Professor Michael Orfanopoulos
A tribute

This special issue of Arkivoc is dedicated to Professor Michael Orfanopoulos on the occasion of his 67th birthday and at his official retirement, to acknowledge his contribution to physical and synthetic organic chemistry

DOI: http://dx.doi.org/10.3998/ark.5550190.p001.466

Michael (Mike) Orfanopoulos was born in Patras (Greece) in 1948 and studied chemistry at the University of Patras where he took his bachelor's degree in 1971. He then moved overseas and in 1976 obtained a M.Sc. degree at the University of Toledo (Ohio, USA) working with Professor J. Fry on the reduction of carbonyl compounds to alcohols or hydrocarbons, employing the organosilane-BF_3 reducing system. In 1979 he finished his Ph.D. at Case Western Reserve University under the supervision of Professor L. M. Stephenson. In his doctoral thesis, Professor Orfanopoulos studied the mechanism of the singlet oxygen ene reaction with olefins, a topic that he continued to elaborate throughout his academic carrier. The most impressive achievements from that period are two publications in JACS (*J. Am. Chem. Soc.***1979**, *101*, 275, "Site specificity in the singlet oxygen-trisubstituted olefin reaction"; and *J. Am. Chem. Soc.***1979**, *101*, 3111, "The stereochemical dependence of isotope effects in the singlet oxygen/olefin reaction"). These two contributions provided substantial information on the mechanism of this unusual reaction and are known to the singlet oxygen scientific community as the "*cis effect*" and "*Stephenson's isotope effect test*", respectively. Immediately afterwards (1980-1981), he worked as a postdoctoral fellow with the late Professor Harry S. Mosher at Stanford University.

Between 1981 and 1985 he worked as a Research Scientist at the National Centre of Scientific Research "Demokritos" Athens (Greece) and in 1985 was appointed as an Assistant

Professor in the newly established Department of Chemistry at the University of Crete (Greece). Here he was one of a small number of pioneer professors who built up the new department giving it the strong foundations on which it thrives today. In 1993, he was promoted to full Professor, and has held this position since. Throughout his 30 years at the University of Crete, Professor Orfanopoulos held many administrative positions, including Chairman of the department for 8 years (1994-1998 and 2010-2014), member of the Research Committee of the University of Crete, Scientific Director of the M.Sc.'s Graduate Program "Synthesis and Isolation of Natural Products with Biological Activity", member of the International Scientific Committee of "European Symposium of Organic Chemistry" (ESOC) and was part of the team that organized the ESOC-17 in July 2011 in Crete. He was a Visiting Professor at the California Institute of Technology (2006, guest of Professor Robert H. Grubbs), and at The Scripps Research Institute, La Jolla (2000, guest of Professor Kyriakos C. Nicolaou). In addition, he has been an associate member of the Organic and Biomolecular Chemistry Division of IUPAC since 2012, member of the editorial board of referees in ARKIVOC (1994-present), and member of the international advisory board of *ChemPlusChem* (2011-present). He is co-author of more than 120 publications and 5 book chapters and has lectured over 70 times at international conferences and symposia. He has supervised over 25 graduate students throughout his career, 7 of which hold academic positions in Greece or elsewhere.

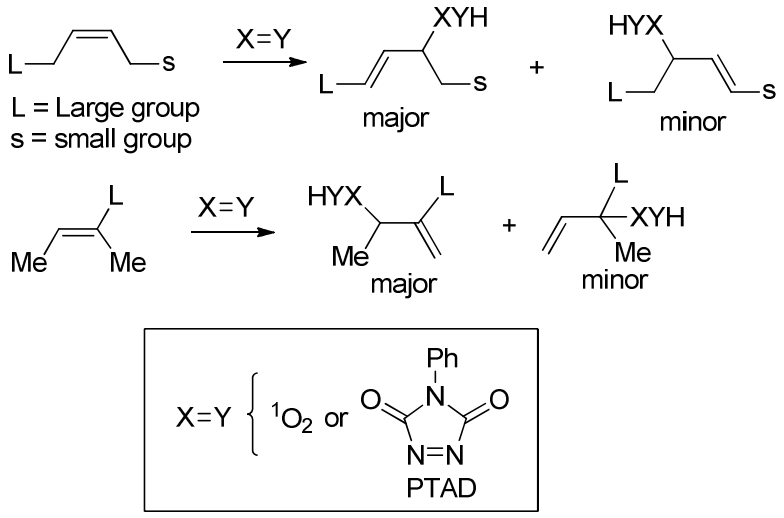
Professor Orfanopoulos is a highly socialized person with a unique ability to communicate and motivate his students. He enjoys fishing, cooking, gardening and hiking.

