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One- and Two-Photon Processes in the Photochemistry of 1,3-Bis(1-naphthyl)-2-propanone: An Example of a "Reluctant" Norrish Type I Reaction[1]

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Abstract: Photoexcitation of 1,3-bis(1-naphthyl)-2-propanone in the carbonyl or naphthalene chromophore leads to the formation of a carbonyl-localized singlet state in the subnanosecond time scale. This singlet decays (τ_s = 1.4 ns in isooctane), presumably to yield the carbonyl triplet, which rapidly populates the naphthalene-localized triplet state. This intermediate can be readily detected by laser flash photolysis and shows typical naphthalene-like characteristics (TT absorption, λ_{max} = 430 nm). Product and quenching studies indicate that the Norrish type I cleavage occurs from the singlet state with $\Phi \approx 0.002$. Excitation of the triplet state with the pulses from a dye laser (430 nm) leads to cleavage of the CH_2–CO bond to yield 1-naphthylmethyl radicals in a process that we describe as a "reluctant" Norrish Type I reaction. The quantum yield for this process is ~0.06. The structural features required for this type of process to occur are discussed.

Naphthalene derivatives are frequently used as triplet-state quenchers in studies of the photochemistry of carbonyl compounds. 1,3-Bis(1-naphthyl)-2-propanone (BNP) incorporates both the ketone and naphthalene chromophores in the same molecule; not surprisingly its photochemistry is quite inefficient. Cerfontain et al.[2] report that BNP is photostable toward irradiation at λ ~ 300 nm in acetonitrile at room temperature, while some decomposition to 1,2-bis(1-naphthyl)ethane (BNE) takes place upon irradiation at 254 nm. Earlier laser photolysis studies from our laboratory have qualitatively confirmed that BNP is a poor source of 1-naphthylmethyl radicals when excited by 308-nm pulses.[3] The reported observation of no reaction is somewhat surprising in view of the fact that while naphthalenes are excellent triplet quenchers, they are also well-known to be good sensitizers of singlet photoprocesses in aliphatic ketones.[4] In fact, Wagner has proposed the use of 1-methylnaphthalene as a solvent to selectively study singlet photoreactions.[4] Part of this paper is devoted to the study of one-photon photoreactions from BNP, including product studies and a detailed characterization of its singlet and triplet states.

Several halomethylnaphthalenes are known to undergo one-photon cleavage to yield naphthylmethyl radicals;[3,5,6] the lowest lying excited singlet states are clearly involved in these processes, although it is not clear if other states (triplet or upper singlets) are also involved. The possibility of enhancing a similar cleavage in the case of BNP by laser excitation of the triplet state has been examined in this paper; our results confirm that two-photon excitation leads to Norrish type I cleavage of BNP.[7]

Results

Unless otherwise indicated our experiments were carried out in deaerated solutions at room temperature.

Fluorescence Spectrum and Lifetime. BNP shows typical carbonyl fluorescence upon excitation at either 295 or 325 nm.[8] At wavelengths below 315 nm the absorption spectrum of BNP (Figure 1) indicates that absorption must lead to initial excitation of the naphthalene moiety while at 325 nm only the low-lying carbonyl singlet would be populated directly. We must, therefore, assume that energy transfer to the lowest singlet state of BNP, localized on the carbonyl group, is a very fast (subnanosecond) process. The fluorescence spectrum of BNP in isooctane is also shown in Figure 1.

The fluorescence lifetime of BNP was measured by time-correlated single-photon counting in isooctane, and a typical decay trace has been included as an insert in Figure 1. Greater than 98% of the decay could be fit to a single exponential with a lifetime of 1.4 ns.[8] For comparison the singlet lifetime of dibenzyl ketone in isooctane under the same experimental conditions is 2.8 ns;[9] in contrast, the lifetime for 1-methylnaphthalene is ~100 ns. Fluorescence intensities and basic spectral features from the two ketones were similar for 300-nm excitation.

