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Laser Flash Photolysis Study of Chlorocarbene

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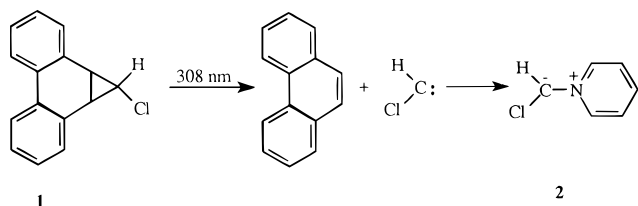
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Laser flash photolysis (308 nm) of *endo*-7-chlorodibenzo[*a,c*]bicyclo[4.1.0]heptane produces phenanthrene and chlorocarbene, which can be trapped with pyridine to form an ylide. The ylide absorbs strongly at 374 nm, and its lifetime is many tens of microseconds. It was not possible to resolve the growth of the ylide due to the rapid reaction of chlorocarbene with solvent. It was possible, however, to deduce the lifetimes of chlorocarbene in various solvents by measuring the yield of ylide as a function of [pyridine] and assuming that the absolute rate constant of reaction of chlorocarbene is the average of those of dichlorocarbene and alkylchlorocarbenes, which have been previously reported. Absolute rate constants for the reaction of chlorocarbene with alkenes were then deduced by the Stern–Volmer method, and the relative reactivity of chlorocarbene toward alkenes was found to be in good agreement with the relative reactivities of the lithium–chlorocarbene complex or carbenoid determined by analysis of product mixtures reported by Closs and Schwartz.

Introduction

The simplest carbenes are, of course, triatomic. Methylene (CH₂) has been studied by an enormous number of experimental and theoretical techniques² including nanosecond laser flash photolysis (LFP)³ methods. Dichlorocarbene (CCl₂) has also been studied by LFP methods.⁴ Herein we are pleased to report LFP studies of chlorocarbene (CHCl). Perhaps unsurprisingly our data indicate that the absolute reactivity of CHCl is somewhat intermediate in behavior to that of CH₂ and CCl₂. As per the LFP work with CCl₂,⁴ chlorocarbene will be generated by LFP of a known dihydrophenanthrene type of precursor (e.g. *endo*-1).⁵



endo-7-Chlorodibenzo[*a,c*]bicyclo[4.1.0]heptane (**1**) was prepared as previously described⁵ from the phenanthrene–dichlorocarbene adduct by low-temperature lithiation with *n*-butyllithium, followed by quenching with methanol. Only the *endo* isomer is produced by this reaction. Material for photochemical and LFP studies was purified by radial chromatography followed by multiple recrystallization.

Photolysis of dilute solutions of **1** at 254 nm in a Rayonet photoreactor afforded high yields of phenanthrene, which was isolated by chromatography over silica gel. No other aromatic products were detected. To prove that chlorocarbene was generated, the carbene was trapped by cycloaddition with cyclohexene. Authentic samples of the *endo*- and *exo*-7-

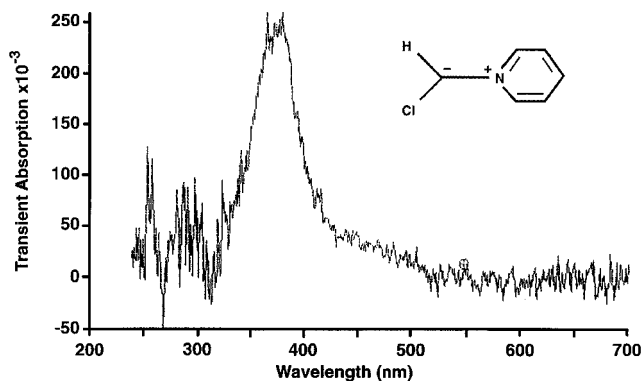
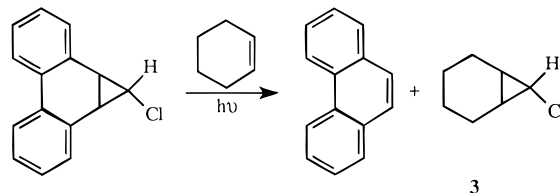


Figure 1. Transient spectrum of ylide **2** produced upon LFP of **1** in pentane containing 0.59 M pyridine at 295 K. The spectrum was recorded over a window of 400 ns approximately 1.1 μ s after the laser pulse.

