Pergamon

Tetrahedron Vol. 51, No. 35, pp. 9569-9580, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00532-3

Preparation of Silyl Enol Ethers Derived from α-Phenylseleno aldehydes and α-Phenylseleno ketones

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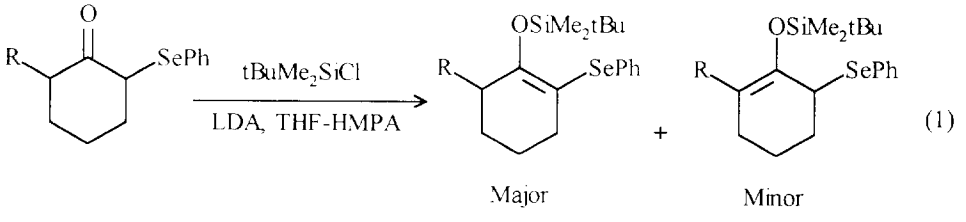
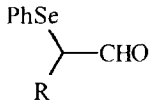
Abstract : The best experimental conditions for the preparation of trimethylsilyl enol ethers **3** from α-phenylseleno aldehydes **1**, compatible with a limited deselenenylation of the substrate, were studied. Starting from α-phenylseleno ketones **2**, the enoxysilanes **4**, bearing a vinylic PhSe group, are the major products when triethylamine is the base. Trimethylsilyl enol ethers **5** with an allylic PhSe group are also formed beside **4** when LDA or KH are used at lower temperatures.

Silyl enol ethers are pivotal intermediates in modern organic chemistry allowing efficient and selective carbon-carbon bond formations in aldol and Michael type reactions.[1,2,3] Since House's work,[4] concerning the preparation of easily hydrolysable trimethylsilyl enol ethers, other experimental procedures have been described.[2,5,6] The synthesis of the more stable t-butyldimethylsilyl[7] and tri(isopropyl)silyl[8] derivatives has also been proposed. The synthesis and the reactivity of β-bromo, β-alkoxy, β-alkylthio and β-phenylthio silyl enol ethers have been studied and reviewed.[9] We observe that a single paper was devoted to the access of some trialkylsilyl enol ethers derived from α-phenylseleno ketones.[10] Using t-butyldimethylsilyl chloride and LDA as base in a mixture THF-HMPA, 2-phenylselenocyclohexanone gave the silyl enol ether bearing a vinylic phenylseleno group as the major product. (reaction 1).



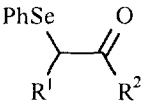
(1)

The growing interest of selenium intermediates in organic synthesis,[11,12] has led us to initiate a study of silyl enol ethers derived from α-phenylseleno aldehydes **1**[11,13] and α-phenylseleno ketones **2**.[11,14] The use of these carbonyl compounds, in the synthesis of unsaturated functional and polyfunctional structures, is studied in our laboratory.[15] We present here our results concerning the access to trimethylsilyl enol ethers **3**, **4** (and **5**).



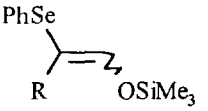
1

a R = H
b R = Me
c R = Et
d R = Ph
e R = Bn
f R = iPr

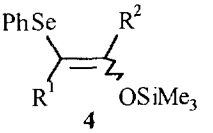


2

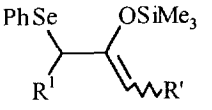
a R^1 = H R^2 = Me
b H Ph
c Me Ph
d H tBu
e Me Me
f Me Et
g Et Me
h $-(CH_2)_3-$
i $-(CH_2)_4-$



3



4



5

($R^2 = CH_2R'$)

Preparation of enoxysilanes 3 from α-phenylseleno aldehydes 1.

The α-phenylseleno aldehydes **1**, selected for these studies, were prepared by the action of N-phenylselenomorpholine on the corresponding aldehydes.[13] The simplest term **1a** was obtained by addition of PhSeBr on ethylvinylether in ethanol, followed by the hydrolysis of the intermediate acetal[16] and **1d** was the result of the reaction of PhSeCl on the trimethylsilyl ether derived from phenylethanal. In this last case, the general method leads to a complex mixture. The classical methods[4,5,6] were tested for the access to the silyl enol ethers **3** but the yields were modest and a partial deselenenylation of the substrate (10-20 % of PhSeSePh isolated) was observed. The yield was improved when THF was used as solvent instead of CH_3CN or DMF, the reaction being carried out at room temperature. Me_3SiCl and Et_3N were added to the substrate in ratios determined for the formation of **3a** from **1a** (Table 1).

Table 1. Experimental Conditions tested for the synthesis of **3a** in THF

Entry	Me_3SiCl (eq.)	Et_3N (eq.)	Temp. °C	React time (h)	Conversion % [a]	E/Z ratio [a]
1	6	2	+ 20	1	47	75/25
2	6	2	+ 20	3	80	85/15
3	3	3	+ 20	6	100	85/15
4	6	3	- 20	10	100	90/10
5	6	2	+ 50	10	100	87/13

a) Determined by ^1H NMR-200 MHz on crude product.

