of reaction are CF_3NF^- and $(CF_3)_2N^-$. $CF_2{=}N^-$ is consistently defeated as a nucleophile, but FCN can be used as an electrophilic substrate with a suitably nucleophilic anion. The list of imines that have been successfully attacked by CF_3NF^- includes the $CF_2{=}NX$ series (X = F, Cl, Br)[4,18,29] and $CF_3N{=}CF_2$, but other qualified substrate imines should behave similarly.

Alkali metal fluoride promoted reactions of the other *N*-halodifluoromethylenimines, $CF_2{=}NX$ (X = Cl, Br), offer little evidence of nucleophilic anions like CF_3NF^-. Neither the CF_3NCl^- anion near the CF_3NBr^- anion, both far less stable over the metal fluoride surface, have reacted nucleophilically with any of the substrates that we have examined.[18]

In summary, the competitive reactions of the perfluorinated imines, $CF_2{=}NF$ and $CF_3N{=}CF_2$, and FCN in the presence of KF and CsF generate new compounds that include fluorinated *N*-cyano compounds and a stable symmetric diaziridine. These reactions establish a relative order of reactivity for these substrates with alkali metal fluoride and the corresponding order of nucleophilicity for the related anions. Some derivatives of the *N*-cyano compounds, including two *N*,*N*-dichloramines and an *N*-bromimine, have been synthesized.

Acknowledgment. The support of the U.S. Army Research Office and the National Science Foundation is gratefully acknowledged.

Registry No. FCN, 1495-50-7; $CF_3N{=}CF_2$, 371-71-1; $(CF_3)_2NCN$, 54657-79-3; $(CF_3)_2NCF{=}NCF_3$, 686-39-5; $CF_3\overline{NCF_2N}CF_3$, 123837-30-9; $CF_3N(F)CF{=}NCF_3$, 666-95-5; $(CF_3)_2NCF_2NCl_2$, 123837-31-0; $CF_3N(F)CF_2NCl_2$, 123837-32-1; $(CF_3)_2NCF_2NF_2$, 123837-33-2; $(CF_3)_2NCF{=}NBr$, 123837-34-3; $CF_2{=}NF$, 338-66-9; $CF_3N(F)CN$, 123837-35-4.

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(29) Bauknight, C. W., Jr.; DesMarteau, D. D. *J. Org. Chem.* **1988**, *53*, 4443.

The Mechanism of Formation of *m*-Xylylene Type Biradicals Produced by Photolysis of Polymethyl Benzenes or Dihalomethyl Benzenes

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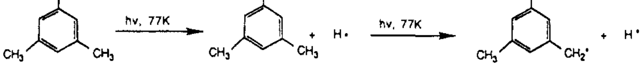
Abstract: The mechanism of formation of the mesitylylene biradical (**3**) produced by short-wavelength photolysis of matrix-isolated mesitylene (**1**) has been investigated. The data rule out a mechanism involving the sequential formation of the biradical **3** via photolysis of the *m*-methylbenzyl radical **2**. The data are most consistent with a mechanism in which the nascent H atom formed by initial scission of a benzylic carbon-hydrogen bond partitions between reaction with the matrix (MH) and abstraction from the *m*-methylbenzyl radical (**2**). The monoradical is produced by photolysis of the triplet state of mesitylene with 249-, 337-, or 405-nm excitation. Laser-induced fluorescence (LIF) experiments using a dihalide precursor produces the emission spectrum of *m*-xylylene. This is the first ambient temperature spectroscopic detection of *m*-xylylene.

The short-wavelength photolysis of matrix-isolated *m*-dimethylbenzene derivatives produces a mixture of persistent mono- and biradicals. These fragments are produced by the dissociation of the C–H bonds of one or two methyl groups of the parent molecule. Both the mono- and biradicals have been detected by their fluorescence spectra in a rigid matrix.[1]

Several years ago, Albrecht and co-workers[2] studied the photochemically induced benzyl C–H bond scission reactions of durene, which produced the duryl monoradical. Upon studying the yield of duryl radical as a function of the radiation intensity, it was concluded that the formation of duryl radical changed from a two-photon to a one-photon process upon raising the photon energy from 4.51 eV (275 nm) to 4.66 eV (252 nm). Such studies have never been extended to the biradicals produced from methylated benzenes, where the key mechanistic question is whether the biradical is formed directly from the parent molecule or by a stepwise mechanism involving secondary photolysis of a *m*-methylbenzyl monoradical.

The aim of the present work is to determine the mechanism of formation of *m*-xylylene type biradicals. We have recently reported[3] that *m*-xylylene can be prepared by photolysis of α,α'-dichloro-*m*-xylene in addition to the original aromatic hydrocarbon precursor. Our previous studies have shown that the biradical derived from mesitylene (1,3,5-trimethylbenzene) is more easily detected than that derived from *m*-xylene. Herein we propose an explanation of this observation and a mechanism for the formation of *m*-xylylene type biradicals produced by photolysis of matrix-isolated mesitylene and α,α'-dichloro-*m*-xylene.

Scheme I



1 2 3

Results and Discussion

Methylbenzene Precursors. The 254-nm photolysis of mesitylene in low-temperature matrices (77 K) produces 3,5-dimethylbenzyl monoradical and the mesitylylene (3-methyl-*m*-xylylene) biradical whose fluorescence spectra originate around 487 and 452 nm, respectively. Since both species are always

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[†] The Ohio State University.

[‡] CNRS.

(1) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400.

(2) Schwartz, F. P.; Albrecht, A. C. *Chem. Phys. Lett.* **1971**, *9*, 163.

