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Aminosilanes in Organic Synthesis. Addition of Organocopper Reagents on γ-Bis(trimethylsilyl)amino-α-Acetylenic Amides, Esters and Ketones. Stereochemistry and Some Synthetic Uses.

Robert, J.P. Corriu*; Geng Bolin; Javed Iqbal; Joël, J.E. Moreau* and Claude Vernhet

Laboratoire Hétérochimie et Aminoacides, Associé au CNRS n° 1097, Département de Chimie Organique Fine, Université de Montpellier II, Sciences et Techniques du Languedoc, F 34095 Montpellier Cedex 05 - France.

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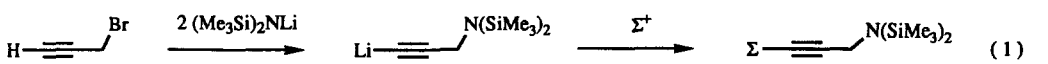
Summary : The stereochemical outcome of the carbocupration of γ-bis(trimethylsilyl)amino-α-acetylenic amide, esters and ketone was studied. A judicious choice of substrate, reagent and(or) reaction conditions allows to perform highly stereoselective cis or trans addition. The intermediate vinylic copper adducts, with (E) or (Z) configuration, react with electrophilic reagents to provide short routes to substituted pyrrolinones and pyrroles.

Introduction.

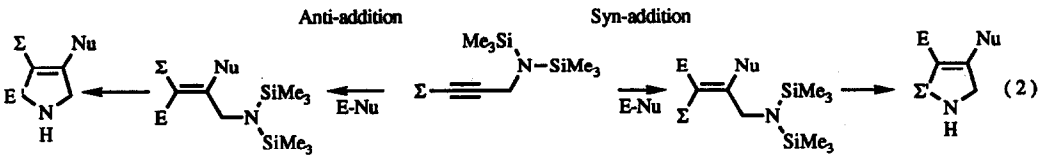
Owing to its reactivity, the silicon-nitrogen bond of aminosilanes can interestingly play two roles. It can withstand a variety of reaction conditions and therefore silylation at nitrogen provides an efficient protection for a primary amino group [1-6]. On the other hand, the silicon-nitrogen bonds can nevertheless be cleaved by electrophilic reagents [7]. The formation of nitrogen to carbon bond can be obtained from aminosilanes providing useful chemical transformations and new synthetic routes [8-14].

We previously reported a short route to substituted and functional protected propargylic amines [15] (eq-1)



(1)

and showed that these are precursors of various unsaturated amines [16]. These readily available functional propargyl amines are also of potential interest as precursors of nitrogen heterocycles. In these trifunctional three-carbon molecules, the silyl amino group could be used both as a protected primary amine and as a reactive functional group. Owing to the presence of the carbon carbon triple bond, one can carry out a stereospecific addition reaction which will lead either to Z or E functionalized allylic amines (eq-2). The latter compounds can then cyclize to nitrogen heterocycles upon reaction of the cis-orientated functional groups.



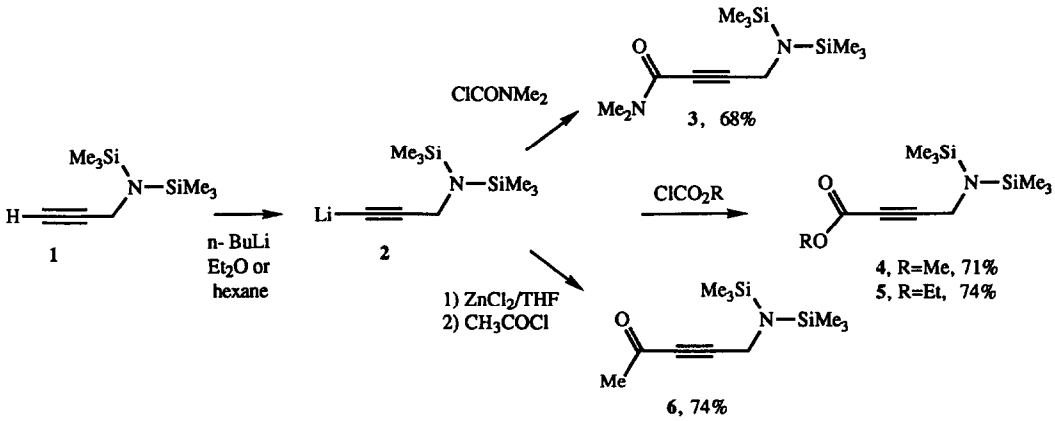
(2)

In connection with our studies on the use of aminosilanes for the synthesis of nitrogen heterocycles[11,17,18], we explored some possible short synthetic routes according to equation 2, via carbometallation reactions of functionalized propargylic amines. We first investigated the addition of organocopper reagent to γ-bis(trimethylsilyl)amino-α, β-acetylenic amide, esters and ketone. We were particularly interested to determine the stereochemistry and selectivity of the addition reaction in order to examine its use for new heterocyclizations reactions. We wish to report here the results of this study and to show that the stereochemical outcome can be controlled by judicious choice of substrate, reagent and (or) reaction conditions. Highly stereoselective trans or cis addition can be performed and further reactions of the various vinylic organo copper adducts provides facile route to five membered nitrogen heterocycles. A portion of this study has been communicated [17].

Results and Discussion.

1-Preparation of γ-bis(trimethylsilyl)amino-α,β-Acetylenic Amide, Esters and Ketone.

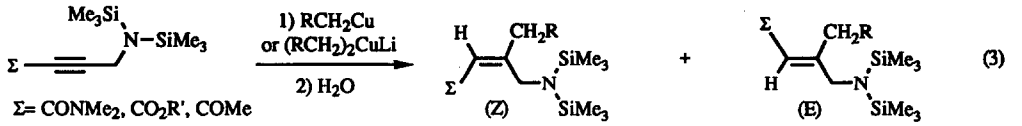
The functionalized propargylic amines used in this study were prepared from N,N-bis(trimethylsilyl) propargyl amine[16] in one step according to scheme 1. The quantitative metallation of the protected amine **1** led to ether or hexane solutions of the lithium acetylide **2**. Addition of N,N-dimethyl carbamoyl chloride at -20°C allowed isolation of a 68% yield of the acetylenic amide **3**. Similarly the reaction of **2** with methyl or ethyl chloroformate gave esters **4** (71%) and **5** (74%), respectively. The preparation of the ynone **6** was also achieved from **2** via conversion to the intermediate zinc derivative [19] with $ZnCl_2$ in THF and condensation with acetylchloride. It is worth noting that compounds **3-5** can also be prepared directly from propargyl bromide in a one-pot reaction [15], however we found large preparations to be carried out more easily from propargyl amine **1.** Using this procedure hundred grams quantities of functionalized propargyl amines were routinely obtained.



Scheme 1: Preparation of γ-Bis(trimethylsilyl)amino α,β–Acetylenic Amide **3**, Esters **4,5** and Ketone **6**

2-Carbocupration Reactions of γ-bis(trimethylsilyl)amino α,β–Acetylenic Amide (3), Esters (4, 5) and Ketone (6).

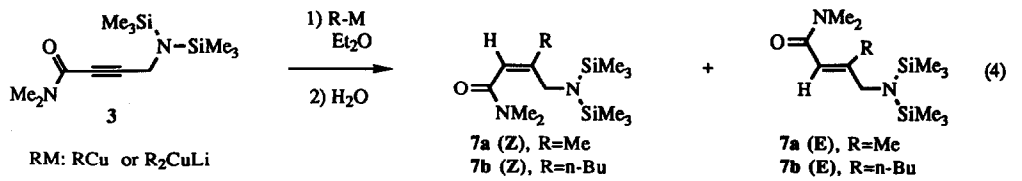
The conjugate addition of organocopper reagents to α, β -acetylenic esters or amides has been widely used in the synthesis of substituted acryclic derivatives [20-26]. The stereochemistry of the reaction was found to be dependent on the nature of the reagent, the substrate, and the reaction conditions (solvent, reaction time, temperature). Reactions which allow an overall cis-addition of the organocopper reagent are readily accomplished. A stereoselective trans-addition was reported only in a few cases [17,24]. We studied the carbocupration of compound **3-6** having a protected γ–amino substituent under various reaction conditions. The addition reaction of organocopper reagent, followed by protonolysis of the vinyl copper intermediate led to a mixture of (E) and (Z) isomeric adducts (eq-3). The E/Z ratio was determined by ^{1}H NMR analysis. The stereo-



chemistry of the adducts was assigned on the basis of the chemical shift of the protons situated on the carbon α to the C = C bond [23c, 24e]. For both allylic carbons : CH_2R and CH_2-$N(SiMe_3)_2$, the protons situated on the α carbon cis to the functional group (Σ = $CONMe_2$,CO_2R , COMe) resonate at lower field than the proton on the carbon trans to the functional group. This was realized for each pair of isomers. The structural assignments were also confirmed on a chemical basis. Some reactions of the intermediate vinyl copper reagent which led to the above (E) and (Z) acrylic derivatives allowed the formation of heterocyclic compounds, in agreement with the proposed stereochemistry (vide infra).

