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SYNTHESIS OF α-SELENOALKYLLITHIUM COMPOUNDS

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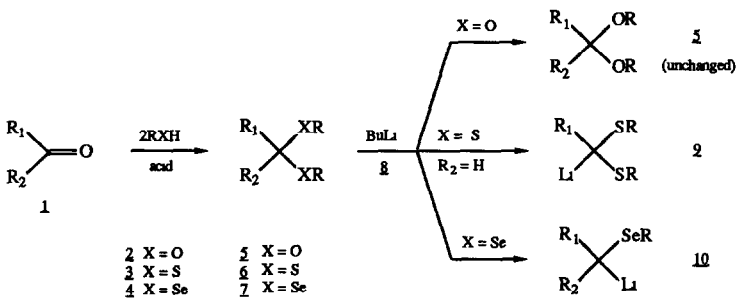
Abstract: α-Phenylselenoalkyllithiums and α-methylselenoalkyllithiums have been prepared from the corresponding selenoacetals and alkyllithiums. Several features of this reaction are disclosed. For example,the reaction is more readily achieved on phenylselenoacetals than on methylseleno analogues. Those derived from hindered carbonyl compounds are less readily cleaved.s-BuLi/THF proved superior to n-BuLi in THF, itself better than n-BuLi in ether.

The acetal family has played an increasingly important role in organic synthesis. The members of this series are usually directly available from aldehydes or ketones 1 by reaction with alcohols [1] 2, thiols [2] 3 or selenols [3] 4 in acidic media. They often possess the same type of reactivity towards for example acids and the same inertness towards most of the nucleophiles including alcoholates, enolates and Grignard reagents. But they display a very diversified reactivity towards alkyllithiums (Scheme 1).

Scheme 1



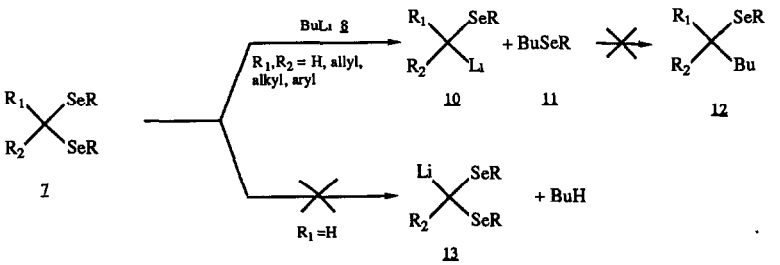
Oxygen derivatives 5 are completely inert towards alkyllithiums 8 and are used for the protection of the carbonyl group [4] of aldehydes and ketones. Although thioacetals 6 derived from ketones display usually a similar inertness [2], those derived from aldehydes are readily and almost quantitatively metallated in THF already at low temperature and produce 1-lithio-1,1-dithioacetals 9. These proved valuable acyl anion equivalents.[5] They play an important role in synthetic methodology and in synthesis. Selenoacetals 7 behave differently since they are reduced by butyllithiums to α-selenoalkyllithiums 10. This transformation originally disclosed by Seebach [3f,g] on bis(phenylseleno)methane and bis(phenylseleno)ethane was later found to be of wide applicability.[3d-g,6] Thus, phenylselenoacetals as well as their methylseleno analogues derived not only from aliphatic but also from aromatic and cyclic carbonyl compounds are very good precursors of the corresponding α-selenoalkyllithiums.[3c,g,6] These belong to the well known family of α-heterosubstituted organometallics [3e] which proved particularly useful in organic synthesis and have been extensively used the last two decades. Among the various organometallics which fall in this category those whose heteroatom is not partially or fully charged are the most difficult to prepare and prior to our work none of those who bear two alkyl groups on the carbanionic center were known [7] except the special case of α-thiophenyl cyclopropyllithium.[8] Butyllithiums [7] which have been successfully used for the metallation of related sulfides such as dimethyl sulfide,[9a] primary alkyl phenyl sulfides [9b,c] and cyclopropyl phenyl sulfide [8] react with selenides in a different manner. An exchange of ligand rather takes place on the selenium atom and leads to a butyl selenide and a novel organolithium *which invariably proved to be the one which possesses the most stabilized carbanion.* [3d,e,6a,10] Thus Gilman [10a] described in the early forties that n-butyllithium reacts with methyl phenyl selenide in ether and slowly produces (20°C, 4 days) phenyllithium which has been trapped with carbon dioxide and led to benzoic acid in modest yield. We later found [6c] that this reaction is by far more rapid

when carried out in THF since the same organometallic is produced almost quantitatively and much more rapidly at a much lower temperature (0°C, 0.5 h). This original route to organolithium reagents which implies the selenium-metal exchange on a selenide or a functionalized selenide proved to be at different occasions a good alternative to the more conventional methods involving the hydrogen-, halogen- or tin-lithium exchange which are usually performed by alkyllithiums [3e,7] or the oxygen- or sulfur-lithium exchange which requires the use of the less attractive lithium naphthalenides.[11]

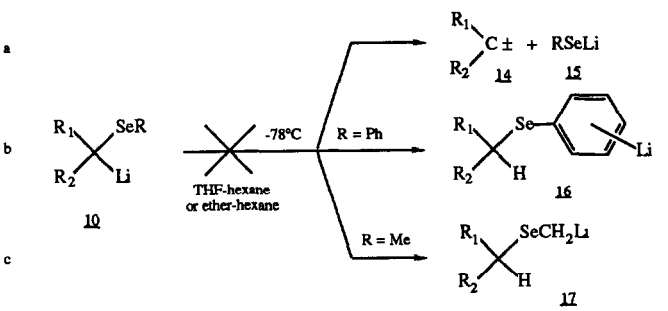
The selenium-metal exchange has been successfully used [3c-e,6a,b] *inter alia* for the synthesis of benzyl [6c,g,10c,e,f] and allyllithiums [6c,10b,d] from the corresponding selenides, α-thioalkyllithiums [6d,e,12] from mixed S,Se acetals, α-selenoalkyllithiums [3c-f,g,6a-f,i,j,13] from selenoacetals, α-metalloselenoacetals [3f,13] from selenoorthoesters and α-silylalkyllithiums [14] from α-silylalkyl selenides.

α-Selenoalkyllithiums proved particularly useful reagents since: **(i)** Selenoacetals, their precursors, are stable compounds which can be prepared [3a,c,g,i,15] efficiently by selenoacetalisation of readily available aldehydes or ketones. **(ii)** The selenium-metal exchange on selenoacetals takes place [3d,e,6a] readily with butyllithiums (THF-hexane or ether-hexane, usually at -78°C) and under these conditions metallation is not a competing reaction even with selenoacetals derived from aromatic aldehydes [6g] (Scheme 2). **(iii)** α-Selenoalkyllithiums 10 are usually stable under these conditions (THF-hexane or ether-hexane, -78°C) for several hours and do not possess a high propensity to decompose to carbenes 14 (scheme 3a). Phenylseleno derivatives do not transform at this temperature to their ring metallated isomers 16 (scheme 3b) and methylseleno analogues do not isomerise to the more stable α-alkylselenomethyllithiums 17 (scheme 3c). Interestingly they are not alkylated by the butyl selenide 11 concomitantly formed (scheme 2). **(iv)** They are highly nucleophilic species especially towards carbonyl compounds.[6f,16]

Scheme 2



Scheme 3



They allow [3c-e,6a,b,17] a large variety of valuable synthetic transformations such as : **(i)** The synthesis of alcohols, [16a] allyl alcohols, [6c-e,16a,18a] α,β-unsaturated carbonyl compounds,[18b] olefins,[16a,17,19] epoxides,[6f,16a,20] ring expanded ketones [16a,20b,21] starting from two carbonyl compounds, one of them being activated as a selenoacetal. **(ii)** The synthesis of oxetanes, [22] homoallyl alcohols, [23] enones [23] from a carbonyl compound and an epoxide. **(iii)** The homologation [24] of alkyl halides and the homologation [22] of epoxides to oxetanes and to tetrahydrofuranes. **(iv)** The reduction, [23] the reductive alkylation [25a] or the reductive allylation

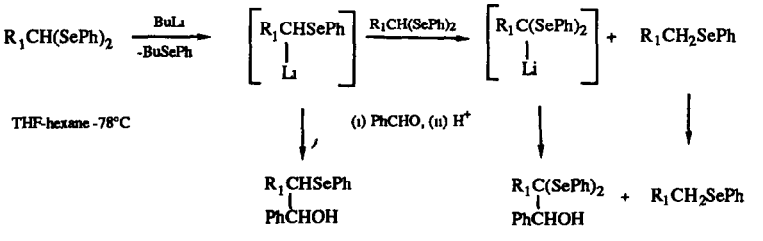
[25e] of the carbonyl group of aldehydes and ketones. (v) The geminal dialkylation of the carbonyl group of aromatic carbonyl compounds.[10e]

We report in this and in the following paper the full account of our work directed towards the synthesis of various α-selenoalkyllithiums from selenoacetals and alkyllithiums. Other methods such as the cleavage of the C-Se bond of selenoacetals by metals [26] or alkali-metal naphthalenides,[26] the metallation of selenides,[3f,g,10d,e,27] the addition of alkyllithiums to phenyl vinyl selenide,[28] and the bromine-metal exchange on α-bromoselenides [29] which are less general and have therefore found limited uses in synthesis will be reported separately.

The reaction between selenoacetals and butyllithiums has been generalized to selenoacetals derived from aliphatic and aromatic aldehydes and ketones including hindered ones. Limitations to the previous experimental descriptions have been observed and have been overcome. With that respect a comparative study of the reactivity of the different butyllithiums (n,s,t-) in different solvents (THF, ether) became necessary and is reported. A clear cut difference of reactivity between selenoacetals belonging to the phenylseleno and methylseleno series has been observed. In the less reactive cases, the reactions have been tentatively performed at a temperature higher (-50°C to 0°C) that the one usually used (-78°C). Therefore we have studied the stability towards the temperature of some of the α-selenoalkyllithiums produced. We also attempted to use the ^{77}Se NMR method to follow the advancement of the reactions, to see if any intermediate can be observed and to gather some comparative results concerning the aptitude of the seleno moiety to stabilize an α-carbanion.

In a standard procedure, 1 molar equivalent of primary or secondary butyllithium 8 in alkane solution has been added to a precooled (-78°C) solution (1 molar) of the selenoacetal 7 in THF or in ether. In a preliminary run the advancement of the reactions has been qualitatively followed by ^{77}Se NMR. Then in separate experiments, the reactions have been quenched at different intervals of time with benzaldehyde or heptanal (1 molar equiv.). The different products have been separated and their respective yields calculated. They usually consist of the β-hydroxyalkyl selenide 18 and the butyl selenide 11 resulting from the cleavage of the C-Se bond of the selenoacetal 7. In the case of incomplete reactions, the starting selenoacetal 7 as well as alcohols resulting from the butylation of the aldehyde have been also isolated. The different results of this study are gathered in the Table 1. In only two cases which involve bis(phenylseleno)methane and 1,1-bis(phenylseleno)ethane ,we observed the presence of some amounts of β-hydroxyalkyl selenoacetals beside the expected β-hydroxyalkyl selenides (scheme 4 entries a and b). We found that these compounds arise from the metallation of the α-selenoacetal not by the butyllithium but by the selenoalkyllithium 10 just produced. In fact, methyl phenyl selenide and ethyl phenyl selenide are respectively formed as by-products (Scheme 4). This side reaction which can be minimized by slow reverse addition of the reagents (Scheme 4 entry c, table 1 entries 1aA, 2aA) does not take place with higher homologues in the phenylseleno series and with all the methylselenoacetals.