(3) Haider, K. W.; Platz, M. S.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318, 1988.

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Scheme II

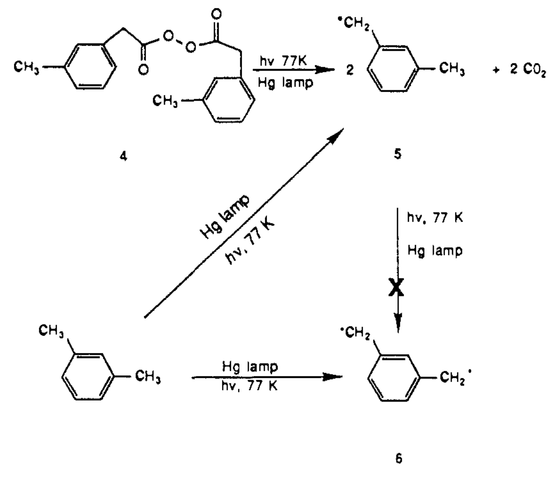

Table I. Relative Ratios of Biradical/Monoradical (**3**/**2**) Fluorescence Intensities Produced from Photolysis of Matrix-Isolated Mesitylene, as a Function of Light Intensity[a]

sample	light intensity, %	3/2
mesitylene (1.6×10^{-2} M)	100	0.40
mesitylene (1.6×10^{-2} M)	60	0.42
mesitylene (1.6×10^{-2} M)	29	0.43
mesitylene (1.6×10^{-2} M)	9	0.45
mesitylene (3.0×10^{-3} M)	100	0.36
mesitylene (3.0×10^{-3} M)	9	0.42

[a] Samples were photolyzed at 77 K in glassy 3-methylpentane with the 249-nm line of the Lumonics excimer laser. The ratio was determined by monitoring the intensity of the fluorescence emission at the maxima for both the biradical (452 nm) and the monoradical (487 nm). The excitation wavelength was 296 nm throughout. The light intensity was modulated by means of neutral density filters whose absorption properties were measured before and after laser photolysis.

simultaneously detected in the same sample, one might imagine a stepwise mechanism in which the photolysis of the parent molecule produces a monoradical which is subsequently photolyzed to form a *m*-xylylene biradical (Scheme I).

In order to test this mechanism, we have prepared the monoradical from an independent precursor, *m*-tolylacetyl peroxide (**4**). An extensive photolysis of the latter molecule in glassy 3-methylpentane at 77 K with the unfiltered light of a medium pressure mercury arc lamp produces 3-methylbenzyl monoradical which is easily detected by its fluorescence (Scheme II).

A subsequent photolysis of this trapped monoradical with 254-nm radiation does not reveal any fluorescence attributed to *m*-xylylene, whereas this biradical is easily detected under identical photolysis conditions when *m*-xylene is the precursor. This result is inconsistent with the stepwise mechanism of biradical formation described previously.

In addition, we have found that the relative yield of mono- and biradicals produced by photolysis of matrix-isolated mesitylene is independent of light intensity (see Table I) and photolysis times (see Figure 1). These experiments demonstrate that the mono- and biradicals are each formed by processes involving the same number of photons.

The Berson Mechanism. Another mechanism was suggested to us by Berson[4] in which the nascent hydrogen atom produced by photochemical scission of *m*-xylene or mesitylene partitions between reaction with the matrix (MH) or reaction with the monoradical to produce the biradical (Scheme III).

Reaction of a hydrogen atom with **2** or MH is certainly exothermic[5] and we assume can proceed rapidly at 77 K by quantum mechanical tunneling[6] or perhaps even by thermal activation. The Berson mechanism predicts that decreasing the H-atom-donating ability of the matrix will increase the yield of biradical relative to monoradical. This expectation is borne out in Table II where the ratio of biradical/monoradical (**3**/**2**) is shown to be larger in hydrocarbon matrices than in methanol. One could argue that this is a consequence of different matrix-packing arrangements.[7] However, perdeuteration of the matrix should not distort the packing of mesitylene within the host significantly. Furthermore, there should be large isotope effects on the reaction of hydrogen atoms with the glass.[6] In fact a dramatic increase in the ratio of biradical to monoradical was observed upon perdeuteration of either the methanol or the *n*-hexane host matrices (see Table II). Although significant, the isotope effect is still much less than

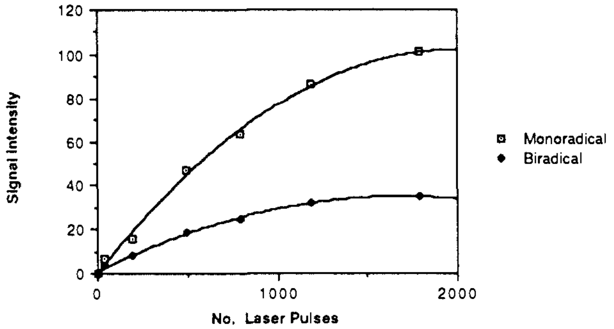

Figure 1. The growth of monoradical **2** and biradical **3** produced from mesitylene as a function of photolysis time. Photolyses were carried out at 77 K using a 249-nm excimer laser with a pulse rate of ~5 Hz. The monoradical and biradical were monitored by their fluorescence emission at 487 and 452 nm, respectively. The excitation wavelength was 296 nm.

