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CONJUGATE ADDITION OF GRIGNARD REAGENTS TO α,β-UNSATURATED ESTERS : PREPARATION OF ALKYLSILYLKETENEACETALS.

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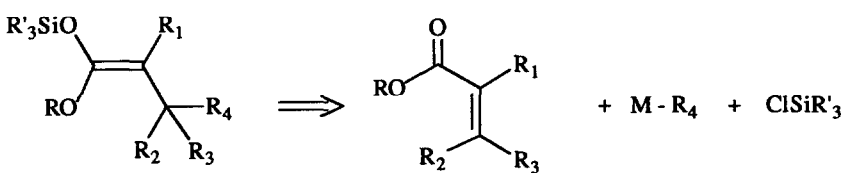
Abstract: *Alkylsilylketeneacetals have been prepared by a one-step copper-catalyzed 1,4-addition of Grignard reagents to acrylic, crotonic, methacrylic and 3,3-dimethylacrylic esters in the presence of $ClSiMe_3$. Their Z/E ratio could be modified using Cu^I (in the presence of HMPA) or Cu^{II} salts (without HMPA).*

It has been previously shown that ω-alkynylenoxysilanes can be easily cyclised into 2-alkylidene-1-(1-oxoalkyl)cycloalkanes by treatment with mercury (II) chloride [1]. We have envisioned to extend such a methodology to analogous alkynyltrimethylsilylketeneacetals.

Alkylsilylketeneacetals can generally be prepared by 1,4-hydrosilylation of α,β-unsaturated esters [2], by reaction of esters with trialkylsilyl perchlorates in the presence of an amine [3] or by action of chlorotrialkylsilanes on ester enolates formed by a strong base deprotonation of esters [4]. They can also be obtained by reaction of sodium with alkylmalonates [5] or by action of metals on α-haloesters [2b,4b,6], in the presence of trimethylsilyl chloride. However, extension of such methods to acetylenic compounds appears unattractive [7].

Retrosynthesis shows a more direct method through C-C bond formation by 1,4-addition of an organometallic compound to an acrylate derivative followed by one-pot reaction with a chlorotrialkylsilane, since the carbon framework and the enol double bond are built up in the same step. The conjugate addition of



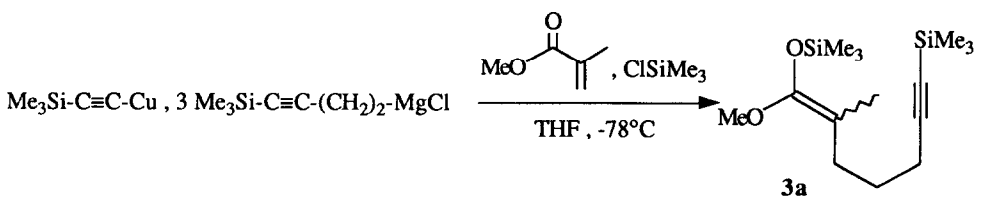
organocopper reagents represents probably the most valuable synthetic procedure for the formation of such C-C bonds. Since the early catalytic reaction reported by Kharasch in 1941 [8a] many papers have been devoted to the

improvement and the understanding of the reaction. In the case of α,β-unsaturated aldehydes and ketones, the use of polyalkyllithiocuprates have been emphasized. Until the beginning of the 80's 1,4-addition of R_2CuLi to enoates was not considered a synthetically useful process, because 1,2-addition is often preferred [8b]. The use of $RCu.BF_3$ [9] or high order cuprates $R_2Cu(CN)Li_2$ [10] have allowed the conjugate addition to enoates to take place but a large excess of the R group containing reagent (100 to 200%) was necessary to obtain good yields. This problem was partially overcome with the use of $Me(R)Cu(CN)Li_2$ in which the methyl group acts mainly as a "dummy" ligand [10]. However, to avoid the limitations introduced by the preparation of alkyllithiums (precursors of the lithiocuprates) we have focused our work since 1975 on Grignard reagents [11].

