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VINYL COPPER DERIVATIVES 30[1]
REACTIVITY OF γ-SILYLATED VINYL COPPER REAGENTS

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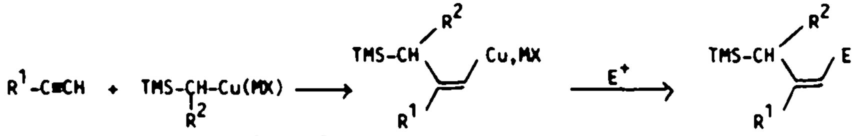
Abstract - γ-silylated vinyl copper reagents react with electrophiles with total retention of configuration of the C=C double bond. Oxidation, allylation, vinylation and acylation lead to fonctionalized dienes with a given geometry.

γ-silylated vinylcopper reagents[1] react with electrophiles according to the following scheme :



M : MgX or Li, X=Br,Cl ; R^1 or R^2=H or alkyl ; TMS=Me_3Si

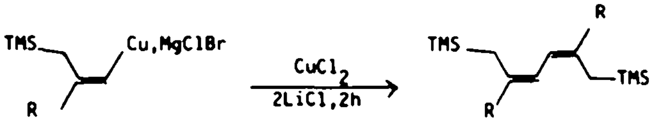
1. OXIDATION

Thermal decomposition of vinylcopper reagents leads to symmetrical 1,3-dienes[3]. A best result is obtained by oxygen or oxidizing agents as $CuCl_2$,2LiCl[4].

In the present case this reaction gives access to dienes bearing two allylic silyl moieties (Table 1).

These bis allylsilanes are isomers of those described by Trost et al.[4] : they show a pure Z,Z configuration (E,E for entry 4 Table 1).

TABLE 1 -



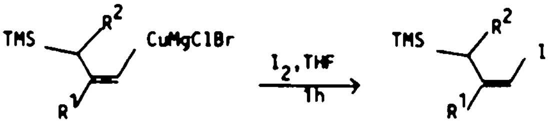
Entry	R	Temp(°C)	Product	Yield %[a]
1	Pent	20	**1**	60
2	Bu	20	**2**	52
3	H	20	**3**	42
4	OEt	-10	**4**	55

a/ calculated from RC≡CH

2. IODINATION

Iodinolysis of vinyl copper reagents gives iodo alkenes with complete retention of configuration[5]. The problem here, was to avoid interaction of iodine with the allylsilane (Table 2).

TABLE 2 -



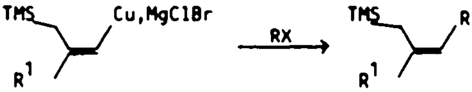
Entry	R^1	R^2	Temp(°C)	Product	Yield %[a]
1	OEt	H	-10	5	54
2	Bu	H	+20	6	45
3	H	Pr	+10	7	38

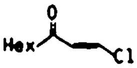
a/ Yield calculated from $R^1C{\equiv}CH$

Compound 5 shows a higher stability, as compared to its non silylated analog[5]. The iodo silyl alkene 7 allows to check by NMR ^1H that syn addition had occurred exclusively ($J_{1,2}$ H_1H_2=7Hz) in the carbocupration step.

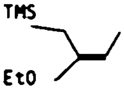
3. ALKYLATION

TABLE 3 -



Entry	R^1	RX	Solvent	Addend	Temp (°C)	t (h)	Product	Yield[a] %
1	OEt	MeI	ether	$3P(OEt)_3$ 1 HMPT	30	20	8	41
2	Pent	 Br	ether/THF 1 2	LiI	25	3	9	65
3	OEt	"	"	"	20	3	10	41
4	"		"	$5\%Pd(P\phi_3)_4$	20	2	11	78
5	"		"	"	20	2	12	65

a/ Yield calculated from $R^1C{\equiv}CH$



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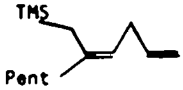

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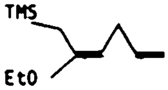

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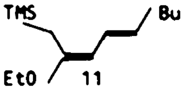

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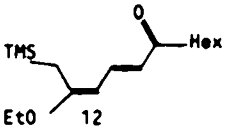