Phosphorescence. Within our limits of detection BNP does not show phosphorescence in solution at room temperature. However, in glasses at 77 K phosphorescence is readily detectable. These results contrast with the fluorescence in that the phosphorescence is clearly that from the naphthalene moiety. As in the case of the fluorescence, the fact that the luminescence observed arises from the lowest state (for that multiplicity) in the molecule indicates that intramolecular energy transfer is a very fast process. The phosphorescence spectrum in a methylcyclohexane glass at 77 K is shown in Figure 1 and exhibits the vibrational structure which is one of the main features of naphthalene phosphorescence. The triplet lifetime under these conditions is too long to be measured with our instrumentation (≫25 ms). From the 0,0 band (481 nm) we estimate a triplet energy of 59.4 kcal/mol for BNP, very similar to that for naphthalene itself (60.9 kcal/mol).[10]

In soft glasses such as 2-methylbutane the phosphorescence shows somewhat less vibrational resolution than in methylcyclohexane and there is an additional component in the 400–450-nm region. This was assigned to delayed fluorescence due to triplet–triplet annihilation on the basis of its similarity to BNP fluorescence and the fact that the contribution from the 400-nm signal to the total emission decreased substantially by attenuating the excitation beam with neutral density filters.

Product Studies (Lamp Irradiation). Irradiation of BNP at λ ~ 300 nm in either benzene or acetonitrile leads to photodecomposition to yield 1,2-bis(1-naphthyl)ethane (BNE) as the major product (Table I). In benzene BNE accounts for >90% of the

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[1] Issued as NRCC No. 27885.

[2] Roof, A. A. M.; van Woerden, H. F.; Cerfontain, H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1546.

[3] Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368.

[4] Wagner, P. J.; Capen, G. *Mol. Photochem.* **1969**, *1*, 173.

[5] Slocum, G. H.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 2177.

[6] Hilinski, E. F.; Huppert, D.; Kelley, D. F.; Milton, S. V.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 1951.

[7] Scaiano, J. C.; Johnston, L. J. *Pure Appl. Chem.* **1986**, *58*, 1273.

[8] Careful purification by liquid chromatography was required to remove a very minor impurity which caused additional fluorescence at λ > 450 nm when DNP was excited at λ > 310 nm. A minor long-lived component in the fluorescence decay is attributed to this impurity.

[9] The singlet lifetime of dibenzyl ketone in benzene has been reported to be 3.6 ns: Engel, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 6074.

[10] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973; p 30.

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Table I. Product Distributions in the Photolysis of BNP under Conditions of Lamp Irradiation[a]

[BNP], mM	solvent	excitation[b]	% conv	BNE,[c] mol %	1-$NpCH_3$[c] mol %	1-$NpCH_2OH$, mol %
0.755	benzene	310/2 h	57[d]	44	3.8	1.4
0.755	benzene + 1.5 mM 1,3-cyclohexadiene	310/2 h	53[d]	26	5.8	1.3
1.14	CH_3CN	310/2 h	69[d]	36	9.3	3.5
0.50	benzene	350/4 h	4[e]	1.9	1.3	3.7
0.50	benzene + 6.2 mM benzophenone	350/4 h	3[e]	0.7	2.8	1.3

[a] All irradiations for 2-mL samples. [b] Either 310-nm or 350-nm Rayonet lamps. [c] Based on moles of starting ketone. [d] Based on recovered ketone. [e] Based on three products.

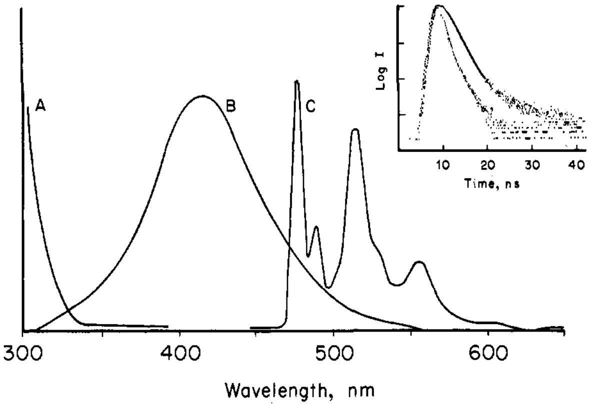


Figure 1. Absorption (A) and fluorescence (B, 290-nm excitation) spectra for BNP in isooctane at 298 K and phosphorescence (C, 295 nm excitation) spectrum in a methylcyclohexane glass at 77 K. Insert: A fluorescence decay trace from BNP in isooctane (290-nm excitation; emission monitored at λ > 375 nm). The solid line represents the fit of the calculated decay to the observed decay and the short-lived signal is the lamp pulse profile.

