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SYNTHESIS OF SELENOACETALS

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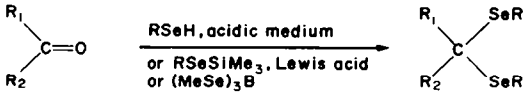
Abstract—This paper reports our results concerning the syntheses of various bis(alkylseleno)alkanes and some of their arylseleno analogues by different methods. The scope and limitation of each of them are presented.

We present in this paper a full account of our work directed towards the synthesis of selenoacetals from the corresponding carbonyl compounds (Scheme 1). Selenoacetals belong to a class of compounds practically unknown some 15 years ago.[1,2] They have nevertheless played a crucial role in the development of modern organoselenium chemistry.[3-6]

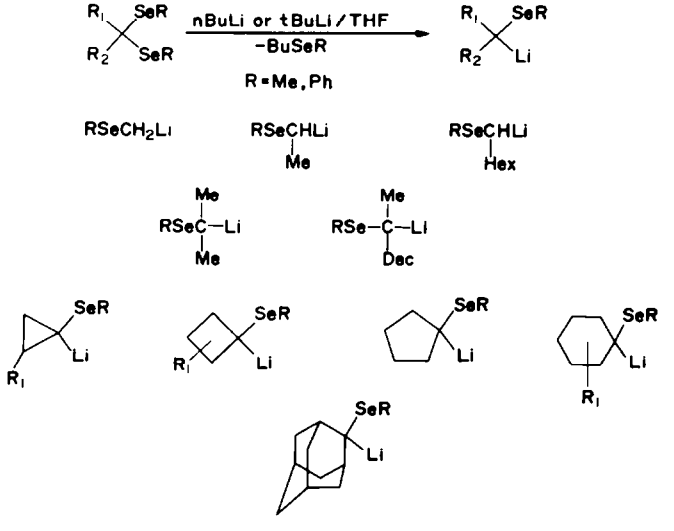
As expected they share similar behaviour with their oxygen[7,8] and sulfur[9-12] analogues; like them they are inert to Grignard reagents and are valuable precursors of carbonyl compounds.[13,14] They, however, possess the unique property to be reduced quantitatively to α-selenoalkyllithiums on reaction with butyllithiums.[3-6] This reaction had allowed the synthesis of a large variety of α-phenylseleno- and α-methylselenoalkyllithiums including those bearing two hydrogens,[15-17] one hydrogen and one alkyl,[4,17-20] one aryl group and even two alkyl groups[4,17-20] or cycloalkyl groups[4,21,22] on the carbanionic centre (for a selection of α-selenoalkyllithiums prepared see Scheme 2).



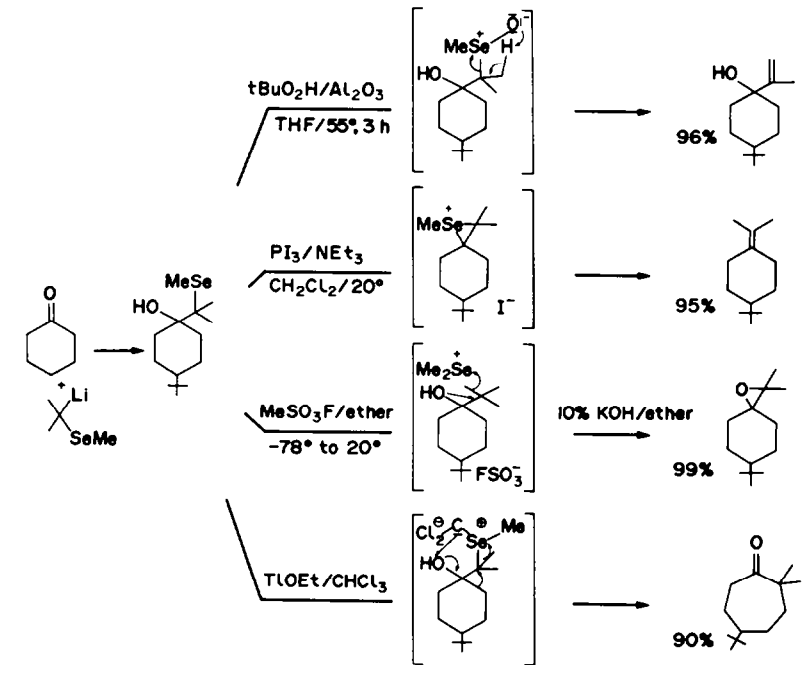
Scheme 1.

It is worthwhile to mention that these reagents where the first α-heterosubstituted organometallics bearing a non-charged heteroatomic moiety and two alkyl groups on the carbanionic centre to be prepared.[4,6] They were found to be highly reactive towards a large array of functional groups including aldehydes and ketones, even the relatively hindered[17,23] or enolizable ones,[17] and have been found to be very good precursors, *inter alia*, of allyl alcohols,[18-20,22-24] epoxides,[17,22,23,25-27] olefins,[23,28-31] and ketones[23,26,30,31-35] from carbonyl compounds (Scheme 3) as well as α-enones,[36] homoallyl alcohols,[36] halogenohydrins,[37] oxetanes,[37] allyl alcohols[36] and alcohols[38] from epoxides (Scheme 4). Metallation of phenylselenoacetals was achieved with metallo amides[16,30,39] and the resulting α-metallo phenylselenoacetals proved to be valuable acyl anion equivalents[4,13,39,40] (Scheme 4).

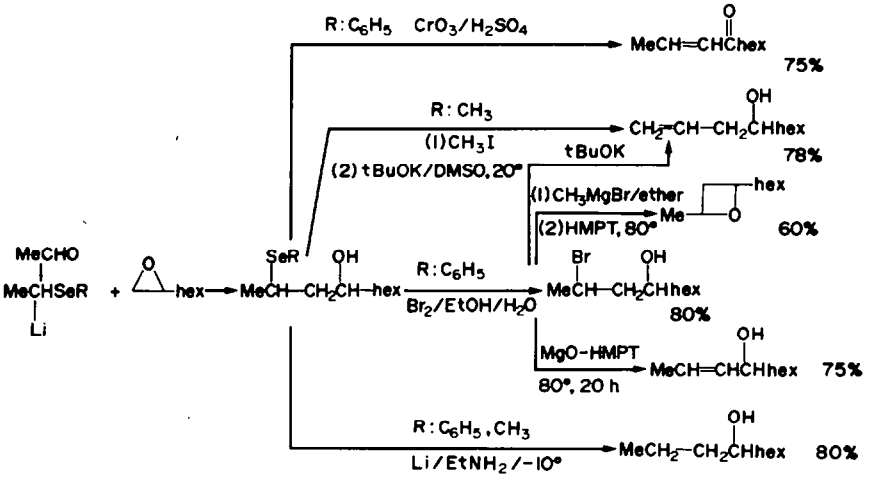
Selenoacetals have been selectively transformed to vinyl selenides on reaction with methyl iodide[42] at reflux of DMF or with P_2I_4 or PI_3[43] at room temperature (Scheme 5), and have produced aldehydes and ketones when reacted with copper chloride/copper



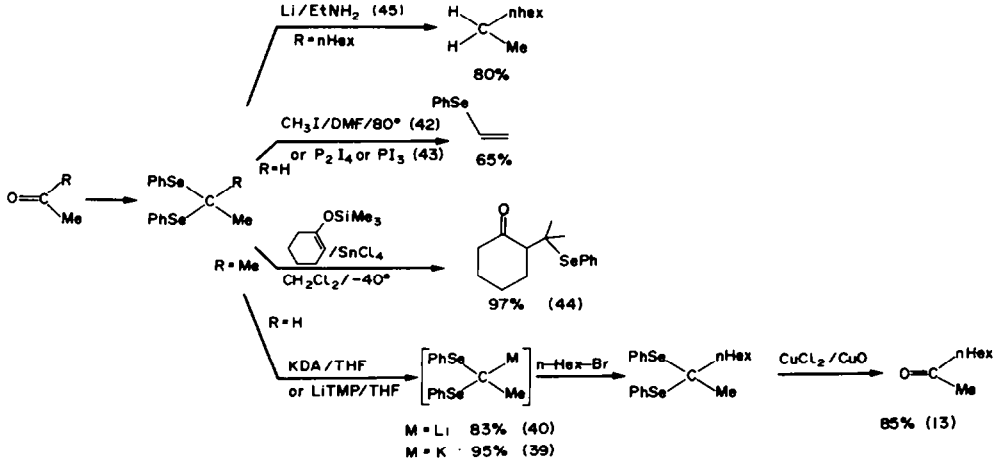
Scheme 2.



Scheme 3.



Scheme 4.

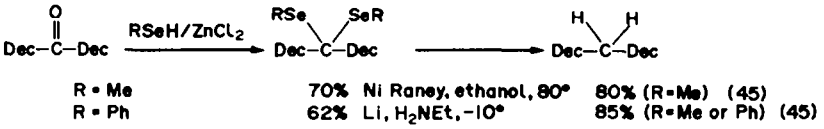


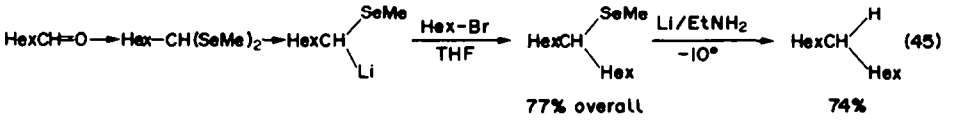
Scheme 5.

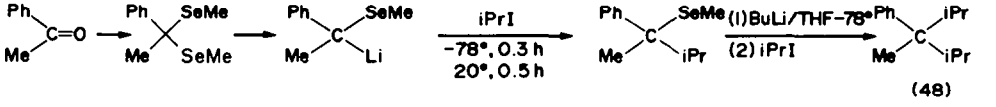
oxide,[13,41] mercuric chloride,[13] seleninic anhydrides,[13] or hydrogen peroxide[13] (Scheme 5). They are also valuable precursors of α-selenocarbenium ions[44] which have been successfully reacted with nucleophiles including silyl enols ethers[44] (Scheme 5).

Finally, the C—Se bond in selenoacetals is efficiently transformed to a C—H bond by several reducing agents (Schemes 5 and 6) such as lithium in ethylamine at −10°,[45] Raney nickel in ethanol[45] at 80° or tin hydride.[46,47] Under the latter conditions selenoacetals can be selectively reduced to selenides or alkanes depending upon the number of equivalents (1 or 2) of tin hydride used.

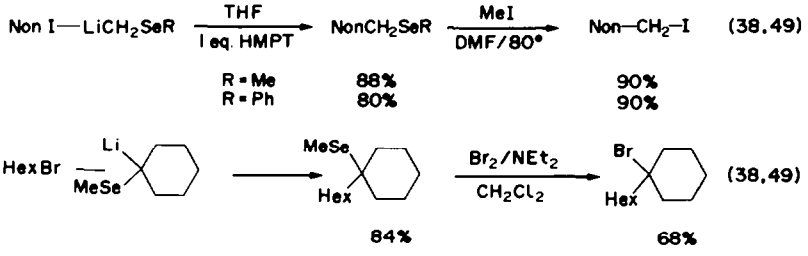
These reactions have been successfully used for various interesting reactions such as the ones cited in Schemes 3 and 4, but also for the reduction and the alkylative reduction of the carbonyl group of aldehydes and ketones (Schemes 5 and 6),[45–47] the geminal dialkylation of aromatic aldehydes and ketones[48] (Scheme 6) the ring enlargement of cyclic ketone[31–34] (Scheme 3), the homologation of alkylhalides,[38,49] (Scheme 7), the vicinal dialkylation of electrophilic olefins[14,50] (Scheme 8) and the oxidative cleavage of carbonyl compounds[42] (Scheme 9). They are also precursors of other heteroatom stabilized organometallics such as α-thio[18,20,51] and α-silyl[52,53] alkyllithiums some of which are not available by other methods (Scheme 10).



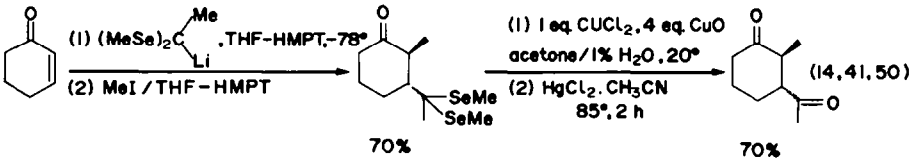




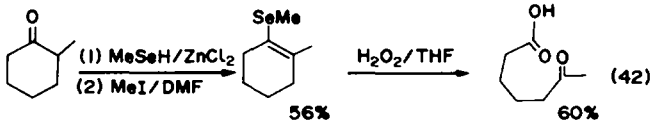
Scheme 6.



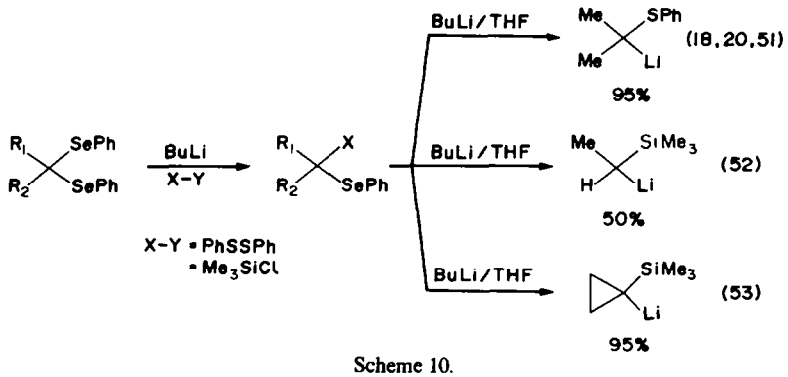
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

It is, therefore, important to have efficient methods which allow the synthesis of a wide range of selenoacetals from cheap and readily available starting materials. It is also interesting to have mild conditions which permits the synthesis of the selenoacetal moiety part of a complex molecule possessing various other functional groups sensitive to acid and/or to basic reagents.

When we started to work in that area ten years ago, only a few selenoacetals were known and little was known about their reactivity. During that period, we have prepared around 100 different selenoacetals under various experimental conditions. We have learned more about the limitation of each method and have tried in some cases to overcome the difficulties encountered. We have already disclosed some of our preliminary results[13,17,21,22,54–57] and we would like to present now the full account of our work devoted to the synthesis of selenoacetals directly from carbonyl compounds. We must also mention the work of Clive and Menchen,[46,58] which appeared during that period.

1. ABOUT PREVIOUS SYNTHESIS OF SELENOACETALS

As we already pointed out, few selenoacetals were described when we began our work. The parent compounds have been prepared by reaction of diiodomethane with sodium selenolate[16] or trifluoroalkylselenomercury,[59,60] from α-chloromethylether, zinc and selenols[61] and from diphenyldiselenide or dibenzyldiselenide and diazomethane.[63,64]

Several arylselenoacetals were obtained from carbonyl compounds and arylselenols under quite drastic conditions which require saturation of the medium with gaseous hydrochloric acid.[16,65,66]

Finally, the selenoacetal moiety is also present in selenacycloalkanes.[67–71] Some of them have been obtained in attempting[70,71] to prepare selenals and selones from carbonyl compounds and hydrogen selenide. 1,1-Bis(phenylseleno)ethane was also prepared[15,16] from 1,1-bis(phenylseleno)methyllithium. Related reactions were later successfully applied to the synthesis of various phenylseleno- and methylselenoacetals including functionalized ones.[14,21,39,40]

2. OUR RESULTS

2.1. *Selenoacetalization of carbonyl compounds with selenols and protic acids*

2.1.1. *Selenoacetalization of carbonyl compounds with selenols in the presence of hydrochloric acid.* Ten years ago, we became interested in generalizing the synthesis of α-selenoalkyllithiums from selenoacetals and alkyl lithium reagents whose first example was previously reported by Seebach and Peleties.[15,16] At that time, we needed a large variety of aryl and alkyl selenoacetals derived from aldehydes, as well as from alicyclic and cyclic ketones. We decided to use the published method[16,65,66] which consisted of treating a mixture of a selenol and a carbonyl compound by gaseous hydrogen chloride. In this way, we synthesized in good yield several methylselenoacetals[17] derived from aldehydes or ketones (Table 1). We also prepared without any difficulties some phenylselenoacetals derived from ketones (Table 1).

