromide to give a 55% yield of allylamine **30** which was desilylated by stirring with aqueous oxalic acid in acetone.

ii) Hydrometallation reactions.

Trimethylsilylalkynes can undergo hydrometallation reaction to give reactive vinyl organometallics. The hydroalumination[25] of silyl propargylamine **4** was achieved in ether at -40°C (eq - 4). The intermediate vinylalane was then treated with bromine to give the 3-bromo allyl amine **31** which desilylated to the free amine

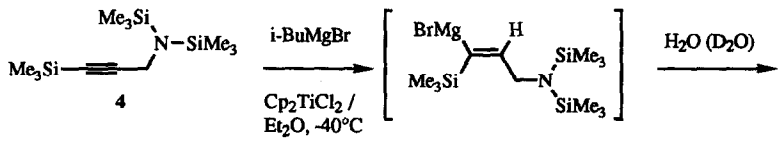


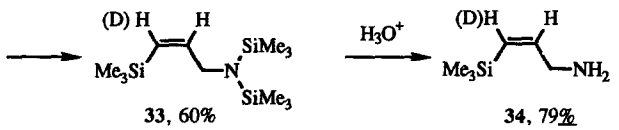


(4)

under acidic conditions. The initially formed vinylalane was also tentatively reacted with 1-iodohex-1-ene according to Neghishi et al[26]. The expected dienic amine formed but no pure sample was isolated.

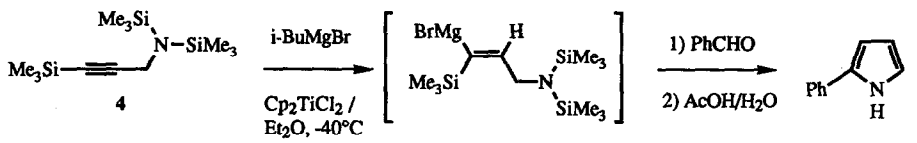
The hydromagnesation[27] of propargyl amine was also carried out (eq - 5). At -40°C the formation of the vinyl Grignard was established upon quenching with water to give Z-allylamine **33**[28]. The vinyl Grignard





(5)

however appeared of a low reactivity. It reacted with benzaldehyde unexpectedly to give 2-phenylpyrrole in a 70% yield (eq - 6). The formation of a pyrrole ring may result from a cyclisation of an intermediate allenyl

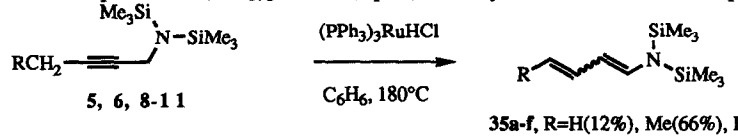


(6)

amine initially produced by a Peterson type reaction of the vinyl Grignard with benzaldehyde. The reaction however could not be extended to other aldehydes. Owing to the low reactivity of the vinyl organometallics produced by hydrometallation of **4**, this method although selective does not seem of general interest to obtain allylamines. We recently reported a much more general route to Z or E allylamines *via* hydrostannation[29].

3 - Preparation of dienic amines

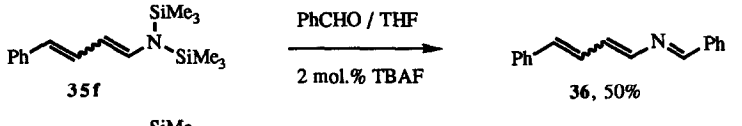
In order to have an access to dienic amines we studied some possible preparations from N,N-bis-(silyl)propargyl amines. We found that the ruthenium complex : $(PPh_3)_3RuHCl$, which is known to isomerise propargylic silyl ether[30], was also effective for the isomerisation of α-acetylenic silyl amines. Thus, the amines **5-11** were converted into conjugated dienamines by heating benzene solution at 180°C in sealed tubes in the presence of 1 mole percent of $(PPh_3)_3RuHCl$ (eq - 7). Good yields of the isomerised products were obtained in



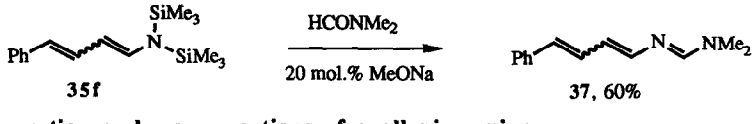
5, 6, 8-11 (7)

35a-f, R=H(12%), Me(66%), Et(59%), n-Pr(75%), n-Bu(69%), Ph(78%).

most cases, except for but-2-ynylamine **5** for which 80% of the starting material was recovered after prolonged heating. The slow isomerisation of **5** may be due to the formation of a stable ruthenium complex with the unsubstituted dienamine **35a**. Related iron complexes have been characterised[7]. The dienamines **35a-f** were formed as a mixture of Z and E isomers which were not separated. They are very stable and exhibit a reactivity similar to that of N,N-bis(silyl)enamines[5]. Nucleophilic activation of the silicon-nitrogen bond by fluoride ion or sodium methoxide allowed reaction of benzaldehyde or dimethylformamide (eq - 8,9). The reactions of dienamine **35f** led to 2-aza-1,3,5-hexatrienes **36, 37** respectively in 50 and 60% yields.



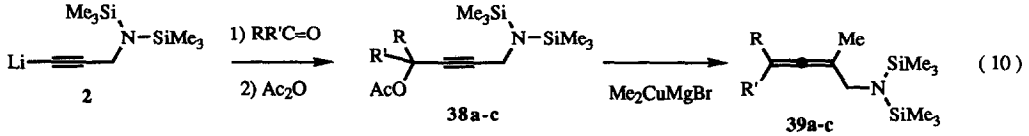
35f **36**, 50% (8)



35f **37**, 60% (9)

4 - Preparation and some reactions of α-allenic amines

Functional acetylenic amines are also of interest since they can be converted to α-allenyl amines[31]. We studied some possible preparations starting from the readily accessible acetylenic amino ethers (eq - 2,3). We first examined the reaction of di-alkyl cuprates with propargyl acetates which is known to lead to allenic derivatives[32]. As shown in eq-10 the 4-amino propargylic acetates **38** obtained by reaction of the lithium acetylide **2** with carbonyl compounds gave the substituted α-allenic amines **39a-c** in 60 to 65% overall yields.

