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Review

Selenium Stabilized Carbenium Ions on Organic Synthesis

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Este artigo resume as aplicações sintéticas de íons de carbenio estabilizados por grupos organoselênio. São descritas reações de diferentes tipos de íons de carbenio estabilizados por selênio com compostos aromáticos, éteres enólicos de silício, alilsilanos/alilestananas e alcenos.

This review summarizes the synthetic application of selenium stabilized carbenium ions. Are presented reactions of different types of selenium stabilized carbenium ions with aromatic compounds, silyl enol ethers, allylsilanes/allylstannanes and alkenes.

Keywords: *selenium, carbenium ions, organic synthesis*

Introduction

Organoselenium compounds have been known for a long time as versatile reagents in organic chemistry. In the last years there has been a considerable development of selenium-based methods for organic synthesis[1]. Many of these methods are currrently been used as standard procedures to introduce new functional groups under mild conditions. From the several areas of interest in organoselenium chemistry, selenium stabilized carbocations has emerged as a useful class for interesting transformations and new methods for carbon-carbon bond formation.

Aspects related to heterosubstituted carbenium ions, like their formation, structure and stability, has been very well studied and revised by Hevesi in the last years[2], and will not be the subject of this article. In the following chapter we will detail synthetic aspects of selenium stabilized carbocations as electrophiles.

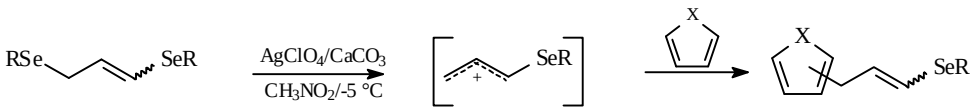
Synthetic Applications

Several new reactions were developed in the last years using the capability of an organoselenium group to stabilize an adjacent carbenium ion. These carbenium ions were generated from different selenium species and reacted with several nucleophiles, like silyl enol ethers, alkenes, allylsilanes/allylstannanes and aromatic compounds. In the following, we will be presenting these reactions in detail.

Reaction of selenium stabilized carbenium ions with aromatic compounds

The first aplication of this chemistry in order to produce a new carbon-carbon bond, was made by the use of selenoallyl cations in reaction with *N*-methyl-pyrrole (**1**) and furan (**2**)[3]. These carbocations, stabilized by both selenium and allylic resonance, were generated *in situ* from a mixture of *E* and *Z* 1,3-bis(methylseleno)-propene (**3**) and 1,3-bis(phenylseleno)-propene (**4**) mediated by silver perchlorate and sodium carbonate in nitrometane to give adducts like **5**, as depicted in Fig. 1.

The reaction proceed smothly, with relatively good yields and stereospecificity. In the case of N-methyl-pyrrole variable ratios of regioisomers were obtained. After reaction are recovered important quantities of the starting material but one the isomers when are used as *Z* and *E* mixture.There have not been detected products derived of



R=CH_3 (**3**)
R=Ph (**4**)

X=CH_3-N (**1**)
X=O (**2**)

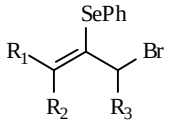
5

Figure 1.

a [4 + 3 → 7] cycloaddition. This latter reaction occurs with allyl cations substituted at position 2, especially with 2-oxyallyl systems[3].

The same type of reaction have been exploited using other sources of allylic cationic species, like β-bromovinyl selenides **6a-f** and electron-rich aromatic compounds as furan, *N*-methyl-pyrrole, thiophene and 1,3,5-trimethoxy-benzene[4].

Reagents like **6a** and **6b** have been prepared by addition



6 a: R_1= H, R_2= Cl, R_3= H; b: R_1= H, R_2= Br, R_3= H; c: R_1=R_2= R_3= H; d: R_1= H, R_2=R_3= CH_3 (*Z* + *E*); e: R_1= C_2H_5, R_2=R_3= H (*Z* + *E*); f: R_1=R_2= CH_3, R_3= H

of benzeneselenenyl chloride or bromide to propargyl bromide in dichloromethane solution at room temperature in 91% and 69%, respectively. In an analogous fashion **6c-f** have been prepared by the addition of benzeneselenenyl bromide to the corresponding allenes in quantitative yields[4].

In Fig. 2 below, are presented some of the results obtained on the reaction of selenium stabilized carbenium ions with N-methyl pyrrole, thiphene, furan and 1,3,5-trimethoxybenzene. In the case of N-methyl pyrrole or thiophene the products are obtained as a mixture of substituion at 2- and 3-position.

Although 1-selenoallyl cations **7** also undergo Friedel-Crafts reactions with electron rich heterocycles, the nature of the final product is highly dependent on the susbstitution pattern of **8** and **9** as well as on the reaction solvent. This is illustred in Fig. 3 for the case of *N*-methyl pyrrole[5].

Unsubstituted **8** and **9** (R_1=R_2=H) suffers nucleophilic attack by *N*-methyl pyrrole to give **10** (path a), whereas disubstituted **8** and **9** (R_1=R_2=alkyl, aryl) follows path b. Compound **11** cannot be isolated most likely because of the high stability of cation **12** which in turn reacts with a second molecule of *N*-methyl pyrrole to give **13** or **14**, depending on the solvent used. Paths a and b also shows some sensitivity to solvent, but the most spectacular effect is seen at the last stage of the reaction, *i.e.* attack of **12** by *N*-methyl pyrrole. 1,3-dipyrryl propenes **13** are almost exclusively formed in nitromethane, while regioisomers **14** are largely predominant when the reaction is carried out in DMF. The amounts of **15** and/or **14** can in each case be minimized by the use of an excess of *N*-methyl pyrrole.

One of the most interesting examples is the synthesis of porphyrins by this type of reagents. The high selective access to 1,1-dipyrryl propenes **14**, suggest a straightforward synthesis of phorphirins bearing substitited vinyl groups at their *meso*-positions. Indeed, with the vinylselenoacetal **16** (**a**-**g**) like source of electrophile, a series of porphyrins **17** (**a**-**g**) have been prepared under the mild