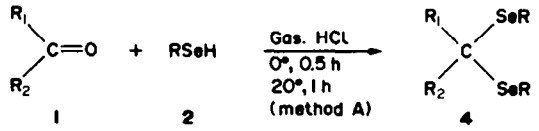
However, in contrast with the reports of the literature,[66] this method was found to be of low efficiency for the synthesis of 1,1-bis(phenylseleno)alkanes.[62] The reaction between selenophenol and an aliphatic aldehyde (acetaldehyde[66] or n-heptanal) in the presence of gaseous hydrogen chloride gave under the usual conditions a mixture of three products: the selenoacetal, the corresponding α-chlorophenylselenide and an unknown product. Under prolonged HCl bubbling, we finally got a mixture of the first two compounds from which the acetal was isolated in modest yield after tedious purification [1,1-bis(phenylseleno)ethane: 40%; 1,1-bis(phenylseleno)heptane: 35%]. In order to overcome these difficulties we decided to look in more detail at the selenoacetalization reaction of carbonyl compounds.

We found that neither heptanal nor acetone deliver the corresponding selenoacetal when they are mixed with 2 equiv of phenyl- or methylselenol neat or in a non-polar solvent. However, whereas heat is evolved and 1-hydroxy 1-selenoalkanes 3 are formed besides the starting material in the case of heptanal (neat, 30°, 3/1 ratio: R = Ph, 90/10, 0.1 or 15 hr; R = Me > 95/5, 0.1 or 15 hr), the starting materials remain the only products present in the case of acetone whatever the selenol used.

From these results, it seems obvious that the presence of an acid is required for the success of the selenoacetalization. We have therefore looked at the reaction of selenols, carbonyl compounds and sulfuric acid, which possess a conjugated base of low nucleophilicity, in order to avoid the complication observed in the hydrochloric acid method.

We have also tried to perform the reaction in the presence of Lewis acids ($MgCl_2$, $ZnCl_2$, $SnCl_4$, $TiCl_4$) and we have searched for the mildest conditions compatible with the presence of other functional

Table 1.



1 2 4

Entry	R_1	R_2	R		% Yield in 4
1	Me	H	Me	4a	80
2	n-Hex	H	Me	4b	70
3	Me	Me	Me	4e	90
4	$-(CH_2)_5-$		Me	4m	80
5	$-(CH_2)_2-CH(t\text{-}C_4H_9)-(CH_2)_2-$		Me	4o	93
6	Me	Me	Ph	4e′	98
7	$-(CH_2)_5-$		Ph	4m′	95
8	Me	H	Ph	4a′	40
9	n-Hex	H	Ph	4b′	35

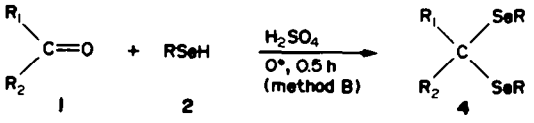
groups sensitive to acid. With that respect we have also looked at the reactivity of aldehydes and ketones with trimethylsilyl methylselenide, trimethylsilyl phenylselenide and tris(methylseleno)borane. We did not use tris(phenylseleno)borane since a paper from Clive's Laboratory disclosing the use of this reagent for phenylselenoacetalization appeared[46] in the meantime.

2.1.2. *Selenoacetalization of carbonyl compounds with selenols in the presence of sulfuric acid.* We have concentrated our efforts to the case of phenylselenoacetals derived from aliphatic aldehydes which were not easily available by the hydrochloric acid method (method A). We found that performing the reaction at room temperature in the presence of one molar equivalent (vs the carbonyl compounds) of concentrated (18 M) sulfuric acid led to various 1,1-bis(phenylseleno)alkanes (Table 2, entries 1–3) in good yield (~75%).

The same procedure was more or less successfully applied to phenylselenoacetals derived from aliphatic ketones (Table 2, entries 4–6) but completely failed for the synthesis of all methylselenoacetals (Table 2, entries 7 and 8). In all the cases diselenides are formed: as by-products in the phenylseleno series, but nearly quantitatively in the methylseleno ones. These results led us to suspect that concentrated (18 M) sulfuric acid has a high propensity to oxidize selenols and that this reaction competes with the selenoacetalization. We found, in separate experiments, that it is effectively the case since both phenyl- and methylselenols are rapidly (<0.5 hr) and quantitatively oxidized to diselenides with 1 molar equivalent of 18 M aqueous sulfuric acid at room temperature. Using 13 M instead of 18 M sulfuric acid again leads to the quantitative formation of dimethyl diselenide but phenylselenol is only oxidized to a 25% extent (20°, 0.5 hr).

Interestingly, we found that the propensity of sulfuric acid to transform selenoacetals to carbonyl compounds and diselenides through an oxidative process (Table 3) parallels the results reported above.

Table 2.

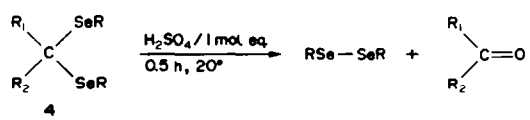


1 2 4

Entry	R_1	R_2	R		% Yield in 4†
1	Me	H	Ph	4a′	70
2	n-Hex	H	Ph	4b′	73
3	n-Dec	H	Ph	4c′	75
4	Me	Me	Ph	4e′	75
5	n-Hex	Me	Ph	4f′	57(78)
6	$-(CH_2)_5-$		Ph	4m′	75
7	n-Non	Me	Me	4g	0
8	n-Dec	H	Me	4c	0(67)

† An equimolar amount of 18 M sulfuric acid vs the carbonyl compound was used except for yields quoted in parentheses which were observed in reactions carried out with 13 M sulfuric acid.

Table 3.



4

Entry	R_1	R_2	R		H_2SO_4 molarity	% Recovered in 4
1	n-Nonyl	Me	Me	4g	18 M	0
2	n-Nonyl	Me	Me	4g	13 M	20
3	n-Decyl	H	Ph	4c′	18 M	50
4	n-Decyl	H	Ph	4c′	13 M	80

The results of these separate experiments suggest that 13 M sulfuric acid could be more suitable than the 18 M solution for carrying out the selenoacetalization in the problematic cases we reported above and this was indeed observed (Table 2, entries 5 and 8 results in parentheses).

2.2. *Selenoacetalization of carbonyl compounds with selenols in the presence of Lewis acids*

Most of our work on selenoacetalization of carbonyl compounds has been performed in the presence of Lewis acid. Phenyl- and methylselenols were the most frequently used, although ethaneselenol, benzylselenol, isopropylselenol as well as 1,3-propanediselenol and 1,4-butanediselenol have been on the occasion successfully reacted.

2.2.1. *Selenoacetalization of aliphatic carbonyl compounds with methylselenol.* We choose for prospective purposes magnesium dichloride, zinc dichloride,[13,54,89] tin tetrachloride and titanium tetrachloride,[72] among the various Lewis acid candidates. Model experiments involved undecanal or 2-undecanone and methylselenol and were routinely performed at 20° or at lower temperature in dichloromethane. Our results are summarized in Table 4.

Magnesium dichloride proved to be inefficient whereas the other metal salts used in that study produced the desired selenoacetals.

Under optimal conditions, the selenoacetalization was carried out with 0.2–0.5 molar equivalents of Lewis acid depending upon its nature. The reaction is not complete when catalytic amounts are used and on the other side, increasing the quantities of Lewis acid to 5 molar equivalents leads to a deviation of the reaction in the case of 2-undecanone: 2-methylselenoundecane[72] instead of 2,2-bis(methylseleno)undecane is formed quite exclusively (Table 4, entries 6, 9 and 12). Under the same condition 1,1-bis(methylseleno)undecane is still obtained in good yield and is not contaminated by the corresponding selenide[72] (Table 4, entry 4).

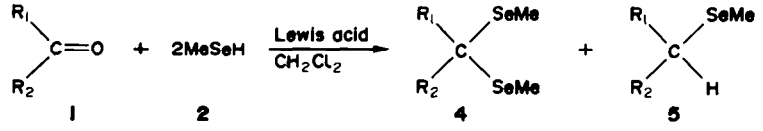
The mechanistic implications of this surprising reductive process are not yet elucidated and will be investigated in the near future.

The results we just reported for two specific cases apply also to a wide range of carbonyl compounds. Several aliphatic aldehydes and alicyclic and cyclic ketones have been successfully transformed to their corresponding methylselenoacetals on reaction with two equivalents of methylselenol and zinc dichloride (0.5 equiv, at 20°, method C), tin tetrachloride (0.2 equiv, at 20° or −78°, method D), or with titanium tetrachloride (0.35 equiv, usually at −78°, method E). Our results are gathered in Table 5.

The reaction takes place usually in a few hours but is sensitive to steric hindrance when ketones are involved. In those cases, the titanium tetrachloride method (method E) was found to be by far superior to other methods (C or D), at the condition that the reaction is performed for the shortest time at the lowest temperature possible. Diisopropyl ketone is a good representative of this type of compound and produced 69% of the desired selenoacetal when the reaction in the presence of $TiCl_4$ is conducted at −50° for 8.5 hr. Performing the reaction at higher temperature (20°) or at low temperature (−50°) but for a long period of time leads to much lower yields of the acetal and concomitant formation of 2,4-dimethyl 3-methylselenopentane, the selenide formally resulting from the reduction of the selenoacetal (61% of selenide formed instead of the acetal when the reaction is performed at −50° for 20 hr).

On the other hand, we were unable to prepare the methylselenoacetals derived from very crowded 2,2,6,6-tetramethyl cyclohexanone or diterbutyl ketone under these conditions or more drastic ones (higher temperature, longer reaction time, higher amounts of catalyst) and in most cases the two ketones were recovered unchanged.

Table 4.

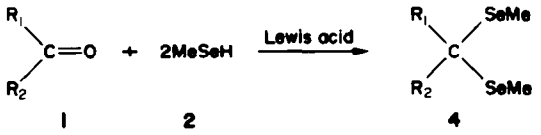


1 2 4 5

Entry	R_1	R_2		Structure	Lewis acid Rel. amount† (molar equiv)	Time (hr)	Temp (°)	% Yield in 4	% Yield in 5
1	n-Decyl	H	c	$MgCl_2$	5	2	20	0	0
2	n-Nonyl	Me	g	$MgCl_2$	5	2	20	0	0
3	n-Decyl	H	c	$ZnCl_2$	0.5	3	20	97	0
4	n-Decyl	H	c	$ZnCl_2$	5	16	20	98	0
5	n-Nonyl	Me	g	$ZnCl_2$	0.5	3(2.5)	20(−50)	91(76)	0(0)
6	n-Nonyl	Me	g	$ZnCl_2$	5	16	20	0	91
7	n-Decyl	H	c	$TiCl_4$	0.3	2(3)	20(−78)	76(81)	0(0)
8	n-Nonyl	Me	g	$TiCl_4$	0.3	1.7(5)	20(−78)	85(83)	0(0)
9	n-Nonyl	Me	g	$TiCl_4$	5	4	20	0	94
10	n-Decyl	H	c	$SnCl_4$	0.2	4.7	−78	72	0
11	n-Nonyl	Me	g	$SnCl_4$	0.2	3.5(5.5)	10(−78)	86(92)	0(0)
12	n-Nonyl	Me	g	$SnCl_4$	5	5	20	0	56‡

† Versus the carbonyl compound.
‡ 2-Undecanone is also recovered.

Table 5.



1 2 4

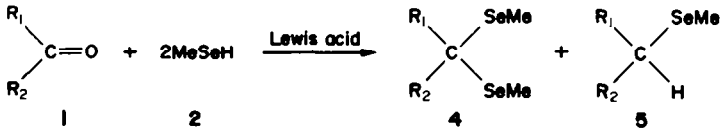
Entry	R_1	R_2		$ZnCl_2$ (0.5 molar equiv;† 20°) (method C) Time (hr)	% Yield in 4	$SnCl_4$ (0.2 molar equiv;† −78°) (method D) Time (hr)	% Yield in 4	$TiCl_4$ (0.35 molar equiv)† (method E) Time (hr)	Temp (°)	% Yield in 4
1	Me	H	**4a**	1	91					
2	n-Hexyl	H	**4b**	3	72					
3	t-Butyl	H	**4d**	0.75	90	2	80	4.8	−78	75
4	Me	Me	**4e**	3	90			3	−78	86
5	n-Hexyl	Me	**4f**	3	77					
6	t-Butyl	Me	**4h**	1.5	81					
7	n-Hexyl	n-Hexyl	**4i**	24	66					
8	iso-Propyl	iso-Propyl	**4j**	3.2	16	8	0	8.5	−50	69
9		$-(CH_2)_3-$	**4k**	0.5	89					
10		$-(CH_2)_4-$	**4l**	0.5	87					
11		$-(CH_2)_5-$	**4m**	0.5	91	1.5	87	5	−78	90
12		$-(CH_2)_4-CH(CH_3)-$	**4n**	1	64					
13	$-(CH_2)_2-CH(t\text{-}C_4H_9)-(CH_2)_2-$		**4o**	5.5	85	4	92	1.5	−78	89
14	2-Adamantyl		**4p**	1	88					

† Versus the carbonyl compound.

As previously reported in the models (Table 4) the use of higher amounts (5 mol equiv) of Lewis acids should be avoided when aliphatic ketones are involved since reductive selenenylation of the carbonyl group takes place rather than selenoacetalization.[72]

2.2.2. *Methylselenoacetalization of aromatic aldehydes and ketones.* Methods C and E permit also the methylselenoacetalization of a large variety of aromatic aldehydes (Table 6). However when applied to aromatic ketones the zinc chloride method (method C) led, especially in the case of *p*-methyl and *p*-methoxy acetophenone (Table 6, entries 6–8), to substantial amounts of selenides at the expense of the desired selenoacetal. As already pointed out the amount of selenides increases by increasing the reaction time (Table 6, entries 7 and 8) or increasing the amount of catalyst. As a general trend in these last cases, the $TiCl_4$ method proved highly efficient (method E). We have also tried to perform this last reaction in the presence of triethylamine, the reaction times are much increased

Table 6.



1 2 4 5

Entry	R_1	R_2		$ZnCl_2$ (0.5 molar equiv;† 20°) (method C) Time (hr)	% Yield in 4 and (5)	$TiCl_4$ (0.35 molar equiv)† (method E) 0.25 hr at −50° and 2 hr at 20° % Yield in 4 and (5)	$TiCl_4$ (1 molar equiv;† 20°) Et_3N (1 molar equiv)† (method F) Time (hr)	% Yield in 4 and (5)
1	Ph	H	**4q**	2[2]‡	92(0)[67(29)]‡	89(0)	17	62(8)
2	p-EtO—C_6H_4—	H	**4r**	2	93(0)	84(0)		
3	p-NO_2—C_6H_4—	H	**4s**	2	91(0)	78(0)		
4	o-Cl—C_6H_4—	H	**4t**	2	78(0)	62(0)		
5	Ph	Me	**4u**	2	68(26)	70(15)	1	72(0)
6	p-Me—C_6H_4—	Me	**4v**	2	39(7)	94(0)	17	49(10)
7	p-MeO—C_6H_4—	Me	**4w**	3	47(20)	43(0)		
8	p-MeO—C_6H_4—	Me	**4w**	10	< 5(49)		17	63(10)
9	p-Cl—C_6H_4—	Me	**4x**	3	35(55)	79(0)		
10	p-NO_2—C_6H_4	Me	**4y**	3	74(15)			

† Versus the carbonyl compound.

