

[Heterocycles, **38**, 2165-2169 (1994)]

[Lab. of Pharm. Synthetic Chemistry]

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

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Small cyclic ethers, epoxides and oxetanes, possessing etheral groups on the side chain, were found to rearrange by means of Lewis acid catalysts, $\text{BF}_3 \cdot \text{Et}_2\text{O}$, to give ring expanded cyclic ethers accompanied by transfer of the etheral groups. Formation of tetrahydrofuran and pyran ring and transposition of benzylic and allylic groups of the etheral function were observed to be favorable.

[Tetrahedron Lett., **35**, 7961-7964 (1994)]

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

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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)]

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

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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.