Tetrahedron Vol. 41, No. 24, pp. 5939 to 5954, 1985
Printed in Great Britain.

0040-4020/85 $3.00+.00

PREPARATION OF 3-HYDROXYL-VINYL SELENIDES AND 1,3-BIS(SELENO)-PROPENES

M. Renard and L. Hevesi *

Facultés Universitaires Notre-Dame de la Paix,
Laboratoire de Chimie Organique
61, Rue de Bruxelles, B-5000 Namur (Belgium)

(*Received in UK* 19 *June* 1985)

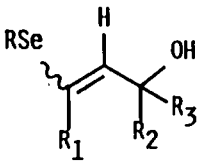
Abstract : Z and E 3-hydroxy-vinyl selenides can be prepared with very high stereoselectivity respectively by nucleophilic addition of selenolates to propargyl alcohols and by selenylation followed by $LiAlH_4$ reduction of the same propargyl alcohols. 1,3-Bis(seleno)-propenes are available either from the reaction of 3-hydroxy-vinyl selenides with selenols in the presence of zinc chloride or by Wittig condensation of α-selenoaldehydes with selenophosphorus ylids. Both reactions lead to mixtures of E and Z products which undergo sigmatropic rearrangements under acidic conditions.

Heterosubstitued allylic systems are interesting and widely used compounds in synthetic organic chemistry. Considerable effort has been devoted recently to the regiochemistry of alkylation of the resulting carbanions with various electrophiles as well as their use [1]. Recently we have reported that vinyl selenides bearing heteroatomic substituents in the allylic position are valuable precursors for selenium stabilized allyl cationic species [2-4].

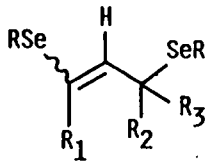
While numerous methods leading to simple vinyl selenides have been described [5], with the exception of specific examples [6], 3-hydroxy vinyl selenides 1 were unknown compounds prior to the start of this work. A similar situation arises for 1,3-bis(seleno)-propenes 2 where only 1,3-bis (phenylseleno)-propane 2e has been described previously [1e].

In this paper we show that a number of derivatives of the type 1 and 2 can easily be prepared in good yield from commercially available starting materials.

While we are able to prepare the alcohols 1E and 1Z with high stereoselectivity, the 1,3-bis (seleno)-propenes 2 could only be obtained as mixtures of E and Z isomers.



1 (E or Z)



2 (E or Z)

a	R=Me ; $R_1=R_2=R_3=H$
b	R=Me ; $R_1=R_2=H$; $R_3=Me$
c	R=Me ; $R_1=H$; $R_2=R_3=Me$
d	R=Me ; $R_1=Me$; $R_2=R_3=H$
e	R=Ph ; $R_1=R_2=R_3=H$
f	R=Ph ; $R_1=R_2=H$; $R_3=Me$
g	R=Ph ; $R_1=H$; $R_2R_3=Me$
h	R=Ph ; R_1Me ; $R_2R_3=H$

a	R=Me ; $R_1=R_2=R_3=H$
b	R=Me ; $R_1=R_2=H$; $R_3=Me$
c	R=Me ; $R_1=H$; $R_2=R_3=Me$
d	R=Me ; $R_1=Me$; $R_2=R_3=H$
e	R=Ph ; $R_1=R_2=R_3=H$
f	R=Ph ; $R_1=R_2=H$; $R_3=Me$
g	R=Ph ; $R_1=H$; $R_2R_3=Me$
h	R=Ph ; $R_1=Me$; $R_2=R_3=H$

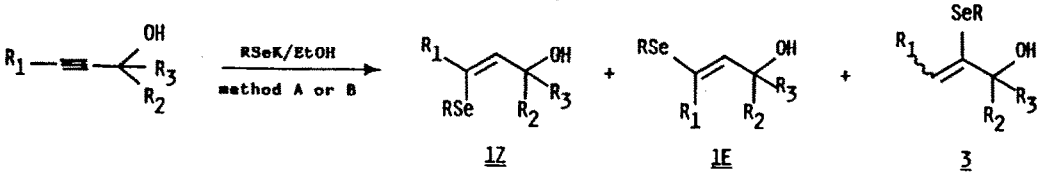
Results and Discussion.

1. Synthesis of 3-hydroxy-vinyl selenides 1.

One possible access to heterosubstituted vinylic compounds is by way of nucleophilic addition to alkynes [7]. This reaction is known to occur in good yield between arylselenols and mono-and dialkylacetylenes in basic medium to give the corresponding aryl vinyl selenides of cis stereochemistry [8-11]. We have therefore performed a series of reactions in order to test whether or not propargyl alcohols bearing 1,2 or 3 methyl substituents would react in the same fashion with selenolate ions ($MeSe^-$) and ($PhSe^-$).

The results displayed in Scheme I show that both methane and benzene selenolates add to the triple bond of propargyl alcohols in good to excellent yields. The addition reactions appear to be highly stereoselective since in all cases only 1Z could be isolated from the reaction mixtures with the exclusion of the 1E isomers. This is a quite remarkable result [12] since the reactions are performed at 80°C for 72 hours. Although the stereoselectivity is generally excellent, the regioselectivity is rather modest, as indicated by variable amounts of regioisomers 3 present in all the product mixtures except in the most hindered cases (Scheme I, entry 4). As expected on steric grounds, the more encumbered the carbon bearing hydroxyl substituent is the less isomer 3 is formed, regardless of whether methaneselenolate or benzeneselenolate is used as the nucleophile (Scheme I, entries 1 and 6). Finally, both methods A (RSeH/KOH/EtOH/80°C/72 hrs) and B ($PhSeSePh/HOCH_2N_2$-KOH/EtOH/80°C/72 hrs) give comparable results (Scheme I, entries 6,7 and 9,10).

Scheme I

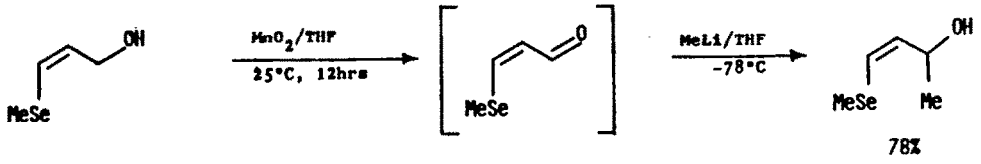


Entry	R	R_1	R_2	R_3	Method ×	1Z : 1E : 3	Yield (%)
1	Me	H	H	H	A	50 : 0 : 50	80
2		H	H	Me	A	63 : 0 : 37	76
3		H	Me	Me	A	61 : 0 : 39	95
4		H	iPr	iPr	A	100 : 0 : 0	83
5		Me	H	H	A	66 : 0 : 34	85
6	Ph	H	H	H	A	72 : 0 : 28	67
7		H	H	H	B	56 : 0 : 44	83
8		H	H	Me	A	83 : 0 : 17	88
9		H	Me	Me	A	89 : 0 : 11	81
10		H	Me	Me	B	89 : 0 : 11	90
11		Me	H	H	A	75 : 0 : 25	64

×Method A : RSeH, 1 eq. KOH, EtOH, 80°C, 72 hrs
Method B : PhSeSePh, $HOCH_2SO_2Na.H_2O$/KOH, EtOH, 80°C, 72 hrs

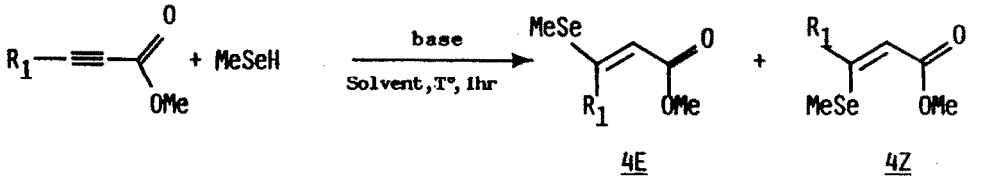
Despite the presence of regioisomer 3 in the products, nucleophilic addition of selenolate ions to propargyl alcohols appears to be a viable route to cis 3-hydroxy-vinyl selenides (1Z) since the undesirable isomer 3 can easily be separated from the stereochemically pure 1Z compound. In one case we have also tried to carry out methylation of the allylic position of 1. Manganese dioxide oxidation of 1a (MnO_2/THF/R.T./12 hrs) led to β-methylseleno-acrolein which was treated without prior purification with methyllithium in THF at -78°C to give 1b of pure 1Z stereochemistry in 78 % overall yield (Scheme II). Since oxidation of 1b to the corresponding ketone should also proceed without difficulty, repeated methylation would lead to 1c. This is however a less straightforward procedure and was not pursued.

