Pergamon

Tetrahedron, Vol. 53, No. 49, pp. 16767-16782, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)10117-X

Synthesis and Reactivity of β-Phenylselanyl α-oxoesters

Stéphane Boivin, Francis Outurquin and Claude Paulmier*

Laboratoire de Synthèse Thio- et Séléno-organique (IRCOF), Université de Rouen, UFR des Sciences et des Techniques, F-76821 Mont-Saint-Aignan Cedex, France.

Abstract *: β-Phenylselanyl α-oxoesters* ***2*** *were prepared by N-phenylselanyl morpholine treatment of α-oxoesters* ***1****, oxidized into β-unsaturated α-oxoesters* ***5*** *and subjected to the Wittig-Horner olefination. The diethyl (1-phenylselanylalkyl)maleates* ***6*** *have led, after [2,3]sigmatropic rearrangement of the corresponding selenoxides, to the diethyl 3-alkylidene-2-hydroxysuccinates 7. The 2-(t-butoxycarbonylamino)-3-alkylidenesuccinates* ***8*** *were prepared in a similar way. The decomposition of halo-adducts derived from compounds* ***6*** *has allowed the synthesis of the diethyl 3-alkylidene-2-halosuccinates* ***9*** *and* ***10****.* © 1997 Elsevier Science Ltd.

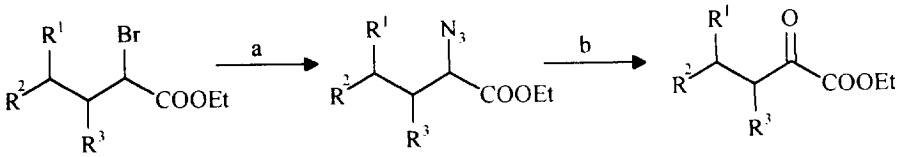
We have been interested for several years in the reactivity of α-phenylselanyl aldehydes. The reactions studied concern the carbonyl group, the selenium substituent , the α-carbon and have led to various unsaturated and functionalized structures.[1] Benzeneselenenamides ($PhSeNR_2$, NR_2 = diethylamino,[2a] morpholino[2b] groups) have been used as selenenylating agents of enolisable aldehydes for the preparation of α-phenylselanyl aldehydes. Mixture of regioisomers and low yields were observed with ketones.[3] Better results have been obtained for the α-selenenylation of cyclanones with N-phenylselanyl phthalimide.[4] The reaction of enolates or silyl enol ethers derived from aliphatic ketones with PhSeX (X = Cl, Br) has been proposed.[5] A general method, using $PhSeCl_3$, can be applied to aldehydes and ketones.[6]

We have also observed that areneselenenamides are selenenylating agents for α-oxoesters.[7] Using N-phenylselanyl morpholine, we have prepared the ethyl β-phenylselanyl α-oxoesters **2a-h**. We propose, here, a new method for the synthesis of β-unsaturated α-oxoesters **5** and of diethyl 3-alkylidenesuccinates **7-10** through the rearrangement of the diethyl (phenylselanylalkyl)maleates **6** formed by olefination of the α-oxoesters **2**.

The α-oxoesters **1** were prepared by two known methods, except for ethyl 2-oxo-4-phenylbutanoate **1e** and ethyl 3-methyl-2-oxobutanoate **1g** which are commercial compounds (Scheme 1). In method A,[8] the α-azidoesters, obtained by sodium azide treatment of the corresponding α-bromoesters, were deprotonated using a catalytic amount of lithium ethoxide in a THF/ethanol mixture. α-Oxoesters **1a**[8] (75 %), **1b**[9a] (78 %), **1c**[9a] (84 %) were synthetized by this way. The reaction of a Grignard reagent on diethyl oxalate has allowed the preparation of **1d**[9b] (75 %), **1f**[9b] (74 %), and the ethyl 2-cyclohexyl-2-oxoacetate **1h**, a new α-oxoester (72 %) (Method B[9b]).

Fax : 02-35-52-29-59

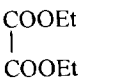
Scheme 1



Method A

a) $R^1=R^2=R^3=H$
b) $R^1=Me$, $R^2=R^3=H$
c) $R^1=Et$, $R^2=R^3=H$
d) $R^1=nBu$, $R^2=R^3=H$
e) $R^1=Ph$, $R^2=R^3=H$
f) $R^1=R^2=Me$, $R^3=H$
g) $R^1=R^2=H$, $R^3=Me$
h) $R^1=H$, $R^2=R^3=-(CH_2)_4-$

Method B



Method A : a) NaN_3, DMF ; b) EtOLi, EtOH, THF.
Method B : $R^1R^2CHCH(R^3)MgX$, THF, -80°C.

The selenenylation of compounds **1** was achieved as for enolisable aldehydes.[1,7] The reaction using N-phenylselanyl morpholine[2b] occurs more slowly and the β-phenylselanyl α-oxoesters **2** were prepared in fair to good yields with a slight excess of reagent. (Scheme 2, Table 1). The β,β-bis(phenylselanyl) α-oxoesters **3a** ($R^1=R^2=H$), **3b** (R^1= Me, R^2 =H), **3c** (R^1=Et, R^2=H) were isolated in 50, 43 and 39 % yields respectively with two equivalents of selenenamide and a longer reaction time (2 days) from α-oxoesters **1** (R^3=H). A modest yield (41 %) was observed for **2h**. The selenenylation was improved (72 %) by PhSeBr treatment of the lithium enolate derived from ethyl 2-cyclohexyl-2-oxoacetate **1h**. LiHMDS is used as a base. We have observed that LDA caused the reduction of **1h** into ethyl 2-cyclohexyl-2-hydroxyacetate **4**. This unexpected hydride transfer from LDA to the carbonyl group is a known reductive behavior of this lithium amide in the case of sterically hindered ketones.[10]

Scheme 2

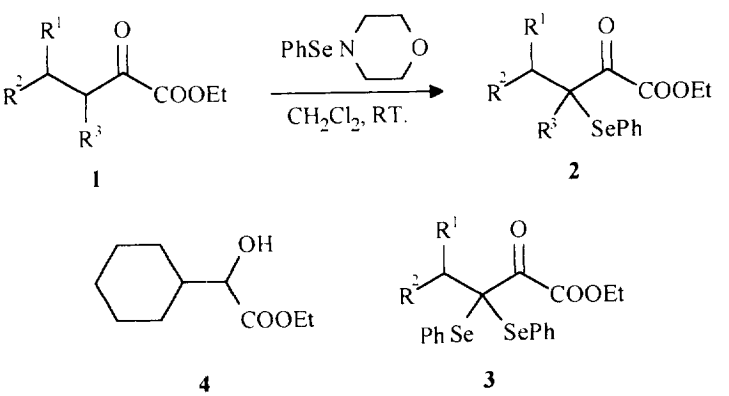


Table 1

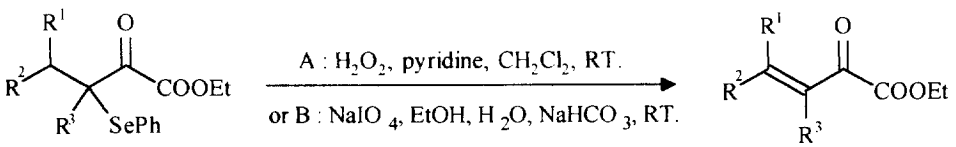
β-Phenylselanyl α-oxoesters **2** and β,β-bis(phenylselanyl) α-oxoesters **3**

N°	R^1	R^2	R^3	**2** Yield (%)	**3** Yield (%)[a]
2a	H	H	H	69	50
2b	Me	H	H	73	43
2c	Et	H	H	75	39
2d	nBu	H	H	76	-
2e	Ph	H	H	80	-
2f	Me	Me	H	80	-
2g	H	H	Me	58	-
2h	H	$-(CH_2)_4-$		41(72)[b]	-

a) 2 eq. N-phenylselanyl morpholine were used. b) Reaction achieved with LiHMDS and PhSeBr in THF.

The oxidation of the β-phenylselanyl α-oxoesters **2b-2h** was carried out as for other α-phenylselanyl carbonyl compounds.[11] H_2O_2 or $NaIO_4$ were used as oxidizing reagents (Scheme 3). The selenoxides have led immediately to the β-unsaturated α-oxoesters **5** after syn-elimination reaction. **5a**, however, cannot be isolated whatever the oxidizing agent and the reaction conditions. The E isomers were only formed in good yields (Table 2). We propose, here, an efficient two steps process for the preparation of esters **5** from α-oxoesters **1**.

Scheme 3



2 **5**

Table 2

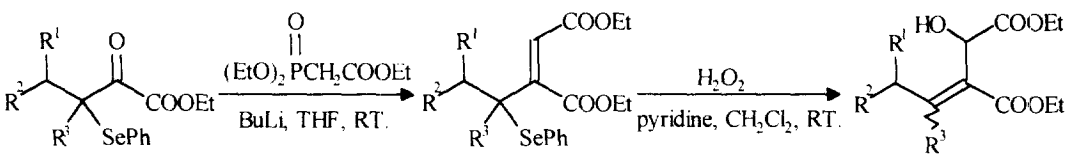
β-Unsaturated α-oxoesters **5**

N°	R^1	R^2	R^3	Method	Yield (%)	^1H NMR (δ, ppm) H_β (R^3)	H_γ (R^2)	J (Hz)
5b	Me	H	H	A	87	6.54	7.08	15.8
5c	Et	H	H	A	93	6.57	7.16	15.9
5d	nBu	H	H	A	90	6.50	7.16	15.8
5e	Ph	H	H	B	92	7.34	7.84	16.2
5f	Me	Me	H	B	85	6.70	-	-
5g	H	H	Me	A	92	-	6.03 6.12	-
5h	H	$-(CH_2)_4$		A	82	-	6.92	-

A few methods have been proposed for the synthesis of these compounds. The unsaturated α-oxoesters **5b**, **5d** and **5e** have been prepared by reaction of an alkenyl Grignard reagent with diethyl oxalate.[9b] **5c**[12] and **5g**[13] were obtained by oxidation of the corresponding β-unsaturated α-hydroxyester. The Wittig reaction between benzaldehyde and the phosphorane Ph_3P=CHCOCOOEt has allowed the access to the unsaturated α-oxoester **5e**.[14]

The diethyl(1-phenylselanyl)alkylmaleates **6** were prepared stereoselectively, in good yields, through the Wittig-Horner olefination of the α-oxoesters **2** with triethylphosphonoacetate (Scheme 4, Table 3). The E-stereochemistry was assigned from NOESY experiments. This finding agrees with results given for the general reaction between α-oxoesters and phosphonate anions derived from α-bromoesters.[12]

Scheme 4



The diesters **6**, bearing an allylic phenylselanyl substituent , were oxidized with H_2O_2. The [2,3]-sigmatropic rearrangement of the corresponding selenoxides has led to the diethyl 3-alkylidene-2-hydroxysuccinates **7** in very good yields. NOESY experiments have allowed the assigment of the Z configuration to the major isomer for **7a-7f** (Scheme 4, Table 3). The formation of a dienic diester, resulting from a syn-elimination reaction, has never been observed as for the oxidation of γ-phenylselanyl α,β-unsaturated esters or alkyl 5-phenylselanylpenta-2,4-dienoates.[1a]

Table 3

Diethyl (1-phenylselanyl)alkylbutenedioates **6**[a] and diethyl 3-alkylidene-2-hydroxysuccinates **7**.

