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# 1-Naphthylcarbene: Spectroscopy, Kinetics, and Mechanisms[1]

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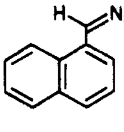
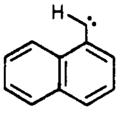
**Abstract:** The reactions of 1-naphthylcarbene have been examined by using laser flash photolysis techniques. Generation of the carbene from the diazo precursor in hydrocarbon solvents leads to the formation of 1-naphthylmethyl radicals, which were characterized by their absorption at 363 nm. However, product studies in cyclohexane and cyclohexane-$d_{12}$ reveal that the main reaction path is carbene insertion into the C–H bond rather than H abstraction. 1-Naphthylcarbene reacts readily with nitriles to yield nitrile ylides which can also be generated from the corresponding azirine. For example, the carbene reacts with acetonitrile with a rate constant of $4.6 \times 10^5$ $M^{-1}$ $s^{-1}$ at 300 K to yield an ylide that can be trapped readily with electron-deficient olefins, such as diethyl fumarate. Reaction of the carbene with oxygen ($k = 3.5 \times 10^9$ $M^{-1}$ $s^{-1}$) yields the carbonyl oxide ($\lambda_{max}$ 435 nm). Other reactions examined include halogen abstraction, addition to ketones, and reactions with triethylamine, pyridine, and ethers. The absolute kinetics of the various reactions were examined by monitoring the formation of the products (e.g., ylides, radicals, etc.), since the carbene spectrum was not detected directly.

Laser flash photolysis has become a widely used technique in the study of the kinetics and spectroscopy of carbenes. Diphenylcarbene (DPC), fluorenylidene (Fl), dimesitylcarbene, dibenzocycloheptadienylidene, boranthranylidene, and the aryl halocarbenes have been studied in considerable detail.[4,5] All these species are disubstituted with two aryl groups or an aryl group and a halogen on the carbene carbon. At the outset of this work there were no reports of the time-resolved spectroscopy of a simple monoaryl carbene. This led us to study the laser flash photolysis of 1-naphthyldiazomethane (**1**).[6] 1-Naphthylcarbene (**2**) was studied rather than phenylcarbene due to the convenient diazo absorption of **1** at the laser wavelength and the ease of handling of **1** relative to phenyldiazomethane. During the course of our work Horn has reported a study of the laser flash photolysis of 2-naphthyldiazomethane.[8]



**1**



**2**

Previous studies of 1-naphthylcarbene are relatively limited. Trozzolo et al.[9] observed the triplet EPR spectrum of **2** at 77 and 4 K, indicating that the carbene has a triplet ground state. There are no reports of a matrix absorption spectrum of triplet **2**, presumably because **2** is quite reactive in organic glasses even at 77 K.[10] Jones[11] has studied the gas-phase thermal rearrangements of **2**, but no traditional solution-phase chemical studies of **2** have been reported. In this work the laser experiments have systematically preceded the product studies; this illustrates how laser flash photolysis techniques can be used to map out the reaction mechanisms and kinetics of a novel reaction intermediate and to identify systems requiring careful product analyses. This is the reverse of the traditional approach in which the chemistry of a reactive intermediate is developed and then used to interpret spectroscopic data.

## Results and Discussion

Unless otherwise indicated, all experiments in this section were carried out under a nitrogen atmosphere. Time-resolved experiments were carried out in static samples (usually 1 or 2 mL) with the 337.1-nm pulses from a nitrogen laser for excitation.

This section has been divided according to the solvent used. Given the high reactivity of **2**, this is equivalent to a mechanistic subdivision of the experiments, since the type of solvent usually determines the main mode of decay of **2**.

**1. Hexafluorobenzene.** Initial experiments were directed toward the direct observation of triplet **2** in relatively unreactive solvents. Earlier work by us[12] and others[13] on fluorenylidene demonstrated that there is no truly inert solvent for this carbene. One of the longest lifetimes for Fl was observed in hexafluorobenzene, a solvent that had also been used for earlier product studies.[14] Accordingly, laser experiments on **1** were carried out in this solvent. No transient absorption could be observed between 350 and 700 nm which could be assigned to triplet **2**. A very long-lived (microseconds) weak absorption signal was observed at about 500 nm, but control experiments demonstrated that this spectrum may not be due to triplet **2**. There must be at least one other (longer lived) unknown transient contributing to the absorption at this wavelength. Given the expected absorption maximum for the carbene (vide infra), biphotonic processes probably play some role in the generation of the 500-nm signal. The dominant feature of the transient spectrum is in fact the bleaching around 330 nm that can be attributed to the decomposition of **1**.

The failure to detect **2** can be rationalized by comparison with triplet DPC,[15,16] Fl,[12,13] and dibenzocycloheptadienylidene.[17] The main absorption maxima of these triplets are at a wavelength ca.

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(1) Issued as NRCC-25421.

(2) Ohio State University.

(3) National Research Council of Canada.

(4) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Acc. Chem. Res.* **1984**, *17*, 283.

(5) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Tetrahedron* **1985**, *41*, 1525.

(6) Two communications relating to nitrile ylides have been published.[7]

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(8) Horn, K. A.; Chateauneuf, J. E. *Tetrahedron* **1985**, *41*, 1465.

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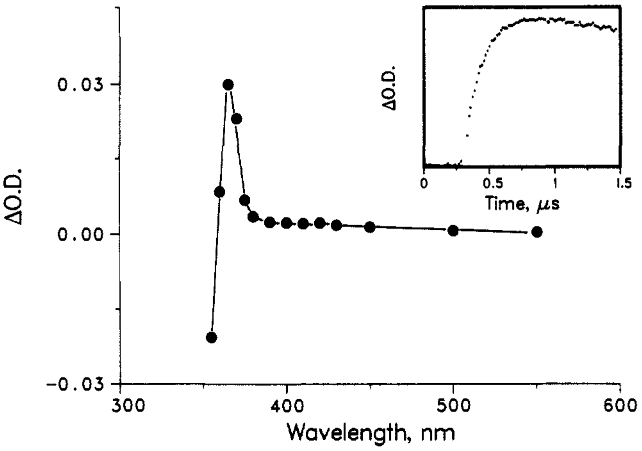


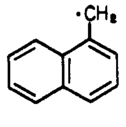
**Figure 1.** Absorption spectrum obtained 1 μs after laser excitation of **1** in cyclohexane at 300 K and (inset) a growth trace monitored at 363 nm.

**Table I.** Kinetics for the Formation of the 363-nm Absorption of the 1-Naphthylmethyl Radical

| solvent | $k_{obsd}$[a] | solvent | $k_{obsd}$[a] |
|---|---|---|---|
| cyclohexane | $7.0 \times 10^6$ | cyclopentane[b] | $8.7 \times 10^6$ |
| cyclohexane-$d_{12}$ | $3.5 \times 10^6$ | methylcyclohexane[c] | $9.3 \times 10^6$ |

[a] At 300 K in $s^{-1}$. [b] Arrhenius parameters (195–280 K): $E_a$ = 3.1 kcal/mol, log ($A/s^{-1}$) = 9.2. [c] Arrhenius parameters (205–294 K): $E_a$ = 4.3 kcal/mol, log ($A/s^{-1}$) = 10.6.

30 nm shorter than the corresponding radicals (e.g., benzhydryl from DPC). As pointed out by Trozzolo,[18] it is reasonable to expect triplet carbenes and their corresponding radicals to have similar electronic spectra, as they have similar π electronic structures. The absorption maximum of the 1-naphthylmethyl radical (**3**) is reported to be 363 nm.[7,19] Applying the 30-nm "rule of thumb" correction predicts the absorption maxima for triplet **2** to be at ~333 nm. This is quite close to the laser excitation wavelength (337.1 nm) and overlaps extensively with the absorption spectrum due to **1** ($\lambda_{max}$ at 329 nm with a shoulder at 343 nm). As a result it is not practical to monitor signals in this region. Similar detection problems were found in other solvents. Horn has also found that carbene **2** cannot be observed in aromatic solvents due to overlapping absorption by the diazo precursor. He has been able to observe **2** in alkanes between 340–350 nm.[20]



**3**

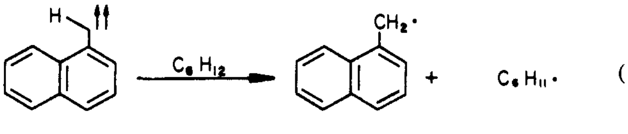
It should however be emphasized that detection of the carbene is not really necessary in order to establish the kinetics and mechanisms of its reactions as long as the rate of formation of its reaction products can be monitored.[21]

**2a. Alkanes in the Absence of Oxygen.** Photolysis of **1** in cyclohexane produces a transient with a sharp absorption maximum at 363 nm (Figure 1). This is the absorption maxima for the 1-naphthylmethyl radical **3**, first observed by Porter.[19] This species is formed in a process that follows first-order kinetics with a growth lifetime of 144 ns at 300 K (see Table I and inset in Figure 1); its decay follows clean second-order kinetics. The species absorbing at 363 nm can therefore be confidently assigned to radical **3** produced in reaction 1.

**Table II.** Percent Product Distribution Obtained by Photolysis of **1** in $C_6H_{12}$ and $C_6D_{12}$ at 298 K

| condns | [**1**], M | **4** | **5** | **6** | **8** | tot |
|---|---|---|---|---|---|---|
| $C_6H_{12}$ | 0.012 | 67 | 2.5 | 3.0 | *a* | 72 |
| $C_6D_{12}$ | 0.026 | 64 | 3.2 | ≤1 | *a* | 67 |
| $C_6H_{12}$, $O_2$[b] | 0.012 | 34 | *a* | 0.5 | 23 | 57 |

[a] Not detected. [b] Initial oxygen concentration (1 atm partial pressure, 0.0115 M).

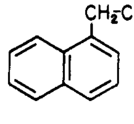


(1)

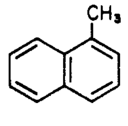
**³2** **3**

Laser photolysis of **1** in oxygen-containing solutions leads to different photoprocesses as a result of the formation of carbonyl oxides.[23-26] These processes are discussed in a separate section.

