Photochemistry of Organic Reaction Intermediates: Novel Reaction Paths Induced by Two-Photon Laser Excitation[1]

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Pulsed lasers have been used in the study of photochemical reactions for close to a quarter of a century.[2] It is well-recognized that under certain conditions the consequences of laser excitation can differ from those of conventional (e.g., lamps or ambient light) irradiation at the same wavelength.

Laser and conventional excitation of organic materials can lead to different consequences for a variety of reasons. Three of the major origins for these differences are the following:

(i) This Account deals with the case where laser excitation can generate a sufficiently high concentration of intermediates (typically 10–100 μM) to compete with the ground-state precursor for the exciting photons. Under these conditions, photolysis of the intermediates (excited states, free radicals, etc.) can lead to new chemical processes, quite different from those induced by conventional excitation. We avoid the use of the term "biphotonic" since these two-photon processes involve *stepwise* photon absorption in which the second photon is normally absorbed by a chemical species quite distinct from the original ground-state precursor.

The other two common examples leading to "lamp vs laser" differences are as follows:

(ii) Simultaneous two-photon absorption can lead to the population of high-energy excited states, not usually accessible by one-photon excitation. This interesting area will not be covered in this Account.

(iii) When the reaction intermediates (e.g., free radicals) produced by photolysis of their precursor decay by a mechanism that involves a competition of first- and second-order processes, laser excitation will favor the product of the latter. For example, photolysis of 6-heptenoyl peroxide in benzene leads to radical I, which can isomerize to II.[3] Under 308-nm laser excitation the main product is 1,11-dodecadiene (>90%, III), while under lamp irradiation III is not observed and the main
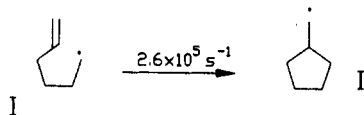
product is 1,2-dicyclopentylethane (>60%, IV), along with smaller amounts of 7-cyclopentyl-1-heptene (V). In this system the lamp vs laser differences can be fully understood on the basis of one-photon processes.

This Account covers primarily recent work from our laboratory,[4] although the subject has received attention in other laboratories. In particular, contributions from Argonne, Notre Dame, Columbia, and Kanazawa have stimulated some aspects of our own work.

Development of Techniques for the Study of Two-Photon Processes. While two-photon processes can frequently be initiated by single-pulse laser excitation, this does not provide sufficient control of the experiment to adequately understand the mechanisms or reaction kinetics. The stepwise nature of the processes requires control of the two excitation steps. Thus, we utilize two lasers, such that the wavelength, energy dose, and timing can be independently controlled for each step. This approach is similar to that of organic chemists, who prepare and characterize a molecule before examining its chemistry (or photochemistry). The only difference is that the substrates in which we are interested are short-lived, and therefore their characterization and the study of their reactions need to be performed on a short time scale. The first laser pulse is used for synthesis purposes, i.e., to make the intermediate whose photochemistry will be studied. We refer to this laser as the "synthesis laser", while the second pulse, which excites the intermediate, is referred to as the "photolysis laser". The same experimental setup is used for transient and preparative studies; the latter are an essential part of our work.[5]

We illustrate the technique used in our experiments with one example which can be carried out with either lasers or lamps. Aberchrome 540 is a commercial fulgide which undergoes the efficient photoreversible transformation outlined in Scheme I. Heller et al.[6,7] have calibrated Aberchrome 540 for use as a photochemical actinometer. VII is quite stable, and the VII → VI photoreaction does not require the precise timing which characterizes most of our other experiments. Figure 1 summarizes the details of the experiment.

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(3) For the kinetics of the rearrangement, see: Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981,** *103,* 7739.
(4) For a brief review of our work on naphthalene derivatives, see: Scaiano, J. C.; Johnston, L. J. *Pure Appl. Chem.* **1986,** *58,* 1273.
(5) For some details of our two-laser setup, see: Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985,** *107,* 4396.
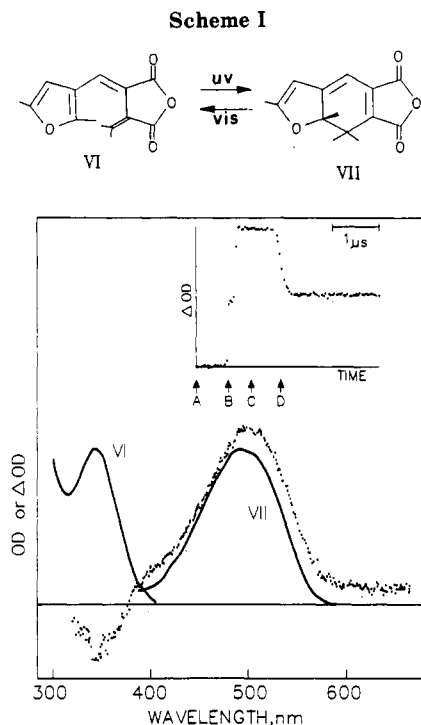(6) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981,** 341.
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Scheme I

