High-Intensity Laser Photochemistry of Organic Molecules in Solution

R. Marshall Wilson*

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172

Karlyn A. Schnapp*

Department of Chemistry, Northern Kentucky University, Highland Heights, Kentucky 41099-1905

Received July 28, 1992 (Revised Manuscript Received November 18, 1992)

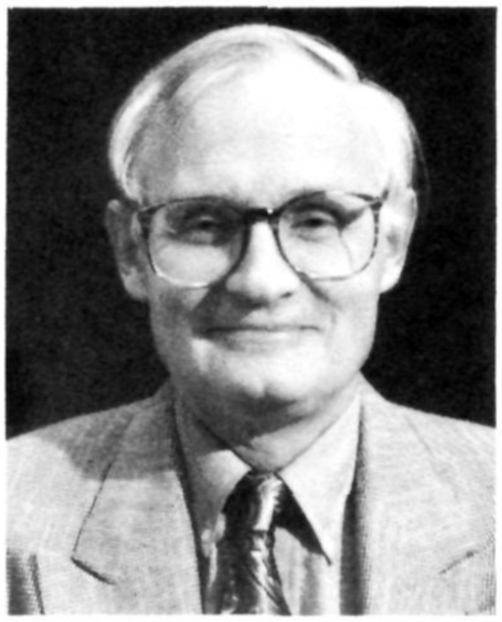
Contents

I. Introduction

The science of photochemistry might be partitioned into several domains according to the intensity of the light required to produce a particular type of photochemical phenomenon. While the boundaries of these domains are not always sharply defined, in general, they might be characterized as follows: (1) The single-photon domain is accessed with light intensities of less than about 10^{22} photons/cm^2 s. All photochemical processes initiated by a single photon occur within this domain, and thus, the bulk of present photochemical knowledge has been derived from studies in this low-intensity domain. (2) The multiple-photon domain is accessed with light intensities that extend from roughly 10^{23} to 10^{28} photons/cm^2 s. In this high-intensity domain, sequential double, triple, and other low-order multiple-photon processes become important and even dominant. Finally, (3) the plasma domain is accessed with light intensities greater than about 10^{28} photons/cm^2 s. In this extreme high-intensity range, simultaneous double-photon absorption, dielectric breakdown, and plasma formation become the dominant photochemical events. In this review, we have restricted ourselves to those photochemical reactions and processes that occur in the second, the multiple-photon domain, and have further restricted this discussion to exclude those processes involving infrared and other low-energy photons.

In general, there are two types of photochemical processes that have their thresholds in the multiple-photon domain: (1) Intertransient reactions or reactions that occur between two transient species. These processes become rather common in this domain. Under low-intensity conditions, the same transient species will be formed, but in such low concentrations that there is only a very low probability that they will encounter one another within their lifetimes. Under high-intensity conditions, concentrations of short-lived reactive intermediates as high as 10^{-3} to 10^{-5} M might be produced, and at these concentration levels, the probability for reactions between these species becomes appreciable. (2) Intratransient reactions become possible when a photochemically generated transient species is sufficiently long-lived for the absorption of additional photons. One variation on this type of process occurs when the target transient is a reactive intermediate such as a radical, biradical, carbene, radical ion, or other type of open-shell or highly reactive species. In these cases, excited states of the transient are produced. In a second variation, the target transient is an excited state itself. Usually, longer-lived excited triplet states provide more suitable target species than the corresponding shorter-lived excited singlet states. In either case, the absorption of the second photon produces a higher excited state.

It should be noted that the production of higher excited states under multiple-photon conditions will almost always arise from the sequential absorption of one or more photons by conventional, lowest excited states that exist for an appreciable time period, Δt, before the absorption of the subsequent photons as outlined in Figure 1. In contrast, "simultaneous", or uncertainty principle-governed, multiple-photon absorption is a fundamentally different phenomenon[1] in which the exciting photon has insufficient energy, ΔE, to produce a stable excited state (Figure 1). However, the pseudostate that does result from the "absorption" of the first photon may exist for a time period Δt as determined by the uncertainty principle and shown in



R. Marshall Wilson was born on October 18, 1939 in Reading, PA. He attended more than a dozen schools including schools in Tokyo, Japan, and Orleans, France. In 1957, he entered The Pennsylvania State University as a Chemical Engineer. During these undergraduate years, he worked in the University nuclear reactor and held positions with Texas Instruments, Inc., American Cyanamid Company, and Johnson Service. Upon graduation in 1961, he entered the Ph.D. program in Organic Chemistry at the Massachusetts Institute of Technology. Under the direction of Prof. John C. Sheehan, he developed one of the first photolabile protecting groups for carboxylic acids that had application to peptide synthesis. In 1965, he moved to Harvard University where he did postdoctoral research addressing synthetic approaches to dodecahedrane with Prof. Robert B. Woodward. In 1967, he joined the faculty of the Department of Chemistry at the University of Cincinnati where he gained valuable practical experience with lasers in the laboratories of Dr. Leon Goldman at the Children's Hospital. His research has emphasized the development of applications of the laser for the study of photochemical intermediates and synthesis of unusual molecules. Among his most significant achievements in this area have been the development of laser methods for the generation and study of biradicals including the trapping of laser-generated biradicals with oxygen. In recent years, he has developed laser techniques for the study of photochemical processes that occur only with very high light intensities. This methodology has led to the discovery of new photochemical processes that may serve as the basis for many future applications of the laser. In addition, he has made significant contributions to the chemistry of natural products with the synthesis of insect pheromones and the development of new strategies for their applications in the control of pest species. More recently, the chemistry of radical cations has been studied and found to mimic the biosynthesis of lignan natural products some of which are known to be important anticancer agents. Finally, he has developed a number of useful synthetic methods including the condensations of triazolinedione ylides.

Karlyn A. Schnapp was born and raised in Ohio. She received her B.S. in Chemistry, with Honors, from the University of Cincinnati in 1984. She received her Ph.D. from the University of Cincinnati in 1989, under the direction of Prof. Marshall Wilson. She has worked at Mead Imaging as a research scientist and was also a postdoctoral fellow at The Ohio State University, working with Prof. Matthew S. Platz. In 1991, she joined the faculty at Northern Kentucky University where she is currently an assistant professor. Her research interests include the photochemistry of short-lived intermediates and higher excited states on both preparative and spectroscopic levels. She is also interested bioorganic photochemistry and has an active collaboration with Prof. Wilson. In addition to her research, Prof. Schnapp is actively involved in teaching and is in the process of encouraging young students, especially women, to pursue careers in science. She is a member of the Inter-American Photochemical Society and the Council on Undergraduate Research.

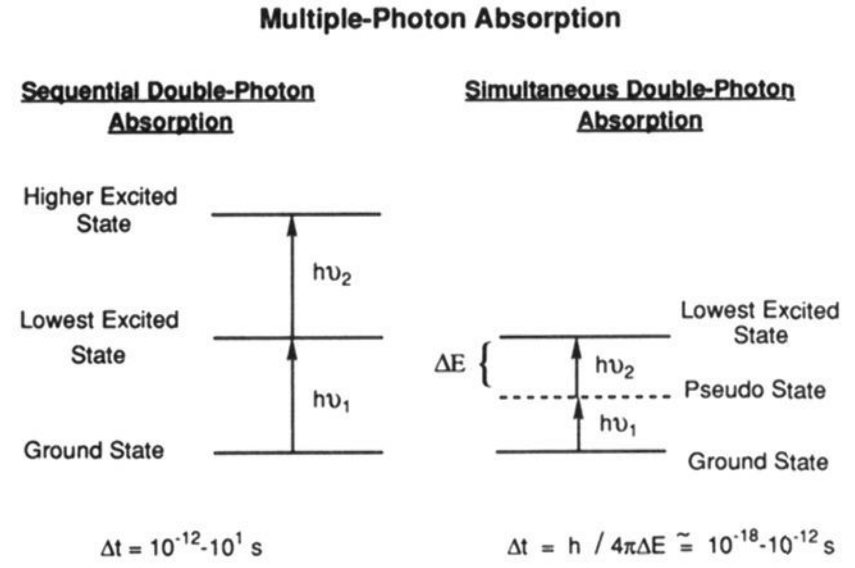


Figure 1.

Figure 1. If this pseudostate encounters a second photon during that time period, the second photon may be absorbed to produce a stable, conventional excited state. Thus, "simultaneous" double-photon absorption differs from sequential double-photon absorption in that it does not involve an intermediate, conventional excited state and in that the selection rules for absorption are altered so that forbidden transitions may become allowed and vice versa. In the vast majority of cases, simultaneous double-photon absorption has its threshold in the plasma domain.

Kleinermanns and Wolfrum have reviewed laser photochemistry with emphasis on its practical applications. They have incorporated a number of examples of multiple-photon processes.[2a] Reviews by Scaiano, Johnston, and co-workers have covered multiple-photon photochemistry through about mid 1988.[2b-d] These reviews provide detailed discussions of multiple-photon processes and are excellent sources of spectroscopic and kinetic data. In the present review, we shall emphasize the more recent developments in this area up to early 1992, and organize the rapidly growing number of known high-intensity reactions in a manner that will attempt to emphasize the emerging reactivity trends of the species encountered in the multiple-photon domain.

II. High-Intensity Techniques

In the past, the study of high-intensity photochemistry has been exceedingly difficult for several reasons. First, single-photon photochemistry will usually occur in competition with the multiple-photon processes. In most cases, the more probable single-photon products will be the dominant products in often rather complex reaction mixtures. If one attempts to increase the light intensity in an effort to increase the yield of multiple-

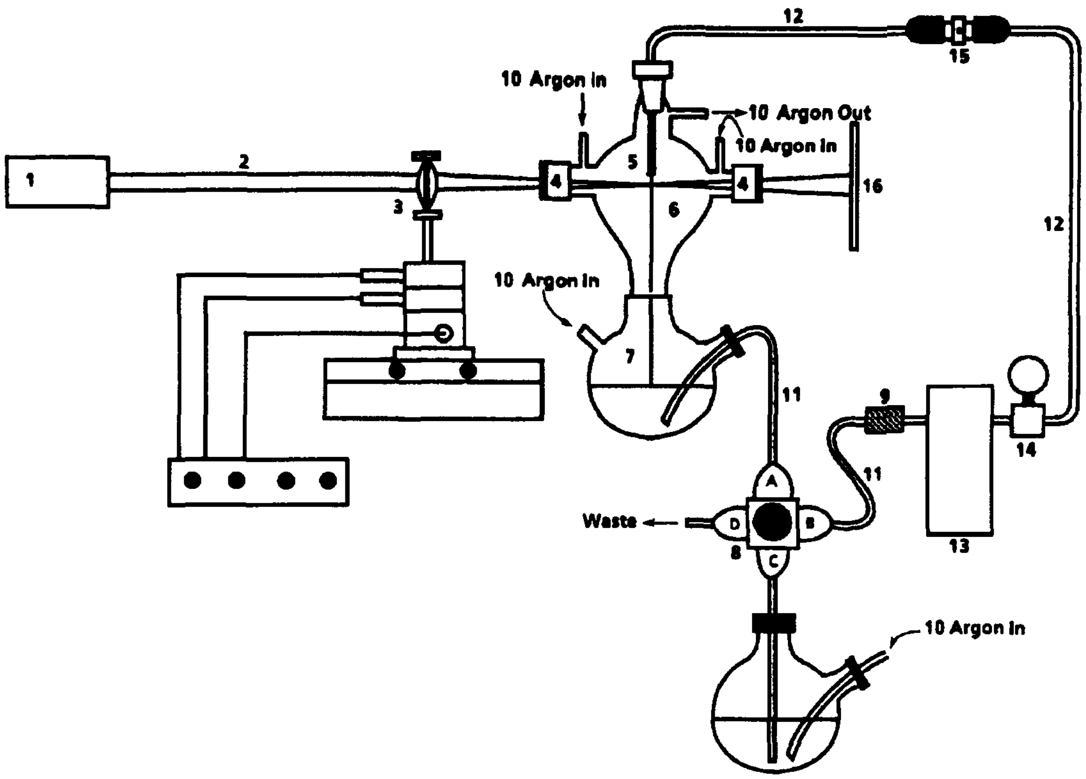


Figure 2. Laser–jet apparatus: (1) argon ion laser, (2) laser beam, (3) lens on motorized micropositioner, (4) demountable reaction chamber windows, (5) capillary nozzle, (6) reaction chamber, (7) reservoir receiving flask, (8) 4-way valve, (9) filter, (10) inert atmosphere ports, (11) low-pressure tubing, (12) high-pressure tubing, (13) HPLC pump, (14) pressure gauge, (15) shut-off valve, and (16) projection screen.

photon products, the formation of color centers or hot spots will often lead to low-threshold dielectric breakdown and plasma formation. Furthermore, high-intensity light suitable for studies of this type is more readily available from pulsed laser sources such as excimer lasers. Unfortunately, the relatively long duty cycle of this type of laser requires a very large number of pulses under carefully controlled conditions in order to produce isolable quantities of multiple-photon products even from relatively efficient photochemical reactions. In recent years, two methods have been developed that can effectively deal with these problems and produce useful structural information about the products of high-intensity photochemical processes.

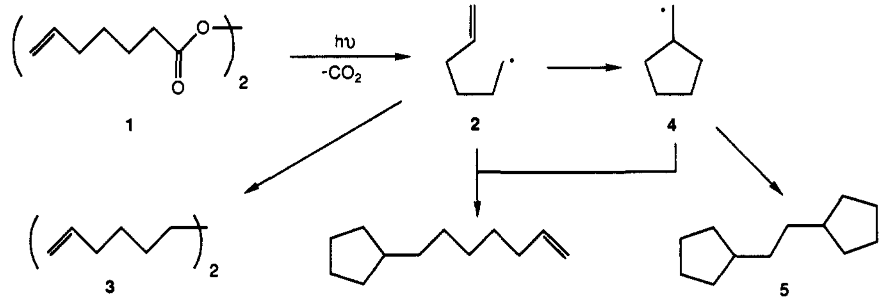
A. The Two-Pulse Technique

The first of these is the two-laser pulse technique developed by Scaiano and co-workers.[3] In this method, the target transient intermediates are produced with an excimer laser pulse (the "synthesis" pulse). After a suitable delay time which often is necessary for the optimum development of the targeted species, this transient is irradiated with a second laser pulse (the "photolysis" pulse). The second laser pulse has a wavelength selected to optimize absorption by the targeted species. This two-pulse technique is ideally suited for the acquisition of spectroscopic data bearing on the photochemical reactivity of a wide variety of transient species. In favorable cases, it can be used to produce isolable quantities of multiple-photon products. More typically, however, the duty cycle problem mentioned above, and intrinsic to all pulsed laser techniques, makes it a difficult task to obtain characterizable quantities of multiple-photon products from all but the most efficient of reactions. Furthermore, without access to the mechanistic information provided by these products, it can be most difficult, if not impossible, to obtain interpretable data from spectroscopically cluttered systems containing many, often closely related, transient species.

B. The CW Laser–Jet Technique

In a second high-intensity irradiation technique, a single CW (continuous wave) argon ion laser beam (333.6–363.8 nm) is focused on a high velocity microjet (50 to 100 μm in diameter) of a solution containing the substrate to be studied (Figure 2).[4] This technique takes advantage of the intensity amplification properties of microbodies that can effectively amplify light intensities by factors of 10^6 or more over that which would be obtained had the light been focused in a homogeneous medium.[5] In essence, the microjet serves as a resonance cavity for the light which becomes trapped within the microcylinder of the jet by total internal reflection. This leads to the formation a mode structure of concentric rings of light around the periphery of the jet. Modes with circumferences that correspond to an integral number of light wavelengths are greatly amplified.[5c] Light intensity amplification by this technique provides CW intensities comparable to those available from pulsed lasers. Since a CW laser is used, the duty cycle problem is avoided, and it is possible to obtain much larger quantities of multiple-photon products per unit of irradiation time. In fact, sufficient quantities of multiple-photon products can usually be obtained for characterization by conventional spectroscopic methods such as NMR, IR, and mass spectrometry. The disadvantage of this method relative

Scheme 1



Low Intensity	----	Minor	>60%
High Intensity[a]	>90%	----	----

[a] 308 nm, excimer laser

to the aforementioned two-pulse technique is that presently it provides no spectroscopic information that can be used to determine the nature of the targeted species. In order to obtain information of this type, separate experiments must be conducted with more conventional transient spectroscopic equipment. Nevertheless, it is perhaps worth noting that in all jet experiments a coherent disk of light is produced normal to the jet axis. The spectroscopic properties of this light disk have never been examined. Given the very high concentrations of transient species present at the origin of this disk, this disk light might provide valuable spectroscopic information about these species. If so, then the laser–jet technique might be developed into a form of steady-state transient spectroscopy. This is certainly an area deserving of further investigation.

On occasion, other photochemical methods have been applied in the study of high-intensity processes. However, when these methods do not incorporate *both* spectroscopic characterization of the transient species involved and structural characterization of the products formed, great care must be exercised in providing mechanistic interpretations for the phenomenon observed.

Finally, it is important to emphasize that the lifetimes of most of the target species involved in high-intensity photochemistry can be greatly extended at low temperature. Thus, the generation of these species in low-temperature matrices often makes it possible to study their photochemistry using conventional low-intensity light sources.[6] Unfortunately, this parallelism breaks down for those reactions that are either thermally activated or require some degree of mobility of the species involved, such as in the case of the aforementioned intertransient reactions.

III. Intertransient Reactions

A. Radical and Biradical Coupling

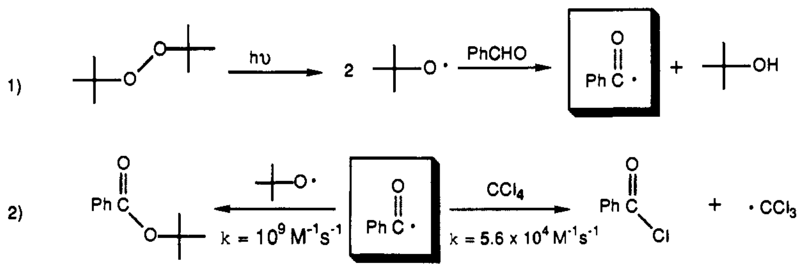
The classical example of an intertransient reaction is the coupling of simple radicals. Of course, a given radical will only survive long enough to undergo coupling in the absence of more efficient competing reactions. In general, any photochemical reaction involving the coupling of radicals should exhibit a light intensity dependence, while competing ground-state radical reactions with other substrates will not. Indeed, this effect has been recognized for a number of years and was originally studied with conventional light sources.[7]

An instructive variation of this type of competition utilizes the well-known radical clock reaction shown in Scheme 1.[2c,8] When **1** is irradiated under low-intensity conditions, the resulting radical **2** is formed in concentrations insufficient to undergo coupling to **3** in competition with cyclization to radical **4**. Thus, the major product is the coupling product **5** of the cyclized radical **4**. In contrast, excimer laser irradiation of **1** affords concentrations of **2** well in excess of 10^{-5} M which results in nearly exclusive formation of the uncyclized radical coupling product **3**.

In a similar type of experiment, Adam and Schulte Oestrich have generated benzoyl radicals in carbon tetrachloride via the photolysis of *tert*-butyl peroxide as outlined in Scheme 2.[9a,c] With low intensities, the exclusive product was benzoyl chloride arising from a rather slow chlorine abstraction from carbon tetrachloride. While under argon laser–jet conditions, *tert*-butyl benzoate was formed as the major product. On the basis of this competitive trapping experiment (*tert*-butyl peroxide:CCl_4 = 50:50, [CCl_4] = 5.4 M), they estimated the concentration of *tert*-butoxy radical to be about 1.5×10^{-3} M which is quite remarkable considering that the extinction coefficient of *tert*-butyl peroxide at the laser lines is only 0.4 M^{-1} cm^{-1}. It also is interesting to note that the trichloromethyl radical formed by the route shown in Scheme 2 dimerizes exclusively to form hexachloroethane with no cross-coupling to α,α,α-trichloroacetophenone being observed. In contrast, when benzoyl radical is generated in the two-photon cleavage of benzil in carbon tetrachloride (see section V.B), formation of α,α,α-trichloroacetophenone is favored over dimerization to hexachloroethane.[9c] This observation is ascribed to a cage effect. Since this process produces two benzoyl radicals in a carbon tetrachloride cage, chlorine atom abstraction results in formation of benzoyl radical and trichloromethyl radical within the same solvent cage and, consequently, favors the cross-coupling process.

Irradiation of perfluoroazoethane displays the same type of intensity-dependent behavior.[10] In this case, the competition is between trapping of the perfluoroethyl radical by the starting azoalkane and coupling of these radicals (Scheme 3).