‡ [ ] Refers to experiment carried out in CH_2Cl_2 instead of CCl_4.

and although the amount of selenide remains low, the method does not seem to offer, at least in the cases studied, substantial advantages (Table 6, entries 1, 5, 6 and 8).

2.2.3. *Synthesis of functionalized selenoacetals.* The methaneselenol/zinc dichloride or titanium tetrachloride methods (methods C and E) permit also the high yield synthesis of a wide range of functionalized methylselenoacetals from functionalized carbonyl compounds (Table 7) such as from aldehydes or ketones bearing an ester, a primary hydroxyl group or another carbonyl group (Table 7). Selenoacetals bearing a halogen or a selenenyl group are respectively available from carbonyl compounds possessing these moieties but with the condition that these groups are not in an α position to the carbonyl group (Table 7). In the latter cases a reduction takes place concomitantly leading to the selenoacetal free from any halogen.

Selenoacetals possessing a carbon–carbon double bond have also been prepared from unsaturated carbonyl compounds (Table 7) but α,β-unsaturated aldehydes lead under the standard conditions to intractable mixtures of compounds which contain, *inter alia*, β-selenenyl selenoacetals. On the other hand citronellal is partially cyclized and produces several unidentified products.

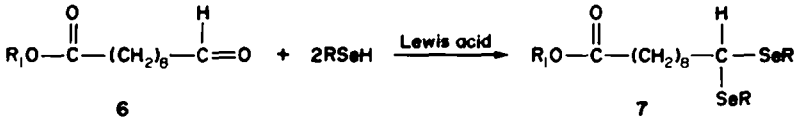
2.2.4. *Synthesis of other alkylselenoacetals.* A few selenoacetalizations involving primary and secondary selenols or β- and γ-diselenols have also been successfully carried out using the zinc dichloride method (method C). These results are presented in Table 8.

2.2.5. *Synthesis of arylselenoacetals.* Most of the work was done with phenylselenol and zinc dichloride or titanium tetrachloride methods under standard conditions (methods C and E). The reaction features are very similar to the ones we reported for the methylselenoacetalization and the results are gathered in Tables 7 and 9. Some differences must be noticed: under these conditions the phenylselenoacetalization seems to be less easy. This is observed in those cases such as hindered carbonyl compounds, with some aromatic aldehydes and with most of the aromatic ketones (Table 9, entries 8, 9, 15, 16, 20). In those cases, all or part of the starting material was recovered unchanged even after long reaction times (17 hr). Thus the reductive selenenylation of the carbonyl group leading to selenides, often observed under similar conditions in the methylseleno series, is no longer the crucial problem in the phenylseleno series.

2.3. *Selenoacetalization of carbonyl compounds with selenosilanes and selenoboranes*

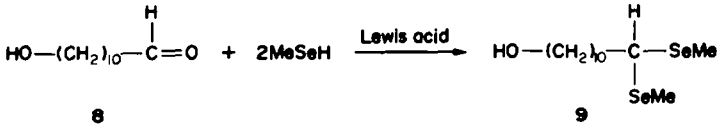
All the selenoacetalizations reported above have required the presence of an acidic medium which could be incompatible with some other functionalities present in the molecule. We became interested, therefore, in

Table 7.



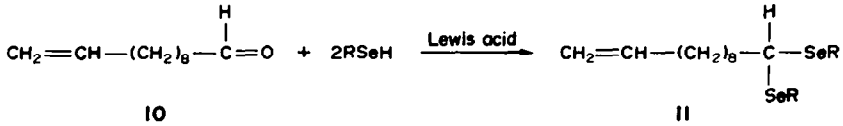
6 7

R = Me	R_1	Method	Time (hr)†	% Yield in 7	R = Ph	R_1	Method	Time (hr)†	% Yield in 7
7a	H	C	4.5	94	**7a'**	H	C	5	95
7a	H	E	5[−78]	73	**7b'**	Me	C	5.5	82
7b	Me	C	5	84	**7b'**	Me	E	5.5 [−50]	56
7b	Me	E	5[−78]	76					



8 9

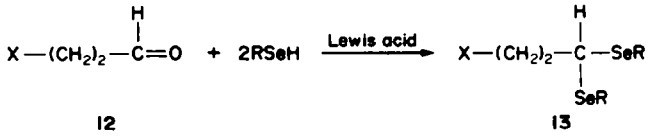
Method	Time (hr)†	% Yield in 9
C	6	89
E	6[−78]	56



10 11

R = Me	Method	Time (hr)†	% Yield in 11	R = Ph	Method	Time (hr)†	% Yield in 11
11a	C	3	86	**11a'**	C	5	97
11a	E	2[−78]	82	**11a'**	E	5[−45]	75

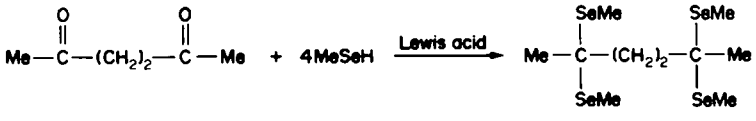
Table 7. *Cont.*



12 13

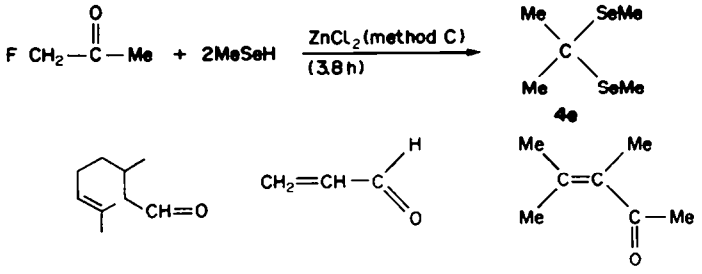
R = Me	X	Method	Time (hr)†	% Yield in 13
13a	Cl	A	0.5[0] 1[20]	65
13b	PhSe	C	2	69
13b	PhSe	E	2.5[−78]	52

R = Ph	X	Method	Time (hr)	% Yield in 13
13a′	Cl	C	2	75
13b′	PhSe	C	3.8	60



14 15

Method	Time (hr)†	% Yield in 15
C	4	85
E	8[−78] 15[0]	74



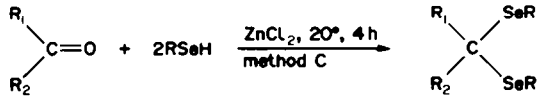
† Unless otherwise mentioned, [ ], the reactions were performed at 20°.

finding selenoacetalization reagents which could avoid these conditions. Both selenosilanes and tris-selenoboranes were expected to be valuable candidates due to the well-known oxygenophilic properties of the silicon or boron atoms. Moreover, precedents existed in the sulfur series where thioanalogues [Me_3SiSPh,[73,74] $B(SR)_3$[75–76]] were reported to efficiently perform the thioacetalization of carbonyl compounds in the absence of acid catalyst.[74] We have investigated the reaction of $Me_3SiSePh$, $Me_3SiSeMe$ and $B(SeMe)_3$ with carbonyl compounds.

Our expectations were, at least partly confirmed in the case of the boron reagent, but not at all in the case of the selenosilanes where an acid catalyst was required in order to achieve the selenoacetalization.

Thus we found that tris(methylseleno)borane[77–79] readily available from dimethyldiselenide, lithium aluminium hydride and boron trifluoride etherate, and free, by two consecutive distillations, from the aluminium trifluoride concomitantly formed, is able to provide in methylene dichloride and at room temperature the selenoacetalization of various aliphatic aldehydes and ketones (Table 10) without the requirement of an acid catalyst. The reaction occurs at room temperature, is usually slow and becomes slower when steric hindrance around the carbonyl group increases. It is therefore not surprising that under these conditions diisopropyl ketone does not react.

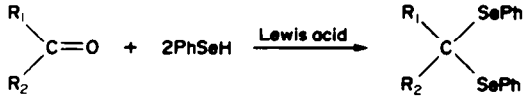
Table 8.



1 17 18

Entry	R_1	R_2	R		% Yield in 18
1	Me	H	n-Butyl	18a	55
2	Me	H	2-Heptyl	18b	60
3	n-Hexyl	H	Et	18c	55
4	n-Hexyl	H	n-Butyl	18d	50
5	n-Hexyl	H	$-(CH_2)_3-$	18e	82
6	n-Hexyl	H	$-(CH_2)_4-$	18f	80
7	n-Hexyl	H	$Ph-CH_2$	18g	93
8	n-Hexyl	H	iso-Propyl	18h	35
9	n-Hexyl	H	2-Heptyl	18i	71
10	Me	Me	2-Heptyl	18j	43

Table 9.



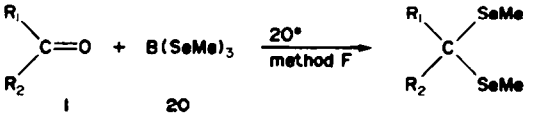
1 4

Entry	R_1	R_2		$ZnCl_2$ (0.5 molar equiv;‡ 20°) (method C) Time (hr)	% Yield in 4	$TiCl_4$ (0.35 molar equiv)‡ (method E) Time (hr)	Temp (°)	% Yield in 4
1	Me	H	4a'	2.5	90			
2	n-Hexyl	H	4b'	3	79			
3	n-Decyl	H	4c'	5	80	6	−50	87
4	t-Butyl	H	4d'	3	90	7.7	−50	87
5	Me	Me	4e'	3	85			
6	n-Hexyl	Me	4f'	5	80			
7	n-Nonyl	Me	4g'	5	92	7.8	−50	79
8	t-Butyl	Me	4h'	24	32	5	0	6
9	n-Hexyl	n-Hexyl	4i'	4	16			
10		$-(CH_2)_3-$	4k'	3	84			
11		$-(CH_2)_4-$	4l'	1	81	7.6	−50	93
12		$-(CH_2)_5-$	4m'	1	81			
13	$-(CH_2)_4-CH(CH_3)-$		4n'	4	62			
14	$-(CH_2)_2-CH(t\text{-}C_4H_9)-(CH_2)_2-$		4o'	2.5	70			
15	2-Adamantyl		4p'	5	27			
16	Ph	H	4q'	2	Trace (5)†	0.25 2	−50 20	64(2)†
17	$o\text{-}ClC_6H_4$	H	4t'	2		0.25 2	−50 20	55
18	Ph	Me	4u'			0.25 2	−50 20	39
19	p-Me—Ph	Me	4v'		0(34)†	0.25 2	−50 20	
20	p-MeO—Ph	Me	4w'	2	0(10)†	0.25 2	−50 20	10

† The corresponding selenide 5 was also isolated and yields are quoted in parentheses.
‡ Versus the carbonyl compound.

Most of the functionalized carbonyl compounds we already successfully transformed to functionalized selenoacetals by the methylselenol/$ZnCl_2$ method were also transformed using $B(SeMe)_3$ (Table 10). Moreover, the later reagent permits the synthesis in 60% yield of the methylselenoacetal derived from citronellal and although in modest yield (33–47%) it allows the synthesis of a methylselenoacetal of an aldehyde leaving untouched a dioxolane group.[64] These two transformations were not possible, as already pointed out, with methylselenol/$ZnCl_2$. Unfortunately, tris-(methylseleno)borane does not allow, under these

Table 10.



1 20

Entry	R_1	R_2		Time (hr)	% Yield in selenoacetal
1	Me	H	4a	2.5	63
2	n-Decyl	H	4c	8	74
3	t-Butyl	H	4d	24	65
4	Me	Me	4e	15	45
5	$-(CH_2)_5-$		4m	4.5	65
6	$-(CH_2)_2-CH(t\text{-}C_4H_9)-(CH_2)_2-$		4o	31	84
7	$CH_2=CH-(CH_2)_8-$	H	11a	2	76
8	$(CH_3)_2C=CH-(CH_2)_2-CH(CH_3)-CH_2-$	H	26	5	60
9	$HO_2C-(CH_2)_8-$	H	7a	5	84
10	$MeO_2C-(CH_2)_8-$	H	7b	1.5	62
11	$PhSe-(CH_2)_2-$	H	13b	6	63

conditions, the formation of selenoacetals derived from aromatic carbonyl compounds, and selenides are often formed instead. Simultaneously Clive and Menchen reported the synthesis of phenylseleno- and methylselenoacetals using tris(phenylseleno)- and tris(methylseleno)boranes.[46] However, most of their reactions were performed with an acid catalyst.

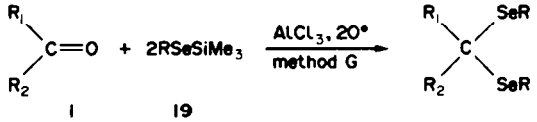
We have also reacted trimethylsilylphenylselenide and its methylseleno analogue with various carbonyl compounds in order to achieve their selenoacetalization. The desired silyl selenides were prepared according to known procedures[86] from the diselenides, lithium aluminium hydride and chlorotrimethyl silane. The first experiments were performed with bi-distilled silylselenides thus avoiding the presence of the aluminum trichloride concomitantly formed during the synthesis. Contrary to our expectation no reaction takes place at 20° in the absence of an acid catalyst (neither neat nor in solvents such as carbon tetrachloride, diethylether or acetonitrile). On addition of magnesium bromide (0.5 equiv) to heptanal (1 equiv) and trimethylsilylmethylselenide (2 or 1 equiv), the corresponding α-O-(trimethylsilyl)selenide is, however, obtained in 79% yield[54,87,88] but the methylselenoacetal is not formed. Increasing the amount of catalyst to 1 equiv leads to the formation of some selenoacetal **4** (27%) besides the α-O-trimethylsilylselenide (59%). 1,1-Bis(methylseleno)heptane is, however, formed quite exclusively if stronger acids such as $ZnCl_2$ (0.5 equiv; **4**: 92%) or $AlCl_3$ (0.5 equiv; **4**: 65%) are used.[54,55] On the basis of these results, we have set up a new procedure which allows the synthesis of various selenoacetals from diselenides. This procedure requires the *in situ* formation of a $Me_3SiSeR/AlCl_3$ mixture using the experimental condition we described above: ether was removed *in vacuo* leaving a residue which is taken up with chloroform, instead of to be distilled. The resulting suspension, which can be stored at 0°, was used for several weeks without decomposition. The supernatant (expected to titer 2.6 M, based on quantitative formation of $RSeSiMe_3$) is very efficient for the direct acetalization of carbonyl compounds. The reaction usually occurs at 20° with a supernatant/carbonyl compound ratio of 3 ml mmol^{-1} (Table 11). The results are similar, occasionally better, than those obtained by the selenol/$ZnCl_2$ method. Both methods have the same advantages and suffer from the same limitations. The selenosilane method avoids the use of selenols. This is particularly interesting in the methylseleno series where methylselenol is volatile (b.p. 25°/760 mm Hg), has a bad smell and has also to be prepared from dimethyldiselenide. The selenosilane used in this method does not need to be purified and the manipulations are reduced to the change of solvent (chloroform instead of ether). This change is important for the success of the reaction.

2.4. *Selenoacetalization of carbonyl compounds by miscellaneous methods*

During the course of this work we also tried other experimental conditions. For instance tin tetrachloride leads to results closely related to the one we reported with titanium tetrachloride, but was unable to promote the methylselenoacetalization of diisopropylketone. Tetra(methylseleno)tin[90] and tetra(methylseleno)-silane[86] did not give more interesting results. Unfortunately we were unable to prepare tetra(methylseleno)-titanium. We have also extended the reaction of diphenyldiselenide and diazomethane[63] to dimethyldiselenide: bis(methylseleno)methane[64] was obtained in 81% but we were unable to apply it to higher homologues.

