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Allylation and Benzylation of enolates derived from β-Phenylselanyl Silyl Enol Ethers.

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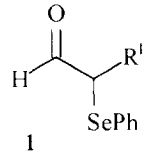
Abstract *: α-Phenylselanyl γ-unsaturated ketones were obtained through allylation of enolates generated by potassium t-butoxide cleavage of β-phenylselanyl silyl enol ethers derived from α-phenylselanyl ketones. With enoxysilanes prepared from α-phenylselanyl aldehydes, O-allylation and O-benzylation of the corresponding enolates were also observed.* © 1997 Elsevier Science Ltd.

α-Phenylselanyl aldehydes **1** and ketones **2** are useful bifunctional synthons which have received a great attention during the last two decades.[1] We have recently reported efficient procedures for the preparation of these compounds,[2] and of their corresponding β-phenylselanyl enoxysilanes **3** and **4**.[3] We present here our results concerning the allylation reaction of enolates formed by potassium t-butoxide cleavage of enoxysilanes **3** and **4**. Starting from silyl enol ethers **3** derived from aldehydes **1**, the products of C- and O-allylation **5** and **6** were obtained and the α-allyl ketones **7** were only formed from silyl enol ethers **4** prepared from ketones **2**.



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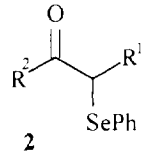

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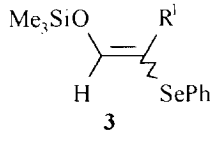

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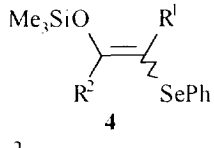
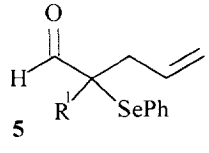


4

	R^1
1, 3, 5	a) Me
	b) Et
	c) Ph
	d) Bn
	e) iPr

	R^1	R^2
2, 4, 7	a) H	Me
	b) H	Ph
	c) H	tBu
	d) Me	Me
	e)	$-(CH_2)_4-$



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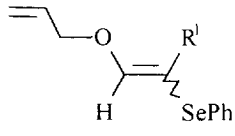
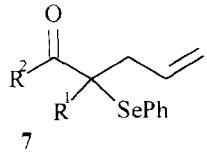


6 c) Ph
d) Bn
e) iPr

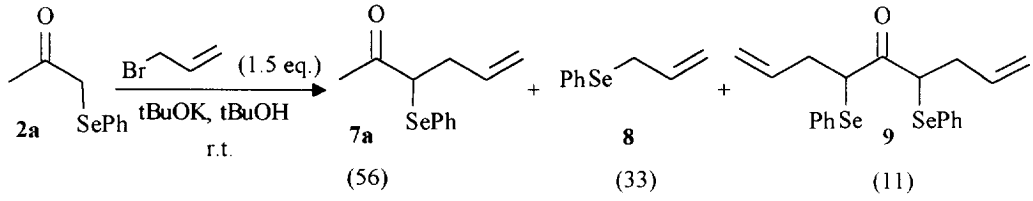


7

Since the first works of Grieco,[4] Tsuji[5] and Reich[6] relative to the allylation of enolates derived from α-phenylselanyl ketones, α-allyl α-phenylselanyl cyclanones were also obtained from the corresponding α-phenylselanyl α, β-unsaturated cyclanones,[7] but no exhaustive studies were undertaken on this subject.

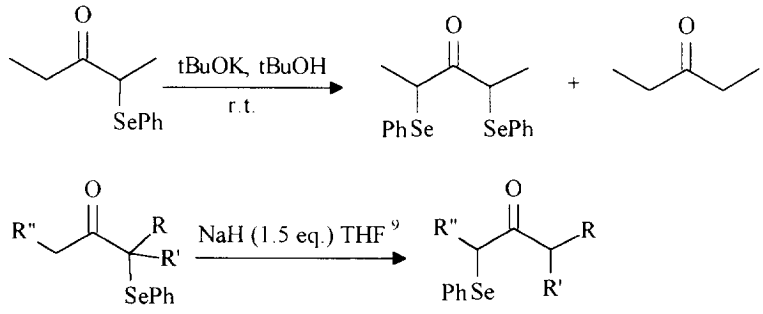
When the Tsuji's conditions were applied to the phenylselanyl propanone **2a**, allyl phenylselenide **8** and 4,6-bis(phenylselanyl)nona-1,8-dien-5-one **9** were formed besides the expected 3-phenylselanyl hex-5-en-2-one **7a** (Scheme 1). We also observed that the use of LiHMDS instead of potassium t-butoxide has led to a mixture of allyl phenylselenide **8** and of the starting ketone **2a** (**2a/8** : 4/5).

Scheme 1



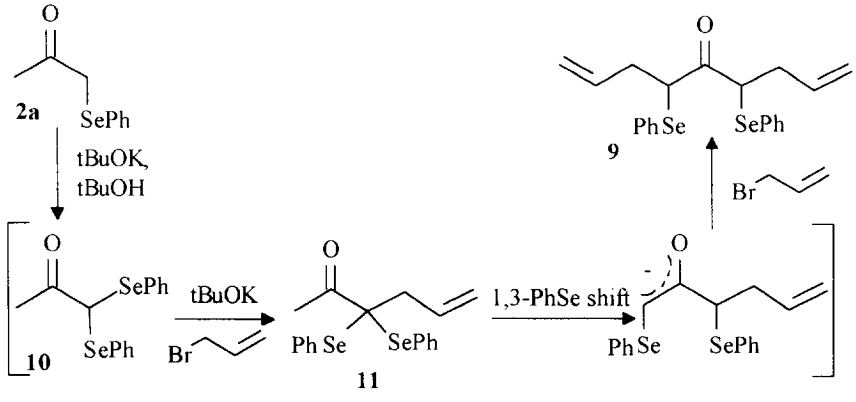
In a recent work devoted to the preparation of α,α-bis(phenylselanyl)ketones,[8] we have observed the 1,3-rearrangement of the phenylselanyl group as already described by Liotta and Coll.[9] In these reactions, involving the intermolecular migration of a PhSe substituent through a selenophilic attack of the substrate by the kinetic enolate, the driving force is the formation of the more stable enolate (Scheme 2).

Scheme 2



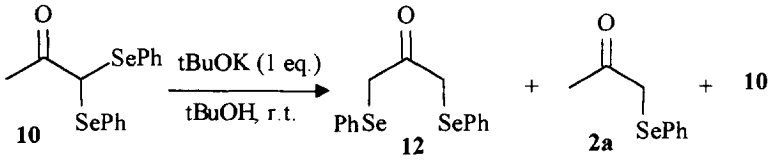
We have first imagined that the formation of the diallylated product **9** can be explained by the initial formation of the α,α-bis(phenylselanyl)propanone **10**[8] whose enolate formed on the selenylated carbon is then allylated giving the ketone **11** which undergoes a 1,3-PhSe shift through its kinetic enolate.[9, 10] A second allylation on the same position completes the processes (Scheme 3).