Scheme 2



Low Intensity	----	>99%
High Intensity[a]	81%	16%

[a] Argon Laser-Jet, 333 nm

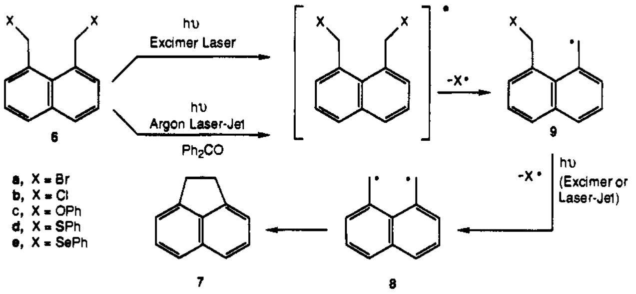
Scheme 3

$CF_3CF_2—N{=}N—CF_2CF_3 \xrightarrow{h\nu} (CF_3CF_2)_2N—N(CF_2CF_3)_2 + CF_3CF_2—CF_2CF_3$

Low Intensity	85%	15%
High Intensity[a]	10%	90%

[a] 308 nm, excimer laser

Scheme 4



In general, molecular weight distributions of polymers formed in photopolymerizations initiated with azoalkanes and benzoin ethers are intensity dependent.[11,12] Thus, in cases where low-intensity irradiation results in high molecular weight polymers, high-intensity laser irradiation results in decreasing molecular weight distributions with increasing laser peak power,[12] laser pulse repetition rate,[13] and initiator concentration.[14] These effects are all due to the formation of high radical concentrations which cause premature radical chain termination.

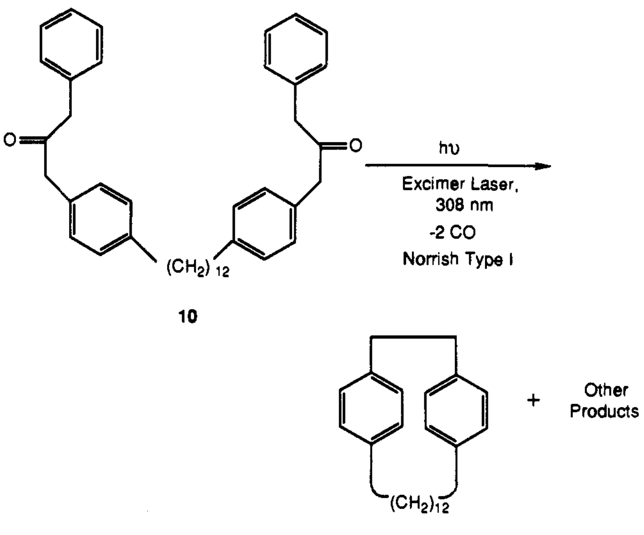
The same general intensity-dependent behavior is observed with biradicals in which the two radical termini are formed in two separate steps. For example, the bichromophoric molecule 1,8-bis(bromomethyl)naphthalene (**6a** in Scheme 4) seems to form oligomers and polymers upon low-intensity irradiation. In contrast, irradiation at intensities greater than ca. 1.4 × 10^{23} photons/cm^2 s^1 with a variety of excimer laser lines (ArF, 193 nm; KF, 248 nm; XeCl, 308 nm) affords acenaphthene (**7**).[15a,b] This reaction is thought in involve the sequential absorption of two photons to yield the biradical **8** as outlined in Scheme 4. The same reaction can be produced in about twice the yield using the argon ion laser–jet technique.[16] Under these conditions, the starting naphthalene **6a** does not absorb in the wavelength region of the argon laser UV laser lines (333–364 nm). Therefore, the formation of the intermediate monoradical **9a** must be sensitized with benzophenone. Once formed, **9a** readily absorbs an argon laser photon directly, and extrudes the second bromine atom to yield the biradical **8**. Since many potential substrate molecules do not absorb in the wavelength region of the argon laser UV lines, and yet, once excited, yield transients that absorb strongly in this region, the technique of sensitized multiple-photon absorption promises to be an extremely useful tool in high-intensity photochemistry.

Further examples of this type of sequential biradical generation have been described in more recent work.[15b,c] A variety of potential radical leaving groups have been examined in this capacity (**6b–e** in Scheme 4), and the phenylselenyl group (**6e**) was found to give the highest yields of acenaphthene (**7**). Of this series, **6a–e**, only **6e** can be excited directly under argon laser–jet conditions, and thus, does not require sensitized initiation. Comparison of the unsensitized and benzophenone-sensitized reactions of **6e** indicated that comparable yields of **7** were obtained by either method (unsensitized, 13.4 ± 0.6% and sensitized, 12.3 ± 0.7%).[15c]

Sequential biradical generation also has been used in the synthesis of macrocyclic molecules (Scheme 5).[17] In this approach, two sequential Norrish type I cleavages were used to form a biradical from the bis-dibenzyl ketone **10**. It was found that excimer laser irradiation of **10** at 308 nm was about three times more effective in producing the macrocycle **11** than was low-intensity irradiation.

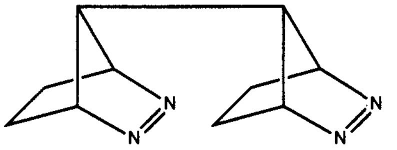
Biradicals in which both radical termini are formed by a single-photon process have been observed to dimerize upon high-intensity irradiation. For instance, 1,3-cyclopentanediyl has a lifetime of ca. 100 ns[18] and undergoes efficient collapse to bicyclo[2.1.0]pentane with no evidence of dimer formation under low-intensity conditions. In contrast, argon laser–jet generation of 1,3-cyclopentanediyl affords up to 45% yield of dimers.[19] It is instructive to note that the novel bis-azoalkane **12**

Scheme 5



11

did not afford the corresponding tetraradical under the high-intensity conditions available at the time. This was indicated by the exclusive formation of bi-5,5′-bicyclo[2.1.0]pentane isomers upon high-intensity irradiation.[20a] These isomers apparently arise through nitrogen extrusion and collapse of the first biradical unit before the second biradical unit can be formed. This observation is consistent with the drastic reduction in biradical lifetime caused by carbon substituents in the 2-position between 1,3-biradical termini (2,2-dimethyl-1,3-cyclopentanediyl, $\tau < 0.1$ ns).[20b]

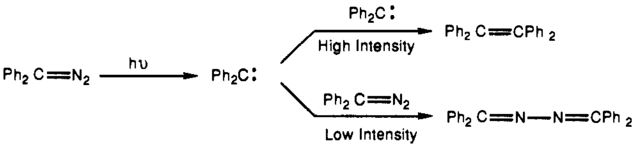


12

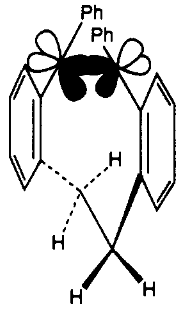
B. Carbene Coupling

Carbenes follow this same intensity-dependent reactivity pattern.[21] At low light levels and correspondingly low carbene concentrations, both singlet and triplet diphenylcarbene react with the precursor diphenyldiazomethane to form benzophenoneazine (Scheme 6).[21] While under high-intensity, laser irradiation conditions, the diphenylcarbene dimerization product, tetraphenylethylene, becomes dominant.

Scheme 6



In a striking example of how intensity-dependent carbene dimerization might be used to synthesize olefins not available through other routes, Hannemann and Wirz have obtained the strained *trans*-olefin 13 in moderately good yield from the high-intensity, excimer laser irradiation (248 nm) of the bis-diazo compound 14 (Scheme 7).[22] At low light levels, 14 affords a series of hydrocarbons and a cyclic azine via sequential carbene formation. In comparison, excimer laser irradiation affords the bis-carbene 15 which collapses to a mixture of *cis*- and *trans*-olefins. Interestingly, the more strained *trans*-olefin predominates in this mixture. Since it was shown that this high-intensity, cis–trans isomer mixture contained much more *trans*-olefin than the photostationary state, the preferential formation of 13 must be a consequence of a kinetically controlled coupling of the bis-carbene 15. This can be readily understood in terms of the approach geometry shown in structure 16 which would force a trans geometry in the product olefin. The constraints imposed on the system by the two-carbon tether make it very difficult to achieve an approach geometry that would result in the *cis*-olefin.



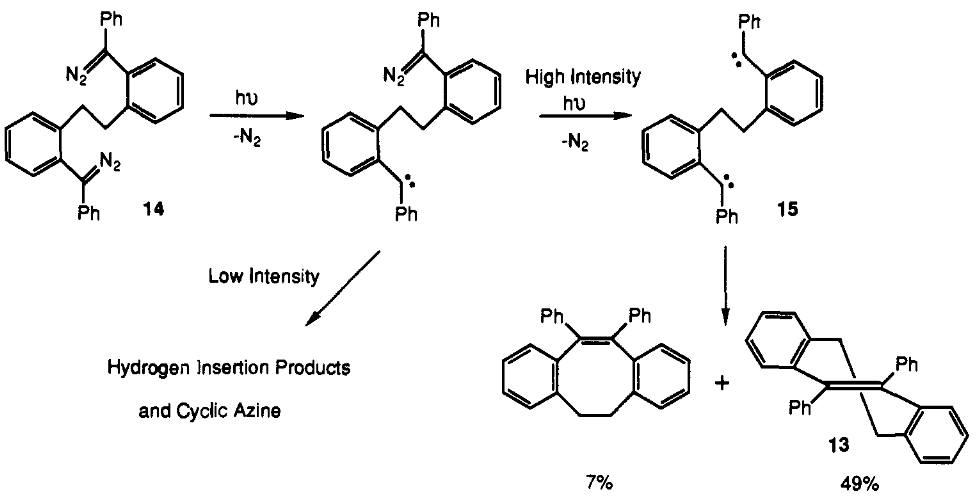
16

C. Nitrene Coupling

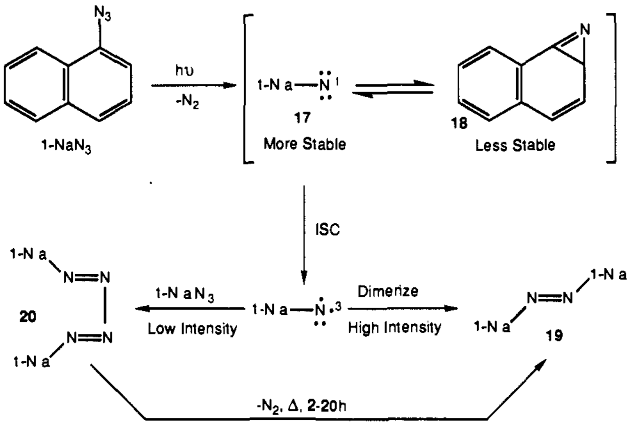
The intensity dependence of aryl nitrene behavior is considerably more complex than that of carbenes described above. The behavior of aryl nitrenes is highly dependent on the aryl substituents and their pattern of substitution. Two basic situations are encountered. In the first of these,[23] shown in Scheme 8, the singlet naphthyl nitrene 17 is thought to be more stable than its azirine valence tautomer 18, and ISC to the triplet nitrene is facile. Under these circumstances, high-intensity laser irradiation affords large concentrations of the triplet nitrene which dimerizes to the azo compound 19. Under low-intensity conditions, 19 is also formed, but, unlike the high-intensity reaction, the generation of 19 continues in the dark for a period of several hours. This observation is rationalized by invoking the putative tetrazine intermediate 20 which might arise from reaction of the triplet nitrene with the starting azide, a process which would be favored by low nitrene concentration. It was suggested that 20 might undergo a slow thermal extrusion of nitrogen to form the azo compound 19. In this scenario, formation of azo compounds usually is enhanced by high-intensity irradiation.

It is interesting to contrast the reaction shown in Scheme 9 with that outlined in Scheme 8. Irradiation of 1,8-diazidonaphthalene (21) with conventional light sources apparently affords the rather long-lived nitrene 22.[24] Under these conditions, the azo compound 24 is not formed in solution, although it is formed at 77 K in a matrix.[25] On the other hand, excimer laser irradiation of 21 does afford 24 in appreciable yields. Thus, even though the nitrene functionality in 22 would seem to be ideally situated for reaction with the adjacent azido group to form a tetrazine species analogous to 20 in Scheme 8, this apparently does not happen, since 24 is not observed under low-intensity conditions. Only

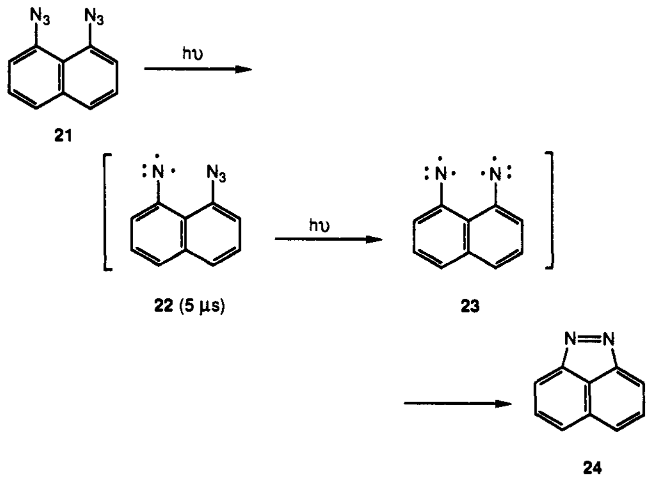
Scheme 7



Scheme 8



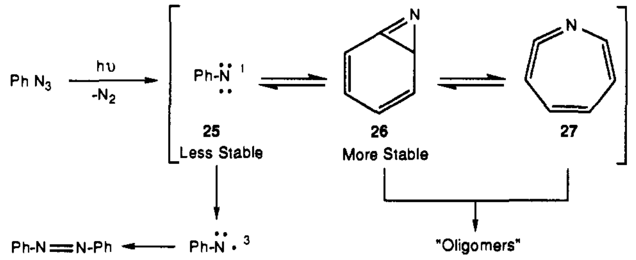
Scheme 9



under high-intensity conditions and in low-temperature matrices is the second nitrene unit formed within the lifetime of the first nitrene to yield the dinitrene **23** which collapses to the azo compound **24**.

The second situation encountered in aryl azide photochemistry is exemplified by phenyl azide itself (Scheme 10).[26] The singlet nitrene **25** derived from phenyl azide is thought to be less stable than the azirine **26**. In this system, the dehydroazepine **27** also participates in the equilibrium. Under low-intensity conditions, **26** and **27** serve as nitrene "sinks", and slowly leak triplet nitrene via the singlet nitrene. Consequently, at low initial concentrations of phenyl azide, appreciable amounts of azobenzene are produced. While at high concentrations of phenyl azide or under high-intensity conditions, the yield of azobenzene is drastically reduced and replaced with undefined polymers. Apparently, **26** and **27** are prone to polymerization and, when formed in high concentrations, react with each other and perhaps nitrenes to form polymer. Consequently, in this scenario, azo compound formation is suppressed by high-intensity irradiation.

Scheme 10

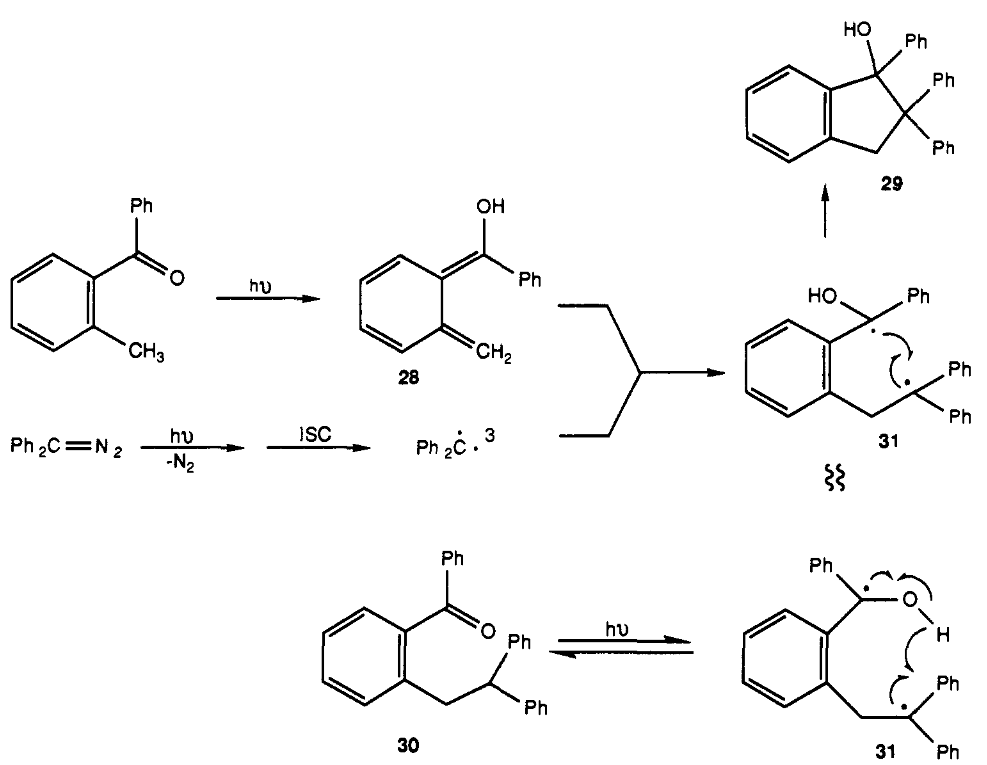


D. Transient Targeting

It is clear from the above examples that high-intensity photochemistry provides an effective, and by now well-established, method for studying the reactions of transient intermediates with each other. However, in the great majority of these cases, the reactions studied have been the simple dimerization of transient species. Therefore, one of the next steps in the exploration of this fascinating area of high-intensity photochemistry will be to study of reactions between different transient intermediates.

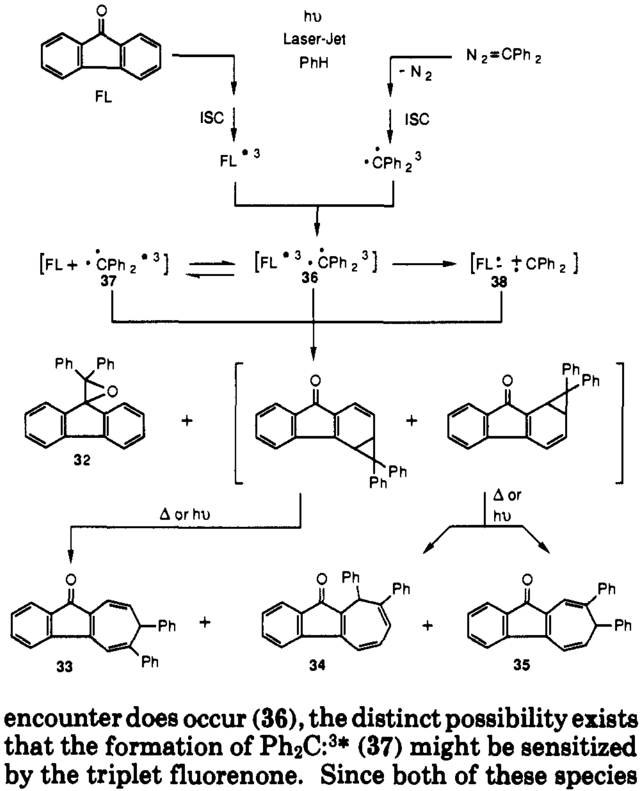
Several early examples of this type of intertransient reaction are the reactions of singlet oxygen with tetramethyl-*o*-xylylene[27] and the photoenol of 2-methylacetophenone.[28] The transient photoenol of 2-methylbenzophenone (**28**) reacts with diphenylcarbene as shown in Scheme 11.[29] Argon laser-jet irradiation of mixtures of 2-methylbenzophenone and diphenyldiazomethane simultaneously generates the photoenol **28** and triplet diphenylcarbene in high concentrations. From the rather complex reaction mixture that results, two products that incorporate the elements of the photoenol **28** and diphenylcarbene have been isolated and shown to have structures **29** and **30**.

