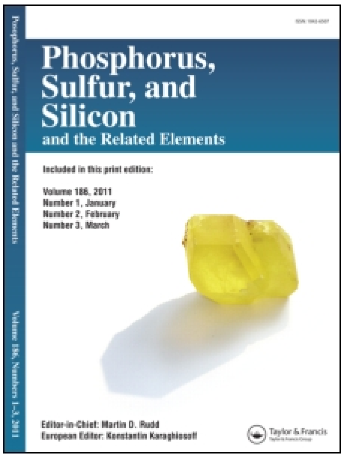

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SELENIUM STABILIZED CARBENIUM IONS: STRUCTURE AND USEFUL REACTIONS

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SELENIUM STABILIZED CARBENIUM IONS: STRUCTURE AND USEFUL REACTIONS

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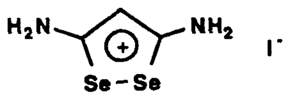
Abstract Carbocations bearing one or two seleno moieties can be generated in solution by Lewis acid mediated heterolytic C-X (X = OR, SeR) bond cleavages. Some of these species, e.g. bis(methylseleno)benzylcarbenium hexachloroantimonate, can be isolated in crystalline form and in high yield. Spectroscopic and X-ray data demonstrate a substantial stabilization of the positive charge by the two methylseleno groups which is comparable to that provided by the corresponding thio substituents. Reactions of various selenium stabilized cationic species with carbon nucleophiles such as silyl enol ethers or electron rich heteroatomic compounds are described, and synthetic applications to the preparation of conjugated carbonyl derivatives as well as of novel meso-tetravinyl porphyrins are provided.

Although the history of organoselenium chemistry is nearly as long as that of organic chemistry, to the author's knowledge selenium substituted carbenium ions have not been mentioned in the literature before 1967.[1] Whereas most of the 1,2-diselenolylium[2] 1 and 1,3-diselenol-2-ylium[3,4] 2 salts have been described as stable compounds, the aliphatic selenocarbenium ions of type 3 have only been proposed as reasonable intermediates in seleno-Pummerer rearrangements.[5] Our initial efforts have therefore been directed towards the latter class of carbenium ions bearing one or two selenium substituents.

Kinetic studies of the acidic hydrolysis of various methyl vinyl selenides have shown that the mechanism of these reactions



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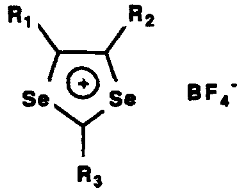

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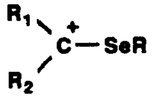

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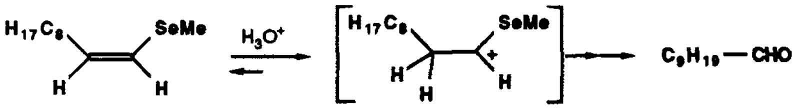
differs from that of the corresponding sulfur and oxygen analogues in that protonation of the starting vinyl selenides is a partially reversible event[5] (Scheme 1).

Scheme 1



Partially reversible protonation : $k(H_2O)/k(D_2O) = 1.8$

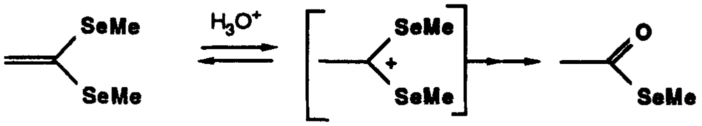
25% D incorporation

25% cis → trans isomerisation

Interestingly, such reversibility of the protonation step has not been detected in the case of aryl vinyl selenides[6] which hydrolyzed according to the mechanism (A-S_E2) prevailing for vinyl ethers and vinyl sulfides.

