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A Laser Flash Photolysis Study of Dibromocarbene and Bromochlorocarbene

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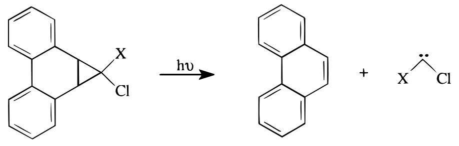
Laser flash photolysis (LFP, XeCl, 308 nm) of 11,11-dibromotricyclo[4.4.1.0$^{1.6}$]undeca-2,4,8-triene (**1**) or 10,10-dibromotricyclo[4.3.1.0^{1,6}]deca-2,4-diene (**2a**) produces CBr_2 and an aromatic compound. Bromochlorocarbene is produced by LFP of 10-bromo-10-chlorotricyclo[4.3.1.0^{1,6}]deca-2,4-diene (**2b**). The carbenes are trapped by pyridine to form ylides. The lifetimes of CBr_2 and CBrCl and their absolute reactivities toward pyridine and alkenes have been determined. The relative reactivity of CBr_2 toward alkenes determined by LFP methods is in excellent agreement with that determined previously by chemical analysis of reaction mixtures, and the rate constant data reveal that the absolute reactivity of CBrCl more closely resembles that of CBr_2 rather than that of CCl_2.

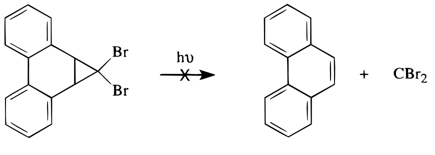
I. Introduction

Dibromocarbene was one of the first carbenes to be thoroughly studied by chemical analysis.[1] Because of the lack of a suitable precursor, it has not been studied by laser flash photolysis (LFP) methods. Herein we are pleased to report LFP studies of dibromocarbene (CBr_2) that complement previous laser flash photolysis studies of dichlorocarbene[2] and of chlorocarbene.[3] The chlorinated carbenes were generated from 7,7-dichloro- and *endo*-7-chlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane.



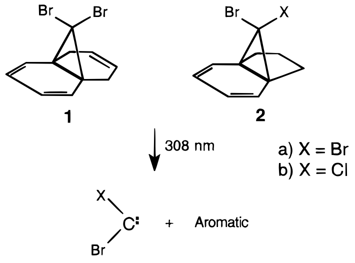
X = H, Cl

However, this reaction fails to produce CBr_2 in the corresponding precursor[4]



necessitating the use of another source of the carbene. Dibromocarbene and bromochlorocarbene have been generated by LFP of precursors **1** and **2**. Jones and Bickelhaupt have used these compounds as a photochemical source of dibromocarbene and shown that it leads to carbene addition products in good yield in the presence of various olefins.[5,6] Jones et al. have also used diene **2a** as a dibromocarbene source to demonstrate the feasibility of 1,4 addition to 1,3-dienes and of "homo 1,4 addition" to norbornadiene.[6]

In this paper we report absolute rate constants of reaction of dibromocarbene and bromochlorocarbene with alkenes and pyridine.



II. Results and Discussion

Recent calculations indicate that dihalocarbenes are ground state singlets[7] presumably because of the stabilization the two halogen substituents provide the carbene center. The singlet state of dibromocarbene, for example, has been calculated to be 12.48 kcal/mol lower in energy than the corresponding triplet state, while the singlet state of bromochlorocarbene is calculated to be 16.12 kcal/mol lower in energy than the corresponding triplet state.[7b] Provided theoretical studies dealing with the singlet−triplet energy gaps in dihalocarbenes use configuration interaction (CI)[7d] and d basis functions,[7e] reliable measurement of singlet−triplet energy gaps in dihalocarbenes can be obtained. For example, the calculated results are consistent with the organic chemistry of CBr_2, and the singlet−triplet energy gap for dichlorocarbene shows good agreement between theory (20.04 kcal/mol)[7b] and experiment (20.5 kcal/mol).[8] It is interesting to note that the calculated singlet−triplet energy gap for bromochlorocarbene (16.12 kcal/mol) is approximately midway between the singlet−triplet energy gaps calculated for dibromocarbene (12.48 kcal/mol) and dichlorocarbene (20.04 kcal/mol).

