

Inter-American Photochemical Society Newsletter



I-APS Internet Address <http://www.chemistry.mcmaster.ca/~iaps>

This newsletter is available in pdf format from the web site.

Volume 23 Number 1

May 2000

I-APS Officers	2
Election Results	4
Letter from Linda Johnston, I-APS President	5
2001 I-APS Award in Photochemistry and I-APS Fellowship Award: Call for Nominations	6
Announcement.....	7
Nick Turro Awarded Gibbs Medal.....	8
6th International Conference On Methods And Applications Of Fluorescence Spectroscopy	10
Report on the Inter-American Photochemical Society 11 th Winter Conference.....	13
A Decade of Closure and Surprises: Dr. Peter Wagner's 2000 I-APS Award Address.....	17
The Photophysics of Organic Molecules with Long-Lived Second Excited Singlet States.....	34
Electronic Spectroscopy of Matrix Isolated Singlet Carbenes – Simple Models, Conformational Dependence, and Photochemistry	39
Upcoming Meetings	49
Registration Form for the I-APS	51

I-APS Officers

President

Linda J. Johnston
Steacie Institute for Molecular Science
National Research Council
Ottawa, ON K1A 0R6
ljj@ned1.sims.nrc.ca

Vice President

Frederick D. Lewis
Department of Chemistry
Northwestern University
Evanston, IL 60208-3113
lewis@chem.nwu.edu

Secretary

Russell H. Schmehl
Tulane University
Department of Chemistry
New Orleans, LA 70118
schmehl@mailhost.tcs.tulane.edu

Treasurers

Lisa Kelly (USA)
Department of Chemistry and Biochemistry
University of Maryland, Baltimore County
1000 Hilltop Circle
Baltimore, MD 21250
lkelly@umbc.edu

Cornelia Bohne
Department of Chemistry
University of Victoria
P.O. Box 3055
Victoria, B.C.
Canada V8W 3P6
bohne@uvic.ca

Frank H. Quina (South America Secretary)
Instituto de Química
Universidade de São Paulo
São Paulo, Brazil
frhquina@quim.iq.usp.br

Editor's Note: With this issue, we happily welcome a new advertiser/sponsor, Applied Photophysics, Ltd. Their web address is <http://www.apltd.co.uk>. Our advertisers, including Ace Glass, Edinburgh Instruments, IBH, OLIS, and Opotek help defray the cost of this newsletter and thus keep our dues down. Please thank them by considering these companies when you make a purchase.

Advisory Committee

Cornelia Bohne
Department of Chemistry
University of Victoria, B.C.
P.O. Box 3055
CANADA V8W 3P6
bohne@uvic.ca

Frank H Quina
Instituto De Química
Universidade de São Paulo
São Paulo, Brazil
frhquina@quim.iq.usp.br

Richard G. Weiss
Department of Chemistry
Georgetown University
Washington DC 20057
weissr@gusun.georgetown.edu

Newsletter Editor

William S. Jenks
Department of Chemistry
Iowa State University
Ames, Iowa 50011-3111
wsjenks@iastate.edu

Lisa McElwee-White
Department of Chemistry
P.O. Box 117200
University of Florida
Gainesville, FL 32611
lmwhite@chem.ufl.edu

Ian R. Gould
Department of Chemistry
Arizona State University
Box 871604
Tempe, AZ 95287-1604
igould@asu.edu

Irene E. Kochevar
Department of Dermatology
Massachusetts General Hospital WEL-224
Harvard Medical School
Boston, MA 02114
kochevar@helix.mgh.harvard.edu

I-APS Webmaster

William Leigh
Department of Chemistry
McMaster University
1280 Main St. West
Hamilton, ON L8S 4M1 Canada
leigh@mcmaster.ca

Election Results - New Officers

The election results are in! There was a strong slate of excellent candidates and many races were close. The new officers and Advisory Board members are as follows:

Vice President/President Elect

Edwin F. Hilinski

Department of Chemistry
Florida State University
Tallahassee, FL 32306-4390
hilinski@chem.fsu.edu

Secretary

Steven A. Fleming

Department of Chemistry
Brigham Young University
Provo, UT 84602
fleming@byu.edu

Advisory Board Members

Pedro F. Aramendia

INQUIMAE. Departamento de Química Inorgánica
FCEN. Universidad de Buenos Aires
Pabellón 2. Ciudad Universitaria
1428 Buenos Aires. ARGENTINA
pedro@q1.fcen.uba.ar

Mary K. Boyd

Department of Chemistry
Loyola University Chicago
6525 N. Sheridan Road
Chicago, IL 60626
mboyd@luc.edu

Gerald J. Meyer

Department of Chemistry
The Johns Hopkins University
3400 North Charles Street
Baltimore, MD 21218
Meyer@JHUVMS.HCF.JHU.EDU

The terms for the new officers and Board Members begin on July 1, 2000. Ed Hilinski will serve as Vice President for 2 years, followed by 2 years as President. The Secretary serves a 2 year term and the Advisory Board Members serve 4 year terms. The continuing members of the present Advisory Board are Cornelia Bohne, Ian Gould and Irene Kochevar.

2001 I-APS Award in Photochemistry: Call for Nominations

The Inter-American Photochemical Society Award was established in 1988 to recognize outstanding contributions by members of the Society to the advancement of the photochemical and photophysical sciences. The award recognizes achievements during the last ten years. The 2001 I-APS Award will be presented at the I-APS Conference to be held in Cordoba, Argentina in May 2001.

Nominations should include a detailed justification that clearly outlines the nominee's scientific achievements during the last ten years, along with a curriculum vita and publications list. Seconding letters from colleagues familiar with the nominee's work are also helpful to the committee. All documents should be forwarded to the Chair of the Awards Committee at the address below. The deadline for receipt of nominations is August 1, 2000.

I-APS Fellowship: Call for Nominations

The society established the honor of Fellowship in 1993. Fellowship recognizes outstanding lifetime scientific achievements in photochemistry or contributions to either the science of photochemistry as a discipline or the furtherance of the Society through service. Fellowship is limited to 4% of the membership of the Society and no more than two Fellows can be elected in a given year. Fellows may be requested to make a short presentation at the next Winter Conference and will receive a waiver of membership dues.

Nominations should include a statement describing the merit of the contribution to be recognized and should state clearly whether the award is for contributions in science or service. Seconding letters are not required, but may be submitted. Nominees should be members of the Society. Exceptions to this requirement require special justification by the nominator. All documents should be forwarded to the Chair of the Awards Committee at the address below. The deadline for receipt of nominations is August 1, 2000.

Nominations for the I-APS Award and Fellowship should be sent to:

Frederick D. Lewis
Chair, I-APS Awards Committee
Department of Chemistry
Northwestern University
Evanston, IL 60208-3113

**X111TH INTER-AMERICAN PHOTOCHEMICAL SOCIETY
CONFERENCE**

ASCOCHINGA, CÓRDOBA, ARGENTINA, MAY 20-25, 2001



The I-APS meeting will take place for the second time in South America (the first South American meeting was at Foz do Iguaçu, Brazil, in May 1996). The location is Ascochinga, a small village in the hills of Central Argentina, 50 km to the north of the city of Córdoba, and 40 km from its International Airport.

Córdoba is the second largest city in Argentina and is located 700 km NW of Buenos Aires. Córdoba has a great cultural tradition and the University of Córdoba, established in 1613, is one of the first institutions of higher education in the Americas. The International Airport is well connected to Buenos Aires, Sao Paulo and Rio de Janeiro. Direct flights to Miami, New York, and Europe are less frequent. The conference will be held at a hotel specially booked for the meeting. We invite you to visit the Web page: <http://www.unc.edu.ar/iaps2001>

Gerardo Argüello	Univ. Córdoba, Argentina	gerardoa@fisquim.fcq.unc.edu.ar
Gustavo Argüello	Univ. Córdoba, Argentina	gaac@fisquim.fcq.unc.edu.ar
Cornelia Bohne	Univ. Victoria, Canada	bohne@uvic.ca
Carlos Chesta	Univ Río Cuarto, Argentina	cchesta@exa.unrc.edu.ar
Miguel García Garibay	UCLA, USA	mgg@chem.ucla.edu
Frank Quina	Univ. Sao Paulo, Brazil	quina@usp.br
Robert Redmond	Harvard Medical School, USA	redmond@helix.mgh.harvard.edu
Russel Schmehl	Tulane Univ., USA	russ@mailhost.tcs.tulane.edu
<i>Richard Weiss</i>	Georgetown Univ., USA	weissr@gusun.georgetown.edu
Pedro Aramendía	Univ. Buenos Aires, Argentina	pedro@q1.fcen.uba.ar

NICK TURRO AWARDED GIBBS MEDAL

Frederick D. Lewis



Nicholas J. Turro, William P. Schweitzer Professor of Chemistry at Columbia University received the Willard Gibbs Medal of the ACS Chicago Section on May 19, 2000. The Gibbs Medal was first awarded in 1911 to Svante Arrhenius and since then has been awarded annually to a stellar list of chemists, many of whom have subsequently been awarded the Nobel Prize. The Gibbs medal is considered among the most prestigious of awards conferred by a ACS local section. Nick, as he is called by photochemists world-wide, is the first member of I-APS to receive this award. The award was presented at a gala banquet in Skokie, IL at which Nick was introduced by his former postdoc, Fred Lewis, a member of the Chicago Section and Vice-President of I-APS. Nick's wife Sandy and other past members of the Turro group were in attendance.

Nick was honored for pioneering and interdisciplinary research on the interaction of light and organic molecules, for the invention of novel and general methods for investigations of organic reactions of supramolecular systems, and the development of organic systems whose reactivity is extremely sensitive to the application of weak magnetic fields.

Nick was born in Middletown, Connecticut on May 18, 1938. Remaining in Middletown, he received his B.A. degree *summa cum laude* from Wesleyan University in 1960. He attended graduate school at Cal Tech where he received his Ph.D. degree with G. S. Hammond in 1963, during the blossoming of the new field of mechanistic

organic photochemistry in the Hammond group. Following a postdoctoral year at Harvard with P. D. Bartlett (the 1963 Gibbs Medallist) he joined the faculty at Columbia University in 1964. He is the author of over 650 scientific papers and two influential books, "Molecular Photochemistry" published in 1965 and "Modern Molecular Photochemistry" published in 1978. His scientific accomplishments have been recognized by numerous awards, lectureships, and honorary degrees. Among these are election to the National Academy of Sciences, the Porter Medal, and several American Chemical Society awards including the Award in Pure Chemistry, the James Flack Norris Award, and the Cope Scholar Award, and the 1991 I-APS Award.

Nick's research interests have centered on organic photochemistry with a focus that has evolved with time from molecular to supramolecular. He was among the first to broadly apply the methods of kinetic spectroscopy to the study of photochemical and chemiluminescent reactions mechanisms. Early targets of investigation included acyclic and cyclic ketones and dioxetanes. He was a pioneer in the study of photochemical reactions in organized media such as micelles and zeolites, first investigating the effects of such media on photochemical reactions and then using photochemistry to probe the environment. Investigations of cage effects and magnetic field effects on the behavior of photochemically generated radical pairs have revealed remarkable radical pair phenomena, including isotopic separations induced by differential hyperfine interactions.

Synthetic polymers, dendrimers, and biopolymers including DNA have also fallen within the scope of his investigations.

No less impressive are Nick's accomplishments as an educator and administrator. He has served as mentor to dozens of graduate students and postdocs, many of whom occupy leadership positions in universities and industrial laboratories world-wide. Generations of Columbia undergraduates have also benefited from Nick's dynamic classroom presentations, educational innovations, and departmental leadership. Nick has also been tireless in the service of photochemical science and has served as chair or organizer of the leading conferences in the field. Nick's presence at a conference ensures that it will be a lively and stimulating event.

Both as a scientist and a teacher, Turro has sought to develop simple models for complex phenomena. The model is intended as a stimulus for thought, research, and debate - not as irrefutable dogma. In collaboration with Bill Dauben and Lionel Salem he helped popularize the use of potential energy surfaces to explain photochemical reactivity. His second book spread the gospel. Having played a key role in the development molecular photochemistry, he became a prime mover in the emerging field of supramolecular photochemistry. His lectures are enlivened with colorful illustrations and language: what listener will forget the roach motel or paradigm shift? As a teacher, mentor, collaborator, lecturer, interpreter, and guide he has influenced the thinking of photochemists for over three decades. His energy and enthusiasm show no sign of abating.

Nick's friends and colleagues congratulate him on the receipt of the Gibbs Medal.

**6th INTERNATIONAL CONFERENCE ON METHODS AND
APPLICATIONS OF FLUORESCENCE SPECTROSCOPY (MAFS6)
PARIS, September 12-15, 1999.**

René Lapouyade and Jean Kossanyi

The sixth International Conference on Methods and Applications in Fluorescence Spectroscopy was organized by a committee headed by Prof. Bernard Valeur and Dr. Jean-Claude Brochon and was held at the Centre Chaillot-Galliera near the Champs-Élysées Avenue in Paris. This conference series was founded by Prof. Otto Wolfbeis starting with the first MAFS Conference in Graz in 1990.

The lectures and posters presentations as well as the number of participants (ca 300) demonstrated the continued growth of fluorescence and its numerous applications to the physical and life sciences. It was the objective of the organizers to maintain the balance between basic science and applications on one hand, and life sciences and physical sciences on the other hand.

The conference started on Sunday night with a minihistorical session: Prof. Mario N. Berberan-Santos (Instituto Superior Técnico, Lisboa) and Prof. Dave Jameson (University of Hawaii, Honolulu) taught us "where we come from", with the pioneering works of Jean and Francis Perrin and Gregorio Weber, respectively. From the demonstration of the reality of atoms and molecules, the establishment of model for quenching, the quantitative theory of resonance energy transfer and of fluorescence polarization (Perrin's father and son) to the applications of fluorescence spectroscopy to biological sciences through the development and even the marketing of fluorescence methodologies, the contributions of these pioneers have been emphasized.

Lectures in physical sciences

Jean-Claude Mialocq (CEA, Saclay) described the use of fluorescence up-conversion, a method particularly well-suited for studying the dynamics of Stokes shifts, electron or hydrogen transfer, etc.

F.V. Bright (State university of New York at Buffalo) probed molecular-level events in supercritical fluids, with time-resolved fluorescence spectroscopy.

M. Van der Auweraer (university of Leuven) showed that dyes incorporated in monomolecular layers or assemblies, tend to aggregate and from the analysis of the fluorescence decay of these aggregates acting as traps, he observed that generally the distribution of the dimers and aggregates is inhomogeneous.

Three lectures were devoted to ion or molecule recognition (a) Jean-Pierre Desvergne (LCOO, university of Bordeaux) described fluorescent macrocyclic ditopic receptors composed of aromatics doubly linked with polyethylene oxide chains, for which he measured the equilibrium constants with alkali and alkaline-earth cations. The first complexation enhances or decreases the second complexation (stoichiometry 1:2) in relation with the structure of the host. The stationary fluorescence suggests partial cleavage between the cations and the phenolic oxygen, while the fluorescence anisotropy relaxation demonstrates that the receptor and the cations are not separated during the lifetime of the fluorescing state. (b) Seiji Shinkai (Kyushu university) reported selective recognition of sugars in water by boronic acids. New supramolecular systems composed of diboronic acids part of PET sensors have been designed which show enhanced specificity and better absorption and emission characteristics. (c) Luigi Fabbrizzi (Università di Pavia) reported a new platform in which a Zn(II) ion is

coordinated by the tripodal tetramine tren, and offers a vacant coordination site available for anion binding. The platform has been equipped with photoactive fragments in different supramolecular systems which allowed the recognition and signalling of tryptophan and linear amidinate anions.

Mitchell A. Winnik (university of Toronto) examined and modelled the quenching kinetics of excited dyes by oxygen in carefully designed polymer resins (Prof. I. Manners). The applications concerns aviation and racing car design: coating the models with these polymers containing phosphorescent dyes, illuminating in the wind tunnel and measuring the intensity profile across the model with a digital TV camera leads to the air pressure profile across the surface of the object.

The last lecture was given to Otto S. Wolfbeis (university of Regensburg) who described the state of the art regarding luminescent sensors: "Where are we? Where are we going?". After a short semantic lesson about the word sensor (a device capable of continuous monitoring) and probes (which involve recognition and associated signal at a molecular level) he described the sensors needed (pH, oxygen, CO₂, K⁺, Na⁺, Ca²⁺, Cl⁻, glucose,...). The present MUSTS in optical sensors include "cost reduction, miniaturization, replacement of biological receptors by more stable (e.g. artificial) receptors, improvements in the limits of detection, probe design".

Lectures in life sciences

Enrico Gratton (university of Illinois) developed a novel method for the analysis of intensity fluctuations within the framework of two photon excitation fluorescence correlation spectroscopy.

Philippe Bastiaens (London) extended a frequency domain fluorescence lifetime imaging microscopy (FLIM) set-up to encompass 3D-multi-frequency detection. Quantitative assessment of biochemical processes, such as protein interactions and protein phosphorylation can be obtained *in vivo*.

Arthur G. Szabo (University of Windsor, Ontario) investigated the local interacting segments of protein-protein complexes when tryptophan has been biosynthetically replaced by unnatural tryptophan analogues.

Joseph M. Beechem (Vanderbilt university, Nashville) obtained millisecond structural motion-pictures of protein folding reactions using 3-D resolved multi-site stopped-flow fluorescence energy transfer.

Markus Sauer (university of Heidelberg) reported new improvements in the methods of single molecule detection for DNA sequencing, using diode laser-based time-resolved fluorescence detection.

Manfred Auer (Novartis Forschungsinstitut, Vienna) described fluorescence intensity distribution analysis (FIDA), from confocal fluorescence technique, as an appropriate tool for resolving the molecular mechanism of complex biochemical interactions.

Gérard Mathis (CIS Biointernational, Bagnols/Cèze) showed the particular well-suited rare earth cryptates for the study of different models chosen from the signalling pathways involved in cellular communication and expression. This results from the antenna effect of the ligands and their amplification effect by non radiative energy transfer related to their long-lived excited state.

All contributors were invited to submit a manuscript for publication in a special issue of the Journal of Fluorescence. Moreover a book published by Springer-Verlag will collect the articles written by the invited speakers at MAFS6 and other delegates on invitation.

Side Programmes

Beside the heavy scientific programme which included two poster sessions (for which the time devoted was

found too short by several participants), an important instrumentation exhibit was presented during the whole conference with several fluorimeters including two new instruments.

A social programme was organized on tuesday afternoon for which the participants were invited to choose one out of the three following sites of interest : visit of the Louvre museum, visit of the (renewed) Musée du Conservatoire des Arts et Métiers, tour of the main points of interest of the City of Paris. The Conference Banquet was held on a "bateau-mouche" on tuesday evening and took the participants in an unforgettable trip for a magnificent sightseeing of the main monuments built 100 to 900 years ago along the Seine river and cleaned in the recent years.

Next Conference

The next conference (MAFS7) will be held in Amsterdam in september 2001 under the chairmanship of Professor Kraayenhof.

