

The Laser-Drop Technique: A Semipreparative Method for the Study of Multiphotonic Processes

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A excitação por laser de moléculas orgânicas em solução leva, frequentemente, à geração de produtos bastante diferentes dos obtidos usando irradiação de baixa intensidade, como lâmpadas ou luz solar. Os mecanismos responsáveis por essas diferenças podem envolver a decomposição de intermediários de vida curta, tais como radicais livres, cetenas, birradicais, etc. Os mecanismos de reações multifotônicas podem ser estudados usando a técnica de *flash photolysis* com dois lasers, embora esses estudos em geral não produzam quantidades de produto suficientes para sua completa caracterização. A técnica de laser-gota permite estudos semipreparativos voltados para a caracterização dos produtos de reação. Neste método cada pequena gotícula (de alguns μL) é excitada por um único pulso de laser. Neste artigo apresentamos um relato atualizado de nossas pesquisas usando a técnica de laser-gota. Os sistemas químicos examinados incluem radicais difenilmetila e cumiloxila, birradicais, cetenas e fotoenóis. Os resultados da técnica de laser-gota são comparados com os obtidos usando o método de *laser-jet* ou as técnicas de dois lasers, nos casos em que foram pesquisados sistemas similares por essas técnicas.

Laser excitation of organic molecules in solution frequently leads to the generation of products which are quite different from those formed under conditions of low intensity irradiation using lamps or sunlight. The mechanisms that are responsible for these differences may involve the photodecomposition of short lived intermediates such as free radicals, ketenes, biradicals, etc. The mechanisms of multiphotonic reactions can be studied employing two-laser flash photolysis techniques, although these studies normally do not produce enough products to allow their full characterization. The laser-drop technique allows semipreparative studies aimed at the characterization of reaction products. In this method each small droplet (a few μL) is excited by a single laser pulse. This paper is an account of our research to date using the laser-drop technique; the chemical systems examined include the diphenylmethyl radical, cumyloxyl radical, biradicals, ketenes and photoenols. When similar systems have been examined, the results of the laser-drop technique are compared with those obtained using the laser-jet method or two-laser techniques.

Keywords: *laser-drop photolysis, multiphotonic reactions*

Introduction

A number of techniques are now available for the study of multiphoton processes in organic chemistry. These take advantage of the wide availability of reliable high power lasers. The two-laser two-color technique¹ has provided a reliable mechanistic and kinetic tool, widely used during the last decade. The laser-jet technique² has made it possible to obtain products from multiphoton processes in a small preparative scale. The technique is extremely useful, but requires a large investment in laser equipment of a type (cw) which is not usually available in laboratories that routinely perform laser flash photolysis work. The present

article presents an account of the development, implementation and representative results obtained with a new technique, which we have called *laser-drop photolysis* (LDP) and which allows semipreparative experiments using the same type of lasers normally employed in time resolved laser photolysis studies. This technique makes it possible for laboratories already equipped with pulsed lasers to perform small scale preparative work without the need for a major investment in new, dedicated equipment.

The specific systems described herein have appeared in earlier publications on the subject. The reader is referred to these articles for a full description of the experiments and product characterizations.

Description of the experiment

One of our earlier ideas, that one could run a pulsed laser at high frequency and focus it onto a microjet did not prove useful. An excimer laser with 10 ns pulses operated at 100 Hz would irradiate the sample only one millionth of the time. Depending on beam and jet size, only 1-5% of the solution would be irradiated under these extreme conditions³.

The idea of irradiating free falling drops of solution was, while feasible, very impractical. The simplest approach proved to be to excite the drop shortly before it was ready to fall from the tip of a needle. The output pulses from an excimer laser (308 nm, ~6 ns, 60-130 mJ/pulse) were focused onto a drop of solution suspended from a nearly-horizontal syringe needle. A syringe pump delivered the photolysis solution and was set at a flow leading to a spontaneous droplet rate slightly lower than the laser repetition rate. Excitation of droplets causes them to burst, presumably as a result of a shock wave generated within the drop, since thermal changes are not sufficient to induce this effect. Once the drop has been destroyed, a new drop begins to form. Figure 1 shows a schematic representation of the timing of a laser-drop experiment.

Several aspects must be taken into account for the design of an adequate laser-drop cell; i) since the droplets explode upon irradiation, the ejected material must be contained to ensure that the photolysate can be efficiently collected, ii) ablation of quartz is not uncommon under these irradiation conditions⁴ and the drop must be far enough away from the cell window to keep the focal point of the laser from destroying the quartz window, iii) it is usually desirable to keep the photolysis solution under an inert atmosphere to avoid oxygen contamination, and iv) if for some reason there is sufficient oxygen present, the solvent mist may ignite and cause an explosion. It is prudent to have a pressure release point to avoid rupture of the container and possible injury to the experimenter. Figure 2 shows the design for the laser-drop cell built and used for these studies. It must be stressed that there is the possibility for explosion during the course of these experiments; how-

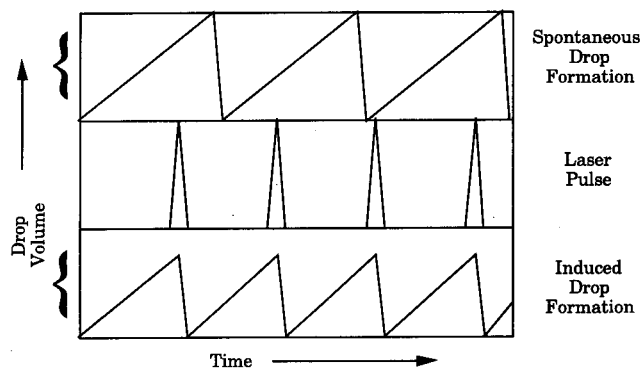


Figure 1. Schematic diagram of the timing sequences for laser-drop irradiations.

ever, provided the experimenter is aware of this and takes the necessary precautions, this technique is no more dangerous than many typical synthetic organic procedures.

Laser-drop and laser-jet photolysis

In order to assess the feasibility of this new method, we examined the laser-drop photochemistry of two systems. The first example deals with diphenylmethyl radicals³ which have been extensively studied by two-laser two-color and related techniques.^{1,5,6} The second example deals with the photoenol produced upon the photolysis of *ortho*-methylbenzophenone.⁷ This system has also been examined by the laser-jet technique⁸ and more recently by pulse radiolysis/LFP.⁹ These systems provide a direct comparison of the results from laser-drop and laser-jet photolysis.