Scheme II



In an effort to avoid formation of the undesired regioisomer 3 we also studied 1,4-additions of selenolates to methyl propiolate and methyl butynoate (Scheme III). These reactions take place in a totally regioselective manner and essentially in quantitative yield. Unfortunately, satisfactory stereoselectivity could not be attained and methyl β-selenoacrylates 4E and 4Z were formed in about 20:80 ratio. This ratio was found to be insensitive to the reaction solvent and was only slightly modified by changing the temperature from +21 to -80°C (Scheme III). The stereoisomeric mixture of β-methylselenoacrylates could not be resolved by column chromatography on silica gel. However, lithium aluminum hydride reduction of and methyllithium addition to the ester mixtures proceeded cleanly (Scheme IV a and b). The resulting 1E and 1Z components of the 3-hydroxy-vinyl selenides could be separated by chromatography.

Scheme III



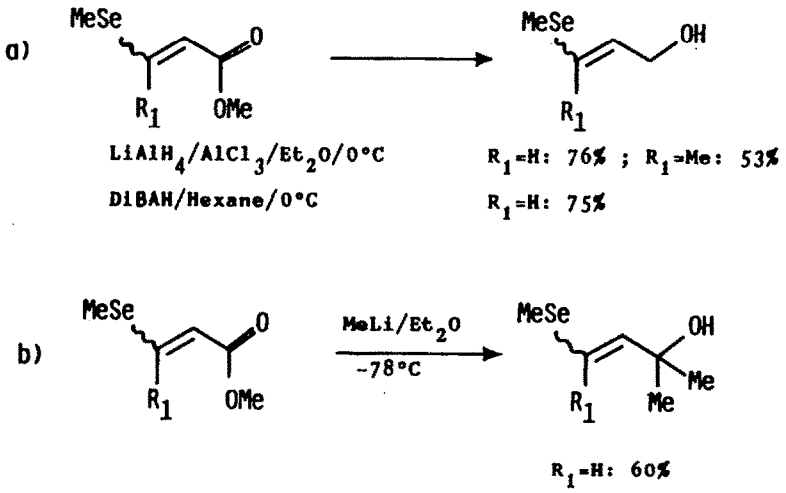
4E 4Z

Entry	R_1	Base[a]	Solvent	T(°C)	4E : 4Z[b]
1	H	A	Et_2O	21	22 : 78
2	H	A	Et_2O	0	20 : 80
3	H	A	Et_2O	-65	19 : 81
4	H	A	Et_2O	-80	17 : 83
5	H	B	Et_2O	21	20 : 80
6	H	C	EtOH	21	20 : 80
7	H	None	$CDCl_3$	21	20 : 80
8	Me	A	Et_2O	21	19 : 81

(a) A = catalytic amount of piperidine (0.1 mol.eq.); B = 1 eq. piperidine; C = 1 eq. KOH

(b) 100 % yield in all cases

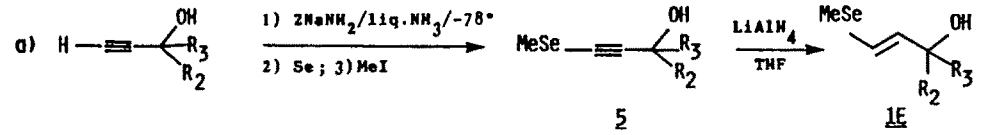
Scheme IV



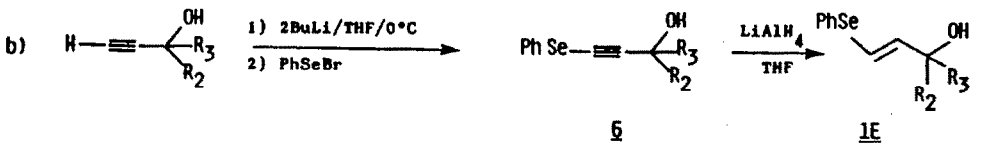
Furthermore, it is worth noting the trend of the E/Z ratios observed in nucleophilic additions to acetylenic ketones and esters on going from alcohol to thiol to selenol nucleophiles. The adducts formed from alcohols and methyl propiolate possessed essentially E stereochemistry ,[13] thiols gave nearly 1:1 mixtures of E and Z adducts [10,14,15], while methaneselenol predominantly gave the Z isomer (Scheme III).

Our method of preparation of 3-hydroxy-vinyl selenides 1E is based on the highly trans stereoselective reduction of acetylenic selenides by means of lithium aluminum hydride [5,16]. The method of Brandsma [17] was adapted for the production of the necessary acetylenic selenides 5 and 6 by forming the dianions of propargylic alcohols (Scheme V) either with sodium amide (liq. NH_3/-78°) or with butyllithium (THF/0°C) and reacting these with metallic selenium followed by methyl iodide [17] or with benzeneselenenyl bromide [18]. Reduction of 5 in THF gave the expected 3-hydroxy-vinyl selenides 1 of pure E stereochemistry (Scheme V a and b). Obviously this route does not allow the preparation of 1d(E) and 1h(E), therefore these compounds are at present only accessible as mixtures of stereoisomers by the methods of Kuwajima [6c] and Gravel [6a].

Scheme V



R_2	R_3	Yield (%) in 5	Yield (%) in 1E
H	H	55	81 (1a)
H	Me	43	79 (1b)
Me	Me	68	84 (1c)



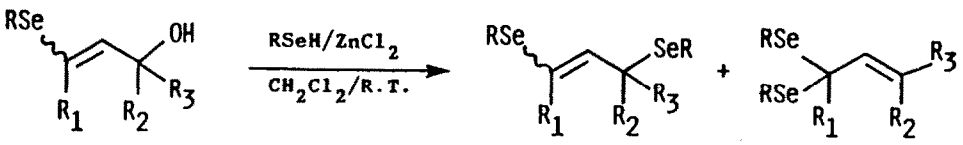
R_2	R_3	Yield (%) in 6	Yield (%) in 1E
H	H	87	83 (1e)
H	Me	98	75 (1f)

2. Synthesis of 1,3-bis(seleno)-propenes 2 from alcohols 1

An (E,Z) mixture of 1,3-bis(phenylseleno)-propenes, unique example of the series 2, has been prepared [1e] from 1,3-dichloropropene [19] and benzeneselenolate in strongly basic medium. However, the method is therefore limited to the unsubstituted derivative 2e.

It has been shown recently that primary, secondary and tertiary alkyl and benzyl alcohols are easily transformed to the corresponding selenides by the action of selenols in the presence of zinc chloride [20], and allylic sulfides are produced under similar conditions [21,22]. Applying this reaction to substrates 1 described in the preceding section we obtained the results given in Scheme VI, which shows that substitution of the hydroxyl group proceeds in good yield in all cases. Thus the original process [20] is not limited to unfunctionalized allyl alcohols. In several instances however two main products are formed, the desired 1,3-bis(seleno)-propenes 2 and 1,1-bis(seleno)-propenes 7. This observation, as well as the stereochemistry of compounds 2 formed, is reminiscent of the intimate mechanisms of the allylic nucleophilic substitution reactions involved [24]. Interpretation of the results displayed in Scheme VI is however complicated by the fact that the reactions were performed under heterogeneous conditions and that allyl selenides are known [25,26] to undergo thermal, light or acid catalyzed sigmatropic rearrangements.