In a previous work in enoxysilanes chemistry [12] we reported the successful 1,4-addition of the poorly transferable 4-trimethylsilyl-3-butynyl chain (R') on methacrolein using the mixture $Me_3Si\text{-}C{\equiv}C\text{-}Cu$, 3R'MgCl, the so formed enolate being trapped by addition of t-butyldimethylchlorosilane in the presence of HMPA. With methyl methacrylate using the same reagents and the same stepwise procedure no product resulting from the 1,4-transfer of the butynyl chain was detected even in the presence of $BF_3.Et_2O$.

Since the study of Normant and al [13] on conjugate addition of organocuprates to unsaturated aldehydes in the presence of trimethylchlorosilane, the great influence of halosilanes on the rate and the selectivity of the addition of organocopper reagents to α,β-unsatured carbonyl compounds was demonstrated [13b,14,15,16,17]. With unsaturated esters the presence of chlorotrimethylsilane increases the reaction rate and improves the selectivity towards 1,4- over 1,2-addition [14b,e,15,16,17]. The chlorosilane accelerated 1,4-addition of Grignard reagents to enoates in the presence of $Cu^{I}Br/Me_2S$, HMPA [15] or $Cu^{II}Br_2$ [17] seemed particularly interesting because the excess in Grignard reagent was only 20 and 50% and yields of isolated esters were good. In the case of unsaturated aldehydes and ketones, the 1,4-addition of copper reagents in the presence of halosilanes allowed the direct synthesis of silylenol ethers, [14a,c,d,15], and recently the formation of silylketeneacetals by 1,4- addition of methylcopper to methyl cinnamate in the presence of $ISiMe_3$ was reported [18].

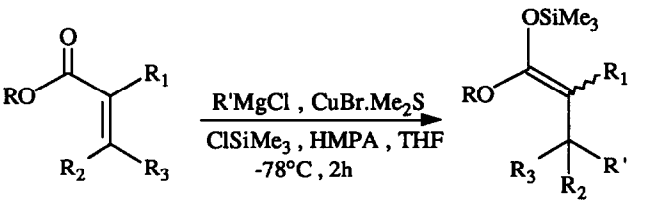
As we observed (vide supra) that no reaction took place in the stepwise addition of the mixture $Me_3Si\text{-}C{\equiv}C\text{-}(CH_2)_2MgCl$, $Me_3Si\text{-}C{\equiv}C\text{-}Cu$ and $ClSiMe_3$ to methyl methacrylate, we performed the slow addition of a mixture of methyl methacrylate and $ClSiMe_3$ to the mixed polyalkynylmagnesiocuprate (60% excess of Grignard reagent) maintained at -78°C : the expected methyltrimethylsilylketeneacetal **3a** formed was isolated using a non-aqueous work-up [19].



3a

Owing to the simplicity of the $ClSiMe_3$ accelerated addition of Grignard reagents in the presence of catalytic copper bromide [15], we have thus explored the scope of this reaction with various esters in order to prepare alkynyl- and alkylsilylketeneacetals.

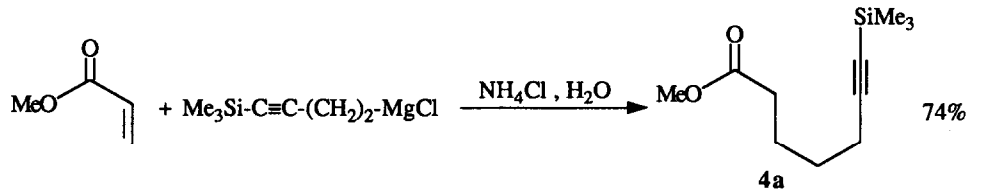
After reaction in THF of the organomagnesium reagent (1.2 eq) with the unsaturated ester at - 78°C, during 2 hours in the presence of $CuBr.Me_2S$ (0.06 eq), HMPA (2.4 eq) and $ClSiMe_3$ (2.4 eq) the products were isolated by flash vacuum transfer after a non-aqueous work-up (see experimental part). Our results are reported in Table I. In the cases of methyl acrylate, methacrylate and crotonate (entries 1-7) the alkyltrimethylsilylketeneacetals were isolated in good yields (61 to 74%) using primary and, interestingly, secondary Grignard reagents [20]. With vinylmagnesium chloride and methyl crotonate (entry 8) the low yield of silylated products was partly due to their volatility. With ethyl 3,3-dimethylacrylate (entry 9) the 1,4-addition