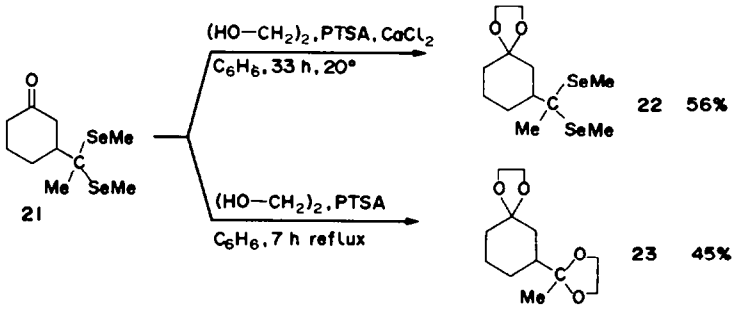
We were unable to promote the transselenoacetalization between carbonyl compounds (undecanal and

Table 11.

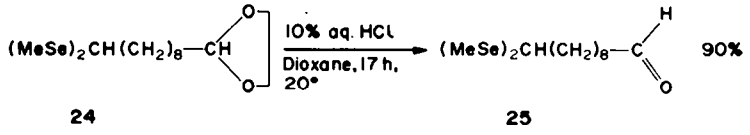


1 19

Entry	R_1	R_2	R		Time (hr)	% Yield in selenoacetal
1	Me	H	Me	**4a**	3	60
2	n-Hexyl	H	Me	**4b**	2	60
3	n-Decyl	H	Me	**4c**	1	80
4	t-Butyl	H	Me	**4d**	2.5	71
5	Me	Me	Me	**4e**	3	65
6	n-Hexyl	Me	Me	**4f**	2	65
7	n-Nonyl	Me	Me	**4g**	1.2	77
8	$-(CH_2)_5-$		Me	**4m**	3	72
9	$-(CH_2)_2-CH(t\text{-}C_4H_9)-(CH_2)_2-$		Me	**4o**	1	90
10	Ph	H	Me	**4q**	3.5	77
11	n-Decyl	H	Ph	**4c'**	3	67
12	t-Butyl	H	Ph	**4d'**	26	40
13	Me	Me	Ph	**4e'**	4.5	44
14	n-Nonyl	Me	Ph	**4g'**	4.5	55
15	$-(CH_2)_2-CH(t\text{-}C_4H_9)-(CH_2)_2-$		Ph	**4o'**	3	82
16	$CH_2=CH-(CH_2)_8-$	H	Me	**11a**	2	89
17	$MeO_2C-(CH_2)_8-$	H	Me	**7b**	2	45
18	$HO-(CH_2)_{10}-$	H	Me	**9**	1	62



Scheme 11.



Scheme 12.

2-undecanone) and orthoselenoformate or orthoselenoacetate with ammonium chloride or ammonium nitrate under various conditions (DMF or CH_3CN) which usually permit the transacetalization of oxygenated analogues.

However, we were able to synthesize an O,O-acetal from a ketone containing a built in methylselenoacetal. This has been achieved with ethylene glycol in benzene using *p*-toluenesulfonic acid as the catalyst and calcium chloride as the dehydrating agent (Scheme 11). It must be pointed out that the reaction must be carried out at 20° since, transacetalization was observed at higher temperature (Scheme 11).

Finally, deprotection of an O,O-acetal can be selectively achieved in the presence of a methylselenoacetal moiety using 10% aqueous hydrochloric acid (Scheme 12).

3. CONCLUSION

In conclusion, we have now a set of reagents and reactions which allow the synthesis of a wide range of selenoacetals from carbonyl compounds. Any time a common carbonyl compound is involved, we suggest the use of the selenol/zinc chloride method (method C). These reagents are stable, readily available and not highly sensitive to moisture or oxidation. However, this method is not suitable for hindered aliphatic ketones, for most of the aromatic ketones especially in the phenylseleno series and for some functionalized derivatives such as citronellal.

The $TiCl_4$ method gave results closely related to the ones just described in the simple cases. However, $TiCl_4$ is less easily handled than $ZnCl_2$ and the reaction is often more violent. This requires the careful control of the temperature when mixing the reagents. It is, however, the method of choice for the selenoacetalization of aromatic compounds especially for the synthesis of methylselenoacetals derived from aromatic ketones.

Finally trisselenoborane is the only efficient reagent when an acid catalyst has to be avoided.

4. EXPERIMENTAL

M.ps are taken on a Kofler apparatus and are uncorrected. IR data reported in cm^{-1} were obtained using a Perkin–Elmer model 377 spectrophotometer. The spectra were performed on neat liquids or on solids in KBr or dissolved in CCl_4.

^{1}H-NMR spectra were taken on Jeol MH 100, JNM 60 Si, or FX 90 Q spectrometers. ^{1}H-NMR were recorded in $CDCl_3$ or CCl_4 using TMS as internal standard. Mass spectra were obtained on AEI MS 30 or HP 5995 AGC/MS spectrometers. In the experimental part M refers to M^+ and only a few characteristics are reported. A general discussion of complete spectral data of selenoacetals (including ^{77}Se-NMR and UV spectra) will be soon disclosed. The microanalyses were performed in the Microanalysis Laboratory of the Paris VI University.

Layer chromatography: analytical TLC was performed on premade, glass-backed plate SiO_2, 60 PF254, 250 μm (Merck 5719). Compounds were visualized by UV illumination and by heating to 150° after spraying phosphomolybdic acid in EtOH. PLC was performed on SiO_2 plates prepared as follows: 440 g of silica gel 60 PF254 (Merck 7747) (for fifteen 20 × 20 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 adsorbent (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 hr. The hot water bath was removed after 1 hr and the plates were allowed to dry in the closed hood for 20 hr. The dried plates were activated (140°, 10 hr) prior to use (> 95% success on > 50,000 plates prepared).

Unless otherwise noted, selenoacetalizations were performed in a two-necked round bottomed flask equipped with serum stoppers and an argon filled balloon. The liquids were transferred by syringe.

4.1. *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 aldehydes and ketones were distilled or recrystallized prior to use. Magnesium dichloride,

titanium tetrachloride and tin tetrachloride were used without any pretreatment whereas zinc dichloride was calcinated and allowed to cool in a desiccator filled with dry nitrogen.

Few aldehydes or ketones non-commercially available were prepared according to classical procedures outlined below. 8-Formylnonanoic acid **6a** was obtained from 10-undecen-1-al in a two-step procedure which involved the pyridinium dichromate oxidation (84%) of 10-undecen-1-al followed by ozonolysis (70%) of the resulting unsaturated acid. 8-Formylmethylnonanoate **6b** was prepared by quantitative esterification of the corresponding acid with diazomethane. 10-Hydroxyundecan-1-al **8** was synthesized in a three-step procedure from 10-undecen-1-al. This unsaturated aldehyde was acetalized in 95% yield under usual conditions (ethyleneglycol, PTSA, water–benzene azeotropic distillation). The resulting 11-(ethylenedioxy)-1-undecene was submitted to hydroboration (borane–dimethyl sulfide complex) and gave, after treatment with hydrogen peroxide, the corresponding hydroxyacetal. This last compound was finally reacted with a 10% aq HCl soln to give the desired 10-hydroxyundecan-1-al (33% for the last two steps). 3-Chloropropanal **12a** was prepared by bubbling gaseous HCl into cooled (0°) acroleine. 2-Phenylselenopropanal **12b** was obtained in 70% yield according to described procedure.[91] Compound **21** (Scheme 11) was synthesized in 78% yield by the HMPA promoted addition of 1-lithio-1,1-bis(methylseleno)ethane to cyclohexenone.[50]

Finally **24** (Scheme 12) was derived in two steps from 11-(ethylenedioxy)-1-undecene (see above): treatment of this compound with osmium tetroxide followed by reaction with sodium periodate gave 9-(ethylenedioxy)decan-1-al (86%) which was transformed in modest yield (33%) to 10-(ethylenedioxy)-1,1-bis(methylseleno)decane **24** using tris(methylseleno)borane[55,79] (24 hr, 20°).

4.2. *Synthesis of selenols*

The selenols used in this work were prepared by known procedures starting from the corresponding alkyl bromides, diselenides or selenocyanates. Detailed experimental conditions are described below. The reactions are performed in a well-ventilated hood.

Dimethyldiselenide.[81] A 3 l three-necked flask is fitted with a dropping funnel, whose stem is immersed in the reaction mixture, a mechanical stirrer and a distillation head connected through a condenser to a 1 l flask cooled to 0°. The side tube of the receiver adapter is connected to a set of three gas-washing bottles, the first being empty and the last two containing a 50% aq KOH soln. In the 3 l flask are successively introduced under stirring sodium bisulfite (380 g, 2 mol), water (700 ml), KOH (560 g, 10 mol) and again water (700 ml). After complete dissolution of the reagents, black Se powder (316 g, 4 mol) is added in small portions and the mixture is heated to the boiling point of the solvent. Dimethylsulfate (504 g, 4 mol) is then added slowly from the dropping funnel and the orange oily dimethyldiselenide is continuously removed by steam distillation. The steam distilled oil is separated from the aqueous phase which is extracted twice with 500 ml portions of ether. The organic layers are combined and dried over $MgSO_4$. Cautious removal of the solvent *in vacuo* affords crude dimethyldiselenide (302 g) sufficiently pure for the synthesis of selenomethanol.

Note: On standing, some crystalline material (usually 3–5 g) may appear in the crude dimethyldiselenide. This is probably due to the presence of a slight amount of dimethylsulfate in this crude product. This problem may become more important if the addition of dimethylsulfate to the reaction mixture was too fast. If pure dimethyldiselenide is needed, the solid is filtered off and the liquid residue distilled (b.p. 63–65°, 15 mmHg, 277 g, 73%).

Selenomethanol.[81] A mixture of crude dimethyldiselenide (190 g, ≃ 1 mol) and 50% aq hypophosphorous acid (158 g, 1.2 mol) is placed into a 1 l flask fitted with a magnetic stirrer, a nitrogen inlet and a distillation head connected through a condenser to a 0.5 l flask immersed in a dry ice–acetone bath. The side arm of the receiver adapter is linked to a set of three gas-washing bottles, the first being empty and the last two containing 30% aq H_2O_2. N_2 is passed slowly through the apparatus, while the content of the flask is heated to 90° under stirring. The evolution of gas set in almost immediately and slightly wet methylselenol (b.p. 24–26°) is condensed in the cold flask. The crude methylselenol is redistilled through a 20 cm Vigreux column (the receiving flask being again immersed in a dry ice–acetone bath and connected to a set of gas-washing bottles fitted as above). Pure selenomethanol (163 g, 85%) is obtained and stored at −30° on 4 Å molecular sieves in a flask fitted with a septum.

Selenophenol.[82] Magnesium (72 g, 3 mol) and a few crystals of iodine are introduced into a 2 l flask fitted with a mechanical stirrer, a reflux condenser (with a $CaCl_2$ tube) and a dropping funnel. The Mg is covered with anhyd ether and bromobenzene (5–10 g) is introduced. After the reaction started, the remaining amount of bromobenzene (total amount: 471 g, 3 mol) dissolved in dry ether (750 ml) is slowly added under stirring, the mixture being allowed to reflux gently). Thirty minutes after the end of the addition, the dropping funnel is replaced by a plastic pipe (in which is inserted a needle for N_2 inlet) connected to a flask containing black Se powder (228 g, 3 mol). A slow stream of N_2 is passed through the apparatus and the Se is introduced in small portions. An hour after the end of the addition, the contents of the flask are poured upon a mixture of cracked ice (2 kg) and conc HCl (250 ml). The aqueous layer is separated and extracted once with ether (500 ml). The combined extract and main product are dried over $MgSO_4$. The solvent is evaporated *in vacuo* and the residue distilled through a 20 cm Vigreux column to afford pure selenophenol (b.p. 72–75°/15 mmHg, 292 g, 70%) which is stored at −30° under argon in a flask fitted with a septum.

Diphenyldiselenide.[83] Selenophenol (666 g, 4.24 mol) in EtOH (1 l) is stirred with KOH (7.8 g, 0.14 mol) for 60 hr under slightly positive O_2 pressure. After this treatment, there still remains some selenophenol and the reaction is achieved by O_2 bubbling for 6 hr which results in mass crystallization. Pure diphenyldiselenide is filtered off and dried *in vacuo* (665 g, 99%, m.p. 62–63°). This product can be recrystallized from pentane.

Selenocyanates.[84,85] Potassium selenocyanate (10 g, 0.069 mol) and DMF or acetone (see Table 12) (60 ml) are placed into a 250 ml two-necked flask fitted with a magnetic stirrer, a septum and a condenser connected to an argon filled balloon. The soln is heated under stirring to 60° and the suitable alkylbromide is slowly introduced by a syringe. The resulting mixture is stirred for 4 hr at 60°, then hydrolyzed (30 ml water) and extracted twice with 50 ml portions of ether. The ethereal fractions were combined, washed with water (5 × 15 ml), brine (10 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo*, leaving the crude selenocyanate sufficiently pure for the next step.

Selenols **17** *from selenocyanates.* Sodium borohydride (2.6 g, 0.068 mol) and dry EtOH (50 ml) are placed in a two-necked flask fitted with an argon filled balloon and a septum (or a plastic pipe connected to a flask). The suspension is stirred and cooled to 0° and the selenocyanate (see Table 13) is slowly introduced by syringe (or via the plastic pipe for solids). After addition, the mixture is stirred for 1 hr at 0° and for 1 hr at 20°, hydrolyzed with 10% aq HCl (until a 3–4 pH is obtained) and extracted twice with 50 ml portions of ether. The ethereal fractions are combined, washed with 1% aq HCl (3 × 15 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo* (except for ethaneselenol, n-butaneselenol and 2-iso-propaneselenol which are too volatile and whose ethereal solutions are directly used for selenoacetalization reactions) leaving the crude selenols which will be used without further purification.

4.3. *Trimethylsilyl methylselenide* **19**[54,55,86–88]

Dimethyldiselenide (8.55 g, 0.045 mol) in dry ether (10 ml) is slowly added to a stirred suspension of lithium aluminium hydride (0.875 g, 0.023 mol) in dry ether (10 ml) at 0° under

Table 12.

Starting bromide Structure	Amount (g) (mol)	Solvent	Selenocyanate Amount (g)	% Yield	m.p. (°)
Et Br	7(0.065)	DMF	4.5	66	—
n-Butyl Br	8.9(0.065)	DMF	8.6	97	—
$Br(CH_2)_3$ Br	6.5(0.032)	Acetone	7.9	97	52
$Br(CH_2)_4$ Br	6.9(0.032)	Acetone	7.8	91	68–69
Ph—CH_2 Br	11.1(0.065)	Acetone	12.5	98	71.5
iso-Propyl Br	8.6(0.065)	Acetone	7.9	83	—
2-Heptyl Br	11.6(0.065)	DMF	10.8	81	—

Table 13.

Selenocyanate Structure	Amount (g) (mol)	Selenol Amount (g)	Yield
EtSeCN	6.75(0.05)	—	—†
n-Butyl—SeCN	8.15(0.05)	—	—†
$NCSe(CH_2)_3SeCN$	6.35(0.025)	3.5	69
$NCSe(CH_2)_4SeCN$	6.7(0.025)	3.5	65
Ph—CH_2SeCN	9.85(0.05)	5	58
iso-Propyl—SeCN	7.4(0.05)	—	—†
2-Heptyl—SeCN	10.25(0.05)	7.5	83

† See note at the end of the general procedure.

argon. After the end of the addition, the mixture is stirred for 0.3 hr at 0°. Then, neat trimethylsilyl chloride (9.7 g, 0.09 mol) is slowly syringed into the reaction mixture at 0°. The content of the flask is then allowed to heat at 20°, stirred for 1 hr and finally refluxed for 0.7 hr. At this stage, either we proceed to isolate pure trimethylsilyl methylselenide or we prepare a $CHCl_3$ soln of trimethylsilyl methylselenide containing a suspension of aluminium trichloride which has been formed during the reaction.