The best conditions found for the synthesis of compounds **3** were those of entry 3 (Table 1). Enoxysilanes **3** were obtained in convenable yields (Table 2) but we cannot avoid the formation of small

amounts of diphenyldiselenide (~ 5 %). We must also point out that the formation of **3f** (R = iPr) was complete after one week, using the same experimental conditions. The enoxysilanes **3** are very hydrolysable compounds and are stored at - 10°C and protected from moisture. Despite their instability during a classical distillation under reduced pressure, they could be purified by Kugelrohr distillation or by chromatography on basic alumina. They were used, in crude form, in various reactions with electrophilic reagents.[17]

The enoxysilane **3a** appears as a mixture of the two geometric isomers (E/Z : 85/15). The characterization of the two forms and those of the other trimethylsilyl enol ethers **3** result from a ^{1}H, ^{13}C, ^{77}Se NMR study which will be described elsewhere. The E/Z ratio of **3a** is not modified after three hours of heating at 40°C in CH_2Cl_2.

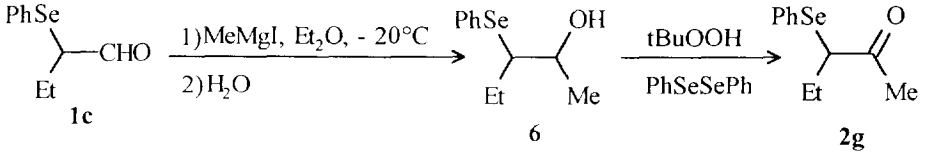
Table 2. Preparation of β-phenylseleno trimethylsilyl enol ethers **3**

N°	R	Purification	Yield %	Geometric Isomers
3a	H	a	78	85/15 (E/Z)[c]
3b	Me	a	75	100/0
3c	Et	a	80	100/0
3d	Ph	b	80	68/32[c]
3e	Bn	b	73	100/0[c]
3f	iPr	b	68	94/6[c]

a) Kugelrohr distillation. b) Chromatography on basic alumina.
c) Determined by G.C - Masse spectra.

Preparation of enoxysilanes 4 (and 5) from α-phenylseleno ketones 2.

The same transformation into enoxysilanes **4** (and **5**) was carried out on α-phenylseleno ketones **2a-2i**. The ketones **2a**[14f], **2b**[14e], **2c**[14e], **2d**[14e], **2e**[14g], **2f**[14e], **2h**[14c], **2i**[14e] were prepared according to known procedures. The 3-phenylseleno 2-pentanone **2g** was synthesized in two steps from 2-phenylseleno butanal **1c** (reaction 2). The formation of the intermediate 3-phenylseleno 2-pentanol **6** was achieved as described for analogs derived from phenylselenoethanal.[16] The oxidation step was carried out with a good yield using the method described by Kuwajima and Coll.,[14h] with a good yield.



The access to the trimethylsilyl enol ethers **4** derived from the α-phenylseleno ketones **2** was expected to be more difficult, taking into account the lower reactivity of the carbonyl group, despite the more acidic character of the proton linked to the carbon atom bearing the PhSe group.[11,18] The work of Kuwajima[10] indicates that trialkylsilyl enol ethers such as **4** are the major products, but the formation of the regioisomers **5**

could be observed. More over, we have observed a partial deselenenylation of the α-seleno ketones. The intermediate enolate ions could be selenophilic towards the substrates.[11,17,19]

As for the aldehydes **1**, the classical methods[4-6] are not well adapted for this purpose. We have applied five experimental procedures (methods A, B, B', B" and C). The results are gathered together in table 3.

Method A : Me_3SiCl (3.2 eq.), Et_3N (3 eq.), THF, RT, 18 h.

Method B : LDA (1.1 eq.), Me_3SiCl (1.2 eq.), THF, - 78°C, 5 h. (Internal Quench).

Method B' : LDA (1.1 eq.), THF, O°C, 0.5 h then Me_3SiCl (1.2 eq.), - 78°C, 12 h. (External Quench).

Method B" : LDA (1.1 eq.), THF, - 78°C, 0.5 h then Me_3SiCl (1.2 eq.), - 78°C, 12 h. (External Quench).

Method C : KH (1.1 eq.), THF, O°C, 0.5 h then Et_3N (2 eq.), Me_3SiCl (2.1 eq.), - 40°C, 5 h.

Table 3. Preparations of trimethylsilyl enol ethers **4** (and **5**)