Inter-American Photochemical Society 11th Winter Conference

Clearwater Beach, Florida

January 2-6, 2000

Reported by William Jenks

The 11th Winter Conference of the IAPS was held last January in the Clearwater Beach Hilton, as usual. A great debt of thanks are due to Ed Hilinski, Joe Hupp, and the rest of the organizing committee for putting on another excellent meeting and arranging the excellent weather. Ed was in fine form, making sure everything went smoothly during the meeting itself. Though we switched hotels, he managed to use the one that had that same old comfortable name from years past to make us all feel at home.

The first talk of the meeting on Monday morning was **Gary Schuster's** discussion of long distance radical cation migration in DNA. He reviewed his work with anthraquinone derivatives that abstract a single electron from DNA bases, but primarily cut at GG sites, with apparent migration of the radical cation site down the DNA strand. Much of the talk was dedicated to the mechanism of this site hopping, with the conclusion that a "phonon-assisted polaron-like hopping" mechanism is in force in which conformational distortion induced by the radical cation formation plays a key role in hole migration. **Richard Keene** discussed his work on polymetallic assemblies. The structures, based on the classic Ru(bpy)₃ complexes, were modified with ligands with multiple nitrogen-based binding sites, such that Ru-Ru and Ru-Os complexes, each a pseudo-Ru(bpy)₃, were prepared. Molecules with different stereochemical arrangements with the same number of bonds were isolated and studied. The key result from lifetime studies was that charge separation lifetimes differed for various *cis* and *trans* isomers in a way that did not correlate well with physical distance between the metal centers. **Irena Bronstein** summarized the state of the art of an instrument from Tropix Inc that takes advantage of the chemiluminescence of dioxetanes. Enzyme-catalyzed hydrolysis of a phosphate on the dioxetane structure triggers dioxetane cleavage that is detected using a secondary fluorescer and CCD cameras for multiple well plates. In this way, very high throughput analysis is possible. A new dioxetane substrate that emits in the visible was described that allowed simultaneous study of more than one hydrolysis enzyme. **William Jenks** presented his work on the degradation of 4-chlorophenol under TiO₂-mediated conditions. Hydroxylation reactions are generally observed until ortho HO groups are obtained, after which and oxidative ring opening is possible. A mechanism for the ring opening was suggested.

Monday afternoon saw a new group of talks. **Norbert Scherer** described his collaborative research with Keith Moffat connecting ultrafast protein fluctuations to reactivity. The particular system involved the photochemical isomerization of coumaric acid in Photoactive Yellow Protein of cyanobacteria. Time-resolved X-ray studies were coupled to theoretical modeling. **Herbert Meier** described the photophysics and photochemistry of stilbenoid dendrimer systems. At larger generations, the conformation of the macromolecule is cylindrical and the photochemical 2+2 reactions can be run essentially to completion. "Belt cyclophanes" were produced with

related structures, interestingly only at elevated temperature. It was postulated that this effect was due to needing the higher temperature to achieve the right conformation for the first chemical step. **Gerald Babcock** reviewed his group's work in photosystem II, with particular emphasis on the Mn-dependent chemistry that involves radical formation. An interesting thermodynamic problem, in which the phenoxy radical of tyrosine appears to end up abstracting a hydrogen from water was explored, with the proposition that the Mn-bound water had a considerably smaller HO bond strength. **Howard Zimmerman** described a computational chemistry method he had developed to predict the photochemical reactivity of organic systems. The method is based on calculating a ρ -density matrix between excited and ground states. Its utility was demonstrated with a series of prototypical systems in which bond order changes were consistent with reactivity.

The night session consisted of two talks. **Joerg Rockenberger** presented his work with functionalized semiconductor nanocrystals. An example system consisted of a CdSe core, surrounded by a CdS shell, the latter to improve the characteristics of the core and make the surface less critical to performance. A silica coating is further added that can be functionalized to make the nanoparticles water soluble or cause them to bind to various substrates. The fluorescent properties of the particle can then be taken advantage of as a "stain" for biological materials. **Ya-Ping Sun** talked about his work with functionalized C₆₀ and carbon nanotubes. The essential innovation with the nanotubes is to put them onto soluble polymers to facilitate solution phase photophysical study. The photophysical behavior complex, but they also behave in fairly expected ways, such as being quenched at or near the diffusion controlled limit by anilines.

Richard Givens opened up the Tuesday morning session with a review of his work on "caged" biologically active compounds (e.g., phosphate derivatives). Flash photolysis results were presented that shed light on the mechanism of the desyl trigger. Modifications of the basic *p*-hydroxyphenacyl phototrigger structures meant to shift the absorption to the red also led to changes in photochemical behavior. Progress on collaborative projects implementing the Givens phototriggers in biological systems was also presented.

The second talk of the morning was given by **Christine Clancy, winner of the 2000 Closs award**. Using ns/ μ s-time resolved EPR, she studied the photoionization of tyrosine. Ionization was found to come primarily from the triplet state, but singlet ionization was detected when 2-bromomethylpropionic acid was added as an electron acceptor, probably via an exciplex. **Michele Régimbald-Krnel** described work of her Ottawa group to develop photo-decrosslinking polymers. The rather sensitive application is to try to improve the current methods for growing protein crystals in microgravity. The main approach has been to use iodonium-based photoacids to de-crosslink polymers held together with orthoesters. Ideally, the membranes would be indefinitely stable in the dark, but quickly degraded on exposure to light. Several promising variations on the basic theme were discussed, but the ideal system has yet to emerge. **Albert Stiegman** presented his results on photochemical and photophysical characteristics of some exotic xerogels based on doping silica with transition metals, primarily vanadium. These porous glasses contain well isolated catalytic sites for alkyne or olefin polymerization, for instance. An interesting approach to making a "teflon" coating on glass or Si was based on making a thin layer of metal/silica xerogel and polymerizing difluoroethylene.

The final talk Tuesday morning was **Doug Neckers' 1999 I-APS Award Address**. After taking advantage of his high position as the awardee to give an incredibly vague title and abstract, his presentation was a thorough review of the history and recent developments by his and other groups on several photoinitiator families, notably the borates. The role of electron transfer vs. direct radical formation through various systems was a recurring theme.

David McMillin opened the afternoon session with his work on cationic porphyrins that bind to DNA. Using hairpin turns to simplify his systems, he noted that in GC rich sequences the porphyrins intercalated, whereas external binding was observed in AT rich sequences. First binding constants were rather high, of the order of 10^8 M^{-1} . Competitive binding studies were used to determine affinities of particular base pairs and probe various steric issues in the binding by using "altered" base pairs. The second talk of the afternoon was **Ana Paola Cione's Cilento Award address** in which she described her work on the photochemistry and photophysics of several aromatic substrates adsorbed to clays. The materials examined included montmorillonites and hectorites from various sources and the major probe technique was fluorescence. Clays from Wyoming, for instance quenched fluorescence uniquely well because of high iron content. Similar to some zeolite systems, fluorescence could be changed to phosphorescence by exchanging natural Na cations with heavy atoms such as Rb, and Tl.

Lisa Kelly described her work with various imide and diimide aromatic systems as DNA photocleavage agents. Flash photolysis studies on the basic quenching rate constants for reductive solution phase quenching of the imide triplets were reported, as were some binding constant studies. An important issue in her systems is to get chemistry from the triplet state, rather than from the singlet, to insure good cutting quantum yields. **Keith Walters** from Kirk Schanze's group gave his talk on the photophysics of π -conjugated phenylene-acetylene oligomers that contain bipyridyl type units for metal binding. Effects of the length of the oligomer on the equilibrium of excited state types were of significant interest. A particularly clever synthetic scheme was ultimately used to prepare well-defined systems en route, at least intellectually, to the polymeric systems. **Franz De Schryver** gave his talk on a series of highly branched aromatic dendrimers. The details of time- and spatial resolution of his spectroscopy were a major focus. He outlined the confocal imaging, coupled with laser trapping of the assemblies and interpretation of the data. To inject a brief non-scientific note, it was also notable that Franz was able to light up the whole room during a brief power outage with his extraordinarily powerful green laser pointer.

Wednesday morning's session was opened by **Pedro Aramendia**. He discussed the photochromism of merocyanine/spirooxazine couples in several different polymer systems, including the methyl, ethyl and isobutyl methacrylates. The essence of his talk was the interpretation of the non-exponential fluorescence decays. He proposed that, instead of the usual Gaussian distribution of decays that is often invoked in heterogeneous systems, a "relaxation model" should be used. In addition to the simple photophysics of the emitter, it also accounts for the relaxation of the matrix. **Roseanne Sension** gave her presentation on some femtosecond flash work on polyene systems. Direct observation of the S_2 to S_1 internal conversion is observable with excitation pulses a few 10s of fs wide. S_2 lifetimes were on similar 10s of fs timescales. Applications of the fs-timescale spectroscopy to a couple of biological problems was also discussed. **Peter Wagner** was to have given his **2000 I-APS Award address** at this time, but he had fallen ill and gone home. The talk he was to give is printed elsewhere in this issue.

After a free Wednesday afternoon, talks started up again in the evening, beginning with **Josef Michl**. He discussed the reversible photochemistry of an intramolecular photochemical $6 + 6$ electron cycloaddition based on the isodrine-pagodane system. The system has wavelength-dependent ratio of fluorescence and chemistry, suggesting meaningful competition between relaxation and chemistry for S_2 . A different temperature dependence was also observed at different irradiation wavelengths. An interesting "benzene excimer" fluorescence was reported. The back reaction (to the two benzenes) was found to be at least partly adiabatic. A kinetic model that included measurement of the forward quantum yield in the presence of product absorption was presented. **Michael Kasha** followed, discussing the photophysics of related hydroxyflavones. Independently

occurring “normal” and post-proton-transfer fluorescence was observed in some systems by inducing rotation of the OH group adjacent to the carbonyls with a hydrogen bonding matrix. A mechanistic basis of the general non-luminescence of the systems involving a pseudo-Jahn-Teller potential was discussed. And as always, general bits of wisdom were tossed in, this time discussing the relationship of chemists to medical research.

This reporter had to return home Thursday morning, and his students spent the morning sick, so our notes from the last set of talks are unfortunately poor. Our apologies are laid out to the presenters for the Thursday morning session, whose talks we summarize largely from the abstracts. **Robert Dickson** opened the session with his talk on probing the three dimensional orientation of individual molecules using spectroscopic methods. Using a wide-field optical microscope with a single detector, it is possible **Don Arnold** reviewed his recent work on the photo-NOCAS reaction between cyanobenzenes and electron rich olefins or allenes in polar solvent. Favorable electron transfer energetics lead to the titled substitution reaction, whereas an exciplex-mediated cycloaddition reaction exists as an alternative in less favorable circumstances. **Richard Weiss** spoke about his work functionalizing polystyrene and *n*-alkanes with pyrene irradiated at small wavelengths (high energy). A preliminary version of this work was presented in a recent issue of this newsletter. Also discussed was the use of MeV energy range protons and electrons instead of light. A remarkable efficiency of functionalization was achieved with the protons, and remarkably, 1-pyrenyl functionalization is done quite selectively. **Gerald Meyer** closed out the conference with his talk on TiO₂ sensitization by Na₂[Fe(bpy)(CN)₄]. Both ground and excited state sensitization pathways are found, each having different dynamics and efficiencies. Time dependent optoelectronic responses can be tuned by excitation wavelength and subtle manipulation at the molecular level.

The Photophysics of Organic Molecules with Long-Lived Second Excited Singlet States

Ron Steer, Department of Chemistry, University of Saskatchewan, Saskatoon SK, Canada S7N 5C9

In the late 1960s when I was a graduate student studying photochemistry and spectroscopy, my labmates and I learned a great deal about the photochemistry of carbonyl compounds and about the "rules" governing the electronic relaxation processes of the excited states of polyatomic molecules. *Photochemistry*, the text by Jack Calvert and Jim Pitts published in 1964, was regarded as a work of near biblical importance, particularly to those of us doing research on gas phase systems. The theory of radiationless transitions was just past its infancy; it was truly exciting (and educational!) to follow the controversies in the literature surrounding the early ideas of intra- and inter-molecular vibrational and electronic relaxation, and to learn the fundamental basis for the empirical rules of excited state behaviour. One must be indelibly imprinted by the earliest of one's research experiences, because my research group and I have now followed variations on these themes for thirty years. This brief, personal review describes some of that research.

In the early 1970s, my group became interested in photochemical reactions which yield small thioaldehydes and thioketones as products - reactions such as the photodecomposition of cyclic organic sulfides in the gas phase. Inevitably, this interest prompted us to examine the spectroscopy of these thiocarbonyl-containing products and to find new spectroscopic ways to analyze for them *in situ* by fluorometry. To this end, we built a classical gas phase fluorescence apparatus which we dutifully calibrated and tested for sensitivity using the only volatile thiocarbonyl compound commercially available, thiophosgene, Cl₂CS. We were actually interested in thiophosgene's red emission from S₁ which had been recently (then!) reported in the literature, but to our surprise (because we had been conditioned by "Kasha's Rule") we also found an enormously intense, broad feature in the emission spectrum in the uv/blue - emission which we assigned to S₂ - S₀ fluorescence, i.e. "anomalous" prompt fluorescence from an upper excited singlet state. We duly reported this in a Chem. Phys. Letters paper in 1974,¹ and soon learned that Paul de Mayo and his group, quite coincidentally, had already observed S₂-specific photochemistry in thiobenzophenone in solution.² This chance observation of S₂ - S₀ emission in thiophosgene set the course for much of my group's research through to the end of the century.

Azulene is the first-identified, best-studied and most often cited example of closed-shell-ground-state organic molecules which fluoresce strongly from their relatively long-lived upper excited singlet states (S₂) but only weakly from their very short-lived lowest excited singlet states (S₁) in condensed fluid media. However, the thiones are actually easier model compounds to use in studies of upper excited state photophysics because they provide a larger number of readily accessible experimental observables and are amenable to several pump-probe methods that are difficult or impossible to use in the azulene system.³ First, the presence of a "heavy" sulfur atom in the thiones results in extensive singlet-triplet mixing by spin-orbit coupling so that relatively strong radiative singlet-triplet transitions can be readily observed. In many thiocarbonyls, for example, one can easily excite T₁ cleanly by direct one-photon absorption in the red or near infrared region of the spectrum, and can observe intense T₁ - S₀ phosphorescence in fluid media at room temperature.⁴ Sequential two photon excitation of S₂ is possible via T₁, i.e. S₀ - T₁ - S₂, as well as via S₁.⁵ The triplet sublevels also exhibit unusually large zero-field splittings (D*) so that at low temperature the kinetics of inter-sublevel transitions can provide a good experimental handle on spin-lattice relaxation

phenomena.⁶ Finally, S_1 is not "dark" in many thiones and its emission provides a third experimental measurable in the form of either prompt or thermally activated delayed fluorescence.⁷ Thus many aromatic thiones in inert fluid solution at room temperature exhibit emission from three states, $S_2 - S_0$, $T_1 - S_0$ and $S_1 - S_0$ (thermally activated delayed fluorescence) following initial excitation of an ensemble of them to S_2 .

Thiones also provide interesting variations on the process of excited state annihilation; examples of both singlet-singlet annihilation (SSA) for small thiocarbonyls in the gas phase⁸ and triplet-triplet annihilation (TTA) for aromatic thiones in fluid solution⁹ are known. The energy level spacings in the thiocarbonyls are such that both $S_1 + S_1$ SSA and $T_1 + T_1$ TTA can populate the fluorescent upper singlet, S_2 . The kinetics of these electronic energy pooling processes can thus be followed by observing the decay of emission from the lower state and the growth and decay of P-type delayed fluorescence from S_2 following pulsed laser excitation in the $S_0 - T_1$ or $S_0 - S_1$ absorption bands. Measurements of the efficiency of energy pooling and the determination of the physical factors which control the dynamics of this process are ongoing in our laboratories.

Of course thioaldehydes and thioketones are not ideal in other respects. They are often not particularly thermally stable - some tend to polymerize at room temperature - and the volatile compounds stink. They also are oxygen and moisture sensitive, and will react to form the corresponding ketone and various decomposition products if exposed to air for any length of time. They are photochemically reactive to an extent determined by their structure, the nature of the solvent and the wavelength of their excitation. Excited thiones are ubiquitous H atom abstractors¹⁰ and this can be a nuisance (from a photophysical perspective only, of course!) when hydrocarbons are used as solvents. We often minimize such unwanted reactions by carrying out our measurements in inert perfluorinated solvents,³ but this severely limits the solute concentration ranges which can be explored.

Studying the photochemistry and photophysics of thiones in solution can also be a bit tricky. The S_2 states of some alicyclic thiones, for example, are very short-lived and appear to relax rapidly by a mechanism which involves reversible intramolecular photochemistry.¹¹ In addition, the S_2 and T_1 states of most thiones are quenched by ground state thione at diffusion limited rates.³ In earlier work this latter fact was not always recognized, and measurements of rate constants, excited state lifetimes and emission quantum yields gave data which were of limited use. To overcome this difficulty and obtain rate constants and quantum yields which are genuine functions of only the solute and solvent system employed, it is necessary to extrapolate measurements of quantum yields and lifetimes to infinite dilution of the thione.³

It is always dangerous to generalize, but for dilute solutions of many photostable aromatic thiones in fluid inert solvents at room temperature, the most important excited state decay processes are nonradiative and follow the general route $S_2 - S_1 - T_1$. The relative magnitudes of the rate constants for $S_2 - S_1$ internal conversion are determined by the Franck-Condon factors for the two weakly coupled states which, in turn, are determined by their $S_2 - S_1$ electronic energy spacings according to the energy gap law. $S_1 - T_1$ intersystem crossing occurs with near unit quantum efficiency, but the decay of T_1 is determined by a number of factors, including the temperature of the system and the $S_1 - T_1$ and $T_1 - S_0$ electronic energy spacings. Quantum yields of phosphorescence can be remarkably large.³ At room temperature, back intersystem crossing to S_1 followed by $S_1 - S_0$ internal conversion is significant in thiones with small $S_1 - T_1$ spacings. At lower temperatures, when back intersystem crossing is suppressed, $T_1 - S_0$ intersystem crossing accounts for the majority of the decay. At still lower temperatures, less than 4 K, the rate of spin-lattice relaxation among triplet spin sublevels begins to play an important role in the dynamics. All of this can be complicated by the reordering of T_1 and T_2 in more strongly interacting solvents, such as benzene, in which the lowest triplet is of π character compared with n character in most weakly interacting solvents.¹² Indeed, the observation of interesting solvation effects in the thiones has spawned a small cottage industry among spectroscopists with access to supersonic expansion equipment.¹³

Once the photophysics of a thione's lower valence states (S_0 through S_2) has been determined, it becomes possible to identify some of the major decay paths of still higher states, even though these states are very short-lived and essentially non-fluorescent. Both higher valence and low-lying Rydberg states are accessible in the near uv, and excitation of them invariably results in emission from lower excited valence states populated during the system's electronic relaxation, provided that photochemical pathways are not dominant. Quantum efficiencies of $S_n - S_2$ ($n > 2$) internal conversion are large (but often not 1) for photostable thiones in inert condensed media at room temperature.¹⁴

Azulene and its derivatives have been extensively studied over the years, but still present many challenges. Several years ago we acquired a laser system for time-resolved pump-probe studies, expecting to use it to measure the lifetimes of the short-lived S_1 states of the thiones which had interested us for some time. Of course we dutifully tried out our new gear on the "well-known" azulene system, and were dismayed, initially, that we were unable to reproduce, accurately, measurements of azulene's picosecond S_1 lifetime which had been in the literature for many years. Azulene is not nearly as experiment-friendly as some aromatic thiones because the only quantity which can be easily and directly observed is its $S_2 - S_0$ fluorescence. In solution at room temperature its triplet state is non-phosphorescent and is very short-lived because it undergoes fast back-intersystem crossing to S_1 (small $S_1 - T_1$ electronic energy gap) followed by very fast crossing to the ground state (by a mechanism which is now known to involve an $S_1 - S_0$ conical intersection). In any event, our initial difficulties led us to carry out a systematic study of the photophysics of azulene and many of its derivatives in a wide variety of solvents using a range of pump and probe excitation energies. We learned that our initial experiments were, in fact, correct, but that we weren't considering all of the important variables such as the effect of solvent shift.

