

[Phosphorus Sulfur, **67**, 169-172 (1992)]

[Lab. of Pharm. Chemistry]

Reduction of Sulfonium and Selenonium Salts with Samarium Diiodide.

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Treatment of sulfonium and selenonium salts with 2 equiv of a THF solution of samarium diiodide nicely caused the reductive cleavage of the C-S or C-Se bonds. The bond cleavage took place regioselectively between the positive sulfur or selenium atom and an allylic carbon or the carbon atom with an electron-withdrawing group such as a cyano, an ester, or an amide group. Some medium-sized cyclic sulfides or selenides were synthesized in high yields by this method.

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[Lab. of Pharm. Chemistry]

Synthesis of Medium-sized Cyclic Sulfides and Selenides by Crosspiece C-X Bond Cleavage of Bicyclic Onium Salts bearing a Bridgehead Sulfur or Selenium Atom.TADASHI KATAOKA*, TETSUO IWAMA, KAZUHIRO TSUTSUMI, YOSHIHIDE NAKAMURA,
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Medium-sized cyclic sulfides and selenides were synthesized by reductive cleavage of the crosspiece C-X bond of bicyclic sulfonium and selenonium salts, respectively. Reducing agents used were magnesium metal, sodium borohydride and samarium diiodide. Samarium diiodide reduction of simple sulfonium and selenonium salts was also carried out. Application of this method to the C-S bond cleavage of lactam-sulfonium salts provided sulfur-containing medium-sized lactams in high yields. Treatment of the sulfonium salts bearing an allylic double bond with a base gave an olefinic sulfide or a cyclopropane derivative.

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[Lab. of Medicinal Chemistry]

First Synthesis of 5,6,7,8-Tetrahydro-8-deaza-8-thiafolic Acid.

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5,6,7,8-Tetrahydro-8-deaza-8-thiafolic acid (**1**) was synthesized as a diastereoisomeric mixture *via* thermal condensation of 5-hydroxyisocytosine (**2**) with diethyl *N*-[*p*-(2-amino-3-mercaptopropyl)aminobenzoyl] glutamate after activation of the C(6)-position in (**2**) with *N*-bromosuccinimide/ethanol. The compound (**1**) was fairly stable even in solution compared with the parent 5,6,7,8-tetrahydrofolic acid. The corresponding *N*₅,*N*₁₀-methylene derivative was also prepared upon treatment of (**1**) with formaldehyde.