Scheme III

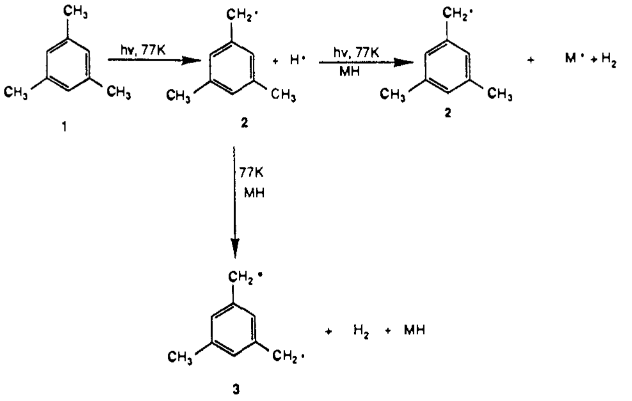

Table II. Relative Ratios of Biradical/Monoradical (**3**/**2**) Fluorescence Intensities Produced from Photolysis of Matrix-Isolated Mesitylene, as a Function of Matrix[a]

sample	matrix	3/2
mesitylene (3.0×10^{-3} M)	3-methylpentane	0.42
mesitylene (4.7×10^{-3} M)	CH_3OH	0.24
mesitylene (4.7×10^{-3} M)	CD_3OD	0.32
mesitylene (5.0×10^{-3} M)	*n*-hexane	0.54
mesitylene (5.0×10^{-3} M)	*n*-hexane-d_{14}	1.26
mesitylene (5.0×10^{-3} M)	methylcyclohexane	0.69

[a] Samples were photolyzed at 77 K with the 249-nm line of a Lumonics excimer laser. The ratio was determined by monitoring the intensity of the fluorescence emission at the maxima of both the biradical (452 nm) and the monoradical (487 nm). The excitation wavelength was 296 nm throughout.

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(4) Berson, J. A., Dept. of. Chemistry, Yale University. Personal communication.

(5) Benson, S. W. *Thermochemical Kinetics*; John Wiley and Sons: New York, 1968.

(6) (a) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; John Wiley and Sons: New York, 1980. (b) Sprague, E. D. *J. Phys. Chem.* **1973**, *77*, 2066. (c) Weiss, M. A.; Willard, J. E. *J. Phys. Chem.* **1975**, *79*, 783. (d) Hudson, R. L.; Shiotani, R. M.; Williams, F. *Chem. Phys. Lett.* **1977**, *48*, 193.

(7) (a) Sprague, E. D. *J. Phys. Chem.* **1973**, *77*, 2066. (b) Neiss, M. A.; Willard, J. E. *J. Phys. Chem.* **1972**, *76*, 546. (c) Siebrand, W.; Wildman, T. A. *Acc. Chem. Res.* **1986**, *19*, 238.

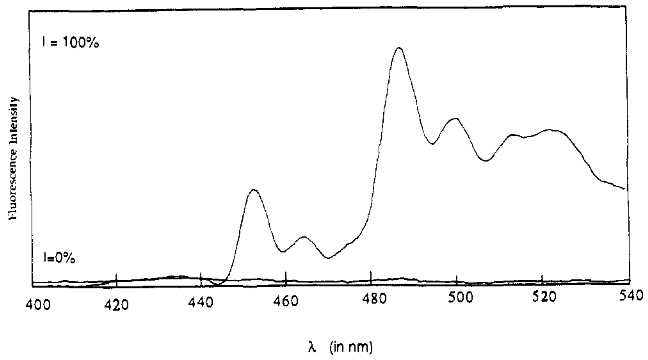

Figure 2. Fluorescence emission spectra recorded at 77 K of the 3,5-dimethylbenzyl monoradical **2** (487, 498 nm) and mesitylylene biradical **3** (452, 463 nm). The spectrum was produced by excimer laser irradiation of mesitylene (5 × 10^{-3} M) in glassy 3-methylpentane at 77 K. The excitation wavelength was 296 nm (upper trace; 50 pulses, 249 nm, 5 Hz) (Lower trace; 50 pulses, 249 nm, 0.05 Hz).

predicted at 77 K for a tunneling or even for a classical reaction.[6] This demonstrates that very few of the nascent hydrogen atoms are generated on a trajectory which allows them to partition between reaction with a *m*-methyl group or a matrix CH(D) bond.

Finally, we note that the Berson mechanism easily explains the increased yield of biradical from mesitylene relative to that derived from *m*-xylene, as a consequence of the increased number of target methyl groups in the former precursor.

Variation of the Laser Pulse Repetition Rate. Since the biradical is formed by a thermal reaction of a hydrogen atom with a matrix-isolated monoradical, the remaining question is the mechanism of formation of the mesityl monoradical. As previously mentioned, Albrecht[2] has reported that the photochemical conversion of durene into duryl radical at 77 K is biphotonic with 275-nm radiation but can be achieved monophotonically with 252-nm excitation. We will demonstrate that photolysis of durene and mesitylene at 249 nm and (presumably at 252 nm) is a biphotonic process.

Excitation of mesitylene in glassy 3-methylpentane at 77 K with a single pulse of an excimer laser at 249 nm produces the guest triplet state via the first excited singlet state. The mesitylene phosphorescence is clearly visible to the unaided eye and persists for several seconds after the photolysis is terminated. When the glass containing mesitylene is subjected to 50 rapid laser pulses (5 Hz) at 77 K, relatively large amounts of mono- and biradicals are produced, as shown by their fluorescence spectra displayed in Figure 2. Under these conditions, mesitylene in both the singlet ground state and in its lowest excited triplet state is irradiated with the 249-nm light.