Scheme II
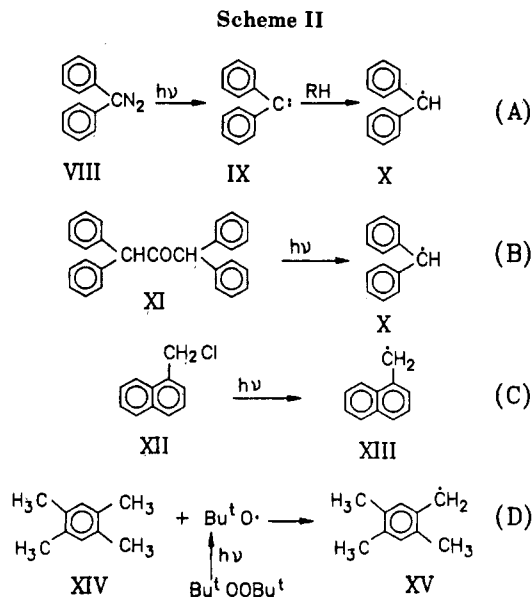

Figure 1. Absorption spectra for VI and VII in toluene and transient absorption spectrum (dotted line) measured 500 ns (point C in insert) after 308-nm excitation of 2.1×10^{-6} M VI in toluene. Insert: A kinetic trace monitored at 494 nm for 308-nm plus dye laser (517 nm) excitation of VI. Points A, B, C, and D correspond to the beginning of detection, the 308-nm pulse, the time at which the spectrum was recorded, and the dye laser pulse, respectively.

Under UV irradiation VI leads to VII ($\lambda_{max} = 494$ nm), which in turn photobleaches back to VI upon visible ($\lambda > 400$ nm) irradiation. The insert trace in Figure 1 was monitored at 494 nm and shows the formation of VII (point B) upon 308-nm laser excitation; after ~1-μs delay about half of VII is bleached by dye laser irradiation at 517 nm. Under our experimental conditions the forward reaction occurs with a quantum yield (Φ) of 0.20, while the reverse process has $\Phi = 0.06$.[6] Note (point D) that high chemical yields of bleaching can be obtained in spite of the modest quantum yields. The spectrum in the bottom part of Figure 1 was obtained at point C in the insert. Transient spectra usually depict ΔOD, rather than OD, and therefore have negative segments where an absorbing species is depleted (see Figure 1 at $\lambda < 380$ nm). Note that the individual segments in the insert are essentially horizontal; this reflects the fact that VII is not strictly a "transient". Other species covered in this Account usually show some decay during the experiment. We have calibrated the reactions of Scheme I and Figure 1 for use as an actinometer in two-laser experiments.[8]

In closing this section we would like to raise two points. Firstly, there is an interesting analogy between our two-laser studies and some aspects of matrix isolation work;[9] in our work the intermediates are examined by fast techniques in which short-lived species are

accessed during their lifetime, while in matrix isolation the technique remains "slow", but the lifetime of the intermediates has been extended to the point where they become accessible to the techniques. Secondly, while our studies usually involve two lasers, it is important to emphasize that the same chemistry can frequently (but not always) be induced by a single laser pulse. The two lasers are often needed only to facilitate the study of these processes.

Luminescence from Excited Reaction Intermediates. Laser-induced fluorescence is a common technique in the study of reaction intermediates in the gas phase. Fluorescence from reaction intermediates in solution is frequently less intense due to the increased efficiency of deactivation pathways. This section presents a limited selection of data on the luminescence of various reaction intermediates; all have aromatic rings α to the functional site, and this frequently leads to readily detectable emission.

Free Radicals. Excited radicals such as 1-naphthylmethyl,[10-13] diphenylmethyl,[5,14-16] and benzophenone ketyl[17-20] show readily detectable fluorescence in solution. For example, Ph_2CH^* has a fluorescence quantum yield (Φ_f) of 0.3 for the $1^2A_2 \rightarrow 1^2B_2$ transition and a lifetime of 255 ns in cyclohexane at room temperature. The parent radical, $PhCH_2$, does not fluoresce in solution at ambient temperature,[21] despite the fact that at 77 K its excited lifetime is longer than that for Ph_2CH^*.[22,23] Recent studies[21] have shown that the

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(9) Interesting examples where lamp irradiation at 77 K leads to similar effects as laser-induced processes at room temperature are provided by several compounds of the acenaphthylene family. See: Plaas, D.; Schäfer, F. P. *Chem. Phys. Lett.* **1986**, *131*, 528. Kolc, J.; Michl, J. *J. Am. Chem. Soc.* **1970**, *92*, 4147, 4148. Menwald, J.; Samuelson, C. E.; Ikeda, M. *J. Am. Chem. Soc.* **1970**, *92*, 7604.

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Table I.
Fluorescence Lifetimes and Spectral Parameters for Excited Free Radicals in Solution at Room Temperature