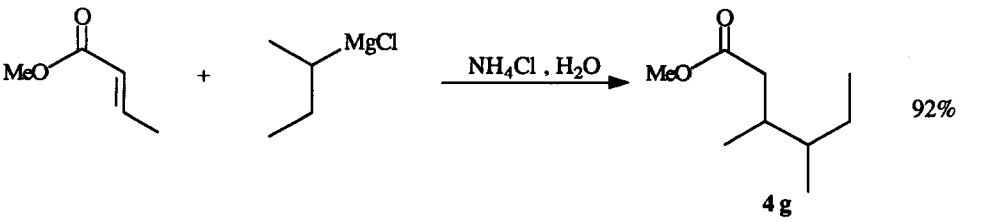
1 **3**

was also observed but the poorer yield probably reflects the higher energy required to build the sterically crowded quaternary center. One limitation of this methodology appears with α,β-disubstituted unsaturated esters : no products resulting from 1,4-transfer to methyl cyclohexenecarboxylic (entries 10 and 11) and tiglic (entry 12) esters were detected [21].

Generally the alkylsilylketeneacetals were obtained free of the corresponding esters. The esters could however be obtained by subsequent hydrolysis. Nevertheless the isolation of the keteneacetal could be avoided when performing an aqueous work-up after the chlorosilane accelerated 1,4-addition. This "direct" synthesis of the undescribed esters **4a** and **4g** was performed in this fashion [22]. The higher yields so obtained are indicative of an incomplete recovery of the corresponding keteneacetals in the previous experiments (entries 1, 7).



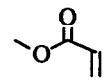
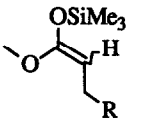
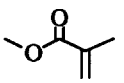
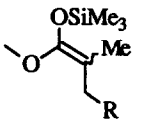
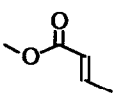
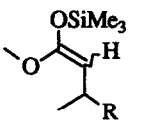
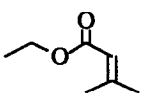
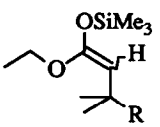
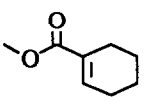
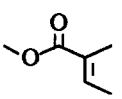
4a



4 g

mixture of diastereoisomers (55/45)

TABLE I - Preparation of alkylsilylketeneacetals by copper catalysed addition of Grignard reagents to enoates in the presence of $ClSiMe_3$ / HMPA at -78°C.

entries	unsaturated esters 1	RMgX	products		Z/E [23]	yield
1		$Me_3Si-C\equiv C-(CH_2)_2-MgCl$		**3a**	94/6	65%
2		sec-C_4H_9-MgCl		**3b**	66/34	63%
3		n-C_4H_9-MgCl		**3c**	21/79	62%
4		sec-C_4H_9-MgCl		**3d**	31/69	61%
5		n-C_6H_{13}-MgCl		**3e**	29/71	74%
6		n-C_6H_{13}-MgCl		**3f**	79/21	68%
7		sec-C_4H_9-MgCl		**3g**	79/21 [a]	69%
8		H_2C=CH-MgCl		**3h**	57/43	23% [b]
9		n-C_4H_9-MgCl		**3i**	86/14	46% [b]
10		n-C_6H_{13}-MgCl	*			
11		sec-C_4H_9-MgCl	*			
12		n-C_6H_{13}-MgCl	*			

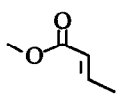
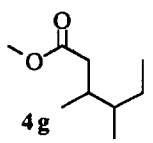
* No alkylsilylketeneacetals detected.

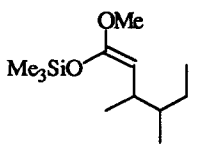
a The NMR spectra shows for the E and Z isomers, mixtures of diastereoisomers 45/55. The relative configurations were not assigned.

