

Generation, Spectroscopy, and Reactivity of Excited 1-Naphthylmethyl Radicals¹

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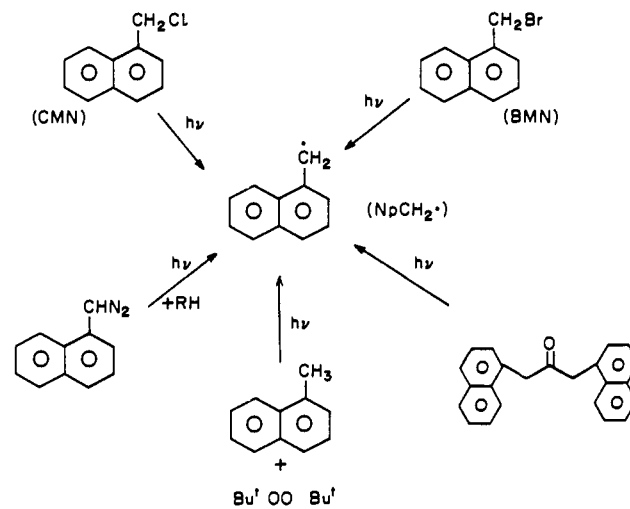
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Abstract: The excited state of the 1-naphthylmethyl radical has been characterized with use of laser flash photolysis techniques. Lifetimes measured at its absorption maxima (430 nm, compared with 365 nm for the ground state) are typically around 35 ns at room temperature and agree well with values obtained monitoring the fluorescence of the excited radical. Excited 1-naphthylmethyl radicals react readily with oxygen and methyl viologen with rate constants of $(4.7 \pm 0.8) \times 10^9$ and $(3.8 \pm 1.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The former leads to the recovery of ground-state radical (rather than formation of peroxy radicals). Reaction with methyl viologen involves electron transfer. Chlorine abstraction from carbon tetrachloride ($k = 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) is believed to occur via a charge-transfer mechanism. The excited radicals are rather poor hydrogen abstractors. Altogether the results suggest that the excited 1-naphthylmethyl radical has typical excited-state properties rather than enhanced free radical characteristics. The resemblance of its absorption spectrum with that of triplet naphthalenes may be a further reflection of this similarity.

The photophysics and photochemistry of haloaromatics and halomethylaromatics have been the subject of several recent publications. In particular, Rentzepis et al.,³⁻⁵ Thomas et al.,⁶ and Schuster et al.^{7,8} have examined the problem using picosecond techniques, pulse radiolysis, and nanosecond laser photolysis, respectively. While there is some consensus that dissociation eventually occurs from a $T(\sigma, \sigma^*)$ state, the state responsible for the population of $T(\sigma, \sigma^*)$ has been suggested to be S_1 , S_2 , and T_1 . In fact, more than one state may be responsible for C-X bond homolysis, depending on the excitation energy and the nature of the C-X bond involved (i.e., X = Cl, Br, or I). As far as we can determine from published reports, it has never been demonstrated that the initial radical pair is indeed a triplet. In spite of the various questions that still remain in the photochemistry of halomethylaromatics, the fact that their direct and sensitized photolysis leads to the efficient formation of arylmethyl radicals is now well established.

A few recent reports have been concerned with the spectroscopy and chemistry of excited free radicals, particularly benzophenone ketyl,^{9,10} diphenylmethyl,¹¹⁻¹⁴ and a few related species.^{13,15,16} In the case of the excited diphenylmethyl radical we have carried out a study of its intermolecular reactivity;¹¹ the excited radical is an excellent electron donor and a moderate acceptor, and it reacts with oxygen 14 times faster than its ground state but does not lead to peroxy radical formation. The excited radical was observed to abstract chlorine atoms readily in a process that is believed to involve charge-transfer interactions.

Scheme I



The fluorescence from excited naphthylmethyl radicals has been detected by Rentzepis et al.,^{3,4} who used this property to monitor the formation of the ground-state radical in the photochemistry of halomethylnaphthalenes. In particular, excited 1-naphthylmethyl radicals were reported to have a lifetime of 13 ± 3 ns in hexane at room temperature and to fluoresce with $\lambda_{\text{max}} \sim 600$ nm. The absorption spectrum of the excited radicals has never been reported.

In this paper we report the excited-state spectrum of the 1-naphthylmethyl radical and its lifetime and reactivity. We also compare the kinetics of some of its reactions with those of excited diphenylmethyl radicals. In addition, we have examined several sources of ground-state 1-naphthylmethyl radicals and compare some of their characteristics.