The hydrolytic behavior of ketene selenoacetals is even more intriguing since we have found[7] that protonation of most of these compounds takes place via a rapid equilibrium and thus the mechanism is completely changed from A-S_E2 to rate limiting nucleophilic attack (by water) of the intermediate bis(methylseleno)carbenium ion (Scheme 2). The same phenomenon was described simultaneously to occur during acid catalyzed hydrolysis of ketene thioacetals.[8]

Scheme 2

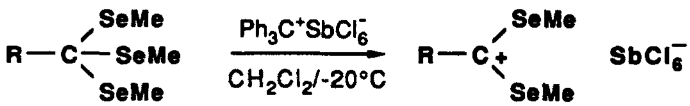


Fully reversible protonation : $k(H_2O/k(D_2O) = 0.4 - 0.8$

100% D incorporation

More detailed insight into the nature of selenocarbenium ions was gained[9] when we discovered that crystalline bis(methylseleno)carbenium salts could be prepared easily by reaction of triphenylcarbenium hexachloroantimonate with tris(methylseleno)-orthoesters[9] (Scheme 3). Indeed, ^1H NMR spectroscopy revealed,

Scheme 3



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R = Et	75%
R = $PhCH_2$	97%

in the case of bis(methylseleno)benzyl carbenium ion and its thio analogue, the existence of hindered rotations around the C^+-Se and C^+-S bonds having Arrhenius activation energies of 13 and 14 kcal/mole, respectively. These figures are very much the same as those found for bis(oxo)carbenium ions indicating thereby an extensive delocalization of the selenium lone pairs which creates a C^+-Se double bond character comparable to that of the C^+-S and C^+-O bonds.[9] That the amounts of positive charge on C^+ in the seleno- and thiocarbenium ions are also similar is mirrored by their ^{13}C chemical shifts: 263 ppm for the selenium species and 245 ppm for its sulfur analogue.[9]

Recently we have been able to measure ^{77}Se chemical shifts for bis(methylseleno)benzylcarbenium hexachloroantimonate.[10] At -30°C one can see two ^{77}Se signals (due to the unsymmetrical conformation exclusively present at this temperature[9]) located at 788 and 836 ppm relative to MeSeMe. Taking into account that trialkyl selenonium salts resonate in the region of 250-400 ppm[11] we think that the observed low field shifts can in part be attributed to the relatively high sp^2 character of the Se atoms.

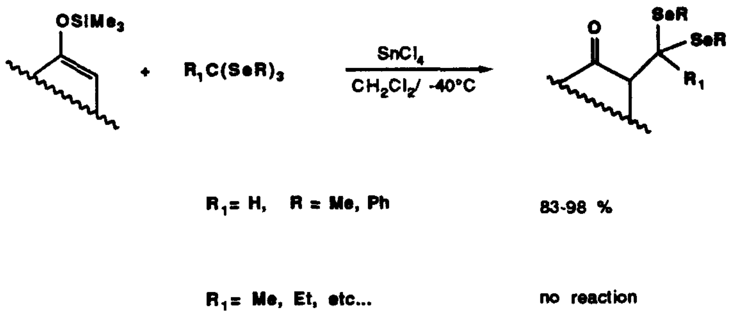
The above results and interpretations are fully corroborated by the X-ray diffraction data of bis(methylseleno)- and bis-(methylthio)benzylcarbenium hexachloroantimonates collected at -100°C and +25°C, respectively.[9] Scheme 4 shows the most salient feature of these structures.

It appears that bis(methylseleno)- and bis(methylthio)-carbenium ions exhibit very similar thermodynamic stability which is however less pronounced than that of the oxygen analogues. Therefore the kinetic behavior of these ions can not be rationalized on the basis of their intrinsic stability, but rather by the existence of a high kinetic barrier towards nucleophilic attack in the case of the sulfur and selenium species leading to the equilibrium protonation mentioned above[7,8] (Schemes 1 and 2). We feel that this kinetic barrier arises from the high polarization of the electron clouds surrounding the S and Se atoms by the positive center. Attacking nucleophiles would thus be repelled by this screen of electrons rather than by convenional steric effect. Such a polarization should be much less effective in the case of oxocarbenium ions.

