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VINYL COPPER DERIVATIVES n° 29[1]. ADDITION OF α-SILYLATED ORGANOCOPPER REAGENTS TO ALKYNES, ACCESS TO γ-SILYLATED VINYL COPPER REAGENTS

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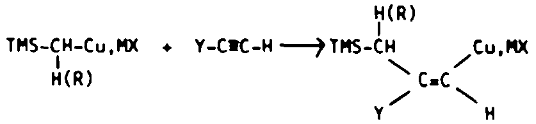
Abstract - α silylated organocopper reagents add regio- and stereo-selectively to alkynes. Experimental procedures (temperature, solvent, ligands, main group metal salts) are highly dependent on the structure of the various simple or functionalized alkynes.

Allylsilanes are important agents in organic synthesis, their chemistry has been reviewed, these last years[3-6]. In order to enhance their synthetic potential, allylic silanes, metalled on one of the two sp^2 carbon atoms have been prepared (i) from the corresponding halo derivatives[7-11] or by (ii) carbometallation of alkynes bearing a silyl substituent on propargylic position[12,13]. The carbocupration by trimethylsilylmethyl copper of a very electrophilic substrate (dimethyl 2-butyn dioate) has been disclosed[14].

We have studied the scope of such carbocupration on various simple alkynes according to the following scheme :



M : MgCl,MgBr,Li
TMS : Me_3Si
X : halogen
Y : hydrocarbon chain or function

The optimum conditions for the addition to 1-hexyne have been studied first, and then extended to functionalized alkynes[15].

RESULTS and DISCUSSION -

1/ Preparation of the organocopper reagent

Me_3SiCH_2MgCl can be prepared from the commercially available chloromethyl silane in ether, THF[16], or dibutyl ether[17]. Use of crushed glass for the activation of magnesium has a powerful effect and allows reproducible yields in ether as well as in THF (≈90%).

Me_3SiCH_2Li can be prepared in pentane[18], ether or THF[19] ; our best results come from the use of freshly cut pieces of Li (2% Na content) and crushed glass in ether between 25 and 30°C, yields ≈80%).

The organocopper reagent is prepared from CuI in ether[20] (with the lithium reagent) and from CuBr in THF at room temperature with the Grignard reagent[21]. The latter can also be prepared in ether, from CuBr at -10°C, yielding a yellow precipitate which dissolves completely in the presence of lithium iodide.

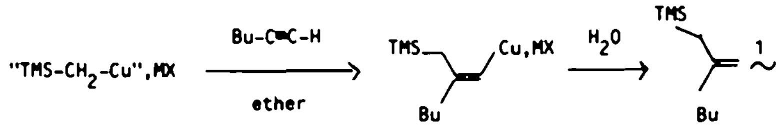
The lithium cuprate is prepared from CuI in ether (purple solution), the transformation is quantitative at -10°C within a few minutes.

2/ Carbocupration of 1-hexyne

The results quoted in table 1 show that the best conditions are obtained with the Grignard derived alkyl copper species in the presence of LiI or $P(OEt)_3$ in ether. Lithium iodide speeds up the reaction, and magnesium salts are required for the addition reaction.

Addition of lithium bromide destabilizes the formed vinyl copper species (leading to a symetrical diene). Adding dimethyl sulfide slows down the rate of addition. As for lithio- and magnesio-cuprates, they both fail to react.

TABLE 1 - Addition of trimethylsilylmethylcopper reagents to 1-hexyne



Entry	Reagent	Ligand	Temp °C	Time (h)	Yield %
1	$TMSCH_2Cu,MgClBr$	none	-13	72	40
2	"	LiBr	-10	19	17
3	"	Me_2S	+20	48	17
4	"	LiI	+10	18	78
5	"	$P(OEt)_3$	+35	62	78
6	$(TMSCH_2)_2CuMgCl$	LiBr [b]	+20	24	0
7	$(TMSCH_2)_2CuLi$	none [c]	+20	24	0

a/ yield of distilled product

b/ performed in THF

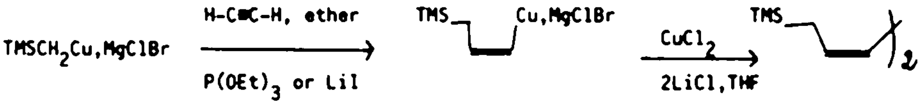
c/ all copper reagents are prepared from CuBr except this one from CuI

It is worthy of note that not only the starting silylated organocopper is unusually stable as quoted by Lappert[20], but also is the derived γ-silylated vinyl copper which resists temperatures as high as +15°C (vinyl copper species usually decompose above -10°C).