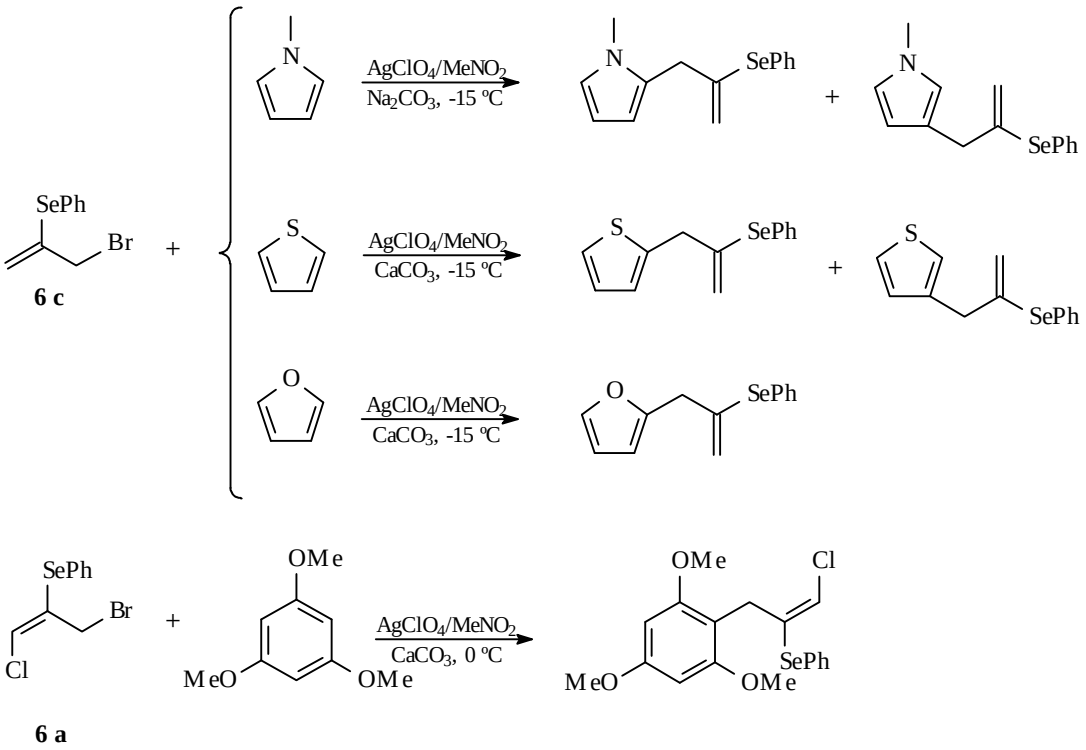


Figure 2.

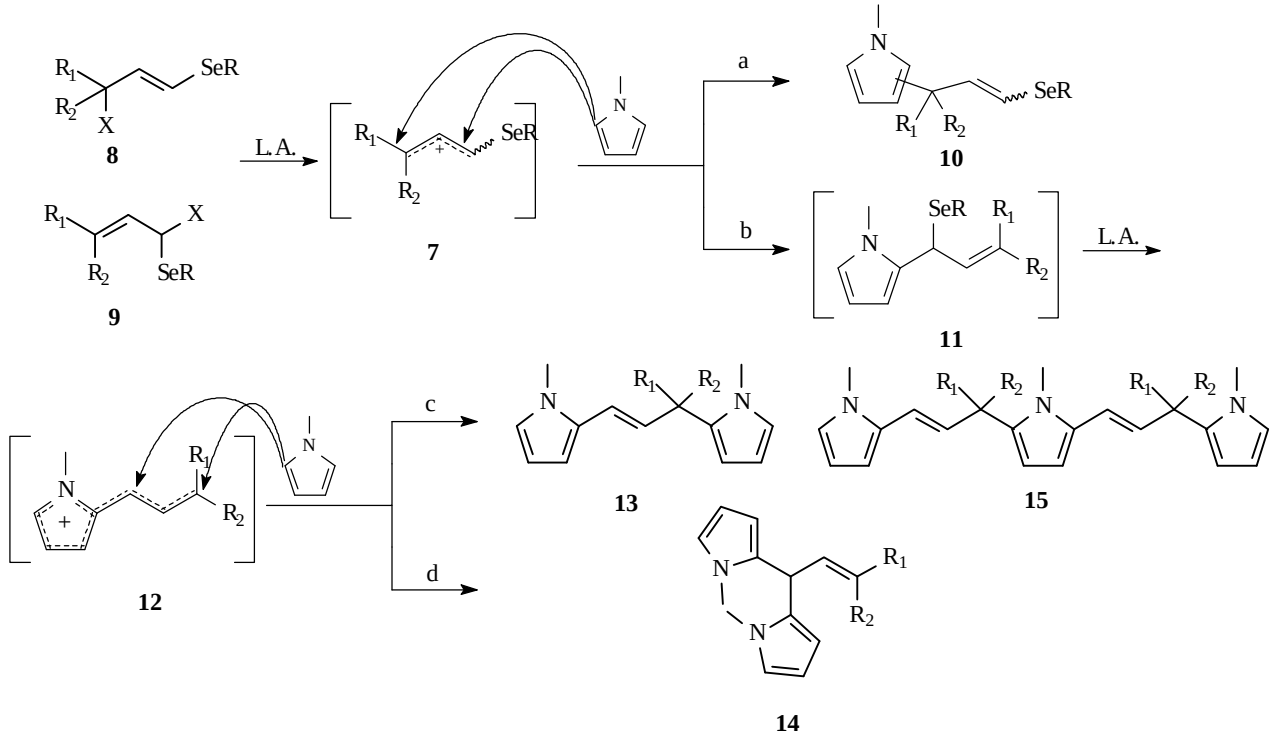


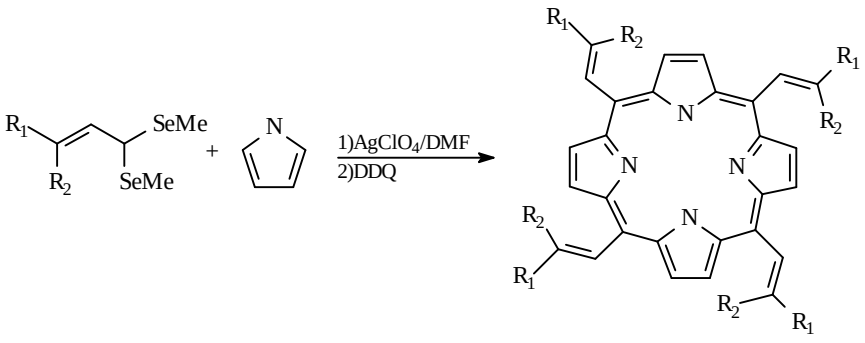
Figure 3.

conditions[6] using the one pot reaction sequence outlined in Fig. 4.

Another synthesis of an interesting class of *meso*-porphyrins have been developed in the same fashion[7]. In this case, *meso*-tetraalkynyl porphyrins have been obtained from selenoacetals **18a-b** derived from 2-butynal and 3-phenylpropynal, with pyrrole and silver perchlorate in DMF. A further treatment with DDQ furnish the porphyrin **19a** and **19b** albeit in low yield (Fig. 5).

The use of selenocarbenium ions containing an acyl moiety and generated under Friedel-Crafts conditions have proved to be an efficient route to aromatic derivatives of phenyl acetic acids[8]. The interest in this synthetic route is due to that direct introduction of a two carbon unit containing an acyl group with an α-substituent, under these conditions, into an aromatic ring is expected to be difficult, owing to the desactivation of the intermediary electrophilic complex by the electronegative acyl group. The presence of an organoselenium moiety at the α-position of the acyl group could circunvent this problem.

The synthetic procedure involves treatment of aromatic hydrocarbons with a mixture of ethyl α-bromo-α-phenylseleno acetate **20a** and ethyl α-α-bis-(phenylseleno) acetate **20b** and $TiCl_4$ at room temperature, affording the related benzylic selenides **22a-h** as shown in Fig. 6. The mixture of ethylacetate derivative **20a** and **20b** is easily avaiable from reaction of ethyldiazoacetate with phenylselenenyl bromide in THF at 0 °C (Fig. 6). We observed lately



R_1	R_2	Yied (%)
Me	Me	10
Et	Et	20
i-Pr	*i*-Pr	25
Ph	Ph	28
Me	Ph	28
o-NO_2Ph	H	4
Ph	H	0

Figure 4.