Photochemistry of 1,1-diphenylacetone (1)

Diphenylmethyl radicals (**2**) are readily produced upon the 308 nm photolysis of **1** (see Scheme 1 below). The radical has an extinction coefficient of $88,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 330 nm and $40,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 315 nm.¹⁰ The excited radical **2*** is readily produced in a single laser pulse with an appropriate precursor^{5, 10, 11} and also has a large extinction coefficient ($80,000 \text{ M}^{-1} \text{ cm}^{-1}$ and $24,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 360 and 270 nm, respectively¹⁰). The lifetime of the excited radical in acetonitrile has been reported to be about 260 ns and about 235 ns in several alcohols.^{5, 12}

Ground state **2** is a relatively inert radical and does not readily abstract hydrogen atoms from most solvents, but prefers to undergo radical-radical recombinations in the absence of oxygen. While **2*** shows some increased reactivity towards hydrogen donors such as 1,4-cyclohexadiene and tri-*n*-butyltin hydride⁵, it is a surprisingly poor hydro-

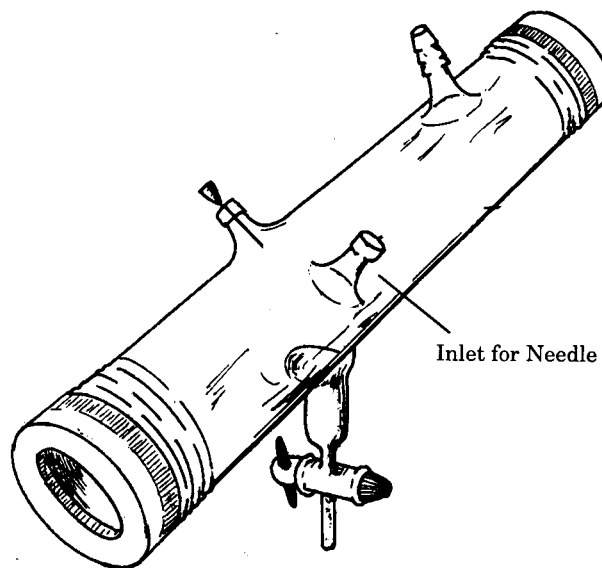
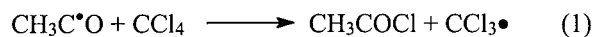


Figure 2. Diagram of the cell employed for laser-drop experiments. The overall length is 12 in. and the cell is equipped with removable quartz windows.

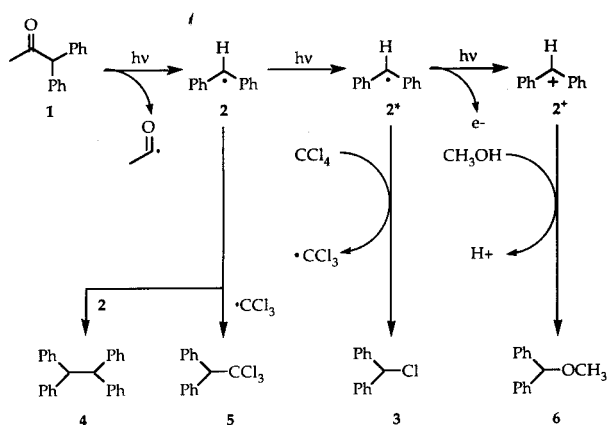
gen abstracting species, even though this reaction would be more exothermic than abstraction of hydrogen by a phenyl radical. The reactivity towards tri-*n*-butyltin hydride is five times less than that of *t*-butyl radicals.⁵ This species can be quenched by oxygen to give singlet oxygen and ground state radicals.¹³ The excited radical also reacts with electron acceptors, leading to the diphenylmethyl cation.¹¹ The reaction of **2*** with halogenated compounds involves electron transfer leading to abstraction of the halogen to produce benzhydryl halide and the corresponding radical^{5, 11} (*vide supra*).

Laser-drop photolysis of a solution containing 10 mM of **1** in carbon tetrachloride shows benzhydryl chloride (**3**) as the main (>98%) reaction product. In contrast, lamp photolysis yields very little **3**, while tetraphenylethane (**4**) and 1,1,1,-trichloro-2,2-diphenylethane (**5**) are now the main products. Product distributions for the irradiation of **1** under lamp and laser-drop conditions are given in Table 1 along with results reported for the laser-jet photolysis of benzhydryl phenyl ketone (**7**).¹⁴

While the acetyl radical products were not quantified, it is evident that **5** results from the combination of **2** with trichloromethyl radicals, which under lamp irradiation would be the expected product of reactions of acetyl radicals with the solvent (Reaction 1).



Recent time resolved infrared spectroscopy work has demonstrated the reactivity of acyl radical towards the C-Cl bond. Ingold and coworkers¹⁵ report a rate constant of $5.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for abstraction of chlorine from carbon tetrachloride by benzoyl radicals. Acetyl radicals should be at least as reactive towards a C-Cl bond as the benzoyl radical. Note that the absence of **5** under laser-jet and laser-drop excitation conditions cannot be due to failure to produce $\text{CCl}_3\cdot$, since excited diphenylmethyl radicals abstract chlorine to provide an additional source of $\text{CCl}_3\cdot$ under these conditions.^{5, 11}



Scheme 1.

Preparative experiments for LDP of **1** in carbon tetrachloride were done by recycling the photolysate four times. Two separate experiments were performed; i) deaerating the photolysate between cycles, and ii) deaerating only before the first cycle. The percent conversions were 57% and 52%, respectively, with product distributions similar to those listed in Table 1. No additional products were detectable.

The effect of drop size on product distribution was also investigated by LDP of CCl_4 solutions of **1**. The flow rate was varied while the laser repetition rate was kept constant. It was found that drop size (5 to 25 μL) had little effect on product distribution, as long as the energy of the laser was kept constant and the drops remained in the same focal region of the laser. Drop size did, however, have a direct effect on the percent conversion, with the smaller drops having the highest conversion. This is not surprising since the drops are always larger than the laser cross section at the focal point. Drops were kept as small as possible while remaining slightly larger than the cross section of the focused laser.

The photolysis products of **1** (10 mM) in methanol again showed a strong dependence on light intensity. Under lamp irradiation, the major product (>98%) is 1,1,2,2-tetraphenylethane (**4**), formed by the combination of radicals **2**, while under laser-drop conditions the ether **6** accounts for 92% of the products. Product distributions for **1** in methanol are given in Table 2. A solution of **1** in methanol- d_1 was also irradiated under laser-drop conditions and analyzed by GC-MS. The $M^+/M^+ + 1$ ratio for the ether **6** was 3.7 as compared to a ratio of 6.4 for the ether produced upon LDP of **1** in undeuterated methanol.

In a recent paper, Adam and Schulte-Oestrich⁶ examined the high intensity photochemistry of benzhydryl

Table 1. Photolysis of diphenylmethyl radical (**2**) precursors in CCl_4 .

Method	Precursor	% Conv.	3	4	5
Rayonet ^a	1	87	10	38	52
Laser-jet ^b	7	22	96	5	—
Laser-drop	1	15	≥ 98	—	—

^a Lamp irradiation at 300 nm.

^b Data from Ref. 6.

Table 2. Photolysis of diphenylmethyl radical precursors in methanol.

Method	Precursor	% Conv.	4	6
Rayonet ^a	1	98	≥ 98	—
Laser-jet ^b	7	27	59	34
Laser-drop	1	19	8	92

^a Lamp irradiation at 300 nm.