Pure trimethylsilyl methylselenide. Ether and volatile impurities are distilled from the crude mixture (b.p. < 65°, 760 mmHg). Most of the solid material contained in the residue is eliminated by complete distillation *in vacuo* (15 mmHg, 5.7 g). This distillate is again fractionated under normal pressure to give pure trimethylsilyl methylselenide (b.p. 114–116°, 4.6 g, 30%).

Chloroform solution of trimethylsilyl methylselenide containing a suspension of aluminium trichloride. The crude mixture is cautiously concentrated under slight vacuum (100 mmHg). Then, dry $CHCl_3$ (20 ml) is added and the whole content of the flask (34 ml) is transferred by syringe into a bottle filled with argon and stopped by a septum. This crude mixture (which should be 2.6 molar in trimethylsilyl methylselenide assuming a quantitative reaction) is stored at −30°.

4.4. *Trimethylsilyl phenyselenide* **19**[54,86–88]

Preparation of a solution of trimethylsilyl phenylselenide containing a suspension of aluminium trichloride. Diphenyldiselenide (21.84 g, 0.07 mol) in dry ether (60 ml) is slowly added to a stirred suspension of lithium aluminium hydride (1.42 g, 0.0375 mol) in dry ether (20 ml) at 0° under argon. After the end of the addition, the mixture is stirred for 0.5 hr at 20°. Then, neat trimethylsilyl chloride (15.2 g, 0.14 mol, 17.8 ml, d: 0.856) is slowly syringed into the reaction mixture which is stirred for 15 hr at 20°. The resulting mixture (which should be approximately 2.4 molar in trimethylsilyl phenylselenide), is stored at −30° and the supernatant is used for selenoacetalization.

4.5. *Tris(methylseleno)borane* **20**[55,79]

Dimethyldiselenide (14.1 g, 0.075 mol) in dry ether (12 ml) is slowly added to a stirred suspension of lithium aluminium hydride (1.42 g, 0.0375 mol) in dry ether (25 ml) at 0° under argon. After the end of the addition, the mixture is stirred for 0.3 hr at 0°. Then, neat boron trifluoride etherate (6.3 ml, d: 1.125, 0.05 mol) is syringed into the reaction mixture which is allowed to heat to 20°. After 20 hr, the solid material is rapidly filtered off under argon and washed with ether (50 ml). The filtrate is then evaporated *in vacuo* and the semi-solid residue is quickly distilled. All the distillate (b.p. < 100°/0.5 mmHg) is again fractionated to give pure tris-(methylseleno)borane (b.p. 75–78°/0.3 mmHg) as a slightly yellow oil which crystallizes on cooling to 0° (10.4 g, 47%).

4.6. *Selenoacetalization reactions from aldehydes or ketones and selenols*

Method A. Reaction in the presence of gaseous HCl. Selenol (0.2 mol) and aldehyde or ketone (0.1 mol) are introduced in a three-necked flask fitted with an N_2 inlet, a gaseous HCl inlet and a condenser equipped with a $CaCl_2$ tube. The flask is cooled to 0° and slow streams of N_2 and HCl are passed through the reaction mixture during 0.5 hr. The gas inlets are then replaced by stoppers and an N_2 balloon is placed on the top of the condenser. The reaction is then allowed to proceed for 1 hr at 20° under magnetic stirring. The crude mixture is diluted with ether (250 ml), washed with small portions of sat aq bicarbonate until basic, then with water (2 × 15 ml) and dried over $MgSO_4$ and filtered. The solvents are removed *in vacuo* and the selenoacetal is purified using the appropriate procedure (see later). Yields are given in Table 1.

Method B. Reaction in the presence of 18 M H_2SO_4. Selenol (0.2 mol) and aldehyde or ketone (0.1 mol) are introduced in a two-necked flask fitted with a septum and a condenser surmounted by an argon filled balloon. The flask is cooled to 0° and 18 M H_2SO_4 (5.5 ml, ≃0.1 mol) is syringed quickly into the magnetically stirred mixture. At the end of the strongly exothermic reaction which initially takes place, the mixture is stirred for 0.5 hr at 20°, diluted with ether (250 ml), washed successively with small portions sat aq bicarbonate and water (2 × 15 ml), dried over $MgSO_4$ and filtered. Ether is removed *in vacuo* and the selenoacetal is purified using the appropriate procedure (see later). Yields are given in Table 2. As pointed out in this table, selenoacetals **4c** and **4f'** were synthesized following the general procedure above but using 13 M H_2SO_4 (7.5 ml).

Method C. Reaction in the presence of $ZnCl_2$. A soln of the carbonyl compound (0.1 mol) and the selenol (0.2 mol) in CCl_4 (30 ml) is slowly added to a stirred suspension of $ZnCl_2$ (6.8 g, 0.05 mol) in the same solvent (20 ml) at 0° under argon. The mixture is stirred at 20° for the time listed in Tables 5–9, diluted with ether (250 ml) and washed with 5% HCl (2 × 50 ml) sat aq bicarbonate and water. The organic phase is dried over $MgSO_4$, the solvents are evaporated *in vacuo* and the selenoacetal is purified using the appropriate procedure (see later). Yields are given in Tables 5–9.

(1) Phenylselenoacetals derived from aromatic aldehydes and ketones are acid and water sensitive and a particular procedure must be used (see later).

(2) HCl treatment may be suppressed in case of acid sensitive substrates. This results in a more tedious elimination of the Zn salts by washing with aq sodium hydrogenocarbonate.

Method D. Reaction in the presence of $SnCl_4$. A soln of the carbonyl compound (0.001 mol) and selenol (0.002 mol) in CH_2Cl_2 (0.5 ml) is added to a soln of $SnCl_4$ (0.23 g, 0.0005 mol) in the same solvent (0.5 ml) at −78° under argon. The mixture is stirred at −78° then allowed to heat at 20°. Specific times and temperatures are listed in Tables 4 and 5. Ether (50 ml) is finally added and the soln is washed with 10% aq HCl (2 × 10 ml), sat aq bicarbonate and water, dried over $MgSO_4$ and filtered. The solvents are removed *in vacuo* and the selenoacetal is isolated by PLC (SiO_2, pentane). Yields are given in Tables 4 and 5.

(1) See method C, note 2.

(2) This method was only applied for some examples in the methylated series.

(3) Due to its lack of interest as compared to methods C and E, this procedure was never scaled up to larger quantities.

Method E. Reaction in the presence of titanium tetrachloride. A solution of the carbonyl compound (0.025 mol) and the selenol (0.05 mol) in dichloromethane (20 ml) is added to a solution of titanium tetrachloride in the same solvent (10 ml) at −50° under argon. The reaction mixture is then stirred under conditions listed in Tables 5–7 and 9, diluted with ether (100 ml) with aqueous saturated bicarbonate and water, dried over $MgSO_4$ and filtered. The solvents are evaporated *in vacuo* and the selenoacetal is isolated by the appropriate procedure (see later). Yields are quoted in Tables 5–7 and 9.

(1) See method C, note 1.

(2) Some reactions (see Tables 5–7 and 9) were completely performed at −78°.

4.7. *Selenoacetalization reactions of carbonyl compound without selenols*

Method F. Using tris(methylseleno)borane **20**. Neat tris(methylseleno)borane (0.325 g, 0.0011 mol) is added at 20° under argon to a soln of the carbonyl compound (0.001 mol) in dry $CHCl_3$ (1 ml). The mixture is stirred at 20° for the time listed in Table 10, diluted with ether (50 ml), washed with water (2 × 20 ml), dried over $MgSO_4$ and filtered. The selenoacetal is isolated by PLC (SiO_2, pentane). Yields are quoted in Table 10.

Method G. Using a soln of trimethylsilyl selenide containing a suspension of aluminium trichloride **19**. The reagent's solns were prepared as described above. For 0.001 mol of the carbonyl compound, these solns of trimethylsilyl methylselenide and trimethylsilyl phenylselenide were respectively used in 1.2 and 2.9 ml amounts.

The appropriate amount of the reagent's soln is added to a soln of the carbonyl compound (0.001 mol) in dry $CHCl_3$ under argon at 20°. The reaction mixture is stirred at 20° for the time listed in Table 11, diluted with ether (50 ml), washed with aq sat NH_4Cl, water, dried over $MgSO_4$ and filtered. The solvents are evaporated *in vacuo* and the selenoacetal is isolated by PLC (SiO_2, pentane). Yields are quoted in Table 11. Note: methods F and G were never scaled up to larger quantities.

4.8. *Purification of the selenoacetals from the crude reaction mixtures*

For experiments on small quantities (0.001–0.003 mol), the selenoacetal was always purified by PLC (SiO_2, pentane as element) (procedure a). For experiments on a larger scale, the selenoacetal was purified by column chromatography over silica gel (Merck, pentane as eluent) (procedure c), by distillation under reduced pressure (procedure d) or by recrystallization from pentane (procedure e). If the crude mixture is soiled by a significant amount of diselenide (estimated by ^{1}H-NMR), the following pretreatment (procedure b) is effected before the final purification. The crude mixture (obtained using 0.1 mol of carbonyl compound) is dissolved in ether (50 ml) and this soln is slowly added to a stirred suspension of lithium aluminium hydride (1.5 g) in ether (150 ml) under argon. The mixture is refluxed for 0.5 hr, cooled to 0° and carefully treated with the minimum amount of 50% aq KOH until H_2 evolution has subsided. The mixture is then immediately filtered through Celite and dried over $MgSO_4$. The ether is removed *in vacuo* and the selenoacetal is purified by one of the procedures described above.

For phenylselenoacetals derived from aromatic aldehydes and ketones, any treatment with acid or water must be avoided. The crude mixture is simply evaporated and fractionated by column chromatography over alumina using pentane as eluent until the diphenyldiselenide comes out, then a pentane/ether: 9/1 mixture (procedure f).

The specific purification procedures used in each case are presented in Section 4.13.

4.9. *Reaction between undecanal and 2-undecanone with methylselenol in the presence of various amounts of different Lewis acids*

A soln of the carbonyl compound (0.17 g, 0.001 mol) and methylselenol (0.192 g, 0.002 mol) in CH_2Cl_2 (2 ml) is added to a soln or suspension of the Lewis acid (structures and amounts are listed in Table 4). The reaction mixture is then stirred in the conditions indicated in Table 4. When the reaction is carried out at 20°, the mixing of the reagents is effected at 0°. Ether (50 ml) is finally added to the mixture and the organic soln is washed with sat aq bicarbonate (3 × 10 ml) and water (2 × 10 ml), dried over $MgSO_4$ and filtered. After evaporation of the solvents *in vacuo*, the selenoacetal and the selenide are isolated by PLC (SiO_2, pentane). Yields are quoted in Table 4.

4.10. *Reaction between a carbonyl compound and selenomethanol in the presence of titanium tetrachloride and triethylamine*

Triethylamine (0.1 g, 0.001 mol) in dry CH_2Cl_2 (0.5 ml) is added at 0° under argon to a soln of titanium tetrachloride (0.2 g, 0.001 mol) in the same solvent (0.5 ml). A solution of the carbonyl compound (0.001 mol) and methylselenol (0.192 g, 0.002 mol) in CH_2Cl_2 (0.5 ml) is then syringed into the mixture which is allowed to reach 20° and then stirred for the time listed in Table 6. The crude mixture is diluted with ether (50 ml), washed with sat aq bicarbonate (3 × 10 ml), water (2 × 10 ml), dried over $MgSO_4$and filtered. After evaporation of the solvents *in vacuo*, the selenoacetal generally soiled by the selenide is isolated by PLC (SiO_2, pentane/ether: 95/5). Yields estimated by ^{1}H-NMR are listed in Table 6.

4.11. *Reaction of compound* **21** *with ethyleneglycol*

At 20°. Compound **21** (0.312 g, 0.001 mol), ethyleneglycol (0.31 g, 0.005 mol) and APTS (0.04 g) are stirred at 20° for 33 hr, in benzene (5 ml) in the presence of a minute amount of $CaCl_2$. The mixture is diluted with ether (20 ml), washed with sat aq bicarbonate and water and dried over $MgSO_4$. The solvents are evaporated *in vacuo* and the residue fractionated by PLC (SiO_2, pentane/ether: 75/25) to give pure **22** (0.2 g, 56%). R_f 0.6 (ether/pentane: 3/7). Oil. IR (neat) 2950, 2880, 1455, 1430, 1380, 1370, 1360, 1345, 1320, 1300, 1280, 1260, 1240, 1175, 1100, 1055, 1030, 955, 930, 900, 850, 815 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.1–2.1 [m, 18H, —$(CH_2)_3$—CH—CH_2—, CH_3—C (s at 1.7) and CH_3Se (s at 1.94)], 3.88 (s, 4H, CH_2—O). Mass spectrum 263 (M − $SeCH_3$), 219 (M − $SeCH_3$—C_2H_4O).

Exact mass spectrum (no parent but $M-SeCH_3$), calc, 263.0550; found, 263.0543. (Found: C, 40.41; H, 6.44. Calc for $C_{12}H_{22}O_2Se_2$: C, 40.46; H, 6.22%.)

4.12. *Synthesis of 9,9-bis(methylseleno)decan-1-al* **25**

Compound **24** (0.25 g, 0.00064 mol) is stirred for 16 hr at 20° in a dioxane (5 ml), 10% aq HCl (5 ml) mixture. Ether (20 ml) is then added and the organic soln is washed with sat aq bicarbonate, water, dried over $MgSO_4$ and filtered. After evaporation of the solvents *in vacuo*, the crude mixture is fractionated by PLC (SiO_2, pentane/ether: 8/2) to give 9,9-bis(methylseleno)decanal **25** (0.2 g, 90%). IR (neat) 3030, 2960, 2720, 1730, 1470, 1435, 1420, 1270, 1125, 800 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.2–2.1 [m, 2OH, $(\underline{CH_2})_7$—CH($SeCH_3$)$_2$ and CH_3Se (s at 1.9)], 2.3 (t, 2H, $\underline{CH_2}$—CHO), 3.85 (t, 1H, $\underline{CH}(SeCH_3)_2$), 9.7 (t, 1H, CHO). Mass spectrum 249 ($M-SeCH_3$). Exact mass spectrum (no parent but $M-SeCH_3$), calc, 249.0757; found, 249.076. (Found: C, 42.40; H, 7.06. Calc for $C_{12}H_{24}OSe_2$: C, 42.11; H, 7.07%.)

4.13. *Summary of spectral and physical data of selenoacetals*

4a. Purified according to method(s) a or d. R_f 0.72 (ether/pentane: 2/8). B.p. 79° (17 mmHg). IR (neat) 2990, 2950, 2920, 2850, 2810, 1440, 1420, 1370, 1270, 1240, 1140, 1120, 1040, 960, 900, 780, 785, 620 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.8 (d, 3H, CH_3—C), 1.98 (s, 6H, $SeCH_3$), 4.02 (q, 1H, CH). Mass spectrum 218 (M), 123 ($M-SeCH_3$). Exact mass spectrum, calc for $M-SeCH_3$, 122.971; found, 122.972. (Found: C, 22.39; H, 4.89. Calc for $C_4H_{10}Se_2$: C, 22.24; H, 4.67%.)

4b. Purified according to method(s) a or d. R_f 0.76 (ether/pentane: 2/8). B.p. 140° (18 mmHg). IR (neat) 2990, 2950, 2920, 2870, 2850, 1465, 1455, 1420, 1380, 1270, 1130, 900, 730, 680 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.88 (t, 3H, CH_3), 1.3 (m, 1OH, CH_2), 1.94 (s, 6H, CH_3Se), 3.75 (t, 1H, CH). Mass spectrum 288 (M), 192 ($M-CH_3SeH$). Exact mass spectrum, calc for $M-SeCH_3$, 193.049; found, 193.050. (Found: C, 37.73; H, 7.23. Calc for $C_9H_{20}Se_2$: C, 37.77; H, 7.04%.)