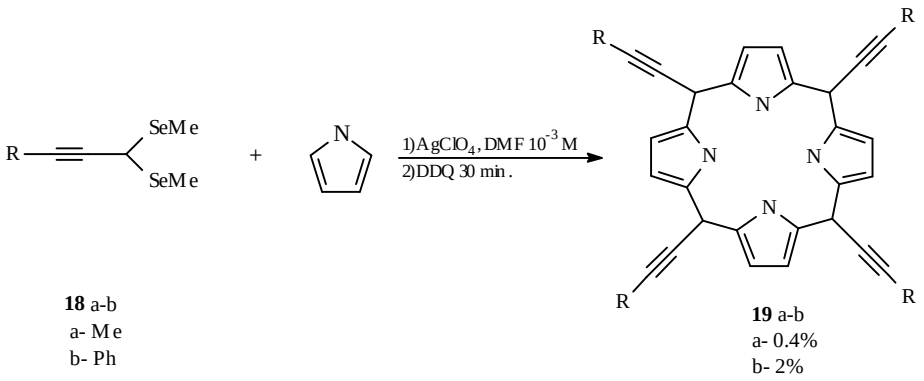


Figure 5.

that pure ethyl α-bromo-α-phenylseleno acetate can be obtained exclusively if the reaction is made by adding ethyl diazoacetate to a reflux benzene solution of PhSeBr. The chloro derivative may also be prepared by the reaction of PhSeCl and ethyldiazo acetate, as the sole product[9]. Both these reagents gives the Friedel-Crafts reaction under the same conditions described. Also, has been developed an efficient way to remove the phenylseleno group from the alkylation products. By treatment of benzylic selenide **22** with catalytic amounts of thienylditelluride in ethanol and equimolar amounts of sodium borohydride under basic conditions[10] the corresponding deselenate derivative **23** is formed, as depicted in Fig. 6. The result obtained by the Friedel-Crafts reaction are presented in Table 1.

Table 1.

21	Aromatic hydrocarbon	Yield (%) [isomer ratios]	Reaction time (min)
a	benzene	87	50
b	toluene	68 [2:1]	75
c	ethylbenzene	75 [1.5:1]	30
d	naphtalene	94	50
e	phenantrene	76	40
f	*p*-cymene	64 [1:2]	60
g	mesitylene	82	60
h	*p*-xylene	76	45

Reaction of α-phenylseleno carbenium ions with silyl enol ethers

The use of selenoacetals **24a-f** in order to produce synthetically available carbenium ions have been developed succesfully[11]. The reaction of these compounds with silyl enol ethers like **25a** mediated by a Lewis acid catalyst, gave the β-seleno carbonyl derivative **26** in good to excellent yields as depicted in Fig. 7.

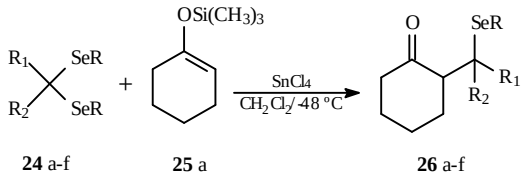


Figure 7.

In Table 2 are reproduced the yields obtained in the former reaction, using 2 eq. of cyclohexanone silyl enol ether, 1 eq. of selenium reagent and 2 eq. of Lewis acid in dichloromethane.

By inspection of values reflected in the previous table, can be observed that the presence of bulkier groups arround the cationic center decrease the yields of the reaction (entries d and e), while the presence of a phenyl group increase

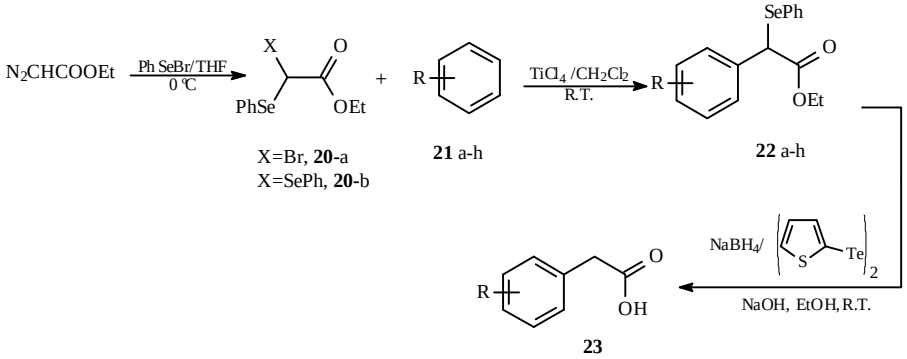


Figure 6.

Table 2.

24	R	R_1	R_2	React. time (h)	Yield (%)
a	CH_3	CH_3	CH_3	1.5	84
b	CH_3	C_6H_5	H	2	89
c	CH_3	C_6H_5	CH_3	1.5	81
d	CH_3	CH_3CH_2	CH_3	1.5	61
e	CH_3	CH_3CH_2	CH_3CH_2	1.5	49
f	C_6H_5	CH_3	CH_3	1.5	97

the yields by the effect of making the formation of cation easier.

Furthermore the seleno alkylation of **24a** with a variety of silyl enol ethers (Fig. 8), in the conditions described previously, gave raise to good yields.

In a similar methodologie, we found that α-halo-α-phenylseleno alkanes **27** reacts with silyl enol ethers in the presence of $TiCl_4$ to give the corresponding aducts **28** in high yields[12], as described in Fig. 9.

α-Halo-α-(organoseleno)-alkanes **27** are easily accesible throgh the reaction of arylselenenyl bromide with diazoalkanes[13], addition of hydrogen halides to vinylic selenides[14] and by reaction of carbonyl compounds with selenophenol in presence of hydrogen halides[14].

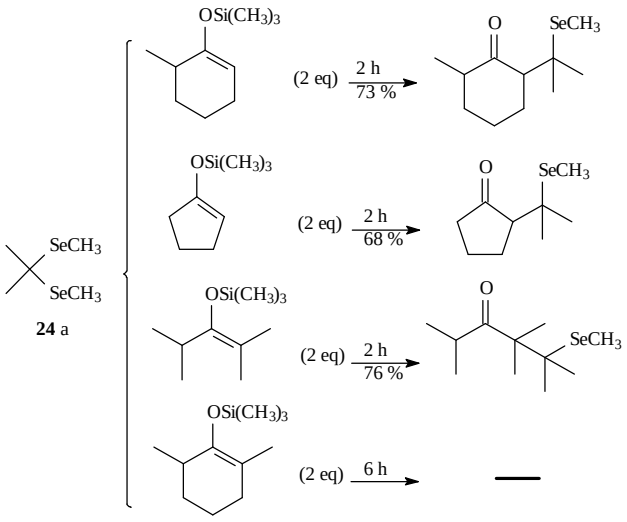


Figure 8.

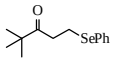
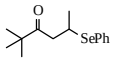
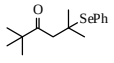
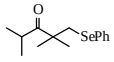
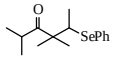
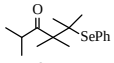
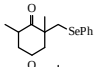
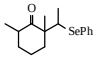
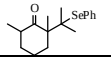
In the Table 3 are presented the results of this study, showing the generality of the method.

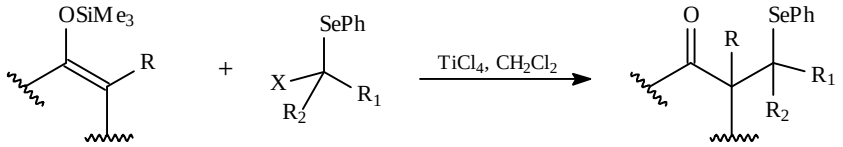
Worth of note it is that by this methodology it was posible to obtain the alkylation products of silyl enol ethers with α-bromo-α-(phenylseleno)-methane and 1-bromo-1-(phenylseleno)-ethane, products not formed by the reaction of alkylation of silyl enol ethers with selenoacetals described above[11]. This result suggests that the stability of the carbenium ion it is not the only factor affecting the reaction course. Also, we were able to alkylate the sterically crowded 1-trimethylsilyloxy-2,3-dimethylcyclohexene in good yileds using 1-bromo-1-(phenylseleno)ethane.