Scheme 4

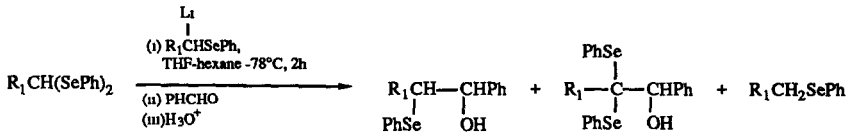


a	"normal addition"	R_1 = H	61	23	16
b	"normal addition"	R_1 = Me	70	8	8
c	"reverse addition"	R_1 = H	82	6	5

In order to confirm the above results, we reacted at -78°C 1,1-bis(phenylseleno)ethane with one equivalent of 1-phenylseleno-1-ethyllithium (generated independently in THF-hexane, from equimolar amounts of the same phenylselenoacetal and n-BuLi) and the resulting mixture has been quenched with benzaldehyde after 2 hours (Scheme 5a). 2,2-Bis(phenylseleno)-1-hydroxy-1-phenylpropane (76 % yield) and ethyl phenyl

selenide (90 % yield) resulting from the metallation of the selenoacetal by the α-selenoalkyllithium have been recovered. We have extended the above reaction to higher homologues and found that it becomes more and more difficult as can be shown for the specific case of 1,1-bis(phenylseleno)heptane reported in the scheme 5b.

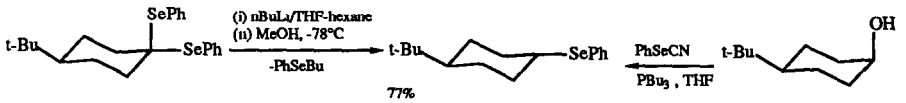
Scheme 5



a	R_1 = Me	0	76	90
b	R_1 = Hex	66	17	35

The reaction between butyllithiums and 1,1-bis(phenylseleno)-4-tert-butylcyclohexane and 1,1-bis(methylseleno)-2-methylcyclohexane requires further comments since only one of the two possible stereoisomeric selenides has been obtained after quenching the reaction mixture with methanol (1 mol. equiv. n-BuLi, THF-hexane, -78°C, 0.5 h then MeOH, -78°C to +20°C). In the former case, trans 1-phenylseleno-4-tert-butylcyclohexane is exclusively produced (Scheme 6). We have ascertained its stereochemistry by comparison with an authentic sample [30] prepared from cis 4-tert-butylcyclohexanol and phenylselenocyanate. These results do not tell if the axial or the equatorial seleno moiety is preferentially cleaved and therefore if the resulting anions are conformationally stable. Work is now in progress to clarify this point.

Scheme 6

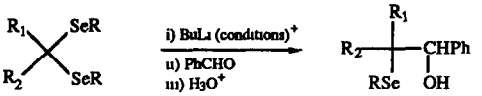


The results presented in the table 1 clearly show that the structure of the selenoacetal, the nature of the alkyllithium and the solvent used have all an important influence on the reaction of alkyllithiums with selenoacetals. **(i)** All structural features which allow a better stabilization of the carbanionic center greatly favor the reaction, enhance its rate and allow the use of a less reactive organolithium reagent (see below). Thus phenylselenoacetals are usually more reactive than their methylseleno counterpart (Table 1 compare entries a to b) and selenoacetals derived from aromatic carbonyl compounds and cyclopropanone are more reactive than those derived from aliphatic carbonyl compounds (table 1). **(ii)** Steric bulk around the reactive site dramatically lowers the reactivity of the selenoacetals. For example, there is a clear cut difference of reactivity between selenoacetals derived from aldehydes, which are more reactive than those derived from ketones (compare for example Table 1 entries 4bA to 7bA; 5aA, 5bA to 8aA, 8bA). Even so, the cleavage of the C-Se bond in 7 becomes more and more difficult when the selenoacetals are derived from carbonyl compounds increasingly substituted around the carbonyl group. This effect is perfectly perceptive **(a)** within the series of 1,1 -bis-(phenylseleno)methane, 1,1-bis (phenylseleno)ethane and 1,1-bis (phenylseleno)heptane (compare Table 1 entries 1aD, 2aD, 4aD) when the reaction is carried out with n-butyllithium in ether-hexane solution and **(b)** within the series of methylselenoacetals derived from cyclic ketones such as 1,1-bis(methylseleno)cyclohexane, 1,1-bis(methylseleno)-2-methylcyclohexane and 2,2-bis(methylseleno)adamantane when reacted with n-butyllithium in THF-hexane (compare Table 1 entries 14bA, 16bA and 17bA respectively).

In order to have some insight on the reactivity of alkyllithiums towards selenoacetals, we have carried out the reaction under standard conditions (1 molar solutions, -78°C) and in different solvents. As it can be observed from table 1 (columns A and B) n-butyllithium in THF-hexane (1-1), under the conditions originally described 3f,g,6c,d, allows complete reaction in a reasonable time of all the selenoacetals derived from aldehydes (few minutes) and of most of those derived from ketones (usually in less than 5h). In the case of selenoacetals derived from long chain or hindered ketones such as 7-tridecanone and adamantanone, the reaction is however much slower (Table 1, entries 9aA, 9bA and 17aA, 17bA). A great enhancement of its rate can be observed if secondary butyllithium is instead used. With that respect, those reactions which required one to four hours are now completed within less than 0.5 hour (Table 1, compare entries 9bB to 9bC ; 16bB to 16bC and 17bB to 17bC). It is interesting to notice that in those cases, the more hindered organolithium reagent is the most reactive although more unfavorable steric interactions are expected. Since the aggregation status of both

organolithium reagents seems to be nearly the same in this mixture of solvent [7], the higher reactivity observed with s-butyllithium may be due to electronic factors.

Table 1



Entry	R_1	R_2	H	n-BuLi THF-hexane,-78°C A*	n-BuLi THF-hexane,-78°C B*	s-BuLi THF-hexane,-78°C C*	n-BuLi ether-hexane, -78°C D*	s-BuLi ether-hexane, -78°C E*
1a	H	H	Ph	82(00)0.1h°			88(00)1h	82(00)0.5h
1b			Me	80(00)0.1h				
2a	Me	H	Ph	70(00)0.1h°			73(16)1h	
2b			Me	81(00)0.1h				
3a	Et	H	Ph	80(00)0.1h				
3b			Me	83(00)0.1h				
4a	n-Hex	H	Ph	89(00)0.1h			40(46)1h	74(00)0.5h
4b			Me	84(00)0.1h				82(00)0.5h
5a	t-Bu	H	Ph	92(00)0.1h				
5b			Me	82(10)0.1h				
6a	Me	Me	Ph	94(00)0.1h				83(00)0.5h
6b			Me	75(16)0.1h	92(00)0.5h			80(00)0.5h
7a	n-Hex	Me	Ph	81(00)0.1h				
7b			Me	50(40)0.1h	90(00)2h			
8a	t-Bu	Me	Ph	59(25)0.1h				
8b			Me	32(60)0.1h	77(05)2h			
9a	n-Hex	n-Hex	Ph	47(48)0.1h				
9b			Me	17(80)0.1h	93(00)4h	91(00)0.5h		
10b	i-Pr	i-Pr	Me	27(69)0.1h	77(05)2h			
11a	CH_2----------CH_2		Ph	91(00)0.1h			35(64)1h	
11b			Me	80(00)0.1h				68(00)0.5h
12a	CH_2----------CH_2---------CH_2		Ph	90(00)0.1h				
12b			Me	87(00)0.1h				
13a	CH_2---------$(CH_2)_2$--------CH_2		Ph	91(00)0.1h				
13b			Me	82(00)0.1h				
14a	CH_2---------$(CH_2)_3$--------CH_2		Ph	88(00)0.1h				
14b			Me	62(35)0.1h	87(00)2h			
15a	CH_2-CH_2-CH(t-Bu)CH_2-CH_2		Ph	80(08)0.1h				
15b			Me	65(34)0.1h				
16a	CH_2 - CH (Me) $(CH_2)_2$ - CH_2		Ph	55(43)0.1h				79(00)0.5h
16b			Me	25(72)0.1h	82(00)4h	87(00)0.1h		78(00)0.5h
17a	2-adamantane		Ph	00(89)0.1h				
17b			Me	00(97)0.1h	00(93)2h	81(00)0.5h		
18b	4-CNPh	H	Me	81(00)0.1h				
19b	4-ClPh	H	Me	77(00)0.1h				
20a	Ph	H	Ph	83(00)0.1h			81(00)1h	
20b			Me	87(00)0.1h			89(00)1h	
21b	4-MeOPh	H	Me	79(00)0.1h				
22b	2-MeOPh	H	Me	77(00)0.1h				
23a	Ph	Me	Ph	82(00)0.1h				
23b			Me	87(00)0.1h				
24b	4-MeOPh	Me	Me	81(00)0.1h				
25b	4-MePh	Me	Me	90(00)0.1h			80(00)1h	

+ all the reactions, except these noted with a dot °, have been performed by adding the butyllithium on the selenoacetal.

* refer respectively to the yield in β-hydroxyalkyl selenide %, (recovered selenoacetal %) and reaction time with BuLi.

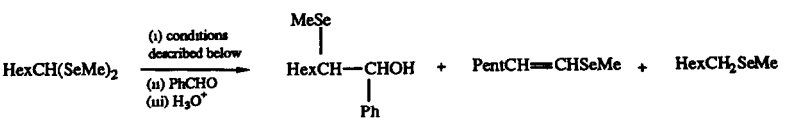
In a parallel work, we have performed the reactions in an ether-alkane instead of a THF-alkane mixture (Table 1, column D and E). This medium offers valuable advantages over the previous one. Thus not only the α-selenoalkyllithiums (especially those bearing two alkyl substituents on the carbanionic center) have a lower tendency to decompose (allowing thus further reaction with less reactive electrophiles) but they also exhibit an original reactivity especially towards carbonyl compounds [3d,e,6a,16a,b]. They have a higher propensity to add across the carbonyl group of hindered [16a] or highly enolisable ketones and to react in an axial mode with rigid cyclohexanones [16b].

We found that s-butyllithium in ether-cyclohexane exhibits a reactivity closely related to the one observed with n-butyllithium in THF-hexane (Table 1 compare columns E to A) whereas n-butyllithium in ether-hexane (Table 1 entry D) tends to be more selective and only selenoacetals derived from aromatic carbonyl compounds (Table 1 entries 20bD to 25bD) and bis(phenylseleno)methane (Table 1 entry 1aD) are completely cleaved after 1 h at -78°C . Phenylselenoacetals derived from aliphatic aldehydes (Table 1 entries 2aD, 4aD) and from cyclopropanone (Table 1 entry 11 aD) are partially cleaved under similar conditions but react completely if the reaction is instead performed at -50°C for 0.5h. Under the last conditions, the phenylselenoacetals derived from ketones react very slowly and methylselenoacetals from aliphatic aldehydes remain unchanged. Therefore some chemoselectivity can be expected under the last conditions between selenoacetals possessing different structures. Preliminary results towards this purpose will be presented in the following paper.

During this work, we had occasion to study the behaviour of other organometallics towards selenoacetals. We found that tert-BuLi possesses, all being otherwise identical, a reactivity similar to that of s-BuLi . It is more reactive than n-BuLi, itself being by far more reactive than methyllithium or phenyllithium. Others organometallics including α-selenoalkyllithiums, benzyllithiums and allyllithiums have exhibited from time to time a somewhat different reactivity towards selenoacetals: they have acted as bases (see for example schemes 4 and 5) or as carbon nucleophiles.[31] Other organometallics including for example organosodiums, metal acetylides, organocoppers (especially RCu : BF_3), organozincs and organotitaniums are being tested. The selenium metal exchange reaction proved to be more effectively achieved when performed in THF-hexane than in ether-hexane or in hydrocarbons (hexane)(table 1 compare columns A,B to D). Therefore the following order of reactivity of the systems towards selenoacetals can be derived: tert-BuLi / THF-hexane ~ s-BuLi / THF-hexane > n-BuLi / THF-hexane ~ s-BuLi / ether-hexane > n-BuLi ether-hexane >>> MeLi / THF-ether > tert-BuLi / hexane ~ n-BuLi / hexane.