Scheme 11



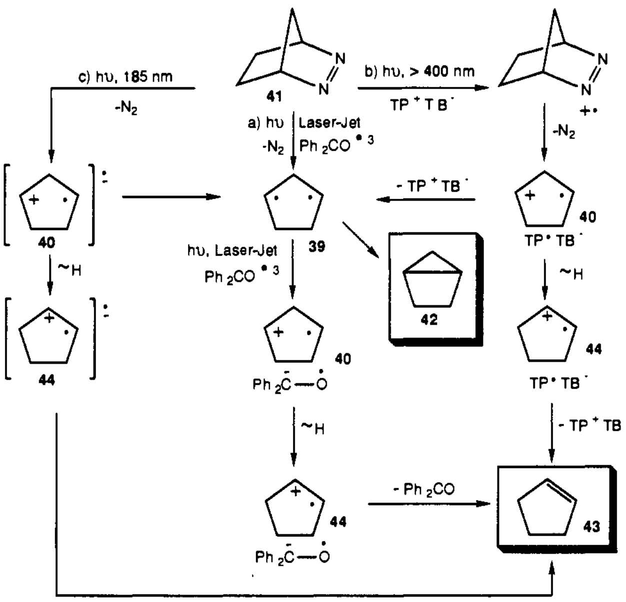
These products apparently arise through the stepwise addition of the triplet carbene to the photoenol via the biradical **31** as outlined in Scheme 11. Collapse of this biradical with carbon–carbon bond formation affords **29**, and intramolecular disproportionation affords **30**. The same biradical, **31**, accessed through the conventional irradiation of **30**, has been shown to collapse to the indanol **29**. Reactions of this type are expected to be much more difficult to realize than many of the radical couplings described above, since closed-shell transients such as photoenols usually will react with rate constants far below the diffusion limit, and thus, must be present in much higher concentrations in order for appreciable reaction to occur.[30]

Scheme 12

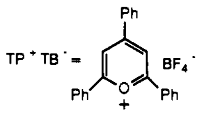


Another type of transient species that might be targeted by a reactive intermediate is an excited state itself. A particularly appealing target species for this type of study is the triplet excited state of 9-fluorenone which has an unusually long lifetime (1 ms, benzene, room temperature).[31] Thus, irradiation of mixtures of 9-fluorenone and diphenyldiazomethane under argon ion laser-jet conditions generates high concentrations of fluorenone and diphenylcarbene triplets as outlined in Scheme 12.[32] This reaction affords not only the oxirane **32**, but the highly colored, and novel dihydrobenz[*a*]azulenes **33**–**35**, as well as other products (see Scheme 48 and associated discussion). The mechanistic origins of these high-intensity products is not entirely certain. Nevertheless, it seems highly likely that the fluorenone triplet is involved due to its unusually long lifetime. The excited state of diphenylcarbene ($\mathrm{Ph_2C}{:}^{3*}$) may also be involved, but its involvement can not be straightforward, since its lifetime is too short (4.2 ns, benzene, room temperature)[21c] for efficient reaction with fluorenone under the dilute reaction conditions used. Therefore, the most likely initial encounter is between triplet fluorenone and the ground state of triplet diphenylcarbene. Once encounter does occur (**36**), the distinct possibility exists that the formation of $\mathrm{Ph_2C}{:}^{3*}$ (**37**) might be sensitized by the triplet fluorenone. Since both of these species have very similar excited triplet energies ($\mathrm{Ph_2C}{:}^{3*}$, $E_T = 52$ kcal/mol,[33] and triplet fluorenone,[34] $E_T = 53$ kcal/mol), there does not seem to be a distinct bias for either of these scenarios shown in Scheme 12. In addition, the possibility of electron transfer between these species to form the ion pair **38** might be considered (see Scheme 13 and associated discussion). This latter alternative seems unlikely, since this same ion pair should be formed in an exothermic electron-transfer reaction between triplet fluorenone and diphenyldiazomethane

Scheme 13



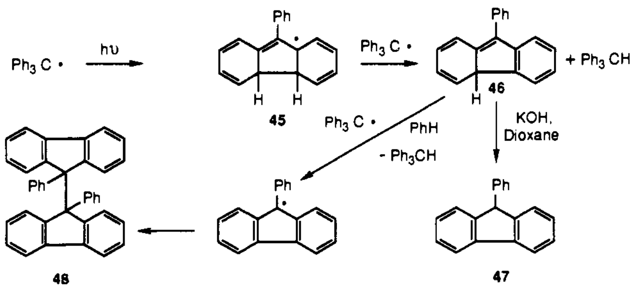
Route	42	43
a	45%	10%
b	20%	80%
c	52%	38%



under low-intensity conditions[35] which, if it does occur, does not lead to the products **32–35**. Finally, it has to be mentioned at this point that oxirane formation via the reaction of aryl ketones with excited diphenylcarbene is unexceptional under high-intensity conditions, and will be elaborated upon in a subsequent section. In contrast, diphenylcarbene attack at the aromatic rings of aryl ketones is unique to fluorenone as of this writing.[36]

Adam and co-workers have recently reported another interesting example involving the use of an excited-state aryl ketone to target a biradical (Scheme 13).[19,37] In this case, triplet benzophenone not only sensitizes the formation 1,3-cyclopentanediyl (**39**), but subsequently appears to oxidize **39** to its radical cation **40**. This mechanistic sequence is based upon the observation that laser–jet irradiation of 2,3-diazobicyclo[2.2.1]heptene (**41**) and benzophenone not only forms the typical product of this reaction, bicyclo[2.1.0]pentane (**42**), but also cyclopentene (**43**) (pathway a, Scheme 13). Since **43** is the major product when **41** is subjected to photochemical electron transfer conditions (pathway b, Scheme 13), the authors suggest that 1,3-cyclopentanediyl radical cation (**40**) is a common intermediate in both reactions and that **40** undergoes a facile 1,2-hydride shift to afford the radical cation of cyclopentene (**44**). In a further most interesting comparison, it was shown that these same species (**40** and **44**), or closely related species, are apparently generated when **41** is irradiated with high-energy, 185-nm photons (pathway c, Scheme 13). This work is particularly significant, since it demonstrates the feasibility of sequential double sensitization for the generation of high-energy species from nonabsorbing species of lower energy. Furthermore, the correlation established between 1,3-diyl photochemistry and radical cation chemistry may prove quite useful in interpreting earlier observations in the photochemistry of biradicals (see Scheme 28 and associated discussion).

Scheme 14



IV. Intratransient Reactions

In this, the second major area of high-intensity photochemistry, the host of transient intermediates that have been generated in photochemical reactions become potential targets for the absorption of secondary photons. Thus, radicals, biradicals, carbenes, nitrenes, ylides, and all varieties of absorbing intermediates might be excited to higher energy species many of which will display unique and, as yet, undefined chemistry.

A. Arylmethyl Radicals

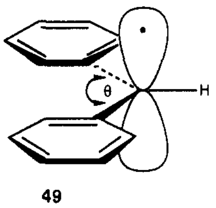
Arylmethyl radicals constitute the most thoroughly studied class of transient photochemical intermediates. In fact, the first example of the photochemistry of a transient radical species was that of triphenylmethyl radical which has such a long lifetime that its photochemistry can be studied easily with conventional low-intensity light sources[38] including the relatively weak light source of a fluorimeter.[39] This photochemistry has been most succinctly characterized by Letsinger[40] as outlined in Scheme 14. Thus, upon excitation, the triphenylmethyl radical cyclizes to the dihydrofluorenyl radical (**45**) which subsequently undergoes disproportionation with the ground state of triphenylmethyl radical to form triphenylmethane and the fluorene tautomer **46**. In the presence of base, **46** is aromatized to the much more stable 9-phenylfluorene (**47**), but if aromatization proceeds too slowly, further hydrogen abstraction can lead to the dimer **48**.

While triphenylmethyl and related triarylmethyl radicals are generally sufficiently long-lived to exhibit photochemistry at low light intensities, the relatively short-lived diarylmethyl analogs, which display analogous photochemistry, require significantly higher light intensities. Furthermore, since arylmethyl radicals have been widely applied as "reporter" groups in transient spectroscopy, their photochemistry has been of considerable interest. Unfortunately, until very recently, most of the work on the photochemistry of these species has relied heavily on transient spectroscopic data with very little data being derived from product isolation. Scaiano, Johnston, and co-workers[2b,c] have provided excellent reviews of the transient properties of these arylmethyl species. Consequently, we shall only present more recent results and selected older results which provide an overview of the modes of excited arylmethyl chemistry.

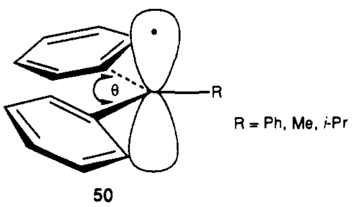
Two detailed studies of the sequence of steps involved in the photoconversion of triphenylmethyl radicals to

4a,4b-dihydro-9-phenylfluorenyl radicals have been reported. Hilinski has observed what is most likely an excited state of the triphenylmethyl radical using three-pulse, picosecond-resolved absorption spectroscopy.[41] This work indicates that the excited triphenylmethyl radical cyclizes to the dihydrofluorenyl radical within ca. 10 ns. The stable perchloro analog[42] has been studied by Fox[43] who found that its photoconversion to the analogous perchlorofluorenyl radical is somewhat more complex. In this system, the initially formed excited state decays to a 560-nm transient within ca. 10 ns. before cyclizing to the perchloro-4a,4b-dichloro-9-phenylfluorenyl radical. The nature of the intermediate 560-nm transient is uncertain, but may be some type of intramolecular charge-transfer species, perhaps Ar_2C^+–$Ar^{\bullet-}$. Photoacoustic spectroscopy has been applied in this work in order to determine the relative energies of the various species. Photoacoustic spectroscopy has also been combined with Scaiano's two-pulse technique for producing excited states of transient intermediates.[44] In this initial work, the quantum yield for the fluorescence of the excited state of diphenylmethyl radical was determined. This method should provide previously difficult to obtain data for the energetics and quantum yields of upper excited states.

As indicated in the above discussion, the most widely encountered mode of diarylmethyl radical photochemistry is cyclization to the corresponding dihydrofluorenyl radical (first step in Scheme 14). This type of cyclization only occurs with diarylmethyl radicals that are substituted on the central carbon atom.[45] Apparently, the less demanding steric requirements of a hydrogen atom on this central carbon (**49**) leads to an expansion of the angle Θ between the two phenyl groups. This in turn results in the two phenyl groups being able to assume a more nearly coplanar geometry.[46] On the other hand, substitution of the central carbon atom with any larger group (**50**) produces a buttressing effect which forces the two phenyl groups closer together through a reduction of the angle Θ. This additional crowding apparently results in the propeller-like geometry shown for **50** with phenyl twist angles of 30–40°. These out-of-plane phenyl groups will have significantly better interaction between their ortho positions, and hence, be more favorably disposed for cyclization to the dihydrofluorenyl radical.



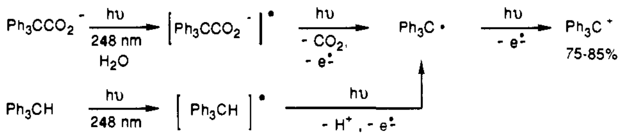
49



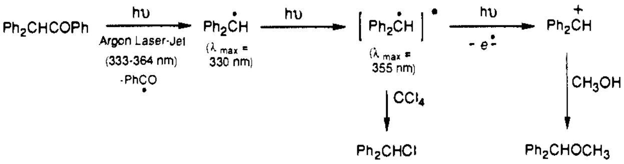
50

Closely related photocyclizations of arylamines and *cis*-stilbenes are well known,[47] and being photochemically allowed 6n electrocyclic processes, are conrotatory processes forming dihydroisomers with a trans geometry about the newly formed bond. In contrast, the stereochemical course of reactions involving an odd number of electrons, such as these diphenylmethyl radical cyclizations, is not clear. While there presently are no experimental data addressing this point, Fox, who has analyzed the problem from a theoretical perspective, suggests that diphenylmethyl radical cyclizations are probably also conrotatory, and thus, should lead to *trans*-dihydrofluorenyl radicals.[43]

Scheme 15



Scheme 16



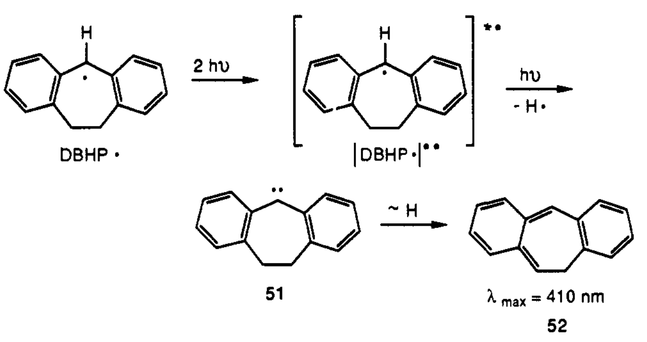
The existence of other photochemical reaction modes of diphenylmethyl radicals was first suggested by Meisel and co-workers.[45] They found that both diphenylmethyl radical itself and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptenyl radical (DBHP) were both unreactive in their lowest excited states. However, upon excitation to a higher excited state, they both underwent solvent-dependent chemistry. The exact nature of this photochemistry remained somewhat speculative until recent studies indicated that there may be at least two additional modes of excited diphenylmethyl radical chemistry other than the aforementioned cyclization to dihydrofluorenyl radicals.

The first and most thoroughly studied of these alternative modes is photoionization. This process has been demonstrated spectroscopically by Faria and Steenken for the triphenylmethyl radical excited at 248 nm in polar solvents as outlined in Scheme 15.[48] The high yield of triphenylmethyl cation produced by this method clearly shows that the traditional cyclization to dihydrofluorenyl radical can be bypassed with the aid of sufficiently polar solvents and high-energy photons. These same workers have extended this photoionization process to the spectroscopic observation of a variety of ring-substituted diphenylmethyl cations.[49] In this work, the corresponding cations were formed using a sequence of two excimer laser pulses, a 248-nm pulse to generate the radicals and a 308-nm pulse to excite the radicals and cause electron ejection.

Scaiano and co-workers had previously attempted to observe the diphenylmethyl cation through the photooxidation of the corresponding radical with CCl_4 (Scheme 16).[3] They showed that the lowest excited state of diphenylmethyl radical can be efficiently trapped by CCl_4 in what appears to be an electron transfer reaction to form Ph_2CHCl. Since free diphenylmethyl cation could not be observed in these experiments, this cation, if it is formed, must undergo reaction within the geminate ion pair. Of further significance, is the observation that this same lowest excited state of diphenylmethyl radical is unreactive toward alcohols which apparently did effectively trap its higher excited states.[45,50]

Adam and Schulte Oestrich have nicely applied the above information in a series of argon ion laser–jet experiments and product isolation studies.[9a] These authors generated the parent diphenylmethyl radical in a Norrish type I cleavage of benzhydryl phenyl ketone

Scheme 17



(Scheme 16), and studied the competitive trapping of its different excited states with CCl_4 and methanol. At low CCl_4 concentrations, this trapping is highly intensity dependent with CCl_4 trapping predominating at low light intensities and methanol trapping predominating at high intensities. Furthermore, it was shown that the methanol-d_1 trapping product, benzhydryl methyl ether, contained no deuterium. These deuterium labeling results are consistent with the higher excited states of diphenylmethyl radical either undergoing facile electron ejection to form the cation, or being an incipient carbocation with highly electrophilic character. In addition, these labeling results also clearly exclude the possibility that the higher excited states have carbene character (see Scheme 17 and the associated discussion). Thus, the mechanistic speculation, based solely on spectroscopic studies, that different diphenylmethyl radical excited states display distinctly different reactivity modes has now been confirmed by preparative laser–jet studies.

The second alternative, and much less well understood, mode of diphenylmethyl radical photochemistry is carbene extrusion. The existence of this mode again stems from Meisel's observation that the lowest excited state of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptenyl radical [DBHP•]* (Scheme 17) is unreactive, but that higher excited states, [DBHP•]**, undergo photochemistry.[45] The nature of this [DBHP•]** photochemistry was based primarily upon two spectroscopic observations. The first of these was that [DBHP•]**, or some product derived from it, reacts irreversibly with alcohol solvents. The reactivity pattern of various alcohols suggests that this reaction occurs at the alcohol oxygen. The second observation, made in acetonitrile as the solvent, was the formation of a new transient absorbing at 410 nm. Since this transient had an absorption spectrum reminiscent of a species formed in the decay of carbene **51** which tentatively had been assigned the *o*-xylylene structure **52**,[51] the primary photoproduct of the reaction of [DBHP•]** was suggested to be the carbene **51**. It also was suggested that a similar carbene extrusion might account for the observed reactivity of the higher excited states of diphenylmethyl radical,[45] but this possibility seems to have been excluded by the more recent experiments described above.[9a]

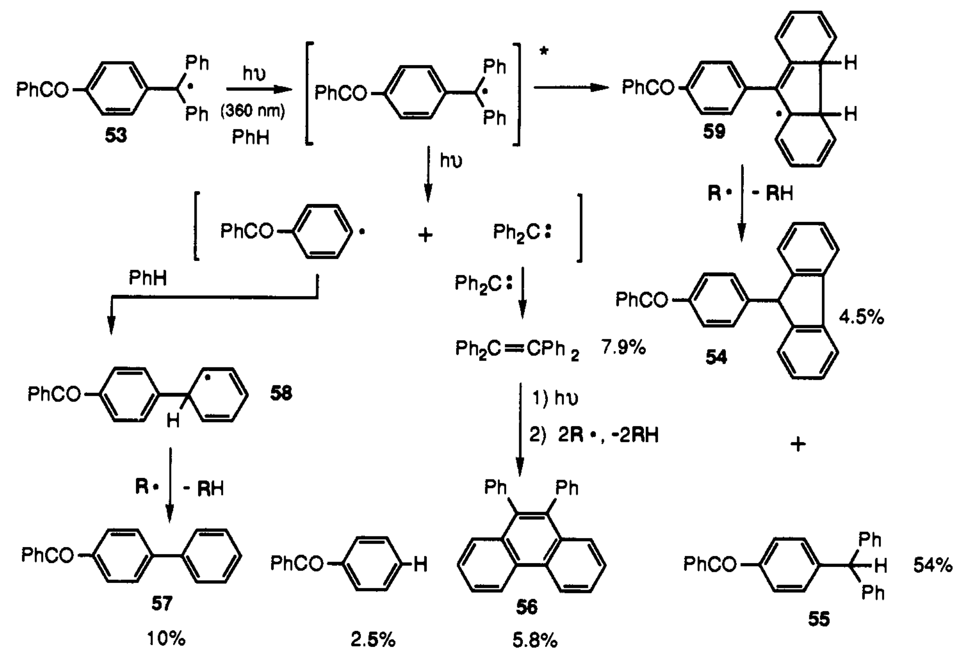
These arguments for carbene extrusion have been based entirely upon spectroscopic data, and must be considered tentative until they can be verified by products analysis. It is interesting to note that there is a single, low-intensity reaction where just this type of carbene extrusion seems to have been observed in a related system, and the products from this reaction have been thoroughly characterized.[52] Neckers and coworkers have studied the photochemistry of the triarylmethyl radical **53** and isolated the products shown in Scheme 18. Thus, the observation of the 9-arylfluorene **54** and the triarylmethane **55** are unexceptional, but the other products, **56**, **57**, tetraphenylethylene, and benzophenone are precisely the products that one would expect from a carbene extrusion reaction as shown by the mechanism outlined in Scheme 18. It should be mentioned that deuterium labeling studies were conducted using benzene-d_6. However, deuterium incorporation was only evaluated for **55**.[53] Since the source of abstractable hydrogen (deuterium) in this type of reaction will be the mono and dihydro species such as **58**, **59**, and the dihydrophenanthrene precursor to **56** rather than the benzene-d_6 itself (see Scheme 14), low deuterium incorporation in **55** is to be expected. A second point is that Meisel's examples of carbene extrusion all seem to arise from higher excited states of diphenylmethyl radicals rather than the lowest excited state.[45] In the present example, the lowest excited state would seem to be the most likely source of this chemistry. However, the *p*-benzoyl substituent may stabilize the lowest excited state of **53** to the extent that it might have a sufficiently long lifetime for further excitation to occur even under low-intensity conditions.

Clearly the factors that direct the course of diarylmethyl radical photochemistry along these three possible reaction channels, (1) cyclization to dihydrofluorenyl radicals, (2) photoionization, and (3) carbene extrusion, warrant further study.

