



Prof. Michael Orfanopoulos

Physical Organic

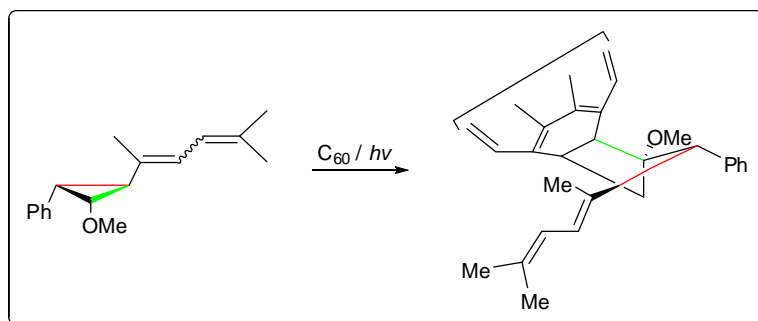
Reaction Mechanisms

Organic Photochemistry

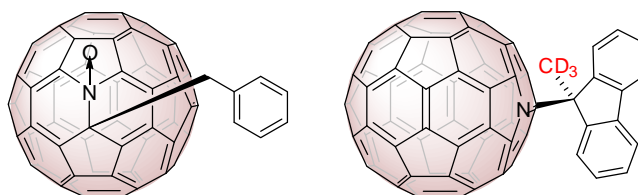
Research Interests

The discovery of [60]fullerenes, the third allotropic form of carbon (1996 Nobel Prize in Chemistry), opened new avenues for research in Chemistry, Physics and Material science. Research in our group is primarily aimed toward the exploratory chemistry and photochemistry of fullerene-based carbon nanostructures. Particular attention is paid to the synthesis of [60]fullerenes and aza[60]fullerenes derivatives that might have novel reaction chemistry.

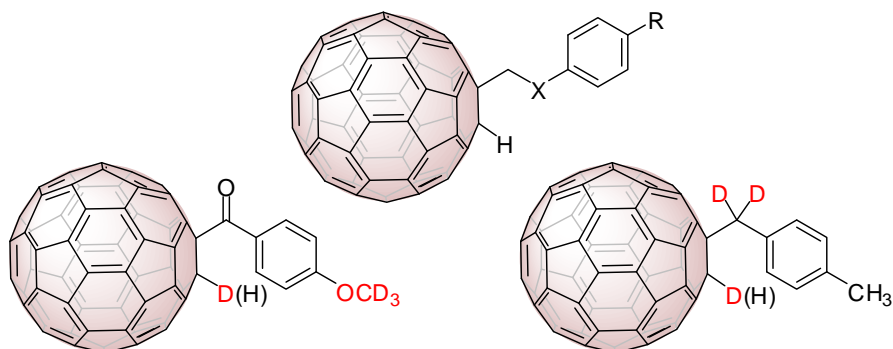
For instance, the investigation of the [2 + 2] photocycloaddition of dienes and alkenes to [60]fullerene revealed the presence of a biradical intermediate, whereas the corresponding [4 + 2] cycloaddition led to stereospecific Diels-Alder adducts. Moreover, the photocycloaddition of dienyl cyclopropanes to C_{60} enabled the stereospecific construction of five-, seven-, and nine-membered rings on the C_{60} core.



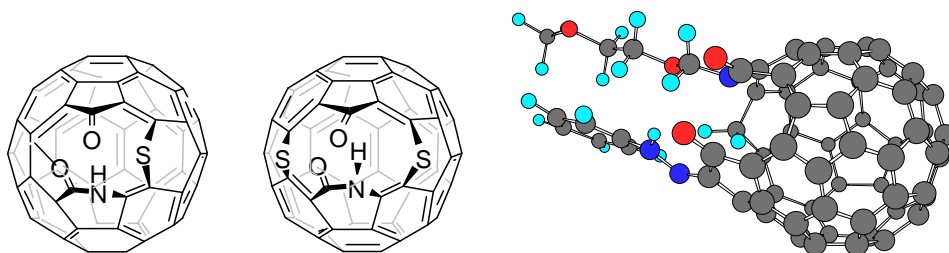
Studies on the physicochemical characteristics and applications of the $C_{59}N^+$ PET reactivity have been also successfully elaborated in our laboratory. Primary and secondary kinetic isotope effects have been widely used for the elucidation of reaction mechanisms (i.e., the reaction of aza fullerene radical $C_{59}N^{\bullet}$ with aromatic compounds).



