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Review

VINYLIC SELENIDES

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INTRODUCTION

Although vinyl ethers and sulphides are useful intermediates in organic synthesis, their selenium analogs have received little attention. In recent years, however, a number of methods for preparing vinylic selenides, as well as some valuable synthetic applications of these compounds have appeared in the literature. The aim of this article is to emphasize the synthetic potentialities of this class of organic compounds, and in the forthcoming pages, the methods available for preparing vinylic selenides, as well as some synthetic transformations that can be done by using them as starting materials, are described.

1. PREPARATION OF VINYLIC SELENIDES

(A) From vinyl halides (vinyl Grignard reagents)

The reaction of vinyl Grignard reagents with diaryldiselenides or arylselenenyl halides (eqn.1) is the most convenient method for preparing vinylic selenides, provided that the corresponding vinyl halide is easily available. The reaction occurs in few minutes, at 0ºC, in tetrahydrofuran (THF). Some vinylic selenides which have recently been synthesized by this method are listed in table 1 |1|.

Table 1

$$\mathrm{RCH{=}CHMgBr} \quad + \quad \mathrm{ArSeX} \xrightarrow[0^\circ C]{THF} \mathrm{RCH{=}CHSeAr} \qquad (1)$$

X = Br, ArSe

R	Ar	yield %	ref.
H	Ph	67	1,2
H	$m\text{-}CF_3C_6H_4$	60	1
CH_3	Ph	92	1

(B) From olefins

The reaction of ethylene with arylselenenyl halides in chloroform leads to the corresponding β-haloarylselenide I |3,4|. Dehydrohalogenation of these intermediates with potassium t-butoxide in t-butyl alcohol, leads to the vinylarylselenide II in good yields |4| (eqn.2, Table 2).

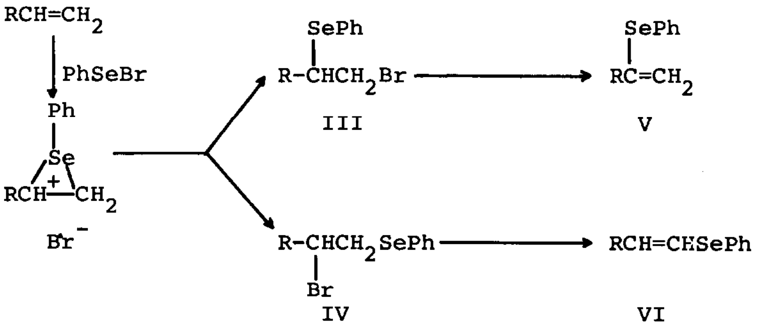
Table 2

$$\mathrm{ArSeX} + \mathrm{CH_2{=}CH_2} \xrightarrow{\mathrm{CHCl_3}} \underset{\mathrm{I}}{\mathrm{ArSeCH_2CH_2X}} \xrightarrow[\text{t-BuOH}]{\text{t-BuOK}} \underset{\mathrm{II}}{\mathrm{ArSeCH{=}CH_2}} \qquad (2)$$

Ar	X	I yield%	II yield%
p-$CH_3OC_6H_4$	Cl	69	78
p-$CH_3C_6H_4$	Cl	75	75
p-ClC_6H_4	Cl	80	69
p-BrC_6H_4	Cl,Br	72	79
m-BrC_6H_4	Br	—	74
p-$NO_2C_6H_4$	Cl	81	81

On the other hand, the addition of phenylselenenyl bromide to substituted olefins leads to a mixture of β-bromoalkylphenylselenides, the ratio of products depending upon the reaction conditions. Under kinetic control (PhSeBr,THF,-78°C) the main product is the anti Markownikoff adduct III (Scheme I), but under thermodynamic control (PhSeBr,CH_3CN,25°C) the Markownikoff product IV predominates |5|. Dehydrohalogenation of the β-bromoalkylphenylselenide III or IV with potassium t-butoxide in tetrahydrofuran produces the vinylic selenides V and VI, respectively, in high yield (Table 3). In most cases, mixtures of the Z and E isomers are formed |5|.

Scheme 1



In an analogous way has been prepared 2,2-difluoroethylphenylselenide VII. Addition of phenylselenenyl chloride or bromide to vinylidene fluoride gave the respective 2,2-difluoroethylphenylselenides VII in 90% yield (eqn.3) |6|.

Table 3
Vinylic selenides obtained from dehydrohalogenation of β-bromoalkylphenylselenides* |5|.

R	Kinetic Control[a] V/VI**	Thermodynamic Control[b] V/VI**
CH_3	85:15	9:91
$n\text{-}C_4H_9$	90:10	8:92
$n\text{-}C_6H_{13}$	90:10	9:91
$n\text{-}C_{14}H_{29}$	90:10	7:93
$i\text{-}C_4H_9$	90:10	8:92
$PhCH_2$	98:2	2:98
$i\text{-}C_3H_7$	98:2	3:97
$t\text{-}C_4H_9$	100:0	0:100
$CH_3(CH_2)_3C(CH_3)_2$	100:0	0:100

* The yields are always >85%.

** Ratio of anti-Markownikoff/Markownikoff product.

a) PhSeBr (THF,-78°C); t-BuOK(THF,-78°C to 25°C)

b) PhSeBr (CH_3CN,25°C);t-BuOK(THF,25°C)

$$PhSeX \quad + \quad CH_2{=}CF_2 \longrightarrow PhSeCH_2CF_2X \qquad (3)$$

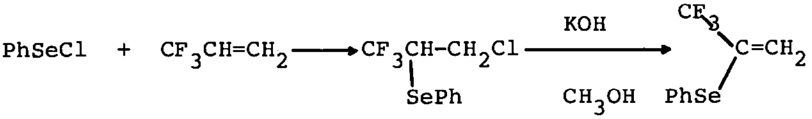
VIIa X = Cl
VIIb X = Br

Treatment of VIIa with anhydrous potassium fluoride in acetonitrile containing a catalytic amount of 18-Crown-6 at 60°C (eqn.4) yielded a mixture of the vinylic selenide VIII and trifluoride IX |6|.

$$VIIa \longrightarrow \underset{VIII}{PhSeCH{=}CF_2} \longrightarrow \underset{IX}{PhSeCH_2CF_3} \qquad (4)$$

In contrast, the bromide VIIb, under identical conditions, gave only the vinylic selenide VIII in 85% yield.

In the same way phenylselenenyl chloride adds to 3,3,3-trifluoropropene X giving the adduct XI in 95% yield. This last compound eliminates HCl upon treatment with potassium hydroxide in methanol at 10°C leading to the corresponding vinylic selenide XII in 95% yield (Eqn.5) |7| .



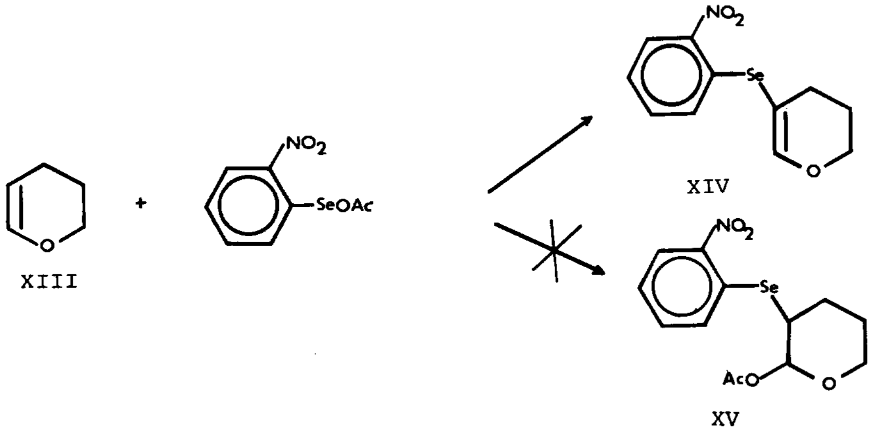
$$PhSeCl + CF_3CH{=}CH_2 \longrightarrow \underset{\textstyle SePh}{CF_3\overset{|}{C}H}{-}CH_2Cl \xrightarrow[CH_3OH]{KOH} \begin{matrix} CF_3 \\ PhSe \end{matrix}\rangle C{=}CH_2 \qquad (5)$$

X XI XII

(C) From activated olefins

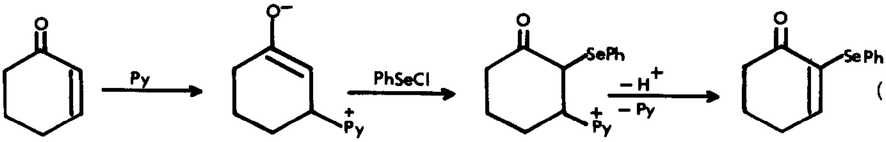
Reaction of seleneny1 acetates in acetic acid with olefins bearing an activating group, e.g. dihydropyran XIII, gives vinylselenides XIV rather than the addition product XV (Scheme 2) |8|.

Scheme 2



The reaction probably proceeds through an addition-elimination pathway. Substitution of acetic acid for pyridine as solvent allows the reaction to occur with seleneny1 bromides and cyanates (Table 4) |8|.

The reaction of the phenylseleneny1 chloride/pyridine complex with α-β unsaturated ketones leads to the corresponding α-phenylseleno enones (Eqn.6) |9|. The reaction pathway depicted below has been proposed to account for this transformation.

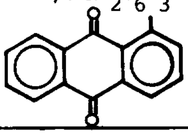


(6)

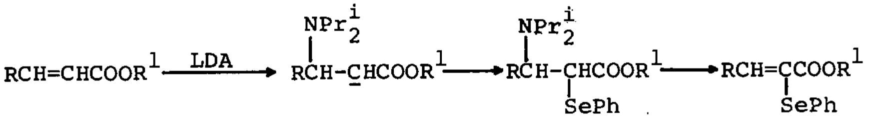
Examples of the products (XVI) are given in Table 5.

Table 4

$X_2C{=}CH_2 + ArSeY \longrightarrow X_2C{=}CHSeAr$

X	Ar	Y/solvent
Ph	$o\text{-}NO_2C_6H_4$	OAc/HOAc
$p\text{-}CH_3OC_6H_4$	$o\text{-}NO_2C_6H_4$	OAc/HOAc
$3,4\text{-}(CH_3O)_2C_6H_3$	$o\text{-}NO_2C_6H_4$	OAc/HOAc
$2,4\text{-}(CH_3O)_2C_6H_3$	$o\text{-}NO_2C_6H_4$	OAc/HOAc
$p\text{-}(CH_3)_2NC_6H_4$	$o\text{-}NO_2C_6H_4$	OAc/HOAc
$p\text{-}(CH_3)_2NC_6H_4$	$o\text{-}NO_2C_6H_4$	Br/py
$p\text{-}(CH_3)_2NC_6H_4$	$o\text{-}NO_2C_6H_4$	OAc/py
$p\text{-}(CH_3)_2NC_6H_4$	$2,4\text{-}NO_2C_6H_3$	OAc/py
$p\text{-}(CH_3)_2NC_6H_4$	$2,4\text{-}NO_2C_6H_3$	C≡N/py
$p\text{-}(CH_3)_2NC_6H_4$		Br/py

α-β Unsaturated esters react with lithium diisopropylamide (LDA), giving the ester enolate anion XVII (eqn.7). Quenching of these anions with phenylselenenyl bromide gives the α-phenylseleno enoic ester XVIII |10| (Table 6).



$$RCH{=}CHCOOR^1 \xrightarrow{LDA} \underset{XVII}{\overset{NPr^i_2}{RCH}\text{-}\underline{C}HCOOR^1} \longrightarrow \overset{NPr^i_2}{RCH}\text{-}\underset{SePh}{C}HCOOR^1 \longrightarrow \underset{XVIII}{RCH{=}\underset{SePh}{C}COOR^1} \quad (7)$$

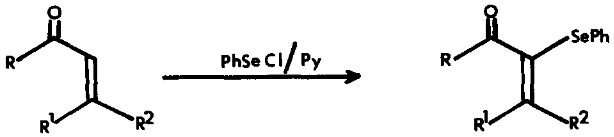
XVII XVIII

(D) Vinylic selenides from acetylenes

(a) Addition of selenols to acetylenes

The first method developed to prepare vinylic selenides was the addition of a selenol to an acetylene |11,12,13|. The regio and stereo chemistry of the products depends upon the experimental conditions. Two procedures have been employed: i) Reaction of neat arylselenols and acetylenes; ii) Reaction under basic conditions in an appropriate solvent.

