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Solution Photochemistry of Azulene

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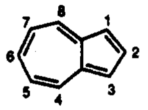
Photochemical reactivity has been observed in solution-phase azulene. Experiments are described which confirm photoinduced deuteration, chlorination, and polymerization. The threshold for the observed chemistry is at the origin of S_2 which is at 27956 ± 8 cm^{-1} (357.7 ± 0.1 nm) in chloroform. Only one photon is required to induce the observed chlorine substitution reactions. Although no naphthalene is formed, this chemical channel appears to be the equivalent of a thermal reaction, with the substitutions taking place at the two equivalent positions on the small ring of azulene. The mechanism of these reactions is bimolecular in nature. Chlorination provides a complex mixture of products in most cases; however, deuteration proceeds cleanly giving only 1,3-d_2-azulene.

Introduction

Azulene **1** is a fused-ring, planar, aromatic isomer of naphthalene **2**; both compounds have similar spectra in the ultraviolet which arise from π–π^* electronic transitions.[1] Naphthalene is not polar, while azulene has a permanent dipole moment of 0.80 ± 0.02 D, with the smaller of the two rings being the negative end of the molecule.[2] As a result of its permanent dipole and its asymmetric structure, azulene has an electronic transition in the visible. It is this transition at 694 nm, resulting from an intramolecular charge transfer, that is responsible for the blue color of azulene.[1]



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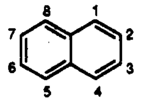

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Azulene is probably the best known example of a molecule that does not obey Kasha's Rule.[3] The fluorescence quantum yield from the first excited singlet state, S_1, is $<10^{-6}$,[4] but from S_2 it is 0.03.[5] This is probably due more to the exceptional behavior of S_1, its intramolecular charge-transfer characteristics and its "faster than usual" internal conversion rate, than the behavior of S_2 of azulene. Because of this exceptional behavior, azulene has attracted substantial interest for decades.[1,4–20]

There has only been one reported observation of the photochemical behavior of azulene in solution; Lok et al. were able to photolytically induce a reaction between azulene and the nucleophile CN^-.[21] The photochemical reaction of 1-nitroazulene with nucleophiles has also been reported.[22] In this article, we document the observed photochemical behavior of azulene with electrophiles in the solution phase, following ultraviolet irradiation.

Experimental Section

Azulene (Aldrich, 98%) concentrations ranged from 1.0×10^{-5} M to 5.0×10^{-3} M in CH_2Cl_2, $CHCl_3$, CCl_4, and CD_3OD (all from Aldrich, spectral or HPLC grade). All chemicals were used without further purification. To avoid the possibility of reaction with oxygen, samples were generally deoxygenated by repeated exposure to vacuum prior to irradiation, and some of the samples were stirred with Teflon-coated stir bars during irradiation. The solutions were irradiated in a standard 1 cm × 1 cm quartz cuvette or a 1 in. × 1 in. quartz vacuum cell.

Light sources used for this study include a Mercury pen-lamp (Ultra-Violet Products), low power D_2 (75 W, Oriel) and Xe (75 W, Oriel) lamps, and YAG (355 nm, Lumonics and Continuum-660), dye (Lumonics and Lambda Physik FL2002), and excimer (308 nm, Lambda Physik EMG 102) lasers. Irradiation times depended upon light intensity, concentration, and solvent. In CCl_4 using a mercury pen-lamp, irradiation times as short as 45 s resulted in a noticeable color change in the solution.

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Photochemical products were separated on a silica gel column using either 1- or 2-propanol followed by CH_2Cl_2. The propanols were the only solvent system found that would result in product separation. However, many of the photoproducts underwent solvolysis in the propanols so that separation and identification of the initial photoproducts were not possible.

