SYNTHESIS OF 2-HETEROSUBSTITUTED 1,3-OXATHIANES AND THEIR REACTION WITH STRONG BASES

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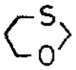
A series of 2 heterosubstituted 1,3-oxathianes were synthesized and their reactivity toward strong bases (sec.BuLi and lithium dicyclohexylamide) were studied.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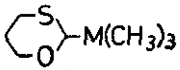
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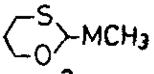
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The reaction of the anion derived from 1,3-oxathiane (1) with trimethylmetal halide [$(CH_3)_3SiCl$, $(CH_3)_3GeCl$, $(CH_3)_3SnCl$] or acetate [$(CH_3)_3PbOAc$] afforded 2 (M = Si, Ge, Sn, Pb). Dimethyl disulfide and diselenide were used as an elecrophile to prepare the derivatives 3 (M = S, Se). 2-Methoxy-1,3-oxathiane (3, M = O) was synthesized by the methanolysis of the N-tosylsulfilimine of 1,3-oxathiane (1). Transacetalization between 3-mercapto-1-propanol and N,N-demethylformamide dimethylacetal gave 2-dimethylamino-1,3-oxathiane.

Detailed inspection of ^{1}H and ^{13}C NMR spectra of these compounds revealed the following facts: the substituent at C-2 in the derivative 2 (M: group IV element) took equatorial orientation, while that in the derivative 3 (M: group VI element) took axial orientation.

With the derivative 2 sec.BuLi removed the proton at C-2 (for Si, Ge) or attacked the metal atom to leave 1,3-oxathianyl anion (for Sn, Pb) depending upon the heteroatom at C-2. Nucleophilic displacement at C-2 giving 2-sec.butyl-1,3-oxathiane was observed in the reaction of the group VI derivatives (3, M = O, S, Se). In the case of 2-methylseleno-1,3-oxathiane the nucleophilic attack at the metal atom was also recognized.

2-Dimethylamino-1,3-oxathiane on the reaction with sec.BuLi or lithium dicyclohexylamide gave a complex mixture with recovery of starting material.

Lithium dicyclohexylamide was proved to be not enough basic to abstract the proton at C-2 of 2-heterosubstituted 1,3-oxathianes.