Carbocupration of acetylenic amide (3):

The reaction of organocopper reagents with the acetylenic amide **3** in diethylether was studied as a function of temperature and reagents (eq-4). The addition of the copper reagent was carried out at low temperature and the mixture was then eventually warmed to 0°C or +20°C before quenching and hydrolytic workup. The stereochemistry was determined by ^{1}H NMR analysis of the crude reaction mixture. The results are



presented in Table 1. The reaction of butyl copper at - 20°C (entry 1) led to the predominant formation of the Z isomer **7b(Z)** corresponding to a selective cis addition of the organometallic reagent. Upon raising the temperature to 0 or + 20°C, the selectivity decreased and a 3/1 mixture of Z and E isomers was obtained (entries 2,3). The reaction of organocuprate reagents (entries 4,7) at low temperature similarly gave a preferential cis-addition, although the selectivity is slightly lower than with the corresponding organocopper reagent. Moreover

Table 1 : Addition of organocopper reagents to the acetylenic amide (3)

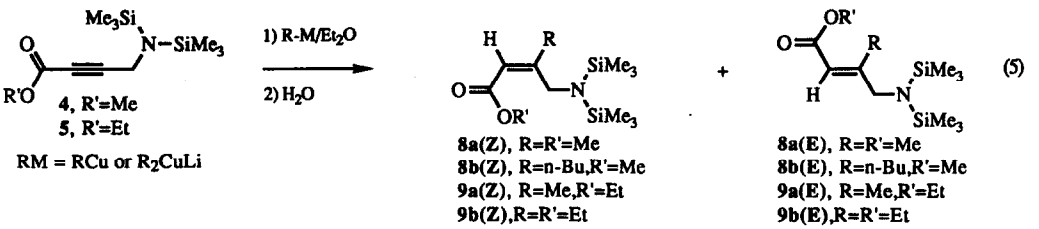
Entry	Reagent	Reaction conditions[a] Temp. (time)	Products ratio[b] Z : E	Yield[b] (%)
1	n-BuCu	-20°C (3h)	92 : 08	76[c]
2	n-BuCu	-20°C(3h) then 0°C (1h)	83 : 17	90
3	n-BuCu	-20°C(3h) then +20°C(1h)	75 : 25	90
4	n-Bu_2CuLi	-50°C (3h)	88 : 12	90
5	n-Bu_2CuLi	-50°C (3h) then 0°C (1h)	25 : 75	90
6	n-Bu_2CuLi	-50°C(3h) then + 20°C (1h)	16 : 84	90
7	Me(Hexynyl)CuLi	-50°C (1.5h)	75 : 25	95[c]
8	Me(Hexynyl)CuLi	-50°C (1.5h) then 0°C (1h)	10 : 90	95
9	Me(Hexynyl)CuLi	-50°C (1-5h) then +20°C (18h)	05 : 95	95[c]

a) An ethereal solution of 3 was added to the organocopper reagent at -20°C or -50°C and stirred for a few hours. The mixture was eventually warmed to 0° or + 20°C for some time before quenching by addition of saturated aqueous NH_4Cl solution or MeOH for low temperature experiments. b) Determined by ^1H NMR unless otherwise stated.c) Isolated yield.

upon warming the reaction mixture to 0 or +20°C, a reverse stereoselectivity was found (entries, 5, 6, 8, 9). The major product was the E-isomer **7(E)** corresponding to an overall trans-addition of the organometallic reagent. A quite high stereoselectivity was found upon reaction of a mixed cuprate after standing at + 20°C. It is also worth noting that the intermediate vinyl copper formed are stable for several hours at room temperature. Therefore the carbocupration of the acetylenic amide 3 seemed to proceed via a cis-addition at low temperature leading to Z-adducts with a high selectivity. At higher temperatures E-adducts can be obtained selectively from the reaction of organocuprate reagents.

Carbocupration of acetylenic esters (4) and (5):

The addition of copper reagents to esters 4 and 5 was similarly studied (eq-5). The results are presented



8a(Z), R=R'=Me
8b(Z), R=n-Bu,R'=Me
9a(Z), R=Me,R'=Et
9b(Z),R=R'=Et

8a(E), R=R'=Me
8b(E), R=n-Bu,R'=Me
9a(E), R=Me,R'=Et
9b(E),R=R'=Et

in Table 2. The main features can be summarized as follows:

The reaction of **organocopper reagents (RCu)** at - 40°C gave a highly selective cis addition (entries 1,4). Upon warming the reaction mixture to 0°C a 30 : 70 mixture of Z and E adducts was isolated.

The reactions of **organocuprate reagents (R_2CuLi)** were more complex :

i) at -40°C the adducts resulting from a selective trans-addition were isolated (entries 5-9). Up to 96% of the E isomer was formed (entry 8);

ii) when the reaction mixture was warmed to 0°C before quenching (entry 10) the selectivity decreased and a 25 : 75 mixture of Z and E isomers was obtained. The mixture composition is close to the one produced from the reaction of n-BuCu under the same reaction conditions (entry 3);

Table 2 : Addition of organocopper reagents to the acetylenic esters (4) and (5)

Entry	Acetylenic Ester	Reagent	Reaction conditions[a] Temp. (time)	Prod. ratio[b] Z : E	Yield[b] (%)
1	4	n-BuCu	-40°C (9h)	95 : 05	79[c]
2	4	n-BuCu	-40°C(9h) then 0°C (2h)	29 : 71	75[c]
3	4	n-BuCu	-40°C(9h) then 0°C (2h)[d]	30 : 70	78[c]
4	5	EtCu	-40°C (24h)	93 : 07	86[c]
5	5	Me_2CuLi	-40°C (2h)	05 : 95	77[c]
6	5	Et_2CuLi	-40°C (2h)	15 : 85	75[c]
7	4	$n\text{-}Bu_2CuLi$	-40°C (2h)	13 : 87	60[c]
8	4	Me (Hexynyl)CuLi	-40°C (2h)	04 : 96	67[c]
9	5	Me (Hexynyl)CuLi	-40°C (2h)	05 : 95	78[c]
10	5	Me (Hexynyl)CuLi	-40°C (2h) then 0° (2h)	25 : 75	90
11	5	Me (Hexynyl)CuLi	-40°C (2h) then 0° (2h) [d]	05 : 95	90
12	5	Me (Hexynyl)CuLi	-40°C (3h) then 0° (2h) [e]	25 : 75	90
13	5	Me (Hexynyl)CuLi	-40°C (3h) then 0° (2h) [d,e]	05 : 95	90
14	5	EtCu/EtLi [f]	-40°C (24h)	32 : 68	75[c]

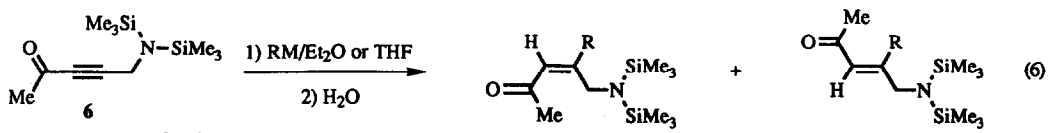
a) An ethereal solution of 4 or 5 was added to the copper reagent at -40°C and stirred for several hours .The mixture was then eventually warmed to 0°C for two hours and quenched by addition of saturated aq. NH_4Cl solution.b) Determined by ^1H NMR unless otherwise stated .c) Isolated yield.d) The mixture was cooled again at -40°C before quenching.e) The reaction was carried out in the presence of 1 mol.% of Et_3N. f) The ester 5 was first treated with EtCu at -40°C and stirred for 20h , then one mole of EtLi was added and the mixture was quenchedwith water after 2h.

iii) interestingly, when the reaction mixture warmed to 0°C was then cooled once again to-40°C (entry 11) a highly selective formation of the E isomer, identical to that obtained when the reaction was kept at - 40°C (entry 5), was observed. Similar observations were made when the reactions were performed in the presence of Et_3N. This peculiar behavior was not found in the case of the reaction of n-BuCu. Finally the reaction of EtCu at -40°C followed by treatment of the intermediate initially formed vinyl copper with EtLi (entry 14) is no longer a stereoselective cis addition but a mixture of Z and E adduct are obtained, although the isomer ratio is different from the one obtained in the reaction of Et_2CuLi (entry 6).

In summary the carbocupration of acetylenic esters **4** and **5** is highly stereoselective at low temperatures (-40°C). Organocopper reagents yielded cis addition products, whereas organocuprates reagent gave trans addition products. At a higher temperature (0°C), a mixture of E and Z adducts of similar composition is obtained for both organocopper and organocuprate reagents.

Carbocupration of the acetylenic ketone (6):

We finally examined the addition of organocopper reagents to the ynone derivative **6** (eq-6). The results are presented in Table 3. Whatever the reaction conditions the conjugate addition of n-BuCu or $n\text{-}Bu_2CuLi$ gave a predominant formation of the E adduct **10b(E)**. The percent formation of the Z adduct was higher at very low temperature (entries, 1,3,4) but never exceeded 30%. The E adduct was already formed with a good selectivity at



(6)

RM: RCu, R_2CuLi

10a (Z), R=Me
10b (Z), R=n-Bu

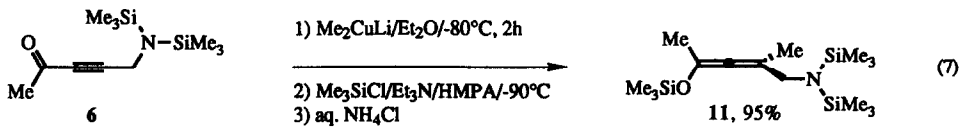
10a (E), R=Me
10b (E), R=n-Bu

Table 3 : Addition of organocopper reagents to the acetylenic ketone (6)

Entry	Reagent	Reaction conditions [a] Temp. (time)	Products ratio [b] Z : E	Yield (%)
1	n-BuCu	-100°C (3.5h)	23 : 77	95
2	n-BuCu	-50°C (3h)	10 : 90	95
3	Me_2CuLi	-90°C (1.5h)	30 : 70	95
4	$n\text{-}Bu_2CuLi$	-100°C (4h)	25 : 75	95
5	$n\text{-}Bu_2CuLi$	-50°C (1h)	05 : 95	95

a) An ethereal or THF solution of **6** was added to the copper reagent at low temperature, the mixture was then stirred for a few hours and quenched by addition of methanol. b) Determined by ^1H NMR.

-50°C. Although the adducts **10(Z),10(E)** formed upon protonolysis of the reaction mixture were not isolated, the treatment with chlorotrimethylsilane prior to the hydrolytic work up allowed trapping of the intermediate to yield the silyl allenolate **11** (eq-7). Interestingly, **11** reacted with MeLi to give, after quenching the lithium allenolate with MeOH, a 2 : 3 mixture of compounds **10a(Z)** and **10a(E)**, respectively.



(7)

3-Mechanistic Considerations.

The stereochemistry of the Michael addition of organocopper (I) species to acetylenic esters has been interpreted in term of kinetic cis addition to the carbon-carbon triple bond [20-26]. The observed cis-stereoselectivity of the addition at low temperature was explained by the initial formation of a cis-vinyl cuprate intermediate, while the loss of stereoselectivity at higher temperature was attributed to the formation of the trans vinyl cuprate possibly via a copper allenolate intermediate.