In ether, the addition is totally regioselective, and also stereoselective as shown infra.

3/ Carbocupration of acetylene

Due to the volatility of trimethylallylsilane, the vinylcopper reagent obtained by carbocupration of acetylene has been oxydized by cupric ions following Trost[22]. Among the various silylated methyl copper reagents, only $Me_3SiCH_2Cu,MgClBr$ adds to acetylene in ether, in the presence of LiI or $P(OEt)_3$.



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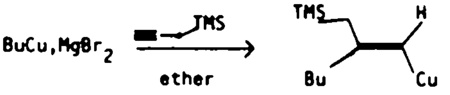
The corresponding lithio cuprate does not add in ether, but metallates acetylene instead. Inspection of the NMR spectrum of the 1,6-bistrimethylsilyl 2,4-hexadiene shows a Z,Z stereochemistry which implies that syn addition has occurred.

Access to the (E) isomer of γ-silylated vinyl copper species

Methylalanation of propargyltrimethylsilane has been shown to lead to the corresponding allylsilane[10]. A generalization of this reaction is obtained with alkylcopper reagents according to table 2.

TABLE 2 - Carbocupration of propargyltrimethylsilane



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Entry	Ligand	T°C	Time(h)	Yield % [a]
1	$P(OEt)_3$	+20	20	50
2	LiI	-10	10	56

a/ yield of hydrolyzed product after distillation

In this case, the starting alkylcopper reagents are unstable, and use of ligands is required. LiI has a pronounced accelerating effect and regioselectivity is total.

Reagent 2(E) is less stable than its (Z)isomer, but both are more stable than non silylated vinylcopper reagents. Thus, according to the use of a silylated copper reagent, or a γ-silylated alkyne, both stereoisomers of (E) and (Z) γ-silylated vinyl reagents may be prepared.

4/ Generalization : addition to functionalized alkynes

We have studied four distinct cases : ethoxyacetylene, 2-propyn 1-al diethylacetal, ethyl propynoate, and 1-propyn 3-ol.

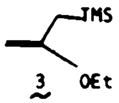
TABLE 3 - Addition of "$TMSCH_2Cu$" to functionalized alkynes in ether

Entry	Alkyne	Reagent	Temp°C	Time(h)	Product[a]	Yield%
1	H-C≡C-OEt	$TMSCH_2Cu,MgClBr$	-40	3	**3**	68
2	$H-C≡C-CH(OEt)_2$	$(TMSCH_2)_2CuLi$	-10	6	**4**	80
3	H-C≡C-COOEt	$TMSCH_2Cu,MgClBr$	-50	2	**5**	55[b]
4	$H-C≡C-CH_2OMgBr$	$(TMSCH_2)_2CuLi$[c]	-20,+20	18	**6**	50

a/ after hydrolysis

b/ Z/E=1/3

c/ in THF/ether (1/3)



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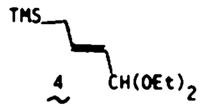

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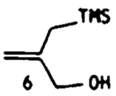

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Ethoxyacetylene :

The best reagent is the organocopper species derived from the Grignard reagent[23]. LiI accelerates the reaction (2h) to give the same yield. In this case, THF or ether behave similarly. The organocopper derived from the parent lithium compound gives only metallation of the terminal sp carbon, and the lithium cuprates initiate a polymerisation reaction (which is not observed with the "normal" R_2CuLi reagents).

