

THE PREPARATION OF SELENIRANIUM AND SELENIRENIUM IONS<sup>1</sup>

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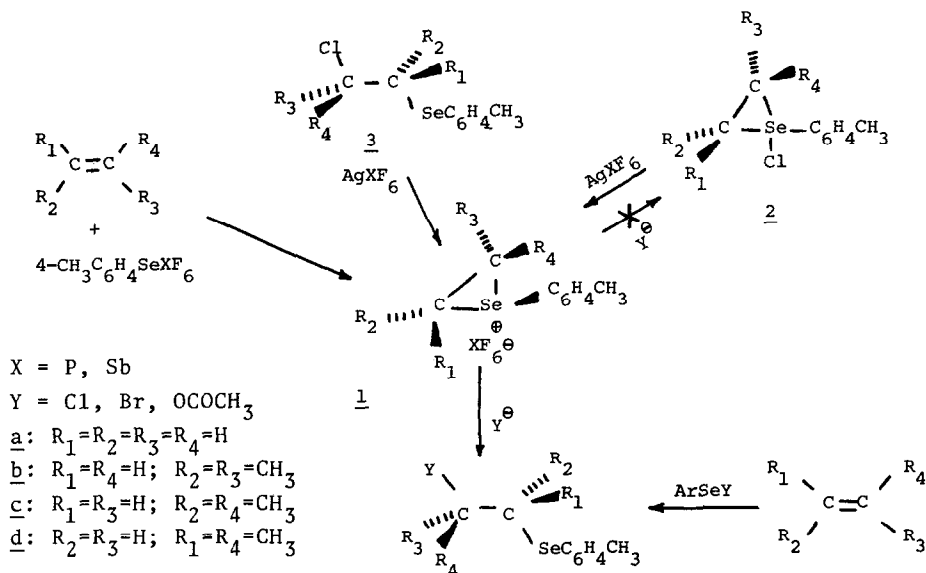
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We wish to report the synthesis and characterization of a number of novel organoselenium compounds containing the selenium atom in a three member ring.

Seleniranium ions 1a-c can be quantitatively prepared as either their hexafluorophosphate or hexafluoroantimonate salts by the addition of a CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>NO<sub>2</sub> solution of the areneselenenyl hexafluorophosphate or -antimonate respectively to an equimolar solution of the appropriate alkene. For example, 0.315 g.



X = P, Sb

Y = Cl, Br, OCOCH<sub>3</sub>

a: R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=H

b: R<sub>1</sub>=R<sub>4</sub>=H; R<sub>2</sub>=R<sub>3</sub>=CH<sub>3</sub>

c: R<sub>1</sub>=R<sub>3</sub>=H; R<sub>2</sub>=R<sub>4</sub>=CH<sub>3</sub>

d: R<sub>2</sub>=R<sub>3</sub>=H; R<sub>1</sub>=R<sub>4</sub>=CH<sub>3</sub>

(1 mmole) 4-tolueneselenenyl hexafluorophosphate in 20 ml CH<sub>2</sub>Cl<sub>2</sub> (prepared in situ from 0.206 g (1 mmole) 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SeCl and 0.253 g (1 mmole) AgPF<sub>6</sub> followed by filtration in an anhydrous atmosphere to remove AgCl) reacts readily with ethylene to give a single product

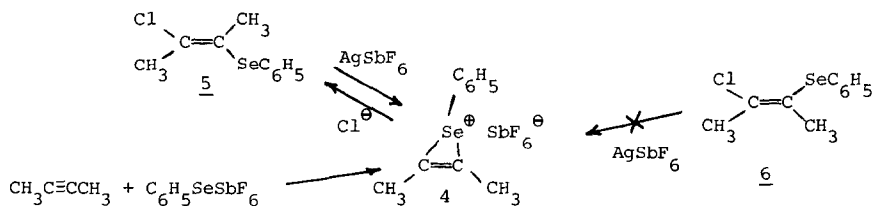
identified as 4-tolyl ethyleneseleniranium hexafluorophosphate 1a. The pmr spectrum of 1a shows a tightly coupled AA'BB' spin system centered at  $\delta$  4.2 ppm relative to internal TMS. The cmr spectrum of 1a has a single resonance at  $\delta$  45.46 ppm (acetone- $d_6$ ), consistent with magnetically equivalent carbons in the three member ring. The aryl methyl group is observed at  $\delta$  5.31 ppm. Aromatic carbons are found at 120.81, 114.81, 116.61, 122.50 ppm. Alternatively 1a can be prepared from either the episelenurane<sup>2</sup> 2a or 2-chloroethyl 4-tolyl selenide 3a by reaction with  $\text{AgPF}_6$  or  $\text{AgSbF}_6$  in  $\text{CH}_2\text{Cl}_2$ . Reactions of the areneseelenenyl hexafluorophosphates and -antimonates were carried out over the temperature range  $-60^\circ$  to  $28^\circ\text{C}$ . Half-lives for the ions at temperatures greater than  $20^\circ\text{C}$  are usually less than 48 hours.