chloronorcaranes (**3**) were prepared following the method of Closs and Closs⁶ and purified by preparative gas chromatography. NMR spectral data were in agreement with the literature.⁷



Results and Discussion

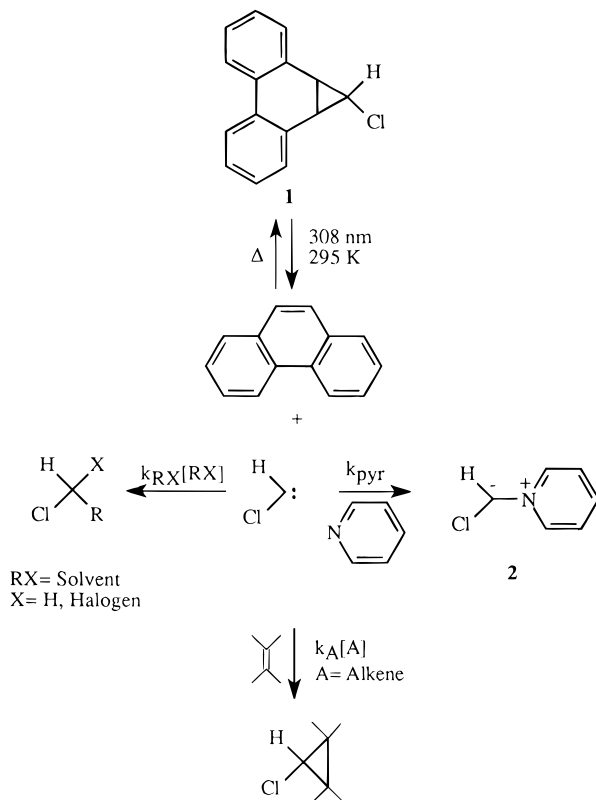
Laser Flash Photolysis. LFP (308 nm) of **1** in deoxygenated hydrocarbon solvents at 295 K fails to produce a UV–vis active transient intermediate. However, LFP of **1** in the same solvents, in the presence of pyridine, leads to an intensely absorbing transient with $\lambda_{\text{max}} \approx 374$ nm (Figure 1, Table 1). The transient

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TABLE 1: Absorption Maxima of Ylide 2 and the Deduced Lifetimes of Chlorocarbene in Various Solvents

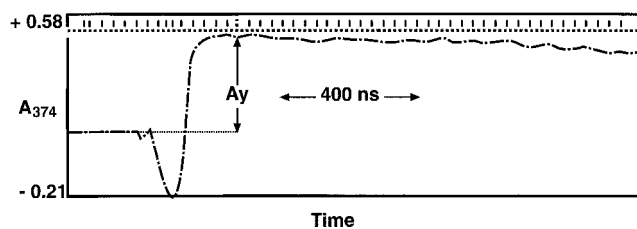
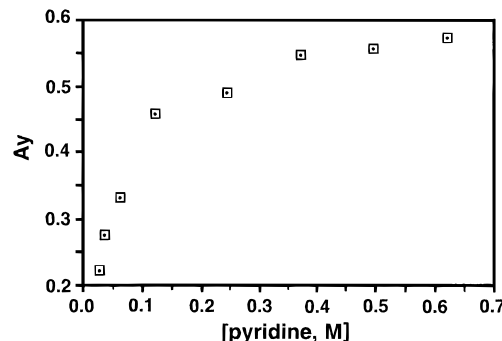
solvent	λ_{\max} [2, (nm)]	$k_{\text{pyr}}\tau$ (M^{-1})	τ (ns) ^a
pentane	373.5	16–24	2–3
cyclohexane	375	2.8–3.6	0.35–0.45
cyclohexane- <i>d</i> ₁₂	375	3.6–4	0.45–0.5
acetonitrile	374	0.48–1.2	0.06–0.15
benzene	374.5	0.56	0.07
Freon-113	375		

^a Assuming $k_{\text{pyr}} = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