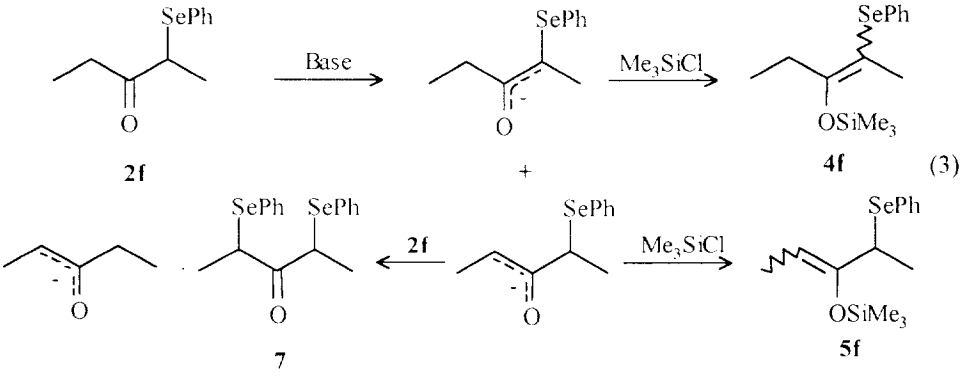
Entry	N° Substrate	R_1	R_2 (CH_2R')	Method	Yield %	Products **4** **5** ratio[g]	Geometric Isomers **4**[g]
1	**2a**	H	Me	A	70[a,b]	100 0	85/15
2	**2a**	H	Me	B	-[c]	100 0	100/0
3	**2b**	H	Ph	A	60[a,b]	-	100/0
4	**2c**	Me	Ph	A	0		
5	**2c**	Me	Ph	B	70[d]	-	75/25
6	**2c**	Me	Ph	C	65[d]	-	75/25
7	**2d**	H	tBu	A	0		
8	**2d**	H	tBu	B	50[d]	-	100/0
9	**2d**	H	tBu	C	55[d]	-	100/0
10	**2e**	Me	Me	A[e]	81[a,b]	100 0[h]	89/11[h]
11	**2f**	Me	Et	A	0		
12	**2f**	Me	Et	B or C	-[f]		
13	**2g**	Et	Me	A[e]	75[a,b]	100 0[h]	97/3[h]
14	**2h**	-$(CH_2)_3$-		A	55[d,b]	100 0[h]	-
15	**2h**	-$(CH_2)_3$-		B	65[b]	55 45	-
16	**2i**	-$(CH_2)_4$-		A	55[d,b]	100 0	-
17	**2i**	-$(CH_2)_4$-		B	65[b]	45 55[h]	-
18	**2i**	-$(CH_2)_4$-		B'	85[b]	95 5	-
19	**2i**	-$(CH_2)_4$-		B"	75[b]	20 80	-
20	**2i**	-$(CH_2)_4$-		C	70[d]	90 10	-

a) Flash chromatography on silicagel. b) Kugelrohr distillation. c) Presence of unidentified compounds. d) Flash chromatography on neutral alumina. e) Acetonitrile as solvent. f) **4f**, and **5f**, the substrate **2f**, and the 2,4-bis(phenylseleno) 3-pentanone **7** were present in similar amounts. g) Determined by ^1H NMR-200 MHz. h) Determined by GC-MS analysis.

Inspection of table 3 shows that method A (triethylamine as base) gave only the silyl enol ethers **4** but no reaction occurs for **2c**, **2d** and **2f** (entries 4, 7 and 11). The silyl enol ethers **5**, corresponding to **2a**, **2e**, **2g**, **2h** and **2i**, are not formed. We observed the formation of these products (**5f** and **5i**) beside enoxysilanes **4** when method C was used (entries 12 and 20). With LDA as base, the ketones **2f**, **2h** and **2i** lead to mixtures of enoxysilanes **4** and **5** in similar amounts (entries 12, 15 and 17). The trimethylsilyl enol ether **5i**, derived from 2-phenylseleno cyclohexanone **2i**, was the major product using method B" (entry 19).

The GC-MS analysis was very useful to distinguish the enoxysilanes **4** and **5**. In fact, the loss of the PhSe radical was more important for the allylic selenide **5** than for the enoxysilanes **4**, having a PhSe group in a vinylic position.

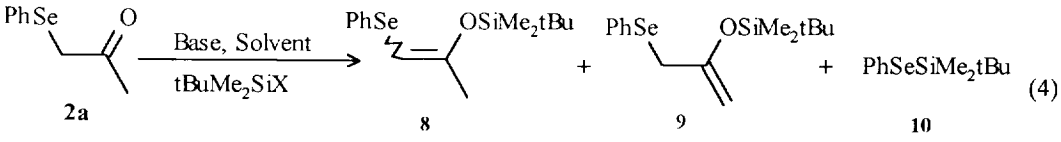
We must point out that the silyl enol ether **4f** derived from 2-phenylseleno 3-pentanone **2f** cannot be prepared conveniently. Using method A, formation of diphenyldiselenide was observed (entry 11). No explanation could be given for the deselenylation of the substrate in non-selenophilic conditions. With method B or C (entry 12), the 2,4-bis(phenylseleno) 3-pentanone **7** appears beside the silyl enol ethers **4f** and **5f** which are formed in similar amounts. The presence of the diseleno-ketone **7** means that the enolate derived from **2f** having the PhSe group in the α'-position is selenophilic towards the substrate[17] (reaction 3).



When the reaction was carried out on **2f**, in the presence of Lewis acid[6] (Et_3N, MeCN, Me_3SiCl, $ZnCl_2$, RT), a 33/67 mixture of **4f** and **5f** was obtained with a modest yield (50 %) without formation of the ketone **7**.

Trimethylsilyl enol ethers **4** are more stable that enoxysilanes **3**. They can be purified by flash chromatography on neutral alumina or by Kugelrohr distillation without hydrolysis or decomposition. The determination of the E or Z configuration of enoxysilanes **4** is under investigation by means of a ^1H, ^{13}C, ^{77}Se NMR study.

