

Renaissance of “Photoredox Catalysis” for Organic Molecules

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The concept of “Photoredox Catalysis” for organic molecules was reported by Sakurai and Pac in 1977 [1], and they called it a “Redox-Photosensitized Reaction” in 1978 [2], because they wanted to make sure the difference in redox reactions using TiO_2 was recognized as a “Photocatalyst”. In their studies, a radical cation of phenanthrene (Phen) or a radical anion of 1,4-dicyanobenzene (DCB) serves as an oxidant or a reductant, respectively, through photoinduced electron transfer (PET) between Phen and DCB, to provide unique products. From the 1980s, a lot of similar photoredox organic reactions, mainly with UV irradiation, were developed by Arnold [3], Albini [4], Griesbeck [5], Okada [6], Fukuzumi [7], Mizuno [8], etc. However, the scopes of the substrate, reagent, and product were quite limited, and the control of reactive intermediates, such as radicals and radical ions, was not efficient at this time. Thus, the synthetic application of “Redox-Photosensitized Reaction” to useful organic reactions was unsuccessful. These facts caused a decrease in this type of reports from the latter half of the 1990s. On the other hand, advances in the knowledge of radical reactions using alkyl halides, AIBN, and Bu_3SnH from the 1980s showed that radical reaction is a versatile and powerful tool for the transformation of organic compounds, due to the unique reactivity of radicals, their high tolerance for unprotected functional groups compared to ionic reactions, and the well-established reaction pathway of the generated radicals [9–11]. This is despite environmental problems, such as the toxicity of these substrates and reagents, difficulties associated with the removal of tin-containing byproducts (Bu_3SnX), and harsh conditions (high temperature). Accordingly, there have been efforts to make “Photoredox Catalysis” a more environmentally friendly and cleaner process that can generate reactive species, such as radicals under mild conditions. For example, Yoshimi reported PET-induced decarboxylative alkyl radical generation from aliphatic carboxylic acids using a “Redox-Photosensitized Reaction” system at room temperature in 2007 [12], and, finally, the decarboxylative aryl radical generation of benzoic acids in 2020 [13], which minimize the use of hazardous substances without heating or cooling. MacMillan reported the excellent “Photoredox Catalysis” with visible photoredox catalysts in the 2010s [14], and the number of studies on the visible-light-induced redox reaction rapidly increased. In addition, new technology such as LED and flow reactors that “Photoredox Catalysis” is easily accessible to researchers.

At present, “Photoredox Catalysis” is the most exciting topic in organic chemistry, because photoredox catalysts can provide unique and environmentally friendly processes of organic synthesis. Therefore, this Special Issue aims to illustrate recent developments related to photoinduced reactions with photoredox catalysts. Contributions will focus on a broad range of organic reactions by effective photoredox catalysts.

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