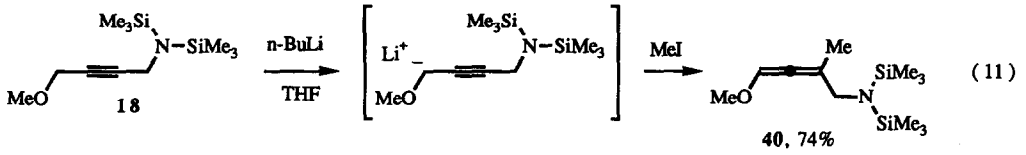


2 **38a-c** **39a-c** (10)

R,R'=Ph,H,(62%);i-Pr,H(60%);Me_2,(65%)

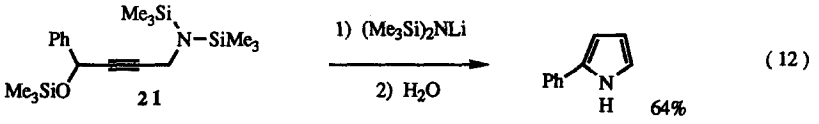
A second route to allenic structures was obtained from the methyl ether **18** (eq - 11). The treatment of **18** with n-BuLi in THF led to metallation at C-4 [33]. The alkylation of the intermediate conjugated anion with MeI led to the α-amino allenyl ether **40** in a 74% yield. Functional allenes of that type are of interest since they can lead

to primary γ-amino enones from which heterocyclisations reaction can be obtained. We already observed a spontaneous cyclisation to pyrrole ring when E-γ-bis(trimethylsilyl)amino enones were generated[34].We therefore



(11)

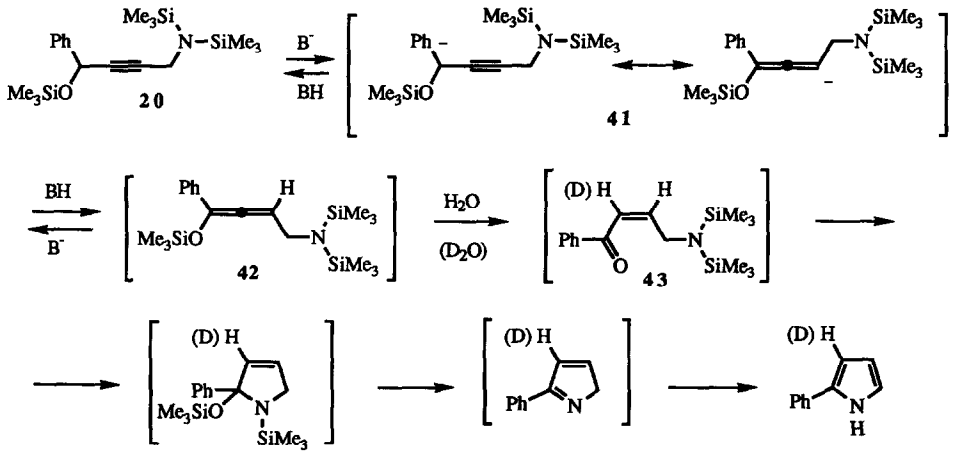
studied the metallation and isomerisation of a γ-amino-α-acetylenic silyl ethers (eq-12). Compound **21** was treated by $(Me_3Si)_2NLi$ at -78°C and warmed to 0°C. The mixture was then hydrolysed to give a 64% yield of 2-phenylpyrrole.The pyrrole ring formation can arise from the cyclisation of a γ - amino enone formed according to



(12)

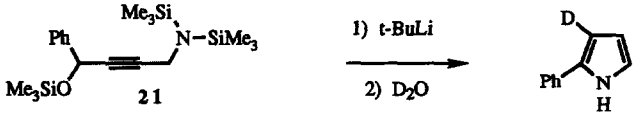
scheme 4. Initial deprotonation at the more acidic site of the propargylic silyl ether **21** led to an α-acetylenic anion **41**.The delocalised anion can be reprotonated to give rise to an allenic isomer derivative **42**.The hydrolysis

Scheme 4: Proposed scheme for the formation of 2-phenyl pyrrole.



of the resulting allenoxysilane then generate the γ-amino enone **43**. The latter can cyclize upon reaction of the bis(silyl)amino substituent with the adjacent carbonyl group.We attempted to react or to trap the intermediate carbonionic specie **41** with electrophiles[35]. Thus the metallation of silyl ether **21** according to eq-12 was followed by addition of allyl bromide, methyl iodide, or chlorotrimethylsilane. In all three cases, hydrolytic work up of the reaction mixture only allowed isolation of 2-phenyl pyrrole in a 60 to 62% yield. No indication for any alkylation or silylation of the intermediate **41** was obtained. A similar behaviour was noted when t-butyllithium

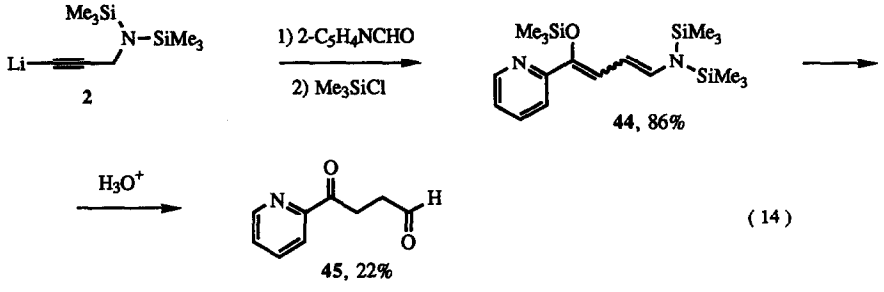
was used instead of the lithium amide base. It seems that the lithiated species **41** are either non reactive or formed in a low concentration in the reaction medium. A further evidence was obtained from a deuterolysis experiment (eq - 13). Treatment of the acetylenic amino alcohol **21** as previously, followed by quenching of the reaction



(13)

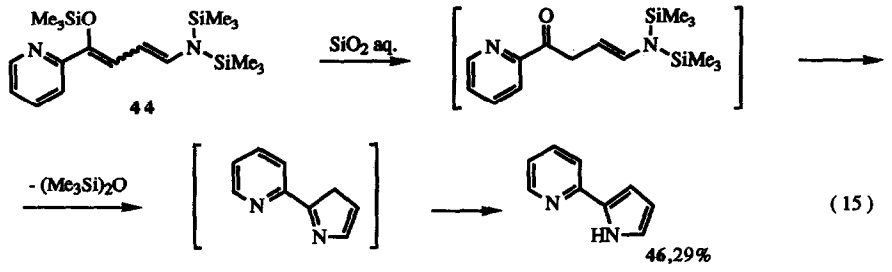
mixture with D_2O allowed recovery of deuterated phenyl pyrrole. The 3-position of the deuterium atom was established by ^1H NMR analysis at 250 MHz. In particular no introduction of a deuterium atom at the 4-position was noted. The formation of deuterated pyrrole clearly arises from the deuterolysis of allenoxysilane **42** (scheme 4). It shows that the species **42** is formed prior to hydrolysis via a base catalysed isomerisation of the acetylenic silyl ether **21**. Whereas the conjugate acid can act as a proton donor in the case of $(Me_3Si)_2NLi$, the substrate **21** itself may act as a proton source in the case of t-BuLi.