In order to prepare more stable compounds allowing a better study of reactions with electrophiles[17], we have envisaged to synthesize t-butyldimethylsilyl enol ethers. Various experimental conditions were tested with phenylseleno propanone **2a** as substrate (reaction 4).



(4)

Using method A, previously cited for the access to enoxysilanes **4**, no reaction was observed. The same is true with acetonitrile as solvent (X = Cl, I) or when LiHMDS, was used as base. In a reaction with triethylamine and t-butyldimethylsilyl triflate, a 30 % conversion was obtained. The reaction mixture contains **8** (7 %), **9** (7 %) and t-butyldimethylsilyl phenylselenide **10** (15 %). The selenide **10** is only formed (5 %) using LDA in THF at - 78°C. Better yields were observed with triethylamine in acetonitrile in the presence of $ZnCl_2$ at room temperature,[6] (method D) (50 % yield, ratio **8/9** : 1/2) and with KH, diisopropylamine, in THF at - 40°C (method E) (55 % yield, ratio **8/9** : 85/15). These two procedures (using t-butyldimethylchlorosilane as reagent), produced a small amount of **10** (~ 5 %). The formation of the selenide **10** is not clearly elucidated and was the sole compound formed when the reaction was carried out in THF at 0°C, with KH as base.

In conclusion, we have found good experimental conditions for the synthesis of enoxysilanes derived from α-phenylseleno aldehydes and α-phenylseleno ketones. For the latter and when the two silyl enol ethers regioisomers could be produced, we have observed that enoxysilanes **4** having a vinylic phenylseleno group can be obtained in a pure form. Mixtures of the two enoxysilanes **4** and **5** are obtained using LDA or KH as bases at low temperatures.

Acknowledgements

We thank Professor J. C. Combret for his help concerning the GC-MS analysis of the β-phenylseleno enoxysilanes.

EXPERIMENTAL SECTION

Triethylamine was refluxed over potassium hydroxide pellets, simply distilled and then distilled once more from calcium hydride. Acetonitrile was refluxed over P_2O_5, distilled and stored under argon over molecular sieves (3A°). Tetrahydrofurane was distilled over sodium-benzophenone. All the reactions were carried out under argon atmosphere in a standard apparatus composed with a 50 ml three necked round bottomed flask equipped with a reflux condenser fitted with a drying tube containing calcium chloride, a pressure-equalizing dropping funnel and a magnetic stirring bar. Infrared spectra were recorded on a Perkin Elmer FTIR 1600 spectrophotometer. ^1H NMR spectra were recorded on a Jeol PMX 60 and on a Brücker AC 200. For simplification, the proton signals of the phenylseleno groups are not indicated.

The purity of the enoxysilanes **3**, **4** (and **5**), **8** (and **9**) was verified by microanalysis or by Mass Spectra which were obtained on a Hewlett Packard HP 5890 mass spectrometer (70 eV) using GC-MS coupling with a glass capillary column HP1 (25 m, 0,22 mn, He carrier gas).

Phenyl phenylseleno ethanal 1d. To a stirred solution of 2-phenyl 1-trimethylsilyloxy ethylene (1.92 g, 10 mmol) in anhydrous THF (15 ml) at - 20°C, the benzeneselenenyl chloride (1.91 g, 10 mmol) dissolved in the same solvent (10 ml) was added dropwise. The mixture was then stirred for 10 mn and treated with a saturated solution of sodium hydrogenocarbonate. After separation and extraction of the aqueous phase with ether, the organic fractions were washed with water, dried over magnesium sulfate and concentrated. The aldehyde **1d** was obtained in 90 % yield after chromatography. Elution with petroleum ether separates diphenyldiselenide from the product which was eluted with a mixture petroleum ether/dichloromethane (85/15). ^{1}H NMR ($CDCl_3$), δ : 9.64 (1H, d, J = 5.0 Hz, C*H*O), 4.77 (1H, d, J = 5.0 Hz, C*H*SePh). ^{13}C NMR ($CDCl_3$), δ : 191.3 (C=O), 56.0 (CHSePh). IR $\nu_{C=O}$ = 1712 cm^{-1}. GC-MS (70 eV) m/z 276 (M^+, 17), 247 (40), 167 (32), 155 (5), 119 (12), 91 (100), 77 (18), 65 (31), 51 (19), 39 (21).

3-Phenylseleno 2-pentanol 6. To a stirred solution of MeMgI (11 mmol) in anhydrous ether (15 ml) at - 20°C, the aldehyde **1c** (2.27 g, 10 mmol) dissolved in the same solvent (10 ml) was added dropwise. The mixture was stirred for 4 h and treated with a saturated solution of ammonium chloride (20 ml). After separation and extraction of the aqueous phase with ether, the organic fractions were washed with water, dried over magnesium sulfate, and concentrated. The oily residue shows no traces of aldehyde **1c** (^{1}H NMR) and was purified by Kugelrohr distillation (87 % yield). ^{1}H NMR ($CDCl_3$), Major isomer (85 %) : 3.87-3.84 (1H, m, C*H*OH), 3.24-3.15 (1H, m, C*H*SePh), 1.80-1.50 (2H, m, CH_2), 1.18 (3H, d, J = 7.3 Hz, CH_3), 1.08 (3H, t, J = 7.3 Hz, CH_3CH_2). Minor isomer (15 %) : 3.80-3.65 (1H, m, C*H*OH), 3.00-2.90 (1H, m, C*H*SePh), 1.80-1.50 (2H, m, CH_2), 1.25 (3H, d, J = 6.3 Hz, CH_3), 1.08 (3H, t, J = 6.3 Hz, CH_3CH_2).