2-propyn 1-al diethylacetal :

The silylated lithium cuprate reagent adds regioselectively to give the linear product in good yields, just as the non silylated lithium cuprates do[24], but the former leads to no β-elimination (to an allenic ether) at -10° as the latter do when they are handled above -30°.

An other difference has to be noted : the latter reagent add both alkyl groups, whereas the silylated species transfers only one moiety after 6 hours, and half the second moiety after 12h. That syn addition has occurred may be checked in the hydrolysis product : its ^1H NMR spectrum shows a coupling constant of J=16Hz between the two ethylenic hydrogen atoms. Use of the silyl copper species $Me_3SiCH_2Cu,MgCl$ in ether or THF gives low yields (15-20%) of addition product.

Ethyl propynoate :

Best yields are obtained from the silyl copper reagent prepared from the Grignard in ether, but as with aliphatic copper reagents[25], the stereochemistry is lost through formation of an allenolate intermediate (Z/E=1/3).

1-propyn 3-ol :

As with non silylated species[26], the lithio cuprate is the best reagent when added to preformed magnesium alcoholate. The total regioselectivity leads to an interesting synthon[27], which is thus prepared in a one stage process.

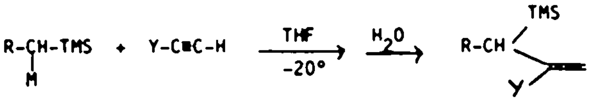
Generalization : Case of α-trimethyl silyl alkyl copper reagents

These higher homologs are prepared according to[28] by addition of alkyl lithium reagents to vinyl silanes, and further transformation to a copper derivative in the presence of lithium salts, or of added magnesium salts : see table 4.

Both of these two reagents add regioselectively to ethoxyacetylene.

The addition to acetylene requires the use of three equivalents of CuBr,2LiCl with these substitued silanes. Such beneficial effect of an excess of Cu(I) salts in difficult carbocupration reactions has already been noted[29], but addition to higher terminal alkynes (i.e. hexyne) failed with these reagents.

TABLE 4 -

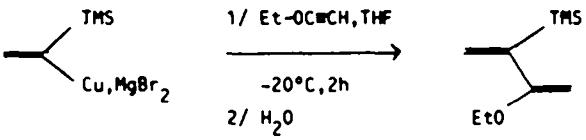


$$\underset{M}{R\text{-}CH\text{-}TMS} + Y\text{-}C\equiv C\text{-}H \xrightarrow[-20°]{THF} \xrightarrow{H_2O} R\text{-}CH(TMS)\text{-}C(Y)=CH_2$$

Entry	Y	R	M	Product	Time(h)	Yield %
1	EtO	Pr	Cu(LiCl)	7	1	60
2	EtO	Pr	Cu(MgClBr)	7	1	62
3	H	Pent	Cu(MgClBr)[a]	8	2	56

[a] : three fold excess of CuBr,2LiCl

Previous works have shown[23,30] that α-substituted vinyl copper reagents add to alkynes under precise conditions. We have now been able to add an α-silylated vinyl copper reagent to ethoxy-acetylene



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The diene is formed in 100% yield according to GLC, but is obtained in only 66% yield after distillation.

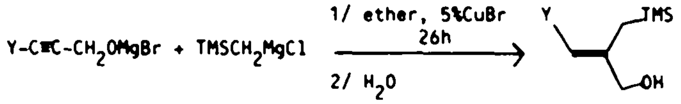
It is not necessary to stabilize the reagent by dimethyl sulfide[31] or trimethylphosphite[32] : the reaction is fast and totally regioselective : this bis functionalized dienyl copper reagent represents a versatile synthon, presently under study.

5/ Use of catalytic amounts of Cu(I) : Addition of α-trimethylsilyl Grignard reagents to some alkynes, under Cu(I) catalysis :

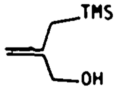
We have selected two examples : 1-propyn 3-ol and propynal diethylacetal.