Most of the reactions described in this work have been carried out at-78°C since except rare cases such as the one of phenylselenomethyllithium [3g,h] and methylselenobenzyllithium [31] which are still present in appreciable amount after 12h and 1h at 20°C respectively, most of the α-selenoalkyllithiums tend to decompose between -50°C and 0°C. However, the exact temperature at which this process starts, the rate of decomposition and the nature of the products formed clearly depend upon their structure. Those bearing two alkyl groups on the carbanionic center often decompose above -50°C. The resulting products are not always identical and in most cases their structures have not yet been identified. A more detailed work has been carried out on 1-seleno-1-heptyllithiums. Their thermal behaviour has been studied in THF-hexane and in ether-hexane both by ^{77}Se NMR and by trapping experiments after raising the temperature to 0°C and further addition of benzaldehyde to the medium prior hydrolysis. In the methylseleno series, whatever the solvent used, only a trace amount of the expected 1-methylseleno-1-heptyllithium is present after standing for 3.5 hrs at 0°C (compare table 1 entry 4b to scheme 7 entries a and b). 1-Methylselenoheptane which probably results from the protonation of the organometallic by the solvent and 1-methylseleno-1-heptene resulting from an hydride elimination are produced instead (Scheme 7). Such types of decomposition have been already described for other organolithium compounds [7].

Scheme 7

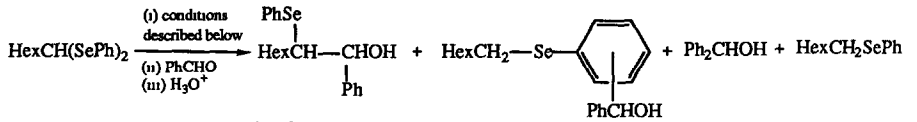


a	(i) nBuLi THF-hexane, -78°C, 0.2h then -78°C to 0°C, then 0°C, 1h	25	27	small amount
b	(i) nBuLi THF-hexane, -78°C, 0.2h then -78°C to 0°C, then 0°C, 3 5h	trace	36	35

The decomposition takes another course with 1-phenylseleno-1-heptyllithium (Scheme 8). In ether and THF the reagent is still present (±20 %) after 3,5 h at 0°C beside heptylselenophenyllithiums resulting from the isomerisation of the original organometallic to the more stabilized aryllithium. Heptyl phenyl selenide (15 %) arising from the protonation of the organometallic by the solvent and substantial amounts of phenyllithium [trapped as diphenyl carbinol: (±21%)] from unknown origin are also found as by-products when the reaction is carried out in THF-hexane or in ether-hexane respectively.

Such an isomerisation leading to ring metallated derivatives has been also observed in attempting the synthesis of α-selenoalkyllithiums from phenyl vinyl selenide and n-butyllithium in ether [28c] and of α-thioalkylithiums from alkyl phenyl sulfides and butyllithiums. [9b,c]

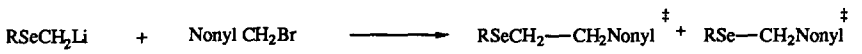
Scheme 8



a	(i) nBuLi THF-hexane, -78°C, 0.2h then -78°C to 0°C, then 0°C, 3.5h	25	11	trace	15
b	(i) nBuLi ether-hexane, -78°C, 0.2h then -78°C to 0°C, then 0°C, 3.5h	21	25	21	0

It has been noticed that methylseleno and phenylselenomethyllithium react, around -20°C,with primary alkyl halides [25a] (Scheme 9, entries a and c), epoxides [23] and oxetane [22] and produce beside the expected products, compounds resulting from the direct substitution of these electrophiles by selenolates. This suggests for these two specific cases a decomposition pathway which involves the intermediate formation of lithium methylselenolate and probably methylene. Surprisingly however the same organometallics react with carbonyl compounds at the same temperature and produce the corresponding β-hydroxyalkyl selenide [3g,h] almost quantitatively.

Scheme 9



a	R = Me	THF, -20°C	48	41
b	R = Me	THF - HMPT, -78°C	90	02
c	R = Ph	THF, -20°C	41	59
d	R = Ph	THF - HMPT, -78°C	84	03

‡ These selenides have been compared to authentic samples prepared from sodium selenolates and decylbromide and undecylbromide respectively.

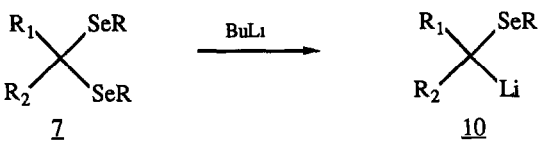
As already mentioned, most of the reactions described in this study have been routinely monitored by ^{77}Se-NMR.[3b,17b] This method combines (i) good receptivity which is about three times that of ^{13}C-NMR. (ii) simplicity of proton decoupled spectra due to the few atoms of selenium generally present in organic molecules. (iii) very large chemical shift range (2500 ppm). (iv) narrow peaks (2 to 8 Hz) which in general allow a very important differentiation even between organoselenium compounds possessing closely related structures. Thus the selenoacetal as well as the α-selenoalkyllithium and the butyl selenide resulting from its cleavage by butyllithiums exhibit in both methyl- and phenylseleno series well differentiated chemical shifts and therefore it is quite easy, at least when the reaction is not instantaneous, to follow qualitatively its advancement. The ^{77}Se NMR spectra of differently substituted selenoacetals 7 and α- selenoalkyllithiums 10 are collected in the table 2.

In some cases, the chemical shifts of 10 are substantially different when the reactions are carried out in THF-hexane or in ether-hexane in which an upfield shift is observed. Line width is dependent upon the temperature when the reaction is carried out in ether-hexane (MeCHLiSeR, ± 15 Hz at -40°C, ± 85 Hz at -78°C) whereas only slight changes are observed in THF-hexane (MeCHLiSeR, ± 15 Hz at -40°C, ± 26 Hz at -78°C). Although it is difficult to forecast the reasons of these differences, one may assume a greater aggregation of the organometallic in ether [7].

We tried without success to detect by ^{77}Se NMR an eventual intermediate which could provide some insight on the intimate mechanism of such selenium metal exchange reaction. This can be expected to proceed **(i)** by a concerted metathesis via a four center transition state, **(ii)** via an ate complex generated by nucleophilic attack of the organolithium compound on one of the selenium atoms of the selenoacetal or **(iii)** by a stepwise electron transfer (SET) mediated process. Related mechanisms have been proposed for the halogen-metal exchange reaction but up to now a definite answer has not been ascertained [32] even for this well established reaction.

The case of α-selenobenzyllithiums [33] merits further comments since decreasing electron attracting ability of the para substituent X leads to an upfield shift of the ^{77}Se signal of para substituted benzyl selenides (Table 3, columns a,d and g) reasonably attributed to the change in electron density around the selenium atom and an unexpected downfield shift on the corresponding α-selenobenzyllithiums (Table 3, columns b,e and h).

Table 2



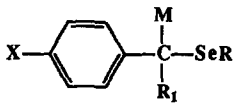
7 10

R_1	R_2	7 R=Ph	7 R=Me	10 R=Ph	10 R=Me	R_1	R_2	7 R=Ph	7 R=Me	10 R=Ph	10 R=Me
H	H	324	104	278	61	H	4-CN-Ph	450	244	237	32
H	Me	422	194	389	180	H	4-Cl-Ph	442	241	249	53
H	Et	378	155	335	126	H	Ph	442	237	254	54
H	$C_{10}H_{21}$	388	163	347	138	H	4-MeO-Ph	437	237	264	69
H	t-Bu	382	155	307	95	Me	4-CN-Ph		371		138
Me	Me	530	277	475	249	Me	4-Cl-Ph		367		159
Me	Et	479	241	408	187	Me	Ph		359		168
Me	$C_{10}H_{21}$	490	249	425	202	Me	4-Me-Ph		361		180
Me	t-Bu	479	247	397	179	Me	4-MeO-Ph		363		193
Hex	Hex	448	207	405	182						
CH_2	CH_2	527	297	492	184						
CH_2---CH_2---CH_2		479	253	452	213						
CH--$(CH_2)_2$--CH_2		439	235	401	186						
CH_2-$(CH_2)_3$--CH_2		558-402	313-166	476	246						

* The value presented refer to ^{77}Se NMR shifts in ppm. The measurements have been performed in THF - hexane at -78°C on a Jeol FX 90 Q spectrometer. Dimethyl selenide was used as an external standart.

This effect is even more pronounced when Δδ values (difference between the shift of the selenobenzyllithiums and of the corresponding selenides) are compared (Table 3, compare entries 1 to 5 in columns c,f,i). The figures 1, 2 and 3, where these results are presented, show excellent linear correlation (r) between the δ ^{77}Se of the organometallics or the corresponding Δδ ^{77}Se and the Hammet σρ value for the ring substituents in para positions.

Table 3

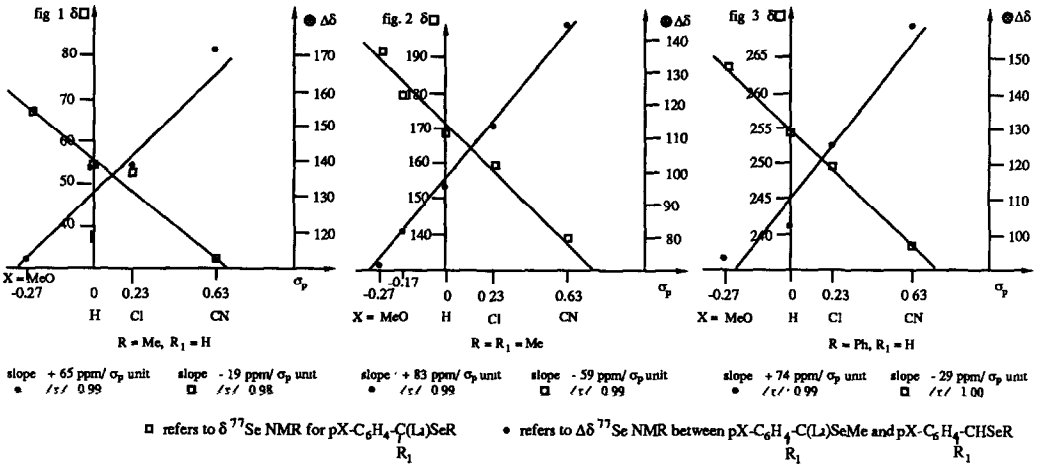


18 M = H
10 M = Li

		a	b	c	d	e	f	g	h	i
		R = Me, R_1 = H			R = R_1 = Me			R = Ph, R_1 = H		
	X	M=H*	M = Li*	Δδ	M=H*	M = Li*	Δδ	M=H*	M = Li*	Δδ
1	CN	204	32	172	283	138	145	394	237	157
2	Cl	193	53	140	272	159	113	374	249	125
3	H	182	54	128	264	168	96	357	254	103
4	Me	—	—	—	262	180	82	—	—	—
5	MeO	182	69	113	264	193	71	357	264	93

* The values presented above refer to ^{77}Se NMR shifts. The measurements have been performed in THF-hexane at -78°C on a JEOL FX 90Q spectrometer. Dimethyl selenide was used as an external standard

Figures 1,2,3



The negative slope of the δ vs σ lines for the lithium derivatives indicates that these unexpected chemical shifts must arise from two or more factors operating in opposite directions. Undoubtedly one of these factors is charge density which should generate a positive slope. Clearly another more important phenomenon having an inverse effect is superimposed, leading thereby to the observed overall negative slope. We feel that this phenomenon may be identified as a change in hybridization of the selenium atom from sp^3 to something in between sp^3 and sp^2 reflecting delocalization of the negative charge towards this atom on going from an electron attracting to an electron donating para substituent (X). With that respect, it may be recalled that the δ ^{77}Se NMR data for selone (R_2C = Se) ranges [34] from 1600 to 2100 ppm. Indeed, in the former case, one would expect the carbanionic negative charge to be delocalized towards the substituted phenyl ring, whereas delocalization would be more efficient towards the selenium atom with electron donating substituants (X), and leads to increased sp^2 character and therefore to a downfield shift of the ^{77}Se NMR signal. Such a delocalization has been recently proposed [35] to explain ^{13}C and ^{6}Li NMR spectra of α-selenoalkyllithiums possessing a labeled ^{6}Li and ^{13}C carbanionic center.