In contrast, when mesitylene is irradiated with 50 laser pulses which are spaced far apart in time (0.05 Hz) so as to ensure complete decay of the triplet state of the hydrocarbon prior to the next pulse, the yield of mono- and biradical decreases by greater than 10-fold as shown in Figure 2. Under these conditions only the ground state of mesitylene can be irradiated with the 249-nm light. Similar results were obtained with durene. This experiment demonstrates that two photons of 249-nm radiation are required to produce the mono- and biradicals and that the second photon is absorbed by a long-lived species. The most reasonable assignment of this species is the triplet state of the parent molecule. The second photon excites the molecule into its upper triplet levels where the dissociation of a methyl C–H bond can occur.

Laser flash photolysis (249 nm) of mesitylene in solution at ambient temperature produces the transient absorption spectrum shown in Figure 3. The transient absorption spectrum is in good agreement with previous studies of triplet absorption spectra of the methyl-substituted benzenes.[8] Triplet mesitylene has a broad

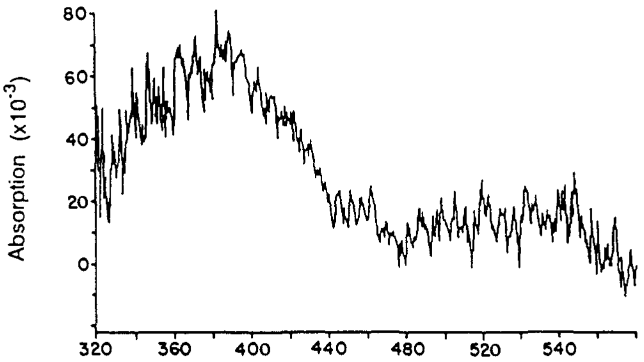

Figure 3. Absorption spectrum of triplet mesitylene produced by flash photolysis (249 nm) of mesitylene in 3-methylbenzene at ambient temperature.

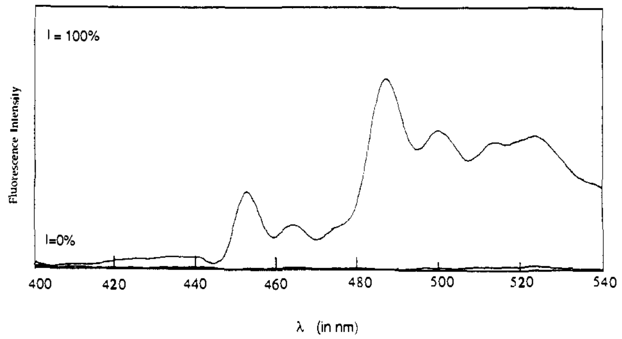

Figure 4. Two-laser experiment (see text). Fluorescence emission spectra recorded at 77 K for 3,5-dimethylbenzyl monoradical **2** (487, 498 nm) and mesitylylene biradical **3** (452, 463, nm). Upper trace: the sample was prepared by simultaneous exposure to an excimer laser (50 pulses, 249 nm, 0.05 Hz) and a N_2 laser (337 nm, 50 Hz) of mesitylene (5 × 10^{-3} M) in glassy 3-methylpentane at 77 K. Lower trace: photolysis of an identical sample with the N_2 laser alone. The excitation wavelength was 296 nm.

absorption extending into the visible region of the spectrum. This prompted a "two-beam" experiment in which a 249-nm pulse was used to generate ^{3}**1** and a second beam is used to photolyze ^{3}**1** to monoradical **3**. The experiment is similar to one described by Joussot-Dubien[9] and co-workers.

The Two-Beam Experiment. In the present work, matrix-isolated mesitylene is irradiated simultaneously with two beams of different wavelength. The first beam at 249 nm is provided by an excimer laser which promotes the guest molecule to its first excited triplet state. The second beam is either a nitrogen laser (337.1 nm) operating at a repetition rate of ~50 Hz or a mercury–xenon arc lamp fitted with a filter transmitting only the 405 nm wavelength line. In both cases, the second beam is absorbed only by the guest triplet state to produce monoradicals.

When mesitylene or durene in glassy 3-methylpentane at 77 K is subjected to 50 excimer laser pulses spaced at relatively long intervals (~20 s), the yield of mono- and biradicals is very small, as mentioned previously. This yield becomes at least 10-fold larger when the sample is simultaneously irradiated with a nitrogen laser. The fluorescence spectra of mono- and biradicals thus obtained from mesitylene are presented in Figure 4. Similar results were obtained when the nitrogen laser is replaced with a beam of 405-nm radiation. The photolysis of the samples with nitrogen laser or 405-nm radiation alone produces no detectable yield of either mono- or biradicals. The ratio of **2**/**3** formed from this two-laser experiment is identical with that formed when **1** is irradiated with 249-nm light alone.