We have also investigated a number of reactions of potential synthetic interest using selenium stabilized carbenium ions as electrophiles.

In the presence of silyl enol ethers, cations of type 4 (R = H) [generated as in Scheme 3] gave the corresponding alkylation products (i.e. monoselenoacetals of β-dicarbonyl compounds) in low yield, confirming our earlier findings on the hydrolysis of ketene selenoacetals. However, tris(methylseleno)- and tris-(phenylseleno)orthoformates activated by $SnCl_4$ react with the same carbon nucleophiles in an extremely efficient manner since the β-ketoselenoacetals 5 are formed in very high yields[12] (Scheme 4). Whereas the synthetic utility of species 4 is limited to formylation reactions, a large variety of cation 3, generated from the easily available selenoacetals, can undergo reaction with various silyl enol ethers to give β-selenoketones in a connective fashion[13] (Scheme 5) and with very high regioselectivity[13] (Scheme 6).

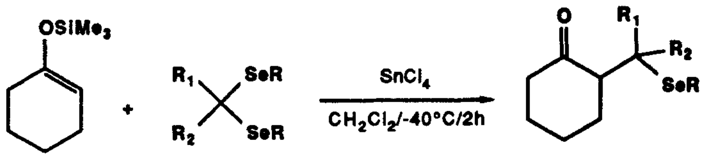
Scheme 4



One interesting example of application of the above reactions to the selective preparation of lactone 6 or of the enone 7 is shown in Scheme 7. Treatment of the alkylation product β-selenoketone with a large excess of H_2O_2 leads predominantly to the unsaturated lactone 6, while oxidation with 1 eqn. mCPBA gives mainly the enone.[13]

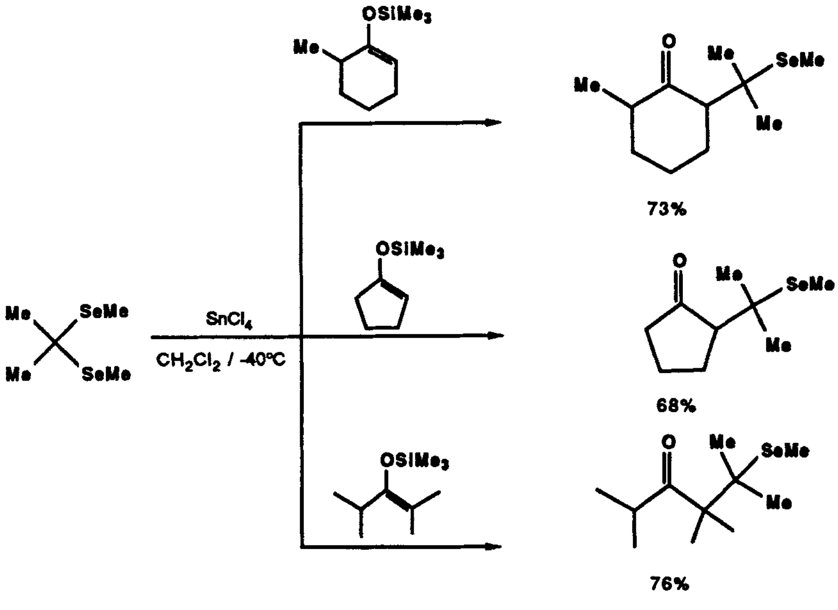
Selenium substituted allyl cations 8 and 9 (Scheme 8) also proved valuable electrophiles, especially towards five-membered heterocyles such as pyrrole and furan.

