

VII-F Development of New Carbonylation Reactions

Carbonylation is recognized as one of useful, reliable, and powerful synthetic methods of carbonyl compounds, such as aldehydes, ketones, esters, lactones, and so on. 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-F-1 Ru₃(CO)₁₂-Catalyzed Coupling Reaction of *sp*³ C–H Bonds Adjacent to a Nitrogen Atom in Alkylamines with Alkenes

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Catalytic reactions which involve the cleavage of an *sp*³ C–H bond adjacent to a nitrogen atom in *N*-2-pyridynyl alkylamines are described. The use of Ru₃(CO)₁₂ as the catalyst results in the addition of the *sp*³ C–H bond across alkene bond to give the coupling products. A variety of alkenes, including terminal, internal, and cyclic alkenes, can be used for the coupling reaction. The presence of directing groups, such as pyridine, pyrimidine, and an oxazoline ring, on the nitrogen of the amine is critical for a successful reaction. This result indicates the importance of the coordination of the nitrogen atom to the ruthenium catalyst. In addition, the nature of the substituents on the pyridine ring has a significant effect on the efficiency of the reaction. Thus, the substitution of an electron-withdrawing group on the pyridine ring as well as a substitution adjacent to the *sp*² nitrogen in the pyridine ring dramatically retards the reaction. Cyclic amines are more reactive than acyclic ones. The choice of solvent is

also very important. Of the solvents examined, 2-propanol is the solvent of choice.

VII-F-2 Catalytic Carbonylation Reactions of Benzyne Derivatives

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Carbonylation reactions of benzyne are described. The treatment of 2-trimethylsilylphenyl trifluoromethanesulfonate (**1**) with CsF and a catalytic amount of Co₄(CO)₁₂ in CH₃CN at 10 atm of CO at 60 °C gives anthraquinone (**2**). The product **2** consists of two molecules of benzyne, which is generated from the reaction of **1** with CsF, and two molecules of CO. The use of substituted benzyne precursors gives a nearly 1:1 mixture of regioisomers, indicating that a benzyne mechanism is operating. The reaction of **1a** with allyl acetate under CO (1 atm) in CH₃CN in the presence of [(π -C₃H₅)PdCl]₂, dppe, and CsF at 80 °C gives 2-methyleneindanone (**3**). The results on the reaction of substituted benzyne precursors clearly support the intervention of a free benzyne or similar species. The present reaction demonstrates the first example of the catalytic carbonylation of benzyne.

VII-G Development of Cycloisomerization Reactions

Cycloisomerization of enynes is useful methods for the construction of various ring systems from structurally simple acyclic starting materials. An issue critical to the synthetic utility of the cycloisomerization is whether complete conversion with formation of only one product can be attained, because difficulty in separation of the unreacted starting material from the product is foreseen. Simple metal halides, such as [RuCl₂(CO)₂]₂, PtCl₂, [IrCl(CO)₃]_n, and AuCl₃ was found to be the effective catalyst for the skeletal reorganization of enynes. The catalysis is initiated by the electrophilic addition of these metal halides to alkynes. This project focuses on the development of new catalytic reaction that consists of the new activation method of C–C triple bonds by metal halides.

VII-G-1 Cycloisomerization of ω -Aryl-1-Alkynes: GaCl₃ as a Highly Electrophilic Catalyst for Alkyne Activation

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Cycloisomerization of a variety of ω -aryl-1-alkynes, where ω = 5 or 6, in the presence of a catalytic amount of GaCl₃ provided dihydronaphthalene derivatives or dihydrobenzocycloheptenes, respectively, in high yields. The reactions of the substrates containing electron-withdrawing groups on the aromatic ring were

significantly improved with GaCl_3 catalyst, compared with the previously reported catalytic system.