In conclusion, butyllithiums are particularly suitable for the preparation of a large array of α-selenoalkyllithiums belonging to the methylseleno and phenylseleno series. s-BuLi proved the most valuable reagent for the cleavage of the C-Se bond of selenoacetals even for the most hindered ones. Selenoacetals derived from aldehydes are more reactive than those derived from ketones and phenylselenoacetals are more rapidly cleaved than their methylseleno analogues. These observations have been used to perform chemoselective reactions which are reported in the following paper.

Experimental

General

^{1}H-NMR spectra have been performed on JEOL MH 100 (100 MHz), JNM 60 Si (60 MHz) and FX 90 Q (90 MHz) spectrometers. The spectra were measured in CCl_4 or $CDCl_3$ with TMS as an internal standard (δ : 0.00). ^{77}Se-NMR spectra were obtained on an JEOL FX 90 Q (17.04 MHz) spectrometer. The spectra measured in THF or ether with dimethylselenide as an external standard (δ:0.00). IR data reported in cm^{-1} were obtained using a Perkin-Elmer model 337 spectrophotometer. The spectra were performed on neat liquids or on solids in KBr or in CCl_4. Mass spectra were obtained on AEI MS30 or HP 5995 A GC / MS spectrometers. In the discussion M refers to M^+ and only a few characteristics are reported. High resolution mass spectra were obtained on the AEI MS30 spectrometer with perfluorokerosene as an internal standard. Microanalyses were performed in the Microanalysis Laboratory of the Paris VI University Paris, France. Layer chromatography : Analytical thin-layer chromatography (TLC) was performed on premade, glass-backed plate SiO_2, 60PF254, 250 microns (Merck 5719). Compounds were visualized by UV illumination and by heating to 150°C after spraying phosphomolybdic acid in ethanol. Preparative layer chromatography (PLC) was performed on SiO_2 plates prepared as follows : 440 g of silica gel, 60 PF254 (Merck 7747) (for fifteen 20x20 plates) were shaken with 880 ml of distilled water to obtain a free-flowing slurry. Using a CAMAG 21602 automatic preparative spreader, the plates were covered with an even coating of absorbent (1.5 mm). Just after coating, the plates were put down in a nonventilated closed hood with a water-saturated atmosphere (obtained by boiling water) for 1 h. The hot water bath was removed after 1 h and the plates were allowed to dry in the closed hood for 20 h The dried plates were activated (140°C, 10 h) prior to use (>95% success on > 150,000 plates prepared).

All the reactions were performed in two necked round bottomed flasks equipped with a septum stopper and an argon filled balloon. Theses monitored by ^{77}Se NMR were performed under argon in NMR tubes (10 mm x 17 cm Wilmad 513-7PP) fitted with a screw cap equipped with a teflon septum. All transfers of reagents were performed via syringes. When the reactions needed to be cooled at -78°C, the flasks and tubes were immersed in a Dewar filled with a dry-ice acetone mixture.

Reagents and solvents.

Unless otherwise noted, the reagents and solvents used in this work have been purchased from Janssen Chimica (Beerse, Belgium). The solvents and the carbonyl compounds were distilled prior to use. Anhydrous THF or ether were distilled from sodium benzophenone ketyl just prior to use. n-BuLi (1.6M in hexane) and s-BuLi(1.0M in cyclohexane) have been titrated prior to use. Bis(phenylseleno)methane 3fg and bis (methylseleno)methane[6f] have been synthesized from diiodomethane and the corresponding potassium selenolates. 1,1-Bis(methylseleno)cyclopropane has been prepared 25e from 1-ethoxy-1-silyloxycyclopropane and methylselenol and its phenylseleno analogue 6i from 1,1-bis(phenylseleno)-3-chloropropane and LDA. The other selenoacetals used in this study have been prepared from the corresponding carbonyl compounds and selenols as previously described 3i.

Synthesis of α-selenoorganolithium compounds for ^{77}Se NMR analysis. General procedure.

1.00 Mmol of selenoacetal dissolved in 1 ml of anhydrous THF (or ether) was placed in an NMR tube, at -78°C, under argon. and n-butyllithium (0.63 ml,1.6 M in hexane) (or s-butyllithium, 1 ml, 1.0 M in cyclohexane) was injected. The mixture was shaken manually for a time given in the discussion. Then, the NMR tube was placed in the NMR probe cooled at -78°C.

Reactions of selenoacetals with butyllithiums.

To a solution of 1.00 mmol of selenoacetal dissolved in 1 ml of anhydrous THF or ether, was added 1 equiv of butyllithium in alkane at -78°C (procedure A and B : n-BuLi / THF, procedure C : s-BuLi / THF, procedure D : n-BuLi / ether, procedure E : s-BuLi / ether). The mixture was stirred at this temperature for a time given in the discussion for each example cited then 1 equiv of benzaldehyde dissolved in 1 ml of the same solvent was added. The resulting mixture was stirred for 0.25 h at -78°C. The reaction was then quenched with water saturated with NH_4Cl and was allowed to warm up to room temperature. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were dried over anhydrous $MgSO_4$. Purification of the product was carried out by SiO_2 preparative layer chromatography. Specific details as well as spectroscopical and analytical data are described below for the conditions which allow the complete reaction of the selenoacetal.

Synthesis of 1-phenyl-2-phenylselenoethane-1-ol.

To a solution of 0.63 ml of n-butyllithium in 1 ml of anhydrous THF was added 0.328 g of bis(phenylseleno)methane. Then the general procedure A, was followed. We obtained 0.228 g (82%) of the corresponding β-hydroxyalkylselenide.Tlc Rf 0.3 eluent pentane-ether (8:2, v/v). ^{1}H NMR (CCl_4) δ 2.60-2.80 (m, 1H, OH), 3.1 (m, 2H, CH_2-Se), 4.58 (dd,J = 10.0 and 6.0 Hz, 1H, CH-O), 7.00-7.50 (m, 10H, arom.), IR (neat) 3440, 3070, 3030, 2930, 1960, 1890,1810, 1590, 1500, 1490, 1460, 1450, 1200, 1060, 1040, 760, 710 cm^{-1}. HRMS Calcd. for M 278.021. Found 278.018. MS (m/e) 278 (M), 260 (M-H_2O), 158 (PhSeH), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd for $C_{14}H_{14}OSe$ C 60.66, H 5.09 . Found C 60.86, H 5.00.

Synthesis of 1-phenyl-2-methylselenoethane-1-ol.

Following the general procedure A , 0.204 g of bis(methylseleno)methane and 0.63 ml of n-butyllithium gave 0.172 g (80%) of the corresponding β-hydroxyalkylselenide. Tlc Rf 0.3 eluent pentane-ether (8:2, v/v). ^{1}H NMR (CCl_4) δ 1.70 (s, 3H,

MeSe), 2.65 (m, 2H, CH_2-Se), 2.83-3.04 (m, 1H, OH), 4.50 (dd, J = 8.0 and 6.0, Hz, 1H, CH-O), 6.90-7.10 (m, 5H, arom.). IR (neat) 3450, 3070, 3030, 2970, 2930, 2870, 1610, 1505, 1465, 1435, 1390, 1340, 1285, 1250, 1200, 1120, 1080, 1035, 910, 770, 710 cm^{-1}. HRMS Calcd. for M 216.006. Found 216.005. MS (m/e) 216 (M), 198 (M-H_2O), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_9H_{12}OSe$ C 50.24, H 5.62. Found C 50.53, H 6.00.

Synthesis of 1-phenyl-2-phenylselenopropane-1-ol.

Following the general procedure A , 0.342 g of 1,1-bis(phenylseleno)ethane and 0.63 ml of n-butyllithium gave 0.204 g (70%) of a diastereoisomeric mixture (55/45) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.3 eluent pentane-ether (8:2, v/v). ^1H NMR (CCl_4) δ 1.12 (d, J = 8 Hz, 3H, Me), 2.50-3.60 (m, 2H, OH+CH-Se), 4.14 and 4.50 (2d in a ratio of 55:45, J = 7.0 and 3.0 Hz, CH-O), 6.90-7.40 (m, 10H, arom.). IR (neat) 3460, 3070, 3030, 2970, 2930, 2870, 1960, 1890, 1870, 1810, 1590, 1500, 1490, 1450, 1390, 1190, 1080, 1030, 750, 710 cm^{-1}. HRMS Calcd. for M 292.037. Found 292.037. MS (m/e) 292 (M), 274 (M-H_2O), 185 (M-PhCHOH), 158 (PhSeH), 135 (M-PhSe), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{15}H_{16}OSe$ C 61.86, H 5.54. Found C 61.53, H 5.74.

Synthesis of 1-phenyl-2-methylselenopropane-1-ol.

Following the general procedure A , 0.218 g of 1,1-bis(methylseleno)ethane and 0.63 ml of n-butyllithium gave 0.185 g (81%) of a diastereoisomeric mixture (55/45) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.3 eluent pentane-ether (8:2, v/v). ^1H NMR (CCl_4) δ 1.12 and 1.18 (2d, J = 7.0 and 7.0 Hz, 3H, Me-C), 1.75 (s, 3H, MeSe), 2.60-3.20 (m, 2H, CH-Se + OH), 4.18 and 4.52 (2d in a ratio of 55:45, J = 8.0 and 4.0 Hz, 1H, CH-O), 6.80-7.10 (m, 5H, arom.). IR (neat) 3460, 3070, 3030, 2930, 1615, 1605, 1500, 1465, 1430, 1200, 1065, 920, 775, 715 cm^{-1}. HRMS Calcd. for M 230.021. Found 230.021. MS (m/e) 230 (M), 212 (M-H_2O), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{10}H_{14}OSe$ C52.41, H 6.16. Found C 52.80, H 6.00.

Synthesis of 1-phenyl-2-phenylselenobutane-1-ol.

Following the general procedure A , 0.356 g of 1,1-bis(phenylseleno)propane and 0.63 ml of n-butyllithium gave 0.245 g (80%) of a diastereoisomeric mixture (55/45) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.6 eluent pentane-ether (8:2, v/v). ^1H NMR (CCl_4) δ 0.80-1.64 (m, 5H, Et), 2.60-3.30 (m, 2H, CH-Se+OH), 4.14 and 4.52 (2d in a ratio of 55:45, J = 6.0 and 4.0 Hz, 1H, CH-O), 6.80-7.30 (m, 10H, arom.). IR (neat) 3460, 3070, 3030, 2970, 2880, 1960, 1890, 1810, 1590, 1500, 1490, 1460, 1450, 1390, 1190, 1110, 1035, 770, 755, 710, 680 cm^{-1}. HRMS Calcd. for M 306.052. Found 306.054 MS (m/e) 306 (M), 199 (M-PhCHOH), 158 (PhSeH), 149 (M-SePh), 91 (tropylium ion). Anal. Calcd. for $C_{16}H_{18}OSe$ C 62.95, H 5.94. Found C 62.53, H 6.04.