SCHEME 1

has a lifetime in excess of several microseconds and is attributed to ylide **2** (Scheme 1). This conclusion is supported by analogy to the very similar transient spectra observed with the pyridine ylides derived from dichlorocarbene ($\lambda_{\max} = 390 \text{ nm}$)⁴ and alkylchlorocarbenes ($\lambda_{\max} = 370\text{--}379 \text{ nm}$)⁸ and by detection of phenanthrene by gas chromatography after photolysis at 300 nm. It was not possible to resolve the rate of formation of ylide **2** in any solvent system studied. This demonstrates that chlorocarbene is a very short-lived ($\tau < 20 \text{ ns}$) intermediate relative to dichlorocarbene, which has a lifetime of microseconds in hydrocarbon solvents.⁴ This result is not surprising because chemical analysis of the reactions of chlorocarbene⁹ indicates that this species inserts readily into the C–H bonds of hydrocarbon solvent (RX, Scheme 1).

As ylide **2** is formed faster than the time resolution of our apparatus, the optical yield (A_y) as a function of pyridine concentration was measured. In the absence of pyridine, A_y is close to zero and increases steadily as the concentration of pyridine is increased (Figures 2 and 3). At high concentrations of pyridine, the yield of ylide is saturated (A_y^∞); every carbene produced in the laser pulse is then trapped prior to reaction with solvent. The quantum yield of ylide formation (ϕ_y) and the optical yield of ylide are given in eq 1, where ϕ_c is the quantum yield of carbene formation, k_{pyr} is the rate constant of quenching by pyridine, and k_0 is a pseudo-first-order rate constant that is the sum of all the processes consuming the carbene.

**Figure 2.** Formation of ylide **2** in pentane at 295 K after the laser pulse, monitored at 374 nm (A_{374}). The value of A_y is defined.**Figure 3.** Optical yield of ylide **2** (A_y) determined as a function of [pyridine] in pentane at 295 K.

$$\phi_y = \frac{\phi_c k_{\text{pyr}} [\text{pyridine}]}{k_0 + k_{\text{pyr}} [\text{pyridine}]} \quad (1)$$

and

$$A_y = \phi_y A_y^\infty \quad (2)$$

Equation 3 follows immediately from eqs 1 and 2.

$$\frac{1}{A_y} = \frac{k_0}{\phi_c A_y^\infty k_{\text{pyr}} [\text{pyridine}]} + \frac{1}{\phi_c A_y^\infty} \quad (3)$$

Thus a plot of $1/A_y$ versus $1/[\text{pyridine}]$ is predicted and found to be linear (Figure 4). Division of the intercept by the slope gives the ratio (k_{pyr}/k_0) , which is equal to $k_{\text{pyr}}\tau$, where τ is the lifetime of chlorocarbene in the absence of pyridine.¹⁰ The value of k_{pyr} is taken to be equal to the average of the previously determined values with chloromethyl, chlorobenzyl, and dichlorocarbenes ($8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).^{4,8} Lifetimes obtained in this manner are listed in Table 1. The results presented here have been reproduced twice in each solvent, except in benzene. Chlorocarbene is likely to be more reactive than dichlorocarbene and alkylchlorocarbenes for steric and electronic reasons. Thus, a value of k_{pyr} is assumed, which is a lower limit, and the lifetime values are likely to be upper limits. The lifetime of chlorocarbene is significantly smaller than other alkylchlorocarbenes: 330 ns with methylchlorocarbene, 90 ns with *tert*-butylchlorocarbene, 15 ns with benzylchlorocarbene, and 10 ns with ethylchlorocarbene (all results obtained at 298 K in isooctane).^{8,11} This indicates that the chemical reaction(s) consuming the carbene (mainly insertion into a C–H bond of the solvent in the case of the chlorocarbene) is (are) faster with the chlorocarbene than with dichlorocarbene and alkylchlorocarbenes.

The data of Table 1 demonstrate that the kinetic isotope effect on the insertion of chlorocarbene is too small to be measured ($\tau_{\text{H}}/\tau_{\text{D}} \approx 1$). This is surprising because isotope effects on the C–H insertion reactions of other singlet carbenes have previously been found to be close to 2.¹² The lack of an isotope effect indicates that readdition of chlorocarbene to phenanthrene