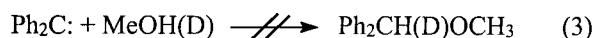
^b Data from ref. 6.

phenyl ketone (Ph_2CHCOPh , **7**) in carbon tetrachloride and in methanol. The process involves the intermediacy of excited electronic states of the diphenylmethyl radical, 2^* . Adam's results⁶ on the laser-jet photolysis of **7** are very similar to those from the laser-drop photolysis of **1** (see Tables 1 and 2). In CCl_4 , the formation of **3** can be readily explained by the reaction of 2^* with the solvent, *i.e.*



It has been reported that Reaction 2 occurs with a rate constant of $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at room temperature, and that the lifetime of 2^* in CCl_4 is less than 5 ns.⁵ It was proposed several years ago that quenching of 2^* by CCl_4 probably involved charge transfer interactions.⁵ Arnold *et al.*¹⁰ have recently established this mechanism by characterizing the corresponding carbocation, Ph_2CH^+ , as an intermediate in the reaction in acetonitrile. In non-polar media (*e.g.* in CCl_4 solvent), geminate recombination of the ions (Ph_2CH^+ and Cl^-) may predominate and account for the high yield of **3** (> 98%).

When the solvent is methanol, the charge transfer mechanism is no longer efficient for 2^* , and its lifetime is 236 ns, a value close to those typically observed in inert solvents.^{5, 16} Under high intensity excitation conditions (laser-jet or laser-drop) a significant yield of diphenylmethyl methyl ether, **6**, was formed (see Table 2). Meisel *et al.*¹⁶ and later Arnold *et al.*¹⁰ showed that 2^* can be further excited to 2^{**} . Meisel¹⁶ suggested that 2^{**} may lose a hydrogen atom to form diphenylcarbene. In this case one would expect the carbene to insert into the O-H bond of methanol to form ether **6**, Reaction 3. However, no deuterium incorporation in **6** was detected under laser-jet⁶ excitation of **7** in a 5% solution of methanol-*d*₁ in benzene. Laser-drop photolysis of **1** in neat methanol-*d*₁ shows some deuterium incorporation, as shown by the change in the $M^+/M^+ + 1$ ratio. However, the incorporation is small and could result from proton exchange of the ether with the deuterated solvent after photolysis. Since the insertion of diphenyl carbene into the O-D bond would result in extensive deuterium incorporation, these results suggest that the ether is formed by the nucleophilic trapping of the cation, 2^+ , by methanol. That this is the case is further supported by Steenken's report on the photoionization of aryl substituted methyl radicals,¹⁷ and by the photoionization of diphenylketyl radicals in polar solvents.¹⁸



Adam was also able to show that the ratio of products **6/3** increased as a function of laser intensity when the laser-jet photolysis of **7** was carried out in a 1:99 mixture of methanol and CCl_4 .⁶ This result indicates that the reaction with methanol to form **6**, requires more photons than the reaction with carbon tetrachloride to form **3**. Thus, different species must be responsible for the different prod-

uct distributions resulting from increasing the light intensity. This experiment, combined with Meisel's observation of irreversible photobleaching of 2^* in methanol, suggests that the formation of **6** results from the successive absorption of three photons. Thus, we find that the photochemistry of **1** under laser-drop conditions parallels that observed by Adam⁶ for **7** under laser-jet conditions. The origin of the products of laser-drop photolysis of **1** is outlined in Scheme 1.

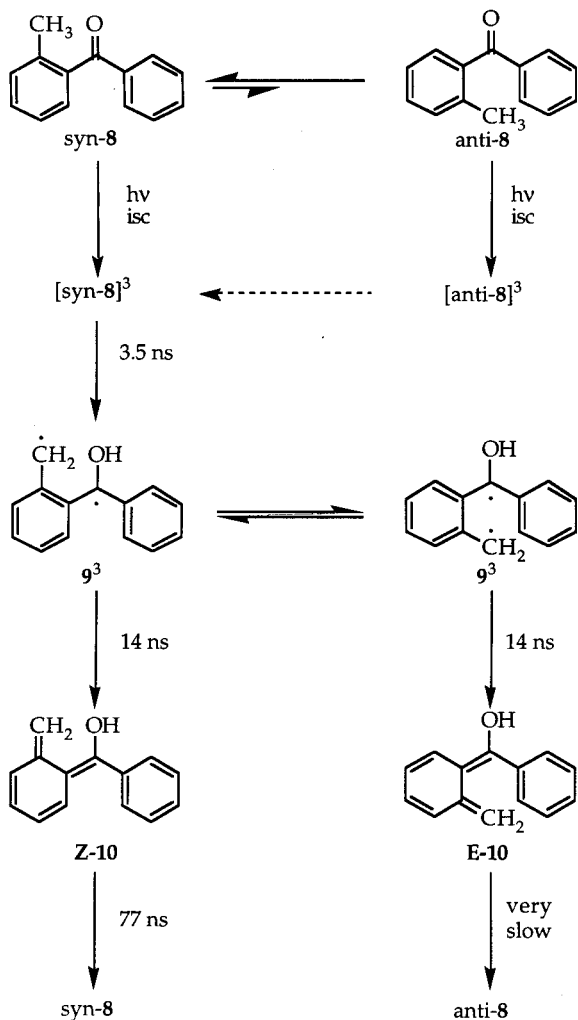
Ether **6** accounted for 92% of the diphenylmethyl radical products under laser-drop irradiation of **1**, compared with 34% reported for the photolysis of **7** under laser-jet conditions (see Table 2). Note that the conversion of the 10 mM solution of starting material is similar for both experiments, suggesting comparable efficiencies for both the laser-drop and laser-jet techniques in producing multiple-photon products. In fact, the conversion to three photon products is much higher in the laser-drop technique, suggesting that this method should be preferred for processes requiring more than two photons. It is also noteworthy that both methods can recycle the photolysate to increase the conversion of starting material. Although our experiments indicate that oxygen contamination is not a problem when recycling (the photolysate is kept under an inert atmosphere), transfer of the photolysate should be done with care to avoid oxygen contamination problems since radicals, triplets, carbenes and other reactive intermediates are often reactive towards oxygen.

Photochemistry of *ortho*-methylbenzophenone (**8**)

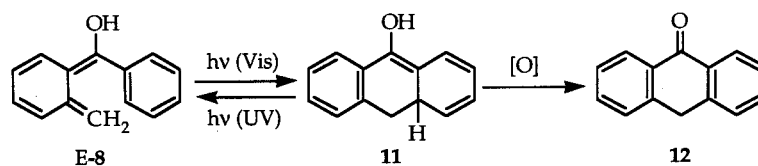
The photoreduction of benzophenone in the presence of readily abstractable hydrogens to give benzopinacol is a well known reaction¹⁹. However, this reaction does not occur if the benzophenone is substituted at the *ortho* position by an alkyl group containing an α -hydrogen. Numerous investigations have been reported on the photochemistry of *ortho*-alkylbenzophenones.^{7,9,20-25} Although early investigations incorrectly assigned many of the transients involved in its photochemistry,^{20,22} it is now well established that the lack of photoreduction products is due to the sequence of reactions outlined in Scheme 2.^{9,23}

As early as 1965, Ullman and Huffman²⁶ reported that broadband irradiation of **8** in oxygenated solutions produced anthrone (**12**) in about a 1% yield. Porter and Tchir²² detected an absorption signal ($\lambda_{\text{max}} = 390 \text{ nm}$) which persisted for hours during the conventional flash photolysis of 2,4-dimethylbenzophenone. This signal was not present when 90% of the photolysis light between 380 and 550 nm was removed. They attributed the long-lived signal to the dihydroanthrone enol **11**, which was formed by the long wavelength photolysis of E-**8** (Scheme 3).