Synthesis of 1-phenyl-2-methylselenobutane-1-ol.

Following the general procedure A , 0.232 g of 1,1-bis(methylseleno)propane and 0.63 ml of n-butyllithium gave 0.203 g (83%) of a diastereoisomeric mixture (60/40) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.5 eluent pentane-ether (8:2, v/v). ^1H NMR (CCl_4) δ 0.70-1.80 (m, 8H, CH_2 + Me-C + MeSe (2s at 1.56 and 1.58)), 2.24-3.20 (m, 2H, CH-Se + OH), 4.16 and 4.46 (2d in a ratio of 60:40, J = 7.0 and 4.0 Hz, 1H, CH-O), 6.70-7.20 (m, 5H, arom.). IR (neat) 3450, 3070, 3030, 2970, 2930, 2880, 1610, 1505, 1460, 1390, 1285, 1200, 1110, 1055, 910, 770, 710 cm^{-1}. HRMS Calcd. for M 244.037. Found 244.035 MS (m/e), 244 (M), 226 (M-H_2O), 149 (M-SeMe), 137 (M-PhCHOH), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{11}H_{16}OSe$ C 54.35, H 6.63. Found C 53.79, H 7.08.

Synthesis of 1-phenyl-2-phenylselenooctane-1-ol.

Following the general procedure A ,0.412 g of 1,1-bis(phenylseleno)heptane and 0.63 ml of n-butyllithium gave 0.321 g (89 %) of a diastereoisomeric mixture (60/40) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.6 eluent pentane-ether (8:2, v/v). ^1H NMR (CCl_4) δ 0.70-1.80 (m, 13H, n-Hex), 2.80-3.60 (m, 2H, CH-Se + OH), 4.44 and 4.74 (2d in a ratio of 60:40, J = 8.0 and 4.0 Hz, 1H, CH-0), 7.00-7.80 (m, 10H, arom.). IR (neat) 3460, 3070, 3040, 2920, 2870, 1610, 1590, 1505, 1490, 1465, 1450, 1390, 1190, 1070, 1035, 770, 750, 710 cm^{-1}. HRMS Calcd. for M 362.115 Found 362.121 MS (m/e) 362 (M), 344 (M-H_2O), 255 (M-PhCHOH), 205 (M-SePh). Anal. Calcd. for $C_{20}H_{26}OSe$ C 66.47, H 7.25. Found C 66.31, H 7.35.

Synthesis of 1-phenyl-2-methylselenooctane-1-ol.

Following the general procedure A ,0.286 g of 1,1-bis(methylseleno)heptane and 0.63 ml of n-butyllithium gave 0.252 g (84 %) of a diastereoisomeric mixture (65/35) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.7 eluent pentane-ether (8:2 v/v). ^1H NMR (CCl_4) δ 0.70-1.80 (m, 16H, n-Hex + MeSe (2 s at 1.60 and 1.68)), 2.60-3.20 (m, 2H, OH + CH - Se), 4.30 and 4.64 (2d in a ratio of 65:35, J = 6.0 and 4.0 Hz, 1H, CH-O), 7.00-7.40 (m, 5H, arom.). IR (neat) 3450, 3070, 3030, 2940, 2870, 1610, 1505, 1480, 1465, 1390, 1200, 1060, 910, 770, 715 cm^{-1}. HRMS Calcd. for M 300.099. Found 300.104. MS (m/e) 300 (M), 282 (M-H_2O), 205 (M-SeMe), 193 (M-PhCHOH). Anal. Calcd. for $C_{15}H_{24}OSe$ C 60.10, H 8.08. Found C 60.21, H 8.23.

Synthesis of 1-phenyl-2-phenylseleno-3,3-dimethyl-butane-1-ol.

Following the general procedure A,0.384 g of 1,1-bis(phenylseleno)- 2,2-dimethyl-propane and 0.63 ml of n-butyllithium gave 0.306 g (92%) of a diastereoisomeric mixture (60/40) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.6 eluent pentane-ether (8:2, v/v). ^1H NMR (CCl_4) δ 0.90 and 1.10 (2s in a ratio of 60:40, 9H, t-Bu), 2.5-2.9 (m, 1H, OH) 2.93-3.00 and 3.36 (m+d, J = 4.0 Hz, 1H, CH-Se), 4.84 and 5.00-5.20 , (d, J = 4.0 Hz + m, 1H, CH-O), 6.8-7.6 (m, 10H, arom.). IR (neat) 3460, 3070, 3030, 2970, 2910, 2870, 1960, 1890, 1810, 1710, 1590, 1500, 1490, 1460, 1450, 1400, 1380, 1245, 1080, 1045, 780, 760, 710

cm^{-1}. HRMS Calcd. for M 334.084. Found 334.077. MS (m/e) 334 (M), 316 (M-H_20), 227 (M-PhCHOH), 158 (PhSeH). Anal. Calcd. for $C_{18}H_{22}0Se$ C 64.86, H. 6.65. Found C 64.53, H 6.40.

Synthesis of 1-phenyl-2-methylseleno-3,3-dimethyl-butane-1-ol.

Following the general procedure A, 0.260 g of 1,1-bis(methylseleno)- 2,2-dimethyl propane and 0.63 ml of n-butyllithium gave 0.114 g (42%) of a β-hydroxyalkyl selenide and 0.109 g (40%) of its diastereoisomer. Tlc Rf 0.8 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 0.90 (s, 9H, t-Bu), 1.80 (s, 3H, MeSe), 2.72-2.96 (m, 2H, OH + CH - Se (d, J= 6.0 Hz at 2.78)), 4.64 (d, J = 6.0 Hz, 1H, CH-O), 6.90-7.30 (m, 5H, arom.). IR (neat) 3460, 3070, 3030, 2970, 2930, 1610, 1500, 1490, 1460, 1400, 1380, 1245, 1210, 1100, 1070, 1035, 750, 710 cm^{-1}. HRMS Calcd. for M 272.068. Found 272.068. MS (m/e) 272 (M), 215 (M-t-Bu), 169 (M-PhCHOH), 107 (PhCHOH). Anal. Calcd. for $C_{13}H_{20}OSe$ C 57.56, H 7.43. Found C 57.99, H 7.43. Tlc Rf 0.6 eluent pentane-ether (8:2, v/v). ^{1}H NMR (CCl_4) δ 1.12 (s, 9H, t-Bu), 1.20 (s, 3H, MeSe), 2.60-2.80 (m, 2H, CH-Se + OH), 4.80-5.00 (m, 1H, CH-O), 7.00-7.20 (m, 5H, arom.), IR (neat) 3460, 3070, 3030, 2970, 2930, 1610, 1500, 1490, 1465, 1400, 1375, 1280, 1245, 1220, 1040, 1035, 780, 710 cm^{-1}. HRMS Calcd. for M 272.069. Found 272.069. MS (m/e) 272 (M), 215 (M-t-Bu), 165 (M-PhCHOH), 107 (PhCHOH). Anal. Calcd. for $C_{13}H_{20}OSe$ C 57.56, H 7.43. Found C 57.99, H 7.33.

Synthesis of 1-phenyl-2-phenylseleno-2-methyl-propane-1-ol.

Following the general procedure A , 0.356 g of 2,2-bis (phenylseleno)propane and 0.63 ml of n-butyllithium gave 0.287 g (94%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.45 eluent pentane-ether (8:2, v/v). ^{1}H NMR (CCl_4) δ 1.16 and 1.20 (2s, 6H, Me), 3.04 (s, 1H, OH), 4.18 (s, 1H, CH-O), 6.90-7.50 (m, 10H, arom.). IR (neat) 3610, 3470, 3070, 3030, 2970, 2930, 2870, 1960, 1890, 1820, 1760, 1720, 1615, 1500, 1490, 1460,1390, 1375, 1330, 1190, 1120, 1060, 960, 930, 700 cm^{-1}. HRMS Calcd. for M 306.052. Found 306.053. MS (m/e) 306 (M), 288 (M-H_2O), 198 (M-PhCHOH), 158 (PhSeH), 148 (M-PhSeH). Anal. Calcd. for $C_{16}H_{18}OSe$ C 62.95, H 5.94. Found C 63.29, H 6.18.

Synthesis of 1-phenyl-2-methylseleno-2-methyl-propane-1-ol.

Following the general procedure B, 0.232 g of 2,2-bis (methylseleno)propane and 0.63 ml of n-butyllithium gave 0.225 g (92%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.4 eluent pentane-ether (8:2, v/v). ^{1}H NMR (CCl_4) δ 1.14 and 1.24 (2s, 6H, Me), 1.72 (s, 3H, MeSe), 2.90-3.00 (m, 1H, OH), 4.24 (s, 1H, CH-O), 6.80-7.10 (m, 5H, arom.). IR (neat) 3460, 3070, 3030, 2970, 2930, 2890, 1610, 1500, 1460, 1400, 1375, 1200, 1130, 1060, 910, 760, 715 cm^{-1}. HRMS Calcd. for M 244.039. Found 244.037 MS (m/e) 244 (M), 226 (M-H_2O), 149 (M-SeMe), 137 (M-PhCHOH), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{11}H_{16}OSe$ C 54.33, H 6.63. Found C 54.06, H 6.85.

Synthesis of 1-phenyl-2-phenylseleno-2-methyl-octane-1-ol.

Following the general procedure A , 0.424 g of 2,2-bis (phenylseleno)octane and 0.63 ml of n-butyllithium gave 0.305 g (81%) of a diastereoisomeric mixture (90/10) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.8 eluent pentane-ether (8:2, v/v). ^{1}H NMR (CCl_4) δ 0.70-2.00, (m, 16H, n-Hex + Me (2s at 1.16 and 1.20)), 3.26 and 3.46 (2s, 1H, OH), 4.36 and 4.46 (2 s in a ratio of 90:10, 1H, CH-O), 7.1-7.8 (m, 10H, arom.). IR (neat) 3470, 3070, 3040, 2940, 2870, 1615, 1590, 1505, 1490, 1470, 1450, 1390, 1340, 1215, 1255, 1200, 1060, 750, 710 cm^{-1}. HMRS Calcd. for M-SePh 219.175. Found 219.179. MS (m/e) 358 (M-H_2O), 269 (M-PhCHOH), 219 (M-SePh), 158 (PhSeH). Anal. Calcd. for $C_{21}H_{28}OSe$ C 67.19, H 7.52. Found C 66.88, H 7.73.

Synthesis of 1-phenyl-2-methylseleno-2-methyl-octane-1-ol.

Following the general procedure B, 0.302 g of 2,2-bis (methylseleno)octane and 0.63 ml of n-butyllithium gave 0.280 g (90%) of a diastereoisomeric mixture (60/40) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.75 eluent pentane-ether (8:2, v/v). ^{1}H NMR (CCl_4) 0.70-1.80 (m, 19H,n-Hex + Me-C (s at 1.1) + MeSe (2s at 1.68 and 1.74)), 2.80-3.20 (m, 1H, OH), 4.38 and 4..48 (2s in a ratio of 60:40, 1H, CH-O), 7.00-7.40 (m, 5H, arom.). IR (neat) 3460, 3070, 3030, 2940, 2870, 1610, 1510, 1460, 1390, 1200, 1060, 910, 770, 720 cm^{-1}. HRMS Calcd. for M 314.115. Found 314.115. MS (m/e) 314 (M), 296 (M-H_2O), 219 (M-SeMe), 207 (M-PhCHOH), 107 (PhCHOH), 95 (MeSe). Anal. Calcd. for $C_{16}H_{26}OSe$ C 61.33, H 8.36. Found C 61.06, H 8.27.