Table 5



XVI

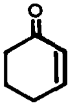
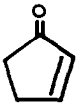
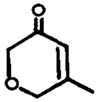
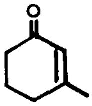
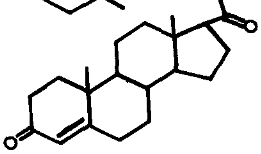
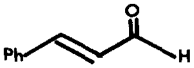
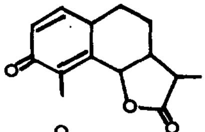
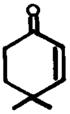
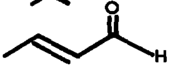
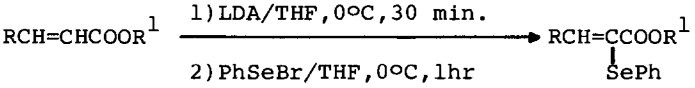
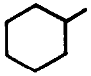
Substract	XVI yield%	reaction time/ temp. (°C)
	71	2 hr/25
	88	30 min/25
	88	3 hr/25
	45	3 days/25
	no reaction	2 days/60
	70	6 hr/25
	no reaction	2 days/60
	40	20 hr/25
	75	2 hr/25

Table 6



$$RCH{=}CHCOOR^1 \xrightarrow[2)\,PhSeBr/THF,0^oC,1hr]{1)\,LDA/THF,0^oC,30\ min.} RCH{=}\underset{\substack{|\\SePh}}{C}COOR^1$$

R	R^1	XVIII yield %
H	CH_3	18
CH_3	CH_3	64
$CH_3(CH_2)_2$	CH_2CH_3	66
$(CH_3)_2CHCH_2$	CH_2CH_3	71
$CH_3CH{=}CH$	CH_2CH_3	38
	CH_2CH_3	no reaction
$-(CH_2)_5-$	CH_2CH_3	no reaction

i) Reaction of neat arylselenols and acetylenes

Under these conditions the addition of selenophenol to phenylacetylene is immediate and exothermic, leading to the Z isomer in 90% yield |12,13,14,15,16|. The addition to aryl- and alkyl disubstituted acetylenes, as well as to monoalkylacetylenes is slow at room temperature, requiring a long reaction time, but becomes faster at higher temperatures. When the reaction is performed at room temperature or at 50°C, the vinylic selenides which result exhibit predominantly the Z configuration (95%Z) and only the regioisomer XIX showed in table 7 could be detected |16|, but at 120°C the stereoselectivity is lost and approximately equal amounts of the Z and E vinylic selenides are formed |16|. At 120°C besides the expected vinylic selenide, a "rearrangement" product XX is formed (eqn.8) |16|.

$$PhC{\equiv}C{-}R \xrightarrow[120^oC]{PhSeH\ neat} XIX + \underset{XX}{PhCH_2(PhSe)C{=}CHR^1} \qquad (8)$$

XXa $R^1 = CH_3$
XXb $R^1 = C_2H_5$
XXc $R^1 = n\text{-}C_3H_7$

Table 7

$$R^1C{\equiv}CR^2 \xrightarrow[\text{neat}]{\text{PhSeH}} R^1CH{=}C(SePh)R^2$$

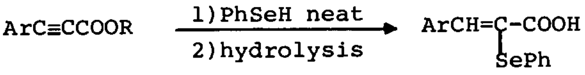
XIX

R^1	R^2	yield %*			
		a	b	c	d
Ph	H	90			
Ph	CH_3		90	85	64
Ph	C_2H_5		80	80	65**
Ph	$n\text{-}C_3H_7$		45	76	69**
Ph	$n\text{-}C_4H_9$		45	74	76**
$n\text{-}C_3H_7$	H		44	46	64
$n\text{-}C_4H_9$	$n\text{-}C_4H_9$		45	42	69
$n\text{-}C_4H_9$	$n\text{-}C_4H_9$				45

* Freshly distilled acetylenes must be used; ** Yield of the normal and rearranged addition products;a) the reaction is completed in few minutes at room temperature;b) 240 hr/r.t.;c) 48 hr/50°C; d) 24 hr/120°C.

Addition of selenophenol to arylpropiolates XXI , under the above conditions (eqn.9), proceeds easily, furnishing the α-substituted cinnamates XXII |17|. This reaction has been previously reported as giving the β-substituted cinnamate |12,18|. A radical mechanistic pathway was suggested to account for the regiochemistry of this reaction |17|.

Table 8



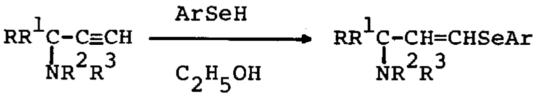
$$ArC{\equiv}CCOOR \xrightarrow[\text{2)hydrolysis}]{\text{1)PhSeH neat}} ArCH{=}\underset{\displaystyle SePh}{\underset{|}{C}}{-}COOH \qquad (9)$$

XXI XXII

Ar	yield%
Ph	73
$p\text{-}CH_3OC_3H_4$	78
$2,5\text{-}(CH_3O)_2C_6H_3$	62
$2\text{-}CH_3OC_{10}H_6$	82

Acetylenes containing an amino group attached to position 3 (eqn.10), react with selenols to give the corresponding vinylic selenide XXIII of predominant cis configuration |19,20,21|.

Table 9



$$\mathrm{RR^1\underset{NR^2R^3}{C}\text{-}C{\equiv}CH} \xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{ArSeH}} \mathrm{RR^1\underset{NR^2R^3}{C}\text{-}CH{=}CHSeAr} \qquad (10)$$

XXIII

R	R^1	R^2	R^3	yield% a	yield% b	yield% c	yield% d
CH_3	CH_3	H	H	74	80	90	96
CH_3	C_2H_5	H	H	76	87	90	93
C_2H_5	C_2H_5	H	H	78	80	90	93
$-(CH_2)_4-$		H	H	59	91	91	92
$-(CH_2)_5-$		H	H		89	90	75
CH_3	CH_3	H	CH_3				80
CH_3	CH_3	$(CH_2CH_2)_2O$					72
CH_3	CH_3	$-(CH_2)_5-$					65

Ar = a) $p\text{-}CH_3C_6H_4$; b) $o\text{-}CH_3C_6H_4$; c) $p\text{-}ClC_6H_4$; d) α-naphthyl

ii) Reaction under basic conditions

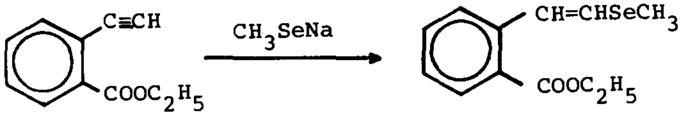
Under basic conditions the regiochemistry of the addition of selenols to arylpropiolates XXI, is the reverse of the one observed in the preceding method. The reaction affords exclusively β-substituted cinnamates XXIV of predominant Z stereochemistry (Michael addition) (eqn.11) |17|.

Table 10

$$\underset{\mathrm{XXI}}{\mathrm{ArC{\equiv}CCOOR}} \xrightarrow[\text{2) hydrolysis}]{\text{1) } \mathrm{PhSeH/CH_3ONa/CH_3OH}} \underset{\mathrm{XXIV}}{\mathrm{Ar(SePh)C{=}CHCOOH}} \qquad (11)$$

Ar	yield%
Ph	81
$p\text{-}CH_3OC_6H_4$	96
$2,5\text{-}(CH_3)_2C_6H_3$	40
$2,5\text{-}(CH_3O)_2C_6H_3$	68
$2\text{-}CH_3OC_{10}H_6$	55

In the same way ethyl o-ethynylbenzoate XXV undergoes regiospecific nucleophilic β-addition, by reacting with the methanoselenolate anion, affording the corresponding vinylic selenide XXVI in 64 % yield(Z:E ratio 9:1)|22|.

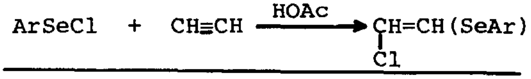


XXV XXVI

(b) <u>Addition of arylselenenyl halides to acetylenes</u>

The addition of arylselenenyl chlorides to acetylene occurs easily and in high yield by mixing the two reagents in acetic acid at room temperature (Table 11) |23|.

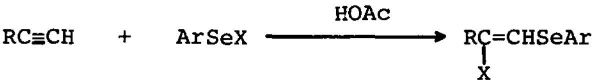
Table 11



$$\mathrm{ArSeCl} + \mathrm{CH{\equiv}CH} \xrightarrow{\mathrm{HOAc}} \underset{\mathrm{Cl}}{\mathrm{CH}}\mathrm{{=}CH(SeAr)}$$

Ar	yield%
p-$CH_3OC_6H_4$	85
p-$CH_3C_6H_4$	77
p-ClC_6H_4	78
p-BrC_6H_4	75
m-BrC_6H_4	69
p-$NO_2C_6H_4$	78

The addition of arylselenenyl halides to monosubstituted alkynes (eqn.12) has been reported as leading to the respective vinylic selenides XXVII with the <u>trans</u> configuration in 25-90% yield |24,25,26,27|.



$$\mathrm{RC{\equiv}CH} + \mathrm{ArSeX} \xrightarrow{\mathrm{HOAc}} \mathrm{R}\underset{\mathrm{X}}{\mathrm{C}}\mathrm{{=}CHSeAr} \qquad (12)$$

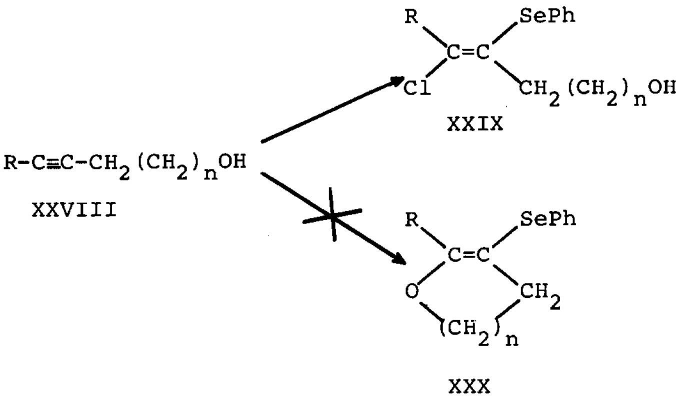
XXVII

Ar = p-$CH_3OC_6H_4$, p-$CH_3C_6H_4$, p-ClC_6H_4 X = Cl, Br
p- and m-BrC_6H_4

R = H, n-C_4H_9, p-$CH_3OC_6H_4$, p-$CH_3C_6H_4$, Ph, p-ClC_6H_4, p- and m-C_6H_4, p-$NO_2C_6H_4$

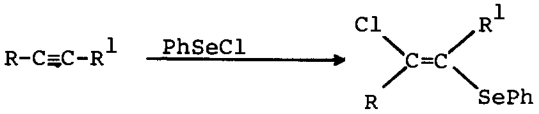
Reaction of phenylselenenyl chloride with a number of hydroxyalkynes XXVIII produced the corresponding vinylic selenides XXIX rather than the expected cyclization product XXX (Scheme 3) |28|.

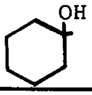
Scheme 3



The yields varied from poor to excellent (Table 12) and the products exhibited preferentially the trans stereochemistry.

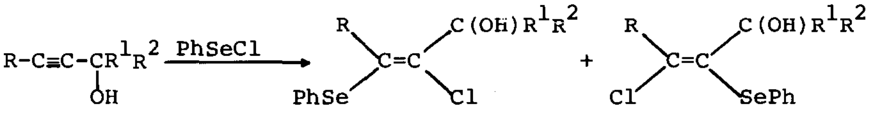
Table 12
Addition of phenylselenenyl chloride to hydroxyalkynes |28|



R	R^1	yield % a	yield % b
H	$(CH_2)_2OH$	84	89
CH_3	$(CH_2)_2OH$	44	66
H	$(CH_2)_3OH$	43	17
H	$(CH_2)_3OAc$	–	90
H	$(CH_2)_4OH$	55	60
H		80	90

a) Reaction performed in CH_3COOH at 24°C
b) Reaction performed in CH_2Cl_2 at -78°C

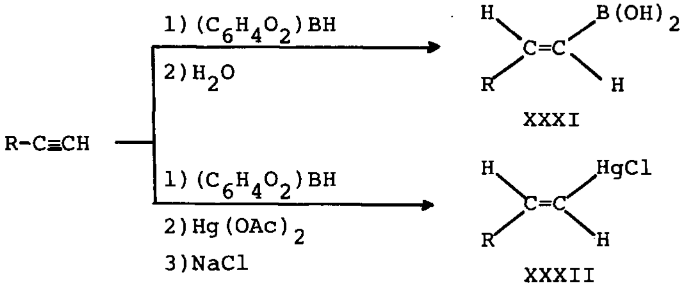
Addition of phenylselenenyl chloride to propargyl alcohols affords a mixture of the Markownikoff and anti-Markownikoff adducts. The regioselectivity was found to be dependent upon the nature of the substituents geminal to the alcoholic moiety. In general, the presence of bulky geminal substituents favours the formation of the anti-Markownikoff adduct under kinetic control (eqn.13) |29|.


(13)

(c) Reaction of phenylselenenyl halides with vinyl derivatives of boron and mercury

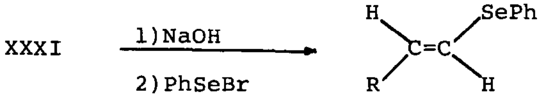
The vinyl derivatives of boron XXXI and mercury XXXII of E configuration, can be obtained from the corresponding acetylenes according to Scheme 4 |30|.

Scheme 4



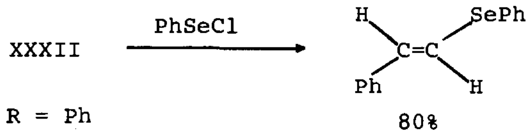
Treatment of the alkenylboronic acid XXXI with one equivalent of sodium hydroxide, followed by reaction with phenylselenenyl bromide (eqn.14), gives stereoselectively (E)-1-(phenylseleno)-1-alkenes in good yields (Table 13) |30|.

Table 13


(14)

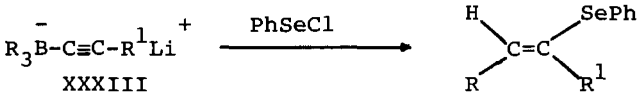
R	Yield %
n-C_4H_9	70
Ph	90

Likewise, reaction of alkenylmercuric chloride XXXII with phenylselenenyl chloride gives stereoselectively (E)-1-(phenylseleno)-2-phenylethene (Eqn.15) |30|.



(15)

Reaction of phenylselenenyl chloride with trialkylalkynylborate salts XXXIII followed by acid hydrolysis, gives a vinylic selenide (eqn.16) |31|.

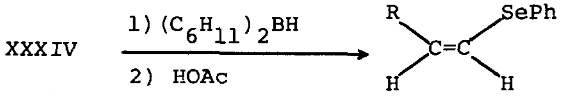


(16)

(d) Reduction of phenylselenoacetylenes

Reduction of phenylselenoacetylenes XXXIV with dicyclohexylborane followed by protonolysis with acetic acid, gives the corresponding vinylic selenide of Z configuration in 85-90 % yield (eqn.17) |30|.

