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The Pummerer Reaction of 2-Vinylcyclopropyl Sulfoxides: Generation and Reactions of Butadienylthionium Ion Intermediates.

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Generation of butadienylthionium ions in the Pummerer reactions of 2-vinylcyclopropyl sulfoxides and their benzothiazinone derivatives was investigated. Although the Pummerer reactions of 2-vinylcyclopropyl sulfoxides with trifluoroacetic anhydride were complicated, benzothiazinone derivatives smoothly reacted with trifluoroacetic anhydride to give 1,3-dienes in good yields. The reactions proceed *via* butadienylthionium ions by proton abstraction of the 2'-methyl group or the cyclopropane ring. Reactions of disubstituted benzothiazinones provided cyclic dienes while treatment of mono- or un-substituted derivatives gave acyclic conjugated dienes.

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A New Synthesis of α-Amino Acid Thioesters by Pummerer Reaction of 3-Substituted-4-sulfinyl-β-sultams.

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α-Amino acid thioesters were synthesized by the Pummerer reaction of 3-substituted-4-sulfinyl-β-sultams with TFAA. The 3-substituted-4-sulfinyl-β-sultams were prepared from the corresponding β-sultams by sulfenylation with diphenyl disulfide followed by *m*-CPBA oxidation. Diastereoselective synthesis of β-sultams by 1,3-asymmetric induction in [2+2] cycloaddition of a sulfene intermediate and chiral imines in solution-phase was studied. The use of imines derived from (*R*)- and (*S*)-α-methylbenzylamine followed by separation of the major and minor diastereomers gave enantiopure 3-substituted-*N*-methylbenzyl-β-sultams. These β-sultams were then converted to *N*-methylbenzyl-α-amino acid thioesters *via* sulfenylation and the Pummerer rearrangement with high or complete retention of configuration.

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Reactions of Diphenyl(phenylethynyl)selenonium Salts with Active Methylene Compounds and Amides: First Isolation of Oxyselenuranes [10-Se-4(C3O)] as a Reaction Intermediate

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The reaction of the diphenyl(phenylethynyl)selenonium triflate with active methylene compounds and *t*-BuOK in THF gave furan derivatives. The [10-Se-4(C3O)] selenuranes could be isolated from the reactions with benzoylacetonitrile and with 1,3-indandione, respectively, as reaction intermediates. The structures of the selenuranes were elucidated by X-ray crystallography and ^{77}Se high-resolution solid-state NMR spectroscopy. The selenuranes underwent ligand coupling on standing at room temperature or refluxing in chloroform and gave the furan derivatives and the ring-opened product. Similarly, the reaction of the selenonium salt with benzamide and pivalamide in the presence of NaH in THF afforded oxazole derivatives.

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Activation of the 41/43 kDa Mitogen-activated Protein Kinase Signaling Pathway Is Required for Hepatocyte Growth Factor-induced Cell Scattering.

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Hepatocyte growth factor (HGF) markedly induced the spreading, dissociation and scattering of Madin-Darby canine kidney epithelial cells (MDCK) and human stomach adenocarcinoma cells (TMK1). Scattering of MDCK and TMK1 was induced by 12-*O*-tetradecanoylphorbol-13-acetate (PMA) and epidermal growth factor (EGF), respectively. HGF-, PMA- and EGF-induced scattering of MDCK and TMK1 was inhibited at doses of 2-(2-amino-3-methoxyphenyl)chromone similar to those that gave comparable levels of inhibition of the activities of MEK, 41/43 kDa MAP kinases and p90^{rsk}. Activation of the 41/43 kDa MAP kinase signaling pathway is required for the motility response of MDCK and TMK1 induced by agents such as HGF, PMA and EGF.