Simple energetic arguments based on this dual-beam experiment provide additional support for the Berson mechanism. The triplet energy of mesitylene is 80.3 kcal/mol.[10] Thus after absorption

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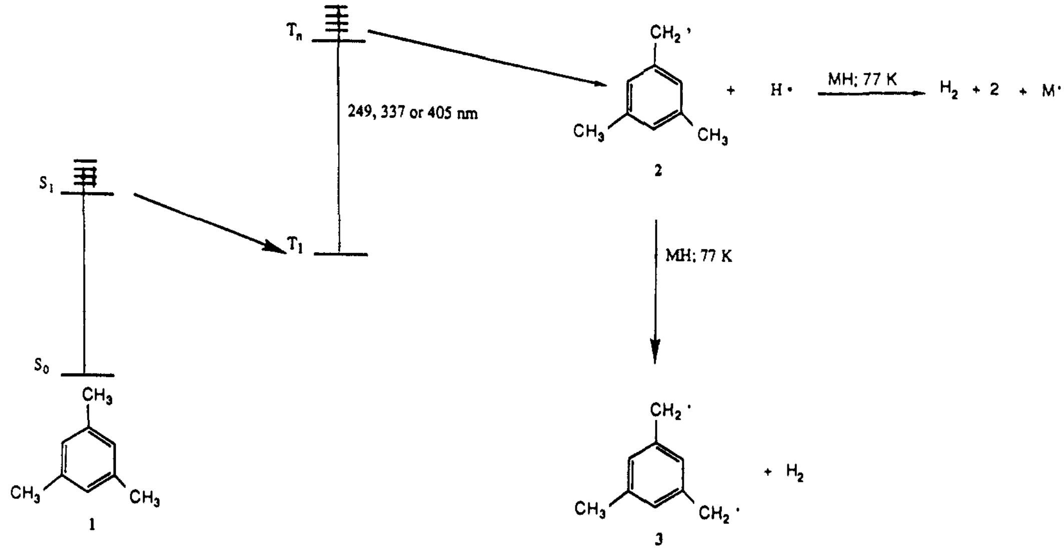
(8) (a) Leclercq, J.; Leclercq, J. M. *Chem. Phys. Lett.* **1973**, *18*, 411. (b) Astier, R.; Meyer, Y. H. *Chem. Phys. Lett.* **1969**, *3*, 399. (c) Astier, R.; Bokobza, A.; Meyer, Y. *J. Chim. Phys.* **1970**, 137.

(9) Joussot-Dubien, J.; Lamotte, M.; Pereyre, J. *J. Photochem.* **1981**, *17*, 347.

Scheme IV



of a second photon of 337 nm, the doubly excited triplet state of mesitylene has 165.3 kcal/mol, which is sufficient energy to fragment the mesitylene into the monoradical **2** and a hydrogen atom. However, 165.3 kcal/mol is not sufficient to simultaneously cleave two benzylic C–H bonds of mesitylene. This would require 170 kcal/mol (the benzylic C–H bond of toluene is 85 kcal/mol),[5] assuming that the second C–H bond dissociation energy of mesitylene is the same as that of the first. Admittedly, due to the necessarily apporoximate nature of the second C–H bond dissociation energy of *m*-xylene, this argument is rendered less convincing. However, when the wavelength of the second beam is 405 nm (from a mercury–xenon arc lamp), similar results are obtained. The sum of the triplet energy of mesitylene (80.5 kcal/mol) plus the energy provided by a 405-nm photon (70.7 kcal/mol) is clearly insufficient to break two C–H bonds in a purely photochemical process. These data are consistent with the Berson mechanism, in which the cleavage of the second benzylic C–H bond occurs in a dark reaction rather than through a photochemical process. The proposed mechanism is illustrated in Scheme IV.

The Dichloride Precursor. We have previously reported[3] that the 254-nm photolysis of α,α′-dichloro-*m*-xylene (**7**) in glassy ethanol at 77 K gives rise to benzyl type monoradicals and *m*-xylene biradicals, which are detected by their fluorescence starting at 471 and 438 nm, respectively. The ratio of biradical/monoradical is, however, much higher with the dihalide precursor than that produced when the methylbenzenes are photolyzed under similar conditions. This suggests that the pathways by which the mono- and biradicals are formed differ with the two precursor systems.

The fluorescence spectra of the mono- and biradicals produced by photolysis of α,α′-dichloro-*m*-xylene (**7**) in ethanol at 77 K with an excimer laser pulsed at high frequency (5 Hz) at 249 nm are presented in Figure 5. In the early stages of the photolysis (10 pulses), only the fluorescence of the *m*-xylylene biradical can be detected. When the number of pulses to which the sample is exposed increases, the fluorescence of the monoradical appears and increases along with that of the biradical. The ratio of biradical/monoradical actually decreases as the photolysis progresses (Figure 6). Eventually the ratio of biradical/monoradical becomes essentially independent of photolysis time. These results are very different from those obtained with the methylated benzene precursors. In these systems the monoradical was the major absorbing species in the matrix, even at very brief photolysis times, and the ratio of monoradical/biradical was essentially time independent throughout the experiment.

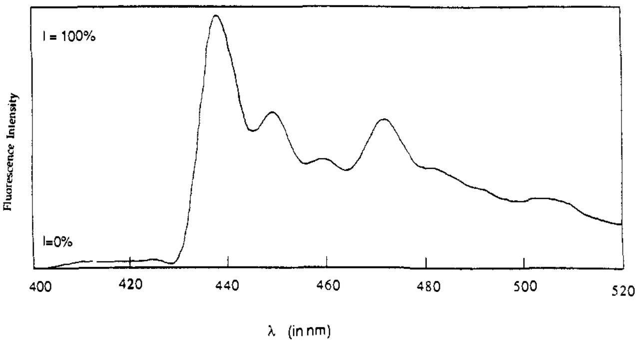


Figure 5. The fluorescence of the *m*-xylylene biradical **6** (438 nm) and *m*-methylbenzyl radical **5** (471 nm), produced from photolysis of α,α′-dichloro-*m*-xylene (**7**) (8.0×10^{-3} M) in glassy ethanol at 77 K with an excimer laser (249 nm, 350 pulses, 5 Hz). Excitation wavelength was 296 nm.