Scheme VI



1 2 7

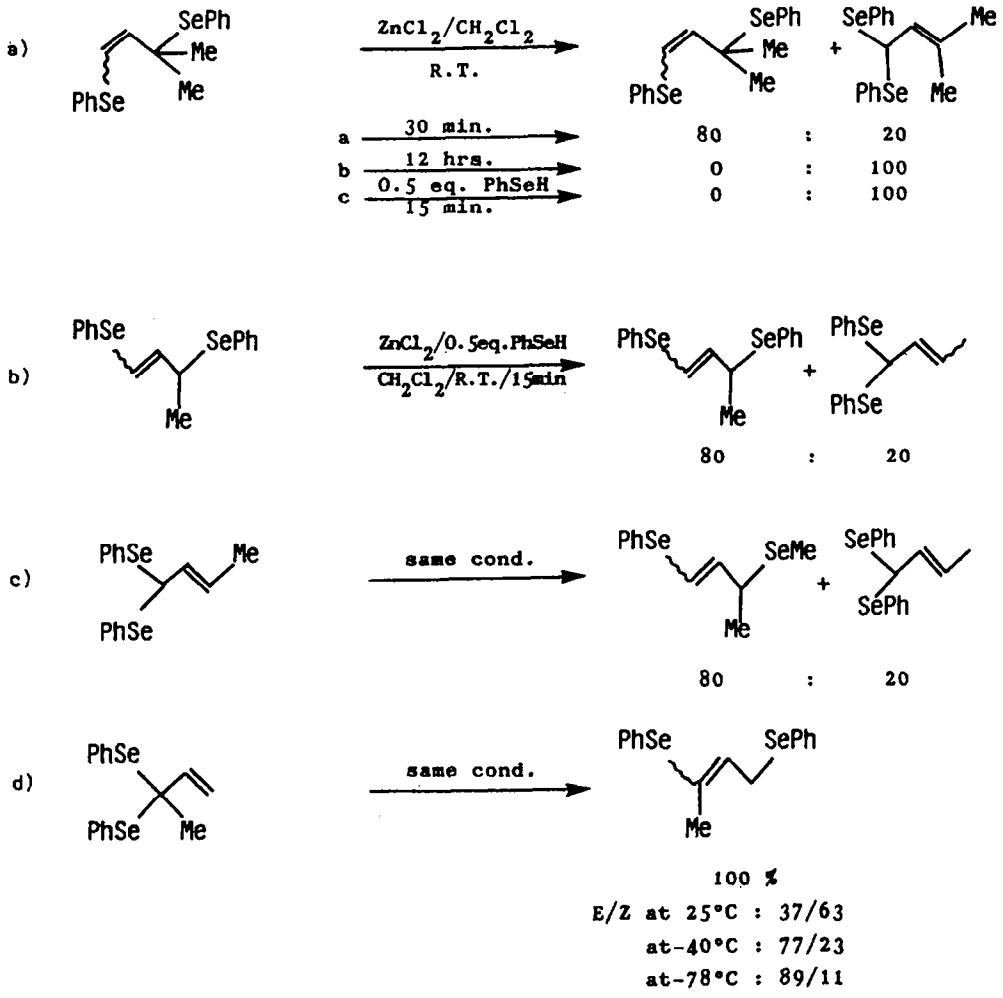
Entry	Starting 1				R	2 (E : Z)	: 7	Yield (%)
	R_1	R_2	R_3					
1	Me	H	H	Z	Me	100 (34:66)	: 0	54
2	H	H	H	Z	Me	100 (40:60)	: 0	73
3	H	H	H	E	Me	100 (100:0)	: 0	82
4	H	Me	H	Z	Me	68 (66:34)	: 32	60
5	H	Me	H	E	Me	70 (70:30)	: 30	63
6	H	Me	Me	Z	Me	0	: 100	79
7	H	iPr	iPr	Z	Me	0	: 100	72
8	H	Me	Me	E	Me	0	: 100	80
9	H	H	H	Z	Ph	100 (50:50)	: 0	75
10	H	H	H	E	Ph	100 (100:0)	: 0	79
11	H	Me	H	Z	Ph	67 (70:30)	: 33	68
12	H	Me	H	E	Ph	66 (100:0)	: 34	70
13	H	Me	Me	Z	Ph	0	: 100	63
14	H	Me	Me	E	Ph	0	: 100	61
15	Me	H	H	Z	Ph	100 (37:63)	: 0	81

It is seen (Scheme VI, entries 1,2,9,15) that even primary Z-alcohols change the double bond configuration to a large extent (35-50 %), while primary E-alcohols undergo substitution with complete retention of configuration (entries 3,10). This result is quite different from that observed in solvolysis [27] or in substitution with organometallics [24].

In isolated cases we have checked the effect of temperature and solvent on the double bond isomerization during reaction. When (Z)-3-phenylseleno-2-buten-1-ol 1h was subjected to substitution ($PhSeH/ZnCl_2/CH_2Cl_2$) at 21, 0, -40 and -78°C the product 2h was obtained with E/Z ratios of 37/63; 37/63; 16/84 and 12/88 respectively. On the other hand, the same reaction carried out on (Z)-3-phenylseleno-2-propen-1-ol in benzene, carbon tetrachloride, dichloromethane, 1,2-dichloroethane and nitromethane [28] almost invariably produced 1:1 mixtures of E and Z 1,3-bis (phenylseleno)-propenes.

Substantial evidence has been obtained showing that acid catalyzed rearrangements of compounds 2 and 7 during their formation determine to a large extent the net regiochemical results of these allylic substitutions. We have prepared some representative derivatives 2 and 7 of the phenylseleno series by independent synthesis (see next section) and examined their rearrangements (Scheme VII). It was observed that while 2g (E + Z) rearranged slowly in the presence of $ZnCl_2$ alone, it was rapidly transformed to the corresponding acetal 7 when selenophenol was added to the reaction mixture (Scheme VII a). As expected, the same regioisomeric mixture was produced on rearrangement of 1,3-bis(phenylseleno)-but-1-ene and of 1,1-bis(phenylseleno)but-2-ene (Scheme VII b and c). Finally, 3,3-bis(phenylseleno)-but-1-ene rearranged completely to 1,3-bis(phenylseleno)-but-2-ene under the same conditions (Scheme VII d). Quite remarkably E/Z ratios of the rearranged product mixtures in the latter case as a function of temperature closely resemble those given for the substitution of (Z)-3-phenylseleno-2-buten-1-ol.

Scheme VII



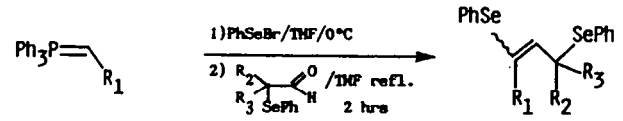
Unfortunately, we were unable to prepare acrolein phenylseleno-acetal although this was attempted by two different approaches (vide infra). Nevertheless, the above results allow us to draw some conclusions concerning the mechanisms of the allylic substitution reaction. Thus, SN_2 mechanism does not appear to operate except in the cases of primary E alcohols where the double bond stereochemistry is retained. Of the two alternatives, SN_1 (or ion pair) and SN_2' mechanism, we prefer SN_2' for two reasons. Firstly, it is known that γ-substitution of primary allylic substrates occurs especially with soft organometallics [29,30] and secondly, that parallelism between stereochemical results for substitution and rearrangement make it plausible that even primary alcohols 1 suffer γ-attack by the soft nucleophile selenol to give 7 as the first product. Under the influence of the acidic reaction medium, the latter would rearrange rapidly and completely to 2. Such a scheme is increasingly possible for secondary and tertiary alcohols with less likelihood of rearrangement of product 7.

3. Synthesis of 1,3-bis(seleno)-propenes 2 by the Wittig reaction

This method is based on the availability of selenophosphoranes [31] and selenophosphonates [32] and their reactions with carbonyl compounds to produce vinyl selenides [16,33,34]. Phenylselenoacetaldehyde was prepared in high yield (95 %) from ethyl vinyl ether and benzeneselenenyl bromide according to Petrzilka [35]; α-phenylseleno isobutyraldehyde was obtained by direct selenylation of the aldehyde with benzeneselenenyl chloride in ethyl acetate [36] and 2,2-bis(phenylseleno)-propanal was prepared in excellent yield from 1,1,1-tris(phenylseleno)-ethane and DMF by the method of Krief [37]. With these compounds in hand we studied various Wittig reactions the results of which are shown in Scheme VIII. Similarly to vinyl selenides [16], these reactions required heating in THF to occur in acceptable yields so long as the reactants were not heavily substituted (Scheme VIII a). The products 1,3-bis(phenylseleno)-propenes were isolated as mixtures of E+Z isomers. Their ratio could not be greatly changed neither under "salt free" conditions nor in the presence of added lithium bromide.

Scheme VIII

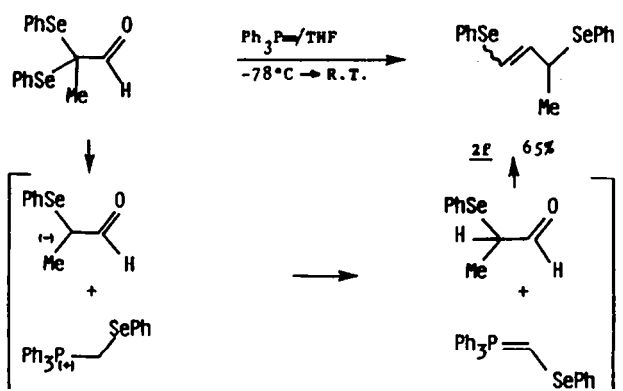
a)



R_1	R_2	R_3	2 Yield (%)	E/Z
H	H	H	2e 60	50/50
Me	H	H	2h 52	50/50
H	Me	Me	2g 63	19/81 (24/76)*
Me	Me	Me	0	

