JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 2, 623–630 (1989)

THE DOUBLE PHOTODISSOCIATION OF A GEMINAL DICHLORIDE: EVIDENCE FOR THE STEPWISE FORMATION OF A DIARYL CARBENE

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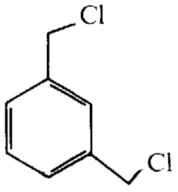
ABSTRACT

Photolysis of dichlorodiphenylmethane in glassy 2-methyltetrahydrofuran at 77 K results in the formation of diphenylcarbene and the diphenylchloromethyl radical, which were detected by their fluorescence emission and excitation spectra. The relative yields of the carbene and biradical are shown to vary dramatically as a function of photolysis time. The photolability of the diphenylchloromethyl radical is also demonstrated. These results were interpreted in terms of a two-step mechanism, in which the diphenylchloromethyl radical is an intermediate in the formation of diphenylcarbene.

INTRODUCTION

The photodissociation of benzylic halides to produce arylmethyl radicals is a well known process. By photolysis of appropriate arylmethyl halides, various arylmethyl radicals, including benzyl,[1] naphthylmethyl[2] and diphenylmethyl,[3] have been produced and spectroscopically characterized. The photodissociation is believed to be initiated by promotion to the S_2 ($\pi-\pi^*$) state of the aromatic system. This energy is ultimately transferred into the carbon—halogen bond T (σ^*) state, which results in dissociation. Internal conversion of S_2–S_1 ($\pi-\pi^*$) and ISC to the T_1 ($\pi-\pi^*$) state followed by dissociation may also be a contributing pathway.[4] In recent work,[5] we have demonstrated that photolysis of suitable dihalides in rigid organic glasses at low temperature leads to the formation of the corresponding biradicals. It was shown that photolysis of α,α′-dichloro-*m*-xylene (**1**) or α,α′-dichloro-*o*-xylene (**2**) gives the parent *m*-quinodimethane biradical (**3**) or the *o*-quinodimethane biradicaloid (**4**), respectively.



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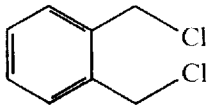

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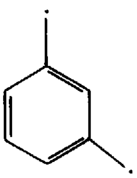

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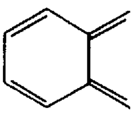

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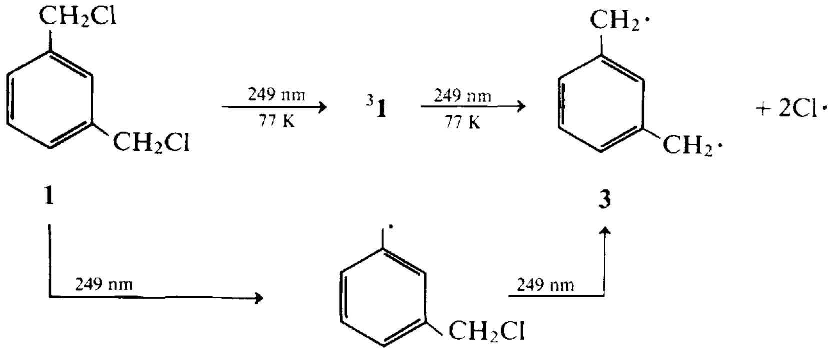
0894–3230/89/080623–08$05.00

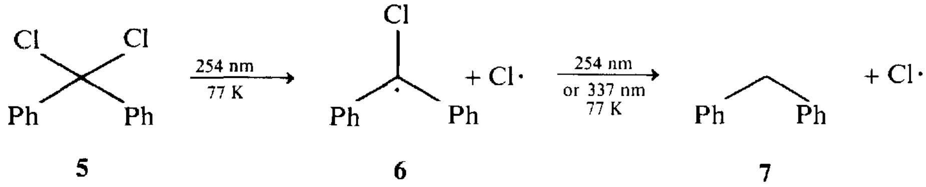
Received 6 October 1988
Revised 12 December 1988