Scheme 3



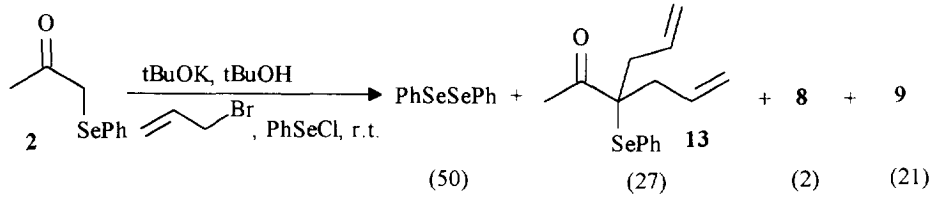
In fact, when the ketone **10** was treated with one equivalent of KOtBu and allyl bromide according to the same conditions, the allylated ketones **7a** and **9** and other unidentified products were formed. Without allyl bromide, the treatment of the ketone **10** with KOtBu (1 eq.) in tBuOH has led to a partial isomerization into 1,3-bis (phenylselanyl)propanone **12**[8] (Scheme 4). This result seems to indicate that the 1,3-PhSe shift precedes, at least partially, the first allylation reaction.

Scheme 4



To increase the yield of the ketone **9**, PhSeCl (0.3 eq.) was added to the reaction achieved with the same procedure. Surprisingly, the crude mixture afforded the α,α-bisallyl α-phenylselanyl ketone **13** along with diphenyldiselenide, the expected nonadienone **9** and traces of allyl phenylselenide **8** in ratio given in Scheme 5.

Scheme 5



It must be noticed that in the reaction described in Scheme 1, no traces of ketone **12** were detected and when PhSeCl was used with an excess of allyl bromide (1.5 eq.), neither monoallylation reaction nor allyl phenylselenide formation were observed. These complications, resulting from this double allylation reaction and from the 1,3-PhSe shift, led us to study the reactivity of enolates formed by cleavage of silyl enol ethers **3** or **4** according to well-known procedures.[11, 12] In fact, the methyllithium cleavage of the silyl enol ether **4a** gave only traces of allylated product and α-phenylselanyl ketone **2a** was recovered after work-up. The same result was observed when the cleavage was achieved with tetrabutylammonium fluoride.[13] The enolate formation was successful by the enoxysilane treatment with potassium t-butoxide as proposed by Duhamel and Coll.[14] Under these conditions, the monoallylation can be achieved but the formation of allyl phenylselenide **8** cannot be avoided. A small amount of the original ketone **2** was also present in the reaction mixture (Scheme 6). The results are gathered in Table 1.

Scheme 6

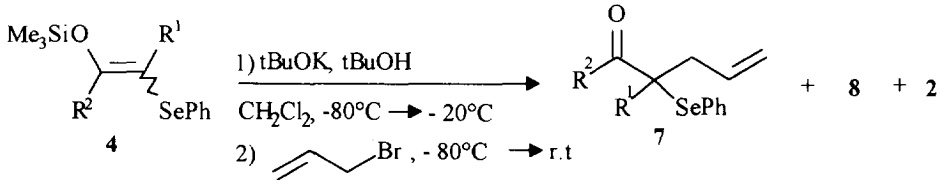


Table 1

Allylation of potassium enolates derived from β-phenylselanylenoxysilanes **4**

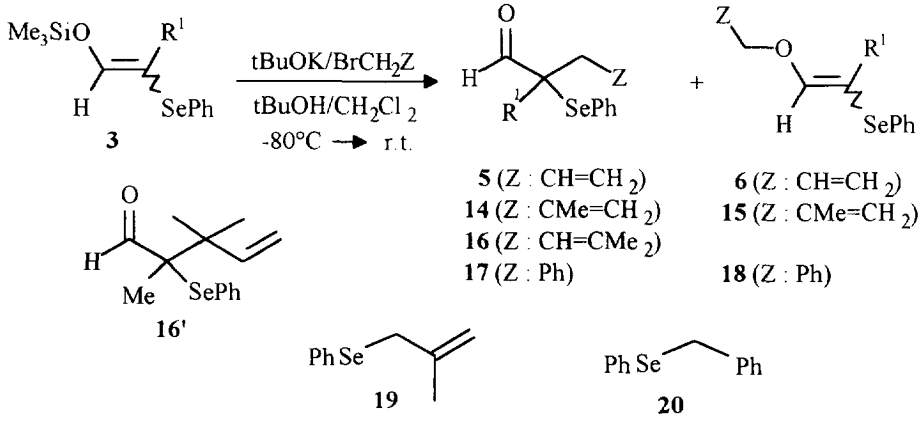
Entry	Enoxysilane	R^1	R^2	Yield [a] (%)	Product ratio[b] 7	8	2
1	**4a**	H	Me	57	63	25	12
2	**4b**	H	Ph	72	81	11	8
3	**4c**	H	tBu	65	74	13	13
4	**4d**	Me	Me	68	73	14	13
5	**4e**	$-(CH_2)_4-$		56	64	25	11

a) Yield of purified product. b) Determined by ^1H NMR on the crude product.

The bisallylated ketone **9** was not detected when this reaction was applied to the silyl enol ether **4a**. tBuOK (1 eq.) acts only for the cleavage of the silicium-oxygen bond but does not allow the 1,3-shift of the phenylselanyl group. Moreover, no formation of the α,α'-diallylated ketone **12** was observed despite the excess of allyl bromide (1.5 eq.). We must notice that α-allyl α-phenylselanyl ketones **7** have been prepared by α-phenylselenenylation of the corresponding γ-unsaturated ketones.[15] When R^1 is a carbonyl group, N-phenylselenophthalimide was added without base. When R^1 is an alkyl or aryl group, the use of NaH was needed to form the corresponding enolate.

The potassium t-butoxide cleavage was also achieved on silyl enol ethers **3**. After addition of allyl bromide, no formation of allyl phenylselenide **8** was observed but the O-allyl enol ethers **6** were formed besides the expected pent-4-enals **5** for **3c**, **3d** and **3e** (**5**/**6** ≃ 80/20). (Scheme 7, Table 2, entries 8, 9 and 10).