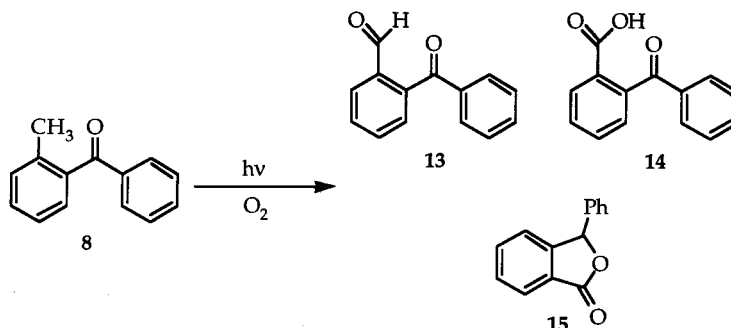
Heindel *et al.*²⁷ showed that irradiation of **8** in benzene under a steady stream of air with a 350 nm Rayonet lamp supplemented by a long wavelength incandescent tungsten



Scheme 2.



Scheme 3.

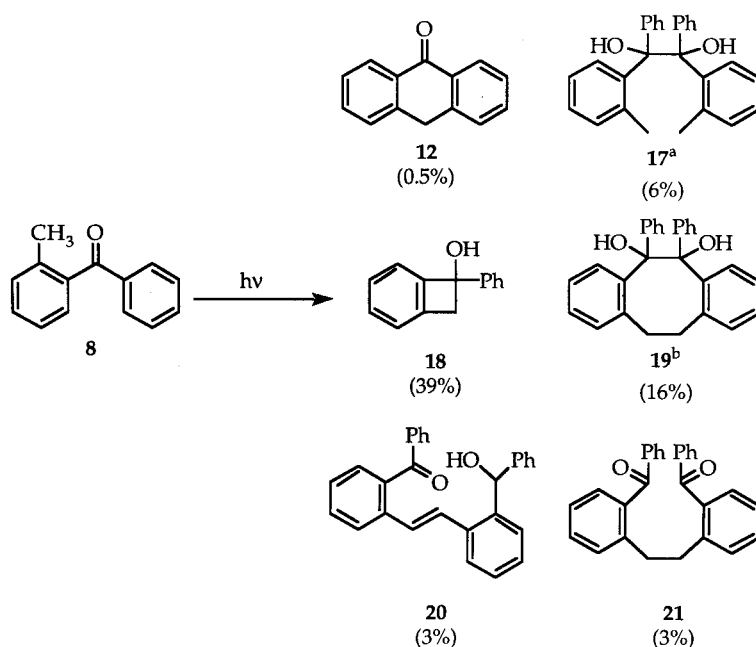


Scheme 4.

lamp produced anthraquinone (**16**) in a 28% yield, along with 2-benzoylbenzaldehyde (**13**), 2-benzoylbenzoic acid (**14**) and 3-phenylphthalide (**15**). Irradiation with 350 nm alone produced only **13**, **14**, and **15** but no anthraquinone (Scheme 4). These authors postulated that the anthrone produced as described by Porter and Tchir²² could be photo-oxidized to produce **16**.

Wilson and coworkers⁸ have recently reexamined the photochemistry of **8** by laser-jet and lamp photolysis. Low intensity irradiation (20 hours, 350 nm Rayonet lamp) of 54 mM deaerated solutions of **8** in benzene led to 89% conversion of the starting material to give a complex mixture of products (see Scheme 5 for products and percent yields). Laser-jet photolysis (argon ion cw laser, 2.85 W, 334 D 364 nm) of 20 mM deaerated solutions of **8** in benzene, also led to a complex mixture of products. The yield of anthrone (**12**) increased from 0.5% under low intensity conditions to 23% under laser-jet conditions (the yields of the other products were not reported). A second laser-jet experiment was done with the crossed beams from two argon ion lasers, one with the UV output mentioned above and a second with 9.0 W output in the 458 to 514 nm range. In this experiment, the yield of anthrone was further enhanced to account for 34% of the products.

In our lab, low-intensity irradiations (Rayonet reactor, 300 nm) of deaerated 1.0 mM solutions of **8** in benzene showed no depletion of starting material after two hours. In contrast, irradiation of an identical solution saturated with oxygen showed 37% conversion after 30 minutes. The three major products were **13**, **14**, and **15**. The distribution of these products varied, with **15** being larger at longer



Scheme 5.

irradiation times, seemingly at the expense of **13**. Anthrone (**12**) was also present, but in much smaller amounts. The highest yield of **12** was ~1.5%. Another three minor products were not identified. The product distributions of a typical photolysis run are given in Table 3.

Laser-drop photolysis (308 nm) of 1.0 mM deaerated solutions of **8** in benzene also showed no product formation. However, 308 nm LDP of oxygen saturated solutions in benzene resulted in ~4% conversion after one cycle and the formation of **12** in a 15% yield, along with **13** and **14**. There was one other major product (detected by HPLC) which could not be identified. No phthalide **15** was detected from laser-drop photolysis. The product distributions for the 308 nm LDP of **8** are given in Table 3.

Although Wilson *et al.*⁸ reported that photolysis of **8** under deaerated conditions in benzene and isopropanol resulted in considerable conversion of starting material, we were unable to detect the loss of starting material during either low intensity irradiations or laser-drop photolysis. We note that the irradiation times reported by Wilson were considerably longer than those employed here. Further, laser-jet photolysis in benzene required 7 cycles to achieve ~30% conversion. The high conversions which we have

been able to achieve during LDP of other substrates, and the long irradiation times reported by Wilson suggests that the efficiency for product formation from the enols is very small.

In contrast, the oxidation of the enol to form benzoylbenzaldehyde (**13**) and benzoylbenzoic acid (**14**) is efficient enough to convert 37% of the starting material. The formation of 3-phenylphthalide (**15**) is most likely a result of the secondary photolysis of **13**. Scaiano *et al.*²⁸ have shown that the photolysis of this compound in benzene forms **15** in high yields. Confirmation of this secondary photolysis mechanism can be found in the LDP of oxygen saturated solutions of **8** in benzene. Under these conditions **15** could not be detected. Since the oxidation of the enol to form **13** would not occur within the duration of the laser pulse, **13** cannot be further photolysed to form **15**.

The lifetime for the triplet biradical which mediates the photoenolization has been reported to be 14 ns⁹ in benzene; thus, the enols **10** would have been formed in significant quantities during the laser pulse to be capable of absorption of a second photon to produce **11**. The 308 nm LDP of **8** shows a definite increase in the anthrone yield when compared to low intensity irradiations. However, it seems that the laser-jet is more efficient for the production of anthrone from the photolysis of **8**. Not only are the yields of anthrone higher in the laser-jet, but the yields reported by Wilson⁸ were for the photolysis of deoxygenated solutions.