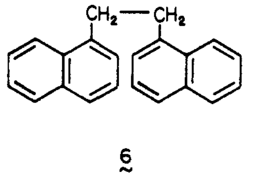
In cyclohexane-$d_{12}$ the growth kinetics at 363 nm led to $k \simeq 3.5 \times 10^6$ $s^{-1}$ ($\tau$ = 286 ns), approximately half as fast as in cyclohexane-$d_0$. In addition, the optical density due to **3** was reduced considerably. For example, in a pair of matched cells the change in optical density (ΔOD) at the absorption maximum of **3** (363 nm) was 0.029 in cyclohexane-$d_0$ and 0.017 in cyclohexane-$d_{12}$. Interestingly, if hydrogen abstraction was the only reaction path for the carbene, no change would have been anticipated. The change in the value of ΔOD indicates that another process competes with hydrogen abstraction and that its relative importance increases upon deuteration; further, the true (H/D) isotope effect for hydrogen abstraction by triplet **2** must be larger than the value of ≃2 determined from the observed experimental rate constants. This prompted us to examine the chemistry of **2** in considerable detail. Preparative photolysis at 350 nm of a 12 mM solution of **1** in cyclohexane at 298 K gave a rather clean product mixture with a good material balance (Table II). Formal C–H insertion led to **4** in 67% yield. Small amounts of 1-methylnaphthalene (**5**) and radical dimer **6** were present. Analysis for bicyclohexyl **7** showed that its yield was ≪1%.



**4**



**5**



**6**

**7**

1-Naphthylcarbene can react with cyclohexane via its singlet state by direct insertion to give **4**; alternatively, **2** can react via its triplet ground state to give initially the 1-naphthylmethyl–cyclohexyl radical pair (reaction 1) and ultimately species **4**–**7**. The low yields of products **5**–**7** suggest that the major route for carbene decay is insertion via the singlet state. This interpretation is unambiguously confirmed by the isotopic distribution of **4**

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(18) Gibbons, W. A.; Trozzolo, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 172.

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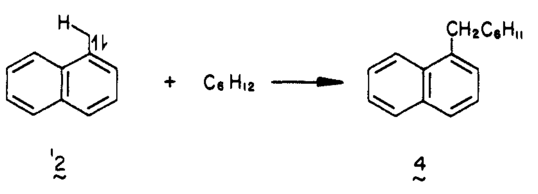
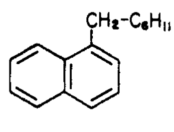
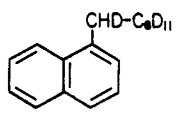


(2)

formed by reaction of **2** in a 1:1 cyclohexane/cyclohexane-$d_{12}$ mixture. If **2** reacts exclusively by singlet insertion, then only **4**-$d_0$ ($M_{224}$) and **4**-$d_{12}$ ($M_{236}$) will be formed. However, if **2** reacts

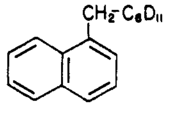


4-$d_0$

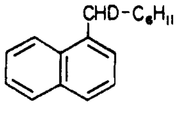


4-$d_{12}$

by triplet hydrogen atom abstraction (reaction 1) to form radical **3**, then the radical crossover products **4**-$d_{11}$ ($M_{235}$) and **4**-$d_1$ ($M_{225}$) will also be formed.



4-$d_{11}$



4-$d_1$

Since the $d_0$–$d_1$ and $d_{11}$–$d_{12}$ peaks are fully separated by capillary GC, the comparison of the mass distributions is straightforward (see Experimental Section). Quite simply, the mass spectra do not show any evidence for crossover (<10%) and can be fully explained by a concerted mechanism. Of course, the laser data do require some free radical contribution; however, the product data show that **4** is formed predominantly by a concerted reaction, presumably that of direct insertion of the singlet state.

Similar conclusions can be drawn from an analysis of the cross combination ratio ($\mathbf{4}^2/\mathbf{6} \times \mathbf{7}$) which leads to values much higher than the statistical one.

It is frequently assumed that the singlet–triplet equilibration of arylcarbenes is much faster than chemical reaction from either spin state. This assumption seems appropriate for the 1-naphthylcarbene/cyclohexane system, where the carbene lifetime exceeds 100 ns (Scheme I). Although we prefer the mechanism of Scheme I, we note that the insertion products and kinetics of reaction do not strictly require the assumption of this mechanism. It is equally consistent with the data to assume that in addition to hydrogen abstraction the triplet also inserts into the C–H bond by a concerted mechanism.

Under the conditions of Scheme I the lifetime of triplet **2** is controlled by both the singlet and triplet decay channels. It is important to note that the rate of growth of the radical should equal the reciprocal of the lifetime of triplet **2**. The experimental values of $k_{obsd}$ listed in Table I are a composite of the singlet and triplet reactivities according to eq 3, where it has been assumed that $[\mathbf{2}^S] \ll [\mathbf{2}^T]$.[27]

$$k_{obsd} = k_T[C_6H_{12}] + k_SK[C_6H_{12}] \tag{3}$$

where

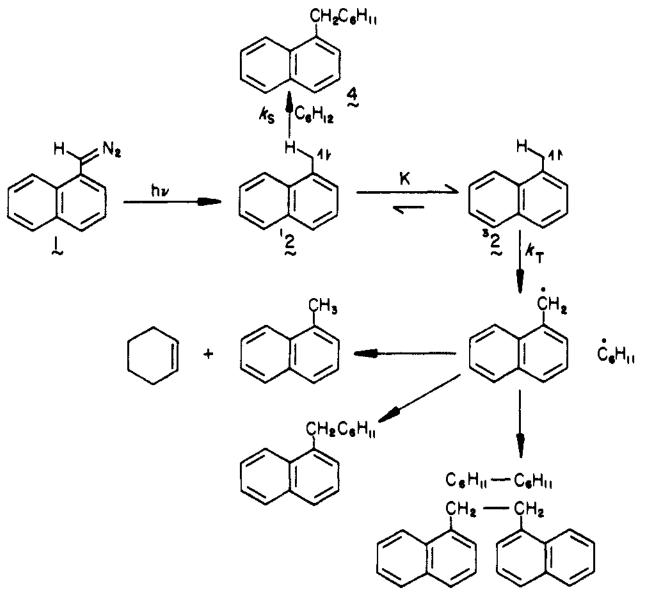
$$K = [\mathbf{2}^S]/[\mathbf{2}^T]$$

If we further assume that

$$\frac{\%\text{ concerted insertion}}{\%\text{ radical reaction}} = \frac{k_SK}{k_T} \tag{4}$$

and if, as expected, the isotope effect for triplet hydrogen abstraction is larger than for singlet CH insertion,[16,28-30] then one would expect the actual yield of radical **3** to be considerably decreased in deuterated solvents due to a change in the way in which the carbene partitions between abstraction and insertion. This, of course, agrees with the ratio of optical densities due to **3** observed in cyclohexane and cyclohexane-$d_{12}$.

**Scheme I**



The combined primary–secondary isotope effect for the insertion reaction can be readily determined from the integration of the GC peaks for the $d_0$–$d_1$ and $d_{11}$–$d_{12}$ products (in the solvent mixture). This leads to $k_S(H)/k_S(D) = 2.1$, a value that is very close to that reported for the reaction of singlet phenylcarbene with cyclohexane (2.0)[31] and close to that reported by Horn[20] for 1-naphthylcarbene (1.7).

The fact that the isotope effect derived from the ratio of insertion products agrees well with the value obtained in the laser experiments supports the idea that insertion dominates the rate of radical growth at 363 nm. It is important to emphasize that the rates of signal growth at 363 nm include *all modes of carbene decay*, regardless of whether these modes yield **3**. In fact, our measurements of the quantum yield for the formation of **3** (see Experimental Section) suggest that this is quite low, probably around 0.1.

It is possible to use the data to estimate the isotope effect for triplet hydrogen atom abstraction. As before

$$\frac{\text{yield of insertion product}^H}{\text{yield of radical}^H} = \frac{k_S{}^HK}{k_T{}^H}$$

$$\frac{\text{yield of insertion product}^D}{\text{yield of radical}^D} = \frac{k_S{}^DK}{k_T{}^D}$$

where superscripts H and D refer to reaction in cyclohexane and cyclohexane-$d_{12}$, respectively. As the singlet insertion process predominates in both cyclohexane and cyclohexane-$d_{12}$, (yield of insertion product$^H$) ≈ (yield of insertion product$^D$), and since the equilibrium constant $K$ is assumed to be independent of the solvent isotope composition

$$\frac{\text{yield of radical}^D}{\text{yield of radical}^H} = \frac{k_S{}^H}{k_S{}^D}\,\frac{k_T{}^D}{k_T{}^H}$$

and

$$k_T{}^H/k_T{}^D = 3.6$$

Laser photolysis of **1** in cyclopentane and methylcyclohexane also leads to the formation of **3**. These solvents remain fluid at much lower temperatures than cyclohexane; hence, it was possible

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[27] The superscripts indicate the multiplicities.

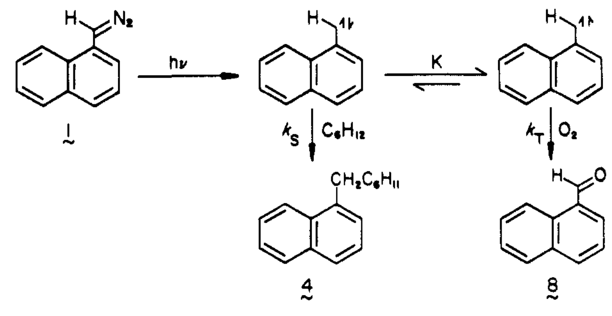
[28] Ring, D. F.; Rabinovitch, B. S. *Can. J. Chem.* **1968**, *46*, 2435.

[29] Isotope effects for triplet H atom abstraction of diphenylcarbene and dibenzocycloheptadienyldiene have been reported, ref 16 and 17.

[30] Savino, T. G.; Soundararajan, N.; Platz, M. *J. Phys. Chem.* **1986**, *90*, 919.