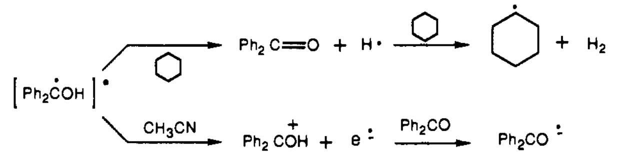
Finally, it should be emphasized that excited diphenylmethyl radicals display a much greater tendency to undergo electron-transfer reactions than hydrogen abstraction reactions.[2b,c,3] Thus, excited diphenylmethyl radical itself is rapidly quenched by electron acceptors such as methyl viologen and carbon tetrachloride ($k_q > 10^8\ M^{-1}\ s^{-1}$) and electron donors such as triethylamine ($k_q = 2.1 \times 10^8\ M^{-1}\ s^{-1}$), while it undergoes surprisingly slow hydrogen abstraction with substrates such as 1,4-cyclohexadiene ($k_q = 1.1 \times 10^6\ M^{-1}\ s^{-1}$) and *n*-$Bu_3SnH$ (k_q = ca. $4 \times 10^5\ M^{-1}\ s^{-1}$). In the case of molecular oxygen, excited diphenylmethyl radical is quenched to form singlet oxygen ($k_q = 8.7 \times 10^9\ M^{-1}\ s^{-1}$) rather than reacting with oxygen to form a hydroperoxy radical.[2b,c,3] These reactivity properties apparently are characteristic of other excited arylmethyl radicals as well. For instance, excited 1-naphthylmethyl radical displays very similar rate constants for reactions with each of the quenching species listed above.[54]

Diphenylketyl (diphenylhydroxymethyl) and related ketyl radicals constitute a widely encountered subclass of substituted diphenylmethyl radicals. The parent diphenylketyl radical is typically formed in any of several photochemical reactions: (1) hydrogen abstraction by excited benzophenone,[55] (2) hydrogen abstraction from benzhydrol,[55] and (3) Norrish type I cleavage of α,α-diphenyl-α-hydroxyacetophenone.[9b] Diarylketyl radicals have excited-state lifetimes that are about 2 orders of magnitude shorter than their diarylmethyl counterparts, $Ph_2C^\bullet OH$, τ = 2–4 ns, $Ph_2C^\bullet H$, τ = 255–280 ns.[2b] In spite of this greatly attenuated lifetime, the excited-state behavior of diarylketyl radicals closely parallels that of excited diarylmethyl radicals in many

Scheme 18



Scheme 19



instances. They undergo electron-transfer reactions with onium salts, carbon tetrabromide, and methyl methacrylate at nearly diffusion-controlled rates (k_q = 10^8–10^{10} M^{-1} s^{-1}),[56] and hydrogen abstraction reactions are moderately fast (cyclohexane, $k_q = 4 \times 10^7$ M^{-1} s^{-1}, isopropyl alcohol, $k_q = 5 \times 10^8$ M^{-1} s^{-1}).[57]

However, the dominant mode of reaction of excited-state ketyl radicals does deviate from the reaction pathway observed for the excited diphenylmethyl radical. Thus, excited ketyl radicals undergo β-scission with loss of the hydroxyl hydrogen atom as shown in Scheme 19.[55] This process forms the ground-state ketone and a hydrogen atom which may then abstract another hydrogen atom from the solvent to form molecular hydrogen. The hydrogen gas formed in this fashion has been detected by Raman spectroscopy in reactions run in cyclohexane as the solvent. This type of hydrogen cleavage is characterized by a significant extension of the excited ketyl lifetime upon substitution of the hydroxyl hydrogen with deuterium ($[Ph_2C^{\bullet}OH)]^*$, τ = 3.9 ns, $[Ph_2C^{\bullet}OD]^*$, τ = 8.7 ns), as well as an associated pronounced isotope effect (k_H/k_D = 5.8 for hydrogen cleavage and k_H/k_D = 1.9 for the sum of other radiative and nonradiative processes).[55,58]

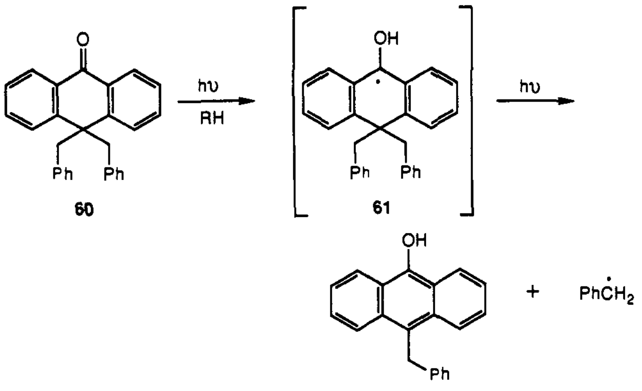
In contrast, when diphenylketyl radical is formed from benzophenone by hydrogen abstraction in polar solvents such as acetonitrile, its excitation leads to photoionization by electron ejection (Scheme 19).[59] In the absence of electron scavengers, the ejected electron is scavenged by benzophenone to form diphenylketyl radical anion which exhibits a broad absorption in the 710–720-nm region.

Contrary to expectations based on the relatively simple behavior of benzophenone, decafluorobenzophenone apparently undergoes rather complex photochemistry.[60] For instance, a 475-nm transient has been observed upon excitation of decafluorobenzophenone ketyl radical. It was suggested that this species might be a cyclized radical analogous to the dihydrofluorenyl radicals discussed above.[2b] However, in further studies of the photoreduction of decafluorobenzophenone, the same authors make no reference to this 475-nm species.[61] It may be of significance that the photoreduction of decafluorobenzophenone leads to the loss of a fluorine atom and formation of tetrafluorophenylpentafluorophenyl ketone.[52] While this particular example seems to be a single-photon process, it is to be expected that many halogenated aromatics will exhibit halogen cleavage, especially from higher excited states. Furthermore, since the aryl radicals associated with this halogen cleavage process are very difficult to detect spectroscopically, product studies will be essential in the analysis of the decafluorobenzophenone ketyl decay pathway, as well as those of other halogenated aromatics.

The photochemistry of the ketyl of anthrone is complicated by the presence of the anthranol tautomer.[62] This tautomerization can be eliminated by blocking the 10-position with substituents. Consequently, 10,10-dimethylanthrone affords a ketyl that displays fairly typical, uncomplicated photochemistry involving the cleavage of the O–H bond.[63] In contrast, 10,10-dibenzylanthrone (60 in Scheme 20) affords the ketyl 61 which upon excitation undergoes cleavage of a benzyl group as its primary mode of chemical reaction rather than the typical O–H bond cleavage.

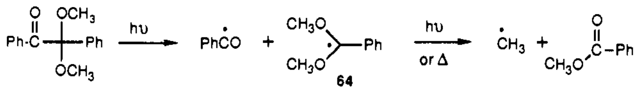
At this point, it is instructive to note the effect of light intensity upon the classical photoreduction of benzophenone even though, for the most part, this chemistry is intertransient in origin. Under the traditionally applied low-intensity conditions, the photoreduction of benzophenone in the presence of hydrogen donors such as alcohols leads almost exclusively to benzopinacol and other mixed pinacols (Scheme 21). For years, it has been known that this reaction is

Scheme 20



adversely affected by the formation of light-absorbing transients (LAT's).[64] These LAT's are highly unstable, especially to oxygen which rapidly destroys them during attempts at their isolation. It has been speculated that the LAT's arise from the coupling of radicals with the diphenylketyl radical at one of its aromatic ring positions. This type of coupling should afford unstable enols related to **62** in Scheme 21. This hypothesis is supported by the isolation of substituted benzophenones related to **63** from high-intensity reactions.[7c,9b] In addition, a reduction of benzopinacol yield and a very significant increase in benzhydrol yield are observed under these high-intensity conditions.[9b] This is consistent with the mechanism outlined in Scheme 21. On the basis of these observations, Adam and Schulte Oestrich have suggested that diphenylketyl radical and its excited state may exhibit different modes of coupling.[9b] They postulate that the ground-state ketyl radical may undergo highly regioselective coupling at the central carbon atom to form the usual pinacol products, and that the excited ketyl radical might display a greater tendency to undergo coupling at a ring position to form LAT's such as **62** and subsequently **63**. It should be noted, however, that in order for excited diphenylketyl radical to couple with $CH_3C^{\bullet}HOH$ radical with any degree of efficiency, the $CH_3C^{\bullet}HOH$ radical concentration would have to be in excess of 10^{-2} M which seems rather high. Furthermore, in this polar alcoholic medium, the possibility exists that photoionization of the diphenylketyl radical may play a role in LAT formation (see Scheme 19 and associated discussion). Nevertheless, the question of the regiospecificity of the coupling of diphenylketyl radical and its excited state is extremely interesting, and certainly deserves further attention.

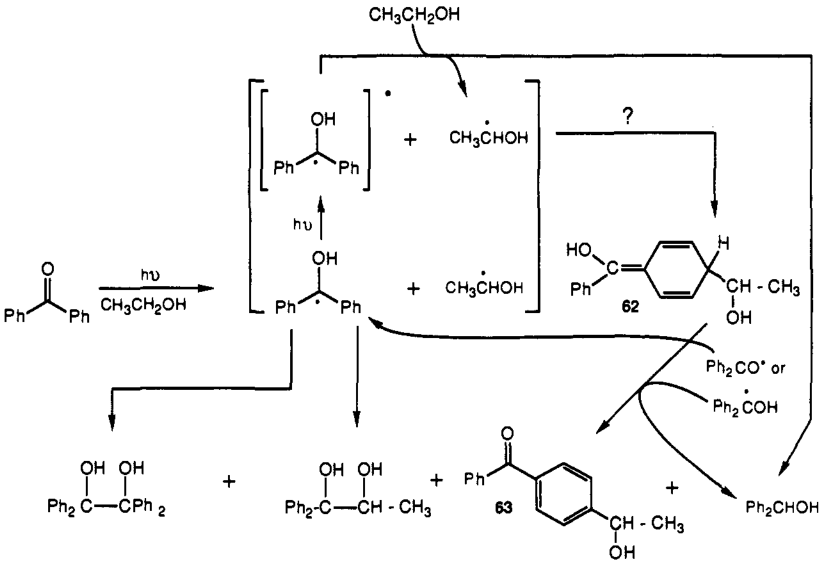
Scheme 22



Recently, it has been shown that the methyl ethers of ketyl radicals undergo photochemical cleavage analogous to the β-scission of the O–H hydrogen in diphenylketyl radical (Scheme 22).[65] In the case of dimethoxybenzyl radical (**64**), cleavage occurs both photochemically and thermally to form methyl radical which ultimately dimerizes to ethane. Most recently, it has been shown that the thermal cleavage of unsymmetrical α,α-dialkoxybenzyl radicals is governed by the stability of the resulting alkyl radical. Thus, the relative ease of alkyl group cleavage is $CH_3/CH_2CH_3/i\text{-}C_3H_7 = 1{:}6.5{:}78$. In contrast, the photochemical cleavage of these alkyl groups occurs with more or less equal efficiencies.[66] These observations are particularly significant, since the system shown in Scheme 22 and related molecules are widely used as initiators in photopolymerization reactions.

Also of note in the area of polymer chemistry is the recent development by Guillet of a high-intensity method for labeling polystyrene and poly(methyl methacrylate) with fluorescent groups.[67] This is accomplished by generating the excited states of either 1-naphthylmethyl or 9-anthrylmethyl radicals in the

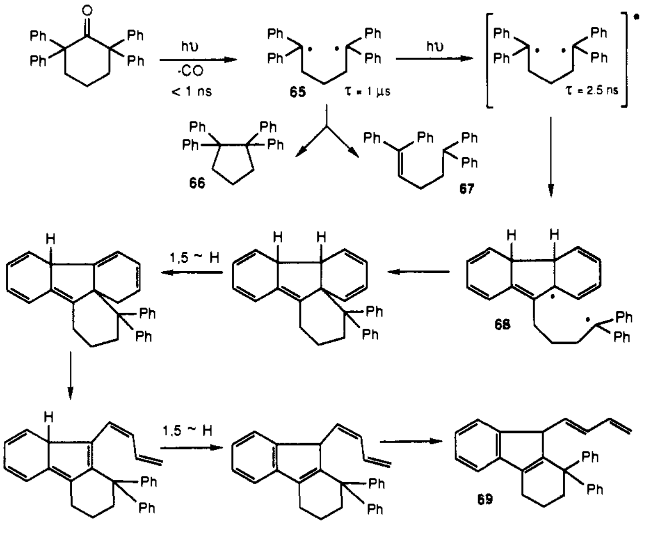
Scheme 21



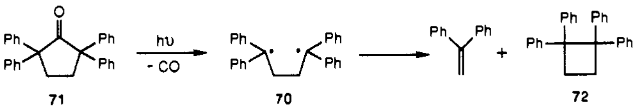
Low Intensity	47%	50%	1%	2%
High Intensity[a]	20%	46%	18%	16%

[a] Laser-Jet

Scheme 23



Scheme 24



presence of the polymer to be labeled. It is proposed that the excited states of these radicals abstract the more labile hydrogen atoms from the polymer backbone to form radicals which subsequently couple with the arylmethyl radicals.

B. Biradicals[68]

Diphenylmethyl radicals provide ideal light-absorbing terminal groups for the preparation of photochemically reactive biradicals. Johnston and Scaiano[69] were the first to investigate this possibility when they prepared the biradical **65** in which the two diphenylmethyl radicals are separated by a tether of three methylene units (Scheme 23). This unusually long-lived biradical (τ = ca. 1 μs) slowly collapses to the hydrocarbons **66** and **67**. Most interestingly, upon excitation, **65** undergoes cyclization at one of its diphenylmethyl termini to form the dihydrofluorenyl radical **68** and, following a complex series of orbital symmetry allowed steps, ultimately comes to rest at **69**. It should be noted that the cyclization of excited **65** is significantly faster than is the comparable cyclization of the simple methyl-substituted diphenylmethyl radical.[45] This may be a consequence of the greater steric bulk of the tethering chain and its terminal diphenylmethyl radical unit.[46] In Scheme 23, the sequencing of the orbital symmetry allowed steps may be somewhat arbitrary. Nevertheless, these are included in the schemes of this review, since the involvement of orbital symmetry governed processes seems to be a common occurrence in the "fallout" reactions that follow the collapse high-energy excited states. It is to be hoped that the reaction patterns for these "fallout" sequences will be more obvious as data become available (vide infra). Finally, it is worth mentioning that **69** can be obtained in about 12% yield using the two-laser pulse technique while up to about 40% yield of **69** has been obtained using the CW argon ion laser–jet technique.[70]

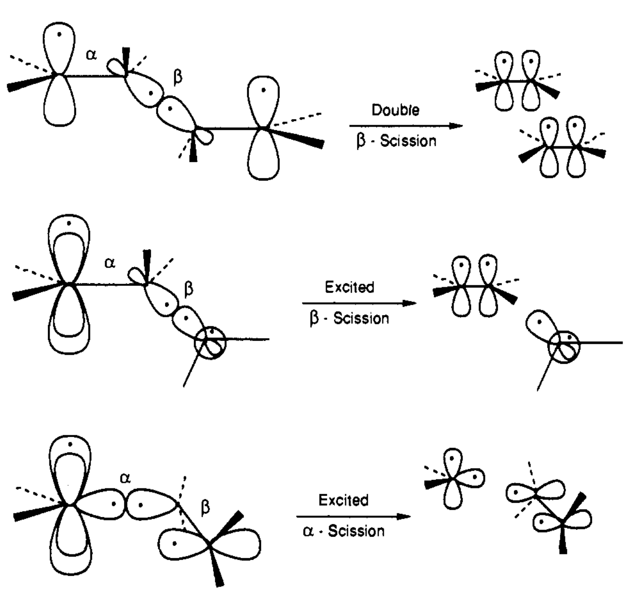
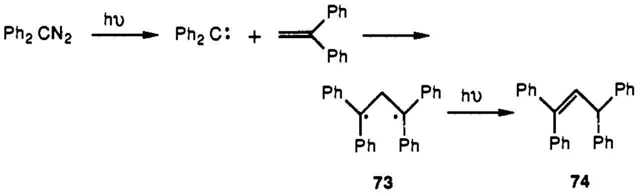


Figure 3. Scission modes of decay for biradicals: double β-scission for 1,4-biradicals; excited β-scission and excited α-scission for 1,3-biradicals.

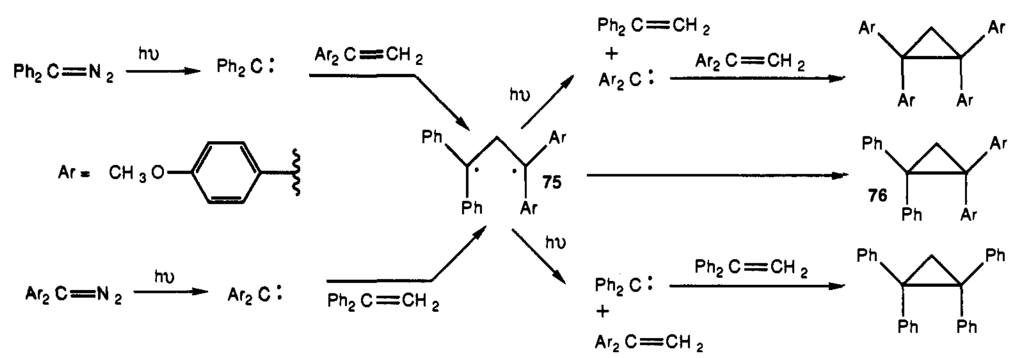
Scheme 25



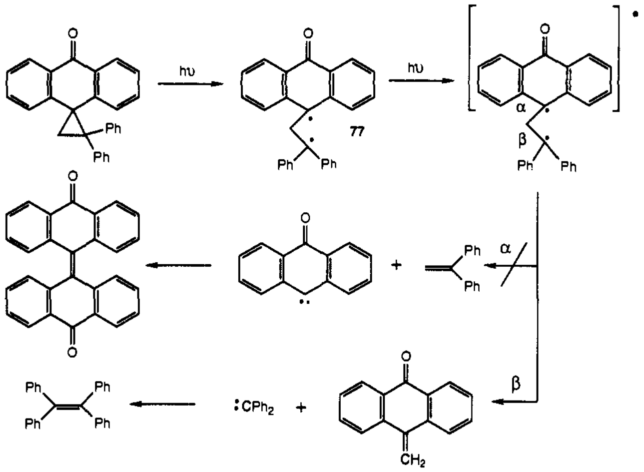
The related diphenylmethyl-terminated biradical tethered by only two methylene groups, **70**, can be formed via the analogous decarbonylation of the ketone **71** (Scheme 24). Thus, low-intensity irradiation of **71** has been observed to form 1,1-diphenylethylene and the cyclobutane **72**.[71] Unfortunately, biradical **70** is not formed efficiently. Under the same conditions that were so effective in generating **65**, the transient spectrum of **70** was found to be only ca. 3% as intense as that of **65**, even though, the quantum yield for the disappearance of the cyclopentanone **71** was ca. 50% that for the cyclohexanone analog. Apparently extremely rapid photochemical processes are inhibiting the formation of **70**. This failure to observe significant quantities of **70** cannot be due to its undergoing very rapid chemical reactions, since **70** has a lifetime about half as long as that of **65**. The somewhat accelerated decay of **70** can probably be attributed in part to the availability of the well-known double β-scission reaction shown in Figure 3. Thus, the inefficient access to **70** along with the expected enhanced dominance of an excited double β-scission from of the excited state of **70** may have, perhaps unduly, inhibited the further study of this interesting system.

The lowest member of the diphenylmethyl-terminated biradical series is **73** containing a tether of a single methylene unit (Scheme 25). This biradical can be accessed through the addition of diphenylcarbene to 1,1-diphenylethylene. Under laser–jet conditions, the only apparent, high-intensity photoproduct from this reaction was the olefin **74**.[72] The formation of **74** is readily rationalized via excitation of **73** followed by a 1,2-H shift of the type first reported by Michl[73] (Scheme

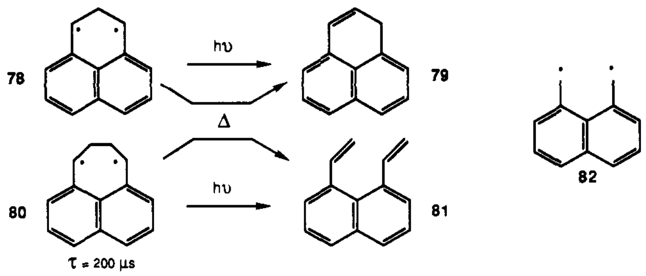
Scheme 26



Scheme 27



Scheme 28



28) and more recently by Adam as outlined in Scheme 13.[37]

The possibility that the photochemistry of biradical 73 was obscured by the coincidence of starting materials and products was confirmed in the high-intensity photochemistry of the unsymmetrical biradical 75 (Scheme 26).[72] This unsymmetrical species could be generated by either of the two possible routes shown in Scheme 26. Since 75 apparently has a lifetime in the range of 100 ns,[68,71,74] it is easily excited under laser–jet conditions before it collapses to its usual product, the unsymmetrical cyclopropane 76. Furthermore, since the excited state energies of either terminal diarylmethyl chromophore in 75 will be more or less equal, both termini should be excited to a similar extent. As a result, two modes of excited biradical decay might be expected, one from the excited $Ph_2C^{\bullet}$ terminus and the other from the excited $Ar_2C^{\bullet}$ terminus. This expectation was confirmed when it was observed that no matter which of the two photosynthetic routes is used to form 75, one of these two alternative modes of decay leads to regenerated starting materials and, thus, is "invisible". Consequently, the application of both photosynthetic routes to 75 was necessary in order to observe the two complementary modes of decay shown in Scheme 26.

