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Novel Oxidative Ring Contraction of Dihydroselenopyrans to Selenophenes.

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Oxidation of 3,6-dihydro-*2H*-selenopyrans bearing an electron-withdrawing group at 2 position with sodium periodate caused an unprecedented ring-contraction to afford selenophenes, whereas oxidation with *m*-chloroperbenzoic acid provides selenopyrans, 2-(*m*-chlorobenzoyloxy)dihydroselenopyrans and a trace amount of selenophenes. The ring contraction would proceed *via* some intermediates, selenopyran *Se*-oxides, 2-alkoxyselenopyrans, episelenonium betaines and selenophenium ylides.

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Versatile Cyclisation Reactions Using Selenoboranes.

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Tris(phenylseleno)borane and tris(methylseleno)borane reacted with terminal acetylenes to afford (*Z*)-vinyl selenides. This reaction was initiated by oxygen or azobisisobutyronitrile, and the intermediates were vinyl radicals. This radical reaction could be applied to the intramolecular free radical cyclisation of enynes and some heterocycles and carbocycles were synthesized. This novel method could be also employed in the synthesis of α-kainoid derivatives.

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Novel Rearrangements of Cyano-stabilised Cyclic Sulfur Ylides, 2-Alkyl-1-cyano-3,4-dihydro-*1H*-2-thionianaphthalen-1-ides: Spiro-compound Formation and Ring Expansion Reactions.

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Thermal reaction of 1-cyano-2-methyl-3,4-dihydro-*1H*-2-thionianaphthalen-1-ides **1** in ethanol or treatment with succinimide afforded the spiro compounds in good yields, which underwent thermal rearrangement and Diels-Alder reaction to give tetrahydro-3-benzothiepine and a pair of cycloadducts, respectively. In contrast, treatment of **1** with *N*-chlorosuccinimide, chloramine B or T formed chloroketenimines *via* an S→N [2,3]sigmatropic rearrangement of the *exo*-methanide.