Under 308 nm irradiation at room temperature, both compounds **1** and **2a** produce two weak, overlapping absorption

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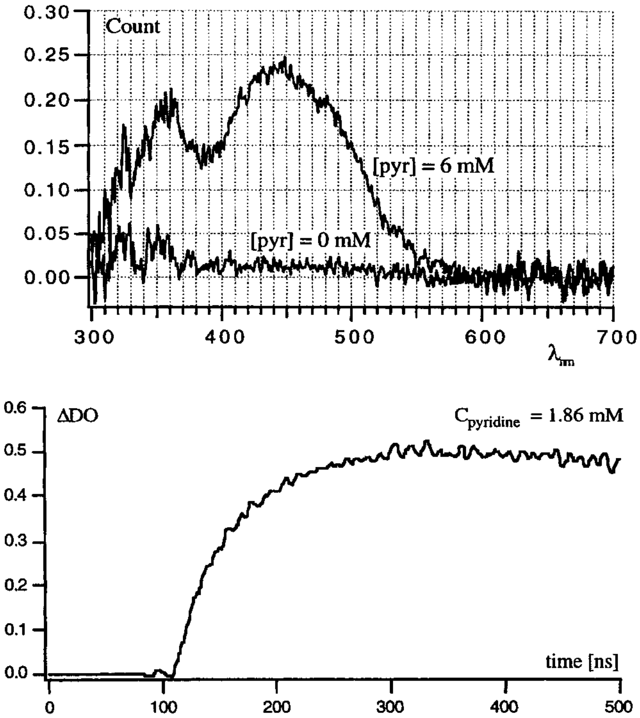
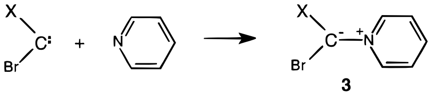


Figure 1. Top: Transient spectrum obtained upon LFP of precursor **2a** in cyclohexane. The spectrum was recorded approximately 1.3 μs after laser pulse over a window of 300 ns. Bottom: Kinetic trace of pyridine-ylide in isooctane monitored at 436 nm (obtained by LFP of precursor **1**).

bands with maxima around 330 and 370 nm, respectively. Upon addition of pyridine, even in extremely small concentrations, a very intense band centered around 440 nm appears (Figure 1). The same results were obtained in different solvents (pentane, isooctane, cyclohexane, cyclooctane, and $CF_2ClCFCl_2$−Freon-113). This transient is attributed to the ylide **3a** resulting from the quenching of singlet dibromocarbene by pyridine.



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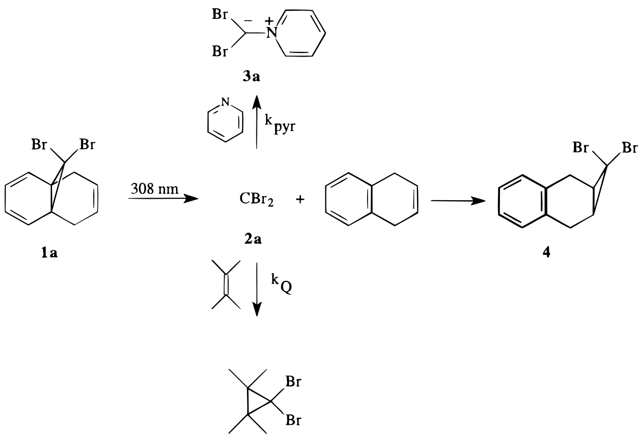
X = (a) Br (b) Cl

Ylide **3a** is formed in an exponential process following the laser pulse (Figure 1) which can be analyzed to yield an observed rate constant k_{obs}. This observed rate constant can be related to Scheme 1 via eq 1

SCHEME 1



$$k_{obs} = 1/\tau + k_{pyr}[pyr] \qquad (1)$$

where k_{pyr} is the absolute rate constant of reaction of CBr_2 with pyridine and τ is the lifetime of CBr_2 in the absence of pyridine. As expected, a plot (Figure 2) of k_{obs} versus [pyridine] is linear with a slope of k_{pyr} (Table 1).

The yield of ylide **3a** increases as the pyridine concentration increases from 0 to 5 mM. Above this pyridine concentration there is no further increase in the yield of ylide. Thus, every carbene produced upon LFP of **1** in isooctane containing 12.4 mM pyridine is captured by pyridine to form an ylide. Upon addition of alkene, however, the yield of ylide will drop because of competitive capture of the carbene (Scheme 1, Figure 3). Under these conditions, it can be shown that

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

where A_y is the optical yield of ylide formed in the presence of 12.4 mM pyridine and alkene. Thus a plot of A_y^∞/A_y versus alkene will be linear with a slope equal to k_A/k_{pyr}[pyridine] (Figure 3). Values of k_A determined in this manner are given in Table 2.