The isomerisation reaction appeared however limited to acetylenic alcohols such as **21** leading to a benzylic type carbanion. For example, no reaction was observed upon treatment of the silyl ether **24** having a 2-ethyl substituent, with $(Me_3Si)_2NLi$ or t-BuLi. We then attempted the reaction of pyridine carbaldehyde with lithium acetylide **2** (eq. 14) . The reaction did not lead to the expected propargylic alcohol derivative but to a mixture of dienic amino alcohol isomers **44.** Examination of the high field ^1H NMR spectrum showed multiplets for the vinylic protons in agreement with a mixture of the 4 possible isomers. The structure and relative proportions were not determined. Compound **44** presenting both the enoxysilane and bis(silyl)enamine[7] functionalities was formed in a good yield. However a lower yield of pure material was isolated owing to a moderate thermal stability. The dienic structure of **44** was further confirmed by the hydrolysis reaction. Treatment with an



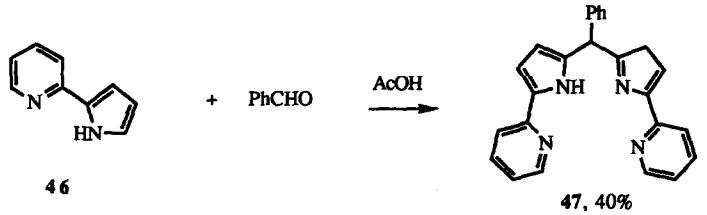
(14)

aqueous HCl solution allowed isolation of the keto-aldehyde **45**. The obtention of dienic amino alcohol derivatives may arise from an in-situ base catalysed isomerisation reaction owing to the probably high basicity of the 2-pyridylmethanolate formed prior to silylation. Interestingly the treatment of compound **44** with silicic acid in THF led to the isolation of 2-pyridylpyrrole **46** (eq-15). The ring closure reaction probably occured through the initial hydrolysis of the enoxysilane moiety to a keto bis(silyl)enamine. The latter via a nucleophilic attack of the nitrogen atom at the carbonyl group underwent a cyclisation with C=N double bond formation and elimination of hexamethyldisiloxane[5]. The resulting intermediate then tautomerises to 2-pyridyl pyrrole **46.**



(15)

It appears that 2-substituted pyrroles can be obtained from the reaction of lithium bis(silyl)aminomethyl acetylide with aldehyde. Although limited to aromatic aldehyde, the reaction can give a short access to polyheterocyclic compounds[36]. We for example observed that pyrrole **46** with a free 2-position easily formed dipyrryl methane derivatives. The reaction of benzaldehyde in acetic acid (eq-16) gave the dipyridyl dipyrryl methane **47**.



(16)

Experimental :

General remarks : All reactions were carried out in an inert atmosphere. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer in the from indicated. The ^1H NMR spectra were measured on a Varian EM 360 or EM 390 spectrometer, and ^{13}C NMR on a Brucker WP 200 apparatus. Chemical shifts (δ, ppm) are relative to Me_4Si. The Mass spectrum were obtained on a JEOL JMS D100 apparatus elemental analyses were carried out by the Service Central Microanalyse du CNRS.

N,N-bis(trimethylsilyl)propargylamine 3 ; Hexamethyldisilazane (12.9g, 80 mmol.) was slowly added to 65 mL of a 1.2 M solution of n-BuLi in ether at -78°C. After addition, the mixture was warmed to room temperature and stirred for 1h. The mixture was then cooled to -20°C and propargyl bromide (4.5g, 38 mmol.) in ether was added slowly. After stirring overnight, the reaction mixture was added to a cold water solution of phosphate buffer (3.8g KH_2PO_4; 4.5g Na_2HPO_4, $4H_20$). The organic layer was collected after filtration, washed rapidly and dried over Na_2CO_3. Evaporation of the solvent and distillation afforded 6.2g (78%) of propargyl amine **3**, Bp. 80°C, 20 mm Hg. ^1H NMR (CCl_4): 0.15(18H,s), 2.05(1H, t, J=3Hz), 3.5(2H, d, J= 3 Hz); ^{13}C NMR (C_6D_6): 1.7($SiCH_3$), 34.1(CH_2), 70.2(H-C≡C), 86.0(H C≡C), IR (CCl_4) 3320 cm^{-1}; Mass spect., m/e: 199(M^+); Anal. calcd. for $C_9H_{21}NSi_2$; C, 54.20;H, 10.61; N, 7.02. Found: C, 54.03,H, 10.54; N, 6. 90

1-Trimethylsilyl-N,N-bis(trimethylsilyl)propargylamine 4 : 11g of trimethylchlorosilane (0.1 mol.) were added at -20°C to an ethereal solution of lithium acetylide **2** prepared as above from 42g (0.26 mol.) of HMDS and 12.5g (0.105 mol.) of propargyl bromide. The mixture was warmed to room temperature and stirred for 2 hours. The hydrolytic work up as above gave 12.5g (78%) of trisilylated propargyl amine **4**, Bp : 120°C, 20 mm Hg. ^1H NMR (CCl_4) : 0 (27H, s); 3.35 (2 H,s); IR (CCl_4) : 2180 cm^{-1}; Mass spectrum, m/e : 271(M^+); Anal. calcd. for $C_{12}H_{29}NSi_3$: C, 53.06; H, 10.75; N, 5.16. Found : C, 53.01; H, 10.70; N, 5.04.

Alkylation reactions of lithium acetylide 2 : General procedure : A solution containing 22 mmol. of MeLi or n-BuLi in ether was added at -78°C to 4g of bis(silyl)propargyl amine **3** in 50 mL of ether or THF. The mixture was warmed to room temperature and stirred for 30 mn. The alkyl halide (20 mmol) was then added and the mixture was heated at 40 to 65°C for 3 to 48 h. The THF was removed, the residue hydrolysed with 100