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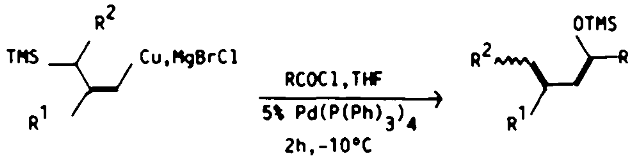
- Methylation (see table 3 entry 1) necessitates the combined addition of HMPT and triethylphosphite[5], the yield is only fair ;
- Allylation is better performed, without HMPT or phosphite, and activation by lithium iodide is more rewarding in THF as solvent ;
- Vinylation : as already reported for the non silylated reagents, vinyliodides couple with Grignard derived vinylcopper reagents in the presence of $Pd^\circ L_4$[6] ; on the other hand Me_3SiCH_2MgCl itself has been condensed with vinylic halides in the presence of Pd° or Ni°[7,8]

The silylvinylcopper reagents can be condensed with vinyl iodides (product 11) or chlorovinyl ketones (product 12) under catalysis with total retention of configuration. Dienone 12 is remarkably stable.

4. ACYLATION

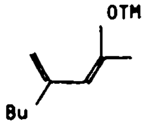
Acylation by acid chlorides in the presence of a catalytic amount of palladium (0) complex[9] does not allow to stop at the γ silylated α,β-ethylenic ketone stage. ^1H NMR of the reaction mixture shows the presence of the latter product, accompanied by a silyloxy 1,3-diene resulting from the migration of the trimethylsilyl moiety[10]. Heating the crude product for distillation yields only the rearranged product (see Table 4).

TABLE 4 - Acylation



Entry	R^1	R^2	R	Product	Yield%[a]
1	Bu	H	Me	13	42
2	OEt	H	Me	14	59
3	OEt	Pr	Me	15	48
4	OEt	H		16	76

a/ yield calculated from R^1-C≡CH



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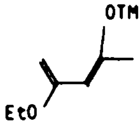

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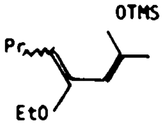

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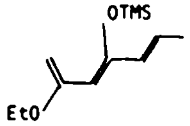

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A NOE experiment on compound 14 shows that the trisubstitued C=C double bond is exclusively of Z configuration.

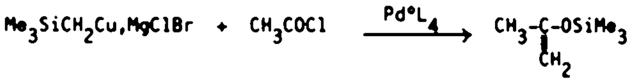
This fact suggests a sigmatropic (1-5) σ + π rearrangement of the transient ketone :

It must be pointed out that ketone 12 (Table 3) although (E) vinylogous of the precursor of 14 does not lead to such a rearrangement.

Compound 14 is a regioisomer of dienol diethers described by Danishefsky[11].

In the case of alkyl substitued derivatives such as 15, we observe a mixture (E/Z) of two isomers : although the silyloxy moiety still ends up on a Z double bond, there is no selectivity for the formation of the second double bond of the diene.

Remark :
We have observed that the organocopper reagent TMSCH$_2$Cu,MgClBr reacts (in THF) with acyl halides in the presence of Pd°L$_4$(2h,-10°C) to give silyl enol ethers :

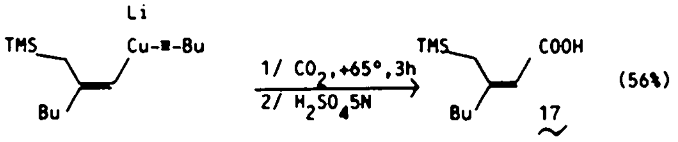


$$Me_3SiCH_2Cu,MgClBr + CH_3COCl \xrightarrow{Pd°L_4} CH_3-\underset{\underset{CH_2}{\|}}{C}-OSiMe_3$$

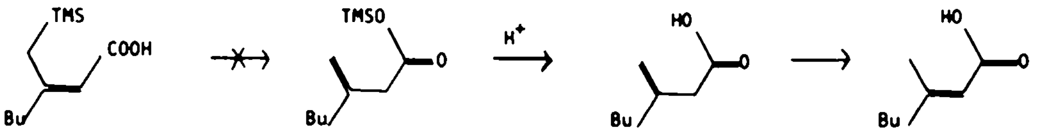
in analogy with the reaction of the organocuprate (TMSCH$_2$)$_2$CuLi with acid halides catalyzed by trimethylsilyltriflate[12] and the isomerisation of α-trimethylsilylketones into trimethylsilyl enol ethers under the following conditions : heat, HRh(CO)(P(Ph)$_3$)$_3$, and Me$_3$SiI catalysis[13].