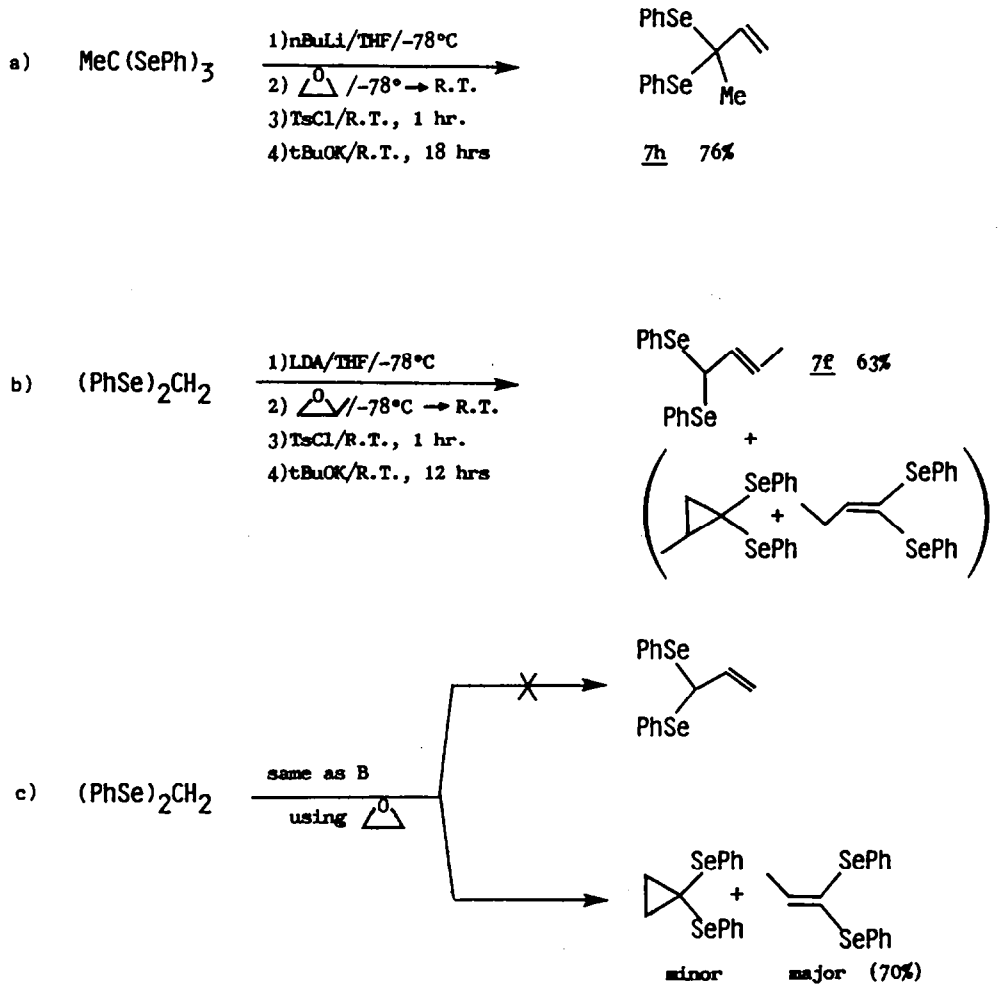
(*) : in the presence of 10 eq. LiBr

b)



We attempted preparation by this methodology of 3,3-bis(phenylseleno)-but-1-ene necessary experiments on allylic rearrangement. Methylene triphenylphosphorane and 2,2-bis(phenylseleno)-propanal react to produce 2f (E+Z) presumably by the route outlined in Scheme VIII b. 1,1-Bis (phenylseleno)-prop-2-ene could not be prepared for the same reasons. Synthesis of these types of compounds was also studied using yet another method which has met with some success (Scheme IX), the major side reactions being cyclopropanone [38] and ketene selenoacetal formation.

Scheme IX



In conclusion, a variety of 3-hydroxyl-vinyl selenides and 1,3-bis(seleno)-propenes can now be prepared usually in good yield and with satisfactory regio- and stereoselectivity. Currently, we are using a number of these compounds as precursors for the in situ generation of 1-selenoallyl cationic species whose efficient reactions with electron rich heterocycles such as furan and pyrrole lead to new synthetic applications of allylic derivatives 1 and 2. These results will be reported separately.

Acknowledgement. We thank F.N.R.S. for financial support and I.R.S.I.A. for predoctoral fellowships to one of us (M.R.).

Experimental Part

All organic and inorganic reagents and solvents were purchased from Janssen Chimica (Beerse, Belgium) or from Merck (Belgolabo, Overijse, Belgium). Tetrahydrafuran (THF) and diethyl ether were distilled before use from benzophenone ketyl in a recycling still; dichloromethane, acetonitrile and nitromethane were distilled from phosphorus pentoxide and stored on 4 Å molecular sieves.

Methaneselenol was prepared by hydrophosphorous acid reduction of dimethyl diselenide according to Günther [39]; selenophenol was obtained by the method of Foster [40]; formaldehyde diphenyl selenoacetal [41] and triphenyl orthoselenoacetate [41,42] were prepared according to literature procedures.

Preparation of 3-hydroxy-vinyl selenides 1

Method A: Potassium hydroxide (2.8 g, 50 mM) is dissolved in a minimum amount of water (~3ml). 150 ml of degassed ethanol is added followed by 7.85 g (50 mM) of selenophenol under argon and by 4.21 g (50 mM) of 3-methyl-butyn-3-ol. The mixture is refluxed until disappearance of all the propargyl alcohol (3 days, monitored by IR). After cooling the deep brown reaction mixture is acidified by 1N HCl, extracted with ether; the ether layer washed with water, dried over magnesium sulphate. Evaporation of the solvent leaves 10.03 g of viscous yellowish liquid which, besides of a little diphenyl diselenide, contains 1g(Z) and 3g in the ratio 89:11 (81 % overall yield) as determined by ^{1}H NMR. Pure 1g(Z) is isolated by column chromatography (SiO_2, pentane/ ether, 80/20 v/v).

Method B[1e]: 4.68 g (15 mM) of diphenyl diselenide and 2.7 g of rongalite ($HOCH_2SO_2Na.H_2O$) are dissolved in 100 ml degassed ethanol under argon. A solution of 5.6 g of KOH in 20 ml ethanol is added with stirring; the mixture, heated to 60°C for 1 hour, completely decolorizes. At this stage 2.52 g (30 mM) of 3-methyl-butyn-3-ol and 8.4 g of powdered KOH are introduced and the mixture is refluxed for 3 days. After cooling 0.36 g of monochloroacetic acid are added and reacted for 10 min. The mixture is extracted with ether; the ether layer is washed with water, dried over magnesium sulphate and purified as in method A. Compounds 1g(Z) and 3g are obtained in the same (89:11) ratio but in somewhat better yield (90 %) as above.

Preparation of 1b from 1a

A suspension of 8 g of activated MnO_2 in 30 ml of dry THF containing 604 mg (4 mM) of 1a is stirred 24 hrs at room temperature. The solid is separated by filtration through celite and magnesium sulphate and the solution is cooled to -78°C. Methyl lithium (2.6 ml of 1.55 N solution in ether, 4 mM) is added. The mixture is kept at -78°C for 1hr, hydrolyzed with aqueous ammonium chloride and extracted with ether. The ether layer is washed with water, dried over magnesium sulphate and concentrated under vacuum. The crude product is purified by PLC (Si_2O) eluent pentane/ether 75/25, v/v) to yield 500 mg (78 %) of 1b as a pale yellow liquid.

Addition of methaneselenol to methyl but-2-ynoate

196 mg (2 mM) of methyl but-2-ynoate are dissolved in 5 ml dry ether under argon. 190 mg (2 mM) of methane selenol and one drop of piperidine are injected and the solution is stirred for 4 hrs at room temperature. Evaporation of solvent and purification by PLC (SiO_2, pentane/ ether 95/5, v/v) gives a quantitative yield of an E+Z mixture of 4 (R_1 = Me, Scheme III).

Reduction of 4 to 1

380 mg (10 mM) of $LiAlH_4$ and 441 mg (3.3. mM) of $AlCl_3$ are placed in 10 ml dry ether under argon at 0°C. A solution of 591 mg (3.3 mM) of 4 (R_1 = H) in 1 ml ether is added slowly. After 1 hr the temperature is allowed to reach 25°C and the mixture is hydrolyzed carefully with a minimum of water. Filtration through celite and $MgSO_4$ and evaporation of the solvent leaves 380 gm (76 %) of pure 1a. Similarly, the same ester is reduced to 1a using iBu_2AlH in hexane (0°C, 1 hr) in 75 % yield.

Reductive methylation of 4

1.79 g (10 mM) of methyl β-methylselenoacrylate 4 (R_1 = H) are dissolved in 20 ml of dry ether, cooled to -78°C and treated with 14 ml of methyllithium (1.55 N in ether, 20 mM) and stirred under argon for 2 hrs. The mixture is hydrolyzed, the ether layer washed with 10 % HCl, dried and concentrated under vacuum. Purification by chromatography (SiO_2, pentane/ether, 75/25, v/v) yields 0.8 g (60 %) of 1c as a pale yellow liquid.

Preparation of compounds 5 and 6

These are obtained by a combination of literature procedures [17] as follows.
Compounds 5 : Sodium amide is prepared as a liquid ammonia (100 ml) suspension at -78°C from 2.3 g (0.1 M) of sodium. Butyn-3-ol (3.5 g, 0.05 M) is added dropwise and the mixture stirred at -78°C for 30 min. Metallic grey selenium (4g, 0.05 M) is added, followed rapidly by 7.1 g (0.05 M) of methyl iodide. Temperature is then allowed to reach room temperature until all the solvent is evaporated. The resulting dark solid is hydrolyzed with ice water, extracted with ether, washed with 1N HCl, saturated brine and dried over $MgSO_4$. Evaporation of solvent ether and chromatography (SiO_2, pentane/ether 5/5, v/v) yields 3.5 g (43 %) of 5 (R_2 = H, R_3 = Me) as a pale yellow liquid.