mL of water and extracted with 3 x 50 mL of ether. The organic layer was dried over Na_2CO_3 and the ether was evaporated.Distillation of the residue afforded the alkylated products **5-19. Compound 5** : The addition of MeI (2.85g, 20 mmol.) was followed by stirring 3h at 40°C. As indicated above 3.6g (88%) of propargyl amine **5** was isolated. Bp : 92-94°C, 20 mm Hg ; ^1H NMR (CCl_4) : 0.06 (18H, s), 1.75 (3H, t), 3.4 (2H, q); Mass spectrum, m/e : 213 (M^+); Anal. calcd. for $C_{10}H_{23}NSi_2$: C, 56,27; H, 10.85; N, 6.56; Found : C, 55.80; H, 10.79; N, 6.42. **Compound 6** : As above, the reaction of 3.1g of EtI (20 mmol.) gave 3.85g (88%) of propargylamine **6**. Bp : 109-110°C, 20 mm Hg; ^1H NMR (CCl_4) : 0.13 (18H, s), 1.15 (3H, t); 2.1 (2H, m), 3.55 (2H, t); Mass spectrum, m/e : 227 (M^+); Anal. calcd. for $C_{11}H_{25}NSi_2$: C, 58.08; H, 11.07; N, 6.17; Found : C, 58.40; H, 11.27; N, 5.98. **Compound 7** : Reaction of 4.2g of 1-iodo hex-6-ene (20 mmol.) for 16h in refluxing THF gave 4.0g (72%) of **7**. Bp : 123-125°C, 0.2 mm Hg; ^1H NMR (CCl_4) : 0.13 (18H, s), 1.5 (4H, m), 2.1 (4H, m), 3.45 (2H, t), 4.9 (2H, m), 5.5 (^1H, m); IR (CCl_4) : 1645 cm^{-1}. Mass spectrum, m/e : 281 (M^+); Anal. calcd. for $C_{15}H_{31}NSi_2$: C, 63.99; H, 11.09; N, 4.98; Found : C, 63.43; H, 11.22; N, 5.10. **Compound 8** : The reaction of 2.45g of n-PrBr (20 mmol) in THF (48h, reflux) gave 2.9g (75%) of **8**. Bp 124°C, 20 mm Hg. ^1H NMR (CCl_4) : 0.13 (18H, s), 1.0 (3H, m) 1.5 (2H, m), 2.1 (2H, m), 3.5 (2H, m), 3.5 (2H, t); Mass spectrum, m/e : 241 (M^+); Anal. calcd. for $C_{12}H_{27}NSi_2$: C, 59.68, H, 11.26; N, 5.80; Found : C, 59.04; H, 11.42; N, 5.94. **Compound 9** : A above, the use of 2.8g of n-BuBr (20 mmol) gave 3.5g (69%) of **9**. Bp : 138-139°C, 20 mm Hg; ^1H NMR (CCl_4) : 0.13 (18H, s), 0.9 (3H, m), 1.4 (4H, m), 2.1 (2H, m), 3.45 (2H, t); Mass spectrum, m/e : 253 (M^+); Anal. calcd. for $C_{13}H_{28}NSi_2$: C, 61.10; H, 11.43; N, 5.48; Found : C, 61.10; H, 11.44; N, 5.17. **Compound 10**: 3.0g of n-$C_5H_{11}Br$ (20 mmol.) gave 3.6g (67%) of **10**. Bp 68-71°C, 0.05 mm Hg. 1H NMR (CCl_4) : 0.13 (18H, s), 0.9 (3H, m), 1.4 (6H, m), 2.1 (2H, m), 3.45 (2H, t); Mass spectrum, m/e : 269 (M^+); Anal. calcd. for $C_{14}H_{31}NSi_2$: C, 62.38; H, 11.58; N, 5.20; Found : C, 62.39; H, 11.78; N, 5.30. **Compound 11** : 3.4g of $PhCH_2Br$ gave 1.5g (26%) of **11**. Bp. 94°C, 0.08 mm Hg, ^1H NMR (CCl_4) : 0.13 (18H, s), 3.55 (4H, m), 7.25 (5H, m); Mass spectrum, m/e : 289 (M^+); Anal. calcd. for $C_{16}H_{27}NSi_2$: C, 60.34; H, 9.39; N, 4.84; Found C, 60.46; H, 9.50; N, 4.77. **11** (1.0g, 3.5 mmol.) was dissolved in 20 mL of MeOH containing 0.1g of KF and allowed to stir for 3 hours. Evaporation of the solvent and extration of the residue afforded 0.5g of **20**. ^1H NMR ($CDCl_3$) : 1.45 (2H, m), 3.4 (2H, t), 3.55 (2H, t), 7.3 (5H, m); IR ($CHCl_3$) : 3460, 3400 cm-1. Mass spectrum, m/e : 145 (M^+); Anal. calcd. for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.64; Found : C, 82.52; H, 7.50; N, 9.40. **Compound 14** : The reaction of 2.4g of allyl bromide (20 mmol.) led to 1.2g (43%). Bp 145-150°C, 20 mm Hg. ^1H NMR (CCl_4): 0.13 (18H, s), 2.2 (2H, m), 2.9 (1H, m), 3.5 (2H, d), 5.0 (4H, m) 5.5 (2H, m). Mass spectrum, m/e: 279 (M^+); Anal. calcd. for $C_{15}H_{29}NSi_2$: C, 64.45; H, 10.44; N, 5.01; Found : C, 64.11; H, 10.84; N, 5.05. **Compound 15** : 2.4g of 1.5-dibromopentane (10 mmol.) after 72h reflux yielded 2.4g of **15**. Bp. 150-154°C, 0.1 mm Hg. ^1H NMR (CCl_4) : 0.13 (36H, s) 1.5 (6H, m), 2.1 (4H, m), 3.45 (4H, t); Mass spectrum, m/e : 466 (M^+); Anal. calcd. for $C_{23}H_{50}N_2Si_4$: C, 59.15; H, 10.79; N, 6.00; Found : C, 59.45; H, 10.70; N, 5.85. **Compound 16** : From the reaction of 3.1g of 1-bromo-3-chloro propane at reflux for the 72 h, 3.8g (72%) of **16.** Bp. 81-83°C, 0.05 mm Hg; ^1H NMR (CCl_4) : 0.13 (18H, s) 1.9 (2H, m), 2.3 (2H, m), 3.4 (2H, t), 3.5 (2H, t); Mass spectrum, m/e : 277 (M^+,^{37}Cl); Anal. calcd. for $C_{12}H_{26}NClSi_2$: C, 52.22; H, 9.43; N, 5.07 ;Found: C, 51.90; H, 9.39; N, 5,20. **Compound 17** : Similarly 3.4g of 1-bromo-4-chloro butane gave 4.1g (73%) of **17**. Bp. 91°C, 0.05 mm Hg; ^1H NMR (CCl_4) : 0.13 (18H, s), 1.75 (2H, m), 2.15 (4H, m), 3.4 (2H, t), 3.5 (2H, t,); Mass spectrum, m/e 291 (M^+,^{37}Cl); Anal. calcd. for : $C_{13}H_{28}NClSi_2$: C, 53.84; H, 9.73; N, 4.83. Found : C, 54.01; H, 9.85; N, 5.05. **Compound 18** : 1.7g of CH_3OCH_2Cl in THF at 50°C for 24 h gave 3.8g of **18**. Bp. 125°C, 20 mm Hg; ^1H NMR (CCl_4) : 0.18 (18H, s), 3.3 (3H, s), 3.6 (2H, t), 4.05 (2H, t); Mass spectrum, m/e: 243 (M^+); Anal. calcd. for : $C_{11}H_{25}NOSi_2$; C, 54.26; H, 10.34; N, 5.75. Found : C, 54.47; H, 10.39; N, 5.57. **Compound 19** : 3.4g of $(CH_3O)_2CHCH_2Br$ (20 mmol.) gave 1.5g (49%) of **19**. Bp. 83-85°C, 0.08 mm Hg; ^1H NMR (CCl_4), 0.15(18H, s); 2.4(2H, m); 3.3(6H, s), 3.5(2H, t), 4.45(1H, t). Mass spectrum, m/e: 287 (M^+). Anal. calcd. for $C_{13}H_{29}NO_2Si_2$: C,54.30; H, 10.16; N, 4.87. Found : C, 54.55: H, 9.92; N, 5.03.