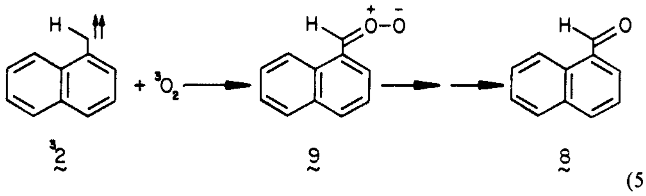
[31] Savino, T. G.; Platz, M. S. *J. Org. Chem.*, submitted.

**Scheme II**



to monitor the kinetics of radical formation over a wide temperature range. The corresponding Arrhenius parameters for cyclopentane and methylcyclohexane derived from a first-order kinetic analysis of the data lead to the values included as footnotes in Table I. It is interesting to note that the activation energy associated with the decay of 1-naphthylcarbene by predominantly singlet insertion is very similar to the activation energy for triplet H atom abstraction by diphenylcarbene in alkanes. The 10-fold difference in lifetime of $^3$**2** and $^3$DPC in alkanes is due solely to the differences in the preexponential terms (log $(A/s^{-1}) = 7-8$ for DPC).[16] At 300 K the lifetimes of $^3$**2** are 114, 144, and 107 ns in cyclopentane, cyclohexane, and methylcyclohexane, respectively. The lifetime of $^3$DPC in cyclohexane is in excess of 2 μs.

**2b. Alkanes in the Presence of Oxygen.** The chemistry of **2** in oxygenated cyclohexane has also been examined. Oxygen reacts rapidly with triplet carbenes to give carbonyl oxides.[23,26,32] In this case **9** will be formed and will ultimately lead to 1-naphthaldehyde (**8**) (see Table II).



(5)

In fact, **9** can be readily detected when samples of diazo compound **1** are photolyzed in oxygen-containing solutions. Figure 2 shows the spectrum obtained in cyclohexane, giving $\lambda_{max}$ 435 nm. For comparison, the corresponding carbonyl oxides from fluorenylidene[26] and diphenylcarbene[24] give $\lambda_{max}$ 450 and 410 nm, respectively. A plot of the pseudo-first-order rate of carbonyl oxide formation as a function of oxygen concentration (inset in Figure 2) yields $k_T^{O_2} = (3.5 \pm 0.7) \times 10^9$ M$^{-1}$ s$^{-1}$ from the slope. Typical lifetimes for the carbonyl oxide were a few microseconds (somewhat shorter than in earlier examples)[23-27] and decayed with predominantly second-order kinetics with $2k_t/\epsilon \sim 3.2 \times 10^6$ cm s$^{-1}$, where $\epsilon$ is the molar extinction coefficient of **9** at 435 nm.

If we assume that products **8** and **4** are formed from the triplet and singlet states of 1-naphthylcarbene, respectively, then Scheme II will hold and leads to eq 6.

$$\frac{\text{yield of } \mathbf{8}}{\text{yield of } \mathbf{4}} = \frac{k_T^{O_2}}{k_S K} \frac{[O_2]}{[C_6H_{12}]} \tag{6}$$

Analysis of the data in Table I using this equation leads to

$$\frac{k_T^{O_2}}{k_S K} = 4000$$

from which we obtain

$$k_S K = 8.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

Since the upper limit for $k_S$ is diffusion controlled ($\sim 10^{10}$ M$^{-1}$ s$^{-1}$) and the upper limit of $K$ (by EPR) is around unity

$$9 \times 10^{-5} < K < 1$$

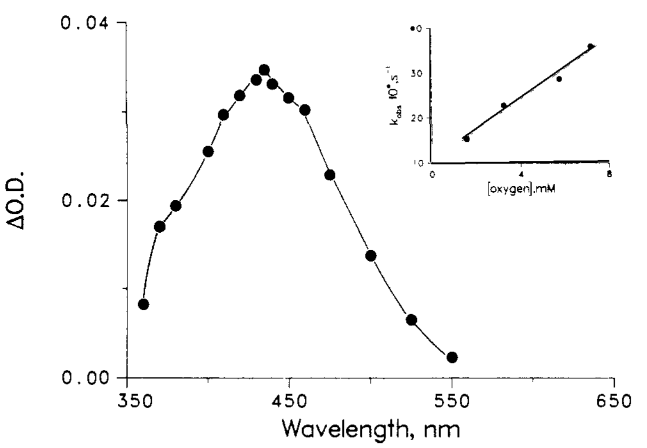


**Figure 2.** Absorption spectrum obtained 1.5 μs after laser excitation of **1** in cyclohexane containing 0.006 M oxygen at 300 K and (inset) a plot of the rate of carbonyl oxide formation as a function of oxygen concentration.

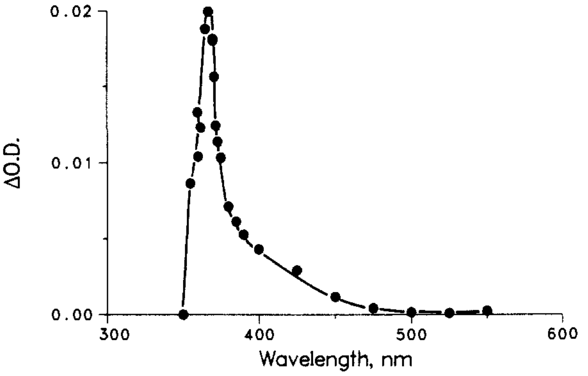
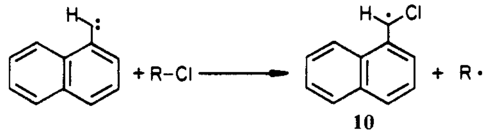


**Figure 3.** Absorption spectrum obtained 1 μs after laser excitation of **1** in Freon 113 at 300 K.

This suggests that the free energy gap between the singlet and triplet states is only a few kilocalories per mole ($0 < \Delta G_{ST} < 5.5$ kcal/mol), which is small enough to allow a significant population of the singlet state at normal temperatures. The singlet–triplet energy gaps in DPC and Fl have been estimated as 3–5 kcal/mol and ~1 kcal/mol, respectively, using similar arguments based on kinetic and chemical trapping data.[12,13]

The chemistry of diphenylcarbene in cyclohexane is primarily triplet in nature,[16] whereas that of fluorenylidene is primarily of singlet origin.[12,13] It is possible that these differences are mainly due to changes in the singlet-triplet gap ($K$) and only to a lesser extent to a variation in triplet reactivity ($k_T$).

**3. Halogenated Solvents.** Laser flash photolysis of **1** in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) leads to a strongly absorbing transient with a sharp maximum at 367 nm (Figure 3). This transient forms with a lifetime of 1.06 μs and subsequently decays over a period of several hundred microseconds with predominantly second-order kinetics. We assign the 367-nm band to the chloro(1-naphthyl)methyl radical (**10**) formed in reaction 7 (RCl = Freon 113).



(7)

**10**

The assignment was confirmed by independent generation of the radical by laser photodecomposition of di-*tert*-butyl peroxide in the presence of 1-(chloromethyl)naphthalene (**11**) according to reactions 8 and 9.

*tert*-Butoxyl radicals react rapidly with hydrogen donors[22] but do not abstract chlorine atoms. The transient spectrum of **10** produced via the *tert*-butoxyl radical is entirely consistent with that produced in the carbene reaction with Freon 113. The

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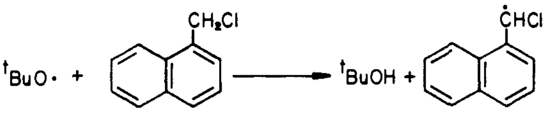
[32] Kirmse, W.; Horner, L.; Hoffmann, H. *Ann.* **1958**, *614*, 19.

$$^{t}BuOO^{t}Bu \xrightarrow{h\nu} 2\,^{t}BuO\cdot \qquad (8)$$



**11** **10** (9)

corresponding fluoro(1-naphthyl)methyl radical can be expected to have a spectrum similar to that assigned to **10**, but fluorine abstraction from the solvent is a very unlikely process.

The 1.06-μs growth lifetime of radical **10** must also be the decay lifetime of the triplet carbene **2** according to Scheme I. The triplet lifetime is again controlled by its reaction with the solvent, as well as by reactions of the thermally populated singlet carbene, which is presumed to be in rapid equilibrium with the triplet ground state. Roth,[33] using CIDNP techniques, has demonstrated that both singlet and triplet methylene abstract chlorine atoms from carbon tetrachloride. Singlet phenylcarbene preferentially abstracts chlorine atoms from chloroform, whereas the triplet carbene preferentially abstracts hydrogen atoms from this solvent.

The kinetics of the reaction of spin-equilibrated 1-naphthylcarbene (**2**) with various quenchers can be followed by monitoring the effect of added quenchers on the rate of growth of the chlorinated radical **10** in Freon 113. Under these conditions the observed growth rate constant, $k_{obsd}$, is given by

$$k_{obsd} = k_0 + k_q[Q] \qquad (10)$$

where $k_0$ is the sum of the rate constants for all first- or pseudo-first-order processes by which **2** decays in the absence of quencher Q. This term ($k_0$) will be dominated by reaction 7 (RCl = Freon 113), with possible contributions due to azine formation and/or reaction with traces of water or oxygen. The observed quenching rate constant, $k_q$, refers to the spin-equilibrated carbene and will normally (i.e., as long as the spin equilibrium is not disrupted) be given by

$$k_q = k_q^{T} + k_q^{S}K \qquad (11)$$

where the superscripts T and S refer to the spin multiplicity and $K$ is the same equilibrium constant as in eq 3. It should be emphasized that nanosecond laser techniques cannot separate $k_q^{T}$ and $k_q^{S}$ under these conditions and that further elaboration is usually based on the interpretation of temperature studies, disruption of the equilibrium, product studies, or simply chemical intuition.

Diphenylcarbene and fluorenylidene react with methanol at room temperature with observable rate constants of (0.6–1) × $10^7$ $M^{-1}$ $s^{-1}$ and (2–4) × $10^8$ $M^{-1}$ $s^{-1}$, respectively. The addition of methanol to a Freon 113 solution of **1** shortens the growth lifetime for the radical **10** in accord with eq 10. The slope of a plot of $k_{obsd}$ vs. [$CH_3OH$] gives $k_q = 1.6 \times 10^7$ $M^{-1}$ $s^{-1}$. This provides additional support for the assignment of carbene **2** as the precursor of radical **10**.