Table 14

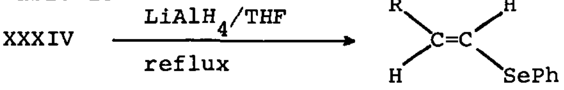


(17)

R	yield %
n-C_4H_9	85
Ph	90

Alternatively, phenylselenoacetylenes XXXIV can be reduced with lithium aluminium hydride in refluxing tetrahydrofuran, furnishing the vinylic selenides of the E configuration (eqn.18) |16|. The yields (Table 15) are, however, lower than in the preceding method.

Table 15



(18)

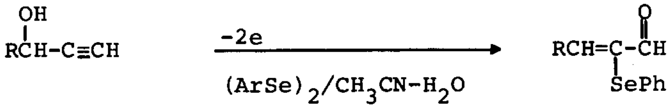
R	yield%
Ph	62
n-C_3H_7	62
n-C_4H_9	68

The starting phenylselenoacetylenes XXXIV can be prepared easily and in high yield from the corresponding lithium acetylides and phenylselenenyl bromide in THF (eqn.19) |16,32|.

$$R\text{-}C\equiv CH \xrightarrow[\text{2) PhSeBr/THF}]{\text{1) n-BuLi/THF}} \text{XXXIV} \qquad (19)$$

(e) Electrochemical oxidation of 3-hydroxyalkynes

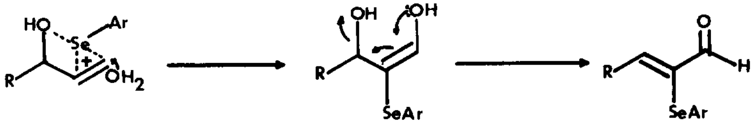
Electrochemical oxidation of 3-hydroxyalkynes in CH_3CN/H_2O in the presence of diaryldiselenides provides α-arylseleno enals XXXV in good yield (eqn.20) |33|.



$$R\overset{\displaystyle OH}{\overset{|}{C}}H\text{-}C\equiv CH \xrightarrow[(ArSe)_2/CH_3CN\text{-}H_2O]{-2e} RCH{=}\underset{\displaystyle SePh}{\underset{|}{C}}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}H \qquad (20)$$

XXXV

The triple bond is attacked in an anti-Markownikoff fashion by the electrooxidatively generated selenenylating reagent, followed by hydrolysis of the selenirenium type cation XXXVI from the less hindered side to give the enol XXXVII, which undergoes dehydration to the vinylic selenide XXXV.



XXXVI XXXVII XXXV

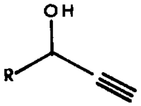
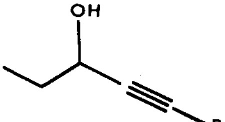
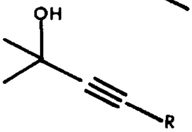
The substituent on the phenyl ring affects the yield. The most satisfactory results were obtained with p-chlorodiphenyldiselenide (Table 16) |33|.

(E) Vinylic selenides from allenes

Addition of phenylselenenyl chloride to allenes

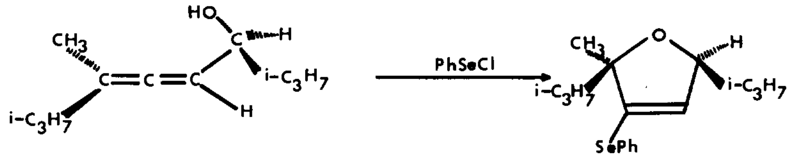
Phenylselenenyl chloride reacts with allenes in methylene dichloride at room temperature, generating vinylic selenides in quantitative yield (eqn.21) |34|. The phenylseleno moiety attacks regiospecifically the central allenic carbon. The resulting olefin XXXVIII exhibits the Z configuration preferentially. Unsymmetrical allenes furnish a mixture of products, whose relative amounts depend on the electron donating character and steric bulk of the alkyl substituent: the carbon atom bearing the most electron donating and sterically bulky substituent is preferentially attacked (Table 17) |34|. The role of steric versus electronic effects in the reaction of arylselenenyl halides with allenes has been studied |35|.

Table 16
Vinylic selenides from electrooxidative hydroxyselenation of 3-hydroxyalkynes |33|.

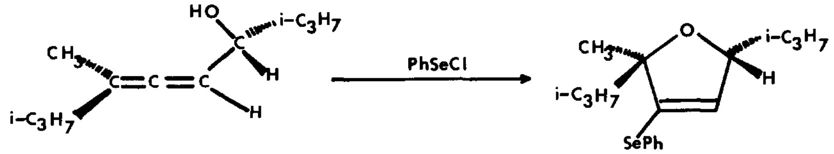
substracts	R	F/mol	XXXV yield %
	CH_3[b]	15	87
	C_2H_5[b]	26	81
	C_5H_{11}[b]	35	81
	Ph[b]	36	74
	Ph[b]	19	90
	C_4H_9[b]	30	94
	H[c]	30	62
	Ph[d]	16	65

a) Isolated yields based on p-chlorodiphenyldiselenide.
Electrolyte: b)Et_4NClO_4;c)Et_4NBr;d)Et_4NOTs.

Addition of phenylselenenyl chloride to α-allenic alcohols leads to 2,5-dihydrofurans (eqn.22). The yields are excellent (Table 18) |36|. The ring closure is stereospecific. Thus, reaction of phenylselenenyl chloride with (3-RS,5RS)-2,6,7-trimethyl-4,5-octadien-3-ol XXXIX yields Z-2,5-diisopropyl-2-methyl-3-phenylseleno-2,5-dihydrofuran XL, stereospecifically, whereas the corresponding (3-RS,5-SR) allenic alcohol XLI gives the analogous E-2,5-dihydrofuran XLII.

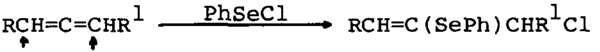


XXXIX XL



XLI XLII

Table 17
Vinylic selenides from the addition of phenylselenenyl chloride to allenes |34|.



$$\underset{\beta}{\mathrm{RCH}}\!=\!\mathrm{C}\!=\!\underset{\alpha}{\mathrm{C}}\mathrm{HR}^1 \xrightarrow{\mathrm{PhSeCl}} \underset{\mathrm{XXXVIII}}{\mathrm{RCH{=}C(SePh)CHR^1Cl}} \qquad (21)$$

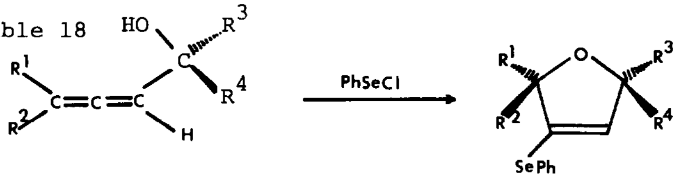
R	R^1	symmetric allenes	asymmetric allenes		
		E:Z ratio	α/β	α	β
				E:Z	E:Z
CH_3	CH_3	26:74			
C_2H_5	C_2H_5	40:60			
$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	36:64			
$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	0:100			
$-(CH_2)_6-$		100:0			
$-(CH_2)_{10}-$		36:64			
CH_3	C_2H_5		33:67	27:73	30:70
CH_3	$i\text{-}C_3H_7$		56:44	30:70	43:57
CH_3	$t\text{-}C_4H_9$		76:24	9:91	39:61

(F) Vinylic selenides from carbonyl compounds

(a) Dehydrohalogenation of α-haloalkylselenides

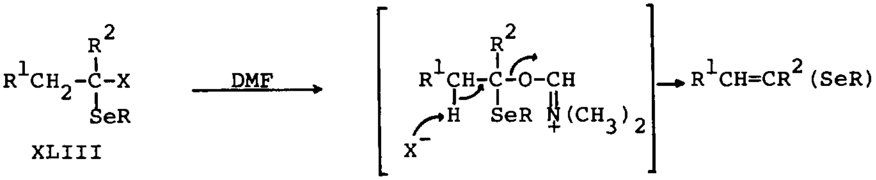
α-Halogenoalkyl selenides XLIII can be prepared in high yield from the reaction of a carbonyl compound with selenols in the presence of a haloacid |37|, or by reaction of arylselenenyl halides with diazoalkanes |32,38|. The bromo derivatives are transformed into vinylic selenides in good yield simply by heating in dimethylformamide (DMF) or dimethylacetamide (eqn.23) |39|. The α-chloroalkyl selenides do not react under these conditions, but are transformed into the vinylic selenides when NaBr is added to the reaction mixture (Table 19) |39|. The following mechanistic pattern has been proposed to account for this transformation.

Table 18



(22)

R^1	R^2	R^3	R^4	yield %
CH_3	CH_3	CH_3	C_2H_5	90
CH_3	CH_3	CH_3	$i\text{-}C_3H_7$	98
CH_3	CH_3	CH_3	$t\text{-}C_4H_9$	92
CH_3	CH_3	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	97
CH_3	$i\text{-}C_3H_7$	CH_3	$i\text{-}C_3H_7$	85
CH_3	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	CH_3	88
H	$i\text{-}C_3H_7$	H	$i\text{-}C_3H_7$	89
H	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	H	93
CH_3	C_2H_5	H	$i\text{-}C_3H_7$	79
CH_3	C_2H_5	$i\text{-}C_3H_7$	H	86
CH_3	$i\text{-}C_3H_7$	H	$i\text{-}C_3H_7$	90
CH_3	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	H	91
H	H	C_2H_5	C_2H_5	83
H	H	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	70
H	H	CH_3	$t\text{-}C_4H_9$	98
H	$i\text{-}C_3H_7$	C_2H_5	C_2H_5	95



XLIII

(23)

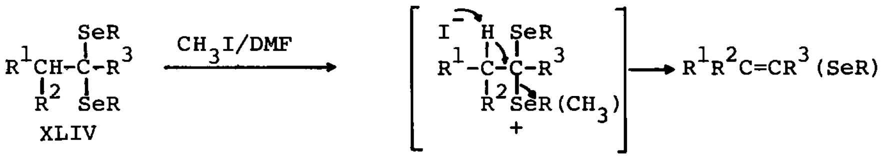
(b) Reaction of selenoketals with methyl iodide

Selenoketals XLIV are easily prepared from carbonyl compounds |40|. Reaction of these intermediates with methyl iodide in dimethylformamide (DMF) at 80°C produces vinylic selenides in moderate yields (eqn.24, Table 20) |41|. A mixture of olefins is formed, the most substituted one predominating |41|. A β-elimination on an intermediate selenonium ketal has been proposed.

Table 19

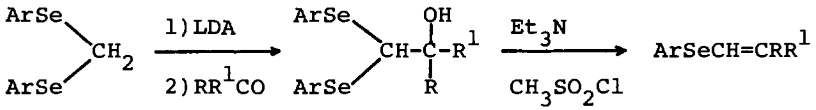
Vinylic selenides from dehydrohalogenation of α-haloalkylselenides |39|.

R	R^1	R^2	X	yield%
Ph	H	H	Br	66
Ph	C_9H_{19}	H	Br	75
Ph	H	CH_3	Br	70
Ph	C_5H_{11}	CH_3	Br	75
CH_3	C_9H_{19}	H	Br	70
CH_3	C_5H_{11}	CH_3	Br	60
Ph	H	H	Cl	60
Ph	C_9H_{19}	H	Cl	75
Ph	H	CH_3	Cl	62
Ph	C_5H_{11}	CH_3	Cl	70


XLIV

(24)

On the other hand, the selenoacetal XLV can be efficiently deprotonated with lithium diisopropylamide (LDA) to give bis-(arylseleno)methyllithium |42,43,44|, which reacts easily with aldehydes and ketones furnishing β-hydroxyselenoketals XLVI|43,45|. A "reductive elimination" of these intermediates leads to vinylic selenides (eqn.25) |1,46|. The yields of both reactions are good to excellent (Table 21).


XLV XLVI XLVII

(25)

Table 20

Vinylic selenides from reaction of selenoketals with methyl iodide |41|.

R	R^1	R^2	R^3	yield %
CH_3	H	C_5H_{11}	H	50
CH_3	H	C_9H_{19}	H	65
CH_3	H	C_8H_{17}	CH_3	65
CH_3	H	C_5H_{11}	CH_3	60
CH_3	H	$-(CH_2)_4-$		65
CH_3	CH_3	$-(CH_2)_4-$		53
Ph	H	H	H	65
Ph	H	C_5H_{11}	H	65
Ph	H	H	CH_3	60

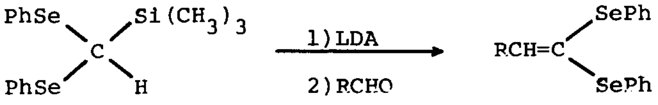
Table 21

Vinylic selenides from β-hydroxyselenides by reductive elimination

Ar	R^1	R	XLVI yield%	XLVII yield%
Ph	Ph	H	95	74
Ph	CH_3	H	92	84
Ph	C_2H_5	H	98	74
Ph	$i\text{-}C_3H_7$	H	77	81
Ph	CH_3	CH_3	95	77
$m\text{-}CF_3C_6H_4$	Ph	H	-	85
$m\text{-}CF_3C_6H_4$	Ph	H	91	63
$m\text{-}CF_3C_6H_4$	C_2H_5	H	98	72
$m\text{-}CF_3C_6H_4$	$i\text{-}C_3H_7$	H	98	79
$m\text{-}CF_3C_6H_4$	CH_3	CH_3	98	73

(c) Reaction of bis-(phenylseleno)(trimethylsilyl) methyllithium with aldehydes

The reaction between bis-(phenylseleno)(trimethylsilyl)-methyllithium XLVIII and aldehydes leads to ketenediselenoketals XLIX through a Petterson olefination reaction (eqn.26) |47|.