There is a good agreement between the relative reactivity of the photochemically generated species, which reacts with pyridine, and the product-forming species trapped by Moss[1d] and earlier by Skell[1e] and Doering[1f] (Table 3). The most meaningful comparison is with the data of Moss et al. because any involvement of carbenoid species was eliminated by the use of 18-crown-6. Thus, there is no doubt that we are

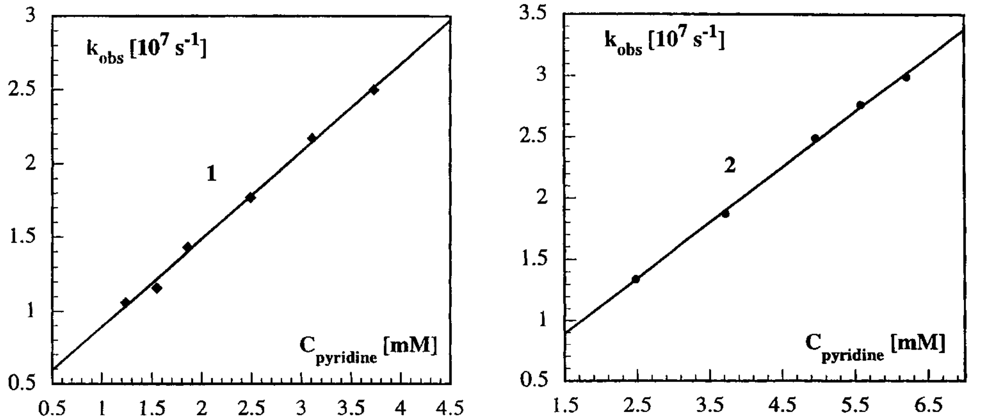


Figure 2. Plots of k_{obs} vs [pyridine] in Freon-113 (left, precursors **1** and **2a**) and in cyclooctane (right, precursor **1**).

TABLE 1: Dibromocarbene Lifetimes and Rate Constants of Addition to Pyridine Measured at the Absorption Maxima of the Pyridinium Ylide

precursor	solvent	viscosity[a] (295 K) (cP)	lifetime (ns)	k_{pyr} (10^{-9} M^{-1} s^{-1})
1	isooctane	0.49	250 ± 10	9.5–10
	freon-113	0.72	330 ± 30	4.9
	cyclohexane	0.95	340 ± 30	4.9–5
	cyclohexane-d_{12}		560 ± 20	~4
	cyclooctane	2.2	150	4
2a	isooctane	0.49	290	10.8
	freon-113	0.72	455 ± 10	4.5
	cyclohexane	0.95	350 ± 5	4.95
	cyclohexane-d_{12}		600 ± 30	~5.4

[a] See ref 14.

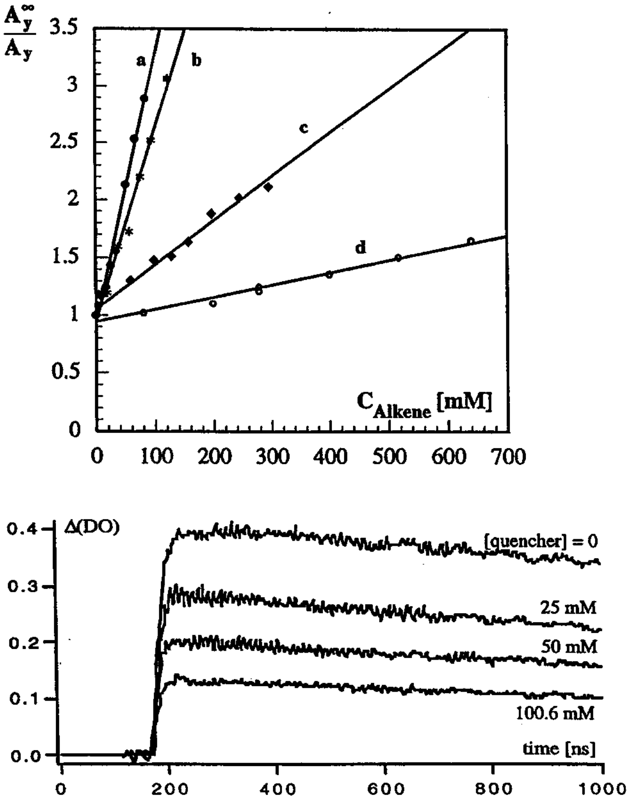


Figure 3. Top: Stern–Volmer treatment of the quenching of the yield of ylide with alkene, at constant pyridine concentration (a, TME; b, 2-methyl-2-butene; c, cyclohexene; d, 1-hexene). Bottom: Kinetics of the pyridine-ylide in isooctane at 436 nm and constant pyridine concentration (from precursor **1**). Drop of the infinite yield of ylide by addition of increasing amounts of quencher (TME).