5. CARBONATATION

The γ silylated vinyl copper reagents react with carbon dioxide only at a relatively high temperature, and stabilizing agents are necessary (1LiI ; 4HMPT ; 0.1 P(OEt)$_3$) in ether, leading however to low yields (≃ 20%) of acid 17.
Use of the mixed lithium vinyl-hexynyl cuprate (in boiling THF), without addends, gives much better results :



The intermediate cuprous carboxylate requires strong hydrolyzing conditions (H$_2$SO$_4$5N,1h). Acid 17 Z is then isolated. Surprisingly, no protolysis of the allylsilane moiety is observed, and contrary to the above result with ketones, no sigmatropic (1-5) rearrangement is to be observed :



Since no 3-Butyl 3-butenoic acid nor 3-Methyl 2 heptenoic acid are found in this case.
The alkynyl moiety is partly transferred (formation of 2-heptynoïc acid separated by chromatography on silica gel.

CONCLUSION -

γ-silylated vinyl copper reagents are interesting synthons on the way to allylsilanes bearing a C=C double bond of defined geometry, as well as other functionalities. Their acylation or carbonatation followed by a rearrangement show that they formally behave as geminated allylic bianions :

This potential double nucleophilicity is the subject of further investigation.

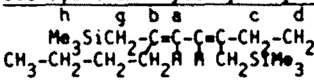
EXPERIMENTAL[14]

$Pd(P(Ph)_3)_4$ is prepared according to[15] stored at room temperature; it is stable, in the dark, for months.
1-iodohexene is synthetised by Zweifel's method[16]
1-chloro 1-nonene 3-one is prepared according to[17]
1-bromo 1-trimethylsilyl ethylene is prepared according to[18]

1. GENERAL PROCEDURE FOR OXIDATION

15 mmol of γ-silylated vinyl copper reagents are prepared as above[1]. To the mixture cooled at -40°C are added 100ml of THF. The oxidation reagent solution (15mmol of Li_2CuCl_4 dissolved in 50ml of THF) is introduced at the desired temperature (see Table 1). The mixture is stirred during 2h, hydrolyzed with 100ml of ammonia buffer solution, filtered, decanted. The organic layers are washed with sat. aqueous NaCl, dried over Na_2CO_3. Distillation under reduced pressure gives the following dienes.

bis 5,8-trimethylsilymethyl 5,7-dodecadiene (Z,Z) : **2**

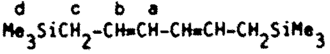


$$\begin{array}{l} \quad\mathrm{\overset{h}{Me_3Si}\overset{g}{CH_2}{-}\overset{b}{C}{=}\overset{a}{C}{-}C{=}C{-}\overset{c}{CH_2}{-}\overset{d}{CH_2}{-}\overset{e}{CH_2}{-}\overset{f}{CH_3}} \\ \mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2\;H\;\;H\;CH_2SiMe_3} \end{array}$$

(52%) bp = 115°C/0.1mmHg

NMR $^1H(CCl_4)$: Ha(2H,s,5.86) ; Hc(4H,t,2.04) ; Hg(4H,s,1.88) ; Hd and He(8H,m,1.32) ; Hf(6H,t,0.92) ; Hh(18H,s,0.04)
NMR $^{13}C(CDCl_3)$: eight peaks ; 136.8(Cb) ; 119.2(Ca) ; 39.9(Cc) ; 31.8(Cg) ; 28.1 and 22.7(Cd and Ce) ; 14.9(Cf) and -0.5(Ch).
Mass spectrum (m/e) : 338(M^+) 10%, 73 ($SiMe_3$) 100%.