The second excited singlet states of azulene and its simple derivatives in inert solvents at room temperature behave in a more-or-less understandable way. The majority of S_2 relaxation events are nonradiative; quantum yields of $S_2 - S_0$ fluorescence are typically a few percent. In azulene and its light-atom containing derivatives, including alkyl- and fluorine-substituted ones, the vast majority of nonradiative events involve $S_2 - S_1$ internal conversion.¹⁵ The relative rates of the process are in accordance with the energy gap law, i.e. they are determined by the relative magnitudes of the Franck-Condon factors involved in the weak coupling of S_2 and S_1 . 1,3-Difluoroazulene has the largest $S_2 - S_1$ gap and has the largest quantum yield of $S_2 - S_0$ emission (0.20) and the longest S_2 lifetime (9.5 ns) yet reported for an organic compound in condensed media at room temperature.¹⁵ (Okay, so it is not a Guinness world record - you take what you can get!) The addition of free or restricted rotors (e.g. alkyl groups) to an otherwise rigid azulene frame increases the nonradiative decay rate by an increment which can be rationalized in terms of changes in the electronic energy gap and the increased effective number of coupled vibrational states. Substitution by chlorine or bromine atoms also results in an increase in the nonradiative rate, this time by enhancement of the rates of intersystem crossing associated with greater spin-orbit coupling in the heavy atom-containing molecules.

The photophysics of the S_1 states of azulene and its derivatives is even more interesting. Relevant empirical observations are as follows.¹⁶⁻¹⁸ (i) The lifetime of S_1 is short - is about 1 ps for azulene itself - and $S_1 - S_0$ relaxation is all physical (no significant photochemistry in most media). (ii) There is no significant deuterium isotope effect (for azulene-d₈ is the same as for azulene-h₈ in the same solvent). (iii) The rate constants for S_1 nonradiative decay of azulene and its simple derivatives in many different solvents exhibit an energy gap law-like relationship, i.e. $\ln k_{NR}$ decreases approximately linearly with increasing $S_1 - S_0$ electronic energy gap. (iv) Shifts in the $S_1 - S_0$ energy gap produced by both ring-substitution and solvent shift are correlated with the nonradiative rate constants in the same way. Substitution of methyl groups or other free and restricted rotors only affects the rate constant for the nonradiative decay through the changed $S_1 - S_0$ energy spacing. Even the value of the nonradiative rate constant for the decay of *isolated* supersonically-expanded azulene in its S_1 zero-point level falls squarely on the same linear energy gap law correlation. (v) The vibrational structure of the solvent has little effect on the S_1 lifetime - only the effect of the solvent on azulene's $S_1 - S_0$ energy gap has a measurable effect. (vi) For azulene itself, excitation of S_1 with

pump wavelengths that provide up to ca. 1650 cm^{-1} of incremental vibrational energy produce no measurable effect on the S_1 lifetime in solution at room temperature.

In 1996 Mike Robb and coworkers¹⁹ published a revealing set of calculations which demonstrated that the S_1 and S_0 potential energy surfaces of azulene exhibit a conical intersection at large C-C bond displacements. This immediately provided a satisfying explanation for both the short S_1 lifetime and the lack of an observable deuterium isotope effect, but left several loose ends, the most obvious of which is a rationale for the apparent energy gap law correlation in the nonradiative decay rates. We are currently working to answer at least some of these open questions.

Thirty years ago learning about the photochemistry of ketones, the spectroscopic underpinnings of photophysics and the theory of radiationless transitions occupied much of my group's time. Today contributing in some way to our understanding of the photochemistry, photophysics and spectroscopy of thiones, azulene derivatives and other compounds which exhibit unusually long-lived S_2 states still occupies a significant minority of our time. Only our perceptions have changed. Then we were conditioned by Kasha's Rule: "*the emitting electronic level of a given multiplicity is the lowest excited level of that multiplicity.*"²⁰ Now we are conditioned by the experience that all bound excited electronic states of all multiplicities emit – it is just that we're not always clever enough to detect the emission!

Acknowledgements:

The research described in this article arising from my lab has all been supported by grants from the Natural Sciences and Engineering Research Council of Canada through their thoroughly enlightened Equipment, Research and Scholarships and Fellowships programs. Many students, post-docs and colleagues around the world have contributed greatly, and I owe them a lot of thanks. Prominent among these individuals from my lab are Osama Abou-Zied, Alfredo Bruno, Dennis Clouthier, Ken Falk, Darin Latimer, Andrzej Maciejewski, Benoit Simard, Hemant Sinha, Marek Szymanski, Dietrich Tittelbach-Helmrich and Brian Wagner, and at the MPI, Göttingen, Bernhard Nickel in whose lab the TTA experiments were done. I apologise to the many whose work has not been quoted in this brief, personal review.

References:

1. S.Z. Levine, A.R. Knight and R.P. Steer, *Chem. Phys. Lett.* **1974**, 29, 73.
 2. P. de Mayo and H. Shizuka, *J. Am. Chem. Soc.* **1973**, 95, 3942.
 3. A. Maciejewski and R.P. Steer, *Chem. Rev.* **1993**, 93, 67.
 4. M. Szymanski, A. Maciejewski and R.P. Steer, *Chem. Phys.* **1988**, 124, 143.
 5. B. Simard, V.J. MacKenzie, P.A. Hackett and R.P. Steer, *Can. J. Chem.* **1994**, 72, 745.
 6. M.R. Taherian and A.H. Maki, *Chem. Phys. Lett.* **1983**, 96, 541.
 7. A. Maciejewski, M. Szymanski and R.P. Steer, *J. Phys. Chem.* **1986**, 90, 6314.
 8. D.J. Clouthier, A.R. Knight, P.A. Hackett and R.P. Steer, *J. Chem. Phys.* **1980**, 72, 1560.
 9. H. Eisenberger, B. Nickel, A.A. Ruth and R.P. Steer, *J. Chem. Soc. Faraday Trans.* **1996**, 92, 741.
 10. See, for example, the review by J.D. Coyle, *Tetrahedron* **1985**, 41, 5393.
 11. K.J. Falk and R.P. Steer, *J. Am. Chem. Soc.* **1989**, 111, 6518.
 12. A. Maciejewski, M. Szymanski and R.P. Steer, *Chem. Phys. Lett.* **1988**, 143, 559.
 13. H.K. Sinha, O.K. Abou-Zied, M. Ludwiczak and R.P. Steer, *Chem. Phys. Lett.* **1994**, 230, 547.
 14. M. Szymanski, A. Maciejewski and R.P. Steer, *J. Phys. Chem.* **1988**, 92, 2485.
 15. N. Tétreault, R.S. Muthyala, R.S.H. Liu and R.P. Steer, *J. Phys. Chem.* **1999**, 103, 2524.
 16. B.D. Wagner, M. Szymanski and R.P. Steer, *J. Chem. Phys.* **1993**, 98, 301.
-

17. D. Tittelbach-Helmrich, B.D. Wagner and R.P. Steer, *Chem. Phys. Lett.* **1993**, 209, 413.
 18. D. Tittelbach-Helmrich, B.D. Wagner and R.P. Steer, *Can. J. Chem.* **1995**, 73, 303.
 19. M.J. Bearpark, F. Bernardi, S. Clifford, M. Olivucci, M.A. Robb, B.R. Smith and T. Vreven, *J. Am. Chem. Soc.* **1996**, 118, 169.
 20. M. Kasha. *Disc. Faraday Soc.* **1950**, 9, 14.
-

Electronic Spectroscopy of Matrix Isolated Singlet Carbenes - Simple Models, Conformational Dependence, and Photochemistry

Robert S. Sheridan
University of Nevada, Reno

Introduction

For over 15 years our group has been studying the low temperature spectroscopy, structure, reactivity, and photochemistry of a wide variety of ground state singlet carbenes. We have often been struck by the parallels between organic carbenes and transition metal based systems. To wit, carbenes afford an opportunity for ligand-based multiplicity control that is rare in organic molecules, but quite conventional for transition metal complexes. Moreover, we have observed that singlet carbenes in particular exhibit a remarkably rich and varied absorption spectroscopy, exquisitely sensitive to substitution, and ranging throughout the UV and visible. Matrices containing trapped singlet carbenes routinely are vividly colored.

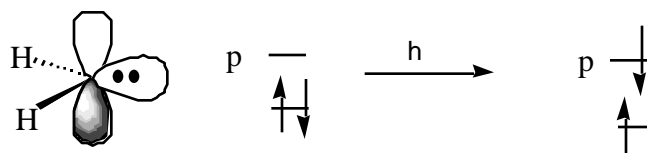
We wish now to take this opportunity to catalog our results on the absorption spectra of a broad array of singlet carbenes, and to take advantage of this "friendly" setting to describe our very simple-minded models for rationalizing our observations. We are by no means the only workers in this area. We apologize up front for concentrating on our own previously published results, but these provide a wide enough variety to illustrate the principles of our crude analysis. In particular, we will not venture into the rapidly evolving field of stabilized "Arduengo" carbenes,¹ nor into the extensively investigated simple halocarbene realm.² Finally, we will not cover the fine contributions of Dailey and McMahon to this area.³ Despite these limitations in scope, however, we hope that others in the field will find this discussion of interest and of use perhaps in their own investigations.

Results and Discussion

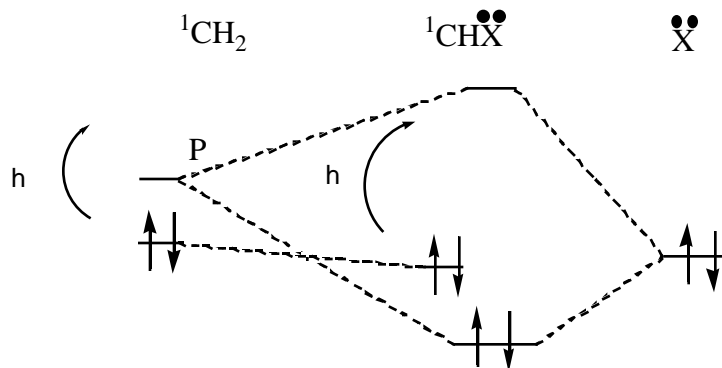
Matrix isolation has become a routine tool for studying the spectroscopy of reactive intermediates under static conditions, and a handy complement to laser time resolved solution studies. In short, we freeze precursor molecules in solid Ar or N₂ at 10 K. Irradiation at wavelengths carefully selected to be absorbed by precursor, but not by the targeted intermediate, leads to fragmentation (diazirine or diazo compounds), or in select cases rearrangement, to the desired carbene. In most cases (but not all), the inert surroundings and low temperatures render the intermediate indefinitely stable in the dark. The sample can be most conveniently interrogated by IR and UV/vis spectroscopy. In all cases discussed herein, we have confirmed the identity of the intermediates by various combinations of in situ trapping, photochemical conversion to identifiable products, and calculational modeling.

It is the photochemistry and, in certain fascinating cases, the thermal chemistry of the carbenes that attracts our primary interest. But again here we want to focus on our attempts to understand, in simplest terms, the UV/vis spectra of these species. In particular, we have found that depending on substitution the longest wavelength electronic

absorption of singlet carbenes can range from the high energy end of the UV to the farthest reaches of the visible. This first excited state for singlet carbenes can nominally be ascribed to a $\sigma \rightarrow p$ (or more formally, $^2 \rightarrow ^1p^1$) transition as shown below.



This significantly non-vertical transition generally appears as a very broad absorption in the visible (e.g. singlet CH_2 absorbs from 550 - 950 nm),⁴ although certain substituents can move this band into the UV. Although the excited state (and indeed the ground state in some cases) is certainly more complicated electronically, with considerable configurational mixing, this zeroth order picture is sufficient to rationalize trends in substituent effects on this absorption. From this starting point, we then consider structural and substituent perturbations on the energies of these two orbitals, varying the HOMO-LUMO gap, and with it to a gross approximation, the absorption energy. We thus consider a simple frontier MO mixing picture, illustrated below for electronegative lone-pair donors.



The same effects which stabilize closed shell singlet carbenes relative to the triplet states will clearly increase the energy gap to the excited open shell singlet as well. Our picture thus parallels discussions of substituent influences on triplet-singlet energies in carbenes, where two effects have been recognized to be important.^{5,6} Specifically, σ -donor atoms (O, Cl, F, Br) raise the carbene p-orbital energy, increasing the $\sigma \rightarrow p$ energy gap in line with donor ability. Moreover, the inductive electron withdrawal, by increasing the p-character in the C-X bond, lowers the carbenic lone-pair energy to some extent. Both effects serve to stabilize the carbene singlet state, and at the same time blue-shift the lowest energy electronic absorption.

In Table 1, and graphically in Figure 1, we summarize the data we have published for this key lowest energy $\sigma \rightarrow p$ transition in a variety of singlet carbenes, matrix isolated in Ar or N_2 . In the absence of more precise information on the spectral origins of these bands, we have simply recorded the apparent λ_{max} values, along with calculated numbers when available. In cases where different geometric isomers are observed (vide infra), we list the approximate average maximum. It should be noted that singlet carbenes often show more intense, higher energy absorptions in the UV, but these fall outside our scope here.

Table 1. λ_{max} Absorption Maxima for Matrix Isolated Singlet Carbenes

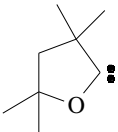
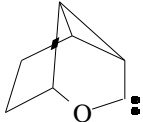
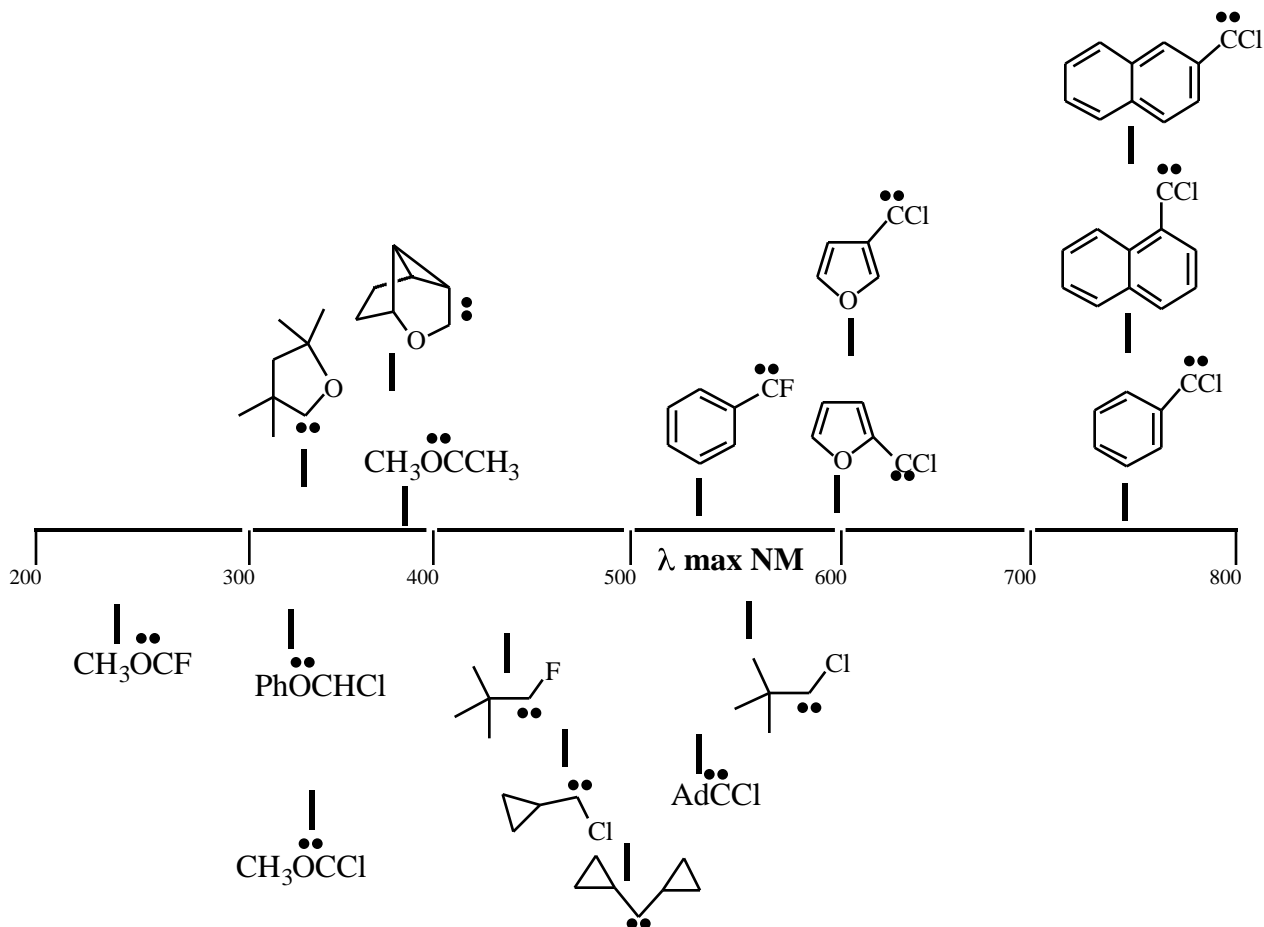
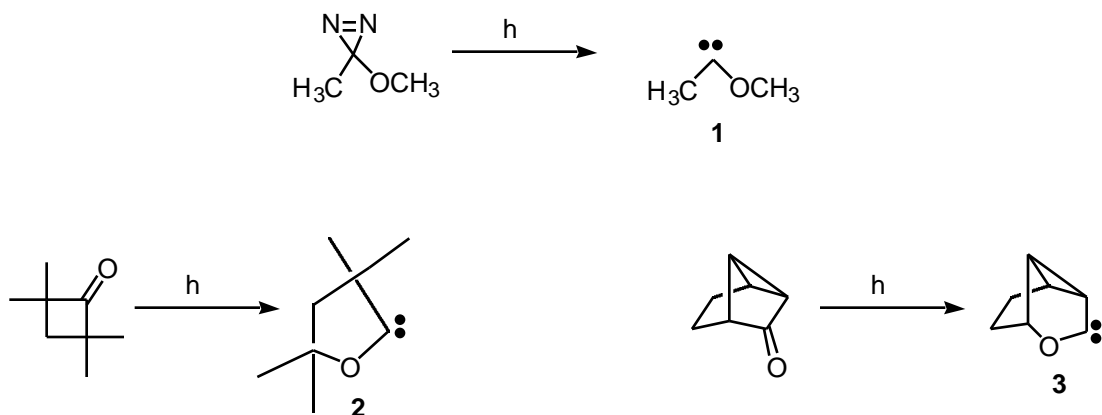
Carbene	λ_{max} (nm)	Calculated (method)	Ref.
MeOCMe (1)	385	376 <i>trans</i> , 385 <i>cis</i> (INDO/S) 357 <i>trans</i> , 397 <i>cis</i> (CIS/6-31G*)	7 8
 (2)	360	346 (CIS/6-31G*)	8
	396	396.9 (CIS/6-31G*)	8, 9
MeOCCl (4)	318	297 <i>trans</i> , 285 <i>cis</i> (CIS/6-31G*)	11, 14
PhOCCl (5)	320		12
MeOCF (6)	245	254 <i>trans</i> , 240 <i>cis</i> (INDO/S)	13
t-butCCl (7)	570	566 (CIS/6-31G**)	15
t-butCF (8)	447	421 (CIS/6-31G**)	Unpublished
AdCCl (9)	540		16
C ₃ H ₅ CCl (10)	460	470 (INDO/S)	18
(C ₃ H ₅) ₂ C (11)	490	475 (CIS/6-31G*)	19
PhCCl (13)	740	560 (CIS/6-31G*) 716 (CASPT2)	21 23
1-NpCCl (14)	750	540 (CIS/6-31G*)	24
2-NpCCl (15)	750	540 (CIS/6-31G*)	24
PhCF (16)	550	470 (CIS/6-31G*)	25
2-furylCCl (17)	600	471 <i>syn</i> , 489 <i>anti</i> (CIS/6-31G**)	26
3-furylCCl (18)	600	507 <i>syn</i> , 464 <i>anti</i> (CIS/6-31G**)	27