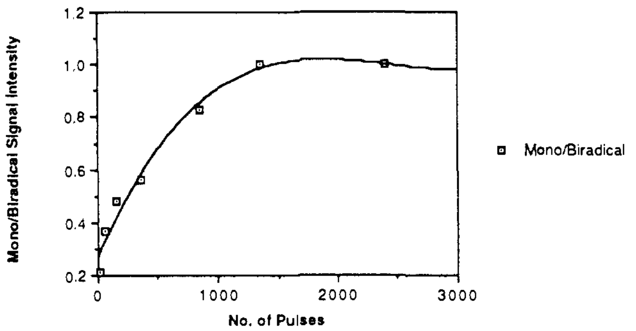
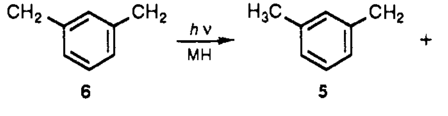


Figure 6. The ratio of the monoradical/biradical (**5**/**6**) produced from the photolysis of dichloride **7** (see text) versus the number of laser pulses delivered. The ratio is calculated by measuring the emission intensities at the maxima of the monoradical and the biradical (471 and 438 nm, respectively), with the $\lambda_{\text{excitation}}$ held constant at 296 nm.

The increase in the ratio of the fluorescence intensities of the monoradical/biradical produced by extended photolysis of **6** may be due to secondary photolysis of the biradical, leading to a slow photochemical hydrogen transfer reaction of *m*-xylylene with the matrix to form the monoradical **5**.



The effects of variation of the excimer laser pulse rate on the photochemistry of dihalide **7** also differed dramatically from those observed with the methylated benzene precursor. Photolysis of

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(10) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973; p 34.

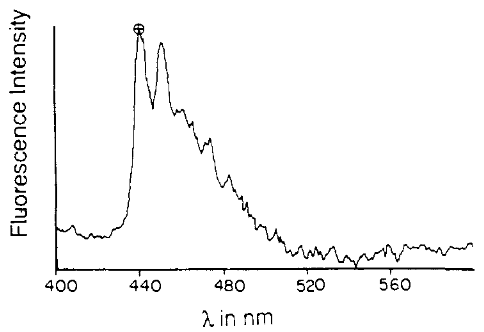
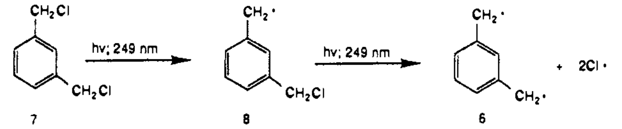


Figure 7. Room-temperature laser-induced fluorescence (LIF) spectrum of *m*-xylylene **6**. Spectra produced from α,α'-dichloro-*m*-xylene (**7**). The spectrum was recorded in isopentane solution at room temperature. Fluorescence was collected beginning co-incident with the laser pulse for a total of 100 ns. (Optical density of the dihalide was 1.2 at 249 nm.)

Scheme V



dichloride **7** at 77 K with 50 rapid 249-nm laser pulses produces primarily the *m*-xylylene biradical **6** and only traces of monoradical **5** emission. However, exposure of dichloride **7** to 50 laser pulses spaced 20 s apart are equally effective in producing **5** and **6**, in marked contrast to the results with mesitylene as precursor. The biradical must therefore be produced from **7** within the 10 ns pulse width of the excimer laser pulse.

The results obtained by solution-phase laser-induced fluorescence (LIF) experiments performed at ambient temperature are in good agreement with the results obtained at low temperature. In these experiments, a single pulse from an excimer laser (249 nm, 10 ns) was used to irradiate a fluid solution of the dichloride **7**. The laser pulse serves to dissociate the precursor, as well as to excite the nascent radicals or biradicals. The LIF emission spectrum recorded in this manner (Figure 7) from dihalide **7** is in excellent agreement with the matrix fluorescence emission spectrum previously assigned to *m*-xylylene. An identical LIF spectrum was recorded with α,α'-dibromo-*m*-xylene as the precursor. Only a very low intensity band corresponding to the 0–0 transition of monoradical **5** can be seen along with the liquid-phase emission spectrum of *m*-xylylene. To our knowledge this is the first ambient temperature direct spectroscopic detection of *m*-xylylene in fluid solution.

The mechanism of the photolytic conversion of dichloride **7** to *m*-xylylene is not known. It is not clear whether a single 249-nm photon has sufficient energy (115 kcal/mol) to cleave both carbon–chloride bonds of **7**, because the required bond dissociation energies of this substance are not known. Thus it is not known whether this reaction is a one- or a two-photon process.