bis 1,6-trimethylsilyl 2,4-hexadiene (Z,Z) : **3**

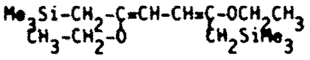


$$\mathrm{\overset{d}{Me_3SiCH_2}{-}\overset{c}{CH}{=}\overset{b}{CH}{-}\overset{a}{CH}{=}CH{-}CH_2SiMe_3}$$

(42%) bp = 67°C/0.1mmHg

NMR $^1H(CCl_4)$: Ha(2H,d,6.10) ; Hb(2H,dt,5.42) ; Hc(4H,d,1.6) ; Hd(18H,s,0.04) ;
J_{HaHb}=8Hz=J_{HbHc}.

2,5-diethoxy 1,6-bis trimethylsilyl 2,4-hexadiene (E,E) : **4**



$$\begin{array}{l} \mathrm{\overset{f}{Me_3Si}{-}\overset{d}{CH_2}{-}\overset{b}{C}{=}\overset{a}{CH}{-}CH{=}C{-}\overset{c}{OCH_2}\overset{e}{CH_3}} \\ \quad\mathrm{CH_3{-}CH_2{-}O\qquad\quad CH_2SiMe_3} \end{array}$$

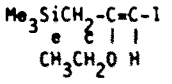
(55%) bp = 50°C/0.05mmHg

NMR $^1H(CCl_4, K_2CO_3)$: Ha(2H,s,4.68) ; Hc(4H,q,3.72) ; Hd(4H,s,1.92) ; He(6H,t,1.24) ; Hf(18H, s,0.08).

2. GENERAL PROCEDURE FOR IODINATION

The procedures for iodination and oxidation are about the same, instead of Li_2CuCl_4 solution, a solution of 15mmol iodine (3,8g) in 50ml THF is used. The mixture is treated as above. Distillation gives the following derivatives :

2-ethoxy 1-iodo 3-trimethylsilyl 1-propene (E) : **5**

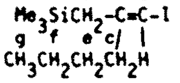


$$\begin{array}{l} \mathrm{\overset{f}{Me_3Si}\overset{d}{CH_2}{-}\overset{b}{C}{=}\overset{a}{C}{-}I} \\ \qquad\mathrm{e\;\;c\;\;|\;\;|} \\ \quad\mathrm{CH_3CH_2O\;H} \end{array}$$

(54%) ; bp =52°C/0.2mmHg

NMR ^1H (CCl_4, Na_2CO_3) : Ha(1H,s,4.75ppm) ; Hc(2H,q,3.76) ; Hd(2H,s,1.96) ; He(3H,t,1.24) ; Hf(9H,s,0.08).
NMR ^{13}C ($CDCl_3$, Na_2CO_3) : six peaks ; 160.0(Cb) ; 63.6(Ca) ; 41.7(Cc) ; 26.7(Cd) ; 15.7(Ce); -1,9(Cf).

1-iodo 2-trimethylsilyl methyl 1-hexene (Z) : **6**



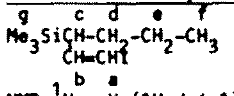
$$\begin{array}{l} \mathrm{\overset{h}{Me_3Si}\overset{d}{CH_2}{-}\overset{b}{C}{=}\overset{a}{C}{-}I} \\ \mathrm{g\;\;f\;\;e\;\;c/\;\;|} \\ \mathrm{CH_3CH_2CH_2CH_2H} \end{array}$$

(45%) ; bp = 45°C/0.05mmHg

NMR $^1H(CCl_4)$: Ha(1H,s,5.68) ; Hc(2H,t,2.08) ; Hd(2H,s,1.76) ; He and Hf(4H,m,1.12-1.48) ; Hg (3H,t,0,88 ; Hh(9H,s,0.2).

NMR $^{13}C(CDCl_3)$: eight peaks ; 150.4(Cb) ; 71.1(Ca) ; 38.5(Cc) ; 30.2, 28.5, 29.2 (Cd,Ce,Cf); 13.9(Cg) ; -0.36(Ch).

