論文 / 著書情報
Article / Book Information

題目(和文)	フォトレドックス触媒によるオ レフィン類からの有機硫黄化合物 の合成法に関する研究
Title(English)	Photoredox catalyzed synthesis of organosulfur compounds from olefins
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学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	化学環境学 専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （工学）
学生氏名： Student’s Name	LI Yanjie	指導教員（主）： Academic Advisor(main)	穐田宗隆
		指導教員（副）： Academic Advisor(sub)	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this thesis, the author describes a series of novel radical reactions for synthesis of organosulfur compounds from olefins by using visible-light-induced photoredox-catalysis.

This thesis consists of five chapters:

In Chapter 1, the author introduces the research background. Radical species which contain unpaired valence electron(s) have many advantages such as mild reaction conditions, different behavior from that of non-radical species, and tolerance to functional groups. However, radical generation by conventional methods has many drawbacks such as requirement of toxic and explosive reagents, UV light, the use of a stoichiometric amount of a reductant or an oxidant, and so on. The visible-light-induced photoredox catalysis has been regarded as useful and green processes because the drawbacks of the conventional methods can be overcome. These photocatalysts include organic dyes and coordination and organometallic compounds. Among them, ruthenium (II) polypyridine complexes and the relevant cyclometalated iridium (III) derivatives show outstanding photochemical properties. Firstly, they can be easily excited by visible light or sunlight. Secondly, the lifetime of the excited state is long enough for chemical transformations. Thirdly, the excited state of photocatalysts can serve either as a single electron oxidant or reductant. Thus, the author decided to develop new radical reactions by visible-light-induced photoredox catalysis by the Ir or Ru complexes. On the other hand, organosulfur compounds are valuable in medicinal and materials science because of their unique features. But green, simple, mild, and effective synthetic methods for them are still

demanded. In the present thesis, the author describes the results obtained to pursue development of new radical synthesis of organosulfur compounds from olefins by photoredox catalysis. In addition, the author reviews synthetic reactions for thioether and pentafluorosulfanylphenyl (SF_5-phenyl) compounds which are useful functional groups in material and medical chemistry. The research goal and the significance of present study are also described.

In Chapter 2, the author describes radical oxy-trifluromethylthiolation of styrenes promoted by using the photoredox catalysis of $Ir(mppy)_3$ (mppy = 2-(pyrid-2-yl)-5-methoxyphenyl). In this reaction, four kinds of SCF_3 reagents were examined, and 1-trifluoromethylthiopyrrolidine-2,5-dione turned out to be the best SCF_3 radical source following the oxidative quenching cycle of the photoexcited $Ir(mppy)_3$ catalyst. SCF_3 radical shows better reactivity toward styrenes which carry electron donating substituents on the benzene ring presumably because of the electrophilic nature of the SCF_3 radical. This reaction affords various β-SCF_3-substituted alcohols and ethers from styrene derivatives through solvolytic processes. In addition, not only terminal but also internal olefins afford the oxy-trifluromethylthiolated products.

In Chapter 3, the author describes radical alkyl- and aryl-thioalkylation of olefins by photocatalysis of $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ ($dF(CF_3)ppy$: 2-(5-trifluoromethylpyrid-2-yl)- 3,5-difluorophenyl, bpy: 2,2’-bipyridine). The photocatalytic reactions of aryl- and alkyl-thioalkyltrifluoroborates followed the reductive quenching cycle to generate the corresponding α-thioalkyl radicals via deboronation, and the resultant α-thioalkyl radicals smoothly reacted with electron-deficient olefins to afford the addition products in moderate to good yields. Electron-deficient terminal olefins and highly electron-deficient internal olefins can be applied to the present dithianylation. For the arylthioalkylation of olefins, the arylthiomethylborates gave the corresponding products in acceptable yields with the formation of a considerable amount of arylthiomethanes as a by-product. For alkylthioalkylation of olefins, alkylthiomethylborate (phenethylthiomethylborate) gave a good result on the electron-deficient terminal and internal olefins presumably

because it owns better nucleophilic property. The present photocatalytic method provides us with a simple and new access to a range of alkylsulfides under mild reaction conditions.

In Chapter 4, the author describes radical SF_5-phenylation of styrenes by the photoredox catalysis following oxidative quenching cycle of the $[Ru(bpy)_3](PF_6)_2$ catalyst. SF_5-phenyliodonium salts, which are easily accessible from the corresponding aryl iodides, serve as the precursors of the SF_5-phenyl radicals. Hydroxy-SF_5-phenylation was first investigated as a representative example of the SF_5-phenylation reactions. As a result, the reaction turned out to be effective for both terminal and internal styrenes, and a variety of functional groups can be tolerant to this reaction. In addition, the solvolytic reaction or deprotonation in other solvents led to the methoxy-, amino-, and Heck-type SF_5-phenylated compounds.

In Chapter 5, the author describes summary and outlook. The author has developed three new synthetic reactions for organosulfur compounds from olefins by the photoredox catalysis. In particular, the useful moieties, such as SCF_3, α-thioalkyl, and SF_5-phenyl groups can be easily incorporated into the target organic skeletons under mild reaction conditions. In addition, these photocatalytic reactions afford a variety of compounds which have great potential applications in the field of medicinal chemistry and material chemistry. On the basis of the results of the present research, the author proposes that development of highly redox-powerful photocatalysts and stable and active radical reagents are challenging problems for synthesis of organosulfur compounds by photoredox catalysis.