^1H NMR spectra of unirradiated and irradiated azulene in CD_3OD were obtained with a 200-MHz Bruker NMR. NMR spectra of other reaction mixtures were too complex to be of value in product identification. Even after chromatographic separation the products were either present in low concentrations or were contaminated with unreacted azulene and polymer, making NMR spectra complex. A Hewlett-Packard GCMS (5890/5970) with a 10-m methyl silicone-coated capillary column was also used to help in photochemical product identification. All GCMS runs were performed with a beginning temperature of 60 °C, a temperature ramp beginning at 2 min at the rate of 20 °C/min up to 200 °C and holding at this final temperature for the remainder of the 12-min run. UV-vis spectra were obtained on a variety of different scanning and diode array spectrophotometers.

A Gentec ED 200 power meter was used to measure the light powers both before and after the sample cell to determine the amount of energy that was absorbed by the sample. Screens and/or apertures were used to vary the light intensity.

The frequency range for the threshold of the observed photochemical reaction was determined by scanning the second harmonic of a YAG pumped dye laser using DCM (Exciton) as the dye. The laser was set so that the wavelength was at the red (low frequency) end of the dye range and then scanned toward the blue by 0.1-nm intervals. A sample of azulene in chloroform was exposed to 20 laser pulses at each wavelength until a color change was observed.

In order to examine these reactions at 77 K in a glass, an azulene solution (1.0×10^{-4} M) was prepared by using a mixture of 2 g of methylcyclopentane (Aldrich, filtered through silica gel) and 1 g of camphene (Aldrich, filtered through silica gel) as the solvent. This solvent mixture was used in order to obtain an optically clear glass when frozen. Another solution was prepared with the same mixture, but also included dimethyl acetylenedicarboxylate (DMAD) (Aldrich, 99%) so that its concentration was 10 times larger than the azulene. A third solution contained CCl_4, again in a 10:1 mole ratio with the azulene, in the same mixed solvent system. Approximately 0.5 mL of these solutions were placed into a quartz NMR tube which sat in a Dewar flask that had quartz windows. These glasses were irradiated with a Hg pen-lamp and their UV-vis spectra were monitored with an HP diode array spectrometer as a function of irradiation time.

Results and Discussion

Characteristics of Chlorination Reactions. When exposed to ultraviolet irradiation, solutions of azulene in methylene chloride, chloroform, or carbon tetrachloride exhibited color changes. In dilute samples, the color initially changed to yellow. If a small portion of the sample is irradiated (either with a laser or by focusing the light with a lens), the volume in which the reaction occurs can be observed since the products are differently colored from the azulene. Color changes in the various azulene solutions were visible evidence that azulene was undergoing chemical reactions.[23]

After irradiation, small amounts of these reaction mixtures were injected into the GCMS. Authentic samples of azulene and naphthalene have different retention times under our GC conditions, and the mass spectral library search assigned correct structures to each. In this study, virtually no naphthalene was formed even though this was the only photochemical product (gas phase) reported in the literature.[24-27] The Hewlett-Packard library does not contain any azulene derivatives, but most of the nonpolymeric photoproducts seem to exhibit parent peaks. Polymeric azulenes do not elute off the GC column and were not observed in the GCMS. The mass spectral library searches of the photoproducts suggest naphthalene skeletal products, but with low (≤0.80) probabilities. One might expect the probability of the matches to be lower, but there are two complications: (1) the mass spectra of azulene and naphthalene are very similar; (2) the 70-eV electrons used to form the ions have more than enough energy to also isomerize azulene to naphthalene.[28] The GCMS of substituted naphthalenes showed that they did not elute at the same times as observed for the photoproducts of azulene. Reasonable guesses for the molecular formulae of the products could be made from mass spectral analysis, although the positions of substitution could not be unambiguously assigned. The photoproducts identified from the GCMS are listed in Table 1.

Table 1. Azulene Photolysis Products Identified from the Various Solvents

product	solvent CH_2Cl_2	 $CHCl_3$	 CCl_4
chloroazulene	x	x	x
dichloroazulene*			x
chloromethylazulene	x		
dichloromethylazulene		x	
trichloromethylazulene			x
polymer	x	x	
(dichloromethyl)chlorodihydroazulene**		x	
chloro(trichloromethyl)dihydroazulene**			x
dichloro(trichloromethyl)dihydroazulene			x

* Up to three different isomers of this product have been observed. The 1,3 dichloroazulene is always produced in the largest concentration. ** Several isomers of this product are observed.