For the quinodimethanes, we have considered a mechanism of stepwise double photodissociation in which the dichloride is photolyzed to yield first a halogen-containing monoradical, which is then further photolyzed under the conditions of the experiment to fragment to form a second Cl atom together with the biradical[6] (Scheme 1). Alternatively, photolysis of **1** may produce an excited triplet state ($^{3}\mathbf{1}$) at 77 K which, on absorption of a second photon, simultaneously ejects two chlorine atoms to produce *m*-xylylene (**3**).



Scheme 1

We now report that in analogy to the *m*-xylylene system, photolysis of the geminal dihalide dichlorodiphenylmethane (**5**) at 77 K leads to the formation of diphenylcarbene (**7**) via a two-step photodissociation mechanism involving initial formation of the diphenylchloromethyl radical (**6**) (Scheme 2). This represents a new entry for matrix isolation studies of carbenes which may be of use when diazo compounds or diazirine precursors are inconvenient.



Scheme 2

EXPERIMENTAL

1,1-Diphenylacetone (**8**), dichlorodiphenylmethane (**5**) and chlorodiphenylmethane (**9**) were purchased from Aldrich and used without further purification. 1,1,2,2-Tetraphenylethylene oxide (**10**) was a generous gift from G. W. Griffin. 2-Methyltetrahydrofuran (2-MeTHF) (Aldrich) was refluxed over $KMnO_4$, distilled and dried over molecular sieves prior to use. All fluorescence spectra were obtained on a Perkin-Elmer Model LS-5 spectrofluorimeter. The sample compartment of the LS-5 was modified so that fluorescence spectra can be recorded on samples in a Dewar flask at the temperature of boiling liquid nitrogen. Samples were prepared by syringing 0·5 ml of solution into a quartz tube (4 mm o.d.). The samples were then degassed