Scheme 7



Prenyl bromide, benzyl bromide and methallyl bromide were also used as electrophilic reagents (Scheme 7). As seen in Table 2, the C-alkylation was exclusive for the enoxysilane **3a** (entries 1, 3 and 4) excepted for methallyl bromide (entry 2). For the silyl enol ether **3b** (R^1 = Et), 14 and 10 % of O-alkylated products **15b** and **18b** were formed besides **14b** and **17b** respectively (Table 2, entries 6, 7). With a bulky substituent (entries 8 , 9, 10 and 12), the O-alkylation increased. The complex mixture obtained from methallyl bromide

and the silyl enol ether **3e** (R^1 = iPr), was not completely analyzed. The O-methallyl product **15e** was isolated in a poor yield (entry 11). The C-alkylated compounds **5**, **14**, **16**, **17** and the two geometric isomers of O-alkylated products **6**, **15**, **18** were separated by silicagel chromatography. These alkyl vinyl ethers **6**, **15**, **18** are new compounds. The literature only indicates the synthesis, by an indirect procedure,of the corresponding phenyl ether derived from α-phenylselanyl acetophenone.[16]

Table 2

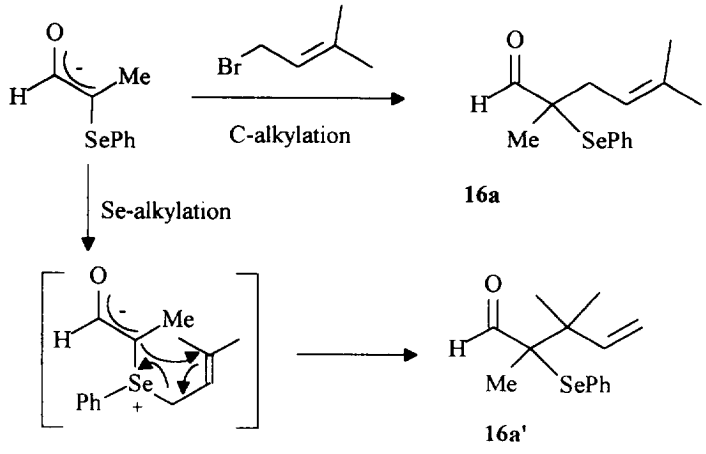
Allylation of potassium enolates derived from β-phenylselanylenoxysilanes **3**.

Entry	Product N°	R^1	Z	C/O alkylation[a]	Isolated yield (%)[b] C-alkylated compounds **5, 14, 16, 17**	O-alkylated compounds **6, 15, 18**	**6, 15, 18** (E/Z)[c]
1	**5a**	Me	$CH=CH_2$	100/0	65	-	-
2	**14a, 15a**	Me	$CMe=CH_2$	> 95/5[e]	86	d	0/100
3	**16a** **16a'**	Me	$CH=CMe_2$	100/0	71 (60 / 40)	-	-
4	**17**	Me	Ph	100/0	79	-	-
5	**5b**	Et	$CH=CH_2$	100/0	79	-	-
6	**14b, 15b**	Et	$CMe=CH_2$	86/14[e]	78	12	40/60
7	**17b, 18b**	Et	Ph	90/10[f]	81	5	d
8	**5c, 6c**	Ph	$CH=CH_2$	79/21	70	17	-
9	**5d, 6d**	Bn	$CH=CH_2$	81/19	72	15	50/50
10	**5e, 6e**	iPr	$CH=CH_2$	73/27	65	21	40/60
11	**15e**	iPr	$CMe=CH_2$	c, g	-	15	50/50
12	**17e, 18e**	iPr	Ph	53/47[f]	39	41	40/60

a) From the ^1H NMR spectra of the crude product. b) Purified products. c) Stereochemistry assigned from NOESY experiments. d) One geometric isomer only isolated. Stereochemistry not assigned. e) Trace of methallyl phenylselenide **19** . f) Trace of benzyl phenylselenide **20** . g) Complex mixture. **15e** was only isolated.

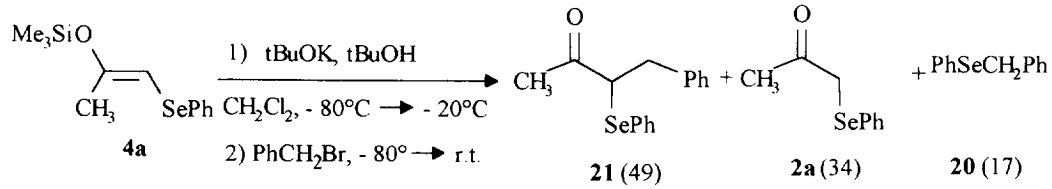
The two regioisomers **16a** and **16'a** (60/40) were formed with prenyl bromide (entry 3). To explain this result, we suppose that the C-alkylation of the enolate was competitive with the Se-alkylation as proposed by Reich and Coll.[6] The direct SN_2' bromide displacement is not considered as likely with this enolate (Scheme 8). The alkylation of the selenium atom, leading to an intermediate ylid, could also explain the minor formation of allyl phenylselenide **8**, of methallyl phenylselenide **19** and of benzyl phenylselenide **20**. However, its decomposition giving a carbene was not underlined.

Scheme 8



We have also carried out the benzylation of the enoxysilane **4a** (Scheme 9). 4-Phenyl 3-phenylselanyl 2-butanone **21** was isolated in a fair yield but the original ketone **2a** and benzyl phenylselenide **20** were also formed in substantial amounts.

Scheme 9



In conclusion, we have shown that the allylation of enolates generated by potassium t-butoxide cleavage of β-phenylselanyl silyl enol ethers **3** and **4**, derived from the corresponding aldehydes **1** and ketones **2**, gave C-allylated products leading to γ-unsaturated α-phenylselanyl aldehydes **5**, **14**, **16**, **17** and γ-unsaturated ketones **7**. O-allylation was partially observed in the case of enoxysilanes **3**. The benzylation of such enolates has led to similar results. The formation of the allylic phenylselenides **8**, **19** and benzyl phenylselenide **20** can be explained by the intermediate formation of an ylid resulting from the Se-alkylation of the α-phenylselanyl enolates.

EXPERIMENTAL SECTION

CH_2Cl_2 was distilled over P_2O_5 and then over calcium hydride. Allyl bromide, benzyl bromide, methallyl bromide, prenyl bromide and t-butyl alcohol were purified before use. The enoxysilanes **3** and **4** were prepared according to the a previous work[3]. All the reactions were carried out under argon. IR spectra were recorded on a Brucker AC 200. The purity of the α-allyl α-phenylselanyl carbonyl compounds **5**,**7**, **14**, **16**, **17** and O-alkyl vinyl ethers **6**, **15**, **18** were controled by microanalysis and Mass Spectrometry on a Hewlett Packard HP 5890 mass spectrometer (70 eV) using GC-MS coupling with a glass capillary column HP1 (25m, 0.22 mm, He carrier gas).