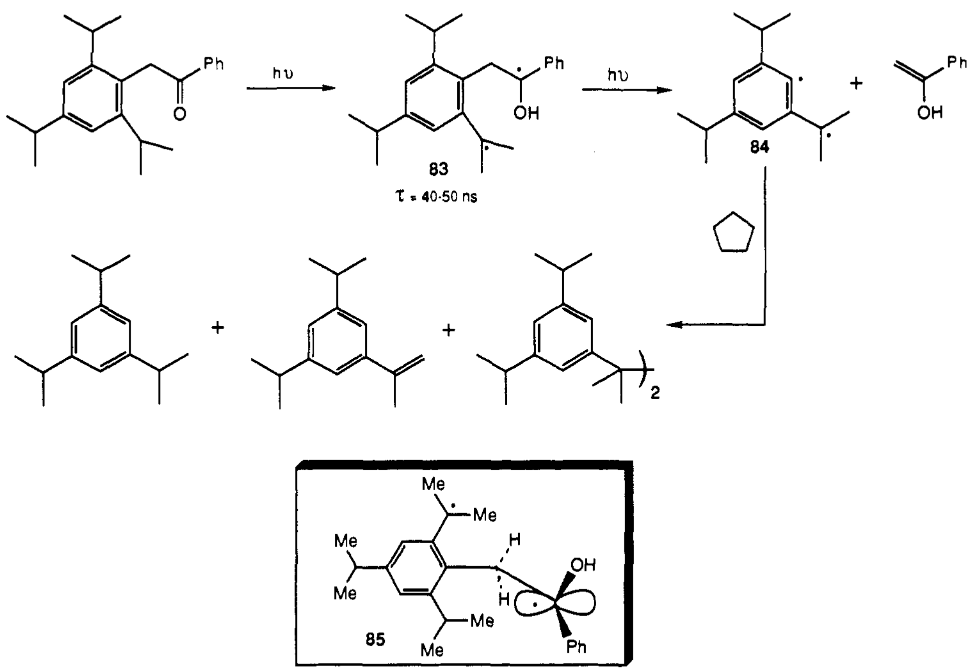
Carbene extrusion of the type shown in Scheme 26 might occur by either an excited α- or β-scission of a 1,3-biradical (Figure 3). In order to determine which of these alternative scissions was occurring, the highly unsymmetrical biradical 77 was generated as shown in Scheme 27. Since the anthronyl radical is known to absorb at about 500 nm[75] and the diphenylmethyl radical at about 330 nm,[45] there was little doubt that excitation would reside in the anthronyl terminus of 77. Consequently, the observation of only tetraphenylethylene and methyleneanthrone from the high-intensity photolysis of 77 confirmed the excited β-scission mode shown in Figure 3 as the principal contributor to the photochemistry of excited 1,3-biradicals.[4a,b]

Prior to the above work, Michl had studied the photochemistry of the triplet biradical 78 at 77 K (Scheme 28).[73] An excited β-scission in this symmetrical biradical system probably also would be "invisible" due to recyclization of the resulting carbene–olefin to 78. Thus, the major photochemical pathway in 78 is apparently 1,2-hydrogen migration to form the olefin 79. This same type of hydrogen shift also is found as an activated process in a thermal reaction that occurs at higher temperature. The authors expect that the relative ease of hydrogen migration in 1,3-biradicals is likely to be $S_1 > S_0 > T_1$. Consequently in this scenario, excitation of the triplet biradical 78 would have to provide access to singlet states above the activation barrier. For a somewhat different view of hydrogen migration processes in 1,3-biradicals, see Scheme 13.[37]

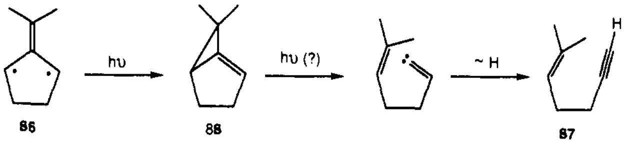
Wirz and Pagni have examined the related 1,4-biradical 80 which was generated photochemically from an azo precursor at 77 K (Scheme 28).[76] Excitation of 80 under these conditions affords an excited double β-scission to the diene 81. Here again, this reaction occurs both photochemically and thermally at higher temperatures. Thus, when viewed from the perspective of the azo precursor of 80, this reaction becomes monophotonic at room temperature. It is perhaps of interest that these authors comment on the photosensitivity of biradical 82 (Scheme 28), but do not elaborate on this observation.[76a] Also, it should be noted that biradicals related to 78 and 80 are probably involved in the multiple-photon chemistry of the parent hydrocarbons (see Scheme 51 and associated discussion).

A further example of an excited β-scission is that of the 1,5-biradical 83 reported by Scaiano and Wagner

Scheme 29



Scheme 30



(Scheme 29).[77] This ketyl radical **83** is generated photochemically via an intramolecular hydrogen abstraction. The ketyl radical terminus is then excited by a second photon which leads to cleavage of the rather strong carbon–carbon bond to the phenyl ring forming the triisopropylphenyl biradical **84**. An interesting aspect of this reaction is that, if the isopropyl groups are replaced by methyl groups, the β-scission seems to occur with greatly reduced efficiency. Perhaps, this is a consequence of the very bulky isopropyl groups forcing the ketyl radical out of the plane of the phenyl ring and into a conformation that favors β-scission such as **85** in Scheme 29.

Finally, a classic reaction that is not easily compartmentalized has been reported by Berson.[78] The irradiation of the trimethylenemethane biradical **86** at 77 K affords the alkyne **87** in high yield (Scheme 30). This reaction is thought to proceed through the highly strained olefin **88** followed by carbene extrusion and a 1,2-hydrogen shift. Since carbene extrusions of the type shown here are almost always photochemically initiated,[79] the carbene extrusion from **88** may be photochemical as well. Alternatively, these reactions may all be taking place on an excited-state hypersurface without returning to the ground state (see the discussion of tandem excited state reactions below).

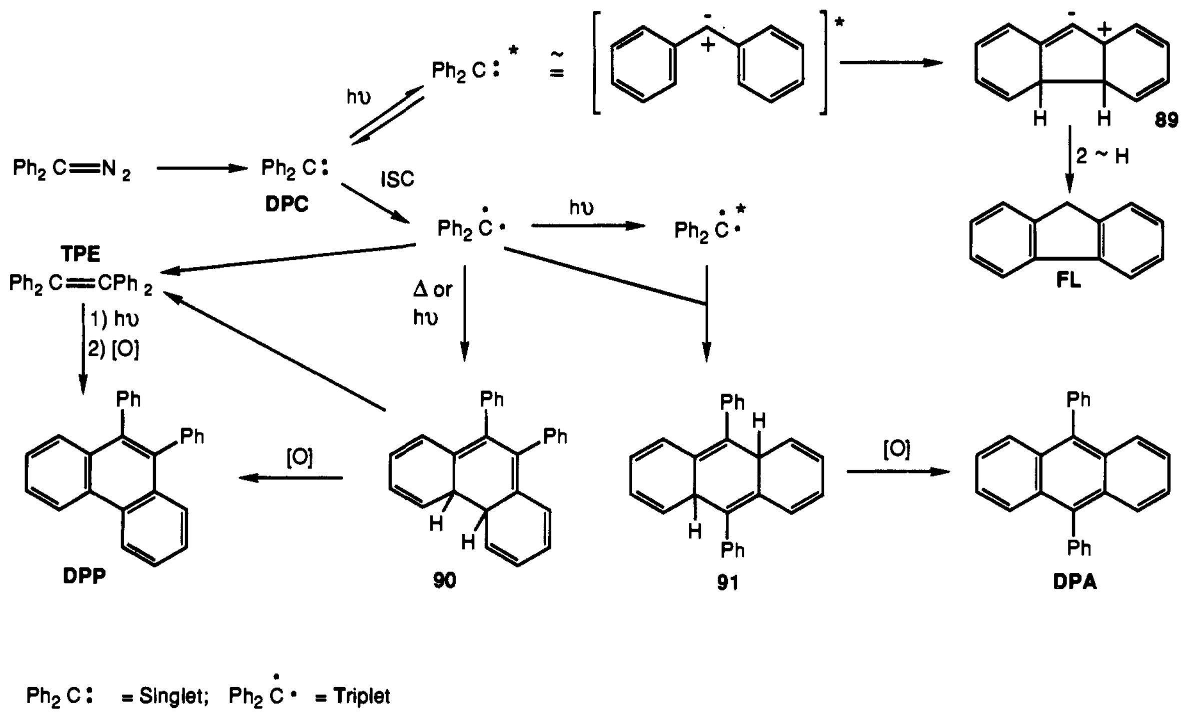
In summary, while examples of biradical photochemistry are still rather uncommon, reactivity trends are beginning to become more obvious. At this point, it is probably safe to say that 1,2-hydrogen shifts and β-scissions are among the most frequently encountered processes in this area.

C. Carbenes

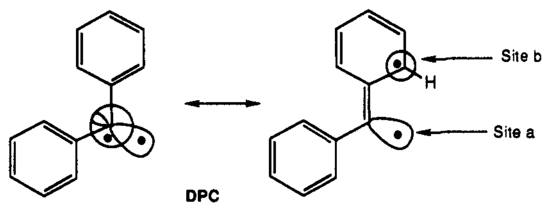
The photochemistry of carbenes has focused on the study of diarylcarbenes, since these are conveniently excited with the available laser light sources. For instance, diphenylcarbene (DPC) displays an intense absorption band at 314 nm with a much weaker band system in the visible region around 465 nm.[80]

Turro and co-workers provided one of the first structurally explicit examples of high-intensity solution photochemistry of DPC (Scheme 31).[21c] Irradiation of diphenyldiazomethane with an excimer laser at 249 nm produces DPC in high concentrations. Under these conditions, tetraphenylethylene (TPE) (see Scheme 6), 9,10-diphenylphenanthrene (DPP), 9,10-diphenylanthracene (DPA), and fluorene (FL) are formed. We have examined the same reaction under argon laser–jet conditions and found all of the above products except FL.[72] Under laser–jet conditions, the yields of these products decrease in the order that they are listed above. On the basis of these studies, it seems likely that the intensity-dependent formation of FL occurs via excited singlet DPC (^{1}DPC*). Since ^{1}DPC might be expected to have the π-system of a diphenylmethyl cation, it should undergo photochemical cyclization to **89**[81] followed by hydrogen migration to form FL. The TPE and DPP probably arise through the coupling of ^{3}DPC and ^{3}DPC*. Since this coupling constitutes a triplet–triplet reaction, spin statistics would indicate that only about 25% of the productive ^{3}DPC collisions will result in the direct formation of singlet products, and the other 75% would pass through a triplet intermediate before arriving at a singlet ground state. Thus, it seems probable that the dihydrophenanthrene **90** might result from the coupling of two ^{3}DPC units in this latter stepwise fashion. The dihydrophenanthrene intermediate might, then, either undergo electrocyclic ring opening to TPE or be oxidized to DPP via DPC hydrogen abstraction. Apparently, the oxidative photocyclization of TPE to DPP is a minor process under these conditions. The simplest explanation for the

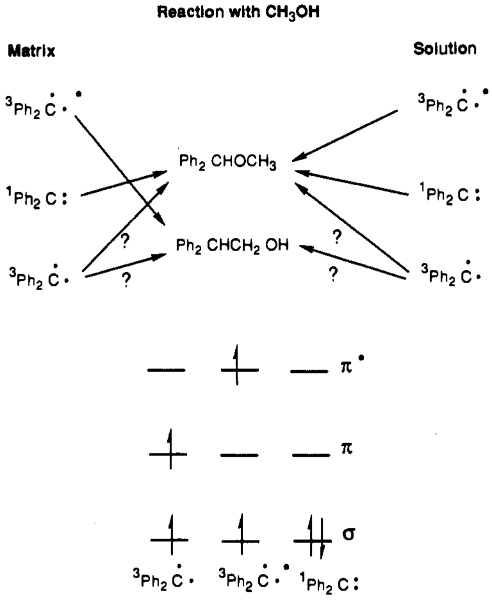
Scheme 31



Scheme 32



Scheme 33



intensity-dependent formation of DPA is that it occurs via a cross coupling of ^{3}DPC and ^{3}DPC*. As shown in Scheme 32, DPC has two sites, a and b, that are involved in these dimerizations. Thus, TPE would result from initial bond formation between two a sites, **90** from initial bond formation between either two a sites or two b sites, and **91** from initial bond formation between an a and a b site. This correlation would seem to imply that ^{3}DPC* has greater spin density in the rings than does ^{3}DPC. Finally, oxidation of **91** would afford DPA.

The intermolecular ground-state chemistry of carbenes in general and DPC in particular is extraordinarily complex. With only two carbene states of concern in ground-state chemistry, the lowest singlet and triplet states, a significant portion of the physical organic community can find few points of accord. Platz and Maloney have provided a very useful discussion of the divergent mechanistic viewpoints in this area.[82] Judging from the degree of controversy that has arisen over the relationship of just these two states and their chemistry, the elucidation of the chemistry of the large number of excited states that might potentially be encountered in carbene photochemistry should occupy mechanistic chemists for many years to come.

The photochemistry of DPC involves primarily its triplet excited state (^{3}DPC*) which has a sufficiently long lifetime (τ = 4–9 ns) to react with external reagents.[83] Attention has been focused on the relative reactivities of ^{3}DPC and ^{3}DPC* with alcohols in general and methanol in particular (Scheme 33). Apparently, DPC undergoes two very different types of reactions with alcohols. The first of these is a formal insertion into the O–H bond to form benzhydryl ethers, and the second is an abstraction of a hydrogen atom on carbon followed by radical coupling to form a new alcohol. The extremely short-lived ^{1}DPC (τ = 310 ps)[84] is assumed to react via the O–H insertion route. While the much longer-lived ^{3}DPC (τ = 1.5–7.8 μs)[80b] might react by either pathway. In contrast, its excited state, ^{3}DPC*, behaves more like ^{1}DPC displaying a reactivity pattern and isotope effect in its reaction with methanol-d_1 that are consistent with reaction at the O–H bond.[85] For example, the rate for methanol quenching of ^{3}DPC* (k = 3.1×10^6 M^{-1} s^{-1})[85b] is intermediate between that for quenching of ^{3}DPC (k = $(1.2–2.0) \times 10^7$ M^{-1} s^{-1})[80b,86] and ^{1}DPC (k = 2.1×10^{10} M^{-1} s^{-1}).[85b]

On the basis of these observations, a model for the reactivity patterns of the various DPC states has been proposed (Scheme 33).[87] Thus, the empty π-orbitals of ^{1}DPC and ^{3}DPC* are thought to make these species better Lewis acids, and hence, more reactive toward the alcohol O–H. In contrast the half-filled π-orbital of ^{3}DPC might inhibit reaction at the alcohol O–H and should favor the hydrogen-abstraction pathway.

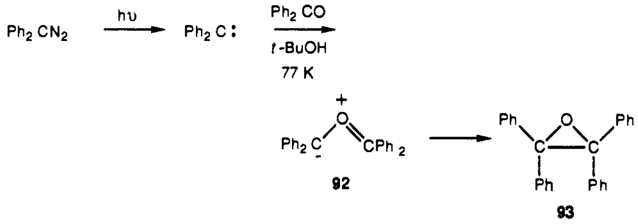
Unfortunately, product studies cause one to question this simple model. At least for DPC, hydrogen abstraction reactions do not seem to occur at all in solution. In various solvents, DPC reacts with methanol to form only the ether via formal insertion into the O–H bond in 90% yield or greater (96% mass balance). Even more puzzling are the observations of Platz and co-workers, who have noted that in matrices, hydrogen abstraction by DPC only becomes prominent upon extended irradiation or irradiation with high light intensities.[88] They attribute these effects to the excitation of ^{3}DPC, presumably to ^{3}DPC*, and subsequent hydrogen abstraction by this excited state species. Consequently, on the basis of these DPC product studies, it would appear that hydrogen abstraction, at least from methanol, only occurs in matrices, and then only upon excitation to ^{3}DPC* (Scheme 33).

Since ^{3}DPC*[89] and related excited carbenes[90] are known to have reasonable long lifetimes at 77 K (^{3}DPC*, τ = 123 ns), it would be of interest to examine spectroscopically the effect of methanol and other quenchers under low-temperature conditions. In this regard, Griller and co-workers have found that dimesitylcarbene is formed in a nonequilibrium conformation when generated from the diazo compound at 77 K.[91] Therefore, the possibility exists that the different modes of reactivity of excited diarylcarbenes in solution and matrices (Scheme 33) are associated with the formation of abnormal excited-state carbene geometries in low-temperature matrices. In the case of dimesitylcarbene, annealing the matrix to 188 K permits the carbene to assume its more linear equilibrium conformation.[91] Since excitation of this type of equilibrated carbene at 77 K would very likely generate an excited carbene in a nonequilibrated geometry, it would seem that quenching studies in the vicinity of the annealing temperature might be very useful in resolving some of these questions about the differences observed in carbene reactivity in solutions and low-temperature matrices.

The effect of quenching agents other than alcohols on ^{3}DPC* has also been investigated. Amines have been found to quench ^{3}DPC*. Since the quenching rates of these reactions correlate with the ionization potentials of the amines,[83,92] they apparently involve an electron-transfer or charge-transfer mechanism. In a similar fashion, ^{3}DPC* is found to be much more reactive toward carbon tetrachloride than is ^{3}DPC, $k = 1.1 \times 10^9$ M^{-1} s^{-1} and $k \sim 2 \times 10^6$ M^{-1} s^{-1}, respectively.[93] As in the case of the reaction of diarylmethyl radicals with carbon tetrachloride, an electron-transfer mechanism seems likely for these carbene processes as well.

Another reaction that might be influenced by the carbene electronic state is that outlined in Scheme 34. While ^{3}DPC does not react with carbonyl compounds,[94] it is possible that ^{3}DPC* would be significantly more reactive toward carbonyl groups due to its expected enhanced electrophilicity (Scheme 33).[87] The example shown in Scheme 34 was the only known case in which an oxirane is formed in a reaction of DPC with a carbonyl compound.[95] Apparently, DPC will react with benzophenone only in a polycrystalline *t*-BuOH matrix at 77 K where it forms the ylide **92** which subsequently collapses to the oxirane **93**. This oxirane formation might involve either the direct excitation of ^{3}DPC to ^{3}DPC* or the excitation of the benzophenone followed by benzophenone triplet sensitized generation of ^{3}DPC* (see Scheme 12 and associated discussion).[94]

Scheme 34



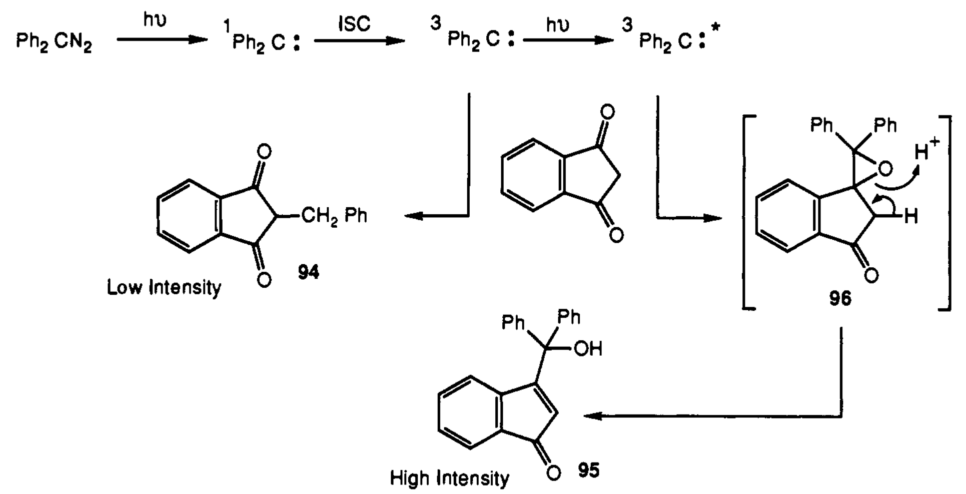
In support of this hypothesis, it has been observed that a variety of aromatic carbonyl compounds afford oxiranes derived from DPC under high-intensity argon laser–jet conditions.[32] A possible example of this type of behavior might be fluorenone which does not form the oxirane **32** under conventional low-intensity conditions but, in the laser–jet, forms **32** to an appreciable extent (Scheme 12).[32] Unfortunately, an alternative route to **32** exists in this system, and that route does not involve a direct attack of DPC on the carbonyl oxygen (see Scheme 48 and associated discussion). The reaction of 1,3-indandione with DPC is more straightforward and seems to provide strong support for the concept that ^{3}DPC functions primarily as a hydrogen-abstracting agent[96] while its excited state, ^{3}DPC*, is a much more effective Lewis acid (Scheme 35).[87] If this reaction is conducted under low-intensity conditions, the major product is the substituted indandione **94** which most probably arises via a hydrogen abstraction pathway. In contrast, under argon ion laser–jet conditions, the alcohol **95** is formed as the major product. The formation of **95** is most simply rationalized by the cleavage of the oxirane ring of **96** as outlined in Scheme 35. These reactions plus the fact that other aryl ketones including anthraquinone and benzil form oxiranes under high-intensity conditions[32] lend support to the hypothesis that excited triplet carbenes serve as better Lewis acids than their ground-state counterparts.