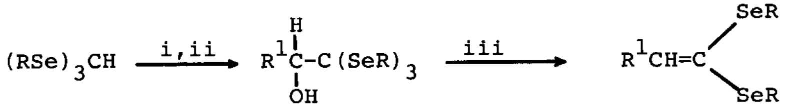


XLVIII XLIX

(26)

R = H; C_2H_5; Ph

Similarly, deprotonation of orthoselenoesters L generates the corresponding carbanion, which react with aldehydes to give β-hydroxyorthoselenoesters LI. These intermediates react with P_2I_4 or PI_3, furnishing the vinylic derivatives LII in good yield (eqn.27, Table 22) |50|.



L LI LII

(27)

i,LDA/THF,-78°C;ii, R^1CHO;iii, P_2I_4 or PI_3

Table 22

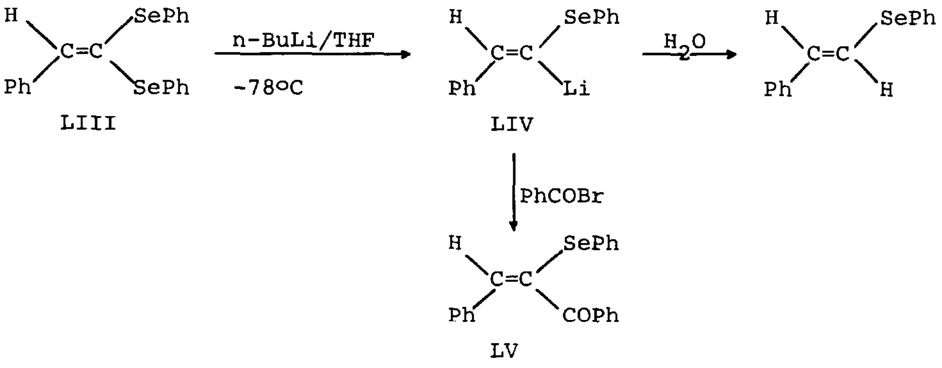
Ketenediselenoketals from β-hydroxyorthoselenoesters

R	R^1	yield%		
		a	b	c
CH_3	n-$C_{10}H_{21}$	85	70	18
CH_3		85		
CH_3	Ph	70	86	
Ph	Ph	70	86	

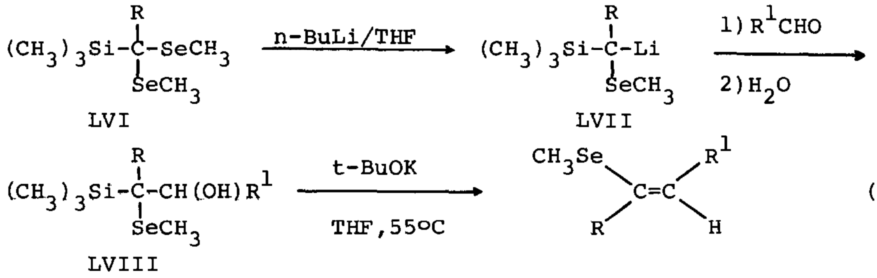
Reagent used: a)P_2I_4; b)PI_3;c)$SOCl_2$

The ketenediselenoketal LIII can be lithiated by reaction with one equivalent of n-butyllithium in THF at -78°C. The lithiated species LIV, when trapped with water, lead to trans-phenylselenostyrene, showing that the Se-Li exchange reaction occurs stereoselectively. Reaction of LIV with benzoyl bromide gives the vinylic selenide LV in 55% yield (Scheme 5) |48|.

Scheme 5



Reaction of LVI with n-butyllithium in THF generates α-lithio-α-silylselenides LVII |48,49,51|, which react with aldehydes leading, after hydrolysis, to the corresponding alcohol LVIII. The alcohol LVIII, by treatment with potassium t-butoxide in THF at 55°C, produces vinylic selenides (eqn.28).



(28)

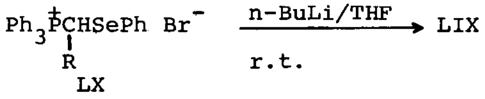
		yield %
R = H;	$R^1 = C_{10}H_{21}$	78
CH_3;	$C_{10}H_{21}$	89

(d) Wittig and Horner-Emmons reaction of (phenylseleno)-alkylidenephosphoranes and (phenylseleno)phosphonates carbanions

The first systematic approach to the synthesis of vinylic selenides was the Wittig reaction between a phenylselenophosphorane LIX and a carbonyl compound (eqn.29) |32,52|.

$$\underset{\text{LIX}}{Ph_3P{=}CR(SePh)} \xrightarrow{R^1R^2CO} R^1R^2C{=}CR(SePh) \qquad (29)$$

Phenylselenophosphoranes LIX can be generated either by direct deprotonation of a phenylselenophosphonium salt LX with n-BuLi in tetrahydrofuran (eqn.30), or through a transylidation reaction, using PhSeBr as electrophile (eqn.31)|32,52|.



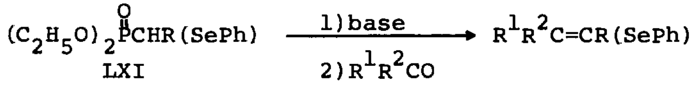
$$\underset{\text{LX}}{Ph_3\overset{+}{P}(R)CHSePh\ Br^-} \xrightarrow[\text{r.t.}]{\text{n-BuLi/THF}} \text{LIX} \qquad (30)$$

$$2\ Ph_3P{=}CHR \xrightarrow[\text{r.t.}]{\text{PhSeBr/THF}} \text{LIX} + Ph_3\overset{+}{P}CH_2R\ Br^- \qquad (31)$$

Alternatively the phenylselenophosphonium salt LX can be deprotonated under phase transfer conditions using NaOH as base. The use of a phase transfer catalyst is unnecessary |53|.

The Wittig reaction affords good to excellent yields with aromatic and aliphatic aldehydes, when R is H or CH_3. When R is larger than CH_3, the yields become very poor |54|. In all instances the formation of a mixture of Z and E vinylic selenides was observed, but the use of phase transfer conditions leads to a predominance of the Z isomer. With ketones the reaction takes an unexpected route and the only product detected is the α-phenylseleno ketone |52|.

Treatment of the carbanion of a phenylselenophosphonate LXI with both aldehydes and ketones results in the production of the desired vinylic selenide in moderate to good yield (eqn.32 , Table 24) |55|. The phenylselenophosphonate LXI can be deprotonated with n-BuLi in tetrahydrofuran at -78°C |55|, with NaH in the presence of a carbonyl compound in tetrahydrofuran at reflux temperature |55|, or with NaOH under phase transfer conditions using an ammonium salt as catalyst |53|. Under the last conditions, ketones and aliphatic aldehydes do not react.



$$\underset{\text{LXI}}{(C_2H_5O)_2\overset{O}{\overset{\|}{P}}CHR(SePh)} \xrightarrow[2)R^1R^2CO]{1)\text{base}} R^1R^2C{=}CR(SePh) \qquad (32)$$

Table 23

Vinylic selenides from reaction between selenophosphoranes and aldehydes

$$Ph_3P{=}CR(SePh) \xrightarrow{R^1CHO} R^1CH{=}CR(SePh)$$

R	R^1	yield%	ref.
H	Ph	99	|32|
		75*	|53|
H	$p\text{-}CH_3C_6H_4$	95	|32|
		56*	|53|
H	$p\text{-}NO_2C_6H_4$	90	|32|
		77*	|53|
H	C_2H_5	66	|32|
		70*	|53|
H	$n\text{-}C_6H_{13}$	65	|32|
CH_3	Ph	99	|32|
CH_3	$p\text{-}CH_3C_6H_4$	95	|32|
CH_3	$p\text{-}NO_2C_6H_4$	91	|32|
CH_3	C_2H_5	65	|32|
CH_3	$n\text{-}C_6H_{13}$	63	|32|
C_2H_5	Ph	60	|54|
$n\text{-}C_3H_7$	Ph	53	|54|
$n\text{-}C_4H_9$	Ph	40	|54|
$n\text{-}C_5H_{11}$	Ph	50	|54|
$n\text{-}C_6H_{13}$	Ph	40	|54|
C_2H_5	$n\text{-}C_6H_{13}$	20	|54|
$n\text{-}C_3H_7$	$n\text{-}C_6H_{13}$	15	|54|
$n\text{-}C_4H_9$	$n\text{-}C_6H_{13}$	10	|54|
$n\text{-}C_5H_{11}$	$n\text{-}C_6H_{13}$	10	|54|

*Reaction under phase transfer conditions

As expected for a Horner-Emmons reaction, in all instances the products are of predominant E stereochemistry.

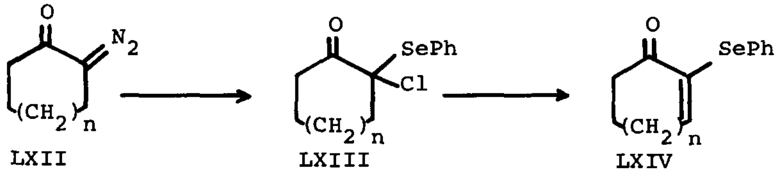
(G) Reaction of α-diazoketones with phenylselenenyl chloride followed by dehydrochlorination

Table 24

Vinylic selenides from (phenylseleno)alkylphosphonates carbanions and carbonyl compounds |53,55|.

R	R^1	R^2	yield %
H	H	Ph	80
H	H	p-$CH_3C_6H_4$	72
H	H	p-$NO_2C_6H_4$	74
H	H	n-C_3H_7	57
H	H	n-C_6H_{13}	45
H	H	C_2H_5	70
H	Ph	CH_3	50
H	Ph	Ph	52
H	-$(CH_2)_5$-		78
H	-$(CH_2)_5$-		50
CH_3	H	Ph	86
CH_3	H	p-$CH_3C_6H_4$	70
CH_3	-$(CH_2)_5$-		60
C_2H_5	H	Ph	70
C_2H_5	H	p-$CH_3C_6H_4$	51
n-C_4H_9	H	Ph	66
n-C_4H_9	H	p-$CH_3C_6H_4$	55
n-C_8H_{17}	H	p-$CH_3C_6H_4$	52

The reaction of a diazoalkane with arylselenenyl halides leads to α-haloalkylphenylselenides |32,38|. This reaction can be sucessfully applied to α-diazoketones LXII producing α-chloro-α-(phenylselenenyl) ketones LXIII, which by treatment with anhydrous sodium carbonate in boiling xylene affords the α-phenylseleno enones LXIV (eqn.33) |56|.



(33)

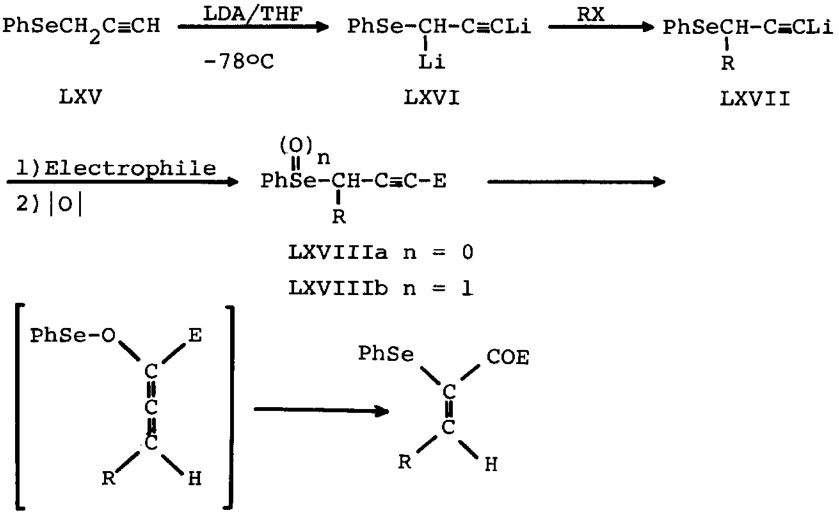
Table 25
α-phenylseleno enones from diazoketones

n	LXIII yield %	LXIV yield %
0	100	50
1	100	55
2	100	60

(H) Vinylic selenides from rearrangement of propargyl phenyl selenides

Oxidation of propargyl phenyl selenides LXVIII at low temperature leads to vinyl phenyl selenides LXX presumably via an allene intermediate LXIX |57,58|. The Scheme 6 shows the reaction sequence that transforms propargyl phenyl selenide LXV into vinyl phenyl selenides LXX.

Scheme 6



LXV LXVI LXVII

LXVIIIa n = 0
LXVIIIb n = 1

LXIX LXX

Propargyl phenyl selenide LXV is rapidly deprotonated by 2 equivalents of lithium diisopropylamide in THF or glyme at -78°C. Alkyl halides react with LXVI exclusively at the α-position giving the lithium acetylide LXVII, which can be treated with a variety of electrophiles to give 1,3-disubstituted propargyl selenides LXVIIIa in good yield. Oxidation of these intermediates at low temperature furnishes a mixture of Z and E phenylseleno enones LXX (Table 26).

Table 26

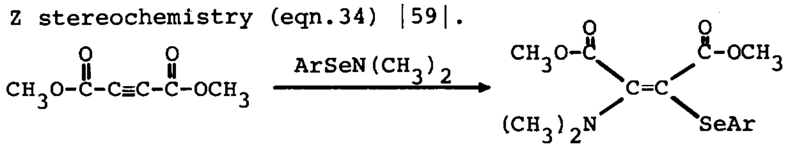
Vinylic selenides obtained from rearrangement of propargyl phenyl selenides |57,58|.

RX	Electrophile	oxidant	yield %
$Ph(CH_2)_3I$	H_2O	O_3,CH_2Cl_2	68
$Ph(CH_2)_3I$	CH_3I	RCO_3H,CH_2Cl_2	59
$PhCH_2Br$	CH_3CHO	O_3,CH_2Cl_2	61
CH_3CH_2Br	CH_3COCH_3	RCO_3H,CH_2Cl_2	53
$(CH_3)_2CHI$	H_2O	RCO_3H,CH_2Cl_2	60
*	CH_3I	RCO_3H,CH_2Cl_2	61
CH_3I	$(CH_3)_3SiCl$	RCO_3H,CH_2Cl_2	42

* The monoanion of propargyl phenyl selenide LXV was alkylated.