TABLE 2: Stern–Volmer Rate Constants k_A (10^{-9} M^{-1} s^{-1}) for the Reaction of Dibromocarbene, Bromochlorocarbene, and Dichlorocarbene with Alkenes

alkene	CBr_2	CCl_2[a]	CClBr[a]
2,3-dimethyl-2-butene (TME)	2.80	3.80	5.97
2-methyl-2-butene	1.99	2.23	
cyclohexene	0.464	0.035	0.343
isoprene			2.80
2,3-dimethyl-1,3-butadiene			1.57
1-hexene	0.128	0.0108	
1-pentene			0.150
cis-4-methyl-2-pentene			1.93
spread	22	352	38

[a] Data of dichlorocarbene, see ref 2.

monitoring ylide **3a** and the dynamics of CBr_2. Dibromocarbene is less selective than dichlorocarbene. The spread or range of reactivity is about 22 with the latter species whereas it is about 350 with the former (Table 2).[2] The Br substituent must provide less electronic stabilization to the carbene than does Cl, and hence the greater selectivity of dichlorocarbene.

TABLE 3: Relative Reactivity of Dibromocarbene toward Alkenes As Determined by Chemical Analysis and LFP

alkene	k_A/k_{TME}[a] (chemical analysis)	k_A/k_{TME} (LFP)
2,3-dimethyl-2-butene	1	1
2-methyl-2-butene	0.65	0.71
cyclohexene	0.115–0.145	0.165
1-hexene	0.02–0.03	0.045

[a] See ref 1.

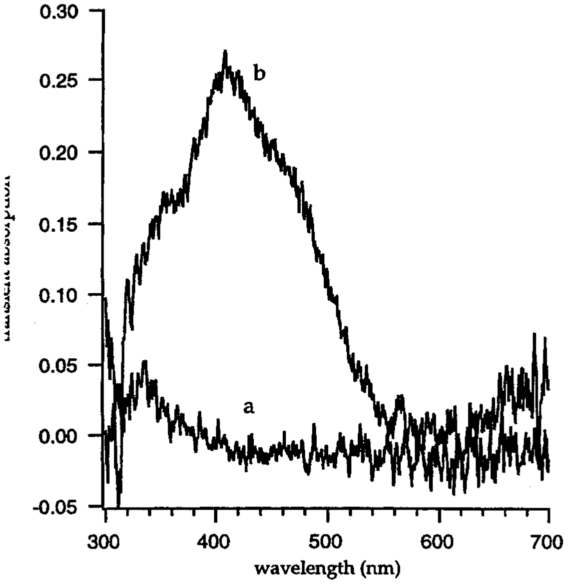


Figure 4. Transient spectrum of ylide **3b** produced by LFP of **2b** in cyclohexane containing: (a) 0.00 mM pyridine; and (b) 3.1 mM pyridine at ambient temperature. The spectra were recorded over a window of 200 ns, at 200 ns after the laser pulse.

How can one be sure that this new band arises from an ylide and not from a charge transfer complex resulting from the association of pyridine and bromine radicals? First, recall that photolysis of triene **1** leads to carbene addition products in good yield in the presence of various olefins.[5] Second, if bromine radicals were produced, then the transient spectrum in benzene should exhibit the characteristic broad absorption band of the ensuing complex, with $\lambda_{max} \sim 550$ nm.[10] However, the transient spectrum produced upon LFP of **1** in isooctane in the presence of benzene (up to 2.25 M) did not exhibit a new band. Third, it is known that alkylbromocarbene–pyridine adducts absorb at approximately 25 nm longer wavelengths than the corresponding chloro adducts.[11] Since λ_{max} for the dichlorocarbene–pyridine adduct has been found to be near 390 nm,[2] one would expect a maximum for the absorption of the dibromocarbene–pyridine ylide in the 415–440 nm region. This is exactly what has been observed.