radical	solvent	$\lambda_{00}{}^a$	$\lambda_{max}{}^a$	τ, ns	source[b]	ref
duryl	toluene		508	5	D	c
pentamethylbenzyl	toluene		503	5.5	C, D	c
4-phenylbenzyl	benzene	576	576	13	C, D	25
4-(p-tolyl)benzyl	benzene	582	582	10	D	25
1-naphthylmethyl	cyclohexane	586	586	35	C, D	12
2-naphthylmethyl	cyclohexane	589	589	27	C	4
diphenylmethyl	cyclohexane	528	547	255	A, B	5
diphenylmethyl-d_{10}	cyclohexane	527	545	390	A	16
diphenylmethyl-d_1	cyclohexane			250	B	25
4-methyldiphenylmethyl	cyclohexane	535	552	218	A	16
4-cyanophenylmethyl	cyclohexane		560	80	A	16
2-phenanthrylmethyl	toluene	593	593	79	C	25
$Ph_2\dot{C}OH$	toluene		574	3.9	E	19
$Ph_2\dot{C}OD$	toluene-d_8		574	8.7	E	19
$(C_6D_5)_2\dot{C}OH$	toluene		570	4.2	E	19
$(p\text{-}CH_3C_6H_4)_2\dot{C}OH$	toluene		588	3.1	E	26
$(p\text{-}CNC_6H_4)(C_6H_5)\dot{C}OH$	toluene		613	7.8	E	26
$(o\text{-}C_5H_4N)(C_6H_5)\dot{C}OH$	toluene		567	5.9	E	27
$(m\text{-}C_5H_4N)(C_6H_5)\dot{C}OH$	toluene		580	4.2	E	27
$(p\text{-}C_5H_4N)(C_6H_5)\dot{C}OH$	toluene		559	7.4	E	27
$(4\text{-}BrC_6H_4)\dot{C}(OH)CH_3$	benzene	593	593	6.1	E	27
$(4\text{-}C_6H_5C_6H_4)\dot{C}(OH)CH_3$	benzene	587	587	5.6	E	27

^{a} In nanometers, λ_{00} included only when the spectrum shows vibrational resolution. ^{b} A–D, see Scheme III; source E corresponds to photoreduction of the carbonyl triplet. ^{c} Unpublished results.

unusual temperature dependence of benzyl radical fluorescence is due to the proximity of the two lowest lying excited states, 1^2A_2 and 2^2B_2, the latter providing an efficient thermally activated pathway for radiationless deactivation. Structural changes in benzyl can lead to increased separation of these two doublet levels and thus eliminate this deactivation path.

We have generated benzylic radicals by one or several of the routes exemplified in Scheme II. These have been selected so that a 308-nm laser would provide a suitable "synthesis" pulse. The fluorescence from excited free radicals frequently shows vibrational structure; in the case of $Ph_2\dot{C}H$ and its derivatives typical vibrational spacing is in the 1200–1500-cm^{-1} range.[24] Table I summarizes spectroscopic and lifetime data for a partial list of radicals examined in our laboratory. Figure 2 shows the fluorescence spectra of representative radicals.

Excited diarylmethyl radical lifetimes exhibit an inverse dependence with the 1^2A_2–1^2B_2 energy gap.[16] For example, the parent and 4-cyanodiphenylmethyl radicals have lifetimes of 255 and 80 ns, respectively, while the positions of the 0,0 fluorescence bands are 528 and 560 nm.[16]

Deuterium substitution has a substantial effect on the lifetimes of diphenylmethyl radicals, e.g., 255 and 390 ns for $(C_6H_5)_2\dot{C}H$ and $(C_6D_5)_2\dot{C}H$, respectively.[5] Interestingly, for benzophenone ketyl radicals (see Table I) deuterium substitution at the ring positions has virtually no effect, while at the –OH position the effect is large.[19] We have also been able to detect the luminescence from substituted acetophenone ketyl radicals; thus, for the 4-bromo derivative λ_{max} is 593 nm and $\tau = 6.1$ ns.[27] Species of this type have not been reported before, perhaps because their fluorescence is
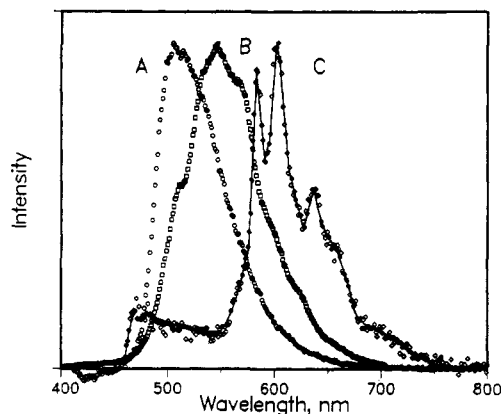

Figure 2. Room-temperature radical fluorescence spectra from duryl in toluene (A), $(C_6D_5)_2\dot{C}H$ in benzene (B), and 1-naphthylmethyl in cyclohexane (C).

less intense than that from benzophenone ketyls.

We limit our coverage of the fluorescence of free radicals to those basic elements that are relevant to the understanding of the chemical reactions covered elsewhere in this Account. It is clear from the data in Table I that some excited radicals are sufficiently long-lived that they can be expected to undergo intermolecular reactions in solution at room temperature. Luminescence quenching has been used in a number of cases to examine the interaction of excited free radicals with several species. Unfortunately, such studies do not lead to any direct evidence for the transient or final products of reaction, although an educated guess is sometimes possible. Transient absorption measurements and product studies can in many cases overcome these limitations.