4c. Purified according to method(s) a or d. R_f 0.29 (pentane). B.p. 135–137° (0.05 mmHg). IR (neat) 2960, 2920, 2860, 1470, 1420, 1375, 1270, 900 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.85 (t, 3H, CH_3), 1–2 [m, 24H, CH_2, CH_3Se (s at 1.95)], 3.82 (t, 1H, CH). Mass spectrum 344 (M), 342, 249 ($M-SeCH_3$). Exact mass spectrum, calc, 344.0521; found, 344.0522. (Found: C, 45.59; H, 8.38. Calc for $C_{13}H_{28}Se_2$: C, 45.62; H, 8.24.)

4d. Purified according to method(s) a or d. R_f 0.3 (pentane). B.p. 60° (0.1 mmHg). IR (neat) 3000, 2960, 2920, 2900, 2860, 2820, 1480, 1465, 1425, 1395, 1370, 1270, 1230, 1150, 1105, 900 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.1 (s, 9H, CH_3—C), 2 (s, 6H, $SeCH_3$), 3.65 (s, 1H, CH). Mass spectrum, 260 (M), 258, 165 ($M-SeCH_3$). Exact mass spectrum, calc 259.9582; found, 259.957. (Found: C, 32.38; H, 6.34. Calc for $C_7H_{16}Se_2$: C, 32.57; H, 6.25%.)

4e. Purified according to method(s) a or d. R_f 0.56 (ether/pentane: 2/8). B.p. 85° (25 mmHg). IR (neat) 3000, 2970, 2950, 2920, 2860, 1420, 1380, 1370, 1270, 1150, 1110, 900 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.78 (s, 6H, CH_3—C), 1.96 (s, 6H, $SeCH_3$). Mass spectrum 232 (M), 136 ($M-CH_3SeH$). Exact mass spectrum, calc for $M-CH_3SeH$, 135.979; found, 135.978. (Found: C, 25.95; H, 5.14. Calc for $C_5H_{12}Se_2$: C, 26.10; H, 5.26%.)

4f. Purified according to method(s) a or d. R_f 0.26 (pentane). B.p. 90° (0.5 mmHg). IR (neat) 2960, 2930, 2860, 1470, 1460, 1430, 1375, 1270, 1150, 1065, 900 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.9 (t, 3H, $\underline{CH_3}$—CH_2), 1–1.8 [m, 13H, CH_2 and CH_3—C—Se (s, 1.7)], 1.9 (s, 6H, CH_3Se). Mass spectrum 302 (M), 207 ($M-CH_3Se$). Exact mass spectrum, calc, 302.0051; found, 302.0055. (Found: C, 40.10; H, 7.54. Calc for $C_{10}H_{22}Se_2$: C, 40.01; H, 7.39%.)

4g. Purified according to method(s) a or d. R_f 0.34 (pentane). B.p. 120–125° (0.015 mmHg). IR (neat) 3000, 2960, 2920, 2850, 1465, 1430, 1375, 1270, 1140, 1060, 900, 790, 625 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.85 (t, H, $\underline{CH_3}$—CH_2), 1.1–1.5 (m, 16H, CH_2), 1.7 (s, 3H, CH_3—C—Se), 1.9 (s, 6H, $SeCH_3$). Mass spectrum 344 (M), 249 ($M-SeCH_3$). Exact mass spectrum, calc, 344.0521; found, 344.0522. (Found: C, 45.27; H, 8.37. Calc for $C_{13}H_{28}Se_2$: C, 45.62; H, 8.24%.)

4h. Purified according to method(s) a or d. R_f 0.33 (pentane). B.p. 68° (0.1 mmHg). IR (neat) 2965, 2925, 2870, 2820, 1480, 1470, 1460, 1430, 1420, 1395, 1375, 1360, 1270, 1225, 1090, 1065, 900 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.2 (s, 9H $(CH_3)_3C$), 1.8 (s, 3H, $\underline{CH_3}$—C($SeCH_3$)$_2$), 2.04 (s, 6H, CH_3Se). Mass spectrum 274 (M), 178 ($M-CH_3SeH$). Exact mass spectrum, calc, 273.9738; found, 273.963. (Found: C, 35.57; H, 6.78. Calc for $C_8H_{18}Se_2$: C, 35.31; H, 6.67%.)

4i. Purified according to method a. R_f 0.3 (pentane). Oil. IR (neat) 2910, 2845, 1450, 1420, 1375, 1300, 1260, 1220, 1180, 1115, 1015, 885, 720 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.9 (t, 6H, $\underline{CH_3}$—CH), 1.2–2 [m, 26H, CH_2 and CH_3Se (s at 1.9)]. Mass spectrum 277 ($M-SeCH_3$). (Found: C, 48.98; H, 8.98. Calc for $C_{15}H_{32}Se_2$: C, 48.65; H, 8.71%.)

4j. Purified according to method a. R_f 0.49 (pentane). Oil. IR (neat) 2960, 2930, 2900, 2880, 1465, 1420, 1380, 1360, 1320, 1310, 1270, 1180, 1120, 1085, 895 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.05 (d, 12H, CH_3—C), 1.9–2.2 [m, 8H, CH and CH_3Se (s at 1.93)]. Mass spectrum 288 (M), 193 ($M-SeCH_3$). Exact mass spectrum, calc, 287.9895; found, 287.989. (Found: C, 37.55; H, 7.24. Calc for $C_9H_{20}Se_2$: C, 37.77; H, 7.04%.)

4k. Purified according to method(s) a or d. R_f 0.3 (pentane). B.p. 80° (15 mmHg). IR (neat) 3000, 2960, 2940, 1435, 1280, 1250, 1105, 900 cm^{-1}. ^{1}H-NMR (CCl_4) δ1.9 (s, 6H, CH_3Se), 2.04–2.64 (m, 6H, —$(CH_2)_3$—). Mass spectrum 244 (M), 149 ($M-SeCH_3$). Exact mass spectrum, calc, 243.9269; found, 243.9269. (Found: C, 29.69; H, 4.80. Calc for $C_6H_{12}Se_2$: C, 29.77; H, 5.00%.)

4l. Purified according to method(s) a or d. R_f 0.2 (pentane). B.p. 75° (0.8 mmHg). IR (neat) 3000, 2960, 2920, 2860, 1445, 1420, 1305, 1265, 1170, 895 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.64–2.2 [m, CH_2 and CH_3Se (s, 1.94)]. Mass spectrum 163 ($M-SeCH_3$). Exact mass spectrum (no parent but $M-SeCH_3$), calc, 163.002; found, 163.003. (Found: C, 32.79; H, 5.45. Calc for $C_7H_{14}Se_2$: C, 32.83; H, 5.51%.)

4m. Purified according to method(s) a or d. R_f 0.54 (ether/pentane: 8/2). B.p. 86° (0.7 mmHg). IR (neat) 2995, 2930, 2850, 1450, 1430, 1270, 1250, 1190, 1130, 1010, 905, 880, 825, 720 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.4–1.8 (m, 10H, CH_2), 1.92 (s, 6H, $SeCH_3$). Mass spectrum 272 (M), 176 ($M-CH_3SeH$). Exact mass spectrum, calc for $M-SeCH_3$, 177.018; found, 177.019. (Found: C, 35.24; H, 6.07. Calc for $C_8H_{16}Se_2$: C, 35.58; H, 5.97%.)

4n. Purified according to method(s) a or d. R_f 0.25 (pentane). B.p. 105° (0.8 mmHg). IR (neat) 2900, 2840, 1440, 1415, 1380, 1350, 1330, 1250, 1210, 1125, 1075, 1050, 890, 820, 775, 710 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.1 (d, 3H, $\underline{CH_3}$—CH), 1.2–2.3 [m, 15H, CH_2, CH and CH_3Se (2 s at 1.88 and 1.92)]. Mass spectrum 190 ($M-CH_3SeH$). (Found: C, 38.06; H, 6.59. Calc for $C_9H_{18}Se_2$: C, 38.04; H, 6.39%.)

4o. Purified according to method(s) a or d. R_f 0.26 (pentane). B.p. 125° (0.05 mmHg). IR (neat) 2940, 2860, 2840, 1480, 1450, 1490, 1400, 1370, 1315, 1270, 1240, 1190, 1100, 1020, 1005, 900, 830 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.84 (s, 9H, $(CH_3)_3C$), 1.4–2.2 [m, 15H, CH_2, CH and CH_3Se (2s, 1.88 and 1.93)]. Mass spectrum 328 (M), 233 ($M-CH_3Se$). Exact mass spectrum, calc, 328.028; found, 328.020. (Found: C, 44.42, H, 7.56. Calc for $C_{12}H_{24}Se_2$: C, 44.18; H, 7.41%.)

4p. Purified according to method a. R_f 0.25 (pentane). M.p. 56–57°. IR (CCl_4) 2980, 2880, 2860, 2640, 1465, 1440, 1425, 1350, 1335, 1310, 1265, 1195, 1180, 1090, 1060, 1030, 955, 890 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.5–2.2 [m, 16H, CH_2 and CH_3Se (s at 1.9)], 2.45–2.85 (m, 4H, CH). Mass spectrum 324 (M), 229 ($M-SeCH_3$). (Found: C, 44.82; H, 6.46. Calc $C_{12}H_{20}Se_2$: C, 44.73; H, 6.26%.)

4q. Purified according to method(s) a or c. R_f 0.17 (pentane). Liquid. IR (neat) 3060, 3020, 2000, 2920, 2820, 1600, 1580, 1495, 1450, 1420, 1330, 1275, 1210, 1100, 1075, 1030, 905, 780, 705 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.9 (s, 6H, $SeCH_3$), 4.9 (s, 1H, CH—Se), 7.1–7.4 (m, 5H, arom). Mass spectrum 280 (M), 185 ($M-SeCH_3$). Exact mass spectrum, calc, 279.9269; found, 279.927. (Found: C, 39.15; H, 4.42. Calc for $C_9H_{12}Se_2$: C, 38.87; H, 4.35%.)

4r. Purified according to method a. R_f 0.5 (ether/pentane: 5/95). Oil. IR (neat) 2960, 2900, 2860, 2800, 1600, 1575, 1500, 1470, 1410, 1390, 1300, 1240, 1170, 1105, 1090, 1040, 920, 895, 825, 730 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.4 (t, 3H, $\underline{CH_3}$—CH_2), 1.9 (s, 6H, CH_3Se), 3.9 (q, 2H, CH_2), 4.9 (s, 1H, CH), 6.7 (d, 2H, arom), 7.3 (d, 2H, arom). Mass spectrum 229 ($M-SeCH_3$). (Found: C, 41.05; H, 5.10. Calc for $C_{11}H_{16}OSe_2$: C, 41.01; H, 5.01%.)

4s. Purified according to method a. R_f 0.5 (ether/pentane: 1/9). Oil. IR (neat) 3080, 3050, 2980, 2900, 2840, 2800, 1585, 1500, 1485, 1410, 1335, 1270, 1170, 1100, 1010, 900, 850, 810, 750, 740, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 2.03 (s, 6H, CH_3Se), 5.03 (s, 1H, CH), 7.41 (d, 2H, arom), 8.16 (d, 2H, arom). Mass spectrum 325 (M), 230 ($M-SeCH_3$). (Found: C, 33.47; H, 3.44. Calc for $C_9H_{11}NO_2Se_2$: C, 33.46; H, 3.43%.)

4t. Purified according to method a. R_f 0.8 (ether/pentane: 4/96). Oil. IR (neat) 3050, 2980, 2910, 2800, 1585, 1565, 1460, 1440, 1415, 1265, 1090, 1050, 1030, 900, 755, 730 cm^{-1}. ^{1}H-NMR (CCl_4) δ 2 (s, 6H, CH_3—Se), 5.45 (s, 1H, CH), 7–7.7 (m, 4H, arom). Mass spectrum 315 (M for ^{36}Cl), 314 (M for ^{35}Cl), 219 ($M(^{35}Cl)-SeCH_3$). (Found: C, 34.81; H, 3.57. Calc for $C_9H_{11}Se_2Cl$: C, 34.59; H, 3.55%.)

4u. Purified according to method a. R_f 0.2 (pentane). Liquid. IR (neat) 3090, 3060, 3030, 3000, 2990, 2960, 2920, 2860, 1600, 1580, 1495, 1450, 1430, 1380, 1270, 1060, 1040. 900, 775, 700, 650 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.85 (s, 6H, CH_3Se), 2.2 (s, 3H, CH_3—C), 7.1–7.4 (m, 3H, arom), 7.5–7.7 (m, 2H, arom). Mass spectrum 199 ($M-CH_3Se$), 198 ($M-CH_3SeH$). (Found: C, 41.08; H, 5.27. Calc for $C_{10}H_{14}Se_2$: C, 41.11; H, 4.83%.)

4v. Purified according to method a. R_f 0.2 (pentane). Liquid. IR (neat) 3010, 2980, 2940, 2920, 1610, 1510, 1460, 1420, 1370, 1270, 1180, 1020, 900, 820, 780 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.95 (s, 6H, CH_3Se), 1.22 and 1.32 (2s, 6H, $\underline{CH_3}$, —$C(SeCH_3)_2$ and $\underline{CH_3}$—C_6H_4), 7.1 (d, 2H, arom), 7.55 (d, 2H, arom). Mass spectrum 212 ($M-CH_3SeH$). (Found: C, 43.27; H, 5.18. Calc for $C_{11}H_{16}Se_2$: C, 43.15; H, 5.27%.)

4w. Purified according to method a. R_f 0.44 (ether/pentane: 5/95). Oil. IR (neat) 3000, 2960, 2920, 2840, 1610, 1580, 1515, 1470, 1440, 1420, 1380, 1330, 1300, 1260, 1190, 1125, 1035, 900, 840 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.85 (s, 6H, CH_3Se), 2.2 (s, 3H, CH_3—C), 3.75 (s, 3H, CH_3O), 6.8 (m, 2H, arom), 7.5 (m, 2H, arom). Mass spectrum 324 (M), 229 ($M-SeCH_3$). (Found: C, 40.98; H, 5.10. Calc for $C_{11}H_{16}OSe_2$: C, 41.01; H, 5.01%.)

4x. Purified according to method a. R_f 0.5 (ether/pentane: 3/97). Liquid. IR (neat) 3000, 2980, 2960, 2920, 2860, 2820, 1580, 1480, 1450, 1430, 1400, 1375, 1270, 1105, 1095, 1055, 1015, 900, 835, 790, 760, 725 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.85 (s, 6H, CH_3Se), 2.2 (s, 3H, CH_3—C), 7.2 (d, 2H, arom), 7.5 (d, 2H, arom). (Found: C, 36.62; H, 4.07. Calc for $C_{10}H_{13}Se_2Cl$: C, 36.80; H, 4.00%.)

4y. Purified according to method a. R_f 0.3 (ether/pentane: 3/97). Liquid. IR (neat) 3120, 3080, 3010, 2960, 2940, 2860, 1610, 1600, 1520, 1500, 1450, 1425, 1410, 1380, 1350, 1325, 1280, 1120, 1060, 905, 865, 790, 770, 710 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.8 (s, 6H, CH_3Se), 2.3 (s, 3H, CH_3—C), 7.8 (d, 2H, arom), 8.2 (d, 2H, arom).