Bromochlorocarbene. Laser flash photolysis of **2b** in the presence of pyridine generates a transient intermediate with λ_{max} = 407 nm (Figure 4). As in the case of **3a**, this transient is attributed to ylide **3b** because its rate constant of formation is linearly dependent on the concentration of pyridine (Figure 5). The yield of ylide **3b** in cyclohexane at ambient temperature also increases as [pyridine] increases and reaches a saturation value at $\approx 1 \times 10^{-3}$ M pyridine (Figure 6).

Stern–Volmer quenching studies with alkenes were performed in cyclohexane using [pyridine] = 7.47×10^{-3} M, which is well above the concentration of pyridine required to capture

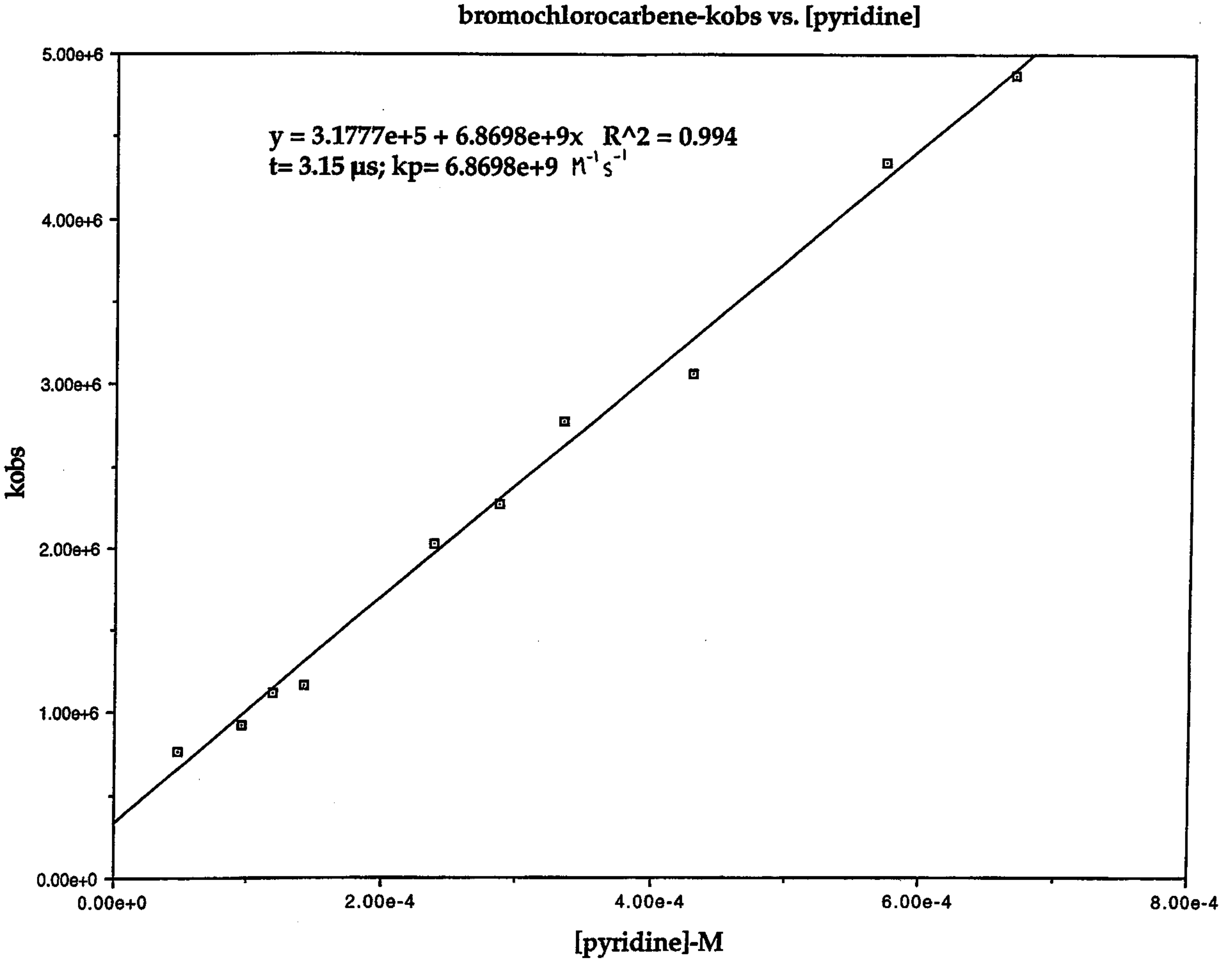


Figure 5. A plot of the observed rate constant of formation (k_{obs}) of ylide **3b** in cyclohexane as a function of [pyridine] at ambient temperature.