N° olefination	R^1	R^2	R^3	Yield (%)	N° oxidation	Yield (%)	E/Z[b]
6a	H	H	H	61	**7a**	83	15/85
6b	Me	H	H	72	**7b**	88	15/85
6c	Et	H	H	77	**7c**	90	15/85
6d	Bu	H	H	78	**7d**	91	15/85
6e	Ph	H	H	70	**7e**	82	10/90
6f	Me	Me	H	80	**7f**	79	20/80
6g	H	H	Me	69	**7g**	80	-
6h	H	-$(CH_2)_4$-		71	**7h**	80	-

a) The E stereochemistry was assigned from NOESY experiments. b) The Z stereochemistry was assigned from NOESY experiments carried out on the major isomer.

The Hopkin's group has studied the nitrogen version of this rearrangement leading to allylic amines derivatives.[15] The treatment of allylic selenides with anhydrous chloramine-T has led to N-allylated p-toluenesulfonamides. N-Allyl carbamates were prepared by N-chlorosuccinimide oxidation in the presence

of an alkyl carbamate. Methyl 2-aminobut-3-enoate[15d] derivatives and methyl 2-(1-aminoalkyl)propenoates[16] were prepared by this way.We have applied this reaction to the unsaturated phenylselanyldiesters **6**. They were treated with N-chlorosuccinimide in the presence of t-butyl carbamate. The rearrangement of the intermediate selenilimine derivatives has occured very easily providing the alkylideneaminosuccinates **8** in fair to good yields (Scheme 5, Table 4).

Scheme 5

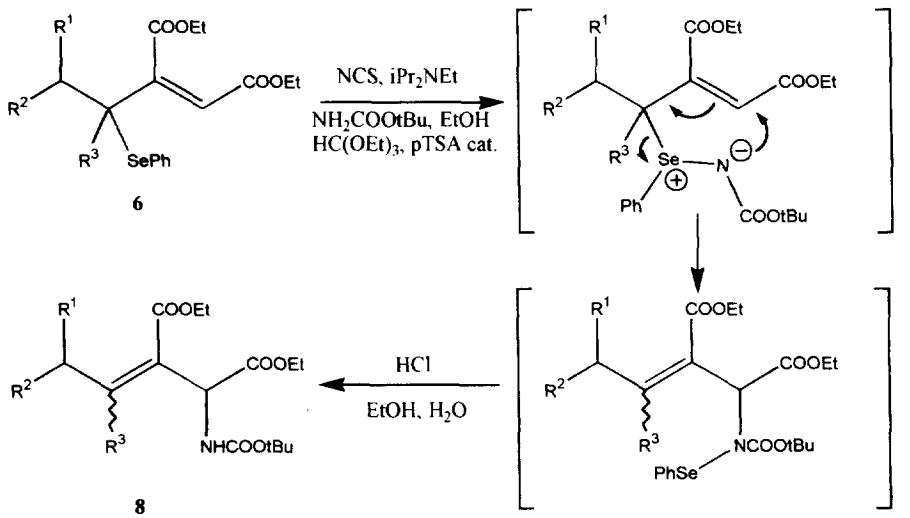


Table 4

Diethyl 3-alkylidene-2-t-butoxycarbonylaminosuccinates **8**

N°	R^1	R^2	R^3	Yield (%)	E/Z ratio
8a	H	H	H	69	70/30
8b	Me	H	H	72	65/35
8c	Et	H	H	79	60/40
8d	nBu	H	H	71	60/40
8e	Ph	H	H	69	60/40
8f	Me	Me	H	63	60/40
8g	H	H	Me	58	-

It must be noticed that traces of water induce a partial hydrolysis of the selenilimine derivative leading to the formation of the allylic alcohol **7** besides the carbamate **8**. The two geometric isomers of **8** were separated . NOESY experiments have allowed the assignment of the E stereochemistry for the major isomer. Two mixed multiplets, corresponding to the allylic proton on the carbon bearing R^1 and R^2, appear in the ^1H NMR spectra of the Z isomer.

Finally, we have studied the reaction between sulfuryl chloride or bromine and the unsaturated phenylselanyldiesters **6** (Scheme 6). This work is the continuation of a study carried out on γ-phenylselanyl α,β-unsaturated esters[1e] and on propargylic phenylselenides.[17] The unstable halo-adducts decompose with

rearrangement providing the diethyl 2-alkylidene-3-halosuccinates **9** (X = Cl) and **10** (X = Br) with excellent yields. (Table 5). The addition of ethyl vinyl ether as a trap of PhSeX was not needed[1e] to avoid the formation of the corresponding isomeric halide **11** or **12**. These compounds were expected by an addition-elimination process favoured by the conjugation of the double bond with the two ester groups. NOESY experiments have allowed the assignment of the E stereochemistry for the major isomer which is more abundant for the chloroesters **9** than for the corresponding bromoesters **10**.

Scheme 6

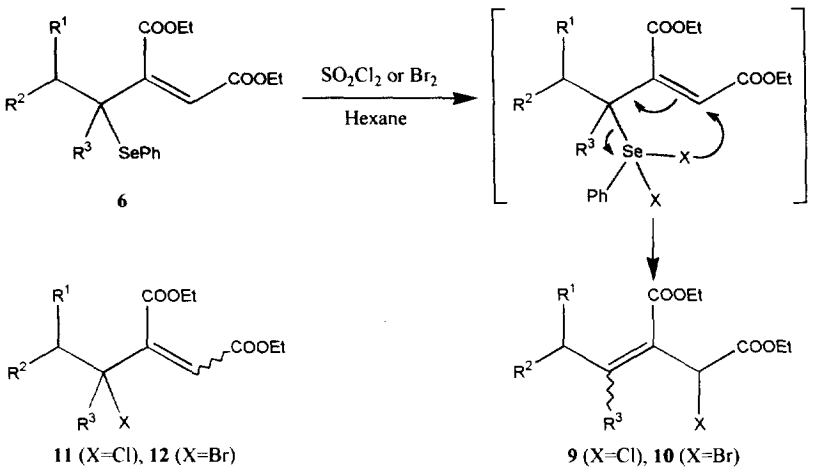


Table 5

Diethyl 2-alkylidene-3-halosuccinates **9** (X=Cl) and **10** (X=Br)

N°	R^1	R^2	R^3	Yield (%)	E/Z ratio
9a	H	H	H	78	75/25
10a	H	H	H	82	60/40
9b	Me	H	H	94	75/25
10b	Me	H	H	96	60/40
9c	Et	H	H	92	70/30
10c	Et	H	H	87	60/40
9d	nBu	H	H	88	80/20
10d	nBu	H	H	86	70/30
9e	Ph	H	H	85	85/15
10e	Ph	H	H	88	80/20
9f	Me	Me	H	95	75/25
10f	Me	Me	H	88	60/40
9g	H	H	Me	67	-
10g	H	H	Me	70	-
9h	H	$-(CH_2)_4-$		68	-
10h	H	$-(CH_2)_4-$		74	-

The decomposition of the unstable halo-adducts occurs with an allylic substitution of the selenonium group in spite of the conjugation of the double bond with the two esters functions. The chloroester **9g** has been already described.[18]

In conclusion, we have prepared β-phenylselanyl α-oxoesters **2**. They were oxidized into β-unsaturated α-oxoesters **5** providing a new method for the preparation of this class of compounds and were converted into diethyl (1-phenylselanyl)alkylbutenedioates **6** through Wittig-Horner olefination. The oxidation of these bifunctional allylic selenides has led to 3-alkylidene-2-hydroxysuccinates **7**. The formation of a deconjugated structure was also observed in the case of the selenilimine derivatives and the corresponding 2-aminoesters **8** were isolated. The decomposition of the halo-adducts derived from compounds **6** caused also a displacement of the double bond and diethyl 2-alkylidene-3-halosuccinates **9** and **10** were obtained with very good yields.

EXPERIMENTAL SECTION

All reactions were performed under argon atmosphere. Ethyl 2-oxobutanoate **1a**,[8] ethyl 2-oxopentanoate **1b**,[9a] ethyl 2-oxohexanoate **1c**,[9a] ethyl 2-oxooctanoate **1d**,[9b] ethyl 4-methyl-2-oxopentanoate **1f**[9b] were prepared according to literature procedures. All solvents and eluents were distilled before use. Light petroleum refers to the fraction with b.p. 40-60°C. THF was freshly distilled from sodium-benzophenone under argon. GC/mass-spectrometry analysis was performed on a Hewlett-Packard HP5890 with an HP-1 capillary column (25 m, 0.22 mm, He carrier gas) at 70eV. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AC 200 spectrometer operating at 200 MHz. ^{13}C NMR spectra were recorded on the same spectrometer. For simplification, the proton signals of the PhSe groups are not indicated.

Ethyl 2-cyclohexyl-2-oxoacetate 1h. A solution of diethyl oxalate (4.38 g, 30 mmol) in dry ether (30 ml) and dry THF (30 ml) was cooled to -80°C and the Grignard reagent (36 mmol) was added dropwise. The reaction was warmed up to -60°C after stirring (1 h), treated with 2N HCl (50 ml) and extracted with ether (3 x 50 ml). The organic layer was washed with brine (50 ml), dried ($MgSO_4$) and evaporated to give an oil which was distilled under reduced pressure giving **1h**. Yield : 3.97 g (72 %). bp 148°C/20 mmHg. ^{1}H NMR, δ : 4.24 (q, J=7.1 Hz, 2H), 2.97 (m, 1H), 1.84-1.25 (m, 13H). ^{13}C NMR, δ : 197.1, 161.7, 61.7, 45.9, 27.2, 25.5, 25.0, 13.7. Anal. Calc. for $C_{10}H_{16}O_3$: C, 65.20 ; H, 8.75. Found : C, 65.45 ; H, 8.52. GCMS m/z 184 (M^+, 1), 111 (27), 83 (100), 67 (6), 55 (55), 41 (21), 29 (13).