Scheme 5



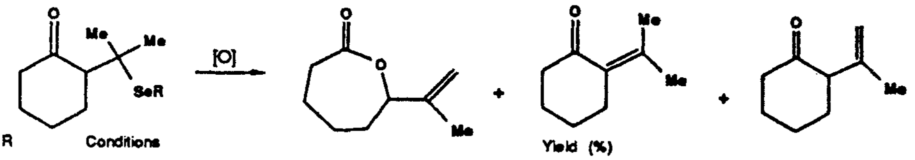
R	R_1	R_2	Yield (%)
Me	Me	Me	84
Me	Ph	H	89
Me	Et	Et	49
Ph	Me	Me	97

Scheme 6



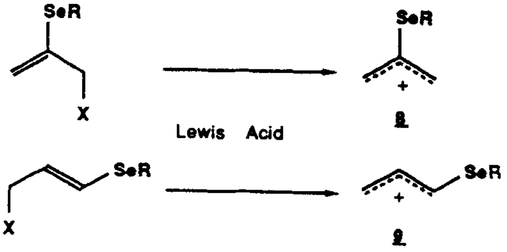
Detailed studies[14,15] have shown that 2-phenylselenoalkyl cations <u>8</u> (R = Ph) do not form 4 + 3⇒7 cycloaddition products when reacted with furan, N-methyl pyrrole or thiophene; rather

Scheme 7



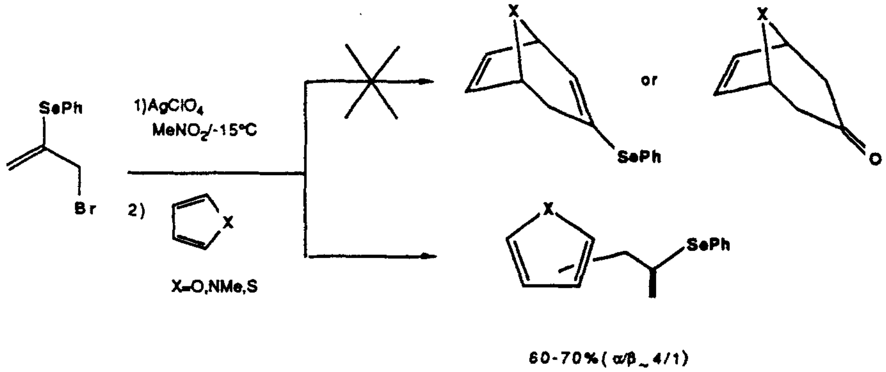
R	Conditions	Yield (%)		
Ph	10 eq. H_2O_2/THF/0°C/10 min.	62	trace	trace
Me	ibid.	58	14	4
Me	1.2 eq. mCPBA/CH_2Cl_2 -78°C/15 min.	00	72	trace

Scheme 8



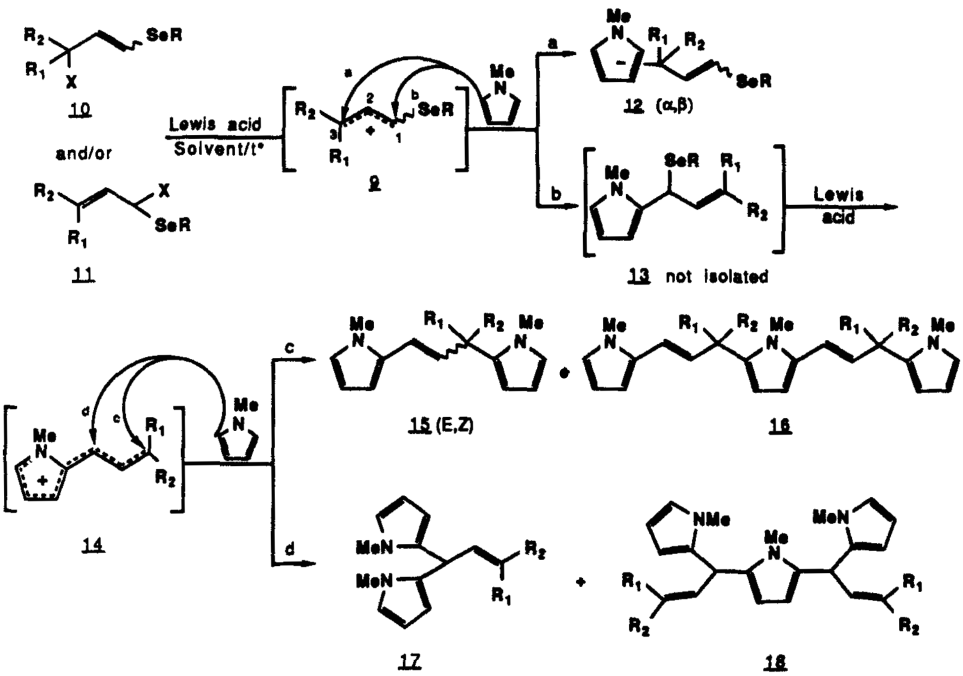
they undergo Friedel-Crafts reactions to give the selenoallyl substituted heterocycles (Scheme 9).