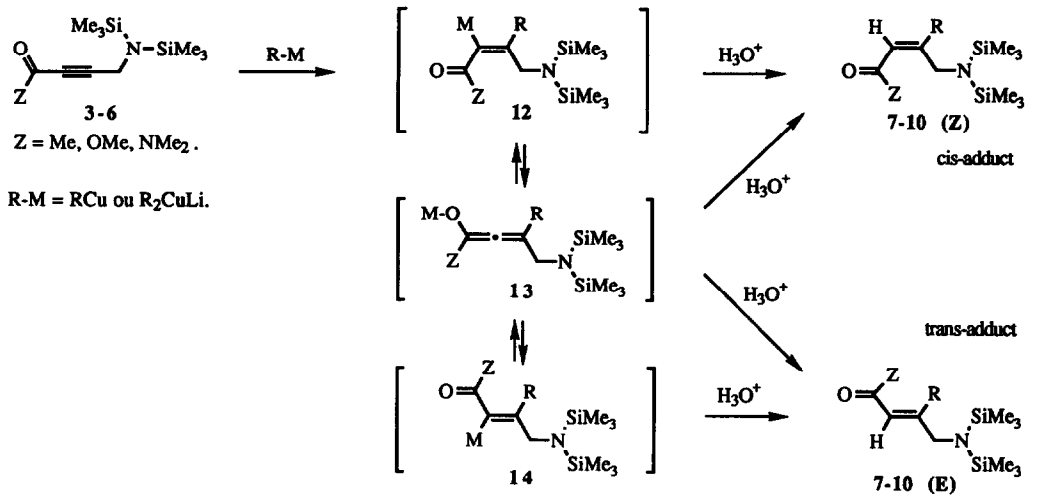
An analogous mechanistic scheme can account for the carbocupration of γ-amino acetylenic derivatives **3-6** (scheme 2). A kinetic cis addition leads to the vinyl copper species **12** which then can isomerize to the trans vinyl copper species **14** through the intermediate allenolate **13.** Although structures of type **12-14** are simplistic representation of the intermediates, the structures of which are more complex [26], they have been proposed as intermediates and used for clarity [20-25]. The protonolysis of intermediates **12** and **14** should selectively lead to the cis and trans adducts respectively, while the protonolysis of **13** should give a mixture of adducts.

The stereochemical results obtained (table 1-3) are consistent with a kinetic cis-addition followed by a more or less rapid isomerisation.

When the isomerisation is slow, the kinetic cis-addition gave in most cases (Table 1, entries 1,4,7 ; Table 2, entry 1) a selective formation of the cis adducts. Under conditions where the kinetic vinyl copper species **12** are allowed to isomerise, a mixture of cis and trans adducts was obtained (Table 1, entries 5,6 ; Table 2, entries 2,3,6,7,10). The E : Z ratio is related to the relative stability of intermediates **12-14.** The rate of isomerisation **12-14** is dependent both on the substrate and on the reagent : i) organocopper adducts of amide **3** (Z = NMe_2) isomerised much slower than those of the esters **4, 5** (Z = OR) and ketone **6** (Z = OMe). A kinetic low

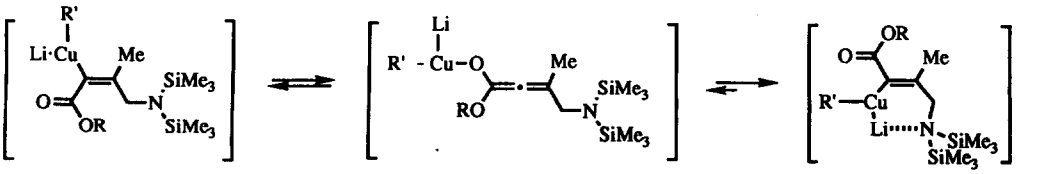
temperature cis addition was observed in all cases of table 1, while predominant trans adduct were formed in all experiments of table 3. ii) The isomerisation of RCu adducts is slow (a major cis-addition to amide 3 was observed even at room temperature) while the isomerization of organocuprates R_2CuLi adduct is more rapid (trans addition to esters **4, 5** was already observed at low temperature).

Scheme 2 : Organo Copper Addition to Compounds 3-6



However the mechanistic scheme 2 does not perfectly account for the stereoselectivity of the addition of methyl cuprate to esters **4** and **5** (Table 2, entries 5, 8, 9, 11, 13). Whereas a rapid isomerization of the kinetic cis-adducts occurs even at low temperature, the thermodynamic mixture was obtained at 0°C and selective trans addition was found to occur at - 50°C. The selective obtention of the trans-adduct cannot be accomodated for by a protonolysis of the intermediates **12** and **13** which should lead to the exclusive or predominant formation of cis adducts. The selective formation of trans adducts seems to arise from protonation of the vinyl copper species **14.** The reason for the stability of this structure may lie in an intramolecular coordination of the nitrogen atom (scheme 3). An intramolecular stabilisation has been shown for example to reverse the regioselectivity of organocuprates addition on propargylic dialkylamines [27]. An isomerization favoring one stereoisomer by intramolecular chelation was also observed in the carbometallation of functionalized silylalkynes by Grignard reagents [28]. In the present case, owing to the low nucleophilicity of the $(Me_3Si)_2N$ groups, an intramolecular coordination is less favorable. Nevertheless, a lithium-nitrogen interaction in **14** (scheme 3) can account for the change in selectivity between butyl copper and organocuprate reagents and for a highly selective trans addition to

Scheme 3: Intramolecular Stabilisation of Vinyl Cuprate **14**, (R=Me, Et; R'=Me, Hexynyl)



acetylenic esters at low temperature. It was however not observed in the case of organocuprate addition to amides. In this case, intramolecular stabilization can be provided by the amino group [29] whatever the Z or E stereochemistry of the intermediates **12-14** and may also account for the high thermal stability of the amino vinyl copper species.

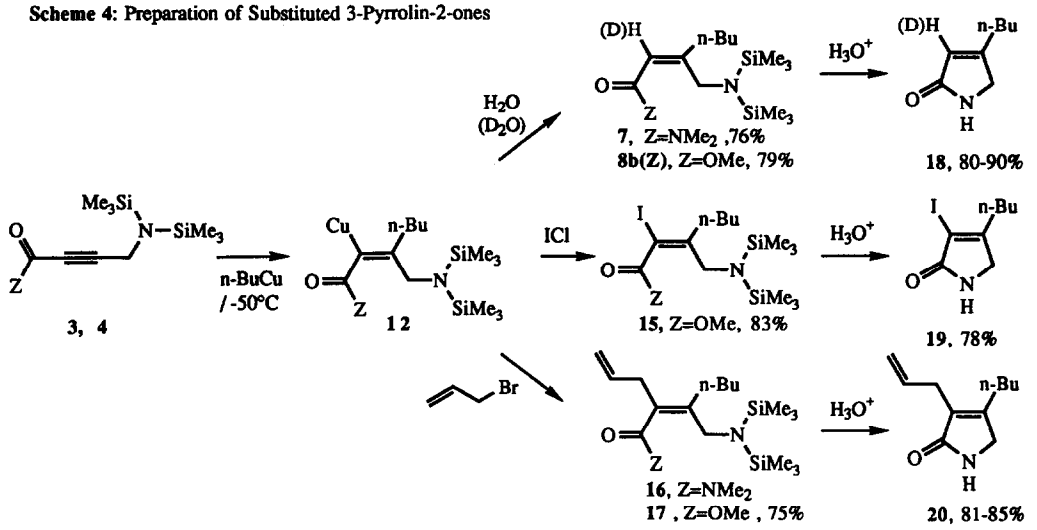
4-Synthetic Uses.

From a synthetic point of view, the addition reactions of organocopper reagents to γ-amino acetylenic amide, esters and ketone are of interest since they allow selective preparation of acryclic derivatives with Z or E configuration. A judicious choice of substrate, reagent and (or) reaction conditions should allow generation and t reaction of either the copper intermediate **12** and **14** (scheme 2). Moreover, reactions of the allenolate form **13** should also be obtained upon prior trapping with chlorotrimethylsilane (eq-7). We wish to show below that the reactions of the γ-bis (trimethylsilyl)amino copper species **12-14** are of potential interest for the synthesis of 5-membered nitrogen heterocycles.

i) Cis-addition of n-butyl copper : synthesis of substituted 3-pyrrolin-2-ones:

The reactions of n-butyl copper with the γ - amino acetylenic amide **3** or ester **4** at low temperature allow the selective formation of the cis-addition species **12.** Quenching of this vinyl copper intermediate with electrophiles such as H_2O, D_2O, ICl or allylbromide, led to the expected adducts **7, 8, 15-17**(scheme 4) in 75 to 83%

Scheme 4: Preparation of Substituted 3-Pyrrolin-2-ones

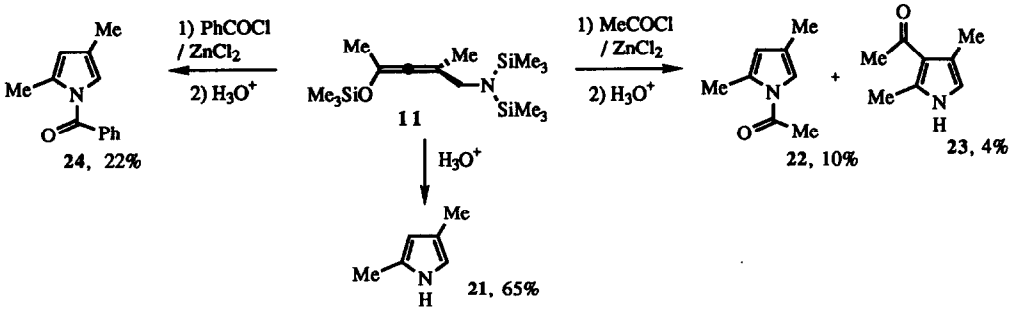


isolated yields. These γ-bis (silyl)amino acrylic derivatives underwent desilylation and cyclization under weak acidic conditions. The treatment of compounds **8b(Z), 8b(Z)(D),15,17** with oxalic acid in acetone afforded the lactams **18-20** in 78 to 90% yield. It is also worth noting that the substituted 3-pyrrolin-2-ones can be obtained in a one pot reaction. It is not necessary to isolate the acrylic intermediate compounds, the treatment of crude reaction product with acid gave the cyclic derivatives in 50 to 60% overall yields based on the starting ester or amide.

ii) Reactions of the allenoxysilane (11).