Arylcarbenes. Few studies have dealt with the luminescence of excited triplet carbenes in solution, although such processes are well-known in low-temperature matrices.[28] In fact, when carbenes are generated according to reaction A in Scheme II, their luminescence can be readily detected, even in single-laser ex-

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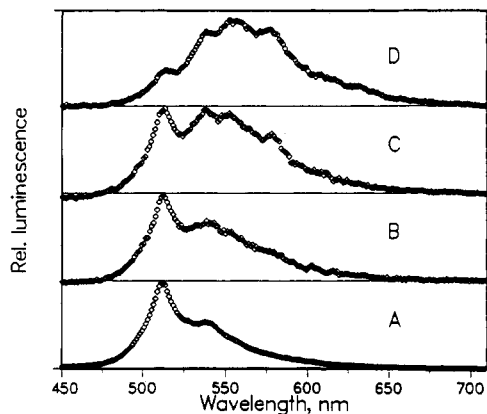
Figure 3. Room-temperature luminescence spectra from 6×10^{-5} M solution of diphenyldiazomethane in cyclohexane irradiated with a 308-nm synthesis laser, followed by a 337-nm photolysis laser after a variable time delay (t_d). A 20-ns detection gate was timed to coincide with the 337-nm pulse. The following are the relative signal intensities (I) and time delays: (A) $I = 100$, $t_d = 0$; (B) $I = 9.3$, $t_d = 1$ μs; (C) $I = 6.1$, $t_d = 2$ μs; (D) $I = 8.0$, $t_d = 5$ μs. Note that (A) may incorporate carbene excitation by the 308-nm pulse also.

Table II.
Fluorescence Lifetimes and Spectral Parameters for Excited Carbenes[a]

		λ_{max}[b]		decay at 293 K	
carbene	solvent	293 K	77 K	solvent	τ, ns
Ph_2C:	benzene	505 (30)	480 (31)	acetonitrile	3.8 (32)
				acetonitrile	9.1 (33)
				cyclohexane	4.2 (33)
$(4\text{-}CNC_6H_5)\overset{..}{C}Ph$	benzene	536 (30)	510 (34)		
$(4\text{-}CH_3C_6H_5)\overset{..}{C}Ph$	benzene	511 (30)	487 (31)		
$(4\text{-}BrC_6H_5)\overset{..}{C}Ph$	benzene	517 (30)	488 (31)		
$(4\text{-}ClC_6H_5)\overset{..}{C}Ph$	benzene	516 (30)	487 (31)		
$(4\text{-}CH_3C_6H_5)_2C$:	benzene	515 (30)		benzene	7.2 (35)
				acetonitrile	5.6 (35)
				isooctane	8.0 (35)

^{a}References given in parentheses. ^{b}In nanometers.

periments (e.g., $\lambda_{max} = 507$ nm for diphenylcarbene).[29] Figure 3 shows the luminescence spectra observed upon nitrogen laser excitation of a cyclohexane solution in which Ph_2C: had been generated by 308-nm excitation of Ph_2CN_2; the early spectra show carbene luminescence, while at longer times only radical emission is observable. Under these conditions the ground-state carbene lifetime is ~ 1.8 μs.

Several representative examples of carbene fluorescence have been summarized in Table II. A comparison with Table I shows that carbene fluorescence is typically blue-shifted by 20–30 nm with respect to the corresponding free radical; the parallel may indicate that similar factors control the lifetimes in both cases. Interestingly, carbene fluorescence in solution is red-shifted ($\sim$25–30 nm) from the position reported in matrices at 77 K. Low-temperature luminescence is likely to arise from an unrelaxed excited state (perhaps

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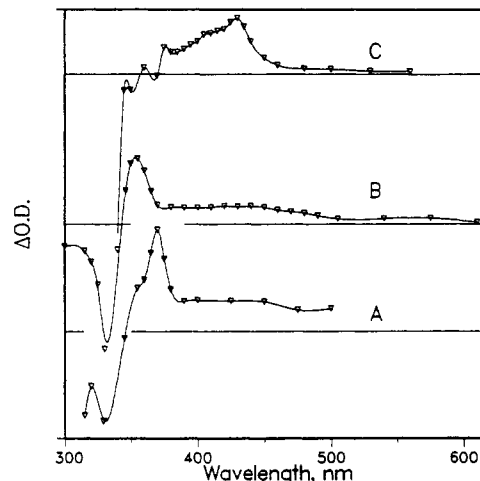(30) Weir, D.; Scaiano, J. C. *Can. J. Chem.*, in press.
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Figure 4. Transient absorption spectra for excited di-p-tolyl-carbene in acetonitrile (A),[35] excited diphenylmethyl in cyclohexane (B),[5] and excited 1-naphthylmethyl radical in methanol (C).[12]

retaining to a considerable degree the ground-state geometry).

Biradicals. Few studies of biradical luminescence in solution have been reported in the literature. We have examined the fluorescence from XVI which shows λ_{max}

Ph Ph Ph Ph

XVI
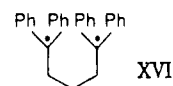
= 520 nm and $\tau = 2.5$ ns in benzene at room temperature.[36] The λ_{max} and general features of the spectrum closely resemble those for diphenylmethyl radicals (see Table I), but the presence of the second radical center reduces the lifetime by 2 orders of magnitude.

Transient Absorption Spectra from Excited Reaction Intermediates. Transient absorption spectra from excited reaction intermediates are much more difficult to measure than fluorescence spectra, but they can provide more information on reaction mechanisms than can be obtained from luminescence measurements alone. Meisel et al.[15] were the first to detect the absorption from excited diphenylmethyl radicals in solution. Figure 4 shows representative absorption spectra for several excited intermediates. Transient spectra, which normally report ΔOD, show negative regions where the precursor absorption is stronger than that of the intermediate. In two-laser experiments, the precursor for the excited intermediate is its ground state, not the initial stable precursor; thus, the bleaching (see Figure 4) provides a "fingerprint", which can help to identify the precursor of the excited species.