Table 2. TLC Retention Factors for Some of the Photoproducts Arising from the Irradiation of Azulene in a Chlorinated Solvent (CCl_4, CCl_3H, or CCl_2H_2). The Solid Phase was Silica, While the Mobile Phase was 2-Propanol

color of photoproduct	tentative photoproduct identity	R_f value
blue/violet	azulene	0.9
red/orange	chloroazulene	0.75
yellow	dichloroazulene	0.6
aqua	polymer	0.43
aqua	polymer	0.2
aqua	polymer	0.1

For any given chlorinated solvent system at room temperature, the products obtained were different except for chloroazulene. As shown in Table 1, both addition and substitution products were formed. This paper will be mainly concerned with the substitution photoproducts that were observed. All of the photoproducts were visibly colored, facilitating TLC separations. Their colors and R_f values (silica plates using 2-propanol as the liquid phase) are listed in Table 2. Irradiation of azulene in CH_2Cl_2 resulted in the formation of large amounts of azulene polymers that absorbed strongly in the visible.[23] When the irradiated solutions in the original solvent were left to stand at room temperature under fluorescent lights, they were stable for months. When these colored photoprod-

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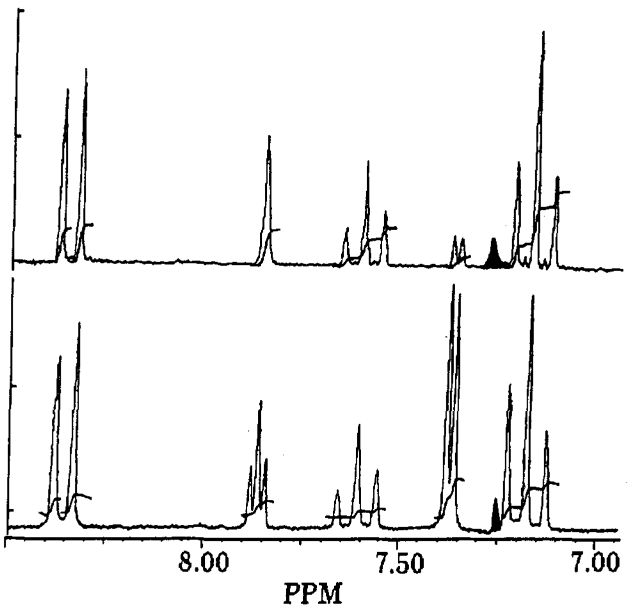

Figure 1. ^1H NMR spectra for azulene in methanol-d_4 before irradiation (bottom spectrum) and after 3 h of irradiation at 308 nm.

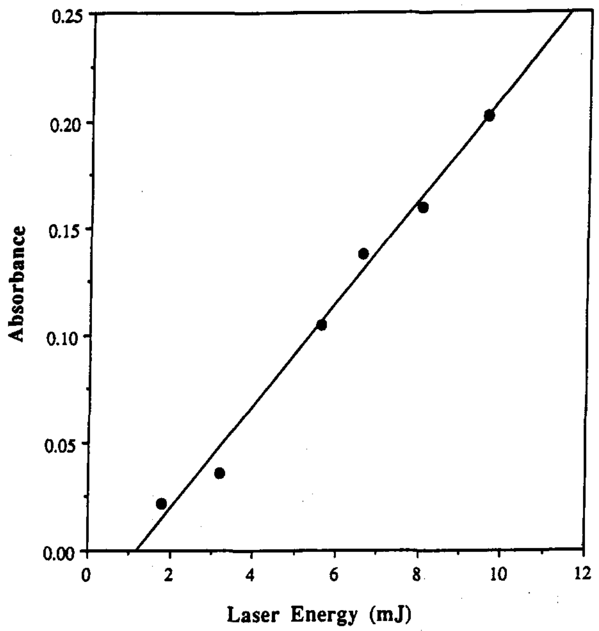

Figure 2. Polymer production monitored via absorbance at 700 nm as a function of 308-nm irradiation power.