D. Ylides

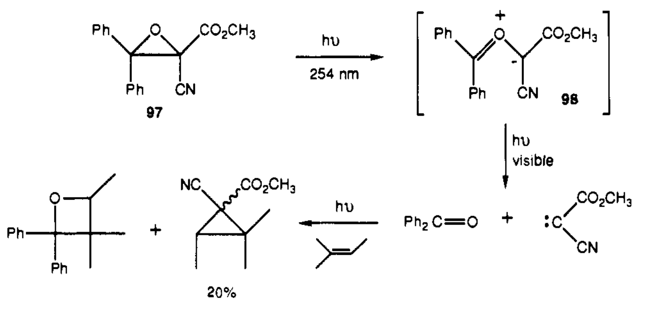
The photochemistry of oxiranes has been studied extensively, especially in low-temperature matrices. While these processes are frequently multiphotonic, they often are not high-intensity reactions, since the intermediate carbonyl ylides are sufficiently photolabile and long-lived to undergo secondary photochemistry under low-intensity conditions.[97] Nevertheless, it is important to record the reaction patterns of these ylide systems, since they are encountered with increasing frequency in high-intensity reactions.

Griffin and co-workers have emphasized the double-photon nature of the extrusion of carbenes from oxiranes by means of the double irradiation techniques shown in Scheme 36.[98] Using conventional light sources, these workers simultaneously irradiated oxirane **97** with both

Scheme 35



Scheme 36



254-nm and visible light and detected the carbene extrusion shown in Scheme 36. The 254-nm light serves to cleave the oxirane and form the highly colored carbonyl ylide **98**. The visible light is then absorbed by **98** and serves to complete the cleavage to benzophenone and the carbene which are both trapped by the added olefin. Apparently, it is important that the second photon be of low energy, since if **97** is irradiated with 254-nm light alone, barely detectable levels of these same trapping products are formed.

In other cases, carbene generation occurs equally well in thermal reactions of carbonyl ylides once the ylides have been formed photochemically.[97] In still other systems, excitation of the carbonyl ylides does not lead to carbene formation at all, but to accelerated closure of the ylides to the oxiranes.[99] An example of this type of behavior is shown in Scheme 37 where the carbonyl ylide **99** is formed through the reaction of fluorenylidene with acetone. In this work, both possible modes of photochemical carbene extrusion were excluded. The only effect of the irradiation of **99** with visible light is to hasten the closure of **99** to oxirane **100**, a reaction that also occurs via a slower thermal mechanism.

As indicated by these results, the photochemical opening of many oxiranes to carbonyl ylides is photoreversible.[100] This is especially true for bicyclic epoxides such as 1,5-diphenyl-6-oxabicyclo[3.1.0]hexane which upon irradiation with ultraviolet light opens to the corresponding cyclic carbonyl ylide (λ_{max} = 525 nm). Subsequent irradiation with visible light results in its quantitative reversion to the starting oxirane.

An interesting parallel with carbonyl ylide photochemistry is found in the photochemistry of carbonyl oxides such as **102** (Scheme 38).[101] These species are typically generated by the reaction of carbenes with oxygen and can be so photolabile that they undergo photochemistry even when irradiated with the visible light from an infrared glow bar. Thus, irradiation of **102** with visible light (>630 nm) results in two modes of decomposition.[102] The minor mode is usually extrusion of an oxygen atom which is analogous to carbene extrusion from carbonyl ylides, and the major mode is cyclization to a dioxirane such as **103** which would correspond to the photoreversion of carbonyl ylides to epoxides. Finally, irradiation of dioxiranes with shorter wavelength light leads to cleavage of the oxygen–oxygen bond in **103** and the formation of stable oxidation products.

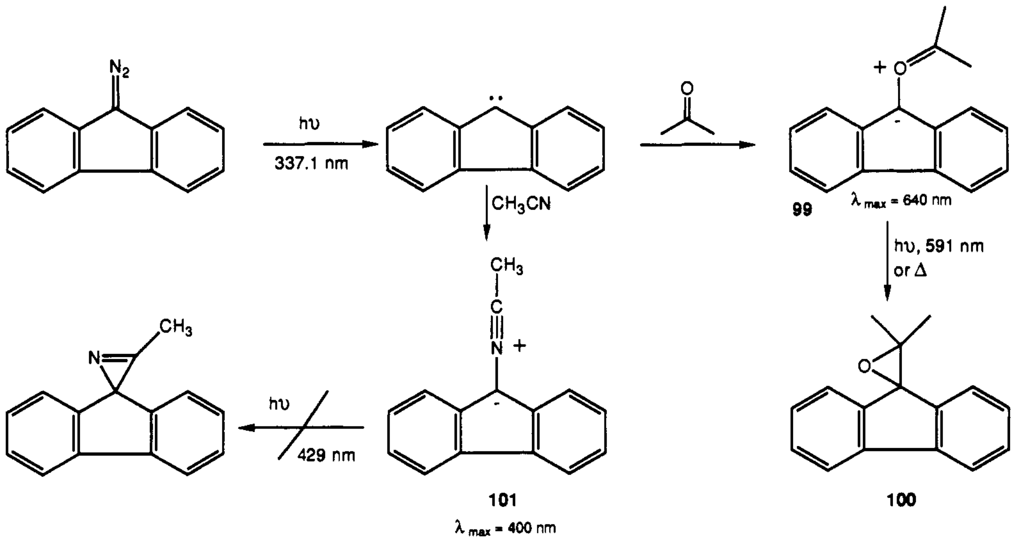
In comparison, nitrogen ylides are significantly more reluctant to undergo photocyclization. For instance, the nitrile ylide **101** (Scheme 37) did not undergo cyclization when it was irradiated in its visible absorption band.[99] The same reluctance to cyclize has been observed for the azimine **104** which Kaupp reports to be stable under a variety of low-intensity conditions.[103] However, upon excimer laser irradiation in a MTHF matrix at temperatures up to 85 K, **104** undergoes cyclization to the triaziridine **105** (Scheme 39). It was suggested that this cyclization proceeds from an upper excited state of **104** that is populated in a multiple-photon excitation.

E. *o*-Xylylenes and Related Species

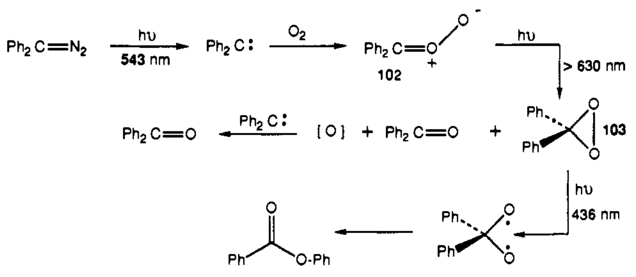
Intermediates in this group frequently are rather long-lived (1 s to 10 min), and thus, provide excellent substrates for the development of high-intensity reaction strategies that can be later applied to much shorter-lived intermediates (see Scheme 11). In general, *o*-xylylenes are formed photochemically, and many of them subsequently undergo photochemical reactions (Scheme 40).[104] The parent *o*-xylylene cyclizes photochemically to benzocyclobutene,[105] and tetramethyl-*o*-xylylene forms the stable isomer **106** via a [1,5] sigmatropic shift.[106] This sigmatropic shift occurs either thermally, $[1_s,5_s]$, or photochemically, $[1_s,5_a]$[107] with the photochemical reaction proceeding 10^{10} times faster than the thermal reaction.

The triphenyl analog **107** shown in Scheme 41 undergoes photochemical cyclization to the dihydroanthracene **108**.[108] Overall this is a double-photon process with the starting ketone absorbing in the ultraviolet

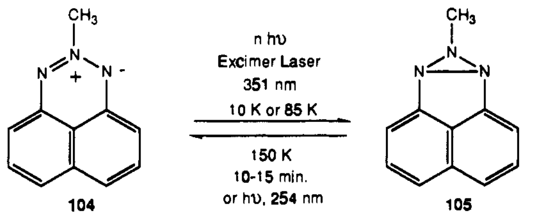
Scheme 37



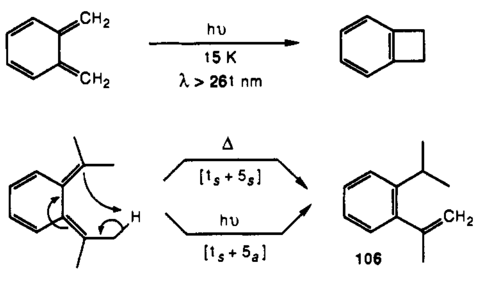
Scheme 38



Scheme 39

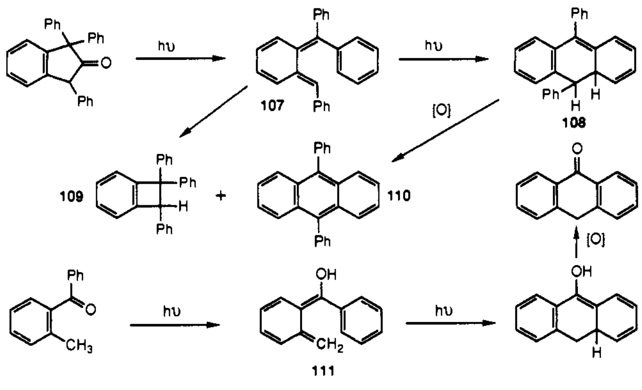


Scheme 40



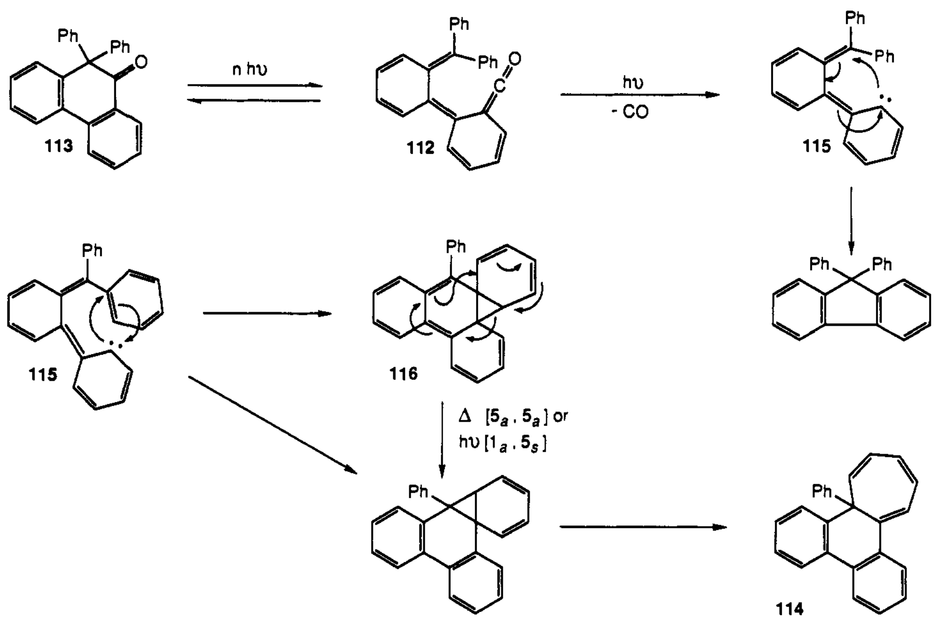
and 107 absorbing in the visible. The final products isolated from this reaction are the single-photon product 109 and 9,10-diphenylanthracene (110) formed from the dehydrogenation of 108. A very similar sequence of steps is involved in the conversion of 2-methylbenzophenone to anthrone via the photoenol 111 (Scheme 41). Both of these reactions have been found to proceed in significantly enhanced yields, if they are conducted with two intense light sources, an ultraviolet source to form the *o*-xylylene and a visible source to cause its cyclization. Thus, in the case of xylylene 107, a single low-intensity source (300–320 nm) affords a ratio of 110/109 = 0.94, while two pulsed high-intensity laser sources (308 nm, 2-μs delay, 480 nm) afford a ratio of 3.93.[108] The same effect is observed in the reaction of photoenol 111 which when conducted with a single low-intensity source (350 nm) affords anthrone in ~0.5% yield, while in a laser–jet apparatus with crossed laser beams (334–364 nm and 458–514 nm), anthrone is formed in 34% yield.[109]

Scheme 41



The rather exotic *o*-xylxylene 112 might conceivably be obtained through a photochemical ring opening of the ketone 113 (Scheme 42). However, this does not occur under low-intensity conditions where 113 is quite stable.[110] Transient spectroscopy indicates that the lowest excited state of 113 resembles a biphenyl triplet. Therefore, 113 does not exhibit typical n,π^*, Norrish type I carbonyl photochemistry which should afford 112. Furthermore, either the lowest π,π^* biphenyl triplet has insufficient energy for the formation of ketene 112, or perhaps less likely, 112 rapidly recyclizes to 113 before it can undergo further photochemistry. In contrast, high-intensity, argon laser–jet irradiation produces, two new decarbonylation products. Both of these products, 9,9-diphenylfluorene and triene 114, seem to have a common origin in the multiple-photon electrocyclic ring-opening of 113 to form ketene 112 followed by a photochemical decarbonylation to afford the pivotal carbene 115. Simple cyclization of 115 will result in 9,9-diphenylfluorene. Several possible mechanisms might account for the conversion of carbene 115 to the triene 114. The most interesting of these involves the carbene insertion into the overlapping

Scheme 42



phenyl ring which would initially lead to the novel spiro bis norcaradiene **116**. This spiro adduct could then collapse to **114** via either a thermally allowed $[5_a,5_a]$ or photochemically allowed $[1_a,5_s]$ sigmatropic shift as shown in Scheme 42. This is another case where orbital symmetry seems to play an important roll in the "fallout" reactions.

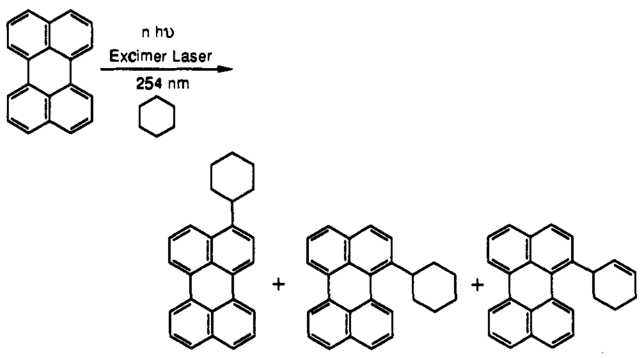
V. Higher Excited States

A. Triplet States

The generation of higher excited states is a common occurrence with high-intensity light. Of course, higher excited triplet states are much more easily formed than are the corresponding upper singlet states, since the parent, absorbing triplet state generally will be much longer-lived than its singlet counterpart. Furthermore, these upper excited states can have lifetimes as long as several hundred picoseconds[111] and, thus, can be easily quenched by solvents such as benzene and concentrated solutes that do not affect the lowest excited states.[111,112] For example, excitation of the lowest triplet state of benzophenone with 525-nm light in benzene solution leads to strong bleaching of this triplet without any significant accumulation of the excited triplet state. Instead, it appears the benzophenone ground state is repopulated via quenching of the higher excited state by benzene.[113]

In fact, many solvents including hydrocarbons such as cyclohexane will quench high-energy upper excited states.[114] While it is generally agreed that this solvent quenching can lead to free radical production, very little structurally explicit work has been devoted to determining the products of these reactions. The sole exception seems to be the work of Lamotte, Joussot-Dubien, and co-workers.[115] They have investigated the products from the high-intensity irradiation of perylene and pyrene in cyclohexane and found solvent radical addition products of the type shown in Scheme 43.

Scheme 43



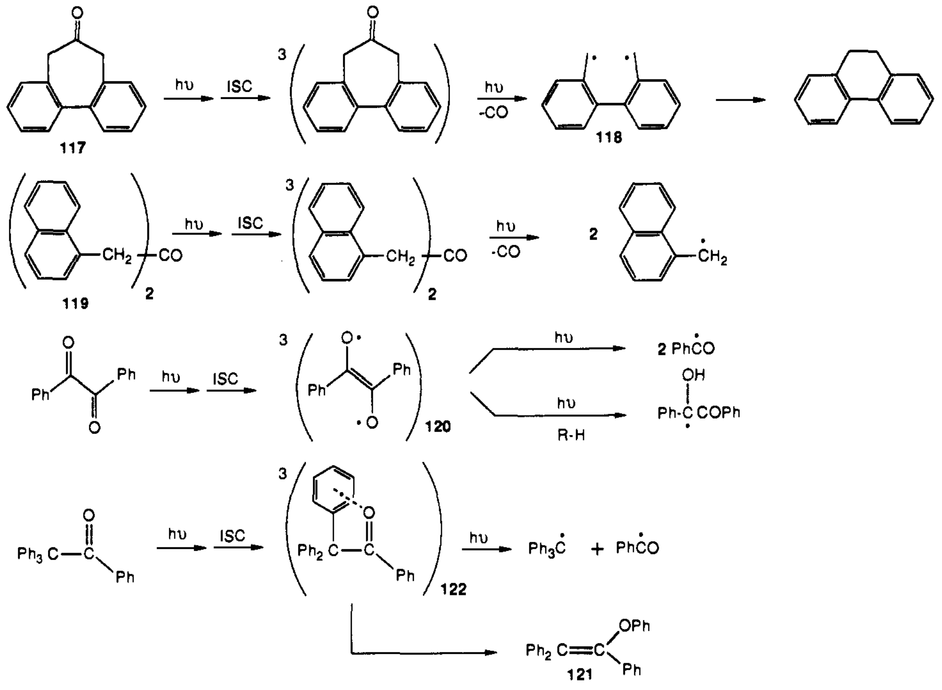
Another, less frequently encountered photophysical process of the lowest excited triplet state is reverse intersystem crossing, or return of triplets to the singlet manifold. This process is much more favorable from an upper triplet state than from the ground triplet state. Thus, excitation of the ground triplet state of 9,10-dibromoanthracene to a higher triplet level results in fluorescence from the lowest singlet excited state which is populated via reverse intersystem crossing.[116] This molecule also exhibits an inefficient loss of bromine from an upper triplet level.

B. Reluctant Norrish Type I Reactions

A number of molecules such as **113** in Scheme 42 afford photochemically unreactive lowest excited states, and yet upon excitation to a higher excited state become quite reactive. Frequently, the type of chemistry produced by these upper excited states is very similar to the much better known chemistry observed from the lowest excited state. When this occurs the unreactive system is said to be "reluctant". There are a variety of possible reasons for this reluctance. In the case of ketone **113**, the lowest excited state is not an aryl ketone n,π^* triplet which might be expected to undergo a Norrish type I cleavage to form **112**. Instead, the lowest energy state is an unreactive π,π^* biphenyl triplet which has insufficient energy to undergo a ring opening with loss of aromaticity in two benzene rings.

