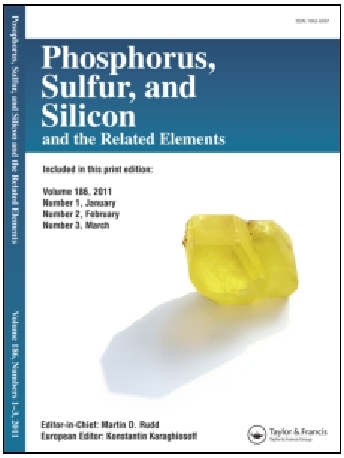

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Twenty Years of Chemistry of Selenium Stabilized Carbenium Ions

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Twenty Years of Chemistry of Selenium Stabilized Carbenium Ions

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This overview summerizes the most important aspects of our present day knowledge about the title species. The material is presented in two sections; the first one reminds salient physico-chemical results related to the stabilization of carbenium ions by selenium moieties and the second one gives examples of the synthetic usefullness of these electrophiles.

Gas phase proton affinity measurements complemented by ab initio MO calculations revealed that the intrinsic carbocation stabilizing ability of the Group 16 elements decreases from oxygen to tellurium. However, this ability is not connected in a straightforward manner to the dispersion of the cation's positive charge. The latter is the largest for the most stable species, i.e. oxocarbenium ions, and it decreases downwards in Group 16. Therefore, coulombic (i.e. electrostatic) factors must play a significant role in the overall stabilization. It follows that oxocarbenium should be considered as hard electrophiles undergoing rapid charge contolled reactions with hard nucleophiles, whereas seleno- and tellurocarbenium ions are soft electrophiles giving rise to slow reactions with the same hard nucleophiles. The ability of a series of selenocarbenium ion precursors to undergo useful inter- and intramolecular C,C bond forming reactions is illustrated.

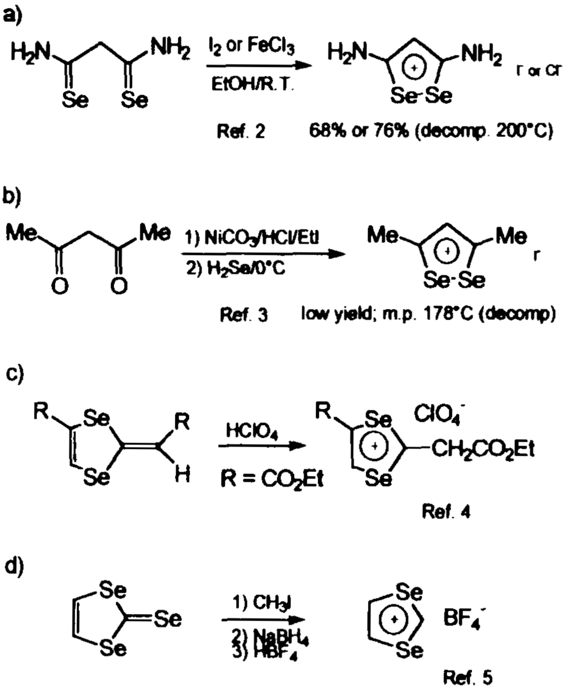
Keywords: Slenium stabilized carbenium ions; selenium; carbenium ions

1. STABILITY OF SELENOCARBENIUM IONS

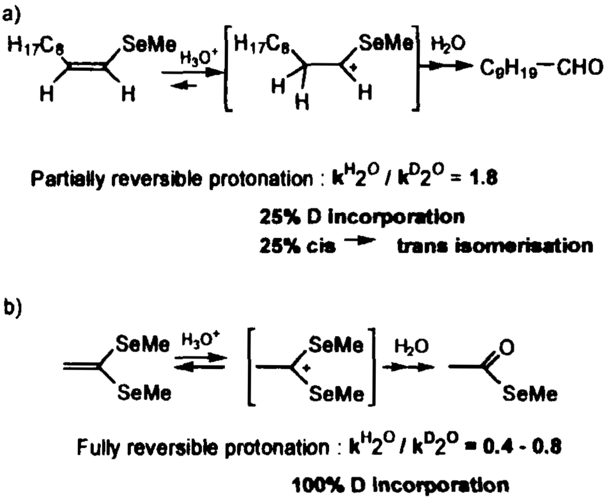
Aromatic carbocationic systems involving one or more selenium atoms have been known since more than twenty years (Scheme 1); and aliphatic selenocarbenium ions have been postulated as reasonable intermediates in various Pummerer type rearrangement reactions[1].