β-Phenylselanyl α-oxoesters 2. (General procedure).

A solution of the α-oxoester **1** (9 mmol) in CH_2Cl_2 (5 ml) was added dropwise to N-phenylselanyl morpholine (2.42 g, 10 mmol) in the same solvent (100 ml). The mixture was stirred for 12 h. at room temperature and then for one hour after addition of a 1N HCl solution (50 ml). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 ml) and the organic fractions were dried and concentrated. The β-phenylselanyl α-oxoesters **2** were purified by chromatography on silica gel (elution with a mixture of light petroleum/CH_2Cl_2 : 70/30).

Ethyl 2-oxo-3-phenylselanylbutanoate 2a. (69 % yield). ^{1}H NMR, δ : 4.49 (q, J=6.9 Hz, 1H), 4.33 (m, 2H), 1.39 (d, J=6.9 Hz, 3H), 1.36 (t, J=7.1 Hz, 3H). ^{13}C NMR, δ : 185.4, 162.8, 62.4, 40.5, 14.1, 13.9. Anal. Calc. for $C_{12}H_{14}O_3Se$: C, 50.53 ; H, 4.95. Found : C, 50.62 ; H, 4.67.

Ethyl 2-oxo-3-phenylselanylpentanoate 2b. (73 % yield). ^{1}H NMR, δ : 4.33 (m, 2H), 4.26 (t, J=7.3 Hz, 1H), 1.66 (m, 2H), 1.36 (t, J=7.1 Hz, 3H), 1.02 (t, J=7.3 Hz, 3H). ^{13}C NMR, δ : 184.5, 162.2, 62.4, 48.7, 21.2, 13.9, 12.2. Anal. Calc. for $C_{13}H_{16}O_3Se$: C, 52.18 ; H, 5.39. Found : C, 52.05 ; H, 5.24.

Ethyl 2-oxo-3-phenylselanylhexanoate 2c. (75 % yield). ^{1}H NMR, δ : 4.33 (m, 3H), 1.61 (m, 4H), 1.36 (t, J=7.1 Hz, 3H), 0.89 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 184.5, 162.2, 62.4, 46.6, 29.7, 20.7, 13.6. Anal. Calc. for $C_{14}H_{18}O_3Se$: C, 53.68 ; H, 5.79. Found : C, 53.61 ; H, 5.62.

Ethyl 2-oxo-3-phenylselanyloctanoate 2d. (76 % yield). ^{1}H NMR, δ : 4.34 (m, 3H), 1.62 (m, 4H), 1.36 (t, J=7.2 Hz, 3H), 1.35-1.24 (m, 4H), 0.85 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 184.5, 162.1, 62.3, 46.9, 31.3, 27.7, 27.1, 22.3, 13.9, 13.8. Anal. Calc. for $C_{16}H_{22}O_3Se$: C, 56.30 ; H, 6.50. Found : C, 56.38 ; H, 6.53.

Ethyl 2-oxo-4-phenyl-3-phenylselanylbutanoate 2e. (80 % yield). ^{1}H NMR, δ : 7.40-7.18 (m, 5H), 4.69 (t, J=8.0 Hz, 1H), 4.33 (m, 2H), 3.16 (dd, J=14.0 Hz, J=8.0 Hz, 1H), 2.99 (dd, J=14.0 Hz, J=8.0 Hz, 1H), 1.36 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 184.1, 161.8, 138.3, 129.2, 128.5, 126.7, 62.6, 47.4, 34.4, 13.9. Anal. Calc. for $C_{18}H_{18}O_3Se$: C, 59.84 ; H, 5.02. Found : C, 60.02 ; H, 4.80.

Ethyl 4-methyl-2-oxo-3-phenylselanylpentanoate 2f. (80 % yield). ^{1}H NMR, δ : 4.32 (m, 2H), 4.10 (d, J=10.0 Hz, 1H), 1.95 (m, 1H), 1.35 (t, J=7.0 Hz, 3H), 1.25 (d, J=6.6 Hz, 3H), 0.97 (d, J=6.6 Hz, 3H). ^{13}C NMR, δ : 183.2, 162.1, 62.4, 56.3, 26.3, 21.3, 20.5, 13.9. Anal. Calc. for $C_{14}H_{18}O_3Se$: C, 53.68 ; H, 5.79. Found : C, 53.75 ; H, 5.85.

Ethyl 3-methyl-2-oxo-3-phenylselanylbutanoate 2g. (58 % yield). ^{1}H NMR, δ : 4.36 (q, J=7.2 Hz, 2H), 1.59 (s, 6H), 1.39 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 189.2, 163.3, 61.9, 51.5, 24.3, 14.0. Anal. Calc. for $C_{13}H_{16}O_3Se$: C, 52.18 ; H, 5.39. Found : C, 52.12 ; H, 5.54.

Ethyl 2-oxo-2-(1-phenylselanylcyclohexyl)acetate 2h. The general procedure has given a modest yield (41 %) of **2h**. It was improved (72 %) by the following method. A 1M solution of LiHMDS in hexane (5 ml, 5 mmol) was added dropwise at - 78°C to a solution of the α-oxoester **1h** in dry THF (30 ml). The mixture was stirred for one hour at - 78°C, and a solution of PhSeBr (1.18 g, 5 mmol) in dry THF was added dropwise. The mixture was warmed up slowly to 0°C over 2 h. and then treated with a saturated solution of $NaHCO_3$. The organic layer was separated, dried and evaporated. The residue was purified by chromatography on silica gel (light petroleum/CH_2Cl_2 : 70/30) to afford **2h**, as a yellow oil. ^{1}H NMR, δ : 4.36 (q, J=7.2 Hz, 2H), 2.20-1.42 (m, 10H), 1.40 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 188.1, 163.4, 61.7, 58.7, 32.5, 25.4, 23.9, 14.0. Anal. Calc. for $C_{16}H_{20}O_3Se$: C, 56.63 ; H, 5.90. Found : C, 56.38 ; H, 6.04.

β,β-Bis(phenylselanyl) α-oxoesters 3

The general procedure was used with the following modifications : the reaction was carried out with 2 equivalents of N-phenylselanyl morpholine and the mixture was stirred for 2 days. The β,β-bis(phenylselanyl) α-oxoesters **3** was obtained after flash chromatography on silica gel (light petroleum/CH_2Cl_2 : 70/30).

Ethyl 2-oxo-3,3-bis(phenylselanyl)butanoate 3a. (50 % yield). ^{1}H NMR, δ : 4.45 (q, J=7.2 Hz, 2H), 1.45 (t, J=7.2 Hz, 3H), 1.42 (s, 3H). ^{13}C NMR, δ : 186.6, 162.9, 62.6, 50.4, 24.0, 14.0. Anal. Calc. for $C_{18}H_{18}O_3Se_2$: C,49.11 ; H, 4.12. Found : C, 49.50 ; H, 4.37.

Ethyl 2-oxo-3,3-bis(phenylselanyl)pentanoate 3b. (43 % yield). ^{1}H NMR, δ : 4.40 (q, J=7.0 Hz, 2H), 1.74 (q, J=7.0 Hz, 2H), 1.41 (t, J=7.0 Hz, 3H), 1.00 (t, J=7.0 Hz, 3H). ^{13}C NMR, δ : 185.1, 162.6, 62.5, 51.8, 27.2, 14.0, 10.9. Anal. Calc. for $C_{19}H_{20}O_3Se_2$: C, 50.23 ; H, 4.43. Found : C, 49.98 ; H, 4.65.

Ethyl 2-oxo-3,3-bis(phenylselanyl)hexanoate 3c. (39 % yield). ^{1}H NMR, δ : 4.41 (q, J=7.0 Hz, 2H), 1.63 (t, J=7.0 Hz, 2H), 1.48-1.40 (m, 5H), 0.88 (t, J=7.0 Hz, 2H). ^{13}C NMR, δ : 185.0, 162.5, 62.4, 50.1, 34.5, 22.1, 14.0, 13.6. Anal. Calc. for $C_{20}H_{22}O_3Se_2$: C, 51.29 ; H, 4.73. Found : C, 51.36 ; H, 4.84.

Ethyl 2-cyclohexyl-2-hydroxyacetate 4. n-BuLi in hexane (2.5 M, 4.2 ml, 10.5 mmol) was added slowly, under argon, to a solution of diisopropylamine (1.11 g, 11 mmol) in THF (20 ml) at 0°C. After stirring for 0.5 h. the temperature was lowered to -78°C and the α-oxoester (10 mmol) in THF (10 ml) was added dropwise. The mixture was then stirred for 2 h. at this temperature and treated with water (30 ml) and hexane (30 ml). After separation and concentration, the crude product was purified by silica gel chromatography (light petroleum/CH_2Cl_2 : 70/30). ^{1}H NMR, δ : 4.21 (q, J=7.1 Hz, 2H), 3.95 (brs, 1H), 2.69 (brs,1H), 1.80-1.17 (m, 14H). ^{13}C NMR, δ : 174.6, 74.8, 61.1, 47.8, 28.9, 26.3, 26.0, 25.8, 14.0. Anal. Calc. for $C_{10}H_{18}O$: C, 64.49 ; H, 9.74. Found : C, 64.68 ; H, 10.01. GCMS m/z 186 (M^+, 1), 113 (30), 95 (100), 83 (9), 76 (44), 55 (35), 41 (27), 29 (24).

β-Unsaturated α-oxoesters 5. (General procedures).

Method A : A solution of β-phenylselanyl α-oxoester **2** (1 mmol) and pyridine(0.16 g, 2 mmol) in dichloromethane (15 ml) was stirred at room temperature. H_2O_2 (35 % aqueous solution, 0.675 ml) was added dropwise and the mixture stirred for one hour. The mixture was treated with a 1N HCl solution (20 ml) and with water (20 ml). After separation and extraction of the aqueous layer with dichloromethane, the organic fractions were dried and concentrated. The oily residue was purified by silica gel chromatography (elution light petroleum/CH_2Cl_2 : 80/20).

Method B : To a solution of β-phenylselanyl α-oxoester **2** (2 mmol) and sodium hydrogenocarbonate (0.167 g, 2 mmol) in ethanol (30 ml) sodium periodate (1.71 g, 8 mmol) dissolved in water (10 ml) was slowly added at 0°C. The mixture was stirred for 2 h. at room temperature,filtered and extracted with dichloromethane (3 x 20 ml). The organic fractions were dried and concentrated. The unsaturated ester **5** was obtained by silica gel chromatography. Light petroleum eliminates diphenyldiselenide and the product was obtained from a mixture light petroleum/CH_2Cl_2 : 80/20.