3-Phenylseleno 2-pentanone 2g. According to the literature[14h], diphenyldiselenide (3.46 g, 11.1 mmol) was added to a solution of t-butyl hydroperoxide (2.00 g, 22.2 mmol) in benzene (100 ml). The solution was heated at reflux during 10 mn and the alcohol **6** (4.50 g, 18.5 mmol) dissolved in benzene (50 ml) was then introduced. The mixture was refluxed 5 h, stirred one hour at room temperature and washed with water (30 ml). The aqueous solution was extracted by ether and the organic phases were dried ($MgSO_4$) and concentrated. The ketone **2g** was obtained in 70 % yield by silicagel chromatography. Elution with petroleum ether eliminates diphenyldiselenide and the product was eluted with a mixture petroleum ether/CH_2Cl_2 (90/10). ^{1}H NMR ($CDCl_3$), δ : 3.55 (1H, t, J = 7.6 Hz, C*H*SePh), 2.26 (3H, s, CH_3), 1.96-1.59 (2H, m, CH_2CH_3), 0.98 (3H, t, J = 7.3 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$), δ : 203.5 (C=O), 53.75 (CHSePh), 27.1 (CH_3CO), 23.1 (CH_2), 12.3 (CH_3). IR $\nu_{C=O}$ = 1704 cm^{-1}. Anal. Calc. for $C_{11}H_{14}OSe$: C, 54.78 ; H, 5.85. Found : C, 54.85 ; H, 5.78.

General procedure for the synthesis of enoxysilanes 3. Chlorotrimethylsilane (1.04 g, 9.6 mmol) in THF (6 ml) was added dropwise at room temperature to a solution of aldehyde **1** (3 mmol), triethylamine (0.91 g, 9 mmol) in THF (30 ml). The mixture was stirred six hours except for **1f**, for which one week was necessary to carry out the reaction to completion. After solvent elimination under reduced pressure, the triethylammonium salt was filtered and washed with pentane. After elimination of the solvent, ^{1}H NMR spectra of the crude oily product shows no trace of the aldehyde. Enoxysilanes **3a** appear as a 85/15 mixture of E and Z isomers (78 % yield).

2-Phenylseleno 1-trimethylsilyloxy ethylene 3a. ^{1}H NMR ($CDCl_3$), E isomer : δ : 6.86 (1H, d, J = 12.1 Hz, C*H*OSiMe_3), 5.89 (1H, d, J = 12.1 Hz, C*H*SePh), 0.28 (s, 9H) ; Z isomer : δ : 6.73 (1H, d, J = 4.7 Hz, C*H*OSiMe_3), 5.53 (1H, d, J = 4.7 Hz, C*H*SePh). IR $\nu_{C=C}$ = 1595 cm^{-1}. Anal. Calc. for $C_{11}H_{16}OSeSi$: C, 48.70 ; H, 5.94. Found : C, 48.35 ; H, 5.39. GC-MS (70 eV) m/z : 272 (M^+, 17), 257 (5), 243 (1), 192 (35), 177 (9), 157 (6), 135 (18), 91 (16), 73 (100), 45 (26).

2-Phenylseleno 1-trimethylsilyloxy propene 3b. ^{1}H NMR ($CDCl_3$), δ : 6.78 (1H, s, C*H*OSiMe_3), 1.99 (3H, s, CH_3), 0.25 (9H, s). IR $\nu_{C=C}$ = 1620 cm^{-1}. Anal. Calc. for $C_{12}H_{18}OSeSi$: C, 50.52 ; H, 6.36. Found : C, 50.15 ; H, 6.00.

2-Phenylseleno 1-trimethylsilyloxy 1-butene 3c. ^{1}H NMR ($CDCl_3$), δ : 6.81 (1H, s, C*H*OSiMe_3), 2.42 (2H, q, J = 7.5 Hz, CH_2), 1.09 (3H, t, J = 7.5 Hz, CH_3), 0.29 (s, 9H). IR $\nu_{C=C}$ = 1600 cm^{-1}. Anal. Calc. for $C_{13}H_{20}OSeSi$: C, 52.16 ; H, 6.73. Found : C, 52.45 ; H, 6.43.

2-Phenyl 2-phenylseleno 1-trimethylsilyloxy ethylene 3d. ^{1}H NMR ($CDCl_3$), Maj. isomer (68 %) : δ : 6.96 (s, 1H, C*H*OSiMe_3), 0.27 (s, 9H). Min. isomer (32 %) : 0.19 (s, 9H). IR $\nu_{C=C}$ = 1597 cm^{-1}. Anal. Calc. for $C_{17}H_{20}OSeSi$: C, 58.78 ; H, 5.80. Found : C, 58.50 ; H, 5.90. GC-MS (70 eV) m/z 348 (M^+, 20), 333 (2), 268 (17), 253 (4), 215 (2), 179 (20), 165 (7), 135 (6), 102 (7), 73 (100), 45 (20).