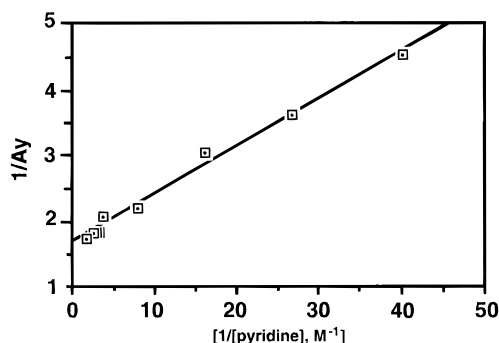
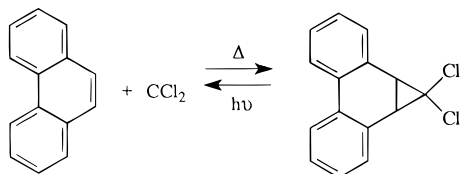


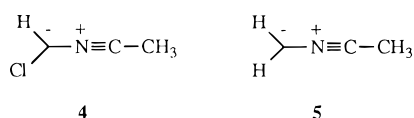
Figure 4. Double reciprocal treatment of the data of Figure 3.

may substantially limit the lifetime of this carbene, under the conditions of this work. The readdition reaction cannot be considered surprising as dichlorocarbene (which is less reactive than CHCl) adds readily to the 9,10 position of phenanthrene.^{4,5}

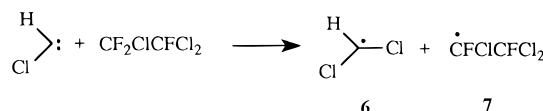


The very short lifetime of **1** in benzene is likely due to facile addition of the carbene to the aromatic, a reaction discovered by Jones and co-workers.¹³ As chlorocarbene reacts rapidly with benzene, it seems again likely that this carbene will react quickly with the phenanthrene that is generated in the same solvent cage upon LFP of **1**. This will also lead to small values of the deduced lifetimes.

A transient intermediate is detected upon LFP of **1** in acetonitrile (no pyridine). This transient is attributed to ylide **4** formed by reaction of the carbene with solvent (Figure 5A). Turro et al. have observed the transient spectrum of ylide **5** upon LFP of diazirine in acetonitrile.³ LFP of **1** in acetonitrile containing pyridine again produces a transient with $\lambda_{\text{max}} = 374$ nm, attributed to ylide **2** (Figure 5B). The rather short lifetime of chlorocarbene in acetonitrile is due to the rapidity of acetonitrile–ylide formation.



It was not possible to deduce the lifetime of **1** in Freon-113 ($\text{CF}_2\text{ClCFCl}_2$). A double reciprocal treatment of the transient absorption data is not linear. We speculate that chlorocarbene abstracts chlorine atoms from Freon-113 to form radicals **6** and **7** and that these radicals react with pyridine and/or phenanthrene to produce radical species whose absorption may overlap that of ylide **2**.



Stern–Volmer Quenching with Alkenes. Chlorocarbene is known to react with alkenes (A, Scheme 1) to form cyclopropanes.⁹ Every carbene produced upon LFP of **1** in cyclohexane containing 1.24 M pyridine is captured by pyridine to form ylide **2**. Upon addition of alkene, however, the yield of ylide will drop due to competitive capture of the carbene.