Laser photolysis of **1** in carbon tetrachloride gives results very similar to those in Freon 113 (RCl = $CCl_4$ in eq 7). The traces usually show a combination of "jump-and-growth" similar to those described recently for other carbenes.[34] The slow step is comparable to that in Freon 113, while the fast component follows the laser pulse. Transient spectra taken immediately after the laser pulse and after a 2-μs delay are identical with that of radical **10**. Further, studies of the power dependence of the "jump-to-growth" ratio did not show any dependence with the laser dose. This leads us to believe that a substantial fraction of the reaction with $CCl_4$ precedes singlet–triplet equilibration. In this solvent the reaction of singlet **2** to yield **10** is competitive with singlet-to-triplet intersystem crossing (ISC). This represents the first step ("jump") observed, while the slow process represents either the direct reaction of triplet **2** with $CCl_4$ or a mixture of triplet and singlet (by reverse ISC) reaction with $CCl_4$. Similar observations and conclusions have been reported by Horn.[20]

**Table III.** Rate Constants for the Reaction of Spin-Equilibrated **2** with Various Substrates at 300 K

| substrate | solvent | $k_q$, $M^{-1}$ $s^{-1}$ | species monitored |
|---|---|---|---|
| methanol | Freon 113 | $(1.6 \pm 0.2) \times 10^7$ | **10** |
| acetonitrile | benzene | $(4.6 \pm 0.2) \times 10^5$ | **12a** |
| oxygen | cyclohexane | $(3.5 \pm 0.7) \times 10^9$ | **9** |

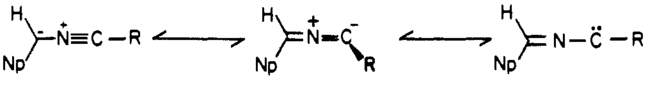
**Table IV.** Kinetic Data Based on the Yields of Nitrile Ylide in Acetonitrile at 300 K, according to Eq 12

| quencher | $k_q\tau$, $M^{-1}$ |
|---|---|
| methanol | 3.3 |
| methanol-*O-d* | 2.2 |
| *tert*-butyl alcohol | 0.82 |
| water | 2.0 |
| 2,3-dimethyl-2-butene | 5.0 |
| 2,5-dimethyl-2,4-hexadiene | 2.8 |
| *cis*-1,2-dichloroethylene | 2.5 |
| *trans*-1,2-dichloroethylene | 5.9 |
| acrylonitrile | 52[a] |

[a] Upper limit only; see text.

**4a. Nitrile Ylides: Formation.** Laser flash photolysis of **1** in acetonitrile produces the spectrum of a strongly absorbing transient with $\lambda_{max}$ 386 nm.[7a] This transient is formed with pseudo-first-order kinetics with a lifetime of 100 ± 10 ns and decays over several hundred microseconds. Very similar spectra can be obtained by laser flash photolysis of **1** in benzonitrile and pivalonitrile, where the growth lifetimes are 86 and 198 ns, respectively. The transients are again very long-lived.

These observations led us to propose[7] that the transient was the nitrile ylide **12**, depicted below in its various tautomeric forms.



**12**

R = $CH_3$; *t*-Bu; phenyl
Np = 1-naphthyl

The middle tautomer has two orthogonal π-systems that may be responsible for the insensitivity of the transient spectra to variations in R. There is considerable precedent for the reaction of carbenes with electron donors to form ylides,[36–41] and in various cases stable ylides can actually be isolated.

The rate of growth of the 386-nm transient was a function of the nitrile concentration, as expected. Thus, the rate of growth of **12a** (R = $CH_3$) was a function of acetonitrile concentration in benzene as solvent. A sixfold variation in acetonitrile concentration led to a linear change in $k_{obsd}$, leading to $k_q = (4.6 \pm 0.2) \times 10^5$ $M^{-1}$ $s^{-1}$ at 300 K, Table III (see ref 7a for the corresponding plot). This treatment assumes that benzene is a relatively inert solvent; this is supported by the small value of the intercept, $k_0$. Extrapolation of this plot would predict that the carbene lifetime in neat acetonitrile (~19 M) should be 114 ns, in good agreement with the observed lifetime of 100 ± 10 ns. As

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(33) Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85.

(34) Johnston, L. J.; Scaiano, J. C. *Chem. Phys. Lett.* **1985**, *116*, 109.

(35) Wang, Y.; Sitzmann, E. V.; Novak, F.; Dupuy, C.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 3238. Sitzmann, E. V.; Wang, Y.; Eisenthal, K. B. *J. Phys. Chem.* **1983**, *87*, 2283. Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *Chem. Phys. Lett.* **1983**, *102*, 446. Horn, K. A.; Allison, B. D. *Chem. Phys. Lett.* **1985**, *116*, 114.

(36) Magee, W. L.; Shechter, H. *Tetrahedron Lett.* **1979**, 4697.

(37) Sheppard, W. A.; Gokel, G. W.; Webster, O. W.; Betterton, K.; Timberlake, J. W. *J. Org. Chem.* **1979**, *44*, 1717.

(38) Kende, A. S.; Hebeisen, P.; Sanfilippo, P. J.; Toder, B. H. *J. Am. Chem. Soc.* **1982**, *104*, 4244.

(39) Kirmse, W.; Loosen, K.; Sluma, H.-D. *J. Am. Chem. Soc.* **1981**, *103*, 5935.

(40) de March, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4952.

(41) (a) Hamaguchi, M.; Ibata, T. *Tetrahedron Lett.* **1974**, 4475. (b) Ibata, T.; Hamaguchi, M.; Kiyohara, H. *Chem. Lett.* **1975**, 21. (c) Hamaguchi, M.; Ibata, T. *Ibid.* **1975**, 499.

**Table V.** Quenching of **12a** by Various Substrates in Acetonitrile at 300 K

| quencher | $k_q$, $M^{-1}$ $s^{-1}$ | precursor |
|---|---|---|
| 2,3-dimethyl-2-butene | $(1.1 \pm 0.2) \times 10^5$ | **1** |
| 2,5-dimethyl-2,4-hexadiene | $(3.5 \pm 0.5) \times 10^4$ | **1** |
| *cis*-1,2-dichloroethylene | $(2.3 \pm 0.2) \times 10^4$ | **1** |
| *trans*-1,2-dichloroethylene | $(3.8 \pm 04) \times 10^4$ | **1** |
| methanol | $<10^4$ | **1** |
| *tert*-butyl alcohol | $<10^4$ | **1** |
| acrylonitrile | $(4.8 \pm 0.3) \times 10^6$ | **16** |
| acrylonitrile[a] | $(5.4 \pm 0.2) \times 10^6$ | **1** |
| diethyl fumarate | $(5.9 \pm 0.2) \times 10^8$ | **1** |
| diethyl fumarate | $(5.0 \pm 0.7) \times 10^8$ | **16** |

[a] Measured within minutes of sample preparation; see text.

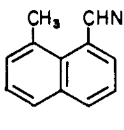
usual (see eq 10 and 11) these rate constants and lifetimes refer to the spin-equilibrated carbene, although chemical intuition favors a singlet pathway.

Kinetic data for **2** can also be derived from a Stern–Volmer type of approach. In this case, the reciprocal of the ylide yield, $\Phi_y^{-1}$, is related to the product $k_q\tau$ according to

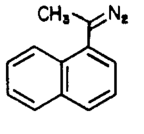
$$\frac{1}{\Phi_y} = \frac{1}{\Phi_y{}^0} + \frac{k_q\tau}{\Phi_y{}^0}[Q] \qquad (12)$$

where $\tau$ is the carbene lifetime in the absence of quencher Q, and $\Phi_y$ and $\Phi_y{}^0$ are the ylide yields in the presence and absence of quencher, respectively. $\Phi_y$ and $\Phi_y{}^0$ are proportional to the corresponding transient optical densities. The data obtained with this approach have been summarized in Table IV.

It is possible to prevent the formation of nitrile ylides in acetonitrile and related solvents by structural modification of the diazo compounds and corresponding carbenes. This achieves in an intramolecular fashion essentially the same result as the bimolecular quenching plots (eq 12) in the intermolecular case. Laser flash photolysis of (8-methyl-1-naphthyl)diazomethane (**13**) or 1-$\alpha$-naphthyldiazoethane (**14**) in acetonitrile does not produce detectable nitrile ylides. Presumably, in these systems the intramolecular reaction of the singlet carbene is too rapid for bimolecular reactions to compete effectively.[42]

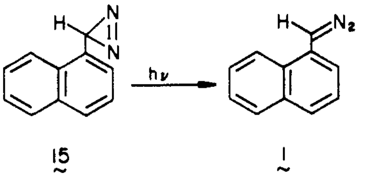


**13**



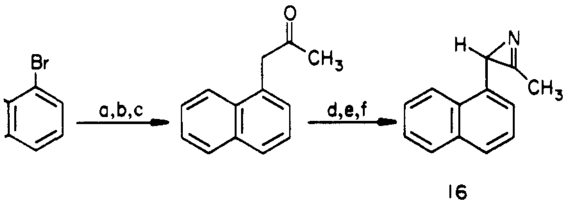
**14**

Nitrile ylides can also be generated from alternate precursors. Thus, laser flash photolysis of 1-naphthyldiazirine (**15**) in acetonitrile gives the same transient spectrum observed with 1-naphthyldiazomethane (**1**) as precursor. However, the spectrum of **12a** obtained with **15** as precursor was considerably less intense than that from **1**, suggesting a lower quantum yield for carbene generation. This may be the result of partial photoconversion of the diazirine **15** to the diazo compound, i.e.[42,43]



(13)

Another route to the nitrile ylides is possible via the photodecomposition of the corresponding azirines. Similar experiments have been reported for the ylides formally derived from diphenylcarbene[44] and fluorenylidene.[45] Azirine **16** was synthesized as shown in eq 14.

