Tetrahedron Vol. 41, No. 12, pp. 2527 to 2543, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

CAPTODATIVE SUBSTITUENT EFFECTS XXI.[1]
SYNTHESIS OF SELENENYLATED CAPTODATIVE OLEFINS VIA SELENENYL HALIDE ADDITION TO OLEFINS BEARING ELECTRON-WITHDRAWING SUBSTITUENTS

S. PIETTRE, Z. JANOUSEK, R. MERENYI and H.G. VIEHE.

Laboratoire de Chimie Organique, Université de Louvain,
Place Louis Pasteur 1, B-1348 Louvain-la-Neuve (Belgium)

(*Received in UK 25 March* 1985)

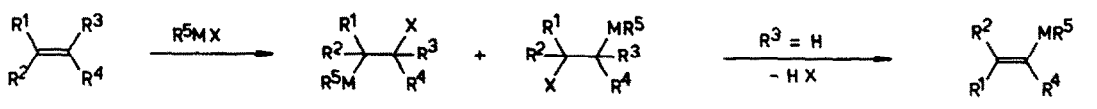
Abstract: *Addition of methane- and benzeneselenenyl bromide or chloride and benzene sulfenyl chloride to carbon-carbon double bonds substituted by electron-withdrawing groups is achieved in solvents of different polarity. Two regioisomeric adducts 6 and 7 or 8 and 9 are generally formed, which can be interconverted by equilibration in refluxing acetonitrile. It is of mechanistic interest that the regioisomers may also derive from selenenyltrihalide adducts. In comparison to acrylic esters, the propiolic ester reacts more slowly, producing mainly the α-selenenyl adduct. Dehydrohalogenation of adducts provides a general and valuable method for the preparation of olefins carrying methyl or phenylselenenyl groups in α-position to electron-withdrawing substituents.*

Selenenylated olefins have been found to be particularly useful radicophiles. Compared to their sulfur analogs, these olefins 1 show even more interesting aspects. Thus for example, adduct-dimers 3 lose diphenyl diselenide, leading generally to symmetrical fumaric acid derivatives 4[2] :

1 2 3 4 (65-75%)

R^1 = CN, $COOCH_3$
R^2 = $(CH_3)_2(CN)C^{\cdot}$, $(CH_3)_2(COOCH_3)C^{\cdot}$

In order to develop a general method for the preparation of selenenylated olefins, we have conducted an extensive study of the addition of selenenyl halides (and sulfenyl halide in some cases) to olefins 5 substituted by electron-withdrawing groups. The adducts 6 and 7 or 8 and 9 can be conveniently dehydrohalogenated to olefins 10 and 11.



5

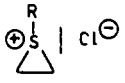
6 M = S 7 M = S 10 M = S
8 M = Se 9 M = Se 11 M = Se

X = Cl, Br ; R^1, R^2, R^3 = H, CH_3 ; R^4_5 = electron-withdrawing group
R = CH_3, C_6H_5

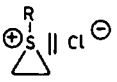
Addition of Selenenyl Halides

Since the work of Kharash[3,4,5], the addition of sulfenyl halides and also of selenenyl halides to carbon-carbon double bonds has been widely developed because of the mechanistic concern and the synthetic potential of the arising adducts[6]. Although these additions generally appear to be of electrophilic nature, even electron poor-olefins react well. These additions proceed via tight or solvent separated ion-pairs such as 13 or 14 rather than via covalent cycles 12 or episulfonium ions 15[4]. Theoretical studies support this mechanistic view[7].

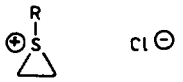
12



13

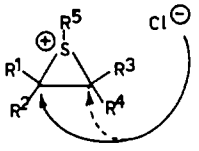


14



15

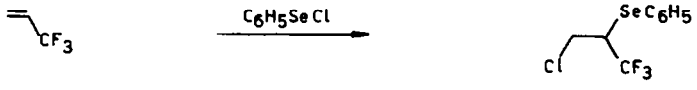
The isomerization of transient cyclic intermediates to the adducts takes place almost generally with trans-stereospecificity[3,4,5]. In the case of non-symmetrical olefins, two regioisomers are generally formed resulting from nucleophilic attack by the halide at either carbon[5]. The amount of each regioisomer is dependent on the experimental conditions, temperature, solvent and on the substituents at the α or β carbon.



The isomerization of the kinetic product to the thermodynamic one is achieved either thermally or by acid catalysis[5]. The rate of addition of sulfenyl halides to acrylic acid derivatives 5 decreases with increasing electron-withdrawing character of the substituent R^4. The following order of reactivity has been established[8] :

$$R^4 = CN < COCl < COOH < COOCH_3 < CONHC_6H_5$$

The reaction between the olefins 5 and methanesulfenyl chloride leads to a mixture of kinetic and thermodynamic adducts already at -65° C[8a]. In the case of vinyl sulfones, however, the important steric bulk of the sulfonyl group leads to ring-opening at the less-hindered carbon and isomer 7 is the only one observed[8a,9]. The addition of selenenyl halides follows essentially the same pathway as with the sulfur analogs[5]. Only a slight difference in the positive charge distribution between the thiyl and selenenyl cyclic intermediates was reported[10]. Electron-poor olefins, however, have received only scant attention, and to our knowledge, phenylselenenyl chloride has been reacted only with 3,3,3-trifluoropropene, leading to adduct 9[11].



5 9

Results and discussion

Additions of selenenyl halides to acrylic or crotonic acid derivatives 5 is strongly solvent-dependent and proceeds much faster in acetonitrile than in chloroform solution; both cases were studied and are discussed below.

1) RSeX additions to olefins in chloroform solution.

In this solvent, the additions are generally quantitative with the exception of the nitriles 5r,s,t, which react too slowly and complete addition can be achieved only in acetonitrile (see below). Approximate rates and product concentrations were monitored by ^1H NMR (200 MHz) spectroscopy. Both the regioisomers 8 and 9 are initially formed and the mixture evolves toward equilibrium. The relative amounts of regioisomers formed after 90 minutes are compiled in Table I.

Table I : Addition of R^5SeX to Olefins 5 (R^2 = H) in $CHCl_3$. Relative Amounts of 5, 8, 9 after 90 minutes.

	R^1	R^3	R^4	R^5	X	5 (%)	8 (%)	9 (%)
a	H	CH_3	$CONH_2$	C_6H_5	Cl	0	82	18
b	H	H	$CONH_2$	C_6H_5	Br	0	14	86
c	H	H	$CONH_2$	C_6H_5	Cl	0	38	62
d	H	H	$CON(CH_3)_2$	C_6H_5	Cl	0	56	43
e	H	H	$COCH_3$	C_6H_5	Br	0	20	80
f	H	H	$COCH_3$	C_6H_5	Cl	0	49	51
g	H	H	CHO	C_6H_5	Br	0	15	85
h	H	H	CHO	CH_3	Br	0	7	93
i	H	H	CHO	C_6H_5	Cl	0	45	55
j	CH_3	H	CHO	C_6H_5	Cl	0	24	70
k	H	H	$COOCH_3$	C_6H_5	Br	0	38	62
l	H	H	$COOCH_3$	CH_3	Br	3 (d)	0	88
m	H	H	$COOCH_3$	C_6H_5	Cl	12 (d)	37	46
n	H	H	$COOC_4H_9$-t	C_6H_5	Cl	9 (d)	34	47
o	CH_3	H	$COOCH_3$	C_6H_5	Cl	10 (d)	9	81
p	H	H	COOH	C_6H_5	Cl	15 (d)	37	45
q	H	H	COCl	C_6H_5	Cl	52 (d)	17	20
r	H	H	CN (a)	CH_3	Br	75	0	25
s	H	H	CN (b)	C_6H_5	Cl	30	13	56
t	CH_3	H	CN (c)	C_6H_5	Cl	39	15	27

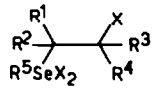
(a) : after 18 hours at room temperature ; (b) : after reflux in $CHCl_3$ during 120 hrs ; (c) : after reflux in $CHCl_3$ during 360 hrs ; (d) : reaction is not complete.

It is noteworthy that in the thermodynamically favored adduct 9, the electron-withdrawing and the electron-donating substituent i.e. selenenyl group, are located at the same carbon (captodative substitution). Regioisomers 8 show characteristic ABX or AMX (AB) patterns from which coupling constants were calculated, whereas products 9 mostly exhibit ABC patterns (sometimes AMX or AB). The NMR data are collected in Table II.

Table II : ^{1}H-NMR data of 8 and 9 (R^2 = H) ($CDCl_3$)

	R^1	R^3	R^4	R^5	X	patterns	8 δ_A	8 $\delta_{B(M)}$	8 δ_X	8 $J_{AB(AM)}$ (Hz)	8 J_{AX} (Hz)	8 $J_{BX(MX)}$ (Hz)	9 δ_A	9 $\delta_{B(M)}$	9 $\delta_{C(X)}$	9 $J_{AM(AB)}$ (Hz)	9 J_{AX} (Hz)	9 J_{MX} (Hz)
a	H	CH_3	$CONH_2$	C_6H_5	Cl	AB+AB	3.49	3.58	-	-12.74	-	-	3.70	4.11	-	-10.96	-	-
b	H	H	$CONH_2$	C_6H_5	Br	ABX+ABC	3.41	3.62	4.44	-12.3	11.0	4.0		3.72-4.0		-	-	-
c	H	H	$CONH_2$	C_6H_5	Cl	AMX+ABC	3.30	3.60	4.45	-12.96	6.35	6.73		3.74-3.84		-	-	-
d	H	H	$CON(CH_3)_2$	C_6H_5	Cl	AMX+AMX	3.12	3.57	4.54	-12.2	4.5	10.5	3.68	4.05	4.19	3.5	9.5	-11.5
e	H	H	$COCH_3$	C_6H_5	Br	AMX+AMX	3.25	3.51	4.45	-12.5	4.3	11.5	3.63	3.77	4.0	9.7	4.3	-11.2
f	H	H	$COCH_3$	C_6H_5	Cl	ABX+ABC	3.44	3.24	4.40	-12.74	9.79	5.14		3.78-3.98		-	-	-
g	H	H	CHO	C_6H_5	Br	AMX+ABC	3.32	3.95	4.45	-	-	-		3.60-3.80		-	-	-
h	H	H	CHO	CH_3	Br	ABC	-	-	-	-	-	-		3.57-4.04		-	-	-
i	H	H	CHO	C_6H_5	Cl	ABX+ABC	3.40	3.30	4.36	-12.90	9.01	5.72		3.74-3.88		-	-	-
j	CH_3	H	CHO	C_6H_5	Cl	AB+AB	3.82	4.33	-	6.65	-	-	3.78	4.32	-	9.7	-	-
k	H	H	$COOCH_3$	C_6H_5	Br	AMX+ABC	3.28	3.50	4.32	-12.80	4.0	12.0		3.60-3.90		-	-	-
l	H	H	$COOCH_3$	CH_3	Br	ABC	-	-	-	-	-	-		3.60-3.83		-	-	-
m	H	H	$COOCH_3$	C_6H_5	Cl	ABX+ABC	3.46	3.29	4.39	-12.78	10.77	4.94		3.78-4.0		-	-	-
n	H	H	$COOC_4H_9$-t	C_6H_5	Cl	ABX+ABC	3.40	3.25	4.25	-12.48	10.72	4.86		3.72-3.94		-	-	-
o	CH_3	H	$COOCH_3$	C_6H_5	Cl	AB+AB	3.53	4.23	-	10.3	-	-	3.72	4.32	-	10.9	-	-
p	H	H	COOH	C_6H_5	Cl	ABX+ABC	3.47	3.31	4.43	-12.69	10.51	4.91		3.89-4.0		-	-	-
q	H	H	COCl	C_6H_5	Cl	ABX+ABC	3.44	3.34	4.61	-13.11	9.96	5.33		3.72-3.88		-	-	-
r	H	H	CN	CH_3	Br	ABX+ABC	3.48		4.53	-	-	-		3.58-3.84		-	-	-
s	H	H	CN	C_6H_5	Cl	ABX+ABC	3.35	3.29	4.42	-13.03	5.44	10.47		3.60-3.83		-	-	-
t	CH_3	H	CN	C_6H_5	Cl	AB+AB	3.80	4.39	-	6.8	-	-	3.98	4.17	-	4.50	-	-