Allylation of ketone 2a. To a stirred solution of tBuOK (0.118 g, 1.05 mmol) in tBuOH (5ml), the ketone **2a** (0.213 g, 1 mmol) and allyl bromide (0.113 g, 1.1 mmol) dissolved in tBuOH (4 ml) were added dropwise at room temperature. The mixture was stirred for 3 hours and treated with water (10 ml). After separation and extraction of the aqueous phase with dichloromethane (3 x 10 ml), the organic fractions were dried, concentrated, and chromatographied. Allyl phenylselenide **8** was eluted by petroleum ether elution and allylated products **7a** and **9** were then separated (petroleum ether/CH_2Cl_2 : 80/20).

3-(Phenylselanyl)hex-5-en-2-one 7a. (46 % yield). ^1H NMR ($CDCl_3$), δ : 7.57-7.48 (2H, m, Ph), 7.34-7.22 (3H, m, Ph), 5.94-5.67 (1H, m, H-5), 5.11-5.01 (2H, H-6), 3.67 (1H, t, J = 7.7 Hz, H-3), 2.68-2.34 (2H, m, H-4), 2.27 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$), δ : 203.3, 135.6, 134.9, 134.6, 129.1, 129.0, 128.6, 117.2, 50.8, 34.3, 27.5. IR $\nu_{C=O}$ = 1698 cm^{-1}. Anal. Calc. for $C_{12}H_{14}OSe$: C, 56.92 ; H, 5.57. Found : C, 57.02 ; H, 5.50. GCMS (70 eV) m/z 254 (M^+, 15), 211 (7), 183 (8), 157 (32), 130 (33), 97 (33), 77 (27), 43 (100), 27 (25).

4,6-Bis(phenylselanyl)nona-1,8-dien-5-one 9. (5 % yield). m.p : 61°C (Petroleum ether/CCl_4 : 90/10). ^1H NMR ($CDCl_3$), δ : 7.51-7.14 (10H, m, 2Ph), 5.97-5.74 (2H, m, H-2, H-8), 5.25-5.03 (4H, m, H-1, H-9), 3.86 (2H, t, J = 7.4 Hz, H-4, H-6), 2.75-2.37 (4H, m, H-3 + H-7). ^{13}C NMR ($CDCl_3$), δ : 197.3, 137.4, 137.0, 136.2, 135.8, 135.2, 129.3, 129.0, 128.7, 117.3, 48.9, 34.2. IR $\nu_{C=O}$ = 1685 cm^{-1}. Anal. Calc. for $C_{21}H_{22}OSe_2$: C, 56.26 ; H, 4.95. Found : C, 56.17 ; H, 5.02. GCMS (70 eV) m/z 448/450 (M^+, 34/33), 314 (37), 293 (62), 252 (1), 234 (6), 211 (52), 183 (21), 157 (100), 130 (80), 91 (26), 77 (70), 53 (48), 27 (30).

Isomerisation of ketone 10. The ketone **10**, already decribed[8] was treated by tBuOK (1 eq) in tBuOH at room temperature as for another α-phenylselanyl ketone[8]. A mixture of the isomerized ketone **12** with **10** and **2a** (24/44/32) was obtained.

1,1-Bis(phenylselanyl)propanone 10. ^1H NMR ($CDCl_3$), δ : 7.65-7.23 (10H, m, Ph), 5.51 (1H, s, H-1), 2.33 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$), δ : 196.8, 135.7, 131.2, 129.5, 129.2, 127.5, 125.9, 60.6, 25.0. IR $\nu_{C=O}$ = 1683 cm^{-1}. Anal. Calc. for $C_{20}H_{16}OSe_2$: C, 55.83 ; H, 3.75. Found : C, 55.94 ; H, 3.67. GCMS (70 eV) m/z 370 (M^+, 64), 327 (22), 314 (10), 247 (7), 234 (6), 213 (64), 167 (25), 157 (37), 132 (70), 117(9), 105 (33), 91 (26), 77 (5), 65 (11), 51 (46), 43 (100), 39 (15), 27 (10).

1,3-Bis(phenylselanyl)propanone 12. ^1H NMR ($CDCl_3$), δ : 7.65-7.23 (10H, m, Ph), 3.73 (2H, s, CH_2). ^{13}C NMR ($CDCl_3$), δ : 191.6, 133.2, 129.2, 128.4, 127.9, 33.8. IR $\nu_{C=O}$ = 1695 cm^{-1}. Anal. Calc. for $C_{20}H_{16}OSe_2$: C, 55.83 ; H, 3.75. Found : C, 57.73 ; H, 3.84. GCMS (70 eV) m/z 370 (M^+, 25), 312 (1), 293 (1), 234 (2), 213 (41), 185 (5), 171 (33), 157 (20), 132 (8), 117 (5), 105 (4), 91 (100), 77 (31), 51 (26), 39 (11).

Allylation - selenenylation of ketone 2a. The ketone **2a** was treated with tBuOK and allyl bromide as described above. The mixture was then stirred for 10 min. and PhSeCl (57 mg, 0.3 mmol) was introduced. The stirring was continued for 3 hours. The work-up led to an oil which was chromatographied. Diphenyldiselenide was eliminated by petroleum ether elution and the ketones **13** and **9** were separated with a mixture petroleum ether / CH_2Cl_2 (80/20).

3-Allyl-3-(phenylselanyl)hex-5-en-2-one 13. (21 % yield). ^1H NMR ($CDCl_3$), δ : 7.47-7.21 (5H, m, Ph), 5.90-5.74 (2H, m, C*H*=CH_2), 5.19-5.05 (4H, m, CH_2=CH), 2.51 (4H, d, J = 6.9 Hz, CH_2), 2.40 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$), δ : 181.0, 137.2, 135.8, 133.0, 131.3, 129.0, 127.6, 118.8, 60.8, 36.4, 25.1. IR $\nu_{C=O}$ =

1692 cm^{-1}. Anal. Calc. for $C_{15}H_{18}OSe$: C, 61.43 ; H, 6.19. Found : C, 61.51 ; H, 6.07. GCMS (70 eV) m/z 294 (M^+, 4), 251 (7), 217 (2), 195 (2), 171 (4), 157 (8), 137 (14), 93 (16), 77 (19), 43 (100).

Allylation of enoxysilanes 4. To a stirred solution of tBuOK (0.112 g, 1 mmol), in CH_2Cl_2 (12 ml) containing tBuOH (2ml) , cooled to - 78°C, the enoxysilane **4** (1 mmol) in CH_2Cl_2 (3 ml) was added dropwise. The mixture was warmed up to - 20°C for 30 minutes and then lowered to - 78°C. A solution of allyl bromide (0.181 g, 1.5 mmol) in CH_2Cl_2 (3 ml) was added slowly. The reaction was then warmed up to room temperature and stirred for 8 hours. After work-up, the chromatography allowed the separation of allyl phenylselenide **8.** The ketone 7 was obtained by elution with petroleum ether/CH_2Cl_2 (90/10).