Reactions of lithium acetylide 2 with carbonyl compounds : Benzaldehyde : A solution of 6.95 of N,N-bis(trimethylsilyl)propargylamine **3** in 35 mL of dry THF, was cooled to -40°C and treated with 14 mL of a 2.5 M solution of n-BuLi in hexane. The mixture was warmed to room temperature and the resulting solution of lithium acetylide **2** was cooled again to -40°C. A THF solution containing 3.6**g** (35 mmol.) of benzaldehyde was then slowly added and after warming to room temperature, the mixture was stirred for 12 h. It was then treated by addition of 3.8g (35 mmol.) of Me_3SiCl from -40°C to room temperature and stirred for an additional 5 h. The mixture was then hydrolysed with a saturated aqueous NH_4Cl solution at 0°C, extracted with ether and dried over Na_2SO_4. Evaporation of the solvents and distillation of the residue allowed isolation of 9.0g (68%) of **21**.Bp. 125°C, 0.1 mm Hg; ^1H NMR (CCl_4) : 0.10(18H,s), 0.15(9H, s), 3.5(2H, d), 5.3(1H, t), 7.3 (5H, m); IR (CCl_4) : 1255, 1030cm-1; Mass spectrum, m/e : 377 (M^+). 3.0g of **21** was stirred with methanol in

the presence of 10 mol. % of KF. Evaporation of the solvent and crystallisation from toluene gave 1.0g (78%) of desilylated derivative. Mp. 79-80°C; ^{1}H NMR ($CDCl_3$) : 2.9 (3H, m), 3.3 (2H, d), 5.35 (1H, t), 7.3 (5H, m); IR ($CHCl_3$): 3600, 3380, 3320 cm^{-1}; Anal. calcd. for : $C_{10}H_{11}NO$: C, 74.51; H, 6.87; N, 8.69; O,9.93. Found : C, 74.62; H, 6.91; N, 8.35; O, 10.06. **Cyclopentanone**: As above, the reaction of 3.15g of cyclopentanone (35 mmol.) afforded 8.7g (70%) of **22**. Bp. 90-96°C, 0.05 mm Hg. ^{1}H NMR (CCl_4) 0.13 (27H,s), 1.6 (8H, m), 3.6 (2H, s); Mass spectrum, m/e: 355 (M^+); Anal. calcd. for $C_{17}H_{37}NOSi_3$: C, 57.39; H, 10.48; N, 3.94; Found: C, 58.05; H,10.52; N, 3.58. **Cyclohexenone**: The reaction of 3.3g of cyclohex-2-one (35 mmol.) gave 11.8g (92%) of **23**. ^{1}H NMR (CCl_4): 0.13 (27H,s), 1.9 (6H, m), 3.5 (2H, s), 5.6 (2H, s); Mass spectrum, m/e: 367 (M^+); Anal. calcd. for $C_{18}H_{37}NOSi_3$: C, 58.78; H, 10.14; N, 3.81; Found: C, 58.78; H,10.14; N, 3.81. **Propanal**: Hexamethyldisilazane (6.4g, 40 mmol.) was added to 20 mmol. of n-BuLi in ether at -78°C and then warmed to 0°C. 2.4g of propargyl bromide (20 mmol.) in ether was added and stirred at room temperature. To the mixture was then added 1.2g of propanal (20 mmol.), after stirring for 10 hours it was cooled to 0°C and treated with 2.2g of Me_3SiCl (20 mmol.). The usual work up allowed isolation of 2.7g (41%) of **24**. Bp. 75-78°C, 0.05 mm Hg. ^{1}H NMR (CCl_4): 0.13 (9H, s), 0.16 (18H, s), 1.0 (3H, m), 1.6 (2H, m), 3.6 (2H, d), 4.25 (1H, tt); Mass spectrum, m/e: 329 (M^+); Anal. calcd. for : $C_{15}H_{35}NOSi_3$: C, 54.64; H, 10.70; N, 4.25 : Found : C, 54.35; H, 10.50; N, 3.95. **2-Methyl-pent-2-enal** : As above using 2.0g of α,β-unsaturated aldehyde (20 mmol.) gave 2.9g (53%) of **25**; bp 105°C, 1 mm Hg; ^{1}H NMR (CCl_4); 0.13 (27H, s), 0.95 (3H, m) 1.65 (3H, m), 2.0 (2H, m), 3.55 (2H, d), 4.6 (1H, m), 5.4 (1H, m); IR (CCl_4) : 1635 cm^{-1}; Mass spectrum, m/e : 369 (M^+); 1.8g of **25** was treated with methanol containing 10 mol. % KF. Evaporation of the solvent and crystallisation gave 0.7g (90%) of the desilylated amino alcohol. mp. 72-75°C. ^{1}H NMR ($CDCl_3$) : 0.95 (3H, t), 1.8 (3H, m), 2.1 (2H, m), 2.45 (3H, m), 3.5 (2H, d), 4.8 (1H, m), 5.0 (1H, m); IR ($CHCl_3$) : 3600, 3400, 3320, 3200 cm^{-1}. Anal. calcd. for : $C_9H_{15}NO$: C, 70.56; H, 9.86; N, 9.14, O, 10.44. Found : C, 70.45; H, 9.95; N, 9.24; O, 9.98. **Chalcone:** As above upon reaction of 4.2g of chalcone (20 mmol.) led to 2.0g (40%) of **26**. ^{1}H NMR (CCl_4) : 0.13 (27H, s), 3.65 (2H, s), 6.15 (1H, d), 6.75 (1H, d), 7.3 (10H, m). Desilylation in MeOH/KF gave after crystallisation 1.0g (92%) of the corresponding amino alcohol. mp. 89-90°C; ^{1}H NMR ($CDCl_3$) : 2.6 (3H, m), 3.5 (2H, s), 6.3 (1H, d), 6.85 (1H, d), 7.2 (8H, m), 7.6 (2H, m); IR ($CHCl_3$) 3600, 3400, 3320 cm^{-1}. Anal. calcd. for : $C_{18}H_{17}NO$: C, 82.10; H, 6.50; N, 5.32; O, 6.08. Found: C, 82.00, H, 6.40; N, 5.10; O, 6.40.