The ^{1}H-NMR spectra reveal also that a third product is formed, the concentration of which increases during the first stages of the reaction but drops to zero at the end. The structure 16 is assigned on the basis of ^{1}H-NMR data (see below). Direct chemical evidence is obtained by chlorination of 8f and 9f which leads to the corresponding selenoether dichlorides. Chemical shifts of 16 and concentrations after 5 and 90 minutes reaction times are shown in Table III.



16

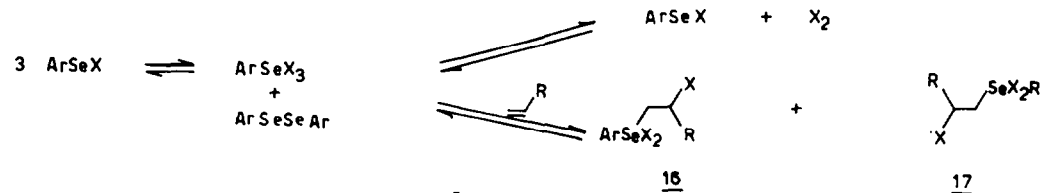
R^1 = H, CH_3
R^2, R^3 = H
R^4 = electron-withdrawing group
R^5 = CH_3, C_6H_5
X = Cl, Br

Table III : Chemical Shifts and Concentrations of 16 (R^2, R^3 = H) after 5 and 90 minutes.

	R^1	R^4	R^5	X	δ_A	δ_B	δ_X	Chemical Shifts of the phenyl group	Other Chemical shifts (ppm)	(%) after 5'	(%) after 90'
					(ppm)						
d	H	$CON(CH_3)_2$	C_6H_5	Cl	4.65		5.55	7.55(m,3H),7.95(m,2H)	3.06(s,3H), 3.17(s,3H)	9	0
f	H	$COCH_3$	C_6H_5	Cl	4.62		5.42	7.60(m,3H),8.0(m,2H)	2.52(s,3H)	15	0
g	H	CHO	C_6H_5	Cl	4.66	4.62	5.45	7.66(m,3H),8.0(m,2H)	9.70(s,1H)	18	0
j	CH_3	CHO	C_6H_5	Cl	5.12	5.48	-	7.62(m,3H),8.09(m,2H)	1.80(d,3H), 9.60(d,1H)	4	0
k	H	$COOCH_3$	C_6H_5	Br	4.68		5.49	7.80(m,3H),8.0(m,2H)	3.93(s,3H)	6	0
l	H	$COOCH_3$	CH_3	Br	4.42		5.37	-	2.92(s,3H), 3.83(s,3H)	20	0
m	H	$COOCH_3$	C_6H_5	Cl	4.68		5.49	7.80(m,3H),8.0(m,2H)	3.93(s,3H)	15	2
n	H	$COO^tC_4H_9$	C_6H_5	Cl	4.66		5.40	7.82(m,3H),8.05(m,2H)	1.55(s,9H)	15	3
o	CH_3	$COOCH_3$	C_6H_5	Cl	4.99	5.50	-	7.75(m,3H),8.05(m,2H)	1.80(d,3H), 3.84(s,3H)	10	0
p	H	COOH	C_6H_5	Cl	4.73		5.57	7.71(m,3H),8.04(m,2H)	11.74(s,1H)	6	3
q	H	COCl[a]	C_6H_5	Cl	4.80	4.71	5.74	7.80(m,3H),8.05(m,2H)	-	5	11[a]

(a) reaction is not complete

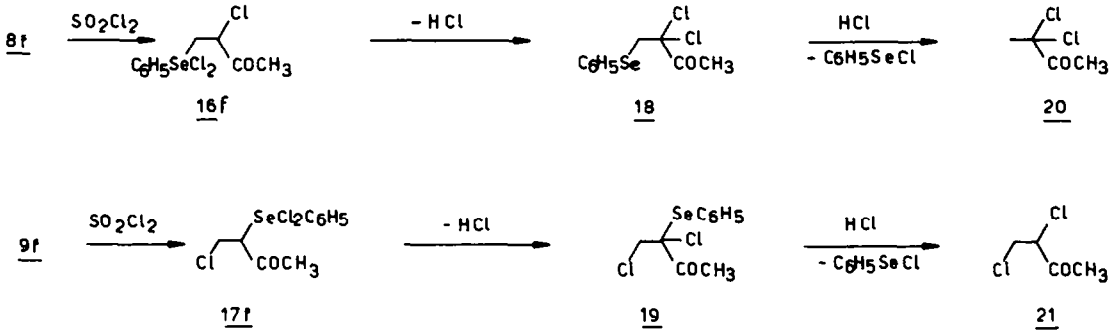
The calculated coupling constants of ABX systems in the case of acrolein (entry 16g; J_{AB} = - 11.29 Hz; J_{AX} = 6.58 Hz; J_{BX} = 8.78 Hz) and acryloyl chloride (entry 16q; J_{AB} = - 11.35 Hz; J_{AX} = 5.82 Hz; J_{BX} = 9.11 Hz) are characteristic of an acyclic structure. The formation of 16 can be explained by assuming an equilibrium between areneselenenyl halides and the dismutation products, namely, areneselenenyl and trihalides and diselenide[12]. Actually, selenenyl trihalides are known to add to alkyl substituted olefins producing two regioisomers 16 and 17 [5,13].



In contrast, the addition of R^5SeX_3 to electron-poor olefins 5 studied in this work is regiospecific. Selenomonohalide adducts 8 could arise from the reduction of 16 by diselenide present in the equilibrium.

The involvement of $ArSeCl_3$ in the addition of p-tolueneselenenyl chloride to ethylene has already been shown [13c]. Compound 16f can also be obtained together with its isomer 17f by chlorinating (SO_2Cl_2) the mixture of regioisomers 8f and 9f

obtained from benzeneselenenyl chloride and methyl vinyl ketone (^{1}H-NMR values for the ABX system of 17f : δ_A = 4.20; δ_B = 4.0; δ_X = 5.42 ppm; J_{AB} = - 12.18; J_{AX} = 9.96; J_{BX} = 2.87 Hz). The deshielding increments permit the structure assignements[13]. The NMR study of the chlorination of 8f and 9f show that the subsequent HCl elimination from 16f and 17f gives 18 and 19 thereby finally leading to 20 and 21[14].



The comparison between RSeCl and RSeBr additions shows that the more bulky and polarizable bromine atom favors the captodative isomer 9 rather than 8 (see Table I : entries b and c, e and f, g and i, k and m). Such a product is also predominant in the case of CH_3SeBr addition to acrolein (entry h), methyl acrylate (entry l) and vinyl phenyl sulfoxide (see below).

2) RSeX additions to olefins in acetonitrile solution.

Compared to the reaction of RSeX in $CHCl_3$ solution, these additions are much faster in CH_3CN, and accordingly the thermodynamic equilibrium is reached more rapidly (Table IV). In practice, all these additions can be performed at room temperature. Table IV shows that when $R^1 = CH_3$, 9 is produced almost exclusively (entries o and t) while methacrylamide ($R^3 = CH_3$) gives predominantly 8 (entry a).

Table IV : Ratio of Regioisomers 8 and 9 resulting from the Addition of C_6H_5SeCl to olefins 5 (R^2 = H) in CH_3CN.

	R^1	R^3	R^4	Ratio 8/9 At r.t. (%)[a]		Ratio 8/9 Upon heating (%)		Time of heating (hrs)
				8	9	8	9	
a	H	CH_3	$CONH_2$	32	68	82	18	3
d	H	H	$CON(CH_3)_2$	68	32	27	73	1.5
f	H	H	$COCH_3$	70	30	21[c]	79[c]	1.5
i	H	H	CHO	76	24	27[c]	73[c]	1.5
m	H	H	$COOCH_3$	65	35	22	78	5
o	CH_3	H	$COOCH_3$	50	50	0	100	1
p	H	H	COOH	48	52	13	87	1
q	H	H	COCl	60	40	30	70	4.5
s	H	H	CN	33[b]	67[b]	30	70	2
t	CH_3	H	CN	22[b]	77[b]	7	93	2

a) after 5' at room temperature ; b) after 18 hours at room temperature : reaction non complete ; c) partial degradation occurred.

Additions of RSeX (or C_6H_5SCl) to olefins 5 substituted by sulfinyl, sulfonyl or nitro group occur in $CHCl_3$ solution at room temperature. The captodative regioisomer 7 (M = S) or 9 (M = Se) is largely predominant in the case of vinyl sulfoxide and vinyl sulfones, whereas complete reversal of regiochemistry occurs with nitroethylene, producing only the adduct 6 or 8 (Tables V and VI).

Table V : Isomer Ratios Formed in the Addition of R^5SeX or C_6H_5SCl to Olefins 5 (R^1,R^2,R^3 = H) Substituted by Sulfinyl, Sulfonyl or Nitro Groups.