Ethyl 2-oxopent-3-enoate 5b.[9b] (87 % yield). ^{1}H NMR, δ : 7.08 (dq, J=15.8 Hz, J=7.0 Hz, 1H), 6.54 (dq, J=15.8 Hz, J=1.6 Hz, 1H), 4.24 (q, J=7.2 Hz, 2H), 1.90 (dd, J=7.0 Hz, J=1.6 Hz, 3H), 1.27 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 183.8, 162.8 , 150.1, 126.7, 62.1, 18.8, 13.8.

Ethyl 2-oxohex-3-enoate 5c.[12] (93 % yield). ^{1}H NMR, δ : 7.16 (dt, J=15.9 Hz, J=6.3 Hz, 1H), 6.57 (dt, J=15.9 Hz, J=1.6 Hz, 1H), 4.28 (q, J=7.2 Hz, 2H), 2.28 (m, 2H), 1.32 (t, J=7.2 Hz, 3H), 1.06 (t, J=7.4 Hz, 3H). ^{13}C NMR, δ : 183.8, 164.0, 156.0, 124.1, 62.1, 26.0, 13.8, 11.6.

Ethyl 2-oxooct-3-enoate 5d.[9b] (90 % yield). ^{1}H NMR, δ : 7.16 (dt, J=15.8 Hz, J=6.4 Hz, 1H), 6.50 (dt, J=15.8 Hz, J=1.5 Hz, 1H), 4.21 (q, J=7.2 Hz, 2H), 2.19 (m, 2H), 1.37-1.17 (m, 7H), 0.77 (t, J=7.0 Hz, 3H). ^{13}C NMR, δ : 183.3, 161.5, 154.9, 124.9, 62.0, 29.6, 22.1, 13.8, 13.5.

Ethyl 2-oxo-4-phenylbut-3-enoate 5e.[9b] (92 % yield). ^{1}H NMR, δ : 7.84 (d, J=16.2 Hz, 1H), 7.63-7.38 (m, 5H), 6.50 (d, J=16.2 Hz, 1H), 4.37 (q, J=7.2 Hz, 2H), 1.39 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 182.6, 162.0, 148.0, 133.8, 131.4, 128.9, 120.4, 62.2, 13.9.

Ethyl 4-methyl-2-oxopent-3-enoate 5f. (85 % yield). ^{1}H NMR, δ : 6.70 (m, 1H), 4.23 (q, J=7.2 Hz, 2H), 2.17 (s, 3H), 1.95 (s, 3H), 1.29 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 182.1, 164.5, 129.2, 119.0, 62.0, 28.3, 21.6, 13.9. Anal. Calc. for $C_8H_{12}O_3$: C, 61.52 ; H, 7.74. Found : C, 61.43 ; H, 7.66.

Ethyl 3-methyl-2-oxobut-3-enoate 5g.[13] (92 % yield). ^{1}H NMR, δ : 6.12 (m, 1H), 6.03 (m, 1H), 4.23 (q, J=7.0 Hz, 2H), 1.87 (m, 3H), 1.31 (t, J=7.0 Hz, 3H). ^{13}C NMR, δ : 188.7, 164.0, 140.4, 132.3, 61.9, 15.8, 13.9.

Ethyl 2-cyclohex-1-enyl-2-oxoacetate 5h. (82 % yield). ^{1}H NMR, δ : 6.92 (m, 1H), 4.29 (q, J=7.2 Hz, 2H), 2.29-2.20 (m, 4H), 1.68-1.58 (m, 4H), 1.33 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 188.2, 164.7, 149.2, 135.8, 61.6, 26.4, 21.8, 13.8. Anal. Calc. for $C_{10}H_{14}O_3$: C, 65.91 ; H, 7.74. Found : C, 65.68 ; H, 7.89.

Diethyl (1-phenylselanyl)alkylbutenedioates 6. (General procedure).

A solution of n-BuLi in hexane (2.5 M, 1.2 ml, 3 mmol) was added slowly, under argon, to triethyl phosphonoacetate (0.74 g, 3.3 mmol) in anhydrous THF (30 ml) at 0°C. After stirring for 0.5 h. at room temperature, the β-phenylselanyl α-oxoester **2** (3 mmol) in THF (5 ml) was added dropwise. The mixture was stirred for 2 h., quenched with a saturated aqueous NH_4Cl solution and extracted with diethylether. The organic extracts were dried over magnesium sulfate and concentrated under vacuum. The residue was purified by silica gel chromatography **6** (light petroleum/CH_2Cl_2 : 60/40). The E configuration was assigned to the sole isomer formed by NOESY experiments.

Diethyl (1-phenylselanyl)ethylbutenedioate 6a. (61 % yield). ^{1}H NMR, δ : 5.43 (s, 1H), 4.28 (q, J=7.2 Hz, 2H), 4.12 (q, J=7.2 Hz, 2H), 4.01 (q, J=7.0 Hz, 1H), 1.52 (d, J=7.1 Hz, 3H), 1.32 (t, J=7.2 Hz, 3H), 1.23 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 167.7, 164.8, 149.3, 119.5, 61.4, 60.7, 39.0, 19.5, 14.0, 13.9. Anal. Calc. for $C_{16}H_{20}O_4Se$: C, 54.09 ; H, 5.67. Found : C, 54.39 ; H, 5.89.

Diethyl (1-phenylselanyl)propylbutenedioate 6b. (72 % yield). ^{1}H NMR, δ : 5.32 (s, 1H), 4.27 (q, J=7.2 Hz, 2H), 4.10 (q, J=7.1 Hz, 2H), 3.68 (t, J=7.1 Hz, 1H),1.72 (m, 1H), 1.31 (t, J=7.2 Hz, 3H), 1.21 (t, J=7.2 Hz, 3H), 1.03 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 167.2, 164.8, 148.2, 120.1, 61.4, 60.6, 47.7, 26.0, 14.0, 13.9, 12.7. Anal. Calc. for $C_{17}H_{22}O_4Se$: C, 55.29 , H, 6.00. Found : C, 55.01 ; H, 6.16. GCMS m/z 370 (M^+, 18), 324 (22), 213 (45), 185 (15), 167 -31), 139 (100), 111 (40), 83 (17), 67 (27), 29 (60).

Diethyl (1-phenylselanyl)butylbutenedioate 6c. (77 % yield). ^{1}H NMR, δ : 5.32 (s, 1H), 4.28 (q, J=7.2 Hz, 2H), 4.10 (q, J=7.2 Hz, 2H), 3.78 (t, J=7.0 Hz, 1H), 1.69 (m, 2H), 1.51 (m, 2H), 1.31 (t, J=7.2 Hz, 3H), 1.21 (t, J=7.2 Hz, 3H), 0.88 (t, J=7.2 Hz,3H). ^{13}C NMR, δ : 167.1, 164.7, 148.3, 120.0, 61.3, 60.6, 45.6, 34.7, 21.1, 14.0, 13.9. Anal. Calc. for $C_{18}H_{24}O_4Se$: C, 56.40 ; H, 6.31. Found : C, 56.28 ; H, 6.41.

Diethyl (1-phenylselanyl)hexylbutenedioate 6d. (78 % yield). ^{1}H NMR, δ : 5.30 (s, 1H), 4.27 (q, J=7.2 Hz, 2H), 4.10 (q, J=7.1 Hz, 2H), 3.76 (t, J=7.1 Hz, 1H), 1.68 (m, 2H), 1.49 (m, 2H), 1.33-1.17 (m, 10H), 0.83 (t, J=7.0 Hz, 3H). ^{13}C NMR, δ : 167.0, 164.7, 148.3, 119.9, 61.3, 60.5, 45.5, 32.6, 27.6, 22.3, 14.0, 13.9, 13.9. Anal. Calc. for $C_{20}H_{28}O_4Se$: C, 58.39 ; H, 6.86. Found : C, 58.45 ; H, 7.05.

Diethyl (2-phenyl-1-phenylselanyl)ethylbutenedioate 6e. (70 % yield). ^{1}H NMR, δ : 7.26-7.17 (m, 5H), 5.40 (s, 1H), 4.31 (q, J=7.1 Hz, 2H), 4.11 (q, J=7.1 Hz, 2H), 4.07 (t, J=8.0 Hz, 1H), 3.20 (dd, J=14.0 Hz, J=8.0 Hz, 1H), 3.01 (dd, J=14.0 Hz, J=8.0 Hz, 1H), 1.34 (t, J=7.1 Hz, 3H), 1.22 (t, J=7.1 Hz, 3H). ^{13}C NMR, δ : 167.0, 164.6, 147.4, 138.2, 129.0, 128.4, 126.7, 121.0, 61.5, 60.7, 47.1, 39.1, 14.0, 13.9. Anal. Calc. for $C_{22}H_{24}O_4Se$: C, 61.25 ; H, 5.56. Found : C, 61.49 ; H, 5.38.

Diethyl (2-methyl-1-phenylselanyl)propylbutenedioate 6f. (80 % yield). ^{1}H NMR, δ : 5.41 (s, 1H), 4.27 (q, J=7.0 Hz, 2H), 4.08 (q, J=7.2 Hz, 2H), 3.50 (d, J=9.1 Hz, 1H), 2.01 (m, 2H), 1.29 (t, J=7.2 Hz, 3H), 1.20 (t, J=7.0 Hz, 3H), 1.14 (d, J=6.5 Hz, 3H). ^{13}C NMR, δ : 167.1, 164.7, 147.8, 121.1, 61.3, 60.5, 56.4, 30.8, 21.7, 21.5, 14.0, 13.9. Anal. Calc. for $C_{18}H_{24}O_4Se$: C, 56.40 ; H, 6.31. Found : C, 56.48 ; H, 6.33.

Diethyl (1-methyl-1-phenylselanyl)ethylbutenedioate 6g. (69 % yield). ^{1}H NMR, δ : 5.17 (s, 1H), 4.34 (q, J=7.2 Hz, 2H), 4.10 (q, J=7.1 Hz, 2H), 1.54 (s, 6H), 1.35 (t, J=7.1 Hz, 3H), 1.21 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 167.2, 164.6, 154.4, 117.1, 61.3, 60.5, 45.0, 28.1, 14.1, 14.0. Anal. Calc. for $C_{17}H_{22}O_4Se$: C, 55.29 ; H, 6.00. Found : C, 55.48 ; H, 6.11.

Diethyl (1-phenylselanyl)cyclohexylbutenedioate 6h. (71 % yield). ^{1}H NMR, δ : 4.86 (s, 1H), 4.33 (q, J=7.3 Hz, 2H), 4.07 (q, J=7.0 Hz, 2H), 1.80-1.37 (m, 10H), 1.34 (t, J=7.3 Hz, 3H), 1.18 (t, J=7.0 Hz, 3H). ^{13}C NMR, δ : 167.1, 164.6, 152.0, 117.1, 61.1, 60.2, 52.1, 35.2, 25.5, 23.1, 14.1, 13.9. Anal. Calc. for $C_{20}H_{26}O_4Se$: C, 58.68 ; H, 6.40. Found : C, 58.61 ; H, 6.29.

