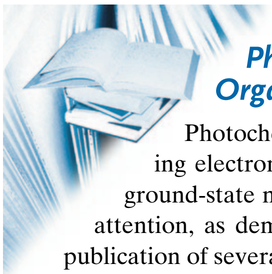


Modern Molecular Photochemistry of Organic Molecules

Photochemical reactions involving electronic (and spin) isomers of ground-state molecules continue to get attention, as demonstrated by the recent publication of several books in this field, e.g., two other books besides this one within the last few months.[1,2] A problem often encountered in connection with photochemical reactions is that they are still considered too "exotic" and unpredictable for wide synthetic application. On the other hand, predicting how an organic molecule will behave upon absorption of light, difficult as that may be, is of crucial importance for introducing photochemical reactions into the armory of synthetic methods. Accordingly, the authors of the present book (Turro, Ramamurthy, and Scaiano, well-known experts in the field) embarked on the ambitious aim of defining the "paradigms for proceeding from the possible to the plausible to the probable photochemical processes", as they state in Chapter 1.

Chapter 2 presents a detailed treatment of the overall configurations of excited states, and the construction of the energy diagrams of such states. This is not the easiest part of the book, but it is mandatory for understanding the interaction of light with matter. It is worth mentioning the didactic value of the presentation, even when treating such difficult topics. Chapters 3–5 are concerned with photophysical processes. These are the main competing paths of a photochemical reaction, and limit the extent to which the absorption of light is productive for a chemical transformation. The chapter includes detailed examples of the deactivation paths (radiative or radiationless transitions) leading back to the ground state, as well as useful generalizations and predictions for identifying the chromophores that are more prone to these processes.

From Chapter 6 on, the authors lay the basis for a theory of molecular organic photochemistry. Plausible reaction pathways are discussed by having recourse to potential energy surfaces and to the modern concepts of conical intersections and funnels as critical regions between an excited-state surface and another surface. It has been recognized that an excited-state molecule can lead to any one of three primary photochemical processes, namely: the formation of an intermediate I (mostly diradical in nature), or the intervention of a funnel (F), or the formation of an excited state of an intermediate or product.

An exhaustive and elegant treatment of energy transfer and electron transfer in photochemistry, both of which are crucial processes for photosynthesis in natural systems, is presented in Chapter 7, where the most interesting part is the explanation and implications of the "normal" and "inverted" regions on the basis of the Marcus theory.

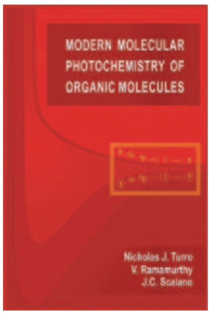
The most innovative part of the book starts from Chapter 8, and is concerned with the possible mechanisms occurring in photochemical reactions and with techniques to detect the intermediates involved. In fact, the main photochemical processes are attributed to the formation of either a radical (whether a biradical, a diradical, or a radical pair) or a zwitterion, except when a funnel is involved. Accordingly, the authors also describe some key characteristics of radicals and the chemistry expected from such species.

At this point, in contrast to the previous book *Modern Molecular Photochemistry* written by Turro more than 30 years ago, the photochemical reactions are discussed according to the chromophore present rather than according to the process occurring. The simple analysis of the photophysical parameters and of the orbital and correlation diagrams of a selected molecule containing a given chromophore enables one to predict which excited state will react, and whether concurrent photophysical paths can have a role.

The authors recognize that in practice most of the photochemical processes arise from just two excited state types, namely the $n\pi^*$ and $\pi\pi^*$ states (either singlet or triplet) that are generated by excitation of carbonyl compounds or olefins, respectively. Accordingly, the photochemistry of other chromophores, including enones and aromatics, can be (in part) rationalized as a particular case of the above two chromophores.

Chapter 9 provides an innovative description of the photoreactions of carbonyl-containing compounds, based on frontier orbital interactions. These photoreactions can be divided into four classes: hydrogen atom abstraction, homolytic cleavage of a C−C bond, addition to a C=C bond, and electron transfer reactions. Some recent advances, such as the work by Garcia-Garibay's group on the photoelimination of CO from crystalline ketones, are not cited. Chapter 10 describes the photochemical reactions of olefins, which, in addition to the processes listed for the C=O bond, include frontier-orbital-controlled reactions such as electrocyclic, sigmatropic, and cycloaddition reactions. Chapter 12 gives a broad overview of the photochemistry that occurs in aromatic molecules. However, the recently reported ArS_N1 reactions via photo-heterolytic cleavage of an Ar−X bond should also have been mentioned.

The book is completed by two chapters on photoreactions in organized media and photoreactions involving singlet oxygen, and the interesting Chapter 15, in which the concepts developed earlier are applied to predict the photochemistry of



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other chromophores (e.g., nitro, azo, and thioketone groups). I strongly recommend this comprehensive and brilliant book to graduate and advanced undergraduate students.

Maurizio Fagnoni
Dipartimento di Chimica Organica
Universitá di Pavia (Italy)

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[1] P. Klan, J. Wirz, *Photochemistry of Organic Compounds*, John Wiley&Sons, Chichester **2009**.
[2] *Handbook of Synthetic Photochemistry* (Eds.: A. Albini, M. Fagnoni), Wiley-VCH, Weinheim **2010**.