Intramolecular Reactions in the Photolysis of Ground-State Reaction Intermediates. The short lifetimes of many excited reaction intermediates restrict the study of their intermolecular reactions, but intramolecular processes are frequently observed, even in cases where the excited state is too short-lived to be detected. A few examples illustrating photoinduced cleavage, rearrangement, and ring closure are discussed below.
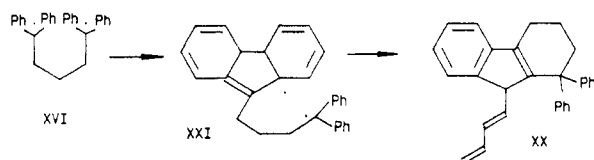
An interesting example of laser-induced biradical cleavage is provided by XVII, derived from α-(2,4,6-triisopropylphenyl)acetophenone.[37] The triplet bi-

(36) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2349.

radical is formed sufficiently rapidly that it can be reexcited within a single intense laser pulse (5 ns, 308 nm, excimer laser). Cleavage of XVII to yield the 1,3-biradical XVIII and acetophenone enol was demonstrated by the observation of long-lived transient signals attributable to these intermediates and identification of the expected new products.
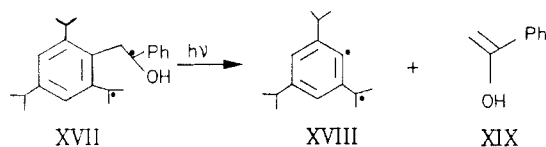

Excitation of biradical XVI derived from 2,2,6,6-tetraphenylcyclohexanone leads to XX.[36] In this case there is no indication of cleavage. As already pointed out, excited XVI fluoresces with $\tau \sim 2.5$ ns. An ad-


ditional longer lived transient absorption with $\lambda_{max} = 480$ nm was shown to result from a two-photon process and was tentatively assigned to biradical XXI formed by initial cyclization of one of the diphenylmethyl centers in XVI. Cyclization of XXI followed by ring opening and hydrogen shifts leads to a 12% yield of XX relative to the normal one-photon products in our experiments.[36] Recently, Wilson et al.[38] reported 40% yields under intense argon laser excitation using jet techniques.

The reaction of fluorenylidene with acetone provides another variation on the intramolecular reactivity of excited intermediates.[39] Although the carbonyl ylide XXIII shows efficient and irreversible bleaching upon
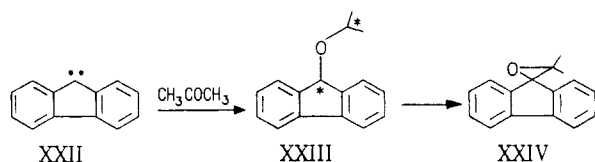
dye laser excitation, product studies indicate that lamp and two-laser photolysis give the same product distribution, with the oxirane and its rearranged product being the major components of the mixture. Control experiments demonstrated that excitation of XXIII does not lead to C–O bond cleavage. We concluded that excited XXIII undergoes the same processes as its ground state, although much more rapidly, perhaps because excitation leads to the bond rotation required for ring closure.

Benzophenone ketyl radicals ($\lambda_{max} = 540$ nm) undergo efficient and irreversible bleaching upon excitation in their visible absorption band.[26] Two-photon product studies for $Ph_2\dot{C}OH$ showed a decreased yield of ketyl radical derived products and a corresponding increase in the amount of benzophenone when the radical was generated from either benzhydrol plus *tert*-butoxyl

Scheme III
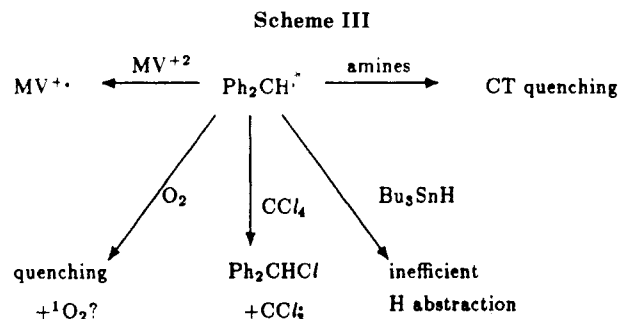
radicals or benzophenone triplet plus a hydrogen donor such as cyclohexane. Photobleaching of ketyl radicals derived from the photoreduction of benzophenone in cyclohexane ($\Phi = 0.27$) occurs with a concomitant increase in solvent-derived products. The modest quantum yield suggests that the reaction leading to bleaching is not solely responsible for the short lifetime (ca. 4 ns) of the excited radical.

The above examples demonstrate that excited intermediates may undergo a variety of intramolecular reactions with great selectivity in spite of the high excitation energies involved.

Intermolecular Reactions of Excited Free Radicals and Carbenes. This section concentrates on the reactions of diphenylmethyl and 1-naphthylmethyl radicals, which are sufficiently long-lived (see Table I) to make the study of their reactions much easier than those of other intermediates. Perhaps the main feature observed in our studies is that excited free radicals have enhanced charge-transfer capabilities, as do the excited states of most stable molecules. The high energy content of these intermediates does not generally lead to enhanced radical reactivity commensurate with the energy available.[40] The reactions of excited free radicals have been examined by using transient absorption techniques which make it possible to establish which processes lead to permanent chemical change and in some cases (such as methylviologen, MV^+)[5] to identify the transient products of reaction. Scheme III illustrates reactions of $Ph_2\dot{C}H^*$, and Table III gives rate data for various free radicals and carbenes which we have examined.