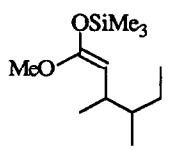
b Reaction conditions were not optimized.

As reported for the chlorosilane accelerated 1,4-addition of organomagnesium reagents to enones [15], reactions with acrylic, crotonic and 3,3-dimethylacrylic esters gave predominantly the Z-alkylsilylketeneacetals (the same Z selectivity was observed in the $ClSiMe_3$ assisted addition of MeCu to methyl cinnamate [18]): a synthetically useful 94/6 Z/E ratio was reached with the butynyl Grignard reagent and the acrylic ester (entry 1). After reaction of sec-butylmagnesium chloride with methyl crotonate in the presence of $ClSiMe_3$ and cupric bromide in THF without HMPA, according to ref. [17], followed by a non aqueous work-up, a mixture of silylketeneacetals **3g** was isolated where the E-isomer was predominant (see A in Table II). The origins of the Z-selectivity in the reaction of enoates with the cupric salt are obscure, but they could be related to the presence of HMPA: the keteneacetal E/Z ratios observed above using either $CuBr.Me_2S$, HMPA, $ClSiMe_3$ or $CuBr_2$, $ClSiMe_3$ are close to the ratios obtained, as expected [4b], from $ClSiMe_3$ trapping of the enolates prepared by lithium diisopropylamide deprotonation of ester **4g**, working respectively with or without HMPA (see B in Table II).

TABLE II - Selectivity in the preparation of the silylketeneacetals **3g**.

starting material	method *	conditions	silylketeneacetals Z	silylketeneacetals E
	A	$CuBr_2$, Et_2O-THF (4-1)	19 [d]	81 (~65/35) [c]
	A	$CuBr.Me_2S$, THF, HMPA	79 (~55/45) [c]	21 (~55/45) [c]
 **4g**	B [a]	THF	4	96
	B [b]	THF, HMPA	73	27





* A - $ClSiMe_3$ accelerated 1,4-addition of sec-BuMgCl.
B - LDA deprotonation of **4g**.
a Ester was added to a mixture of LDA and $ClSiMe_3$ maintained at -78°C.
b $ClSiMe_3$ was added after formation of the ester enolate at -78°C.
c Ratio of diastereoisomers (relative configurations were not attributed).
d Ratio of diastereoisomers not determined.

In summary we have partly examined the scope of the copper-catalyzed conjugate addition of Grignard reagents to enoates in the presence of trimethylchlorosilane. The 1,4- transfer of primary and, more importantly, secondary reagents have occurred with acrylic, methacrylic, crotonic and 3,3-dimethylacrylic esters. Alkylsilylketeneacetals were isolated after a non-aqueous work-up in good yields using only 1.2 equivalent of Grignard reagent.

Acknowledgement : *We warmly thank Dr Jacqueline SEYDEN-PENNE for helpful discussions and useful suggestions.*

EXPERIMENTAL PART

All reactions were performed under argon and with dried equipment. THF was distilled just before use from sodium benzophenone. HMPA and triethylamine were distilled from CaH_2. Hexane was distilled from P_2O_5 and Me_3SiCl just before use from quinoleine. Celite was dried and stored in an oven at 130°C. Alkylmagnesiumchlorides were prepared in THF. Chromatographic purifications of products were achieved with 70/200 mesh silica gel using hexane/ether (4:1) as eluent.

^1H NMR spectra were taken at 200 MHz and 250 MHz on Bruker instruments (AC200 and AM250). Spectra are reported in part per million from tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 682 instrument ; absorptions are reported in cm^{-1} . Mass spectrometry was performed on a GC-MS Nermag R10-10 equiped with a CpSil 5 (25 m) column.

Synthesis of esters by 1,4-addition. General procedure.

