学位論文の要旨		
Abstract of Thesis		
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Studies on Transition-Metal-Catalyzed Decarbonylative Transformations of Acyl Fluorides with Alkynes (遷移金属触媒によるフッ化アシルとアルキンの脱カルボニルを伴う変換反応に関する研究)

学位論文の要旨 Abstract of Thesis

In the past decade, acyl fluorides have emerged as powerful building blocks to construct various ketones, biaryls, alkylarenes, heteroarenes, and organometallic compounds, etc. The versatile transformations of acyl fluorides and their easy accessibility from naturally abundant carboxylic acids make them a viable alternative to aryl halides and, even in some cases, potentially superior to aryl halides and other carboxylic acid derivatives. Because acyl fluorides eliminate the requirement for excess bases, they can be compatible with base-sensitive substrates. However, the coupling reaction between acyl fluorides and alkynes remains unexplored.

In this PhD Thesis, the Author focused on the study on decarbonylative transformations of acyl fluorides with alkynes. First, various alkynylsilanes were produced via nickel-catalyzed decarbonylative cross-coupling reactions of acyl fluorides with silylated terminal alkynes. Second, the resulting alkynylsilanes were utilized as coupling partners in the "sila"-Sonogashira–Hagihara reaction with acyl fluorides to furnish an array of unsymmetrical diarylethynes. Finally, a new strategy was developed to synthesize tetrasubstituted alkenylsilanes from readily available starting materials, internal alkynes, acyl fluorides, and silyboranes. This Thesis not only demonstrates the unique property of acyl fluorides to selectively react with silylated terminal alkynes and alkynylsilanes to form various $C(sp^2)-C(sp)$ bonds by tuning the reaction conditions, but also extends the scope of carboxylic acid derivatives as alternatives to aryl halides in three-component coupling reactions.

Chapter 2. Nickel-Catalyzed Decarbonylative Alkynylation of Acyl Fluorides with Terminal Alkynes



As a powerful synthetic method, the Sonogashira-Hagihara reaction has been widely applied to the preparation of an array of conjugated arylethynes and enynes. However, this kind of palladium/copper-cocatalyzed coupling reaction has always been associated with the generation of homocoupled byproducts, and in most cases, aryl and vinyl (pseudo)halides were utilized as coupling partners and expensive palladium was used as the catalyst. In this

Chapter, the Author describes a nickel-catalyzed Sonogashira-Hagihara reaction under copper-free conditions, which succeed in inhibiting the formation of homocoupled byproducts. Moreover, since acyl fluorides, which can be easily prepared from naturally abundant carboxylic acids, were used as the starting materials, a broad substrate scope was achieved, providing a direct method for conversion of acyl fluorides to alkynes.

Chapter 3. Palladium/Copper-Cocatalyzed Decarbonylative Alkynylation of Acyl Fluorides with Alkynylsilanes



As described in Chapter 2, the copper-free Sonogashira-Hagihara reaction was developed to avoid the formation of homocoupled byproduct. Additionally, replacing the terminal alkynes with silylated ethynes in this reaction is also known as the "sila"-Sonogashira-Hagihara reaction. In this Chapter, the Author disclosed the palladium/copper-cocatalyzed "sila"-Sonogashira-Hagihara reaction of acyl fluorides with silylated ethynes in a decarbonylative manner. Since this newly developed method does not require a base, base-sensitive substrates were well tolerated, exhibiting a broad substrate scope. Moreover, benzoyl chloride was also examined as a coupling partner under optimal reaction conditions, but the desired product was obtained in a poor yield, indicating the unique property of acyl fluorides in this transformation.

Chapter 4. Palladium/Copper-Cocatalyzed Arylsilylation of Internal Alkynes with Acyl Fluorides and Silylboranes: Synthesis of Tetrasubstituted Alkenylsilanes by Three-Component Coupling



Tetrasubstituted alkenylsilanes, which are useful precursors of tetrasubstituted olefins and are difficult to synthesize by conventional approaches, can be efficiently prepared by transition-metal-catalyzed three-component coupling reactions. However, the present three-component coupling reactions for the synthesis of tetrasubstituted alkenylsilanes are still limited by electron-rich electrophiles and require strong bases in most cases. In this Chapter, the palladium/copper-cocatalyzed three-component coupling reaction of internal alkynes, acyl fluorides, and silyborances was developed with the assistance of KF. Various acyl fluorides bearing electron-donating and - withdrawing groups were smoothly converted to the desired highly substituted alkenylsilanes. Furthermore, the steric effect of acyl fluorides in this reaction was also investigated. As a result, it was confirmed that increasing the bulk of the substituents of acyl fluorides from Me to Ph, even to a mesityl group did not reduce the yields of the desired products. Moreover, this is the first example of a decarbonylative three-component coupling reaction utilizing acyl fluorides, which expands the scope of carboxylic acid derivatives as alternatives to aryl halides in three-component coupling reactions.