3-Phenyl 2-phenylseleno 1-trimethylsilyloxy propene 3e. ^{1}H NMR ($CDCl_3$), δ : 6.92 (1H, s, C*H*OSiMe_3), 3.70 (2H, s, CH_2), 0.29 (9H, s). A GC-MS analysis shows only the presence of one geometric isomer. IR $\nu_{C=C}$ = 1605 cm^{-1}. Anal. Calc. for $C_{18}H_{22}OSeSi$: C, 59.82 ; H, 6.14. Found : C, 59.42 ; H, 6.00. GC-MS (70 eV) m/z 362 (M^+, 56), 347 (2), 281 (10), 271 (21), 254 (2), 179 (13), 157 (7), 130 (7), 115 (17), 91 (11), 73 (100), 45 (27).

3-Methyl 2-phenylseleno 1-trimethylsilyloxy 1-butene 3f. ^{1}H NMR ($CDCl_3$), δ : 6.73 (1H, s, C*H*OSiMe_3), 2.87-3.30 (1H, m, $CHMe_2$), 0.24 (s, 9H). The geometric isomer ratio : 94/6 was determined with GC-MS analysis. IR $\nu_{C=C}$ = 1609 cm^{-1}. GC-MS (70 eV) m/z 314 (M^+, 34), 299 (5), 271 (2), 243 (2), 233 (4), 209 (9), 179 (20), 157 (12), 145 (10), 128 (5), 73 (100), 45 (26).

Procedures used for the access to enoxysilanes 4 (and 5).

Method A : (Table 3, entries 1, 3, 4, 7, 10, 11, 13, 14 and 16). The experimental procedure is the same as for the synthesis of enoxysilanes **3**, except for the reaction with ketones **2e** and **2g**. In these cases, THF was replaced by acetonitrile as the solvent. The trimethylsilyl enol ethers **4** were only formed and were purified by flash chromatography or by Kugelrohr distillation (table 3).

Method B ("Internal Quench") : (Table 3, entries 2, 5, 8, 12, 15, and 17). A solution of n-BuLi (10.5 mmol) in hexane was added slowly, under argon, to diisopropylamine (1.11 g, 11 mmol) in THF (20 ml) at 0°C. After stirring for 30 mn and lowering the temperature to - 78°C, chlorotrimethylsilane (1.30 g, 12 mmol) was introduced dropwise. The ketone **2** (10 mmol) in THF (10 ml) was added dropwise 20 mn later, under stirring. The mixture was then stirred for 5 h at - 78°C and treated with water (30 ml) and hexane (30 ml) cooled to 0°C. After the usual work-up, the oily enoxysilane was purified as for method A. The ketones **2h** (entry 15) and **2i** (entry 17) lead to mixtures of enoxysilanes **4** and **5** in similar amounts.

Method B' ("External Quench") : A solution of LDA, prepared as for method B, was added dropwise at 0°C, under argon to the ketone **2** (10 mmol) in THF (10 ml). The mixture was stirred for 10 mn, cooled to - 78°C, quenched with chlorotrimethylsilane (1.30 g, 12 mmol), stirred for 5 h to - 78°C and then treated as in method

B. Applied to ketone **2i** (table 3, entry 18), the ^1H NMR spectra of the residual oil shows the presence of the two regioisomers **4i** and **5i** in a ratio 95/5.

Method B'' ("External Quench") : The experimental procedure is the same as for method B' except that the solution of ketone **2** in THF was added dropwise at - 78°C. The work-up of the reaction was carried out as for method B. Applied to **2i** (table 3, entry 19), the ^1H NMR analysis of the crude oil indicates a **4i/5i** ratio 20/80.

Method C : (table 3, entries 6, 9, 12 and 20) The ketone **2** (3 mmol) in THF (3 ml) was introduced dropwise, under argon, to THF (5 ml) containing potassium hydride (0.132 g, 3.3 mmol, washed two times with hexane) at 0°C. The mixture was then stirred at this temperature until the formation of hydrogen has stopped, and cooled to - 78°C. Triethylamine (0.606 g, 6 mmol) and chlorotrimethylsilane (0.717 g, 6.6 mmol) were added dropwise and successively. The work-up was carried out as described for method A.

1-Phenylseleno 2-trimethylsilyloxy propene 4a. ^1H NMR ($CDCl_3$), E isomer : δ : 5.69 (1H, C*H*SePh), 2.16 (3H, s, Me), 0.36 (9H, s) ; Z isomer : 5.51 (1H, C*H*SePh), 2.04 (3H, s, Me), 0.35 (9H, s). IR $\nu_{C=C}$ (E) = 1605 cm^{-1} , $\nu_{C=C}$ (Z) = 1615 cm^{-1}. Anal. Calc. for $C_{12}H_{18}OSiSe$: C, 50.51 ; H, 6.36. Found : C, 50.89 ; H, 6.36. The E isomer was isolated by flash chromatography on silicagel (eluent : petroleum ether). The configuration of this major isomer was deduced from NOE experiments involving the vinylic proton and the trimethylsilyl group.