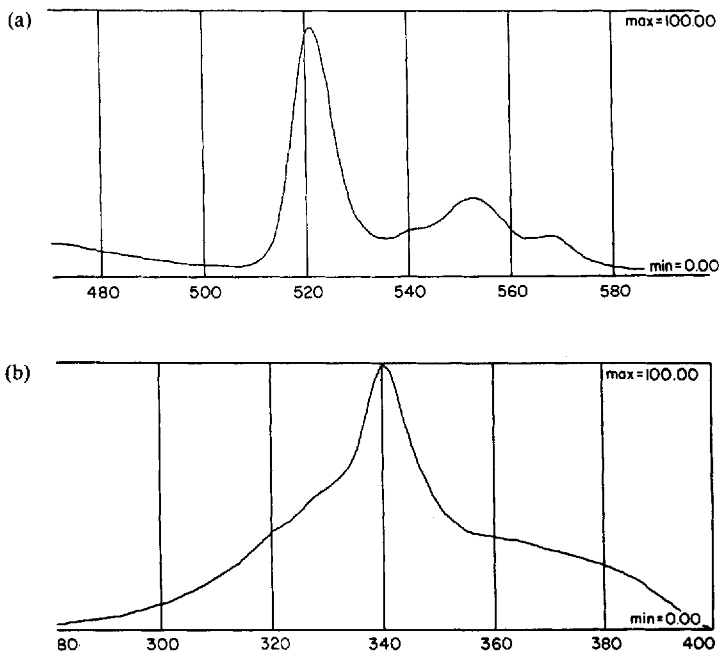


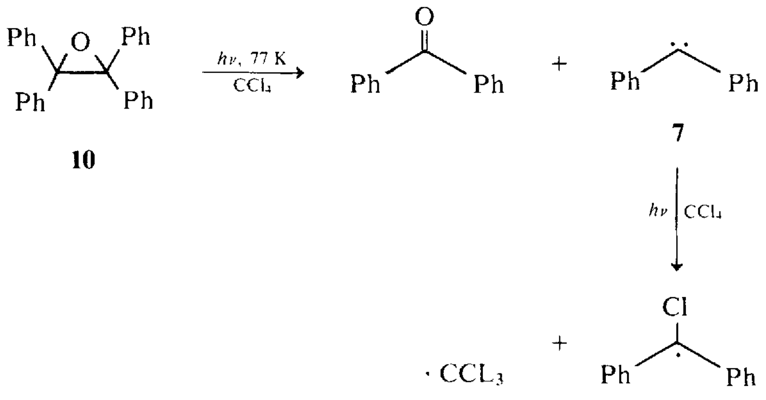
Figure 1. (a) Fluorescence emission spectrum and (b) fluorescence excitation spectrum of the diphenylchloromethyl radical (**6**) produced by 254 nm photolysis of a 0·01 M solution of **5** in glassy 2-MeTHF at 77 K. The excitation wavelength was 340 nm and emission was monitored at 520, 550 or 570 nm

by multiple freeze–pump–thaw cycles prior to sealing under vacuum. Irradiation was carried out using either a Rayonet photoreactor (5-RPR-2540 bulbs) or the 337·1 nm line of a nitrogen laser (Molectron-UV-24 laser operated in their repetitive pulse mode; 5 pulses s^{-1}; up to 8 mJ per pulse).

RESULTS AND DISCUSSION

Spectroscopy of diphenylchloromethyl radical

Brief photolysis (254 nm, 5 s) of a 0·01 M solution of **5** in 2-MeTHF at 77 K produces only a single fluorescent species (λ_{max} emission 522 nm; λ_{max} excitation 341 nm) whose emission and excitation spectra are shown in Figure 1, and attributed to the diphenylchloromethyl radical **6**, on the basis of several pieces of evidence. First, the carrier of the spectra in Figure 1 was readily demonstrated to be a thermally unstable intermediate. Photolysis at 77 K yielded the emission assigned to **6**, but warming the sample to room temperature and recooling to 77 K led to the disappearance of this emission. Further, the spectra in Figure 1 are not present in samples which have not been irradiated. This excludes the possibility that the species detected at 77 K is a stable reaction product or a fluorescent impurity present in the starting material. Also, the fluorescence excitation and emission spectra of **6** are very similar in position and appearance to those previously reported for the diphenylmethyl radical,[3] and the excitation maximum agrees with the position of the absorption maximum of the diphenylchloromethyl radical.[7] However the fluorescence emission maximum in Figure 1 is blue shifted relative to that observed by Fessenden and co-workers[8] for the monochlororadical **6**. It is important to note that Fessenden and co-workers' spectrum was obtained in solution and ours in a rigid glass at 77 K, a difference which may well be responsible for the discrepancy between the two observations. A very similar phase-dependent shift in fluorescence maxima is well known for aromatic carbenes.[9,10] Owing to the large matrix shift in the fluorescence emission spectrum of **6**, we searched for an additional precursor to the chlorinated radical in order to strengthen the assignment of the emission spectrum. Johnston and Scaiano[7] and Horn and Allison[11] have independently demonstrated that an electronically excited state of diphenylcarbene (^{3}**7***) will abstract a Cl atom from carbon tetrachloride. We therefore attempted to generate the diphenylchloromethyl radical **6** in polycrystalline CCl_4 by photolysis of the oxirane **10** at 77 K (Scheme 3).