1-iodo 3-trimethylsilyl 1-hexene (Z) : **7**



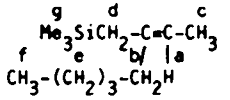
$$\begin{array}{l} \mathrm{\overset{g}{Me_3Si}\overset{c}{CH}{-}\overset{d}{CH_2}{-}\overset{e}{CH_2}{-}\overset{f}{CH_3}} \\ \qquad\mathrm{\underset{b}{CH}{=}\underset{a}{CHI}} \end{array}$$

(38%) ; bp = 60°C/0.3mmHg

NMR ^1H : Ha(1H,d,6.1) ; Hb(1H,dd,5.88) ; Hc(1H,dt,2.0) ; Hd and He(4H,m,1.2-1.6) ; Hf(3H,t,0.86) ; Hg(9H,s,0.06) ; J_{HaHb}=8Hz=J_{HbHc}.

3. ALKYLATION : 3-trimethylsilyl methyl 2-octene (Z) : 8

To a solution of CuBr (15mmol, 2.2g), $P(OEt)_3$ (15mmol, 2.49g) and heptyne (12.5mmol, 1.2g) in 50ml of ether is added at -20°C Me_3SiCH_2MgCl (15ml, 15 mmol, 1N ethereal solution). The obtained brown solution is stirred at 30°C for two days. 30mmol of $P(OEt)_3$ (5g) and 15mmol of HMPT are added dropwise at -20°C : the mixture turns dark green and 30mmol of CH_3I(4.2g) are then added. The mixture is refluxed at 30°C during 20h and then hydrolyzed as above, filtered, extracted with ether, decanted ; the organic layers are washed with sat NaCl, dried over $MgSO_4$. The crude product is purified by chromatography (Kieselgel 60) and eluted with hexane to give 1.7g (41%) of pure 8 :



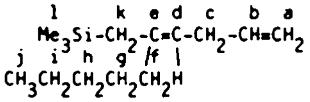
$Me_3SiCH_2{-}C{=}C{-}CH_3$, $CH_3{-}(CH_2)_3{-}CH_2H$

bp = 94°C/12mmHg

NMR ^1H : Ha(1H,q,5.1) ; Hc(3H,d,1.56) ; Hd(2H,s,1.54) ; He(6H,m,1.32) ; Hf(3H,t,0.92) Hg(9H,s,0.04).

ALLYLATION : 5-trimethylsilyl methyl 1,4-decadiene (Z) : 9

To a suspension of CuBr (15mmol, 2.2g) and LiI (20mmol, 10ml of 0.2mol l^{-1} ethereal solution) in 15ml of ether is added at 0°C : $TMSCH_2MgCl$ (15mmol). This mixture is stirred at 0°C for 1h. After addition of heptyne (12.5mmol, 1.2g), the mixture is allowed to warm to 20°C and stirred at room temperature for 20h. A solution of allyl bromide (20mmol) in 50ml of THF is introduced dropwise at this temperature. The mixture is stirred during 3h and hydrolyzed with 100ml of ammonia buffer solution, filtered, extracted with pentane ; the organic layers are washed with sat. NaCl. Distillation afforded 1.8g (65%) of pure 9 :



$Me_3Si{-}CH_2{-}C{=}C{-}CH_2{-}CH{=}CH_2$, $CH_3CH_2CH_2CH_2CH_2H$

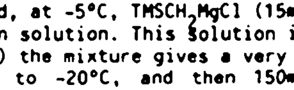
bp = 77-78°C/0.01mmHg

NMR ^1H : Hb(1H,m,5.8-5.92) ; Ha and Hd(3H,m,4.88-5.2) ; Hc(2H,dd,2.68) ; Hf(2H,t,1.92) ; Hk(2H,s,1.5) ; Hg,Hh,Hi(6H,m,1.5-1.2) ; Hj(3H,t,0.92) ; Hl(9H,s,0.06).

NMR ^{13}C : twelve peaks ; 138.4(Ce) ; 137.8(Cd) ; 118.4(Cb) ; 114.8(Ca) ; 39.2(Cc) ; 32.8, 31.8, 28, 22.8 and 21.2 (Ck,Cg,Ch,Ci) ; 14.1(Cj) ; -0.6(Cl).
Mass spectrum (m/e) : $224(M^+)$ 0.2%, $209(M^+{-}CH_3)$ 0.4%, $94(M^+{-}SiMe_3{-}C_4H_9)$ 2%, $73(SiMe_3)$ 100%.