(I) Miscellaneous

N,N-Dialkyl benzeneselenenamides react with dimethyl acetylenedicarboxylate to give the corresponding adduct LXXI of predominant Z stereochemistry (eqn.34) |59|.

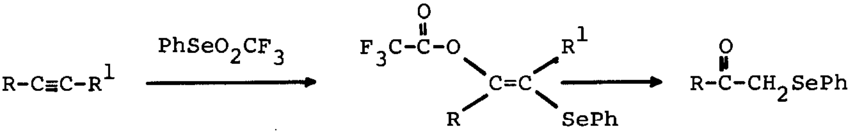


LXXI

(34)

Ar = Ph; $p\text{-}CF_3C_6H_4$

Phenylselenenyl trifluoroacetate adds rapidly to acetylenes giving phenylseleno enol trifluoroacetates LXXII, which upon hydrolysis give α-phenylseleno ketones (eqn.35) |60|.



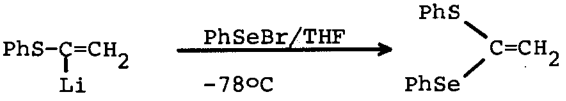
LXXII

(35)

Allyl phenyl selenide can be transformed into 1-propenyl selenide by reaction with a base in an appropriate solvent (eqn.36) |41,61|.

$$PhSeCH_2\text{-}CH{=}CH_2 \xrightarrow[\text{solvent}]{\text{base}} PhSeCH{=}CH\text{-}CH_3 \qquad (36)$$

Reaction of α-lithiovinyl phenyl sulphide LXXIII with phenylselenenyl bromide in THF at -78°C leads to the respective thioselenoketeneacetal LXXIV in 84 % yield (eqn.37) |62|.



LXXIII LXXIV

(37)

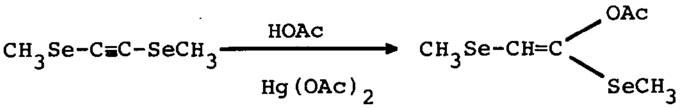
Elemental selenium reacts with acetylene in aqueous dimethylsulfoxide (DMSO) in the presence of potassium hydroxide to give the divinyl selenide LXXV in 17 % yield (eqn.38) |63|.

$$CH{\equiv}CH + Se \xrightarrow[\text{KOH}]{H_2O,\text{DMSO}} \underset{\text{LXXV}}{CH_2{=}CH\text{-}Se\text{-}CH{=}CH_2} \qquad (38)$$

Analogously, selenium adds to vinylacetylene to give the divinyl selenide LXXVI in 17 % yield (eqn.39) |64|. In both cases, by-products other than the vinylic selenides are formed.

$$CH{\equiv}C\text{-}CH{=}CH_2 + Se \xrightarrow[\text{KOH}]{H_2O/\text{DMSO}} \underset{\text{LXXVI}}{CH_2{=}CH\text{-}CH{=}CH\text{-}Se\text{-}CH{=}CH\text{-}CH{=}CH_2} \qquad (39)$$

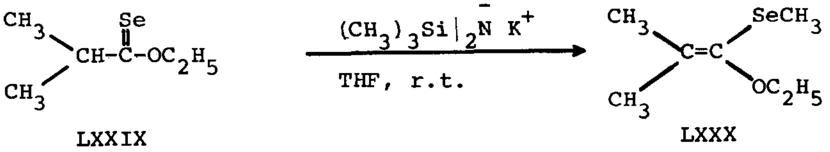
Bis(methylseleno)ethylene LXXVII reacts with acetic acid in the presence of mercuric acetate to give the corresponding vinylic selenide LXXVIII in 19 % yield (eqn.40) |65|.



LXXVII LXXVIII

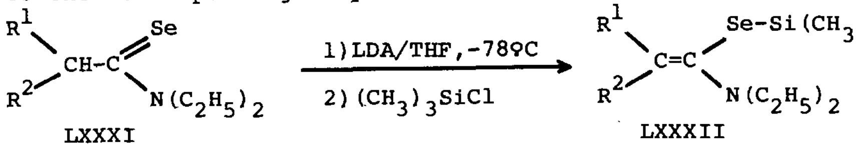
(40)

Reaction of O-ethyl selenoisobutyrate LXXIX with potassium bis-(trimethylsilyl) amide gives, on work up with methyl iodide, a 54% yield of the dimethylketen monoselenoacetal LXXX (eqn.41) |66|.



(41)

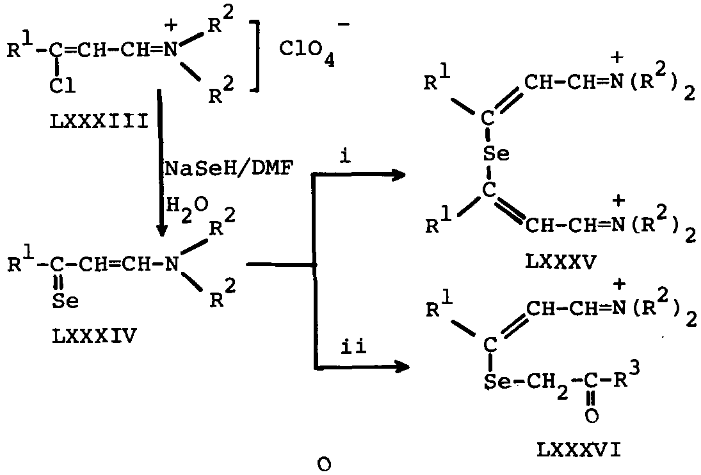
Treatment of selenoamides LXXXI with lithium diisopropylamide, followed by reaction with trimethylsilylchloride (eqn.42), leads to the corresponding vinylselenosilanes LXXXII in good yield |67|.



(42)

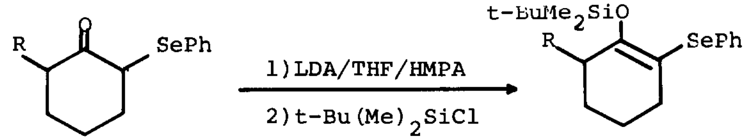
2-Aminovinyl selenoketones LXXXIV react with 2-chloro-2-alkeniminium salts LXXXIII in DMF to give the divinyl selenides LXXXV |68|. In contrast, the reaction of 2-aminovinyl selenoketones LXXXIV with α-haloketones furnishes monovinyl selenides LXXXVI (Scheme 7). These compounds are intermediates in the synthesis of substituted selenophenes |68|.

Scheme 7



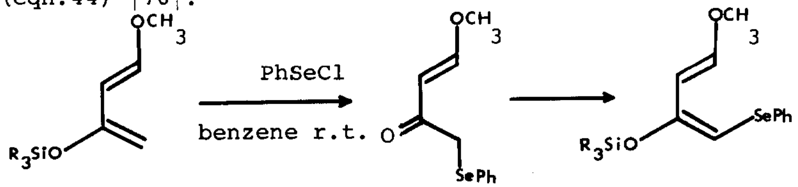
i, $DMF/HClO_4$; ii, $XCH_2\overset{O}{\overset{\|}{C}}R^2/C_2H_5OH/C_2H_5ONa$

The lithium enolates of α-phenylseleno ketones react with trialkylsilylchlorides to give the corresponding vinylsilylethers in good yield (eqn.43) |69|.



(43)

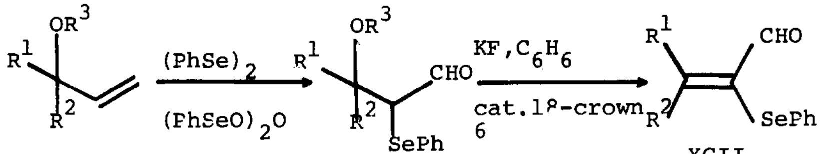
Reaction of the diene LXXXVII with phenylselenenyl chloride gives the α-phenylseleno ketone LXXXVIII in 82 % yield |70,71|. Resilylation leads to the vinylsilylether LXXXIX in 80 % yield (eqn.44) |70|.



LXXXVII LXXXVIII LXXXIX

(44)

Oxidation of allyl ethers XC with diphenyldiselenide and phenylseleninic anhydride gives the corresponding α-phenylseleno-aldehydes XCI, which furnish α-phenylseleno enals XCII (eqn.45) |72| upon treatment with potassium fluoride in the presence of a catalytic amount of 18-crown-6.



XC XCI XCII

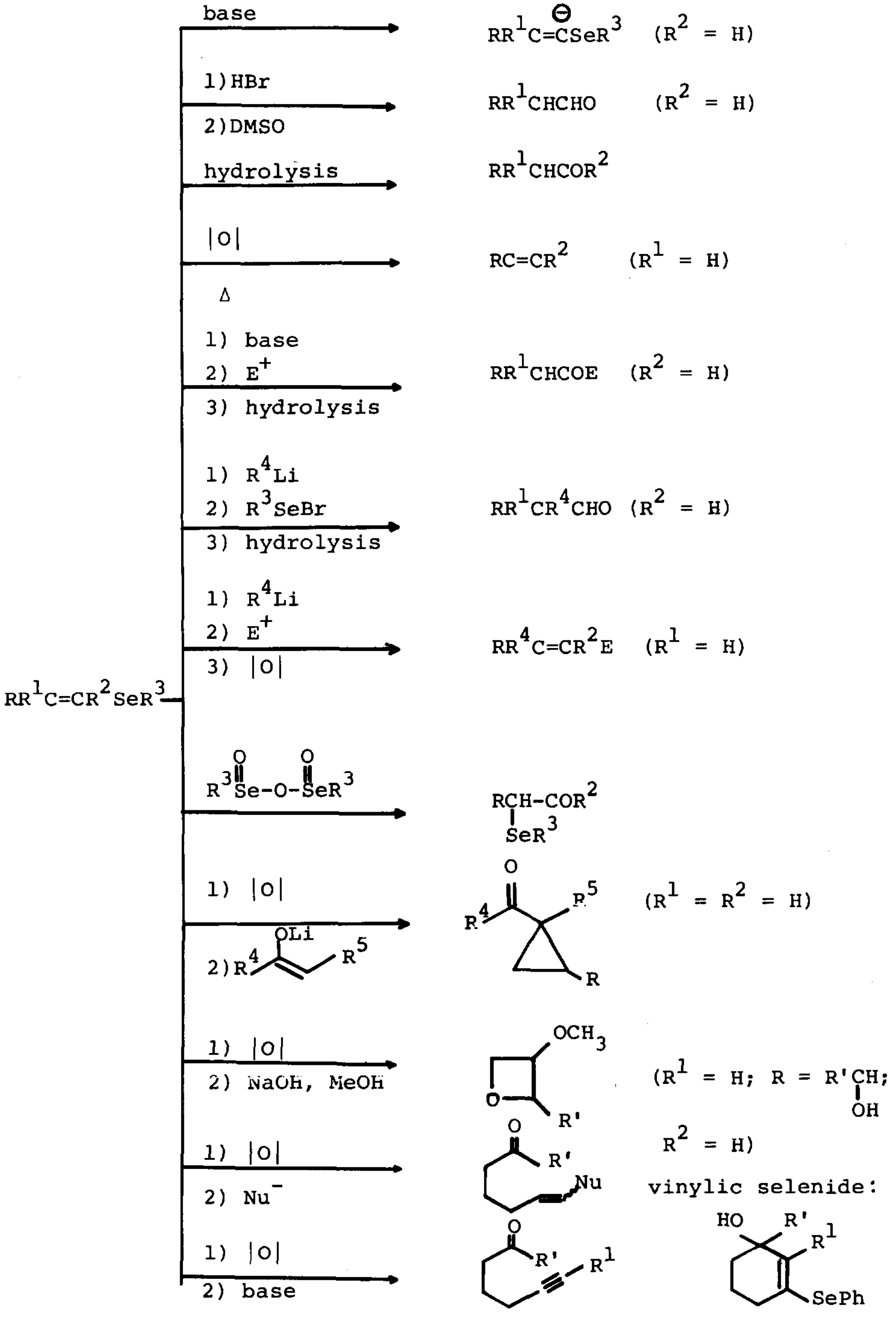
(45)

2. SYNTHETIC APPLICATIONS OF VINYLIC SELENIDES

Vinylic selenides are intermediates of great synthetic potential, since they combine the functional transformations achieved by the well known reactions of the organoselenium compounds |73,74,75,76| with the ability of carbon-carbon bond-forming reactions involving the double bond. This ability is associated with the capacity of selenium to stabilize carbanions |42,43,45,74|, as can be inferred from the Scheme 8.

Following the scheme, we will discuss these transformations in detail.

Scheme 8


RR^{1}C=CR^{2}SeR^3
base
RR^{1}C=$\overset{\ominus}{C}$SeR^3 (R^2 = H)
1) HBr
2) DMSO
RR^{1}CHCHO (R^2 = H)
hydrolysis
RR^{1}CHCOR^2
|O|
Δ
RC≡CR^2 (R^1 = H)
1) base
2) E$^+$
3) hydrolysis
RR^{1}CHCOE (R^2 = H)
1) R^{4}Li
2) R^{3}SeBr
3) hydrolysis
RR^{1}CR^{4}CHO (R^2 = H)
1) R^{4}Li
2) E$^+$
3) |O|
RR^{4}C=CR^{2}E (R^1 = H)
R^{3}Se(O)-O-Se(O)R^3
RCH(SeR^3)-COR^2
1) |O|
2) R^{4}C(OLi)=CHR^5
O
R^4
R^5
R
(R^1 = R^2 = H)
1) |O|
2) NaOH, MeOH
OCH$_3$
O
R'
(R^1 = H; R = R'CH(OH); R^2 = H)
1) |O|
2) Nu$^-$
O
R'
Nu
vinylic selenide:
HO
R'
R^1
SePh
1) |O|
2) base
O
R'
R^1

(A) Hydrolysis of vinylic selenides to carbonyl compounds

The first demonstration of the synthetic utility of vinylic selenides was provided by their hydrolysis to ketones |32,55|. Both aromatic and aliphatic vinylic selenides are hydrolytically cleaved either with $HgCl_2/H_2O$ in acetonitrile or with trifluoroacetic acid, furnishing the corresponding ketones in high yield (eqn.46,Table 27)|32,76,77,78|. Mechanistic studies of the acidic hydrolysis of vinylic selenides have been recently reported|79,80, 81|.