Whereas the intermediate allenolate **13** cannot be reacted directly, as shown in equation 7 it was trapped by silylation with chlorotrimethylsilane. The allenoxysilanes which were first described by Dunogues et al. are interesting functional molecules[30] and silyl enol ethers have been widely used in organic synthesis[31]. Compound **11** with a protected γ- amino group is a bifunctional molecule from which heterocyclization products should be obtainable. The reaction of electrophiles with **11** gave pyrrole derivatives **21-24** (scheme 5).

Scheme 5: Reactions of the Allenoxysilane **11**

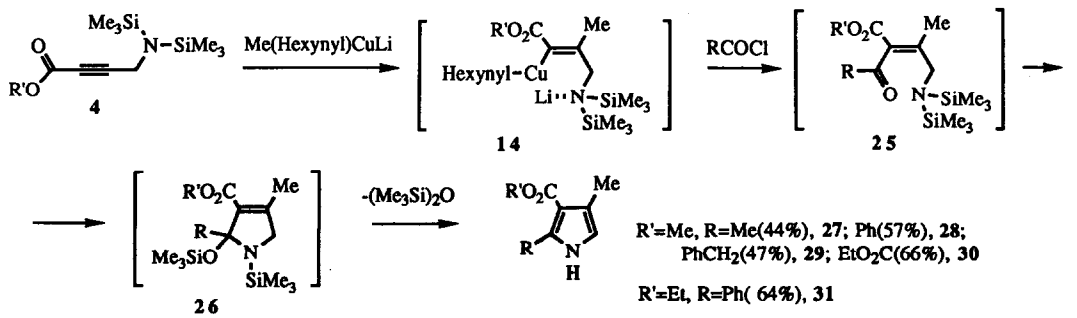


The acid hydrolysis afforded 2,4 - dimethyl pyrrole **21** in 65% yield. It arises from an intramolecular reaction of the γ - amino group with the carbonyl function liberated upon protonolysis of the enoxysilane moiety in **11**. The reaction of acid chlorides in the presence of zinc chloride also allowed isolation of pyrrole derivatives **22, 23** and **24** however in low yield. The formation of N-acyl and N-benzoyl derivatives probably results from an initial attack of the electrophilic reagent at the nitrogen atom of the bis(silyl)amino group. The synthetic uses of **11** therefore seem somewhat limited.

iii) Trans-addition of organo cuprates: synthesis of substituted pyrroles.

The reaction of organocuprates with the γ- aminoacetylenic esters **4, 5** at low temperature selectively led to the trans-addition species **14**. The reaction of the vinyl cuprate **14** offers the possibility to introduce a new functional group in a cis position with respect to the amino methyl substituent. It opens new possibilities of cyclization to nitrogen heterocycles. We found that acid chlorides readily reacted to give substituted pyrroles (scheme 6). The reaction of the acid chloride probably led to the expected protected γ - amino enone **25**. It was

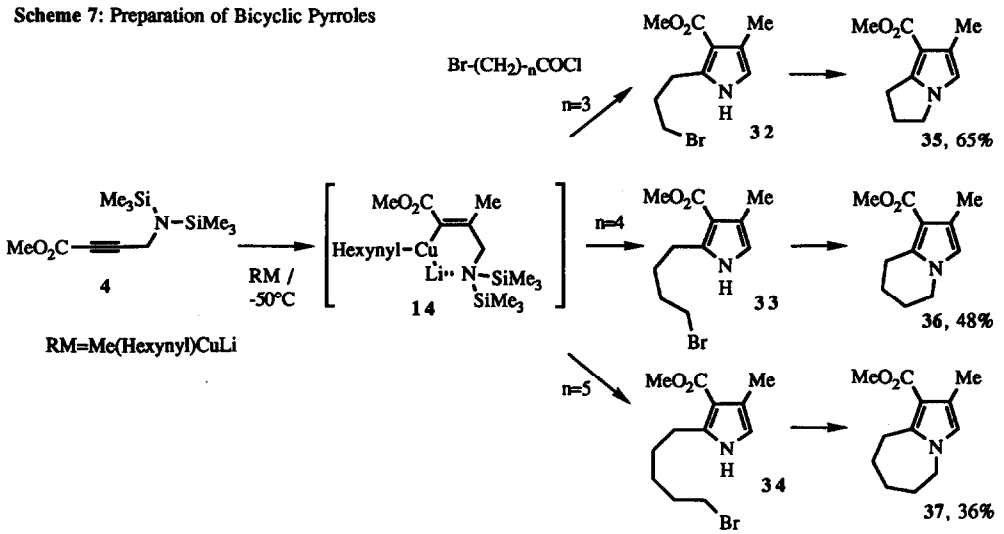
Scheme 6: Preparation of Substituted Pyrroles



not isolated and underwent cyclization to intermediate **26** probably via an intramolecular reaction of the cis orientated silylamino group and carbonyl function. Then upon elimination of siloxane the cyclic intermediate **26** afforded the aromatic pyrrole derivatives **27-31** in 44 to 66% yield. According to this method, functional pyrroles are obtained from readily available starting materials [32].

The synthesis of pyrrole according to scheme 6 is an interesting illustration of the versatility of the silicon -nitrogen bond in organic synthesis. The bis-(trimethylsilyl)amino group $(Me_3Si)_2N$ play three successive roles in this one-pot pyrrole synthesis. First, it is a protected primary amino group allowing the cuprate reaction. Then it directs the stereochemisty of the cuprate addtion by stabilizing the trans - adduct via chelation. Finally, it is reactive enough to cause cyclization upon nucleophilic attack at the cis-orientated carbonyl group. The synthetic interest of this new route to functional pyrroles was illustrated in a short preparation of bicyclic molecules (scheme 7). The reaction of the vinyl cuprate species **14** with ω-bromoalkyl acid chlorides gave the ω-bromo alkyl pyrroles **32-34**. The latter were not isolated and the treatment of the crude reaction products with KOH in the presence of TDA_1 as phase transfer catalyst [33] resulted in the obtention of the bicyclic compounds **35-37** in 36 to 65% yields based on the starting aminomethylpropiolate **4**. Such ring systems are well represented as structural subfeatures in alkaloïds [34].

Scheme 7: Preparation of Bicyclic Pyrroles



Experimental

General Remarks :

All reactions were performed under an atmosphere of nitrogen and using standard vacuum line and Schlenk tube techniques [35]. Melting points were determined using a Gallenkamp apparatus and are uncorrected. Solvents were dried and distilled before use. IR spectra were recorded on a Perkin-Elmer 298 or Perkin-Elmer 1600 FT spectrometer in the form indicated. ^1H NMR spectra were recorded on a Bruker AW-60, AW-80 or AC-250 spectrometer. ^{13}C spectra were recorded on Bruker WP 200 instrument. Chemical shifts are relative to Me_4Si. Mass spectra were obtained on a Jeol-JMS DX 300 instrument. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS.