Several reluctant Norrish type I reactions are shown in Scheme 44. In the first case, the lowest triplet state of ketone **117** again is an unreactive π,π^* biphenyl triplet, and thus, **117** fails to lose carbon monoxide via

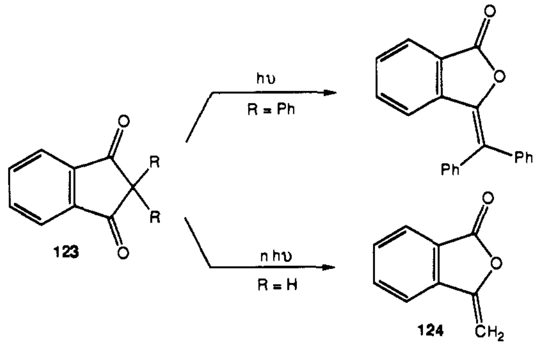
Scheme 44



a Norrish type I cleavage from its lowest excited state.[117] However, biradical **118** is formed upon further excitation to an upper excited state. In the case of the naphthyl ketone **119**, failure to exhibit a Norrish type I loss of carbon monoxide has been shown to be due the lowest excited state being an unreactive naphthalene π,π^* triplet rather than a reactive carbonyl n,π^* state.[118] The lowest n,π^* excited state of benzil is rather unreactive and does not cleave efficiently to benzoyl radicals.[119] This behavior can probably be attributed to a higher bond order between the carbonyl carbons in the n,π^* state as indicated in **120**. Both Norrish type I cleavage[9c,119] and ketyl radical formation[120] become much more efficient from the upper triplet excited states of benzil. Surprisingly, benzopinacolone, which might be considered to be an ideal candidate for Norrish type I cleavage, is quite unreactive in this regard at low light intensities. Instead, benzopinacolone displays an unusual phenyl migration to form the enol ether **121** as the major reaction product under conventional conditions.[121] This behavior has been attributed to charge-transfer complex formation between the excited carbonyl and one of the adjacent phenyl rings as indicated by **122** in Scheme 44.[122] This complexation would be expected to reduce the electrophilicity of the half-filled nonbonding orbital on the carbonyl oxygen which in turn should inhibit Norrish type I cleavage. Only upon high-intensity, laser–jet irradiation does the Norrish type I cleavage become the dominant mode of reaction for benzopinacolone.[4a,b]

Enol lactone formation from 1,3-indandiones occurs with a variety of substituents in the 2-position (Scheme 45).[123] However, the parent molecule **123**, R = H, is unreactive under low-intensity conditions. Apparently the lack of any stabilizing substituent on the α-carbon atom inhibits this rearrangement. This inhibition is readily overcome in higher excited states, since **124** is formed easily under argon laser–jet conditions.[124]

Scheme 45



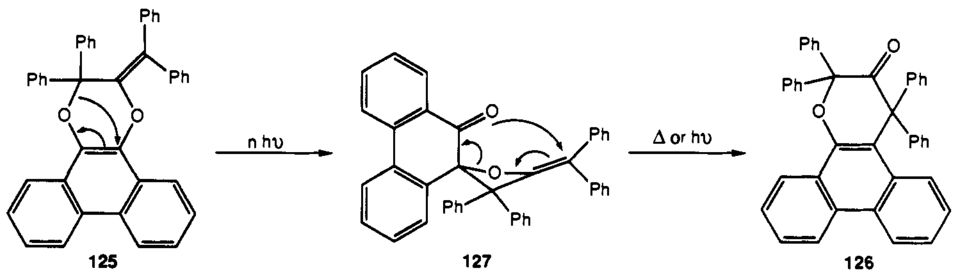
C. Reluctant [1,3] Sigmatropic Shifts

The 1:1 photoadduct of tetraphenylallene with phenanthraquinone (**125**) is transformed into the rearranged ketone **126** only upon argon ion laser–jet irradiation (Scheme 46).[4b,125] Transient spectroscopy indicates a lack of long-lived intermediates ($\tau > 20$ ns) in this reaction. Consequently, this unusual skeletal reorganization might be an example of a reluctant [1,3] sigmatropic shift to form the highly strained oxetane **127** followed by an oxo-Claisen rearrangement to **126**. The reluctance of this rearrangement at low intensities might be associated with the high strain energy of the oxetane ring in **127** which could make the oxetane inaccessible from the lowest excited state of **125**. It is interesting to note that the reverse of this dioxene–oxetane rearrangement has been observed in analogous systems,[126] but this appears to be the first example of the rearrangement proceeding in the endothermic direction. Finally, the last step of this process might occur either thermally or photochemically.[127]

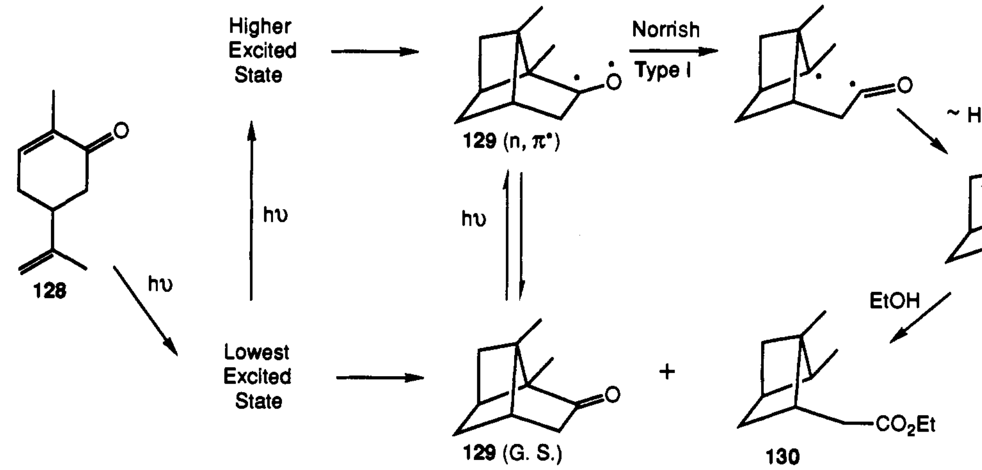
D. Tandem Excited-State Reactions

After many years of adjusting conditions, the yield of the intramolecular cycloaddition of carvone (**128**) to form carvone–camphor (**129**) has been raised from just 9% to 88% (Scheme 47).[128] This was achieved by using

Scheme 46



Scheme 47



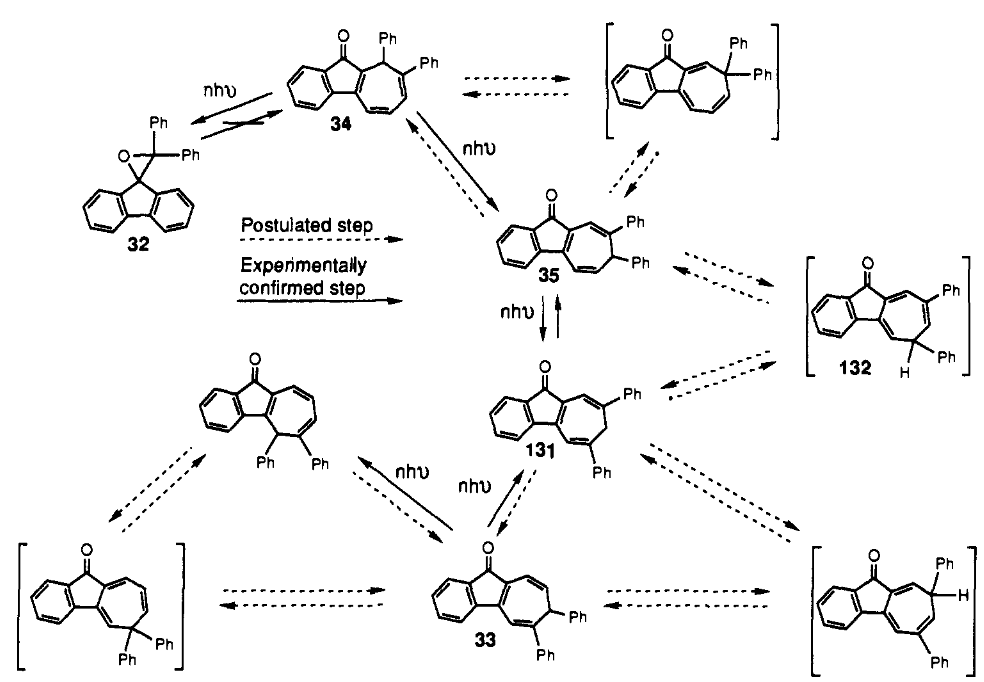
the 350.7- and 356.4-nm lines of a krypton ion laser which are absorbed by **128**, but not by **129**. Even with these highly optimized conditions, it has not been possible to completely eliminate formation of the ring-cleaved ester **130**. It has subsequently been found that a pulsed XeF excimer laser (350 nm) provides an even better yield of **129**, and that this cycloaddition is probably a two-photon process.[129] Most interestingly, this study also suggested that **130** is a primary photoproduct.

Consequently, the conversion shown in Scheme 47 may be an example of tandem excited-state processes. When dealing with higher excited states, the possibility exists that sufficient energy is available for several photochemical transformations to occur before the molecule returns to its ground state. In Scheme 47, the conventional pathway would be to go through the lowest excited state of **128** to **129**. Then **129** would require further excitation to its n,π^* state before it could undergo the Norrish type I cleavage leading to the final ester **130**. Alternatively, double-photon excitation of **128** would lead to an energy-rich, higher excited state which might cyclize to form the n,π^* excited state of **129** directly without passing through the ground state of **129**. If this occurs, then both **129** and **130** would be primary photoproducts. This point is stressed, since there seems to be several instances of this type of tandem photochemical reaction occuring under high-intensity conditions. To the best of our knowledge, the following example may be the most extreme case of this type of behavior.

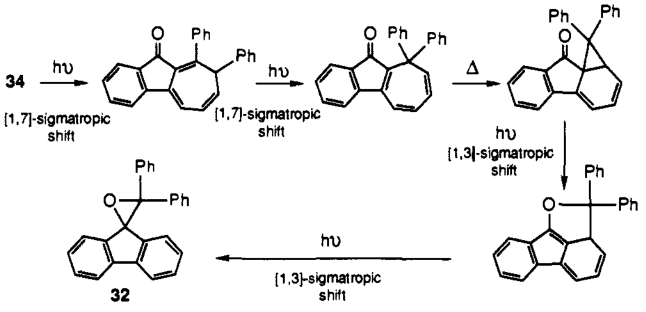
As described earlier in Scheme 12, the laser–jet addition of diphenylcarbene to fluorenone has been found to produce a variety of intensity-dependent adducts.[32] These adducts also display intensity-dependent photochemistry which may be due to the population of upper excited states. The apparent relationships between these products are outlined in Scheme 48. In order to test these correlations, **32**–**35** and **131** have been isolated and reexposed to the laser–jet conditions used in their formation. The solid arrows in Scheme 48 indicate transformations that have been confirmed experimentally in this way. All of the dihydrobenz[*a*]azulene isomers isolated from this system can be correlated, at least formally, by sequences of two tandem photochemical [1,7] sigmatropic shifts. For example, the most unusual dihydrobenz[*a*]azulene isomer **131** is photochemically equilibrated with isomer **35** only under high-intensity conditions. In this model, 1,7-phenyl migration would convert **35** to the quinodimethane isomer **132** and a second 1,7-hydrogen migration would transform **132** to **131**. The fact that none of the quinodimethane isomers, shown in brackets, have been isolated from these reactions may indicate that these isomers are either too unstable to be isolated or that each of these transformations proceeds through a set of two tandem excited-state reactions. In this latter case, the ground-state quinodimethanes would not be formed.

The most surprising transformation observed in these studies is the formation of the epoxide **32** from the dihydrobenz[*a*]azulene **34**. This as well as the other reactions shown in Scheme 48 do not seem to involve the extrusion and readdition of diphenylcarbene, since no tetraphenylethylene or other diphenylcarbene-derived products were detected in these reactions. A possible mechanism for the conversion of **34** to the epoxide **32** is outlined in Scheme 49, and again this overall transformation might involve tandem excited-state processes. Confirmation of these most interesting, but rather speculative mechanisms must await the development of methods for the synthesis of the

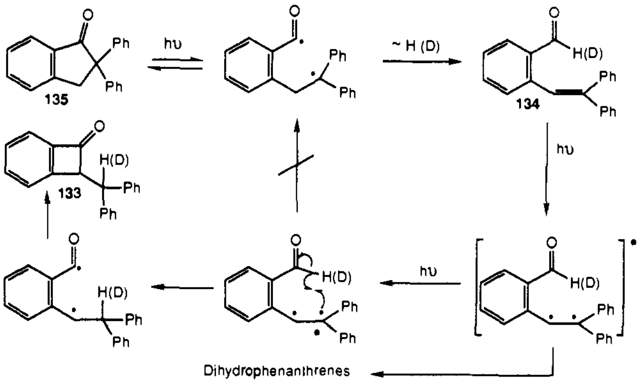
Scheme 48



Scheme 49



Scheme 50



dihydrobenz[*a*]azulene isomers, since they are presently only available in very small quantities from the high-intensity reactions shown in Schemes 12 and 48. Nevertheless, these and other examples (Scheme 30) seem to indicate that tandem excited-state reactions may be rather widespread in high-intensity photochemistry. Consequently, this is an important area in need of much more detailed theoretical and experimental study.

E. Hydrogen Abstraction by Olefins

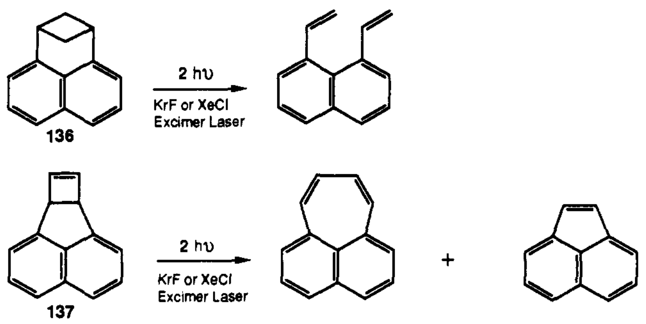
Another aspect of conventional photochemistry that has received very little attention is hydrogen abstraction by olefins. While reactions of this type do occur,[130] they are rarely observed, if the olefin is not conjugated to a heteroatom or incorporated into a small ring. Therefore, the formation of the cyclobutanone **133** from the olefin **134** or ketone **135** under argon ion laser–jet conditions is particularly interesting (Scheme 50).[131] Deuterium-labeling studies have clearly established the source of the diphenylmethyl hydrogen in **133** as shown in Scheme 50. The major products from the low-intensity irradiation of the olefin **134** are phenanthrenes arising from excitation of the triphenylethylene unit. Consequently, it is most likely that the formation of **133** originates from a higher excited state of this same unit. While the mechanistic aspects of this reaction are still unclear, it is interesting to observe that the hydrogen abstraction step is highly regiospecific occurring principally, if not exclusively, at the diphenylmethyl olefin terminus. If olefin hydrogen abstraction proves to be simply another "reluctant" photoreaction, then the high-intensity version of this type of reaction may be quite useful.

F. Miscellaneous Aromatic Systems

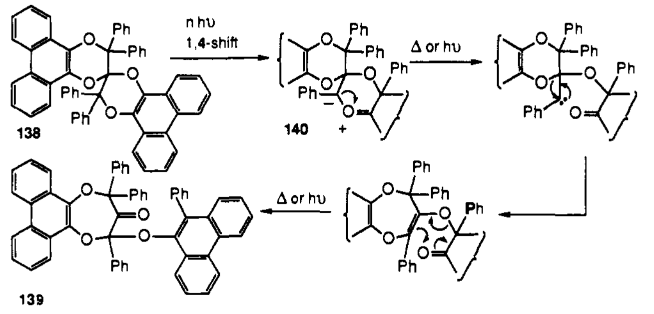
The naphthylcyclobutane **136**, cyclobutene **137**, and related systems are unreactive when irradiated with low-intensity light.[132] However, they do display photochemistry when irradiated at 77 K or with excimer laser pulses (Scheme 51). This photochemistry seems to require excitation to a higher triplet level as the reaction from the ground triplet state is forbidden by symmetry.[133] In this same area of aryl olefin chemistry, it has been noted that stilbene undergoes much more rapid cis–trans isomerization when excited to an upper singlet state.[134]

Finally the 2:1 phenanthraquinone–tetraphenylallene adduct **138** undergoes an extensive rearrangement to **139** when irradiated in an argon ion laser–jet (Scheme 52).[125] This reaction seems to arise from excitation to a higher excited state of a phenanthrene unit. Apparently this initiates an unprecedented 1,4-phenyl migration which generates a carbonyl ylide species **140**.

Scheme 51



Scheme 52



The presence of 140 early in the reaction sequence is indicated by transient spectroscopy which displays a broad absorption band at 466 nm that is quenchable with fumaronitrile. The subsequent "fallout" steps in this extensive rearrangement are, of course, speculative, but they do provide an economical route to the product using one massive injection of energy followed by a cascade of more or less conventional chemistry.

These latter examples provide some idea of the degree of complexity encountered in this area of chemistry even in what would appear to be relatively simple systems (Schemes 12, 48, and 49 for example). Furthermore, they convincingly demonstrate the need for thorough product characterization which is often difficult due to the small amounts of material obtained, and since the most effective multiple-photon substrates tend to be highly aromatic molecules the products of which afford rather uninformative spectroscopic data. Therefore, in most of our work cited here, the high-intensity products have been characterized by X-ray crystallography.

VI. Summary and Conclusions

From the account provided above one can see that high-intensity photochemistry provides access to a domain of chemistry not previously available for study. Since this area has just begun to be explored, relatively few examples of high-intensity photochemistry have been described and these are usually in need of much more thorough mechanistic study. In fact, so little is known about the characteristic chemistry of this domain that no serious theoretical studies of the behavior of higher excited states have been reported to date. Thus, virtually every aspect of high-intensity photochemistry provides fertile ground for further study. An effort has been made in this review to emphasize particularly intriguing areas such as intertransient reactions or transient targeting. In this area, potential reactions between any of the classical or nonclassical transient species offer an enormous variety of fascinating possibilities for exotic chemistry. The availability of very high steady-state concentrations of some of these transient species should offer the possibility for their characterization by conventional, nontransient spectroscopic methods. Access to higher excited states in significant concentrations and under controlled conditions makes their study much more practical. In the past, access to these high-energy states was only available by means of vacuum ultraviolet irradiation. Since absorption by solvent in this spectroscopic region usually interferes with absorption by the substrate molecules, the study of these states has had to be conducted in the vapor phase. Now that these high-energy intermediates are accessible with relatively low-energy photons and can be generated in appreciable quantities in conventional solvent environments, their study becomes much more attractive. This accessibility only serves to emphasize our lack of knowledge of these high-energy species. How might one best view their geometries, charge distributions, spin densities, and associated reactivity patterns? Theoretical models for the correlation of high-energy states would be of great value in developing an understanding of the "fallout" and tandem excited-state processes that follow the multiple-photon absorption events.

At its present state of development, high-intensity photochemistry provides one the most fertile areas for observing truly novel chemical reactions. In our experience, more than half of the classical photochemical reactions that have been reexamined under laser–jet conditions afford new products, many of which have yet to be characterized. Clearly this area is in a *re*search phase of development. Practical applications of the reactions and processes characteristic of this high-intensity domain may be relatively distant. Nevertheless, future chemical applications of lasers will certainly depend upon developments in this area.

Finally, in its upper regions the multiple-photon domain merges with the plasma domain and it should be mentioned in this review that this plasma domain can be readily accessed using the argon ion laser–jet technique.[135] If the nozzle of the laser–jet apparatus shown in Figure 2 is very *briefly* exposed to the focal region of the laser beam, a plasma is ignited. This plasma can be maintained indefinitely upon moving the focal region away from the nozzle. Preliminary studies have shown that, if this type of plasma is generated in a benzene–argon atmosphere, polycyclic aromatic hydrocarbons are generated in substantial quantities. These hydrocarbons include anthracene, phenanthrene, pyrene, and a series of other C_nH_{10} hydrocarbons. It is most interesting, that a very similar series of polycyclic aromatic hydrocarbons has recently been produced by the discharge of a carbon arc into a hydrogen-donating atmosphere (propylene).[136] While no fullerenes have yet been detected from these laser plasma experiments, these experiments seem to be one of the first examples of the generation of a sustainable plasma with a CW laser. Thus, the laser–jet technique for accessing the multiple-photon domain can be easily extended into the plasma domain.

In summary, the tools for investigating high-intensity processes are now in place. Sophisticated spectroscopic techniques when coupled with the ability to obtain and characterize small amounts of high-intensity photoproducts provide a much greater degree of understanding of multiple-photon chemistry than does either of these techniques alone. During the past 10 years, the majority of the work in this field has been directed toward the development of a basic understanding of the fundamental species involved in high-intensity reactions. More recently, it has become possible to extend these techniques to much more complex molecules. Since reactions in this area can span the full range of available states, they are likely to be rather complex, but the probability of encountering truly unique chemistry in this area is very high, and we suspect will remain so for many years to come.

VII. Acknowledgments

We thank Professors W. Adam, M. S. Platz, D. C. Neckers, and Dr. A. Ouchi for helpful discussions and for providing unpublished material to us. Furthermore, we are most grateful to the National Science Foundation for providing the financial support over many years that has made our contribution to laser chemistry possible.