Cis-2-butene when reacted with  $\text{ArSeXF}_6$  ( $\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ,  $\text{X} = \text{P, Sb}$ ) gave two ions 1b & 1d in approximately a 40:60 distribution. These results may be interpreted in terms of the expected pyramidal geometry of selenonium selenium,  $\text{R}_3\text{Se}^+$ , with the aryl group syn to the methyls in one isomer and anti in the other. The presence of two isomers is readily observed in both pmr (see Table) and cmr spectra: 1b  $\delta$  76.46 CH 15.74 CH<sub>3</sub>, 1d  $\delta$  76.05 CH 16.35 CH<sub>3</sub>. After approximately 48 hours only the anti isomer could be observed. In contrast trans-2-butene gives only a single ion 1c cmr  $\delta$  74.32 CH 18.94 CH<sub>3</sub> as expected. It is of interest that the ring carbons although shifted downfield relative to the corresponding acyclic  $\beta$ -chloroalkyl aryl selenide are considerably upfield from resonances reported<sup>3</sup> for carbonium ions thus suggesting considerable charge localization on selenium. Alternatively 1b, 1c and 1d are also prepared from the appropriate  $\beta$ -chloroalkyl aryl selenide.

The reaction of 1a-c with external nucleophiles such as  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{OAc}^-$  in  $\text{CH}_2\text{Cl}_2$  free of any  $\text{AgCl}$  results in attack at carbon. The products are identical in all respects to those formed independently by the addition of  $\text{ArSeY}$  ( $\text{Y} = \text{Cl, Br, OAc}$ ) to the appropriate alkene<sup>4</sup>. Attack at selenium to give the corresponding episelenurane is not observed.

Similarly the corresponding selenirenium ions may be synthesized from  $\text{ArSeXF}_6$  and an alkyne. For example, benzeneseelenenyl

hexafluoroantimonate plus 2-butyne in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$  yields quantitatively phenyl 2-butyne-selenirenium hexafluoroantimonate 4



Compound 4 may also be prepared from E-2-chlorobuten-2-yl phenyl selenide 5 by reaction with  $\text{AgSbF}_6$  in  $\text{CH}_2\text{Cl}_2$ . The reaction is complete within five minutes. The corresponding Z-isomer 6 was not observed to react during 36 hours of observation. The pmr spectrum of 4 consists of a singlet at  $\delta$  2.8 ppm (6H) plus aromatic protons. The cmr spectrum shows resonances at  $\delta$  24.20  $\text{CH}_3$  and 136.13  $\text{CH}_3\text{C}=\text{C}$ . Reaction of 4 with external chloride below  $20^\circ\text{C}$  gave 5 stereospecifically.

The chemical reactions of 1a-c and 4 are identical<sup>5</sup> and their pmr spectral parameters are similar<sup>6</sup> to the analogous sulphur compounds recently prepared. A comparison of the pmr parameters are given in the Table.

Table  
A Comparison of the PMR Chemical Shifts\* of Ions Containing S<sup>6,7</sup>  
and Se in Three Member Rings

Configuration			Chemical Shifts		
<u>1b</u>	cis-syn	Se <sup>+</sup>	1.67 d (6H)	4.90 m (2H)	
<u>1d</u>	cis-anti	Se <sup>+</sup>	1.72 d (6H)	4.40 m (2H)	
	cis-anti	S <sup>†</sup>	1.85 d (6H)	4.32 m (2H)	
<u>1c</u>	trans	Se <sup>+</sup>	1.70 d (3H)	1.86 d (3H)	4.3 m (2H)
	trans	S <sup>†</sup>	1.84 d (3H)	1.96 d (3H)	4.0 m (2H)
<u>4</u>		Se <sup>+</sup>	2.80(s) 6H		
		S <sup>†</sup>	2.77(s) 6H		
	+ in $\text{CD}_2\text{Cl}_2$ at $28^\circ$		† in $\text{SO}_2$ at $-60^\circ$ * $\delta$ relative to internal TMS.		

We believe that this data firmly supports the conclusion that stable three membered ring compounds with a selenium atom in the ring do exist.

### Acknowledgement

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