Turro et al. have compared the reactivity of ground- and excited-state benzophenone ketyl radicals with various electron acceptors.[18] The excited-state interaction with diazonium salts was 3 times faster than the ground-state reaction, although the former process was diffusion limited. For triphenylsulfonium tetrafluoroborate the rate enhancement was a factor of 370.

The reaction of excited radicals with halides (see Scheme III) is believed to be driven by charge transfer, possibly involving the intermediacy of the ion pair $[Ph_2CH^+,CCl_4^{\cdot-}]$. Product studies indicate a large increase in Ph_2CHCl yield upon excitation of the radical.[5] For $Ph_2\dot{C}OH^*$ Turro et al. report diffusion-controlled quenching (3.8×10^{10} M^{-1} s^{-1}) by CBr_4.[18]

Interestingly, amines, which tend to be good excited-state quenchers, are only modest quenchers of excited diphenylmethyl radical and do not appear to yield

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(40) Excited nitroxides do show enhanced free-radical character, e.g.: Johnston, L. J.; Tencer, M.; Scaiano, J. C. *J. Org. Chem.* **1986**, *51*, 2806.
(41) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *Chem. Phys. Lett.* **1983**, *102*, 446.
(42) Wang, Y.; Sitzmann, E. V.; Novak, F.; Dupuy, C.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 3238.

Table III.
Representative Intermolecular Reactivity of Excited Free Radicals and Carbenes at Room Temperature

| radical or carbene	quencher	solvent	k, $M^{-1} s^{-1}$	ref
Free Radicals				
diphenylmethyl	O_2	cyclohexane	8.7×10^9	5
1-naphthylmethyl	O_2	cyclohexane	4.7×10^9	12
2-phenanthrylmethyl	O_2	benzene	5.7×10^9	25
diphenylmethyl	CCl_4	methanol	1.6×10^8	5
1-naphthylmethyl	CCl_4	methanol	4×10^6	12
2-phenanthrylmethyl	CCl_4	toluene	1×10^6	25
diphenylmethyl	methyl methacrylate	cyclohexane	4.0×10^6	5
diphenylketyl-d_1	methyl methacrylate	toluene-d_8	3.6×10^9	19
diphenylmethyl	triethylamine	cyclohexane	5.2×10^8	5
1-naphthylmethyl	triethylamine	neat	$<2 \times 10^6$	12
diphenylmethyl	methylviologen	acetonitrile:water	1.3×10^{10}	5
diphenylmethyl	1,4-cyclohexadiene	cyclohexane	1.1×10^6	5
Carbenes				
diphenyl	diethylamine	acetonitrile	9×10^8	33
diphenyl	dibutyl sulfide	acetonitrile	3.2×10^8	41
diphenyl	methanol	acetonitrile	3.1×10^8	42
di-p-tolyl	CCl_4	isooctane	1.1×10^9	35

radical ions. Further, excited 1-naphthylmethyl radical can be generated in neat triethylamine with no detectable reduction in lifetime or change in the emission spectrum, compared to other inert solvents. Oxygen quenching of excited radicals is much faster (14 times for $Ph_2\dot{C}H$) than that of the ground state. However, interaction of $Ph_2\dot{C}H^*$ with O_2 leads to the repopulation of ground-state $Ph_2\dot{C}H$! i.e., it does not lead to formation of the peroxy radical, $Ph_2CHOO^\bullet$. The reaction mechanism is still under study, but singlet oxygen formation appears probable.[5]

Excited diphenylmethyl and 1-naphthylmethyl radicals are poor hydrogen abstractors, despite the fact that their high energy content would make hydrogen abstraction a very exothermic process. Thus, their lifetimes are essentially the same in benzene, cyclohexane, or 2-propanol. Perhaps most striking is the fact that Bu_3SnH can be used as a solvent, with only minor lifetime reductions; e.g., $Ph_2\dot{C}H^*$ has lifetimes of 255 and 170 ns in benzene and Bu_3SnH, respectively. However, poor hydrogen-abstracting ability is not a property of all excited radicals, but rather one that is common for benzylic species. For example, nitroxides, such as TEMPO, become efficient abstractors upon photoexcitation.[40]

A few recent studies have examined the reactivity of excited carbenes, although their short lifetimes limit the measurements primarily to luminescence techniques which provide little information on the nature of the changes taking place. Table III gives representative rate constants. For diphenylcarbene, the excited triplet state, $^3Ph_2\ddot{C}:^*$, reacts with alcohols at rates comparable with those for the lowest singlet state and 100 times faster than $^3Ph_2\ddot{C}:$. For CCl_4 (where product studies show halogen abstraction), the triplet carbene reactivity is enhanced by a factor of 1000 upon excitation.