ucts were separated on either an LC column or on a TLC plate using propanol as the solvent, most of the colors faded within 1 h. This is presumably due to solvolysis of the products by either propanol or water. In the case of the TLC plates, it is even possible that they reacted with air as occurs in some other cases.[29]

Formation of Doubly Deuterated Azulene. When azulene in CD_3OD was photolyzed with a low-pressure mercury lamp, the only observed photoproduct was doubly deuterated azulene. This single product is remarkable because of the myriad of products obtained in chlorinated solvents. The observed photoinduced deuteration was useful in allowing us to determine the specific substitution sites. A solution of azulene in CD_3OD was made at a concentration of approximately 2×10^{-2} M and an NMR spectrum obtained. When this solution was irradiated for 5 h with 308-nm light (at 10 Hz, 100 mJ/pulse), the GCMS indicated that there was a large amount of singly (129 amu) and doubly deuterated (130 amu) azulene present in the sample. The simplicity and quantitative nature of this process was revealed by following the reaction by ^1H NMR. The NMR spectra (Figure 1) of azulene in CD_3OD before and after irradiation are readily interpreted. Clearly, after irradiation the triplet at 7.86 ppm collapsed into a singlet and the doublet at 7.35 ppm reduced in intensity. On the basis of the previous assignment by Schneider, Bernstein, and Pople, the triplet at 7.86 ppm is due to the proton at C2 (apex of the small ring), while the doublet at 7.37 ppm is due to the equivalent protons at C1 and C3.[30,31] Therefore, upon irradiation, deuterons are being substituted for protons in azulene at the 1 and 3 carbon positions. Extended exposure to irradiation failed to give further deuteration.

Determination of Chlorination Sites. Since large enough amounts of the chlorinated photoproducts could not be isolated for NMR spectra analysis, an aliquot of deuterated azulene in CD_3OD was mixed with a small volume of CCl_4 and the mixture was irradiated with a mercury pen-lamp. An aliquot of this mixture was injected into the GCMS to determine whether the chlorine atoms were displacing deuterons (at C1 and C3) or hydrogens (at C2 or C4–C8). The base peaks observed were also the parent ions and had masses of 130 amu for dideuteroazulene, 163 amu for the chloroazulene, and 196 amu for the dichloroazulene peaks. For the chlorinated azulenes, the ^{37}Cl isotopes could be seen at higher masses (with the appropriate intensity ratios), but there were no other heavier mass peaks. The GCMS data on the chlorination of the deuterated azulene showed that the monochloroazulene was formed by replacement of one of the deuterons. Similarly, the dichloroazulene showed no deuterons present. These results unambiguously confirm that chlorination is occurring at C1 and C3.

Characterization of the Dynamics of the Photochemical Process. For azulene in chloroform, the threshold for the photochemical reaction was determined to be at 27956 ± 8 cm^{-1} (357.7 ± 0.1 nm). This frequency corresponds to the origin of the S_2 transition for azulene in chloroform solutions.[32] The actual threshold for the photochemical reaction could be lower but is not observed due to the lower absorption cross section in the S_1 transition. Since this photochemical behavior of azulene had never before been reported, a plot of the absorbance of the polymer product versus the energy absorbed by the sample was made to determine how many photons were required to induce this reaction. The linear slope in Figure 2 shows that only one photon was needed for the reaction. Linear plots can also be obtained by using the GCMS data of chloroazulene from any of the chlorinated solvents. Since the photochemical reaction can be induced by the 0.1-W output of a mercury pen-ray lamp, the absorption of more than one photon could occur only if there is a long-lived excited state involved in this reaction.

