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The total number of articles received for the January/February 1993 special issue of Chemical Reviews on "Photochemistry" was too great to be accommodated by a single issue, and four of the articles have overflowed into the present issue. The "Photochemistry" Introduction is reprinted below, and the remaining "Photochemistry" articles follow.

Photochemistry: Introduction

Ancient civilizations recognized the importance of *light* for the maintenance and sustenance of life on earth. The sun, the ultimate source of light that provides the energy that drives life as we know it, has been an object of worship since antiquity. A number of folk medicines which date back hundreds of years suggest that exposure of the patient to sunlight was an integral part of medical treatments. However, orderly investigations of the connection between the absorption of light by matter and its chemical and physical consequences were not reported in the scientific literature until about the turn of this century, when systematic efforts revealed that exposure of matter to sunlight led to a rich range of transformations that are now termed photochemical reactions. During this period many photoreactions that are still the object of investigation and practical use today were discovered: dimerization of cinnamic acids, styrene derivatives, quinones, and anthracenes; photoreduction, intramolecular cycloaddition, and cleavage reactions of carbonyl compounds; photoreduction of aromatic nitro compounds; photoisomerization of olefins; etc.

After the early part of this century, studies of photoreactions received only sporadic attention, possibly due to the lack of experimental tools for investigation or to the lack of theoretical concepts as a basis for understanding photochemical transformations. During the 1930s and 1940s gas-phase photochemistry was a popular area of study and in the early 1940s the theoretical concept of the triplet state of organic molecules was confirmed with striking experimental evidence. The "rules" of the photophysics of organic molecules were established by 1950, and correlations were made between spectroscopic properties of molecules and the orbital configurations of electronically excited states. In the 1950s a number of experimental and theoretical advances were made. Photochemical reactions initiated by "short" pulses of light allowed the direct spectroscopic characterization of electronically excited states and relatively long-lived reaction intermediates. Theoretical and experimental studies of triplet–triplet energy transfer and radiationless transitions provided a firm scientific platform and background for the birth of modern molecular photochemistry during the 1960s.

The 1960s marked a period when many photoreactions were discovered (or rediscovered!). The mechanisms of these reactions were investigated with a cluster of powerful new spectroscopic techniques (laser flash spectroscopy, emission spectroscopy, single photon counting, ESR spectroscopy, etc.) and theories (Woodward–Hoffmann rules, theories of radiationless transitions, quantum mechanical calculations, etc.). The triplet state ruled as an early and ubiquitous reactive intermediate. A symbiotic relationship between photochemists and spectroscopists emerged, and the first generation of the new wave of photochemists were trained and began to set up their own laboratories. Soon the triplet state was forced from "front stage" as the dominant excited state involved in photoreactions, and the viability of singlet states and excimers and exciplexes as excited-state intermediates in photoreactions was clearly demonstrated. These were heady days of great intellectual and experimental activity, fired with excitement and certainly not free of controversy. During this period the power of mechanistic investigations was demonstrated and the field of molecular photochemistry gained the status of a truly new and emerging discipline.

The development of new techniques continued, unabated, into the next decade as well. The phenomenon of CIDNP was interpreted and applied to photochemical mechanisms; shorter and shorter laser pulses were developed to assist in mechanistic investigations; matrix isolation techniques were developed; and previously unthinkable structures were prepared and characterized at low temperatures, etc. Structures which had previously been considered by many to be "transition states" were now being routinely characterized by time-resolved laser flash spectroscopy. Carbenes, nitrenes, radicals, biradicals, zwitterions, and so forth became the objects of routine investigations. The theory of photoreactions shifted from emphasis on the state level to the potential energy surface level in the 1970s. The ability to discuss reaction mechanisms in terms of energy surfaces (Salem diagrams) added not only a new richness to the intellectual aspects of organic reaction mechanisms but also served to stimulate experimental activity previously unimaginable. Theoretical concepts for processes such as upper excited-state reactivity, adiabatic photoreactions, and chemiluminescent reactions were quickly coupled with experimental counterparts. Electron-transfer processes began to appear as a potentially important class of photochemical reactions. Photobiological problems were being attacked with the powerful techniques and concepts that had been developed for small organic molecules. By this time molecular photochemistry had truly become "modern" and was thriving.