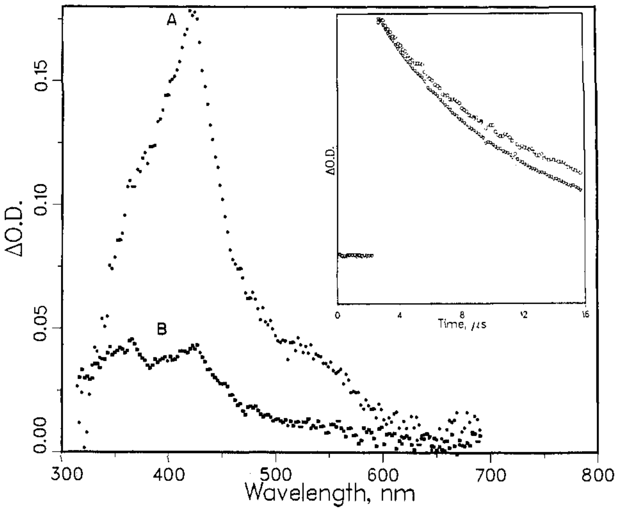
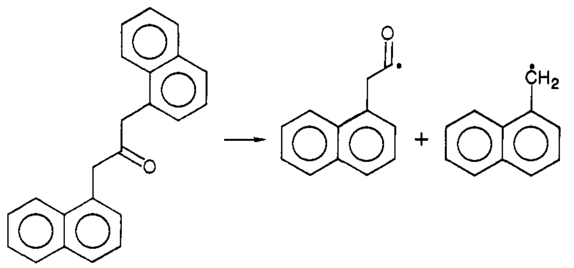


Figure 2. Transient absorption spectra obtained by 308-nm excitation of 0.2 mm BNP in benzene and recorded 250 ns (A) and 8 μs (B) after the laser pulse. Insert: Normalized decay traces for the above sample monitored at 370 nm (○) and 430 nm (▽).

products with small amounts of 1-methylnaphthalene (1-$NpCH_3$) and 1-naphthylmethanol (2–3% each) and traces of (1-naphthyl)phenylmethane also being produced. Similar results were obtained in acetonitrile (Table I). These results clearly show that the dominant process in the photochemistry of BNP is the Norrish type I cleavage (reaction 1). Quantum yields for product for-


(1)

mation (BNE, 1-$NpCH_3$, and alcohol) of ~0.002 were measured for 313-nm excitation of BNP in benzene with valerophenone as an actinometer.[11] Given such low quantum yields, it is not surprising that BNP had previously been reported to be photostable at 300 nm in acetonitrile,[2] particularly since relatively concentrated solutions were irradiated (0.16 M vs. ~0.001 M in our experiments).

Reaction 1 must involve the intermediacy of the 1-naphthylacetyl radical, but its decarbonylation must be sufficiently fast[13] that our product studies do not reveal any information on its behavior.

In order to establish the nature of the excited state responsible for the Norrish type I photocleavage of BNP we carried out a quenching experiment with 1,3-cyclohexadiene.[16] In the presence of 1.5 mM diene there was only ~10% decrease in the consumption of BNP, relative to photolysis in benzene alone. However, laser flash studies (vide infra) show that this concentration is sufficient to quench over 95% of the triplets. These results clearly suggest a singlet reaction for the monophotonic type I cleavage.[17]

While BNP consumption was essentially unaffected by the presence of diene, the products formed by photolysis of BNP in the presence of diene were considerably different from those in benzene alone (Table I). There was a substantial decrease in the amount of BNE as well as an increase in the amount of methylnaphthalene. GC–MS analysis also indicated the presence of a complex mixture of new products resulting from the addition of 1-naphthylmethyl radicals to 1,3-cyclohexadiene.