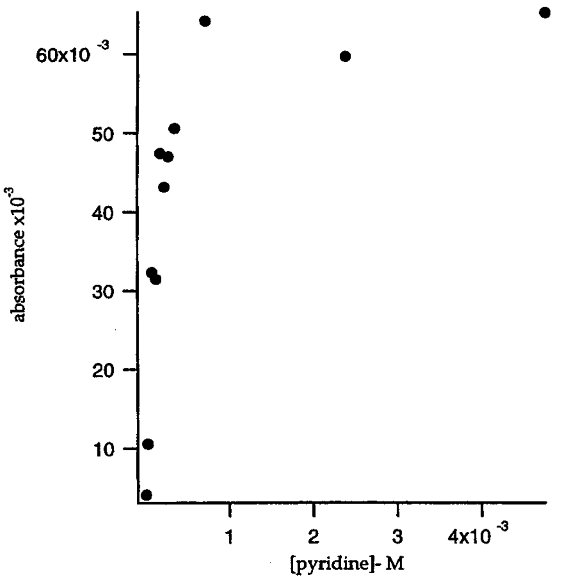


Figure 6. Yield of **3b** produced by LFP of **1b** as a function of [pyridine] in cyclohexane at ambient temperature.

every carbene generated by the laser pulse. These plots were linear (Figure 7). The slopes of these plots are equal to $k_A\tau$, where $\tau = 3.1\ \mu$s (the lifetime of CBrCl). The lifetime of CBrCl was determined from the intercept of the plot in Figure 5.

The rate constant data (Table 2) demonstrate that the absolute reactivity of CBrCl more closely resembles that of CBr_2 rather than that of CCl_2.

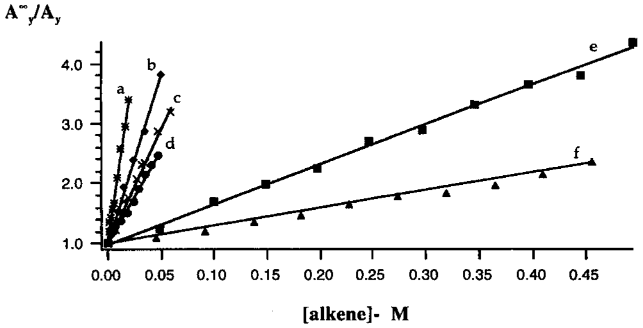
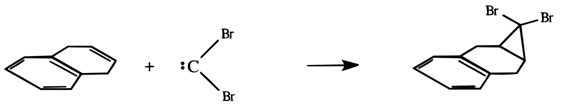


Figure 7. Stern−Volmer treatment of the quenching of bromochlorocarbene with alkenes in cyclohexane at ambient temperature with [pyridine]= 7.47×10^{-3} M: a, TME; b, isoprene; c, *cis*-4-methyl-2-pentene; d, 2,3-dimethyl-1,3-butadiene; e, cyclohexene; f, 1-pentene.

Effects on the Lifetime of CBr_2. It was possible to resolve the growth of ylide **3a** in Freon-113, cyclohexane, and isooctane (from both precursors **1** and **2a**), and in cyclooctane (from precursor **1**) as a function of pyridine concentration (Figure 2). As stated earlier, plots of k_{obs} versus [pyridine] are found to be linear (Figure 2), allowing us to extract the rate constant of reaction between the carbene and pyridine and the lifetime of the carbene (Table 1). The carbenes described in this work all are relatively long-lived; thus the τ values may be limited in part by reaction with adventitious water and oxygen.

The lifetimes of CBr_2 are generally shorter when **1** is used as a precursor (Table 1). Photolysis of **1** produces CBr_2 and 1,4-dihydronaphthalene in the same solvent cage. The nascent carbene may add to the olefinic double bond of the dihydronaphthalene or escape from the solvent cage. However, even outside the original solvent cage the local concentration of dihydronaphthalene will be extremely high in the small region of the cuvette excited by the focused excimer laser beam. Upon photolysis of **2a**, the carbene is formed in a solvent cage with a less reactive partner, indane, which lacks an isolated double bond. Thus, when precursor **2a** is used, the carbene lifetime is generally longer. This interpretation is supported by studies of the kinetics of CBr_2. We have determined that the absolute rate constant of CBr_2 with 1,4 tetrahydronaphthalene is 0.5×10^9 M^{-1} s^{-1} using standard Stern−Volmer quenching methodology. As the concentration of precursor is approximately 1 mM, the recombination reaction to form **4** limits the lifetime of CBr_2 to at most 2 μs. Thus the small effects on the lifetime we observe as a function of precursor are consistent with recombination contributing to the decay of dibromocarbene when generated from precursor **1**. However, dibromocarbene decays in cyclohexane primarily by reaction with solvent as evidenced by the large solvent isotope effect which is characteristic of singlet carbenes.[12]