A hypothetical two-photon mechanism of formation of *m*-xylylene from **7** implies that there is a light-sensitive intermediate connecting the two species. The two most reasonable candidates which can undergo secondary photolysis are the lowest triplet state of the dichloride (^{3}**7**) or the *m*-(chloromethyl)benzyl radical **8** formed by rapid fragmentation of an excited state of **7** (Scheme V). However, the chlorinated monoradical **8** is not detected by fluorescence spectroscopy upon brief photolysis of **7** with 254 nm arc lamp radiation or with a 249 nm excimer laser, at 77 K or at ambient temperature. Laser flash photolysis (LFP) of α,α'-dichloride **7** in liquid solution, produces a transient with λ_{max} = 324 nm. This transient absorption is at the exact wavelength of the maximum on the fluorescence excitation spectrum[11] of the *m*-methyl-substituted benzyl radical **9** (Figure 8 and Scheme V). Assignment of the transient spectrum of Figure 8 to radical **9** would require that a single 10 ns laser pulse breaks both carbon–chlorine bonds of **7** and promotes hydrogen abstraction from the solvent (SH). Radical **9** is not detected in emission upon laser flash photolysis of **7** (Figure 7) in liquid solution, but this is perhaps unsurprising as the parent benzyl radical itself is not fluorescent in liquid solution at temperatures higher than 180 K.[12] Another possibility is that the transient absorption spectrum depicted in Figure 8 is due to *m*-(chloromethyl)benzyl radical **8**, the absorption spectrum of which should be very similar to that of radical **9**. The formation of **8** in a single laser pulse is certainly a conceptually simpler process than the formation of **9** as the former process requires cleavage of only a single bond. However, if the latter assignment of the transient absorption depicted in Figure 8 is correct than monoradical **8** must be assumed to be nonfluorescent at ambient temperature as per benzyl radical[12] and at 77 K where it is not observed upon brief photolysis of dichloride **7**. At this time a clear assignment of the carrier of the transient absorption of Figure 8 is not possible.

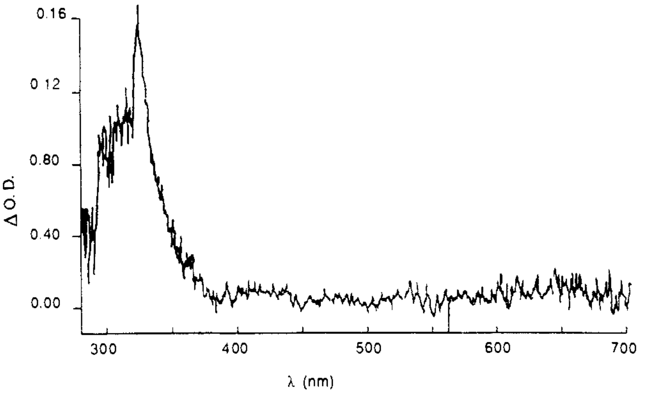
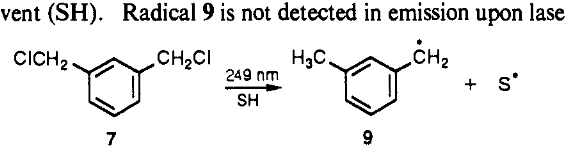
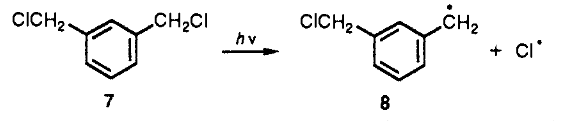


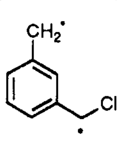
Figure 8. Transient absorption spectrum produced from laser flash photolysis (LFP) of α,α'-dichloro-*m*-xylene (**7**). Spectrum recorded 250 ns followed the laser pulse of a 3-methylpentane solution of dichloride **7** (optical density = ~1.0 at 249 nm).





The transient absorption spectrum produced by LFP of dichloride **7** does not resemble that of a derivative of triplet *m*-xylene (cf. Figure 3). However, this spectrum might not be observed if ^{3}**7** is very short lived due to heavy atom acceleration of singlet–triplet radiationless transitions.[13]

A Berson type of mechanism appears unlikely with dichloride precursor **7** because a photochemically generated chlorine atom is expected to abstract a hydrogen atom from the matrix or the monoradical rather than a second chlorine atom from monoradical **8**. The latter reaction would produce **10** rather than *m*-xylylene **6**. The biradical fluorescence emission and excitation spectra we observe from dichloride **7** are identical with those of *m*-xylylene **6**, and we suspect quite different from **10** which is unknown.



10

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[11] (a) Branciard-Larcher, C.; Migirdicyan, E.; Baudet, J. *Chem. Phys.* **1973**, *2*, 95. (b) Branciard-Larcher, C. Ph.D. Thesis, Université Paris-Sud, Orsay, France, 1972.

[12] Meisel, D.; Das, P. K.; Hug, G. L.; Bhattacharyya, K.; Fessenden, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 4706.

[13] (a) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905. (b) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice Hall Inc.: New Jersey, 1969; pp 183–284.

Regardless of mechanism of photolysis of dichloride **7**, this is the precursor of choice for generating *m*-xylene in liquid or solid solution.

Conclusions

Photolysis of polymethylbenzenes can produce *m*-xylylene type biradicals. The mechanism involves the secondary photolysis of the polymethylbenzene triplet state which cleaves a benzylic carbon–hydrogen bond. The nascent hydrogen atom produced can then abstract a second benzylic hydrogen from a nearby methyl group to produce the biradical and molecular hydrogen.

A liquid solution phase fluorescence spectrum of *m*-xylylene is produced by 249 nm laser photolysis of dichloride **7**. The mechanism of biradical formation from dichloride **7** is not known.

Experimental Section

Mesitylene (gold label), α,α'-dibromo-*m*-xylene, α,α'-dichloro-*m*-xylene, 2-methylbutane, methylcyclohexane, *n*-hexane, *n*-hexane-d_{14}, ethanol, ethanol-d_6, and 3-methylpentane were purchased from Aldrich Chemical Co. (spectral or HPLC grade where available) and used without further purification. Durene (technical grade) was purchased from Humble Oil and Refining Co. and purified by elution through neutral alumina (hexanes as eluent) immediately prior to preparation of a sample tube. 2-Methyltetrahydrofuran (Aldrich) was refluxed over $KMnO_4$, distilled, and stored over molecular sieves prior to use.