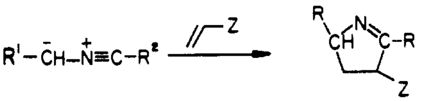


(14)

(a) Butyl lithium (b) $CH_2\overset{O}{—}CHCH_3$
(c) Oxallylchloride-DMSO (d) $NH_2N(CH_3)_2$
(e) $CH_3I$ (f) NaH

Laser flash photolysis of **16** at 308 nm (the absorption of **16** is too weak at 337.1 nm for nitrogen laser flash photolysis) leads to a transient spectrum for **12a** totally consistent with that obtained from 1-naphthyldiazomethane in acetonitrile using 337.1 nm excitation.[7a] The rate constants for reactions of **12a** derived from **16** were identical with values obtained with other precursors (vide infra).

**4b. Nitrile Ylides: Reactions.** It is possible to examine the kinetics of reactions of nitrile ylides by observing directly their decay rates in the presence of various quenchers. Our choice of quenchers was dictated by the extensive product studies of Huisgen, Padwa, and Schmidt,[46] who have demonstrated that nitrile ylides are efficiently captured by electron-deficient olefins to give $\Delta^1$-pyrrolines. Reaction 15 illustrates the reaction of **12a** with acrylonitrile (Z = CN).



(15)

**17**

$R^1$ = 1-Np, $R^2$ = $CH_3$

The same reactivity pattern was observed for **12a**, which reacts with diethyl fumarate ≃ 100 times more rapidly than with acrylonitrile and nearly 6000 times more rapidly than with 2,3-dimethyl-2-butene, Table V.

We have also obtained chemical evidence in support of the nitrile ylide assignment. The chemistry of **2** in acetonitrile is expected to be a function of quencher concentration: i.e., at high quencher concentration carbene reactions with the quencher will be favored, while low quencher concentrations will enable carbene reaction with solvent to form **12a**, which will subsequently react to give pyrrolines. Acrylonitrile was used in the chemical studies, as the photolysis of **16** in the presence of this olefin gives synthetically useful yields of pyrrolines. Unfortunately, 1-naphthyldiazomethane (**1**) reacts within minutes with 1 M acrylonitrile to give appreciable yields of cyclopropanes **18Z** and **18E**.

The diazirine **15** proved to be a more stable precursor of **2**. Photolysis of **15** in acetonitrile containing 1 M acrylonitrile gives

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(42) (a) Chapman, O. L.; Chang, C. C.; Kolc, J.; Jung, M. E.; Loew, J. A.; Barton, T. J.; Tumey, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 7844. (b) Chedekel, M. R.; Skoglund, M.; Kreeger, R. L.; Shechter, H. *J. Am. Chem. Soc.* **1976**, *98*, 7846.

(43) We are confident that the nitrile ylide signals arise from carbene produced via direct photolysis of **15** rather than secondary photolysis of photogenerated **1**. Two arguments support this conclusion: (i) the nitrile ylide signals are present in fresh, diazo-free samples, and (ii) experiments with acrylonitrile (vide infra) rule out the diazo route because **1** is unstable in the presence of acrylonitrile.

(44) Turro, N. J.; Hrovat, D. A.; Gould, I. R.; Padwa, A.; Dent, W.; Rosenthal, R. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 625. Padwa, A.; Rosenthal, R. J.; Dent, W.; Filho, P.; Turro, N. J.; Hrovat, D. A.; Gould, I. R. *J. Org. Chem.* **1984**, *49*, 3174.

(45) Zupancic, J. J.; Grasse, P. B.; Lapin, S. C.; Schuster, G. B. *Tetrahedron* **1985**, *41*, 1471.

(46) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633. Padwa, A. *Acc. Chem. Res.* **1976**, *9*, 371. (c) Orhovats, A.; Heimgartner, H.; Schmid, H.; Heinzelmann, W. *Helv. Chim. Acta* **1975**, *58*, 2662.

(47) This relationship is derived by assuming a rapid equilibrium between singlet and triplet **2**. If one assumes the steady-state condition for ylide **12**, then $d[\mathbf{12}]/dt = 0 = k_q{}^b[CH_3CN][\mathbf{2}] - k^y[CH_2CHCN][\mathbf{12}] = 0$. Then $[\mathbf{2}]/[\mathbf{12}] = k^y[CH_2CHCN]/k_q{}^b[CH_3CN]$ and yield **18**/yield **17** = $k_q{}^a[CH_2CHCN][\mathbf{2}]/k^y[CH_2CHCN][\mathbf{12}] = (k_q{}^a/k_q{}^b)[CH_2CHCN]/[CH_3CN]$, where $k^y$ is the rate constant for reaction of **12** with acrylonitrile and $k_q{}^a$ and $k_q{}^b$ are as defined in the text.

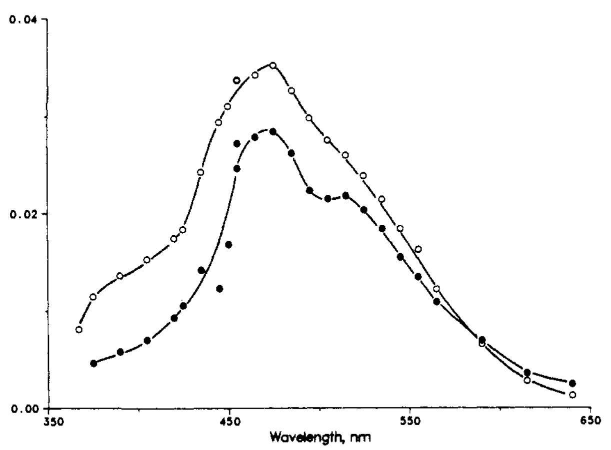
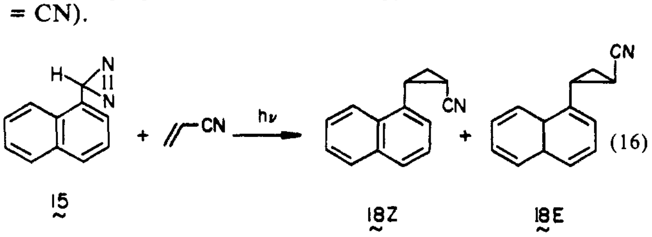


**Figure 4.** Absorption spectrum of the carbonyl ylide **19** obtained 100–200 ns (●) and 3 μs (○) after laser excitation of **1** in acetone at 300 K.

both cyclopropanes **18Z** and **18E** and pyrrolines **17Z** and **17E** (Z = CN).



(16)

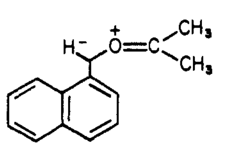
15 18Z 18E

A plot of the ratio of cyclopropanes to pyrrolines as a function of quencher concentration leads to a slope $k_q\tau \sim 3.6\ M^{-1}$.[7b] The slope of a plot of (cyclopropanes/pyrrolines) vs. acrylonitrile should be directly comparable with the ratio obtained by flash photolysis, Table IV, i.e.,

$$\frac{k_q^{\,a}}{k_q^{\,b}[\text{acetonitrile}]} = 52\ M^{-1} = k_q^{\,a}\tau$$

where a and b denote the rate constants for the spin-equilibrated carbene with acrylonitrile and acetonitrile, respectively. This is more than 14 times larger than the value obtained by chemical analysis. The source of the discrepancy is most likely due to an overestimation of $k_q^{\,a}$. This value was obtained by Stern–Volmer analysis of the yield of ylide, as measured by flash photolysis as a function of the concentration of acrylonitrile. As acrylonitrile reacts rapidly with 1-naphthyldiazomethane, thermal depletion of the precursor can also account for the diminished yield of ylide signal. Hence the value of $k_q\tau$ for acrylonitrile in Table IV must be considered suspect.

**5. Ketones.** Laser flash photolysis of **1** in acetone gives rise to the spectrum of Figure 4; this is assigned to the corresponding carbonyl ylide by analogy with earlier studies with fluorenylidene.[48] The lifetime of **19** is 2.3 μs at 300 K. The spectrum of **19** is



**19**

blue-shifted with respect to a similar ylide formed by the reaction of fluorenylidene with acetone ($\lambda_{max}$ 640 nm), which has a lifetime of 3.4 μs.[48] The temperature dependence for the decay of **19** gives log $(A/s^{-1}) = 6.9$ and $E_a = 1.5$ kcal/mol.

Figure 4 shows transient spectra obtained in time windows from 100 to 200 ns and 3 μs after laser excitation. There are small but reproducible changes with time in the transient spectra of the ylide. We do not have a conclusive explanation for these changes; however, it seems possible that they reflect conformational changes in the ylide, similar to those observed recently by Das et al. for ylides derived from the stilbene oxides.[49] It is possible that the initial mixture of ylide conformers (which will be kinetically controlled) is different from the thermodynamically favored composition and that the small spectral changes that occur shortly after ylide formation reflect a relaxation toward this composition.

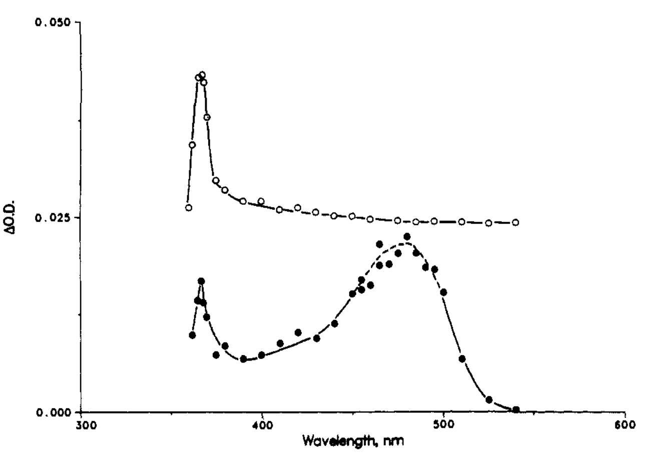
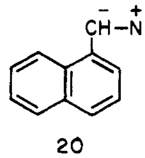


**Figure 5.** Absorption spectrum obtained following laser excitation of **1** in triethylamine at 300 K recorded 100 ns (●) and 1 μs (○) after the laser pulse. The late spectrum has been offset by ΔOD = 0.025.