Heindel *et al.*²⁷ have shown that the production of anthraquinone during the photolysis of **8** in aerated benzene does not occur in the absence of visible light. Wilson and coworkers⁸ found that the efficiency of anthrone pro-

Table 3. Photolysis of **8** in oxygenated benzene.

Method	% Conv.	13	14	15	12
Rayonet ^a	37	18	32	44	~1
Laser-drop ^b	4	36	33	-	15

^a Lamp irradiation at 300 nm.

^b One cycle irradiation.

duction during the LJP photolysis of **8** was increased by 50% when the visible light from a second laser was also focused on the microjet. These authors suggested that visible light induced the photoisomerization of E-**10** to the dihydroanthrone **11**, but that UV light induces the reverse reaction as shown in Scheme 3. If this was the case, then 308 nm LDP of **8** should not form the anthrone as a product. It is more likely that a pseudo-photostationary state is achieved in the laser-jet and that visible light shifts this pseudo-photostationary state towards **11**. This would explain the production of anthrone in significant yields by 308 nm laser-drop irradiation.

It should be pointed out that the triplet biradical is also sufficiently long lived, and has a suitable absorption at 308 nm to undergo absorption of a second photon during laser-drop photolysis. However, it would not be possible to separate the photochemistry of these two intermediates during laser-drop photolysis.

Laser-drop vs. laser-jet

From the two systems described above, one can see that the efficiencies for these two methods are system dependent. One of the more important factors which governs the efficiency of the method used is the absorption spectrum of the transient intermediate responsible for the absorption of the second (or third) photon. If the transient (generated by the photolysis of the precursor) does not have an appreciable absorption at an available wavelength (frequently 308 nm for LDP and 333, 351, and 364 nm for LJP), the likelihood of it absorbing a photon is small. Figure 3 shows the transient spectra obtained upon 308 nm LFP of **1** and **8**. Upon examination of the two spectra shown in Fig. 3, one can see that the photoenol (**10**) generated upon photolysis of **8** (bottom) has better absorption properties at wavelengths ≥ 350 nm. The argon ion laser used in LJP has lines at 351 and 364 nm and is better suited to excite this transient than 308 nm LDP. The diphenyl methyl radical (**2**) has suitable absorption properties for excitation by either LJP or LDP. Naturally, LDP experiments could also be performed at other wavelengths, such as the 355 nm line from the third harmonic of Nd/YAG lasers.

Selected examples of laser-drop photolysis

In order to implement successfully the laser-drop photolysis technique for the preparation of multiphoton products, the substrates (both the precursor and reactive intermediate) must meet several criteria. These criteria are: i) the precursor molecule must absorb at the wavelength of the photolysis laser; ii) the reactive intermediate must be produced within the duration of the laser pulse in order to absorb a 'second' photon; iii) the reactive intermediate must become a major absorbing species within the laser pulse (again, at the wavelength of the laser used); and iv)

if it is necessary to recycle the photolysate, the products must be photostable at the wavelength of the laser, and they should not become the major absorbing species in the photolysate.

α,α -Disubstituted benzyloxy radicals

Alkoxy radicals are important intermediates in biological,²⁹ atmospheric,^{30,31} and organic^{32,33} chemistry, and have been the subject of numerous studies. The vast majority of studies have centered on the reactions of *t*-butoxy radicals, probably due to the fact that several thermal and photochemical sources for this radical are readily available. Cumyloxy radicals have also received considerable attention because of their involvement in the autoxidation of cumene,³⁴ a major industrial process used in the synthesis of phenol and acetone.

Alkoxy radicals usually decay by one of two pathways, either hydrogen atom abstraction from a suitable donor (Reaction 4) or β -scission to produce a ketone and an alkyl radical (Reaction 5). Reactions 4 and 5 usually represent major pathways in alkoxy radical decay.

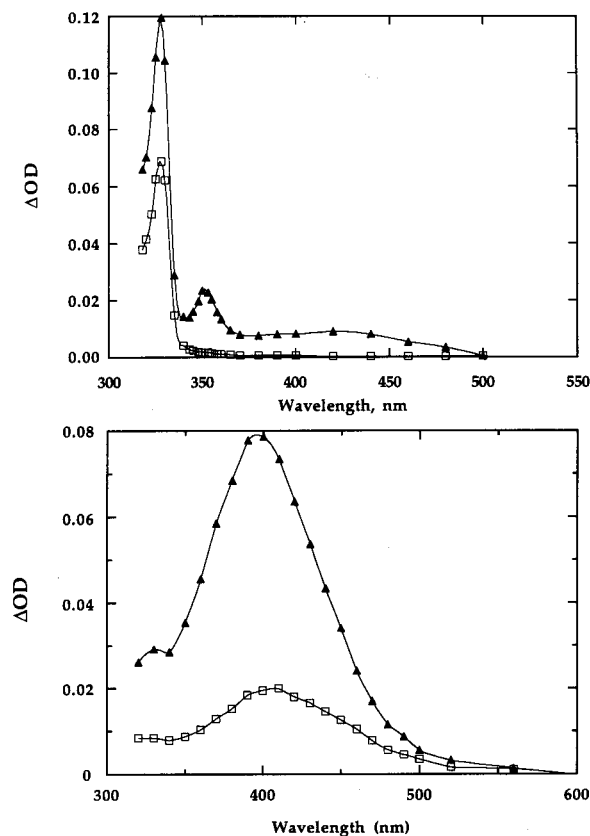
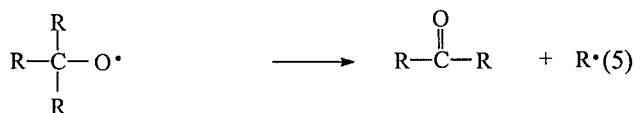


Figure 3. Transient spectra recorded upon 308 nm laser flash photolysis of **1** and **8**, recorded immediately after the laser pulse and about 5 s later. The solvent is acetonitrile for **1** and benzene for **8**.



Recently, Ingold and coworkers³⁵ have reported that cumyloxy radicals (**22**) have a moderate absorption in the visible region of the spectrum, and presented evidence suggesting that this band reflects charge transfer from the aromatic ring to oxygen. When one considers the polar nature of the transition state which has been postulated for the β -scission of alkoxy radicals,³⁶⁻³⁸ it is not unreasonable to attempt a photo-induced β -scission of the cumyloxy radical.

Lamp irradiation (300 nm) of a 10 mM solution of dicumyl peroxide (**23**) in acetonitrile gave acetophenone (**24**) as the only major aromatic product (98%). The β -scission of cumyloxy radical in the absence of readily abstractable hydrogens is well documented.^{39,40} When the photolysis is carried out in methanol as solvent, cumyl alcohol (**25**) becomes the only major aromatic product (> 98%), with only a small amount of acetophenone (**24** < 2%). We attribute this behavior to hydrogen abstraction by **22** from the solvent, as expected from the reactivity observed in laser flash photolysis experiments.⁴¹

Cumyloxy radicals have significant absorption at 308 nm.⁴¹ In contrast, the precursor peroxide (**23**) absorbs very weakly at this wavelength ($\epsilon_{308} \sim 5.7 \text{ M}^{-1} \text{ cm}^{-1}$, corresponding to $A = 0.04$ for a 10 mM solution in a cell with 7 mm optical path). It was possible to use the 308 nm excimer laser for the laser-drop photolysis of **23** by recycling the solution several times until a sufficient concentration of products had accumulated. Five cycles of laser-drop irradiation of 10 mM solutions of **23** in methanol lead to an almost equimolar mixture of **24** and **25**. At this point the conversion was ca. 10%. No other products were detected by HPLC. Table 4 gives the product yields for lamp and laser-drop photolysis of **23**.