1-Phenyl 2-phenylseleno 1-trimethylsilyloxy ethylene 4b. ^1H NMR ($CDCl_3$), δ : 6.31 (1H, s, C*H*SePh), 0.23 (9H, s). IR $\nu_{C=C}$ = 1585 cm^{-1}. Anal. Calc. for $C_{17}H_{20}OSiSe$: C, 58.77 ; H, 5.80. Found : C, 58.57 ; H, 5.66.

1-Phenyl 2-phenylseleno 1-trimethylsilyloxy propene 4c. ^1H NMR ($CDCl_3$), Maj. isomer (75%) , δ : 2.15 (3H, s, C*Me*SePh), 0.05 (9H, s). Min. isomer (25%) , δ 1.81 (3H, s), 0.12 (9H). IR $\nu_{C=C}$ = 1590 cm^{-1}. Anal. Calc. for $C_{18}H_{22}OSiSe$: C, 63.73 ; H, 6.54. Found : C, 63.20 ; H, 6.30. GC-MS (70 eV) m/z 362 (M^+, 98), 347 (7), 282 (17), 209 (9), 177 (20), 135 (17), 115 (18), 73 (100), 45 (22).

3,3-Dimethyl 1-phenylseleno 2-trimethylsilyloxy 1-butene 4d. ^1H NMR ($CDCl_3$), δ : 5.59 (1H, s, C*H*SePh), 1.17 (9H, s, tBu), 0.34 (9H, s). IR $\nu_{C=C}$ = 1580 cm^{-1}. Anal. Calc. for $C_{15}H_{24}OSiSe$: C, 54.84 ; H, 7.18. Found : C, 55.03 ; H, 7.39.

3-Phenylseleno 2-trimethylsilyloxy 2-butene 4e. ^1H NMR ($CDCl_3$), Maj. isomer, δ : 2.20 (3H, s, C*Me*$OSiMe_3$), 2.03 (3H, s, C*Me*SePh), 0.26 (9H, s) , Min. isomer, δ : 2.04 (3H, s, C*Me*$OSiMe_3$), 1.95 (3H, s, C*Me*SePh), 0.23 (9H, s). IR $\nu_{C=C}$ = 1580 cm^{-1}. The geometric isomer ratio : 89/11 was determined with GC-MS analysis. GCMS (70 eV) m/z 300 (M^+, 28), 285 (8), 257 (11), 220 (12), 193 (10), 147 (14), 135 (13), 73 (100), 45 (26).

2-Phenylseleno 3-trimethylsilyloxy 2-pentene 4f and 4-phenylseleno 3-trimethylsilyloxy 2-pentene 5f. ^1H NMR ($CDCl_3$), **4f** : δ : 4.20 (2H, q, J = 6.0 Hz, CH_2), 1.46 (3H, d, J = 6.0 Hz, CH_3), 1.50 (3H, s, CH_3), 0.22 (9H, s). The geometric isomer ratio : 84/16 was determined with GC-MS . GC-MS (70 eV) m/z 314 (M^+, 42), 299 (9), 257 (20), 207 (5), 161 (7), 157 (7), 135 (12), 105 (12), 73 (100), 45 (19) ; **5f** : δ : 4.55 (1H, q, 6.6 Hz, CH=), 3.69 (1H, q, J = 7.8 Hz, C*H*SePh), 1.48 (3H, d, J = 6.6 Hz, CH_3), 1.48 (3H, d, J = 7.8 Hz, CH_3CHSePh), 0.26 (9H, s). The geometric isomer ratio : 80/20 was determined with GC-MS analysis. GCMS (70 eV) m/z 314 (M^+, 13), 233 (7), 215 (4), 157 (66), 91 (20), 75 (100), 73 (59), 45 (15).

2,4-Bis(phenylseleno) 3-pentanone 7. ^{1}H NMR ($CDCl_3$), δ : 4.09 (1H, q, J = 6.9 Hz, CH), 1.49 (3H, d, J = 6.9 Hz, CH_3). IR $\nu_{C=O}$ = 1704 cm^{-1}. Anal. Calc. for $C_{17}H_{18}OSe_2$: C, 51.53 ; H, 4.58. Found : C, 51.30 ; H, 4.42. The ketone 7 appears in mixture with **4f** and **5f** in similar amounts but the two enoxysilanes are the sole products formed when method D was used with trimethylsilyl chloride in place of t-butyldimethylsilyl chloride (see below).

3-Phenylseleno 2-trimethylsilyloxy 2-pentene 4g. ^{1}H NMR ($CDCl_3$), Maj. isomer, δ : 2.36 (2H, q, J = 7.3 Hz, CH_2), 2.16 (3H, s, =C), 0.99 (3H, t, J = 7.3 Hz, CH_3), 0.25 (9H, s). IR $\nu_{C=C}$ = 1615 cm^{-1}. The geometric isomer ratio : 97/3 was determined with GC-MS analysis. GC-MS (70 eV) m/z 314 (M^+, 31), 299 (9), 271 (4), 219 (8), 209 (3), 193 (11), 157 (7), 145 (8), 73 (100), 45 (22), 43 (32).