An attempted sensitization experiment with benzophenone provided further support for the singlet nature of reaction 1. Photolysis of a benzene solution containing 0.5 mM DNP and 6.2 mM benzophenone for 4 h with 350-nm Rayonet lamps yielded only ~3% of the usual BNP photolysis products in addition to several new minor products.[20] Under these conditions, >95% of

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(11) Based on acetophenone production and using $\phi_{ACP} = 0.3$.[12]

(12) Wagner, P. J.; Kelso, A.; Kemppainen, A. E.; McGrath, J. M.; Schott, N. H.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

(13) While the decarbonylation of this radical has not been examined, related systems leading to other stabilized radicals have been reported.[14,15]

(14) Turro, N. J.; Gould, I. R.; Baretz, B. H. *J. Phys. Chem.* **1983**, *87*, 531.

(15) Lunazzi, L.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1983**, *87*, 529.

(16) 1,3-Cyclohexadiene has a triplet energy of 53 kcal/mol and is an excellent triplet quencher in these systems.[10]

(17) The type I reaction is generally a triplet process,[18,19] but when this is prevented the minor contribution from the singlet takes over.

(18) For the type I reaction of dibenzyl ketone see ref 9 and: Robbins, W. K.; Eastman, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6076.

(19) For the type I reaction of cycloalkanones see: Caldwell, R. A.; Sakuragi, H.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 2471. Dalton, J. C.; Pond, D. M.; Weiss, D. S.; Lewis, F. D.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 2564. Weiss, D. S.; Turro, N. J.; Dalton, J. C. *Mol. Photochem.* **1970**, *2*, 91. Wagner, P. J.; Spoerke, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4437.

the light is absorbed by benzophenone and >99% of the benzophenone triplets are quenched by BNP (from laser flash photolysis results (vide infra)). The small amount of product formation is probably due to direct excitation of BNP since irradiation of the ketone alone at 350 nm under identical conditions to the sensitization experiment yields ~4% conversion. The above results demonstrate that triplet BNP is not responsible for the observed photocleavage.

Laser Flash Photolysis at 308 nm. Laser photolysis of BNP at 308 nm in benzene with the pulses from an excimer laser leads to the formation of an intermediate which shows a broad absorption band with a peak at 430 nm (Figure 2). We assign these signals to the triplet state of BNP. This assignment is supported by the similarity of the early spectrum of Figure 2 to those of typical naphthalenes, as well as by the observations that this species is readily quenched by oxygen and 1,3-cyclohexadiene. For the latter, a study of the lifetime dependence for ^{3}BNP with the diene concentration led to $k_q = (4.5 \pm 0.2) \times 10^9$ M^{-1} s^{-1} (errors as $\pm 2\sigma$). The assignment of the above transient to triplet BNP is further substantiated by the fact that the same spectrum can be produced by sensitization with benzophenone. The quenching of triplet benzophenone (produced by 337-nm laser excitation) by BNP occurs with a rate constant of $(6.1 \pm 0.5) \times 10^9$ M^{-1} s^{-1}.

Examination of the triplet decay traces at 420 and 370 nm revealed small differences (insert in Figure 2) that indicate the presence of an underlying species with a longer lifetime at 370 nm. The same effect is observable in the transient spectra recorded following different delays after laser excitation. For example, the spectrum after 8 μs (Figure 2) shows an increase in the relative intensity of bands at $\lambda < 400$ nm. We attribute these effects to the presence of some 1-naphthylmethyl radicals, produced by 308-nm excitation. These ideas are also supported (vide infra) by the results of product studies under conditions of laser excitation.

The decay of the triplet state of BNP typically showed a significant contribution from second-order processes; this is not uncommon for long-lived triplets under conditions of laser excitation and is due to triplet–triplet (T–T) annihilation. The observable lifetimes for ^{3}BNP increased when the initial concentration of triplet was reduced by using a set of calibrated neutral density filters to attenuate the laser dose. Extrapolation to "zero" laser dose[21] suggests a triplet lifetime of ca. 20 μs under our experimental conditions.