Preparation of functional N,N-bis(trimethylsilyl)propargyl amine : **N,N-dimethyl-4-N',N'-bis(trimethylsilyl)amino but-2-yne amide (3).** To a solution of 3 N, N-bis (trimethylsily)amino prop-1-yne **1** (prepared as described [16b]) (40.0 g, 0.20 mol) in 150 mL of hexane at -20°C was added a solution of n- butyllithium in hexane (0.20 mol) . The mixture was warmed to room temperature for 0.5 h and cooled again at - 20°C. Then 21.5 g (0.2 mol) of N,N - dimethyl chloroformate in hexane was added and the resulting solution was stirred for 2h and allowed to warm to room temperature for an additionnal 2h. After filtration, the mixture was washed with aq. NH_4Cl, extracted with ether, dried over $MgSO_4$. The solvents were removed under reduced pressure and distillation of the residue gave 38.0 g (yield, 70%) of the amide **3** as a pale yellow oil. B.p. 95-98°C, 0.05 mmHg. ^1H NMR ($CDCl_3$): 0.08 (s, 18H, 6x$SiCH_3$), 2.81 (s, 3H, NCH_3), 3.05 (s, 3H, NCH_3), 3.61 (s, 2H, CH_2N) ; ^{13}C NMR ($CDCl_3$) : 2.3 ($SiCH_3$), 34.7 (NCH_3), 35.0 (NCH_3), 38.8 (CH_2N) 75.6, 94.4 (C≡C), 155.2 (C=O) ; IR (CCl_4): 2956, 2232, 1643, 1395, 12453, 1070, 1024 cm^{-1} ; EI mass spectrum: m/e(relative intensity): 270 (M^+, 80%), 255 (M^+- Me, 68%), 228 (12%), 73 (Me_3Si, 100%). Anal. Calcd. for $C_{12}H_{26}N_2OSi_2$ (270.52) : C, 53.28 ; H, 9.69 ; N, 10.36 ; Si, 20.76. Found : C, 54.07; H, 9.67 ; N, 10.36 ; Si, 20.77. **Methyl-4-N,N-bis (trimethylsilyl)amino but-2-ynoate (4).** To a solution of 3 - N,N - bis (trimethylsilyl)amino prop-1-yne **1** (prepared as described [16b] (48.0 g, 0.24 mol in hexane (150 mL) at - 40°C was added a solution of n-butyllithium in hexane (0.25 mol.) and the mixture was then warmed to room temperature. It was cooled again to -40°C and methyl chloroformate (23.6 g, 0.25 mol) in 50 ml of hexane was added. The reaction mixture was kept at - 40°C for 2h then warmed to room temperature and stirred for 12h.. After filtration, the solution was concentrated and the residue was extracted with pentane. After evaporation of the solvent, the residual oil was distilled to give 43 g (yield, 71%) of the amino ester **4**. b.p. 77°C, 0.15 mmHg. ^1H NMR (CCl_4) : 0.20 (s,18H, 6x$SiCH_3$), 3.35 (s, 2H, CH_2N), 3.40 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) : 1.73 (CH_3Si), 34.40 (CH_2N), 52.65 (CH_3O), 74.33 (C≡ CCH_2), 90.30 (MeO_2 C - C≡), 154.5 (-CO_2CH_3). IR (CCl_4) : 2230, 1730 cm^{-1}. EI mass spectrum: m/e: 257 (M^+). Anal. Calcd. for $C_{11}H_{23}NO_2Si_2$: C, 51.31; H, 9.00 ; N, 5.44. Found : C, 51.45 ; H, 9.28 ; N, 5.37. **Ethyl-4-N,N-bis(trimethylsilyl)amino but-2-ynoate (5).** The above method, using 96 mL (0.24 mol) of a 2.5 M n-butyllithium solution in hexane, 45.0 g (0.23 mol) of propargylamine **1** and 27.1 g (0.25 mol.) of ethyl chloroformate, allowed isolation of 48.8 g (yield, 78%) of the bis(silyl)amino ester **5**. b.p. 90°C, 0.15 mm Hg. ^1H NMR (CCl_4) : 0.18 (s, 18H, 6x$SiCH_3$), 1.30(t, 3H, CH_3CH_2O), 3.65 (s, 2H, CH_2N), 4.15 (q, 2H, CH_3CH_2O); IR (CCl_4): 2240, 1715 cm^{-1}. Mass spectrum: m/e : 271 (M^+). Anal. Calcd. for $C_{12}H_{25}NO_2Si_2$: C, 53.09; H, 9.28; N, 5.10. Found : C 53.04, H 8.72, N 5.09. **5-N,N-bis(trimethylsilyl)amino pent-3-yne-2-one (6).** To a solution (100 mL) of hexane and THF (1/1 mixture) containing 35 mmol of lithium acetylide **2** prepared as above at - 40°C was added dropwise a solution of 4.77 g (35 mmol) $ZnCl_2$ in 30 mL of THF . The reaction mixture was stirred at -40 °C for 1 h, then a solution of 35 mmol of acetyl chlorid in THF was added, the reaction was stirred for an additional hour then the reaction mixture was allowed to warm to room temperature slowly. After stirring for 12 h at room temperature, the mixture was cooled to -40°C and hydrolysed with saturated aqueous NH_4Cl. After work up, the ethereal solution was concentrated under reduced pressure and the distillation gave 6.2 g (yield, 75%) of ynone **6** as a light yellow liquid. B.p. 85-90°C, 0.03 mm Hg (The ynone is very air/H_2O sensitive and should be stored in schlenk tube under nitrogen at low temperature) .^1H NMR ($CDCl_3$) : 0.08 (s, 18H, 6x$SiCH_3$), 2.10 (s, 3H, CH_3), 3.53 (s, 2H, CH_2N). IR (CCl_4) : 2202, 1681cm^{-1}; ^{13}C NMR ($CDCl_3$) : 1.9 (CH_3Si), 32.8 (CH_3CO), 34.6 (CH_2N), 82.5, 94.5 (C≡C), 184.4 (C=O); EI mass spectrum: m/e (relative intensity): 241 (M^+, 6%), 226 (M^+-Me, 25%), 147 (100%), 73 (84%); Anal. calcd. for $C_{11}H_{23}NOSi_2$ (241.48) : C, 54.71 ; H, 9.60 ; N, 5.80. Found C, 54.41; H, 9.70 ; N, 5.39.

Carbocupration of acetylenic amide (3): The addition of alkyl copper and alkyl cuprate reagents were carried out according to the same general procedure. The reaction conditions are indicated in table 1. The Z/E ratio of the adducts was determined by ^1H NMR analysis of the crude reaction mixture. Representative procedures are given. **Addition of n-BuCu:** To a suspension of CuI (3.8 g, 20mmol) in anhydrous diethylether (50 mL) at - 40°C, was added slowly n-BuLi (8mL, 2.5M, 20mmol) in ether. The black mixture was then stirred for 1h at -20°C. A solution of 4.1g(15mmol) of amide **3** in diethylether(50mL) was added dropwise . After the addition , the reaction mixture was stirred for 3h at -20°C . It was then quenched by addition of 20mL of an aqueous saturated NH_4Cl solution. It was then filtered, washed with aq. NH_4Cl, water and then dried over Na_2SO_4. Evaporation of the solvent and distillation of the residue afforded 3.7 g (76%) of compounds **7b(Z+E)**. B.p. 40-45°C, 0.05 mm Hg. ^1H NMR ($CDCl_3$): (Z:E = 92:8) ,**7b(Z)**, Z isomer : 0.02 (s, 18H, 6x$SiCH_3$), 0.8-2.6 (m, 9H, C_4H_9) , 2.81 (s, 6H, 2xNCH_3), 3.93 (s, 2H, CH_2N) , 5.69 (s, 1H, CH=C-CH_2N). **7b(E)**, E isomer : 0.02 (s, 18H, 6x$SiCH_3$), 0.8-2.6 (m, 9H, C_4H_9), 2.84 (s, 6H,

2xNCH$_3$), 3.34 (s, 2H, CH$_2$N), 6.04 (s, 1H , CH=C-CH$_2$N). EI mass spectrum : m/e: 328 (M$^+$). The same experiment after warming a 0°C for 1h before hydrolysis work up gave Z : E = 83 : 17. Similarly warming the reaction mixture at +20°C for 1h gave Z : E = 75 : 25. **Addition of (n-Bu)$_2$CuLi:** To a suspension of CuI (3.8 g, 20 mmol) in diethylether at -50°C was added dropwise an ethereal solution of BuLi (16mL, 2.5M, 40 mmol). After 20 min., the amide 3 (4.1g , 20 mmol) was added and the mixture was stirred for 3h at -50°C .The reaction was then quenched with aqueous saturated NH$_4$Cl solution and after the above work up the ^{1}H NMR analysis of the crude reaction product revealed **7b(Z+E).** (Z:E = 78 : 12). Upon warming the reaction at 0°C for 1h and + 20°C for 1h before the hydrolytic work up, Z : E ratios of 25 : 75 and 16 : 84 were measured respectively. **Addition of Me(Hexynyl)CuLi:** To a solution of MeLi (20 mmol) in ether at 0°C was added dropwise1.65g (2.2mL, 20mmol) of hex-1-yne in 20 mL of diethyl ether. It was stirred for 30 min until the gas evolution ceased and the mixture was then slowly added to 3.8 g (20 mmol) of CuI in diethylether. The yellow reaction mixture was stirred for 30 min. at 0°C and then cooled to - 30°C. Another 20 mmol. of MeLi in diethylether was added and the mixture was slowly warmed to 0°C and cooled again at -50°C. Addition of 4.0g (15mmol) of 3 was followed by stirring for 1.5h. The above hydrolytic work up afforded a mixture of compound **7a(Z)** and **7a(E)** which was distilled to give 4.0g (95 %). B.p. 30-35°C, 0.01 mm Hg, ^{1}H NMR (CDCl$_3$) (Z:E=75:25) **7a(Z),** Z- isomer : 0.08 (s, 18H, 6xSiCH$_3$), 1.70(s, 3H, CH$_3$), 2.90 (s, 3H, NCH$_3$), 3.08 (s, 3H, NCH$_3$), 3.65 (s, 2H, CH$_2$N), 5.75, (s, 1H, CH=C-CH$_2$N). **7a(E),** E - isomer : 0.08 (s, 18H, 6xSiCH$_3$), 1.8 (s, 3H, CH$_3$), 2.90 (s, 3H, NCH3), 3.30 (s, 3H, NCH$_3$), 3.43(s, 2H, CH$_2$N), 6.03 (s, 1H, CH=C-CH$_2$N). Upon warming to 0°C or +20°C before the work up, Z : E ratios of 10 : 90 and 5 : 95 were determined respectively. ^{13}C NMR (CDCl$_3$) of **7a(E)** : 2.0 (CH$_3$Si), 17.0 (CH$_3$), 35.2 (NCH$_3$) , 38.0 (NCH$_3$), 52.3 (CH$_2$N), 116.0 , 152.9 (C = C) ,169.2 (C=O); IR (CCl$_4$) : 2960, 1630, 1390, 1250 cm^{-1}; EI mass spectrum : m/e: 286 (M$^+$, 15%), 271 (M$^+$-Me,28%), 242 (m$^+$ - NMe$_2$, 8%), 174 [CH$_2$N(SiMe$_3$)$_2$, 98%], 73 (SiMe$_3$, 100%).