Photolysis of dicumyl peroxide (**23**) yields two cumyloxy radicals (**22**), which in the absence of a suitable

Table 4. Photolysis of **23** in acetonitrile and in methanol.

Method	Solvent	% Conv.	24	25
Rayonet ^a	acetonitrile	39	98	—
Rayonet ^a	methanol	48	—	98
Laser-drop ^b	methanol	10	46	54

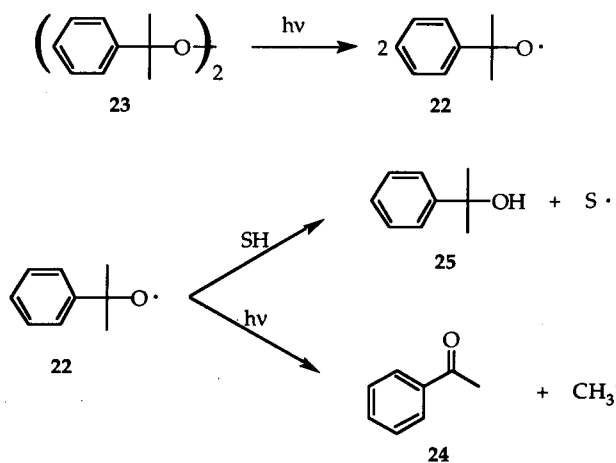
^a Lamp irradiation at 300 nm.

^b Five cycle irradiation.

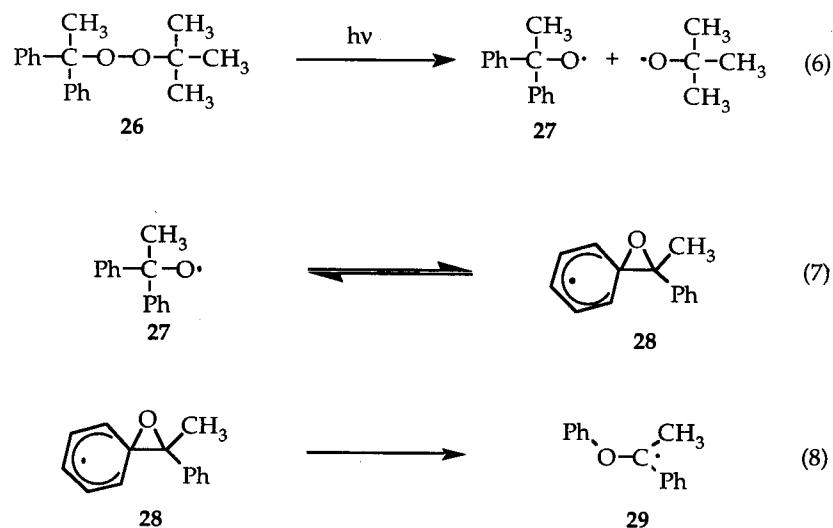
hydrogen donating species, undergo β -scission to give acetophenone, **24**, and methyl radicals. In order to insure that **24** was a product of the cumyloxy radical photodecomposition, it was necessary to suppress the thermal β -scission reaction. This was easily done by using a good hydrogen donating solvent such as methanol. Thus, low-intensity irradiation of **23** in methanol yields cumyl alcohol, **25**, as the major product with only small amounts of **24** (< 2%). In contrast, laser-drop irradiation produces almost equimolar amounts of **24** and **25**. This represents a greater than 23 fold increase in the relative yield of acetophenone under laser-drop conditions, indicating that **22** undergoes a photoinduced β -scission reaction. Scheme 6 shows the main reaction paths taking place in the laser-drop photolysis of dicumyl peroxide in methanol.

Two-laser two-color laser flash photolysis experiments were also attempted to see if bleaching of **22** could be detected spectroscopically.¹ The radical was produced with a pulse from the 248 nm laser and irradiated 250 ns later with either a 308 nm pulse from the excimer laser or a 480 nm pulse from the dye laser; no bleaching could be found in either experiment. Luszyk and coworkers also attempted to bleach this radical with similar results.^{35,42} Failure to detect bleaching of the signal from a second laser does not necessarily imply that a photocleavage cannot occur. Under laser-flash conditions, the absorbance change due to the radicals at the wavelengths of the second lasers is small (0.008 or less), which corresponds to a concentration on the order of about 10 μM . In contrast, under laser-drop conditions the radical concentration may be in the millimolar range. Further, if the excited state of the radicals is very short-lived, it is possible that under laser-drop conditions the radicals are re-excited several times during the laser pulse.

When more than one of the substituent groups in tertiary alkoxy radicals are aryl, the β -scission reaction no longer



Scheme 6.



Scheme 7.

occurs; instead, there is migration of an aryl group to produce the corresponding phenoxy-methyl radical, presumably according to Reactions 7 and 8 in Scheme 7. It is interesting to note that the migration of a phenyl group in triphenylmethoxyl radicals to form phenoxy-diphenylmethyl radicals was the first reported free-radical rearrangement.⁴³ The 1,2-migration of an aryl group in free radicals, known as the neophyl rearrangement, has been extensively studied.⁴⁴⁻⁴⁶ Although it is generally accepted to occur via a bridged-radical intermediate, direct evidence for this type of intermediate is scarce. ESR^{44, 45} and CIDNP⁴⁶ studies for the rearrangement of 2-arylpropyl type radicals failed to detect signals for any bridged-radical intermediates.

Recently, Schuster and coworkers⁴⁷ have reported the detection of an intermediate with λ_{max} 535 nm and a lifetime of ~310 ns in acetonitrile upon 266 nm LFP of 1,1-diphenylethyl-*t*-butyl peroxide, (**26**), at room temperature. These authors assigned this intermediate to the bridged radical **28**. This assignment was based upon the similarity to the absorption of the spiro[2.5]octadienyl radical reported by Scaiano and coworkers,⁴⁸ and the fact that *no known alkoxy radicals possess absorptions in the visible region of the spectrum*.⁴⁷ We have recently shown that the alkoxy radical **27** is a better assignment for the visible absorption produced upon LFP of **26**.⁴⁹ Avila *et al.*⁴² have also reached the same conclusion.

Lamp photolysis (300 nm, < 20 min.) of deaerated 10 mM solutions of **26** in acetonitrile leads to dimer **30** (formed by the recombination of radicals **29**) as the major product. At conversions below ~10%, no acetophenone or benzophenone (products from β -scission) were detected. Under prolonged irradiation (12 h, complete consumption of starting material) the reaction mixture becomes quite complex, and a significant amount of acetophenone is

formed. This is probably due to oxygen contamination, since Ingold⁵⁰ has shown that acetophenone, phenol and *p*-benzoquinone are formed by a complex mechanism when oxygen is present. Benzophenone is not formed at all under lamp irradiation. Further, no acetophenone or benzophenone was produced when peroxide **26** was decomposed thermally at 169 °C.