Synthesis of 1-phenyl-2-phenylseleno-2,3,3-trimethyl-butane-1-ol.

Following the general procedure A ,0.398 g of 2,2-bis (phenylseleno)-3,3-dimethyl-butane and 0.63 ml of n-butyllithium gave 0.205 g (59%) of a diastereoisomeric mixture (75/25) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.8 eluent pentane-ether (8:2, v/v). ^{1}H NMR (CCl_4) d 0.75 and 1.14 (2s, 12H, t-Bu + Me-C) 2.50-2.90 (m, 1H, OH), 4.60-4.90 (2s in a ratio of 75:25, 1H, CH-O), 6.90-7.60 (m, 10H, arom.). IR (CCl_4) 3590, 3430, 3050, 3020, 2940, 2900, 2870, 1945, 1875, 1805, 1750, 1705, 1600, 1580, 1450, 1440, 1380, 1365, 1325, 1215, 1180, 1020, 895, 690 cm^{-1}. HRMS Calcd. for M 348.099. Found 348.099. MS (m/e), 348 (M), 330 (M-H_2O), 291 (M-t-Bu), 173 (M-H_2O-SePh), 158 (PhSeH). Anal. Calcd. for $C_{19}H_{24}OSe$ C 65.70, H 6.96. Found C 65.35; H 7.04.

Synthesis of 1-phenyl-2-methylseleno-2,3,3-trimethyl-butane-1-ol.

Following the general procedure B ,0.247 g of 2,2-bis (methylseleno)3,3-dimethyl-butane and 0.63 ml of n-butyllithium gave 0.220 g (77%) of a diastereoisomeric mixture (75/25) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.8 eluent pentane-ether (8:2, v/v). ^{1}H NMR (CCl_4) δ 0.96 and 1.06 (2s, 12H, t-Bu + Me-C), 1.32 and 1.42 (2s, 3H, MeSe), 2.60-2.90 (m, 1H, OH), 4.50 and 4.74 (2s in a ratio of 75:25, 1H, CH-O), 7.00-7.60 (m, 5H, arom.). IR (neat), 3450, 3080, 3060, 3020, 2960, 2930, 2870,

1710, 1610, 1500, 1460, 1400, 1380, 1370, 1225, 1125, 1090, 1075, 1050, 1030, 1010, 910, 770, 735, 710 cm^{-1}. HRMS Calcd. for M 286.084. Found 286.084. MS (m/e) 286 (M), 268 (M-H_2O), 229 (M-t-Bu), 173 (M-H_2O-SeMe), 96 (MeSeH). Anal. Calcd. for $C_{14}H_{22}OSe$ C 58.94, H 7.77. Found C 58.57, H 7.91.

Synthesis of 1-phenyl-2-phenylseleno-2-hexyl-octane-1-ol.

Following the general procedure A, 0. 496 g of 7,7-bis (phenylseleno) tridecane and 0.63 ml of n-butyllithium gave 0.210 g (47%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.8 eluent pentane-ether (8:2, v/v). ^1H NMR (CCl_4) δ 0.60-1.70 (m, 26H, n-Hex), 2.90-3.20 (m, 1H, OH), 4.30 (s, 1H, CH-O), 6.90-7.60 (m, 10H, arom.). IR (neat) 3460, 3070, 3030, 2970, 1960, 1890, 1820, 1610, 1590, 1500, 1490, 1460, 1445, 1390, 1340, 1250, 1195, 1035, 750, 715, 705 cm^{-1}. HRMS Calcd. for M 446.209. Found 446.209. MS (m/e) 446 (M), 428 (M-H_2O), 339 (M-PhCHOH), 289 (M-SePh), 91 (tropylium ion). Anal. Calcd. for $C_{26}H_{38}OSe$ C 70.09, H 8.60. Found C 70.14, H. 8.99.

Synthesis of 1-phenyl-2-methylseleno-2-hexyl-octane-1-ol.

Following the general procedure B, 0.372 g of 7,7-bis (methylseleno) tridecane and 0.63 ml of n-butyllithium gave 0.356 g (93%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.8 eluent pentane-ether (8:2, v/v). ^1H-NMR (CCl_4) δ 0.70-1.80 (m, 29 H, n-Hex, + MeSe (s at 1,44)), 2.50-2.70 (m, 1H, OH), 4.40 (s, 1H, CH-O), 7.00-7.30 (m, 5H, arom.). IR (neat) 3440, 3070, 3030, 2960, 2930, 2860, 1610, 1500, 1480, 1465, 1390, 1240, 1200, 1090, 1060, 1035, 910, 750, 735, 710 cm^{-1}. HRMS Calcd. for M 384.193. Found 384.193. MS (m/e) 384 (M), 366 (M-H_2O), 289 (M-SeMe), 277 (M-PhCHOH). Anal. Calcd. for $C_{21}H_{36}OSe$ C 65.78, H 9.46. Found C 65.94, H 9.50.

Synthesis of 1-phenyl-2-methylseleno-2-isopropyl-3-methyl-butane-1-ol.

Following the general procedure B, 0.283 g of 3,3-bis (methylseleno) 2,4-dimethyl-pentane and 0.63 ml of n-butyllithium gave 0.230 g (77%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.8 eluent pentane-ether (8:2, v/v). ^1H-NMR (CCl_4) δ 0.9-1.3, m,12H, Me-C),1.74 (s, 3H, SeMe), 1.80-2.30 (m, 2H, CH-Me), 2.60-2.80 (m, 1H, OH), 4.94 (s, 1H, CH-O), 6.90-7.40 (m, 5H, arom.). IR (neat) 3440, 3070, 3040, 2970, 2940, 2890, 1610, 1500, 1480, 1460, 1395, 1380, 1340, 1190, 1050, 1049, 910, 780, 765, 715, cm^{-1}. HRMS Calcd. for M 300.099. Found 300.101. MS (m/e) 300 (M), 205 (M-SeMe), 193 (M-PhCHOH), 107 (PhCHOH). Anal. Calcd. for $C_{15}H_{24}OSe$ C 60.19, H 8.08. Found C 59.94, H 8.22.

Synthesis of phenyl-[(1-phenylseleno)cyclopropyll-methanol.

Following the general procedure A, 0.354g of bis (phenylseleno) cyclopropane and 0.63 ml of n-butyllithium gave 0.276 g (91%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.6 eluent pentane-ether (8:2, v/v). ^1H-NMR (CCl_4) δ 0.80-1.10 (m, 4H, cycl.), 2.65 (s, 1H, OH), 4.36 (s, 1H, CH-O), 6.90-7.4 (m, 10H, arom.). IR (neat) 3450, 3080, 2860, 1590, 1495, 1440, 1200, 1190, 1025 cm^{-1}.

Synthesis of phenyl-[(1-methylseleno)cyclopropyll-methanol.

Following the general procedure A , 0.228g of bis (methylseleno) cyclopropane and 0.63 ml of n-butyllithium gave 0.194 g (80%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.5 eluent pentane-ether (8:2, v/v). ^1H-NMR (CCl_4) δ 0.80-1.05 (m, 4H, cycl.), 1.60 (s, 3H, MeSe), 2.60 (s, 1H, OH), 4.28 (s, 1H, CH-O), 7.15-7.30 (m, 5H, arom.). IR (neat) 3450, 3080, 3015, 2930, 1600, 1500, 1450, 1050, 1030 cm^{-1}. HRMS Calcd. for M 242.021. Found 242.022. MS (m/e), 242 (M), 135 (M-PhCHOH), 95 (MeSe). Anal. Calcd. for $C_{11}H_{14}OSe$. C 54.80, H 5.80. Found C 54.57, H 5.89.

Synthesis of phenyl-[(1-phenylseleno)cyclobutyll-methanol.

Following the general procedure A, 0.366 g of bis (phenylseleno) cyclobutane and 0.63 ml of n-butyllithium gave 0.285 g (90%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.6 eluent pentane-ether (8:2, v/v). ^1H-NMR (CCl_4) δ 1.20-2.80 (m, 7H-$(CH_2)_3$ - + OH), 4.40 (s, 1H, CH-O), 7.00-7.50 (m, 10H, arom.). IR (neat) 3460, 3070, 3040, 2990, 2950, 2870, 1610, 1590, 1570, 1490, 1460, 1450, 1390, 1340, 1250, 1190, 1030, 930, 750, 710 cm^{-1}. HMRS Calcd. for M 318.052. Found 318.053. MS (m/e) 318 (M), 300 (M-H_2O), 211 (M-PhCHOH), 158 (PhSeH), 91 (tropylium ion). Anal. Calcd. for $C_{17}H_{18}OSe$ C 64.35, H 5.72. Found C 64.18, H 5.74.

Synthesis of phenyl-[(1-methylseleno)cyclobutyll-methanol.

Following the general procedure A , 0.242g of bis (methylseleno) cyclobutane and 0.63 ml of n-butyllithium gave 0.220 g (87%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.5 eluent pentane-ether (8:2, v/v). ^1H-NMR (CCl_4) δ 1.40-2.60 (m, 9H,-$(CH_2)_3$- + MeSe (s at 1.4)), 2.88-3.00 (m, 1H, OH), 4.36 (s, 1H, CH-O), 7.00-7.30 (m, 5H, arom.). IR (neat) 3450, 3060, 3020, 2980, 2940, 1600, 1560, 1500, 1480, 1450, 1440, 1380, 1330, 1020, 740, 700 cm^{-1}. HRMS Calcd. for M 256.037. Found 256.038. MS (m/e), 256 (M), 161 (M-MeSe), 149 (M-PhCHOH), 96 (MeSeH), 91 (tropylium ion). Anal. Calcd. for $C_{12}H_{16}OSe$ C 56.47, H. 6.32. Found C 56.48, H 6.67.

Synthesis of phenyl-[(1-phenylseleno)cyclopentyll-methanol.

Following the general procedure A, 0.380g of bis (phenylseleno) cyclopentane and 0.63 ml of n-butyllithium gave 0.300 g (91%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.65 eluent pentane-ether (8:2, v/v). ^1H-NMR (CCl_4) δ 1.20-2.10 (m, 8H,-$(CH_2)_4$-), 3.30 (s, 1H, OH), 4.55 (s, 1H, CH-O), 7.10-7.70 (m, 10H, arom.). IR (neat) 3460, 3070, 3030, 2970, 2880, 1610, 1590, 1505, 1480, 1460, 1450, 1400, 1330, 1190, 1030, 750, 720, 710 cm^{-1}. HRMS Calcd. for M 332.068. Found

332.068. MS (m/e) 332 (M), 314 (M-H_2O), 225 (M-PhCHOH), 175 (M-SePh), 158 (PhSeH), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{18}H_{20}OSe$ C 65.25, H 6.08. Found C 65.25, H 6.20.

Synthesis of phenyl-[(1-methylseleno)cyclopentyl]-methanol.

Following the general procedure A, 0.256g of bis (methylseleno) cyclopentane and 0.63 ml of n-butyllithium gave 0.220 g (82%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.65 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 1.20-2.00 (m, 11H,-$(CH_2)_4$-+MeSe (s at 1.64)), 3.00-3.30 (m, 1H, OH), 3.60 (s, 1H, CH-O), 7.20-7.50 (m, 5H, arom.). IR ($CDCl_3$) 3440, 3040, 2920, 2870,1500, 1450, 1330, 1230, 1180, 1040 cm^{-1}. HRMS Calcd. for M 290.052. Found 290.053. MS (m/e) 270 (M), 252 (M-H_2O), 175 (M-MeSe), 163 (M-PhCHOH), 107 (PhCHOH), 96 (MeSeH), 91 (tropylium ion). Anal. Calcd. for $C_{13}H_{18}OSe$ C 57.99, H 6.74. Found C 58.02, H 6.77.