Experimental Section

Materials. 1-(Chloromethyl)naphthalene, CMN (Aldrich), was recrystallized twice from hexane/ether. 1-(Bromomethyl)naphthalene, BMN, was prepared by a literature procedure:¹⁷ mp $55-56^\circ\text{C}$ (lit.¹⁷ mp $55-56^\circ\text{C}$). Naphthylidiazomethane was prepared by a literature procedure.¹⁸ Methyl viologen (K and K) was recrystallized twice from

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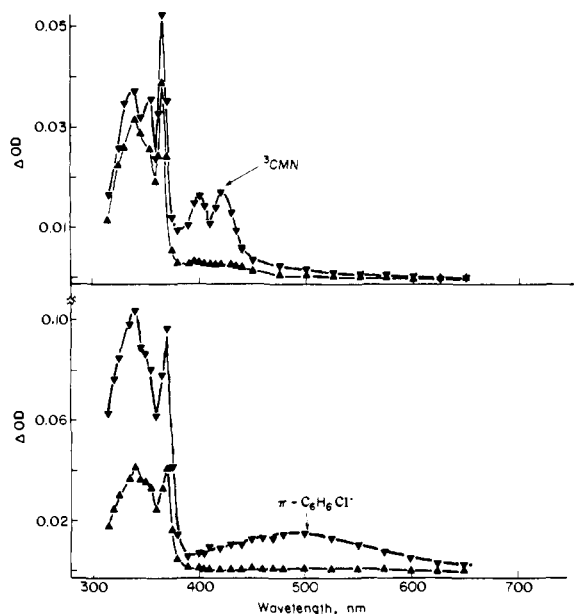


Figure 1. Transient absorption spectra obtained upon 308-nm excitation of 1-chloromethylnaphthalene in cyclohexane (A: ▼, 400 ns after laser; ▲, 2.5 μ s after laser) and benzene (B: ▼, 300 ns after laser; ▲, 6 μ s, after laser).

methanol. All other reagents and solvents were commercially available and were used as received.

1,3-Di(1-naphthyl)-2-propanone. The ketone was prepared by condensation of ethyl 1-naphthylacetate and 1-naphthylacetonitrile in sodium ethoxide followed by hydrolysis and decarboxylation of the resulting α -cyano ketone, according to a literature procedure for 1,3-diphenyl-2-propanone.¹⁹ The ketone was purified by passing it through a short silica gel column and then recrystallizing from chloroform/hexane to give slightly yellowish crystals: mp 109–110 °C (lit.²⁰ mp 108–109 °C); NMR (60 MHz, CDCl_3) δ 7.1–7.7 (m, 14 H), 4.0 (s, 4 H); mass spectrum, m/e (relative intensity) 310 (8.9), 141 (100), 115 (23.9). Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{O}$: C, 89.0; H, 5.8. Found: C, 88.9; H, 5.8.

Sample Preparation. Samples of CMN and BMN for laser flash photolysis were $6\text{--}7 \times 10^{-4}$ M in the appropriate solvent and were contained in 7×7 mm² quartz cells and degassed by nitrogen purging. All spectra and most quenching experiments were done with use of a flow system to prevent depletion of starting material and buildup of fluorescent products.

Laser Photolysis. The laser photolysis facility has been described in detail in an earlier publication.²¹ Recent modifications required to carry out two-laser experiments have also been reported.¹¹ All two-laser experiments reported herein used a Lumonics TE-860-2 excimer laser with a Xe–HCl gas mixture (308 nm, ~ 5 ns pulses, ≤ 80 mJ/pulse) as the synthesis laser for 1-naphthylmethyl radicals ($\text{Np}\dot{\text{C}}\text{H}_2$) and a Moletron UV-24 nitrogen laser (337.1 nm, ~ 8 -ns pulse, ≤ 10 mJ/pulse) for excitation of $\text{Np}\dot{\text{C}}\text{H}_2$.

Results and Discussion

Unless otherwise indicated, all experiments have been carried out in deaerated solutions at 300 K.

Generation of 1-Naphthylmethyl Radicals. The possible routes leading to 1-naphthylmethyl radicals ($\text{Np}\dot{\text{C}}\text{H}_2$) are outlined in Scheme I.