Allyl phenylselenide 8. ^1H NMR ($CDCl_3$), δ : 7.51-7.46 (m, 2H, Ph), 7.28-7.23 (m, 3H, Ph), 6.04-5.84 (m, 1H, H-2), 5.01-4.91 (m, 2H, H-3), 3.54-3.49 (m, 2H, H-1).

1-Phenyl-2-(phenylselanyl)pent-4-en-1-one 7b. (72 % yield). ^1H NMR ($CDCl_3$), δ : 7.91-7.17 (10H, m, 2Ph), 5.96-5.74 (1H, m, C*H*=CH_2), 5.11-5.01 (2H, m, CH_2=CH), 4.53 (1H, t, J = 8.4 Hz, H-2), 2.91-2.44 (2H, m, CH_2). ^{13}C NMR ($CDCl_3$), δ : 194.2, 136.6, 136.2, 135.5, 132.8, 129.0, 128.4, 123.3, 117.4, 44.6, 35.1. IR $\nu_{C=O}$ = 1671 cm^{-1}. Anal.Calc.for $C_{17}H_{16}OSe$: C, 64.77 ; H, 5.12. Found : C, 64.90 ; H, 5.01.

4-(Phenylselanyl)-2,2-dimethylhept-6-en-3-one7c. (65 % yield). ^1H NMR ($CDCl_3$), δ : 7.56-7.21 (5H, m, Ph), 5.76-5.56 (1H, m, H-6), 5.07-4.96 (2H, m, H-7), 4.00-3.93 (1H, m, H-4), 2.70-2.37 (2H, m, H-5), 1.15 (9H, s, tBu). ^{13}C NMR ($CDCl_3$), δ : 210.3, 136.0, 135.3, 128.8, 128.6, 117.4, 43.5, 43.3, 36.7, 27.0. IR $\nu_{C=O}$ = 1698 cm^{-1}. Anal. Calc. for $C_{15}H_2OSe$: C, 61.01 ; H, 6.83. Found : C, 60.88 ; H, 6.91. GCMS (70 eV) m/z 296 (M^+, 9), 211 (16), 183 (9), 157 (23), 139 (12), 130 (39), 77 (21), 57 (100), 41 (70).

3-Methyl-3-(phenylselanyl)hex-5-en-2-one 7d. (68 % yield). ^1H NMR ($CDCl_3$), δ : 7.48-7.23 (5H, m, Ph), 5.84-5.61 (1H, m, H-5), 5.15-5.03 (2H, m, H-6), 2.58-2.47 (2H, m, H-4), 2.36 (3H, s, H-1), 1.44 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$), δ : 203.1, 137.2, 136.9, 133.3, 129.2, 128.8, 118.6, 56.5, 41.2, 24.8, 21.3. IR $\nu_{C=O}$ = 1691 cm^{-1}. Anal. Calc. for $C_{13}H_{16}Se$: C, 58.43 ; H, 6.04. Found : C, 58.54 ; H, 5.93. GCMS (70 eV) m/z 268 (M^+, 4), 225 (9), 183 (7), 157 (11), 111 (8), 77 (12), 43 (100), 41 (13).

2-Allyl-2-(phenylselanyl)cyclohexanone 7e. (56 % yield). ^1H NMR ($CDCl_3$), δ : 7.45-7.23 (5H, m, Ph), 5.91-5.67 (1H, m, C*H*=CH_2), 5.13-4.94 (2H, m, CH_2=CH), 3.54-3.33 (1H, m, C*H* : cycle), 2.41-2.35 (2H, m, CH_2), 2.34-1.53 (7H, m, cycle). ^{13}C NMR ($CDCl_3$), δ : 205.9, 137.2, 134.4, 129.2, 128.8, 118.8, 58.1, 40.3, 37.1, 36.3, 26.3, 21.8. IR $\nu_{C=O}$ = 1692 cm^{-1}. Anal. Calc. for $C_{15}H_{18}OSe$: C, 61.43 ; H, 6.19. Found : C, 61.32 ; H, 6.24. GCMS (70 eV) m/z 312 (M^+, 1), 294 (8), 253 (1), 225 (1), 213 (2),184 (1), 157 (17), 137 (63), 119 (15), 93 (44), 67 (100), 55 (40), 41 (19).

Benzylation of enoxysilane 4a. The procedure used was the same as for allylation. After work-up, the oily residue was chromatographied. Benzyl phenylselenide **20** was eliminated by petroleum ether elution and the ketone **21** eluted with a mixture petroleum ether/CH_2Cl_2 (90/10).

Benzyl phenylselenide 20. ^1H NMR ($CDCl_3$), δ : 7.50-7.19 (m, 10H, 2Ph), 4.12 (s, 2H, CH_2).

4-Phenyl-3-(phenylselanyl)-2-butanone 21. (41 % yield). ^1H NMR ($CDCl_3$), δ : 7.49-7.16 (10H, m, 2Ph), 3.96-3.80 (1H, m, H-3), 3.77-3.57 (1H, m, H-3'), 3.04-2.93 (1H, m, H-4), 2.22 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$), δ : 203.3, 138.8, 135.6, 131.3, 128.8, 128.3, 52.7, 36.5, 28.1. IR $\nu_{C=O}$ = 1702 cm^{-1}. Anal. Calc. for $C_{16}H_{16}OSe$: C, 63.37 ; H, 5.32. Found : C, 63.45 ; H, 5.22.

Allylation of enoxysilanes 3. The enoxysilane **3** (1 mmol) and allyl bromide (0.181 g, 1.5 mmol) in CH_2Cl_2 (3 ml) were added dropwise to a stirred solution of tBuOK (0.112 g, 1 mmol) in tBuOH (2 ml) and CH_2Cl_2 (12 ml) at - 78°C. The mixture was then slowly warmed up to room temperature and stirred for 8 hours. After work-up, the oily residue was chromatographied. Petroleum ether elution afforded the O-allyl vinyl ether **6.** The two isomers **6d** and **6e** were separated. The aldehyde **5** was isolated by elution with a mixture petroleum ether-CH_2Cl_2 (90/10).