4a'. Purified according to methods a or b+c. R_f 0.2 (pentane). Undistillable oil. IR (neat) 3060, 3040, 2950, 2900, 2840, 1940, 1870, 1790, 1720, 1570, 1470, 1430, 1370, 1320, 1300, 1115, 1060, 1020, 1000, 955, 910, 745, 690 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.75 (d, 3H, CH_3—), 4.42 (q, 1H, CH), 7–7.2 (m, 6H, arom), 7.3–7.6 (m, 4H, arom). Mass spectrum 342 (M), 185 ($M-C_6H_5Se$), 184 ($M-C_6H_5SeH$). Exact mass spectrum, calc, 341.9425; found, 341.942. (Found: C, 50.16; H, 4.42. Calc for $C_{14}H_{14}Se_2$: C, 49.43; H, 4.15%.)

4b'. Purified according to methods a or b+c. R_f 0.2 (pentane). Undistillable oil. IR (neat) 3065, 3050, 2950, 2920, 2870, 2850, 1940, 1870, 1800, 1580, 1475, 1440, 1380, 1300, 1125, 1060, 1055, 1025, 1000, 790, 690 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.9 (t, 3H, CH_3), 1.1–1.7 (m, 8H, CH_3—$(\underline{CH_2})_4$), 1.8–2.0 (m, 2H, $\underline{CH_2}$—CH), 4.26 (t, 1H, CH), 7.1–7.3 (m, 6H, arom), 7.4–7.6 (m, 4H, arom). Mass spectrum 412 (M), 255 ($M-C_6H_5Se$), 254 ($M-C_6H_5SeH$). Exact mass spectrum, calc, 412.0208; found, 412.0182. (Found: C, 53.31; H, 5.37. Calc for $C_{19}H_{24}Se_2$: C, 53.42; H, 5.27%.)

4c'. Purified according to methods a or b+c. R_f 0.2 (pentane). Undistillable oil. IR (neat) 3070, 3060, 2960, 2920, 2850, 1580, 1480, 1440, 1380, 1300, 1130, 1070, 1025, 1000, 740, 690 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.85 (t, 3H, $\underline{CH_3}$—CH_2), 1–2 (m, 18H, CH_2), 4.3 (t, 1H, CH), 7.05–7.2 (m, 6H, arom), 7.3–7.5 (m, 4H, arom). Mass spectrum 311 ($M-SeC_6H_5$). Exact mass spectrum (no parent but $M-SeC_6H_5$), calc, 311.1277; found, 311.1268. (Found: C, 59.55; H, 6.81. Calc for $C_{23}H_{32}Se_2$: C, 59.22; H, 6.92%.)

4d'. Purified according to methods a or b+c. R_f 0.19 (pentane). Undistillable oil. IR (neat) 3060, 3040, 2980, 2930, 1580, 1480, 1440, 1395, 1365, 1305, 1270, 1230, 1150, 1100, 1065, 1025, 1000, 900, 765, 750, 740 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.1 (s, 9H, CH_3), 4.1 (s, 1H, CH), 7–7.4 (m, 10H, arom). Mass spectrum 384 (M), 227 ($M-SeC_6H_5$). Exact mass spectrum, calc, 383.9895; found, 383.9886. (Found: C, 53.58; H, 5.25. Calc for $C_{17}H_{20}Se_2$: C, 53.42, H, 5.27%.)

4e'. Purified according to methods a or (b+c) or e. R_f 0.15 (pentane). M.p. 42°. IR (KBr) 3050, 3040, 3000, 2950, 2940, 2900, 2840, 1940, 1870, 1800, 1750, 1650, 1570, 1470, 1430, 1375, 1360, 1310, 1140, 1090, 1060, 1020, 1000, 910, 840, 740, 690 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.68 (s, 6H, CH_3), 7.2–7.4 (m, 6H, arom), 7.6–7.8 (m, 4H, arom). Mass spectrum 356 (M), 199 ($M-SeC_6H_5$). (Found: C, 50.66; H, 4.72. Calc for $C_{15}H_{16}Se_2$: C, 50.86; H, 4.55%.)

4f'. Purified according to method(s) a or b+c. R_f 0.15 (pentane). Undistillable oil. IR (neat) 3070, 3050, 2950, 2920, 2850, 1580, 1475, 1465, 1455, 1440, 1370, 1300, 1180, 1140, 1120, 1065, 1050, 1020, 1000, 785, 740, 695 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.88 (t, 3H, $\underline{CH_3}$—CH_2), 1.1–1.4 (m, 8H, CH_3—$(\underline{CH_2})_4$), 1.5–1.8 [m, 5H, $\underline{CH_2}$—$C(SeC_6H_5)_2$ and CH_3—C (s at 1.56)], 7.2–7.4 (m, 6H, arom), 7.6–7.8 (m, 4H, arom). Mass spectrum 269 ($M-SeC_6H_5$). (Found: C, 56.29; H, 6.45. Calc for $C_{20}H_{26}Se_2$: C, 56.61; H, 6.18%.)

4g'. Purified according to methods a or b+c. R_f 0.13 (pentane). Undistillable oil. IR (neat) 3080, 3060, 2930, 2860, 1580, 1480, 1460, 1440, 1375, 1305, 1030, 1005, 745, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.9 (t, 3H, $\underline{CH_3}$—CH_2), 1–1.8 [m, 19H, CH_2 and CH_3—C—Se (s at 1.6)], 7.2–7.4 (m, 6H, arom), 7.6–7.7 (m, 4H, arom). Mass spectrum 311 ($M-SeC_6H_5$). Exact mass spectrum (no parent but $M-SeC_6H_5$), calc, 311.1278; found, 311.127. (Found: C, 59.52; H, 6.86. Calc for $C_{23}H_{32}Se_2$: C, 59.23; H, 6.92%.)

4h'. Purified according to method a. R_f 0.15 (pentane). IR (CCl_4) 3070, 3050, 2970, 2900, 2870, 1970, 1950, 1900, 1880, 1820, 1800, 1750, 1660, 1480, 1470, 1460, 1440, 1390, 1370, 1360, 1330, 1300, 1220, 1180, 1160, 1095, 1080, 1060, 1050, 1020, 1000, 920 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.2 (s, 9H $(CH_3)_3C$), 1.4 (s, 3H, tC_4H_9—C—$\underline{CH_3}$), 6.9–7.7 (2m, 10H, arom). Mass spectrum 240 ($M-SeC_6H_5$). Exact mass spectrum (no parent but $M-SeC_6H_5$), calc, 240.0417; found, 240.041. (Found: C, 54.93; H, 6.12. Calc for $C_{18}H_{22}Se_2$: C, 54.55; H, 5.59%.)

4i'. Purified according to methods a or b+c. R_f 0.19 (pentane). Undistillable oil. IR (neat) 3080, 3060, 2960, 2930, 2860, 1580, 1480, 1470, 1440, 1380, 1310, 1030, 745, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.9 (t, 6H, CH_3), 1–1.8 (m, 20H, CH_2), 7.2–7.4 (m, 6H, arom), 7.6–7.8 (m, 4H, arom). Mass spectrum 338 ($M-C_6H_5SeH$). Exact mass spectrum (no parent but $M-C_6H_5SeH$), calc, 338.1512; found, 338.1548. (Found: C, 60.40; H, 7.55. Calc for $C_{25}H_{36}Se_2$: C, 60.73; H, 7.34%.)

4k'. Purified according to methods a or b+c. R_f 0.3 (pentane). M.p. 60°. IR (neat) 3060, 3040, 3000, 2930, 2860, 1580, 1480, 1440, 1380, 1305, 1240, 1180, 1070, 1030, 1000, 745, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.95 (q, 2H, CH_2—$\underline{CH_2}$—CH_2—), 2.40 (t, 4H, $\underline{CH_2}$—CH_2—$\underline{CH_2}$), 7.1–7.3 (m, 6H, arom), 7.5–7.7 (m, 4H, arom). Mass spectrum 368 (M), 211 ($M-SeC_6H_5$). Exact mass spectrum, calc, 367.9582; found, 367.9582. (Found: C, 52.25; H, 4.40. Calc for $C_{16}H_{16}Se_2$: C, 52.48; H, 4.40%.)

4l'. Purified according to methods a or (b+c) or e. R_f 0.2 (pentane). M.p. 75°. IR (CCl_4) 3080, 3060, 3020, 2960, 2870, 1965, 1950, 1895, 1875, 1825, 1805, 1580, 1480, 1450, 1440, 1305, 1175, 1070, 1025, 950, 915, 695 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.5–2 (m, 8H, CH_2), 7.1–7.3 (m, 6H, arom), 7.5–7.7 (m, 4H, arom). Mass spectrum 382 (M), 225 ($M-SeC_6H_5$).

(Found: C, 53.83; H, 4.81. Calc for $C_{17}H_{18}Se_2$: C, 53.70; H, 4.77%.)

4m'. Purified according to methods a or (b+c) or e. R_f 0.2 (pentane). M.p. 75–76°. IR (KBr) 3080, 3060, 2930, 2860, 1950, 1880, 1805, 1715, 1660, 1580, 1480, 1450, 1440, 1340, 1305, 1270, 1255, 1195, 1125, 1070, 1030, 1005, 930, 865, 820, 745, 695 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1–2 (m, 10H, CH_2), 7.1–7.4 (m, 6H, arom), 7.5–7.8 (m, 4H, arom). Mass spectrum 396 (M). Exact mass spectrum, calc, 395.9895; found, 395.9900. (Found: C, 55.10; H, 5.02. Calc for $C_{18}H_{20}Se_2$: C, 54.83; H, 5.11%.)

4n'. Purified according to methods a or (b+c). R_f 0.2 (pentane). M.p. 75–76°. IR (CCl_4) 3050, 2910, 2845, 1960, 1945, 1890, 1870, 1820, 1800, 1750, 1650, 1470, 1450, 1445, 1435, 1375, 1350, 1330, 1315, 1300, 1175, 1125, 1060, 1050 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.9–2 (m, 12H, CH_3, CH_2 and CH), 7–7.9 (m, 10H, arom). Mass spectrum 410 (M), 253 (M – SeC_6H_5). (Found: C, 55.28; H, 5.59. Calc for $C_{19}H_{22}Se_2$: C, 55.89; H, 5.43%.)

4o'. Purified according to methods a or (b+c) or e. R_f 0.2 (pentane). M.p. 82–83°. IR (KBr) 3070, 2950, 2860, 1575, 1470, 1440, 1400, 1370, 1315, 1310, 1255, 1240, 1190, 1100, 1070, 1030, 1005, 920, 830, 780, 750, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 0.8 (s, 9H, CH_3), 1.1–2.1 (m, 9H, CH_2 and CH), 7.2–7.4 (m, 6H, arom), 7.5–7.85 (m, 4H, arom). Mass spectrum 452 (M), 294 (M – C_6H_5Se). Exact mass spectrum, calc, 452.0521; found, 452.0517. (Found: C, 58.51; H, 6.27. Calc for $C_{22}H_{28}Se_2$: C, 58.67; H, 6.27%.)

4p'. Purified according to method a. M.p. 152–153°. ^{1}H-NMR δ 1.45–2.25 (m, 10H, CH_2), 2.6–3 (m, 4H, CH), 7.1–7.5 (m, 6H, arom). These data are in full agreement with the literature.[58,59]

4q'. Purified according to procedure f. R_f 0.35 (ether/pentane: 3/97). Undistillable oil. IR (neat) 3060, 3030, 1580, 1500, 1480, 1470, 1455, 1445, 1070, 1030, 1005, 780, 745, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 5.35 (s, 1H, CH), 6.9–7.5 (m, 15H, arom). Mass spectrum 404 (M), 247 (M – C_6H_5Se). Exact mass spectrum, calc for (M – C_6H_5Se), 247.0026; found, 247.0026. (Found: C, 56.83; H, 4.09. Calc for $C_{19}H_{16}Se_2$: C, 56.73; H, 4.01%.)

4t'. Purified according to procedure f. R_f 0.6 (ether/pentane: 4/96). IR (neat) 3040, 3000, 2920, 2840, 1940, 1910, 1870, 1790, 1570, 1555, 1465, 1455, 1435, 1320, 1295, 1270, 1170, 1155, 1060, 1050, 1030, 1020, 730 cm^{-1}. ^{1}H-NMR (CCl_4) δ 6 (s, 1H, CH), 6.8–7.6 (m, 14H, arom). Mass spectrum 438 (M), 281 (M – SeC_6H_5). (Found: C, 52.17; H, 3.46. Calc for $C_{19}H_{15}Se_2Cl$: C, 52.26; H, 3.46%.)

4u'. Purified according to procedure f. R_f 0.1 (pentane). M.p. 85–86°. IR (CCl_4) 3040, 3010, 2940, 2910, 2860, 1960, 1940, 1885, 1870, 1815, 1795, 1745, 1470, 1435, 1370, 1300, 1040, 1020, 990 cm^{-1}. ^{1}H-NMR (CCl_4) δ 2 (s, 3H, CH_3), 6.9–7.8 (m, 15H, arom). Mass spectrum 261 (M – SeC_6H_5). (Found: C, 57.67; H, 4.58. Calc for $C_{20}H_{18}Se_2$: C, 57.71; H, 4.36%.)

4v'. Purified according to procedure f. R_f 0.15 (pentane). M.p. 85–86°. IR (CCl_4) 3040, 3010, 2950, 2900, 2840, 1580, 1500, 1470, 1430, 1400, 1365, 1060, 1045, 1015, 995, 815, 730, 690 cm^{-1}. ^{1}H-NMR (CCl_4) δ 2 (s, 3H, $\underline{CH_3}C(SeC_6H_5)_2$), 2.35 (s, 3H, $\underline{CH_3}$—C_6H_4), 6.9–7.55 (m, 14H, arom). Mass spectrum 275 (M – SeC_6H_5). Unstable product.

7a. Purified according to method a. R_f 0.5 (ether/pentane: 1/1). Oil. IR (neat) 3500–2300, 2930, 1710, 1470, 1430, 1415, 1290, 1275, 1240, 1220, 1120, 950, 905 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.1–2 [m, 20H, $(\underline{CH_2})_7$—CH and CH_3Se (s at 2.0)], 2.3 (t, 2H, $\underline{CH_2}$—COOH), 3.9 (t, 1H, CH), 11 (m, 1H, COOH). Mass spectrum 264 (M – CH_3SeH). Exact mass spectrum (no parent but M – CH_3SeH), calc, 264.0628; found, 264.0627. **7a** was transformed to **7b** by treatment with diazomethane.

7b. Purified according to method a. R_f 0.35 (ether/pentane: 5/95). Oil. IR (neat) 3000, 2930, 2860, 1740, 1460, 1440, 1360, 1250, 1200, 1185, 1120, 1020, 905, 730 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.1–2 [m, 20H, $(\underline{CH_2})_7$—CH and CH_3Se (s at 1.95)], 2.2 (t, 2H, $\underline{CH_2}$—$COOCH_3$), 3.6 (s, 3H, CH_3O), 3.85 (t, 1H, CH). Mass spectrum 374 (M), 279 (M – CH_3Se), 247 (M – CH_3Se – CH_3OH). Exact mass spectrum, calc, 374.0262; found, 374.0264. (Found: C, 41.80; H, 7.13. Calc for $C_{13}H_{26}O_2Se_2$: C, 41.94; H, 7.04%.)

7a'. Purified according to method a. R_f 0.4 (ether/pentane: 1/1). Oil. IR (neat) 3600–2500 (3080, 3060, 2940, 2860), 1710, 1580, 1480, 1470, 1440, 1410, 1300, 1030, 1005, 745, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.2–2.2 (m, 14H, $(\underline{CH_2})_7$—CH), 2.32 (t, 2H, $\underline{CH_2}$—COOH), 4.52 (t, 1H, CH), 7.28–7.5 (m, 6H, arom), 7.55–7.8 (m, 4H, arom), 10.1 (m, 1H, COOH). **7a'** was reacted with diazomethane to give **7b'** which has been fully characterized.