Like the cumyloxyl radical, 1,1-diphenylethoxyl radicals also have significant absorption at 308 nm, while the precursor peroxide **26** absorbs only weakly, although significantly more than dicumyl peroxide **22** (ϵ_{308} ~20 M⁻¹ cm⁻¹, corresponding to $A = 0.14$ for a 10 mM solution in a cell with 7 mm optical path); thus it was not necessary to recycle the photolysate from LDP in order to obtain ~7% conversion. Laser-drop photolysis of deaerated 10 mM solutions of **26** in acetonitrile (under nitrogen) leads to the formation of acetophenone (**24**) and benzophenone (**31**) in a 1-to-0.8 ratio. No other products were detected by HPLC. Table 5 gives the product yields for lamp and laser-drop photolysis of **26**.

The laser-drop experiments show a remarkable change in the chemistry of **27**. Low intensity photolysis of **26** gives only the dimers **30** (meso and *d,l*) from the recombination of the rearranged radicals **29**. When the photolysis is carried out under laser-drop conditions, these dimers are no longer formed, leading to acetophenone (**24**) and benzophenone (**31**) instead. These results suggest that the photoinduced

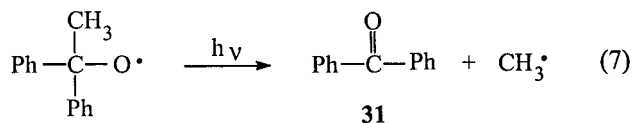
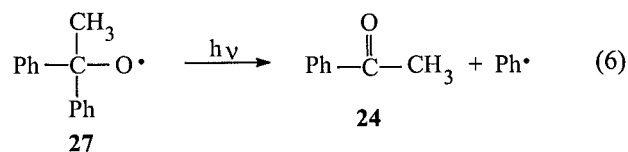
Table 5. Photolysis of **26** in acetonitrile.

Method	% Conv.	24	31	30
Rayonet ^a	10	—	—	~100
Laser-drop ^b	7	56	44	—

^a Lamp irradiation at 300 nm.

^b One cycle irradiation.

β -scission reactions (Reactions 6 and 7) take place under laser-drop conditions.



It is interesting that the phenyl migration is completely suppressed during laser-drop photolysis of **27**. This suggests that the geometry for the excited radical (either **27*** or **28***) is such that it is allowed to cross over to the reaction surface for β -scission, but cannot cross over to the reaction surface which leads to phenyl migration. Of course, it is also possible that the reaction proceeds entirely on the excited state surface. While we cannot rule this out, it would still require that the geometry for the excited radical be such that it is committed to proceed to β -scission rather than phenyl migration. Since the geometry of the excited species responsible for the ketone products must be very similar to the transition state geometry for β -scission of radical **27**, it is likely that this is the radical photolyzed during laser-drop photolysis.

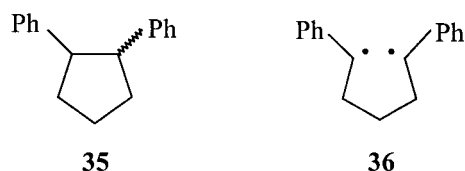
Laser-drop photolysis of the two peroxides (**23** and **26**) show surprising selectivities for the fragmentation reactions of the excited radicals. In the case of cumyloxyl radical, the fragmentation gives only the methyl radical from both the excited and ground states. For 1,1-diphenylethoxyl radical there is little selectivity between the two β -scission reactions from the excited radical; however, the phenyl migration, which is the sole reaction pathway for the ground state radical, is not a competitive process from the excited radical. Reactions 10 and 11 provide a good example where high-intensity laser photochemistry leads to new products, distinct from those obtained under conditions of lamp irradiation.

Hypervalent iodine radicals

Divalent iodine radicals have long been proposed as intermediates in the arylation of nucleophiles by diaryliodonium cations.⁵¹⁻⁵³ There has been some support for such hypervalent halogen radicals,⁵⁴⁻⁵⁷ but direct evidence for these species cannot be found in the literature. Hypervalent sulfur radicals are well known in the literature.^{58,59} In fact, Martin and Perkins⁶⁰ have shown that some sulfuranyl radicals are in equilibrium with their dimers.

We have recently shown that the spectrum and reactivity of the intermediate obtained upon laser flash photolysis of 1,5-diiodo-1,5-diphenylpentane (**32**) is not consistent with the expected spectroscopic properties of radical **33** expected from C-I bond homolysis.⁶¹ We have prepared the intermediacy of the hypervalent iodine radical **34** to account for the laser photolysis results (see Scheme 8).

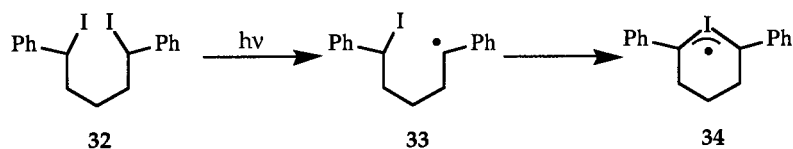
Under conditions of monophotonic excitation **34** decays to typical carbonation disproportionation products. However, under LDP conditions **34** undergoes photoinduced cleavage to produce a mixture of isomers of 1,2-diphenylcyclopentane (**35**). This product is consistent with the formation of biradical **36** via iodine ejection from **34**.



In contrast, **35** could not be detected in low intensity irradiations of **32**. Thus, **32** provides another example where LDP allows the semipreparative study of multiphoton processes leading to very different products compared with the case of low intensity irradiations.

Conclusion

The laser-drop technique provides a versatile tool for the study of multiphoton processes in a semipreparative scale, adequate for full product characterization. In laboratories which routinely perform time resolved laser photolysis work, the LDP technique can be implemented at a minimum cost, since the same laser equipment can be



Scheme 8.

utilized. In numerous systems the products of multiphoton processes are quite different from those resulting from low intensity irradiation.

The laser-jet and laser-drop techniques thus provide novel approaches in the study of high intensity photochemistry; both methods have comparable capabilities and the selection of one method is best based on the availability of continuous (laser-jet) or pulsed (laser-drop) lasers at a given location.