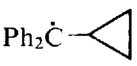


Scheme 3

Under these conditions, an emission spectrum identical with that in Figure 1a was produced, confirming that **6** is the species responsible for the emission spectrum initially observed in the photolysis of dichloride **5** at 77 K. The λ_{max} of the excitation spectrum of **6** is slightly blue shifted (ca 5 nm) relative to that of the unsubstituted diphenylmethyl radical. Similar blue shifts have been reported for various alkyl- and aryl-substituted diphenylmethyl radicals.[3] In the case of **11**–**13**, previous workers have attributed the hypsochromic shifts to an increase in the extent of twisting of the phenyl groups out of the central molecular plane. This presumably results in a decrease in conjugation of the radical center over the entire π system, thus raising the energy of the first electronic transition. Our assignment of the fluorescent carrier as **6** is consistent with this trend. Further, the vibrational structure of **6** is similar to that reported for radicals **11**–**13**. The first observable vibrational spacing in the spectrum of **6** is 1041 cm^{-1}. Similar values were reported for **11**–**13** (1049, 1020 and 1060 cm^{-1}, respectively), which the authors attributed to a C–C stretching mode. Further, radical **6** is photolabile (see below), producing diphenylcarbene on photolysis. We find it difficult to envision a structure other than that of **6** which could be consistent with all of these observations.

$Ph_2\dot{C}CH_3$

11



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$Ph_3C\cdot$

13

Photochemistry of diphenylchloromethyl radical (6)

On exposure of a rigid glass containing **5** and **6** to 254 nm light for long periods, the formation of a second emitting species in the matrix became evident. This second species is readily identified as the diarylcarbene **7**, as its fluorescence excitation and emission spectra agree with those previously reported for diphenylcarbene generated from diphenyldiazomethane.[9] It is interesting that two independent precursors, possessing very different ground-state geometries at the central carbon atom, give rise to similar matrix fluorescence spectra, both of which differ markedly from the solution-phase spectrum obtained at room temperature.[10]

If one monitors the ratio of **6** to **7** as a function of photolysis time, an interesting trend is observed. Clearly, the data shown in Table 1 indicate that the yield of carbene **7** relative to that of radical **6** increases with increasing irradiation time. Photolysis of **5** clearly leads to photodissociative expulsion of a Cl atom and formation of monoradical **6**. However, as the photolysis time increases, the concentration of radical **6** increases, at which point it can undergo secondary photolysis to form **7** by a second fragmentation similar to that observed initially with dihalide **5** (Scheme 2). According to this mechanism, the ratio of **6** to **7** is expected to decrease with increasing photolysis time, as the chlorinated radical **6** becomes photolytically converted to the diarylcarbene **7**. In our hands, the ratio of **6** to **7** could not be decreased below the value of 2·20 shown in Table 1 for a 10 min photolysis time. Admittedly, longer irradiation times actually led to increases in this ratio. This result may at first seem inconsistent with the proposed pathway leading to diphenylcarbene (**7**). However, under the experimental conditions, **7** is both thermally and even more rapidly photochemically destroyed, so as it accumulates in the matrix it too is photochemically destroyed. A possible pathway for decomposition of **7** is via H atom abstraction from the 2MeTHF matrix.[12] Such processes are well documented for diarylcarbenes, and in this case would lead to the diphenylmethyl radical, which could remain undetected owing to its overlapping absorption and fluorescence maxima with those of chlorinated radical **6**. Therefore, prolonged irradiation could lead to an increase in the apparent ratio of **6** to **7**, consistent with the proposed mechanism.

The mechanism proposed in Scheme 2 is neither unreasonable nor unprecedented. A single 254 nm photon does not have sufficient energy to cleave both C—Cl bonds of diphenyldichloromethane. Bromberg and Meisel[13] demonstrated that the diphenylmethyl radical can be photochemically consumed and postulated that the radical photolytically