Two-Laser Transient Phenomena. In these experiments the triplet state of DNP was generated by 308-nm excitation in the same manner described in the previous section. However, in this case the normal decay of the triplet was perturbed by excitation with the ~430-nm pulses from a dye laser.[7] At this wavelength the precursor of the triplet (i.e., ground-state BNP) is transparent (Figure 1) and cannot be excited by the dye laser. Thus, the effects observed are a direct result of excitation of the transient. Figure 3 shows the results of triplet excitation for traces monitored at 410 and 370 nm. It should be noted that, given the high energy per pulse obtained from the dye laser and the relatively long pulse duration (~250 ns), the chemically efficient bleaching of ^{3}BNP (Figure 3, top) should not be taken as indicative of a high quantum yield. In fact, preliminary experiments with Aberchrome-540 as an actinometer indicate a quantum yield in the neighborhood of 0.06.[22] The processes responsible for the photobleaching are presumably sufficiently fast that a 250-ns pulse is for practical purposes the equivalent of irradiation of the transient with a continuous source.

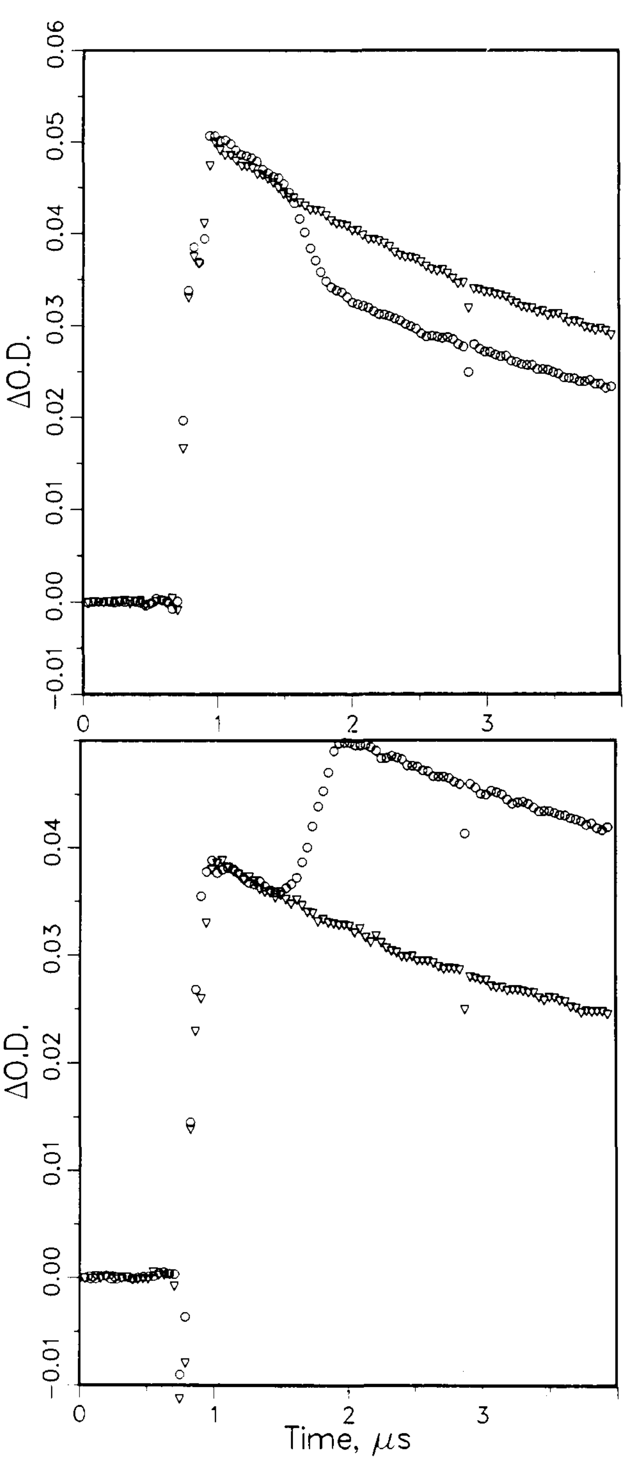

Figure 3. The decay of BNP transients formed by excitation with an initial 308-nm laser pulse followed by a 430-nm laser pulse and observed at 410 nm (top) and 370 nm (bottom).

