

DEVELOPMENT OF RARE-METAL-FREE SYNTHETIC METHODS USING NEW IODINE REAGENTS

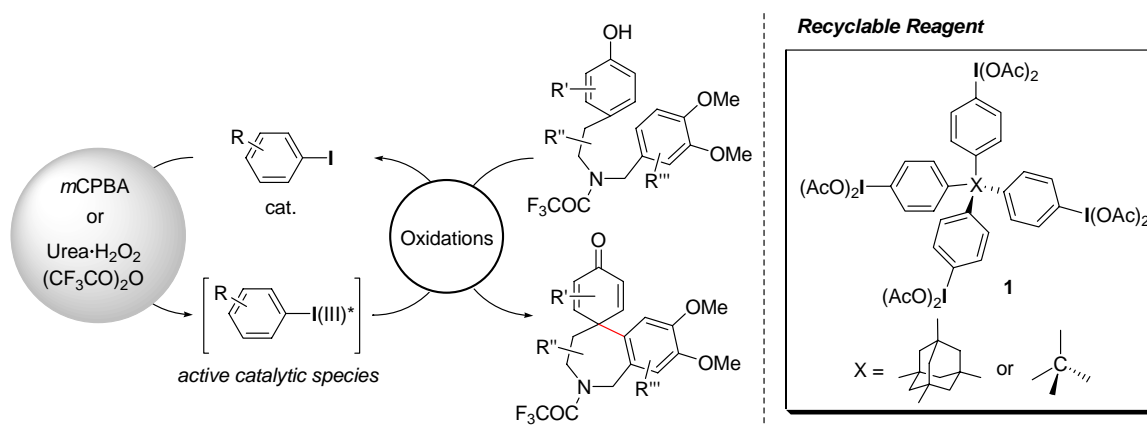
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Oxidation is synthetically important as functional group transformation and bond-forming method, and hypervalent iodines are one of the promising reagents for development of environmentally benign oxidations due to their low toxicities and easy handling. Our research purpose is to enhance the synthetic values of the reagents as useful alternatives to highly toxic heavy metal oxidants and even rare-transition metals, by pioneering their efficient utilization methods and unique new reactivities.

1. Development of New Recyclable Reagents **1** and Their Catalytic Utilizations

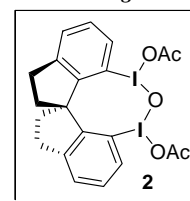
We have designed the new recyclable reagents **1** with adamantane or methane cores having four reactive iodine(III) sites in the molecules. We have confirmed that **1** are practical recyclable reagents that are recoverable by simple washing by methanol after reactions, and possess high reactivities and stabilities against degradation loss during the operations. In this investigation, we noted that *m*CPBA works as an efficient stoichiometric co-oxidant for *in situ* regeneration of **1**, and thus have succeeded in a catalytic utilization of the hypervalent iodine reagents **1** in a variety of useful phenolic oxidations.



2. Design of a Chiral Reagent **2** and Reactions for Asymmetric Oxidations

Asymmetric induction by hypervalent iodine reagents control is a challenging work, and no effective chiral reagents have been appeared thus far. We have designed a new chiral reagent **2** having rigid spirobiindane backbone, and applied it for the first time in highly enantioselective asymmetric oxidations of naphthols.

Chiral Reagent



3. Survey of New Reactivities: Direct Carbon-Hydrogen Bond Functionalizations

We have developed several rare-metal-free direct functionalization methods of carbon-hydrogen bonds using $\text{PhI}(\text{OAc})_2$ (PIDA) and $\text{PhI}(\text{OCOCF}_3)_2$ (PIFA), by inducing selective one- or two-electron oxidations through unique ionic or radical pathways.