Research Contributions

His scientific contributions are superb and well recognized. Most of his work has been published in prestigious journals of organic and general chemistry, including *J. Am. Chem. Soc.*, *J. Org. Chem.*, *Org. Lett., Angew.Chem. Int. Ed.*, *Chem. Commun.*, *Chem. Rev.*, *Chem. Soc. Rev.*, and others. His research has focused on enophilic addition to olefins (singlet oxygen, triazolinediones), functionalization of [60]-fullerene, and organic photochemistry with polyoxometalates, each of which are summarized below:

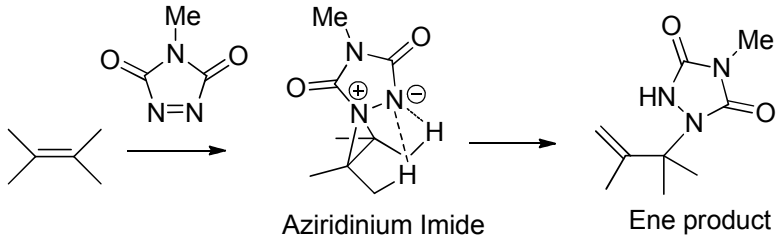
1. Reactions of enophilic singlet oxygen and triazolinediones with alkenes

The early achievements of his independent career focused on the reactivity of enophilic singlet molecular oxygen ($^1O_2$) and triazolinediones(RTAD's) with alkenes. In some of his elegant work Professor Orfanopoulos collaborated with the late Professor Cristopher S. Foote at UCLA, a pioneer in the field of singlet oxygen chemistry. The landmarks from this research are the studies on the regioselectivity of $^1O_2$ and PTAD with alkenes which uncovered and established the so called "*nonbonding large group effect*" (*J. Am. Chem. Soc.* **1990**, *112*, 6417; *J. Am. Chem. Soc.* **1991**, *113*, 3180), which controls and can predict the regioselectivity of double bond formation in the ene products from any given alkene (Scheme 1, Review article: *Tetrahedron* **2000**, *56*, 1595).



Scheme 1. Regioselectivity in the ene reaction of singlet oxygen and triazolinediones with alkenes.

The ene reaction of *N*-phenyl-1,3,5-triazoline-2,5-dione (PTAD) with alkenes, whose mechanism has fascinated organic chemists for two decades, was thoroughly studied in Mike's group. Although it had been established by Professor Orfanopoulos' contribution and by others, that the ene product is formed through an aziridinium imide intermediate (Scheme 2), the triazolinedione/alkene ene reaction mechanistic question was revived by Singleton (*J. Am. Chem. Soc.* **1999**, *121*, 11885), who proposed a biradical mechanism requiring aziridinium imides as "innocent bystanders". The formation of biradicals, not only in the triazolinedione, but also in the singlet oxygen ene reactions, were ruled out on the basis of experiments involving stereoisotopic analysis and hypersensitive cyclopropyl alkenes as probes (Review article: *Chem.-Eur. J.* **2010**, *16*, 9414).

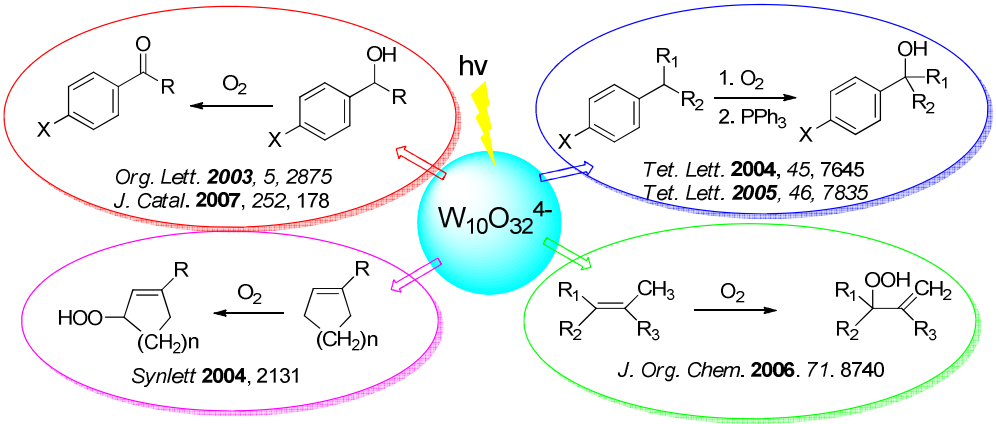


Scheme 2. Mechanism of the ene reaction of triazolinediones with alkenes proceeding through an aziridinium imide intermediate.