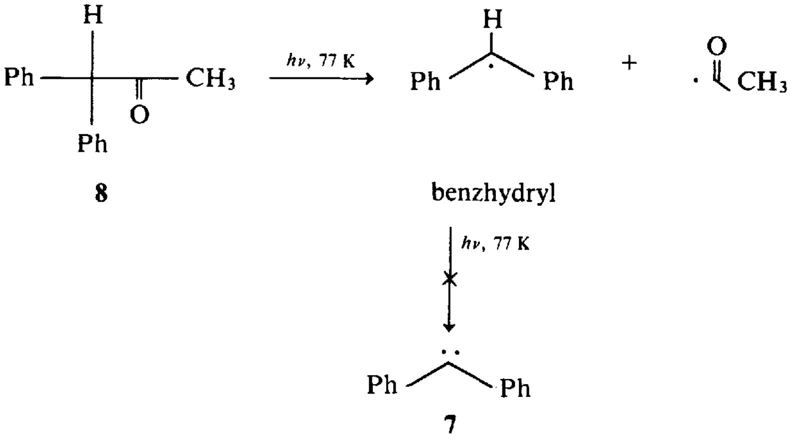
Table 1. Ratio of diphenylchloromethyl radical to diphenyl carbene (**6** : **7**) as a function of irradiation time[a]

Irradiation time (min)	**6** : **7**
0·5	13·2
1·5	4·50
3·0	2·43
5·0	2·41
10·0	2·20

[a] Ratio determined by measuring absolute intensities of the fluorescence emission at the maxima for **6** and **7** (522 and 474 nm) while exciting at 340 and 300 nm, respectively. Ratio determined following photolysis of **5** (0·01 M in 2-MeTHF irradiated (Rayonet RPR 2534, 5 tubes) at 77 K.

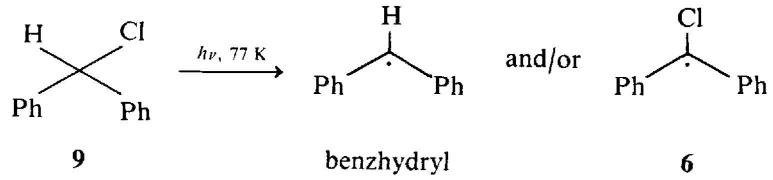
fragments to form **7**. This hypothesis was based on indirect evidence, as the product carbene was not directly detected. To our knowledge, this work represents the first matrix spectroscopic observation of a triplet carbene produced by photolysis of a chlorinated radical.

We have tried without success to produce triplet diphenylcarbene by photolysis of benzyhydryl radical in organic glasses at 77 K. Photolysis (254 nm, 77 K) of 1,1-diphenylacetone (**8**) in 3-methylpentane at 77 K produces benzhydryl radical (Scheme 4), which is easily detected by its fluorescence. Prolonged irradiation of this radical (either 254 nm or broad-band) did not produce any evidence for the formation of diphenylcarbene (**7**).



Scheme 4

Photolysis (254 nm, 77 K) of benzhydryl chloride (**9**) in 3-methylpentane produces a new emission maximum at 525 nm. Because of the similarity in the spectra of **6** and the benzyhydryl radical, it is not immediately clear which radical (or if a mixture of radicals) has been produced (Scheme 5).



Scheme 5

We suspect that photolysis of **9** produces the benzyhydryl radical because prolonged photolysis does not produce diphenylcarbene, as it must if chlorinated radical (**6**) were produced. Preferential cleavage of a C—Cl bond in **9** makes sense intuitively because this is the weakest bond in the molecule. The failure to produce diphenylcarbene from **8** or **9** demonstrates the uniqueness of the diphenyldichloromethane system.

The data presented so far are consistent with, but do not require, the sequential nature of the double photodissociation as described in Scheme 2. The data do not exclude the possibility that **7** is simply formed concurrently with **6**, but by a lower quantum yield process which does not involve the intermediacy of **6**.