It is known[26] that Grignard reagents add to propargylic alcohols in the presence of catalytic amounts of Cu(I) salts in an anti fashion. We have applied this scheme to the case of Me_3SiCH_2MgCl[33] ; the reaction is regioselective but slow and yields are fair. Use of excess of magnesium alcoholate or of the Grignard reagent does not improve the yield ; the dianion $ClMg-C≡C-CH_2OMgCl$ fails to react but the 1-silylated 1-propyn 3-ol also gives the bis silylated allylic alcohol (see table 5).

TABLE 5 -



Entry	Y	Temp °C	Product	Yield
1	H	0 +20	6	46 (55)[a]
2	TMS	+20	10	48 (57)[a]
a : in parentheses GLC yield				



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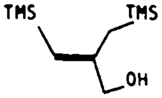

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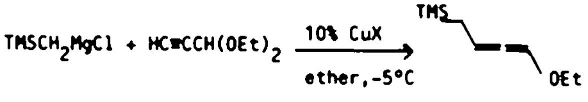
Propynal diethylacetal is known to react with Grignard reagents in the presence of catalytic amounts of Cu(I) to give alkoxyallenes[34]. In the case of $TMSCH_2MgCl$, a similar reaction is observed, leading to δ-silylated alkoxyallenes (allenes bearing a TMS group on allylic position have been already described)[21].

The reaction is slow (see table 6), and use of copper cyanide raises both the rate of the reaction and the yield.

TABLE 6 -



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Entry	X	Time (h) [a]
1	Br	48 (60)
2	CN	62 (80)

a : of distilled product (in parentheses GLC yield)

CONCLUSION -

α-silylated primary and secondary organocopper and cuprate reagents add to simple and functionalized alkynes. The reaction is both regio and stereoselective. α-silylated vinylic copper reagents add to ethoxyacetylene.

A versatile preparation of allylic silanes, metalled on sp2 carbon is thus attained.

The catalytic use of copper (I) salts is even possible in the case of propargylic alcohol or propynal acetal leading to interesting synthons bearing both an allylsilane moiety and an allylic alcohol (or allenic ether) moiety.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Jeol MH100 (CCl_4, δ ppm from TMS), ^{13}C NMR on a Jeol FX90 ($CDCl_3$, δ ppm from TMS); the quotation (K_2CO_3) means that a trace of K_2CO_3 was added to the sample in the NMR tube. IR spectra were obtained on a Perkin Elmer model 457 spectrometer. GLC analysis were performed on a Carlo Erba gas chromatograph model using a 3m glass column (10% SE30).

All reactions are performed under a nitrogen atmosphere in a 250ml flask equiped with a low temperature thermometer, a mechanical stirrer and a pressure equalizing addition funnel.

Starting materials

1-hexyne,2-ethyl propynoate, trimethyl vinylsilane, acetylene are commercially available. 1-propyne 3-ol, ethoxyacetylene, 3-trimethylsilyl 1-propyne are synthetised as previously described[35]. 1-bromo 1-trimethylsilyl ethylene is prepared according to ref.36, CuBr is purified in boiling formic acid[37]. LiI is prepared by reaction of LiH on I_2[38].

The buffer solution used for all hydrolyses is prepared by mixing one volume of sat. ammonia aqueous solution and nine volumes of sat aqueous NH_4Cl solution.

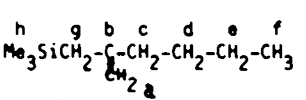
Chloromethyl trimethylsilane (Me_3SiCH_2Cl) is commercially available and must be dried over $CaCl_2$ and distilled before use. Trimethylsilylmethyl magnesium chloride is prepared as described[16]. Use of crushed glass activates the magnesium and allows reproducible yields (≈90%); the titration is performed by Watson's method[39] modified by addition of small amounts of THF to solubilise the magnesium alcoholates ; the Grignard solution is stored at low temperatures (-15°C) and is stable for months.

Trimethylsilylmethyl lithium is prepared as described[19] under an argon atmosphere. Use of crushed glass allows reproducible yields (≈80%) ; titration and storage are identical to those of the Grignard reagent.