2-Methyl-2-(phenylselanyl)pent-4-enal 5a. (82 % yield). ^1H NMR ($CDCl_3$), δ : 9.25 (1H, s, H-1), 7.48-7.22 (5H, m, Ph), 5.28 (1H, m, H-4), 5.14 (2H, m, H-5), 2.46 (2H, d, J = 7.0 Hz , H-3), 1.35 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$), δ : 192.5, 137.6, 132.4, 129.3, 128.9, 124.5, 119.0, 61.9, 38.4, 18.1. IR $\nu_{C=O}$ = 1698 cm^{-1}. Anal. Calc. for $C_{12}H_{14}OSe$: C, 56.92 ; H, 5.57. Found : C, 56.85 ; H, 5.63. GCMS (70 eV) m/z 254 (M^+, 7), 225 (6), 183 (8), 172 (7), 157 (19), 97 (21), 77 (35), 41 (100), 27 (21).

2-Ethyl-2-(phenylselanyl)pent-4-enal 5b. (79 % yield). ^1H NMR ($CDCl_3$), δ : 9.26 (1H, s, H-1), 7.50-7.20 (5H, m, Ph), 5.94 (1H, m, H-4), 5.23-5.10 (2H, m, H-5), 2.55-2.30 (2H, m, H-3), 1.71 (2H, q, J = 7.4 Hz , CH_2), 0.97 (3H, t, J = 7.4 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 192.5, 137.7, 132.6, 129.4, 129.0, 125.1, 118.6, 62.5, 33.6, 23.1, 9.0. IR $\nu_{C=O}$ = 1705 cm^{-1}. Anal. Calc. for $C_{13}H_{16}OSe$: C, 58.43 ; H, 6.04. Found : C, 58.35 ; H, 6.12. GCMS (70 eV) m/z 268 (M^+, 14), 239 (10), 197 (4), 172 (16), 158 (48), 131 (4), 55 (100), 41 (96).

2-Phenyl-2-(phenylselanyl)pent-4-enal 5c. m.p : 66-67°C (70 % yield). ^1H NMR ($CDCl_3$), δ : 9.59 (1H, s, H-1), 7.55-7.20 (10H, m, Ph), 5.94 (1H, m, H-4), 5.63 (2H, m, H-4), 4.99-4.83 (2H, m, H-5), 2.71 (2H, d, J = 6.9 Hz , H-3). ^{13}C NMR ($CDCl_3$), δ : 189.4, 137.9, 135.9, 133.0, 129.7, 129.0, 128.7, 118.4, 65.0, 38.3. IR $\nu_{C=O}$ = 1700 cm^{-1}. Anal. Calc. for $C_{17}H_{16}OSe$: C, 67.77 ; H, 5.12. Found : C, 67.90 ; H, 5.02. GCMS (70 eV) m/z 316 (M^+, 9), 211 (2), 183 (3), 172 (8), 159 (20), 145 (38), 131 (53), 77 (44), 51 (31), 28 (20).

2-Benzyl-2-(phenylselanyl)pent-4-enal 5d. (46 % yield). ^1H NMR ($CDCl_3$), δ : 9.44 (1H, s, H-1), 7.52-7.16 (10H, m, 2Ph), 6.05 (1H, m, H-4), 5.06-5.27 (2H, m, H-5), 3.16 (1H, d, J = 11.2 Hz, CH_2Ph), 3.06 (1H, d, J = 11.2 Hz, CH_2Ph), 2.34 (2H, d, J = 6.7 Hz, H-3). ^{13}C NMR ($CDCl_3$), δ : 191.3, 137.7, 135.8, 132.9, 129.8, 129.5, 129.0, 128.2, 126.8, 125.0, 119.1, 62.0, 37.5, 33.7. IR $\nu_{C=O}$ = 1702 cm^{-1}. Anal. Calc. for $C_{18}H_{18}OSe$: C, 65.65 ; H, 5.51. Found : C, 65.57 ; H, 5.59. GCMS (70 eV) m/z 330 (M^+, 4), 253 (1), 183 (1), 172 (11), 159 (14), 129 (11), 65 (14).

2-Isopropyl-2-(phenylselanyl)pent-4-enal 5e. (65 % yield). ^1H NMR ($CDCl_3$), δ : 9.44 (1H, s, H-1), 7.49-7.25 (5H, m, Ph), 5.94 (1H, m, H-4), 5.10 (2H, m, H-5), 2.40 (2H, d, J = 7.6 Hz, H-3), 2.11 (1H, hept, J = 6.9 Hz, CH(CH_3)$_2$), 1.16 (3H, d, J = 6.9 Hz, CH_3), 1.07 (3H, d, J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 189.4, 137.9, 133.0, 129.7, 129.0, 128.7, 128.4, 128.1, 125.9, 118.4, 65.0, 38.3. IR $\nu_{C=O}$ = 1700 cm^{-1}. Anal. Calc. for $C_{17}H_{16}OSe$: C, 64.77 ; H, 5.12. Found : C, 64.83 ; H, 5.04. GCMS (70 eV) m/z 316 (M^+, 14), 211 (1), 183 (2), 183 (2), 172 (8), 159 (20), 145 (38), 131 (53), 115 (34), 103 (14), 51 (31).

1-Allyloxy-2-phenyl 2-(phenylselanyl)ethene 6c. (17 % yield). The stereochemistry of the only geometric isomer formed was not assigned. ^1H NMR ($CDCl_3$), δ : 7.82-7.06 (11H, m, 2Ph, H-1), 5.90-6.10 (1H, m, CH=CH_2), 5.43-5.27 (2H, m, CH_2=CH), 4.49 (2H, d, J = 5.0 Hz, CH_2). Anal. Calc. for $C_{17}H_{16}OSe$: C, 667.77 ; H, 5.12. Found : C, 67.71 ; H, 5.19.

1-Allyloxy-3-phenyl 2-(phenylselanyl)prop-1-ene 6d. (15 % yield). (Z/E : 50/50). E isomer, ^1H NMR ($CDCl_3$), δ : 7.43-7.12 (10H, m, 2Ph), 6.75 (1H, s, H-1), 6.09-5.90 (1H, m, CH=CH_2), 5.45-5.27 (2H, m,

CH_2=CH), 4.45 (2H, d, J = 5.3 Hz, CH_2), 3.70 (2H, s, H-3). ^{13}C NMR (CDCl3), δ : 152.1, 133.2, 131.6, 130.0, 128.8, 128.0, 126.0, 125.9, 117.9, 107.6, 73.0, 36.1. Anal. Calc. for $C_{18}H_{18}OSe$: C, 65.65 ; H, 5.51. Found : C, 65.72 ; H, 5.47. GCMS (70 eV) m/z 330 (M^+, 4), 315 (2), 259 (1), 234 (1), 209 (1), 183 (2), 173 (8), 157 (9), 129 (17), 91 (100), 77 (30), 65 (23), 39 (17). ^1H NMR ($CDCl_3$), Z isomer, δ : 7.46-7.03 (10H, m, 2Ph), 6.41 (1H, s, J = 1.1 Hz, H-1), 5.98-5.81 (1H, m, C*H*=CH_2), 5.37-5.20 (2H, m, CH_2=CH), 4.39-4.35 (2H,m, CH_2), 3.42 (2H, s, H-3). ^{13}C NMR ($CDCl_3$), δ : 147.0, 133.3, 132.8, 128.6, 126.6, 126.1, 117.8, 73.0, 39.5.