2-Phenylseleno 1-trimethylsilyloxy cyclopentene 4h. ^{1}H NMR ($CDCl_3$), δ : 2.35-2.50 (4H, m), 1.85-2.00 (2H, m), 0.21 (9H, s). IR $\nu_{C=C}$ = 1600 cm^{-1}. Anal. Calc. for $C_{14}H_{20}OSiSe$: C, 54.00 ; H, 6.48. Found : C, 53.90 ; H, 6.70. GCMS (70 eV) m/z 312 (M^+, 22), 297 (3), 232 (77), 217 (5), 157 (5), 135 (10), 117 (23), 73 (100), 45 (25).

5-Phenylseleno 1-trimethylsilyloxy cyclopentene 5h. This compound was a minor component of the mixture isolated, when method B was used (**4h/5h** : 55/45). ^{1}H NMR ($CDCl_3$), δ : 4.70 (1H, s large, -C*H*=), 4.05 (1H, m, C*H*SePh). The two CH_2 signals was masked by those of **4h**.

2-Phenylseleno 1-trimethylsilyloxy cyclohexene 4i. ^{1}H NMR ($CDCl_3$), δ : 2.19-2.26 (4H, m, 3-CH_2 and 6-CH_2), 1.62-1.76 (4H, m, 4-CH_2 and 5-CH_2), 0.30 (9H, s). IR $\nu_{C=C}$ = 1620 cm^{-1}. Anal. Calc. for $C_{15}H_{22}OSiSe$: C, 55.37 ; H, 6.82. Found : C, 55.61 ; H, 6.52. GC-MS (70 eV) m/z 326 (M^+, 84), 311 (19), 246 (37), 234 (5), 173 (3), 155 (14), 135 (10), 73 (100), 45 (22).

6-Phenylseleno 1-trimethylsilyloxy cyclohexene 5i. The enoxysilane **5i** was obtained, as the major product, when method B" was applied to **2i**. ^{1}H NMR ($CDCl_3$), δ : 4.91 (1H, t, J = 3.9 Hz, -CH=), 3.73 (1H, dt, J = 3.0 Hz, C*H*Se), 0.17 (9H, s). GC-MS (70 eV) m/z 326 (M^+, 13), 311 (2), 169 (70), 73 (100), 45 (14).

2-t-Butyldimethylsilyloxy 1-phenylseleno propene 8 and 2-t-butyldimethylsilyloxy 3-phenylseleno propene 9.

Method D : This procedure, described in the literature[6], needs the presence of a Lewis acid. To a solution of the ketone **2a** (1.06 g, 5 mmol) in dry acetonitrile (30 ml), stirred under argon, triethylamine (1.52 g, 15 mmol) and $ZnCl_2$ (5 ml solution 1 M in ether, 5 mmol) were added dropwise successively. t-Butyldimethylchlorosilane (0.90 g, 6 mmol) in acetonitrile (10 ml) was then slowly introduced under strong stirring. The reaction was maintained at 30°C for 24 h and the solvent was eliminated. The ammonium salt was filtered, washed with pentane (3 x 20 ml). The organic layers were washed with water, dried and concentrated. The enoxysilanes **8**, **9** were separated from t-butyldimethylsilyl phenylselenide **10** through chromatography on basic alumina (ratio **8/9** 1/2).(**10** : eluent : petroleum ether - **8/9** : eluent : petroleum ether / CH_2Cl_2 : 95/5).

Method E : Diisopropylamine (1.16 g, 1.15 mmol) in THF (1 ml) was added to potassium hydride (44 mg, 1.1 mmol, washed with dry hexane) in THF (2 ml) at - 78°C. The resulting mixture was stirred at - 40°C for 10 mn and cooled to - 78°C. The ketone **2a** (0.21 g, 1 mmol) in THF (5 ml) was introduced dropwise. The reaction was stirred at - 30°C until the hydrogen bubbling was stopped and warmed to 0°C for 5 mn. The temperature was then lowered to - 78°C and the t-butyldimethylchlorosilane (0.15 g, 1.05 mmol) in THF (2 ml) was added slowly.

The mixture was stirred for 10 mn, warmed to room temperature. After the usual work-up, the oily product was purified as in method D. The enoxysilanes were isolated as a 85/15 mixture of **8** and **9**.
Enoxysilane **8** : ^{1}H NMR ($CDCl_3$), δ : 5.59 (1H, s, CH=), 2.08 (3H, s, CH_3) ; E isomer : 1.01 (9H, s), 0.25 (6H, s) ; Z isomer : 5.39 (1H, s, CH=), 1.99 (3H, s, CH_3), 0.99 (9H, s), 0.24 (6H, s). The attributions were made by analogy with those of the enoxysilane **4a**. Enoxysilane **9** : ^{1}H NMR ($CDCl_3$), δ : 4.09 (2H, d, J = 10.0 Hz, CH_2=), 3.47 (2H, s, CH_2SePh), 0.92 (9H, s), 0.18 (6H, s).

t-Butyldimethylsilyl phenylselenide 10 : ^{1}H NMR ($CDCl_3$), δ : 0.99 (9H, s), 0.20 (6H, s).

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(*Received in Belgium* 30 *January* 1995; *accepted* 27 *June* 1995)