2-trimethylsilylmethyl 1-hexene:1 (table 1 entry 4)

To a suspension of CuBr (15mmol, 2.2g) and LiI (20mmol, 20ml 1N ethereal solution) in ether (50ml) is added at 0°C $TMSCH_2MgCl$ (15mmol, 17ml 0,9N ethereal solution). The mixture first gives a yellow precipitate and then a homogeneous pale green solution. This solution is stirred at -5°C for 1h. After addition of hexyne (12,5mmol, 1.0g) the mixture is allowed to warm to +10°C and stirred at this temperature for 18h (brown solution) and then hydrolyzed with 100ml of buffer ammonia solution. The mixture is filtered and decanted ; the organic layer is washed once with 10ml sat NaCl and finally dried over $MgSO_4$. The solvent is evaporated and the residue is distillated through a 10cm Vigreux column to afford 1.8g (78%) of pure 1. bp=70°C/10mmHg

$C_{10}H_{22}Si$(170.37) calc. C, 70.50 ; H, 13.01. Found C, 70.40 ; H, 13.03.



$Me_3SiCH_2-C(=CH_2)-CH_2-CH_2-CH_2-CH_3$ 1

NMR ^1H : Ha(2H,2s,4.6 and 4.8) ; Hc(2H,t,2.0) ; Hg(2H,s,1.8) ; Hd and He(4H,m,1.4) ; Hf(3H,t,0.98) Hh(9H,s,0.05)

2-trimethylsilylmethyl 1-hexene : 1 (table 1 entry 5)

To a suspension of CuBr (15mmol, 2.2g) in 50ml of ether are added, at +10°C, 15mmol of $P(OEt)_3$ (2.49g), with stirring at this temperature until complete solubilisation occurs (10mn). To this solution are added at 0°C hexyne (12.5mmol ; 1.0g) and Me_3SiCH_2MgCl (15mmol, 17ml ether, 0.9N solution). The mixture is stirred during 1h, and is refluxed for 62h ; we observe a grey precipitate in a green solution. The mixture is hydrolyzed with an ammonia buffer solution as described above, filtered, decanted . The organic layer is washed twice with sat. NH_4Cl and dried over $MgSO_4$. The crude product is purified by chromatography (kieselgel 60, pH=7) and eluted with hexane to give 1.8g (78%) of pure 1, same product as above.

2-trimethylsilylmethyl 1-hexene : 1 (table 2 entry 1)

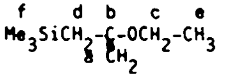
To a solution of CuBr (15mmol, 2.2g) and $P(OEt)_3$ (15mmol ; 2.49g) in 50ml of ether, is added at -20°C BuMgBr (15mmol, 7.5ml ethereal 2N solution) ; the brown solution is stirred during 30mn ; propargylsilane (12.5mmol) is added dropwise at -10°C ; the mixture is stirred at +20°C during 20h and then hydrolyzed and worked up as above 1b. We obtain 1.2g (50%) of pure 1.

2-trimethylsilylmethyl 1-hexene : 1 (table 2 entry 2)

To a suspension of CuBr (15mmol ; 2.2g) and LiI (20mmol) in 50ml of ether is added, at -20°C, ethereal solution of BuMgBr (15mmol). The green solution is stirred 30min ; propargylsilane is added dropwise at -10°C ; the mixture is stirred at -10°C during 10hr, and then hydrolyzed and worked up as above 1a ; we obtain 1.3g(56%) of pure 1.

2-ethoxy 3-trimethylsilyl 1-propene : 3

To a suspension of CuBr (30mmol, 4.4g) in 50ml of ether is added at +5°C 30mmol of Me_3SiCH_2MgCl (30ml of 1N ethereal solution) ; after 1h, freshly distillated ethoxyacetylene (30mmol) is added at -40°C (red color) ; the mixture is stirred 3h at -40°C, hydrolyzed as above, filtered, decanted ; the organic layer is washed twice with sat. NaCl, dried over K_2CO_3 ; the solvent is evaporated. Distillation afforded 3.2g (68%) of pure 3. bp=60°C/70mmHg or 30°C/12mmHg.