Initially, our work aimed at addressing the unknown question of how efficiently these aliphatic carbenium ions could be stabilized by common organoselenium moieties?

As a starting approach, we have studied the mechanisms of the acid catalyzed hydrolyses of methylvinyl selenides[6,7] and ketene (Se,Se)- acetals[8]. Scheme 2 shows the most striking results pointing to the unprecedented finding of ***reversible protonation*** of these substrates[9].



SCHEME 1



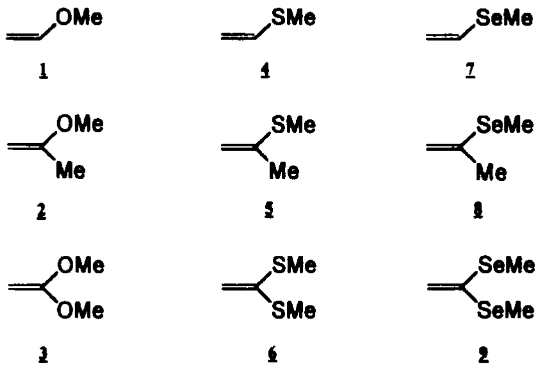
SCHEME 2

Most importantly, such reversible protonation has also been found to occur in the hydrolysis of ketene (S,S)- acetals[10].

In principle, these changes in rate determining steps might arise either from greater thermodynamic stabilities of the corresponding thio- and selenocarbenium ion intermediates, or from the slowing down of their rate of hydration. It has been demonstrated that i) the hydration of methylthio-bis(4-methoxy-phenyl) carbenium ion occurred about 5.000 times slower than that of the methoxy species[11]; ii) the hydrolysis of ketene (S,S)- acetals proceeded through rate limiting hydration of the (S,S)- stabilized cations[10]. Therefore, we have concluded that a high kinetic barrier to hydration of our selenium substituted cations was a more plausible explanation for the above mentionned reversible protonations.

Further investigation of gas phase basicities[12] supported by *ab initio* MO calculations[13] shed some light on the origin of this high kinetic barrier. Thus, proton affinity (PA) of a series of O, S, and Se substituted vinylic derivatives (Scheme 3) has been measured by ion cyclotron resonace (ICR).

The good correlation between the experimental and computed PA values shown in Figure 1 witnesses for the reliability of our relatively lower level 3-21G* calculations. The results demonstrate that i) the monoheterosubstituted derivatives **1**, **4**, **7** possess very similar proton affinities, almost indistinguishable experimentally; therefore, the gas phase stabilizations of the corresponding carbenium ions should also be comparable[14]; ii) compounds **2**, **5** and **8** are a little more differenciated so that 2-methoxy-2-propyl cation appears distinctly more stable than the corresponding methylthio- and methylseleno species; iii) the superior carbenium ion stabilizing ability of oxygen moieties is clearly visible in the series 3, 6 and 9: 1,1-bis(methoxy)ethyl cation being 5.6 kcal/mol more stable than 1,1-bis(methylthio)- ethyl- and 7.2 kcal/mol more stable than 1,1-bis(methylseleno)-ethyl cation.



SCHEME 3

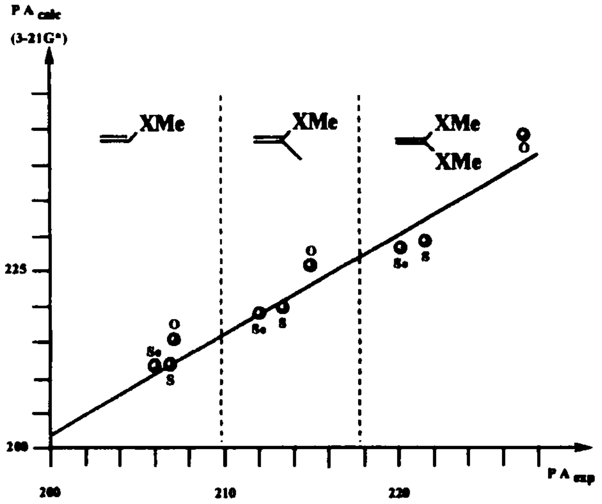


FIGURE 1. Experimental and calculated proton affinities of vinyl chalcogenides 1 – 9 (see Scheme 3).

Additional proofs of the good carbocation stabilizing ability of selenium substituents were gained from the successful synthesis, X-ray structure determination and conformational analysis of bis(methylseleno) phenylcarbenium hexachloroantimonate[15].