Figure 1 - Experimental Carbene σ -p Absorptions

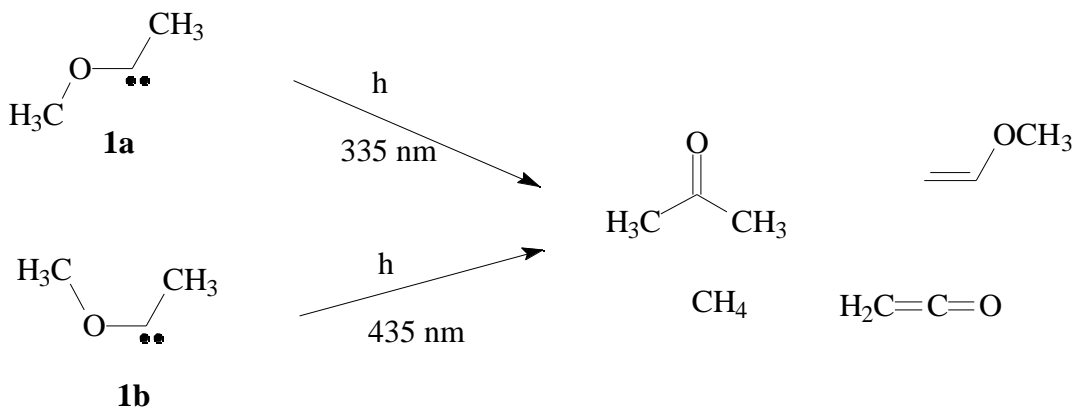
The singlet carbene systems fall naturally into the following groups: alkoxy, alkoxyhalo, haloalkyl, haloaryl, and dialkyl. We will discuss each subtype in turn.

We have used two methods to generate alkoxy-carbenes at low temperatures, diazirine photolysis (**1**)⁷ and ketone photorearrangement (**2**⁸ and **3**⁹).

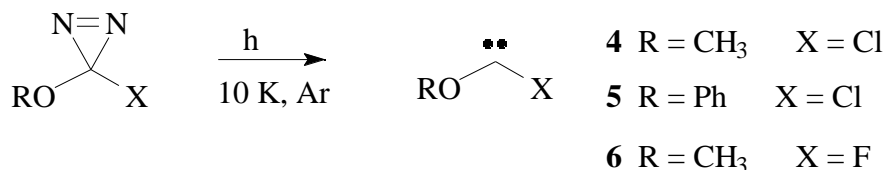


Here, compared to singlet $^1\text{CH}_2$ itself, the lone-pair donation from O raises the energy of the π -p transition significantly, to the range of 360 to 390 nm. We have proposed that the bond angle at the carbenic carbon also plays a role in the position of this absorption.⁸ A smaller angle lends greater s-character to the π -orbital, increasing the energy gap. Accordingly, **2** is calculated (MP2/6-31G*) to have the smallest OCC angle, and has the shortest wavelength absorption of the three carbenes. CIS/6-31G* calculations quite satisfactorily also fit the experimental absorptions, predicting values in the range ca. 350 - 400 nm (Table 1), and supporting the shortest wavelength for **2**.

Interestingly, we saw evidence for two geometric isomers of the acyclic alkoxy carbene, **1a**, and **1b**.⁷ Two sets of IR bands could be discerned for this species, that showed different dependencies on the wavelengths of photolysis. Irradiation on the short wavelength side (335 nm) of the broad π -p absorption centered at 390 nm caused selective conversion of *trans*-**1a** to products. Conversely, *cis*-**1b** was more labile at 435 nm. INDO/S calculations satisfactorily predicted absorptions for the two isomers at 376 nm for **1a** and 385 nm for **1b**. We speculate that the steric repulsion between the two CH_3 groups in **1b** opens the CCO bond angle significantly (114° at HF/6-31G* vs. 108° calculated for *trans*-**1a**),⁸ causing lower energy absorption. The assignments of the IR bands to the different geometric isomers was confirmed by ab initio calculations by Hess and co-workers.¹⁰

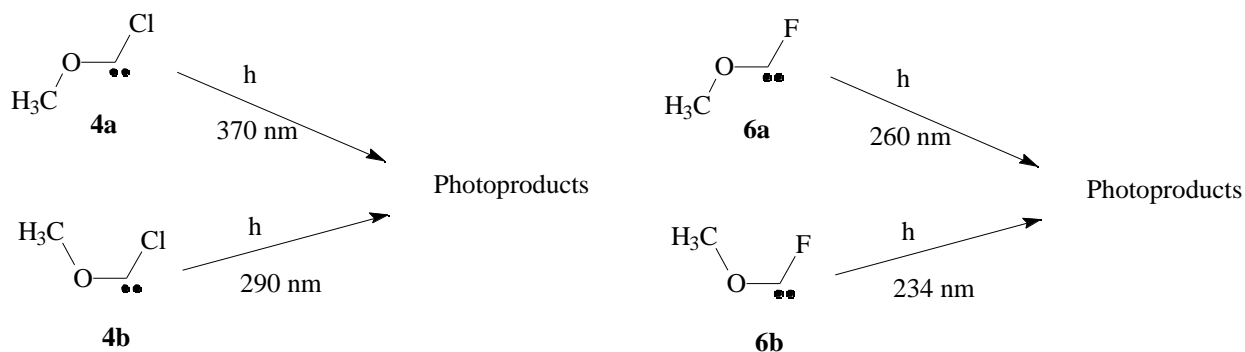


Adding halogen substitution to the alkoxy carbenes, from additional π -donation (and π -inductive withdrawal) increases the π -p energy gap further. Hence, methoxychloro- (**4**),¹¹ phenoxychloro- (**5**),¹² and methoxyfluorocarbene (**6**),¹³ all produced from irradiation of matrix isolated diazirines as shown below, absorb at shorter wavelengths. The effect is most pronounced in the fluorocarbene **6**, where the first excited state is now shifted to 245 nm. CIS/6-31G* calculations again confirm that the observed transitions are predominantly due to carbene π -p (or π) excitation.

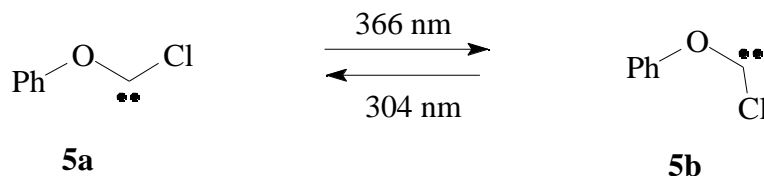


In these carbenes, we again see conformational differences in the electronic spectra, although now the *cis* and *trans* isomers are reversed. For example, methoxychlorocarbene (**4**) exhibits two sets of IR bands which convert to products selectively at different wavelengths.¹¹ On irradiation at 370 nm, it is the bands associated with *trans*-isomer **4a** that disappear more rapidly. And, irradiation of the broad UV band on the short-wavelength side, at 290 nm,

destroys *cis*-**4b** faster. Similarly, *trans*-methoxyfluoro-**6a** appears to react more rapidly at longer wavelengths (260 nm) and *cis*-**6b** is more photolabile at shorter wavelengths (234 nm).¹³ We are not sure what subtle geometric and electronic influences here shift the *trans*-isomers to longer wavelengths in contrast to methoxymethyl-**1** above. However, this conformational trend is confirmed by calculations. CIS/6-31G* calculations predict transitions at 297 and 285 nm, respectively, for *trans*-**4a** vs. *cis*-**4b**.¹⁴ Similarly, INDO/S theory predicts 254 nm for *trans*-**6a** and 240 nm for *cis*-**6b**.¹³

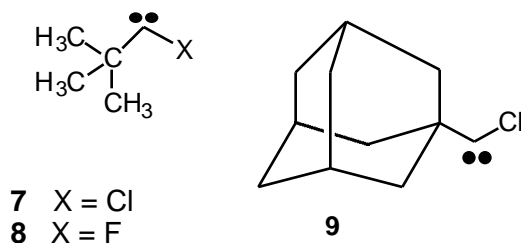


The methoxy carbenes are all quite photolabile, and we do not observe different photoproducts from different conformers, nor do we see any photo-interconversion of isomers. However, when the carbenes are rendered less sensitive to fragmentation, then photochemical *cis-trans* isomerization becomes evident. Irradiation of a *cis-trans* mixture of matrix isolated phenoxychlorocarbene (**5**) at 304 nm on the short wavelength side of its $\sigma \rightarrow \pi^*$ transition not only more rapidly causes conversion of *cis*-isomer **5b** to products, but also produces an increase in the IR bands of *trans*-**5a**.¹² Similarly, at longer wavelengths (366 nm), the *trans*-**5a** isomer is converted to **5b** along with product formation. Although we could not resolve the separate UV absorptions of *cis* and *trans* isomers, we found that long wavelength irradiations caused the apparent UV absorption maximum of the carbene to move to shorter wavelengths. Irradiation at 304 nm had the opposite effect.

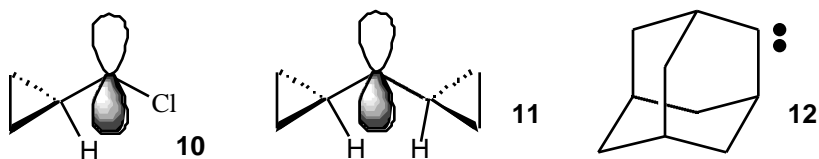


We also have a handful of alkylhalocarbenes to compare, all generated from diazirine matrix photolysis. Here, compared to the alkoxy carbenes the halogen σ -donation is weaker, and the smaller $\sigma \rightarrow \pi^*$ energy gaps are reflected in longer wavelength absorption. Direct halocarbene-to-alkoxy carbene comparisons are more difficult here, because the halocarbenes are inherently less stable and more prone to rearrangement even at 10 K. For example, we and others have tried in vain to observe methylhalocarbenes at low temperatures. But, although *t*-butylchlorocarbene (**7**) undergoes intramolecular CH insertion at 10K through quantum mechanical tunneling, the carbene lives long enough (6 h) for characterization.¹⁵ Its absorption at 570 nm is close in energy to that of the more stable adamantylchlorocarbene **9** (540nm).¹⁶ On the other hand, the fluorocarbene **8** absorbs at significantly shorter

wavelengths (447 nm).¹⁷ Again, CIS calculations model these absorptions quite satisfactorily (566 and 421 nm for **7** and **8**, respectively).



Compared to the t-butyl carbenes, cyclopropylchloro **10** seems out of place at 460 nm.¹⁸ However, calculations indicate that the "empty" p-orbital of the carbene aligns with the strongly electron donating cyclopropane C-C bonds, deriving considerable stabilization. The C-H is constrained into an orientation unfavorable for 1,2-shift, rendering the carbene observable at low temperatures. At the same time, the back π -donation from the Walsh type cyclopropane orbitals again raises the carbene p-orbital energy, expanding the HOMO-LUMO gap and correspondingly shifting absorption to shorter wavelengths.

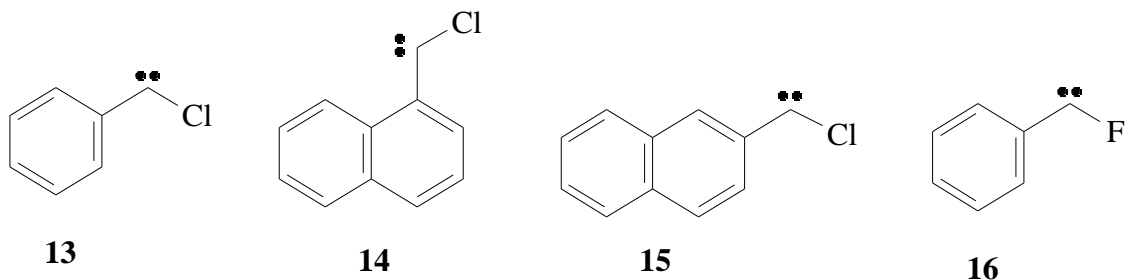


A similar cyclopropylcarbinyl electronic donation effect may be seen in dicyclopentyl carbene **11**, the first directly observed singlet dialkylcarbene.¹⁹ Although there are less systems known for comparison, the observed λ_{max} at 490 nm seems rather short compared to singlet methylene itself. Singlet adamantylidene (**12**) has also been observed under matrix isolation conditions by Bally and Platz.²⁰ They indicated a λ_{max} at 620 nm for this system, at significantly longer wavelengths as might be expected. However, the carbenic bond angle may be substantially different in **11** and **12**, complicating comparison of the two singlets.

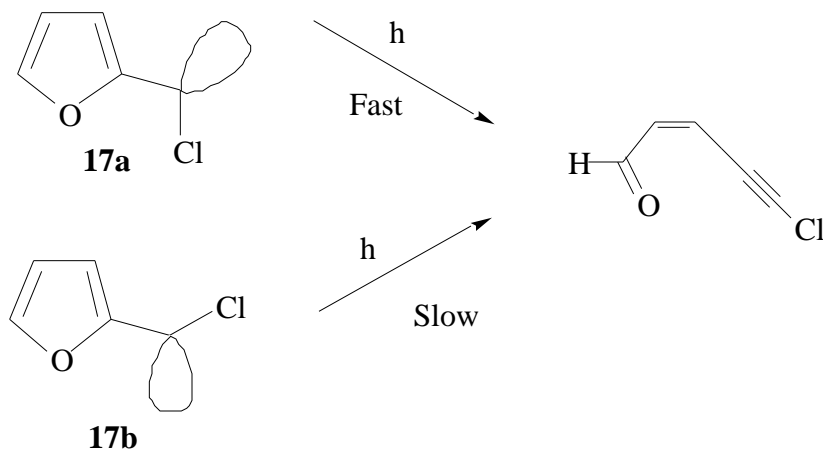
In general, we have found that arylhalocarbenes are shifted to longer wavelengths than their alkyl counterparts. Phenylchlorocarbene **13** has a long history as a prototypical singlet carbene for spectroscopic studies, with a conveniently observed strong absorption at ca. 320 nm, presumably $\pi \rightarrow \pi^*$ in origin. Interestingly, despite earlier matrix isolation studies (including our own), the long-wavelength $\sigma \rightarrow \sigma^*$ transition was not described until our report in 1994.²¹ We found a very broad and weak absorption for **13** centered at a λ_{max} of 740 nm.

It is not so obvious how to rationalize in simple qualitative terms the effect of aryl substitution on these absorptions. It has been suggested, however, that alkyl groups may stabilize the singlet state of carbenes, relative to the triplets, to a greater extent than do aryl groups.²² Thus, it may simply be that the aryl groups also do not stabilize the ground state of the halocarbenes relative to the excited states as well as do alkyls. CIS/6-31G* calculations are also not as successful here at modeling this long wavelength transition in phenylchlorocarbene (**13**), and predict a band at 560 nm, effectively where alkylchlorocarbenes **7** and **8** are calculated to be (and where they are found).

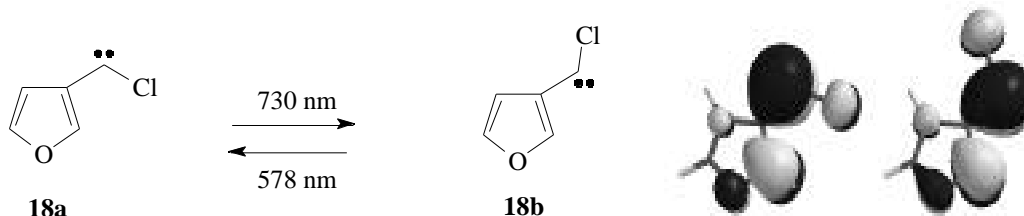
Platz and co-workers²³ have reported recently confirmation of this experimental observation, accompanied by an insightful theoretical analysis of the electronic spectra of **13**. At the CASPT2 level, they predict a weak transition at 716 nm corresponding predominantly to the $\pi \rightarrow \pi^*$ excitation. We have found similar, very weak and broad absorptions in the ca. 750 nm region for 1- (**14**) and 2-naphthylchlorocarbene (**15**).²⁴ Again, CIS calculations (ca. 540 nm) are less satisfactory here, but support the contention that these arylchlorocarbenes should all absorb in the same region of the visible. On the other hand, fluorine substitution has the expected effect of shifting the absorption to higher energies. Phenylfluorocarbene (**16**) absorbs distinctly in the range 450 - 740 nm (λ_{max} 550 nm), turning matrices a vivid blue color.²⁵ As in the chlorocarbenes, CIS calculations predict this transition to be at somewhat shorter wavelengths (470 nm).



Recently we have reported studies on the 2- and 3-furylchlorocarbenes. Each has unique spectral and conformational features, and thus we will describe them separately in turn. With a more electron-rich π -system, the furylcarbenes exhibit blue-shifted visible absorptions compared to the simple aryls, as seen with other π -donors. Thus, 2-furylchlorocarbene **17a,b** absorbs very broadly in the region 400 - 800 nm with a λ_{max} at 600 nm.²⁶ Here, two geometric isomers can be discerned in the IR spectra, *syn-a* and *anti-b*. Interestingly, the *syn*-isomer is significantly more photochemically labile than the *anti*-carbene. Irradiations of matrices containing the two conformers, irrespective of wavelength, causes **17a** to ring-open ca. 4 times faster than does **17b**. No change is observed in the UV/vis bands of the carbene during these irradiations, and thus we believe that both conformers have approximately the same electronic spectra. Indeed, CIS calculations, although again inaccurate in absolute energies, predict only small differences between the two $\pi \rightarrow \pi^*$ transitions (471 nm for **17a** and 489 nm for **17b**). We have suggested that the anti-periplanar alignment between the carbenic lone pair and the C-O bond selectively facilitates cleavage in the *syn* isomer.