A solution of Grignard reagent RMgX in THF (2.11 mmol) and HMPA (770 µl, 4.2 mmol) were added to a stirred suspension of CuBr.Me_2S (20 mg, 0.1 mmol) in THF (4 mL) maintained at -78°C under argon in a 25 mL two-necked flask. After ten minutes a solution of conjugated ester (1.76 mmol) and trimethylsilylchloride (530 µl, 4.22 mmol) in THF (4 mL) was added dropwise over 0.5 hour. Then the yellow mixture was stirred 2 hours at -78°C and triethylamine (0.5 mL) was added. The mixture was allowed to rise up to room temperature and was poured into an NH_4Cl saturated aqueous solution. After 1 hour stirring and ether extraction (3 x 30 mL) the organic layer was washed with water just to neutrality, dried over anhydrous Na_2SO_4 and concentrated. Chromatography of the remainder on silica gel gave the ester resulting from 1,4-addition.

Methyl 7-trimethylsilyl-6-heptynoate **4a** :

^1H NMR ($CDCl_3$, 200 MHz) : 3.66 (s, 3H, OCH_3), 2.34 (t, J = 9.0 Hz, 2H, CH_2-CO), 2.23 (t, J = 8.4 Hz, 2H, CH_2-C≡), 1.82-1.63 (m, 2H, CH_2-CH_2-CO), 1.63-1.44 (m, 2H, CH_2-CH_2-C≡), 0.13 (s, 9H, $SiMe_3$). M.S. ($C_{11}H_{20}O_2Si$, M 212), m/e (relative intensity): 43 (26), 45 (16), 55 (14), 59 (53), 69 (12), 73 (60), 75 (65), 79 (17), 80 (32), 81 (13), 83 (20), 89 (100), 91 (15), 93 (17), 105 (10), 108 (20), 109 (28), 165 (11), 167 (41), 197 (27), 212 (1). IR (film) (cm^{-1}) : 2930 (FF), 2170 (F), 1730 (FF), 1250 (FF), 840 (FF). Anal. calcd. for $C_{11}H_{20}O_2Si$ (212.366) : C 62.21, H 9.49%, found C 61.84, H 9.74%.

Methyl 3,4-dimethylhexanoate **4g** :

^1H NMR ($CDCl_3$, 200 MHz) : 3.69 (s, 3H, OCH_3), 2.21 (m, 2H, CH_2-CO), 1.45-1.03 (m, 4H, CH_2-CH_3 and 2 CH-CH_3), 0.96-0.76 (m, 9H, 3 CH_3). M.S. ($C_9H_{18}O_2$, M 158), m/e (relative intensity): 39 (17), 41 (52), 42 (10), 43 (48), 55 (28), 56 (16), 57 (38), 59 (27), 69 (48), 74 (100), 75 (18), 83 (10), 84 (21), 85 (52), 87 (51), 101 (23), 102 (13), 158 (1). IR (film) (cm^{-1}) : 2950 (FF), 1735 (F), 1240 (F), 830 (F). Anal. calcd. for $C_9H_{18}O_2$ (158.243) : C 68.31, H 11.47%, found C 68.01, H 11.42%.

Synthesis of alkylsilylketeneacetals. General procedure.

The same procedure than that described for the synthesis of esters (vide supra) was used unless the aqueous work-up which was substituted by a non-aqueous one. Experiments were done in a 50 mL two-necked flask and after the addition of triethylamine and the rise to room temperature, THF and the excess of $ClSiMe_3$ were evaporated under reduced pressure (0.1 mmHg). Then hexane (7 mL) and dry celite (3 g) were added to the residue. The mixture was stirred under argon and after settlement the supernatant solution was transferred with a double-tipped needle into a sintered-glass funnel containing dry celite and fitted to a receptor. The sintered-glass funnel and the receptor were always maintained under argon. Washings of the celite impregnated with the residual reaction mixture were repeated 6 times in the same way. Hexane from recovered filtrate was removed under vacuum and the silylketeneacetal was isolated by flash-transfer under reduced pressure (0.1 mmHg).