The *ab initio* 3-21G* calculations also gave access to the charge densities on the heavy atoms as obtained by the Mulliken population analysis[13,14]. In excellent qualitative agreement with earlier[16] and more recent[17-20] results, these calculations gave +1.05, -0.38 and -0.18 charges on the "positive" carbon atoms of the carbocations corresponding to **3**, **6**, and **9**, respectively. In view of lending experimental support to these calculated charge densities, X-ray photoelectron spectra of cystalline 1,1-bis(methoxy)ethyl carbenium tetrafluoroborate and 1,1-bis(methylthio)ethyl carbenium hexachloro antimonate salts have been measured[14]. The charge distributions for these two carbocations as obtained by the Mulliken population analysis and those extracted from the XPS spectra (using the Gelius equation[21]) can be seen in Figure 2.

These and other recent[20] results have important bearing on both the above mentionned kinetic observations and the mechanism of carbenium ion stabilization by O-, S-, Se- and Te-substituents. Indeed, all oxocarbenium ions appear to be *hard electrophiles* whose reactions with the hard nucleophile water are charge controlled processes, and thus should proceed rapidly. In contrast, thio-, seleno- (and possibly telluro-) carbenium ions get *softer and softer* on going down group 16 and on going from 1 to 2 to 3 substituents rendering their reactions with water less and less favoured. Consequently, this decrease in hardness increases the activation energy for the hydration (second step in Scheme 2) of the carbenium ion intermediates which then leads to the observed reversibilities.

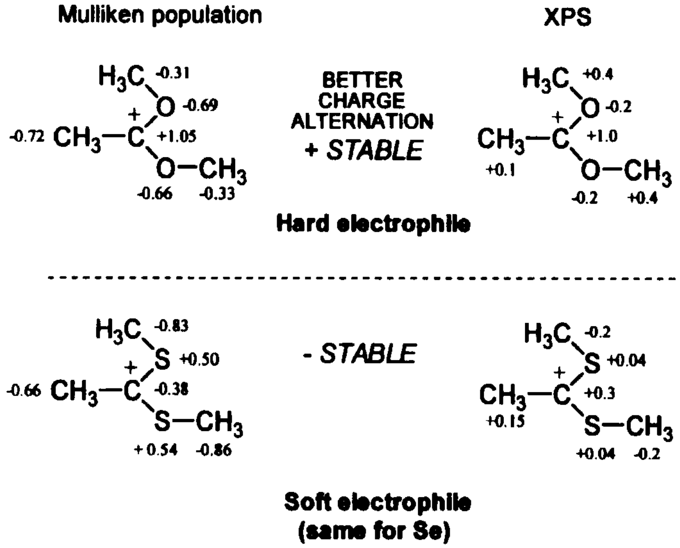


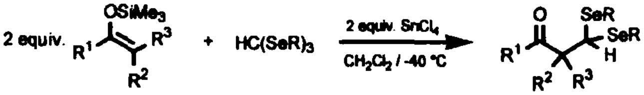
FIGURE 2. Charge densities of O- and S-stabilized carbocations.

It has been concluded some time ago[19] that "*...the correlation between the π-donating ability or the degree of charge dispersal and the stability of a carbenium ion is very limited...*" and that the Coulomb term contributes significantly to the stability[20]. Our experimental results fully support these conclusions.

2. REACTIONS OF SELENOCARBENIUM IONS

Eventhough the term "selenocarbenium ion" will be used throughout of the following description, no such species could be identified as free ions by spectroscopic methods.

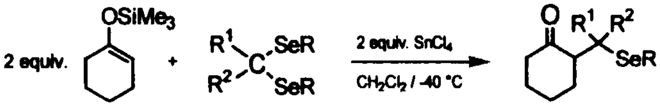
Lewis acid activated *triselenoorthoformates* react efficiently with ***silyl enol ethers*** to produce the corresponding β-oxoselenoacetals in good to excellent yields[22,23] (Scheme 5). Although higher homologues of triselenoorthoesters do not react with silyl enol ethers[24], 2,2-bis(phenylseleno)propionitrile was formed quantitatively from tris(phenylseleno)orthoacetate and trimethyl-silyl cyanide in the presence of tin tetrachloride[25].



