

[Chem. Pharm. Bull., 42, 811-816 (1994)]

[Lab. of Pharm. Chemistry]

**Generation of Selenobenzenes Bearing an Electron-Withdrawing Group at the 2-Position.**

TADASHI KATAOKA\*, YASUHIRO OHE, AKIRA UMEDA, TATSUNORI IWAMURA,  
MITSUHIRO YOSHIMATSU, HIROSHI SHIMIZU

3,6-Dihydro-2*H*-selenopyrans **1** with an electron-withdrawing group at the 2-position were prepared by the Diels-Alder reaction of butadienes with selenoaldehydes. Oxidation of **1** with *m*-chloroperbenzoic acid provided 2*H*-selenopyrans **2** and 3,6-dihydro-2*H*-selenopyran-2-yl *m*-chlorobenzoates **3**. The selenopyrans **2** were methylated with methyl trifluoromethanesulfonate to give *Se*-methyl selenopyranium salts **4**. Deprotonation of **4** with NaH or triethylamine generated the selenabenzene derivatives **5**, which were too unstable to be isolated. Therefore, we confirmed the generation of **5** by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy at -30°C.

[J. Chem. Soc., Chem. Commun., 2107-2108 (1994)]

[Lab. of Pharm. Chemistry]

**A Novel Synthesis of (*Z*)-Enynes and (*Z*)-Eneidyne from Prop-2-ynyl Alcohols.**

MITSUHIRO YOSHIMATSU, HITOMI YAMADA, HIROSHI SHIMIZU, TADASHI KATAOKA\*

The conjugated (*Z*)-enynes and (*Z*)-eneidyne were synthesized by dehydration of prop-2-ynyl alcohols and diyne alcohols with polyphosphoric acid trimethylsilyl ester, respectively.

[J. Org. Chem., 59, 1011-1019 (1994)]

[Lab. of Pharm. Chemistry]

**A New Method of Generation of  $\alpha$ -Selenocarbenium Ions from *Se,O*-Heteroacetals and Their Reactions.**

MITSUHIRO YOSHIMATSU, TAKASHI SATO, HIROSHI SHIMIZU, TADASHI KATAOKA\*

Various *Se,O*-heteroacetals were prepared by the LiAlH<sub>4</sub> reduction of diselenides **1** followed by alkylation with methoxymethyl chloride or (2-methoxyethoxy)methyl (MEM) chloride. Olefinic and acetylenic  $\alpha$ -selenocarbenium ions were generated by the selective C-O bond cleavage of *O*-(2-methoxyethyl)-*Se,O*-heteroacetals with titanium(IV) chloride and cyclized to give the seleno heterocyclic compounds. Olefinic MEM-selenides underwent the *endo*-mode cyclization to afford 4-chloroselenacycloalkanes in good yields, whereas acetylenic MEM-selenides underwent the *exo*-mode cyclization to give 3-(1-chloroalkylidene) selenacycloalkanes.