Recently, a new free-radical approach has been developed for the photochemical functionalization of [60]fullerene with a variety of organic moieties (e.g., benzyl, acyl, ethers etc). A series of mechanistic studies, including intra and intermolecular deuterium isotope effect measurements, have been performed to elucidate the mechanism underlying these reactions.



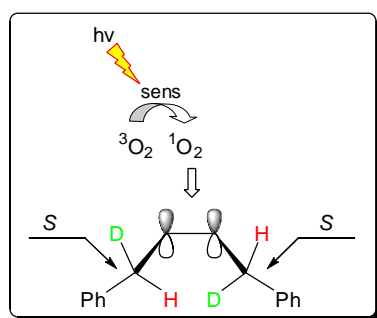
The chemistry of open-cage [60]fullerene derivatives has been also investigated. A series of new open-cage fullerene adducts having up to a 16-membered ring orifice on the fullerene cage has been isolated and characterized.



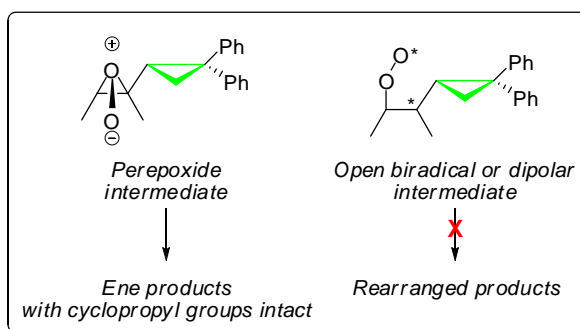
Another major area of investigation involves the chemistry of reactive oxygen species including singlet molecular oxygen ($^1\text{O}_2$). The organic and biological chemistry of molecular oxygen is of extraordinary interest. Oxygen plays an important role in aging, damage of materials in the environment, cellular pathology and many other areas. In particular, our group uses preparative and physical organic methods to study the chemistry of molecular oxygen in photochemical processes.

Earlier and recent work in our laboratory has been devoted on the elucidation of various photooxygenation mechanisms by using powerful tools, such as kinetic isotope effects, the use of hypersensitive radical probes and the fascinating regio/stereoselective reactions of $^1\text{O}_2$ with alkenes.

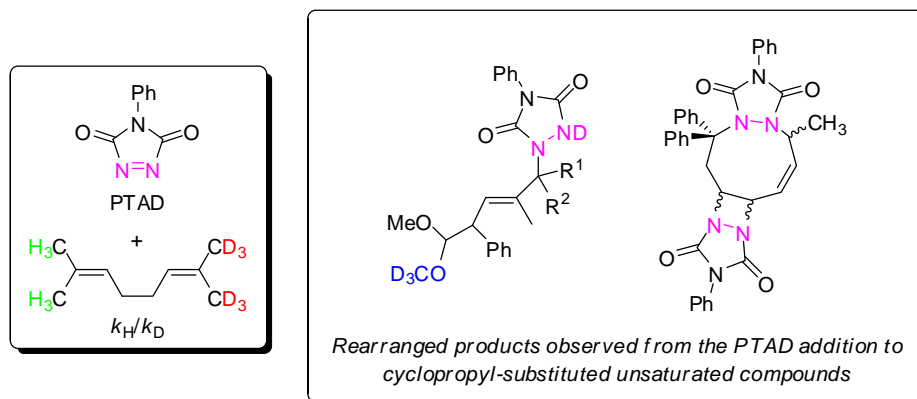
$^1\text{O}_2$ Ene Reaction: A Stereospecific Process



The Use of Hypersensitive Probes in the $^1\text{O}_2$ -Mediated Allylic Oxidation



Mechanistic studies concerning the thermal and photochemical reactions of various reactive enophiles including triazolinediones (i.e., PTAD), tetracyanoethylene (TCNE) and dimethyldioxerane have also been the subject of our research interest.



Another area of investigation involves the study of the catalytic action of “polyoxometalates” in organic chemistry. This family of metallic clusters photocatalyzes a remarkable array of homogeneous oxidations and radical coupling reactions. For instance, several decatungstate ($W_{10}O_{32}^{4-}$) mediated reactions, under either homogeneous or heterogeneous conditions, have been developed for applications in organic synthesis.