The easily available tris-(phenylseleno)methane reacted with trimethylsilyl enol ethers mediated by Lewis acids to give β,β-bis-(phenylseleno)-carbonyl compounds[15], as described on Fig. 10.

In this case the presence of a second selenium atom in the carbenium ion should enhance the stability of the intermediate, facilitating its formation and thus leading to the alkylated product in good yield. The Table 4 presents the results of this study, by reaction with the silyl enol ether from different carbonyl compounds.

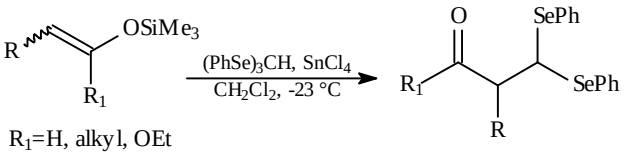
Table 3.

Product	Yield (%)	X	Reaction Temp. (°C)
	57	Br	-23
	85	Br	-23
	65	Cl	-78
	50	Br	-23
	77	Br	-23
	26	Cl	-78
	20	Br	-23
	74	Br	-23
	-	Cl	-78



25 **27** **28**

Figure 9.



29 **30**

Figure 10.

Similar results were described at the same time by Hevesi and Nsunda[16], with additional that tris-(methylseleno)-methane could also be employed as the carbenium ion source.

Soon later Hevesi and Lavoix[17] described the reaction of 1-(trimethylsilyloxy)-ciclohexene with selenium stabilized allylic carbocations, as described on the Fig. 11.

The electrophilic species could be generated from 1,3-bis-(methylseleno)-propenes and 3-hydroxy-vinylselenides. With the former, tin tetrachloride showed to be the best catalyst and zinc chloride for the last one. In both cases the reactivity, the efficient and the regiochemistry of the carbenium ions on these reactions were very dependent on the substituents on the selenium reagent. These results are better resumed on Table 5[17].

In the course of our studies on selenium-stabilized carbenium ions, we observed that α-chloro-α-phenylselenoesters[18] **33a-b** reacted with silyl enol ethers **25** mediated by Lewis acids to give α-phenylseleno-γ-keto esters **34** in fair to high yields, in very clean reactions as depicted in Fig. 12.

Table 4.

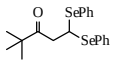
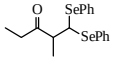
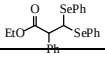
Silyl enol ether	Product	Yield (%)
		52
		78
		92
		83
		81
		83
		93

Table 5.

					Yield %	
31	R^1	R^2	X	Conditions	**32** (**32a:32b**)	**32c**
a (*E*)	H	H	SeMe	2 eq. $SnCl_4/CH_2Cl_2$/-40 °C/6 h	-	27[a]
b[b]	H	Me	SeMe	2 eq. $SnCl_4/CH_2Cl_2$/-40 °C/6 h	32 (0:100)	18
c[c]	Me	Me	SeMe	2 eq. $SnCl_4/CH_2Cl_2$/-40 °C/2 h	69 (80:20)	-
d (*E*)	H	H	OH	1.2 eq $ZnCl_2/CH_3NO_2$/R.T./0.5 h	-	15
e (*Z*)	H	Me	OH	1.2 eq $ZnCl_2/CH_3NO_2$/R.T./3 h	44 (0:100)	9
f (*Z*)	Me	Me	OH	1.2 eq $ZnCl_2/CH_3NO_2$/0 °C/1 h	80 (80:20)	-
				1.2 eq $ZnCl_2/CH_3NO_2$/-40 °C/1.5 h	69 (96:4)	-

a) 51% of **31a** (*E*+*Z*) recovered unreacted;
b) **31b** is a [1,3] sigmatropic mixture of the acetal and the related vinyl selenide;
c) **31c** is in fact the pure acetal.

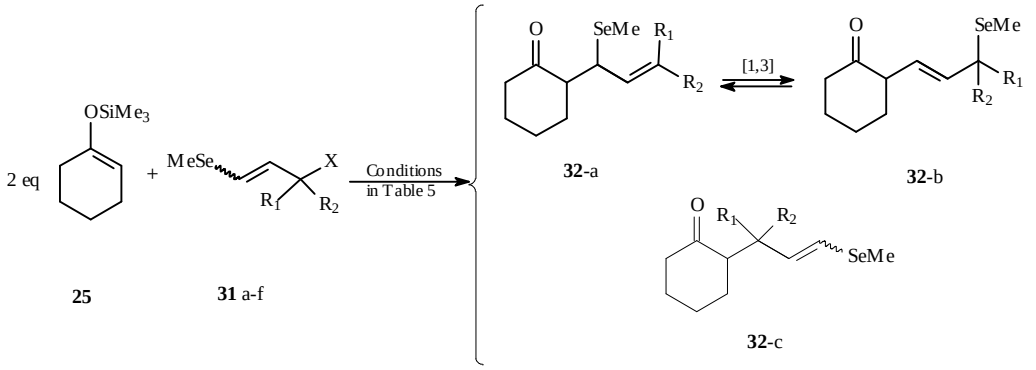
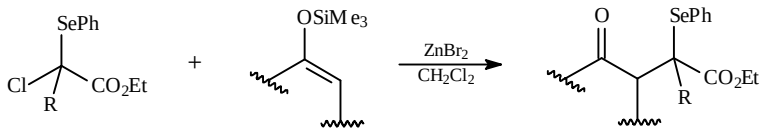


Figure 11.



33-a R=H
33-b R=CH_3

25 a-e

34 a-i

Figure 12.

Thus, the treatment of a dichloromethane solution of **33a-b** with 2.0 equivalents of **25a-e** and $ZnBr_2$ as Lewis acid, produces the desired adducts **34a-i** (Fig. 12; Table 6).

From the results described in Table 6, it can be seen that the presence of an additional methyl group in the halide **33b** causes a beneficial effect on the carbocation stabilization. The yields of the reaction of silyl enol ethers with ethyl α-chloro-α-phenylseleno propionate **33b** in most cases studied are higher than with **33a**, with reaction of silyl enol ether **25b** being one exception (product **34d**; Table 6). The reactions of **33b** were performed at 0 °C, but we observed that for the reaction with ethyl α-chloro-α-phenylseleno acetate, better results could be achieved if the reaction was performed at a somewhat higher temperature (room temperature for cyclic ketones or 42 °C for acyclic ketones) as shown in Table 6. Among the various Lewis acid tried, $ZnBr_2$ gave the best results, although $ZnCl_2$ also reacted efficiently. When $AlCl_3$, $TiCl_4$ and $SnCl_4$ were used, rapid decomposition of the silyl enol ether was observed by TLC and no products were detected.

Yoshimatsu and co-workers[19] described the reaction of *S*-ethyl-*O*-silyl-enol ethers **36** with γ-chalcogen-substituted prop-2-ynyl cations to prepare *S*-ethyl-3-ethoxy-5-(phenylchalcogeno)pent-4-ynethioates **37**. These intermediates were converted to ϖ-chalcogen-substituted alkynyl amides **38** (in moderate yields), which were in sequence cyclized to 5-(phenylselenomethylene)-pyrrol-2-ones **39**, in accordance with Fig. 13.