	R^4	R^5	M	X	6 or 8 (%)	7 or 9 (%)
u	$S(O)C_6H_5$	C_6H_5	S	Cl	24	63
v	$S(O)C_6H_5$	C_6H_5	Se	Cl	6	93
w	$S(O)C_6H_5$	CH_3	Se	Br	0	100
x	$SO_2C_2H_5$	C_6H_5	S	Cl	0	100
y	$SO_2C_2H_5$	C_6H_5	Se	Cl	0	100
z	$SO_2C_6H_5$	C_6H_5	Se	Cl	0	100
aa	$SO_2C_6H_5$	CH_3	Se	Br	0	100
ab	$SO_2CH(SeC_6H_5)-CH_2Cl$	C_6H_5	Se	Cl	0	100
ac	NO_2	C_6H_5	S	Cl	20	0
ad	NO_2	C_6H_5	Se	Cl	100	0

Table VI : Proton-Proton Coupling Constants of ABX (AMX) Systems present in Olefins 5 (R^1,R^2,R^3 = H) Substituted by sulfinyl, sulfonyl or Nitro Groups.

	R^4	R^5	M	X	6 or 8 $J_{AB(AM)}$ (Hz)	6 or 8 J_{AX} (Hz)	6 or 8 $J_{BX(MX)}$ (Hz)	7 or 9 $J_{AB(AM)}$ (Hz)	7 or 9 J_{AX} (Hz)	7 or 9 $J_{BX(MX)}$ (Hz)
u	$S(O)C_6H_5$	C_6H_5	S	Cl	-14.0	8.6	4.0	-	-	(a)
v	$S(O)C_6H_5$	C_6H_5	Se	Cl	-13.6	9.0	3.8	11.5	8.5	5.5 (a)
w	$S(O)C_6H_5$	CH_3	Se	Br	-	-	-	6.9	10.9	7.7
x	$SO_2C_2H_5$	C_6H_5	S	Cl	-	-	-	4.13	7.97	-11.64
y	$SO_2C_2H_5$	C_6H_5	Se	Cl	-	-	-	5.33	6.91	-12.34
z	$SO_2C_6H_5$	C_6H_5	Se	Cl	-	-	-	4.19	8.64	-12.09
aa	$SO_2C_6H_5$	CH_3	Se	Br	-	-	-	4.39	10.89	-12.1
ab	$SO_2CH(SeC_6H_5)-CH_2Cl$	C_6H_5	Se	Cl	-	-	-	5.8 6.0	7.8 7.5	-12.0 (b) -11.6 (b)
ac	NO_2	C_6H_5	S	Cl	-12.31	10.08	4.10	-	-	-
ad	NO_2	C_6H_5	Se	Cl	-12.40	11.08	3.37	-	-	-

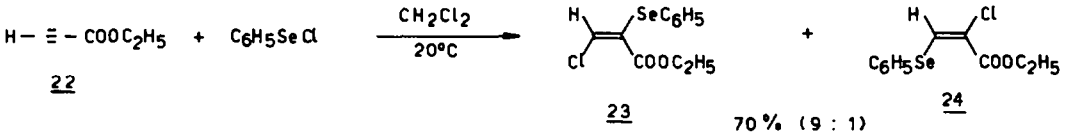
(a) ABC patterns ; b) mixture 1:1 of meso and d,l isomers.

The amount of captodative regioisomers is larger with selenenyl chloride (entry v) than with sulfenyl chloride (entry u), thereby reflecting the larger steric hindrance of selenoether group which obviously disfavors ring-opening in α-position. This view is further supported by the complete absence of isomers 8 when bromine is involved (entry w).

In the case of vinyl sulfones, only the regioisomer 7 or 9 is formed in analogy to the addition of sulfenyl halides[8a,9]. Addition of two equivalents of C_6H_5SeCl to divinylsulfone affords bis-adduct 9 (entry ab). In contrast, reaction of C_6H_5SeCl with nitroethylene leads in $CHCl_3$ quantitatively to the regioisomer 8 after 3 days, while C_6H_5SCl produces only about 20 % of isomer 6 which moreover could not be isolated; adduct 7 could not be detected. It is surprising that in acetonitrile adduct 8ad is obtained in only 20 % yield.

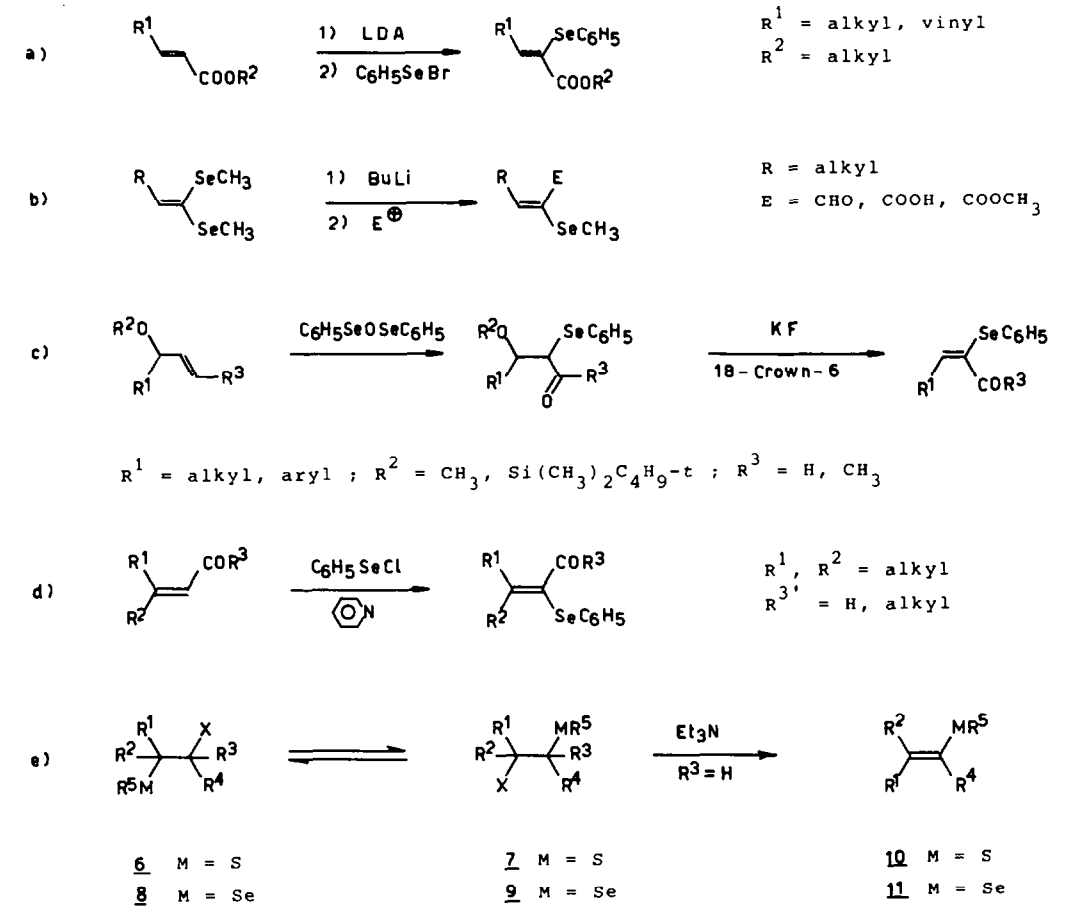
Addition of C_6H_5SeCl to Ethyl Propiolate

In analogy to the addition of C_6H_5SeCl to propiolic acid[15] and the corresponding addition of C_6H_5SCl[16] we found that the addition to ethyl propiolate is much slower and more regioselective as compared to methyl acrylate. The structure of the isomer 23 was determined by ^{13}C-NMR spectroscopy. The value of the ^3J coupling between the carbon of the carboxylic group and the olefinic proton is characteristic of a trans-relationship (10.3Hz).



Synthesis of Selenenylated Olefins 11

Captodative olefins 11 with selenenyl groups as electron-donating substituents have been occasionally mentioned in the literature as deriving from several approaches : a) selenenylation of vinylic carbanions[17], b) lithiation of ketene selenoacetals followed by introduction of the electron-withdrawing group[18], c) oxidation of allylic alcohols followed by elimination[19]. An one-pot reaction using the pyridine/C_6H_5SeCl reagent (equation d) appears to be confined to vinyl ketones and aldehydes[20]. Our synthesis is based on the dehydrohalogenation of the mixture of regioisomers 8 and 9 (equation e) leading to a single product.



The Table VII shows that, using triethylamine as a base, only the isomer 9 undergoes an elimination to give 11. This in turn shifts the equilibrium 8 ⇌ 9 to the right until the elimination is completed. Olefins 10 are obtained in an

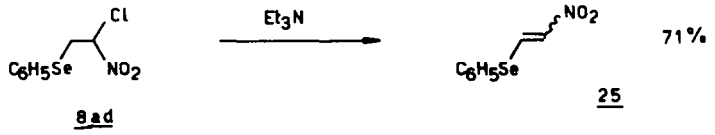
analogous manner (entries n and q). The rates of elimination expectedly depend on the nature of the electron-withdrawing substituent. Thus with sulfonyl or aldehyde groups, the reaction is almost instantaneous but with the sulfinyl substituent, the reaction is complete only after 16 hours at room temperature, whereas the amide necessitates reflux in $CHCl_3$ for two hours.

Table VII : Yield and Coupling Constants of AB systems of Olefins 10 and 11 (R^2=H)

	R^1	MR^5	R^4	Yield(%)[a]	$^2J_{HH}$(Hz)
a	CH_3	SeC_6H_5	CN	65[d]	-
b	H	SeC_6H_5	CN	55	0.4
c	H	$SeCH_3$	CN	35	0.4
d	H	SeC_6H_5	$COOCH_3$	57[17]	0.6
e	H	SeC_6H_5	$COOtC_4H_9$	53	0.6
f	H	$SeCH_3$	$COOCH_3$	81	0.93
g	CH_3	SeC_6H_5	$COOCH_3$	86[17],[c]	-
h	H	SeC_6H_5	$CONH_2$	96	-
i	H	SeC_6H_5	CHO	68[21]	1.10
j	CH_3	SeC_6H_5	CHO	65[17,21],[c]	-
k	H	$SeCH_3$	CHO	40[b]	-
l	H	SeC_6H_5	$COCH_3$	85[21]	1.74
m	H	SeC_6H_5	COC_6H_5	50[21]	1.50
n	H	SC_6H_5	$S(O)C_6H_5$	64[21]	1.4
o	H	SeC_6H_5	$S(O)C_6H_5$	91	1.92
p	H	$SeCH_3$	$S(O)C_6H_5$	70	0.9
q	H	SC_6H_5	$SO_2C_2H_5$	75[8a,9c]	1.60
r	H	SeC_6H_5	$SO_2C_2H_5$	89	1.98
s	H	SeC_6H_5	$SO_2C_6H_5$	92	1.90
t	H	SeC_6H_5	$SO_2-C(SeC_6H_5)=CH_2$	94	2.0
u	H	$SeCH_3$	$SO_2C_6H_5$	89	1.71

(a) yield based on the starting olefins ; (b) isolated as a dihydropiran [4+2]dimer [22] ; (c) only isomer E is obtained ; (d) mixture of E and Z isomers

Nitroethylene adduct which contains the strongest electron-withdrawing group constitutes a special case. Only regioisomer 8 is obtained which does not equilibrate with the captodative isomer. Consequently, the elimination leads exclusively to the β-selenenylated nitroethylene 25 as a 1:1 mixture of cis and trans isomers[23].