Diethyl 3-alkylidene-2-hydroxysuccinates 7. (General procedure).

A solution of β-phenylselanyl diester **6** (1 mmol) and pyridine (0.16 g, 2 mmol) in dichloromethane (15ml) was stirred at room temperature. H_2O_2 (35% aqueous solution, 0.675 ml) was added dropwise and the mixture stirred for 1.5 h. The mixture was treated with a 1N HCl solution (20 ml) and then with water (20 ml). After the usual workup, the crude product was purified by silica gel chromatography (light petroleum/CH_2Cl_2 : 80/20).

Diethyl 3-ethylidene-2-hydroxybutanedioate 7a. (83 % yield). E isomer, ^{1}H NMR, δ : 7.03 (q, J=7.3 Hz, 1H), 4.96 (s, 1H), 4.14 (m, 4H), 3.56 (brs, 1H), 1.89 (d, J=7.3 Hz, 3H), 1.20 (m, 6H). ^{13}C NMR, δ : 172.7, 165.5, 142.3, 130.8, 66.0, 61.6, 60.6, 14.0, 13.9 . Z isomer, ^{1}H NMR, δ : 6.35 (q, J=7.3 Hz, 1H), 4.59 (s, 1H), 4.15 (m, 4H), 3.56 (brs, 1H), 2.02 (d, J=7.3 Hz, 3H), 1.20 (m, 6H). ^{13}C NMR, δ : 172.7, 165.5, 142.6, 130.8, 73.3, 61.7, 60.3, 15.5, 13.9. Anal. Calc. for $C_{10}H_{16}O_5$: C, 55.55 ; H, 7.46. Found : C, 55.89 ; H, 7.59.

Diethyl 3-propylidene-2-hydroxybutanedioate 7b. (88 % yield). E isomer, ^{1}H NMR, δ : 6.94 (q, J=7.2 Hz, 1H), 4.95 (d, J=7.3 Hz, 1H), 4.17 (m, 4H), 3.57 (brd, J=7.3 Hz, 1H), 2.31 (m, 2H), 1.21 (m, 6H), 1.07 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 172.8, 166.0, 148.6, 129.5, 66.3, 61.6, 60.5, 21.7, 13.9, 13.4. Z isomer, ^{1}H NMR, δ : 6.21 (t, J=7.2 Hz, 1H), 4.58 (d, J=5.9 Hz, 1H), 4.17 (m, 4H), 3.50 (brd, J=5.9 Hz, 1H), 2.43 (m, 2H), 1.21 (m, 6H), 0.94 (t, J=7.5 Hz, 3H). ^{13}C NMR, δ : 172.8, 166.0, 149.2, 129.3, 73.4, 61.7, 60.5, 22.7, 13.9, 13.4. Anal. Calc. for $C_{11}H_{18}O_5$: C, 57.40 ; H, 7.88. Found : C, 57.31 ; H, 8.02. GCMS m/z 212 (1), 157 (47), 111 (100), 83 (25), 55 (25), 39 (8), 29 (25).

Diethyl 3-butylidene-2-hydroxybutanedioate 7c. (90 % yield). E isomer, ^{1}H NMR, δ : 6.95 (q, J=7.2 Hz, 1H), 4.96 (s, 1H), 4.17 (m, 4H), 3.31 (brs, 1H), 2.27 (q, J=7.2 Hz, 2H), 1.45 (m, 2H), 1.22 (m, 6H), 0.92 (t, J=6.8 Hz, 3H). ^{13}C NMR, δ : 172.8, 165.5, 147.2, 129.9, 66.3, 61.7, 60.6, 30.2, 21.7, 13.8, 13.5. Z isomer, ^{1}H NMR, δ : 6.24 (t, J=7.4 Hz, 1H), 4.61 (s, 1H), 4.17 (m, 4H), 3.31 (brs, 1H), 2.48 (q, J=7.4 Hz, 2H), 1.45 (m, 2H), 0.89 (t, J=6.8 Hz, 3H). ^{13}C NMR, δ : 172.8, 165.5, 147.6, 129.9, 73.4, 61.7, 60.3, 31.1, 22.0, 13.8, 13.5. Anal. Calc. for $C_{12}H_{20}O_5$: C, 59.00 ; H, 8.25. Found : C, 59.34 ; H, 8.38.

Diethyl 3-hexylidene-2-hydroxybutanedioate 7d. (91 % yield). E isomer, ^{1}H NMR, δ : 6.96 (q, J=7.2 Hz, 1H), 4.97 (s, 1H), 4.16 (m, 4H), 3.51 (brs, 1H), 2.27 (q, J=7.2 Hz, 2H), 1.48-1.19 (m, 12H), 0.87 (t, J=6.6 Hz, 3H). ^{13}C NMR, δ :172.8, 165.4, 147.4, 129.7, 66.20, 61.6, 60.6, 31.1, 29.0, 28.0, 22.2, 13.8. Z isomer, ^{1}H NMR, δ : 6.25 (t, J=7.2 Hz, 1H), 4.61 (s, 1H), 4.17 (m, 4H), 3.51 (brs, 1H), 2.52 (q, J=7.2, 2H), 1.48-1.19 (m, 12H), 0.84 (t, J=6.6 Hz, 3H). ^{13}C NMR, δ :172.8,165.4, 147.7, 129.7, 73.3, 61.6, 60.3, 31.2, 29.1, 28.4, 22.2, 13.8. Anal. Calc. for $C_{14}H_{24}O_5$: C, 61.74 ; H, 8.88. Found : C, 61.99 ; H, 8.92.

Diethyl 3-(2-phenylethylidene)-2-hydroxybutanedioate 7e. (82 % yield). E isomer, ^{1}H NMR, δ : 7.06 (q, J=7.2 Hz, 1H), 5.12 (d, J=6.8 Hz, 1H), 4.18 (m, 4H), 3.82 (d, J=7.2 Hz, 2H), 3.62 (brd, J=6.8 Hz, 1H), 1.24 (t, J=7.0 Hz, 3H), 1.21 (t, J=7.0 Hz, 3H). ^{13}C NMR, δ :172.7, 165.5, 145.2, 138.9, 130.2, 128.5, 126.3, 66.5, 62.0, 60.8, 34.9, 14.0. Z isomer, ^{1}H NMR, δ : 6.38 (t, J=7.2 Hz, 1H), 4.67 (d, J=6.6 Hz, 1H), 4.18 (m, 4H), 3.86 (d, J=7.2 Hz, 2H), 3.67 (brd, J=6.6 Hz, 1H), 1.24 (t, J=7.0 Hz, 3H), 1.20 (t, J=7.0 Hz, 3H). ^{13}C NMR, δ : 172.7, 165.5, 145.3, 139.0, 130.2, 128.5, 126.4, 73.4, 62.0, 60.7, 35.5, 14.0. Anal. Calc. for $C_{16}H_{20}O_5$: C, 65.74 ; H, 6.90. Found : C, 65.38 ; H, 6.69. GCMS m/z 274 (30), 219 (24), 200 (55), 173 (54), 155 (50), 145 (73), 115 (100), 105 (17), 91 (61), 65 (21), 39 (11), 29 (66).

Diethyl 3-(2-methylpropylidene)-2-hydroxybutanedioate 7f. (79 % yield). E isomer, ^{1}H NMR, δ : 6.70 (d, J=9.9 Hz, 1H), 4.91 (d, J=5.9 Hz, 1H), 4.15 (m, 4H), 3.88 (brd, J=5.9 Hz, 1H), 3.08 (m, 1H), 1.17 (m, 6H), 1.00 (d, J=7.1 Hz, 3H), 0.97 (d, J=7.1 Hz). ^{13}C NMR, δ : 172.8, 165.8, 153.8, 127.7, 66.8, 61.7, 60.5, 28.1, 22.2, 22.0, 13.8. Z isomer, ^{1}H NMR, δ : 5.97 (d, J=9.9 Hz, 1H), 4.56 (d, J=5.9 Hz, 1H), 4.15 (m, 4H), 3.46

(brd, J=5.9 Hz, 1H), 3.19 (m, 1H), 1.17 (m, 6H), 1.00 (d, J=7.1 Hz, 3H), 0.97 (d, J=7.1 Hz). ^{13}C NMR, δ : 172.8, 165.8, 153.7, 127.7, 73.4, 61.7, 60.4, 28.2, 22.2, 22.0, 13.8. Anal. Calc. for $C_{12}H_{20}O_5$: C, 59.00 ; H, 8.25. Found : C, 58.85 ; H, 8.14.

Diethyl 3-(1-methylethylidene)-2-hydroxybutanedioate 7g. (80 % yield). ^{1}H NMR, δ : 4.93 (d, J=5.5 Hz, 1H), 4.09 (m, 4H), 3.41 (brd, J=5.5 Hz, 1H), 2.01 (s, 3H), 1.89 (s, 3H), 1.16 (m, 6H). ^{13}C NMR, δ : 173.3, 166.6, 149.6, 126.4, 68.5, 61.7, 60.3, 23.2, 22.4, 13.9. Anal. Calc. for $C_{11}H_{18}O_5$: C, 57.40 ; H, 7.88. Found : C, 57.52 ; H, 7.71. GCMS m/z 212 (1), 157 (28), 111 (100), 83 (8), 67 (3), 55 (16), 39 (6), 29 (14).

Diethyl 3-(cyclohexylidene)-2-hydroxybutanedioate 7h. (80 % yield). ^{1}H NMR, δ : 5.05 (s, 1H), 4.18 (m, 4H), 3.41 (brs, 1H), 2.51-2.29 (m, 4H), 1.75-1.50 (m, 6H), 1.28 (m, 6H). ^{13}C NMR, δ : 173.4, 167.2, 154.1, 123.6, 67.9, 61.8, 60.3, 32.8, 31.9, 26.2, 13.9. Anal. Calc. for $C_{14}H_{22}O_5$: C, 62.20 ; H, 8.20. Found : C, 62.48 ; H, 8.01.

Alkylidene aminosuccinates 8. (General procedure).

