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Development of Carbon Dioxide Incorporation Reaction Using Nickel Complexes and Its Application to the Synthetic Organic Chemistry

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Carbon dioxide (CO₂) is regarded as an important source of C1 due to its abundant reserve and low toxicity. Hence, the development of transition metal-catalyzed reaction for CO₂ incorporation onto organic molecules is of great importance and interest. With the aim of developing novel CO₂ incorporation reactions, we have investigated nickel-mediated or -catalyzed processes by utilizing characteristic properties of low-valent nickel complexes, which can activate carbon-carbon multiple bonds. The results are summarized as follows.

1. Multicomponent Coupling CO₂ Incorporation Reactions into Carbon-Carbon Multiple Bonds

In the presence of a zero-valent nickel complex and DBU, various alkynes reacted with CO₂ and an organozinc reagents through addition of CO₂ and an organozinc reagent to a carbon-carbon triple bond to provide α,β -unsaturated carboxylic acids. On the other hands, 1,3-dienes and 1-trimethylsilyllallenes provided dicarboxylic acids through addition of two equivalent of CO₂ by using dimethyl zinc under the similar conditions. These novel alkylative and double carboxylation reactions proceeded in region- and stereo selective manners, and these methods could be applied to natural products synthesis.

2. Carboxylative Cyclization of α,β -Unsaturated Compounds

In the presence of catalytic amounts of Ni(acac)₂ and PPh₃, various bis-1,3-dienes smoothly reacted with CO₂ and an organozinc reagent under mild conditions. This process was accompanied by carbocyclization followed by alkylation by an organozinc reagent to afford cyclic carboxylic acids with high selectivities. The reaction could be carried out in an enantioselective manner by using MeO-MOP as a chiral ligand. 1,6- and 1,7-enynes also provided carboxylative cyclization products in the presence of a nickel complex.