8ad 25

cis : trans = 1 : 1

Studies concerning the reactivity of these olefins are in progress in this laboratory, in particular the use of β-phenylselenonitroethylene as a synthetic equivalent of the nitroacetylene[24,25].

EXPERIMENTAL

Boiling points are uncorrected ; melting points were measured on a Leitz Wetzlar HM Lux apparatus and are uncorrected. 1H-NMR : spectra were recorded in $CDCl_3$ solution using TMS as internal reference at 200 MHz on Varian XL-200 spectrometer. For coupling constants, see Tables in the text. 13C-NMR spectra were recorded in $CDCl_3$ solution on Varian CFT-20 spectrometer (multiplicity due to one-bond couplings : S=singlet, D=doublet, T=triplet, Q=quadruplet, M=multiplet; long-range couplings : s,d,t,q,m).Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrometer. Mass spectra on Varian MAT-445 spectrometer and are given for the 80 Se isotope. Benzeneselenenenyl halides were synthesized as described in litterature [26] and methaneselenenyl bromide was formed in situ from equimolar amounts of dimethyl diselenide and bromine. Microanalyses were performed by the Microanalyses Laboratory of the University of Wien.

Addition of selenenyl and sulfenyl halides : general procedure :

An equimolar amount of the selenenyl halide or sulfenyl chloride and olefin is stirred at room temperature in CH_2Cl_2 or acetonitrile (with nitriles, sulfones and acryloyl chloride) until discoloration of the solution. The reaction is essentially quantitative. Attemps to distil the adducts generally lead to partial degradation. In some cases, purification of slighly impure products may be achieved by column chromatography. Products are generally obtained as a mixture of both regioisomers.

2-Methyl-2-chloro-3-phenylselenopropionamide 8a and 2-methyl-2-phenylseleno 3-chloropropionamide 9a : purified by chromatography on silicagel (Pet.ether/AcOEt = 6/4), a pale yellow oil.
1H-NMR : **8a** : δ = 1.60(s,3H), 3.70(d,1H,J=10.96Hz), 4.11(d,1H), 6.66(br,2H), 7.25(m,3H), 7.58ppm(m,2H) ; **9a** : δ = 1.87(s,3H), 3.49(d,1H,J=12.74 Hz), 3.58(d,1H), 6.66(br,2H), 7.25(m,3H), 7.58ppm(m,2H)
IR(film) : ν_1= 3470, 3340, 3190, 3080, 2990, 2940, 1675, 1580, 1480, 1440, 1025, 740, 690 cm^{-1}
M.S.(EI) : m/e = 277 ; 242, 233, 157, 120, 77

2-Bromo-3-phenylselenopropionamide 8b and 2-phenylseleno-3-bromopropionamide 9b: obtained by crystallization in CH_2Cl_2 as colorless crystals.
1H-NMR : **8b** : δ = 3.41(m,1H), 3.62(m,1H), 4.44(m,1H), 5.9-6.55(br,2H), 7.45(m,3H), 7.70ppm(m,2H) ; **9b** : δ = 3.72-4.0(m,3H), 5.90-6.55(m,2H), 7.42(m,3H), 7.70ppm(m,2H)
IR(CH_3CN) : ν = 3440, 3235, 3040, 2955, 1690, 1610, 1580, 1415, 740, 690 cm^{-1}
M.S.(EI) : m/e = 307 and 309 ; 263 and 265, 228, 157, 77, 51

2-Chloro-3-phenylselenopropionamide 8c and 2-phenylseleno-3-chloropropionamide 9c : obtained by crystallization in CH_2Cl_2 as colorless crystals.
1H-NMR : **8c** : δ = 3.32(dd,1H), 3.61(dd,1H), 4.46(dd,1H), 6.10(br,2H), 7.36(m,3H), 7.58ppm(m,2H) ; **9c** : δ = 3.74-3.84(m,2H), 4.12(m,1H), 5.84(m,2H), 7.3(m,3H), 7.62ppm(m,2H).
IR(CH_3CN) : ν = 3440, 3235, 3040, 2960, 1685, 1610, 1580, 1410, 690, 740 cm^{-1}
M.S.(EI) : m/e = 263 ; 228, 219, 157, 106, 77, 51.

N,N-Dimethyl 2-chloro-3-phenylselenopropionamide 8d and N,N-dimethyl 2-phenylseleno 3-chloropropionamide 9d : purified by chromatography on silicagel (Pet.ether/AcOEt: 6/4); a colorless oil.
1H-NMR : **8d** : δ = 2.9(s,3H), 2.93(s,3H), 3.22(dd,1H), 3.69(dd,1H), 4.60(dd,1H), 7.22(m,3H), 7.44ppm(m,2H) : **9d** : δ = 2.88(s,3H), 3.0(s,3H), 3.77(dd,1H), 4.14(dd,1H), 4.29(dd,1H), 7.26(m,3H), 7.52ppm(m,2H).
IR(film) : ν_1= 3060, 2970, 2940, 1650, 1580, 1480, 1440, 1420, 1400, 1070, 1025, 740, 690 cm^{-1}
M.S.(EI) : m/e = 291 ; 256, 157, 134, 77, 51.

3-Bromo-4-phenylseleno-2-butanone 8e and 3-phenylseleno-4-bromo-2-butanone 9e : purified by chromatography on silicagel (benzene) ; a pale yellow oil.
1H-NMR : **8e** : δ = 2.31(s,3H), 3.25(dd,1H), 3.51(dd,1H), 4.45(dd,1H), 7.35(m,3H), 7.55ppm(m,2H) ; **9e** : δ = 2.37(s,3H), 3.63(dd,1H), 3.77(dd,1H), 4.0(dd,1H), 7.32(m,3H), 7.52ppm(m,2H).
IR(film) : ν = 3060, 2990, 1710, 1580, 1480, 1440, 1420, 1365, 1230, 1070, 690 cm^{-1}
M.S.(EI) : m/e = 306 and 308 ; 227, 157, 77, 51.

3-Chloro-4-phenylseleno-2-butanone 8f and 3-phenylseleno-4-chloro-2-butanone 9f : purified as above ; a pale yellow oil.
1H-NMR : **8f** : δ = 2.32(s,3H), 3.24(m,1H), 3.44(m,1H), 4.40(m,1H), 7.3(m,3H), 7.57ppm(m,2H) ; **9f** : δ = 2.41(s,3H), 3.78-3.90(m,3H), 7.3(m,3H), 7.62ppm(m,2H).
IR(film) : ν = 3080, 2990, 1710, 1580, 1440, 1360, 1200, 1070, 1025, 690 cm^{-1}.
M.S.(EI) : m/e = 262 ; 227, 219, 157, 77, 51.

2-Bromo-3-phenylselenopropanal 8g and 2-phenylseleno-3-bromopropanal 9g : purified by chromatography on silicagel (CH_2Cl_2) ; a pale yellow oil.
1H-NMR : **8g** : δ = 3.32(m,1H), 3.95(m,1H), 4.45(m,1H), 7.30(m,3H), 7.74(m,2H), 9.26ppm(d,1H) ; **9g** : δ = 3.57-4.04(m,3H), 7.26(m,3H), 7.51(m,2H), 9.52ppm(d,1H)
IR($CHCl_3$) : ν = 3060, 2950, 2840, 2735, 1720, 1690, 1475, 1440, 1220, 1065, 850, 690 cm^{-1}
M.S.(EI) : m/e = 292 and 294, 263 and 265, 213, 157, 77, 51.

2-Bromo-3-methylselenopropanal 8h and 2-methylseleno-3-bromopropanal 9h : quantitative yield according to NMR spectrum ; an unstable yellow oil.
1H-NMR : **8h** : δ = 1.90(s,3H), 3.26-3.52(m,2H), 4.37-4.44(m,1H), 9.30ppm(s,1H) ; **9h**: δ = 1.90(s,3H), 3.60-3.80(m,3H), 9.30ppm(s,1H)
IR($CHCl_3$) : ν = 2940, 2840, 2735, 1715, 1695, 1440, 1225, 845, 690 cm^{-1}
M.S.(CI/IB) : 231 and 233($M+H^+$), 153.

2-Chloro-3-phenylselenopropanal 8i and 2-phenylseleno-3-chloropropanal 9i : purified by chromatography on silicagel (CH_2Cl_2) ; a pale yellow oil.
1H-NMR : **8i** : δ = 3.30(m,1H), 3.40(m,1H), 4.36(m,1H), 7.33(m,3H), 7.55(m,2H), 9.59ppm(m,1H) ; **9i** : δ = 3.74-3.88(m,3H), 7.33(m,3H), 7.55(m,2H), 9.55ppm(s,1H)
IR($CHCl_3$) : ν = 3080, 2990, 2850, 1725, 1580, 1480, 1440, 1070, 1025, 690 cm^{-1}
M.S.(EI) : m/e = 248 ; 219, 157, 91, 77, 51.

2-Chloro-3-phenylselenobutanal 8j and 2-phenylseleno-3-chlorobutanal 9j : an unstable yellow oil.
1H-NMR : **8j** : δ = 1.84(d,3H), 3.78(dd,1H), 4.32(dq,1H), 7.36(m,3H), 7.56(m,2H), 9.44ppm(d,1H) ; **9j** : δ = 1.74(d,3H), 3.82(dd,1H),4.33(dq,1H), 7.36(m,3H), 7.60(m,2H), 9.57ppm(d,1H).
IR($CHCl_3$) : ν = 3060, 2990, 2940, 2830, 2730, 1710, 1580, 1440, 1360, 1145, 1025, 740, 690 cm^{-1}
M.S.(EI) : m/e = 262 ; 233, 227, 185, 157, 105, 77, 51.