In support of this interpretation, we are able to detect adduct **4** in the photolysis samples when **1** was used as precursor. Authentic **4** was synthesized and used for comparison purposes.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III. Conclusions

Laser flash photolysis (LFP, XeCl, 308 nm) of 11,11-dibromotricyclo[4.4.1.0$^{1.6}$]undeca-2,4,8-triene (**1**) or 10,10-dibromotricyclo[4.3.1.0^{1,6}]deca-2,4-diene (**2a**) produces CBr_2 and an aromatic compound. Bromochlorocarbene is produced by LFP of 10-bromo-10-chlorotricyclo[4.4.1.0$^{1.6}$]undeca-2,4-diene. The carbenes are trapped by pyridine to form ylides. The lifetimes of CBr_2 and CBrCl and their absolute reactivities toward pyridine and alkenes have been determined. The relative reactivity of CBr_2 toward alkenes determined by LFP methods is in excellent agreement with that determined previously by chemical analysis of reaction mixtures. The lifetime of CBr_2 is sensitive to the solvent isotopic composition, and the nature of the precursor. The latter observation demonstrates the importance of recombination reactions of CBr_2 with 1,4-dihydronaphthalene. The rate constant data (Table 2) demonstrate that the absolute reactivity of CBrCl more closely resembles that of CBr_2 rather than that of CCl_2.

IV. Experimental Section

Materials. The cyclohexane used in these studies was distilled from sodium and stored over 4 Å molecular sieves. Isooctane (Aldrich, 99.8%), cyclooctane (Aldrich, 99+%), and cyclohexane-d_{12} (CIL, 99.7%) were used as received. Pyridine was distilled from CaH_2 and stored over 4 Å molecular sieves. Freon-113 (Aldrich, HPLC grade), isoprene, cyclohexene, 2,3-dimethyl-1,3-butadiene, 1-hexene, 1-pentene, *cis*-4-methyl-2-pentene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene were passed through a column of alumina immediately prior to use.

LFP Protocol. The LFP system in use at The Ohio State University has been described previously.[13] Samples of **1** and **2a** 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 using an EG and G Princeton Applied Research Model 1460 optical multichannel analyzer (OMA).

Stock solutions of precursor **1** or **2a** were typically prepared with an optical density ~0.5 at 308 nm. 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 of **1** were performed similarly. In this case, stock solutions consisted of precursor **1** in isooctane containing 12.2 mM pyridine. Quencher concentrations were typically varied from 0 to between 0.1 and 0.6 M for a series of 6−9 cuvettes.

A stock solution of **2b** was prepared to an optical density of 0.95 at 308 nm, and 1.0 mL of this solution was added to Suprasil quartz cuvettes. To each cuvette was added a specific amount of pyridine, and then an appropriate amount of cyclohexane was added to each cuvette such that the total volume in each cuvette was 2.0 mL. Each cuvette was then capped with a rubber septum, wrapped in foil, and degassed by purging with dry, oxygen-free argon for 5 min immediately prior to LFP at 308 nm. Three transient spectra were recorded for each cuvette, and average k_{obs} and A_y values were used in the data analysis. In the lifetime experiments, the [pyridine] was typically varied by a factor of 10 for a series of 8−10 cuvettes.

Stern−Volmer quenching experiments were performed by adding 1.0 mL of the stock solution used in the lifetime experiments that was 7.47×10^{-3} M in pyridine to Suprasil quartz cuvettes. To each cuvette was then added a specific amount of olefin; then an appropriate amount of cyclohexane was added to each cuvette such that the total volume in each cuvette was 2.0 mL. Each cuvette was then capped with a rubber septum, wrapped in foil, and degassed by purging with dry, oxygen-free argon for 5 min immediately prior to LFP at 308 nm. Three transient spectra were recorded for each cuvette, and average k_{obs} and A_y values were used in the data analysis. For a given olefin, the range of quencher concentration was typically varied by a factor of 10 for a series of 8−12 cuvettes.