Compounds 6: Addition of butyllithium (30 ml 1.65 N in hexane, 50 mM) to a cooled (0°C) solution of 1.75 g (25 mM) of butyn-3-ol in 75 ml THF gives a white suspension. Benzeneselenenyl bromide (6 g, 25 mM; prepared from equivalent amounts of diphenyl diselenide and bromine in dichloromethane) dissolved in 20 ml dry THF is added slowly (~ 1 hr). This leads to a yellowish solution which is quenched with aq. NH_4Cl after two more hours of reaction at 0°C. The mixture is extracted with ether; the ether solution is washed with 1 N HCl, water and dried over $MgSO_4$. Evaporation of solvents yields 5.55 g (98 % of essentially pure 6 (R_2 = H, R_3 = Me).

It is important that PhSeBr be added slowly to the dianion, otherwise addition to the C,C triple bond strongly lowers the yield in 6.

Reduction of 6 to 1

Lithium aluminum hydride (0.95 g) is dissolved in 100 ml of THF at 0°C under argon. A solution of 6 (R_2 = H, R_3 = Me; 4.52 g, 20 mM) in 10 ml of THF is added and the mixture is stirred for 1 hr. The reaction is quenched with 2 ml H_2O followed by 1 ml of 1N KOH. Drying agent ($MgSO_4$) is added, the mixture is stirred for a few minutes and filtered over celite. Evaporation of the solvent THF gives 3.4 g (75 %) of essentially pure 1f (E) as a pale yellow liquid.

Transformation of 3-hydroxy-vinyl selenides 1 to 1,3-bis(seleno)-propenes 2 and/or to 1,1-bis (seleno)-propenes 7

81 mg (0.6 mM) of $ZnCl_2$ are suspended in 2 ml of dry CH_2Cl_2 and stirred under argon while a solution of 228 mg (1 mM) of 1f and of 157 mg (1 mM) of PhSeH in 0.5 ml CH_2Cl_2 is added dropwise at 0°C [44]. After 15-30 min the reaction is quenched with aq. $NaHCO_3$, extracted with ether; the ether layer washed with water, brine and dried over $MgSO_4$. Evaporation and PLC (SiO_2, pentane) purification leads to 260 mg (70 %) of a mixture of 2f (E) and 7f in a ratio of 66:34.

α-Phenylselenoisobutyraldehyde is obtained by mixing PhSeCl with isobutyraldehye in 1:1 molar proportion in ethyl acetate for 12 hours. Evaporation of the solvent and purification (SiO_2, pentane/ether 80/20, v/v) gives the desired compound in 86 % yield.

Preparation of 2g by Wittig reaction : Methyl triphenylphosphonium iodide (807 mg, 2mM) is suspended in 2 ml dry THF and treated with butyllithium (2 mM) at 0°C. After 15 min. benzeneselenenyl bromide (236 mg, 1mM dissolved in 0.5 ml THF) is added to the orange ylid solution which turns yellow and deposits a white precipitate. After 30 min. stirring at 0°C α-phenylselenoisobutyraldehyde (227 mg, 1 mM, dissolved in 0.5 ml THF) is added and the mixture is refluxed 2 hrs, cooled to room temperature. Triphenyl phosphine oxide is precipitated with pentane, filtered off and the solvents evaporated. Purification on Al_2O_3 (eluent pentane) gives 240 mg (63 %) of an E + Z mixture of 2g.

Preparation of 7h

2.475 g (5 mM) of triphenyl orthoselenoacetate are dissolved in 50 ml of dry THF and cooled to -78°C under argon. Butyllithium (5.2 eq.) is added followed by, after 45 min., 220 mg (5 mM) of ethylene oxide and the mixture is stirred 12 hrs without cooling bath. p-Toluenesulphonyl chloride (953 mg, 5 mM, dissolved in 5 ml THF) is added. After 2 hrs at room temperature, the mixture is reacted with potassium t-butoxide (561 mg, 5 mM) at the same temperature for 18 hrs. Quenching with aq. $NaHCO_3$, extraction with pentane, washings with water followed by column chromatographic purification (Al_2O_3, pentane/ether 98/2, v/v) gives 1.395 g (76 %) of 7h.

Analytical and spectroscopic data of new compounds §

1a (E)

^{1}H NMR (δ, CCl_4) : 2.07 (3H, s), 3.05 (1H, OH), 4.05 (2H, d, J = 5 Hz), 5.7 (1H, dt, J = 5 Hz, J' = 15 Hz), 6.50 (1H, d, J = 15 Hz)
IR (liq. film, cm^{-1}) : 3300, 2900, 2850, 1600, 1400, 1300, 1265, 1000
Mass spectrum m/e : 154, 152 (M^+), 150, 148, 96, 95, 94, 93, 91, 57
Anal. calc. : C : 31.804, H : 5.388 ; found : C : 32.11, H : 5.38

1a (Z)

^{1}H NMR (δ, CCl_4) : 2.10 (3H, s), 3.50 (1H, OH), 4.10 (2H, d, J = 5 Hz), 6.00 (1H, dt, J = 5 Hz, J' = 10 Hz), 6.27 (1H, d, J = 9 Hz)
IR (liq. film, cm^{-1}) : 3300, 3000, 2900, 2840, 1600, 1400, 1300, 1265, 1000, 970
Mass spectrum m/e (M^+) : 154, 152, 150, 148, 96, 95, 94, 93, 57
Anal. calc. : C : 31.80, H : 5.34 ; found C : 32.11, H : 5.38.

1b (E)

^{1}H NMR (δ, CCl_4) : 1.21 (3H, d, J = 6 Hz), 2.1 (3H, s), 2.5 (1H, OH), 4.23 (1H, p, J = 6 Hz), 5.45 (1H, dt, J = 5 Hz, J' = 6 Hz), 6.41 (1H, d, J = 15 Hz)
IR (liq. film, cm^{-1}) : 3300, 2960, 2920, 2860, 1700, 1605, 1440, 1420, 1365, 1320, 1270, 1200, 1120, 1050, 930, 910, 860, 830, 710
Mass spectrum m/e : 168 (M^+), 166, 151, 123, 121, 95, 93, 71, 55, 53
Anal. calc. : C : 36.38, H : 6.11 ; found C : 36.40, H : 5.92

1b (Z)

^{1}H NMR (δ, CCl_4) : 1.21 (3H, d, J = 6 Hz), 2.10 (3H, s), 2.6 (1H, O-H), 4.4 (1H, p, J = 6 Hz) 5.7→5.95 (1H, m), 6.13 (1H, d, J = 9.5 Hz)
IR (liq. film, cm^{-1}) : 3340, 2960, 2915, 2860, 1600, 1440, 1420, 1360, 1290, 1270, 1180, 1100, 1070, 1050, 1020, 920, 910, 860, 780, 760, 700
Mass spectrum m/e : 168 (M^+), 166, 151, 123, 121, 95, 93, 71, 55, 53
Anal. calc. : C : 36.38, H : 6.11 ; found : C : 36.40, H : 5.92.

1c (E)

^{1}H NMR (δ, $CDCl_3$) : 1.30 (6H, s), 2.10 (3H, s), 3.50 (1H, OH), 5.70 (1H, d, J = 16 Hz), 6.20 (1H,d, J = 16 Hz)
IR (liq. film, cm^{-1}) : 3350, 2950, 2900, 2850, 1600, 1450, 1420, 1350, 1320, 1270, 1230, 1180, 1130, 950, 890, 780, 760
Mass spectrum m/e : 180 (M^+) Anal. calc. : C : 40.23, H : 6.75 ; found : C : 39.95, H : 6.61

1c (Z)

^{1}H NMR (δ, CCl_4) : 4.2 (2H, d, J = 5 Hz), 5.20 (1H, OH), 6.2 (1H, dt, J = 5 Hz, J ' = 9 Hz), 6.50 (1H, d, J = 9 Hz), 7.1→7.6 (5H, m)
IR (liq. film, cm^{-1}) : 3300, 3040, 2900, 2840, 1940, 1860, 1790, 1600, 1570, 1470, 1430, 1290, 1250, 1060, 1030, 1020, 730
Mass spectrum m/e : 215 (M^+), 212, 160, 158, 157, 156, 155, 154, 78, 77
Anal. calc. : C : 50.73, H : 4.30 ; found : C : 50.68 , H : 4.87

1d (Z)

^{1}H NMR (δ, CCl_4) : 2.05 (3H, dd, J = 1.2 Hz, J' = 1.2 Hz), 2.10 (3H, s), 3.2 (1H, OH), 4.10 (2H, dq, J = 5 Hz, J' = 1.2 Hz), 5.80 (1H, tq, J = 5Hz, J' = 1.2 Hz)
IR (liq. film, cm^{-1}) : 3300, 2980, 2950, 2920, 2850, 1625, 1425, 1360, 1270, 1180, 1120, 1075, 1000, 900
Mass spectrum m/e : 166 (M^+), 164, 151, 149, 148, 107, 96, 95, 93, 53