As in the case of $CCl_4$ discussed earlier, the formation of **19** reveals a "jump-and-growth" combination that was independent of laser dose. We believe that this also reflects a combination of reaction before and after singlet–triplet equilibration, both leading to the same ylide. The growths of the acetonitrile and benzonitrile ylides (vide supra) may also show instantaneous jumps in ΔOD. These jumps are not as pronounced as in the case of the acetone ylide but can be readily interpreted as before. In some cases the instantaneous jump may also incorporate an underlying absorption, possibly due to traces of oxygen ylide **9**.

**6. Exploratory Experiments with Triethylamine, Pyridine, and Ethers.** Laser flash photolysis of **1** in deaerated triethylamine gives the transient absorption spectrum in Figure 5. The 1-naphthylmethyl radical (**3**) is quite evident in the 370-nm region, but in addition we detect a second transient with $\lambda_{max}$ 485 nm. Both species are formed "instantaneously" in a nanosecond time scale. The decay of the 485-nm species followed first-order kinetics (225–294 K) with log $(A/s^{-1}) = 9.28$ and $E_a = 3.9$ kcal/mol, corresponding to a lifetime of 380 ns at 300 K. These transient signals may be due to ylide **20** and were too short to allow quenching experiments with diethyl fumarate. The time evolution of the transient spectra (Figure 5, top) shows that at times longer than 1 μs only the radical **3** is present. Further work will be required to establish if **20** in indeed responsible for the absorption at 485 nm.



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Laser flash photolysis of **1** in ethereal solvents such as tetrahydrofuran did not lead to a detectable ylide intermediate, **21**. We cannot say whether the lifetime of this oxonium ylide is too short or its chromophore is too weak to allow detection or whether it is simply not formed.

Laser photolysis of **1** in pyridine leads to a transient with $\lambda_{max}$ 535 nm and a lifetime in excess of 100 μs and which reacts with

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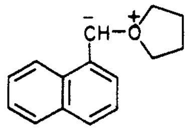
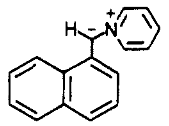
(48) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6631.

(49) Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*, 5639.



21

diethyl fumarate with a rate constant of (5.3 ± 1.0) × $10^5$ $M^{-1}$ $s^{-1}$. Ylide **22** is a possible candidate for this behavior, although a conclusive assignment is not possible at this point.



22

Further work on the nature and formation of these ylides is clearly needed before their characteristics can be established in more detail.

## Conclusion

Laser flash photolysis of 1-naphthyldiazomethane using the 337.1-nm pulses from a nitrogen laser does not lead to any identifiable transients in relatively inert solvents such as benzene or hexafluorobenzene (at $\lambda > 350$ nm). Photolysis in nitrile solvents, such as acetonitrile, leads to nitrile ylides with a characteristic absorption at ~390 nm and long (>100 μs) lifetimes. These ylides react readily with electron-deficient olefins such as diethyl fumarate for which $k_q = 5.9 \times 10^8$ $M^{-1}$ $s^{-1}$. Photolysis in hydrocarbons leads to the readily detectable signals from the 1-naphthylmethyl radical (**3**) although product studies in solvents such as cyclohexane (where $\tau \simeq 100$ ns) indicate that the main mode of decay involves C–H insertion; this process is not detectable in the laser flash experiments. Generation of **2** in oxygen-saturated solution leads to the corresponding carbonyl oxide (i.e., the Criegee intermediate) which has $\lambda_{max}$ 435 nm.

The composite reactivity of 1-naphthylcarbene (i.e., spin equilibrated) is about 30 times lower than that of fluorenylidene. This can be explained by inherently smaller elementary reaction rate constants or, for singlet-like reactions, by a smaller singlet–triplet energy splitting in the case of fluorenylidene.

## Experimental Section

Melting points were taken on an Electrothermal capillary melting point apparatus and are uncorrected. $^1$H NMR spectra were recorded on a Varian EM-360L (60 MHz), EM-390L (90 MHz) or Bruker WP-500 (500 MHz) instrument. All NMR shifts are reported in units of ppm relative to tetramethylsilane (0 ppm). Infrared spectra were recorded on a Perkin-Elmer Model 457 infrared spectrometer. Mass spectra and exact masses were obtained on a Consolidated Electronics MS-9 double-focusing mass spectrometer using an ionization potential of 70 eV.

Acetonitrile (Fisher, HPLC grade) was refluxed and distilled from calcium hydride under a nitrogen atmosphere. Benzene (Aldrich Gold Label) was purified by washing with sulfuric acid, aqueous sodium bicarbonate solution, and water, dried over magnesium chloride, and refluxed over and distilled from calcium hydride. Other solvents were of the highest purity commercially available and were used as received.

Product analyses were performed in the following manner: solutions (2 mL) of 1-naphthyldiazomethane in cyclohexane, cyclohexane-$d_{12}$, or mixtures were deaerated and then photolyzed with 12 RPR-3500 Rayonet lamps until 50–60% of the initial amount of **2** was consumed. Diethyl fumarate (20 μL) was injected, and the samples were allowed to stand until the remaining diazo compound had reacted (1–2 h). The samples were then analyzed on a Hewlett-Packard Model 5995 GC-MS instrument equipped with a 10-m Ultra 1 (OV-101) capillary column. The $d_0$–$d_1$ and $d_{11}$–$d_{12}$ peaks corresponding to **4** were readily separated; while peaks differing by only one deuterium were not resolved, there was a clearly inhomogeneous mass distribution across the peaks, and, for example, the earliest MS sampled in the $d_{11}$–$d_{12}$ peak contained only **4**-$d_{12}$ (higher deuterium content leads to shorter retention times). The MS signal was then integrated across each individual peak, to avoid errors due to inhomogenous mass distribution. For the peak at $d_0$–$d_1$, the distribution is 224 ($M^+$, relative intensity 83.02), 225 (15.74), and 226 (1.23) for the $C_6H_{12}$ sample, while in the 1:1 solvent mixture the relative intensities were 82.97, 15.68, and 1.35, respectively. The differences are within the errors of the experiment; the intensity of the 223 peak is <0.1%. For the $d_{11}$–$d_{12}$ peak the distribution was 235 ($M^+$-$d_{11}$, relative intensity 14.31), 236 ($M^+$-$d_{12}$ 78:31), and 237 (13.94) for the pure $C_6D_{12}$ solvent, and the relative intensities were 13.94, 78.43 and 7.64, respectively, in the solvent mixture. Again, the differences are within experimental error. We note that the 235 peak reflects the isotopic purity (~99%), which corresponds to about one of every eight molecules of cyclohexane being $C_6HD_{11}$. Product yields for the $d_0$–$d_1$ and $d_{11}$–$d_{12}$ peaks were based on flame ionization detection rather than MS data.

**Laser Flash Photolysis.** The samples (1 mL) were contained in cells made of 3 mm × 7 mm rectangular Suprasil tubing. They were deaerated by bubbling with oxygen-free nitrogen. The laser systems use the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a Molectron UV-24 (Ottawa) or UV-22 (Columbus) nitrogen laser for excitation. In the Ottawa system the data, initially acquired by an R-7912 Tektronix transient digitizer, were processed by a PDP 11/23 computer that also provided suitable processing, storage, and hard copy facilities. Further details can be found elsewhere.[50] The measurements of the yield of radical **3** were carried out against di-*tert*-butyl peroxide/1-methylnaphthalene or the photolysis of 1-chloromethylnaphthalene as described in an earlier paper.[51] The yields were much smaller for the diazo compound in cyclohexane and are estimated as ca. 10%, although it should be noted that these measurements are subject to considerable error.

**Photolysis of 1-Naphthyldiazirine in Acetonitrile and Acrylonitrile.** Five solutions of the diazirine (200 μL, 0.02 M) in acetonitrile containing 0.1, 0.2, 0.3, 0.8, and 1.0 M, acrylonitrile were sealed in 4-mm Pyrex tubes after degassing by three freeze–pump–thaw cycles under vacuum. The tubes were then irradiated for 2 h in a Rayonet reactor (350-nm lamps), and the photolysates were analyzed by gas chromatography (10% SE-30) with temperature programming from 150 (10 min initial period) to 220 °C at 2.5 °C/min. The retention times for the cyclopropanes (**18**) were 44.3 and 46.4 min, and for the $\Delta^1$-pyrrolines (**17**), 55.7 and 58.3 min.

The above assignments were confirmed by GCMS analysis and by comparison with authentic samples. The yields of these products reported in the text were corrected for relative response factors.

**Photocyclization of Azirine 16 and Acrylonitrile.** A solution of azirine **16** (180 mg, 0.933 mmol) and acrylonitrile (20 mL) in 150 mL of benzene was irradiated for 30 min under nitrogen with a 450-W Hanovia lamp fitted with a Vycor filter sleeve. Evaporation of the solvent and excess acrylonitrile under reduced pressure gave 230 mg of a yellow oil. Chromatography by MPLC with 1:1 ethyl acetate:hexanes (flow rate 4 mL/min) afforded 111 mg (48%) of *trans*-4-cyano-2-methyl-5-(1-naphthyl)-$\Delta^1$-pyrroline: IR ($CCl_4$) 2985, 2247, 1653, 1429, 1379, 1316 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 3.13 (m, 2 H), 2.92 (br s, 1 H), 7.50–7.88 (m, 7 H); *m/e* 234, 207, 181, 166 (base), 139. The stereochemistry of the products was assigned by the NMR spectra as the proton α to the nitrile unit in the trans isomer is pushed upfield by the deshielding of the aromatic ring.

**1-(1-Naphthyl)-2-cyanocyclopropane (18E,Z).** A solution of 1-naphthyldiazomethane (0.40 g, 1.38 mmol) and acrylonitrile (6.0 mL) in benzene (230 mL) was irradiated under nitrogen for 45 min with a 450-W Hanovia lamp fitted with a Vycor filter sleeve. Evaporation of the solvent and excess acrylonitrile under reduced pressure afforded a brown oil. Chromatography by MPLC eluting with 1:1 ethyl acetate: hexanes (flow rate 4 mL/min) gave two crystalline compounds: 30 mg (mp 84.5–85.5 °C) and 15 mg (mp 80–81 °C). Mass spectroscopic analysis showed that both of these compounds were the desired cyclopropane adducts: *m/e* 193, 178, 165, (base), 139 for each; *m/e* calcd for $C_{14}H_{11}N$ ($M^+$) 193.0891, found 193.0882 for each. However, $^1$H NMR spectroscopy (500 MHz, $CDCl_3$) did not distinguish the stereochemistry of the products: δ 1.56 (m, 2 H), 1.78 (m, 1 H), 3.08 (m, 1 H), 7.20–8.26 (m, 7 H) for each. Double-resonance experiments also gave very similar decoupled spectra.