Somewhat different conformational effects are observed in the 3-furylcarbene.²⁷ Here now the two geometric isomers of the chlorocarbene, **18a,b**, exhibit significantly different UV/vis spectra. In particular, the *syn*-isomer **18a** absorbs at distinctly longer wavelengths (λ_{max} 645 nm) than does *anti*-**18b** (λ_{max} 575 nm). Because the carbene is significantly more photostable than the 2-isomer, we found that the two conformers could be photochemically interconverted selectively depending on irradiation wavelength. Specifically, irradiation at the long-wavelength side of the visible band (730 nm) converted *syn*-**a** to *anti*-**b** rather cleanly. Conversely, irradiation at shorter wavelengths (578 nm) shifts the carbene to the *syn*-**a** isomer. CIS/6-31G* calculations mimic this significant conformational dependence of the carbenes, predicting 507 nm for *syn*-**a** and 464 nm for *anti*-**a**. The calculations suggest that the excited-state for both conformers is dominated by electronic promotion into the π^* -LUMO, as expected. This MO, illustrated below, is predicted to have a much larger coefficient at the 2-carbon than at the 4-carbon of the furyl ring. Moreover, the Cl- lone pair orbital contributes significantly to the MO, producing an orbital reminiscent of the LUMO in 1,3-butadiene. We have thus speculated that transitions populating this orbital are preferentially stabilized in the *syn*-isomer, resulting in longer wavelength absorptions.



Conclusions

The results above illustrate that application of a very simple model of substituent perturbations on frontier orbital energies rationalizes the UV/visible spectra for a variety of singlet carbenes, absorbing over a remarkably broad range of wavelengths. CIS calculations also for the most part parallel the experimental observations. There are clearly limits to the success of these elementary considerations, however. In particular, the π^* transitions in arylhalocarbenes seem somewhat longer wavelength than anticipated in comparison to alkylhalocarbenes. In the aryl singlets, CIS calculations are also a bit inaccurate in predictions of the energies of these absorptions. Nevertheless, this qualitative picture provides a useful guide for predicting the spectra of new species.

Acknowledgments

I am indebted to the excellent graduate, undergraduate, and postdoctoral colleagues who have provided the rich results on which these analyses are based. Long-running financial support by the National Science Foundation and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

References

- (1) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

- (2) See also Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583.
 - (3) (a) Brahms, D. L. S.; Dailey, W. P. *Chem. Rev.* **1996**, *96*, 1585; (b) Seburg, R. A.; McManon, R. J. *J. Org. Chem.* **1993**, *58*, 979.
 - (4) Herzberg, G.; Johns, J. W. C. *Proc. R. Soc., London* **1964**, *295*, 107.
 - (5) Garcia, V. M.; Castell, O.; Reguero, M.; Caballol, R. *Mol. Phys.* **1996**, *87*, 1395.
 - (6) Schwartz, M.; Marshall, P. *J. Phys. Chem. A* **1999**, *103*, 7900.
 - (7) Sheridan, R.S.; Moss, R.A.; Wilk, B.K.; Shen, S.; Wlostowski, M.; Kesselmayer, M.A.; Subramanian, R.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K., *J. Am. Chem. Soc.* **1988**, *110*, 7563.
 - (8) Matsumura, M.; Ammann, J.R.; Sheridan, R.S. *Tetrahedron Lett.* **1992**, *33*, 1843.
 - (9) Kesselmayer, M.A.; Sheridan, R.S. *J. Am. Chem. Soc.* **1987**, *109*, 5029.
 - (10) Hess, B. A., Jr.; Smentek-Mielczarek, L. *J. Mol. Struct. (Theochem)* **1991**, *227*, 265.
 - (11) (a) Kesselmayer, M.A.; Sheridan, R.S. *J. Am. Chem. Soc.* **1984**, *106*, 436. (b) Kesselmayer, M.A.; Sheridan, R.S. *J. Am. Chem. Soc.* **1986**, *108*, 99.
 - (12) Kesselmayer, M.A.; Sheridan, R.S. *J. Am. Chem. Soc.* **1986**, *108*, 844.
 - (13) Du, X-M.; Fan, H.; Goodman, J.L.; Kesselmayer, M.A.; Krogh-Jespersen, K.; LaVilla, J.A.; Moss, R.A.; Shen, S.; Sheridan, R.S. *J. Am. Chem. Soc.* **1990**, *112*, 1920.
 - (14) R. S. Sheridan, unpublished results.
 - (15) Zuev, P.; Sheridan, R. S. *J. Am. Chem. Soc.*, **1994**, *116*, 4123.
 - (16) Yao, G.; Rempala, P.; Bashore, C.; Sheridan, R. S. *Tetrahedron Lett.* **1999**, *40*, 17.
 - (17) P. Zuev, unpublished results.
 - (18) Ho, G-J.; Krogh-Jespersen, K.; Moss, R.A.; Shen, S.; Sheridan, R.S.; Subramanian, R. *J. Am. Chem. Soc.* **1989**, *111*, 6875.
 - (19) Ammann, J.; Ramasamy, S.; Sheridan, R.S. *J. Am. Chem. Soc.* **1992**, *114*, 7592.
 - (20) Bally, T.; Matzinger, S.; Truttmann, L.; Platz, M. S.; Morgan, S. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1964.
 - (21) Zuev, P.; Sheridan, R. S. *J. Org. Chem.* **1994**, *59*, 2267.
 - (22) Bettinger, H. F.; Schleyer, P. v. R.; Schreiner, P. R.; Schaefer, H. F. III in *Modern Electronic Structure Theory and Applications in Organic Chemistry*, E. Davidson, Ed.; 1997.
 - (23) Pliego, J. R., Jr.; De Almeida, W. B.; Celebi, S.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **1999**, *103*, 7481.
 - (24) Rempala, P.; Sheridan, R. S. *J. Chem. Soc., Perkin Trans. 2*, **1999**, 2257.
 - (25) Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.*, **1994**, *116*, 9381.
 - (26) Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 233.
 - (27) Khasanova, T.; Sheridan, R. S. *Org. Letters* **1999**, *1*, 1091.
-

Upcoming Meetings

An up-to-date version of this list is posted on the I-APS website (<http://www.chemistry.mcmaster.ca/~iaps/index.html>). Please send new meeting announcements to: wsjenks@iastate.edu and iaps@mcmaster.ca.

◆ **PHOTOBIOLOGY 2000: JOINT CONGRESS (AIP), ASP AND ESP MEETING**

May 31 – June 4, 2000

San Francisco, CA U.S.A.

Information: Nancy L. Oleinick, Biomedical Res Bldg 3, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, OH 44106-4942, tel: +1 216/368 1117, fax: +1 216/368 1142, email: nlo@po.cwru.edu

◆ **XTH INTERNATIONAL SYMPOSIUM ON LUMINESCENCE SPECTROMETRY-DETECTION TECHNIQUES IN FLOWING STREAMS – QUALITY ASSURANCE AND APPLIED ANALYSIS**

June 4 - 7, 2000

Granada, Spain

Information: Dr. Ana M. Garcia-Campana, Department of Analytical Chemistry, University of Granada, Avenue Fuertenueva s/n, E-18071 Granada, Spain, Tel: +34 9 58 24 85 94, Fax: +34 9 58 24 33 28, email: amgarcia@goliat.ugr.es

◆ **XVIII IUPAC SYMPOSIUM ON PHOTOCHEMISTRY**

July 22 – 27, 2000

Dresden, Germany

Information: Prof. Silvia Braslavsky, Mülheim, fax: +49 208/306 39 51, email: braslavskys@mpi-muelheim.mpg.de (chairperson); Prof. Thomas Wolff, Dresden, fax: +49 351/463 33 91, email: wolff@cech01.chm.tu-dresden.de (chairman local committee).

GORDON RESEARCH CONFERENCE ON ELECTRON DONOR-ACCEPTOR INTERACTIONS

August 13 - 18, 2000

Newport , USA

Information: Prof. Dr. J.W. Verhoeven, Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, NL-1018 WS, Amsterdam, Netherlands, Email: jwv@org.chem.uva.nl.

◆ **25TH EUROPEAN CONGRESS ON MOLECULAR SPECTROSCOPY (EUCMOS XXV)**

August 27 – September 1, 2000

Coimbra, Portugal

Information: Dr. Rui Fausto, Department of Chemistry, University of Coimbra, P-3049 Coimbra, Portugal, Tel: +351 39 85 20 80, Fax: +351 39 82 77 03, email: braslavskys@mpi-muelheim.mpg.de

◆ **11TH INTERNATIONAL SYMPOSIUM ON BIOLUMINESCENCE & CHEMILUMINESCENCE**

September 6 – 10, 2000

Pacific Grove, California, USA

Information: Prof. James F. Case, Department of Ecology, Evolution and Marine Biology, University of California Santa Barbara, Santa Barbara, CA 93106, U.S.A., email: case@lifesci.ucsb.edu

MILLENIUM SOLAR FORUM 2000

September 17 - 22, 2000

Mexico City, Mexico

Information: Millennium Solar Forum 2000, c/o Centro de Investigación en Energía, U.N.A.M., Apartado Postal # 34, Temixco 62580, Morelos, México, Tel: +52 73 25 00 52, Fax: +52 73 25 00 18, Email: ises2000@mazatl.cie.unam.mx.

◆ **PHOTOPHYSICS AND PHOTOCHEMISTRY 2000**

October 19-21, 2000

Oeiras, Portugal

Information: Organizing Committee - PP 2000, Instituto de Technlogia Química e Biológica, Apartado 127, P-2781-901 Oeiras, Portugal, Tel: +351 21 446 97 12, Fax: +351 21 441 12 77, Email: pp2000@itqb.unl.pt•

PACIFICHEM 2000

December 14-19, 2000

Honolulu, Hawaii U.S.A.

Information: <http://www.acs.org/meetings/pacific2000>

XIITH INTER-AMERICAN PHOTOCHEMICAL SOCIETY CONFERENCE

May 20-25, 2001Ascochinga, Córdoba, Argentina

Information: Prof. Pedro Aramendia, INQUIMAE. Departamento de Química Inorgánica, FCEN, University Buenos Aires, Pabellón 2. Ciudad Universitaria. C1428EHA Buenos Aires, ARGENTINA. E-mail: pedro@q1.fcen.uba.ar
Prof. Miguel Garcia Garibay, Department of Chemistry and Biochemistry, University of California Los Angeles, 405 Hilgard Ave, Los Angeles CA 90095-1569 USA. E-mail: mgg@chem.ucla.edu. Web Site: <http://www.unc.edu.ar/iaps2001>

A Decade of Closure and Surprises

The 2000 I-APS Award Address

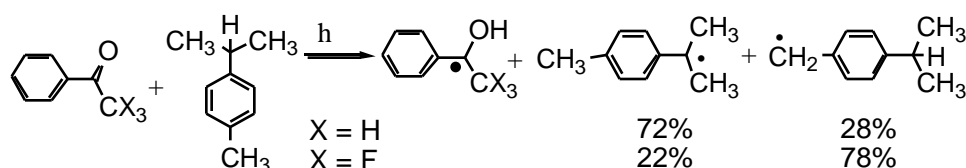
Peter Wagner

Michigan State University

Prologue: I was very disappointed not to be able to present an award talk at this January's IAPS meeting, since I wanted to personally thank the Society and all my fellow photoscientists who have helped and encouraged me over the years. It goes without saying (but I will anyway) that the I-APS award is a great honor that I am both grateful and overjoyed to have earned. The talk I had planned was designed to highlight several of what I consider the most unique and important findings that my group and I have published in the last decade plus. Some of them settled questions that had lain dormant for many years and others revealed previously overlooked or unexpected phenomena, thus the title above. A talk covering the variety of questions that we have addressed seemed more appropriate than one focused on a single question or goal, since it more accurately describes one's *modus operandi*. Moreover, a few papers often do not get the message across when what some would call a paradigm shift (*i.e.* a change in mechanistic thinking) is indicated and I wanted to emphasize our most recent mechanistic contributions. I am very grateful that I was able to provide a written version of my talk in this IAPS newsletter. I hope it is clearer (and certainly more permanent) than my talk would have been.

How much charge separation is there in an exciplex?

Long agoⁱ we showed that – trifluoroacetophenone **TFA** and acetophenone **AP** undergo photoreduction by alkylbenzenes *via* different mechanisms: triplet **TFA** is not subject to primary deuterium isotope effects and reacts 2 times faster with toluene than with cumene, whereas the relative rate constants for reaction of triplet **AP** with cumene, toluene, and toluene-^{-d}₃ are 7:3:1. From these facts we concluded that the rate-determining step for reaction of **TFA** is exciplex formation; for **AP**, hydrogen abstraction. Moreover a linear free energy relationship between the rate constants for reaction of triplet **TFA** with substituted benzenes and the substrates' oxidation potentials indicated a charge transfer mechanism. Later we discovered that triplet **TFA** reacts primarily with the methyl group of p-cymene while triplet **AP** reacts mainly with the isopropyl group.ⁱⁱ The former behavior is well known to demonstrate one-electron oxidation of cymene as opposed to direct hydrogen abstraction.



By the mid-80's there were varying views as to whether exciplexes were contact radical-ion pairs or charge transfer complexes with only partial (but how much?) electron transfer. At that time we learned that both **AP** and benzophenone **BP** triplets react faster with p-xylene than with cyclopentane,ⁱⁱⁱ which was surprising since $n, *$ ketone triplets were by then well known to show the same relative reactivity in hydrogen abstraction as that shown by alkoxy radicals,^{iv} which have the *same* reactivity toward both p-xylene and cyclopentane.^v This realization suggested that all of the phenyl ketone triplets may react with alkylbenzenes by charge transfer followed by hydrogen transfer. Therefore we conducted a study of how various ring-substituted **TFA**'s, **BP**'s, and **AP**'s react with alkylbenzenes.^{vi} For all three we

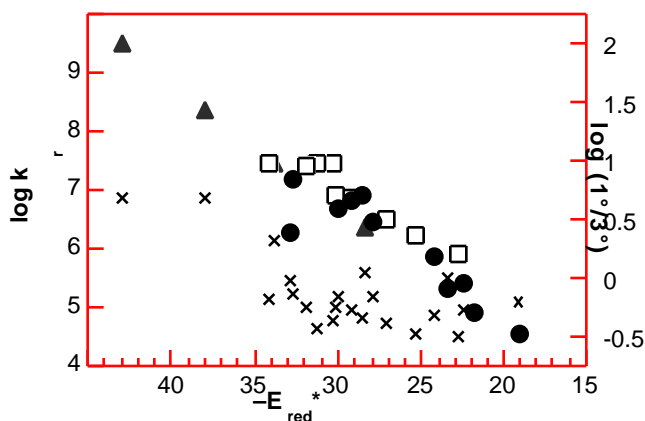
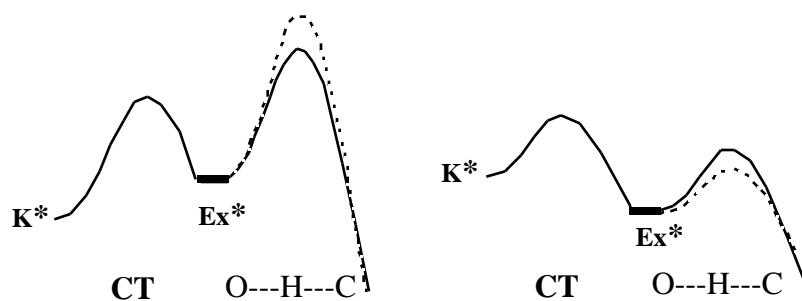


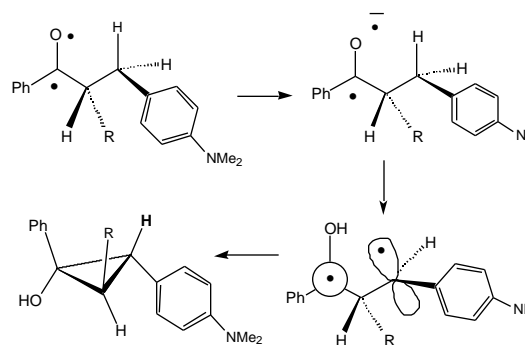
Figure 1. Rate constants for reaction of **TFA**s, **BP** p, and **AP I** triplets with p-xylene; and X primary/tertiary radical ratios from p-cymene .

found that rate constants toward p-xylene, primary/tertiary selectivities toward p-cymene, and H/D kinetic isotope effects all showed strong correlations with the reduction potentials of the triplet ketones. It is noteworthy that $n, *$ and $, *$ triplets with comparable reduction potentials barely differ in their rate constants but do differ in their selectivities toward cymene, likely because of different exciplex orientations. The clear conclusion from these studies was that all the ketones first form charge transfer complexes with varying extents of electron transfer from the alkylbenzene; those with minimal charge transfer undergo rate-determining hydrogen transfer with tertiary selectivity, thus showing an isotope effect; those with maximal charge transfer undergo rapid hydrogen transfer with primary selectivity and show no or little isotope effect.



Thus we determined that the non-emissive exciplexes formed from triplet ketones do have variable extents of charge transfer and that their subsequent chemical behavior measures that extent. It was gratifying to see Gould, Farid and co-workers arrive at an analogous conclusion, based on spectroscopic data, for the singlet exciplexes formed between alkylbenzenes and various arenes.^{vii}

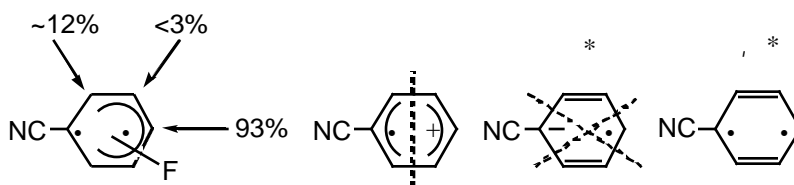
More recently Wilfried Weigel studied several α -(*p*-dimethylaminophenyl)propiophenones to see whether they would behave more like α -phenylpropiophenone, which undergoes rapid internal quenching, or α -dialkylaminopropiophenones, which cyclize to 2-dialkylaminocyclopropanols, both *via* intramolecular exciplex formation. We found that charge transfer from an inverted α -anilino group is extensive enough to promote α -proton transfer to the carbonyl with formation of a 1,3-biradical that cyclizes to a cyclopropanol.^{viii} As an unexpected dividend the exciplex phosphoresces at 77 °K, a very rare occurrence.



Regioelectronic Behavior: How Lucky Can You Get?