1-Allyloxy-3-phenyl 2-(phenylselanyl)but-1-ene 6e. (15 % yield). (Z/E : 60/40). ^1H NMR ($CDCl_3$), E isomer, δ : 7.47-7.14 (5H, m, Ph), 6.58 (1H, s, H-1), 6.05-5.83 (1H, m, C*H*=CH_2), 5.40-5.25 (2H, m, CH_2=CH), 4.38 (2H, m, CH_2), 3.17 (1H, hept, J = 6.8 Hz, H-3), 0.97 (6H, d, J = 6.8 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 152.5, 133.4, 129.4, 128.6, 125.7, 117.7, 116.0, 72.9, 29.2, 21.7. Anal. Calc.for $C_{17}H_{16}OSe$: C, 64.77 ; H, 5.12. Found : C, 64.88 ; H, 5.01. GCMS (70 eV) m/z 282 (M^+, 5), 253 (3), 239 (1), 183 (3), 172 (10), 158 (32), 125 (23), 111 (20), 95 (22), 77 (41), 55 (100), 41 (86), 27 (35). ^1H NMR ($CDCl_3$), Z isomer : δ : 7.43-7.13 (5H, m, Ph), 6.48 (1H, s, J = 0.74 Hz, H-1), 5.91-5.74 (1H, m, C*H*=CH_2), 5.28-5.15 (2H, m, CH_2=CH), 4.33-4.29 (2H, m, CH_2), 2.41 (1H, hept, J = 6.8 Hz, H-3), 1.05 (6H, d, J = 6.8 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 146.6, 133.2, 130.4, 128.5, 125.5, 117.5, 114.3, 72.7, 33.1, 22.5.

Prenylation, methallylation and benzylation of enoxysilanes 3a, 3b and 3e. The procedure used was the same as for allylation.After work-up, the oily residue was chromatographied. Petroleum ether elution afforded O-allyl vinyl ether **15** (or **18**). The aldehyde **14** (or **17**) was isolated by elution with petroleum ether/CH_2Cl_2 (90/10). The isomeric aldehydes **16** and **16a'** were not separated. The 2-methyl prop-2-enyl phenylselenide **19** was also eliminated by petroleum ether elution.

2-Methylprop-2-enyl phenylselenide 19. ^1H NMR ($CDCl_3$), δ : 7.51-7.21 (m, 5H, Ph), 4.68 (m, 2H, H-3), 3.51 (s, 2H, H-1), 1.85 (s, 3H, CH_3). Anal. Calc. for $C_{10}H_{12}Se$: C, 56.88 ; H, 5.73. Found : C, 56.98 ; H, 5.64.

2,4-Dimethyl-2-(phenylselanyl)pent-4-enal 14a. (86 % yield). ^1H NMR ($CDCl_3$), δ : 9.28 (s, 1H, Ha), 7.49-7.23 (m, 5H, Ph), 2.63 (d, 1H, J = 12.2 Hz, H-3), 2.47 (d, 1H, J = 12.2 Hz, H-3), 1.65 (s, 3H, C*H*$_3$-C=), 1.35 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ : 191.7, 140.4, 137.6, 129.2, 128.7, 125.2, 115.3, 102.4, 56.8, 42.6, 23.3, 17.6. IR $\nu_{C=O}$ = 1702 cm^{-1}. Anal. Calc. for $C_{13}H_{15}OSe$: C, 58.65 ; H, 5.68. Found : C, 58.53 ; H, 5.76.

2-Ethyl-4-methyl-2-(phenylselanyl)pent-4-enal 14b. (78 % yield). ^1H NMR ($CDCl_3$), δ : 9.31 (s, 1H, Ha), 7.47-7.25 (m, 5H, Ph), 4.84 (d, 2H, J = 14.3 Hz, H-5), 2.50 (s, 2H, H-3), 1.67 (s, 3H, CH_3), 1.60 (q, 2H, J = 7.3 Hz, CH_2), 1.07 (t, 3H, J = 7.3 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 191.3, 140.2, 137.4, 129.3, 128.9, 125.2, 115.0, 63.7, 38.3, 23.2, 21.2, 8.7. IR $\nu_{C=O}$ = 1698 cm^{-1}. Anal. Calc. for $C_{14}H_{18}OSe$: C, 59.79 ; H, 6.45. Found : C, 59.86 ; H, 6.35.

1-(2-Methylprop-2-enyloxy)-2-(phenylselanyl)propene 15a. (3-4 %). ^1H NMR ($CDCl_3$), Z isomer, δ : 7.40-7.14 (m, 5H, Ph), 6.59 (s, 1H, J = 1.3 Hz, H-1), 4.98 (d, 2H, J = 9.7 Hz, CH_2=), 4.26 (s, 2H, CH_2), 2.03 (s, 3H, J = 1.3 Hz, H-3), 1.76 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ : 151.5, 141.0, 131.4, 129.7, 129.1, 128.9, 126.0, 113.0, 30.0, 19.0, 17.3. Anal. Calc. for $C_{13}H_{15}OSe$: C, 58.65 ; H, 5.68. Found : C, 58.78 ; H, 5.57.

1-(2-Methylprop-2-enyloxy)-2-(phenylselanyl)but-1-ene 15b. (12 % yield). (Z/E : 60/40). ^1H NMR ($CDCl_3$), Z isomer : δ : 7.48-7.17 (m, 5H, Ph), 6.36 (s, 1H, J = 1.1 Hz, H-1), 4.98 (m, 2H, CH_2), 2.11 (q, 2H,

J = 7.2, 1.1 Hz, H-3), 1.69 (s, 3H, CH_3), 0.99 (t, 3H, J = 7.2 Hz, H-4). ^{13}C NMR ($CDCl_3$), δ : 151.5, 145.6, 141.2, 132.0, 128.7, 126.3, 113.0, 109.4, 75.8, 27.1, 19.0, 14.5. Anal. Calc. for $C_{14}H_{18}OSe$: C, 59.79 ; H, 6.45. Found : C, 59.70 ; H, 6.53. ^{13}C NMR ($CDCl_3$), E isomer : δ : 7.47-7.17 (m, 5H, Ph), 6.57 (s, 1H, H-1), 5.01-4.93 (m, 2H, J = 10.1 Hz, CH_2=), 4.26 (s, 2H, CH_2), 2.36 (q, 2H, J = 7.3 Hz, CH_2), 1.76 (s, 3H, CH_3), 0.97 (t, 3H, J = 7.3 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 145.4, 139.2, 131.8, 128.4, 126.0, 112.8, 109.6, 75.9, 29.2, 19.1, 14.6.