2-ethoxy 1-trimethylsilyl 2,5-hexadiene (E) : 10

To a suspension of CuBr (15mmol, 2.2g) and LiI (20mmol, 10 ml 0.2N ethereal solution) in 20ml of ether is added at -10°C $TMSCH_2MgCl$ (15mmol, 19ml, 0.7N ethereal solution). This mixture is allowed to cool to -40°C. After addition of ethoxyacetylene (12.5mmol, 0.87g) the red suspension is stirred 2h at -20°C and allowed to warm to +20°C. After addition of the solution of allylbromide (20mmol, 2.4g) in 50ml of THF the obtained brown solution is stirred at room temperature 4h, and then treated as above. Distillation afforded 1.2g (41%) of pure 10.



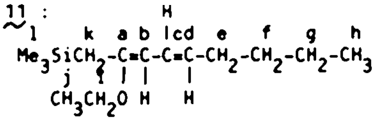
$Me_3SiCH_2{-}C{=}CH{-}CH_2{-}CH{=}CH_2$, $CH_3{-}CH_2{-}O$

bp = 83°C/12mmHg

NMR ^1H : He(1H,m,6.56) ; Hf(2H,m,4.8-5.16) ; Hc(1H,t,4.24) ; Hg(2H,q,3.68) ; Hd(2H,dd,2.68) ; Ha(2H,s,1.6) ; Hh(3H,t,1.24) ; Hi(9H,s,0.06).

2-ethoxy 1-trimethylsilyl 2,4-nonadiene (EE) : 11

To a suspension of CuBr (15mmol, 2.2g) and LiI (20mmol ethereal solution) in 50ml of ether is added, at -5°C, $TMSCH_2MgCl$ (15mmol, 17ml, 0.9 N ethereal solution). The mixture gives a pale green solution. This solution is cooled at -40°C. After addition of ethoxyacetylene (15mmol, 1.1g) the mixture gives a very nice red color and is stirred 2h at -40°C, and is allowed to warm to -20°C, and then 150ml of THF are introduced (dark-blue color). A solution of $Pd(P(Ph)_3)_4$ (5%=0.7g) in 20ml of THF is added at -20°C and finally 12mmol of E 1-iodohexene is added dropwise at 20°C to this mixture (brown or black color) which is stirred 2h at this temperature. The mixture is hydrolyzed with 80ml of buffer ammonia solution, filtered, extracted with ether ; the organic layers are washed with sat. NaCl, dried over Na_2CO_3 ; the solvents are evaporated, and to the residue are added 50ml of pentane (or hexane). The obtained mixture is filtered, the solvents are evaporated. Distillation afforded 2.25g (78%) of pure 11 :



$Me_3SiCH_2{-}C{=}C{-}C{=}C{-}CH_2{-}CH_2{-}CH_2{-}CH_3$, CH_3CH_2O

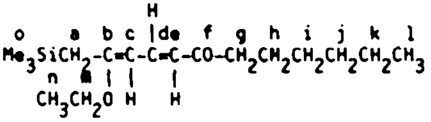
bp = 70°C/0.5mmHg

NMR ^1H : Hc(1H,dd,5.96) ; Hb(1H,d,5.06) ; Hd(1H,dt,5.24) ; Hi(2H,q,3.7) ; He(2H,dt,2.0) ;

Hk(2H,s,1.68) ; Hf,Hg,Hi(7H,m,1.1-1.4) ; Hh(3H,t,0.9) ; Hl(9H,s,0.1) ; J_{HbHc}=10Hz ; J_{HcHd}=15Hz(trans) ; J_{HdHe}=8Hz.

2-ethoxy 1-trimethylsilyl 2,4-dodecadiene 6-one (E,E) : 12

The procedure is analogous to the previous one, the chlorovinylketone being used instead of 1-iodo 1-hexene. The crude product is purified by chromatography (silica column) and eluted with a mixture of ether-hexane (30-70) to give 2.8g (65%) of pure 12.