Carbocupration of acetylenic esters (4, 5): The carbocupration reactions of table 2 were performed as follows: **Addition of n-BuCu:** The reaction was carried out as for the amide 3, using 10 mmol. of n-BuLi in 6 mL of ether, 1.9 g (10 mmol) of CuI and 2.5 g (10 mmol) of methyl ester 4. The above work up afforded 2.6g (79%) of **8b(Z)** . B.p. 120°C, 20 mmHg, ^{1}H NMR (CCl$_4$) Z:E = 95:5 , Z isomer : 0.15 (s, 18H, 6xSiCH$_3$), 0.95 - 2.2 (m, 9H, C$_4$H$_9$), 3.7 (s, 3H, OCH$_3$) 4.18 (s, 2H, CH$_2$N), 5.50 (d, 1H, CH=C-CH$_2$N); IR (CCl$_4$): 1710, 1625cm^{-1}. Anal. calcd. for C$_{15}$H$_{33}$NO$_2$Si$_2$: C, 57.09 ; H, 10.54 ; N, 4.44. Found: C, 57.24 ; H, 10.47 ; N, 4.53. Upon warming to 0°C for 2h, a Z : E ratio of 30 : 70 was found, but cooling the reaction mixture again to -40°C, the above ratio was not changed. **Addition of EtCu:** As above, the reaction of EtCu (prepared from 32 mmol of EtLi in 30 mL of ether and 7.4 g (39 mmol) of CuI with 5 (10.0 g, 37 mmol) at - 40°C for 24h gave after work up 16.7 g (86%) of **9b(Z).** Bp. 110°C, 20 mm Hg. ^{1}H NMR (CCl$_4$) (Z:E = 93:7). 0.10 (s, 18H, 6xSiCH$_3$), 0.82 (t, 3H, CH$_2$CH$_3$), 1.05 (t, 3H, OCH$_2$CH$_3$) 2.05 (q, 2H, CH$_2$CH$_3$), 3.83 (q, 2H, OCH$_2$CH$_3$), 3.9 (s, 2H, CH$_2$N), 5.25 (s, 1H, CH=C-CH$_2$N); IR (CCl$_4$): 1710, 1630cm^{-1}. **Addition of Me$_2$CuLi :** The reaction of Me$_2$CuLi (prepared from 36 mL of a 1.7 M solution of MeLi in diethylether (60 mmol) and 5.7 g (30 mmol) of CuI with 7.5 g (29 mmol) of methyl ester 5 gave 5.2 g of **9a (E)** (77%).Bp. 68-70°C, 0.1 mm Hg ^{1}H NMR (CCl$_4$) : (Z:E = 5:95) E isomer, 0.05 (s, 18H, 6xSiCH$_3$), 1.12 (t, 3H, CH$_3$CH$_2$) 1.90 (s, 3H, CH$_3$), 3.27 (s, 2H, CH$_2$N) , 3.90 (q, 2H, CH$_2$CH$_3$), 5.65 (s, 1H, CH=C-CH$_2$N). IR (CCl$_4$) 1705, 1650 cm^{-1}. **Addition of Et$_2$CuLi:** As above from 9.6 mL (14.8 mmol) of a 1.55 M solution of EtLi in ether, 1.4 g (7.4 mmol) of CuI, and 2.0 g of ethyl ester 5, was isolated 3.2 g (75%) of **9b(E)** ^{1}H NMR (CCl$_4$): 0.10 (s, 18H, 6xSiCH$_3$), 0.83 (t, 3H, CH$_3$CH$_2$), 1.06(t, 3H, OCH$_2$CH$_3$), 2.23(q, 2H, CH$_2$CH$_3$), 3.23 (d, 2H, CH$_2$N), 3.85 (q, 2H, OCH$_2$CH$_3$) , 5.60 (s, 1H, CH=C-CH$_2$N). IR (CCl$_4$) :1705, 1635cm^{-1}.Anal calcd. for C$_{11}$H$_{31}$NO$_2$Si$_2$: C, 55.75 ; H, 10.36; N, 4.64. Found C 54.43 ; H 9.85 ; N 4.77. **Addition of (n-Bu)$_2$CuLi:** 29 mL of n-BuLi (1.72 M solution in diethylether , 50 mmol.), 4.8 g (25 mmol) of CuI and 6.3 g of 4 allowed isolation of 4.6 g (60%) of **8b(E).** Bp. 110°C, 1mm Hg. ^{1}H NMR (CCl$_4$) : Z:E=13:87, E isomer. 0.08 (s, 18H, 6xSiCH$_3$), 0.78 (m, 3H, CH$_3$), 1.22 (m, 4H, CH$_2$CH$_2$-CH$_3$), 2.22 (m, 2H, CH$_2$-CH$_2$CH$_2$CH$_3$), 3.32 (d, 2H, CH$_2$N) , 3.50 (s, 3H, OCH$_3$) 5.71 (t, 1H , CH=C-CH$_2$N). ^{13}C NMR (CDCl$_3$) 1.6 (Me$_3$Si), 13.9, 23.3; 31.0, 31.4(C$_4$H$_9$), 50.8, 51.4 (CH$_2$N, CH$_3$O), 114.0, 166.2 (C = C) , 167.5 (C = O). IR (CCl$_4$) 1718, 1655cm^{-1}. **Addition of Me(hexynyl)CuLi:** By using 36 mL of a 1.7 M solution of MeLi in ether, 3.2 mL (30 mmol) of hex-1-yne, 5.7 g (30 mmol) of CuI and 7.5 g (29 mmol) of methyl ester 4 ; 4.43g of **8a(E)** bp. 65°C, 0.1 mmHg. ^{1}H NMR (CCl$_4$) (Z/E = 4/96) : E isomer : 0.05 (s, 18H, 6xSiCH$_3$) ; 1.87 (s, 3H, CH$_3$) ; 3.27 (s, 2H, CH$_2$N) ; 3.51 (s, 3H,OCH$_3$) ; 6.05 (s, 1H, CH=C-CH2N). ^{13}C NMR (CDCl$_3$) : 1.6 (CH$_3$Si), 30.89 (CH$_3$), 50.78, 52.84 (CH$_2$-N, CH$_2$-O), 114.25 (-CH =), 161.89 (= CCH$_2$N), 167.82 (CO$_2$Me). IR (CCl$_4$) : 1710, 1650 cm^{-1}. Mass spect. m/e : 273 (M$^+$). Anal. calcd. for : C$_{12}$H$_{27}$NO$_2$Si$_2$; C 52.69 ; H 9.95 ; N 5.12. Found : C 53.38 ; H 9.49. N 5.04. The same

reaction performed on ethyl ester **5** gave **9a(E)** (Z/E=5/95) with characteristics similar to those described in the reaction of Me_2CuLi . When the reaction mixture was warmed to 0°C before hydrolytic work up a Z:E ratio of 25:75 was observed. After warming to 0°C, cooling again at -40°C followed by hydrolytic work up gave Z/E = 5/95. No change was observed when Et_3N(0.1 mol) was added to the reaction mixture. **Addition of EtCu/EtLi:** 20 mL (30 mmol) of a 1.5 M solution of ethyllithium in ether were added to a suspension of 5.7 g (30 mmol) of copper (I) iodide in ether at -40°C. The ethyl ester **5** (7.5 g, 29 mmol) was added and the mixture was stirred for 12h at -40°C. It was then added 20 mL (20 mmol) of the ethyllithium solution. The reaction mixture was then quenched by addition of aq. NH_4Cl. The usual work up gave a mixture of **9b(Z), 9b(E)** (Z:E ratio = 32:68) in 75% yield.

Carbocupration of the acetylenic ketone (6): As in the case of the addition of amide **3** and esters **4, 5**. The addition of alkyl copper and cuprate reagent were performed according to the following procedure. **Addition of n-BuCu :** To BuCu prepared from n-BuLi (2.1mL, 2.5M, 5.2mmol) in hexane and Cu I (1.0g, 5.2mmol) in anhydrous diethyl ether (50mL) was added a solution of the ketone **6** (1.0g, 4.1 mmol) in ether or THF. The resulting mixture was kept for the time indicated in table 3. The ^1H NMR analysis of the hydrolysed reaction mixture revealed the ratio of two isomers **10b(Z)** and **10b(E). Addition of Me_2CuLi and $(n\text{-}Bu)_2CuLi$:** It was carried out as for the addition of n-BuCu. The ^1H NMR analysis results are as follows : **10a(Z):** ^1H NMR ($CDCl_3$): 0.05 (s, 18H, 6x$SiCH_3$), 2.10 (s, 3H, CH_3), 2.32 (s, 3H, CH_3CO), 4.00 (s, 2H, CH_2N), 6.00 (s, 1H, C<u>H</u>=C-CH_2N).**10a(E):** ^1H NMR ($CDCl_3$): 0.05 (s, 18H, 6x$SiCH_3$) 2.10 (s, 3H, CH_3), 2.32 (s, 3H, CH_3CO), 3.35 (s, 2H, CH_2N), 6.23 (s, 11H, C<u>H</u>=C-CH_2N). **10b(Z):** ^1H NMR (CDCl3) : 0.05 (s, 18H, 2x$SiCH_3$), 0.8-2.6 (m, 9H, C_4H_9), 2.04 (s, 3H, CH_3CO), 4.03 (s, 2H, CH_2N), 5.58 (s, 1H, C<u>H</u>=C-CH_2N).**10b(E):** ^1H NMR ($CDCl_3$) : 0.05 (s, 18H, 6x$SiCH_3$) ,0.8-2.6 (m, 9H, C_4H_9), 2.04 (s, 3H, MeCO) , 3.39 (s, 2H, CH_2N), 6.28 (s, 1H, C<u>H</u>=C-CH_2N). **Preparation of compound 11**: 20 mmol of ynone **6** were added dropwise to 22 mmol of Me_2CuLi at -80°C. The reaction mixture was stirred at -80°C for 2 hours. A mixture of Me_3SiCl, Et_3N and HMPA (22 mmol/22 mmol/7 mmol : 3/3/1) was added. The resulting reaction mixture was allowed to warm to room temperature slowly , then quenched with NH_4Cl/H_2O saturated solution at -10°C. Extracted with ether, the combined organic phase was dried over $MgSO_4$. After removal of the solvents under vacuum, 6.3g (95%) of allenoxysilane **11** was obtained as light yellow liquid. ^1H NMR ($CDCl_3$) : 0.10 (s, 18H, 6x$SiCH_3$), 0.13 (s, 9H, Me_3SiO), 1.60(s, 3H, CH_3), 1.79 (s, 3H, CH_3), 3.33 (s, 2H, CH_2N) ; ^{13}C NMR ($CDCl_3$) : 0.4 ($OSiMe_3$), 2.2 ($NSiMe_3$) 18.7, 21.5 (2x CH_3), 49.9 (<u>C</u>H_2N), 113.0, 123.0 (<u>C</u> = C = <u>C</u>), 192.3 (C = <u>C</u> = C) ; IR (CCl_4) : 1967.9 (√ C = C = C strong absorption). Anal. Calcd. for $C_{15}H_{35}ONSi_3$ (329.70): C, 54.64 ; H 10.70. Found : C, 54.52 ; H, 11.00