The nature of the new absorption at ~370 nm can be readily resolved by examining the two-photon transient spectrum. This is shown in Figure 4, which compares the corresponding spectra immediately before and immediately after the dye laser pulse. It should be noted that while the actual spectra were recorded a few tenths of a microsecond before and after the dye laser pulse they were normalized (by taking into account the fraction of triplet decay) to the time corresponding to laser excitation. This does not change the features of the spectrum, but it facilitates the comparison of Figure 4. Also included in the same figure is an independently recorded spectrum of the 1-naphthylmethyl radical

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[20] Two additional products were observed by HPLC in the presence of benzophenone which were not present in a sample photolyzed in the absence of sensitizer. GC–MS of the mixture showed these to be high molecular weight material which may result from reaction of benzophenone with DNP.

[21] Evans, C.; Weir, D.; Scaiano, J. C.; MacEachern, A.; Arnason, J. T.; Morand, P.; Hollebone, B.; Leitch, L. C.; Philogène, B. J. R. *Photochem. Photobiol.* **1986**, *44*, 441.

[22] The use of Aberchrome-540 actinometry for determining quantum yields for one- and two-laser experiments and transient extinction coefficients is being developed in our laboratories; the method will be reported elsewhere. The use of Aberchrome-540 as an actinometer in steady-state experiments in both the UV and visible regions has been described: Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341. Heller, H. G., private communication.

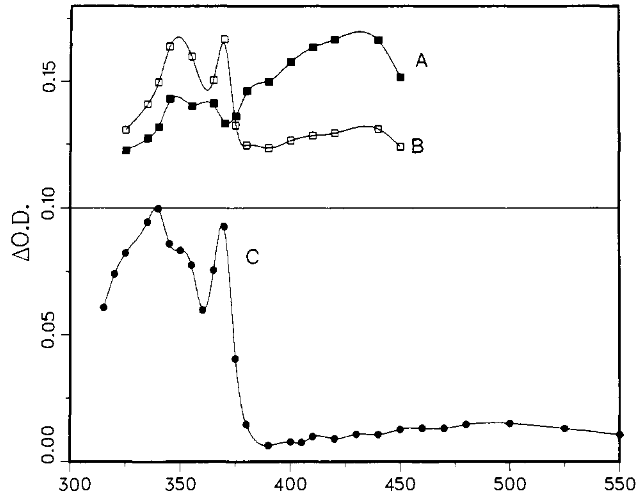

Figure 4. Transient absorption spectra recorded 0.2 μs before (A) and 0.2 μs after (B) the dye laser pulse following 308-nm excitation of BNP in benzene; traces A and B have been normalized to the time corresponding to 308-nm laser excitation and have been offset by 0.1 O.D. units. Trace C shows the transient absorption spectrum of the 1-naphthylmethyl radical produced by 308-nm excitation of 1-(chloromethyl)naphthalene in benzene.[3]

Table II. Comparison of Product Yields from One- and Two-Laser Irradiations of 0.5 mM BNP in Benzene

	product yields		
excitation laser(s)	BNE	1-NpCH$_3$	1-NpCH$_2$OH[a]
308 nm	0.030	tr	0.050
308 nm + 430 nm	0.092	0.010	0.141
430 nm + 308 nm	0.032	tr	0.041

[a] The alcohol product probably arises from traces of residual oxygen. The yields of this product are higher for the laser experiments presumably because the conversions are lower than those for lamp irradiation.

(trace C, bottom). These results unequivocally show that the new species formed by 430-nm excitation of the triplet state should be assigned to the 1-naphthylmethyl radical.

Product Studies (Laser Excitation). Three sets of experiments were carried out under these conditions: (i) a 3-mL sample of 0.5 mM BNP was excited with 500 laser shots at 308 nm; (ii) a second aliquot of the same sample was excited with 500 pairs of 308- and 430-nm pulses with the 430-nm pulses following the 308-nm excitation after ~500 ns; and (iii) the experiment in (ii) was repeated with the laser sequence reversed, i.e., the 308-nm pulse followed the 430-nm dye-laser pulse. The last experiment serves as a control to verify that the effect of the dye laser on the products is not due to thermal effects or secondary photolysis of products generated in earlier laser pulses. Within our experimental error experiments (i) and (iii) gave identical results, while the product yields from experiment (ii) were ca. three times greater. Table II summarizes the product yields and ratios. It should be noted that while comparison of the product ratios from lamp and laser photolysis is valid, the comparison of actual yields is not meaningful unless the appropriate actinometers are taken into consideration.