1-methoxy-7-trimethylsilyl-1-trimethylsilyloxy-1-hepten-6-yne **3a** :

^1H NMR (C_6D_6, 250 MHz) : 3.73 (t, J = 7.3 Hz, 0.06H, =CH of E isomer), 3.35 (t, J = 7.3 Hz, 0.94H, =CH of Z isomer), 3.34 (s, 0.18H, OCH_3 of E isomer), 3.08 (s, 2.82H, OCH_3 of Z isomer), 2.24 (t, J = 6.6 Hz, 4H, CH_2-C≡ and CH_2-CH=), 1.62 (quintuplet, J = 7.0 Hz, 2H, CH-CH_2-CH), 0.22 (s, 9H, $SiMe_3$), 0.21 (s, 9H, $SiMe_3$). M.S. ($C_{14}H_{28}O_2Si_2$, M 284), m/e (relative intensity): 43 (11), 45 (22), 55 (84), 56 (15), 59 (37), 68 (12), 73 (100), 75 (26), 89 (40), 105 (13), 107 (16), 109 (12), 147 (16), 159 (15), 165 (39), 197 (11), 284 (2). IR (film) (cm^{-1}) : 2920 (FF), 2155 (F), 1670 (FF), 1250 (F), 840 (FF).

1-methoxy-4-methyl-1-trimethylsilyloxy-1-hexene **3b** :

^1H NMR (C_6D_6, 250 MHz) : 3.87 (t, J = 8.3 Hz, 0.34H, =CH of E isomer), 3.48 (t, J = 6.9 Hz, 0.66H, =CH of Z isomer), 3.36 (s, 1.02H, OCH_3 of E isomer), 3.16 (s, 1.98H, OCH_3 of Z isomer), 2.35-2.19 (m, 1H),

2.19-2.03 (m, 1H), 1.59-1.35 (m, 2H), 1.35-1.12 (m, 1H), 1.04-0.90 (m, 6H), 0.24 (s, 3.06H, $SiMe_3$ of E isomer), 0.16 (s, 5.94H, $SiMe_3$ of Z isomer). M.S. ($C_{11}H_{24}O_2Si$, M 216), m/e (relative intensity): - Z isomer: 55 (100), 73 (37), 159 (53), 216 (3); - E isomer: 55 (100), 73 (48), 159 (54), 216 (3). IR (film) (cm^{-1}) : 2930 (FF), 1665 (FF), 1230 (FF), 840 (FF).

1-methoxy-2-methyl-1-trimethylsilyloxy-1-heptene **3c** :

^1H NMR (C_6D_6, 250 MHz) : 3.25 (s, 3H, OCH_3), 2.13 (t, J = 7.8 Hz, 1.58H, CH_2-C= of E isomer), 2.05 (t, J = 7.8 Hz, 0.42H, CH_2-C= of Z isomer), 1.67 (s, 0.63H, CH_3-C= of Z isomer), 1.60 (s, 2.37H, CH_3-C= of E isomer), 1.49-1.19 (m, 6H, CH_2-(CH_2)$_3$-CH_3), 0.85 (bt, J = 7.1 Hz, 3H, CH_3-CH_2), 0.15 (s, 1.89H, $SiMe_3$ of Z isomer), 0.13 (s, 7.11H, $SiMe_3$ of E isomer). M.S. ($C_{12}H_{26}O_2Si$, M 230), m/e (relative intensity): - Z isomer: 41 (22), 43 (11), 55 (15), 57 (24), 59 (14), 69 (100), 73 (39), 88 (84), 89 (14), 101 (15), 173 (30), 230 (12); - E isomer: 69 (100), 73 (39), 88 (11), 173 (23), 230 (8). IR (film) (cm^{-1}) : 2940 (FF), 2840 (F), 1690 (FF), 1455 (m), 1240 (FF), 1155 (F), 830 (FF).