Entry	R	R^1	R^2	R^3	Yield (%)
1	Me	-(CH$_2$)$_4$-		H	98
2	Ph	-(CH$_2$)$_4$-		H	95
3	Me	-(CH$_2$)$_4$-		H	72
4	Ph	-(CH$_2$)$_4$-		H	97
5	Me	i-Pr	Me	Me	92
6	Ph	i-Pr	Me	Me	94
7	Me	H	Me	Me	83
8	Ph	H	Me	Me	92

SCHEME 5

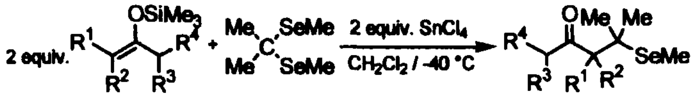
In a similar fashion, *selenoacetals* can be reacted with various carbon nucleophiles to give the corresponding seleno-alkylated products. Both methyl- and phenylselenoacetals derived from aliphatic and aromatic ketones and aldehydes give good yields[24b, 26] (Scheme 6) as long as the reaction is not exposed to severe steric hindrance (Scheme 6, entry 4).



Entry	R	R^1	R^2	Yield (%)
1	Me	Me	Me	84
2	Me	Me	Et	61
3	Me	Et	Et	49
4	Me	Me	*t*-Bu	no reaction
5	Me	Ph	H	89
6	Me	Ph	Me	81
7	Ph	Me	Me	97

SCHEME 6

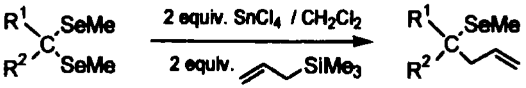
The latter restriction also holds when variously substituted silyl enol ethers are considered[24b, 26] (Scheme 7). Systematic investigation of these reactions has shown their applicability to different types of selenoacetals and silyl enol ethers with the exception of those derived from esters, lactones and β-dicarbonyl compounds[24b, 27].



Entry	R^1	R^2	R^3	R^4	Yield (%)
1	H	$-(CH_2)_3-$		H	84
2	Me	$-(CH_2)_3-$		H	81
3	H	$-(CH_2)_3-$		Me	73
4	Me	$-(CH_2)_3-$		Me	no reaction
5	Me	Me	Me	Me	76
6	Me	Me	H	H	82
7	H	Et	H	H	81

SCHEME 7

We have found that tin tetrachloride activated seleno-acetals also react with *allylsilanes* to produce homoallyl-selenides[28-30] (Scheme 8). The same products can be obtained from *allylstannanes* as carbon nucleophiles; then however, BF_3-OEt_2 or $AlCl_3$ must be used as Lewis acid in order to avoid Sn to Sn transmetallation prior to C,C bond formation[29].



Entry	R^1	R^2	Yield (%)^a
1	n-Hexyl	H	33(50)
2	n-Hexyl	Me	69
3	n-Pr	n-Pr	25(61)
4	4-*t*-Bu-*c*-Hexyl		55
5	Ph	H	48
6	*p*-MePh	H	60
7	*p*-NO_2Ph	H	30
8	Ph	Me	49
9	*p*-NO_2Ph	Me	72

^{a}) In parentheses, yields after addition of a second batch of $SnCl_4$ / allylsilane

SCHEME 8

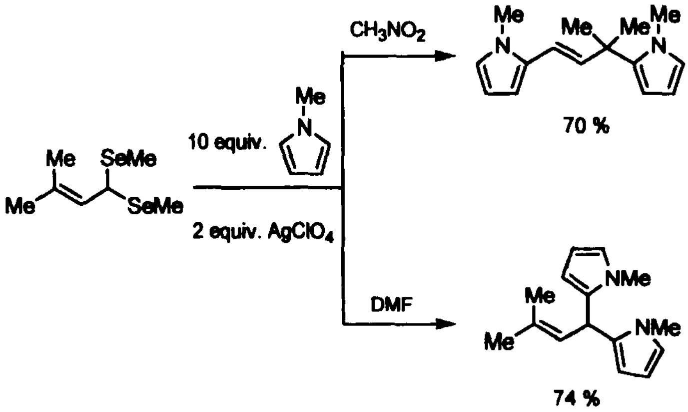
Selenoxide *syn*-elimination being a well established olefin forming reaction[31], the above transformations followed by the oxidation-elimination protocol represent valuable methods for the connective syntheses of α,β-unsaturated aldehydes and ketones, as well as of conjugated dienes.

Further interesting reactions of monoselenocarbenium ion equivalents have been reported. Thus, δ,ε- and ε,η-unsaturated selenoacetals gave cyclized products under appropriate Lewis acid activation[32]. By contrast, intermolecular reaction does not occur with olefins under similar conditions[24b]. On the other hand, on reaction with N-methylpyrrole, $AgClO_4$-activated 1-phenyl-1,1-bis(methylseleno) ethane leads to 1-phenyl-1,1-bis(N-methyl-2'-pyrrolyl)ethane in good yield[24b]. Also, common alkylbenzenes, naphthalene and phenanthrene undergo Friedel-Crafts type reactions with ethyl bis(phenylseleno) acetate in the presence of titanium tetrachloride[33].

