

The Fourth Green and Sustainable Chemistry Award

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Development of Atom-Economical Catalytic Reactions - A Creation of Activation Method of Unreactive Bonds -

One of the goals of synthetic organic chemistry is to provide new and/or useful materials to societies. The development of processes for the removal of byproducts and reducing final waste disposal are important issues. Most importantly, the exploration of new catalytic reactions that are economical in atom count is necessary. Even though such reactions are not directly related to waste disposal, they may have an impact on such processes. The development of reactions that involve new concepts, methodologies, and the discovery of new phenomenon, in order to stimulate significant development of technology, are indispensable for the area of green sustainable chemistry. The focus of our present work is on the creation of new methods for activating unreactive bonds or functional groups, which have not been utilized in chemical reactions, and the application of such research to new catalytic reactions with a 100% atom economy.

The reaction of imidazoles with carbon monoxide and olefins in the presence of $\text{Ru}_3(\text{CO})_{12}$ resulted in regioselective acylation at the 4-position (α to the sp^2 nitrogen). No other regioisomers were formed. The reaction is 100% atom economical, but the most importantly, it involves C-H bonds, which have been believed to be unreactive, can function as a functional group by taking advantage of the coordination of a directing group (the sp^2 nitrogen) to the catalyst. In other words, the reaction does not waste any functional groups, in contrast to the case in substitution reactions. C-H Bonds can be viewed as a functional group. The coordination of the nitrogen to the catalyst is a key step and this methodology is applicable to a wide variety of sp^2 -nitrogen-containing heterocycles. The reaction of benzimidazoles results in the carbonylation of a β C-H bond to the sp^2 nitrogen, however, the carbonylation takes place at a γ C-H bond to the sp^2 nitrogen (ortho position) in the reaction of 2-phenylpyridine derivatives. The carbonylation at the δ -position also is feasible and, not only unsaturated C-H bonds, but also even saturated C-H bonds undergo carbonylation.

Other transformations with a 100% atom economy, such as the skeletal reorganization of enynes and carbonylative cyclization, have also been developed. These reactions involve the generation of electron-deficient species, which are formed by the electrophilic addition of metal halides to acetylenes, and the generation of metalacycles from carbon-oxygen double bonds of aldehydes, ketones, and esters, respectively, as key steps. The reaction of diynes with carbon monoxide with H_2O in the presence of $\text{Ru}_3(\text{CO})_{12}$ gives rise to catechols. This reaction is a rare example for the successive incorporation of two molecules of carbon monoxide into an organic molecule and involves the new activating method of carbon monoxide.

All the reactions described above are atom-economical and new catalytic transformations. They involve the novel creative activation method of unreactive bonds. These methodologies can be expected to be adopted as an innovative methodology.