$Me_3SiCH_2-C(=CH_2)-OCH_2-CH_3$ 3

NMR $^1H(CCl_4$; $K_2CO_3)$: Ha and Hc(4H,m,4-4.2) ; Hd(2H,s,1.9) ; He(3H,t,0.9) ; Hf(9H,s,0.05) ;

NMR ^{13}C ($CDCl_3$, K_2CO_3) : six peaks 164.2(Cb) ; 64.6(Ca) ; 27.8(Cc) ; 16.8(Cd) ; 2.2(Ce) ; 0.3(Cf).

1.1-diethoxy 4-trimethylsilyl 2-butene E : 4

A solution of $(Me_3SiCH_2)_2CuLi$ is prepared by adding at -15°C Me_3SiCH_2Li (20mmol, 75ml of 0,4N ethereal solution) to a suspension of CuI (15mmol, 2.9g) in 35ml of ether. After 1h, 3-diethoxy 1-propyne (15mmol, 1.92g) is introduced dropwise at -40°C ; the mixture is allowed to warm to -10°C during 6h, and hydrolyzed with 150ml of the ammonia buffer solution, filtered, decanted ; the organic layer is washed twice with sat. NaCl, dried over Na_2CO_3. Distillation afforded 2.6g (80%) of pure 4 :

g e a b c d f
$Me_3SiCH_2-CH=CH-CH(OCH_2CH_3)_2$; bp=95°C/18mmHg

NMR $^1H(CCl_4$, $K_2CO_3)$: Ha(1H,dt,5.85) ; Hb(1H,dd,5.4) ; Hc(1H,d,4.85) ; Hd(4H,m,3.5) ; He(2H,d,1.5) ; Hf(6H,t,1.25) ; Hg(9H,s,0.02) ; J_{Ha-Hb}=16Hz).

NMR ^{13}C ($CDCl_3$, K_2CO_3) : seven peaks ; 131.6(Cb) ; 126.3(Ca) ; 102.3(Cc) ; 60.9(Cd) ; 23.9(Ce) ; 15.5(Cf) ; -1.7(Cg).

Ethyl 4-trimethylsilyl 2-butene oate : 5 (E) and (Z)

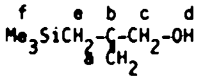
To a suspension of CuBr (15mmol, 2.2g) in THF (30ml) are added dropwise at -10°C Me_3SiCH_2MgCl (15mmol, 15ml of THF 1N solution). The obtained yellow precipitate is cooled to -50°C and ethyl propynoate (15mmol) is added ; the mixture is stirred 2h of and treated as above. Distillation affords 1.4g (55%) of a mixture 5(E) and 5'(Z).

g d c b a e f
$Me_3SiCH_2-CH=CH-COOCH_2CH_3$: 5. bp : 70-85°C/18mmHg.

NMR ^1H : Hc(0.67H,dt,7.18) ; Hc' (0.33H,dt,6.4ppm) ; Hb(0.67H,d,5.76) ; Hb'(0.33H,d,5.72H) ; He and He'(2H,m,4.2) ; Hd(2H,d,1.72) ;Hf(3H,t,1.24) ; Hg(9H,s,0.06).

2-trimethylsilylmethyl 2-propene 1-ol : 6

A solution of $(Me_3SiCH_2)_2CuLi$ is prepared as previously described for 4 at -10°C and allowed to cool to -20°C. To this solution is added the preformed alcoholate solution (addition of EtMgBr (15mmol, THF solution) at -10°C to $HC\equiv C-CH_2OH$ (15mmol, 0.84g). The mixture is allowed to warm to room temperature during 18h, hydrolyzed with 100ml of the usual buffer ammonia solution, filtered, decanted. The organic layer is dried over K_2CO_3, and distillation affords 1.1g (55%) of pure 6.



$$\overset{f}{Me_3Si}\overset{e}{CH_2}-\overset{b}{\underset{\overset{\|}{\underset{a}{CH_2}}}{C}}-\overset{c}{CH_2}-\overset{d}{OH}$$

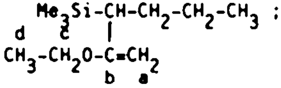
bp. : 32°C/0.2mmHg

NMR ^1H (CCl_4, Na_2CO_3) : Ha(2H,2s,4.85 and 4.95) ; Hc(2H,s,3.95) ; Hd(1H,s,3.00) ; He(2H,s,1.48) Hf(9H,s,0.05).