Under Lewis acid activation, *α-halogenoselenides* have been found valuable precursors of selenocarbenium ion type species which reacted efficiently with silyl enol ethers[34], with allyl-silanes[35], or with aromatic compounds[33]. Similarly, *α-sulfonylselenides* could be reacted with allylsilane under $EtAlCl_2$ activation[36]. The behaviour of *mixed (O,Se) acetals* is more subtle; therefore, the issue and efficiency of their reactions depend on several factors[35,37,38].

1-Selenoallyl- and 2-selenoallyl cationic species have been generated from *α,β-unsaturated selenoacetals*[39-41] and from *2-phenylseleno-3-halogeno-1-propenes*[42,43], respectively. Both types of carbon electrophiles react smoothly with *electron rich heterocycles* such as furan, pyrrole and thiophene to give Friedel-Crafts products without any trace of 4+3 cycloadducts[43].

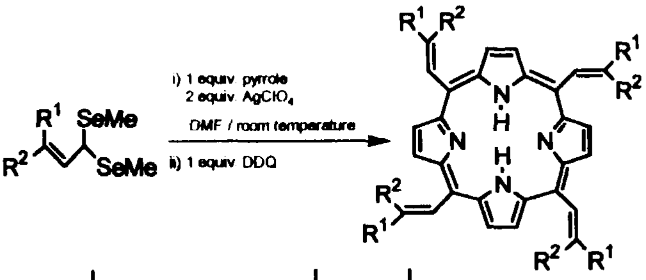
In the case of disubstituted α,β-unsaturated seleno-acetals activated by silver perchlorate both selenium moieties are replaced in the presence of excess N-methylpyrrole[44] (Scheme 9). Moreover, the transformation takes place with a remarkable *solvent dependent regioselectivity*: in nitromethane 1,3-bis(N-methyl-2'-pyrrolyl)propenes are formed in good yield, whereas in DMF pure 1,1 regioisomers are obtained.

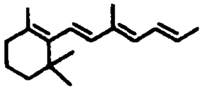


SCHEME 9

This unexpected finding led us to the design of a *novel porphyrin synthesis* giving access to meso-vinyl substituted derivatives[45-47] (Scheme 10).

It can be seen that this synthesis works better when 3,3'-disubstituted selenoacetals are used as precursors; in those cases 10-30% yields of pure porphyrins can be obtained in a very straightforward manner. For the less successful cases (such as entry 2, Scheme 10), even a thorough scrutiny of the reaction conditions did not allow to improve the product yield.



Entry	R^1	R^2	Yield (%)
1	Ph	H	3
2	o-NO_2Ph	H	0.6
3	p-MeOPh	H	0
4	p-NMe_2Ph	H	0
5	p-MePh	H	1
6	o-ClPh	H	2.1
7	p-ClPh	H	0.2
8	o,o'-$(MeO)_2$Ph	H	0
9	Me	Me	11
10	Et	Et	17
11	i-Pr	i-Pr	22
12	Ph	Me	28
13	Ph	Et	17
14	Ph	Ph	30
15	p-MeOPh	Me	10
16	MeOOC	Me	9
17		Me	1.3
18			20
19	- $(CH_2)_5$ -		1.5
20	- CH(Me)-$(CH_2)_3$-CH(Me) -		7

SCHEME 10

Another way of generating *1-selenoallyl cationic* species is to treat 3-hydroxyvinyl selenides with oxygenophilic Lewis acids, for example $ZnCl_2$[44]. Thus, starting from 1-methyl-seleno-3-hydroxy-1-butene[40] and using an iterative procedure we have been able to prepare oligomers of the 1,3-bis(2'-pyrrolyl)propene regioisomer (CH_3NO_2 path in Scheme 9) which led to semi-conducting materials[48].

The same *1-selenoallyl cationic* species led also to synthetically interesting compounds through their reaction with silyl enol ethers followed by oxidative deselenation. Selenoxide syn-elimination gave a conjugated dienone; Baeyer-Villiger oxidation produced lactones and selenoxide [1,3]-σ-tropic rearrangements gave allylic alcohols[49].

Finally, *1-selenopropargyl cations* have been used for the synthesis of *meso*-tetraalkynyl porphyrins[50].

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