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Invited Review

Chirality and stereoselectivity in photochromic reactions

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ABSTRACT

In this review, the chirality and stereoselectivity in photochromic reactions are broadly discussed.

Stereoselectivity is categorized into the two main areas of enantioselectivity and diastereoselectivity.

Enantioselective photochromism was discussed according to the methods of generating chirality, that is: (1) optical resolution of chiral and racemic compounds, (2) spontaneous separation of racemic compounds during crystallization, (3) chiral template-assisted photochromic reactions to preferentially generate an enantiomer or cause chirality-based events, and (4) the generation of a non-racemic mixture of the photoisomers by irradiation of circularly polarized light to the racemic starting photoisomer.

Diastereoselective photochromism was discussed for each family of photochromic reactions, namely, (1) fulgides, (2) diarylethenes, (3) spiro-compounds, (4) azobenzenes, and (5) organometallic complexes.

Chirality-related reactions in overcrowded alkenes are discussed in a separate chapter. These include: (1) the discovery of the light-driven molecular motor, (2) the first generation of light-driven molecular motors with unidirectional rotation, which have two chiral carbon atoms in a molecule, (3) the second generation of light-driven molecular motors with unidirectional rotation, which have a single chiral carbon atom in a molecule.

Finally, two distinctive novel photochromic systems are introduced in which the reactions proceed stereoselectively, although their enantio- or diastereoselectivity during photochromic reactions have yet to be examined.

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1. Introduction

"Stereoselective reactions" are categorized into two main concepts: enantioselective reactions and diastereoselective reactions. When a reaction produces two stereoisomers and one of them is produced predominantly, the reaction is stereoselective. When the relationship of two compounds with different stereochemistries is as enantiomers to each other, it is "enantioselective". When the two compounds are diastereomers to each other, it is "diastereoselective". Generally, enantioselective reactions occur with non-chiral compounds by introducing one or several chiral factors to a molecule through a chiral environment or chiral reagent to generate enantiomers with a biased ratio, i.e., not 50/50. In contrast, diastereoselective reactions occur with compounds already possessing one or several chiral factors on a molecule and the new chiral factors are introduced by the reactions to generate diastereomers with a biased ratio. Therefore, enantioselectivity refers to the degree of the generation of absolute stereochemistry, whereas diastereoselectivity to the degree of the generation of relative stereochemistry with regard to intrinsic chiral factor(s). In this review, we have denoted the enantioselectivity as "er (Enantiomer Ratio, such as 'an er value of 99/1')" and the diastereoselectivity as "dr (Diastereomer Ratio, such as 'the dr value was 99/1')" [1].

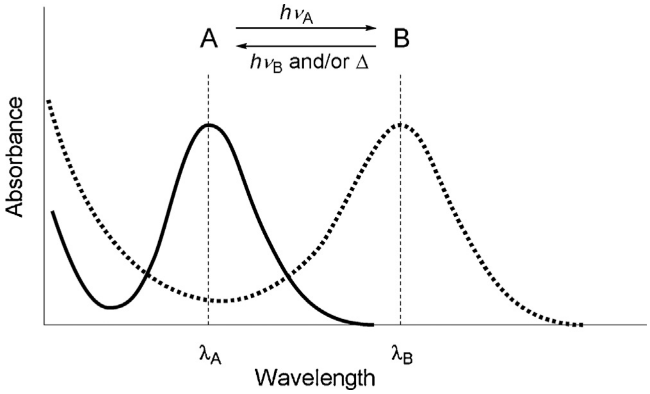

Fig. 1. Schematic absorption spectral change in photochromism.

From the last half of the twentieth century and until the present, countless efforts have been devoted to the development of ground-state stereoselective organic synthesis [2]. However, stereoselective reactions in photochemistry have not received much attention to date, although the recent progress in this field has been remarkable [3–6].

Photochromism is one of the most unique reactions in photochemistry [7–13]. It is defined as the events of photochemically-induced reversible isomerization between two (or more) different compounds possessing substantially different absorption spectra (Fig. 1). When the isomers are thermally stable and revert back to their original state by photoirradiation, they are categorized as "P-type" photochromic compounds. In contrast, when the activation energy of their back reaction is small enough for a return to their original state thermally, they are called "T-type" photochromic compounds [11]. Most, but not all, T-type compounds can also go back photochemically.

Major photochromic reactions are classified according to the reaction modes shown in Fig. 2, and the representative photochromic families are shown in Scheme 1. Except for "*E/Z* isomerization" and "bond cleavage", they all involve the rearrangement of the π-conjugation to make the sp^3 carbon atoms appear and disappear when the photochromic reactions proceed. Since the generation of sp^3 carbon atoms is one of the main reasons for the

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