Photolysis of 1-(chloromethyl)naphthalene (CMN) at 308 nm leads to the formation of 1-naphthylmethyl radicals within the duration of our laser pulse. The radicals exhibit an absorption maximum at 365 nm in methanol and cyclohexane (370 nm in benzene) which agrees well with the position reported earlier,⁸ however, this absorption band is much sharper than suggested by Rentzepis et al.⁴ When the photolysis is carried out in benzene, we observe the simultaneous formation of a broad absorption band

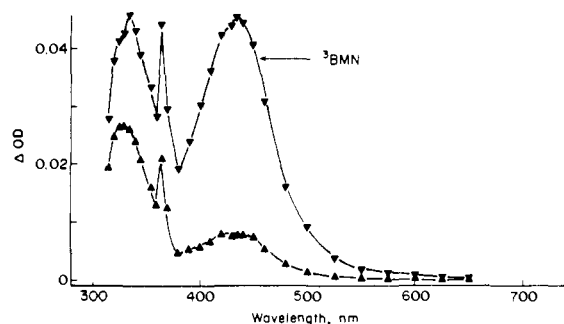


Figure 2. Transient absorption spectra obtained upon 308-nm excitation of 1-bromomethylnaphthalene in cyclohexane: ▼, 400 ns after laser; ▲, 6 μ s after laser.

centered at ca. 490 nm. Under our experimental conditions the decay of this band was 2.5 times faster than that of the 370-nm band. We assign the 490-nm species to the chlorine atom–benzene π -complex ($\pi\text{-C}_6\text{H}_6\text{Cl}\cdot$) in agreement with earlier studies.²² No triplet CMN ($\lambda_{\text{max}} \sim 420$ nm) was detected in benzene.

When the 308-nm photolysis of CMN was carried out in cyclohexane or methanol the 490-nm band assigned to the π -complex was not observed, as expected. However, in these solvents we observe the formation of a band at ca. 420 nm which can be readily characterized as due to triplet CMN. In cyclohexane its lifetime was ~ 0.5 μ s. If sufficient time was allowed for the decay of triplet CMN or $\pi\text{-C}_6\text{H}_6\text{Cl}\cdot$ in cyclohexane or benzene, respectively, the spectra of the longer lived transient were clearly due to the same species (see Figure 1).

Irradiation of CMN at 308 nm is expected to populate predominantly S_1 ,⁴ but the energy is too close to that of S_2 to rule out completely excitation into this level. We carried out a few experiments with use of the 337.1-nm pulses from a nitrogen laser. These experiments required a rather high (close to 0.1 M) concentration of CMN in order to achieve a suitable absorption at the excitation wavelength. The radical, $\text{Np}\dot{\text{C}}\text{H}_2$, was readily formed in these experiments, clearly showing that excitation into S_2 is not a requirement for C–Cl bond homolysis; similar experiments were carried out by Schuster et al.⁸ with 1-(bromomethyl)naphthalene (BMN) and led to the same conclusion. While these experiments undoubtedly bear on the question of the mechanism of bond homolysis in (halomethyl)naphthalenes, this aspect will not be treated in any detail in this report; suffice to say that 308-nm photolysis of CMN leads to the efficient formation of $\text{Np}\dot{\text{C}}\text{H}_2$; the concentrations required (typically 6×10^{-4} M) are sufficiently low that the samples can be regarded as totally transparent at 337.1 nm. This is an important consideration for the two laser experiments (vide infra). Direct photolysis at 337.1 nm is possible with higher concentrations but not convenient for the two laser experiments.

Photolysis of BMN at 308 nm led to the same transient at 365 nm as already discussed for CMN. In methanol we also detected an intense signal at 435 nm (Figure 2) which we attribute to triplet BMN. This signal was substantially shorter lived than that due to $\text{Np}\dot{\text{C}}\text{H}_2$. The higher yield of triplet for BMN compared with CMN is in line with earlier reports that suggest an enhanced yield of intersystem crossing in the case of the bromo derivatives.⁵

Photolysis of 1-naphthyl diazomethane in hydrogen donor solvents also yields $\text{Np}\dot{\text{C}}\text{H}_2$. For example, in cyclohexane $\text{Np}\dot{\text{C}}\text{H}_2$ radicals form with a growth lifetime of 144 ns.²³ However, the signals here are much weaker than in the systems discussed before as a result of extensive insertion (presumably by singlet carbene) into the C–H bonds of the solvent.²³ In this case the short wavelength side of the spectrum due to $\text{Np}\dot{\text{C}}\text{H}_2$ is slightly different

