

## RESEARCH ACTIVITIES VII

### Coordination Chemistry Laboratories

Prof. Nobuhiro Tokito, Prof. Kiyotaka Onizuka took the position of Laboratory of Coordination Bond from April 2001. Prof. Takuzo Aida (Tokyo University) and Assoc. Prof. Kaku Hamachi (Kyushu University) finished their term as Adjunct Prof. of the Synthetic Coordination Chemistry in March 2001. Their effort during their term is gratefully appreciated. Prof. Isao Taniguchi (Kumamoto University) and Assoc. Prof. Yasutaka Tanaka (Shizuoka University) continue the position of the Synthetic Coordination Chemistry.

#### VII-A A Diversity-Based Approach to Novel Chiral Units

Catalytic asymmetric reactions have attracted significant interest for their synthetic utility. One of the most exciting and challenging subjects in research on the catalytic asymmetric synthesis is development of the novel and basic chiral units. Homochiral organic molecules bearing hetero atoms (*e.g.* nitrogen, phosphorus, *etc.*) occupy a prominent position in organic chemistry as both useful synthetic reagents and molecules of biological interest. Highly functionalized optically active bicyclic amines having a pyrrolo[1,2-*c*]imidazolone framework were identified as effective chiral agents through a diversity-based approach to new chiral amine catalysts.

##### VII-A-1 A Parallel Preparation of A Bicyclic *N*-Chiral Amine Library and Its Use for Chiral Catalyst Screening

**UOZUMI, Yasuhiro; MIZUTANI, Kanako; NAGAI, Shin-ichi**

[*Tetrahedron Lett.* **42**, 407 (2001)]

A parallel library of optically active bicyclic tertiary amines bearing *N*-chiral bridgehead nitrogen atoms was readily prepared by condensation of primary amines, cyclic amino acids, and aldehydes. The enantiocontrolling ability of each of the library members was examined for the asymmetric alkylation of benzaldehyde with diethylzinc, and (3*R*,6*R*,7*aS*)-(2,3-diphenyl-6-hydroxy)hexahydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one, which contains  $\beta$ -amino alcohol unit, showed high enantioselectivity.

##### VII-A-2 Enantioselective Desymmetrization of Meso-Cyclic Anhydrides Catalyzed by Hexahydro-1*H*-pyrrolo[1,2-*c*]imidazolones

**UOZUMI, Yasuhiro; YASOSHIMA, Kayo; MIYACHI, Takamasa; NAGAI, Shin-ichi**

[*Tetrahedron Lett.* **42**, 411 (2001)]

Enantioselective desymmetrization of meso compounds is a powerful synthetic means of preparing enantiomerically enriched products where plural stereogenic carbon centers are generated in one step. Enantioselective ring opening of meso cyclic anhydrides is one of the cases. Asymmetric methanolysis of meso cyclic carboxylic anhydrides including hexahydrophthalic anhydride proceeded in toluene in the presence of (6*R*,7*aS*)-(2-aryl-6-hydroxy)hexahydro-1*H*-pyrrolo[1,2-*c*]imidazol-1-one to give the corresponding desymmetrized mono ester acids (*e.g.* (1*S*,2*R*)-2-(methoxycarbonyl)-cyclohexane-1-carboxylic acid) with enantiomeric excesses of up to 89%.

#### VII-B Catalysis in Aqueous Media by Using of Amphiphilic Polymer-Supported Catalysts

Catalytic organic transformations in water using recyclable immobilized catalysts is an important goal in synthetic organic chemistry. We recently reported that several palladium-catalyzed reactions, including  $\pi$ -allylic substitution, carbonylation, the Heck reaction, and Suzuki-Miyaura cross-coupling, took place in water by use of palladium-phosphine complexes bound to an amphiphilic polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) resin. A chiral palladium complex and a quaternary ammonium salt immobilized on PS-PEG resin were designed and prepared, respectively. Allylic alkylation and Michael addition were investigated by using the resin-supported catalysts in water.<sup>aa</sup>

**VII-B-1 Catalytic Asymmetric Allylic Alkylation in Water with a Recyclable Amphiphilic Resin-Supported *P,N*-Chelating Palladium Complex**

UOZUMI, Yasuhiro; SHIBATOMI, Kazutaka

[*J. Am. Chem. Soc.* **123**, 2919 (2001)]

A novel *P,N*-chelate chiral ligand, (3*R*,9*aS*)-(2-aryl-3-(2-diphenylphosphino)phenyl)-tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one was designed, prepared, and immobilized on an amphiphilic polystyrene–poly(ethylene glycol) graft copolymer (PS–PEG) resin. A palladium complex of the PS–PEG resin-supported *P,N*-ligand catalyzed the allylic substitution of both cyclic and acyclic allylic esters in water with high enantioselectivity. Reactions of cyclopentenyl, cyclohexenyl, and cycloheptenyl carbonates with dialkyl malonate gave the corresponding alkylated products with enantiomeric excess ranging from 89 to 98% ee. The PS-PEG supported Pd complex was readily recovered by simple filtration and reused without loss of catalytic activity or enantioselectivity.

**VII-B-2 Michael Reactions in Water Using Amphiphilic Resin-Supported Quaternary Ammonium Hydroxides**

SHIBATOMI, Kazutaka; NAKAHASHI, Toshiyuki; UOZUMI, Yasuhiro

[*Synlett* 1643 (2000)]

Quaternary ammonium hydroxides were immobilized on a polystyrene–poly(ethylene glycol) copolymer resin. The amphiphilic polymer-supported ammonium hydroxides catalyzed Michael reaction of cyclic  $\beta$ -keto esters with several Michael acceptors in water to give corresponding adducts in high yields.