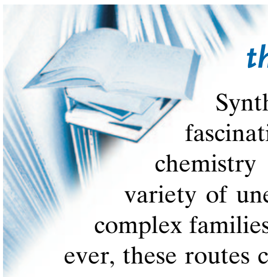

Handbook of Synthetic Photochemistry

Synthetic photochemistry is a fascinating area of organic chemistry and opens up a wide variety of unexpected routes to highly complex families of products. Often, however, these routes can also lead to unexpectedly complex reaction mixtures or can fail to give any conversion at all. This is mostly due to a lack of awareness about the appropriate excitation method: whether by direct excitation or by triplet-energy transfer or electron transfer, choosing the right sensitizer or catalyst, and other reaction conditions. The *Handbook of Synthetic Photochemistry*, edited by Angelo Albini and Maurizio Fagnoni, is a compilation of convincing examples of these diverse excitation routes and the necessary reaction conditions. This handbook demonstrates the potential of synthetic photochemistry, although one cannot expect it to present a comprehensive collection of all known and synthetically relevant processes.

For work on synthetic photochemistry one has to begin by considering basic technical and photophysical conditions (solvents, irradiation reactors and their geometries, lamps, sensitizers, quenchers). These are discussed in a short introductory chapter (Albini), which also presents some basic retrosynthetic concepts for identifying photochemical processes. The first case study relates to photodecarbonylation and photodecarboxylation of simple molecules in the solvent phase and in the solid state (Garcia-Garibay). These processes, as well as photochemical addition to C$-$C multiple bonds (Fagnoni), are highly suitable for the formation of highly substituted C$-$C single bonds.

The photochemical synthesis of ring systems covers 200 pages, and starts with the synthesis of cyclopropanes (Tsuno). The main reactions for this target family are carbene additions, multistage cycloadditions, and rearrangement reactions. For reactions to convert a compound into one of greater complexity (a concept that is, admittedly, not clearly defined), the di-π-methane (DPM) rearrangement and its oxa and aza variants, as well as intramolecular *meta*-photocycloaddition to arenes, are ideal methods. The synthetic possibilities of the DPM rearrangement, as originally developed by Zimmerman, are far from being exhausted. By varying the reactive excited state (sensitization for transfer of energy and electrons as an alternative to direct excitation), by introducing heteroatoms (1-oxa, 1-aza, 2-aza, etc.), or by varying the reaction medium (solution versus solid-state conditions, ionic liquids, chiral environments, zeolites, inclusion compounds) new reactivity patterns are continually being discovered, and even open-chain enones, which for many years were described as unreactive, can be convinced to react.

As expected from orbital symmetry rules, the synthesis of cyclobutanes and heterocyclobutanes are prime examples for photochemical reactions. Consequently, they appear in three different chapters and are described in detail with numerous topical examples: addition of non-activated alkenes to arenes (*ortho*-photocycloaddition reactions) or to other alkenes (Hoffmann), addition of enones to alkenes or to other enones (Bach), and carbonyl-ene photocycloaddition reactions (Abe). Light-induced pathways to larger rings (Pandey, Perez-Prieto, Miranda) are usually initiated by intramolecular H-abstraction or photoinduced electron transfer steps. These processes are particularly important for photochemical aromatic substitution reactions that follow $S_{RN}1$ and S_N1 mechanisms (Arguello).

Chapter 11 deviates somewhat from the general chapter structure, since it explicitly describes one electronically excited reagent, the first excited singlet state of molecular oxygen (Greer). This is definitely justified, as singlet oxygen not only shows a unique reactivity but also is ubiquitous under many reaction conditions. This chapter is further divided according to potential targets: dioxetanes, endoperoxides, allylic hydroperoxides, and the products of tandem photooxygenations. Also this part of the book does not try to be comprehensive, but concentrates on significant examples and topical applications of the products of singlet oxygen photooxygenations. Skeletal rearrangements of heteroaromatic compounds, a group of reactions that are not easily controllable, are described in Chapter 12 (Pace). Finally, the handbook is completed by a highly topical description of photochemically switchable protection groups (Bochet). Especially in this area, light-induced reactions have received attention because light serves as a highly specific reagent to release functional groups.

The book describes many recent applications in different areas of organic photochemistry, with a wealth of up-to-date literature references, and that makes it especially valuable and interesting for all synthetic chemists.

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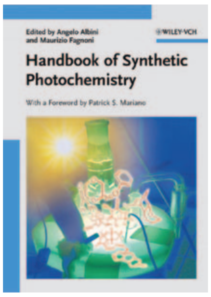
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