Methyl 2-bromo-3-phenylselenopropionate 8k and methyl 2-phenylseleno-3-bromopropionate 9k: purified by chromatography on silicagel (Pet.ether/AcOEt : 9/1) ; a pale yellow oil.
1H-NMR : **8k** : δ = 3.28(dd,1H), 3.5(dd,1H), 3.72(s,3H), 4.32(dd,1H), 7.57(m,3H), 7.78ppm(m,2H) : **9k** : δ = 3.60-3.90(m,3H), 3.70(s,3H), 7.30(m,3H), 7.52ppm(m,3H)
IR(film) : ν = 3060, 2950, 1735, 1580, 1480, 1435, 1350, 1070, 1025, 830, 690 cm^{-1}
M.S.(EI) : m/e = 322 and 324 ; 263 and 265, 243, 157, 77, 51.

Methyl 2-bromo-3-methylselenopropionate 8l and methyl 2-methylseleno-3-bromopropionate 9l : purified by chromatography on silicagel (Pet.ether/AcOEt : 8/2) ; a pale yellow oil.
1H-NMR : **8l** : δ = 2.12(s,3H), 3.05-3.42(m,2H), 3.75(s,3H), 4.20-4.27ppm(m,1H) **9l** ; δ = 2.12(s,3H), 3.60-3.83(m,3H), 3.75ppm(s,3H)
IR(film) : ν = 2990, 2950, 1730, 1440, 1420, 1350, 1205, 1070, 830, 690 cm^{-1}
M.S.(EI) : m/e = 260 and 262 ; 245 and 247, 181, 165 and 167, 95.

Methyl 2-chloro-3-phenylselenopropionate 8m and methyl 2-phenylseleno-3-chloropropionate 9m : purified by chromatography on silicagel (Pet. ether/AcOEt : 9/1) ; a pale yellow oil.
1H-NMR : **8m** : δ = 3.29(m,1H), 3.46(m,1H), 3.75(s,3H), 4.39(m,1H), 7.38(m,3H), 7.60ppm(m,2H); **9m** : δ = 3.74(s,3H), 3.78-4.0(m,3H), 7.35(m,3H), 7.65ppm(m,2H)
IR(film) : ν = 3080, 2990, 2940, 1740, 1580, 1440, 1350, 1070, 1025, 745, 695 cm^{-1}
M.S.(EI) : m/e = 278 ; 243, 157, 121, 77, 51.

Tert-butyl 2-chloro-3-phenylselenopropionate 8n and tert-butyl 2-phenylseleno-3-chloropropionate 9n : purified by chromatography on silicagel (Pet. ether/AcOEt : 95/5) ; a colorless oil.
1H-NMR : **8n** : δ = 1.55(s,9H), 3.25(m,1H), 3.40(m,1H), 4.25(m,1H), 7.36(m,3H), 7.66ppm(m,2H) ; **9n** : δ = 1.50(s,9H), 3.72-3.94(m,3H), 7.33(m,3H), 7.6ppm(m,2H)
IR(film) : ν = 3075, 2985, 2940, 1730, 1580, 1480, 1440, 1370, 1070, 745, 690 cm^{-1}
M.S.(EI) : m/e = 320 ; 285, 247, 219, 157, 77

Methyl 2-chloro-3-phenylselenobutanoate 8o and methyl 2-phenylseleno-3-chlorobutanoate 9o: obtained by distillation as a pale yellow oil of b.p. : 64-66°C/0.01 Torr (both regioisomers).
1H-NMR : **8o** : δ = 1.46(d,3H), 3.62(dq,1H), 3.64(s,3H), 4.23(d,1H), 7.32(m,3H), 7.5ppm(m,2H) ; **9o** : 1.7(d,3H), 3.64(s,3H), 3.72(d,1H), 4.32(dq,1H), 7.3(m,3H), 7.58ppm(m,2H).
IR(film) : ν = 3060, 2985, 2950, 1735, 1580, 1480, 1440, 1290, 1070, 740, 690 cm^{-1}
M.S.(EI) : m/e = 292 ; 257, 233, 157, 135, 77, 51.

2-Chloro-3-phenylselenopropionic acid 8p and 2-phenylseleno-3-chloropropionic acid 9p : obtained by crystallization from diethylether/Pet.ether at -20°C as colorless crystals.
1H-NMR : **8p** : δ = 3.31(m,1H), 3.47(m,1H), 4.43(m,1H), 7.40(m,3H), 7.69(m,2H), 11.74ppm(s,1H) ; **9p** : δ = 3.89-4.0(m,3H), 7.41(m,3H), 7.63(m,2H), 11.74ppm(s,1H)
IR(CH_2Cl_2) : ν = 3500, 2960, 1745 and 1710, 1580, 1480, 1440, 1305, 1025, 690 cm^{-1}
M.S.(EI) : m/e = 264 ; 229, 219, 157, 107, 77, 51.

2-Chloro-3-phenylselenopropionyl chloride 8q and 2-phenylseleno-3-chloropropionyl chloride 9q : a pale yellow oil.
1H-NMR : **8q** : δ = 3.34(m,1H), 3.44(m,1H), 4.61(m,1H), 7.44(m,3H), 7.64ppm(m,2H) ; **9q** : δ = 3.72-3.88(m,2H), 4.15(m,1H), 7.44(m,3H), 7.64ppm(m,2H)
IR(film) : ν = 3080, 2980, 1770, 1580, 1480, 1440, 1070, 1025, 910, 740, 690 cm^{-1}
M.S.(EI) : m/e = 282 ; 247, 219, 157, 77, 51.

2-Bromo-3-methylselenopropionitrile 8r and 2-methylseleno-3-bromopropionitrile 9r : obtained by chromatography on silicagel (pet.ether/CH_2Cl_2 : 7/3) as an unstable pale yellow oil.
1H-NMR : **9r** : 2.33(s,3H), 3.58-3.84 ppm(m,3H)
IR(film) : ν = 2925, 2235, 1440, 1230, 900 cm^{-1} .

2-Chloro-3-phenylselenopropionitrile 8s and 2-phenylseleno-3-chloropropionitrile 9s: purified by chromatography on silicagel (pet.ether/AcOEt : 8/2) ; a pale yellow oil.
1H-NMR : **8s** : δ = 3.29(m,1H), 3.35(m,1H), 4.42(m,1H), 7.5ppm(m,5H) ; **9s** : δ = 3.60-3.83(m,3H), 7.5ppm(m,5H).
IR(film) : ν = 3060, 2950, 2250, 1580, 1480, 1440, 1070, 1025, 745, 690 cm^{-1}
M.S.(EI) : m/e = 245 ; 210, 168, 157, 77, 51.

2-Chloro-3-phenylselenobutanonitrile 8t and 2-phenylseleno-3-chlorobutanonitrile 9t obtained by chromatography on silicagel (pet.ether/AcOEt = 8/2) and distillation as a pale yellow oil of b.p. : 70-72°C/0.01 Torr (both regioisomers).
1H-NMR : **8t** : δ = 1.62(d,3H), 3.8(d,1H), 4.39(dq,1H), 7.4(m,3H), 7.68ppm(m,2H) ; **9t**: δ = 1.72(d,3H), 3.98(d,1H), 4.17(dq,1H), 7.23(m,3H), 7.58ppm(m,2H)
IR(film) : ν = 3070, 2990, 2940, 2250, 1580, 1480, 1440, 1390, 1025, 745, 695 cm^{-1}
M.S.(EI) : m/e = 259 ;224, 182, 157, 77, 51.

1-Chloro-2-phenylthioethyl phenyl sulfoxide 6u and 1-phenylthio-2-chloroethyl phenyl sulfoxide 7u : a colorless oil.
1H-NMR : **6u** : δ = 3.18(m,1H), 3.58(m,1H), 4.42(m,1H), 7.1(s,5H), 7.40ppm(m,5H) ; **7u**: δ = 3.92-4.17(m,3H), 7.17(s,5H), 7.32(m,3H), 7.60ppm(m,2H).
IR(film) : 3060, 2940, 1580, 1480, 1440, 1145, 1090, 1050, 1025, 915, 745, 690 cm^{-1}
M.S.(EI) : m/e = 296 ; 261, 171, 125, 109, 77, 51.

1-Chloro-2-phenylselenoethyl phenyl sulfoxide 8v and 1-phenylseleno-2-chloroethyl phenyl sulfoxide 9v: a pale yellow oil.
1H-NMR : **8v** : δ = 3.17(dd,1H), 3.58(dd,1H), 4.55(dd,1H), 7.10(s,5H), 7.45ppm(m,5H); **9v** : δ = 3.92(dd,1H), 4.07(dd,1H), 4.24(dd,1H), 7.42ppm(m,10H)
IR(CH_2Cl_2) : 3080, 2950, 1580, 1480, 1440, 1055, 1025, 690 cm^{-1}
M.S.(EI) : m/e = 344 ; 309, 267, 219, 157, 125, 77, 51.

1-Methylseleno-2-bromoethyl phenyl sulfoxide 9w : a pale yellow oil.
1H-NMR : **9w** : δ = 2.92(s,3H), 3.50(dd,1H), 3.90(dd,1H), 4.08(dd,1H), 7.48(m,3H), 7.69ppm(m,2H)
IR(film) : ν = 3060, 3020, 2930, 1580, 1475, 1440, 1080, 1040, 910, 750, 715, 690cm^{-1}
M.S.(CI/IB) : m/e = 327 and 329 $(M+1)^+$; 247, 231 and 233, 201 and 203.

1-Phenylthio-2-chloroethyl ethyl sulfone 7x : a colorless oil.
1H-NMR : **7x** : δ = 1.31(t,3H), 3.16-3.28(m,2H), 3.24(m,1H), 4.26(m,1H),4.31(m,1H), 7.36(m,3H), 7.64ppm(m,2H).
IR(film) : ν = 3060, 2990, 2940, 1580, 1475, 1440, 1315, 1130, 1110, 1025, 790, 750, 690 cm^{-1}
M.S.(EI) : m/e = 264 ; 229, 171, 154, 109, 77, 51.

1-Phenylseleno-2-chloroethyl ethyl sulfone 9y : a colorless oil.
1H-NMR : **9y** : 1.34(t,3H), 3.2-3.46(m,2H), 3.96(m,1H), 4.22(m,1H), 4.33(m,1H), 7.32(m,3H), 7.74ppm(m,2H).
IR(film) : ν = 3065, 2985, 2945, 1580, 1480, 1440, 1315, 1135, 1025, 740, 690 cm^{-1}
M.S.(EI) : m/e = 312 ; 277, 235, 219, 157, 155, 77, 51.

1-Phenylseleno-2-chloroethyl phenyl sulfone 9z: purified by washing with pet.ether; a pale yellow oil.
1H-NMR : **9z** : δ = 3.79(m,1H), 4.20(m,1H), 4.35(m,1H), 7.2-7.95ppm(m,10H)
IR(film) : ν = 3070, 2990, 1580, 1480, 1440, 1315, 1150, 1080, 1025, 740, 735, 690 cm^{-1}
M.S.(EI) : m/e = 360 ; 325, 282, 219, 157, 77, 51.