Upper Excited States. The previous sections have dealt with the first excited state of selected reaction intermediates. In this section we present examples where the second laser pulse reexcites a triplet state, thereby leading to an upper excited state of the molecule. While our examples deal largely with two-laser experiments, it should be emphasized that these processes can frequently be induced by a single high-intensity laser pulse. Several systems have been identified

Scheme IV
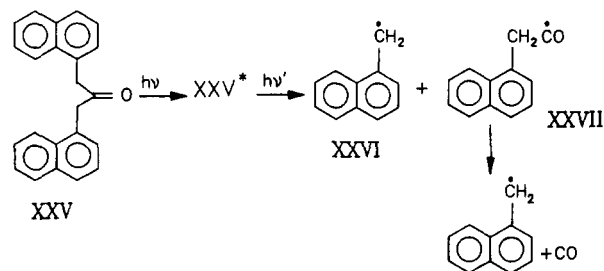
in which excited states have attained high enough local concentrations within the pulse duration to compete efficiently with the ground state for incident photons. In single-pulse experiments it is often difficult to distinguish between singlet and triplet mechanisms; the latter can be studied under controlled conditions by using the two-laser approach.
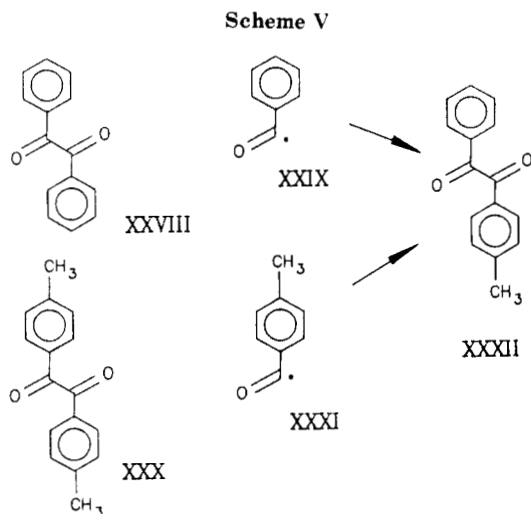
Our work has concentrated on the identification of systems that are inert to conventional one-photon excitation (e.g., UV lamps) but which undergo reaction upon two-photon laser irradiation, i.e., systems in which the low-lying excited states do not have sufficient energy to undergo bond cleavage but which do possess the required energy after reexcitation.

The above statements can be translated into terms of energy requirements. Since many single chemical bonds have bond energies in the 70–100 kcal/mol range, the excited species produced upon one-photon excitation (the triplet in our examples) should store a large fraction of the photon energy and yet stay safely below 70 kcal/mol. Triplet energies around 60 kcal/mol would be ideal. The second photon would then bring the energy well above the threshold for bond cleavage. Many systems, such as benzil, 1,3-di-1-naphthyl-2-propanone (XXV), benzophenone, and dibromoanthracene fulfill these criteria. Triplet reexcitation can lead to different consequences, and in the next few paragraphs we outline the different behaviors that have been observed.

Benzil[43] and XXV[44] both undergo a process referred to as "reluctant" Norrish type I reaction, where the term

(43) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* 1987, *109*, 2179.
(44) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.*, 1987, *109*, 5487.

Scheme V

Figure 5. One (■) and two (□) laser irradiation of a 0.5 mM solution of benzil in benzene. In the two-laser experiment the 308-nm pulse was followed by a 517-nm pulse after 0.75 μs. Insert: Transient spectrum for triplet benzil.
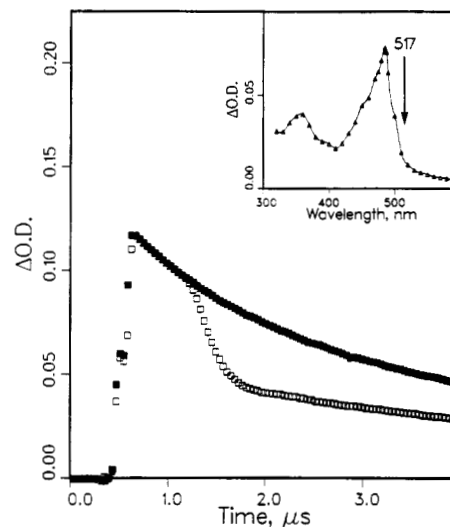
"reluctant" refers to the relatively inert one-photon behavior of these compounds. Scheme IV illustrates the chemistry of XXV. The "one-photon" triplet energy in XXV is localized in the naphthalene moiety and is responsible for the observation that XXV is inert to lamp irradiation at λ > 300 nm.[45] In fact, XXV does undergo some monophotonic cleavage (Φ = 0.002) but this occurs exclusively from the singlet state which is localized on the carbonyl moiety.[44] The behavior of XXV contrasts with that of dibenzyl ketone (where the low-lying triplet is localized in the carbonyl group) which undergoes efficient monophotonic cleavage from the triplet state.[46] Product studies in benzene confirm enhanced yields of 1,2-di-(1-naphthyl)ethane under conditions of two-photon excitation, and transient studies indicate that dye laser excitation of triplet XXV yields the 1-naphthylmethyl radical (λ_{max} = 370 nm). The quantum yield of triplet photocleavage is 0.06 in benzene at room temperature.[44]