Synthesis of substituted 3-pyrrolin-2-ones: **From amide (3) : Compound 18 :** To a solution of the mixture of **7b(Z)** and **7b(E)** (Z:E=92:8, 3.7 g, 11.3 mmol) in 50 ml of CH_3OH was added 0.5 g KF at room temperature. The resulting solution was stirred for 3 days. After evaporation of solvent, the preparative T.L.C. (ether as eluant) gave 1.4 g (90%) of 4-butyl-pyrroline-2-ones **18** mp 62-64°C, ^1H NMR (CCl_4) 0.9 (3H, m), 1.1- 1.8 (4H, m) ; 2.1-2.5 (2H, m) ; 3.8 (2, s), 5.6 (1H, s) ; 8.55 (1H, s). IR (CCl_4) : 3250, 1680 cm-1. Mass spectrum (EI) m/e 139 (M^+). Anal. calcd. for $C_8H_{13}NO$: C 69.02 ; H, 9.41 ; N 10.06. Found C; 69.35 ; H, 9.52 ; N, 9.93.: **Compound 20** : Allylbromide (2.4 g, 20 mmol) reacted with the vinyl copper (20 mmol) which was prepared from the reaction of amide **3** with butyl copper. After 1 hour of stirring at -50°C, the reaction mixture was allowed to warm to room temperature and hydrolysed with aqueous solution of amonium chlorid, extracted with ether. The combined etheral solution was dried over $MgSO_4$. The solvent was removed and the residue was subjected the T.L.C. separation. The pyrroline - 2 - one derivative **20** was obtained directly in 85% yield. Mp : 68-70°C. ^1H NMR (CCl_4) : 0.89 (3H, t) 1.1 - 1.95 (4H, m) ; 2.0-2.5 (2H, m), 2.85 (2H, d); 3.75 (2H, s) ; 4.70 (1H, s) ; 4.90 (1H, d) ; 5.2 - 6.1 (1H, m) ; 8.75 (1H, s). ^{13}C NMR(CDCl3): 14.2, 23.0, 27.8, 27.9, 31.0, 49.1(CH_2N), 115.6, 130.2, 135.3, 155.6, (<u>C</u>H=<u>C</u>H, <u>C</u>H_2=<u>C</u>H), 176.5(<u>C</u>=O); IR (CCl_4) ; 3200, 1680 cm^{-1}. Mass spect. (EI) m/e : 179 (M^+) Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70 ; H, 9.56 ; N, 7.71. Found : C, 73.95 ; H, 9.85 ; N, 7.65. **From ester (4) :** The addition reaction of n-butyl copper to the amino acetylenic ether **4** , follwed by desilylation and cyclisation to pyrrolinones were carried out according to the following procedure. A solution of n-butyllithium (10 mmol) in ether was added at -40°C to a suspension containing (10 mmol) of CuI in ether. The mixture was stirred for 30 min. at -40°C, then a solution containing (10 mmol) of ester **4** in 5 mL of ether was added. The reaction mixture was kept at -40°C for 1.5h and then it was quenched upon addition of an excess of electrophilic reagent. After warming slowly to room temperature the suspension was filtered, the solution eventually dried over Na_2SO_4 and the solvent evaporated. Distillation of the residue, afford the acrylic derivatives **8b(Z), 8b(D)(Z),15,17.** These were dissolved in acetone 10 mL and 10 mL of a saturated aqueous oxalic acid solution was added. The mixture warmed and the acetone was removed in vacuo, extraction of the residue with

ether and neutralization with a saturated aqueous $NaHCO_3$ solution. After washing with water, its was dried over sodium sulfate. The pyrrolinone **18-20** were isolated upon crystallization from pentane. **Compound 18 and 18(D) :** The reaction was carried out, as described above, using 6 mL (10 mmol) of a 1.7 M solution of n-Butyllithium, 1.9 g (10 mmol) of CuI and 2.6 g of methyl ester **4**. Hydrolysis at -40°C afforded 79% of acrylic derivative **8b(Z)** with characteristic identical to those described in exp. Similarly deuterolysis of the reaction mixture afforded the deuterated derivative **8b(Z)(D)** . 2.35 g (75%) B.p. 120-122°C, 20 mmHg. ^1H NMR (CCl_4) 0.10 (18 H, s), 0.92 (3H, t) ; 1.55 (4H, m) ; 2.35 (2H, m) ; 3.65 (3H, s) ; 4.12 (2H, s). IR (CCl_4) : 1710, 1610 cm^{-1}. Compound **8b(Z)** (3.3 g, 10 mmol) was hydrolysed with aq. oxalic acid and led to 1.15 g of 4-butyl pyrrol-3-in-2 one **18** (83%) with the same characteristics as that prepared from amide **3**. The hydrolysis of the deuterated compound **8b(Z)(D)** (2.4 g, 8 mM) afforded 0.9 g (80%) of 3-deutero - 4 - butyl pyrrol-3-in-2-one **18(D)**. Mp. 63-64°C. ^1H NMR (CCl_4) : 0.9 (3H,t), 1.2-1.7 (4H, m), 2.1-2.50 (2H, m, 3.8 (2H,s), 8.6 (1H,s). IR (CCl_4) 3250, 1680 cm^{-1}. mass spect. (EI) m/e : 140 (M^+).**Compound 19** : As above using 7.5mL (10 mmol) of a 1.33 M solution of n-butyllithium, 1.9 g (10 mmol) of CuI, 2.6 g (10 mmol) of methyl ester **4** and 2.0 g (12 mmol) of iodine chloride, gave 3.8 g of crude acrylic derivative **15**(83%). ^1H NMR (CCl_4) /0.10 (18H, s), 0.95 (3H, t), 1.40 (4H, m), 2.32 (2H, m), 3.70 (3H, s), 3.75 (2H, s). IR (CCl_4) 1708, 1610 cm^{-1}. Hydrolysis of crude **15** gave 2.07g of 3 -iodo-4-butyl pyrrol-3- in -2-one **19** (78%). Mp. 70-72°C. ^1H NMR (CCl_4) : 0.95 (3H, t), 1.2-1.8 (4H, m), 2-2 - 2.7 (2H, m), 4.1 (2H, s), 8.8 (1H, s). IR (CCl_4) 3210, 1680 cm^{-1}. Mass spectrum. M/e : 265 (M^+) Anal. calcd. for $C_8H_{12}NOI$: C, 36.23 ; H, 4.56 ; N, 5.28. Found C, 36.55 ; H, 4.67 ; N, 5.14.**Compound 20** : As above using 7.5 mL (10 mmol) of a 1.33 M solution of n-butyl lithium in ether, 1.9 g (10 mmol) of Cu I ; 1.6 g (10 mmol) of methyl ester **4**, 3 mL (14 mM) of allybromide and 2 mL (11mmol) of HMPT afforded 2.75 g (75%) of acryclic derivative **17**. bp. 130°C, 20 mm Hg. ^1H NMR (CCl_4) : 0.10 (18 H, s), 0.9 (3H, t), 1.55 (4H, m), 2.35 (2H, m), 3.10 (2H, d), 3.70 (3H, s), 3.95 (2H, s), 4.90 (1H, m), 5.10 (1H, d), 5.4-6.1 (1H, m). IR (CCl_4) 1710, 1665, 1630 cm^{-1}. Hydrolysis with aq. oxalic acid gave 1.09 g of 3 - allyl- 4 - butyl pyrrol - 3 - in -2 - one **20** (81%) with the identical characteristics as that prepared from the amide **3**.

Reactions of the allenoxysilane 11 : **Hydrolysis** : 0.68 g (2.1 mmol) of allenoxysilane **11** was dissolved in 5 ml of CCl_4. A solution of 3N HCl was added. After 10 mn of stirring, the organic phase was separated. The aqueous phase was neutralized with a solution of $NaHCO_3$, until the pH value > 10. Extracted with ether, the combined etheral solution was dried and concentrated. The residue was subjected the T.L.C. preparative seperation (CH_2Cl_2 as eluant) 0.13 g (65%)of 2,4-dimethyl pyrrole **21** was obtained . ^1H NMR ($CDCl_3$) was identical with the reported value for this compound[36]. **Reactions with Acetyl Chloride :** 1.3 g (4.0 mmol) of allenoxysilane **11** was mixed with 0.54 g (4.0 mmol) of $ZnCl_2$ in CH_2Cl_2 and cooled to -78°C. A solution of 0.62 g (8 mmol) of acetylic chloride in CH_2Cl_2 was added. The reaction mixture was allowed to warm to room temperature. After hydrolytic work up the T.L.C. seperation give 0.05 g of **22** in 10% yield ^1H NMR ($CDCl_3$) : 1.90 (s, 3H, CH_3CO) 2.30 (d, 6H, 2 x Me), 5.6 (s, 1H, H-pyrrolic) 6.6 (s, 1H, H-pyrrilic). IR (CCl_4) : 1721 cm^{-1} 0.02g (4%)of **23** , ^1H NMR ($CDCl_3$): 2.24(s, 3H, CH_3CO), 2.39(s, 3H, CH_3), 2.46(s, 3H, CH_3), 8.66(bs, 1H, NH); IR(CCl_4): 1641, 3462 cm^{-1}[37]. **Reaction with Benzoyl Chloride :** As above, from 1.68g(4.86mmol) of allenoxysilane **11** and 0.7g (5.00mmol), 0.20g(22%) of **24** was obtained ^1H NMR ($CDCl_3$): 1.90(s, 3H, CH_3), 2.50(s, 3H, CH_3), 5.9(s, 1H, H-pyrrolic), 6.50(s, 1H, H-pyrrolic), 7.2-7.8(m, 5H, phenyl) [38]

Synthesis of substituted pyrroles. **General procedure**: To a solution of Me(Hexynyl)CuLi (1 mol) at -40°C, was added the ester **4** or **5** (1 mol. equivalent) and the mixture stirred for 2h. 1 mol. equivalent of acid chloride in ether (0.5 M solution) was finally added. The mixture was stirred for 2h at - 40°C and warmed slowly at 20°C. After 12h, the crude reaction mixture was hydrolysed with aqueous NH_4Cl, filtrated, extracted with ether. The organic layer was collected, washed with water, dried over sodium sulfate. After evaporation of the solvent the crude product was dissolved in THF and refluxed with 10g of silicic acid. After filtration and evaporation of THF the residue was purified by column chromatography over silica gel Et_2O/hexane : 4/1 or crystallization. **2,4-Dimethyl-3-carbomethoxy pyrrole (27)** : The use of 2.9 mL (25 mmol) of hex-1-yne 31.2 mL (50 mmol) of a 1.6 M solution of MeLi in ether, 4.75 g (25 mmol) of CuI, 6.5 g (25 mmol) of ester **4** and 1.8 mL (25 mmol) of acetyle chloride gave 1.7 g (44%) of pyrrole **27**. Mp. 97°C. ^1H NMR (CCl_4) : 2.17 (3H, s), 2.39 (3H, s), 3.79 (3H, s) 6.40 (1H, s), 8.5-8.9 (1H, bs). IR ($CHCl_3$) 3470, 1700, 1260 cm^{-1}. Mass spectr. (EI)) m/e 153 (M^+). Anal. calcd. for $C_8H_{11}NO_2$: C, 62.72; H, 7.23 ; N, 9.14. Found : C, 63.32 ; H, 6.50 ; N, 9.34. **2-Phenyl-3-carbomethoxy-4-methyl pyrrole (28)** : The above method using 4.6 mL (42 mmol) of hex-1-yne, 40 mL (82 mmol) of a 2.05 M solution of methyllithium in ether, 7.92g (41 mmol) of CuI, 7.63 g, 30 mmol. of ester **4** and 4.7 mL (41 mmol.) of benzoyl chloride led to 3.7 g (57%) of **28**. Mp.