In the Table 7 are reproduced the yields obtained for all *S*-ethyl-3-ethoxy-5-(phenylseleno)-pent-4-ynethioates **37**.

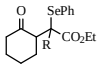
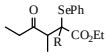
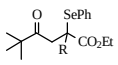
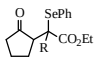
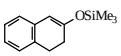
Reaction with allylsilanes and allylstannanes

The first reaction studied of an organo-selenium stabilized carbenium ion with allylsilanes was the reaction described by Hermans and Hevesi[20]. They described the reaction of allyltrimethylsilane with selenoacetals mediated by tin tetrachloride to produce the corresponding

Table 7.

R_1	R_2	Yield %
H	H	90
Me	Me	73
H	Me	65
H	Ph	73
H	*i*-Pr	72

Table 6.

	Silyl Enol Ether	Product		Reaction temp.	Yield (%)[a]
25a			34a, R=H	r.t.[b]	60
			34b, R=Me	0 °C	73
25b			34c, R=H	r.t.	66
			34c, R=H	42 °C	86
			34d, R=Me	0	80
25c			34e, R=H	r.t.	47
			34e, R=H	42 °C	56
			34f, R=Me	0C	71
25d			34g, R=H	r.t.[b]	42
			34h, R=Me	0 °C	81
25e			34i	0 °C	58

[a] Isolated yields;
[b] Lower yields were observed at 42 °C.

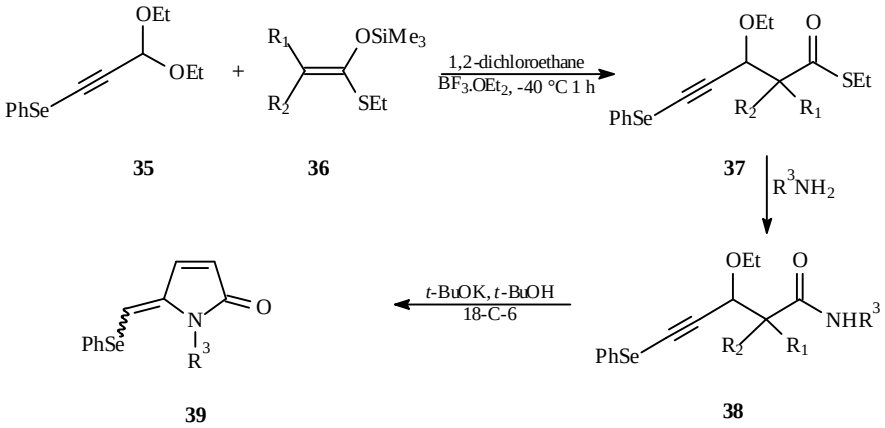


Figure 13.

homoallylselenides **40** in moderate to good yields, in accordance with Fig. 14.

By the results described on Table 7, one can observe that the yields of the products are very dependent on the substitution pattern of the selenoacetal. The ones derived from cyclohexanone or methylketones gives better yields than derived from aldehydes or internal ketones which could be accounted from electronic effects (stabilization of the intermediate carbenium ion for selenoacetals derived from aldehydes) or steric crowding around the electrophilic center (in the case of more substituted ketones). Table 8 presents the results obtained in this study.

Similar reactions of selenoacetals with allyltrimethylstannane were studied, and was observed that they occured at room temperature and in presence of zinc chloride or boron trifluoride etherate as catalyst. Compared to the above described reaction with allylsilane, the reactions with allyltributylstannane, as depicted by Fig. 15, gave yields in the same range and some selenoacetals that fails to react with allylsilanes [like 1,1-bis-(phenylseleno)-4-(*t*-butyl)-cyclohexene] do react with allyltributylstannanes. Besides, the reactions showed good stereoselectivity in some examples depending on the substituion pattern and reaction conditions, as can be seen on Table 9, where are reproduced some examples of interest[20].

Soon after was studied the coupling of mixed (*O*, *Se*) acetals with allyltrimethylsilane and allyltributylstannane mediated by a Lewis acid catalyst[21]. The methodology is illustred in Fig. 16.

In this study was expected that could be possible selectively produce homoallylethers or homoallyl selenides by carefull choice of the Lewis acid. Unfortunatelly this was not the case, since in almost all cases the homoallyl ethers were produced with different Lewis acid (for selected examples see Table 10). The main reason for this result

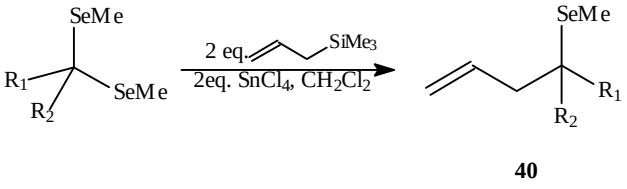


Figure 14.

Table 8.

R_1	R_2	Conditions	Yield %
C_6H_{13}	H	25 °C/ 1 h	33
p-NO_2-C_6H_4	H	-40 °C/ 2 h	30
C_6H_5	H	-40 °C/ 4 h	48
p-CH_3-C_6H_4	H	-40 °C/ 4 h	60
p-MeO-C_6H_4	H	-40 °C/ 2 h	75
C_6H_{13}	CH_3	-40 °C/ 2 h	69
C_3H_7	C_3H_7	-40 °C/ 2.5 h	35
C_3H_7	CH_3	-40 °C/ 5 h	60
C_2H_5	C_2H_5	-40 °C/ 1.5 h	28
-$(CH_2)_5$-	-	-40 °C/ 0.25 h	60
C_6H_5	CH_3	-40 °C/ 2.5 h	49

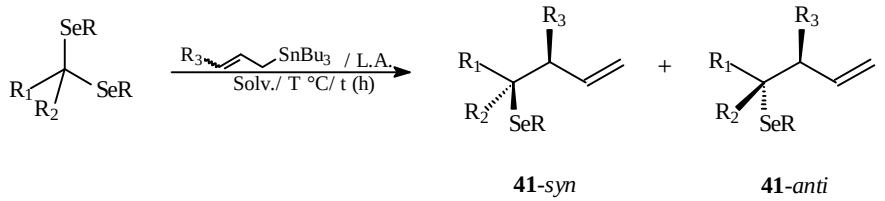
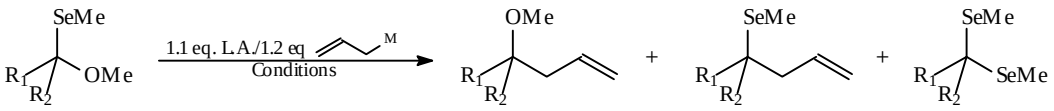


Figure 15.



42 **43** a **43** b **43** c

42 a: R_1= n-Hex. R_2= H M=$SiMe_3$, $SnBu_3$
b: R_1= n-Hex. R_2= Me
c: R_1= Ph R_2= H

Figure 16.

Table 9.