Table 27

Hydrolysis of vinylic selenides

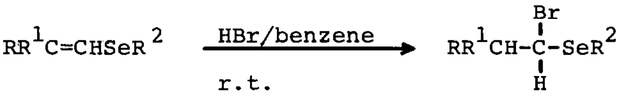
$$RCH{=}CR^1(SePh) \longrightarrow R\text{-}CH_2\text{-}COR^1 \qquad (46)$$

R	R^1	yield %	ref.
Ph	CH_3	84^a	32
		80^b	77
Ph	C_2H_5	80^a	55
		97^b	55
Ph	C_3H_7	80^b	77
Ph	C_4H_9	76^b	77
Ph	C_5H_{11}	78^b	77
C_2H_5	C_6H_{13}	78^b	77
CH_3	C_9H_{21}	63^c	78
CH_3	C_9H_{21}	80^a	76

a) $HgCl_2/H_2O/CH_3CN$,80°C;b) CF_3COOH,r.t.;c) H_2SO_4/H_2O

Vinylic selenides where R^1 is hydrogen, do not hydrolyse to aldehydes under the conditions employed by us to perform the above transformation |82|. However, hydrolysis can be achieved by reacting the vinylic selenide with hydrogen bromide, followed by solvolysis as discussed below.

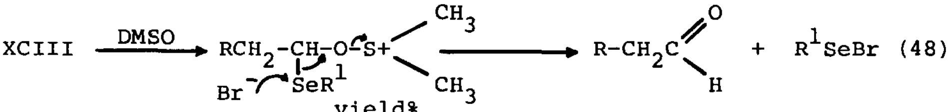
Reaction of vinylic selenides with dry hydrogen bromide in dry benzene leads to α-bromoalkylselenides XCIII (eqn.47)|37,39|.



$$RR^1C{=}CHSeR^2 \xrightarrow[\text{r.t.}]{\text{HBr/benzene}} RR^1CH\text{-}\overset{\displaystyle Br}{\underset{\displaystyle H}{C}}\text{-}SeR^2 \qquad (47)$$

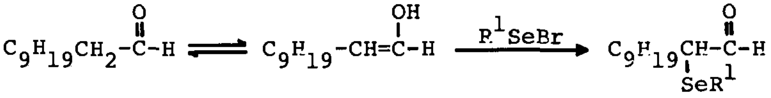
XCIII

The exclusive formation of α-bromoalkyl selenide is observed even when R is the phenyl group |83|, suggesting that the selenium atom has a greater ability than a phenyl group to stabilize a carbonium ion. α-Bromoalkylselenides XCIII can be transformed into the corresponding aldehydes either by reaction with water in acetonitrile in the presence of oxygen or by dissolution in anhydrous dimethylsulfoxide (DMSO) (eqn.48) |39|. The mechanism shown below was proposed to explain this last reaction:



R	R^1	yield%
C_9H_{19}	CH_3	85
C_9H_{19}	Ph	85

If the reaction mixture is not worked up, after about 10 minutes, the selenenyl bromide formed reacts with the aldehyde via enol to give the α-selenocarbonyl compound (eqn.49) |39|.



$$C_9H_{19}CH_2-\overset{\overset{O}{\|}}{C}-H \rightleftharpoons C_9H_{19}-CH=\overset{\overset{OH}{|}}{C}-H \xrightarrow{R^1SeBr} C_9H_{19}\underset{\underset{SeR^1}{|}}{CH}-\overset{\overset{O}{\|}}{C}-H \qquad (49)$$

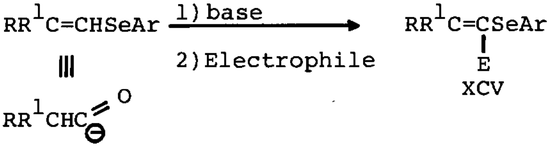
XCIV

In this way α-phenylselenoundecanal XCIV was obtained in 65% yield from α-bromo(phenylseleno)undecane after 24 hr stirring in dimethylsulfoxide at room temperature (eqn.49) |39|.

(B) Deprotonation-alkylation of vinylic selenides

It has been observed that the reaction between vinylic selenides and alkyllithium reagents gives the vinylselenium carbanion, but accompanied by substantial amounts of cleavage and Michael addition products |1,78,84|. However, the use of hindered bases such as lithium diisopropylamide (LDA) or a mixture of potassium t-butoxide-lithium diisopropylamide (KDA) in tetrahydrofuran at -78°C gives the vinyl seleno carbanion in good yield |1, 85|. It has been noted that the substitution of a phenylseleno group by a m-(trifluoromethyl)-phenylseleno group enhances the rate of the deprotonation reaction, due to the greater acidity of the hydrogen linked to the carbon containing the arylseleno moiety |1|.

The vinyl seleno carbanion reacts rapidly with a variety of electrophiles, e.g. primary alkyl halides, epoxides, aldehydes, ketones, giving the corresponding adducts XCV in high yield (Table 28). The deprotonation/alkylation steps occur with retention of configuration about the double bond when KDA is used as base |86|; however, in some cases E/Z mixtures of products are formed when LDA is used as base, irrespective of the stereochemistry of the original vinylic selenide |1| . The resulting structures XCV are of great synthetic potential. As vinylic selenides can be hydrolysed to the corresponding carbonyl compound (eqn.46) |32,39,77|, we can consider these intermediates as acyl carbanion equivalents XCVI.



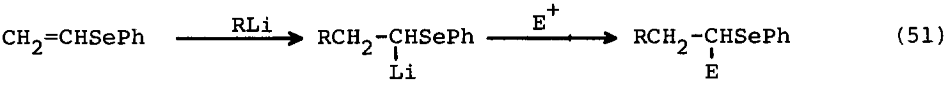
$$RR^1C{=}CHSeAr \xrightarrow[2)\,\mathrm{Electrophile}]{1)\,\mathrm{base}} RR^1C{=}\underset{\underset{XCV}{E}}{C}SeAr$$

$$RR^1C{=}CHSeAr \equiv RR^1CHC(=O)^{\ominus}$$

XCVI

(C) Alkyllithium addition

The ability of a phenylseleno group to stabilize an adjacent carbanion allows the 1,4-addition of a variety of alkyllithiums to vinylphenylselenide XCVII leading to the selenium stabilized carbanion XCVIII which can be trapped with an appropriate electrophile (eqn.51) |87|.

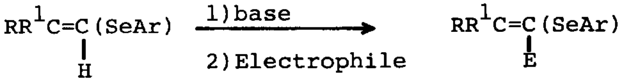


$$CH_2{=}CHSePh \xrightarrow{RLi} RCH_2\text{-}\underset{Li}{C}HSePh \xrightarrow{E^+} RCH_2\text{-}\underset{E}{C}HSePh \qquad (51)$$

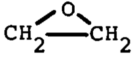
XCVII XCVIII XCIX

The reaction proceeds readily with n- and t-butyllithium and with i-propyllithium in dimethoxyethane or ethyl ether at 0°C. Vinylphenylselenide XCVII is, however, unreactive toward n-BuMgBr. The choice of the reaction conditions is crucial in order to obtain a good yield of the desired product, since alkyllithium can either deprotonate the vinylic selenide or perform a nucleophilic attack at selenium, leading to undesired by-products |1,78,87|. Oxidative elimination of the resulting selenide XCIX affords an olefine C, allowing the vinylphenylselenide XCVII to be considered an efficient $\overset{+}{C}H{=}\overset{-}{C}H$ synthon (eqn.52).

Table 28



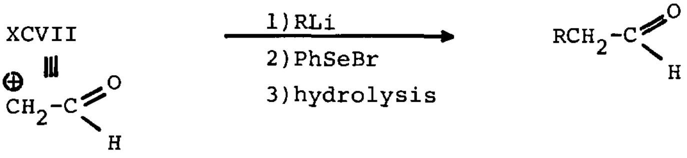
$$RR^1C{=}\underset{H}{C}(SeAr) \xrightarrow[\text{2) Electrophile}]{\text{1) base}} RR^1C{=}\underset{E}{C}(SeAr)$$

R	R^1	Ar	base	E	yield%	ref.
H	H	Ph	KDA	CH_3I	98	|86|
H	H	Ph	KDA	$n\text{-}C_{10}H_{21}Br$	94	|86|
$n\text{-}C_4H_9$	H	Ph	KDA	CH_3I	85	|86|
$(CH_3)_2CH$	H	Ph	KDA	CH_3I	85	|86|
$(CH_3)_2CH$	H	Ph	KDA	$n\text{-}C_{10}H_{21}Br$	88	|86|
H	H	Ph	LDA	CH_3I	75	|1|
H	H	Ph	LDA	$CH_3(CH_2)_3I$	71	|1|
H	H	Ph	LDA	$Ph(CH_2)_3Br$	76	|1|
H	H	$m\text{-}CF_3C_6H_4$	LDA	CH_3I	91	|1|
H	H	Ph	LDA	$CH_3(CH_2)_3I$	85	|1|
H	H	Ph	LDA	$(C_2H_5)_2CO$	75	|1|
H	H	Ph	LDA	$(CH_3)_2CO$	80	|1|
H	H	Ph	LDA	CO_2	77	|1|
H	H	$m\text{-}CF_3C_6H_4$	LDA	CO_2	80	|1|
H	H	Ph	KDA	$(CH_3)_2CHCHO$	92	|86|
H	H	Ph	KDA	2-cyclohexenone	92	|86|
$(CH_3)_2CH$	H	Ph	KDA	$(CH_3)_2CHCHO$	95	|86|
H	H	Ph	KDA		92	|86|
H	H	Ph	LDA	D_2O	82	|1|
H	H	Ph	LDA	CH_3SSCH_3	66	|1|
H	H	Ph	LDA	$(CH_3)_3SiCl$	77	|1|
H	H	$m\text{-}CF_3C_6H_4$	LDA	CH_3SSCH_3	83	|1|
H	H	$m\text{-}CF_3C_6H_4$	LDA	PhSeSePh	89	|1|
H	H	$m\text{-}CF_3C_6H_4$	LDA	$(CH_3)_3SiCl$	99	|1|
H	C_2H_5	$m\text{-}CF_3C_6H_4$	LiTMP	CH_3I	63*	|1|
H	C_2H_5	$m\text{-}CF_3C_6H_4$	LiTMP	$n\text{-}C_3H_7I$	61*	|1|
H	$(CH_3)_2CH$	$m\text{-}CF_3C_6H_4$	LiTMP	CH_3I	62*	|1|
H	$(CH_3)_2CH$	$m\text{-}CF_3C_6H_4$	LiTMP	$n\text{-}C_3H_7I$	63*	|1|

*Mixture of Z/E isomers

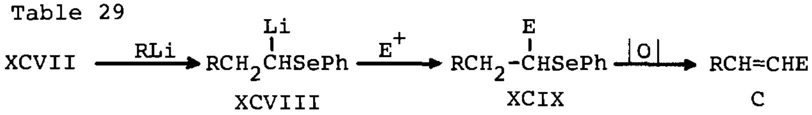
$$\text{XCVII} \xrightarrow[\substack{2)\text{E} \\ 3)|\text{O}|}]{1)\text{RLi}} \text{RCH=CHE} \qquad (52)$$

As bis(phenylseleno)acetals can be hydrolysed to aldehydes (eqn.53), XCVII is also a $\overset{+}{C}H_2CHO$ synthon, since alkyl(phenyl) carbanions react with phenylselenenyl bromide to give the corresponding bis(phenylseleno)acetal in good yield |87|.



(53)

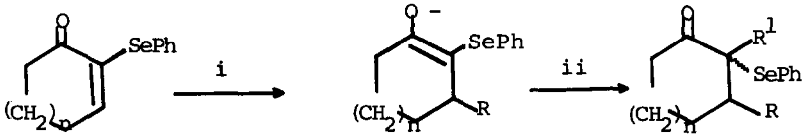
Table 29



$$\text{XCVII} \xrightarrow{\text{RLi}} \underset{\text{XCVIII}}{RCH_2\overset{\overset{\text{Li}}{|}}{C}HSePh} \xrightarrow{E^+} \underset{\text{XCIX}}{RCH_2\text{-}\overset{\overset{\text{E}}{|}}{C}HSePh} \xrightarrow{|O|} \underset{\text{C}}{RCH{=}CHE}$$

RLi	Electrophile	E	XCIX yield%	C yield%
n-BuLi	D_2O	D	97	-
n-BuLi	CH_3I	CH_3	95	-
n-BuLi	$n\text{-}C_{10}H_{21}Br$	$n\text{-}C_{10}H_{21}$	80	-
n-BuLi	PhSeBr	PhSe	84	-
n-BuLi	$(CH_3)_3SiCl$	$(CH_3)_3Si$	90	-
n-BuLi	PhCHO	PhCH(OH)	71	75
n-BuLi	CH_3COCH_3	$(CH_3)_2COH$	60	83
n-BuLi	$PhCOCH_3$	$PhC(CH_3)OH$	-	50
n-BuLi	PhCN	PhCO	-	61
i-PrLi	D_2O	D	92	-
i-PrLi	CH_3COCH_3	$(CH_3)_2COH$	72	81
i-PrLi	$(CH_3)_3SiCl$	$(CH_3)_3Si$	86	-
t-BuLi	D_2O	D	85	-

Vinylic selenides conjugated with a carbonyl group in the α-position undergo 1,4-addition with lithium dialkyl cuprates. The addition of a lithium dialkyl cuprate to CI in ether, followed by reaction with an alkylating agent in THF/HMPA, yields the dialkylated product CII in good yield (eqn.54) |88|.