Synthesis of *m*-Tolylacetyl Peroxide (4). *m*-Tolylacetic acid (3.0 g, 19.9 mmol) was treated with thionyl chloride (10 mL), and the resulting solution was heated to reflux (4.5 h). Removal of thionyl chloride by azeotropic distillation with benzene gave *m*-tolylacetyl chloride which was used immediately without further purification. The acid chloride was taken up in 5 mL of tetrahydrofuran. A solution of sodium peroxide (1 g, 0.013 mol) in 10 mL of water was added to the cold stirred solution of the acid chloride. After 1.5 h, the mixture was extracted with diethyl ether. The ether layer was washed with 10% aqueous bicarbonate solution, dried, and removed in vacuo to yield a pale yellow oil (2.1 g; 35%) which tested positive for a peroxide (KI and starch paper). IR: 1800 and 1730 cm^{-1}.

All matrix fluorescence spectra were obtained on a commercial (Perkin-Elmer Model LS-5) spectrofluorimeter. The sample compartment of the LS-5 has been modified so that fluorescence spectra can be recorded on samples in a Dewar flask at the temperature of boiling liquid N_2. Samples were prepared by transferring approximately 0.5 mL of the desired solution into a quartz tube (4 mm o.d.). The samples were then degassed by multiple freeze–pump–thaw cycles prior to sealing under vacuum. Following preparation, we stored samples which were not used immediately at liquid nitrogen temperature until they could be photolyzed and subsequently analyzed.

LIF experiments were performed by using a laser flash photolysis apparatus similar to that described by Scaiano.[14] Briefly, a degassed solution of the precursor having an optical density of ~1.0 at the 249 nm laser line is prepared in a Suprasil quartz sample cuvette. The focussed output of a Lumonics Model TE-860-4 laser impinges upon the sample cell. This laser pulse serves both to dissociate the precursor molecules, forming the reactive radicals and/or biradicals, as well as to promote these reactive species to an electronically excited state. At a 90° angle to this excitation source, the total fluorescence of the sample is monitored. This emitted light is led via a fiber optics cable through a slit (25 μm) onto an Allied analytical systems spectrograph which serves to disperse the fluorescence. The dispersed fluorescence is then collected using a PARC optical multichannel analyzer (OMA) as the detector. The OMA is gated to coincide with the laser pulse. Extraneous scattered laser light is removed by the use of an Oriel 295 nm long pass glass filter placed between the sample compartment and the fiber optics cable.

For the matrix experiments, samples were irradiated at 77 K in a Dewar flask (quartz windows) with the unfocussed output of either a Lumonics Model TE-860-4 excimer laser (KrF; 249 nm, 10 ns pulse, ~80 mJ per pulse), a Molectron N_2 laser (337 nm, 8 mJ per pulse), or a Rayonet Reactor (5 bulbs PRP 254) or a 1000-W Hg–Xe arc lamp as indicated. The intensity of the laser was varied by the use of wire mesh neutral density filters. The absorbance of the filters was monitored prior to and following irradiation to ensure that the filter was not altered by exposure to the intense excimer laser radiation. Reproducible positioning of the Dewar flask in the excimer beam was achieved by mounting a holder on an optical table, so that the sample, in the Dewar flask, could be reproducibly placed in the path of the laser beam.

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Registry No. 1, 108-67-8; **2**, 19121-63-2; **3**, 57384-02-8; **4**, 123883-43-2; **7**, 626-16-4.

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(14) Scaiano, J. C.; Weir, D. *Can. J. Chem.* **1988**, *66*, 491.

Molecular and Electronic Structure of Pyracylene

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Abstract: Pyracylene (cyclopent[*fg*]acenaphthylene, **1**) is available in two steps from pyrene and, contrary to previous experience, can be crystallized, stored as a solid, and even sublimed without decomposition. The X-ray structure of **1** exhibits a pronounced alternation of bond lengths along the 12-π periphery. The absorption spectrum (with transition moment directions) and the photoelectron spectrum of **1** are reported and analyzed. Pyracylene is quite stable to irradiation both as a solid and in solution. Radiationless deactivation of the lowest excited singlet state is very rapid; fluorescence and intersystem crossing yields were below our limits of detection ($\phi_F < 3 \times 10^{-4}$, $\phi_T < 2 \times 10^{-2}$). The lowest triplet state, observed by flash photolysis with a sensitizer ($\lambda_{max} = 360$ nm, $\epsilon > 10^4$ M^{-1} cm^{-1}; $\lambda_{max} = 520$ nm, $\epsilon = 7500$ M^{-1} cm^{-1}), is also rather short-lived ($\tau = 4.6$ μs). The triplet energy of **1** is bracketed in the range of 103 ± 20 kJ mol^{-1} on the basis of energy-transfer experiments. A major component of flame soots, which had been tentatively attributed to **1** by GC–MS analysis, is shown not to be identical with **1**. The heat of formation of **1** is calculated as $\Delta_f H = 410$ kJ mol^{-1} with the MMP2 force field.

The literature on pyracylene (cyclopent[*fg*]acenaphthylene, **1**) displays a remarkable dichotomy. On the one hand, **1** is held to be very unstable, a prototype "antiaromatic" molecule with a planar 12-π periphery. The first attempts to synthesize **1** by standard procedures have failed,[1] and when the synthesis was achieved by Trost and co-workers,[2] they found that their product

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[‡] This work is part of the Ph. D. thesis of B.F., University of Basel, 1987.

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(1) Anderson, A. G.; Wade, R. H. *J. Am. Chem. Soc.* **1952**, *74*, 2274.