$Me_3SiCH_2\text{-}C{=}C\text{-}C{=}C\text{-}CO\text{-}CH_2CH_2CH_2CH_2CH_2CH_3$ (CH_3CH_2O, H, H; labels o a b c d e f g h i j k l, n m)

IR neat(cm^{-1}) 1675 (C=O) 1600(C=C)

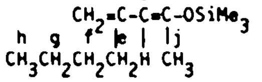
NMR $^1H(CCl_4,TMS)$: Hd(1H,dd,7.60) ; He(1H,d,6.12) ; Hc(1H,d,5.48) ; Hm(2H,q,3.96) ; Hg(2H,t,2.52) ; Ha(2H,s,2.0);Hh(2H,m,1.68) ; Hi,Hj,Hk,Hn(9H,m,1.32) ; Hl(3H,t,0.95) ; Ho(9H,s,0.06) ; J_{HdHe}=16Hz ; J_{HcHd}=12Hz.

NMR ^{13}C : fifteen peaks ; 199.6(Cf) ; 168.8(Cb) ; 141.3(Ce) ; 122.4(Cd) ; 97.1(Cc) ; 63.2(Cg) ; 48.9(Cm) ; 31.8, 29.2, 24.9, 23.8, 22.6(Ca,Ch,Ci,Cj,Ck) ; 14.5, 14.1(Cl,Cn) ; -1,3(Co).

4. GENERAL PROCEDURE FOR ACYLATION

15ml of γ-silylated vinyl copper reagents are prepared as previously described[1]. To the mixture are added, at -40°C, 150ml of THF, a solution of $Pd(P(Ph_3)_4$ (0.7g) in 20ml of THF. The acid chloride (15mmol) is introduced dropwise at -10°C and the mixture is stirred at this temperature during 2h, hydrolyzed with 100ml of buffer ammonia solution, filtered, extracted with ether ; the organic layer is washed with sat. NaCl, dried over Na_2CO_3 ; the solvent is evaporated ; after addition of 50ml of pentane (or hexane), the mixture is filtered and the crude product is distilled under reduced pressure to give the following products :

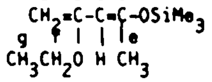
2-butyl 4-trimethylsilyloxy 1,3-pentadiene (Z) : 13


$CH_2{=}C\text{-}C{=}C\text{-}OSiMe_3$ ($CH_3CH_2CH_2CH_2$, H, CH_3; labels d c b a k, h g f e j)

bp = 67°C/0.05mmHg

NMR ^1H (CCl_4,TMS) : Hb(1H,s,5.0) ; Hd(2H,2s,4.88,4.76) ; He(2H,t,2.12) ; Hj(3H,s,1.84) ; Hf,Hg(4H,m,1.12,1.48) ; Hh(3H,t,0.84) ; Hk(9H,s,0.2).

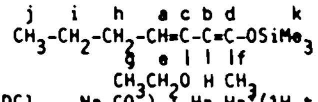
2-ethoxy 4-trimethylsilyloxy 1,3-pentadiene (Z) : 14


$CH_2{=}C\text{-}C{=}C\text{-}OSiMe_3$ (CH_3CH_2O, H, CH_3; labels a b c d h, g f e)

bp = 45-47°C/0.5mmHg

NMR ^1H $(CDCl_3,\ Na_2CO_3)$: Hc(1H,s,4.76) ; Ha(2H,2s,4.28,3.92) ; Hf(2H,q,3.6) ; He(3H,s,1.76); Hg(3H,t,1.2) ; Hh(9H,s,0.12).

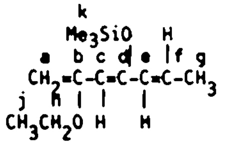
4-ethoxy 2-trimethylsilyloxy 2,4-octadiene : 15 (mixture of (Z,E) 15 and (E,E) 15')