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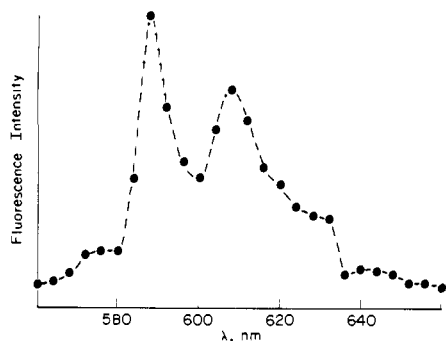


Figure 3. Fluorescence spectrum of excited 1-naphthylmethyl radical in methanol. The radical was produced from 1-chloromethylnaphthalene. The excitation laser was fired 1 μ s after the 308-nm synthesis laser.

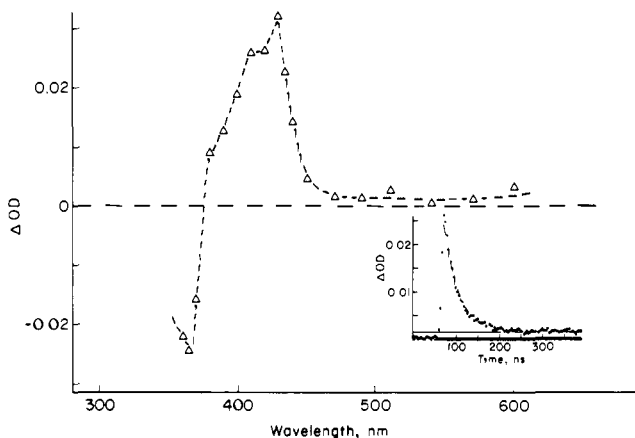


Figure 4. Transient absorption spectrum of excited 1-naphthylmethyl radical in cyclohexane. The radical was produced from 1-bromo-methylnaphthalene. The excitation laser was fired 1 μ s after the 308-nm synthesis laser. The insert shows the transient decay at 430 nm.

than those already shown in Figures 1 and 2; this is due to the fact that transient spectra of this type measure Δ OD, not OD. Thus, they are precursor dependent in the region where the precursors (such as the diazo compound) absorb.

Photolysis of di-*tert*-butyl peroxide at 337.1 nm in the presence of 1 M 1-methylnaphthalene in benzene leads to strong signals due to $\text{Np}\dot{\text{C}}\text{H}_2$ formed with a growth lifetime of 1150 ns which reflects the kinetics of the reaction of *tert*-butoxy radicals with 1-methylnaphthalene. This system is not convenient for 308-nm excitation due to the strong absorption of 1-methylnaphthalene at this wavelength.

The various experiments presented above leave no doubt of the assignment of the 365-nm transient to $\text{Np}\dot{\text{C}}\text{H}_2$. A second band from this transient is centered at ca. 340 nm, ideally located for excitation using the nitrogen (337.1 nm) laser. CMN and BMN are the most convenient sources because at the concentration used they are essentially transparent at 337.1 nm, which makes selective radical excitation straightforward (*vide infra*).

Finally, a few experiments with 1,3-di(1-naphthyl)-2-propanone showed that it is an extremely inefficient source of $\text{Np}\dot{\text{C}}\text{H}_2$ (if any radicals are formed at all). This is in agreement with earlier work showing that the naphthalene chromophore is a good sensitizer for singlet photoprocesses, but a quencher of triplet reaction for carbonyl compounds.²⁴ The Norrish type I reaction of 1,3-diaryl-2-propanones is known to be predominantly a triplet-state reaction.²⁵

Spectroscopy and Lifetimes of Excited 1-Naphthylmethyl Radicals. The efficient generation of excited 1-naphthylmethyl radicals ($\text{Np}\dot{\text{C}}\text{H}_2^*$) requires a two-laser experiment. The first