It was time for photochemistry to advance from the "molecular" level to the "supramolecular" level in terms of external environments, and this happened in the 1980s. By external environment we mean both the atomic environment provided by molecules noncovalently complexed to photochemical substrates and the Coulombic or magnetic environment provided by static and pulsed

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electromagnetic fields. The ability of the "environment" to influence the course of photoreactions opened new fields of photoreactions in "microheterogeneous media", in "constrained spaces", on "interfaces", and so forth. In addition, the fields of "multiphoton" photochemistry and "magnetic effects on photoreactions" were initiated. The expansive role of electron transfer in photoreactions was exposed and was driven by theory and by the goal of finding the "inverted regions" of electron transfer in photochemical reactions. Photochemistry also became the tool to explore the properties of nanoregions of materials science. Commercial applications of photochemical concepts and systems were developed. Thus, before the end of the decade of the 1980s modern molecular photochemistry had become "mature". As is the characteristic of "mature" sciences, *modern supramolecular photochemistry* has become to some extent a connecting link between various branches of chemistry (organic, inorganic, analytical, biological and physical chemistry and materials science).

At the time when photochemical science needed much support, the involvement of photochemical events in processes such as vision, photosynthesis, photoimaging, optical recording, office copying, nonlinear optics, the ozone hole problem, and the greenhouse effect has kept the field in the public eye. Photochemistry is truly an international science, and its future will surely be involved in the solution of global problems from the energy crisis (solar energy storage and conversion) to environmental protection (waste-water treatment, destruction of chemical wastes, etc.).

The physical appearance of the laboratory of a photochemist has undergone remarkable changes since the time of Ciamician. The use of roof tops and solar light sources is no longer common. The laboratory has become sophisticated and is equipped with a number of time-resolved spectrometers and computer-controlled instruments. At the same time the nature of problems handled by today's photochemists has become more complex since the early days of photochemistry. These trends are expected to continue into the 21st century.

This special issue of *Chemical Reviews* attests to the vigor of the field of organic photochemistry as we proceed into the 21st century. In total 28 articles have been contributed from photochemists from all over the world. The articles are representative of much of the current activity in the field, but are by no means comprehensive of the field. The fact that nearly all of the invited authors enthusiastically accepted the invitation to present their reviews is a testament to the continuing excitement and energy in photochemistry. Indeed, the total number of articles received was too great to be accommodated by a single issue of *Chemical Reviews*, and as a result several of the articles will appear in the next issue of the journal.

A group of 11 articles authored by Schuster, Lem, and Kaprindis; Arai and Tokumaru; Kohler; Givens and Kueper; Maciejewski and Steer; Müller and Mattay; Das; Becker; Wan and Shukla; Cornelisse; and Lissi, Encinas, Lempo, and Rubio illustrates how photochemistry has benefited from the development of new concepts, techniques, and synthetic strategies and from the involvement of spectroscopists. A bulk of the research activities of organic photochemists are represented by these articles. Such direction of research often leads to new discoveries and provides a firm base for the field.

A second set of five contributions by van Willigen, Levstein, and Ebersole; Leigh; Gehlen and De Schryver; Wilson and Schnapp; and Johnston summarizes the impact of instrumentation, newer techniques, and methods of data handling on photochemical investigations. Once these methodologies/techniques are firmly established and amply demonstrated, they become common tools to analyze reaction mechanisms and to explore new reactions. The review by Khudyakov, Serebrennikev, Turro and the one by Bhattacharyya and Chowdhury in the third set summarize the effect of external field, in this case magnetic field, on photoreactions. Since its initial discovery, the magnetic field effect has been applied to a number of photoreactions. This strategy may become a routine tool in unraveling reaction mechanisms in the near future. Thus two types of developments, one based on techniques and one based on new theories or concepts, have been vital for the growth of photochemistry.

A fourth set of selections by Kamat, Thomas, Yoon, Fox and Dulay, and Winnik gives a flavor of a recent trend in the activities of photochemists, the study of reactions under microheterogeneous conditions. These articles mostly concentrate on solid substrates although other nonsolid microheterogeneous (organized/confined) media have also occupied the interests of photochemists. Stimulus for interest and activity in this field comes from the fact that a number of photophenomena of commercial and natural importance occur under microheterogeneous conditions.

The final set of presentations by De Keukeleire and He, Duxbury, Monroe and Weed, Law, and Legrini and Braun are on the applications of photochemistry. Except for a few, photoreactions are not routinely used by synthetic chemists to construct large molecules. Not many fine or bulk chemicals are produced in industry with photoreactions as key steps, either. Still, as illustrated by other articles in this set, photochemistry plays an important role in a number of commercial applications. Many more proven and potential applications are not covered in this issue. A number of basic problems still exist in many of the commercial applications and many more inventions need to be made. The role of photochemists in such activities is obvious.

An issue of this magnitude and quality could not have been achieved without the cooperation of the authors. We appreciate their adherence to the time schedule, and their patience in face of demands of multiple revision. The pain of coordinating the activities of photochemists scattered all over the world was mainly borne by Rebecca Baker, the Coordinating Editor, and without her help and dedication this collection of reviews would not have come out on time. We sincerely regret the fact that not all 28 articles could be brought out in a single issue for reasons that were beyond our control.

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