Ethyl orthoformate (1.75 g, 11.8 mmol) and p-toluenesulfonic acid (6 mg) were added successively to a solution of phenylselanyl diester **6** (2 mmol) and t-butyl carbamate (0.70 g, 6 mmol) in ethanol (6 ml) at room temperature. The mixture was stirred for 0.5 h. at the same temperature and N,N-diisopropylethylamine (1.54 g, 12 mmol) was then introduced. The reaction was cooled at 0°C and treated with N-chlorosuccinimide (0.79 g, 6 mmol). The mixture was stirred for one hour and treated with 1N HCl (10 ml). After extraction and concentration, the oily residue was chromatographied on silica gel (light petroleum/ CH_2Cl_2 : 85/15).

Diethyl 2-(t-butoxycarbonylamino)-3-ethylidenebutanedioate 8a. (69 % yield). E isomer, ^{1}H NMR, δ : 7.03 (q, J=7.2 Hz, 1H), 5.60 (brd, J=9.3 Hz, 1H), 5.33 (d, J=9.3 Hz, 1H), 4.13 (m, 4H), 1.99 (d, J=7.2 Hz, 3H), 1.40 (s, 9H), 1.21 (m, 6H). ^{13}C NMR, δ : 170.1, 165.5, 155.0, 141.3, 130.1, 79.7, 61.5, 60.7, 50.0, 28.2, 14.0. Z isomer, ^{1}H NMR, δ : 6.47 (q, J=7.2 Hz, 1H), 5.55 (brd, J=8.6 Hz, 1H), 4.85 (d, J=8.6 Hz, 1H), 4.13 (m, 4H), 2.07 (d, J=7.2 Hz, 3H), 1.40 (s, 9H), 1.21 (m, 6H). ^{13}C NMR, δ : 170.1, 165.4, 154.7, 143.8, 129.2, 79.7, 61.5, 60.2, 57.7, 28.2, 14.3. Anal. Calc. for $C_{15}H_{25}O_6N$: C, 57.13 ; H, 7.99 ; N, 4.44. Found : C, 57.38 ; H, 7.81 ; N, 4.62.

Diethyl 2-(t-butoxycarbonylamino)-3-propylidenebutanedioate 8b. (72 % yield). E isomer, ^{1}H NMR, δ : 6.91 (t, J=7.6 Hz, 1H), 5.59 (brd, J=9.3 Hz, 1H), 5.30 (d, J=9.3 Hz, 1H), 4.13 (m, 4H), 2.41 (m, 2H), 1.40 (s, 9H), 1.22 (m, 6H), 1.07 (t, J=7.2 Hz). ^{13}C NMR, δ :170.2, 165.9, 155.0, 147.9, 128.5, 79.5, 61.3, 60.6, 50.0, 28.0, 21.8, 13.8, 12.8. Z isomer, ^{1}H NMR, δ : 6.31 (t, J=7.6 Hz, 1H), 5.54 (brd, J=9.0 Hz, 1H), 4.88 (d, J=9.0 Hz, 1H), 4.13 (m, 4H), 2.53 (m, 2H), 1.40 (s, 9H), 1.22 (m, 6H), 1.09 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 170.2, 165.6, 155.0, 150.7, 127.8, 79.5, 61.3, 60.3, 57.8, 28.0, 22.7, 13.8, 13.1. Anal. Calc. for $C_{15}H_{25}O_6N$: C, 57.13 ; H, 7.99 ; N, 4.44. Found : C, 57.38 ; H, 7.81 ; N, 4.62.

Diethyl 2-(t-butoxycarbonylamino)-3-butylidenebutanedioate 8c. (79 % yield). E isomer, ^{1}H NMR, δ : 6.93 (t, J=7.6 Hz, 1H), 5.58 (brd, J=9.5 Hz, 1H), 5.33 (d, J=9.3 Hz, 1H), 4.14 (m, 4H), 2.34 (q, J=7.6 Hz, 2H), 1.48 (m, 2H), 1.41 (s, 9H), 1.22 (m, 6H), 0.93 (t, J=7.3 Hz, 3H). ^{13}C NMR, δ : 170.4, 165.5, 155.2, 146.7, 129.2, 79.6, 61.4, 60.7, 50.2, 30.5, 28.1, 21.7, 13.9, 13.5. Z isomer, ^{1}H NMR, δ : 6.32 (t, J=7.2 Hz, 1H), 5.53 (brd, J=9.5 Hz, 1H), 4.88 (d, J=9.5 Hz, 1H), 4.14 (m, 4H), 2.53 (q, J=7.2 Hz, 2H), 1.48 (m, 2H), 1.41 (s, 9H), 1.22 (m, 6H), 0.89 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 170.4, 165.5, 155.2, 149.5, 128.6, 79.6, 61.4, 60.4, 58.1, 31.2, 28.1, 22.0, 13.9, 13.6. Anal. Calc. for $C_{17}H_{29}O_6N$: C, 59.46 ; H, 8.51 ; N,4.08. Found : C, 59.31 ; H, 8.46 ; N, 4.19.

Diethyl 2-(t-butoxycarbonylamino)-3-hexylidenebutanedioate 8d. (71 % yield). E isomer, ^{1}H NMR, δ : 6.92 (t, J=7.6 Hz, 1H), 5.58 (brd, J=9.4 Hz, 1H), 5.31 (d, J=9.4 Hz, 1H), 4.13 (m, 4H), 2.38 (q, J=7.6 Hz, 2H),

1.49-1.35 (m, 11H), 1.28-1.14 (m, 10H), 0.84 (t, J=6.6 Hz, 3H). ^{13}C NMR, δ : 170.2, 165.7, 155.0, 146.7, 129.0, 79.3, 61.2, 60.5, 50.1, 31.2, 28.4, 28.0, 22.2, 13.8, 13.7. Z isomer, ^{1}H NMR, δ : 6.53 (t, J=7.6 Hz, 1H), 5.53 (brd, J=9.4 Hz, 1H), 4.86 (d, J=9.4 Hz, 1H), 4.14 (m, 4H), 2.54 (q, J=7.2 Hz, 2H), 1.49-1.35 (m, 11H), 1.28-1.14 (m, 10H), 0.84 (t, J=6.6 Hz, 3H). ^{13}C NMR, δ : 170.2, 165.7, 155.0, 149.5, 128.9, 79.3, 61.2, 60.2, 57.9, 31.4, 29.2, 28.0, 22.2, 13.8, 13.7. Anal. Calc. for $C_{19}H_{33}O_6N$: C, 61.43 ; H, 8.95 ; N, 3.77. Found C, 61.62 ; H, 9.07 ; N, 3.61.

Diethyl 2-(t-butoxycarbonylamino)-3-(2-phenylethylidene)butanedioate 8e. (69 % yield). E isomer, ^{1}H NMR, δ : 7.29-7.19 (m, 5H), 7.03 (t, J=7.8 Hz, 1H), 5.66 (brd, J=9.2 Hz, 1H), 5.50 (d, J=9.2 Hz, 1H), 4.16 (m, 4H), 3.77 (d, J=7.8 Hz, 2H), 1.44 (s, 9H), 1.24 (m, 6H). ^{13}C NMR, δ : 170.3, 165.9, 155.2, 144.5, 137.9, 129.2, 128.8, 128.5, 126.5, 79.8, 61.6, 61.0, 50.3, 34.9, 28.2, 14.0. Z isomer, ^{1}H NMR, δ : 7.28-7.15 (m, 5H), 6.49 (t, J=7.2 Hz, 1H), 5.55 (brd, J=9.2 Hz, 1H), 4.95 (d, J=9.2 Hz, 1H), 4.16 (m, 4H), 3.92 (m, 2H), 1.42 (s, 9H), 1.24 (m, 6H). ^{13}C NMR, δ : 170.3, 165.8, 155.2, 146.7, 138.9, 128.9, 128.5, 126.3, 79.8, 61.6, 60.7, 57.9, 35.4, 28.2, 14.1. Anal. Calc. for $C_{21}H_{29}O_6N$: C, 64.43 ; H, 7.47 ; N, 3.58. Found : C, 64.38 ; H, 7.52 ; N, 3.42.

Diethyl 2-(t-butoxycarbonylamino)-3-(2-methylpropylidene)butanedioate 8f. (63 % yield). E isomer, ^{1}H NMR, δ : 6.70 (d, J=10.2 Hz, 1H), 5.56 (brd, J=9.3 Hz, 1H), 5.32 (d, J=9.3 Hz, 1H), 4.15 (m, 4H), 2.93 (m, 1H), 1.41 (s, 9H), 1.22 (m, 6H), 1.06 (d, J=7.2 Hz, 3H), 1.04 (d, J=7.2 Hz, 3H). ^{13}C NMR, δ : 170.2, 165.8, 155.0, 148.9, 127.5, 79.6, 61.3, 60.6, 50.2, 28.1, 22.2, 22.0, 13.8. Z isomer, ^{1}H NMR, δ : 6.11 (d, J=10.5 Hz, 1H), 5.49 (brd, J=9.2 Hz, 1H), 4.86 (d, J=9.2 Hz, 1H), 4.15 (m, 4H), 3.30 (m, 1H), 1.41 (s, 9H), 1.22 (m, 6H), 0.99 (d, J=7.2 Hz, 3H), 0.97 (d, J=7.2 Hz, 3H). ^{13}C NMR, δ :170.2, 165.8, 155.0, 149.9, 126.8, 79.6, 61.4, 60.7 , 58.0, 28.1, 22.2, 22.0, 13.9. Anal. Calc. for $C_{17}H_{29}O_6N$: C, 59.46 ; H, 8.51 ; N, 4.08. Found : C, 59.10 ; H, 8.33 ; N, 4.31

Diethyl 2-(t-butoxycarbonylamino)-3-(1-methylethylidene)butanedioate 8g. (58 % yield). ^{1}H NMR, δ : 5.65 (brd, J=9.2 Hz, 1H), 5.50 (d, J=9.2 Hz, 1H), 4.15 (m, 4H), 2.00 (s, 3H), 1.92 (s, 3H), 1.41 (s, 9H), 1.22 (m, 6H). ^{13}C NMR, δ : 170.1, 165.5, 155.1, 147.2, 128.5, 79.5, 61.2, 60.3, 54.5, 28.0, 23.2, 22.4, 13.9. Anal. Calc. for $C_{16}H_{27}O_6N$: C, 58.34 ; H, 8.26 ; N, 4.25. Found : C, 58.12 ; H, 8.15 ; N, 4.29.

Diethyl 2-alkylidene-3-halosuccinates 9 (X = Cl) and 10 (X = Br). (General procedure).

A solution of bromine (1.6 ml, 1 mmol) or of sulfuryl chloride (1.35 ml, 1 mmol) in hexane was added dropwise to the diester **6** (1 mmol) dissolved in hexane (10 ml) at room temperature. The reaction was stirred for 2 h. and treated with water (10 ml). After separation, the aqueous layer was extracted with CH_2Cl_2 (3 x 20 ml) and the organic fractions were dried and concentrated. The crude product was purified by silica gel chromatography (light petroleum/CH_2Cl_2 : 70/30).