Table I. Lifetimes of Excited 1-Naphthylmethyl Radicals in Various Solvents at 300 K

solvent	τ^* , ns	
	absorption	fluorescence
cyclohexane	35.3	35.0
methanol	35.5	35.0
benzene	32.0	31.9
2-propanol	34.0	35.4
1,4-cyclohexadiene	29.4	30.7
carbon tetrachloride	~ 15	
tri- <i>n</i> -butylstannane	~ 14	

pulse (308 nm) can be described as the "synthesis pulse", since its role is to produce $\text{Np}\dot{\text{C}}\text{H}_2$ for further study by using one of the precursors described in the previous section. Following this pulse, we allowed for an appropriate delay so that any transient byproducts, such as triplet precursor or $\pi\text{-C}_6\text{H}_6\text{Cl}$, would decay completely. Fortunately, these transient byproducts were always substantially shorter lived than $\text{Np}\dot{\text{C}}\text{H}_2$ radicals. After this delay (typically between 200 and 1500 ns) the sample was excited with the 337.1-nm "photolysis pulse". The fluorescence spectrum obtained following this second laser pulse (Figure 3) shows $\lambda_{\text{max}} = 590$ nm and agrees well with that reported by Rentzepis et al.^{3,4} This luminescence is not observed when the 308-nm synthesis laser is not used, clearly indicating that it is due to the excitation of a transient photoproduct. The lifetime of this fluorescence (and thus of $\text{Np}\dot{\text{C}}\text{H}_2^*$) was much longer than the value of 13 ± 3 ns reported by Rentzepis et al.^{3,4} Our measurements consistently lead to lifetimes around 35 ns (Table I).

The transient absorption spectrum induced by the second laser pulse is shown in Figure 4. We assign this spectrum to the excited 1-naphthylmethyl radical on the basis of the following observations: (i) Generation of the 430-nm band requires both lasers; i.e., it is not formed when the 337.1-nm laser is not preceded by the 308-nm pulse or when the laser sequence is reversed. (ii) The 430-nm band is not formed when the delay between laser pulses is much longer than the lifetime of the ground-state radical. At intermediate delays the intensity of the 430-nm transient correlates well with the concentration of $\text{Np}\dot{\text{C}}\text{H}_2$ present at the time of excitation. (iii) The lifetime based on this absorption signal (see inset in Figure 4 and Table I) was always in excellent agreement with the values based on fluorescence measurements. (iv) The spectral characteristics of the 430-nm band were independent of the precursor used to generate $\text{Np}\dot{\text{C}}\text{H}_2$ (such as CMN or BMN), and (v) while these signals are not very different from those due to triplet CMN, their lifetime was clearly different, they were not quenched by typical triplet quenchers (such as moderate concentrations of dienes), and they were formed even under conditions where direct excitation does not yield detectable triplet concentrations.

The spectral similarity between $\text{Np}\dot{\text{C}}\text{H}_2^*$ and a wide variety of triplet naphthalenes (including CMN) is rather interesting. Is it possible that $\text{Np}\dot{\text{C}}\text{H}_2^*$ can be considered essentially as a substituted excited naphthalene to which the " $-\dot{\text{C}}\text{H}_2$ " substituent confers some free radical characteristics? Obviously, one cannot answer this question with just one example of this kind, but its consideration suggests a wide range of experiments that may be worth pursuing.

We note that excited-state lifetimes based on absorption need to be corrected to account for some underlying decay due to the tail of the ground-state spectrum. This correction is rather more important in some examples of intermolecular reactions and will be discussed in some more detail in that section. Corrections were very small in the measurements presented in Table I, since the lifetime of $\text{Np}\dot{\text{C}}\text{H}_2$ is much longer than that of $\text{Np}\dot{\text{C}}\text{H}_2^*$.

The reasons for the discrepancies between our lifetimes and those reported by Rentzepis et al.⁴ remain unclear. Even air saturation does not lead to a shortening of the magnitude observed (*vide infra*). It should be noted that picosecond techniques do not allow for a sufficient delay between synthesis and photolysis pulses to permit the complete decay of any transient byproducts

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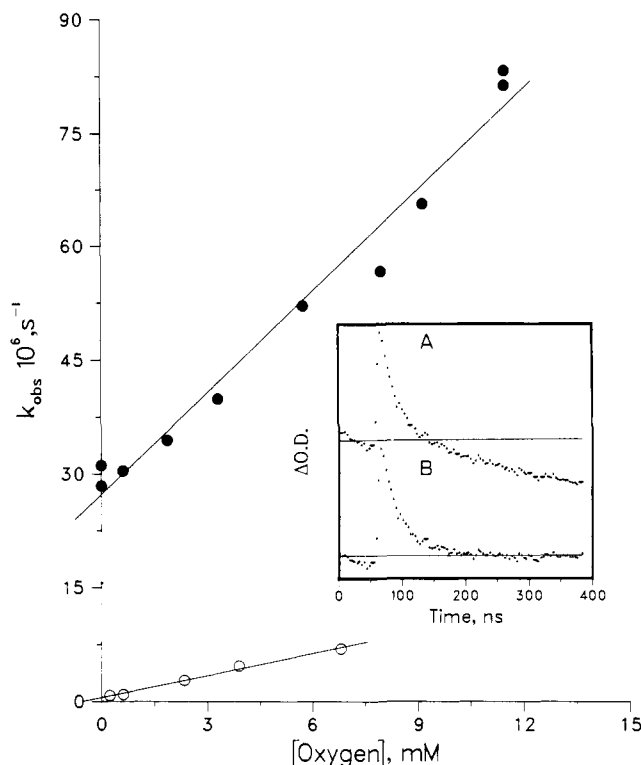