2. Photocatalyzed transformations with polyoxometalates

Another of the active research topics in the Orfanopoulos group was the study of catalytic oxidation usin the most promising catalytic-system from amongst the polyoxometalates namely,

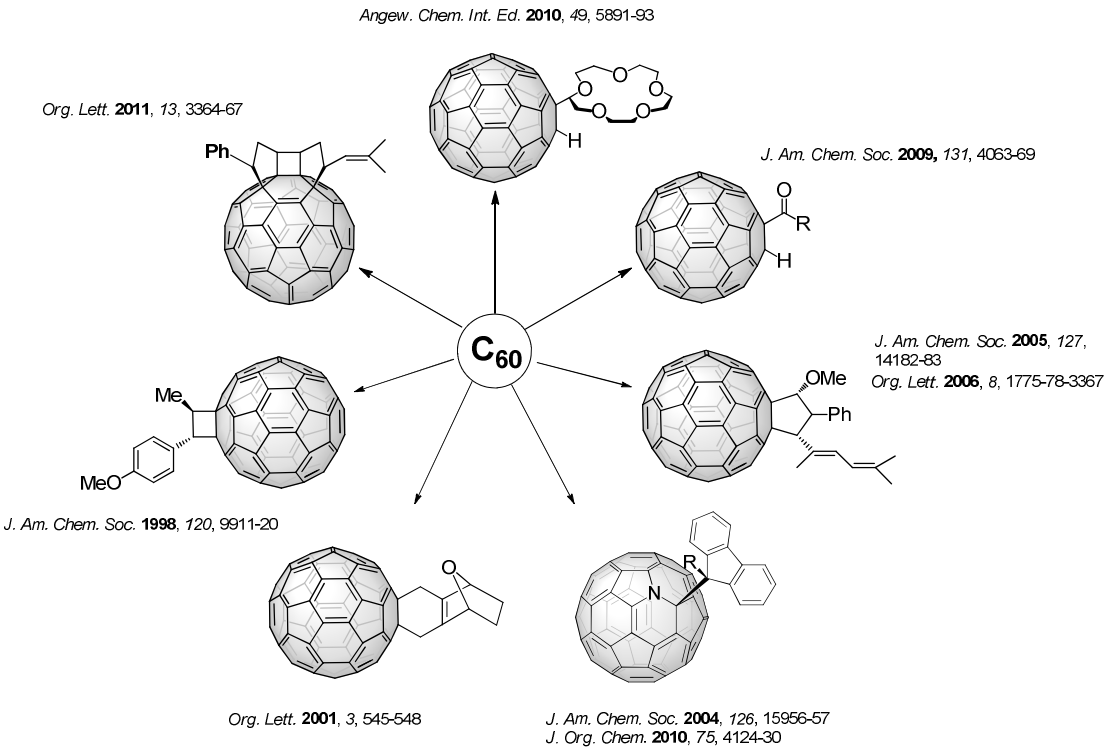
decatungstate $W_{10}O_{32}^{4-}$ as a photo-catalyst. In this field, he collaborated with Professor Charles Tanielian (Strasbourg, France) and studied the catalytic aerobic oxidation of alcohols, alkenes and alkanes (*Chem. Soc. Rev.* **2009**, *38*, 2609) which represented the first mechanistic and synthetic examples of decatungstate-photocatalyzed reactions in organic chemistry.



3. Functionalization of fullerenes

After the observation that [60]-fullerene is an excellent photosensitizer for the production of singlet oxygen capable of promoting the oxidation of alkenes even in water, Professor Orfanopoulos started a systematic and fruitful exploration of ways to functionalize C_{60}. The first examples showed that [2+2] adducts of fullerene and aryl alkenes, or conjugated dienes, could be obtained upon irradiation (e.g. *J. Am. Chem. Soc.* **1997**, *119*, 7394), while mechanistic studies were carried out regarding the thermal [4+2] cycloaddition with conjugated dienes (*Org. Lett.* **2001**, *3*, 545; *J. Am. Chem. Soc.* **1998**, *120*, 9911), or the ene reaction with alkenes (*Org. Lett.* **1999**,*1*, 1909). The use of suitably substituted cyclopropyl alkenes as probes, led to the conclusion that the mechanism of the [2+2] cycloaddition to C_{60} involved biradicals (*J. Am. Chem. Soc.* **2005**, *127*, 14182). Apart from C_{60}, addition reactions to aza[60]-fullerene were also studied (*J. Am. Chem. Soc.* **2004**, *126*, 15956; *Org. Lett.* **2003**, *5*, 4603). Professor Orfanopoulos was also involved in the synthesis of open-cage fullerene derivatives (*Chem. Soc. Rev.* **2010**, *39*, 817) in collaboration with Professor Koichi Komatsu.

A novel photochemical approach for the original functionalization of C_{60} *via* radicals, produced in the presence of a decatungstate polyoxo-anion-cluster, provided access to the synthesis of mono-substituted fullerene derivatives from aldehydes, alcohols, or ethers (*J. Am. Chem. Soc.* **2009**, *131*, 4063; *Chem. Commun.* **2010**, *46*, 8228; *Org. Lett.* **2011**, *13*, 3364; *Chem. Rev.* **2013**, *113*, 5262). The unique characteristic of this approach was that all previous attempts to functionalize C_{60} with radicals had been unselective leading to poly-addition patterns.



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