Highly monochromatic laser radiation can selectively excite one particular component in a mixture of compounds in solution or in a matrix, excluding all others which may be present but do not absorb significantly at the laser line. The monoradical **6** has a strong absorption band centered at 341 nm and the dihalide precursor **5** does not absorb significantly in this region. Thus, by using the 337 nm line of a nitrogen laser one could hope to excite **6** selectively, without depositing energy into **5**. The results of this experiment are shown in Figure 2, where the fluorescence emission spectra of both **6** and **7** are shown before and after exposure to nitrogen laser radiation. Clearly, the intensity of the signal due to the carbene has increased at the expense of the radical **6** following 337 nm photolysis. One is therefore compelled to conclude that monoradical **6** is indeed a photochemical precursor to **7**. This represents direct evidence supporting the stepwise nature of the double photodissociation of a geminal dichloride to a monochloro radical, with subsequent photolysis of the nascent monochlorodiaryl radical to a carbene.

It is interesting that the fluorescent excited state of **6** cannot be the state which undergoes fragmentation, because the energy of this state (523 nm = 54·8 kcal mol^{-1}) is less than that of a typical C—Cl bond dissociation energy.[14] Hence 254 or 337 nm (112·7 and 85 kcal mol^{-1}) excitation must lead to an even higher energy dissociative state of radical **6**.

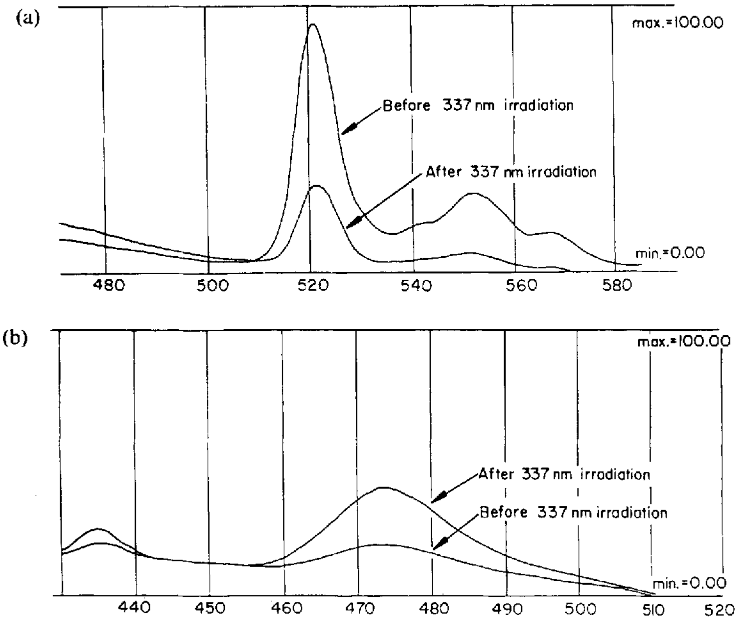


Figure 2. (a) Fluorescence emission spectrum of the chlorodiphenylmethyl radical (**6**) produced by 254 nm photolysis of a 0·01 M solution of **5** in glassy 2-MeTHF at 77 K. Following irradiation with the 337 nm line of a nitrogen laser, the intensity of the signal due to chlorinated radical **6** is shown to decrease. Spectra shown before and after irradiation with a 337 nm laser. The excitation wavelength was 340 nm. (b) Fluorescence emission spectrum of diphenylcarbene (**7**) produced by 254 nm photolysis of a 0·01 M solution of **5** in glassy 2-MeTHF at 77 K, followed by 337·1 nm nitrogen laser irradiation of **6**. Spectra shown both before and after laser irradiation. The excitation wavelength was 300 nm

CONCLUSIONS

Photolysis of **5** at 254 nm at 77 K yields monoradical **6**, which was detected by its fluorescence spectrum. Monoradical **6** can be further photolyzed to **7** either by continued 254 nm photolysis or, more efficiently, by laser radiation. This represents the first case to our knowledge where a dihalide has been photolyzed to the corresponding carbene, and may serve as a viable route to other matrix isolated carbenes and biradicals. This is possible because of the interesting photochemical properties of the intermediate radical **6**, which is able to undergo photodissociation to a carbene. This procedure may readily lend itself to extension into various other systems.

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