VII-B Development of New Carbonylation Reactions

Carbonylation reactions are recognized as useful and reliable transformations for the preparation of a variety of carbonyl compounds, such as aldehydes, ketones, esters, lactones, and lactams. Our research effort is directed towards the discovery of *novel* type of the catalytic carbonylation reactions; (i) direct carbonylation at C–H bonds and (ii) cycloaddition reaction using carbon monoxide as a one-atom assembling unit (carbonylative cycloaddition reaction).

VII-B-1 $Ru_3(CO)_{12}$-Catalyzed C–H/CO/Olefin Coupling of *N*-Pyridylindolines. Direct Carbonylation at a C–H Bond δ to the Pyridine Nitrogen

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[*J. Org. Chem.* **67**, 7557–7560 (2002)]

The reaction of *N*-pyridylindolines with CO and ethylene in the presence of $Ru_3(CO)_{12}$ results in direct carbonylation at a C–H bond δ to the pyridine *sp*^{2} nitrogen, which represents a new type of C–H/CO/olefin coupling. The presence of a pyridine ring as a directing group on the substrates is essential for the reaction to proceed. The choice of *N*,*N*-dimethylacetamide (DMA) as the solvent is crucial for the reaction to proceed efficiently.

VII-B-2 Ruthenium-Catalyzed Reaction of α,β-Unsaturated Imines with Carbon Monoxide and Alkenes Leading to β,γ-Unsaturated γ-Butyrolactams: Involvement of Direct Carbonylation of Olefinic C–H Bonds as a Key Step

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[*J. Org. Chem.* **67**, 7014–7018 (2002)]

The reaction of α,β-unsaturated imines with CO and alkenes in the presence of $Ru_3(CO)_{12}$ as a catalyst results in a three-component coupling reaction that gives α,α-disubstituted β,γ-unsaturated γ-butyrolactams. The reaction proceeds *via* a two-step sequence involving the initial formation of ketone derivatives by catalytic carbonylation at the β-olefinic C–H bonds of α,β-unsaturated imines, followed by the (uncatalyzed) intramolecular nucleophilic attack of the imine nitrogen on the ketonic carbon to generate a tetrahedral intermediate, which then undergoes a 1,2-ethyl migration. The reaction of a cyclic unsaturated imine, derived from the reaction of (1*R*)-(–)-myrtenal with *tert*-butylamine, gives a β-aminocyclopentene derivative, which is formed by an aldol-type condensation of the initially formed ketone, indicating the initial formation of ethyl ketone.

VII-B-3 Ruthenium-Catalyzed Carbonylative Cycloaddition of α-Keto Lactones with Alkenes or Alkynes: The Participation of an Ester-Carbonyl group in Cycloaddition Reactions as the Two-Atom Assembling Unit

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[*J. Org. Chem.* **68**, 1591–1593 (2003)]

The reaction of benzofuran-2,3-dione derivatives with CO and alkenes (or alkynes) results in a carbonylative [2+2+1] cycloaddition in which the ester-carbonyl group is incorporated into a two-atom assembling unit to give spirolactone derivatives. This reaction provides the first example of an ester-carbonyl group participating in a carbonylative cycloaddition reaction.

VII-B-4 Palladium-Catalyzed Carbonylation of 2-(Propargyl)allyl Phosphates Leading to Highly Unsaturated γ-Lactones

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[*Angew. Chem. Int. Ed.* **42**, 1397–1399 (2003)]

The reaction of 2-(propargyl)allyl phosphates with CO in THF in the presence of $[(\eta^3\text{-allyl})PdCl]_2$ and dicyclohexylmethylamine results in the incorporation of two molecules of CO to give highly unsaturated bicyclic lactones in good to high yields. The reaction proceeds smoothly even under an ambient pressure of CO. The experimental data indicates the formation of π-allyl palladium complexes.

VII-C Development of $GaCl_3$-Catalyzed Reaction

We have interested in the development of new catalytic reactions based on a unique reactivity of $GaCl_3$. $GaCl_3$ is a Lewis acid, however it has higher affinity toward an alkyne than oxygen, unlike common Lewis acids, such as $AlCl_3$ and $TiCl_4$. We have already reported that the skeletal reorganization of enynes leading to 1-vinylcycloalkenes is achieved by the presence of a catalytic amount of $GaCl_3$ by taking advantage of a high affinity of $GaCl_3$ toward an alkyne (*J. Am. Chem. Soc.* **124**, 10294–10295 (2002)). Utilization of its lower oxophilicity would have a new possibility to explore new catalytic reactions.

VII-C-1 A $GaCl_3$-Catalyzed [4+1] Cycloaddition of α,β-Unsaturated Carbonyl Compounds and Isocyanides Leading to Unsaturated γ-Lactone Derivatives

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A $GaCl_3$-catalyzed reaction of α,β-unsaturated ketones with isocycanides leading to the formation of unsaturated lactone derivatives is described. This is the first example of the catalytic [4+1] cycloaddition of α,β-unsaturated ketones and isocycanides. $GaCl_3$ is an excellent catalyst due to its lower oxophilicity, which is desirable for all of the key steps, such as *E*/*Z* isomerization, cyclization, and deattachment from the products.