In 1981 we reported that internal quenching of a phenyl ketone triplet by a tertiary amino group tethered to the para position by a four-atom chain occurs only when the lowest triplet is π, π^* , since the corresponding aminobenzophenone undergoes only slow bimolecular triplet quenching by another aminoketone. The difference was ascribed to different localization of the half-empty HOMO's in the two cases, the n -orbital of the benzophenone n, π^* triplet being too far away from the amine to interact with it, unlike the situation for the highest energy benzene orbital.^{ix}

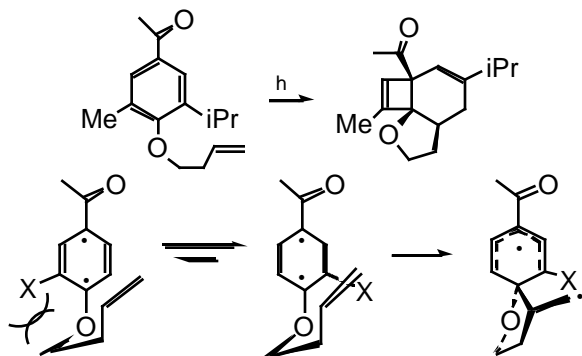
The luck appeared when Keehyung Nahm talked me into trying a similar experiment with vinyl groups as the donor and an oxygen atom anchoring the tether. We found a nearly identical result: very rapid internal quenching for



π, π^* triplet acetophenones and none for the n, π^* benzophenones.^x However, we found a different form of regioselectivity in that no internal quenching occurs in acetophenones with the tether at the meta position. Even better, we found that the rapid quenching in fact represented a previously overlooked chemical reaction, the [2 + 2] cycloaddition of the vinyl group to the benzene ring, a reaction that is followed by a veritable cornucopia of pericyclic rearrangements.^{xi} Further study established that the quenching reaction is a 5-hexenyl radical-like addition of the biradical-like π, π^* triplet to the double bond to generate a 1,4-biradical^{xii} that cyclizes stereoselectively.^{xiii} The ortho/para regioselectivity arises from the 1,4-biradical nature of the π, π^* triplet in

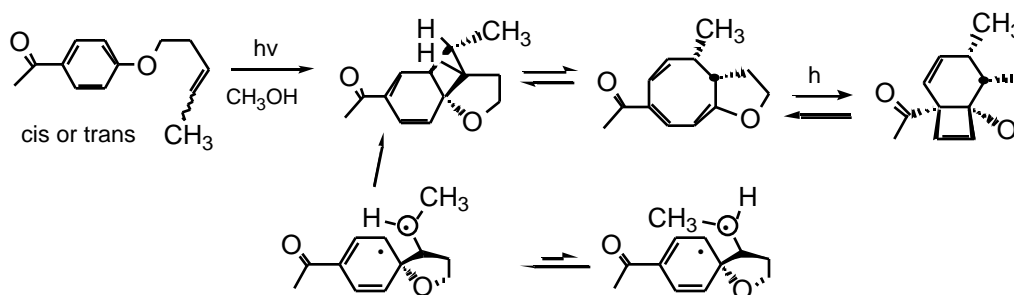
acylbenzenes, there being almost no unpaired electron density at the meta position, as shown by ^{19}F hyperfine splittings in triplet benzonitriles.^{xiv}

The many pericyclic reactions that lead to a variety of products are highly interesting but for the sake of this paper I will focus only on the regio- and stereoselectivity of the initial photoreaction. The effect of substituents ortho to the tether on rate constants indicates a weak charge transfer process^{xv} However,



both electron-withdrawing and alkyl groups direct addition towards themselves,^{xvi} primarily because of steric hindrance to the alternative, as the Scheme portrays. Rather amazingly, all substituents ortho to the carbonyl direct addition towards themselves, for reasons we do not yet fully understand.

The most interesting stereoselectivity is demonstrated by the example below, where a single diastereomer is formed in 95% yield by the cyclization of the 1,4-biradical. There are other reports of 1,4-biradicals cyclizing with modest stereoselectivity; but this one is unique. Despite the free rotation possible for the methyl-substituted end of the biradical, it seems to equilibrate in the obviously more stable geometry, with the methyl pointed away from the ring, before cyclizing. This is the first of several examples in this paper of biradicals obeying the Winstein-Holness principle. We also showed that a chiral amine auxiliary attached as a carboxamide ortho to the tether produces high enantioselectivity in the configuration at the first carbon that bonds to the benzene ring.^{xvii}



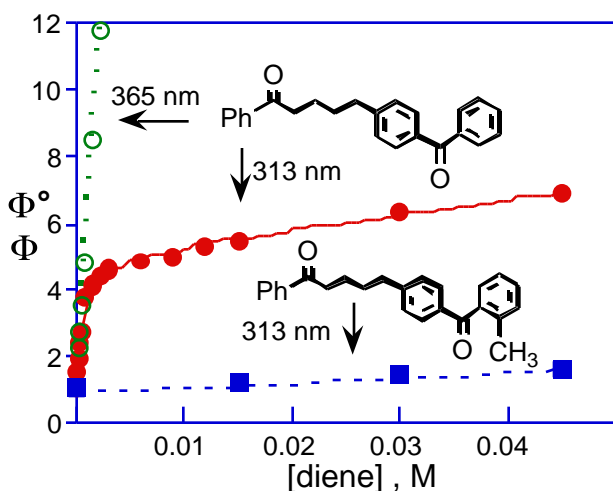
In as yet unpublished work Kevin McMahon found that energy transfer competes with cyclization when the double bond is tri-alkyl substituted. This limitation on the generality of the photocyclization highlights the importance of Caldwell's study of the triplet energies of substituted alkenes.^{xviii}

Speaking of energy transfer...

Gerhard Closs won the IAPS award by demonstrating the importance of through bond interactions in intramolecular electron and energy transfer. The relatively rigid cyclic spacers that he used essentially prevented any through space interactions and Gerhard did acknowledge that the rapidity of bimolecular triplet energy transfer (nearly 10^{11} sec^{-1} for encounter pairs in solution) indicated that through space interactions do occur. At the time we were interested in an exotic kinetics problem, namely how energy transfer between two chromophores in the same molecule affect Stern-Volmer quenching plots of their reactions. The figure shows quenching of the Norrish type II cleavage of δ -(*p*-benzoylphenoxy)valerophenone (δ -(**BP**)**VP**), which is described by the hyperbolic function below.^{xix} The α 's equal the per cent of light absorbed by each chromophore and the subscripts r and u indicate, respectively, the chromophore which is or isn't reacting; k_{12} and k_{21} are the rate constants for state interconversion, k_{ur} being one of them.

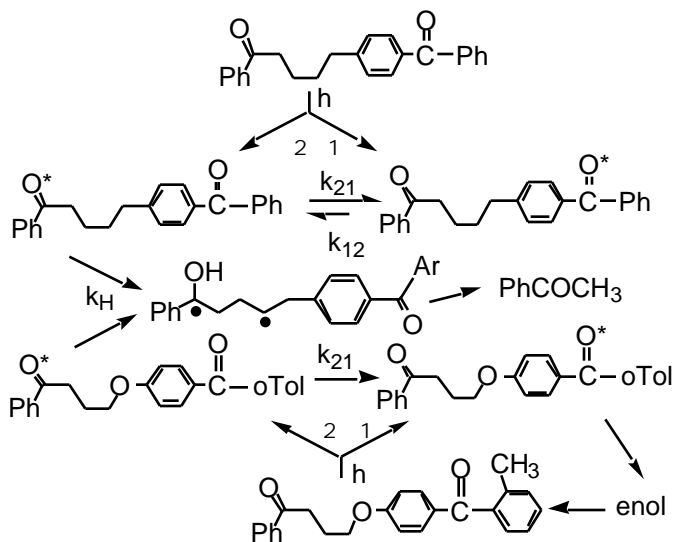
$$D = 1 - \frac{k_{12} \alpha_r \alpha_u}{k_{12} \alpha_r + k_{21} \alpha_u + k_{ur}}$$

$$\frac{r}{r} = \frac{D + (k_{q1} + k_{q2})[Q] + k_{q1}^2 [Q]^2}{D\{1 + r k_{qu}[Q](r + u k_{ur})^{-1}\}}$$



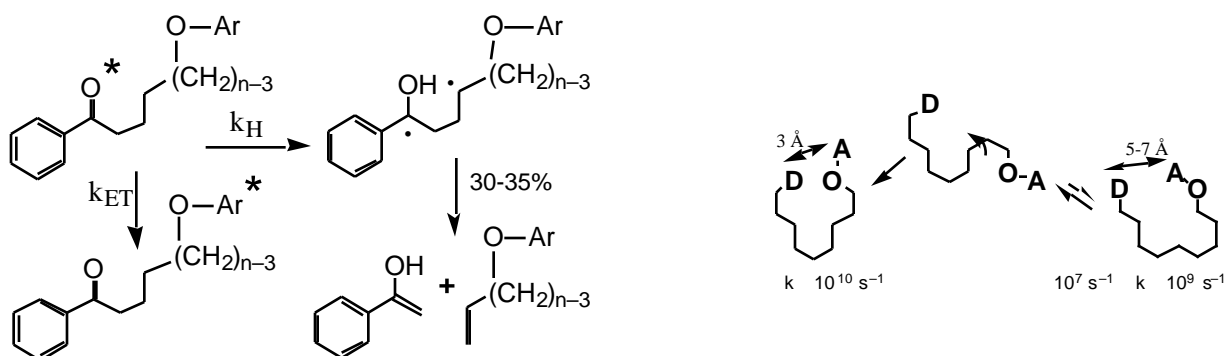
The BP chromophore absorbs most of the light at 365 nm, so the long triplet lifetime indicated by the steep plot reflects slow endothermic energy transfer to the reactive VP carbonyl. At 313 nm both carbonyls absorb; as the long-lived BP triplet is quenched out, the plot becomes dominated by quenching of the short-lived VP triplet. With an *o*-methyl on the BP triplet, very rapid Yang enolization suppresses all energy transfer to the VP such that the plot shows only the short (5 ns) lifetime of the VP triplet, which comprises comparable amounts of γ -hydrogen abstraction and irreversible energy transfer to BP. We decided to exploit this situation by

studying analogous diketones with even longer polymethylene spacers. To my amazement, the rate constants for energy transfer leveled off at $\sim 1.5 \times 10^8 \text{ s}^{-1}$ for spacers containing 5-8 methylene groups. Such behavior for these and similar bichromophores^{xx} indicated the predominance of through-space energy transfer when more than 5 bonds connect donor and acceptor.



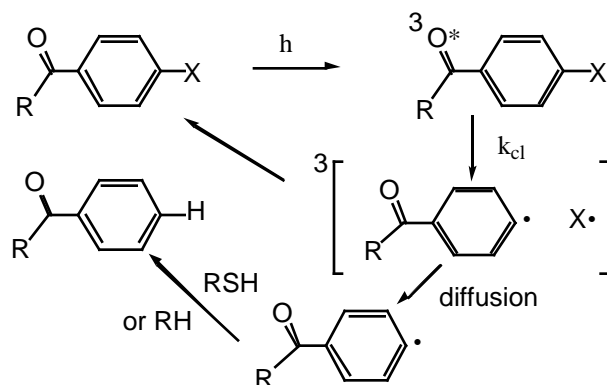
These results prompted a similar study with the same chromophores that Closs used: a benzoyl donor and a naphthyl or biphenyl acceptor. Again, k_{ET} values drop only slightly as the number of connecting bonds increases beyond 4, with the triplet lifetime reflecting from 35-75% energy transfer. Analysis of the various ways the two ends of these γ -benzoyl- γ -aryloxyalkanes can get close enough for energy transfer to compete with hydrogen abstraction leads to the important conclusion that all three of the possible conformational kinetics boundary conditions^{xxi} contribute to the observed rate constants and quantum efficiencies for quenching by energy transfer of hydrogen abstraction, which has a rate

$\sim 1 \times 10^8 \text{ s}^{-1}$. Various Monte Carlo calculations on long alkanes indicate that conformations with their two ends within 3-4 Å comprise only a few per cent of the total; so very rapid ($> 10^{10} \text{ s}^{-1}$) static quenching in these conformers can be responsible for only a small fraction of the energy transfer. The observed k_{ET} values must be dominated by kinetically controlled quenching processes in conformers with their ends farther apart: a mixture of irreversible bond rotations into conformers whose ends are within 3-4 Å; and quenching by equilibrium populations of conformers whose two ends are within 5-7 Å.^{xxii} Calculations of the extent to which each contributes to the overall energy transfer promise to be challenging.



A very different kind of regioelectronic selectivity

The photoinitiated radical cleavage of iodobenzenes often is put to synthetic use. C–I bond cleavage in the parent compound has received a good deal of study with molecular beam type experiments, with the conclusion that a $n, ^3$ triplet rapidly interconverts to a dissociative $n, ^*$ state. In order to see how a strongly interacting acyl group might affect this reaction, we studied various iodo- and bromobenzophenones and acetophenones. From a synthetic view, a key finding was that phenyl-Br bonds can cleave very rapidly. Irradiation of such halophenyl ketones in alkane solvents forms an alkyl halide and the phenyl ketone itself, in modest quantum efficiency that decreases with increasing solvent viscosity.^{xxiii} Apparently, presumably due to the heavy atom effect of the halogen atom, in-cage isc and recombination of the radical pair are faster than diffusion apart and trapping of the acylphenyl radicals.



As mentioned above, the triplets of acylbenzenes have very little unpaired electron density at their meta positions and the kinetics of C–X cleavage reflect this fact for iodophenyl ketones, but not for bromophenyl ketones, as the table below indicates. The 100-fold difference in k_{c1} values for m- and p-iodoBP is due mainly to nonenthalpic factors, the two having nearly identical H^\ddagger values. There are two unusual aspects of the A values. Normally a bond cleavage reaction involving no other molecular motion should have a positive S^\ddagger value. The A values lower than 10^{13} suggest a nonentropic source of inefficiency, which we have suggested is the probability for conversion of the $n, ^3$ triplet into a dissociative $n, ^*$ state at a conical intersection of the two. Since such a conversion involves transfer of an electron from a π^* orbital to a σ^* , the 100-fold greater π^* electron density at the

para position relative to the meta produces the same 100-fold rate difference found for the analogous cleavage of the radical-anions of halophenyl ketones.^{xxiv}

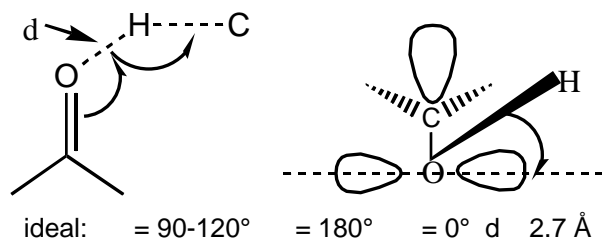
R	X	T ₁	Φ _{Cl}	10 ⁻⁷ s ⁻¹ k _{Cl}	ΔH [‡] , kcal	logA	E _T - kcal	DE
Ph	p-I	n, *	0.30	300	~4.0	~12.5	68	64
Ph	m-I	n, *	0.30	3	4.0	10.5	68	64
Ph	o-I	n, *	0.08	~300			69	~59
Ph	p-Br	n, *	0.003	~0.01	~10	~12	69	78
Ph	m-Br	n, *	0.002	~0.01	~10	~12	68	78
Ph	o-Br	n, *	0.07	6	~6	~12	69.5	~73
Me	p-Br	, *	0.29	10	5.3	12.0	70.6	78
Me	m-Br	n, *	0.19	20	5.3	12.4	72	78
Me	o-Br	, *	0.48	~30	~5	~12	71.5	~73

So why don't the bromophenyl ketones show any para/meta difference? Because cleavage is exothermic for the iodo-**BP**'s and H[‡] is small, only the n, * triplet is involved. Cleavage of bromine is so endothermic that both n, * and , * triplets can be populated before cleavage. Since the bromo**AP**'s, with low-lying , * triplets, undergo endothermic cleavage faster than ³n, * m-**IBP** undergoes exothermic cleavage, it appears that , * triplets can interconvert with a dissociative state more efficiently than do n, * states. This conclusion makes sense when one realizes that one lone pair orbital on the bromine is conjugated with the benzene ring, thereby making the , * transition partially a n_{Br}, * transition and making its mixing with a n_{Br}, * state that much easier.

Finally, the relatively high reactivity of o-Br**BP** is interesting in that the o-bromophenyl ring is twisted out of conjugation with the carbonyl. This presumably negative effect is offset by the significantly lower C-Br bond dissociation energy caused by steric congestion.

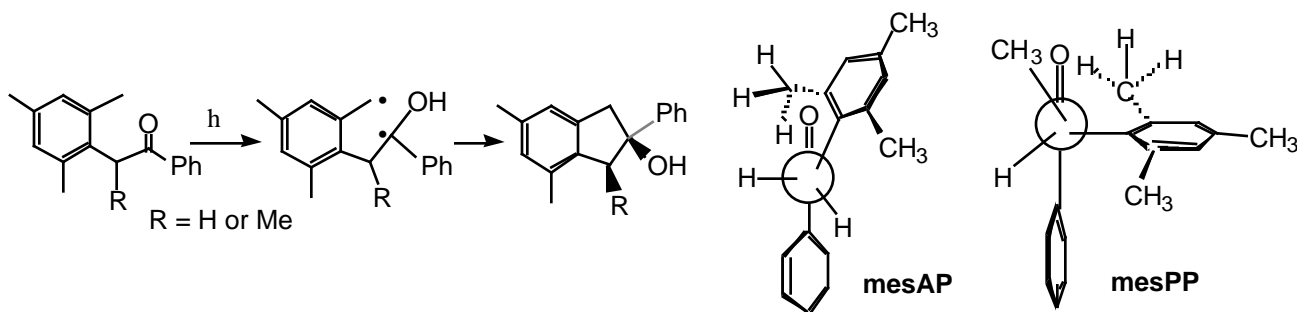
How about some stereoelectronic effects?

My work on biradicals was singled out by the selection committee for this IAPS award; and intramolecular hydrogen abstraction by excited ketones is my favorite way of producing biradicals. There is one aspect of this ubiquitous reaction that has intrigued me for decades, ever since Nick Turro reported the lack of Norrish type II reaction in 2-propylcyclohexanone when the propyl group is axial. He suggested that for a hydrogen atom to be abstracted it should lie along the long axis of the carbonyl n-orbital and in the nodal plane of the orbital, making a dihedral angle of 0° with that plane.^{xxv} This notion was appealing since it recognized the directionality of p orbitals and the fact that the radical reactivity of n, * triplets is centered on the half-occupied n orbital. Moreover, all levels of theory seem to indicate this as the ideal geometry, with the O-H-C atoms aligned linearly in the transition state.^{xxvi} However, many systems have been studied in which such an orientation is impossible; yet efficient hydrogen abstraction occurs.



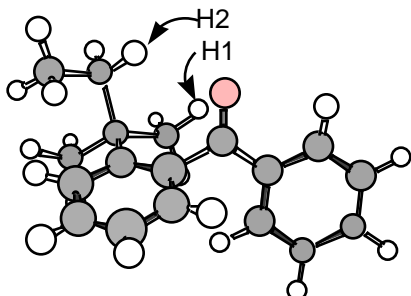
Scheffer has studied a variety of ketones that undergo intramolecular hydrogen transfer in their crystalline states.^{xxvii} He found that d is the most important of the *ground state* parameters depicted above in determining reactivity, with the O-H-C angle and the dihedral angle usually deviating significantly from their ideal values.