R_1	R_2	R_3	R	L.A.	Solvent	T (°C) / t (h)	*syn:anti*	Yield
Ph	H	H	Me	$BF_3.OEt_2$	CH_2Cl_2	20/16	-	49
Ph	H	Me	Me	$BF_3.OEt_2$	CH_2Cl_2	20/16	95:5	12
Ph	H	Me	Me	$BF_3.OEt_2$	CH_2Cl_2	20/72	67:33	52
Ph	H	Me	Me	$ZnCl_2$	CH_2Cl_2	20/24	60:40	44
Ph	H	Me	Me	$AlCl_3$	$C_6H_5CH_3$	-40/2	60:40	46
Ph	H	Me	Me	$AlCl_3$	CH_2Cl_2	-40/2	67:33	50
c-C_6H_{11}	H	H	Me	$AlCl_3$	$C_6H_5CH_3$	20/2	-	78
$PhCH(CH_3)$	H	H	Me	$AlCl_3$	$C_6H_5CH_3$	20/4	40:60	13
n-Pr	H	H	Me	$BF_3.OEt_2$	CH_2Cl_2	20/16	-	25
4-*t*-Bu-$(CH_2)_5$		H	Me	$BF_3.OEt_2$	CH_2Cl_2	20/3	-	30
4-*t*-Bu-$(CH_2)_5$		H	Ph	$BF_3.OEt_2$	CH_2Cl_2	20/3	-	47

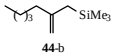
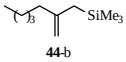
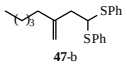
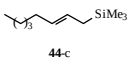
Table 10.

Acetal	M	L.A.	Conditions	**43**-a	**43**-b	**43**-c
a	$SiMe_3$	$TiCl_4$	CH_2Cl_2/-78 °C/ 2 h	54	0	36
a	$SiMe_3$	$SnCl_4$	CH_2Cl_2/-78 °C/ 2 h	55	0	18
a	2 eq. $SiMe_3$	$BF_3.OEt_2$	CH_2Cl_2/-78 °C/ 2 h	40	0	38
a	2 eq. $SiMe_3$	2 eq. BCl_3	CH_2Cl_2/-78 °C/ 2 h	0	0	20
a	$SiMe_3$	$AgClO_4$	CH_3NO_2/-40 °C / 2 h	40	0	0
a	$SiMe_3$	$AgClO_4$	CH_3NO_2/1 eq.$CaCO_3$/-40 °C / 2 h	62	0	0
b	$SiMe_3$	$TiCl_4$	CH_2Cl_2/-78 °C/ 2 h	33	0	18
b	$SiMe_3$	$SnCl_4$	CH_2Cl_2/-78 °C/ 2 h	28	0	20
c	$SiMe_3$	$TiCl_4$	CH_2Cl_2/-78 °C/ 2 h	20	23	22
c	$SiMe_3$	$SnCl_4$	CH_2Cl_2/-78 °C/ 2 h	40	0	35
c	$SiMe_3$	$AgClO_4$	CH_3NO_2/1 eq.$CaCO_3$/-40 °C / 2 h	42	0	0
a	$SnBu_3$	$TiCl_4$	CH_2Cl_2/-78 °C/ 2 h	6	0	42
a	$SnBu_3$	$SnCl_4$	CH_2Cl_2/-78 °C/ 2 h	20	0	7
c	$SnBu_3$	$TiCl_4$	CH_2Cl_2/-78 °C/ 2 h	20	10	30
c	$SnBu_3$	$SnCl_4$	CH_2Cl_2/-78 °C/ 2 h	36	0	30

relies on the much stronger C-O bond as compared to the C-Se bond, giving rise to homoallyl ethers as main products[21].

Recently we have described the reaction of allylsilanes with tris-(phenylchalcogeno)-methane (S,Se), mediated by tin tetrachloride in the case of selenium derivatives and zinc

Table 11.

Allylsilane	Product	t (h)	Yield (%)	Product[b]	t (h)	Yield[b] (%)
 **44**-a	 **46**-a	1	72[a]	 **47**-a	24	55
 **44**-b	 **44**-b	1	58[a](73)[b]	 **47**-b	4.5	73[c]
 **44**-c	 **46**-c	1	65[a](75)[b]	 **47**-c	20	59
 **44**-d	 **46**-d	1	81[a](83)[b]	 **47**-d	7	65
 **44**-e +  **44**-f	 **46**-e	1	54[a](69)[b]	 **47**-e +  **47**-f	24	35

[a] 2.5 eq of allylsilane;
[b] 4 eq of allylsilane;
[c] 10% isomerized product;
[d] 1:1 mixture of allylsilanes.

dibromide on sulphur derivatives, Fig. 17. The reaction was studied in detail with several different allylsilanes, as described on the Table 11[22].

All reactions of allylsilanes and tris-(phenylseleno)-methane were observed to be completed in one hour or less, while the phenylthio derivative **45** reacts slower (4.5 h to 24 h) than the corresponding phenylseleno derivative as indicated in Table 11. In all cases studied on the reaction of allylsilanes with tris-(phenylseleno)-methane, $SnCl_4$ was the most effective catalyst and CH_2Cl_2 was used as solvent. On the other hand, for the sulfur analogue **45**, $ZnBr_2$ was the best catalyst and the use of nitromethane as a co-solvent was more effective.

Along with homoallylselenoacetals, small amounts of the corresponding allylmonoselenides were formed, which were easily separated by column chromatography. The formation of these compounds occurs probably by reaction of the allylsilane with a phenylselanyl species formed in the reaction media. This is in accordance with previous[23] reports that allylsilanes react with C_6H_5SeCl to give allylselenides. In reactions of **44a-f** with **45** the formation of allylsulfides was not observed.

Homoallylselenides have been prepared by the reaction of selenosulphones with allyltrimethylsilane mediated by a Lewis acid[24]. The best results were obtained with $EtAlCl_2$, as can be seen on the Fig. 18. Similar results were also described for the thio analogs.

Reaction with alkenes

Recently was described the reaction of mixed Se,O-heteroacetals with alkenes in a intramolecular pathway to produce cyclohexane derivatives, promoted by $TiCl_4$ at low

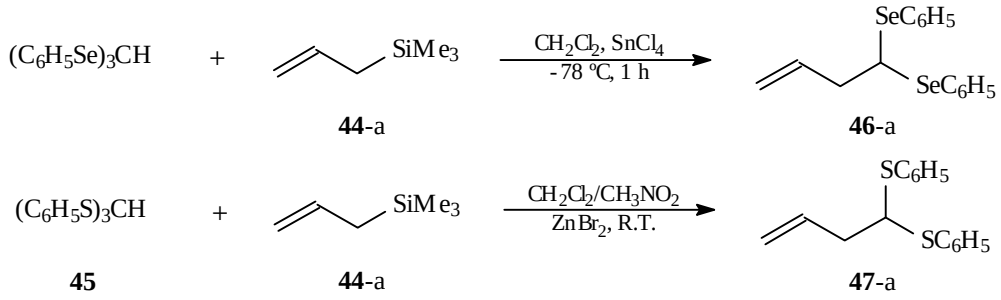
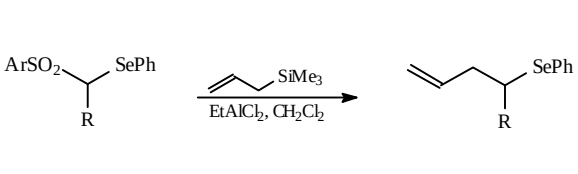


Figure 17.



R	Yield (%)
H	-
Me	51
CH_2Ph	60
$CH_2CH=CH_2$	46

Figure 18.