Substituted allylic amines : Addition of n-Butyl copper : Compound 29. To a suspension of CuI (4.8g, 25 mmol.) in 50 mL of ether at -50°C was added 25 mL of a 1 M solution of n-BuLi in ether. The mixture was slowly warmed to -30°C and stirred for 30 mn. To the resulting clark suspension was then added 5.0g of propargylamine **3** (25 mmol.) in 25 mL of ether. After stirring for 2 hours, water was added and the mixture was washed successively with saturated NH_4Cl solution and water. The combined organic layers were dried over Na_2SO_4. Elimination of the solvent and distillation gave 4.1g (64%) of **29**. Bp 125°C, 25 mm Hg. ^{1}H NMR (CCl_4) : 0.1 (18H, s) 1.1 (7H, m), 1.7 (2H, m), 3.2 (2H, bs), 4.6 (1H, m), 4.8 (1H, m); ^{13}C NMR ($CDCl_3$) : 2.0 ($SiCH_3$), 14.3 (CH_3), 23.0 (CH_2-CH_3), 30.5 (CH_2-CH_2-CH_2), 34.2 (CH_2-C=), 49.7 (CH_2-N), 108.6 (CH_2=C), 151.4 (t, J_{C-H} : 155 Hz) (CH_2=C); IR (CCl_4) : 3095, 1653, 895 cm-1; Mass spectrum, m/e : 257 (M^+); Anal. calcd. for : $C_{13}H_{31}NSi_2$: C, 60.62; H, 12.13; N, 5.44. Found : C, 60.32; H, 12.25; N, 5.16. **Compound 30** : The addition of n-BuCu was performed as above. After addition of propargylamine **3** allylbromide (3.0g, 25 mmol.) and HMPT (3 mL) were added and the mixture stirred at -50°C for 2 h. It was hydrolysed by addition of aqueous NH_4Cl at -20°C. The above work up afforded 4.0g (55%) of **30**; Bp. 120°C, 0.5 mm Hg. ^{1}H NMR (CCl_4) : 0.1 (18H, s), 1.0-1.8 (9H, m), 3.5 (4H, m), 4.7-6.2 (4H, m); Mass spectrum : m/e 297(M^+). **Hydrometallation reactions : Compound 31** : To 2.7g of silylpropargylamine **4** (10 mmol.) in 10 mL of ether was added 10 mL of 1 M at 40°C for 2 h. After cooling at -78°C, 2 mL of pyridine in 15 mL of ether, and 6.7 mL of a 1.5 M solution of bromine in dichloromethane were added. After 30 mn the mixture was hydrolysed. After extraction and washing the organic layers were dried over sodium sulfate. Evaporation of the solvent and distillation afforded 1.9g (54%) of **31**.Bp. 85°C, 0.1 mm Hg. ^{1}H NMR (CCl_4) : 0.15(18H, s), 0.26(2H, s), 3.42 (2H, d), 6.49 (1H, t). The treatment of 1.5g of **31** with 1N aq. HCl gave after neutralisation and extraction with ether 0.7g of **32**. mp 207(dec.) . ^{1}H NMR ($CDCl_3$): 0.20(9H, s), 1.7-2.1 (2H bs), 3.3(2H, d), 6.8(1H, t), ^{13}C NMR (dioxanne): 0.3(Si-C), 40.7(CH_2-N), 106.5(=C-Br), 138.0(=CH-); IR (CCl_4): 3395, 1250 cm^{-1}. **Compound 33** : To 9.0g of silyl propargylamine **4** (33 mmol.) in 30 mL of THF, was added 1.0g of Cp_2TiCl_2 and 20 mL of a 2 M solution of isobutyl magnesium bromide (40 mmol.) in ether. The dark mixture was then stirred for 12 h and hydrolysed with aq. NH_4Cl. Extraction, drying and distillation gave 5.4g (54%) of amine **33** with identical characteristics to the one reported(ref. 28); Treatment with aq. 1 NH_4Cl gave after neutralisation and extraction 1.9g (79%) of the free amine **34** (ref.28). Upon deuterolysis the derivatives were isolated : deuterated-**33**; ^{1}H NMR (CCl_4): 0.12(18H, s), 0.20(9H, s), 3.22(2H,d),6.24(1H,t),

deuterated-**34**; ^{1}H NMR($CDCl_3$): 0.15(9H, s), 2.0-2.75(2H,bs), 3.35(2H,d), 6.30(1H,t).

Dienic amines : Isomerisation reactions : General procedure : The substituted propargylic amine (5 mmol.) was dissolved in 5 mL of benzene together with 50 mg of $(PPh_3)_3RuHCl$, C_6H_6 prepared as described in ref. 37, and transfered in a scaled tube. The mixture was heated for 3 days at 180°C. After cooling, the solvent was removed in vacuo and distillation of the residue afforded the disilylated dienamines **35a-f**. **Compound 35a** : Bp. 90-95°C, 20 mm Hg ^{1}H NMR (CCl_4) : 0.13 (18H, s), 4.4-6.2 (5H, m); IR (CCl_4), 1630, 1595 cm^{-1}; Mass spectrum, m/e : 213 (M^+). **Compound 35b** : 0.8g (66%),Bp. 105-110°C, 20 mm Hg; ^{1}H NMR (CCl_4) : 0.1-0.2 (18H, m) 1.7 (3H, m), 4.9-6.2 (4H, m);IR (CCl_4) : 1645, 1600 cm^{-1}; Mass spectrum , m/e : 227 (M^+), Anal. calcd. for : $C_{11}H_{25}NSi_2$: C, 58.08; H, 11.07; N, 6.17; Found : C, 57.88; H, 11.50; N, 5.83. **Compound 35c** : 0.7g (59%). Bp. 126-130°C, 20 mm Hg; ^{1}H NMR (CCl_4):0.1-0.2(18H,m),1.0(3H,m),2.0(2H,m), 5.0-6-2 (4H, m); IR (CCl_4) : 1645, 1610, 1600 cm^{-1}; Mass spectrum , m/e : 241(M^+), Anal. calcd. for : $C_{12}H_{27}NSi_2$: C, 59.68; H, 11.26; N, 5.80; Found : C, 59.81; H, 11.09; N, 5.40. **Compound 35d** : 0.9g (75%) Bp. 135-139°C, 20 mm Hg; ^{1}H NMR (CCl_4):0.1-0.2(18H,m), 0.9(9H,m), 1.3 (2H,m), 2.0(2H,m), 5.0-6-2 (4H, m); IR (CCl_4): 1645, 1610, 1600 cm^{-1}; Mass spectrum, m/e : 255(M^+); Anal. calcd. for : $C_{13}N_{29}NSi_2$: C,61.10;H,11.43;N,5.48; Found: C,60.70;H,11.05;N,5.12. **Compound 35e** : 0.9g (69%); Bp. 69-70°C, 0.01 mm Hg; ^{1}H NMR: 0.1-0.2(18H, m), 0.9(3H, m), 1.45(4H, m), 2.1(2H, m), 5.0-6.2(5H, m); IR (CCl_4) 1645, 1610, 1600 cm^{-1}; Mass spectrum, m/e : 289(M^+).**Compound 35f**: 1.43g (78%). Bp. 127-130°C, 0.05 mm Hg. ^{1}H NMR (CCl_4): 0.25(18H,m), 5.5-7.2(4H,m), 7.3 (5H,m), IR (CCl_4): 1630, 1615, 1600 cm^{-1}; Mass spectrum, m/e : 289(M^+); Anal. calcd. for : $C_{16}H_{27}NSi_2$: C,66.34; H,9.39; N,4.84; Found: C,65.30;H,9.23;N,4.23. **Formation of azatrienes:Compound 36**; A solution containing 0.7g of dienamine **35f** (24 mmol.) in 20 mL of THF was added slowly at -30°C to 0.5g of benzaldehyde (5 mmol.) and 0.1 mL of a 1M THF solution of TBAF in 30 mL of THF. The mixture was stirred at -30°C for 3 h. After evaporation of the solvent, the residue was extracted with CH_2Cl_2 washed with H_2O. Crystallisation from a mixture of hexane, ethyl acetate gave 0.25g (50%) of **36** : mp. 153-154°C, 1H NMR ($CDCl_3$): 5.5-7.2(4H, m), 7.4(8H, m), 7.8(2H, m); IR ($CHCl_3$); 1640, 1605 cm^{-1}; Mass spect.,m/e: 233(M^+); Anal. calcd. for : $C_{17}H_{15}N$: C,87.52; H,6.48; N,6.00; Found: C,87.28; H,6.65;N, 5.86. **Compound 37** ; A mixture containing 2.9g of **35f** (10 mmol.), 0.1g of dried MeONa (2 mmol.) and 10 mL of DMF was heated at 80°C for 1 h. The solvent was then evaporated and the residue extracted with CH_2Cl_2 and washed with H_2O. The combined organic layers were dried over Na_2CO_3 and the solvent was eliminated in vacuo. Distillation afforded 1.2g (60%) of **37** (Bp. 140-145, 0.05 mm Hg) which yield crystals mp 115-120°C. ^{1}H NMR ($CDCl_3$): 2.9(6H, s), 5.9-7.2(4H, m), 7.3(5H, m), 7.4(1H, s); IR(CCl_4), 1645, 1610 cm-1; Mass spectr., m/e 200(M^+). Anal. calcd. for $C_{13}H_{16}N_2$: C,77.96;H,8.05;N,13.99; Found:C,77.60;H,8.25;N, 13.76.