NMR ^{13}C ($CDCl_3$, K_2CO_3) : 146.6 (Cb) ; 106.6 (Ca) ; 66.4(Cc) ; 23.2(Ce) ; 1.38(Cf)
Mass spectrum (m/e) : 143(M^+-1) 8%, 129(M^+-CH_3) 7%, 73(Me_3Si^+) 100%.

2-ethoxy 3-trimethylsilyl 1-hexene : 7

A solution of $Me_3SiCH(Pr)Li$ is prepared by addition of EtLi (10mmol ethereal solution) to trimethylvinyl silane (10mmol, 1g) dissolved in 150ml of THF at -70°C, then stirring at -30°C for 1h. To this yellow solution are added 10mmol of a CuBr,2LiCl/THF solution and ethoxyacetylene (10mmol). The mixture is stirred during 1h and treated as for 6. Distillation afforded 1g(60%) of pure 7 :



$$\overset{i}{Me_3Si}-\overset{e}{\underset{|}{CH}}-\overset{f}{CH_2}-\overset{g}{CH_2}-\overset{h}{CH_3} \qquad \overset{d}{CH_3}-\overset{c}{CH_2}O-\underset{b}{C}=\underset{a}{CH_2}$$

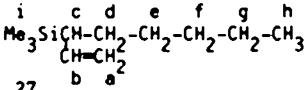
; bp=65°C/20mmHg

NMR ^1H (CCl_4, Na_2CO_3) : Ha and Hc (4H,m,3.95-3.8) ; Hd, He, Hf and Hg (8H,m,1.2-1.8) ; Hh (3H, s,0.9) ; Hi(9H,s,0.02).

NMR ^{13}C ($CDCl_3$, K_2CO_3) : nine peaks ; 167.2(Cb) ; 81.7(Ca) ; 64.9(Cc) ; 38.5(Ce) ; 32.3, 24.9, 17.2 and 16.6(Cd,Cf,Cg and Ch) ; -1.6(Ci).

3-trimethylsilyl 1-octene : 8

A solution of $Me_3SiCH(Pent)Li$ is prepared by addition of nBuLi (10mmol ethereal solution) to trimethylvinylsilane dissolved in 70ml of THF (10mmol, 1g) at -70°C. The reaction is stirred during 3h and allowed to warm to -30°C during 1h. To this homogeneous solution are added $MgCl_2$/THF (10mmol titrated solution) and CuBr,2LiCl/THF solution (30mmol). Acetylene (15mmol, 0.36l) is bubbled at -30°C into the solution which is allowed to warm to -20°C during 2h, treatment as for 6.
Distillation afforded 0.9g (56%) of pure 8 :



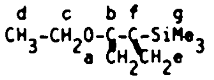
$$\overset{i}{Me_3Si}\overset{c}{\underset{\underset{b\quad a}{CH=CH_2}}{CH}}-\overset{d}{CH_2}-\overset{e}{CH_2}-\overset{f}{CH_2}-\overset{g}{CH_2}-\overset{h}{CH_3}$$

bp.=75°C/15mmHg

NMR $^1H^{27}$: Hb(1H,m,5.8) ; Ha(2H,m,5.0) ; Hc,d,e,f,g (9H,m,1.8-2.1) ; Hh(3H,t,0.96) ; Hi(9H,s,0.04).
NMR ^{13}C : nine peaks ; 140.6(Cb) ; 112.1(Ca) ; 35.3(Cc) ; 32.2, 29.5, 28.8, 23.1(Cd,Ce,Cf,Cg) ; 14.5(Ch) ; -3(Ci).