Synthesis of phenyl-[(1-phenylseleno)cyclohexyl]-methanol.

Following the general procedure A, 0.394g of bis (phenylseleno) cyclohexane and 0.63 ml of n-butyllithium gave 0.304 g (88%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.7 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 0.60-2.20 (m, 10H,-$(CH_2)_5$-), 3.24 (s, 1H,OH), 4.04 (s, 1H, CH-O), 6.80-7.40 (m, 10H, Ph). IR (neat) 3460, 3070, 3040, 2950, 2870, 1610, 1590, 1510, 1490, 1460, 1400, 1340, 1265, 1200, 1050, 1035, 750, 720, 710 cm^{-1}. HRMS Calcd. for M 346.084. Found 346.084. MS (m/e) 346 (M), 239 (M-PhCHOH), 158 (PhSeH), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{19}H_{22}OSe$ C 66.08, H 6.52. Found C 65.76, H 6.72.

Synthesis of phenyl-[(1-methylseleno)cyclohexyl]-methanol.

Following the general procedure B, 0.270g of bis (methylseleno)cyclohexane and 0.63 ml of n-butyllithium gave 0.248 g (87%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.7 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 1.00-1.90 (m, 13H, -$(CH_2)_5$-+MeSe (s at 1.60)), 2.80-3.00 (m, 1H, OH), 4.30 (s, 1H, CH-O), 7.00-7.40 (m, 5H, arom.). IR ($CDCl_3$) 3410, 3070, 3040, 2980, 2910, 2840, 1600, 1490, 1450, 1380, 1330, 1260, 1190, 1130, 1030 cm^{-1}. HRMS Calcd. for M 284.068. Found 284.068. MS (m/e) 284 (M), 266 (M-H_2O), 189 (M-SeMe), 177 (M-PhCHOH), 96 (MeSeMe), 91 (tropylium ion).

Synthesis of phenyl-[(1-phenylseleno-4-tert-butyl)cyclohexyl]-methanol.

Following the general procedure A, 0.452g of 1,1-bis (phenylseleno)- 4-tert-butyl-cyclohexane and 0.63 ml of n-butyllithium gave 0.321 g (80%) of the corresponding β-hydroxyalkylselenide. Tlc Rf 0.55 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 0.70-2.40 (m, 18H, alicycl. + t-Bu (s at 0.76)), 2.50-2.70 (m, 1H, OH), 4.60 (s, 1H, CH-O), 6.7-7.2 (m, 10H, arom.). IR (neat) 3450, 3060,3020, 2940, 2860, 1950, 1880, 1810, 1700, 1600, 1580, 1490, 1480, 1450, 1440, 1390, 1365, 1240, 1040, 1025, 910, 785, 760, 700 cm^{-1}. HRMS Calcd. for M 402.146. Found 402.146. MS (m/e), 402 (M), 384 (M-H_2O), 295 (M-PhCHOH), 245 (M-PhSe), 158 (PhSeH), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{23}H_{30}OSe$ C 68.81, H 7.53. Found C 68.54, H 7.59.

Synthesis of phenyl-[(1-methylseleno-4-tert-butyl)cyclohexyl]-methanol.

Following the general procedure A, 0.328g of 1,1-bis (methylseleno)- 4-tert-butyl-cyclohexane and 0.63 ml of n-butyllithium gave 0.221 g (65%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.55 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 0.80-2.50 (m, 21H, alicycl. + t-Bu (s at 0.82) + MeSe (s at 1.40), 2.2-2.4 (m, 1H, OH), 4.52 (s, 1H, CH-O), 6.80-7.20 (m, 5H, arom.). IR (neat) 3450, 3080, 3030, 2940, 2870, 1700, 1600, 1490, 1480, 1470, 1455, 1390, 1240, 1085, 1050, 1030, 930, 765, 750, 705 cm^{-1}. HRMS Calcd. for M 340.131. Found 340.131. MS (m/e) 340 (M), 322 (M-H_2O), 245 (M-MeSe), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{18}H_{28}OSe$ C 63.70, H 8.32. Found C 63.04, H 8.44.

Synthesis of phenyl-[(1-phenylseleno-2-methyl)cyclohexyl]-methanol.

Following the general procedure A, 0.410g of 1,1-bis (phenylseleno) 2-methylcyclohexane and 0.63 ml of n-butyllithium gave 0.198 g (55%) of a diastereoisomeric mixture (60 /40) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.55 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 0.80-2.40 (m, 13H, alicycl. + Me-C (2d at 1.04 and 1.20, J = 7.0 and 7.0 Hz) + OH), 4.54 and 4.58 (2s in a ratio of 60:40, 1H, CH-O), 6.80-7.40 (m, 10H, arom.). IR (neat) 3450, 3070, 3040, 2940, 2870, 1610, 1590, 1505, 1485, 1465, 1450, 1440, 1390, 1215, 1055, 1035, 800, 755, 710 cm^{-1}. HRMS Calcd. for M 360.099. Found 360.099. MS (m/e) 360 (M), 253 (M-PhCHOH), 203 (M-PhSe), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{20}H_{24}OSe$ C 66.85, H 6.73. Found C 66.77, H 6.70.

Synthesis of phenyl-[(1-methylseleno-2-methyl)cyclohexyl]-methanol.

Following the general procedure B, 0.286 g of 1,1-bis (methylseleno)-2-methylcyclohexane and 0.63 ml of n-butyllithium gave 0.245 g (82%) of a diastereoisomeric mixture (55/45) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.7 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 0.10-2.70 (m, 16H, alicycl. +Me-C+MeSe+OH), 4.32 and 4.70 (2s in a ratio of 55:45, 1H, CH-O), 7.00-7.50 (m, 5H, arom.). IR (neat) 3460, 3070, 3030, 2970, 2930, 2890, 1610, 1500, 1460, 1390, 910, 815, 710 cm^{-1}. HHMS Calcd. for M 298.084. Found 298. 082. MS (m/e) 298 (M), 280 (M-H_2O), 203 (MeSe), 191 (M-PhCHOH), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{15}H_{22}OSe$ C 60.60, H 7.46. Found C 60.52, H 7.38.

Synthesis of phenyl-[(1-methylseleno)adamantyl]-methanol.

Following the general procedure C, 0.324g of 2,2-bis (methylseleno)adamantane and 1.00 ml of s-butyllithium gave 0.272 g (81%) of the corresponding β-hydroxyalkyl selenide. Tlc Rf 0.55 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 0.90 (s, 3H,

MeSe), 1.20-3.80 (m, 15H, alicycl. +OH), 5.00-5.20 (m, 1H, CH-O), 6.90-7.20 (m, 5H, arom.). IR (CCl_4) 3460, 3050, 3020, 2900, 2850, 1700, 1600, 1490, 1450, 1390, 1275, 1245, 1230, 1200, 1100, 1090, 1060, 1025, 960, 890, 860, 695 cm^{-1}. HRMS Calcd. for M 336.099. Found 336.099. MS (m/e) 336 (M), 241 (M-MeSe), 229 (M-PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{18}H_{24}OSe$ C 64.47, H 7.21. Found C 64.47, H 7.40.

Synthesis of 1-phenyl-2-[(4-cyano)phenyl]-2-methylseleno-ethane-1-ol.

Following the general procedure A, 0.308 g of 4-cyano-phenyl bis(methylseleno)methane and 0.63 ml of n-butyllithium gave 0.259 g (81%) of a diastereoisomeric mixture (55/45) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.5 eluent pentane-ether (5:5, v/v). ^{1}H-NMR (CCl_4) δ 1.66 and 1.80 (2s in a ratio of 55:45, 3H, MeSe), 2.66-3.35 (m, 1H, OH), 4.03 and 4.10 (2d, J = 6.0 Hz, J' = 8.0 Hz, 1H, CH-Se), 4.87 and 5.03 (2d, J = 8.0 Hz, J' = 6.0 Hz, 1H, CH-O), 7.00-7.66 (m, 9H, arom.). IR (neat) 3440, 3060, 3020, 2920, 2230, 1605, 1500, 1455, 1415, 1275, 1180, 1050, 910, 840, 790, 765, 700 cm^{-1}. MS (m/e), 317 (M), 222 (M-MeSe), 211 (M-PHCHOH), 116 (cyanotropylium ion), 107 (PhCHOH). Anal. Calcd. for $C_{16}H_{15}OSeN$ C 60.77, H 4.78. Found C 60.77, H 4.73.

Synthesis of 1-phenyl-2-[(4-chloro)phenyl]-2-methylseleno-ethane-1-ol.

Following the general procedure A, 0.315g of 4-chloro-phenyl- bis(methylseleno)methane and 0.63 ml of n-butyllithium gave 0.252g (77%) of a diastereoisomeric mixture (55/45) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.4 eluent pentane-ether (7:3, v/v). ^{1}H-NMR (CCl_4) δ 1.60 and 1.70 (2s in a ratio of 55:45, 3H, MeSe), 2.66-3.10 (m, 1H, OH); 4.00 and 4.07 (2d, J = 7.0 and 7.0 Hz, 1H, CH-Se), 4.77 and 4.93 (2d, J = 7.0 and 7.0 Hz, 1H, CH-O), 6.90-7.33 (m, 9H, arom.). IR (neat) 3420, 3060, 3020, 2920, 1590, 1490, 1450, 1410, 1275, 1190, 1090, 1015, 910, 830, 765, 730, 705 cm^{-1}. MS (m/e) 326 (M), 231 (M-MeSe), 220 (M-PhCHOH), 125 (chlorotropylium ion), 107 (PhCHOH). Anal. Calcd. for $C_{15}H_{15}OSeCl$ C 55.32, H 4.64. Found C 55.33, H 4.76.

Synthesis of 1,2-diphenyl-2-phenylseleno-ethane-1-ol.

Following the general procedure A, 0.404g of phenyl- bis(phenylseleno)methane and 0.63 ml of n-butyllithium gave 0.293g (83%) of a diastereoisomeric mixture (55/45) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.4 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 2.70-3.10 (m, 1H, OH), 4.26 and 4.33 (2d, J = 10.0 and 6.0 Hz, 1H, CH-Se), 4.84 and 4.96 (2d in a ratio of 55:45, J = 10.0 and 6.0 Hz, 1H, CH-O), 6.80-7.40 (m, 10H, arom.). IR (neat) 3420, 3060, 3030, 1600, 1580, 1495, 1480, 1455, 1440, 1180, 1075, 1025, 1000, 915, 775, 750 cm^{-1}. HRMS Calcd. for M 354.052. Found 354.052. MS (m/e) 354 (M), 247 (M-PhCHOH), 197 (M-PhSe). Anal. Calcd. for $C_{20}H_{18}OSe$ C 67.99, H 5.14. Found C 67.46, H 5 26.

Synthesis of 1,2-diphenyl-2-methylseleno-ethane-1-ol.

Following the general procedure A, 0.280g of phenyl- bis(methylseleno)methane and 0.63 ml of n-butyllithium gave 0.254g (87%) of a diastereoisomeric mixture (60/40) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.34 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 1.44 and 1.54 (2s in a ratio 60:40, 3H, Me), 2.68-3.40 (m, 1H, OH), 4.04 and 4.10 (2d, J = 8.0 and 8.0 Hz, 1H, CH-Se), 4.80 and 4.88 (2d, J = 8.0 and 8.0 Hz, 1H, CH-O), 6.75-7.66 (m, 10H, arom.). IR (neat) 3460, 3030, 2920, 1600, 1580, 1495, 1455, 1420, 1390, 1275, 1190, 1075, 1030, 910, 760, 705 cm^{-1}. HRMS Calcd. for M 292.037. Found 292.037. MS (m/e) 292 (M), 275 (M-OH), 197 (M-MeSe), 91 (tropylium ion). Anal. Calcd. for $C_{15}H_{16}OSe$ C 61.86, H 5.54. Found C 61.23, H 5.47.