7b'. Purified according to method a. R_f 0.29 (ether/pentane: 5/95). Oil. IR (neat) 3080, 3060, 2930, 2860, 1740, 1580, 1480, 1470, 1440, 1370, 1305, 1250, 1200, 1180, 1115, 1040, 1030, 1005, 750, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1–2 (m, 14H, $(\underline{CH_2})_7$—CH), 2.2 (t, 2H, $\underline{CH_2}$—$COOCH_3$), 3.60 (s, 3H, CH_3O), 4.4 (t, 1H, CH), 7.2–7.6 (m, 6H, arom). Mass spectrum 498 (M), 341 (M – C_6H_5Se), 309 (M – C_6H_5Se—CH_3OH). Exact mass spectrum, calc, 498.0575; found, 498.0575. (Found: C, 55.38; H, 6.29. Calc for $C_{23}H_{30}O_2Se_2$: C, 55.65; H, 6.09%.)

9. Purified according to method a. R_f 0.43 (ether/pentane: 1/1). Oil. IR (neat) 3250, 2920, 2860, 1470, 1425, 1275, 1125, 1060, 900 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.1–2 [m, 25H, $(\underline{CH_2})_9$—CH, OH and CH_3Se (s at 1.95)], 3.5 (t, 3H, $\underline{CH_2}$—OH), 3.9 (t, 1H, CH). Mass spectrum 360 (M), 265 (M – CH_3Se), 246 (M – CH_3SeH – H_2O). Exact mass spectrum calc for (M – CH_3Se), 265.1070; found, 265.1060. (Found: C, 43.76; H, 7.92. Calc for $C_{13}H_{28}Se_2O$: C, 43.58; H, 7.88%.)

11a. Purified according to method a. R_f 0.17 (pentane). Oil. IR (neat) 3080, 3000, 2980, 2930, 2860, 1640, 1470, 1420, 1275, 1130, 995, 910 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.1–1.65 (m, 12H, $(\underline{CH_2})_6$—CH_2—OH), 1.65–2.1 [m, 10H, CH_2—C≡C, $\underline{CH_2}$—CH and CH_3Se (s at 1.9)], 3.9 (t, 1H, $\underline{CH}$—Se), 5.0 (m, 2H, CH_2=), 5.7 (m, 1H, CH_2=$\underline{CH}$—). Mass spectrum 342 (M), 247 (M – CH_3Se). Exact mass spectrum, calc, 342.0364; found, 342.0360. (Found: C, 45.52; H, 7.94. Calc for $C_{13}H_{26}Se_2$: C, 45.89; H, 7.70%.)

11a'. Purified according to method a. R_f 0.18 (pentane). Oil. IR (neat) 3080, 3060, 2930, 2860, 1645, 1580, 1480, 1470, 1440, 1070, 1030, 1005, 915, 795, 745, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.1–2.2 (m, 16H, CH_2), 4.35 (t, 1H, CH—Se), 4.9 (m, 2H, CH_2=C), 5.7 (m, 1H, CH_2=$\underline{CH}$—), 7.2–7.5 (m, 10H, arom). Mass spectrum 466 (M), 309 (M – C_6H_5Se), 308 (M – C_6H_5SeH). Exact mass spectrum, calc, 466.0677; found, 466.0684. (Found: C, 58.93; H, 6.70. Calc for $C_{23}H_{30}Se_2$: C, 59.48; H, 6.51%.)

13a. Purified according to method c. Oil. ^{1}H-NMR (CCl_4) δ 2 (s, 6H, CH_3Se), 2.28 (q, 2H, $\underline{CH_2}$—CH), 3.65 (t, 2H, CH_2Cl), 4.04 (t, 1H, CH). Mass spectrum 266 (M), 171 (M – $SeCH_3$), 135 (M – $SeCH_3$ – HCl). Exact mass spectrum, calc, 265.887; found, 265.887. **13a** was transformed by reaction with LDA to 1,1-(bismethylseleno)cyclopropane which has been fully characterized.

13a'. Obtained as a crude product which was reacted with LDA to give 1,1-(bisphenylseleno)cyclopropane (this last compound has been fully characterized). ^{1}H-NMR (CCl_4) δ 2.18 (q, 2H, $\underline{CH_2}$—CH), 3.60 (t, 2H, CH_2Cl), 4.48 (t, 1H, CH), 7.1 (m, 6H, arom), 7.44 (m, 4H, arom). Mass spectrum 390 (M), 233 (M – SeC_6H_5), 197 (M – SeC_6H_5 – HCl). Exact mass spectrum, calc, 389.919; found, 389.919.

13b. Purified according to method a. R_f 0.51 (ether/pentane: 3.97). Oil. IR (neat) 3070, 3000, 2930, 1580, 1480, 1440, 1420, 1330, 1270, 1230, 1070, 1030, 800, 740, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.85 (s, 6H, CH_3Se), 2.1 (m, 2H, $\underline{CH_2}$—$CH(SeCH_3)_2$), 3 (t, 2H, $\underline{CH_2}$—SeC_6H_5), 3.9 (t, 1H, CH), 7.2–7.6 (m, 5H, arom). Mass spectrum 388 (M), 292 (M – CH_3SeH). Exact mass spectrum, calc, 387.874; found, 387.874. (Found: C, 34.38; H, 4.14. Calc for $C_{11}H_{16}Se_3$: C, 34.31; H, 4.19%.)

13b'. Purified according to method a. R_f 0.45 (ether/pentane: 3/97). Oil. IR (neat) 3080, 3060, 2940, 1580, 1480, 1440, 1330, 1310, 1230, 1070, 1030, 1010, 745, 700 cm^{-1}. ^{1}H-NMR (CCl_4) δ 2.16 (m, 2H, $\underline{CH_2}$—CH), 3 (t, 2H, $\underline{CH_2}$Se—C_6H_5), 4.48 (t, 1H, $\underline{CH}(SeC_6H_5)_2$), 7–7.6 (m, 15H, arom). (Found: C, 49.82; H, 4.61. Calc for $C_{21}H_{20}Se_3$: C, 49.53; H, 3.96%.)

15. Purified according to methods a or c. R_f 0.55

(ether/pentane: 5/95). M.p. 43–44°. IR (neat) 3000, 2980, 2940, 2920, 2860, 2820, 1445, 1425, 1380, 1270, 1220, 1150, 1060, 1040, 900, 780 cm^{-1}. ^1H-NMR (CCl_4) δ 1.76 (s, 6H, CH_3—C), 1.9–2.2 [m, 16H, CH_2 and CH_3Se (s at 1.95)]. Mass spectrum 462 (M), 367 (M − CH_3Se), 271 (M − $C_2H_7Se_2$), 175 (M − $C_3H_{10}Se_3$). Exact mass spectrum, calc, 461.8332; found, 461.8385. (Found: C, 24.93; H, 4.74. Calc for $C_{10}H_{22}Se_4$: C, 26.22; H, 4.84%.)

18a. Purified according to method c. Liquid. IR (neat) 2950, 2920, 2860, 2850, 1460, 1450, 1440, 1375, 1260, 1200, 1135, 1120, 900, 785, 760 cm^{-1}. ^1H-NMR (CCl_4) δ 0.9 (t, 6H, $\underline{CH_3}$—CH_2), 1.21–1.9 (m, 11H, CH_3— $(\underline{CH_2})_2$— and $\underline{CH_3}$—CH), 2.57 (t, 4H, CH_2—Se), 3.96 (q, 1H, CH). Mass spectrum 302 (M), 165 (M − SeBu). Exact mass spectrum, calc, 302.0051; found, 302.0033. (Found: C, 39.97; H, 7.39. Calc for $C_{10}H_{22}Se_2$: C, 40.018; H, 7.39%.)

18b. Purified according to method c. Liquid. IR (neat) 2950, 2920, 2865, 2850, 1500, 1375, 1240, 1180, 1120, 1030, 1000, 790, 765 cm^{-1}. ^1H-NMR (CCl_4) δ 0.70–0.97 (m, 6H, $\underline{CH_3}$—CH_2), 1.14–1.71 [m, 22H, CH_2 and $\underline{CH_3}$—CH(n-C_5H_{11})], 1.79 (d, 3H, $\underline{CH_3}$—$CHSe_2$), 2.83–3.09 [m, 2H, CH_3—$\underline{CH}$(n-C_5H_{11})], 4 (q, 1H, CH_3—$\underline{CH}Se_2$). Mass spectrum 386 (M), 207 (M − SeC_7H_{15}). Exact mass spectrum, calc, 386.0990; found, 386.100.

18c. Purified according to method c. Liquid. IR (neat) 2950, 2920, 2850, 1460, 1450, 1370, 1230, 1125, 1040, 960, 785, 760 cm^{-1}. ^1H-NMR (CCl_4) δ 0.86 (t, 3H, $\underline{CH_3}$—$(CH_2)_4$), 1.12–1.6 (m, 14H, $\underline{CH_3}$—CH_2Se and CH_3—$(\underline{CH_2})_4$), 1.82 (t, 2H, $\underline{CH_2}$—CH), 2.56 (q, 4H, CH_2Se), 3.88 (t, 1H, CH). Mass spectrum 316 (M), 207 (M − EtSe). Exact mass spectrum, calc, 316.0208; found, 316.0196. (Found: C, 41.70; H, 7.75. Calc for $C_{11}H_{24}Se_2$: C, 42.052; H, 7.696%.)

18d. Purified according to method a. Liquid. IR (neat) 2950, 2920, 2865, 2850, 1460, 1455, 1375, 1280, 1260, 1200, 1125, 1090, 900 cm^{-1}. ^1H-NMR (CCl_4) δ 0.8–1.0 (m, 9H, $\underline{CH_3}$—CH_2), 1.18–2.0 (m, 18H, CH_2 except CH_2Se), 2.5–2.64 (t, 4H, CH_2Se), 3.88 (t, 1H, CH). Mass spectrum 372 (M), 235 (M − SeBu). Exact mass spectrum, calc, 372.0834; found, 372.0830. (Found: C, 48.95; H, 8.80. Calc for $C_{15}H_{32}Se_2$: C, 48.65; H, 8.71%.)

18e. Purified according to method a. Liquid. IR (neat) 2960, 2925, 2870, 2860, 1465, 1420, 1250, 1230, 1130, 890 cm^{-1}. ^1H-NMR (CCl_4) δ 0.89 (t, 3H, $\underline{CH_3}$), 1.17–1.63 (m, 8H, CH_3—$(\underline{CH_2})_4$), 1.75–2.30 (m, 4H, $\underline{CH_2}(CH_2Se)$ and $\underline{CH_2}$—CH), 2.70–3.0 (t, 4H, CH_2Se), 4.20 (t, 1H, CH). Mass spectrum 300 (M), 202 (M − C_7H_{14}). Exact mass spectrum, calc, 299.9895; found, 299.9900. (Found: C, 40.27; H, 7.02. Calc for $C_{10}H_{20}Se_2$: C, 40.28; H, 6.76%.)

18f. Purified according to method a. Liquid. IR (neat) 2960, 2930, 2870, 2860, 1710, 1460, 1415, 1380, 1290, 1260, 1210, 1130, 1110, 790 cm^{-1}. ^1H-NMR (CCl_4) δ 0.9 (t, 3H, $\underline{CH_3}$—CH_2), 1.2–1.56 (m, 8H, CH_3—$(\underline{CH_2})_4$), 1.68–2.01 (m, 4H, Se—CH_2—$(\underline{CH_2})_2$—CH_2—Se), 2.46–2.73 (m, 6H, CH_2Se and $\underline{CH_2}$—CH), 3.82–3.96 (t, 1H, CH). Mass spectrum 314 (M), 216 (M − CHC_6H_{13}). Exact mass spectrum, calc, 314.0051; found, 314.0040. (Found: C, 41.56; H, 7.36. Calc for $C_{11}H_{22}Se_2$: C, 42.32; H, 7.10%.)

18g. Purified according to method a. IR (neat) 3080, 3060, 3010, 1600, 1490, 1450, 1180, 1070, 1030, 800, 700 cm^{-1}. ^1H-NMR (CCl_4) δ 0.84 (m, 3H, $\underline{CH_3}$—CH_2), 1.05–1.40 (m, 8H, CH_3—$(\underline{CH_2})_4$), 1.65–1.87 (m, 2H, $\underline{CH_2}$—CH), 3.52–3.66 (t, 1H, CH), 3.7 (s, 4H, C_6H_5—$\underline{CH_2}$), 7.04 (s, 10H, arom). Mass spectrum 440 (M), 349 (M − $C_6H_5CH_2$), 269 (M − $C_6H_5CH_2Se$). Exact mass spectrum, calc, 440.0521; found, 440.0540.

18h. Purified according to method c. Liquid. IR (neat) 2955, 2920, 2860, 1465, 1440, 1380, 1365, 1220, 1155, 1125, 1025, 925, 880, 790, 765 cm^{-1}. ^1H-NMR (CCl_4) δ 0.8 (t, 3H, $\underline{CH_3}$—CH_2), 1.1–1.60 (m, 20H, CH_3—$(\underline{CH_2})_4$ and $(\underline{CH_3})_2$—CH), 1.87 (t, 2H, $\underline{CH_2}$—CH), 3.13 (q, 2H, CH—Se), 3.92 (t, 1H, CH_2—$\underline{CH}$). Mass spectrum 344 (M), 221 (M − C_3H_7Se). Exact mass spectrum, calc, 344.0521; found, 344.0490. (Found: C, 45.18; H, 9.00. Calc for $C_{13}H_{28}Se_2$: C, 45.618; H, 8.245%.)

18i. Purified according to method c. R_f 0.41 (pentane). Liquid. IR (neat) 2950, 2920, 2865, 2850, 1465, 1455, 1375, 1175, 1140, 1120, 1000, 785, 760 cm^{-1}. ^1H-NMR (CCl_4) δ 0.75–1.77 (m, 39H, CH_3 and CH_2 except CH_2—CH—Se_2), 1.77–1.95 (t, 2H, $\underline{CH_2}$—$CHSe_2$), 2.8–3.16 (m, 2H, CH—Se), 3.8–4 (t, 1H, $CHSe_2$). Mass spectrum 456 (M), 277 (M − $C_7H_{15}Se$). Exact mass spectrum, calc, 456.1883; found, 456.1750.

18j. Purified according to method c. Liquid. IR (neat) 2950, 2920, 2860, 2850, 1465, 1450, 1375, 1360, 1140, 1100, 785, 760 cm^{-1}. ^1H-NMR (CCl_4) δ 0.8–1.02 (m, 6H, $\underline{CH_3}$—CH_2), 1.17–1.77 [m, 22H, CH_2 and $\underline{CH_3}$—$CH(C_5H_{11})$], 1.83 (s, 6H, $(CH_3)_2CSe_2$), 2.77–3.09 (m, 2H, CH). Mass spectrum 400 (M), 301 (M − C_7H_{15}), 221 (M − $C_7H_{15}Se$). Exact mass spectrum, calc, 400.1147; found, 400.1140. (Found: C, 51.01; H, 9.10. Calc for $C_{17}H_{36}Se_2$: C, 51.25; H, 9.11%.)

26. Purified according to method a. R_f 0.19 (pentane). Oil. IR (neat) 2960, 2920, 2860, 1465, 1450, 1430, 1380, 1270, 1120, 920 cm^{-1}. ^1H-NMR (CCl_4) δ 0.9 (d, 3H, $\underline{CH_3}$—CH), 1.2–2.1 [m, 19H, $(CH_3)_2C$=(2 s at 1.56 and 1.64), CH_3Se (s at 1.9), CH_2 and $\underline{CH}$—CH_3], 3.9 (t, 1H, $\underline{CH}(SeCH_3)_2$), 5 (t, 1H, =CH). Mass spectrum 328 (M), 233 (M − $SeCH_3$). Exact mass spectrum, calc, 328.0208; found, 328.0201. (Found: C, 44.44; H, 7.54. Calc for $C_{12}H_{24}Se_2$: C, 44.18; H, 7.42%.)

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