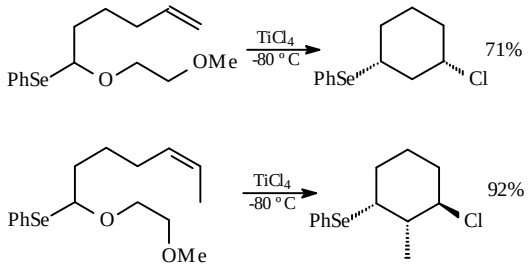


Figure 19.

temperature[25]. In Fig. 19 are presented the results of this study.

A slightly different type of olefin and acetylenic Se,O-heteroacetals gives the corresponding Se-heteroacetals in good yields, as described on Fig. 20[26].

Intramolecular version have been developed emploing cationic cyclizations in the 6-endo fashion, by way of selenonium ion generated from selenoacetals[27].

Representativelly, in Fig. 21 are described the conditions and yields for the related reactions:

E olefin **50** afforded (1R*, 2S*, 3S*)-1-bromo-2-methyl-3-phenylselenocyclohexane **51** and *Z* isomer **52** yielded (1S*, 2S*, 3S*)-1-bromo-2-methyl-3-phenylselenocyclohexane **53**. These findings indicate that the selenonium ions cause stereospecific cyclization. Reactions of phenylselenoacetals were rather slow, since its Se-C bond are more difficult to be cleaved by Lewis acids than that of methylseleno moiety.

Also, heterocycles containing selenium have been synthesized by an [4+2] cationic polar cycloadition. Phenyl α-chlorophenacyl selenide **57** reacts in the former route with trans-stilbene in presence of stannic chloride, to form

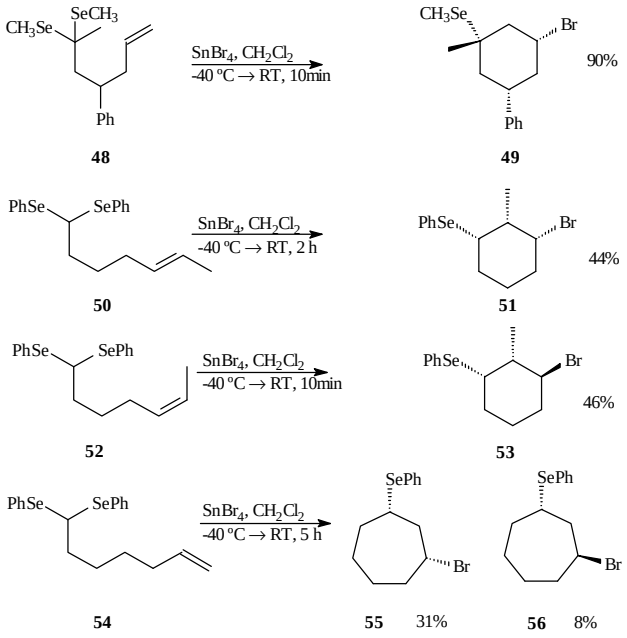


Figure 21.

a trisubstituted selenochroman **58**. The reaction probably takes place trought the following mechanism, illustred in Fig. 22[28]:

Besides these results, we have reported recently our results on the reaction of ethyl α-chloro-α-phenylselenoacetate with alkenes mediated by titanium tetrachloride as Lewis catalyst[29].

We began our study by reacting **33a** with 1-alkenes in an attempt to prepare α-phenylseleno-γ,δ-unsaturated esters **60** in an "ene type" reaction: ethyl α-chloro-α-phenyl-

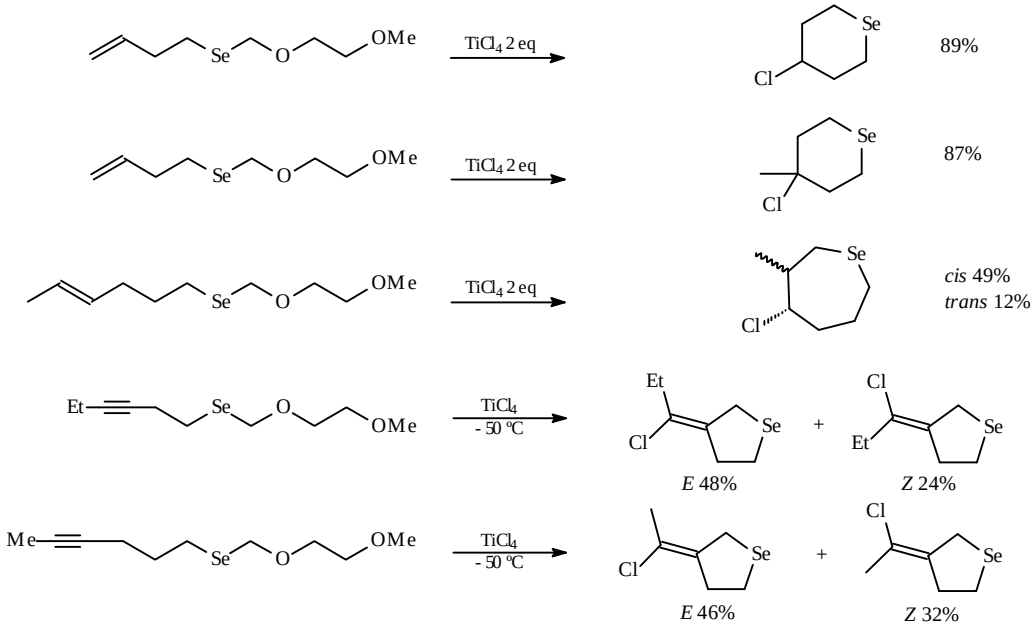


Figure 20.

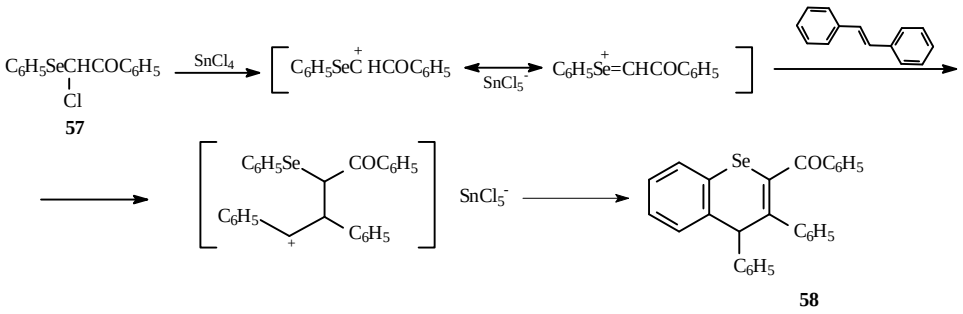


Figure 22.

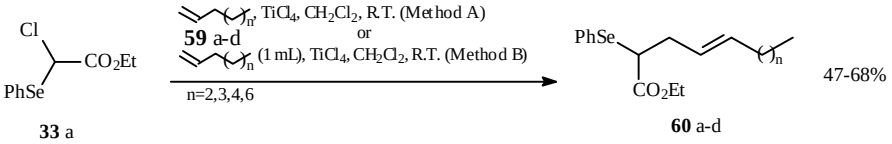


Figure 23.

seleno acetate **33a** was treated with 4 different alkenes **59a-d**, in a reaction mediated by a Lewis acid, producing γ,δ-unsaturated esters **60a-d** in good yields (Fig. 23). The α-phenylseleno-γ,δ-unsaturated esters prepared provide a new convenient way to 2,4-alkanedienoic esters via oxidative deselenation of the adduct **60**.