1-Methylseleno-2-bromoethyl phenyl sulfone 9aa : obtained by chromatography on silicagel (CH_2Cl_2) and crystallization in CH_2Cl_2/n-hexane at -20°C as colorless crystals of m.p. : 99-100°C.
1H-NMR : **9aa** : δ = 2.20(s,3H), 4.04(m,1H), 4.14(m,1H), 4.50(m,1H), 7.62(m,3H), 7.95ppm(m,2H)
IR(film) : ν = 3060, 2940, 1580, 1440, 1320, 1150, 1080, 780, 690 cm^{-1}
M.S.(EI) : m/e = 342 and 344 ; 263, 247 and 249, 201 and 203, 95.

Bis(1-phenylseleno-2-chloroethyl) sulfone 9ab : obtained by washing the crude adduct with pet.ether as a mixture of meso and d,l isomers (1:1) ; a pale yellow oil.
1H-NMR : **9ab** : isomer A : δ = 3.78(dd,2H), 4.18(dd,2H), 5.10(dd,2H), 7.36(m,6H), 7.70ppm(m,4H) ; isomer B : δ = 3.82(dd,2H), 4.18(dd,2H), 5.04(dd,2H), 7.36(m,6H), 7.70ppm(m,4H).
IR(film) : ν = 3075, 2970, 1580, 1480, 1440, 1320, 1135, 1070, 1025, 790, 690 cm^{-1}
M.S.(EI) : m/e = 502 ; 467, 345, 219, 157, 77, 51.

1-Chloro-2-phenylseleno-1-nitroethane 8ad : purified by washing with pet. ether ; a yellow oil.
1H-NMR : **8ad** : 3.89(m,1H), 3.95(m,1H), 5.58(m,1H), 7.25(m,3H), 7.58ppm(m,2H)
IR(film) : ν = 3080, 2980, 1580, 1480, 1440, 1350, 1200, 1070, 1025, 860, 690 cm^{-1}
M.S.(EI) : m/e = 265 ; 219, 157, 77, 51.

Ethyl 2-chloro-3-phenylselenoacrylate 24 and ethyl 2-phenylseleno-3-chloroacrylate 23 : obtained by stirring equimolar amounts of ethyl propiolate and C_6H_5SeCl in CH_2Cl_2 at room temperature for 3 days ; purified by chromatography on silicagel (cyclohexane followed by ether) and distillation as a pale yellow oil of b.p. : 95-100°C/0.01 Torr (both regioisomers).
1H-NMR and 13C-NMR of **23** : δ = 1.21(t,3H), 4.15(q,2H), 6.53(s,1H), 7.20(m,3H), 7.47ppm(m,2H); 13.93(Qm), 61.82(Tq), 125.15(Sd), 125.47(Ds), 127.89(Sm,C-1Ph), 128.54(Dt,C-4Ph), 129.52(Dt,C-2,6Ph), 133.88(Dm,C-3,5Ph), 163.99ppm(Dt)
IR(film) : ν_1 = 3080, 2980, 1725, 1590, 1580, 1480, 1440, 1370, 1305, 1210, 1030, 795, 690 cm^{-1}
M.S.(EI) : m/e = 290 ; 261, 255, 245, 217, 157, 77, 51.

NMR monitoring of selenium dichloride intermediates 16 : olefine **5** (0.5 mmole), PhSeCl (0.156 g, 0.5 mmole) and 1 ml $CDCl_3$ are placed into an NMR tube. The spectra are recorded every 5' during the first hour, then every 10' during the following 30'. The data are collected in Table III.

Chlorination of adducts 8f and 9f : sulfuryl chloride (0.068 gr, 0.5 mmole) is added into a $CDCl_3$ solution of a 1:1 mixture of adducts **8f** and **9f** (0.5 mmole). Selenium dichlorides **16f** and **17f** are immediately formed in a 1:1 ratio as shown by ^{1}H-NMR (200 MHz). NMR data of **16f** and **17f** : see text. Later the signals of **19** (AB system ; δ_A = 3.90, δ_B = 4.56 ppm (d, J_{AB} = 11.78 Hz)) and **18** (A_2 system ; δ = 4.56 ppm (s))appear after 30 min. Compound **21** is observable after 4 hours (ABX system ; δ_A = 3.91, δ_B = 3.78, δ_X = 4.39 ppm (m, J_{AB} = 11.44, J_{AX} = 7.61, J_{BX} = 5.47 Hz) 14H).

Synthesis of Olefins 10 and 11: Unless indicated otherwise, triethylamine (2.53gr, 25 mmoles) in ether (10ml) is added dropwise into the mixture of both regioisomers (10 mmoles) in ether (20ml). After stirring for 16 hours at room temperature, filtration and evaporation, the crude product is purified as specified for each compound.

2-Phenylseleno-2-butenonitrile 11a : purified by chromatography on silicagel [27] (CH_2Cl_2) and distillation ; pale-yellow liquid b.p. : 63-65°C/0.01 Torr.
1H-NMR ($CDCl_3$) : δ = 2.02 and 2.08(2d,3H); 6.87 and 6.94(2q,1H); 7.36(m,3H) ; 7.56 ppm(m,2H).
13C-NMR ($CDCl_3$) : isomer E : δ= 19.42(Qd); 101.14(Ds); 115.89(Sd); 127.71(Sm,C-1Ph) 128.73(Dt,C-4Ph); 129.63(Dm,C-2,6Ph); 133.67(Dm,C-3,5Ph); 152.55ppm(Dq) isomer Z : δ = 18.28(Q,d); 104.68(Ds); 117.45(Sd); 127.17(Sm,C-1Ph); 129.18(Dt,C-4Ph); 129.63 (Dm,C-2,6Ph); 134.21(Dm,C-3,5Ph); 149.42ppm(Dq).
IR(film) : ν = 3070, 2220, 1615, 1580, 1480, 1440, 1380, 1310, 1025, 740, 695 cm^{-1}
M.S.(EI) : m/e = 223 ; 208, 196, 157, 77, 51
Found : C : 53.90, H : 4.09, N : 6.31, $C_{10}H_9NSe$
Requires : C : 54.07, H : 4.08, N : 6.30.

2-Phenylselenopropenonitrile 11b: purified by chromatography on silicagel[27]. (Pet.ether/ACOEt:7/3) and distillation ; pale yellow liquid of b.p. : 54-56°C/0.02 Torr.
1H-NMR($CDCl_3$) : δ = 5.95(d,1H) ; J=0,4Hz), 6.35(d,1H), 7.36(m,3H), 7.60ppm(m,2H)
13C-NMR($CDCl_3$) : δ = 111.13(St), 117.16(Dd), 126.84(Sm,C-1Ph), 130.07(Dt,C-4Ph), 130.45(Dm,C-2,6Ph), 135.54(Dm,C-3,5Ph), 135.73ppm(Ts).
IR(film) : ν = 3090, 3040, 2200, 1580, 1470, 1440, 1370, 1135 cm^{-1}
M.S.(EI) : m/e=209 ; 182, 157, 77, 51
Found : C : 51.79, H : 3.52, N : 6.59, C_9H_7NSe
Requires : C : 51.94, H : 3.39, N : 6.73.

2-Methylselenopropenonitrile 11c : purified as indicated above ; pale yellow liquid[28] of b.p. : 70-72°C/17 Torr.
1H-NMR ($CDCl_3$) : δ = 2.37(s,3H), 6.10(d,1H,J=0,4Hz), 6.42ppm(d,1H)
IR(film) : ν = 3095, 3020, 2940, 2215, 1575, 1440, 1380, 1280, 1155, 910cm^{-1}
M.S.(EI) : m/e = 147, 132, 120, 95, 52.

Methyl 2-phenylselenopropenoate 11d : purified by chromatography on silicagel[27] (CH_2Cl_2) and distillation ; pale yellow oil[17] of b.p.:65-67°C/0.01 Torr
1H-NMR($CDCl_3$) : δ = 3.70(s,3H), 5.15(d,1H, J=0.6Hz), 6.45(d,1H), 7.23(m,3H), 7.50ppm(m,2H)
13C-NMR($CDCl_3$) : δ = 52.54(Qs), 124.90(Ts), 127.05(Sm,C-1Ph), 129.01(Dt,C-4Ph), 129.78(Dm,C-2,6Ph), 135.16(Sm), 136.42(Dm,C-3,5Ph), 164.90ppm(Sm).
IR(film) : ν = 2940, 1700, 1580, 1420, 1365, 1260, 1225, 1090, 1005, 900 cm^{-1}
M.S.(CI/IB) : 243(M+1)$^+$;165, 157, 77, 51.

Tert-butyl 2-phenylselenopropenoate 11e : purified by chromatography on silicagel[27] (pet.ether/AcOEt = 95:5) and distillation ; rather unstable pale yellow oil[29]. b.p. : 64°C/0.005 Torr.

1H-NMR ($CDCl_3$) : δ = 1.53(s,9H), 5.25(d,1H,J=0.6Hz), 6.55(d,1H), 7.14(m,3H), 7.50ppm(m,2H)
IR(film) : ν = 3060, 2940, 1720, 1615, 1580, 1480, 1440, 1245, 1040, 690 cm^{-1}
M.S.(CI/IB) : 273$(M+1)^+$; 195, 157, 77, 51

Methyl 2-methylselenopropenoate 11f : purified by distillation, an unstable pale yellow liquid[29].
b.p. : 55-57°C/2 Torr
1H-NMR($CDCl_3$) : δ = 2.08(s,3H), 3.75(s,3H), 5.52(d,1H,J=0.93Hz), 6.67ppm(d,1H)
IR(film) : ν = 3060, 2940, 1710, 1580, 1480, 1440, 1090, 690 cm^{-1}
M.S.(CI/IB) : 181$(M+1)^+$, 165, 95.

Methyl 2-phenylseleno-2-butenoate 11g : Elimination is performed in refluxing benzene. Distillation affords a pale yellow oil[17] of b.p. : 60-62°C/0.01 Torr
1H-NMR ($CDCl_3$) : δ = 2.04(d,3H), 3.67(s,3H), 7.21(m,3H), 7.36(m,2H), 7.48ppm(q,1H)
13C-NMR ($CDCl_3$) : = 17.71(Qd), 51.29(Qs), 124.49(Sm,C-1Ph), 125.62(Dt,C-4Ph), 128.18(Dm,C-2,6Ph), 129.82(Dm,C-3,5Ph), 130.15(Sm), 147.93(Dq), 164.73ppm(Sm)
IR(film) : ν = 3060, 2950, 1720, 1610, 1580, 1480, 1440, 1245, 1040, 690 cm^{-1}
M.S.(EI) : m/e = 256 ; 197, 157, 99, 77, 51.

