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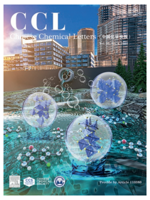

Editorial

Visible light/copper catalysis enabled radial type ring-opening of sulfonium salts

Visible light photocatalytic redox catalysis has become a powerful tool for organic synthesis, and has opened up new avenues for the formation of challenging structural skeletons and chemical bonds. In this respect, diverse photocatalysts, including ruthenium(II), iridium(III), and organic dyes, have been most commonly applied. However, most of these photocatalysts still have some drawbacks, such as lower photostability, potential toxicity, and they are usually expensive as well as environmentally unfriendly, which might hinder their wide applications. As a first-row transition metal, copper is highly economic and low-priced. As an alternative, copper-based photocatalysis has been successfully introduced by Hwang, Lalic, Reiser, Fu, Collins, Peters, Wang, and other research groups. In recent years, research on copper-based photocatalysts has attracted great attention, and various novel photocatalytic organic reactions have been unearthed.

Organosulfur chemistry has attracted increasing attention due to the importance of sulfur-containing compounds in pharmaceuticals, bioactive natural products, and functional materials. Sulfonium salts are common sulfur-containing reagents that have been widely used in synthetic chemistry due to their easy preparation, high reactivity, bench-stable, and broad structural diversity. Traditionally, the chemical transformation of sulfonium salts can be classified as follows: (a) Nucleophilic ring-opening reactions with nucleophiles including Lewis bases and Brønsted bases; (b) Used as one-carbon building blocks for the formation of various ring-sized systems; and (c) transition metal, or visible light-catalyzed desulphurization cross-coupling reactions. Although ionic pathway-based synthetic chemistry of sulfonium salts has been extensively studied, the application of sulfonium salts as radical precursors in radical involved reactions is largely less explored mainly due to lack of controllable and general generation methods. Recently, the research group of Daoshan Yang at Qingdao University of Science and Technology has developed a series of copper- and visible light-promoted radical type ring openings of sulfonium salts with different radical receptors for the formation of various C–C and C-heteroatom bonds (Scheme 1).

Internal alkynes are important skeletons in bioactive molecules, materials and important building blocks in chemical synthesis. In 2023, Yang and co-workers demonstrated an efficient and novel copper-catalyzed Sonogashira reaction bewteen sulfonium salts and alkynes through an anti-Markovnikov ring-opening pathway promoted by visible light/copper catalysis [1]. The coexistence of the phosphorus and nitrogen ligands in the system is the key for the success of this transformation. This radical type ring-opening strategy represents a new reaction mode of sulfonium salts which breaks the restriction that only Brønsted bases and Lewis bases can enable nucleophilic ring-opening reaction of sulfonium salts. Direct difunctionalization of simple alkenes has been treated as a powerful tool for the synthesis of highly functionalized skeletons. In 2023, Yang *et al.* reported a new protocol for the synthesis of α-alkyl-acetophenones from aromatic alkenes and sulfonium salts using $[Cu(TolBINAP)Br]_2$ as a photoredox catalyst, wherein the sulfonium salts serves as alkylating agents [2]. Heterocyclic C–H bond functionalization is an effective strategy for finding effective drugs. In 2022, Yang's group developed a novel radical type *anti*-Markovnikov ring-opening of sulfonium salts with heteroarenes under mild conditions. A detailed mechanistic investigation, involving luminescence quenching expriments, EPR experiments, and kinetic isotope effect experiments was performed to support the proposed plausible mechanism [3]. The development of new alkyl electrophiles for the construction of $Csp^3{-}Csp^2$ bonds through a Heck-like coupling has attracted great interest in synthetic chemistry [4]. Although, great achievements have been made in the synthesis of heterocycles using radical addition/cyclization strategy, developing versatile alkyl radical precursors still remains a huge challenge. In 2024, Yang *et al.* demonstrated an efficient annulation cascade reaction between alkenes and cyclosulfonium salts for the construction of sulfur-containing *N*-heterocycles by visible light/copper catalysis [5]. The C–S bond cleavage/radical cascade reaction affords a variety of corresponding N-heterocycles containing aryl alkyl thioether motifs with good functional group tolerance.

In summary, Yang and co-workers recently reported a series of novel and convenient visible-light-driven copper-catalyzed radical type ring-opening of sulfonium salts with different radical receptors for the formation of various C–C and C-heteroatom bonds under mild conditions. This type of ring-opening mode of sulfonium salts differs fundamentally from the nucleophilic reaction in regioselectivity which will also break the restriction that only Brønsted bases and Lewis bases can enable nucleophilic ring-opening reaction of sulfonium salts. It is highly belive that this strategy will bring new opportunities to sulfonium salt chemistry and copper-based photocatalytic chemistry.

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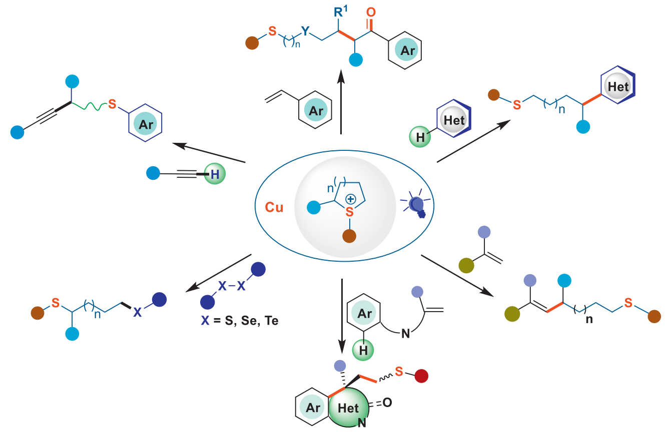

Scheme 1. Visible light/copper catalysis promoted radical type ring openings of sulfonium salts with different radical receptors.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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