$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH{=}C\text{-}C{=}C\text{-}OSiMe_3$ (CH_3CH_2O, H, CH_3; labels j i h a c b d k, g e f)

bp = 75-77°C/0.5mmHg

NMR ^1H $(CDCl_3,\ Na_2CO_3)$: Ha,Ha'(1H,t,5.04 and t, 4.44) ; Hb(1H,s,4.84) ; He(2H,m,3.68) ; Hf(3H,s,1.8) ; Hh,Hh'(2H,m,2,12) ; Hg,Hi(5H,m,1.52-1.04) ; Hj(3H,t,0.90) ; Hk(9H,s,0.12).
NMR ^{13}C $(CDCl_3,\ Na_2CO_3,TMS)$: 150(Cc') ; 149.3(Cd') ; 148.3(Cc) ; 148.2(Cd) ; 113.3(Ca) ; 104.2(Cb) ; 102.5(Ca') ; 100.3(Cb') ; 64.3(Ce) ; 61.3(Ce') ; 28.7(Cf) ; 22.9, 22.6(Ch and Ci) 13.3(Cg and Cj) ; 0.1(Ck).

2-ethoxy 4-trimethylsilyloxy 1,3,5-heptatriene : 16 (Z,E)

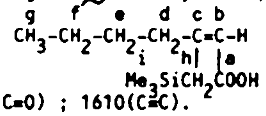

$CH_2{=}C\text{-}C{=}C\text{-}C{=}C\text{-}CH_3$ (Me_3SiO, H above; CH_3CH_2O, H, H below; labels k, a b c d e f g, j h)

bp = 75°C/0.01mmHg

NMR ^1H (CCl_4) : He and Hf(2H,m,5.9) ; Hc(1H,s,5) ; Ha(2H,2s,4.4,4.12) ; Hh(2H,q,3.7) ; Hg(3H,d,1.8) ; Hj(3H,t,1.28) ; Hk(9H,s,0.1).

5. CARBONATATION

To a suspension of CuBr (15mmol, 2.2g), LiI (20mmol, 20ml of 1N ethereal solution) in 20ml of ether, is added at -5°C TMSCH$_2$MgCl (15mmol, 18.3ml of 0.82N ethereal solution). To this pale green solution is added after 1h, at this temperature, hexyne (12.5mmol, 1.02g) ; the mixture is allowed to warm to +16°C and stirred at this temperature for 17h. In this dark green mixture is introduced a hexynyl lithium solution preformed in THF (15mmol in 60ml of THF) and then CO$_2$ is bubbled at 20°C into the mixture which is allowed to warm at 35°C during 1h until ether is evaporated and this solution is refluxed (65°C) during 3h. The grey suspension is hydrolyzed with 50ml of H$_2$SO$_4$5N during 1h, filtered, extracted with ether. The organic layer is washed with sat. NH$_4$Cl and then sat NaCl and dried over MgSO$_4$. The crude product is purified by chromatography (silica Kieselgel 60 column) and eluted with a mixture of hexane-ethylacetate (90-10) : to give **17** 3-methyl 2-hepten oïc acid (44% from hexyne).



$$\overset{g}{CH_3}\text{-}\overset{f}{CH_2}\text{-}\overset{e}{CH_2}\text{-}\overset{d}{CH_2}\text{-}\overset{c}{\underset{\underset{\overset{i}{Me_3Si}CH_2}{h|}}{C}}{=}\overset{b}{\underset{\underset{COOH}{|a}}{C}}\text{-}H$$

IR neat cm^{-1} : 3000(OH) ; 1700(C=O) ; 1610(C=C).

NMR ^{1}H :(CDCl$_3$,TMS) Ha(1H,s,12.0) ; Hb(1H,s,5.48) ; Hh(2H,s,2.36) ; Hd(2H,t,2.06) ; He and Hf(4H,m, 1.2-1.6) ; Hg(3H,t,0.9) ; Hi(9H,s,0,06).

NMR ^{13}C : (CDC13,TMS) nine peaks ; 173.2(Ca) ; 167.8(Cc) ; 111.1(Cb) ; 41(Cd) ; 31,6, 26.7, 22.5(Ce, Cf, Ch) ; 14(Cg) ; -0,7(Ci).
Mass spectrum (m/e) : 214(M$^+$) 0.5% ; 199(M$^+$-Me) 5% ; 157(M$^+$-C$_4$H$_9$) 3% ; 82(M$^+$-Me$_3$SiCH$_2$-COOH) 45% ; 73(SiMe$_3$) 100%.

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