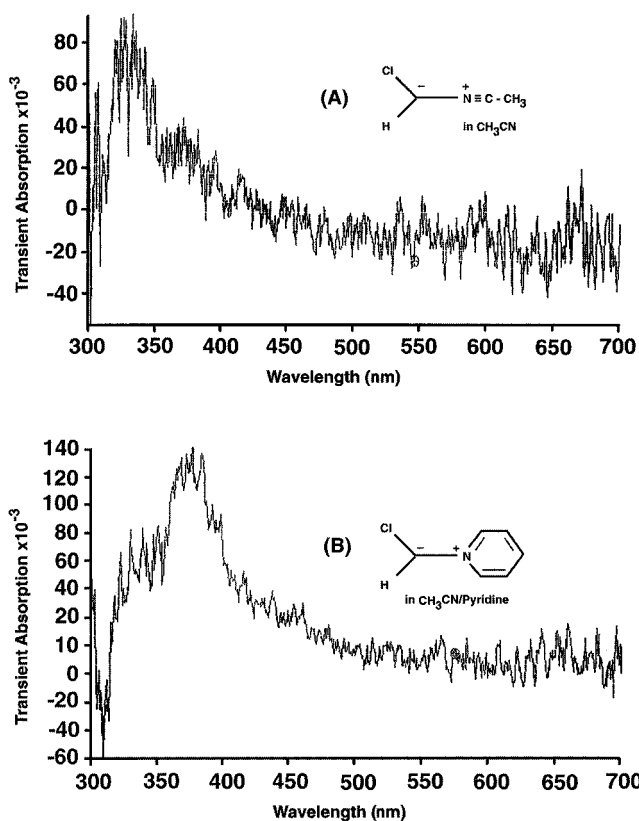


Figure 5. Transient spectra obtained by LFP of **1** in (a) acetonitrile and (b) acetonitrile containing 1.24 M pyridine. The spectra were recorded over a window of 400 ns approximately 600 ns after the laser pulse.

TABLE 2: Stern–Volmer Rate Constants for the Reaction of Chlorocarbene with Alkenes

alkene	k_A/k_{pyr}	k_A ($\text{M}^{-1} \text{s}^{-1}$)	k_A ($\text{M}^{-1} \text{s}^{-1}$)
2,3-dimethyl-2-butene	1.01	8.1×10^9	3.8×10^9
2-methyl-2-butene	0.41	3.3×10^9	2.2×10^9
<i>trans</i> -3-hexene	0.40	3.2×10^9	0.063×10^9 ^c
cyclohexene	0.24	1.9×10^9	0.035×10^9
1-hexene	0.15	1.2×10^9	0.01×10^9
1-pentene	0.125	1.0×10^9	
spread		8.1	380

^a Assuming $k_{\text{pyr}} = 8 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$. ^b Data of dichlorocarbene. ^c *trans*-2-Pentene.

Under these conditions (constant pyridine concentration) it can be shown¹⁰ that

$$\frac{A_y^\infty}{A_y} = 1 + \frac{k_A[A]}{k_{\text{pyr}}[\text{pyridine}]}$$

where A_y is the optical yield of ylide formed in the presence of 1.24 M pyridine and alkene. Thus a plot of A_y^∞/A_y versus alkene will be linear with a slope equal to $k_A/k_{\text{pyr}}[\text{pyridine}]$. Values of k_A/k_{pyr} measured in this manner are given in Table 2 (see Figure 6) along with values of k_A deduced by assuming that $k_{\text{pyr}} = 8 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$. The excellent agreement between the relative reactivity of the photochemically generated intermediate and the product-forming species (probably a carbenoid) trapped by Closs and Schwartz (Table 3)⁹ leaves little doubt that it is chlorocarbene that is generated and trapped with pyridine upon LFP of **1**.

Conclusions

Chlorocarbene is found to be a highly reactive carbene whose lifetime in the absence of quenchers is controlled by reaction

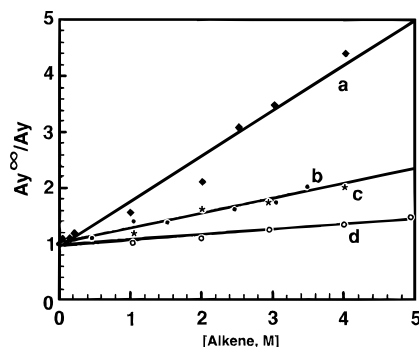


Figure 6. Stern–Volmer treatment of the quenching of the yield of ylide **2** with alkene, at constant pyridine concentration: (a) TME; (b) 2-methyl-2-butene; (c) *trans*-3-hexene; (d) 1-hexene.

TABLE 3: Relative Reactivity of Chlorocarbene toward Alkenes Determined by Chemical Analysis⁹ and LFP

alkene	k_A/k_{TME} (chemical analysis)	k_A/k_{TME} (LFP)
2,3-dimethyl-2-butene (TME)	1	1
2-methyl-2-butene	0.63	0.41
<i>cis</i> -2-butene	0.32	
<i>trans</i> -3-hexene		0.40
cyclohexene	0.21	0.23
1-hexene		0.15
1-pentene	0.08	0.12

with solvent or by readdition to phenanthrene. Unsurprisingly it is found to undergo C–H insertion reactions with alkanes less rapidly than methylene but substantially faster than dichlorocarbene. As per methylene, chlorocarbene forms an ylide with acetonitrile.³

The absolute reactivity of chlorocarbene toward alkenes is greater than that of dichlorocarbene⁴ and the arylhalocarbenes.¹⁴ The rate of reaction of chlorocarbene with tetramethylethylene (TME) approaches the diffusion-controlled limit, and the “spread” or range of reactivity of chlorocarbene toward representative alkenes (Table 2) is quite small (8.1) as opposed to that of dichlorocarbene⁴ (380), in accord with the reactivity-selectivity principle. The absolute rate constants deduced herein are in good agreement with the relative rate measurements of Closs and Schwartz of the lithium–chlorocarbene, carbenoid complex.⁹ This leaves little doubt that the species being trapped is indeed chlorocarbene.