Synthesis of 1-phenyl-2-[(4-methoxy)phenyl]-2-methylseleno-ethane-1-ol.

Following the general procedure A, 0.310g of 4-methoxyphenyl-bis(methylseleno)methane and 0.63 ml of n-butyllithium gave 0.254g (79%) of a diastereoisomeric mixture (75/25) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.40 eluent pentane-ether (7:3, v/v). ^{1}H-NMR (CCl_4) δ 1.53 and 1.70 (2s in a ratio of 75:25, 3H, MeSe), 3.70 (s, 3H, MeO), 4.00 and 4.05 (2d, J = 7.0 and 7.0 Hz, 1H, CH-Se), 4.77 and 4.90 (2d, J = 7.0 and 7.0 Hz, CH-O), 6.5-7.33 (m, 9H, arom.). IR (CCl_4) 3560, 2920, 2840, 2060, 1950, 1880, 1805, 1610, 1580, 1450, 1300, 1110, 1020, 900 cm^{-1}. MS (m/e), 322 (M), 227 (M-MeSe), 215 (M-PhCHOH), 121 (methoxytropylium ion), 107 (PhCHOH), 91 (tropylium ion). Anal. Calcd. for $C_{16}H_{18}OSe$ C 59.82, H 5.65. Found C 59.20, H. 5.42.

Synthesis of 1-phenyl-2-[(2-methoxy)phenyl]-2-methylseleno-ethane-1-ol.

Following the general procedure A, 0.310g of 2-methoxyphenyl-bis(methylseleno)methane and 0.63 ml of n-butyllithium gave 0.252g (77%) of a diastereoisomeric mixture (55/45) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.20 and 0.30 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 1.50-2.00 (m, 3H, MeSe), 2.17-3.17 (m, 1H, OH), 3.63 and 3.66 (2s, 3H, MeO), 4.37 and 4.50 (2d, in a ratio of 55:45, J = 9.0 and 7.0 Hz, 1H, CH-Se), 4.83 and 4.93 (2d, J = 7.0 and 9.0 Hz, 1H, CH-O), 6.50-7.50 (m, 4H, arom.). IR (neat) 3420, 3050, 3020, 2995, 2920, 2830, 1595, 1580, 1490, 1460, 1435, 1290, 1245, 1190, 1050, 1025, 900, 755, 700 cm^{-1}. MS (m/e), 227 (M-MeSe), 215 (M-PhCHOH), 121 (methoxytropylium ion), 107 (PhCHCH), 91 (tropylium ion). Anal. Calcd. for $C_{16}H_{18}OSe$ C 59.82, H 5.65. Found C 59.81, H 5.59.

Synthesis of 1,2-diphenyl-2-phenylseleno-propane-1-ol.

Following the general procedure A, 0.418g of 1-phenyl- 1,1-bis(phenylseleno)ethane and 0.63 ml of n-butyllithium gave 0.302g (82%) of a diastereoisomeric mixture (50/50) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.40 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 1.57 (s, 3H, Me), 2.65-3.10 (m, 1H, OH), 4.73 and 5.63 (2s in a ratio of 50:50, 1H, CH-O),

6.60-7.70 (m, 15H, arom.). IR (neat) 3440, 3050, 3020, 2970, 1600, 1580, 1495, 1475, 1455, 1375, 1190, 1085, 1070, 1025, 775, 745, 700 cm^{-1}. MS (m/e) 368 (M), 261 (M-PhCHOH), 211 (M-PhSe), 77 (Ph). Anal. Calcd. for $C_{21}H_{20}OSe$ C 68.66, H 5.49. Found C 68.75, H 5.68.

Synthesis of 1,2-diphenyl-2-methylseleno-propane-1-ol.

Following the general procedure A, 0.294g of 1-phenyl 1,1-bis(methylseleno) ethane and 0.63 ml of n-butyllithium gave 0.294g (87%) of a diastereoisomeric mixture (55/45) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.55 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 1.56, 1.60, 1.64 and 1.72 (4s, 6H, Me), 2.32-2.90 (m, 1H, OH), 4.96 and 5.20 (2s in a ratio of 45:55, 1H, CH-O), 6.64-7.50 (m, 10H, arom.). IR (neat) 3430, 3050, 3020, 2950, 2930, 2870, 1600, 1490, 1470, 1450, 1445, 1190, 1050, 1030, 900, 770, 750, 705 cm^{-1}. HRMS Calcd. for M 306.052. Found 306.052. MS (m/e) 288 (M-H_2O), 211 (M-MeSe), 199 (M-PhCHOH). Anal. Calcd. for $C_{16}H_{18}OSe$ C 62.95, H 5.94. Found C 63.06, H 6.11.

Synthesis of 1-phenyl-1-methyl-2-[(4-methoxy)phenyl]-2-methylseleno-ethane-1-ol.

Following the general procedure A, 0.324g of 1-(4-methoxyphenyl)-1,1-bis (methylseleno)ethane and 0.63 ml of n-butyllithium gave 0.272g (81%) of a diastereoisomeric mixture (60/40) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.29 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 1.40-1.70 (m, 6H, Me-C-SeMe), 2.3-2.6 (m, 1H, OH), 3.72 (s, 3H, MeO), 4.90 and 5.16 (2s in a ratio of 60: 40, 1H, CH-O), 6.60-7.40 (m, 9H, arom.). IR (neat) 3440, 3060, 3020, 2960, 2920, 2820, 1600, 1540, 1500, 1450, 1300, 1250, 11 80, 1030, 700, 685 cm^{-1}. HRMS Calcd. for M-H_2O 318.052. Found 318.064. MS (m/e) 336 (M), 318 (M-H_2O), 241 (H-MeSe), 229 (M-PhCHOH). Anal. Calcd. for $C_{17}H_{20}O_2Se$ C 60.90, H 6.02. Found C 60.61, H 5.81.

Synthesis of 1-phenyl-1-methyl-2-[(4-methyl)phenyl]-2-methylseleno-ethane-1-ol.

Following the general procedure A, 0.308g of 1-(4-methylphenyl) 1,1-bis(methylseleno)ethane and 0.63 ml of n-butyllithium gave 0.288g (90%) of a diastereoisomeric mixture (60/40) of the corresponding β-hydroxyalkyl selenides. Tlc Rf 0.65 eluent pentane-ether (8:2, v/v). ^{1}H-NMR (CCl_4) δ 1.40-1.70 (m, 6H, Me-C-SeMe), 2.26 (s, 3H, 4-Me-C_6H_4), 2.60-2.90 (m, 1H, OH), 4.80 and 5.10 (2s in a ratio 60:40, 1H, CH-O), 6.60-7.40 (m, 9H, arom.). IR (neat) 3430, 3080, 3060, 3020, 2960, 2920, 1950, 1900, 1800, 1680, 1600, 1500, 1490, 1450, 1370, 1180, 1020, 910, 810, 770, 730, 700 cm^{-1}. HRMS Calcd. for M-H_2O 302.057. Found 302.057. MS (m/e), 320 (M), 302 (M-H_2O), 225 (M-MeSe). Anal. Calcd. for $C_7H_{20}OSe$ C 63.95, H 6.31. Found C 63.43, H 6.64.

Reaction of 1-phenylseleno -1-ethyllithium on 1,1-bis(phenylseleno)ethane

To 1.00 mmol (0.63 ml) of n-butyllithium in 2 ml of anhydrous THF was added at, -78°C, 1.00 mmol (0.342 g) of 1,1-bis(phenylseleno) ethane dissolved in 3 ml of THF. The mixture was stirred for 0.5 h at -78°C. Then, 1.00 mmol (0.342 g) of 1,1-bis(phenylseleno)ethane was introduced and the mixture allowed to react for 2 h at -78°C. Finally, 1.00 mmol (0.106 g) of benzaldehyde was added, followed after 0.2 h at -78°C by methanol and water. The mixture was extracted three times with ether. The combined organic layer was washed with water, dried over anhydrous $MgSO_4$, filtered and the solvents were evaporated under vacuum. The crude mixture was fractionated by preparative layer chromatography (SiO_2, pentane) to give two main fractions. The most eluted one consisted of a 1/1 (estimated by $IGCI^2$) mixture of phenyl butyl selenide and phenyl ethyl selenide (>95 % yield) the less eluted (0.34 g) was pure 1-phenyl 2,2-bis(phenylseleno)propane-1-ol (76 % yield).Tlc Rf 0.35 eluent pentane-ether(8:2 ,v/v).Mp 135°C(pentane). ^{1}H NMR (CCl_4) δ 1.3 (broad s, 3H, Me), 3.7 (m, 1H, OH), 4.65(broad s, 1H, CH-O), 7.1-7.7 (m,15H,arom.).IR(KBr)3479,3047,2964,2919,2855,1954,1887,1769,1574,1557,1520,1505,1495,1474,1450,1435,1386,1364,132 5,1301,1231,1185,1159,1096,1066,1042,1019,919,895,830,731,694cm^{-1}.

Synthesis of trans 4-t-butyl-1-phenylselenocyclohexane.

To a solution of 0.452 g (1.00 mmol) of 1,1-bis(phenylseleno)-4-t-butyl cyclohexane dissolved in 1 ml of anhydrous THF was added 0.63 ml (1.00 mmol) of n-butyllithium in hexane, at -78°C. The mixture was stirred for 0.1 h at -78°C and the reaction was quenched with methanol and was allowed to warm up to room temperature. The organic layer was diluted with 20 ml of ether. Then the organic layer was washed twice with water and was dried over anhydrous $MgSO_4$.Isolation of the product was carried out by SiO_2 preparative layer chromatography. We obtained 0.246 g (83%) of trans 4-t-butyl-1-(phenylseleno) cyclohexane. Tlc Rf 0.4 eluent pentane. ^{1}H NMR (CCl_4) : 0.80 (s, 9 H, t-Bu), 1.00-2.20 (m, 9 H, CH_2 alicycl + CH -t-Bu), 3.04 (m, 1 H, CH-Se), 7.20-7.60 (m, 5 H, arom.). IR (neat) : 3060, 2940, 2860, 1580, 1480, 1450, 1440, 1400, 1350, 1280, 1160, 1030, 1000, 750 cm^{-1}. HRMS Calcd for 296.104. Found 296.105. MS (m/e) 296(M), 281(M-Me), 158(PhSeH), 139(M-PhSeH). Anal. Calcd for $C_{16}H_{24}Se$ C 65.07, H 8.19. Found C 64.86, H 8.21.

Synthesis of 1-methylseleno-2-methylcyclohexane

To 28 mmol (8 g) of 2-methyl 1,1-bis(methylseleno)cyclohexane in 60 ml of anhydrous THF, was added, at -78°C, 28 mmol (17.6 ml) of n-butyllithium. The mixture was allowed to react for 1h at -78°C, then quenched with methanol at this temperature. Water was then added and the mixture extracted three times with ether. The combined organic layer was washed with water, dried over anhydrous $MgSO_4$, filtered and the solvents were evaporated under vacuum. Distillation of the residue gave 4.35 g of 1-methylseleno-2-methylcyclohexane (82% yield, bp 50-52°C/ 0.3 mm Hg) as a single isomer ($IGCI^2$ analysis) whose stereochemistry is not yet determined. Tlc Rf 0.4 eluent pentane. ^{1}H NMR (CCl_4) δ 0.75-2.5 (m with 2 s at 1.05 (MeC) and 1.9

(MeSe). IR (neat) 2924, 2852, 1445, 1375, 1261, 1183, 1115, 1077, 1044, 982, 968, 957, 893, 856 cm^{-1}. ^{77}Se NMR ($CDCl_3$) δ 157.4 .

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