Photochemically-Generated Intermediates in Synthesis

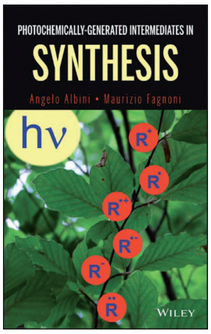
One can reasonably refer to a scientific discipline as “mature” when it is no longer possible to collect the essential material between two book covers. With regard to photochemical organic synthesis, this criterion was already achieved some time ago. The exact time of maturation is difficult to recognize, but there are some clear indications: thus, it is when well-known reaction principles can be applied in a wide range of syntheses without the need for in-depth mechanistic considerations. For the area of organic synthetic photochemistry, the use of aryl cations is a good example. That these highly reactive intermediates are formed during photolysis of aryl diazonium compounds has long been known. However, it was only in the last decade that the use of this reaction, and the generation of aryl cations by photolysis of easily available halogen-substituted arenes, was first investigated, in particular by the authors of the book reviewed here. As another example, the long-established and widely successful use of transition-metal catalysts is beginning to meet unexpectedly strong competition from new applications of photochemical redox catalysis.

In recent years, several comprehensive books and reviews have been published on this topic. This confirms my view that this subject is now scientifically mature and widely applicable. The authors of this book look at this area from another direction, and discuss recent developments in the field of synthetic photochemistry from the perspective of the reaction intermediates involved. Rather than concentrating on the electronically excited states that are present at the beginning of all reactions, or on other electronically excited intermediates, they consider only the ground states, and focus on open-shell intermediates such as free radicals, biradicals, and radical ions, and also closed-shell ionic intermediates and carbenes. Over 1000 literature references, many of them from the period 2000 to 2013, substantiate the relevance of the reactions described in the book, and are evidence of the careful attention to detail in this compilation.

In the first and last chapters, the authors describe basic principles and give valuable information about photochemical techniques (the design of photoreactors, the role of solvent interactions, conventional irradiation sources such as metal vapor lamps, electrical discharge lamps, halogen lamps, and newer light sources such as UV-LEDs, excimer lamps, and solar irradiation facilities), and about the basic methods for generating and manipulating intermediates by photochemical methods (direct homo- or heterolytic cleavage, sensitization, photocatalysis, and photoinduced electron transfer). However, both chapters lack further information about techniques for the determination of structure, energetics, and lifetime of the intermediates, e.g., by static or time-resolved spectroscopic and other kinetic methods. This may be beyond the scope of a textbook, but a tabular compilation of typical data for the intermediates discussed here would have been useful. However, the authors give helpful references. The book’s title might lead to false expectations.

In the central chapters 2–4, the authors describe photochemical reactions in which carbon or heteroatom free radicals, biradicals, or radical pairs are involved. For many examples, the assumptions about the reaction mechanism are justified by results from spectroscopic methods or from radical-specific detection methods, but of course there are many cases where an analogy is sufficient. Carbon radicals can be produced by homolytic cleavage of C–Hal or C–H bonds, by decarboxylation of carboxy radicals, by denitrogenation of azo compounds, or by homolysis of C–S or C–Se compounds. These bond cleavages may be initiated in rare cases also by direct photolysis. Otherwise, transfer radicals can be used, or labile bonds can be incorporated, such as the N–O motif in the case of Barton esters. All methods that generate, as the primary products, two carbon-centered radicals, as in the Norrish Type I and Type II carbonyl reactions, are discussed in the chapters on biradicals and radical pairs. This classification leads to a certain degree of fragmentation, so that reactions that are similar are found in different chapters. Ultimately, however, all the reactions are easy to understand, since the labile bonds and the course of the reaction are clearly identified. Biradicals, a separate chapter, are the most extensively studied photochemically generated intermediates, because they are involved in almost all light-induced cycloadditions, cyclizations, rearrangements, or atom-transfer reactions, especially if initiated from the electronically excited triplet states.

The longest chapter deals with radical ions as intermediates, generated mostly by photoinduced electron transfer (PET). The theory behind these processes, the thermodynamics and kinetics of PET processes, and the use of PET sensitizers, as well as the properties that limit their effectiveness (redox energies, spin states, lifetimes), are not described here; instead, relevant references are cited. The basic processes for PET catalysis are represented by the well-known reaction cycle diagrams. In order to systematize the reaction pathways, which are often complex, the authors start by describing established and intensively studied reaction types such as photo-NOCAS or the photochemical $S_{RN}1$ reaction, which have numerous variations. This



Photochemically-Generated Intermediates in Synthesis
By Angelo Albini and Maurizio Fagnoni. John Wiley and Sons, Hoboken, 2013. 380 pp., hardcover, € 132.00.—ISBN 978-0470915349

leads into the synthetically most powerful and currently most intensively studied applications: additions to or with π-systems, and substitution reactions of aromatic substrates. In the following sections, many current synthetic applications are described, including also organocatalytic versions that can be used for enantioselective additions (enantioselective photoredox catalysis), aromatic ring-closure reactions, aromatic arylations, alkylations, and vinylations. Oxidative heteroatom-initiated PET additions, cycloadditions, and cyclizations (including the synthetically highly valuable iminium ion photochemistry) conclude this chapter. Carbocations and carbanions are treated together in one section. It is important to mention here the contributions of the authors of this book, who have published excellent work in this field.

In summary, this book provides a new and interesting perspective on this highly topical field of organic photochemistry, and it is strongly recommended as a source of motivation for all potential users.

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DOI: 10.1002/anie.201400117