1e (E)

^{1}H NMR (δ, CCl_4) : 3.50 (1H, OH), 4.00 (2H, d, J = 5 Hz), 5.90 (1H, dt, J = 5 Hz, J' = 15 Hz), 7.0→7.5 (5H, m)
IR (liq. film, cm^{-1}) : 3300, 3050, 2900, 2850, 1950, 1870, 1800, 1610, 1580, 1480, 1440, 1360, 1300, 1250, 1075, 1020, 940, 900, 780, 760, 745, 690
Mass spectrum m/e : 215 (M^+), 212, 160, 158, 157, 156, 155, 154, 78, 77
Anal. calc. : C : 50.728, H : 4.729 ; found : C : 50.68, H : 4.87

1e (Z)

^{1}H NMR (δ, CCl_4) : 4.20 (2H, d, J = 5 Hz), 5.20 (1H, OH), 6.20 (1H, dt, J = 5 Hz, J' = 9 Hz), 6.50 (1H, d, J = 9 Hz), 7.1→7.6 (5H, m)
IR (liq. film, cm^{-1}) : 3300, 3040, 2900, 2840, 1940, 1860, 1790, 1600, 1570, 1470, 1430, 1290,

§ In the case of E + Z mixtures Δ designates the E isomer and □ designates the Z isomer.

1f (E)

^{1}H NMR (δ, CCl_4) : 1.2 (3H, d, J = 6 Hz), 3.0 (1H, O-H), 4.26 (1H, p, 6 Hz), 5.7 6.1 (1H, m), 6.56 (1H, d, J = 16 Hz), 7.1→7.6 (5H, m)
IR (liq. film, cm^{-1}) : 3300, 3040, 2960, 2920, 2860, 1940, 1860, 1790, 1605, 1575, 1470, 1435, 1360, 1320, 1275, 1190, 1120, 1050, 1020, 1000, 930, 870, 830, 730, 690
Mass spectrum m/e : 228 (M^+), 226, 185, 183, 158, 157, 156, 155, 78, 71
Anal. calc. : C : 52.87, H : 5.32 ; found : C : 52.88 , H : 5.50

1f (Z)

^{1}H NMR (δ, CCl_4) : 1.27 (3H, d, J = 6.5 Hz), 3.43 (1H, O-H), 4.56 (1H, p, J = 6.5 Hz), 5.8 6.13 (1H, m), 6.40 (1H, d, J = 9 Hz), 7.00→7.60 (5H, m)
IR (liq. film, cm^{-1}) : 3320, 3040, 2960, 2910, 2860, 1940, 1860, 1790, 1600, 1575, 1555, 1470, 1430, 1360, 1285, 1100, 1070, 1050, 1020, 1000, 920, 850
Mass spectrum m/e : 228 (M^+), 226, 185, 183, 158, 157, 156, 155, 78, 71
Anal. calc. : C : 52.87, H : 5.32 ; found : C : 52.88, H : 5.50

1g (Z)

^{1}H NMR (δ, CCl_4) : 1.33 (6H, s), 2.50 (1H, OH), 5.7 (1H, d, J = 10 Hz), 6.4 (1H, d, J = 10 Hz), 7.2→7.5 ($5H_{21}$m)
IR (liq. film, cm^{-1}) : 3400, 3050, 2950, 2920, 1870, 1860, 1800, 1740, 1620, 1580, 1480, 1460, 1440, 1380, 1310, 1200, 1150, 1070, 1020, 1000, 960, 900, 830, 800, 740, 690, 670
Mass spectrum m/e : 242 (M^+), 240, 227, 225, 158, 157, 149, 147, 85
Anal. calc. : C : 54.48, H : 5.85 ; found : 54.46, H : 6.07

1h (Z)

^{1}H NMR (δ, CCl_4) : 1.97 (3H, dd, J = 1.2 Hz, J' = 1 Hz), 3.2 (1H, O-H), 4.23 (2H, dd, J = 6 Hz, J' = 1 Hz), 5.97 (1H, tq, J = 6 Hz, J' = 1,2 Hz), 7.1→7.6 (5H, m)
IR (liq. film, cm^{-1}) : 3280, 3040, 2980, 2940, 2900, 2840, 1940, 1860, 1800, 1630, 1570, 1470, 1430, 1370, 1270, 1220, 1160, 1065, 990, 770, 760, 730
Mass spectrum m/e : 230 (M^+), 158, 157, 156, 78, 77, 71, 69, 53, 51
Anal. calc. : C : 52.87, H : 5.32 ; found : C : 53.13, H : 5.62

(Z)-MeSeCH=CHC(iPr)$_2$OH

^{1}H NMR (δ, CCl_4) : 1.2 (6H, d, J = 6 Hz), 1.23 (6H, d, J = 6Hz), 1.63 (1H, OH), 1.9 (2H, m), 2 (3H, s), 5.6 (1H, d, J = 10 Hz), 6.23 (1H, d, J = 10 Hz)
IR (liq. film, cm^{-1}) : 3500, 2950, 2920, 2875, 1610, 1460, 1420, 1380, 1370, 1340, 1300, 1270 1215, 1140, 1090, 1010, 950, 900, 860, 780, 700

2a (E + Z)

^{1}H NMR (δ, $CDCl_3$) : 1.90 Δ(3H, s), 1.95□ (3H, s), 2.1 (3H, s), 3.12Δ (2H, d, J = 8 Hz), 3.16□ (2H, d, J = 8 Hz), 5.60 Δ(1H, dt, J = 8 Hz, J' = 15 Hz), 5.90 □(1H, dt, J = 8 Hz, J' = 9 Hz), 6.20 Δ (1H, d, J = 15 Hz), 6.24 □ (1H, d, J = 9 Hz)
IR (liq. film, cm^{-1}) : 2990, 2910, 2850, 2820, 1595, 1415, 1320, 1270, 1230, 935, 900, 780, 760, 725
Mass spectrum m/e : 230 (M^+)
Anal. calc. : C : 26.00, H : 4,40 ; found : C : 25.94,H : 4.94

2d (E + Z)

^{1}H NMR (δ, CCl_4) : 1.9 (3H, s), 2.00 Δ(3H, d, J = 1Hz), 2.06 □(3H, s), 2.10Δ(3H, s), 2.13□ 3H, d, J = 1 Hz), 3.2 Δ (2h, d, J = 8 Hz), 3.26 □(2H, d, J = 8 Hz), 5.52 Δ (1H, t, J = 8 Hz), 5.67 □(1H, t, J = 8 Hz)
IR (liq. film, cm^{-1}) : 2980, 2910, 2840, 2800, 1615, 1420, 1370, 1300, 1270, 1175, 1075, 900 840, 780, 760
Mass spectrum m/e : 244 (M^+), 242, 151, 149, 147, 146, 145, 109, 107, 93
Anal. calc. : C : 29.77, H : 5.00 ; found : C : 29.68, H : 5.20

2e (E + Z)

^{1}H NMR (δ, $CDCl_3$): 3.50Δ(2h, d, J = 8 Hz), 3.65 □(2H, d, J = 8 Hz), 6.00Δ(1H, dt, J = 8 Hz, J' = 15 Hz), 6.15□(1h, dt, J = 8 Hz, J' = 9 Hz), 6.24Δ(1h, d, J = 15 Hz), 6.35 □(1H, d, J = 9 Hz), 7.1→7.5 (10H, m)
IR (liq. film, cm^{-1}) : 3100, 3040, 3010, 3000, 2900, 1940, 1870, 1790, 1730, 1590, 1575, 1560, 1470, 1430, 1420, 1380, 1315, 1300, 1270, 1230, 1175, 1160, 1065, 1020, 1000, 940, 900, 850, 760, 730, 690, 670
Mass spectrum m/e : 354 (M^+)
Anal. calc. : C : 51.15, H : 4.01 ; C : 51.28,H : 4.29

2f (E + Z)

^{1}H NMR (δ, CCl_4) : 1.47 (3H, d, J = 6 Hz), 9.85 Δ(1H, dq, J = 6 Hz, J' = 7 Hz), 4.25 □ (1H, dq, J = 6 Hz, J' = 7 Hz), 5.85 → 6.1 (m), 6.07 Δ (1H, d, J = 15 Hz), 6.3 □(1H, d, J = 9 Hz)
IR (liq. film, cm^{-1}) : 3050, 2950, 2900, 1940, 1875, 1850, 1800, 1730, 1595, 1575, 1475, 1435, 1370, 1325, 1300, 1280, 1215, 1150, 1065, 1020, 1000, 950, 921, 840, 800, 730, 690
Mass spectrum m/e : 368, 366 (M^+), 211, 152, 131, 130, 129, 91, 77, 53, 51
Anal. calc. : C : 52.48, H : 4.40 ; found : C : 52.30, H : 4.57