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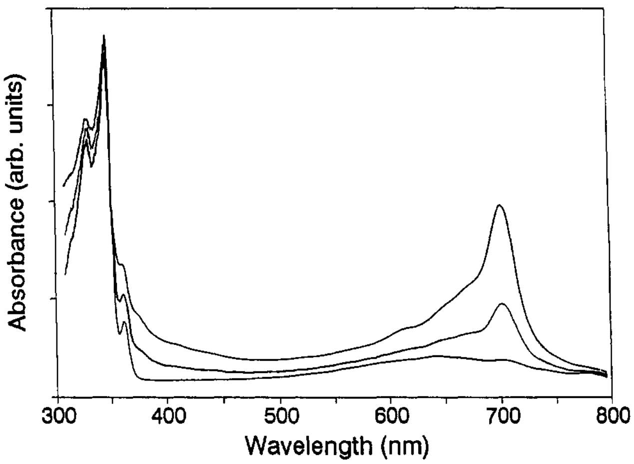


Figure 3. Absorbance of azulene in CH_2Cl_2. The bottom curve is the absorption spectrum of azulene. The middle curve is the spectrum of the azulene solution after it was irradiated for 2 min (308 nm, 8 mJ/pulse, 10 pulses/s, 15-ns pulse). The upper curve is the spectrum of the azulene solution after it was irradiated for 4 min. The azulene solution is blue, but turns green upon irradiation as the polymer is formed.

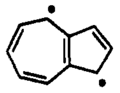
The amount of azulene reacted was estimated by first obtaining the UV-vis spectrum of an unirradiated azulene solution of known concentration. After irradiation, an estimate of the amount of azulene remaining was made. This determination was complicated by the fact that the photoproducts also absorb light in the same spectral region as azulene. A straight line drawn on the spectra from 350 to 375 nm (valley-to-valley) was used as a baseline to estimate the distance to the top of the peak at 352 nm. This "normalized" absorbance was assumed to be proportional to the amount of azulene in the sample. As can be seen in Figure 3, the amount of azulene in the sample decreases upon increasing irradiation with 308-nm light, while the amount of polymer increases. The remaining concentration of azulene following irradiation was subtracted from the concentration in the original sample to obtain the concentration of azulene that reacted during the photolysis.

The photochemical quantum yields were also determined for azulene solutions in CH_2Cl_2 and in CCl_4. The number of azulene molecules reacted was determined by multiplying the concentration of azulene reacted (as determined above) by the volume of the irradiated sample and Avogardro's number. It was also assumed that Beer's Law was obeyed for changes in azulene concentration of about a factor of 2, since this was true up to a factor of 10.

A Gentec power meter was used to measure the amount of light entering the cell and the amount of light that was not absorbed or reflected by the sample in the cell. The difference between these two values was used as the amount of light that was absorbed by the sample. This was converted into the number of photons absorbed. The photochemical quantum yield could then be calculated by dividing the number of molecules that reacted by the number of photons it took to induce that amount of reaction. Using very rough estimates for these values, we obtained calculated quantum yields for the photolysis in carbon tetrachloride of 0.50 ± 0.05 and in methylene chloride of 0.02 ± 0.01. These numbers are much greater than those reported for the gas-phase conversion of azulene into naphthalene by UV irradiation.[24,25]

Triplet-specific quenching compounds (naphthalene, benzophenone, hexatriene, and *p*-phenylphenol (all from Aldrich)) were added to standard solutions of azulene (5.0×10^{-4} M) at concentrations up to 10 times larger than the azulene. UV-vis spectra of each solution (pure azulene solutions as well as with each quencher) were obtained for both the unirradiated samples and samples irradiated at 355 nm. Each irradiation was performed for the same length of time at the same light intensity. The spectra of the unirradiated solutions were subtracted (electronically on a HP diode array UV-vis) from the spectra of the irradiated samples. These difference spectra of the solutions containing the triplet quenchers were compared to the pure azulene solution difference spectrum. None of these spectra indicated a decrease in the amount of photochemistry, regardless of the quencher or its concentration. This indicates that the photochemically active state of azulene is not one of the triplet states of azulene, except maybe T_1 (E_T @ 10000 cm^{-1} which is less than the triplet energies of the triplet quenchers used), but its lifetime is even shorter than that of T_2.[12,19,33] Even though the lifetimes of the triplet states are short, some quenching would have been expected in the solutions with high concentrations of quencher if the triplet states were involved in the reaction.[19]

