

Abstract of Main Thesis

Title of Thesis

Development of Novel Aryl Coupling Reaction Based on the Single-Electron-Transfer (SET) Oxidation Ability of Iodonium Salts

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Abstract on the Content of the Applicant's Thesis

Carbon-carbon (C-C) bond formations in aromatic compounds are very important to synthesize various series of bioactive compounds, ligands for transition-metal catalysis, and organic devices, etc. Although the cross-coupling reactions are known as useful tool for C-C bond formation between two molecules of aromatic compounds and others, the present methods generally require pre-introduction of some active functional group in carbon group and usage of rare metal catalysis.

On the other hand, a research group of our laboratory has preciously achieved the metal-free direct cross-coupling of two different aromatic compounds by using trivalent iodine reagent. The detailed follow-up studies of the intermediates in this reaction now provide a new active intermediate, that is, "iodonium salts". Accordingly, novel C-C bond formation in aromatic compounds proceeding *via* iodonium salts as intermediates has been investigated this time, which has resulted in the achievements.

In this thesis, three subjects have mainly been discussed; 1) development of efficient and versatile synthesis of diaryliodonium salts, which are useful as active intermediates, 2) coupling reaction of aromatic compounds using the thus prepared diaryliodonium salts, and 3) new coupling of aromatic compounds with silyl enol ethers.

In the first topic, aromatic compounds and hypervalent iodine reagents rapidly condensed by our new method and formed the diaryliodonium salts by using fluoroalcohol as solvent. Based on this strategy, application of peracetic acid as green oxidant has enabled one-pot synthesis of diaryliodonium salts directly from iodoarenes. Next, we have clarified that the polyalkoxybenzene-derived iodonium salts that are readily prepared by the above method can be activated by Lewis acid, promoting arylation with aromatic compounds. The detailed mechanistic study has revealed the order of the reactivity of the iodonium salts in abilities of the single-electron oxidation and ligand transfer. Finally, the concept of the single-electron oxidation mechanism has been extended to other salts, and coupling of aromatic compounds with silyl enol ethers has been achieved by efficiently generating activate iodonium intermediates *in situ*. Further investigation and application of this reaction have enabled the concise synthesis of isoflavone structures that are seen in natural products.