1-(2-Methylprop-2-enyloxy)-3-methyl-2-(phenylselanyl)but-1-ene 15e. (15 % yield). (Z/E : 50/50). ^1H NMR ($CDCl_3$), Z isomer, δ : 7.45-7.40 (2H, m, Ph), 7.20-7.16 (3H, m, Ph), 6.54 (1H, s, H-1), 4.98 (2H, m, CH_2=C), 4.27 (2H, s, CH_2), 3.15 (1H, hept, J = 6.7 Hz, H-3), 1.76 (3H, s, CH_3C=), 0.94 (6H, d, J = 6.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 152.6, 141.1, 129.4, 128.6, 125.7, 115.7, 112.9, 76.0, 29.3, 21.7. Anal. Calc. for $C_{15}H_{20}OSe$: C, 61.01 ; H, 6.83. Found : C, 61.12 ; H, 6.77. ^1H NMR ($CDCl_3$), Z isomer, δ : 7.42-7.37 (2H, m, Ph), 7.24-7.12 (3H, m, Ph), 6.46 (1H, s, H-1), 4.91-4.88 (2H, m, CH_2=C), 4.21 (2H, s, CH_2), 2.41 (1H, hept, J = 6.7 Hz, H-3), 1.64 (3H, s, CH_3C=), 1.04 (6H, d, J = 6.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 146.7, 139.0, 130.5, 128.6, 125.6, 113.0, 75.9, 33.2, 22.7, 19.0.

2,5-Dimethyl-2-(phenylselanyl)hex-4-enal 16a. ^1H NMR ($CDCl_3$), δ : 9.25 (s, 1H, Ha), 7.49-7.24 (m, 5H, Ph), 5.16 (m, 2H, H-4), 2.42 (d, 2H, J = 8.5 Hz, H-3), 1.71 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.33 (s, 3H, CH_3).

2-Phenylselanyl-2,3,3-trimethyl-pent-4-enal 16a'. ^1H NMR ($CDCl_3$), δ : 9.63 (s, 1H, Ha), 7.49-7.24 (m, 5H, Ph), 6.07 (m, 1H, H-4), 5.20-5.06 (m, 2H, H-5), 1.29 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.13 (s, 3H, CH_3).

2-Benzyl-2-(phenylselanyl)propanal 17a. m.p : 50-51°C. (Petroleum ether). (79 % yield). ^1H NMR ($CDCl_3$), δ : 9.38 (s, 1H, Ha), 7.54-7.10 (m, 10H, 2Ph), 3.24 (d, 1H, J = 13.8 Hz, CH_2Ph), 2.98 (d, 1H, J = 13.8 Hz, CH_2Ph), 1.28 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ : 192.0, 137.7, 136.0, 129.9, 129.4, 128.9, 128.2, 126.8, 125.4, 58.0, 40.7, 18.1. Anal. Calc. for $C_{16}H_{16}OSe$: C, 63.37 ; H, 5.32. Found : C, 63.45 ; H, 5.23.

2-Benzyl-2-(phenylselanyl)butanal 17b. (81 % yield). ^1H NMR ($CDCl_3$), δ : 9.43 (s, 1H, Ha), 7.56-7.20 (m, 10H, 2Ph), 3.16 (d, 1H, J = 12.3 Hz, CH_2Ph), 3.04 (d, 1H, J = 12.3 Hz, CH_2Ph), 1.55 (q, 2H, J = 7.2 Hz, H-3), 1.10 (t, 3H, J = 7.2 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 191.9, 137.7, 136.4, 131.5, 129.7, 129.2, 128.5, 127.8, 127.0, 125.5. Anal. Calc. for $C_{17}H_{18}OSe$: C, 64.35 ; H, 5.72. Found : C, 64.26 ; H, 5.82.

2-Benzyl-3-methyl-2-(phenylselanyl)butanal 17e. (39 % yield). ^1H NMR ($CDCl_3$), δ : 9.41 (s, 1H, Ha), 7.51-7.22 (m, 10H, 2Ph), 3.26-3.01 (m, 2H, CH_2Ph), 2.01 (hept, 1H, J = 6.9 Hz, H-3), 1.22 (d, 2H, J = 6.9 Hz, CH_3), 0.87 (d, 2H, J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 190.9, 138.0, 135.3, 130.5, 129.6, 129.1, 126.2, 126.8, 68.4, 35.3, 29.6, 19.0, 18.2. IR $\nu_{C=O}$ = 1700 cm^{-1}. Anal. Calc. for $C_{18}H_{20}OSe$: C, 65.25 ; H, 6.08. Found : C, 65.36 ; H, 5.97.

1-Benzyloxy-2-(phenylselanyl)but-1-ene 18b. (5 % yield). ^1H NMR ($CDCl_3$), δ : 7.38-7.17 (m, 10H, 2Ph), 6.68 (s, 1H, Ha), 4.92 (s, 2H, CH_2), 2.41 (q, 2H, J = 7.3 Hz, CH_2), 1.03 (t, 3H, J = 7.3 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 151.5, 129.7, 128.7, 128.4, 128.0, 127.4, 125.8, 74.0, 23.8, 13.2. Anal. Calc. for $C_{17}H_{18}OSe$: C, 64.35 ; H, 5.72. Found : C, 64.44 ; H, 5.63.

1-Benzyloxy-3-methyl-2-(phenylselanyl)but-1-ene 18e. (41 % yield). (Z/E : 60/40). ^1H NMR ($CDCl_3$), E isomer : δ : 7.39-7.13 (m, 10H, 2Ph), 6.63 (s, 1H, Ha), 4.92 (s, 2H, CH_2), 3.19 (hept, 1H, J = 6.7 Hz, H-3),

0.95 (d, 6H, J = 6.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 146.7, 136.8, 131.6, 130.4, 128.5, 128.2, 127.6, 127.1, 125.6, 73.7, 33.1, 22.5. Anal. Calc. for $C_{18}H_{20}OSe$: C, 65.25 ; H, 6.08. Found : C, 65.34 ; H, 5.99. ^1H NMR ($CDCl_3$), Z isomer : δ : 7.41-7.14 (m, 10H, 2Ph), 6.55 (s, 1H, Ha), 4.87 (s, 2H, CH_2), 2.41 (hept, 1H, J = 6.7 Hz, H-3), 1.05 (d, 6H, J = 6.7 Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ : 152.8, 136.7, 130.4, 128.2, 127.4, 125.2, 116.1, 74.2, 29.4, 21.9.

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