2-ethoxy-3 trimethylsilyl 1,3-butadiene : 9

1-trimethyl silyl 1-vinyl magnesium bromide (15mmol, 27.8ml of 0.54 mmol l^{-1} THF solution) is added at 0°C to a suspension of CuBr (15mmol, 2.2g) in 20ml of THF. The mixture is stirred 1h (brown precipitate). Ethoxyacetylene (12.5mmol, 0.9g) is slowly added at 0°C to this mixture (exothermic reaction) which turns dark green, and is stirred at -20°C during 2h and worked up as for 6. Distillation afforded 1.4g (60%) of pure 9 :



$$\overset{d}{CH_3}-\overset{c}{CH_2}O-\overset{b}{\underset{\underset{a}{CH_2}}{C}}-\overset{f}{\underset{\underset{e}{CH_2}}{C}}-\overset{g}{SiMe_3}$$

bp.=60°C/12mmHg

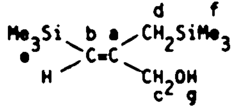
NMR ^1H (CCl_4, K_2CO_3) : He(2H,2d,6.05 and 5.35) ; Ha(2H,2d,4.10-3.85) ; Hc(2H,q,3.70) ; Hd(3H,t,1.25).

2-trimethylsilylmethyl 2-propene 1-ol : 6 (use of a catalytic amount of CuI)

To a solution of propargylic alcohol (15mmol, 0.84g) in 50ml ether is added at -10°C an EtMgBr ethereal solution (15mmol) (white precipitate). CuBr (15mmol, 0.2g) and Me_3SiCH_2MgCl (15mmol ethereal solution) are then introduced. The solution is allowed to warm to room temperature for 26h. After usual work up and distillation pure 6 is obtained.

3-trimethylsilyl 2-trimethylsilylmethyl 2 propene-1-ol : **10**

With 3-trimethylsilyl 2-propyne 1-ol, the same procedure as above is carried out. Distillation afforded 1.3g of pure **10** :



bp = 65°C/0.2mmHg

NMR $^1H(CDCl_3, Na_2CO_3)$: Hb(1H,s,5.40) ; Hc(2H,s,4.0) ; Hg(1H,s,3.60) ; Hd(2H,s,1.90) ; He(9H,s, 0.25) ; Hf(9H,s,0.05).
NMR ^{13}C $(CDCl_3, Na_2CO_3)$: six peaks ; 157.9(Ca) ; 118.6(Cb) ; 69.7(Cc) ; 25.6(Cd) ; 1.8(Ce) ; 0.7(Cf).

1-ethoxy 4-trimethylsilyl 1,2-butadiene : **11**

To a solution of 2 propyn-1al diethylacetal (15mmol) in 50ml of ether are introduced at -5°C CuCN(1.5mmol) and EtMgBr (15mmol ethereal solution). The mixture (yellow precipitate) is stirred at -5°C during 4h and worked up as previously. Distillation afforded 1.8g (62%) of pure **11** :

$$\underset{g}{Me_3Si}\underset{a}{CH_2}\text{-}\underset{b}{CH}\text{=}\underset{c}{C}\text{=}\underset{d}{CH}\text{-}O\underset{e}{CH_2}\underset{f}{CH_3}$$; bp = 72°C/15mmHg ; I.R. neat cm^{-1} ($1950cm^{-1}$)

NMR $^1H(CDCl_3, Na_2CO_3)$; Hd(1H,d,6.9) ; Hb(1H,dt,6.0) ; He(2H,q,3.9) ; Ha(2H,d,1.45) ; Hf(3H,t,1.2) ; Hg(9H,s,0.05).
NMR ^{13}C : seven peaks ; 193.7(Cc) ; 120.7(Cd) ; 120.4(Cb) ; 64.4(Ce) ; 22.9(Ca) ; 15.8(Cf) ; -1(Cg).
Mass spectrum (m/e) : 171(M^++1) 4%, 73(Me_3Si^+) 100%.

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