Synthesis. ***General Methods.*** ^1H NMR spectra were recorded on a General Electric QE 300 spectrometer at 300 MHz in $CDCl_3$. HPLC was performed on a Dynamax SD-200 instrument with a Dynamax 21.4 μm i.d. × 25 cm length microsorb silica column and hexane as solvent. Preparative gas chromatography was performed on a GOW-MAC 580 gas chromatograph with helium as carrier gas, using a 10.5 ft × $^1/_4$ in. i.d. column packed with 10% OV-101 on 80/100 Supelport. GC-MS was conducted on a Hewlett-Packard 5971 instrument with a HP-1701 column (14% cyanopropylphenyl−86% dimethylsiloxane copolymer). Column chromatography was carried out with EM Science silica gel (230−400 mesh). Melting points were determined on a Thomas-Hoover Uni-Melt apparatus and are uncorrected.

10-Bromo-10-chlorotricyclo[4.3.1.0^{1,6}]deca-3-ene. 10-Bromo-10-chloro-tricyclo[4.3.1.0^{1,6}]deca-3-ene was prepared by a slight modification of the procedure of Fedorynski.[15] Chlorodibromomethane (4.16 g, 0.02 mol) was added to a stirred mixture of bicyclo[4.3.0]nona-3,6(1)-diene (2.38 g, 0.02 mol), 50% aqueous sodium hydroxide (6 mL), and dibenzo-18-crown-6 (0.15 g, 0.41 mol) at room temperature. Then the mixture was stirred vigorously at 50 °C for 24 h. Following this, 3 mL of water and 10 mL of dichloromethane were added and the two layers formed were separated. The organic layer was washed with two 5 mL portions of water, dried over magnesium sulfate, and filtered. The dichloromethane was removed with a rotary evaporator. Starting material (1.1 g) was recovered by vacuum distillation. Recrystallization of the residue from ethyl acetate gave 0.8 g 10-bromo-10-chlorotricyclo[4.3.1.0^{1,6}]deca-3-ene (30% after deduction of the recovered starting material). Mp 55−56 °C. ^{1}H NMR δ 5.57 (s, 2 H), 2.29−2.41 (m, 6 H), 2.05−2.13 (m, 2 H), 1.67−1.95 (m, 2 H).

*10-Bromo-10-chlorotricyclo[4.3.1.0^{1,6}]deca-2,4-diene (**2b**).* A mixture of 0.15 g (0.6 mmol) of 10-bromo-10-chlorotricyclo-[4.3.1.0^{1,6}]deca-3-ene, 0.20 g (1.12 mmol) of *N*-bromosuccinimide, 7 mg of benzoyl peroxide, and 10 mL of carbon tetrachloride was heated at 80 °C for 1 h. A green solution was obtained after carbon tetrachloride was removed with a rotary evaporator. Subsequent chromatography on basic alumina gave 0.12 g of 10-bromo-10-chlorotricyclo[4.3.1.0^{1,6}]deca-2,4-diene (81%). Mp 54−55 °C. ^{1}H NMR δ 6.09−6.15 (m, 2 H), 5.86−5.90 (m, 2 H), 2.38−2.50 (m, 2 H), 2.02−2.19 (m, 2 H), 1.63−1.80 (m, 2 H).

*11,11-Dibromotricyclo[4.3.1.0^{1,6}]undeca-2,4,8-triene (**1**).* This compound was prepared by the published procedure.[5,6]

*1,1-Dibromo-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalene (4)***.** A mixture of bromoform (4.1 g, 16 mmol), 1,4-dihydronaphthalene (1.0 g, 8 mmol), benzyltriethylammonium chloride (26 mg, 0.1 mmol), 50% aqueous NaOH (6 mL), and dichloromethane (6 mL) was stirred for 30 h at room temperature. Then, after diluting with 10 mL each of water and dichloromethane, the two layers were separated and the aqueous layer extracted with dichloromethane. The combined organic layers were washed successively with water and brine before the solvent was evaporated. Column chromatography (silica gel/hexanes) gave **4** as an oil that solidified upon standing (0.6 g, 26%): mp 55−58 °C (lit.[16] 67−68 °C). ^{1}H NMR: δ 7.09 (br s, 4 H), 3.27 (dd, J = 8 Hz, 17 Hz, 2 H), 2.74 (d, J = 18 Hz, 2 H), 2.13 (m, 2 H).

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