CIa n = 0

CIb n = 1

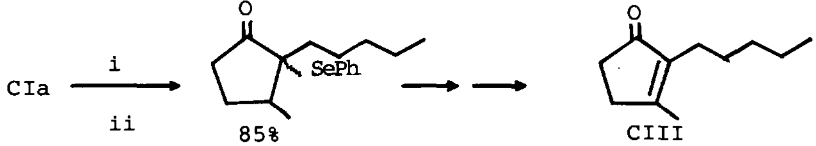
CII

(54)

i,LiR$_2$Cu,Et$_2$O,-20°C;ii,R^{1}X,Et$_2$O/THF/HMPA,25°C

This reaction has been explored in the synthesis of natural products. Thus, as depicted in Scheme 9, dihydrojasmone CIII was easily synthesized from α-phenylseleno cyclopentenone CIa using this methodology |89|.

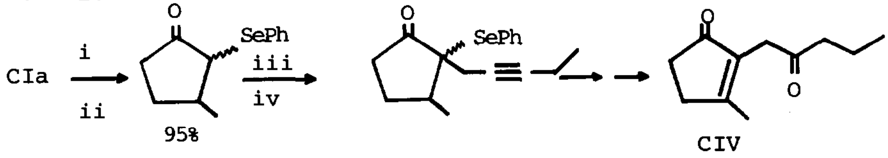
Scheme 9



i, Li(CH$_3$)$_2$Cu,Et$_2$O;ii, n-C$_5$H$_{11}$I,THF/HMPA

An analogous approach was employed in the synthesis of cis-jasmone CIV (Scheme 10) |89|.

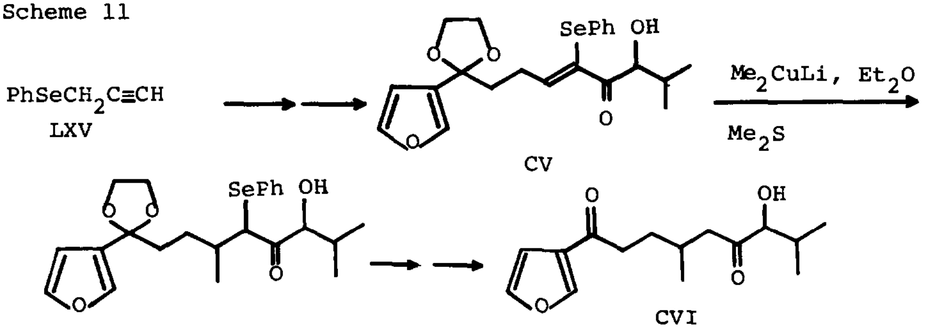
Scheme 10



i, Li(CH$_3$)$_2$Cu,Et$_2$O;ii, NH$_4$Cl;iii, LDA,THF/HMPA;iv, CH$_3$CH$_2$C≡CCH$_2$Br

The addition of a dialkyl cuprate to the phenylseleno enone CV has been used in the synthesis of Epi-7-hydroxymyoporone CVI, as shown in Scheme 11 |58,90|.

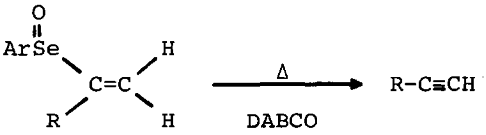
Scheme 11



(D) Oxidation-elimination of vinylic selenides to acetylenes

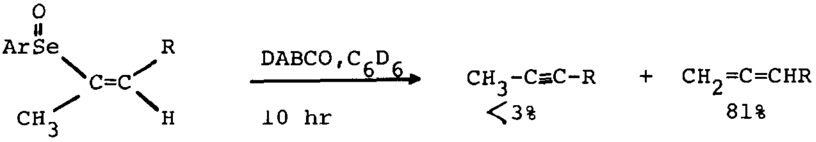
The well known oxidation-elimination sequence of alkyl selenides |73,75| can be successfully applied to vinvlic selenides, producing acetylenes|91|.

The vinyl selenoxide elimination occurs at 95°C. provided an amine is present in order to avoid seleninic acid addition|92| or reduction of the selenoxide. The most effective amine was found to be 1,4-diazabicyclo-2.2.2-octane (DABCO) (eqn.55).



(55)

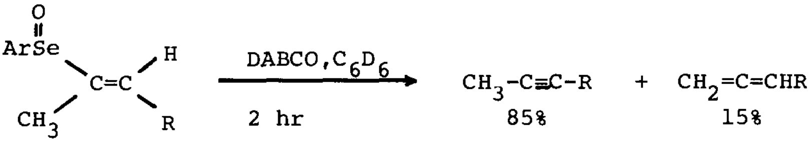
The vinylic selenoxides bearing an alkyl group cis to the arylselenoxide moiety CVIIIa (eqn.56) reacts slower than the corresponding E isomer CVIIIb (eqn.57) and gives predominantly allene.



(56)

CVIIIa

Ar = m-$CF_3C_6H_4$; R = -$CH(CH_3)_2$

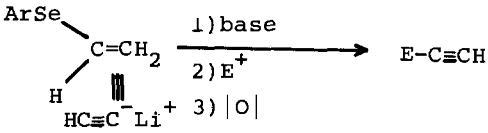


(57)

CVIIIb

Ar = m-$CF_3C_6H_4$; R = -$CH(CH_3)_2$

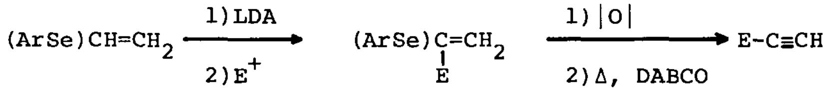
These results are consistent with a pericyclic syn elimination mechanism for the acetylene formation from vinylic selenoxides (eqn.55). The vinyl selenoxide elimination reaction coupled with the reactions described in Section 2(B) allows XCVII to be used as a lithium acetylide equivalent (eqn.58).



(58)

Table 30

Synthesis of acetylenes from vinylic selenoxides |91|



$$(\mathrm{ArSe})\mathrm{CH{=}CH_2} \xrightarrow[2)\,\mathrm{E}^+]{1)\,\mathrm{LDA}} (\mathrm{ArSe})\underset{\mathrm{E}}{\mathrm{C}}{=}\mathrm{CH_2} \xrightarrow[2)\,\Delta,\ \mathrm{DABCO}]{1)\,|\mathrm{O}|} \mathrm{E{-}C{\equiv}CH}$$

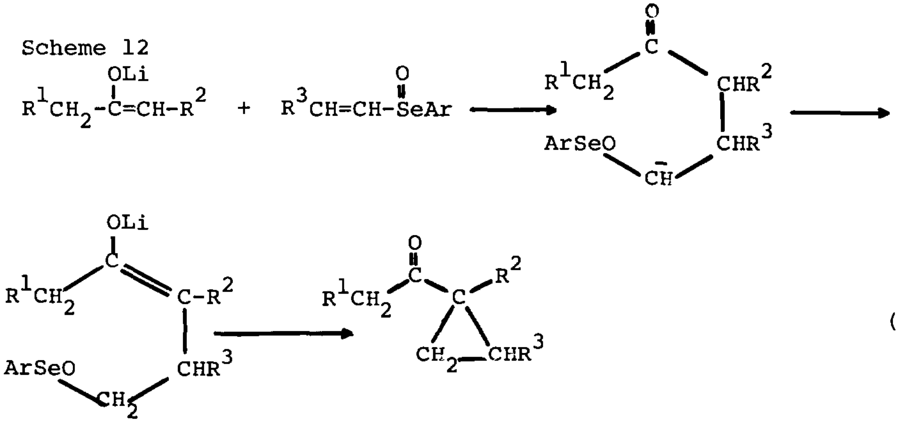
CIX CX

Ar	E	reaction conditions	CIX yield%	CX yield%
m-$CF_3C_6H_4$	CH_3COCH_3	2hr/95°C	80	93
m-$CF_3C_6H_4$	n-C_4H_9I	4hr/95°C	85	90
Ph	$CH_3COCH_2CH_2Ph$	7hr/85°C	67	83
Ph	$Ph(CH_2)_3Br$	7hr/85°C	76	77

(E) Reaction of vinylic selenoxides with enolates ⟶ cyclopropyl carbonyl compounds

As already noted (eqn.51) vinylic selenides are efficient 1,4-addition acceptors. The vinylic selenoxides behave similarly, reacting with lithium enolates of esters and ketones, affording cyclopropyl carbonyl compounds (eqn.59) |93|. The mechanistic pathway depicted below was proposed to account for the reaction.

Scheme 12

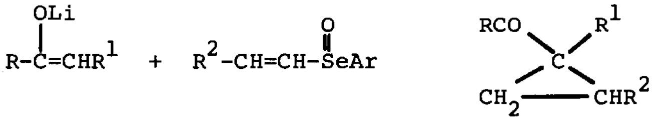


(59)

It has been observed that a p-chloro or a m-trifluoromethyl substituent on the arylseleno moiety enhances the reaction rate, while an o-nitro substituent does not, giving only traces of the desired product.

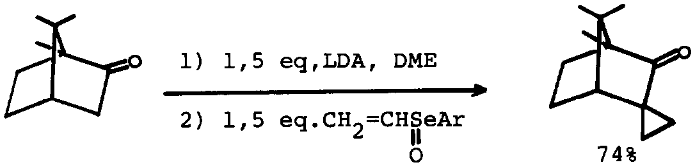
Table 31

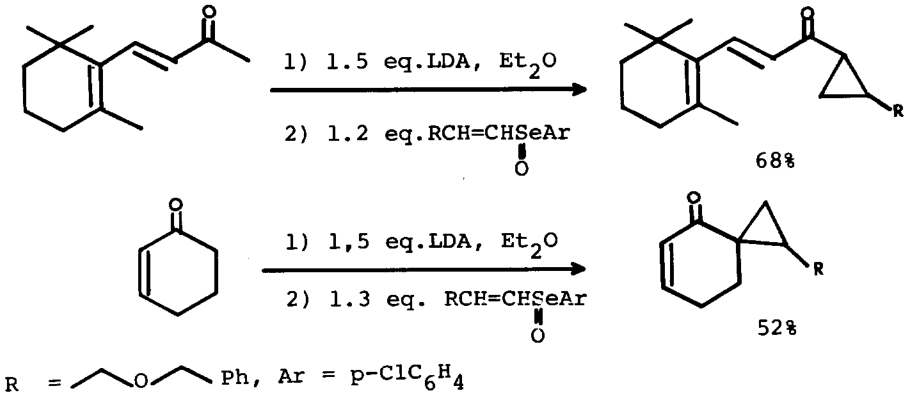
Cyclopropyl carbonyl compounds from vinylic selenoxides |93|.


$$R-\overset{\overset{OLi}{|}}{C}=CHR^1 + R^2-CH=CH-\overset{\overset{O}{\|}}{S}eAr$$

R	R^1	R^2	yield %
Ph	H	H	72
Ph	CH_3	H	59
C_2H_5O	PhS	H	65
Ph	H	$PhCH_2OCH_2$	70
Ph	CH_3	$PhCH_2OCH_2$	84
C_2H_5O	PhS	$PhCH_2OCH_2$	72
$-(CH_2)_{10}-$		$PhCH_2OCH_2$	55
Ph	CH_3	$C_{10}H_{21}$	62
C_2H_5O	PhS	$C_{10}H_{21}$	71
$(CH_3)_3C$	H	$C_{10}H_{21}$	72
$(CH_3)_3CO$	H	$C_{10}H_{21}$	52
$-(CH_2)_4-$		$C_{10}H_{21}$	51
$(CH_3)_2CH$	H	$C_{10}H_{21}$	56
C_5H_{11}	PhS	$C_{10}H_{21}$	47
C_2H_5O	PhSO	$C_{10}H_{21}$	35
C_2H_5O	$PhSO_2$	$C_{10}H_{21}$	13
C_2H_5O	C_2H_5OCO	$C_{10}H_{21}$	23

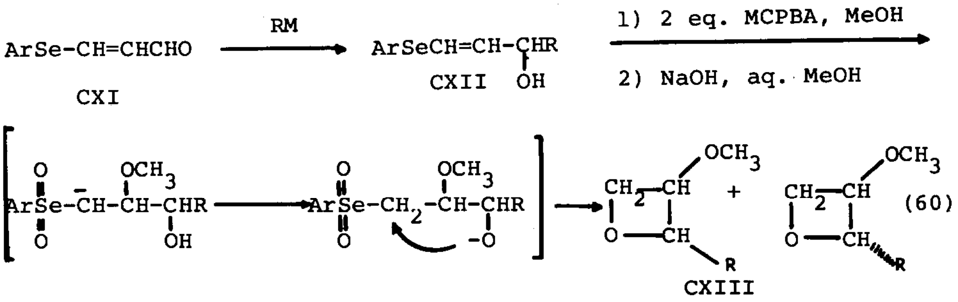
The reaction gives good results with cyclic and α-β-unsaturated ketones, as exemplified below |93|.





(F) Oxetane from vinylic selenoxides and selenones

Reaction of 1-alkyl-3-phenylseleno-1-ols CXII with m-chloroperbenzoic acid (MCPBA) followed by reaction with sodium hydroxide in aqueous methanol gives 2-alkyl-3-methoxyoxetane CXIII (eqn.60) |94|. This makes the easily prepared 3-phenylseleno-2-propenal CXI a valuable building block since oxetanes are important intermediates in the synthesis of a number of compounds |94|.



The hydroxy selenides CXII are easily prepared by reaction of 3-arylseleno-2-propenal CXI with nucleophiles such as Grignard reagents, alkyllithiums and ester or lactone enolates. These intermediates CXII react with two equivalents of MCPBA to give the corresponding selenones, which upon treatment with sodium hydroxide in methanol furnish oxetanes in good yield (Table 32).