2-Phenylselenopropenamide 11h : Elimination is done in refluxing $CHCl_3$ and the mixture is then poured into water (100ml). Extraction (CH_2Cl_2), drying ($MgSO_4$) filtration and evaporation of the solvent leaves a solid which is recrystallized in CH_2Cl_2/n-hexane(8/2), white crystals[30] of m.p. : 108°C
1H-NMR ($CDCl_3$) : δ = 5.94(d,1H), 6.52(br,2H), 6.81(d,1H), 7.28(m,3H), 7.45ppm (m,2H).
13C-NMR ($CDCl_3$) : δ = 124.27(Ts), 129.53(Sm,C-1Ph), 129.86(Dt,C-4Ph), 130.98(Dm,C-2,6Ph), 136.30(Dm,C-3,5Ph), 139.77(Sm), 170.12ppm(Sm)
IR (CH_2Cl_2) : ν = 3500, 3390, 3090, 1680, 1590, 1580, 1565, 1480, 1440, 1390, 1130, 1020, 690 cm^{-1}
M.S.(EI): m/e = 227, 211, 183, 157, 77.

2-Phenylselenopropenal 11i : purified by chromatography on silicagel (CH_2Cl_2) ; unstable pale yellow oil[21]
1H-NMR ($CDCl_3$) : δ = 5.85(d,1H, J=1.1Hz), 6.45(d,1H), 7.4(m,5H), 9.45ppm(s,1H)
IR(film) : ν = 3010, 2850, 2820, 2760, 1680, 1580, 1440, 1020, 980, 690 cm^{-1}.

2-Phenylseleno-2-butenal 11j : elimination must be effected 2.5 hrs after addition of selenenyl halide to crotonaldehyde ; purified by distillation ; pale yellow oil[17,21] of b.p. : 60-62°C/0.01 Torr.
1H-NMR ($CDCl_3$) : δ = 2.18(d,3H), 7.21(m,3H), 7.27(q,1H), 7.36(m,2H), 9.38ppm(s,1H)
13C-NMR ($CDCl_3$) : δ = 18.18(Qd), 126.04(Dt,C-4Ph), 128.39(Dm,C-2,6Ph), 128.97(Sm,C-1Ph), 130.53(Dm,C-3,5Ph), 135.95(Ddq), 158.02(Dq), 189.76ppm(Dd)
IR(film) : ν = 3060, 2820, 2735, 2690, 1695, 1610, 1580, 1480, 1440, 1370, 1170, 1070, 1025, 740, 690 cm^{-1}
M.S.(EI) : m/e = 226, 197, 182, 157, 77, 69, 51.

2-Methylselenopropenal 11k : Elimination effected at -40°C ; this compound undergoes a very rapid dimerization (15 min) to give the dihydropyrane[22]. All attempts to purify **11k** led to isolation of the dimer.
1H-NMR ($CDCl_3$) : δ = 2.20(s,3H), 2.56(s,3H), 6.27(d,1H), 6.65(d,1H), 9.5ppm(s,1H)

3-Phenylseleno-3-buten-2-one 11l : purified by flash chromatography on silicagel (Pet.ether/AcOEt : 9/1) gives a pale yellow oil which can be crystallized from CCl_4 at -20°C. The product is unstable at room temperature[21] ; m.p. : 32°C.
1H-NMR ($CDCl_3$) : δ = 2.4(s,3H), 5.45(d,1H,J=1.74 Hz), 6.40(d,1H), 7.40-7.70ppm (m,5H).
IR(film) : ν = 3010, 1660, 1600, 1580, 1360, 1020, 910 cm^{-1}
M.S.(EI) : m/e = 226 ; 183, 157, 77, 51, 43.

1-Phenylselenovinyl phenyl ketone 11m : purified by flash chromatography on silicagel (benzene), unstable yellow oil[21]
1H-NMR ($CDCl_3$) : δ = 5.87(d,1H, J=1.50Hz), 6.05(d,1H), 7.40ppm(m,10H)
IR(film) : ν = 3070, 1640, 1590, 1570, 1470, 1440, 1260, 1020, 910 cm^{-1}.

1-Phenylthiovinyl phenyl sulfoxide 10n : purified by chromatography on silicagel[27] (CH_2Cl_2) and recrystallized from a mixture AcOEt/Pet.ether (2/8) at -20°C ; colorless crystals ; m.p. : 46-47°C.; b.p. : 140-143°C/0.001 Torr
1H-NMR ($CDCl_3$) : δ = 5.87(d,1H,J=1.40Hz), 6.57(d,1H), 7.10(s,5H), 7.27(m,3H), 7.57ppm(m,2H)
13C-NMR ($CDCl_3$) : δ = 123.09(Ts), 125.0(Dm,C-2,6S(O)Ph), 127.29(Dt,C-4SPh), 128.31(Dm,C-3,5S(O)Ph), 128.70(Dm,C-2,6SPh), 130.31(Dm,C-3,5SPh), 130.92(Dt,C-4S(O)Ph), 131.25(Sm,C-1SPh), 141.93(Sm,C-1S(O)Ph), 149-89ppm(Sm)
IR (CH_2Cl_2) : ν = 3060, 1580, 1480, 1440, 1260, 1090, 1070, 1050, 1025, 690 cm^{-1}.
M.S.(CI/IB) : 521$(2M+1)^+$; 395$(M+135)^+$; 261$(M+1)^+$; 151, 135, 109.
Found : C : 64.39, H : 4.40, O : 6.30, S : 25.28, $C_{14}H_{12}OS_2$
Requires : C : 64.58, H : 4.64, O : 6.14, S : 24.63.

1-Phenylselenovinyl phenyl sulfoxide 11o : recrystallization from CH_2Cl_2/Pet.ether (1/3) at -20°C ; colorless crystals. m.p. : 35°C.

1H-NMR ($CDCl_3$) : δ = 5.95(d,1H,J=1.92Hz),6.85(d,1H), 7.07(m,5H), 7.17(m,3H), 7.48ppm(m,2H)
13C-NMR ($CDCl_3$) : δ = 124.89(Dm,C-2,6S(O)Ph), 125.20(Dd), 127.25(Dt,C-4Se-Ph), 127.64(Dm,C-3,5S(O)Ph), 128.04(Sm,C-1SePh), 128.51(Dm,C-2,6SePh), 130.61(Dt,C-4S(O)Ph), 132.63(Dm,C-3,5SePh), 141.69(Sm,C-1S(O)Ph), 146.35ppm(St).
IR (CH_2Cl_2) : ν = 3090, 3060, 1580, 1480, 1440, 1090, 1070, 1050, 1020, 690 cm^{-1}.
M.S.(CI/CH_4) : 309(M+1)$^+$; 183.

Found : C : 54.81, H : 4.01, O : 5.31, S : 10.40, $C_{14}H_{12}OSSe$
Requires : C = 54.72, H : 3.94, O : 5.21, S : 10.43.

1-Methylselenovinyl phenyl sulfoxide 11p : purified by chromatography on silicagel[27] (CH_2Cl_2)/AcOEt : 9/1) and distillation ; a pale yellow oil ; b.p. : 100-105°C/0.005 Torr.
1H-NMR ($CDCl_3$) : δ = 1.90(s,3H), 5.91(d,1H, J=0.9 Hz), 6.67(d,1H), 7.38(m,3H), 7.60ppm(m,2H)
13C-NMR ($CDCl_3$) :δ = 7.49(Qs), 121.23(Ts), 124.52(Dm,C-3,5Ph), 127.98(Dm,C-2,6Ph), 130.46(Dt,C-4Ph), 141.96(Sm,C-1Ph), 146.90ppm(Sm)
IR(film) : ν = 3060, 2940, 1580, 1440, 1045, 1035, 1025, 910, 775, 690 cm^{-1}
M.S.(EI) m/e = 246 ; 151, 126, 120, 77, 51.
Found : C : 43.86, H : 4.18, $C_9H_{10}OSSe$
Requires : C : 44.08, H : 4.11

1-Phenylthiovinyl ethyl sulfone 10q : purified by chromatography on silicagel[27] (Pet. ether./AcOEt : 9/1) and distillation : a colorless oil of b.p. : 109-110°C/0.01 Torr.
1H-NMR ($CDCl_3$) : δ = 1.30(t,3H), 3.15(q,2H), 5.63(d,1H,J=1.60Hz), 6.33(d,1H), 7.32ppm(m,5H)
IR(film) : ν = 3060, 2990, 2940, 1600, 1580, 1480, 1440, 1315, 1150, 1025, 690 cm^{-1}
M.S.(EI) : m/e = 228 ; 199, 151, 135, 109, 77, 51
Found : C : 52.41, H : 5.40, O : 14.0, S : 28.12, $C_{10}H_{12}O_2S_2$
Requires : C : 52.60, H : 5.30, O : 14.01, S : 28.08.

1-Phenylselenovinyl ethyl sulfone 11r : purified by chromatography on silicagel[27] (CH_2Cl_2) and distillation ;a pale yellow oil of b.p. : 95-97°C/0.001 Torr
1H-NMR ($CDCl_3$) : δ = 1.30(t,3H), 3.2(q,2H), 5.84(d,1H, J=1.98Hz), 6.76(d,1H), 7.40(m,3H), 7.64ppm(m,2H).
13C-NMR ($CDCl_3$) : δ = 6.55(Qt), 46.18(Tq), 126.65(Sm,C-1Ph), 128.23(Dt,C-4Ph), 129.36(Dm,C-2,6Ph), 129.58(Ts), 134.52(Dm,C-3,5Ph), 140.72ppm(Sm).
IR(film) : ν = 3070, 2940, 1590, 1580, 1480, 1440, 1315, 1150, 1090, 790 cm^{-1}.
M.S.(EI) : m/e = 276; 183, 157, 117, 77, 51.
Found : C : 43.67, H : 4.54, S : 11.61, $C_{10}H_{12}O_2SSe$.
Requires : C : 43.64, H : 4.39, S : 11.65.