α-Allenic amines : Compound 39a : The reaction of the lithium acetylide **2** with benzaldehyde was carried out as described previously for the preparation of **21** using 20 mmol. of each reagents. The initially formed lithium alcoholate was treated at -20°C with 20 mmol. of Ac_20 and stirred for 12h at room temperature. The THF was evaporated and the residue was treated with 50 mL H_2O and 100 mL of ether. After extraction washing, and drying the solvent was removed and distillation gave 5.8g (83%) of **38a**; bp 87°C, 0.1 mm Hg; ^{1}H NMR (CCl_4) : 0.15 (18H, s); 1.0 (6H, dd), 1.8 (1H, m), 1.9 (3H, s), 3.5 (2H, d), 5.1 (1H, td); IR (CCl_4) 1750 cm^{-1}; Mass spectrum, m/e : 313(M^+). 3.2g of **38a** (10 mmol.) in 50 mL ether were then added at -50°C to a solution of methyl cuprate (prepared from (30 mmol.) of MeMgBr and 2.9g of CuI (15 mmol.) in a 60 mL of a 1/1 mixture of THF/ether). The mixture was slowly warmed to room temperature and hydrolysed by addition of 50 mL of saturated aq. NH_4Cl and 10 mL of aq. NH_4OH. After filtration the organic layer was washed and dried over Na_2CO_3 and the solvent evaporated. Distillation of the residue gave 2.3g (75%) of **39a**. Bp. 114-116°C, 0.2 mm Hg; ^{1}H NMR (CCl_4) : 0.18 (18H, s), 1.95 (3H, d), 3.6 (2H, m), 6.3 (1H,m), 7.35 (5H, m); IR (CCl_4) : 1960 cm-1; Mass spectrum, m/e 303(M^+). **Compound 39b** : As above **38b** (5.1g, 82%) was isolated upon reaction of 1.45g of isobutyraldehyde (20 mmol.). Bp. 87°C, 0.1 mm Hg. 1H NMR (CCl_4) : 0.15 (18H, s), 1.0 (6H, dd),, 1.8 (1H, m), 1.9 (3H, s), 3.5 (2H, d), 5.1 (1H, td); IR (CCl_4) 1750 cm^{-1} : Mass spectrum, m/e : 313(M^+). The reaction of methyl cuprate with 3.1g of **38b** (10 mmol.) gave 2.0g (73%) of **39b**. Bp 83-86°C, 0.1 mm Hg; ^{1}H NMR (CCl_4) : 0.1 (18 H, s), 1.0 (6H, d), 1.6 (3H, d), 2.1 (1H, m), 3.3 (2H, d), 5.0 1H, m); IR (CCl_4) 1970 cm^{-1}; Mass spectrum, m/e : 269(M^+). **Compound 39c** : As above, **38c** 4.8g, (80%) was obtained from 1.2 of acetone (20 mmol.) Bp. 83-85°C, 0.1 mm Hg ^{1}H NMR (CCl_4) : 0.15 (18H, s), 1.6 (6H, s), 1.9 (3H, s), 3.5 (2H, s); IR (CCl_4) 1750 cm^{-1}; Mass spectrum, m/e : 299(M^+). The reaction of methylcuprate with 3.0g of **38c** (10 mmol.) gave 2.1g (80%) of **39c** ; Bp. 123-125°C, 20 mm Hg; ^{1}H NMR (CCl_4) : 0.1 (18H, s), 1.6 (3H, s), 1.75 (6H, s), 3.35 (2H, s); IR (CCl_4) 1970 cm^{-1}; Mass spectrum,

m/e : 255(M^+). **Compound 40** : 10 mL of 1 M solution of n-BuLi in ether (10 mmol.) were added at -100°C to 2.4g of **18** in 50 mL of THF. After 30 mn the mixture was warmed to -30°C for again 30 mn, then 1.4g of MeI (10 mmol.) were added and the mixture was warmed to room temperature and stirred overnight. Evaporation of THF was followed by hydrolysis with 50 mL of H_2O and extraction with ether. The organic layers were collected, washed with H_2O, dried over Na_2CO_3 and the solvent evaporated. Distillation of the residue gave 1.9g (74%) of **40**. Bp. 80°C, 0.3 mm Hg, ^1H NMR (CCl_4) 0.1 (18H,s), 1.7 (3H, m), 3.3 (3H, s), 3.4 (2H, m), 6.5 (1H, m); ^{13}C NMR (C_6D_6) : 2.08 ($\underline{C}H_3$-Si), 19.4 ($\underline{C}H_3$-C=), 50.1(CH_3-O), 55.8 ($\underline{C}H_2$-N), 119.5 (=$\underline{C}$-CH_3), 124.3 (CH_3O-$\underline{C}$=), 189.6 (=$\underline{C}$=); IR (CCl_4), 1960 cm^{-1}, Mass spectrum, m/e : 257 (M^+). Anal. calcd. for : $C_{12}H_{27}NOSi_2$: C, 55.97; H, 10.56; N, 5.44. Found : C, 55.90; H, 10.75; N, 4.02