Figure 5. Quenching of the transient absorption of ground-state (O) and excited-state (●) 1-naphthylmethyl radical by oxygen. The insert shows the uncorrected (A) and corrected (B) traces for decay of the excited radical at 430 nm in the presence of 0.002 M oxygen.

such as Cl· or solvent derived radicals (vide supra); at this point it is not clear if this could account for the difference.

Temperature Dependence. The effect of temperature on the lifetime of $\text{Np}\dot{\text{C}}\text{H}_2^*$ was monitored in methanol between 297 and 211 K. Over this range the lifetime changed from 35 to 41 ns which gives a rough estimate of the activation energy ($E_a = 0.3 \pm 0.2$ kcal/mol) and A factor [$\log(A/\text{s}^{-1}) = 7.7 \pm 0.2$]. Similar temperature effects on the lifetime of the excited diphenylmethyl radical have been observed.²⁶

Intermolecular Reactions of $\text{Np}\dot{\text{C}}\text{H}_2^*$. This part of our study follows to a considerable extent the pattern of an earlier report on the reactivity of excited diphenylmethyl radicals.¹¹ This allows a comparison of the intermolecular reactivity of the two excited radicals.

Reaction with Oxygen. The reactivities of $\text{Np}\dot{\text{C}}\text{H}_2$ and $\text{Np}\dot{\text{C}}\text{H}_2^*$ toward oxygen were examined in cyclohexane with CMN as the radical source. The measurements are straightforward for the ground state. Figure 5 illustrates a plot of the rate of radical decay (k_{obsd}) as a function of oxygen concentration. The slope corresponds to a bimolecular rate constant of $(9.8 \pm 0.8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (errors as $\pm 2\sigma$) for oxygen quenching.

The measurements for the excited radical were somewhat complicated due to the fact that it was not possible to allow for the complete decay of the underlying absorptions due to triplet CMN. This is due to the fact that decay of triplet CMN and of $\text{Np}\dot{\text{C}}\text{H}_2$ in the presence of oxygen occurs in similar time domains. As a result, the decay of the excited radical was superimposed on that of the triplet state (see trace A in the inset in Figure 5). This can be easily corrected by allowing for a sloping base line by either extrapolating an exponential from the early part of the trace or what we describe as a "beginning-to-end" interpolation. Trace B in Figure 5 shows the result of introducing this correction in trace A. Analysis of the data (see Figure 5) leads to a rate constant of $(4.7 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the quenching of $\text{Np}\dot{\text{C}}\text{H}_2^*$ by oxygen. That is, the excited state interacts with oxygen five times faster than its ground state. For comparison, in the case of diphenylmethyl the excited state was 14 times more reactive than its ground state.¹¹ We observe that

Table II. Reactivities of Excited Free Radicals Toward Various Quenchers at 300 K

quencher	solvent	$k_q^*, \text{M}^{-1} \text{s}^{-1}$	
		$\text{Np}\dot{\text{C}}\text{H}_2^*$	$\text{Ph}_2\dot{\text{C}}\text{H}^*$ ^b
oxygen	cyclohexane	$(4.7 \pm 0.8) \times 10^9$	$(8.7 \pm 0.8) \times 10^9$
diamine 1	cyclohexane	$(2.6 \pm 0.2) \times 10^9$	$(4.5 \pm 0.4) \times 10^9$
methyl viologen	methanol	$(3.8 \pm 1.3) \times 10^{10}$	$(1.3 \pm 0.2) \times 10^{10}$ ^c
carbon tetrachloride	methanol	$\sim 4 \times 10^6$ ^c	$(1.6 \pm 0.1) \times 10^8$
tri- <i>n</i> -butylstannane	cyclohexane	$\sim 1 \times 10^7$ ^d	
1,4-cyclohexadiene	cyclohexane	$\sim 5 \times 10^5$ ^e	$(1.1 \pm 0.2) \times 10^6$

^a Errors as $\pm 2\sigma$. ^b From ref 11. ^c In 4:1 acetonitrile/water. ^d Based on two concentrations only. ^e Based on the lifetime of $\text{Np}\dot{\text{C}}\text{H}_2^*$ in neat solvent.