Some features of this reaction must be emphasized: the use of electron-withdrawing substituents on the arylseleno moiety do not facilitate the oxetane formation, in contrast to the cyclopropane ring formation reaction related in the preceding section |93|. The yields are improved by using water and two equivalents of MCPBA. The water probably prevents the contamination with by-products and the excess MCPBA converts the selenoxides into selenones. It has been observed that selenones are more effective than selenoxides in promoting the oxetane ring formation.

When the reaction is performed with t-butyl acetate or γ-valerolactone enolate, the oxetane formed is easily opened to give α,β-unsaturated esters CXIV or lactone CXV (eqn.61,62,63). In this case the E vinylic selenide (eqn.61) gives better yield than the Z isomer (eqn.62)

Table 32

Preparation of 3-methoxyoxetanes from vinylic selenones |94|.

$$\text{CXI} \xrightarrow{\text{i, ii, iii}} \text{CXIII}$$

i, RM/THF,0°C;ii, 2 eq.MCPBA,MeOH,r.t.,30 min.;iii, NaOH,aq.MeOH, r.t.,18 hr.

Ar	olefin geometry *	RM	yield%
Ph	E	$PhCH_2CH_2MgCl$	80
Ph	Z	$PhCH_2CH_2MgCl$	78
$p\text{-}ClC_6H_4$	Z	$PhCH_2CH_2MgCl$	69
Ph	E	$C_{10}H_{21}MgBr$	78
Ph	Z	$C_{10}H_{21}MgBr$	72
Ph	Z	$C_6H_{13}MgBr$	66
$p\text{-}ClC_6H_4$	Z	PhMgBr	66
Ph	E	PhLi	80
Ph	E	$C_5H_{11}CHLiCO_2t\text{-}Bu$	81

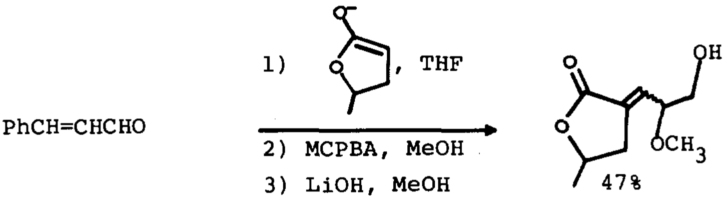
*The <u>cis</u> oxetane is preferentially formed, irrespective of the starting olefin.

$$\underset{\text{E}}{\text{PhSeCH=CHCHO}} \xrightarrow{\text{i,ii,iii}} \underset{\underset{87\%}{\text{CXIV}}}{\text{HOCH}_2\text{CH-CH=CHCOOt-Bu}} \qquad (61)$$

i, $LiCH_2CO_2t\text{-}Bu$,THF;ii,MCPBA,MeOH;iii,LiOH,MeOH

$$\underset{\text{Z}}{\text{PhSeCH=CHCHO}} \xrightarrow{\text{i,ii,iii}} \underset{47\%}{\text{CXIV}} \qquad (62)$$

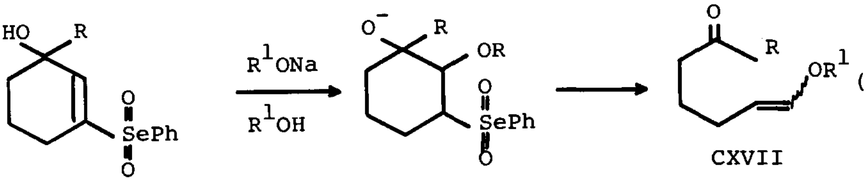
i, $LiCH_2CO_2t\text{-}Bu$,THF;ii,MCPBA,MeOH;iii,LiOH,MeOH



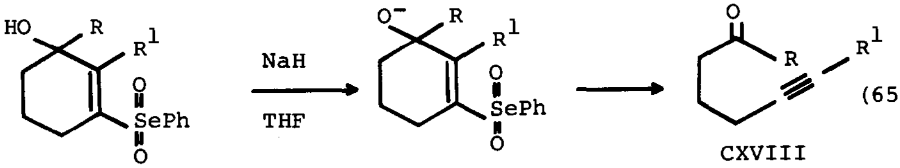
CXV (63)

(G) Ethylenic and acetylenic ketones from vinylic selenones

Treatment of cyclic 3-hydroxyvinyl selenones CXVI with base at room temperature leads to the formation of ethylenic or acetylenic ketones. Two mechanisms were proposed to explain the different products formed: The first consists of an addition of the base (nucleophile) to the double bond, followed by a 1,4-fragmentation furnishing an olefine CXVII (eqn.64);The second, consists of a deprotonation of the alcohol followed by 1,4-fragmentation furnishing an acetylene CXVIII (eqn.65) |95|.



CXVIa CXVII (64)



CXVIb CXVIII (65)

The yields are generally good (Table 33 and 34). The hydroxy vinyl selenones possessing tetrasubstituted olefins give preferentially the acetylenic ketone (eqn.65) rather than the ethylenic one (eqn.64). The use of sodium hydride as base furnishes the acetylenic ketone selectively. Vinyl selenoxides do not undergo the fragmentation reactions described above even on heating.

(H) α-Selenocarbonyl compounds from vinylic selenides

Vinylic selenides react with seleninic anhydride (eqn.66) or

Table 33

Formation of ethylenic ketones from vinylic selenones |95|.

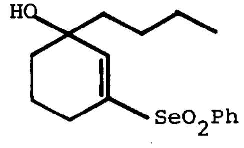
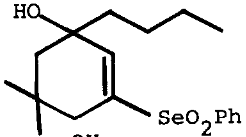
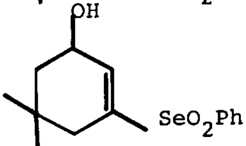
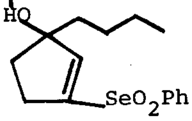
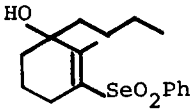
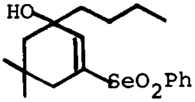
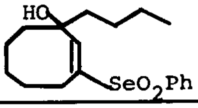
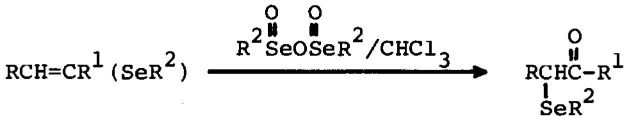
Substrate	nucleophile	olefin E/Z ratio	yield%
	CH_3ONa	20:80	86
	C_2H_5ONa	40:60	84
	PhSNa	-	68
	CH_3ONa	5:95	78
	PhSNa	-	43
	CH_3ONa	15:85	68
	CH_3ONa	80:20	53

Table 34

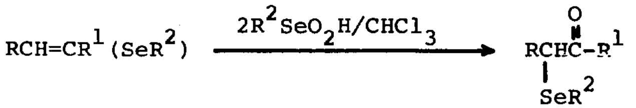
Formation of acetylenic ketones from vinylic selenones |95|.

substrate	base	yield%
	CH_3ONa	40
	NaH	84
	NaH	59
	CH_3ONa	43

or acid (eqn.67) under mild conditions to give α-selenocarbonyl compounds |96|. α-Selenocarbonyl compounds are intermediates of wide applicability in organic synthesis |73,75|.



$$RCH{=}CR^1(SeR^2) \xrightarrow{R^2\overset{O}{\overset{\|}{Se}}O\overset{O}{\overset{\|}{Se}}R^2/CHCl_3} \underset{\underset{SeR^2}{|}}{RCH}\overset{O}{\overset{\|}{C}}{-}R^1 \qquad (66)$$



$$RCH{=}CR^1(SeR^2) \xrightarrow{2R^2SeO_2H/CHCl_3} \underset{\underset{SeR^2}{|}}{RCH}\overset{O}{\overset{\|}{C}}{-}R^1 \qquad (67)$$

The yields (Table 35) varied from very good to poor. The mechanism of this transformation is not known.

Table 35

α-Selenocarbonyl compounds from vinylic selenides |96|.

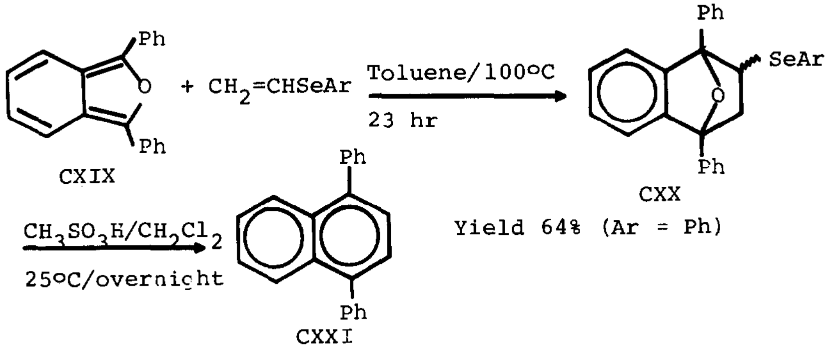
R	R^1	R^2	reaction conditions t°C/time(hours)	yield%
Ph	C_9H_{19}	H	20/40	80^a
			20/15 then 50/2	83^b
Ph	C_8H_{17}	CH_3	20/24	52^a
			50/7	41^b
CH_3	C_9H_{19}	H	20/23	84^a
			20/77	84^b
CH_3	C_8H_{17}	CH_3	20/9	44^a
			50/6	36^b

a) reaction with seleninic anhydride;b) reaction with seleninic acid.

(I) Miscellaneous

Phenyl vinyl selenide XCVII reacts with 1,3-diphenylisobenzofuran CXIX to give the corresponding Diels-Alder adduct CXX. Treatment of CXX with methanesulfonic acid furnishes 1,4-diphenylnaphthalene CXXI (eqn.68) |1|.

Vinylic selenides react with Grignard reagents in the presence of nickel-phosphine complexes to give coupling products free of selenium CXXII (eqn.69) |97,98|. The yields are generally good (Table 36).



Yield 64% (Ar = Ph) (68)

$$RR^1C{=}CR^2(SePh) + R^3MgX \xrightarrow{\text{Ni complex}} RR^1C{=}CR^2R^3 \quad (69)$$

CXXII

Ni complex = $NiCl_2(Ph_3P)$; $NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$

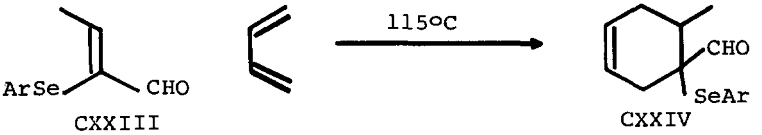
Table 36
Cross-coupling of vinylic selenides with Grignard reagents |98|.

$$PhSeCH{=}CHR \xrightarrow[\text{Ether, reflux, 8hr}]{R^1MgBr\text{,cat. (3mol\%)}} R^1CH{=}CHR + PhR^1$$

R	R^1	yield%	
		A	B
Ph	Ph	88	89
Ph	$n-C_4H_9$	28	76
$n-C_4H_9$	Ph	70	83
$n-C_4H_9$	$n-C_4H_9$	45	86

A = $NiCl_2(Ph_3P)$; B = $NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$

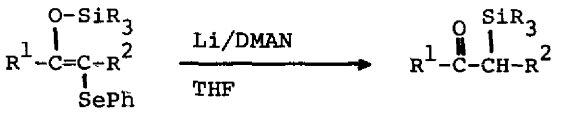
The α-phenylseleno enal CXXIII was found to be an excellent dienophile, giving the corresponding Diels-Alder adduct CXXIV with butadiene in 81% yield (eqn.70) |33|.



CXXIII CXXIV (70)

Trialkylsilyl enol ethers of α-phenylseleno ketones CXXV are converted into the corresponding α-trialkylsilyl ketones CXXVI upon treatment with methallic lithium in the presence of dimethylamino naphthalene (DMAN) (eqn.71, Table 37) |69|.

Table 37

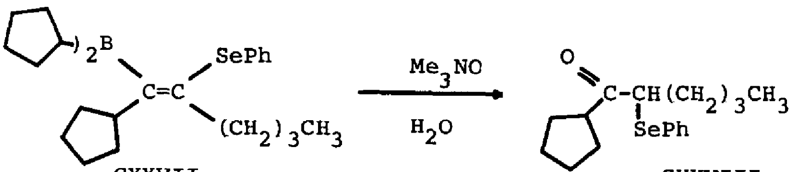


$$R^1-\overset{\displaystyle O-SiR_3}{\overset{|}{C}}=\underset{\displaystyle SePh}{\underset{|}{C}}-R^2 \xrightarrow[\text{THF}]{\text{Li/DMAN}} R^1-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle SiR_3}{\overset{|}{C}}H-R^2 \qquad (71)$$

CXXV CXXVI

R^1	R^2	SiR_3	CXXVI yield%
$-(CH_2)_3-$		$t-BuSiMe_2$	79
$-(CH_2)_4-$		$SiEt_3$	75
$-(CH_2)_4-$		$i-PrSiMe_2$	82
$-(CH_2)_4-$		$t-BuSiMe_2$	85
$-\overset{\displaystyle CH_3}{\overset{|}{C}}H(CH_2)_3-$		$t-BuSiMe_2$	84
$-\overset{\displaystyle n-C_4H_9}{\overset{|}{C}}H(CH_2)_3-$		$i-PrSiMe_2$	81
$-(CH_2)_6-$		$i-PrSiMe_2$	83
$-(CH_2)_{10}-$		$t-BuSiMe_2$	78
Ph	C_2H_5	$i-PrSiMe_2$	67
PhC_2H_5	H	$t-BuSiMe_2$	57
PhC_2H_5	C_3H_7	$i-PrSiMe_2$	65

Bis-vinyl derivatives of the type CXXVII can be transformed into α-phenylseleno ketones CXXVIII by treatment with trimethylamine N-oxide (eqn.72) |99|.



(72)

CXXVII CXXVIII

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