2g (E + Z)

^{1}H NMR (δ, CCl_4) : 1.50 Δ(6H, s), 1.67 □(6H, s), 5.90 □(1H, d, J = 10 Hz), 5.85 Δ(1H, d, J = 16 Hz), 6.23 Δ(1H, d, J = 16 Hz), 6.33 (1H, d, J = 10 Hz), 7.1 → 7.7 (10H, m)
IR (liq. film, cm^{-1}) : 3050, 2950, 2900, 2850, 1945, 1875, 1800, 1735, 1650, 1575, 1475, 1460 1450, 1435, 1380, 1330, 1300, 1270, 1240, 1180, 1140, 1110, 1070, 1020, 1000, 950, 910, 840, 780, 730, 690
Mass spectrum m/e : 381 (M^+), 224, 222, 182, 145, 144, 143, 129, 77, 51
Anal. calc. : C : 53.70, H : 4.77 ; found : C : 53.66, H : 4.80

2h (E + Z)

^{1}H NMR (δ, CCl_4) : 1.70 Δ(3H, d, J = 1.2 Hz), 1.93 □(3H, d, J = 1.2 Hz), 3.43 Δ(2H, d, J = 8 Hz), 3.73 □(2H, dd, J = 8 Hz, J' = 1.2 Hz), 5.86 ΔC(1H, tq, J = 8 Hz, J' = 1.2 Hz), 7.0 → 7.6 (10H, m)
IR (liq. film, cm^{-1}) : 3140, 3040, 3000, 2940, 2900, 2840, 2720, 2600, 1940, 1870, 1800, 1735, 1620, 1575, 1560, 1470, 1430, 1370, 1325, 1300, 1170, 1065, 1020, 1000, 970, 910, 860, 840, 780, 730, 690, 670
Mass spectrum m/e : 366 (M^+), 152, 130, 107, 91, 77, 53, 51
Anal. calc. : C : 52.48, H : 4.4 ; found : C : 52.78, H : 4.53

4 (E + Z) R_1 = Me

^{1}H NMR (δ, CCl_4) : 2.10 (3H, s), 2.26 □(3H, d, J = 1.2 Hz), 2.47 Δ(3H, d, J = 1.2 Hz), 3.66 (3H, s), 5.63 Δ(1H, q, J = 1.2 Hz), 6.10 □(1H, q, J = 1.2 Hz)
IR (liq. film, cm^{-1}) : 2950, 2920, 2840, 1670, 1570, 1430, 1370, 1320, 1260, 1170, 1100, 1030 970, 900, 840
Mass spectrum m/e : 194 (M^+), 192, 181, 179, 177, 175, 163, 135, 99, 93
Anal. calc. : C : 37.52, H : 5.22 ; found : C : 37.23, H : 5.36

4 (E + Z) R_1 = H

^{1}H NMR (δ, $CDCl_3$) : 2.20 (3H, s), 3.70 (3H, s), 5.84 Δ(1h, d, J = 16 Hz), 6.22 □(1H, d, J = 11 Hz), 7.55 □ (1H, d, J = 11 Hz), 8.00 (1H, d, J = 16 Hz)
IR (liq. film, cm^{-1}) : 2980, 2930, 2910, 2820, 1690, 1560, 1425, 1340, 1300, 1250, 1000, 925 900, 800, 750, 650
Mass spectrum m/e : 180 (M^+)
Anal. calc. : C : 33.5, H : 4.50 ; found : C : 33.65, H : 4.43

5 R_2 = R_3 = H

^{1}H NMR (δ, CCl_4) : 2.30 (3H, d), 4.30 (2H, s)
IR (liq. film, cm^{-1}) : 3300, 2900, 2840, 2160, 1400, 1350, 1260, 1240, 1080, 1040, 970, 910
Mass spectrum m/e : 150 (M^+)
Anal. calc. : C : 32.24, H : 4.04 ; found : C : 33.34, H : 4.00

5 R_2 = H ; R_3 = Me

^{1}H NMR (δ, CCl_4) : 1.45 (3H, d, J = 6 Hz), 2.28 (3H, s), 2.83 (1H, O-H), 4.53 (1H, q, J = 6 Hz)
IR (liq. film, cm^{-1}) : 3300, 2960, 2920, 2160, 1445, 1420, 1365, 1340, 1270, 1110, 1070, 1040, 940, 920, 840

5 R_2 = R_3 = Me

^{1}H NMR (δ, CCl_4) : 1.47 (6H, s), 2.25 (3H, s), 2.3 (1H, OH)
IR (liq. film, cm^{-1}) : 3350, 2975, 2920, 2160, 1450, 1420, 1360, 1270, 1220, 1150, 965, 905, 775

6 R_2 = R_3 = H

described earlier [45]

6 R_2 = H ; R_3 = Me

^{1}H NMR (δ, CCl_4) : 1.4 (3H, d, J = 6 Hz), 3.9 (1H, O-H), 4.65 (1H, q, J = 6 Hz), 7.1 → 7.6 (5 H, m)
IR (liq. film, cm^{-1}) : 3300, 3040, 2960, 2860, 2160, 1940, 1860, 1785, 1570, 1470, 1435, 1360, 1320, 1105, 1060, 1035, 1020, 1000, 940, 900, 840, 730, 690, 670

7c

^{1}H NMR (δ, CCl_4) : 1.70 (3H, d, J = 1 Hz), 1.80 (3H, d, J = 1 Hz), 1.99 (6H, s), 4.68 (1H, d, J = 11 Hz), 5.33 (1H, dq, J = 11 Hz, J' = 1 Hz)
IR (liq. film, cm^{-1}) : 2930, 2900, 2650, 1650, 1400, 1360, 1250, 1220, 1075, 880, 840
Mass spectrum m/e : 258 (M^+)
Anal. calc. : C : 32.83, H : 5.51 ; found : C : 32.66, H : 5.47

7f

^{1}H NMR (δ, CCl_4) : 1.55 (3H, dd, J = 5.6 Hz), 4.83 (1H, d, J = 9.2 Hz), 5.1 (1H, dq, J = 5.6 Hz, J' = 15 Hz), 5.57 (1H, dd, J = 9.2 Hz, J' = 15 Hz)
IR (liq. film, cm^{-1}) : 3050, 3010, 2960, 2940, 2860, 2850, 1990, 1870, 1800, 1650, 1580, 1475, 1435, 1375, 1300, 1180, 1100, 1065, 1020, 1000, 995, 785, 760, 740, 690, 670
Mass spectrum m/e : 368, 366 (M^+), 211, 152, 131, 130, 129, 91, 77, 53, 51
Anal. calc. : C : 52.48, H : 4.40 ; found : C : 52.3, H : 4.57

7g

^{1}H NMR (δ, CCl_4) : 1.23 (3H, s), 1.6 (3H, s), 5.1 (1H, d, J = 12 Hz), 5.36 (1H, d, J = 12 Hz), 7.1 7.8 (10H, m)
IR (liq. film, cm^{-1}) : 3040, 2960, 2900, 2850, 1940, 1860, 1800, 1650, 1570, 1470, 1430, 1370, 1325, 1300, 1225, 1175, 1150, 1060, 1020, 1000, 900, 840, 730, 690
Mass spectrum m/e : 381 (M^+), 224, 222, 182, 145, 144, 143, 129, 77, 51
Anal. calc. : C : 53.70, H : 4.77 ; found : C : 53.66, H : 4.80

7h

^{1}H NMR (δ, CCl_4) : 1.73 (3H, s)
ABX : A : 4.56 (1H, d, J = 17 Hz); B : 4.73 (1H, d, J = 10 Hz); X : 6.05 (1H, dd, J = 10 Hz, J' = 17 Hz), 7.1 → 7.6 (10H,)
IR (liq. film, cm^{-1}) : 3050, 2950, 2900, 2850, 1940 , 1870, 1800, 1750, 1620, 1575, 1470, 1435, 1400, 1360, 1300, 1100, 1065, 1050, 1020, 1000, 910, 740, 690
Mass spectrum m/e : 366 (M^+), 152, 130, 107, 91, 77, 53, 51
Anal. calc. : C : 52.48, H : 4.4 ; found : C : 52.78, H : 4.53

$(iPr)_2C{=}CH{-}CH(SeMe)_2$

^{1}H NMR (δ, CCl_4) : 1.03 (6H, d, J = 6 Hz), 1.06 (6H, d, J = 6 Hz), 1.97 (6H, s), 2.35 (1H, h, J = 6 Hz), 2.80 (1H, h, J = 6 Hz), 4.83 (1H, d, J = 11 Hz), 5.33 (1H, d, J = 11 Hz)
IR (liq. film, cm^{-1}) : 2950, 2920, 2860, 2810, 1660, 1630, 1460, 1420, 1380, 1360, 1300, 1265, 1180, 1100, 1080, 1050, 900, 875, 780, 760, 700