Cyclisation of 21 to 2-phenylpyrrole : A solution of 7.54g (20 mmol.) of acetylenic silylaminoether **21** in 30 mL of ether at -78°C was treated with (20 mmol.) of $(Me_3Si)_2NLi$ (prepared by reaction of 3.2g of hexamethyldisilazane with 20 mmol. of n-BuLi in 20 mL of Et_2O). The mixture was stirred for 2 h and warmed to 0°C for 10 h. It was then hydrolysed with a saturated aqueous NH_4Cl solution, extracted with ether and dried over sodium sulfate. After evaporation of the solvent, the residue was chromatographed on a short alumina column. Elution with CH_2Cl_2 gave 1.8g of 2-phenylpyrrole (yield 64%); mp. 128°C (Lit. 129°C). ^1H NMR ($CDCl_3$) : 6.05 (1H, m), 6.30 (1H, m), 6.50 (1H, m), 7.2 (5H, m), 7.85-8.55 (1H, very broad); IR ($CHCl_3$) 3450, 1610, 1590 cm^{-1}. **3-D, 2-phenylpyrrole**: A solution of acetylenic silylaminoether **21** in 15 mL of dry n-hexane was cooled at -78°C and treated with 7.5 mL of a 0.67 M hexane solution of t-BuLi. The mixture was warmed to room temperature and stirred for 5 h. Hydrolysis was then carried out by addition of 1 mL of D_2O, the mixture was then filtered, extracted with ether, dried over magnesium sulfate. After evaporation of the solvents the residue was purified by thin layer chromatography. Elution with CH_2Cl_2 allowed isolation of 0.25g (yield 35%) of deuterated phenylpyrrole. mp. 129°C. 1H NMR ($CDCl_3$) : 6.10 (1H, m), 6.62 (1H, m), 6.93-7.40 (5H, m), 8.2 (1H, very broad).The deuterolysis at C-3 is indicated by the absence of signal at 6.3 ppm

Reaction of lithium acetylide 2 with 2-pyridine carboxaldehyde : As for the preparation of **21** 10g (50 mmol.) of N,N-bis(trimethylsilyl)propargylamine in 50 mL of THF was treated successively with 20 mL of a 2.5 M solution of n-BuLi, 5.3g (50 mmol.) of 2-pyridine carboxaldehyde and 5.4g (50 mmol.) of chlorotrimethylsilane. The previous hydrolytic work up afforded 16.2g of **44** as a crude oil. Distillation gave 5.6g (yield 30%) of **44**. Bp. 130-135°C, 01 mm Hg; ^1H NMR (CCl_4) : 0.10 (18H, s), 0.15 (9H, s), 5.6-6.4 (2H, m), 6.6-6.95 (2H, m), 7.05-7.50 (2H, m), 8.15 (1H, bs); IR (CCl_4). 1620, 1575, 1255, 1070 cm^{-1}; Mass spectrum m/e : 378(M^+). **2-pyridine -γ-oxo butanal 45** : The reaction of lithium acetylide **2** with 2-pyridine carboxadeldehyde was performed as in the preceeding case using 5.0g (25 mmol.) of N,N-bis(trimethylsilyl)propargylamine and 3.2g (30 mmol.) of 2-pyridinecarboxaldehyde. The mixture was hydrolysed, extracted with ether, and dried over magnesium sulfate. After evaporation of the solvents, the residue was purified by TLC (silicagel) to give 0.9g of 2-pyridine-γ-oxo butanal **45** (yield 22%). ^1H NMR ($CDCl_3$) : 3.16 (2H, t), 3.82 (2H, t), 7.4-8.3 (3H, m), 8.9 (1H, bs), 10.0 (1H, s); IR (CCl_4) : 1720, 1695 cm^{-1}; Mass spectrum : m/e : 163(M^+). **2-[Pyridyl-2-]pyrrole 46** : To a solution contraining 1.0g (2.6 mmol.) of enoxysilane 45 in 20 mL of THF was added 5g of silicic acid (Aldrich). The mixture was stirred at 60°C for 4 h. After cooling and filtrating, the solvent was removed in vacuo and the residue was purified using chromatography on neutral alumina to give 0.11g (yield 29%) of 2-[pyridyl-2-]pyrrole **46** ; (mp. 90-91°C, Lit. 88-90°C) having similar characteristic to those reported[38]. ^1H NMR ($CDCl_3$) 6.24 (1H, m), 6.6-7.1 (3H, m), 7.5 (2H, m), 8.4 (1H, d), 10.4-11.0 (1H, bs); ^{13}C NMR ($CDCl_3$) : 107.4, 110.4, 118.3, 120.0, 120.5, 131.8, 136.6, 149.0, 150.9; Mass spectrum, m/e : 144(M^+), Anal. calcd. for : $C_9H_8N_2$: C, 74.92, H, 5.60, N, 19.44. Found : C, 74.74; H, 5.73; N, 19.37. **Reaction of 2-pyridyl-2-]pyrrole 46 with benzaldehyde** : To a solution of 0.5g (3.5 mmol.) of 2-[pyridyl-2-]-pyrrole **46** in 10 mL of acetic acid was added 0.19g (1.8 mmol.) of benzaldehyde. The mixture was heated to 70°C and stirred for 3 h. After cooling, the solvent was removed in vacuo and the residue extracted with ether. The resulting solution was washed first with aqueous $NaHCO_3$ then with water and dried over magnesium sulfate. Purification over an alumina column gave 0.27g (40%) of dipyrryl methane derivative **47**. mp. 209°C; ^1H NMR ($CDCl_3$), 5.68 (1H, s), 6.09 (2H, m), 6.71 (2H, m), 7.09 (2H, m), 7.41 (5H, m), 7.65 (4H, m), 8.58 (2H, m), 9.61 (2H, bs); ^{13}C NMR ($CDCl_3$) : 44.67, 107.72, 109.92, 118.04, 119.85, 120.32, 127.30, 128.67, 128.95, 131.46, 135.02, 136.48, 148.98, 150.85; IR ($CHCl_3$) : 3430 cm^{-1}; Mass spectrum, m/e : 376 (M^+). Anal. calcd. for : $C_{25}H_{20}N_4$: C, 79.76; H, 5.35; N, 14.88; Found : C, 79.51; H, 5.76; N, 14.55.

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