2,4-dimethyl-1-methoxy-1-trimethylsilyloxy-1-hexene **3d** :

^1H NMR (C_6D_6, 200 MHz) : 3.35 (s, 0.93H, OCH_3 of Z isomer), 3.34 (s, 2.07H, OCH_3 of E isomer), 2.22-1.81 (m, 2H, CH_2-C=), 1.71 (s, 0.93H, CH_3-C= of Z isomer), 1.62 (s, 2.07H, CH_3-C= of E isomer), 1.59-1.34 (m, 2H, CH_2-CH_3), 1.34-1.05 (m, 1H, CH-CH_3), 0.96 (d, J = 1.8 Hz, 3H, CH_3-CH), 0.93 (t, J = 7.9 Hz, 3H, CH_3-CH_2), 0.20 (s, 9H, $OSiMe_3$). M.S. ($C_{12}H_{26}O_2Si$, M 230), m/e (relative intensity): - Z isomer: 41 (11), 69 (100), 73 (38), 173 (30), 230 (6); - E isomer: 41 (14), 69 (100), 73 (40), 173 (29), 230 (6);. IR (film) (cm^{-1}) : 2965 (FF), 1705 (F), 1255 (F), 1170 (FF), 845 (FF).

1-methoxy-2-methyl-1-trimethylsilyloxy-1-nonene **3e** :

^1H NMR (C_6D_6, 250 MHz) : 3.42 (s, 3H, OCH_3), 2.35-2.15 (m, 2H, CH_2-C=), 1.81 (m, 0.87H, CH_3-C= of Z isomer), 1.75 (m, 2.13H, CH_3-C= of E isomer), 1.65-1.22 (m, 10H, CH_2-(CH_2)$_5$-CH_3), 1.05 (bt, 3H, CH_3-CH_2), 0.26 (s, 9H, $OSiMe_3$). M.S. ($C_{14}H_{30}O_2Si$, M 258), m/e (relative intensity): - Z isomer: 41 (12), 69 (100), 73 (36), 173 (32), 258 (5); - E isomer: 69 (100), 73 (37), 173 (34), 258 (5). IR (film) (cm^{-1}) : 2930 (FF), 1695 (FF), 1440 (m), 1240 (FF), 845 (FF).

1-methoxy-3-methyl-1-trimethylsilyloxy-1-nonene **3f** :

^1H NMR (C_6D_6, 250 MHz) : 3.68 (d, J = 9.3 Hz, 0.21H, CH-C= of E isomer), 3.37 (s, 0.63H, OCH_3 of E isomer), 3.32 (d, J = 8.9 Hz, 0.79H, CH-C= of Z isomer), 3.15 (s, 2.37H, OCH_3 of Z isomer), 2.76-2.58 (m, 1H, CH-CH_3), 1.57-1.23 (m, 10H, CH_2-(CH_2)$_5$-CH_3), 1.16 (d, J = 13.5 Hz, 3H, CH_3-CH), 0.90 (bt, J = 6.8 Hz, 3H, CH_3-CH_2), 0.24 (s, 9H, $SiMe_3$). M.S. ($C_{14}H_{30}O_2Si$, M 258), m/e (relative intensity): - Z isomer: 69 (100), 73 (32), 89 (12), 173 (45), 258 (8); - E isomer: 69 (100), 73 (23), 173 (25), 258 (1). IR (film) (cm^{-1}) : 2945 (FF), 1665 (FF), 1425 (m), 1230 (FF), 835 (FF).

3,4-dimethyl-1-methoxy-1-trimethylsilyloxy-1-hexene **3g** :

^1H NMR (C_6D_6, 250 MHz) : 3.77 (d, J = 9.6 Hz) and 3.73 (d, J = 9.9 Hz): =CH of E isomers, 3.38 (d, J = 9.3 Hz) and 3.33 (d, J = 9.7 Hz): =CH of Z isomers, 3.35 (s, 0.63H, OCH_3 of E isomers), 3.12 (s, 2.37H, OCH_3 of Z isomers), 2.86-2.55 (m, 1H, CH-C=), 1.70-1.46 (m, 1H, CH-CH_2), 1.46-1.16 (m, 2H, CH_2-CH_3), 1.16-1.02 (m, 9H, CH_3), 0.22 (s, 1.89H, $SiMe_3$ of E isomers), 0.15 (s, 7.11H, $SiMe_3$ of Z isomers). M.S. ($C_{12}H_{26}O_2Si$, M 230), m/e (relative intensity): - Z isomer: 69 (100), 73 (23), 173 (25), 230 (1); - E isomer: 69 (100), 73 (24), 173 (28), 230 (1). IR (film) (cm^{-1}) : 2940 (FF), 1660 (FF), 1240 (FF), 825 (FF).