Acknowledgments

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References

1. J.C. Scaiano, L.J. Johnston, W.G. McGimpsey and D. Weir, *Acc. Chem. Res.* **21**, 22 (1988).
2. R.M. Wilson, W. Adam and R. Schulte-Oestrich, *The Spectrum* **4**, 8 (1991).
3. J.T. Banks, J.C. Scaiano, W. Adam and R. Schulte-Oestrich, *J. Am. Chem. Soc.* **115**, (1993).
4. J. Ihlemann, *Appl. Surf. Sci.* **54**, 193 (1992).
5. J.C. Scaiano, M. Tanner and D. Weir, *J. Am. Chem. Soc.* **107**, 4396 (1985).
6. A. Adam and R. Schulte-Oestrich, *J. Am. Chem. Soc.* **114**, 6031 (1992).
7. R. Haag, J. Wirz and P.J. Wagner, *Helv. Chim. Acta* **60**, 2595 (1977).
8. R.M. Wilson, K. Hanneman, K. Peters and E.M. Peters, *J. Am. Chem. Soc.* **109**, 4741 (1987).
9. A. Ishida, K. Yamamoto and S. Takamuku, *Bull. Chem. Soc. Jpn.* **65**, 3186 (1992).
10. B.R. Arnold, J.C. Scaiano and W.G. McGimpsey, *J. Am. Chem. Soc.* **114**, 9978 (1992).
11. B.R. Arnold and J.C. Scaiano, *Macromolecules* **25**, 1582 (1992).
12. A. Bromberg, K.H. Schmidt and D. Meisel, *J. Am. Chem. Soc.* **106**, 3056 (1984).
13. B.R. Arnold and J.C. Scaiano, *Unpublished Results*. (1993).
14. W. Adam and R. Schulte-Oestrich, *J. Am. Chem. Soc.* **115**, 3455 (1993).
15. A.G. Neville, C.E. Brown, D.M. Rayner, J. Lusztyk and K.U. Ingold, *J. Am. Chem. Soc.* **113**, 1869 (1991).
16. A. Bromberg, K.H. Schmidt and D. Meisel, *J. Am. Chem. Soc.* **107**, 83 (1985).
17. J.L. Faria and S. Steenken, *J. Am. Chem. Soc.* **112**, 1277 (1990).
18. R.W. Redmond, J.C. Scaiano and L.J. Johnston, *J. Am. Chem. Soc.* **112**, 398 (1990).
19. J.C. Scaiano, *J. Photochem.* **2**, 81 (1973/74).
20. E.F. Zwicker, L.I. Grossweiner and N.C. Yang, *J. Am. Chem. Soc.* **85**, 2671 (1963).
21. N.C. Yang and C. Rivas, *J. Am. Chem. Soc.* **83**, 2213 (1961).
22. G. Porter and M.R. Topp, *Proc. R. Soc. London, Ser. A* **315**, 173 (1970).
23. P.K. Das and J.C. Scaiano, *J. Photochem.* **12**, 85 (1980).
24. P.K. Das, M.V. Encinas, R.D. Small Jr. and J.C. Scaiano, *J. Am. Chem. Soc.* **101**, 6965 (1979).
25. T. Nakayama, K. Hamanoue, T. Hidaka, M. Okamoto and H.J. Teranishi, *J. Photochem.* **24**, 71 (1984).
26. E.F. Ullman and K.R. Huffman, *Tetrahedron Lett.* 1863 (1965).
27. N.D. Heindel, J. Molnar and M. Pfau, *J. Chem. Soc., Chem. Commun.* 1373 (1970).
28. J.C. Netto-Ferreira and J.C. Scaiano, *Can. J. Chem.* **71**, 1209 (1993).
29. W.A. Pryor, *Free Radicals in Biology*, (Academic Press, New York, 1976).
30. W.P.L. Carter, K.R. Darnall, A.C. Lloyd, A.M. Winer and J.N. Pitts Jr., *Chem. Phys. Lett.* **42**, 22 (1976).
31. J.N. Pitts and B.J. Finlayson, *Angew. Chem., Int. Ed. Engl.* **14**, 1 (1975).
32. K.U. Ingold, *Pure Appl. Chem.* **15**, 49 (1967).
33. C. Walling, *Pure Appl. Chem.* **15**, 69 (1967).
34. J.A. Howard, J.E. Bennett and G. Brunton, *Can. J. Chem.* **59**, 2253 (1981).
35. D.V. Avila, J. Lusztyk and U. Ingold, *J. Am. Chem. Soc.* **114**, 6576 (1992).
36. C. Walling and A. Padwa, *J. Am. Chem. Soc.* **85**, 1593 (1963).
37. C. Walling and P.J. Wagner, *J. Am. Chem. Soc.* **86**, 3368 (1964).
38. D.V. Avila, C.E. Brown, K.U. Ingold and J. Lusztyk, *J. Am. Chem. Soc.* **115**, 466 (1993).
39. A. Baigne, J.A. Howard, J.C. Scaiano and L.C. Stewart, *J. Am. Chem. Soc.* **105**, 6120 (1983).
40. A.G. Neville, C.E. Brown, D.M. Rayner, J. Lusztyk and K.U. Ingold, *J. Am. Chem. Soc.* **111**, 9269 (1989).
41. J.T. Banks and J.C. Scaiano, *J. Am. Chem. Soc.* **115**, 6409 (1993).
42. D.V. Avila, K.U. Ingold, A.A. DiNardo, F. Zerbetto, M.Z. Zgierski and J. Lusztyk, *J. Am. Chem. Soc.* submitted for publication (1994).
43. H. Weiland, *Chem. Ber.* **44**, 2250 (1911).
44. B. Maillard and K.U. Ingold, *J. Am. Chem. Soc.* **98**, 1224 (1976).
45. J.K. Kochi and P.J. Krusic, *J. Am. Chem. Soc.* **91**, 3940 (1969).
46. P.B. Shevlin and H.J. Hansen, *J. Org. Chem.* **42**, 3011 (1977).
47. D.E. Falvey, B.S. Khambatta and G.B. Schuster, *J. Chem. Phys.* **94**, 1056 (1990).
48. A. Effio, D. Griller, K.U. Ingold, J.C. Scaiano and S.J. Sheng, *J. Am. Chem. Soc.* **102**, 6063 (1980).

49. J.T. Banks and J.C. Scaiano, *J. Phys. Chem.* **99**, 3527 (1995).
50. J.A. Howard and K.U. Ingold, *Can. J. Chem.* **47**, 3796 (1969).
51. J.F. Bunnett and C.C. Wamser, *J. Am. Chem. Soc.* **88**, 5534 (1966).
52. D.L. Brydon and J.I. Cadogan, *J. Chem. Soc. C* 819 (1968).
53. D.L. Brydon and J.I. Cadogan, *J. Chem. Soc., Chem. Commun.* 744 (1966).
54. W. Thaler, *J. Am. Chem. Soc.* **85**, 2607 (1963).
55. K.J. Shea and P.S. Skell, *J. Am. Chem. Soc.* **95**, 283 (1973).
56. D.D. Tanner, D.W. Reed and B.P. Setiloane, *J. Am. Chem. Soc.* **104**, 3917 (1982).
57. R.J. Devoe, M.R.V. Sahyun, E. Schmidt, N. Serpone and S.D.K., *Can. J. Chem.* **66**, 319 (1988).
58. C.W. Perkins, J.C. Martin, A.J. Arduengo, W. Lau, A. Alegria and J.K. Kochi, *J. Am. Chem. Soc.* **102**, 7753 (1980).
59. C.W. Perkins, R.B. Clarkson and J.C. Martin, *J. Am. Chem. Soc.* **108**, 3206 (1986).
60. C.W. Perkins and J.C. Martin, *J. Am. Chem. Soc.* **108**, 3211 (1986).
61. J.T. Banks, H. Garcia, M.A. Miranda, J. Perez-Prieto and J.C. Scaiano, *J. Am. Chem. Soc.* in press (1995).