**1-Naphthyldiazomethane and 1-Naphthyldiazirine.** The preparations of these compounds have been reported elsewhere.[52,53]

**1-Naphthyldiazoethane.** 1-Acetonaphthone was converted into its (*p*-toluenesulfonyl)hydrazone derivative (mp 183–184 °C). Tosylhydrazone (0.2 g) was dissolved in 3–5 mL of tetramethylguanidine and heated on a steam bath under a nitrogen atmosphere until the pink diazo color was formed. The solution was cooled in an ice bath, poured into a 5% aqueous sodium bicarbonate solution, and shaken. Following extraction with ether, the combined extracts were washed 4 times with 5%

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(51) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6378.

(52) See ref 10.

(53) Wright, B. B., Ph.D. Thesis, The Ohio State University, Columbus, OH, 1983. See also ref 7b.

sodium bicarbonate, dried over anhydrous magnesium sulfate, and filtered, and the solvent was removed. The residue was triturated with hexane. Evaporation of the hexane solution gave the desired compound as a red oil in 15–20% yield: NMR ($CDCl_3$) $\delta$ 3.7 (3 H, s), 8.8 (1 H, d of d), and 7.3–8.1 (6 H, m).

**(8-Methyl-1-naphthyl)diazomethane.** 8-Methylnaphthaldehyde was converted into its (*p*-toluenesulfonyl)hydrazone derivative (mp 175–177 °C). The tosylhydrazone (0.1 g) was added to a two-phase mixture of 50% aqueous potassium hydroxide and dioxane. The mixture was stirred and heated for 10 min on a hot plate. After the mixture cooled to room temperature, the orange-red dioxane layer was separated and the solvent removed in vacuo. The residue was triturated with hexane, dried over sodium sulfate, and filtered, and the solvent was removed in vacuo, leaving the product diazo compound as a red oil in 50% yield.

**(1-Naphthyl)cyclohexylmethanol.** In a 50-mL round-bottom flask equipped with a reflux condenser, nitrogen inlet, and magnetic stirrer were placed 500 mg (3.21 mmol, 1 equiv) of 1-naphthaldehyde, 20 mL of dry THF, and 2.0 mL (1.5 equiv) of a 2.0 M solution of cyclohexylmagnesium chloride in ether. The solution was heated to reflux for 1 h and then cooled to room temperature. The solution was acidified with 5% HCl and concentrated in vacuo to remove the THF. The residue was combined with 5 mL of water and extracted 4 times with 5 mL aliquots of methylene chloride. The combined organic layers were dried over sodium sulfate and concentrated in vacuo to give a pale yellow oil. Thin-layer chromatography (10% ethyl acetate/hexane) indicated the presence of (1-naphthyl)cyclohexylmethanol as an impurity as well as an impurity of slightly lower $R_f$ value. The product mixture was purified by flash chromatography using a 14.0 × 2.0 cm silica gel column. Elution proceeded with 5% ethyl acetate/hexane (130 mL), nil; (160 mL), 420 mg (55% yield) of the desired alcohol as a colorless oil: $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 8.10–7.12 (m, 7 H), 4.86 (d, $J$ = 6 Hz, 1 H), 3.46 (s, 1 H), 1.98–0.8 (m, 11 H); IR ($CCl_4$) 3620 $cm^{-1}$ (O–H stretch).

**((1-Naphthyl)methyl)cyclohexane (4).** In a 25-mL round-bottom flask equipped with a nitrogen inlet and magnetic stirrer were placed 280 mg (1.7 mmol, 1.0 equiv) of (1-naphthyl)cyclohexylmethanol and 8.0 mL of freshly distilled trifluoroacetic acid. While the solution was stirred, 0.40 mL (2 equiv) of triethylsilane was added dropwise, and the solution was stirred at room temperature for 18 h; it was then combined with 20 mL of water and extracted 3 times with 10-mL aliquots of ether. The combined organic layers were washed twice with 10-mL aliquots of 5% aqueous sodium hydroxide and 4 times with 10-mL aliquots of saturated sodium bicarbonate solution, dried over sodium sulfate, and concentrated in vacuo to give 580 mg of a pale yellow liquid. The crude product mixture was purified by flash chromatography (14.0 cm × 2.0 cm column) and eluted with hexane (60 mL), nil; (40 mL), 116 mg of the desired product as a colorless oil: $^1H$ NMR (60 mHz, $CCl_4$) $\delta$ 8.05–7.00 (m, 7 H), 2.81 (d, 2 H, $J$ = 6 Hz), 1.90–0.75 (m, 11 H); IR ($CCl_4$) 2925 (s), 2852 (m), 1450 (m), 1397 $cm^{-1}$ (m); *m/e* calcd for $C_{17}H_{20}$ ($M^+$) 224.1565, found 224.1534.

**1-(1-Naphthyl)-2-propanol.**[54] A 1.25 M solution of *sec*-butyllithium (106 mL, 0.133 mol) in cyclohexane was added slowly to a solution of 1-bromonaphthalene (2.40 g, 0.121 mol) in 30 mL of anhydrous THF at −78 °C with stirring under nitrogen. To the solution was added 20 mL of propylene oxide. The mixture was warmed to 0 °C and stirred for 1.5 h, diluted with water (50 mL), and extracted with ether (2 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to afford 24.2 g (89%) of the required alcohol (lit.[54] bp 162 °C (5 torr)). IR (neat) 3400 (br O–H), 3060, 2900, 2950, 1130, 1090, 800 $cm^{-1}$; $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 1.14 (d, 3 H, 6.0 Hz), 1.87 (s 1, H, OH) 3.06 (d, 2 H, 6.0 Hz), 3.90–4.23 (m, 1 H), 7.25–8.23 (m, 7 H).

**1-(1-Naphthyl)-2-propanone.**[55] A solution of oxalyl chloride (5.76 mL, 67.5 mmol) in 30 mL of $CH_2Cl_2$ was placed in a 250-mL, three-necked, round-bottom flask fitted with two pressure-equalizing dropping funnels and a mechanical stirrer under nitrogen. To the solution was added $Me_2SO$ (10.8 mL, 61.3 mmol) in 30 mL of $CH_2Cl_2$ at −78 °C. After stirring for 5 min, a solution of 1-(1-naphthyl)-2-propanol (12.7 g, 61.3 mmol) in 30 mL of $CH_2Cl_2$ was added. After stirring for 15 min, triethylamine (40 mL) was added dropwise and the mixture was warmed to room temperature, diluted with water (50 mL), washed with dilute HCl, dried over $Na_2SO_4$, and evaporated in vacuo. Vacuum distillation afforded 9.56 g (76%) of ketone: bp 111–114 °C (0.4 torr) (lit.[55] bp 121–126 °C (0.75 torr)); IR (neat) 3050, 1690, 1600, 1380, 800, 770 $cm^{-1}$; $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 1.92 (s, 2 H), 3.93 (s, 2 H), 7.29–7.99 (m, 7 H); *m/e* calcd for $C_{13}H_{12}O$ ($M^+$) 184.0888, found 184.0872.

**1-(1-Naphthyl)-2-propanone *N,N*-Dimethylhydrazone.** A mixture of ketone and 15 mL of 1,1-dimethylhydrazine was heated under reflux for 15 h. After the mixture cooled to room temperature, the excess hydrazine was removed by distillation and the residue was dissolved in ether, dried over $Na_2SO_4$, and evaporated in vacuo to afford 5.4 g (89%) of a 2/1 mixture (by $^1H$ NMR integration) of the two isomeric *N,N*-dimethylhydrazones as a yellow oil: IR of the mixture (neat) 3050, 2990, 2960, 2860, 2780, 1600, 1030, 970, 800, 780 $cm^{-1}$; $^1H$ NMR (60 MHz, $CCl_4$) $\delta$ 1.60 (s) and 1.70 (s (major), 3 H), 2.35 (s) and 2.50 (s (minor), 6 H), 3.90 (s) and 4.13 (s (minor), 2 H), 7.26–7.87 (m, 7 H); *m/e* calcd for $C_{15}H_{18}N_2$ ($M^+$) 226.1470, found 226.1482.

**1-(1-Naphthyl)-2-propanone Trimethylhydrazonium Iodide.** A mixture of methyl iodide (30 mL) and the isomeric *N,N*-dimethylhydrazones (5.30 g, 23.4 mmol) was heated under a gentle reflux for 18 h. The excess methyl iodide was evaporated by heating on a steam bath to leave a red viscous salt which crystallized from isopropanol/ethyl acetate: mp 134–136 °C; $^1H$ NMR (60 MHz, $CDCl_3$) $\delta$ 2.39 (s, 3 H), 3.76 (s, 9 H), 4.40 (s, 2 H), 7.36–8.10 (m, 7 H). Evaporation of the mother liquors again provided the oil (mixture of isomers), but no further crystallization could be achieved.

**3-Methyl-2-(naphthyl)-2*H*-azirine (16).** A slurry of the hydrazonium iodide salt (1.00 g, 2.72 mmol) and sodium hydride (0.10 g, 4.17 mmol) in 25 mL of anhydrous THF was stirred for 2 h at room temperature and then heated under a gentle reflux for 3 h under nitrogen. The THF was evaporated under reduced pressure, the residue was triturated with cyclohexane (2 × 75 mL) and filtered, and the cyclohexane was evaporated in vacuo to afford 0.49 g of the crude azirine as a yellow liquid. Chromatography on silica gel, eluting with 1:10 ethyl acetate:hexanes, gave 0.23 g (47%) of the purified azirine (**16**) as a yellow liquid: IR (neat) 3060, 2980, 1770 (C═N), 1430, 1400, 1370, 1270 $cm^{-1}$; $^1H$ NMR (90 MHz, $CCl_4$) $\delta$ 2.43 (s, 3 H), 3.32 (s, 1 H), 7.2–8.3 (m, 7 H). It was found that **16** was an unstable material and probably decomposed to some degree during chromatography. The crude product was of sufficient purity to be used without further purification.

