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The C-O Bond Cleavage of Cyclic Ethers with Tris(phenylseleno)-borane-Lewis Acid.

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Tris (phenylseleno) borane (1) has a hard boron element and a soft selenium element, and therefore it was expected that 1 cleaves the C-O bond. Tetrahydrofuran and tetrahydropyran were cleaved with 1 in the presence of zinc iodide to produce the δ - and ϵ -phenylseleno alcohols. The C(5)-O bond of 2-methyltetrahydrofuran was regioselectively cleaved with 1 and a catalytic amount of tin(IV) chloride to afford the δ -phenylseleno alcohol. The selenoborane (1) was a weak reagent for the C-O bond-cleavage and cleaved cyclic ethers selectively.

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Synthesis and Reactions of a Stable 2-Selenanaphthalene, 1-Cyano-2-methyl-2-selenanaphthalene.

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A stable 2-selenanaphthalene, 1-cyano-2-methyl-2-selenanaphthalene (1) was prepared by deprotonation of 1-cyano-2-methylisoselechromenium salt with triethylamine in ethanol. The selenanaphthalene 1 was air-sensitive and rearranged thermally in aprotic solvents to form 1-cyano-1-methylisoselechromene in good yield. Reaction of 1 with dimethyl acetylenedicarboxylate in benzene afforded a benzocycloheptene derivative 2, whereas the same reaction in sulfolane afforded a naphthalene derivative besides 2. In contrast, the reaction with methyl propiolate gave a 2:1 adduct in addition to the rearranged product and isoselechromene.

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Cyclic Selenonium exo-Ylides (3,4-Dihydro-1H-2-benzoselenin-2-io)-methanides; Syntheses and Reactions.

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Stable cyclic selenonium exo-ylides (3,4-dihydro-1H-2-benzoselenin-2-io)methanides (1a-e) have been synthesized by reactions of 3,4-dihydro-1H-2-benzoselenin 2,2-dichloride or N-(3,4-dihydro-1H-2-benzoselenin-2-io) toluene-p-sulphonamide and active methylene compounds. The reactions of ylides having acetyl group(s) (1a,b) with dimethyl acetylenedicarboxylate afforded the furan derivatives and the dihydrobenzoselenin, while reactions of the ylides having no acetyl group (1c-e) afforded the benzoselenonines. The diacetylmethanide (1a) when heated gave the benzoselenepine, while the bis(ethoxycarbonyl) methanide (1c) afforded the styrene derivative and a tetrasubstituted ethylene.