Even with so much experimental evidence that hydrogen abstraction occurs even when d is nowhere near 0° , there remains a lack of much evidence, either experimental or computational, as to how rate constants change as d varies from 0° to 90° . I pointed out ages ago that reactivity should show a \cos^2 dependence on d , that being the electron density function for a p orbital.^{xxviii} Some of our studies on α -hydrogen abstraction provide reasonably quantitative support for this idea. I'll mention two examples in which ketones undergo photocyclization both in solution and as crystals.



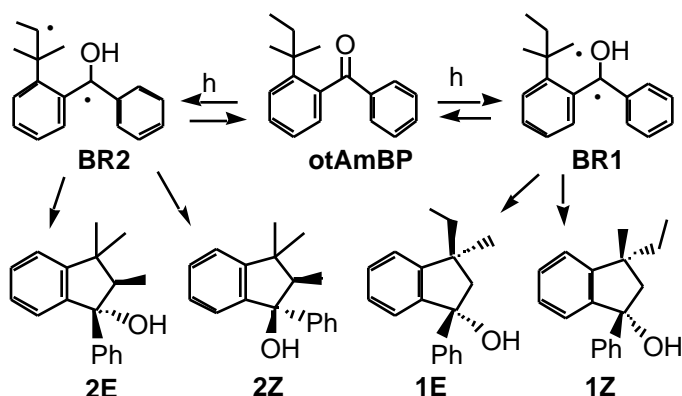
In **mesAP** the mesityl group nearly eclipses the carbonyl, thus allowing a small value of d . The β -alkyl group in **mesPP** forces the mesityl ring to twist and rotate away from the carbonyl, such that its benzylic hydrogen closest to the carbonyl oxygen is 2.7 Å away at an angle d of 66° . Sizable steric barriers prohibit rotation into a more "reactive" geometry within the 6 nsec triplet lifetime. The difference between the \cos^2 values for the two ketones predicts a rate difference of 4. The stereoselectivity for photocyclization of α -(2,4,6-triethylphenyl)propiophenone, to be discussed later, reinforces the notion that the triplet of α -**mesPP** reacts from its preferred ground state geometry.

When we first reported the rapid α -hydrogen abstraction in *o*-*tert*-butylbenzophenone **otBuBP** triplet^{xxix} we noted that two of the methyl groups have H atoms within bonding distance of the oxygen. We then looked at the regioselectivity of hydrogen abstraction by *o*-*tert*-amylbenzophenone **otAmBP**, the x-ray crystal structure of which is on the left.^{xxx} H1 has a d value of 95° ; H2, 45° ; and each is 2.5 Å from the oxygen. Irradiation of **otAmBP** in solution produces roughly equal amounts of indanol products **1** and **2**, a 60:40 ratio in nonpolar



solvents and the opposite in polar solvents. Under such conditions free rotation of the *t*-amyl group can allow more access to methyl hydrogens than is possible in the crystal.

However, at 77°K in methanol or in the solid state, the product ratio is 70-80% **2**. That a primary hydrogen reacts 20-30% as much as a secondary indicates that the latter's better orientation and intrinsically higher reactivity are overcome by some other factor, which almost certainly is



the greater ease of cyclization of **BR1** compared to **BR2** in a frozen environment. In any event, **BR1** is formed despite a near 90°, which may slow down its formation but apparently facilitates its cyclization.

The simple message of these results is that angular orientation does influence rates of hydrogen abstraction but rarely prevents it.

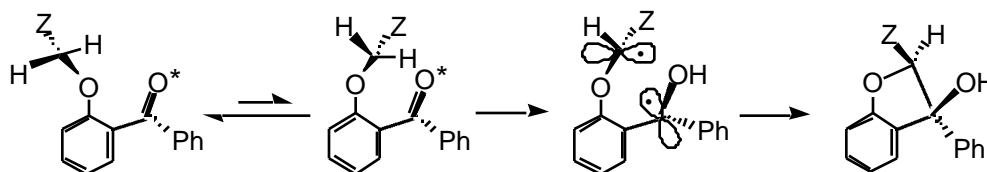
N^+ may be isoelectronic with C but

Although o-alkoxyphenyl ketones are well known to undergo efficient photocyclization *via* γ -hydrogen abstraction (see below), o-(alkylamino)phenyl ketones respond very poorly to irradiation. We decided it would be worthwhile to see how o-acyl-N-alkylanilinium ions respond to light and found that they can photocyclize to indole derivatives.^{xxxii} We expected that the positive charge on nitrogen would slow the hydrogen abstraction. In order to measure this effect we studied o-benzoyl-N-trimethylanilinium salts. The cation has the same geometry as **otBuBP** and photocyclizes in the same way, but with a rate constant for γ -hydrogen abstraction 1/30 that for **otBuBP**. Arrhenius plots indicated that both ketones have the same 2.36 kcal/mole activation energy, the rate difference being entirely entropic.^{xxxii} This is now one of several such examples of inductive effects on hydrogen atom abstraction by electron-deficient radicals having entropic rather than enthalpic causes, lower electron density in the C–H bond decreasing the probability of H atom transfer.

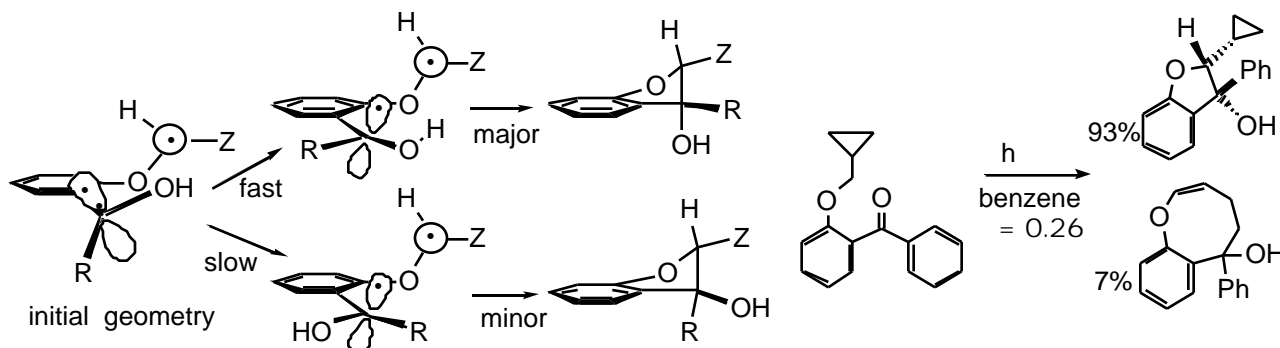
As long as I mentioned o-alkoxyphenyl ketones.....

In the late 80's we decided to study the photochemistry of such ketones more thoroughly than had been done decades earlier, since we found evidence for unprecedented 1,5-biradical rearrangements competing with cyclization and conformational effects that change normal H-abstraction selectivity.^{xxxiii}

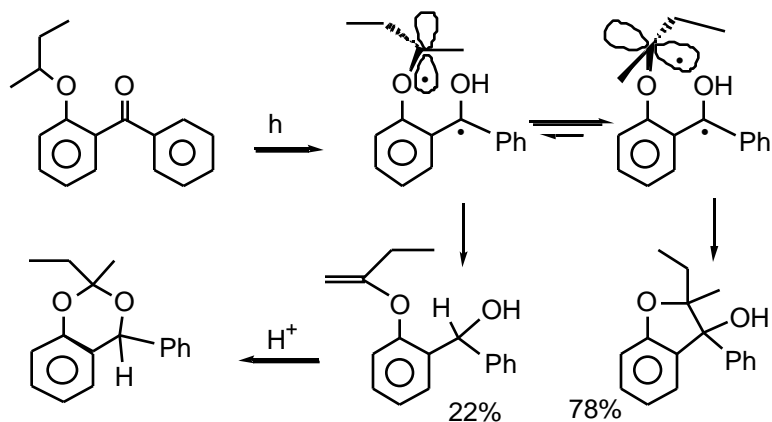
Triplet γ -hydrogen abstraction in **otBuBP** is 1000 times faster than in o-methoxy**BP**, apparently because the methoxy group so prefers an unreactive *anti* conformation that its lower C–H bond energy relative to a simple methyl group becomes unimportant. Thus triplet state kinetics are governed by conformational equilibrium in the triplet state.



When Z = methyl, cyclopropyl or phenyl, cyclization proceeds with relatively high diastereoselectivity (Z and R trans) in hydrocarbon solvents, which is lost in solvents to which the hydroxyl group of the biradical can hydrogen bond. The scheme below depicts the probable conformational preferences that control cyclization. The small amount of cyclopropylcarbiny ring opening found when Z = cyclopropyl indicates a biradical lifetime ~ 2 nsec,^{xxxiv} so the favored geometry for cyclization likely is formed by a least motion bond rotation.

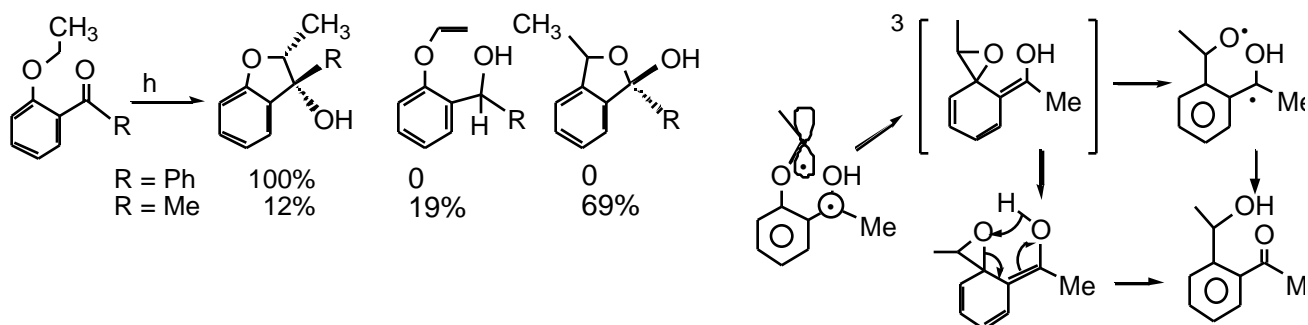


I've come this far without mentioning all the early work showing the strong propensity for Norrish type II 1,4-biradicals to disproportionate as well as cleave and cyclize. However, their disproportionation performs the thermodynamically sensible act of restoring the carbonyl group. We did study one acyclic 1,5-biradical that disproportionates to both the enol and keto forms of the original ketone.^{xxxv} With ortho-isopropoxyphenyl ketones, the biradical does something unusual that had not been fully appreciated in earlier studies of o-alkoxy ketones: it disproportionates to o-(2-propenoxy)benzhydrol, which upon addition of trace acid cyclizes to a 1,3-dioxane. The isobutoxy example adds the interesting twist that the disproportionation is totally regioselective for the methyl group and thus adds another example of stereoselectivity being provided by biradical geometric preferences.

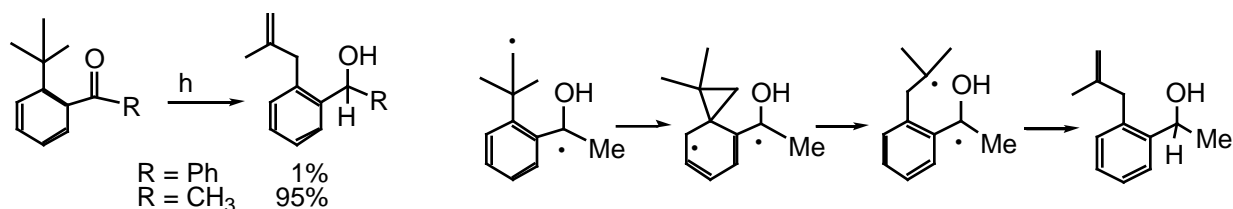


Another interesting aspect of o-alkoxyphenyl ketone photochemistry is the behavior of acetophenones, which undergo a formal 1,2-phenyl shift from oxygen to carbon, generating 2-acylbenzyl alcohols, which equilibrate with their cyclic acetal form. This process predominates over all others, as the example below shows. We have suggested that the difference between the acetophenones and benzophenones lies in the planarity of the hemi-pinacol

radical site of the acetophenone-derived biradical, which fosters coupling of the β -radical site to the benzene ring to form a spiro-epoxy enol intermediate, which can open by a variety of mechanisms to both starting ketone and benzyl alcohol. The lack of this reaction for benzophenones probably reflects the greater rotational flexibility of the diphenyl substituted hemi-pinacol radical site in the biradical, which fosters rapid cyclization.

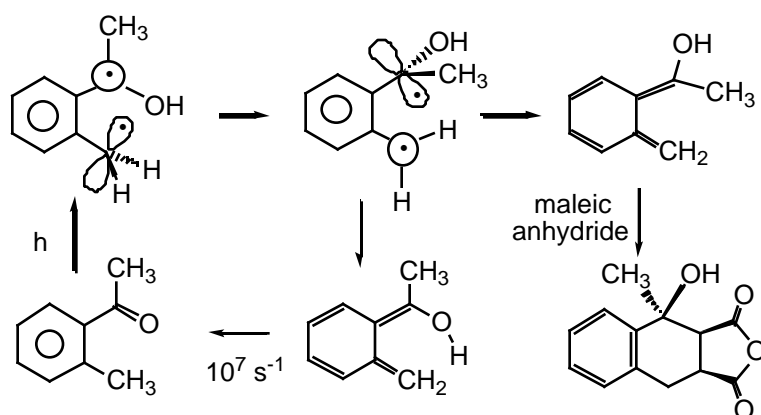


A similar alkyl rearrangement occurs in *o-tert*-alkylacetophenones, but the product is an alcohol rather than a ketone and must arise by the same sort of disproportionation of the rearranged biradical that occurs in *o*-alkoxy ketones.



For both the *o*-alkoxy and *o-tert*-alkyl ketones we have assumed that the spiro-enol intermediate is formed as a triplet and therefore can open to a rearranged biradical which then disproportionates. This is the only mechanism that makes sense for the products formed from the *t*-alkyl ketones, whereas a sigmatropic rearrangement of the ground state epoxy-enol may also occur for the *o*-alkoxy ketones. In either event the spiro-enols are presumed to behave like *o*-xylylenes, which leads me to the next topic:

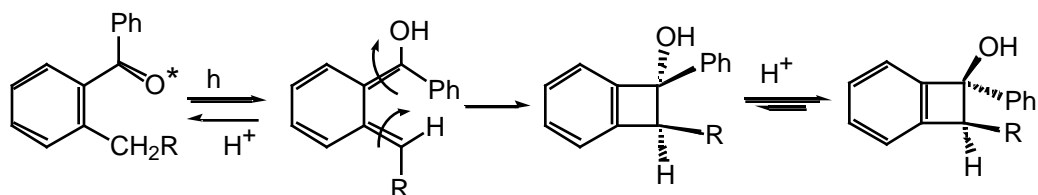
o-xylylenols and the Yang photoenolization



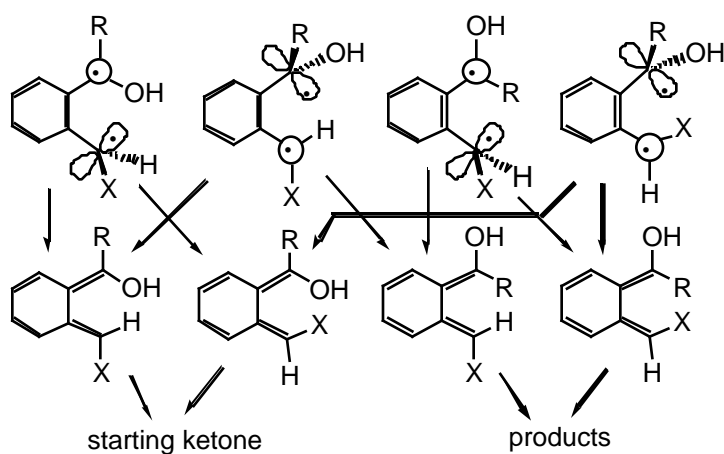
In the nearly 40 years of interest in the photoenolization of *o*-alkylphenyl ketones to *o*-xylylenes, mechanistic knowledge has been acquired in spurts. My contributions began in the mid-70's with the recognition that there are two triplet rotamers, only one of which can rapidly abstract a β -hydrogen from the *o*-alkyl group. This led to a joint project with Jacob Wirz which showed that two isomeric xylylenols are formed: the one

with the OH group pointing in undergoes rapid sigmatropic rearrangement to ground state ketone; the one with OH out lives long enough to be captured by a variety of dienophiles. This finding explained the exclusive endo stereochemistry of the many Diels-Alder adducts that had been formed from these photogenerated *o*-xylylenols.

Our recent contributions began with the finding that many *o*-alkylphenyl ketones photocyclize to thermally labile benzocyclobutenols.^{xxxvi} The fact that benzocyclobutenol formation is quenched by acid proved that the benzocyclobutenols are formed from the *o*-xylylenols, not *vice versa* as had once been postulated and not by direct cyclization of the initially formed 1,4-biradical.

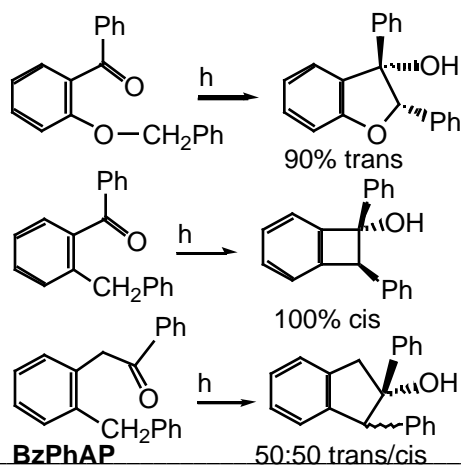


The fact that single benzocyclobutenol diastereomers are formed by conrotatory electrocyclicization prompted a search for an explanation of the stereochemistry of *o*-xylylenol reactions based on how many xylylenol isomers are formed from a given ketone. Our thinking followed early recognition that the terminal bonds of the initially formed biradical must be able to rotate, otherwise the two xylylenols with OH in and out could not both be formed.



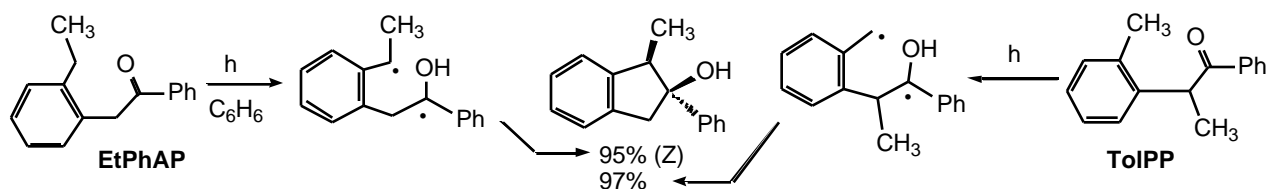
determines what products can be formed.

So biradical geometries can determine product ratios — let's look at some more.

