

# Division of Synthetic Chemistry - Synthetic Organic Chemistry -

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## Visitors

Prof RUANO, Garcia Universidad Autónoma de Madrid, Spain, 21 August 2006

Prof MA, Shengming Shanghai Institute of Organic Chemistry, China, 8 November 2006

## Scope of Research

The research interests of the laboratory include the development of advanced molecular transformation, total synthesis of biologically active products, and molecular recognition. Programs are active in the areas of asymmetric alkylation of carbonyl compounds based on “memory of chirality”, nucleophilic catalysis for fine organic syntheses, synthesis of unusual amino acids and nitrogen heterocycles, visualization of molecular information by functional phenolphthaleins, synthesis and properties of homochiral oligonaphthalenes, and the structural and functional investigation of heterochiral oligomers.

## Research Activities (Year 2006)

### Presentations

Some Aspects of Asymmetric Synthesis under Environmentally Benign Conditions, Kawabata T, IUPAC Second International Symposium on Green/Sustainable Chemistry, 12 January 2006.

Highly Regioselective Acylation of Sugars by Chiral Nucleophilic Catalysts, Kawabata T, The 8th International Symposium on Organic Reactions, 24 April 2006.

Structural and Functional Investigation of D,L-Oligomers, Kawabata T, International Molecular Chirality Conference (MC 2006), 18 May 2006.

Toward the Development of Chiral 2-Metallabiphenyls, Kawabata T, 7th Tetrahedron Symposium, 26 May 2006.

Direct Regioselective Acylation of Sugars by  $C_2$ -Symmetric Chiral Nucleophilic Catalysts, Muramatsu W,

IUPAC International Conference on Biodiversity and Natural Products (ICOB-5 & ISCNP-25), 24 July 2006.

Regioselective Acylation of Sugars by Nucleophilic Catalysis, Kawabata T, 45th Tutzing Symposium: Organocatalysis, 10 October 2006.

Enolate Chemistry at Room Temperature Using Metal Hydroxides, Moriyama K, The 10th International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC-10), 16 November 2006.

Phenolphthalein-based Chemosensors for Diamines and Unprotected Dipeptides in Water, Tsubaki K, The 3rd Seoul-Kyoto-Osaka Joint Symposium on Pharmaceutical Sciences for Young Scientists, 27 November 2006.

### Grants

Kawabata T, Fine Organic Synthesis by Nucleophilic

## Regioselective Acylation of Sugars by Nucleophilic Catalysis

Direct regioselective functionalization of multi-functionalized substrates is one of the goals of current research toward the development of advanced molecular transformation for the next generation. We report here a highly regioselective acylation of sugars with chiral nucleophilic catalysts. Treatment of a glucose derivative with 1 mol% of a catalyst and 1.1 mol eq. of isobutyric anhydride in chloroform at  $-20^{\circ}\text{C}$  gave the 4-acylated glucose derivative and the 3-acylated surrogate in a 99:1 ratio in 98% yield. The corresponding 6-isomer, 2-isomer, and the di-acylated isomers were not detected at all. The corresponding reaction with 10 mol% of DMAP proceeded in a random way, giving 6-, 4-, 3-, and 2-isomer in a ratio of 38:23:38:1 in a combined yield of 69% together with 19% of the di-acylated isomers and 10% recovery. Thus, discrimination of four hydroxyl groups of the glucose derivative has been achieved by the catalyst through fine dynamic molecular recognition.

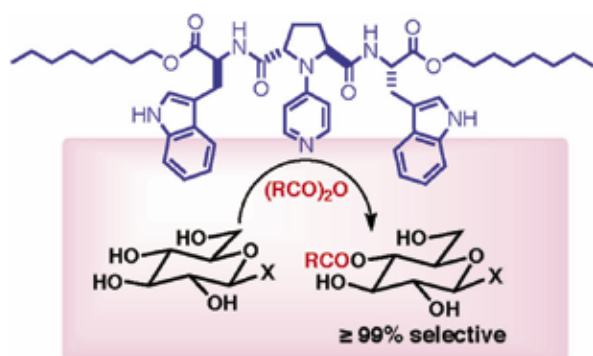
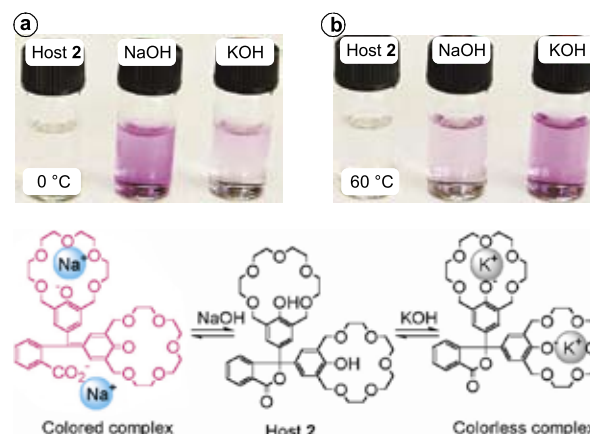


Figure 1. Regioselective Acylation of Sugars with a Nucleophilic Catalyst.

## Bidirectional and Colorimetric Recognition of Sodium and Potassium Ions

Host **2** exhibits fascinating and opposite behavior toward sodium and potassium depending on temperature. Coloration caused by the interaction between **2** and NaOH increased as the temperature decreased (a). In contrast, coloration increased as the temperature increased for **2** and KOH (b). The different behaviors for coloration are assumed to be the result from bidirectional complexation. Complexation between **2** and NaOH preferentially gives a colored carboxylate complex, while that between **2** and KOH leads to a colorless complex with a lactone functionality. Why does the colorless complex dominates in the case of **2** and  $\text{K}^+$ ? One possible explanation is that potassium ion is strongly inclined to occupy the seat of the *pseudo* phenol 18-crown-6 rings. Occupation of the seat may be favored even with sacrificing the conjugation between two phenol crown rings.



Catalysis, Grant-in-Aid for Scientific Research (A), 1 April 2006–31 March 2009.

Kawabata T, Advanced Molecular Transformation with Functional Carbanions, Grant-in-Aid for Scientific Research on Priority Areas, 1 October 2005–31 March 2009.

Tsubaki K, Construction of Molecular Recognition System in Water and Rapid Quantification of Polyamines, Grant-in-Aid for Scientific Research (B), 1 April 2006–31 March 2009.

Tsubaki K, Synthesis and Properties of Optically Active Oligonaphthalene Derivatives, Grant-in-Aid for Exploratory Research, 1 April 2005–31 March 2007.

Kawabata T, Synthesis of Highly Functionalized Heterocycles by Asymmetric Cyclization via Memory of Chirality, Grant-in-Aid for Scientific Research, 30 September 2005–29 September 2007.

### Awards

Kawabata T, Tetrahedron Letters Most Cited Paper 2003–2006 Award, Elsevier Ltd., 10 September 2006.

Moriyama K, Best Poster Award, The Society of Synthetic Organic Chemistry, Japan, 14 September 2006.

Sue D, Best Poster Award, The Society of Functional Host-Guest Chemistry, Japan, 1 December 2006.