Attempted Isolation and Trapping of an Intermediate. Dewar and Merz[28] have discussed the isomerization of azulene to naphthalene, a reaction that occurs thermally and photochemically in the gas phase.[24-27] Initially we anticipated that naphthalene would be an observable photochemical product in solution. The fact that we did not observe naphthalene suggested the possible trapping of an intermediate along the azulene to naphthalene pathway. The most prominent possible intermediates, according to Dewar and Merz,[28] are the diradical **3** or the fused tricyclic isomer **4**. Using techniques successfully used to observe or trap such intermediates,[34-36] we set out to observe or trap **3** or **4**. Azulene glasses were prepared in methylcyclopentane and camphene at 77 K.[34,35] When the azulene glasses at 77 K were irradiated, no reaction was observed to occur visually or via the UV-vis spectra analysis. Addition of the trapping agent DMAD[35,36] and/or CCl_4 to the glass did not result in any observed reaction, even after hours of irradiation with a mercury pen-lamp. Annealing the samples did not reveal any observable reaction either. When the solutions containing CCl_4 were irradiated under the same conditions except at room temperature, the photochemical reaction was observed to occur within minutes.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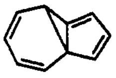
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Since the threshold of this reaction is at the origin of the S_2 state of azulene, the possible photochemically active states are S_0, S_1, S_2, T_1, T_2, or T_3. The two higher triplet states can be eliminated since no photochemical quenching was observed upon addition of triplet specific quenching

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compounds with triplet energies less than the energy of T_2. If this reaction proceeded via a unimolecular mechanism originating on the azulene, such as the formation of intermediate **3** or **4** or some other ionic species, some change in the UV–vis spectrum (200–800 nm) should have been observed in the frozen matrix experiments. DMAD was added to the glass since it forms one type of addition product with radical species and another type of addition product with charge-transfer species.[35,36] Since no addition products were formed between DMAD and azulene (even at room temperature), both of these processes seem unlikely. If any of the electronic excited states were directly responsible for the observed photochemical behavior, one would also expect a unimolecular mechanism with corresponding changes in the electronic spectrum. Since no changes were observed in the UV–vis spectrum, the photochemical mechanism must involve a bimolecular process that is blocked in a rigid matrix.

Implications of the S_0* State. Following electronic excitation, azulene undergoes almost complete internal conversion to form vibrationally excited S_0 azulene.[33,37–39] While in this excited ground state, the reactivities of the hydrogens at C1 and C3 increase.[40] These increased reactivities would facilitate bimolecular substitution reactions. Since we observe bimolecular substitution reactions, it therefore appears that vibrationally excited S_0 is responsible for the observed photochemical process. If this were true, this reaction would behave as if it were thermally induced.

It is interesting that not only do we observe photolytically induced substitution reactions involving electrophilic species occurring at C1 and C3 of azulene, but Lok et al. observed exactly the same phenomenon with nucleophilic species.[21] Apparently, vibrationally excited azulene prefers to react via substitution reactions at the C1 and C3 regardless of whether it is reacting with nucleophilic or electrophilic species.

Conclusions

The photochemical behavior of azulene solutions has been observed and documented. Only one photon is required to induce the substitution reactions that occur with the retention of the azulene skeleton. The threshold for this reaction is at 27956 cm^{-1} (357.7 nm) in chloroform, at the origin of S_2. When light was not present to initiate these reactions, no chemistry was observed.

Substitution of protons by deuterons and chlorines occurs at the two equivalent positions on the smaller of the two rings in azulene. Since Lok et al. observed exactly the same phenomenon with nucleophilic species,[21] vibrationally excited azulene reacts via substitution reactions at C1 and C3 regardless of whether it is reacting with nucleophilic and electrophilic species, probably via bimolecular substitution out of S_0*. This photoinduced reaction is the equivalent of thermal reactions in azulene, due to very efficient internal conversion in azulene.

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