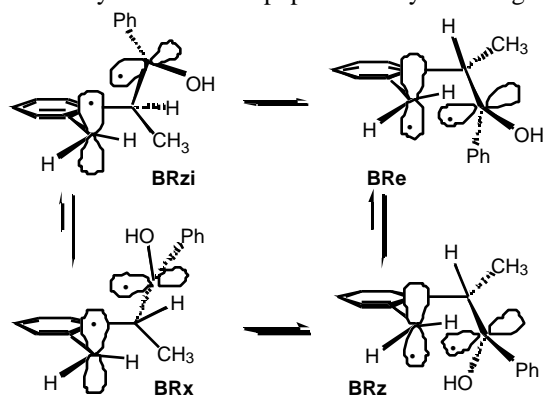


Although the photocyclizations of both *o*-alkoxy and *o*-alkyl phenyl ketones display high diastereoselectivity, the latter, as opposed to the former, form the thermodynamically less stable product, for reasons I just outlined. Upon examining diastereoselectivity in the photocyclization of *o*-(*o*-alkylphenyl) ketones, we found wide variations in selectivity, depending on both structure and conditions, and that conformational dynamics of both ground state ketones and 1,5-biradicals determine the ratios of isomeric indanols.

Our earliest thoughts on this topic were stimulated by Lewis' comparison of the 3:1 trans/cis ratio of cyclobutanols formed from valerophenone to the single isomer formed from *n*-methylbutyrophenone.^{xxxix} Both reveal steric interactions in the intermediate 1,4-biradicals, which are created during cyclization in the former but pre-exist in the latter. Irradiation of *o*-aryl ketones produces a 30:1 ratio of 2-indanols from *o*-(*o*-tolyl)-propiophenone **ToIPP**^{xi} and a 20:1 ratio from *o*-(*o*-ethylphenyl)acetophenone **EtPhAP**.^{xli} I pointed out above how alkyl substitution at the *o*-position changes the geometry of *o*-aryl ketones, so that the aryl group twists and no longer eclipses the carbonyl. This effect produces a pre-existing separation of phenyl and methyl groups in **ToIPP** that persists throughout the reaction. But why do methyl and phenyl groups on the radical sites of the cyclizing **EtPhAP**-derived biradical avoid each other so much more than occurs in the valerophenone-derived biradical? And why a 50:50 ratio from **BzPhAP**?

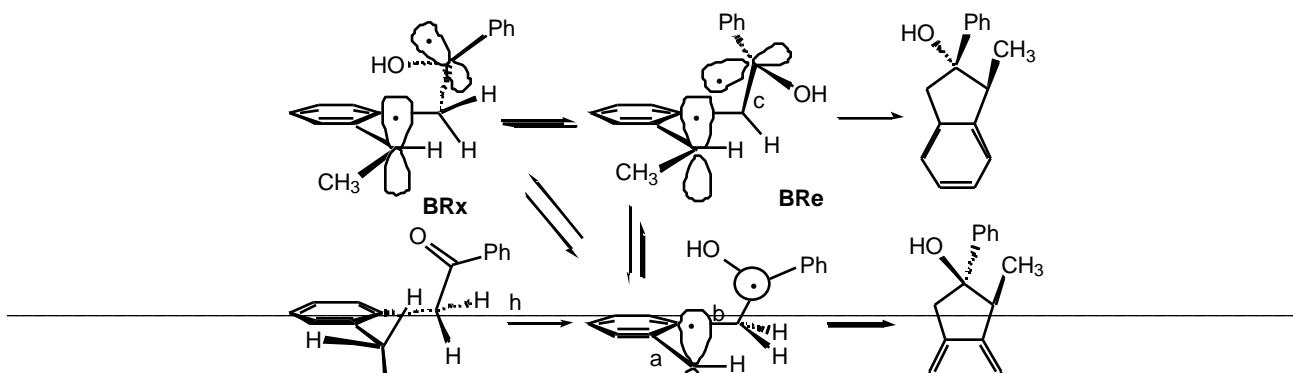


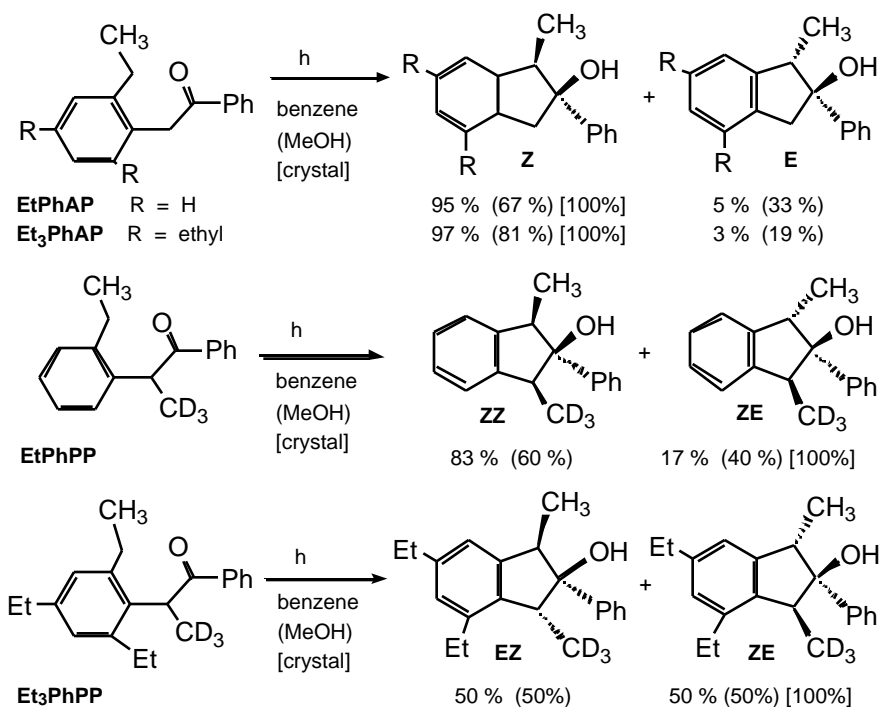
Simple MM2 calculations suggested two conformers of the 1,5-biradical formed from **EtPhAP**; but later studies revealed three conformational minima, two of which require only simple bond rotations to cyclize, as shown below. **BRz** is lower in energy than **BRe** because the OH hydrogen bonds to the benzene ring; **BRx** cannot cyclize directly. Rotating bond *a* such that the methyl points in raises the energy of all conformers by 4 kcal/mole; since they are thus <1% populated they can be ignored. Thus strong conformational preferences at each end of the



biradical are responsible for the stereoselectivity, as described above for other biradicals with benzylic sites. A particularly noteworthy fact is the lack of disproportionation back to ground state ketone, apparently because of the hydrogen bonding in the **BRz** geometry. The lack of stereoselectivity for **BzPhAP** is consistent with our earlier findings that phenyl substitution substantially lowers rotational barriers at benzylic radical sites in a biradical, since both benzene rings do not have to conjugate with the half-occupied p orbital.^{xliii} The biradical can assume several

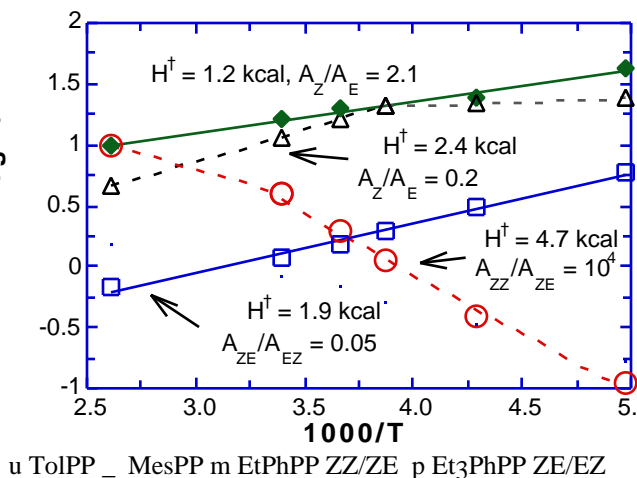
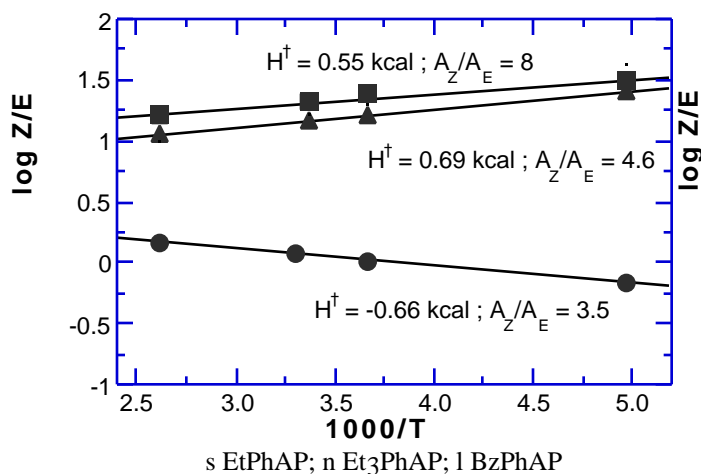
twisted geometries of comparable energies which cyclize differently.





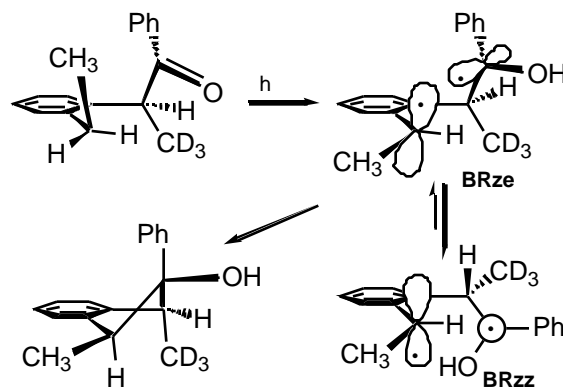
Irradiation of more sterically crowded α -arylpropiophenones produced the unusual effects shown here. Whereas cyclization quantum yields for the α -aryl acetophenones are near 100%, those for the propiophenones are <40%. The latter undergo competing α -cleavage and some biradical reversion to reactant. Diastereoselectivity is highly variable. None of the ketones display much if any in methanol, which solvates the OH group. In benzene at 25°, **EtPhPP** and **Et₃PhPP** each form two indanols, ZE from both with selectivity for ZZ only from **EtPhPP**. In both cases the % ZE isomer increases as the temperature drops. As crystals each ketone forms only the ZE indanol.

It is definitely unusual to see diastereoselectivity invert with changes in temperature; so we measured diastereomer ratios for the various ketones over a 180° temperature range to determine differential activation parameters for forming the two indanol isomers. The resulting Eyring plots shown below provide H^\ddagger and S^\ddagger values for each. The former can represent an enthalpy difference between reactive conformers and/or any enthalpy barriers to cyclization or rotation between conformers that form different isomers. The apparent S^\ddagger values indicate a sizable nonenthalpic preference for biradical cyclization to indanols with phenyl and ethyl-derived methyl groups trans to each other. We have ascribed this apparent entropy effect to differing spin orbit coupling in the different biradical geometries and thus different probabilities for T \leftrightarrow S interconversion during cyclization. What remains perplexing is the extent to which isc can occur separate from reaction. For example, if **BR_x** from **EtPhAP** shifts to a singlet state in its noncyclizable geometry, the Z/E indanol ratio reflects variable enthalpies and entropies for rotation of **BR_x** into some mixture of **BR_z** and **BR_e**.



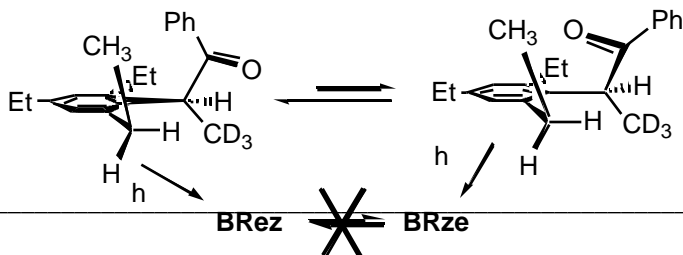
Temperature dependent product ratios in solution may reflect three possible kinetic scenarios: 1) equilibrium between two or more freely interconverting conformers; 2) competition between cyclization of the initial biradical geometry and bond rotation to another conformer; or 3) ground state conformational control (cyclization much faster than bond rotations). Superimposed on these effects there can be inherent differences in the cyclization rates of different conformers, the temperature dependence of which is unknown. Given the ~40 nsec lifetime and 1 kcal/mole activation energy measured for decay of some of the biradicals,^{xliii} we assumed above that the less bulky biradicals from *p*-arylacetophenones have time to equilibrate before cyclizing or reverting to ketone. The *p*-arylpropiophenones demonstrate all three possible boundary conditions, since the already described geometry change caused by the *p*-alkyl substituent translates to the 1,5-biradicals formed by *p*-hydrogen abstraction. In all cases the highest solution selectivity occurs at the lowest temperature and is magnified in the crystal, in which the initially formed biradical cannot escape the ground state geometry, which thus controls product geometry. That molecular immobility in the crystalline state can enforce higher photocyclization stereoselectivity than that observed in solution has been amply demonstrated.^{27,xliv}

The low temperature behavior of **EtPhPP** apparently reflects bond rotation barely competing with cyclization, equilibration being attained only at temperatures too high for us to measure. A linear plot of the low temperature points indicates an A_Z/A_E value which would be impossibly high for inherent differences in biradical cyclization efficiencies but consistent with bond rotation having a much higher S^\ddagger than does $T \rightarrow S$ isc. The ~4.7 kcal H^\ddagger must then represent the barrier to conversion of **BRze** to **BRzz**, minus any activation energy for cyclization of **BRze**. Under equilibrium conditions enough **BRzz** is formed to make the



major product **ZZ**.

For **Et₃PhPP**, the linearity of its temperature dependence and the 1.9 kcal H^\ddagger do not represent equilibration of biradicals but



rather of ground states. Rotation between biradical conformers is too slow because of the large steric congestion. The difference in A values indicates inefficient cyclization by **BRze** relative to **BRez**, similar to that noted for **EtPhAP**. Unfortunately, different computational methods give such different values for the energy differences between conformational minima of the various biradicals that we can make no convincing estimate of how the measured H^\ddagger values can be dissected into biradical equilibria and barriers to cyclization. Take cheer nonetheless, since something must be left for the future.

Epilogue:

After putting the finishing touches on this essay, I'm rather amazed myself at how many different studies I managed to conduct in the past decade with a relatively small number of students. The obvious explanation is that they were a very talented, motivated, and hard-working bunch of whom I am very proud. They are all mentioned in the various footnotes describing their work but I would like to identify them individually anyway. Keepeyung Nahm and Bong-Ser Park have academic positions in Korea, Masami Sakamoto in Japan, Petr Klan in the Czech Republic, Ahmed Madkour in Egypt, Anna Gudmundsdottir in Cincinnati, Bob Smart and Ali Zand in Michigan, and Kevin McMahon in Texas. Boli Zhou and Marty Sobczak have industrial jobs in California; Kung-Lung Cheng in Taiwan. Willie Weigel is currently a postdoc with Fred Lewis. I'm very happy that their time with me was so mutually beneficial and that basic research still prepares people for good jobs. Finally, I must acknowledge my long-time funding from NSF and more recently from NIH.^{1xlv}

References

- (i) Wagner, P. J.; Leavitt, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 3669; Wagner, P. J.; Lam, H. M. H. *J. Am. Chem. Soc.* **1980**, *102*, 4167.
 - (ii) Wagner, P. J.; Puchalski, A. E. *J. Am. Chem. Soc.* **1980**, *102*, 6177.
 - (iii) Wagner, P. J.; Truman, R. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7093.
 - (iv) Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619.
 - (v) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.
 - (vi) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.
 - (vii) Gould, I.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8188.
 - (viii) Weigel, W.; Wagner, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 12858.
 - (ix) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7335.
 - (x) Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 4404.
 - (xi) Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 6528.
 - (xii) Cheng, K.-L.; Wagner, P. J. *J. Am. Chem. Soc.*, **1994**, *116*, 7945.
 - (xiii) Wagner, P. J.; Cheng, K.-L. *Tetrahedron Lett.* **1993**, *34*, 907.
 - (xiv) Wagner, P. J.; May, M. *J. Chem. Phys. Lett.* **1976**, *39*, 350.
 - (xv) Wagner, P. J.; Sakamoto, M. *J. Am. Chem. Soc.* **1989**, *111*, 8723.
 - (xvi) Wagner, P. J.; Sakamoto, M.; Madkour, A. E. *J. Am. Chem. Soc.* **1992**, *114*, 7298.
 - (xvii) Wagner, P. J.; McMahon, K. *J. Am. Chem. Soc.*, **1994**, *116*, 10827.
-

- (xviii) Ni, T.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 457.
- (xix) Wagner, P. J. "Handbook of Organic Photochemistry", CRC Press, Boca Raton, 1989, II, p. 38.
- (xx) Wagner, P. J.; Giri, B. P.; Frerking, H. W., Jr.; DeFrancesco, J. *J. Am. Chem. Soc.* **1992**, *114*, 8326; Wagner, P. J.; El-Taliawi, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 8325.
- (xxi) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461.
- (xxii) Wagner, P. J.; Klan, P. *J. Am. Chem. Soc.* **1999**, *121*, 9625.
- (xxiii) Gudmundsdottir, A., Wagner, P. J., unpublished.
- (xxiv) Andrieux, C. P.; Saveant, J.-M.; Su, K. B. *J. Phys. Chem.* **1986**, *90*, 3815.
- (xxv) N. J. Turro and D. S. Weiss, *J. Am. Chem. Soc.* **1968**, *90*, 2185.
- (xxvi) A. E. Dorigo, M. A. McCarrick, R. J. Loncharich, and K. N. Houk, *J. Am. Chem. Soc.* **1990**, *112*, 7508.
- (xxvii) J. R. Scheffer, *Org. Photochem.*, **8**, 249 (1987).
- (xxviii) Wagner, P. J. *Topics Curr. Chem.* **1976**, *66*, 1.
- (xxix) Wagner, P. J.; Giri, B. P.; Scaiano, J. C.; Ward, D. L.; Gabe, E.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 5483.
- (xxx) Wagner, P. J.; Pabon, R.; Park, B.-S.; Zand, A.; Ward, D. L. *J. Am. Chem. Soc.* **1994**, *116*, 589.
- (xxxi) Wagner, P. J.; Cao, Q. *Tetrahedron Lett.* **1991**, *32*, 3915.
- (xxxii) Wagner, P. J.; Cao, Q.; Pabon, R. *J. Am. Chem. Soc.* **1992**, *114*, 346.
- (xxxiii) Wagner, P. J.; Meador, M. A.; Park, B.-S. *J. Am. Chem. Soc.* **1990**, *112*, 5199.
- (xxxiv) Wagner, P. J.; Yang, J.-S. *J. Am. Chem. Soc.* **1993**, *115*, 7914.
- (xxxv) Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134.
- (xxxvi) Wagner, P. J.; Subrahmanyam, D.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 709.
- (xxxvii) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965.
- (xxxviii) Wagner, P. J.; Sobczak, M.; Park, B.-S. *J. Am. Chem. Soc.* **1998**, *120*, 2488.
- (xxxix) Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1972**, *94*, 3852.
- (xl) Wagner, P. J.; Zhou, B.; Hasegawa, T.; Ward, D. L. *J. Am. Chem. Soc.* **1991**, *113*, 9640.
- (xli) Wagner, P. J.; Park, B.-S. *Tetrahedron Lett.* **1991**, *32*, 165.
- (xlii) Wagner, P. J.; Meador, M. A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7988.
- (xliii) Wagner, P. J.; Meador, M. A.; Zhou, B.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 9630.
- (xliv) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.
-