85°C. ^{1}H NMR (CCl_4) : 2.17 (3H, s) ; 3.50 (3H, s) ; 6.27 (1H, s) ; 7.25 (5H, s) 8.6-9.0 (1H, bs). IR (CCl_4) : 3460, 1685, 1272 cm^{-1}. Mass spectr. (FAB) m/e : 216 ($M+H^+$) Anal. calcd. for $C_{13}H_{13}NO_2$; C, 72.44 ; H, 6.08 ; N, 6.50. Found C, 72.71 ; H, 6.17 ; N, 6.81. **2-Benzyl-3-carbomethoxy-4-methyl pyrrole (29)** : The use of 4.6 mL (42 mmol) of hex-1-yne, 36 mL (84 mmol) of a 2.35 M solution of MeLi in ether, 7.92g (42 mmol) of CuI, 7.63 g (30 mmol) of ester **4** and 6.5 g (42 mmol) of phenylacetyl chloride led to 3.2 g (47%) of pyrrole **29**. Mp. 96°C . ^{1}H NMR ($CDCl_3$) : 2.2 (3H, s), 3.7 (3H, s), 4.15 (2H, s), 6.15 (1H, s) , 7.05 (5H, s), 7.4-8.1 (1H, bs). ^{13}C NMR ($CDCl_3$) 12.54 ($\underline{C}H_3$), 34.18 ($\underline{C}H_2Ph$), 50.51 ($\underline{C}H_3O$), 110.97, 115.21, 126.94, 129.04, 129.31, 131.30, 138.44 (aromatic $\underline{C}$), 166.77 ($\underline{C}$ = O). IR ($CHCl_3$) : 3450, 1690 cm^{-1}. Mass spect/ (FAB) m/e 230 ($M+H^+$). Anal. calcd. for $C_{14}H_{15}NO_2$: C, 73.34 ; H, 6.59 ; N, 6.11. Found : C, 73.12 ; H, 6.66 ; N, 6.26. **2-Carboethoxy-3-carbomethoxy-4-methyl pyrrole (30)** : The use of 2.9 mL (25 mmol) of hex-1-yne 26.7 mL (50 mmol) of a 1.82 M solution of MeLi in ether, 4.8 g (25 mmol) of CuI, 4.63 g (18 mmol) of ester **4** and 2.8 mL (25 mmol) of ethyl oxalyl chloride afforded 2.51g (66%) of pyrrole **30**. Mp. 86°C. ^{1}H NMR ($CDCl_3$) : 1.27 (3H, t) ; 2.10 (3H, s) 3.81 (3H, s) ; 4.19 (2H, q) ; 6.55 (1H, s) ; 9.89 -10.0 (1H, bs). ^{13}C NMR ($CDCl_3$) : 10.90 ($\underline{C}H_3CH_2$), 14.26 ($\underline{C}H_3$Pyr), 51.65 ($\underline{C}H_3O$), 60.87 ($\underline{C}H_2O$), 116.50, 120.21, 122.11, 122.45 (pyrrolic $\underline{C}$), 160.28, 166.04 ($\underline{C}$ = O). IR ($CHCl_3$) : 3450, 1720, 1690 cm^{-1}. Mass spect. (EI) m/e : 211 (M^+). Anal. calcd. for $C_{10}H_{13}NO_4$: C, 56.86 ; H : 6.20 ; N, 6.63. Found : C, 56.65 ; H, 6.20 ; N, 6.28. **2-Phenyl-3-carboethoxy-4-methyl pyrrole (31)** : The use of hex-1-yne (2.3 mL, 20.5 mmol) 21.6 mL (41 mmol.) of a 1.9 M solution of MeLi in ether, 3.98 (20.5 mmol) of CuI, 5.42 g (20 mM) of ester **5** and 2.4 mmol of benzoyle chloride allowed isolation of 2.9 g (64%) of **31**. Mp. 114°C. ^{1}H NMR ($CDCl_3$) : 1.02 (3H, t), 2.15 (3H, s), 3.92 (2H, q), 6.21 (1H, s), 7.12 (5H, m), 8.47 (1H, bs). ^{13}C NMR ($CDCl_3$) 12.50 ($\underline{C}H_3$), 14.14 ($\underline{C}H_3CH_2O$), 59.45 ($\underline{C}H_2O$, 111.52, 116.95, 122.60, 128.03, 129.22, 132.18, 133.33, 137.75 (aromatic C) 166.18 ($\underline{C}$ = O). IR (CCl_4) : 3440, 1690 cm^{-1}. Mass spect. (EI), m/e 229 (M^+). Anal. calcd. of $C_{14}H_{15}NO_2$: C, 73.34 ; H, 6.59 ; N , 6.11. Found : C, 73.70; H, 6.61 ; N, 6.15.

Synthesis of bicyclic pyrrole derivatives: **1-Carbomethoxy-2-methyl-[1,2a]pyrrolopyrrolidine (35)** : To a solution of Me(Hexynyl)CuLi (41 mmol) at -40°C,was added dropwise 7.63 g (30 mmol) of ester **4**. After stirring for 2h., 4.82 mL (41 mmol) of 4-bromobutylryl chloride were introduced in the reaction vessel. The mixture slowly warmed to room temperature overnight and was hydrolysed with aqueous NH_4Cl. Filtration, extraction and drying of the organic layer gave after removal of the solvent an oily residue. The crude reaction product was dissolved in toluene (30 mL) and heated at 70°C with 3.4 g (69 mmol) of KOH in the presence of TDA-1 (3 mmol) as phase transfer catalyst [33] for 5h. Evaporation of the solvent (neutral alumina, Et_2O/hexane : 1/4) gave 3.5 g (65%) of **35** . Mp. 53-54°C. ^{1}H NMR (CCl_4) : 2.10 (3H, s), 2.35 (2H, m), 2.78 (2H, t), 3.6 (3H, s), 3.76 (2H, t), 6.08 (1H, s) ; ^{13}C NMR ($CDCl_3$) : 12.45 ($\underline{C}H_3$), 26.28, 26.63 ($\underline{C}H_2$-$\underline{C}H_2$-CH_2N), 46.92 ($\underline{C}H_2N$), 50.35 ($\underline{C}H_3O$), 87.50, 113.28, 126.50, 144.75 (pyrrolic $\underline{C}$), 166.75 ($\underline{C}O_2Me$). IR (CCl_4) 1670 cm^{-1}. Mass spectr. (EI) m/e : 179(M^+). Anal. calcd. for $C_{10}H_{13}NO_2$: C, 67.02 ; H, 7.31, N, 7.82. Found : C, 67.01, H, 7.50 ; N, 7.75. **1-Carbomethoxy-2methyl-[1,2a]pyrrolopiperidine (36)** : The above procedure using : 2.3 mL (20.5 mmol) of hex-1-yne 25 mL (41 mmol) of a 1.67 M solution of methyllithium in ether, 3.98 g (20.5 mmol) of CuI, 5.2 g (20 mmol) of ester **4** and 4.1 g (20 mmol) of 5-bromovaleryl chloride, led after hydrolytic work up and treatment of the crude product with KOH to 1.87 g (48%) of bicyclic pyrrole. ^{1}H NMR (CCl_4) 1.72 (4H, m), 2.10 (3H, s), 2.87 (2H, t) 3.62 (3H, s), 3.65 (2H, t), 6.0 (1H, s). ^{13} C NMR ($CDCl_3$) : 12.28 ($\underline{C}H_3$), 20.44, 20.72, 20.82 ($\underline{C}H_2\underline{C}H_2\underline{C}H_2CH_2N$), 45.32 ($\underline{C}H_2$-N), 50.16 ($\underline{C}H_3O$), 109.25, 118.32, 121.11, 137.10, (pyrrolic $\underline{C}$) 166.50 ($\underline{C}O_2Me$) IR (CCl_4) 1680 cm^{-1}. Mass spectr. (EI), m/e 193 (M^+). Anal. calcd. fopr $C_{11}H_{15}NO_2$: C, 68.87 ; H, 7.82 ; N, 7.25. Found C, 68.45 ; H, 7.75 ; N, 6.99. **1-Carbomethoxy-2-methyl-[1,2a]pyrroloperhydroazepine (37)** : Using the same procedure with 2.3 mL (20.5 mmol) of hex-1-yne, 19.6 mL (41 mmol) of a 2.1 M solution of MeLi in ether, 3.98 g (20.5 mmol.) of CuI. 3.8 g (15 mmol) of ester **4** and 4.3 g (20 mmol) of 6-bromo hexanoylchloride led to isolation of 1.13 g (36%) of bicyclic pyrrole **37**. ^{1}H NMR (CCl_4) : 1.61 (6H, m), 2.0 (3H, s), 3.05 (2H, m); 3.6 (3H, s), 3.75 (2H, t), 5.98 (1H, s). ^{13}C NMR ($CDCl_3$) : 12.52 ($\underline{C}H_3$-pyr), 25.17, 25.63, 26.11, 26.89, ($\underline{C}H_2$–4) 50.10, 50.28, ($\underline{C}H_3O$, CH_2-N), 110.15, 116.10, 119.94, 142.23 (pyrrolic $\underline{C}$), 166.50 ($\underline{C}O_2Me$). IR (CCl_4) : 1680 cm^{-1}. Mass spect. (FAB) 208 ($M+H^+$). Anal. calcd. for $C_{12}H_{17}NO_2$: C, 69.54 ; H, 8.27 ; N, 6.76. Found : C, 69.47 ; H, 8.18 ; N, 6.16.

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