The reaction of **33a** with alkenes **60a-d** was promoted by several Lewis acids like $TiCl_4$, $SnCl_4$, $ZnCl_2$, $ZnBr_2$ and $AlCl_3$. Among these Lewis acids $TiCl_4$ was found to give the best yields. Dichloromethane was found to be the best solvent (Method A). The use of the 1-alkene as solvent did not improve yields significantly, but reaction times are reduced (Method B; Table 12).

Since the reaction of **33a** with 1-alkenes furnished α-phenyl seleno-γ,δ-unsaturated esters, we continued our studies to the conversion of these species to α-phenylseleno-γ-butyrolactones. The γ,δ unsaturated α-phenylseleno substituted ester **60a** derived from the reaction with 1-hexene were subjected to hydrolysis with an aqueous KOH solution and afforded the corresponding carboxylic acid **61a** in nearly quantitative yield. The acid was submitted to lactonization with some of the more commom electrophiles[29] such as iodine, phenylselenenyl chloride, or phenylsulfenyl chloride, to give the highly functionalized lactones of type **62** (Fig. 24). During the seleno and sulfur-lactonizations reactions, we observed that the use of tributylamine gives a better yield than triethylamine.

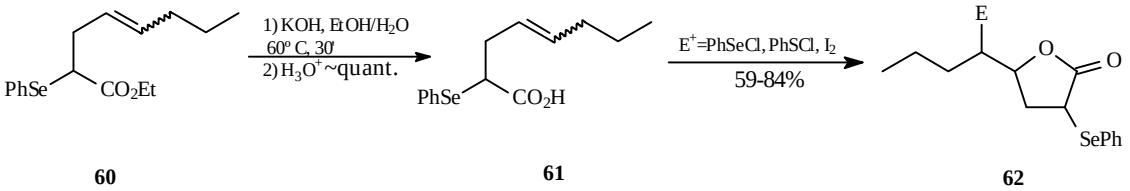
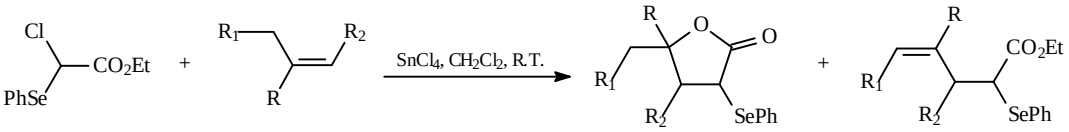


Figure 24.

Table 12.

63	R	R_1	R_2	**64** (%)	**65** (%)
a	CH_3	CH_3	H	56	34
b	CH_3	CH_3	CH_3	64	23
c	*n*-C_4H_9	CH_3CH_2	H	52	17
d	CH_3	-CH_2CH_2-		31	31
e	H	-$CH_2CH_2CH_2$-		44	43
f	CH_3	-$CH_2CH_2CH_2$-		52	32
g	CH_3	-CH_2CH_2CH(*t*-Bu)CH_2-		48	40



33 a **63** a-g **64** a-g **65** a-g

Figure 25.

In view of the formation of α-phenylseleno γ,δ-unsaturated esters when 1-alkenes were employed which need further transformations to give rise to γ-butyrolactones, we decided to explore the use of more substituted alkenes, which would produce γ-butyrolactones directly (Fig. 25, Table 12).

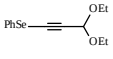
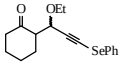
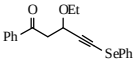
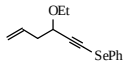
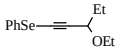
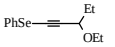
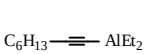
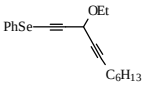
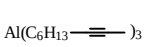
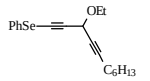
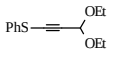
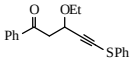
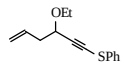
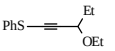
The treatment of a dichloromethane solution of di and tri-substituted alkenes **63a-g** with **33a** in the presence of $SnCl_4$ yields α-phenylseleno-γ-butyrolactones in variable yields, with the corresponding γ,δ-unsaturated ester **65** being formed as by-product. The ratio between lactone and ester was observed to be dependent of the substitution pattern of the alkene. For example, the reaction of **33a** with 1-methyl-cyclohexene gives the corresponding lactone **64f** in 52% yield and the γ,δ-unsatured ester **65f** in 32% yield; in the same way, 2-methyl-2-butene gives the lactone in 64% yield and a 23% yield of the ester. With less substituted alkenes, like cyclohexene, the corresponding lactone **64e** is formed in 44% yield plus a 43% yield of γ,δ-unsaturated ester **65e** (Fig. 26).

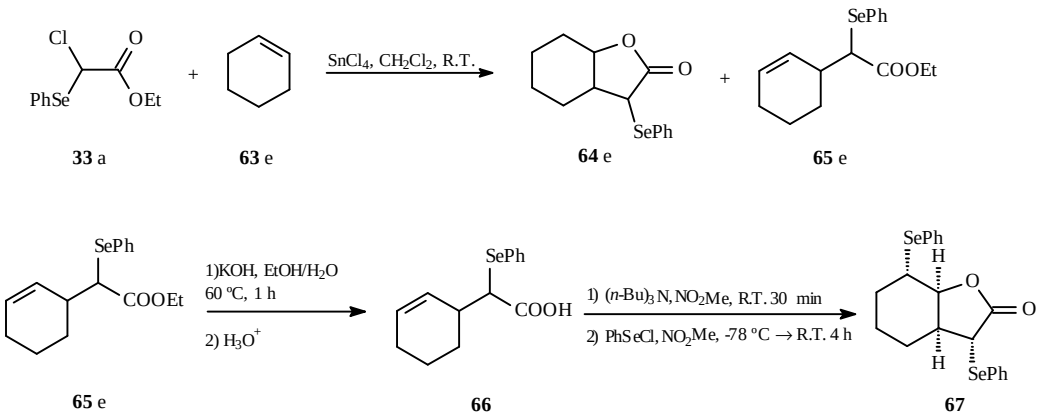
For these lactonizations several Lewis acids were tested ($SnCl_4$, $TiCl_4$, $ZnCl_2$, $ZnBr_2$, $AlCl_3$) the best yields being obtained with $SnCl_4$.

Miscellaneous

Kataoka and co-workers[30] described recently the reaction of γ-chalcogen substituted prop-2-ynyl cations, generated from γ-chalcogen-substituted propynal diethylacetals with several nucleophiles. The starting material **68** were prepared by reaction of propynal diethyl acetal with ethylmagnesium bromide followed by treatment with benzenesulfenyl or benzeneselenenyl chloride (Fig. 27). The reaction of these reagents with nucleophiles are shown in Table 13.

Table 13.

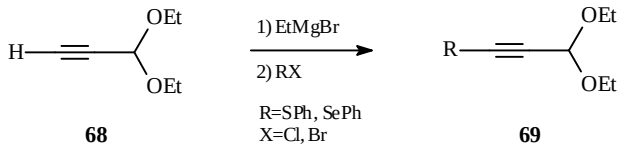
Acetal	Nucleophile	Products	Yield (%)
			42
			61
			60
	$AlEt_3$		81
	$ZnEt_2$		76
			20
			13
			75
			44
	$AlEt_3$		70



33 a **63** e **64** e **65** e

65 e **66** **67**

Figure 26.



68 **69**

Figure 27.

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