1-methoxy-3-methyl-1-trimethylsilyloxy-1,4-pentadiene **3h** :

^1H NMR (C_6D_6, 250 MHz) : 6.10-5.90 (m, 1H, CH=CH_2), 5.17 (dd, J = 17.1 and 1.4 Hz, 1H, =CH(cis)H), 5.01 (dd, J = 10.4 and 1.4 Hz, 1H, =CH(trans)H), 3.78 (d, J = 11.2 Hz, 0.43H, O-C=CH of E isomer), 3.46-3.37 (m, 1H, CH-CH_3), 3.35 (s, 1.29H, OCH_3 of E isomer), 3.29 (d, J = 16.9 Hz, 0.57H, O-C=CH of Z isomer), 3.09 (s, 1.71H, OCH_3 of Z isomer), 1.24 and 1.19 (d, 3H, J = 8.4 Hz, CH_3-CH), 0.23 (s, 3.87H, $OSiMe_3$ of E isomer), 0.15 (s, 5.13H, $OSiMe_3$ of Z isomer). M.S. ($C_{10}H_{20}O_2Si$, M 200), m/e (relative intensity): 45 (17), 53 (10), 59 (15), 68 (24), 69 (19), 73 (74), 81 (100), 89 (23), 96 (13), 200 (10).

3,3-dimethyl-1-ethoxy-1-trimethylsilyloxy-1-heptene **3i** :

^1H NMR (C_6D_6, 200 MHz) : 3.85 (s, 0.14H, =CH of E isomer), 3.77 (quintuplet, J = 7.1 Hz, 0.28H, CH_2O of E isomer), 3.38 (s, 0.86H, =CH of Z isomer), 3.36 (quintuplet, J = 7.5 Hz, 1.72H, CH_2O of Z isomer), 1.67-1.25 (m, 6H, C-(CH_2)$_3$-CH_3), 1.33 (s, 6H, (CH_3)$_2$-C), 0.99 (t, J = 7.1 Hz, 3H, CH_3-CH_2-O), 0.94 (t, J = 3.9 Hz, 3H, CH_3-CH_2-C), 0.27 (s, 9H, $SiMe_3$). M.S. ($C_{14}H_{30}O_2Si$, M 258), m/e (relative intensity): - Z isomer: 73 (26), 75 (15), 83 (100), 125 (12), 201 (12), 258 (1); - E isomer: 73 (25), 75 (11), 83 (100), 125 (11), 201 (16), 258 (4). IR (film) (cm^{-1}) : 2925 (FF), 1665 (FF), 1235 (FF), 835 (FF).

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19) These alkylsilylketeneacetals were always contaminated with 20-30% of the corresponding ester. No product resulting from successive 1,2- and 1,4-addition as reported for similar reactions [15, 8b] were detected.

20) Such 1,4-addition of secondary organometallic species to enoates was only reported very recently in the CuCl catalyzed reaction of organomagnesium and organomanganese reagents in the presence of $ClSiMe_3$ at 20° C and 0°C respectively : G. CAHIEZ and M. ALAMI, *Tetrahedron Lett.*, **1990**, *31*, 7423, 7425.

21) When the temperature of the reaction mixture was slowly raised to -25°C and maintained 40 min at this temperature some alkylsilylketeneacetals were detected by NMR of the resulting product after a non-aqueous work-up.

22) The conjugate addition of the butylmagnesium chloride to the α,β-unsaturated γ-butyrolactone in the same conditions gave the β-butyl γ-butyrolactone in 82% yield.

23) The E and Z stereochemistry of **3a** , **3b** and **3f** - **3i** were assigned from the NMR spectra of mixtures as reported in literature [4b] : in C_6D_6, the signal of the olefinic proton of the Z-isomer appears at higher field than those of the E-isomer. For **3c** - **3e** the Z stereochemistry was tentatively assigned to the minor isomer which shows a small NOE effect on the methoxy singulet when irradiation was performed on the methyl linked to the C=C double bond.