VIII. References

(1) Peticolas, W. L. In *Annual Reviews of Physical Chemistry*; Eyring, H., Christensen, C. J., Johnston, H. J., Eds.; Annual Reviews: Palo Alto, CA, 1967; Vol. 18, p 233. Levine, I. N. *Molecular Spectroscopy*; Wiley-Interscience: New York, 1975; p 133.
(2) (a) Kleinermanns, K.; Wolfrum, J. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 38. (b) Scaiano, J. C.; Johnston, L. J. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1989; Vol. 10, p 309. (c) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* 1988, *21*, 22. (d) Scaiano, J. C. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990; p 353.
(3) This method was first described by Scaiano et al.: Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* 1985, *107*, 4396. It was elaborated in further detail in refs 2b and c.
(4) (a) Wilson, R. M.; Hannemann, K.; Schnapp, K. A.; Memarian, H. R.; Azadnia, A. *SPSE Proc., Summer Symp. Photochem. Imaging* 1988, 167. (b) Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figley, T. M. *Spectrochim. Acta* 1990, *46A*, 551. (c) Wilson, R. M.; Adam, W.; Schulte Oestrich, R. *The Spectrum* 1991, *4*, Fall Issue, 8.
(5) (a) Ashkin, A.; Dziedzic, J. M. *Phys. Rev. Lett.* 1977, *38*, 1351. (b) Ashkin, A.; Dziedzic, J. M. *Appl. Opt.* 1981, *20*, 1803. (c) Owen, J. F.; Chang, R. K.; Barber, P. W. *Opt. Lett.* 1981, *6*, 540. (d) Tzeng, H.-M.; Wall, K. F.; Long, M. B.; Chang, R. K. *Opt. Lett.* 1984, *9*, 499. (e) Qian, S.-X.; Snow, J. B.; Tzeng, H.-M.; Chang, R. K. *Science* 1986, *231*, 486.
(6) (a) Platz, M. S. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990; p 143. (b) Platz, M. S.; Leyva, E.; Haider, K. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 11, p 367. (c) Sheridan, R. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 8, p 159.
(7) (a) Schuster, D. I.; Barile, G. C.; Liu, K.-C. *J. Am. Chem. Soc.* 1975, *97*, 4441. (b) Rubin, M. B.; Inbar, S. *J. Am. Chem. Soc.* 1978, *100*, 2266. (c) Rubin, M. B. *Tetrahedron Lett.* 1982, *23*, 4615.
(8) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4. Griller, D.; Ingold, K. U. *Acc. Chem. Res.* 1980, *13*, 317.
(9) (a) Adam, W.; Schulte Oestrich, R. *J. Am. Chem. Soc.* 1992, *114*, 6031. (b) Adam, W.; Schulte Oestrich, R. *Chem. Ber.*, in press. (c) Adam, W.; Schulte Oestrich, R. *J. Am. Chem. Soc.*, in press.
(10) Kaupp, G.; Sauerland, O. *J. Photochem. Photobiol. A: Chem.* 1991, *56*, 375.
(11) Hoyle, C. E. *Proc. SPIE-Int. Soc. Opt. Eng.* 1990, *1213*, 168.
(12) Kaupp, G.; Sauerland, O.; Marquardt, T.; Plagmann, M. *J. Photochem. Photobiol. A: Chem.* 1991, *56*, 381.
(13) Hoyle, C. E.; Trapp, M. A. *ACS Symp. Ser., Radiat. Curing Polym. Mater.* 1990, *417*, 429. Hoyle, C. E.; Chang, C. H.; Trapp, M. A. *Macromolecules* 1989, *22*, 3607. Hoyle, C. E.; Trapp, M. A.; Chang, C. H. *J. Polym. Sci., Part A: Polym. Chem.* 1989, *27*, 1609. Hoyle, C. E.; Trapp, M. A.; Chang, C. H.; Latham, D. D.; McLaughlin, K. W. *Macromolecules* 1989, *22*, 35.
(14) Hoyle, C. E.; Trapp, M. A.; Chang, C. H.; Latham, D. D.; McLaughlin, K. W. *Macromolecules* 1989, *22*, 3866.
(15) (a) Ouchi, A.; Yabe, A. *Tetrahedron Lett.* 1990, *31*, 1727. (b) Ouchi, A.; Yabe, A. *Tetrahedron Lett.* 1992, *33*, 5359. (c) Ouchi, A.; Adam, W. Unpublished results.
(16) Adam, W.; Ouchi, A. *Tetrahedron Lett.* 1992, *33*, 1875.
(17) Butcher, J. A., Jr.; Hinz, H. R.; Tsou, N.-H.; Shah, S. *Tetrahedron Lett.* 1984, *25*, 5483.
(18) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* 1990, *23*, 165.
(19) Adam, W.; Finzel, R.; Kita, F. *Tetrahedron Lett.* 1991, *32*, 2211.
(20) (a) Adam, W.; Hannemann, K.; Peters, E.-M.; Peters, K.; von Schnering, H. G.; Wilson, R. M. *J. Am. Chem. Soc.* 1987, *109*, 5250. (b) Adam, W.; Günther, E.; Hössel, P.; Platsch, H.; Wilson, R. M. *Tetrahedron Lett.* 1987, *28*, 4407.
(21) (a) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* 1976, *98*, 8190. (b) Griller, D.; Majewski, M.; McGimpsey, W. G.; Nazran, A. S.; Scaiano, J. C. *J. Org. Chem.* 1988, *53*, 1550. (c) Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; Griffin, G. W. *J. Am. Chem. Soc.* 1980, *102*, 5127.
(22) Hannemann, K.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 853.
(23) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* 1984, *106*, 5234. Liang, T.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* 1987, *109*, 7803.
(24) Yabe, A.; Ouchi, A.; Moriyama, H. *J. Chem. Soc., Chem. Commun.* 1988, 1744.
(25) Yabe, A.; Honda, K.; Oikawa, S.; Tsuda, M. *Chem. Lett.* 1976, 823.
(26) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* 1984, *106*, 5228.
(27) Redmond, R. W.; Harwig, C. W.; Scaiano, J. C. *J. Photochem. Photobiol. A: Chem.*, in press.
(28) Redmond, R. W.; Scaiano, J. C. *J. Phys. Chem.* 1989, *93*, 5347.
(29) Wilson, R. M.; Schnapp, K. A.; Patterson, W. S. *J. Am. Chem. Soc.*, in press.
(30) Diphenylcarbene reacts with 1,3-butadiene with a rate constant of $6.5 \pm 2.0 \times 10^5$ M^{-1} s^{-1} (ref 21a). While the photoenol **28** should be somewhat more reactive, its rate of reaction with diphenylcarbene should be considerably less than diffusion controlled.
(31) Andrews, L. J.; Deroulede, A.; Linschitz, H. *J. Phys. Chem.* 1978, *82*, 2304.
(32) Romanova, T. N.; Wilson, R. M.; Ho, D. M.; Krause, J. A. 24th Central Regional Meeting of the American Chemical Society, Cincinnati, OH, May 26–29, 1992; Abstr. no. 478.
(33) Scaiano, J. C.; Weir, D. *Can. J. Chem.* 1988, *66*, 491.
(34) Huggenberger, C.; Labhart, H. *Helv. Chim. Acta* 1978, *61*, 250.
(35) Parker, V. D.; Bethell, D. *J. Am. Chem. Soc.* 1987, *109*, 5066.
(36) The reactions of diphenylcarbene with aromatic molecules is placed in somewhat better perspective by noting that diphenylcarbene does react photochemically with benzene itself to form 7,7-diphenyl-1,3,5-cycloheptatriene, albeit in very low yield (Hannemann, K. *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 284). This benzene adduct is also observed in the fluorenone reaction (Scheme 12), since benzene was used as the solvent. In this reaction, its yield is much lower than those of the dihydrobenz[*a*]azulenes **33–35**. Furthermore, contrary to literature reports (Baron, W. J.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* 1973, *95*, 6286), hexafluorobenzene reacts photochemically with diphenylcarbene to form the analogous cycloheptatriene in good yields. (Wilson, R. M.; Romanova, T. N.; Krause, J. A. Unpublished results.)
(37) Adam, W.; Denninger, U.; Finzel, R.; Kita, F.; Platsch, H.; Walter, H.; Zang, G. *J. Am. Chem. Soc.* 1992, *114*, 5027.
(38) Schönberg, A. *Präparative Organishche Photochemie*; Springer-Verlag: Berlin, 1958; p 124.
(39) Bohne, C.; Boch, R.; Scaiano, J. C. *J. Org. Chem.* 1990, *55*, 5414.
(40) Letsinger, R. L.; Collat, R.; Magnusson, M. *J. Am. Chem. Soc.* 1954, *76*, 4185.
(41) Schmidt, J. A.; Hilinski, E. F. *J. Am. Chem. Soc.* 1988, *110*, 4036.
(42) Luckhurst, G. R.; Ockwell, J. N. *Tetrahedron Lett.* 1968, 4123.
(43) Fox, M. A.; Gaillard, G.; Chen, C.-C. *J. Am. Chem. Soc.* 1987, *109*, 7088.
(44) Redmond, R. W.; Wayner, D. D. M.; Kanabus-Kaminska, J. M.; Scaiano, J. C. *J. Phys. Chem.* 1989, *93*, 6397.
(45) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* 1985, *107*, 83.
(46) Bromberg, A.; Meisel, D. *J. Phys. Chem.* 1985, *89*, 2507.
(47) Mallory, F. B.; Mallory, C. W. *Org. React.* 1984, *30*, 1.
(48) Faria, J. L.; Steenken, S. *J. Am. Chem. Soc.* 1990, *112*, 1277.
(49) Faria, J. L.; Steenken, S. J. XIII IUPAC Symposium on Photochemistry, University of Warwick, Coventry, England, July 22–28, 1990; P236.
(50) For an interesting discussion of the relative efficiencies of producing higher excited states with a single-pulse laser source, see ref 3, p 4402.
(51) Hadel, L. M.; Platz, M. S.; Wright, B. B.; Scaiano, J. C. *Chem. Phys. Lett.* 1984, *105*, 539.
(52) Neckers, D. C.; Rajadurai, S.; Valdes-Aguilera, O.; Zakrzewski, A.; Linden, S. M. *Tetrahedron Lett.* 1988, *29*, 5109.
(53) Neckers, D. C. Personal communication.
(54) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* 1985, *107*, 6368. Scaiano, J. C.; Johnston, L. J. *Pure Appl. Chem.* 1986, *58*, 1273.
(55) Johnston, L. J.; Lougnot, D. J.; Wintgens, V.; Scaiano, J. C. *J. Am. Chem. Soc.* 1988, *110*, 518.

(56) Baumann, H.; Merckel, C.; Timpe, H.-J.; Graness, A.; Kleinschmidt, J.; Gould, I. R.; Turro, N. J. *Chem. Phys. Lett.* 1984, *103*, 497.
(57) Nagarajan, V.; Fessenden, R. W. *Chem. Phys. Lett.* 1984, *112*, 207.
(58) Johnston, L. J.; Lougnot, D. J.; Scaiano, J. C. *Chem. Phys. Lett.* 1986, *129*, 205.
(59) Redmond, R. W.; Scaiano, J. C.; Johnston, L. J. *J. Am. Chem. Soc.* 1990, *112*, 398.
(60) Gauglitz, G.; Kölle, U. *J. Photochem.* 1975, *4*, 309.
(61) Boate, D. R.; Johnston, L. J.; Scaiano, J. C. *Can. J. Chem.* 1989, *67*, 927.
(62) Netto-Ferreira, J. C.; Murphy, W. F.; Redmond, R. W.; Scaiano, J. C. *J. Am. Chem. Soc.* 1990, *112*, 4472.
(63) Netto-Ferreira, J. C.; Scaiano, J. C. *J. Chem. Soc., Chem. Commun.* 1989, 435.
(64) Chilton, J.; Giering, L.; Steel, C. *J. Am. Chem. Soc.* 1976, *98*, 1865.
(65) Jent, F.; Paul, H.; Fischer, H. *Chem. Phys. Lett.* 1988, *146*, 315. Fischer, H.; Baer, R.; Hany, R.; Verhoolen, I.; Walbiner, M. *J. Chem. Soc., Perkin Trans. 2* 1990, 787.
(66) Banks, J. T.; Scaiano, J. C.; Adam, W.; Schulte Oestrich, R. *J. Am. Chem. Soc.*, in press.
(67) Holdcroft, S.; Tang, B.-Z.; Guillet, J. E. *J. Chem. Soc., Chem. Commun.* 1991, 280.
(68) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* 1989, *89*, 521 (this reference provides an excellent compendium of biradical lifetime data that are of great assistance in evaluating the feasibility of targeting various biradical species).
(69) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* 1986, *108*, 2349.
(70) Wilson, R. M.; Hannemann, K.; Adam, W. XI IUPAC Symposium on Photochemistry, Lisbon, 1986; Abstract 2ST-3, p 101.
(71) Barton, D. H. R.; Charpiot, B.; Ingold, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. *J. Am. Chem. Soc.* 1985, *107*, 3607.
(72) Wilson, R. M.; Schnapp, K. A. *J. Am. Chem. Soc.* 1988, *110*, 982.
(73) Muller, J.-F.: Muller, D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* 1978, *100*, 1629; but see also ref 76.
(74) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *Chem. Phys. Lett.* 1987, *134*, 549.
(75) Becker, H.-D.; Elebring, T. *J. Org. Chem.* 1985, *50*, 1319.
(76) (a) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* 1979, *101*, 2216. (b) Burnett, M. N.; Boothe, R.; Clark, E.; Gisin, M.; Hassaneen, H. M.; Pagni, R. M.; Persy, G.; Smith, R. J.; Wirz, J. *J. Am. Chem. Soc.* 1988, *110*, 2527.
(77) Scaiano, J. C.; Wagner, P. J. *J. Am. Chem. Soc.* 1984, *106*, 4626.
(78) Schmidt, S. P.; Pinhas, A. R.; Hammons, J. H.; Berson, J. A. *J. Am. Chem. Soc.* 1982, *104*, 6822.
(79) Brinton, R. K. *J. Phys. Chem.* 1968, *72*, 321. Kende, A. S.; Goldschmidt, Z.; Smith, R. F. *J. Am. Chem. Soc.* 1970, *92*, 7606. Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* 1970, *92*, 7493. Gilbert, J. C.; Luo, T. *J. Org. Chem.* 1981, *46*, 5237.
(80) (a) Trozzolo, A. M.; Gibbons, W. A. *J. Am. Chem. Soc.* 1967, *89*, 239. (b) Hadel, L. M.; Maloney, V. M.; Platz, M. S.; McGimpsey, W. G.; Scaiano, J. C. *J. Phys. Chem.* 1986, *90*, 2488.
(81) Woodward, R. B.; Hoffmann, R. *The Consevation of Orbiral Symmetry*; Verlag Chemie: Weinheim, 1970; p 58.
(82) Platz, M. S.; Maloney, V. M. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990; p 239.
(83) Horn, K. A.; Allison, B. D. *Chem. Phys. Lett.* 1985, *116*, 114.
(84) DuPuy, C.; Korenowski, G. M.; McAuliffe, M.; Hetherington, W. M., III; Eisenthal, K. B. *Chem. Phys. Lett.* 1981, *77*, 272.
(85) (a) Wang, Y.; Sitzmann, E. V.; Novak, F.; Dupuy, C.; Eisenthal, K. B. *J. Am. Chem. Soc.* 1982, *104*, 3238. (b) Sitzmann, E. V.; Wang, Y.; Eisenthal, K. B. *J. Phys. Chem.* 1983, *87*, 2283.
(86) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* 1984, *106*, 198.
(87) Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science* (*Washington, D.C.*) 1984, *225*, 1439.
(88) Leyva, E.; Barcus, R. L.; Platz, M. S. *J. Am. Chem. Soc.* 1986, *108*, 7786.
(89) Ono, Y.; Ware, W. R. *J. Phys. Chem.* 1983, *87*, 4426.
(90) Scaiano, J. C.; Weir, D. *Can. J. Chem.* 1988, *66*, 491.
(91) Nazran, A. S.; Gabe, E. J.; Lepage, Y.; Northcott, D. J.; Park, J. M.; Griller, D. *J. Am. Chem. Soc.* 1983, *105*, 2912.
(92) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *Chem. Phys. Lett.* 1983, *102*, 446.
(93) Johnston, L. J.; Scaiano, J. C. *Chem. Phys. Lett.* 1985, *116*, 109.
(94) Jackson, J. E.; Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, Connecticut, in press. See also: Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* 1984, *106*, 2227.
(95) Tomioka, H.; Miwa, T.; Suzuki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* 1980, *53*, 753.
(96) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* 1984, *106*, 283.
(97) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* 1971, *10*, 537. Trozzolo, A. M.; Leslie, T. M.; Sarpotdar, A. S.; Small, R. D.; Ferraudi, G. J. *Pure Appl. Chem.* 1979, *51*, 261.
(98) Griffin, G. W.; Ishikawa, K.; Lev, I. J. *J. Am. Chem. Soc.* 1976, *98*, 5697.
(99) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Am. Chem. Soc.* 1985, *107*, 7204.
(100) Do-Minh, T.; Trozzolo, A. M.; Griffin, G. W. *J. Am. Chem. Soc.* 1970, *92*, 1402. Arnold, D. R.; Karnischky, L. A. *J. Am. Chem. Soc.* 1970, *92*, 1404. Murata, S.; Ohtawa, Y.; Tomioka, H. *Chem. Lett.* 1989, 853.
(101) Chapman, O. L.; Hess, T. C. *J. Am. Chem. Soc.* 1984, *106*, 1842. Dunkin, I. R.; Shields, C. J. *J. Chem. Soc., Chem. Commun.* 1986, 154. Dunkin, I. R.; Bell, G. A. *Tetrahedron* 1985, *41*, 339. Sander, W. W. *J. Org. Chem.* 1988, *53*, 121. Sander, W. W. *J. Org. Chem.* 1988, *53*, 2091. Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* 1986, *108*, 1517.
(102) Sander, W. W. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 255. Sander, W. W. *J. Org. Chem.* 1989, *54*, 333.
(103) Kaupp, G.; Döhle, J. A. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 828.
(104) Scaiano, J. C.; Wintgens, V.; Netto-Ferreira, J. C. *Pure Appl. Chem.* 1990, *62*, 1557.
(105) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* 1988, *110*, 501.
(106) Wintgens, V.; Netto-Ferreira, J. C.; Casal, H. L.; Scaiano, J. C. *J. Am. Chem. Soc.* 1990, *112*, 2363.
(107) de Fonseka, K. K.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem. Soc.* 1979, *101*, 3277.
(108) Netto-Ferreira, J. C.; Wintgens, V.; Scaiano, J. C. *Tetrahedron Lett.* 1989, *30*, 6851.
(109) Wilson, R. M.; Hannemann, K.; Peters, K.; Peters, E.-M. *J. Am. Chem. Soc.* 1987, *109*, 4741.
(110) Wilson, R. M.; Azadnia, A.; Romanova, T. N.; Krause, J. A., 24th Central Regional Meeting of the American Chemical Society, Cincinnati, OH, May 26–29, 1992; Abstr. no. 480.
(111) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* 1988, *110*, 2299.
(112) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* 1988, *110*, 511.
(113) McGimpsey, W. C.; Scaiano, J. C. *Chem. Phys. Lett.* 1987, *138*, 13.
(114) Siegel, S.; Eisenthal, K. *J. Chem. Phys.* 1965, *42*, 2494.
(115) Lamotte, M.; Pereyre, J.; Lapouyade, R.; Joussot-Dubien, J. *J. Photochem. Photobiol. A: Chem.* 1991, *58*, 225. Lamotte, M.; Pereyre, J.; Joussot-Dubien, J.; Lapouyade, R. *J. Photochem.* 1987, *38*, 177. Joussot-Dubien, J.; Lamotte, M.; Pereyre, J. *J. Photochem.* 1981, *17*, 347.
(116) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* 1989, *111*, 335.
(117) Guerin, B.; Johnston, L. J.; Quach, T. *J. Org. Chem.* 1988, *53*, 2826.
(118) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* 1987, *109*, 5487.
(119) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* 1987, *109*, 2179.
(120) Mukai, M.; Yamauchi, S.; Hirota, N. *J. Phys. Chem.* 1989, *93*, 4411.
(121) Heine, H. G. *Tetrahedron Lett.* 1971, 1473.
(122) Wagner, P. J.; Zhou, B. *J. Am. Chem. Soc.* 1988, *110*, 611.
(123) Rigaudy, J.; Derible, P. *Bull. Soc. Chim. Fr.* 1965, 3047. Rigaudy, J.; Derible, P. *Bull. Soc. Chim. Fr.* 1965, 3055. Rigaudy, J.; Derible, P. *Bull. Soc. Chim. Fr.* 1965, 3061.
(124) Wilson, R. M.; Romanova, T. N. Unpublished results.
(125) Schnapp, K. A.; Wilson, R. M.; Ho, D. M. Submitted for publication.
(126) Farid, S.; Scholz, K.-H. *J. Chem. Soc., Chem. Commun.* 1969, 572. Maruyama, K.; Iwai, T.; Naruta, Y.; Otsuki, T.; Miyagi, Y. *Bull. Chem. Soc. Jpn.* 1978, *51*, 2052.
(127) Dalton, J. C.; Tremont, S. J. *J. Am. Chem. Soc.* 1975, *97*, 6916.
(128) Zandomeneghi, M.; Cavazza, M.; Moi, L.; Pietra, F. *Tetrahedron Lett.* 1980, *21*, 213.
(129) Malatesta, V.; Willis, C.; Hackett, P. A. *J. Org. Chem.* 1982, *47*, 3117.
(130) Hornback, J. M.; Proehl, G. S. *J. Am. Chem. Soc.* 1979, *101*, 7367.
(131) Wilson, R. M.; Patterson, W. S.; Krause, J. A. Unpublished results.
(132) Plaas, D.; Schäfer, F. P. *Chem. Phys. Lett.* 1986, *131*, 528. Kolc, J.; Michl, J. *J. Am. Chem. Soc.* 1970, *92*, 4147. Meinwald, J.; Samuelson, G. E.; Ikeda, M. *J. Am. Chem. Soc.* 1970, *92*, 7604.
(133) Michl, J.; Kolc, J. *J. Am. Chem. Soc.* 1970, *92*, 4148.
(134) Sumitani, M.; Yoshihara, K. *J. Chem. Phys.* 1982, *76*, 738.
(135) Wilson, R. M.; Patterson, W. S. Unpublished results.
(136) Chang, T.-M.; Naim, A.; Ahmed, S. N.; Goodloe, G.; Shevlin, P. B. *J. Am. Chem. Soc.* 1992, *114*, 7603.