Experimental Section

The LFP system in use at The Ohio State University has been described previously.¹⁵ Samples were exposed to the pulses of a 308 nm laser (XeCl, 17 ns, 150 mJ, Lambda Physik LPX100 excimer laser) at right angles to a pulsed 150 W He/Xe arc lamp. Transient spectra were recorded approximately 1 μ s after the laser pulse using an EG and G Princeton Applied Research Model 1460 Optical Multichannel Analyzer (OMA).

Stock solutions of dihydrophenanthrene precursor **1** were typically prepared with an optical density of ~ 1.0 at 308 nm for lifetime experiments and with an optical density of ~ 0.5 for OMA experiments. A constant volume of the stock solution was added to Suprasil quartz cuvettes. To each cuvette was added varying amounts of pyridine. Solvent was added to each cuvette to maintain a constant volume of sample throughout the experiment. Samples were degassed by purging with dry, oxygen-free argon for 3–4 min.

Stern–Volmer quenching studies were performed similarly. In this case, stock solutions consisted of precursor in cyclohexane containing 1.24 M pyridine. Quencher concentrations

were typically varied from 0 to between 4 and 5 M for a series of 6–9 cuvettes.

Pentane (Aldrich, HPLC grade), cyclohexane and acetonitrile (Burdick and Jackson, high-purity grade), and cyclohexane-*d*₁₂ (CIL, 99.7%) were used as received. Benzene was distilled from sodium/benzophenone. Pyridine (Aldrich, 99+%) was distilled over CaH₂ and stored over KOH pellets. Freon-113 (Aldrich, HPLC grade), 2,3-dimethyl-2-butene, 2-methyl-2-butene, *trans*-3-hexene, cyclohexene, 1-hexene, and 1-pentene were passed through an alumina column immediately before use.

endo-7-Chlorodibenzo[*a,c*]bicyclo[4.1.0]heptane (1)⁵. A solution of 7,7-dichlorodibenzo[*a,c*]bicyclo[4.1.0]heptane⁵ (1.51 g, 5.78 mmol) in 30 mL of ether/THF (1:1) was cooled to -78°C (dry ice/acetone) and treated dropwise with 6.5 mL (10.4 mmol) of 1.6 M *n*-butyllithium. The reaction mixture became dark green. After 60 min, methanol (2 mL) was added. The reaction was slowly warmed to room temperature and was stirred overnight before being quenched with brine (4 mL). The organic layer was washed with brine (2×4 mL), dried over MgSO₄, and concentrated under reduced pressure.

Photolysis of endo-7-Chlorodibenzo[*a,c*]bicyclo[4.1.0]heptane (1). Chlorocarbene precursor **1** (10.5 mg, 0.463 mmol) was placed in each of two quartz test tubes. To each tube was added 5 mL of freshly distilled cyclohexene and 15 mL of spectroquality hexane. The tubes were sealed with rubber serum caps and degassed for 15 min with a stream of nitrogen. One tube was irradiated for 30 min at 254 nm and the other for 60 min. After irradiation, the yields of products were determined through analysis by 360 MHz NMR and gas chromatography, with the use of internal standards. Diphenylmethane was used as an internal standard for NMR. Conversion of starting material to phenanthrene for each reaction was $34.3 \pm 3\%$ after 30 min and $62.7 \pm 3\%$ after 60 min. 1,2,3,4-Tetrahydronaphthalene was used as an internal standard for GC analysis. The FID response factor was calibrated versus authentic 7-chloronorcarane. Yields of the trapped products (total for *endo*- and *exo*-7-chloronorcaranes; *endo/exo* 1.1:1) as determined by GC analysis were $86.7 \pm 3\%$ (30 min irradiation) and $86.0 \pm 3\%$ (60 min) based on reacted starting material.

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