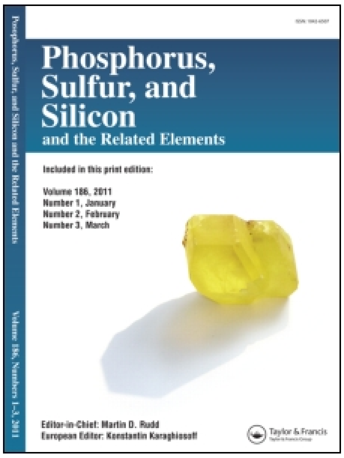

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CYCLIC ALIPHATIC SELENOXIDES AND SE-DIHALIDES: SOME INTER- AND INTRAMOLECULAR REACTIONS

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Investigations of spectral properties, reactions and of stereochemistry of substituted and unsubstituted selenolane Se-oxides and Se-dihalides

Keywords: reactions; stereochemistry; selenolane Se-oxides; selenolane Se-dihalides

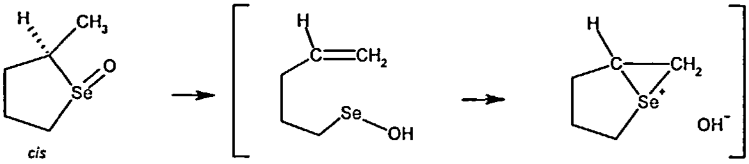
We have performed investigations of spectral properties (UV, CD, MCD, NMR), reactions, and of the stereochemistry of (substituted) selenolane Se-oxides and Se-dihalides, e.g. 2- and 3-methylselenolane derivatives. In comparison with the analogous sulfoxides, the selenoxides show contrasting behavior:

- easy, proton accelerated inversion of the Se pyramid

- facile oxygen elimination yielding the parent compound again
- in steric favorable systems, stereospecific elimination, followed by intramolecular rearrangement
- at more elevated temperatures, intermolecular reactions with alcohols

Unsubstituted selenolane Se-oxide as well as the 3-methylselenolane Se-oxides decompose at elevated temperatures to their parent compounds. In contrast, cis-2-methylselenolane Se-oxide shows an stereospecific elimination/intramolecular addition reaction leading to 2-hydroxymethylselenolane and 3-hydroxyselenane, whereas the trans diastereomer inverts to the cis compound under the same conditions.

In a series of NMR experiments it was shown that the cis- and trans-diastereomeres of 2-methylselenolane Se-oxide give rise to an identical equlibrium mixture before and after protonation of 72:28. At higher temperatures, an external hydroxyl group reacts with the proposed intermediate, as shown by NMR with isotopically labeled methanol. Therefore, we suggest the following reaction mechanism:



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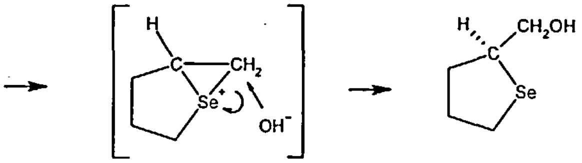

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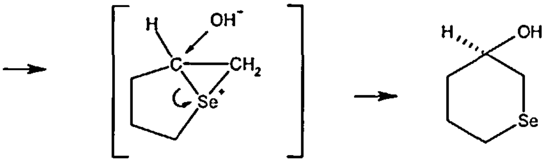
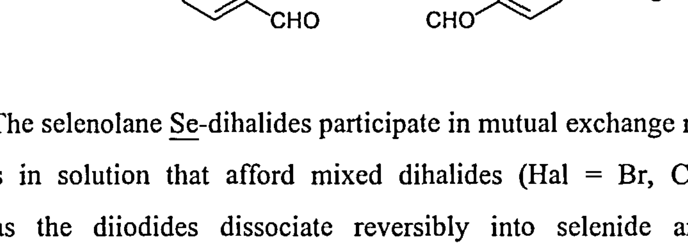
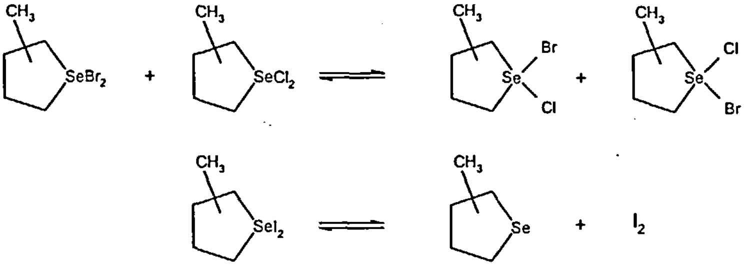


In another series, selenaisochroman-Se-oxide decomposes thermally in a clean stoichiometric reaction:

3



The selenolane Se-dihalides participate in mutual exchange reactions in solution that afford mixed dihalides (Hal = Br, Cl), whereas the diiodides dissociate reversibly into selenide and molecular iodine. As the latter equilibrium cannot be substantiated for the bromides or chlorides, whereas the bromide ion can be detected in polar solvents, an ionic mechanism for the halogen exchange is favored.



MCD and (with optically active substrates) CD techniques are particularly useful for studying these multispecies solutions. For example, the MCD spectrum displayed shows the signal of the bromide ions in a solution of dissociated 3-methylselenolan-Se-dibromide.