Scheme 9



Although 1-selenoallyl cations 9 also undergo Friedel-Crafts reactions with electron rich heterocycles, the nature of the final products is highly dependent on the substitution pattern of 9 as well as on the reaction solvent. This is illustrated in Scheme 10 for the case of N-methyl pyrrole.[16]

Scheme 10

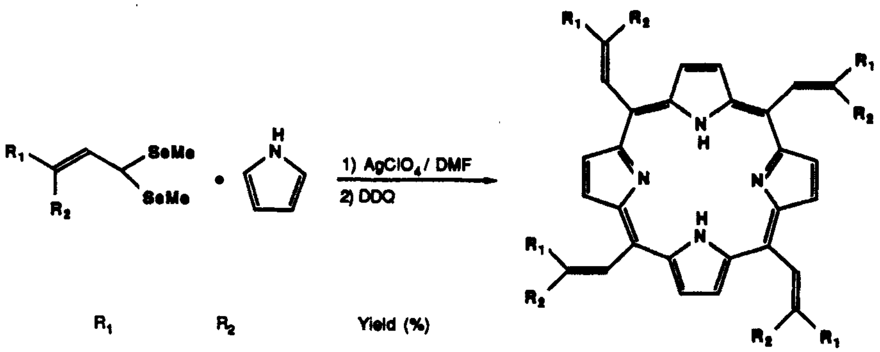


Unsubstituted 9 (R_2 = R_3 = H) suffers nucleophilic attack by N-methylpyrrole to give 12 (path a), whereas disubstituted 9 (R_2 = R_3 = alkyl, aryl) follows path b. Compound 13 cannot be isolated most likely because of the high stability of cation 14 which in turn reacts with a second molecule of N-methylpyrrole to give 15 or 17, depending on the solvent used. Paths a and b also show some sensitivity to solvent, but the most spectacular effect is seen at the last stage of the reaction, i.e. attack of

<u>14</u> by N-methylpyrrole. 1,3-Dipyrryl propenes <u>15</u> are almost exclusively formed in nitromethane, while regioisomers <u>17</u> are largely predominant when the reaction is carried out in DMF. The amounts of <u>16</u> and/or <u>18</u> can in each case be minimized by the use of an excess (10 eqn.) of N-methylpyrrole.

This highly selective access to 1,1-dipyrryl propenes <u>17</u> suggested a straightforward synthesis of a novel class of porphyrins bearing substituted vinyl groups at their meso positions. Indeed, a series of porphyrins could be prepared under mild conditions using the one pot reaction sequence outlined in Scheme 11.[17]

Scheme 11



R1	R2	Yield (%)
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

These examples show that various electrophilic species bearing selenyl moieties can be generated by Lewis acids from easily available precursors and used as valuable carbon-carbon bond forming reagents.

We are currently investigating the structures of the species we call 2- and 1-selenoallyl cations 8 and 9 as well as their further application in synthetically useful transformations.

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