Tetrahedron Letters No. 14, pp 1259 - 1262, 1975. Pergamon Press. Printed in Great Britain.

# NEW PSEUDOAROMATIC RING SYSTEMS: 1,3-THIASELENOLYLIUM AND 1,3-DISELENOLYLIUM CATIONS

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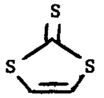
(Received in USA 6 February 1975; received in UK for publication 3 March 1975)

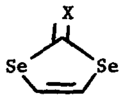
While a considerable literature[1] has accumulated on the resonance stabilized[2] 1,3-dithiolylium cation (I)[3], the corresponding selenium analogs of I (e.g. II and III) have not been reported.


I


II


III


IV

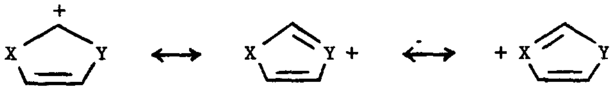

V

Until recently, the only synthetic route available for preparing the parent ring system I involved the oxidation of 1,3-dithiole-2-thione (IV) with a peracid[4]. The analogous treatment of 1,3-diselenole-2-selone (V, X=Se) or even the 2-thione (V, X=S) fails to yield the desired diselenolylium cation (III)[5,6] probably due to attack of the ring seleniums during the oxidation[7]. The new synthetic route[8] to I involves reaction of the methyl iodide salt of IV with NaBH$_4$ followed by treatment with fluoroboric acid. We describe here the extension of this procedure to the preparation of the new pseudoaromatic ring systems, 1,3-thiaselenolylium (II) and 1,3-diselenolylium (III) cations, and report on the changes in the physical properties that accompany the replacement of sulfur with selenium in I.

The synthetic scheme for preparing I and its selenium analogs is outlined in Table 1, along with proton nmr data for the different compounds involved in the syntheses. Essentially the same experimental conditions employed in the sulfur case[8] (reaction 1 in Table 1) were found applicable to the selenium systems (reactions 2-4 in Table 1). Each chemical conversion proceeded in yields typically over 80%. The fluoroborate salt of III was found to be particularly air sensitive. The preparation of the methyl iodide salts (VII) of VI (Table 1) when Z=S involves refluxing the compound with excess methyl iodide in nitromethane for several hours. However, when Z=Se, only gentle heating of the nitromethane solvent below its boiling point for a few minutes is necessary. More vigorous conditions leads to considerable decomposition of the product.

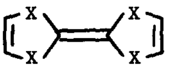
The characterization of the fluoroborate salts of II and III follows from elemental analysis and from comparison of their spectroscopic properties with those for I (Tables 1 and 2). The expected bathochromic shift[9] of the UV absorption maximum in I is seen as sulfur is successively replaced by selenium. In the IR spectra, a similar shift to lower energy of absorptions below 1000 $cm^{-1}$ is observed. These peaks are typically associated with vibrations of groups involving the heteroatom[10]. The intense, broad absorptions around 1150-1000 $cm^{-1}$ are characteristic of the fluoroborate anion[11]. The nmr spectra of I, II and III display weak coupling of the methine and vinyl protons. In the 1,3-thiaselenole ring system, the assignments for the vinyl protons are based on a comparison of its chemical shifts (reaction 2) with those in which the hydrogen gem to sulfur is replaced by a methyl group (reaction 4). We conclude that the proton trans to selenium is shifted to lower field than the gem proton.

Relative to the 1,3-dithiolylium cation, the vinyl protons in the 1,3-diselenolylium cation are shifted to lower field by 0.77 ppm. The methine proton, on the other hand, experiences nearly a 2 ppm shift. This greater displacement to low field of the methine proton is consistent with a change in the charge density distribution upon selenium substitution in I, in which more positive charge is localized on carbon-2 and less on selenium. It is well known that selenium enters into π-bonding with carbon less effectively than sulfur[12]; that is, resonance forms such as X and XI should contribute less when X and/or Y equal selenium than when they equal sulfur. Thus, cations II and III should be less stable than I.



X XI

This conclusion is consistent with the recent finding that substitution of selenium for sulfur in the related system, tetrathiofulvalene (XII, X=S) leads to an increase in the

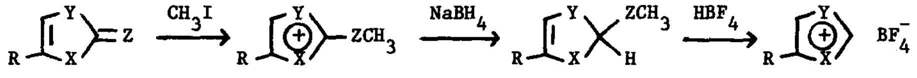


XII

ionization potential, probably due to the reduced stability of the radical cation of XII when X=Se[13]. The redistribution of charge density indicated here for selenium substitution in I provides insights in the changes that may be occuring when X is changed from sulfur to selenium in XII, a system of considerable interest since XII and its derivatives have been found to form highly conducting charge-transfer salts[6,14,15].

Table 1

Proton NMR Chemical Shifts (δ)[a]



| Reaction | VI | VII | | VIII | | | IX | |
|---|---|---|---|---|---|---|---|---|
| | Vinyl | Vinyl | Methyl | Vinyl | Methine | Methyl | Vinyl[b] | Methine[c] |
| 1) X=Y=Z=S<br>R=H | 7.17 | 8.82 | 3.20 | 5.97 | 6.07 | 2.15 | 9.45 | 11.43 |
| 2)[d] X=Z=S,Y=Se<br>R=H | 7.26,<br>7.80<br>J=7.5Hz | 8.82,<br>9.23<br>J=6.5Hz | 3.17 | 6.40,<br>6.68<br>J=6.5Hz | 6.27 | 2.18 | 9.48,<br>10.18<br>J=6Hz | 12.43 |
| 3) X=Y=Z=Se<br>R=H | 8.10 | 9.45 | 3.10 | 7.12 | 6.37 | 2.17 | 10.22 | 13.41 |
| 4)[e] X=Z=S,Y=Se<br>R=$CH_3$ | 7.20,<br>2.28($CH_3$) | 8.82,<br>2.67($CH_3$) | 3.10 | 6.22,<br>2.07($CH_3$) | 6.13 | 2.23 | 9.63,<br>3.07($CH_3$) | 12.27 |

[a] Shifts rel. TMS. Solvents: VI and VIII, $CDCl_3$; VII, DMSO-$d_6$; IX, $CF_3COOD$ and $CF_3COOH$. [b] Doublet, J = 1.5-2.0Hz. [c] Triplet, J = 1.5-2.0Hz. [d] The vinyl proton trans to selenium shifted to lower field than gem proton. Based on shifts of reaction 4. [e] $J_{allylic}$ = 1.0-1.5Hz.

Table 2

UV and IR Data on the Fluoroborate Salts of I, II and III

| | $BF_4^-$ Salt | | |
|---|---|---|---|
| | I | II | III |
| UV λ(ε)<br>(ethanol) | 252(4050)[a] | 258(3700) | 262(3400) |
| IR (cm$^{-1}$)<br>(KBr) | 3120 (s)<br>1455 (m)<br>1140-1020 (br,s)<br>935 (m)<br>812 (m)<br>740 (w) | 3120 (s)<br>1455 (w)<br>1160-1000 (br,s)<br>920 (m)<br>790 (m)<br>725 (w) | 3100 (m)<br>1450 (w)<br>1160-1000 (br,s)<br>910 (vw)<br>760 (m)<br>700 (w) |

[a] Lit. value: λ(ε), 254(3800), reference 4b.

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