1-Phenylselenovinyl phenyl sulfone 11s : obtained by cristallization from diethylether ; colorless crystals ; m.p. : 68-69°C.
1H-NMR ($CDCl_3$) : δ = 5.98(d,1H, J=1.90 Hz), 7.0(d,1H), 7.33(m,5H), 7.63(m,3H), 8.0 ppm(m,2H).
13C-NMR ($CDCl_3$) : δ = 127.53(Sm,C-1SePh), 128.41(Dm,C-2,6SO_2Ph), 128.79 (Dt,C-4SePh), 128.79(Dm,C-3,5SO_2Ph), 129.44(Dm,C-2,6SePh), 130.48(Ts), 133.59(Dt,C-4SO_2Ph), 134.17(Dm,C-3,5SePh), 138.23(Sm,C-1SO_2Ph), 144.08ppm(St).
IR (CH_2Cl_2) : ν = 3070, 1590, 1580, 1480, 1440, 1320, 1310, 1155, 1080, 775, 690 cm^{-1}.
M.S.(EI) : m/e = 324; 298, 183, 157, 141, 77, 51.
Found : C : 51.75, H : 3.82, $C_{14}H_{12}O_2SSe$
Requires : C : 52.02, H : 3.74

Bis-(1-phenylselenovinyl)sulfone 11t : purified by chromatography on silicagel[27] (Pet. ether/AcOEt : 9/1) and recrystallisation from ethanol as colorless crystals. m.p. 49-50°C
1H-NMR ($CDCl_3$) : δ = 5.99(d,2H, J=2.0 Hz), 6.94(d,2H), 7.37(m,6H), 7.58ppm(m,4H).
13C-NMR ($CDCl_3$) : δ = 127.26(Sm,C-1Ph), 129.02(Dt,C-4Ph), 129.64(Dm,C-3,5Ph), 132.33(Ts), 134.64(Dm,C-2,6Ph), 140.87 ppm (Sm).
IR(CH_2Cl_2) : ν = 3070, 3040, 1590, 1580, 1480, 1440, 1300, 1140, 1070, 1015, 780, 690 cm^{-1}
M.S.(EI) : m/e = 430; 273, 183, 157, 77, 51.
Found : C : 44.82, H : 3.25, $C_{16}H_{14}O_2SSe_2$
Requires : C : 44.87, H : 3.29.

1-Methylselenovinyl phenyl sulfone 11u : purified by chromatography on silicagel[27] (CH_2Cl_2) and recrystallization from a mixture CH_2Cl_2/n-hexane (6/4) at -20°C as colorless crystals. M.p. : 63-64°C.
1H-NMR($CDCl_3$) : δ = 2.14(s,3H), 5.98(d,1H, J=1.71 Hz), 6.88(d,1H), 7.56(m,3H), 7.94ppm(m,2H)
13C-NMR($CDCl_3$) : δ = 8.65(Qs), 127.53(Ts), 127.92(Dm,C-2,6Ph), 128.64(Dm,C-3,5Ph), 133.34(Dt,C-4Ph), 138.21(Sm,C-1Ph), 142.97ppm(Sm)
IR(CH_2Cl_2) : δ = 3060, 2940, 1580, 1440, 1315, 1305, 1155, 1075, 915, 690 cm^{-1}
M.S.(EI) : m/e = 262; 121, 95, 77, 51

Found : C : 41.80, H : 3.99, S : 12.53, $C_9H_{10}O_2SSe$
Requires : C : 41.39, H : 3.86, S : 12.27

1-Nitro-2-phenylselenoethylene 25 : purified by chromatography on silicagel (cyclohexane, then CH_2Cl_2) crystallization from a mixture ether/n-hexane (2/3) gives the cis-isomer as yellow needles. m.p.: 69-70°C
b.p.(trans-isomer) : 90-93°C/0.005 Torr as a yellow oil
1H-NMR($CDCl_3$) : cis-isomer : δ = 7.36(m,3H), 7.56(m,3H), 7.91ppm(d,1H, J=7.16Hz) ; trans-isomer : δ = 6.6(d,1H, J=13.40Hz), 7.22(m,5H), 8.38ppm(d,1H)
13C-NMR ($CDCl_3$) : cis-isomer : δ = 129.19(Dt,C-4Ph), 129.72(Dm,C-3,5Ph), 131.32(Sm,C-1Ph), 133.14(Dm,C-2,6Ph), 133.14(Dm), 146.66ppm(Dd)
IR (CH_2Cl_2) : ν = 3090, 3070, 1585, 1570, 1480, 1330, 1300, 1160, 790 cm^{-1}
M.S.(EI) : m/e = 229; 183, 157, 152, 77, 51.
Found : C : 42.10, H : 3.33, N : 6.21, O : 14.12, $C_8H_7NO_2Se$
Requires : C : 42.12, H : 3.09, N : 6.14, O : 14.03.

Acknowledgements : One of us (S.P.) is indebted to I.R.S.I.A.(Belgium) for a grant. Financial support by SPPS grant 79/84-13 is gratefully acknowledged. We further thank Mrs A. Mockel for the recording of ^{1}H-NMR spectra.

REFERENCES and FOOTNOTES

(1) Captodative Substitution Effect Part XX : S. Mignani, Z. Janousek, R. Merényi et H.G. Viehe, Bull. Soc. Chim. France, submitted.

(2) Z. Janousek, S. Piettre, F. Gorissen-Hervens and H.G. Viehe, J. Organometal. Chem.**250**, 197 (1983)

(3) See a) W.H. Mueller, Angew. Chem. Int. Ed. Engl.**8**, 482 (1969) ; b) L. Rasteikiene, D. Greiciute, M.G. Linkova and I.L. Knunyants, Russ. Chem. Rev., **46**, 548 (1977) ; c) G. A. Jones, C.J.M. Stirling and N.G. Bromby, J. Chem. Soc., Perkin Trans II, 385 (1983) ; see also references (4) and (5)

(4) W.A. Smit, N.S. Zefirov, I.V. Bodrikov and M.Z. Krimer, Acc. Chem. Res.**282** (1979) and references cited therein.

(5) G.H. Schmid and D. Garatt in "The Chemistry of Double Bonded Functional Groups", S. Patai Editor, Wiley, New York 1977, Chapter 9.

(6) See for example, a) K. C. Nicoleaou, Tetrahedron Report, Tetrahedron **37**, 4097 (1981) ; b) M. Ihara, Y. Haga, M. Yonekura, T. Ohsawa, K. Fukumoto, T. Kametani, J. Am. Chem. Soc.**105**, 7345 (1983)

(7) V.M. Csizmadia, G.H. Schmid, P.G. Mezey and G.I. Csizmadia, J. Chem. Soc., Perkin Trans. II, 1019 (1977).

(8) a) W.A. Thaler, W.H. Mueller and P.E. Butler, J. Am. Chem. Soc.**90**, 2069 (1968) ; b) see reference (3b) ; c) K.D. Gundermann, Intra-Science Chem. Rept, 6, 91 (1972) ; d) S.A. Heininger and G.H. Birum, U.S. Patent 2,870,209 (1959) C.A. **53**, 9152a.

(9) a) H. Chartier, Bull. Soc. Chim. France 2887 (1972) ; b) M.G. Linkova, D. Greiciute, L. Rasteikiene and I.L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim. 2522 (1971) ; c) F.R. Tantasheva, V.S. Savel'ev, E.A. Bernikov and E.G. Kataev, Zh. Org. Khim.**14**, 478 (1978) ; d) D.I. Relyea and R.A. Davis, Eur. Pat. Appl. 25339 (1981) ; C.A.**95** : 115048a (1981).

(10) G.H. Schmid and D.G. Garratt, Tetrahedron Letters **24**, 5299 (1983).

(11) A.E. Feiring, J. Org. Chem.**45**, 1962 (1980)

(12) D.G. Foster, Rec. Trav. Chim. Pays-Bas,**53**, 405 (1934)

(13) a) D.G. Garratt and G.H. Schmid, Can. J. Chem.**52**, 3599 (1974) ; b) D.G. Garratt and G.H. Schmid, J. Org. Chem.**42**, 1776 (1977) ; c) H.J. Reich and J.E. Trend, Can. J. Chem.**53**, 1922 (1975)

(14) Such a nucleophilic attack at the selenium atom by halide ions was already been observed; a) W. Dumont, M. Sevrin and A. Krief, Tetrahedron Letters **19**, 183 (1978) ; b) H. Gilman and F.J. Webb, J. Am. Chem. Soc., **71**, 4062 (1949) ; c) D.L.J. Clive and al. Ibid. **102**, 4438 (1980) ;

d) J.L. Kice and H.S. Tilk, Ibid. **104**, 7123 (1982) ; e) A. Krief, Bull. Soc. Chim. France, II 519 (1980) ; f) S. Halazy and A. Krief, Tetrahedron Letters **21**, 1997 (1980). g) H.G. Viehe, S. Piettre, unpublished results. h)coupling constants of the ABX pattern of 3,4-dichlorobutan 2-one have been compared with an authentic sample obtained by chlorine addition to methyl vinyl ketone.

(15) E.G. Kataev, T.G. Mannafov and O.O. Saidov, Zh. Org. Khim.**7**, 2229 (1971).

(16) M. Verny and R. Vessière, Bull. Soc. Chim. France **1970**, 746.

(17) T.H. Hase and P. Kukkola, Synth. Commun. **10**, 451 (1980).

(18) J.-N. Denis and A. Krief, Tetrahedron Letters **23**, 3411 (1982).

(19) M. Shimizu, R. Takeda and I. Kuwajima, Tetrahedron Letters **20**, 3461 (1979).

(20) G. Zima and D. Liotta, Synth. Commun. **9**, 697 (1979).

(21) These compounds were independently synthesized by different methods : a) G.M. Ksander, J.E. Mc Murry and M. Johnson, J. Org. Chem. **42**, 1180 (1977); b) H.J. Reich, S.K. Shah, P.M. Gold and R.E. Olson, J. Am. Chem. Soc. **103**, 3112 (1981); c) K. Uneyama, K. Takano and S. Torii, Bull. Chem. Soc. Jpn, **56**, 2867 (1983); d) I. Kuwajima and M. Shimizu, Tetrahedron Lett., **19**, 1277 (1978); e) B. Harirchian and Ph. Magnus, J. Chem. Soc. Chem. Commun. **1977**, 522.

(22) Ch. De Cock, S. Piettre, F. Lahousse, Z. Janousek, R. Merényi and H.G. Viehe, Tetrahedron.: submitted.

(23) The cis.isomer can be easily isolated by crystallization.

(24) R. Verbruggen and H.G. Viehe, Chimia **29**, 350 (1975).

(25) Till now, only tert-butyl nitroacetylene could be isolated in pure state : see V. Jager and H.G. Viehe, Angew. Chem. Internat. Edit. **8**, 273 (1969).

(26) H.J. Reich, J.M. Renga and I.L. Reich, J. Am. Chem. Soc., **97**, 5434 (1975).

(27) Modified Flash Chromatography : D.F. Taber, J. Org. Chem. **47**, 1351 (1982).

(28) Correct elemental analysis could not be obtained, because of rapid dimerization of this olefin at room temperature; cf reference (22).

(29) These olefins easily form oligomeric products at room temperature.

(30) This product decomposes slowly at room temperature.