**1-(1-Naphthyl)-2-propanone Oxime.**[56] A solution of ketone (16.9 g, 91.7 mmol) in 25 mL of ethanol was added to an aqueous solution of hydroxylamine hydrochloride (30.0 mL, 5.0 M) and sodium acetate (30 mL, 5 M) and refluxed for 24 h. After the mixture cooled to room temperature, a dark oil separated, which was extracted with 200 mL of ether and washed with 100 mL of water. The phases were separated and the aqueous layer was back-extracted with 100 mL of ether. The combined organic layers were dried over $Na_2SO_4$ and evaporated in vacuo to afford the oxime mixture as an oil. Flash chromatography, eluting with 20% ethyl acetate/hexanes, gave 14.0 g (77%) of the semisolid product. Trituration with petroleum ether and filtration afforded 7.3 g of a white crystalline solid: mp 73–79 °C (lit.[56] mp of E isomer 96–97 °C), which proved to be a 5:1 mixture of the isomeric oximes (by $^1H$ NMR integration). Evaporation of the petroleum ether gave 4.5 g of an oil, which proved to be a 1:1 mixture of the isomeric oximes: IR (neat) of the mixture 3200 (br, OH), 2900, 1600, 1510, 1430, 1400, 1370, 1260, 1025, 960, 790, 775 $cm^{-1}$; $^1H$ NMR of the solid (60 MHz, $CCl_4$) $\delta$ 1.70 and 1.79 (s, (major), 3 H), 3.92 and 4.16 (s, (minor), 2 H), 7.12–8.05 (m, 7 H), 9.13 (br s, 1 H). The major isomer of this mixture is consistent with the reported spectrum of the E isomer. *m/e* calcd $C_{13}H_{13}NO$ ($M^+$) 199.0997, found 199.1001.

**1-(1-Naphthyl)-2-propanone *p*-Nitrobenzoyloxime.** A solution of oximes (5.00 g, 25.1 mmol) in 25 mL of anhydrous THF was added dropwise over 30 min to a suspension of sodium hydride (0.8 g, 30 mmol) in 25 mL of THF. During this time period, evolution of hydrogen and precipitation of the sodium salt of the oxime was observed. Then a solution of *p*-nitrobenzoyl chloride (5.70 g, 30.7 mmol) in 25 mL of THF was added dropwise over 10 min and the resulting mixture was heated under reflux for 14 h. After cooling to room temperature, the reaction was slowly quenched with 50 mL of water and washed with 200 mL of dilute aqueous KOH. The layers were separated and the aqueous phase was extracted with 100 mL of $CH_2Cl_2$. The combined organic layers were dried over $Na_2SO_4$ and evaporated in vacuo to yield and orange oil, from which 3.4 g of a yellow crystalline solid crystallized from ether: mp 125–127 °C. Evaporation of the ether mother liquor afforded 3.6 g of the crude oil, which was purified by flash chromatography, eluting with 20% ethyl acetate/hexanes to give 2.66 g of the isomeric mixture of the oxime ester, total purified yield 6.06 g (60%): IR (KBr) 1745, 1610, 1530, 1270, 1090, 860, 785, 720 $cm^{-1}$; $^1H$ NMR (90 MHz, $CCl_4$) $\delta$ 1.90 (s, 3 H), 4.06 (s, 2 H), 7.2–7.9 (m, 7 H), 8.10 (s, 4 H); *m/e* calcd for $C_{20}H_{16}N_2O_4$ ($M^+$) 348.1110, found 348.1126.

**3-Methyl-2-(1-naphthyl)-2*H*-azirine (16).** A dispersion of KH (0.40 g, 35%) was washed with anhydrous THF 3 × 25 mL under nitrogen to remove the oil and then covered with a 20-mL layer of THF as solvent. To this slurry, a solution of the above oxime *p*-nitrobenzoate ester (0.95 g, 2.73 mmol) in 40 mL of THF was added dropwise at 0 °C over 30

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min. The mixture was slowly warmed to room temperature and then stirred for 15 h. The solvent was evaporated in vacuo and the residue was triturated with cyclohexane (3 × 75 mL) and filtered. The solvent was removed under reduced pressure to afford 0.45 g (98%) of the crude azirine. IR and NMR of this material were consistent with those reported above and the isolated material was of sufficient purity to be used directly.

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**Registry No. 1**, 10378-55-9; **4**, 64833-56-3; **8**, 66-77-3; **13**, 70840-50-5; **14**, 102421-45-4; **15**, 86602-71-3; **16**, 88235-59-0; **17Z**, 88226-29-3; **17E**, 88226-30-6; **18Z**, 88226-31-7; **18E**, 88226-32-8; acrylonitrile, 107-13-1; 1-acetonaphthone tosylhydrazone, 102421-44-3; 8-methylnaphthaldehyde tosylhydrazone, 102421-46-5; cyclohexyl chloride, 542-18-7; (1-naphthyl)cyclohexylmethanol, 94823-85-5; 1-bromonaphthalene, 90-11-9; propylene oxide, 75-56-9; 1-(1-naphthyl)-2-propanol, 27653-13-0; 1-(1-naphthyl)-2-propanone, 33744-50-2; 1,1-dimethylhydrazine, 57-14-7; (*Z*)-1-(1-naphthyl)-2-propanone *N*,*N*-dimethylhydrazone, 102421-47-6; (*E*)-1-(1-naphthyl)-2-propane *N*,*N*-dimethylhydrazone, 102421-48-7; (*Z*)-1-(1-naphthyl)-2-propane trimethylhydrazonium iodide, 102421-49-8; (*E*)-1-(1-naphthyl)-2-propane trimethylhydrazonium iodide, 102421-50-1; (*Z*)-1-(1-naphthyl)-2-propanone oxime, 20557-52-2; (*E*)-1-(1-naphthyl)-2-propanone oxime, 19534-15-7; (*Z*)-1-(1-naphthyl)-2-propanone *p*-nitrobenzoyloxime, 102421-51-2; (*E*)-1-(1-naphthyl)-2-propanone *p*-nitrobenzoyloxime, 102421-52-3; *p*-nitrobenzoyl chloride, 122-04-3; cyclohexane, 110-82-7; cyclopentane, 287-92-3; methylcyclopentane, 108-87-2; methanol, 67-56-1; oxygen, 7782-44-7; 2,3-dimethyl-2-butene, 563-79-1; 2,5-dimethyl-2,4-hexadiene, 764-13-6; *cis*-1,2-dichloroethylene, 156-59-2; *trans*-1,2-dichloroethylene, 156-60-5; *tert*-butyl alcohol, 75-65-0; diethyl fumarate, 623-91-6.

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# He I Photoelectron Spectra, Valence Electronic Structure, and Back Bonding in the Deltahedral Boron Chlorides, $B_4Cl_4$, $B_8Cl_8$, and $B_9Cl_9$

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**Abstract:** He I photoelectron spectra have been obtained for $B_4Cl_4$, $B_8Cl_8$, and $B_9Cl_9$, the three boron monohalides which have been structurally characterized. The 6 photoelectron bands arising from the 15 highest occupied molecular orbitals of $B_4Cl_4$ are clearly resolved, but the presence of a seventh band at 19.51 eV, which had been previously assigned to the $2a_1$ orbital of $B_4Cl_4$, is not confirmed. The spectra of $B_8Cl_8$ and $B_9Cl_9$ are much more complex and less resolved than that of $B_4Cl_4$. Rather than discrete bands, four broad envelopes of photoelectron activity are found. GAUSSIAN 80 (STO-3G) ab initio calculations on $B_4Cl_4$ and $B_8Cl_8$ and INDO semiemperical calculations on $B_4Cl_4$, $B_8Cl_8$, and $B_9Cl_9$ demonstrate that the four envelopes result from four different types of molecular orbitals. Each type is distinguished by characteristic boron and chlorine contributions to the molecular wave function. Comparison of the ab initio and semiemperical results indicates that they are in remarkably good agreement in the assignment of the $B_8Cl_8$ spectral data. Back bonding in the polynuclear boron chlorides is shown to be much more complex than in smaller molecules like $BCl_3$. The stability of the neutral boron chlorides (which have only $2n$ framework electrons) is found to be one of the results of the differences between the makeup of the HOMO orbitals of the polyhedral boron chlorides and that of the analogous boron hydrides. The average boron–boron overlap populations were examined using the results from both types of calculation. For a series of eight boron chloride structures the average boron–boron overlap population decreases in the order $B_9Cl_9^{2-} > B_9Cl_9 > B_8Cl_8^{2-} > B_8Cl_8 > B_4Cl_4\ (T_d) > B_4Cl_4\ (D_{4h}) > B_2Cl_4\ (D_{2d}) > B_2Cl_4\ (D_{2h})$. Except for $B_8Cl_8$, the core overlap populations correlate well with the experimental thermal stability data where the latter are available.

The polyhedral boron chlorides are a family of volatile cluster compounds which are related in that they have the common molecular formula $B_nCl_n$. The species for which $n = 4$ and 8–12 have been relatively well characterized,[1,2] and the existence of the compounds where $n = 13$–20 has been indicated by mass spectrometry.[3] The structures of only three of the boron monochlorides, $B_4Cl_4$, $B_8Cl_8$, and $B_9Cl_9$, have been determined by crystallographic studies; all three have been found to have closo geometries.

Octaboron octachloride and nonaboron nonachloride are of interest because they are prototypical electron-deficient clusters, clusters which—to the extent that ligand-to-cage bonding can be factored from intracage interactions—possess only $2n$ framework electrons. This is two fewer than the number ($2n + 2$, $n \neq 4$) most frequently observed in $n$-vertex *closo*-boranes, -carboranes, -metalloboranes, and -metal carbonyl clusters.[4,5] The latter number, $2n + 2$, has been referred to as the "magic" number of electrons,[6] the number which gives rise to superaromatic bonding.[7] Similarly, the smallest cluster in the series, $B_4Cl_4$, can also be considered to be electron deficient since there are only 8 framework

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