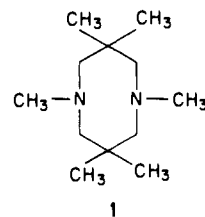
quenching of the excited radical leads to repopulation of the ground state; as in the earlier example, we speculate that quenching of $\text{Np}\dot{\text{C}}\text{H}_2^*$ by oxygen leads to singlet oxygen formation.

Electron-Donor Ability. $\text{Np}\dot{\text{C}}\text{H}_2^*$ radicals were found to be excellent electron donors toward methyl viologen (MV^{2+}), an efficient electron acceptor. Excited-state quenching was accompanied by the formation of the reduced form, MV^+ , readily characterized by its absorption bands at 398 and 603 nm. Measurement of the lifetime of $\text{Np}\dot{\text{C}}\text{H}_2^*$ as a function of the concentration of MV^{2+} led to a rate of electron transfer, reaction 1, of $(3.8 \pm 1.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in methanol.



Table II compares the reactivity of $\text{Np}\dot{\text{C}}\text{H}_2^*$ toward MV^{2+} and other quenchers with those for excited diphenylmethyl radicals. For comparison, triplet naphthalene is quenched by MV^{2+} (also via electron transfer) with a rate constant of $7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.²⁷

Quenching by Amines. $\text{Np}\dot{\text{C}}\text{H}_2^*$ radicals were efficiently quenched by diamine 1. Although the rapid quenching, $k_q = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, suggests charge-transfer interactions, we did not



observe formation of the diamine radical cation which has recently been shown to have a strong absorption band at $\sim 600 \text{ nm}$.²⁸ Apparently the charge-transfer interactions do not lead to full electron transfer to yield radical ions.

Reaction with Carbon Tetrachloride. Excited diphenylmethyl radicals were quenched by carbon tetrachloride with a rate constant of $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Similar studies with $\text{Np}\dot{\text{C}}\text{H}_2^*$ were somewhat more difficult due to its short lifetime and the relatively slower quenching. For example, it was possible to detect $\text{Np}\dot{\text{C}}\text{H}_2^*$ in neat carbon tetrachloride (Table I) under conditions where no signals could be detected for $\text{Ph}_2\dot{\text{C}}\text{H}^*$. The corresponding rate constants have been included in Table II and indicate that $\text{Np}\dot{\text{C}}\text{H}_2^*$ is not nearly as good a halogen abstractor as $\text{Ph}_2\dot{\text{C}}\text{H}^*$. It has been suggested that chlorine abstraction by excited radicals may involve a charge-transfer mechanism.¹¹ Surprisingly, in the case of MV^{2+} , $\text{Np}\dot{\text{C}}\text{H}_2^*$ is at least as good (probably better) as an electron donor as $\text{Ph}_2\dot{\text{C}}\text{H}^*$.

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Interaction with Hydrogen Donors. The lifetime of $\text{Np}\dot{\text{C}}\text{H}_2^*$ was determined in two excellent hydrogen donors, tri-*n*-butylstannane and 1,4-cyclohexadiene. The lifetime in 1,4-cyclohexadiene was ~ 30 ns which is only slightly shorter than that measured in other solvents and corresponds to a rate constant of ca. $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, though this value is subject to rather large errors due to a small difference between lifetimes (see Table I). In tri-*n*-butylstannane the lifetime was ~ 14 ns, which gives a rate constant of ca. $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Furthermore, the insensitivity of its lifetime

Conclusion

1-Naphthylmethyl radicals generated from various sources show a sharp absorption maximum at 365 nm. The radicals were produced by direct photolysis of 1-(chloro- or bromomethyl)-naphthalene at 308 nm and were then excited with the pulses from a nitrogen laser (337.1 nm) leading to the expected fluorescence at 590 nm. The absorption spectrum of $\text{Np}\dot{\text{C}}\text{H}_2^*$ shows $\lambda_{\text{max}} \sim 430$ nm; its lifetime is ~ 35 ns in several hydrocarbon, alcohol, or aromatic solvents but much shorter in carbon tetrachloride, where its decay involves Cl-atom abstraction.