Diethyl 2-chloro-3-ethylidenebutanedioate 9a. (78 % yield). E isomer : ^{1}H NMR, δ : 6.60 (q, J=7.3 Hz, 1H), 5.11 (s, 1H), 4.19 (m, 4H), 2.12 (d, J=7.3 Hz, 3H), 1.28 (m, 6H). ^{13}C NMR, δ : 167.9, 164.5, 144.2, 128.5, 62.3, 60.8, 58.2, 15.8, 13.9. Z isomer : ^{1}H NMR, δ : 7.12 (q, J=7.3 Hz, 1H), 5.39 (s, 1H), 4.19 (m, 4H), 1.94 (d, J=7.3 Hz, 3H), 1.29 (m, 6H). ^{13}C NMR, δ : 167.9, 164.4, 142.9, 130.1, 62.3, 60.9, 52.0, 15.8, 13.9. Anal. Calc. for $C_{10}H_{15}O_4Cl$: C, 51.18 ; H, 6.44. Found : C, 51.36 ; H, 6.62.

Diethyl 2-chloro-3-propylidenebutanedioate 9b. (94 % yield). E isomer : ^{1}H NMR, δ : 6.45 (t, J=7.2 Hz, 1H), 5.11 (s, 1H), 4.20 (m, 4H), 2.59 (m, 2H), 1.24 (m, 6H), 1.05 (t, J=7.4 Hz, 3H). ^{13}C NMR, δ : 167.8, 164.5, 150.8, 127.8, 62.3, 60.8, 58.1, 23.0, 13.9, 13.1. Z isomer : ^{1}H NMR, δ : 6.99 (t, J=7.2 Hz, 1H), 5.37 (s, 1H), 4.19 (m, 4H), 2.30 (m, 2H), 1.25 (m, 6H), 1.10 (t, J=7.4 Hz, 3H). ^{13}C NMR, δ : 167.8, 164.5, 148.3, 129.1, 62.2, 61.1, 52.1, 22.2, 13.9, 12.3. Anal. Calc. for $C_{11}H_{17}O_4Cl$: C, 53.12 ; H, 6.89. Found : C, 53.19 ; H, 6.78.

Diethyl 2-chloro-3-butylidenebutanedioate 9c. (92 % yield). E isomer : ^{1}H NMR, δ : 6.46 (t, J=7.4 Hz, 1H), 5.11 (s, 1H), 4.19 (m, 4H), 2.55 (m, 2H), 1.47 (m, 2H), 1.24 (m, 6H), 0.91 (t, J=7.3 Hz, 3H). ^{13}C NMR, δ : 167.8, 164.5, 149.3, 127.8, 62.2, 60.7, 58.2, 31.3, 22.0, 13.9, 13.5. Z isomer : ^{1}H NMR, δ : 6.97 (t, J=7.4 Hz, 1H), 5.34 (s, 1H), 4.17 (m, 4H), 2.24 (q, J=7.4 Hz, 2H), 1.49 (m, 2H), 1.23 (m, 6H), 0.92 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 167.8, 164.5, 148.0, 129.2, 62.4, 61.1, 52.0, 30.9, 21.7, 13.9, 13.7. Anal. Calc. for $C_{12}H_{19}O_4Cl$: C, 54.86 ; H, 7.29. Found : C, 54.62 ; H, 7.52.

Diethyl 2-chloro-3-hexylidenebutanedioate 9d. (88 % yield). E isomer : ^{1}H NMR, δ : 6.47 (t, J=7.3 Hz, 1H), 5.11 (s, 1H), 4.19 (m, 4H), 2.58 (q, J=7.6 Hz, 2H), 1.50-1.21 (m, 12H), 0.86 (t, J=6.6 Hz, 3H). ^{13}C NMR, δ : 167.7, 164.4, 149.5, 127.8, 62.1, 60.7, 58.2, 31.3, 28.2, 22.2, 13.8. Z isomer : ^{1}H NMR, δ : 6.99 (t, J=7.6 Hz, 1H), 5.35 (s, 1H), 4.19 (m, 4H), 2.26 (q, J=7.6 Hz, 2H), 1.50-1.21 (m, 12H), 0.86 (t, J=6.6 Hz, 3H). ^{13}C NMR, δ : 167.7, 164.4, 148.2, 129.1, 61.7, 61.0, 51.9, 31.4, 29.5, 28.7, 22.2, 13.8. Anal. Calc. for $C_{14}H_{23}O_4Cl$: C, 57.83 ; H, 7.97. Found : C, 58.05 ; H, 7.69.

Diethyl 2-chloro-3-(2-phenylethylidene)butanedioate 9e. (85 % yield). E isomer : ^{1}H NMR, δ : 7.30-7.18 (m, 5H), 6.62 (t, J=7.2 Hz, 1H), 5.15 (s, 1H), 4.22 (m, 4H), 3.97 (d, J=7.2 Hz, 2H), 1.28 (m, 6H). ^{13}C NMR, δ : 167.7, 164.4, 146.9, 138.9, 128.6, 128.1, 126.5, 61.1, 58.2, 35.6, 14.0. Z isomer : ^{1}H NMR, δ : 7.30-7.18 (m, 6H), 5.54 (s, 1H), 4.22 (m, 4H), 3.92 (q, J=7.2 Hz, 2H), 1.28 (m, 6H). ^{13}C NMR, δ : 167.7, 164.4, 145.5, 139.8, 128.6, 128.1, 126.5, 62.5, 61.2, 49.0, 35.4, 14.0. Anal. Calc. for $C_{16}H_{19}O_4Cl$: C, 61.83 ; H, 6.16. Found : C, 61.99 ; H, 6.08.

Diethyl 2-chloro-3-(2-methylpropylidene)butanedioate 9f. (95 % yield). E isomer : ^{1}H NMR, δ : 6.22 (d, J=9.9 Hz, 1H), 5.09 (s, 1H), 4.23 (m, 4H), 3.35 (m, 1H), 1.25 (m, 6H), 1.06 (d, J=7.2 Hz, 3H), 1.04 (d, J=7.2 Hz, 3H). ^{13}C NMR, δ : 167.7,164.3, 155.6, 125.9, 62.2, 60.8, 58.1, 28.5, 21.9, 13.9. Z isomer : ^{1}H NMR, δ : 6.79 (d, J=10.6 Hz, 1H), 5.38 (s, 1H), 4.20 (m, 4H), 2.73 (m, 1H), 1.25 (m, 6H), 1.07 (d, J=7.2 Hz, 3H), 1.06 (d, J=7.2 Hz, 3H). ^{13}C NMR, δ : 167.7, 164.3, 153.4, 127.4, 62.7, 61.1, 52.0, 28.7, 21.6, 20.9, 13.9. Anal. Calc. for $C_{12}H_{19}O_4Cl$: C, 54.86 ; H, 7.29. Found : C, 54.98 ; H, 7.18.

Diethyl 2-chloro-3-(1-methylethylidene)butanedioate 9g.[18] (67 % yield). ^{1}H NMR, δ : 5.36 (s, 1H), 4.18 (m, 4H), 2.14 (s, 3H), 1.98 (s, 3H), 1.25 (m, 6H). ^{13}C NMR, δ : 167.8, 164.3, 152.0, 125.5, 62.4, 60.6, 55.4, 23.5, 22.9, 13.9.

Diethyl 2-chloro-3-cyclohexylidenebutanedioate 9h. (68 % yield). ^{1}H NMR, δ : 5.41 (s, 1H), 4.18 (m, 4H), 2.57-2.55 (m, 2H), 1.66-1.61 (m, 6H), 1.24 (m, 6H). ^{13}C NMR, δ : 173.3, 167.2, 156.8, 122.7, 62.5, 60.7, 55.0, 32.8, 32.5, 28.0, 27.7, 26.0, 13.9. Anal. Calc. for $C_{14}H_{21}O_4Cl$: C, 58.23 ; H, 7.33. Found : C, 58.54 ; H, 7.39.

Diethyl 2-bromo-3-ethylidenebutanedioate 10a. (82 % yield). E isomer : ^{1}H NMR, δ : 6.67 (q, J=7.3 Hz, 1H), 5.20 (s, 1H), 4.19 (m, 4H), 2.10 (d, J=7.3 Hz, 3H), 1.25 (m, 6H). ^{13}C NMR, δ : 167.9, 164.3, 144.9, 128.5, 62.4, 60.8, 46.7, 16.1, 13.6. Z isomer : ^{1}H NMR, δ : 7.06 (q, J=7.3 Hz, 1H), 5.47 (s, 1H), 4.20 (m, 4H), 1.89 (d, J=7.3 Hz, 3H), 1.25 (m, 6H). ^{13}C NMR, δ : 167.9, 164.3, 142.7, 130.8, 62.7, 61.1, 40.4, 16.1, 13.6. Anal. Calc. for $C_{10}H_{15}O_4Br$: C, 43.03 ; H, 5.42. Found : C, 42.89 ; H, 5.36.

Diethyl 2-bromo-3-propylidenebutanedioate 10b. (96 % yield). E isomer : ^{1}H NMR, δ : 6.51 (t, J=7.2 Hz, 1H), 5.19 (s, 1H), 4.19 (m, 4H), 2.56 (m, 2H), 1.24 (m, 6H), 1.06 (t, J=7.5 Hz, 3H). ^{13}C NMR, δ : 167.7, 164.2, 151.3, 127.2, 62.7, 60.8, 46.6, 22.3, 13.9, 13.1. Z isomer : ^{1}H NMR, δ : 6.95 (t, J=7.3 Hz, 1H), 5.46 (s, 1H), 4.19 (m, 4H), 2.27 (m, 2H), 1.25 (m, 6H), 1.10 (t, J=7.5 Hz, 3H). ^{13}C NMR, δ : 167.7, 164.3, 149.0, 129.6, 62.7, 61.1, 40.5, 22.3, 13.9, 12.2. Anal. Calc. for $C_{11}H_{17}O_4Br$: C, 45.07 ; H, 5.84. Found : C,45.29 ; H, 5.99.