Benzil and other α-diketones are known to be inert to conventional one-photon photolysis in deoxygenated non-hydrogen-donating solvents.[47] However, type I fragmentation occurs readily upon laser irradiation. Benzoyl radicals usually undergo self-reaction to yield the parent material, which makes the photocleavage a "transparent" reaction. To probe this mechanism, we have photolyzed mixtures of benzil and 4,4'-dimethylbenzil (XXX) (Scheme V). When a mixture of XXVIII and XXX was irradiated with a lamp, no XXXII could be detected. However, laser photolysis of the same mixture at 308 nm yielded substantial amounts of the cross-product XXXII, indicating that the parent benzils undergo two-photon cleavage.[43] Although the extent of singlet involvement in this reaction is difficult to quantify, it was possible to explore the triplet photocleavage in a controlled two-photon, two-laser experiment. Dye laser excitation of triplet benzil led to extensive photobleaching (Φ = 0.06 in benzene) (Figure 5). In the cross-experiment (Scheme V) we observed a fourfold enhancement of the yield of XXXII compared with the one-laser experiment.[43]
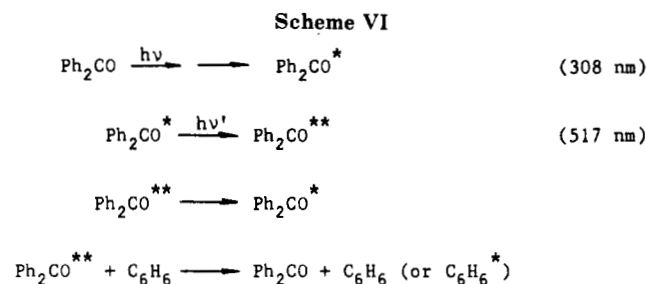
(45) Roof, A. A. M.; van Woerden, H. F.; Cerfontain, H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1546.
(46) Engel, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 6074.
(47) Ledwith, A.; Russell, P. J.; Sutcliffe, L. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1925. Caceres, T.; Encinas, M. V.; Lissi, E. A. *J. Photochem.* **1984**, *27*, 109.

Scheme VI

$$Ph_2CO \xrightarrow{h\nu} \longrightarrow Ph_2CO^* \qquad \text{(308 nm)}$$

$$Ph_2CO^* \xrightarrow{h\nu'} Ph_2CO^{**} \qquad \text{(517 nm)}$$

$$Ph_2CO^{**} \longrightarrow Ph_2CO^*$$

$$Ph_2CO^{**} + C_6H_6 \longrightarrow Ph_2CO + C_6H_6 \text{ (or } C_6H_6^*\text{)}$$

Reluctant Norrish type I processes are currently being examined as potential laser specific photoinitiators which may find applications in polymer chemistry as well as in the areas of photoresists and holographic materials.

The above examples may lead to the erroneous impression that triplet reexcitation systematically leads to cleavage of the weakest bond available. This is not always the case, even when the energy content is well in excess of that required for bond cleavage. For example, reexcitation of benzophenone triplets in benzene with 517-nm dye laser pulses leads to extensive (frequently >50%) irreversible photobleaching; yet, no new products could be detected, in spite of the 25–35 kcal/mol excess over the energy required to cleave the Ph–CO bond.[48] One is forced to conclude that reexcitation of triplet benzophenone provides a radiationless path for ground-state repopulation. A possible explanation for this effect is the quenching of upper excited states by benzene by an energy-transfer mechanism (Scheme VI).[43] A diffusion-controlled quenching mechanism with benzene as solvent would require an upper state (Ph₂CO**) lifetime of 10^{-12}–10^{-11} s to account for the quantum yield of photobleaching of 0.057. Upper excited-state lifetimes of this magnitude are not uncommon. Additional support for this mechanism is provided by the fact that the photobleaching is inefficient in nonaromatic solvents.[48] Upper state energy-transfer mechanisms involving anthracenes have also been postulated.[49]

(48) McGimpsey, W. G.; Scaiano, J. C. *Chem. Phys. Lett.* **1987**, *138*, 13.

Another interesting example is provided by the triplet state of 9,10-dibromoanthracene, which upon dye laser excitation photobleaches with $\Phi \sim 0.04$ to yield its fluorescent singlet state but does not lead to C–Br bond cleavage.[27]

Conclusions. In this Account we have summarized our recent work on two-photon processes. We would like to emphasize that such processes, wanted or unwanted, occur frequently when organic substrates are excited by pulsed laser sources. Their study is not easy under conditions of single-pulse excitation, but their occurrence is not uncommon.

Two-photon processes can provide access to new mechanisms, leading to transformations not accessible by conventional irradiation (e.g., the XVI $\rightarrow$ XX transformation) and to new reactions, such as the reluctant Norrish type I process, that could find wide applications in polymer chemistry. In many cases the lifetimes of excited reaction intermediates are suffi-

ciently long that they can be readily detected by using modern fast techniques (see Table I), and they can and will undergo intermolecular reactions, which frequently differ from from those of the ground-state intermediate. For example, the excited states of free radicals are not "superradicals", but rather they share the electron-transfer and quenching properties of other excited states.

Recently, we have detected two-photon processes in many systems, and a few of those which we have been able to characterize are included in this Account. Many others, including carbonyl oxides, thiocarbonyl ylides, aroyloxy radicals, biradicals, and triplets, await chemical studies that will establish the nature of the photo-transformations responsible for the observable transient phenomena. A basic understanding of the chemistry that underlies the two-photon transformations is essential in the understanding of the transient phenomena observed in these systems.

(49) Liu, R. S. H.; Kellogg, R. E. *J. Am. Chem. Soc.* **1969**, *91*, 250. Liu, R. S. H.; Edman, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 1492.