Reaction of $\text{Np}\dot{\text{C}}\text{H}^*$ with certain amines and with methyl viologen indicates enhanced electron donor/acceptor properties

to solvent and temperature and its rapid reaction with oxygen (with ground-state recovery) indicate that the intermolecular reactivity of $\text{Np}\dot{\text{C}}\text{H}^*$ parallels that observed for excited diphenylmethyl radicals. It would appear that $\text{Np}\dot{\text{C}}\text{H}_2^*$ has predominantly excited state properties, rather than enhanced free radical properties. Obviously, more studies are required to establish whether this is a general characteristic of excited free radicals.

It is interesting to note the similarity between the spectra of the excited 1-naphthylmethyl radical and triplet naphthalenes. This may be a further reflection of the excited-state-like properties of excited radicals.

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Registry No. 1, 17288-12-9; chlorine, 7782-50-5; hydrogen, 1333-74-0; 1-naphthylmethyl radical, 7419-60-5; oxygen, 7782-44-7; methyl viologen, 1910-42-5; carbon tetrachloride, 56-23-5; 1-(chloromethyl)-naphthalene, 86-52-2; 1-(bromomethyl)naphthalene, 3163-27-7; 1,3-di-(1-naphthyl)-2-propanone, 51042-38-7; ethyl 1-naphthylacetate, 2122-70-5; 1-naphthylacetonitrile, 132-75-2; 2,3-di(1-naphthyl)-3-oxo-1-propanoic acid, 98577-45-8; 1-naphthylidiazomethane, 10378-55-9; di-*tert*-butyl peroxide, 110-05-4; 1-methylnaphthalene, 90-12-0.

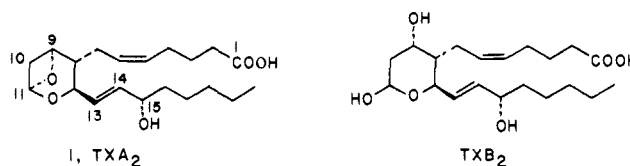
Synthesis of Thromboxane A_2

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Abstract: Thromboxane B_2 (TXB_2) was converted by (1) 1,15-macrolactonization, (2) C11 dehydration, and (3) C10,C11 bromohydrin formation to 10-bromo-1,15-anhydrothromboxane B_2 . On treatment with $\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}/(\text{MeO})_3\text{P}$ in methylene chloride, the bicyclic oxetane formed and was debrominated with tin hydride. The product, 1,15-anhydrothromboxane A_2 , was characterized by high field NMR spectroscopy and single-crystal X-ray crystallography. Saponification of that material gave the proposed Samuelsson bicyclic oxetane structure of thromboxane A_2 (TXA_2) which was shown by a variety of biological assays to be indistinguishable from natural platelet-derived TXA_2 .

We recently described a method for the preparation of the putative thromboxane A_2 (TXA_2) nucleus, an acid-labile 2,6-dioxabicyclo[3.1.1]heptane,¹ and now report application of the method to the synthesis of TXA_2 itself. TXA_2 is an unstable substance ($T_{1/2}(37^\circ\text{C}) = 32$ s in aqueous Krebs medium at pH 7.4) which is derived from the prostaglandin endoperoxide PGH_2 and which is an important blood platelet aggregation factor.² Although TXA_2 has not been previously isolated and characterized, its structure was proposed as **1** on the basis of its lability in neutral aqueous media, isotope incorporation experiments, and the isolation of various TXB_2 -like addition products. In this paper, we describe



the preparation of structure **1** and comparisons of its biological properties with those of natural, platelet-derived TXA_2 .

Our synthesis began with commercially available TXB_2 which was esterified (CH_2N_2 and Et_2O), peracetylated (Ac_2O and pyridine), and selectively deacetylated (catalytic KOME and MeOH , -15°C) at the more reactive C11 anomeric center to **3** in 78% overall yield. Dehydration to the unstable enol ether (MsCl , Et_3N , and CH_2Cl_2), deacetylation (K_2CO_3 and MeOH , 25°C), and immediate bromohydrin formation (NBS , H_2O , and THF) led to 10-bromo- TXB_2 methyl ester **4** in 51% yield. Cyclization to the oxetane proceeded as in the model study leading to **2**¹ by using a modified Mitsunobu reaction³ ($(\text{MeO})_3\text{P}$, $\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$ (DEAD), and CH_2Cl_2 , 25°C , 30 min) to

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