Diethyl 2-bromo-3-butylidenebutanedioate 10c. (87 % yield). E isomer : ^{1}H NMR, δ : 6.54 (t, J=7.4 Hz, 1H), 5.21 (s, 1H), 4.19 (m, 4H), 2.5 (q, J=7.4 Hz, 2H), 1.47 (m, 2H), 1.26 (m, 6H), 0.91 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 167.8, 164.7, 150.1, 127.8, 62.4, 60.8, 46.7, 31.6, 22.0, 13.9, 13.6. Z isomer : ^{1}H NMR, δ : 6.95 (t, J=7.4 Hz, 1H), 5.44 (s, 1H), 4.18 (m, 4H), 2.23 (q, J=7.4 Hz, 2H), 1.52 (m, 2H), 1.24 (m, 6H), 0.94 (t, J=7.2 Hz, 3H). ^{13}C NMR, δ : 166.9, 164.9, 147.6, 130.0, 62.7, 61.1, 40.7, 30.9, 21.3, 14.0, 13.8. Anal. Calc. for $C_{12}H_{19}O_4Br$: C, 46.92 ; H, 6.24. Found : C, 47.32 ; H, 6.36. GCMS (70eV) 263 (13), 261 (13), 227 (100), 199 (14), 181 (54), 135 (20), 125 (45), 97 (25), 79 (46), 29 (98).

Diethyl 2-bromo-3-hexylidenebutanedioate 10d. (86 % yield). E isomer : ^{1}H NMR, δ : 6.54 (t, J=7.3 Hz, 1H), 5.20 (s, 1H), 4.19 (m, 4H), 2.56 (q, J=7.3 Hz, 2H), 1.49-1.22 (m, 12H), 0.86 (t, J=6.6 Hz, 3H). ^{13}C NMR, δ : 167.8, 164.4, 150.0, 127.8, 62.4, 60.8, 46.7, 31.2, 28.5, 22.2, 13.8. Z isomer : ^{1}H NMR, δ : 6.95 (t, J=7.3 Hz, 1H), 5.45 (s, 1H), 4.18 (m, 4H), 2.25 (q, J=7.3 Hz, 2H), 1.49-1.22 (m, 12H), 0.87 (t, J=6.6 Hz, 3H). ^{13}C NMR, δ : 167.8, 164.4, 147.7, 129.3, 62.7, 61.1, 40.7, 31.1, 29.2, 28.5, 22.2, 13.8. Anal. Calc. for $C_{14}H_{23}O_4Br$: C, 50.16 ; H, 6.91. Found : C, 50.28 ; H, 7.04.

Diethyl 2-bromo-3-(2-phenylethylidene)butanedioate 10e. (88 % yield). E isomer : ^{1}H NMR, δ : 7.29-7.18 (m, 5H), 6.68 (t, J=7.5 Hz, 1H), 5.24 (s, 1H), 4.22 (m, 4H), 3.95 (d, J=7.5 Hz, 2H), 1.27 (m, 6H). ^{13}C NMR, δ : 167.7, 164.4, 147.6, 138.7, 128.6, 128.5, 126.5, 62.5, 61.1, 46.6, 35.8, 14.0. Z isomer : ^{1}H NMR, δ : 7.29-7.19 (m, 6H), 5.61 (s, 1H), 4.22 (m, 4H), 3.90 (q, J=7.5 Hz, 2H), 1.28 (m, 6H). ^{13}C NMR, δ : 167.7, 164.4, 146.4, 139.5, 128.6, 128.5, 126.5, 62.6, 61.2, 40.7, 35.3, 14.0. Anal. Calc. for $C_{16}H_{19}O_4Br$: C, 54.10 ; H, 5.39. Found : C, 54.49 ; H, 5.63.

Diethyl 2-bromo-3-(2-methylpropylidene)butanedioate 10f. (88 % yield). E isomer : ^{1}H NMR, δ : 6.26 (d, J=9.9 Hz, 1H), 5.17 (s, 1H), 4.19 (m, 4H), 3.31 (m, 1H), 1.25 (m, 6H), 0.99 (d, J=7.2 Hz, 3H), 1.04 (d, J=7.2 Hz, 6H). ^{13}C NMR, δ : 167.7,164.3, 155.7, 125.8, 62.3, 60.9, 46.7, 28.5, 21.9, 13.9. Z isomer : ^{1}H NMR, δ : 6.70 (d, J=10.6 Hz, 1H), 5.45 (s, 1H), 4.17 (m, 4H), 2.69 (m, 1H), 1.22 (m, 6H), 1.04 (d, J=7.2 Hz, 3H), 1.03 (d, J=7.2 Hz, 3H). ^{13}C NMR, δ : 167.7, 164.4, 153.5, 127.5, 62.7, 61.1, 40.7, 28.6, 21.6, 20.9, 13.9. Anal. Calc. for $C_{12}H_{19}O_4Br$: C, 46.92 ; H, 6.24. Found : C, 46.95 ; H, 6.39.

Diethyl 2-bromo-3-(1-methylethylidene)butanedioate 10g. (70 % yield). ^{1}H NMR, δ : 5.45 (s, 1H), 4.19 (m, 4H), 2.13 (s, 3H), 1.95 (s, 3H), 1.26 (m, 6H). ^{13}C NMR, δ : 167.8, 164.3, 151.5, 125.5, 62.6, 60.6, 44.5, 23.6, 22.9, 13.9. Anal. Calc. for $C_{11}H_{17}O_4Br$: C, 45.07 ; H, 5.84. Found : C, 45.15 ; H, 6.06.

Diethyl 2-bromo-3-cyclohexylidenebutanedioate 10h. (74 % yield). ^{1}H NMR, δ : 5.51 (s, 1H), 4.18 (m, 4H), 2.57-2.54 (m, 2H), 2.30-2.27 (m, 2H), 1.69-1.60 (m, 6H), 1.24 (m, 6H). ^{13}C NMR, δ : 173.3, 167.2, 156.8, 122.6, 62.5, 60.7, 43.7, 32.9, 32.4, 28.1, 27.7, 26.0, 13.9. Anal. Calc. for $C_{14}H_{21}O_4Cl$: C, 50.5 ; H, 6.35. Found : C, 50.29 ; H, 6.31.

REFERENCES AND NOTES

1. (a) Lerouge, P.; Paulmier, C. *Bull. Soc. Chim. Fr.*, **1985**, 1225-1229 ; (b) Paulmier, C.; Outurquin, F.; Plaquevent, J.C. *Tetrahedron Lett.*, **1988**, *29*, 5889-5892. (c) Paulmier, C.; Outurquin, F.; Plaquevent, J.C. *Tetrahedron Lett.*, **1988**, *29*, 5893-5896 ; (d) Outurquin, F.; Paulmier, C. *Synthesis*, **1989**, 690-691 ; (e) Duclos, J.F.; Outurquin, F.; Paulmier, C. *Tetrahedron Lett.*, **1993**, *34*, 7417-7420 ; (f) Ponthieux, S.;

Outurquin, F.; Paulmier, C. *Tetrahedron Lett.*, **1995**, *36*, 6453-6456 ; (g) Ponthieux, S.; Outurquin, F.; Paulmier, C. *Tetrahedron*, **1995**, *51*, 9569-9580.

2. (a) Jefson, M.; Meinwald, J. *Tetrahedron Lett.*, **1981**, *22*, 3561-3564 ; (b) Paulmier, C.; Lerouge, P. *Tetrahedron Lett.*, **1982**, *23*, 1557-1600 ; (c) Lerouge, P.; Paulmier, C. *Tetrahedron Lett.*, **1984**, *25*, 1983-1986 ; (d) Lerouge, P.; Paulmier, C. *Tetrahedron Lett.*, **1984**, *25*, 1987-1990.
3. Hiroi, K.; Sato, S. *Synthesis*, **1985**, 635-638.
4. Cossy, J.; Furet, N. *Tetrahedron Lett.*, **1993**, *34*, 7755-7756.
5. Ryu, I.; Murai, S.; Niwa, I.; Sonoda, N. *Synthesis*, **1977**, 874.
6. Houllemare, D.; Ponthieux, S.; Outurquin, F.; Paulmier, C. *Synthesis*, **1997**, 101-106.
7. Lerouge, P.; Paulmier, C. *Bull. Soc. Chim. Fr.*, **1985**, 1219-1224.
8. Manis, P.A.; Rathke, M.W. *J. Org. Chem.*, **1980**, *45*, 4952-4954.
9. (a) Weinstock, L.M.; Currie, R.B.; Lowell, A.W. *Synth. Commun.*, **1981**, *11*, 943-946 ; (b) Rambaud, M.; Bakasse, M.; Dugay, G.; Villieras, J. *Synthesis*, **1988**, 564-566.
10. Wittig, G.; Reiff, H. *Angew Chem., Int. Edit.*, **1968**, *7*, 7-14.
11. Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press, 1986, chap V. Sonoda, N.; Ogawa, A. *The chemistry of Organic Selenium and tellurium compounds*. Patai, S.; Rappoport, Z.; ed. Wiley, 1986, chap 16.
12. Moppett, C.E.; Sutherland, J.K. *Chem. Commun.*, **1966**, 772-773.
13. Green, D.M.; Long, A.G.; May, P.J.; Turner, A.F., *J. Chem. Soc.*, **1964**, 766-783.
14. Le Corre, M. *C.R. Acad Sci.*, **1970**, *270* (C), 1312-1314.
15. (a) Fankhauser, J.E.; Peevey, R.M.; Hopkins, P.B. *Tetrahedron Lett.*, **1984**, *25*, 15-18 ; (b) Shea, R.G.; Fitzner, J.N.; Fankhauser, J.E.; Hopkins, P.B. *J. Org. Chem.*, **1984**, *49*, 3647-3650 ; (c) Fitzner, J.N.; Pratt, D.V.; Hopkins, P.B. *Tetrahedron Lett.*, **1985**, *26*, 1959-1962 ; (d) Fitzner, J.N.; Shea, R.G.; Fankhauser, J.E.; Hopkins, P.B. *J. Org. Chem.*, **1985**, *50*, 417-419 ; (e) Spaltenstein, A.; Carpino, P.A.; Hopkins, P.B. *Tetrahedron Lett.*, **1986**, *27*, 147-150 ; (f) Shea, R.G.; Fitzner, J.N.; Fankhauser, J.E.; Spaltenstein, P.A.; Peevey, R.M ; Pratt, D.V.; Tenge, B.J.; Hopkins, P.B. *J. Org. Chem.*, **1986**, *51*, 5243-5252 ; (g) Spaltenstein, A.; Carpino, P.A.; Miyake, Fr.; Hopkins, P.B. *J. Org. Chem.*, **1987**, *52*, 3759-3766.
16. Brown, J.M.; James, A.P.; Prior, L.M. *Tetrahedron Lett.*, **1987**, *28*, 2179-2182.
17. Duclos, J.F.; Outurquin, F.; Paulmier, C. *Tetrahedron Lett.*, **1995**, *36*, 2627-2630.
18. Mathew, J.; Alink, B. *J. Org. Chem.*, **1990**, *55*, 3880-3886.

(*Received in Belgium* 28 *May* 1997; *accepted* 23 *September* 1997)