

Edited by Angelo Albini  
and Maurizio Fagnoni

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# Handbook of Synthetic Photochemistry

With a Foreword by Patrick S. Mariano



# Handbook of Synthetic Photochemistry

*Edited by*

*Angelo Albini and Maurizio Fagnoni*



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**Handbook of Synthetic Photochemistry**

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*Angelo Albini and Maurizio Fagnoni*

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## Foreword

From its origin over a century ago, organic photochemistry has undergone a transformation from an area of science populated by a few specialized organic and physical chemists to a field that now attracts the interest of members of the broad synthetic organic chemistry community. Along the way, the basic chemical and physical foundations of the science were developed and the full synthetic potential of photochemical reactions of organic substrates has been realized.

The science of organic photochemistry can be traced back to observations made in the nineteenth century, which showed that ultraviolet irradiation of certain organic substances leads to formation of products that have unique and sometimes highly strained structures. An example of this is found in studies in the early 1800s, which demonstrated that irradiation of the naturally occurring, cross-conjugated cyclohexadienone,  $\alpha$ -santonin, in the crystal state induces a deep-seated, multisteped rearrangement reaction. It is fair to conclude that at that time observations like this could only have been attributed to the magic of Nature, since little if anything was known about the fundamental principles of the light absorption process and the relationships between structures and decay pathways of electronic excited states.

The science of organic photochemistry experienced a significant transformation in the middle part of the twentieth century when it began to attract the interest of organic chemists, who were skilled in the use of valence bond theory, and physical chemists, who were able to probe and theoretically analyze the properties of electronic excited states. These efforts led to a basic mechanistic framework for understanding and predicting how electronic excited states of organic substrates undergo reactions to form products. Clear examples of the insight provided by organic chemists during this era are found in ground-breaking investigations performed independently by Zimmerman and Chapman that probed the photochemistry of simple, cross-conjugated cyclohexadienones. The realization that these processes could be described by utilizing Lewis electron-dot-line structures of excited states and reactive intermediates brought organic photochemistry into the intellectual sphere of organic chemists, who already had learned the benefits of writing arrow-pushing mechanisms for ground-state reactions.

Another important contribution to the field of organic photochemistry arose from investigations of excited state redox processes in the latter part of the twentieth

century. These efforts showed that when the oxidation and reduction potentials and excited state energies of interacting electron donors and acceptors are appropriate, thermodynamically and kinetically favorable excited state single electron transfer (SET) will take place to produce ion radical intermediates. This phenomenon expanded the vista of organic photochemistry, since it enabled the unique and predictable reactivity profiles of charged radicals to be included in the concept library used to design new photochemical transformations. Many examples of the exceptional impact that SET has had on the field of organic photochemistry came from the pioneering work of Arnold and a cadre of other organic chemists who developed synthetic applicable SET photochemical processes.

It is clear that studies in the area of organic photochemistry have led to the discovery of a large number of novel reactions, and that some of these processes meet the high standards needed for use as preparative methodologies. The compilation in this Handbook, which begins with a useful chapter describing practical experimental methods used in photochemistry, reviews several of the more synthetically prominent photochemical reactions of organic substrates.

There is no doubt that the field of organic photochemistry was subjected to intense scrutiny in the latter half of the twentieth century, and that efforts during this period led to a firm understanding of basic photochemical principles and to the discovery of a wealth of highly unique chemical reactions. Moreover, during this period members of the synthetic organic chemistry community recognized that several photochemical processes could be applied as key steps in routes for the construction of complex target molecules. It is likely that activity in the area of organic photochemistry will not diminish in the twenty first century where it will be used in finding matchless solutions to challenging chemical problems. Thus, rather than being caused by the need to prepare sophisticated organic substances made by Nature, problems in the new century are likely to revolve about the search for green methods for promoting chemical reactions and for processes that can be performed in confined spaces (e.g., cells), defined patterns (e.g., lithography), and precisely controlled time domains (e.g., triggers). Organic photochemistry is uniquely applicable to these types of challenges and, as a result, it should continue to be an interesting area in which to work.

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## Preface

Practitioners of organic photochemistry feel that this science has a great potential for synthesis. Indeed, nowadays many reactions are known that lead to useful transformations and have been exploited as key steps in complex synthetic plans. These achievements attract the interest of synthetic chemists. However, photochemical methods are probably less often adopted than they may be, and are still less familiar to the broad chemical community than other methods. In the present handbook it has been attempted to offer an easy approach to the use of photochemical methods in synthesis. Thus, rather than discussing the chemistry of the various chromophores, as usual in photochemistry books, reactions have been grouped according to the molecular transformation involved and care has been given that experimental aspects (much less elaborate with many other methods) are clearly presented. We are convinced that a more general application in nonspecialized laboratories will lead to the discovery of new applications and even new reactions.

It was chosen to have a multiauthor book because this allows a breadth of approaches that could not otherwise be reached. The distinguished photochemists who accepted to participate in this project patiently tolerated the long work required to avoid the risk of discontinuity. We thank them heartily and any deficiency in the book is certainly not their fault. Thanks go to Dr. Heike Nöthe, a friendly and capable help during both the preparation and production phases and to Davide Ravelli and Matteo Albini for the pictures.

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