1-8-6. Asymmetric Photochemistry

Overview

Chiral materials are critically important in organic synthetic chemistry because of their potential applications, such as in pharmaceuticals. Recent advancements using organometallic and biological catalysts have garnered significant attention. Asymmetric reactions have also been extensively studied in photochemistry, involving unique conversion processes that complement thermal synthesis; however, the primary focus has traditionally been on reaction mechanisms. In recent years, advancements in light sources, detailed investigations of reaction mechanisms, and the integration of organic catalysts, have resulted in numerous reports of asymmetric photoreactions that are effective in natural product and stereoselective complex syntheses.

Current Status and Frontiers

Numerous studies on asymmetric photochemistry have been conducted due to the growing interest in the aforementioned reaction mechanisms. Since the 1990s, many researchers, including those in Japan, have been at the forefront of this field. For an overview up to the mid-2000s, refer to Section "1-9. Asymmetric Photochemistry" in the Photochemistry DV Report described in Japanese. URL: https://division.csj.jp/div-report/02/0210900.pdf

Recently, technological advancements, such as new light irradiation sources, including LEDs, and the elucidation of reaction mechanisms through computational science, have facilitated the rapid development of asymmetric photoreactions that are valuable in synthetic chemistry. Below, we present representative examples of current research at the forefront of this field.

1. Electron-transfer chiral photoreaction

In recent years, numerous attempts have been made to impart photoreactivity to organic catalysts within this field. In dual catalyst systems that combine ground-state chiral organic catalysts with photoredox catalysts, active radical species are primarily generated through electron-transfer reactions induced by visible light excitation, leading to stereoselectivity. A key challenge is controlling background reactions that lack stereoselectivity. Additionally, efforts have focused on maintaining both stereoselectivity and photoreactivity within a single catalyst by directly exciting the chiral organic catalyst with light irradiation. In such systems, the reactivity and stereoselectivity are expected to differ from those exhibited by ground-state chiral organic catalysts. Previously, it was widely believed that electronically excited states are short-lived and that achieving high asymmetric recognition is challenging. However, recent research has shown that the characteristics of excited-state reactions can be effectively utilized in asymmetric photoreactions, leading to significant advancements in this field.

2. Energy-transfer chiral photoreaction

The electronically excited states specific to photoreactions can be generated either by direct photoexcitation of the substrate or through energy transfer from other excited species. A concept

of asymmetric induction, similar to that described in Section 1, is also being explored in triplet sensitization reactions. This methodology aims to control the stereoselectivity of excited species after energy transfer by incorporating non-covalent interaction sites, such as hydrogen bonds, into the catalyst to regulate molecular orientation. Recently, stereoselective deracemization reactions have garnered emergent and significant attention in this area. For instance, in the catalytic deracemization of optically active allenes, impressive results have been reported, achieving yields of 98% and enantiomeric excess (ee) values of 97% due to selective energy transfer.

3. Supramolecular chiral photoreactions

Chiral supramolecular host-guest complexes and chiral crystals are also utilized in asymmetric photoreactions. Both porous and non-porous environments, such as crystals, clay, and silica, can restrict the reaction free volume in photoreactions, thereby inducing stereoselective reactions. Compounds such as cyclodextrins, cucurbiturils, and palladium nanocages act as effective supramolecular hosts for these chiral photoreactions.

4. Chiral photoreactions controlled by weak interactions

In the system described in Section 3, the supramolecular complex regulates the stereochemistry of the photoreaction. Weak interactions, known as supramolecular interactions, play a crucial role in host-guest dynamics. Recently, these weak interactions have also been utilized in solution-phase photoreactions, leading to the development of new chiral photoreactions. For example, chiral photoreactions that exploit charge-transfer interactions between electron donors and acceptors have garnered significant attention. In these photoreactions, new absorption bands appear on the long-wavelength side due to the interaction, facilitating selective photoexcitation primarily with the complex using visible light. This approach has correspondingly gained great interest from the perspective of green chemistry.

References

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Future Perspectives and Directions

Challenges to be addressed over the next 10 years include the development of more diverse reaction types that achieve both high product yields and optical yields. Collaboration with the fields of chiral nanomaterials science and biofunctional chemistry will be essential for establishing robust scientific theories and foundations. Additionally, there is significant potential for applying these advancements to the asymmetric synthesis of pharmaceuticals and fine chemical products, with an emphasis on environmentally friendly processes.

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