[Heterocycles, **38**, 2165-2169 (1994)] [Lab. of Pharm. Synthetic Chemistry]

Novel Ring Expansion Reaction of Epoxides and Oxetanes Accompanied by Rearrangement of Ethereal Functional Groups.

AKICHIKA ITOH, YUKIHIRO HIROSE, HIROTAKA KASHIWAGI, YUKIO MASAKI*

Small cyclic ethers, epoxides and oxetanes, possesing ethereal groups on the side chain, were found to rearrange by means of Lewis acid catalysts, $BF_3 \cdot Et_2O$, to give ring expanded cyclic ethers accompanied by transfer of the ethereal groups. Formation of tetrahydrofuran and pyran ring and transposition of benzylic and allylic groups of the ethereal function were observed to be favorable.

[Tetrahedron Lett., **35**, 7961-7964 (1994)] [Lab. of Pharm. Synthetic Chemistry]

Dicyanoketene Acetals, a Novel Type of π-Acid Catalyst for Monothioacetalization of Acetals.

TSUYOSHI MIURA, YUKIO MASAKI*

Dicyanoketene acetals such as dicyanoketene dimethyl acetal and ethylene acetal are introduced to be a novel type of π-acid catalyst for the monothioacetalization of acetals. Particularly, the catalytic activity of dicyanoketene ethylene acetal was found to be superior to that of tetracyanoethylene and chemoselective in the crossover reaction of the monothioacetalization of a ketone-, an aldehyde-acetal and an alcohol THP-ether providing a ketone monothioacetal favorably.

[Chem. Pharm. Bull., **42**, 2625-2628 (1994)] [Lab. of Pharm. Synthetic Chemistry]

Synthesis and Investigation of C2-Symmetric Optically Active Pyrrolidinium Salts as Chiral Phase-Transfer Catalysts.

MIN SHI, KENICHI KAZUTA, YUKIHIRO SATOH, YUKIO MASAKI*

C2-Symmetric optically active pyrrolidinium salts were synthesized by the reaction of 2,3:4,5-di-*O*-benzylidene-(3*R*,4*R*)-dihydroxy-(2*S*,5*S*)-bis(hydroxymethyl)pyrrolidine, (3*R*,4*R*)-dimethoxy-(2*S*,5*S*)-bis(methoxymethyl)pyrrolidine, 2,3:4,5-di-*O*-benzylidene-(3*R*,4*R*)-dihydroxy-*N*-(2-hydroxyethyl)-(2*S*,5*S*)-bis(hydroxymethyl)pyrrolidine, and (3*R*,4*R*)-dimethoxy-N-(2-hydroxyethyl)-(2*S*,5*S*)-bis(methoxymethyl)pyrrolidine with methyl iodide or α,ω-dibromoalkanes. They exhibited low chiral induction activity in the epoxidation of chalcone and in the Darzens condensation of *p*-chlorobenzaldehyde and phenacyl chloride under phase-transfer conditions.