α-phenylseleno-isobutyraldehyde

^{1}H NMR (δ, CCl_4) : 1.4 (6H, s), 7.1 7.6 (5H, m), 9.15 (1H, s)
IR (liq. film, cm^{-1}) : 3400, 3050, 2960, 2920, 2850, 2700, 1950, 1870, 1800, 1700, 1670, 1580 1480, 1450, 1440, 1390, 1365, 1175, 1110, 1070, 1025, 1000, 950, 920, 810, 740, 690
Mass spectrum m/e : 230, 228 (M^+), 199, 158, 157, 155, 119, 115, 78, 77, 51
Anal. calc. : C : 52.87, H : 5.32 ; found : C : 52.73, H : 5.50

2.2-bis(phenylseleno)-propanal

^{1}H NMR (δ, CCl_4) : 1.6 (3H, s), 7.1 7.6 (10H, m), 9.2 (1H, s)
IR (liq. film, cm^{-1}) : 3360, 3140, 3050, 2980, 2960, 2910, 2810, 2700, 1900, 1880, 1800, 1750 1690, 1650, 1575, 1475, 1440, 1360, 1350, 1330, 1275, 1170, 1060, 1020, 1000, 910, 880, 840, 780, 740, 690, 670

References and Notes

1.) See for example :
a.) E.J. Corey, B.W. Erickson and R. Noyori, J. Am. Chem. Soc., 93, 1724 (1971)
b.) E.J. Corey and A.P. Kozikowski, Tetrahedron Lett., 925 (1975)
c.) M. Wada, H. Nakamura, T. Taguchi and H. Takei, Chem. Lett., 345 (1977)
d.) J.J. Fitt and H.W. Gschwend, J. Org. Chem., 44, 303 (1979)
e.) H.J. Reich, M.C. Clark and W.W. Willis, Jr., J. Org. Chem., 47, 1618 (1982)
f.) F.E. Ziegler, J.-M. Feng and C.C. Tam, J. Am. Chem. Soc., 104, 7174 (1982)
g.) B. Costisella, H. Gross and H. Schick, Tetrahedron, 40, 733 (1984)
h.) K. Koumaglo and T.H. Chan, Tetrahedron Lett., 7175 (1984)
i.) K. Ogura, I. Iihama, K. Takahashi and H. Iida, Tetrahedron Lett., 2671 (1984)
j.) Y. Yamamoto, H. Yatagai, Y. Saito and K. Murayama, J. Org. Chem., 49, 1096 (1984)
2.) M. Renard and L. Hevesi, Tetrahedron Lett., 3911 (1983)
3.) M. Renard, Mémoire de Licence, Namur, June 1983
4.) S. Halazy and L. Hevesi, J. Org. Chem., 48, 5242 (1983)
5.) For a review see : J.V. Comasseto, J. Organomet. Chem., 253, 131 (1983)
6.) a.) D. Gravel, R. Déziel and L. Bordeleau, Tetrahedron Lett., 699 (1983)
b.) M. Shimizu and I. Kuwajima, J. Org. Chem., 45, 4063 (1980)
c.) M. Shimizu, R. Ando and I. Kuwajima, J. Org. Chem., 46, 5246 (1981)
7.) D.L. Dickstein and S.I. Miller in "The Chemistry of Carbon-Carbon Triple Bonds", Part 2, Ed. by S. Patai, J. Wiley and Sons, New York, 1978, p. 813
8.) E.G. Kataev and V.N. Petrov, Zh. Obshch. Khim., 32, 3699 (1962)
9.) L.M. Kataeva, L.N. Anonimova, L.K. Yuldasheva and E.G. Kataev, Zh. Obshch. Khim., 32, 3965 (1962)
10.) J. Gosselk, Angew. Chem. Int. Ed. Engl., 2, 660 (1963)
11.) J.V. Comasseto, J.T.B. Ferreira and N. Petragnani, J. Organometal. Chem., 216, 287 (1981)
12.) 3-Hydroxy-vinyl sulfides produced by addition of thiols to propargyl alcohols have been found to be mixtures of E and Z isomers.
a.) O. Ruel, E. Guittet and S. Julia, Tetrahedron Lett., 61 (1983)
b.) M. Julia and J. Lefebvre, Tetrahedron Lett., 109 (1984)
13.) Y. Vo Quang, D. Marais, L. Vo Quang and F. le Goffic, Tetrahedron Lett., 5209 (1983)
14.) V.S. Bozdanov, I.L. Mikhelashvili and E.N. Prilezhaeva, Izv. Akad. Nauk. SSSR, Ser. Khim., 2374 (1972)
15.) R. Möller, N. Engel, W. Steglich, Synthesis, 620 (1978)
16.) N. Petragnani, R. Rodriguez and J.V. Comasseto, J. Organomet. Chem., 114, 281 (1976)
17.) L. Brandsma "Preparative Acetylenic Chemistry", Elsevier, Amsterdam, 1971
18.) Prepared from equivalent amounts of diphenyl diselenide and bromine in dichloromethane. See H. Rheinboldt in Houben-Weyl's Methoden der Organischen Chemie, Ed. E. Möller, G. Thieme Verlag, Stuttgart, 1955, vol. IX
19.) 1,3-dichloropropene is commercially available only in the U.S.A.
20.) M. Clarembeau and A. Krief, Tetrahedron Lett., 3625 (1984)
21.) Y. Guindon, R. Frenette, K. Fortin and J. Rokach, J. Org. Chem., 48, 1357 (1983)
22.) M. Michas-Screttas and C.G. Screttas, J. Org. Chem., 42, 1462 (1977)
23.) Preliminary report : M. Renard and L. Hevesi, Tetrahedron Lett., 26, 1885 (1985)
24.) For a review see: R.M. Magid, Tetrahedron, 36, 1901 (1980), Report n° 87
25.) K.B. Sharpless and R.F. Lauer, J. Org. Chem., 37, 3973 (1972)
26.) T. Di Giamberardino, S. Halazy, W. Dumont and A. Krief, Tetrahedron Lett., 24, 3413 (1983)
27.) C. Georgoulis and G. Ville, J. Chem. Research (S), 248 (1979); J. Chem. Research (M), 3344 (1978)
28.) This reaction could not be performed in ether or in THF, presumably because of too strong inactivation of zinc chloride by these solvents. See also : H. Mayr and I.K. Halberstadt-Kausch, Chem. Ber., 115, 3479 (1982)

29.) R.M. Magid and R.D. Gandow, J. Org. Chem., 35, 269 (1970)
R.M. Magid, E.C. Nieh and R.D. Gandow, J. Org. Chem., 36, 2069 (1971)
30.) K. Maruyama and Y. Yamamoto, J. Am. Chem. Soc., 99, 8068 (1977)
31.) N. Petragnani and M. de Moura Campos, Chem. Ind., 1461 (1964)
32.) N. Petragnani and R. Rodrigues, Chem. Scripta, 8A, 110 (1975)
33.) N. Petragnani, J.V. Comasetto, R. Rodrigues and T.J. Brockson, J. Organomet. Chem., 124, 1 (1978)
34.) J.V. Comasetto and N. Petragnani, J. Organomet. Chem., 152, 295 (1978)
35.) R. Baudat and M. Petrzilka, Helv. Chim. Acta, 62, 1406 (1979). We noticed that instead of using the two phases system H_2O/HCl-ether for hydrolysis of the intermediary phenylseleno-acetyaldehyde diethyl acetal, this reaction could be effected faster in aq. acetone/TsOH/R.T. 2 hrs in 78 % yield
36.) K.B. Sharpless, R.F. Lauer and A.Y. Teranishi, J. Am. Chem. Soc., 95, 6137 (1973); K.B. Sharpless, K.M. Gordon, R.F. Lauer, D.W. Patrick, S.P. Singer and M.W. Young, Chem. Scripta, 8A, 9 (1975)
37.) J.N. Denis, W. Dumont and A. Krief, Tetrahedron Lett., 453 (1976)
38.) S. Halazy, J. Lucchetti and A. Krief, Tetrahedron Lett., 3971 (1978)
39.) W.H.H. Günther, J. Org. Chem., 31, 1202 (1966)
40.) D.G. Foster, Org. Synth., Coll. Vol. 3, 771 (1955)
41.) D. Seebach and N. Peleties, Chem. Ber., 105, 511 (1972)
42.) L. Hevesi, S. Dessauvage, B. Georges, G. Evrard, P. Blanpain, A. Michel, S. Harkema and G.J. van Hummel, J. Am. Chem. Soc., 106, 3784 (1984)
43.) S. Tomoda, Y. Takeuchi and Y. Nomura, Chem. Lett., 253 (1982)
44.) It is recommended to effect these reactions at 0°C or lower instead of room temperature in order to avoid reduction of the bis(seleno)-propenes formed to allyl selenides; see A. Cravador, A. Krief and L. Hevesi, J. Chem. Soc. Chem. Comm., 451 (1980)