It is likely that a fraction of the products from 308-nm excitation (experiment (i) as well as control experiment (iii)) actually result from two-photon excitation, a process that is sometimes unavoidable under conditions of laser excitation. Our laser spectroscopic studies (vide supra) support this idea, as does the fact that the yield of products tends to decrease if the laser beam is defocussed, or if it is attenuated with neutral density filters.

Finally, it should be noted that while BNE is also an interesting substrate for two-laser experiments, our control studies and the progress already achieved in the study of this system clearly show that neither the transient phenomena nor the products of the photochemistry of BNP incorporate contributions due to BNE photochemistry.

Discussion

The one-photon photochemistry of BNP follows the pattern expected from numerous studies of the Norrish type I reaction reported in the literature.[18,19] An interesting molecule of closely related structure, dibenzyl ketone (DBK), undergoes the Norrish type I reaction efficiently and for all practical purposes, exclusively from the triplet manifold;[9,18] not surprisingly, naphthalenes quench the type I reaction of DBK at close to the diffusion-controlled limit.

BNP presents, in an intramolecular form, the same features as DBK in the presence of a naphthalene quencher. Thus, naphthalene singlets can sensitize carbonyl singlets only to quench them following singlet–triplet intersystem crossing. In spite of an earlier report to the contrary,[2] BNP fluorescence is not that from a naphthalene-type excimer, but rather it arises from the carbonyl chromophore and is virtually identical, and of similar intensity to, the fluorescence from DBK. In fact, it would be rather unexpected to see any fluorescence from the naphthalene groups with use of steady state techniques, since the carbonyl unit is expected to have a lower singlet energy.[23]

Our transient spectroscopy studies reveal the presence of a naphthalene-like triplet as the only excited species. On the other hand, product and quantum yield studies tend to reveal the singlet contribution to the Norrish type I reaction. This component is of course minor in most other systems, where the triplet contribution dominates; however, in BNP, where the naphthalene presence prevents the triplet contribution to the Norrish type I process, the singlet component takes over and becomes the only significant (even if inefficient) source of products.

Both the two-laser transient phenomena and the product studies under conditions of two-laser excitation indicate that excitation of triplet BNP results in cleavage to generate 1-naphthylmethyl radicals. This reactivity of the excited triplet contrasts with the stability of the lowest triplet state of BNP. Although the two laser traces monitored at 410 nm show fairly efficient bleaching, the actual quantum yields are quite low (ca. 0.06). Furthermore, the bleaching observed may not all lead to products as there may be decay pathways for the upper triplet which lead to ground-state ketone rather than to the lowest triplet or to cleavage.

Finally, our recent work has led to the identification of two laser-specific free radical sources, BNP and benzil, reported recently in a separate publication.[24] The possibility of identifying molecules that are photostable to conventional irradiation (including, of course, ambient light) but photosensitive toward laser light may lead to the development of a new kind of laser-specific photoinitiator that may find wide use in high-technology applications. It becomes, therefore, interesting to try to understand what structural properties of a molecule make it a good candidate for two-photon lability and one-photon stability. If we are looking for free radical sources, we will clearly need to break chemical bonds. Most single bond energies in molecules containing only C, H, and O are in the 80–100-kcal/mol range. Clearly, excited states with 70 kcal/mol or higher energies will be candidates for one-photon cleavage.

Let us at this point restrict our discussion to triplet states. From the analysis above, we will be looking for triplet states that have the following characteristics: (a) the ability to store a significant portion of the first photon's energy, while having triplet energies significantly below 70 kcal/mol; (b) long triplet lifetimes; (c) "good" triplet absorption characteristics, that will facilitate light absorption by the triplet states; and (d) proximity between the chromophore and the bond to broken. Since we can expect upper triplet states to be short lived, it may be desirable to have a weak bond close to the main chromophore in the molecule. Interestingly, benzil, BNP, and BNE meet all four criteria mentioned above.

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(23) For example, the singlet energies of naphthalene and acetone are 92 and 88 kcal/mol., respectively: ref 10, p 3 and 4.

(24) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2179.

In general, naphthalenes with triplet energies around 60 kcal/mol are almost ideally located to have triplet stability and yet to store a very considerable energy.

Two other questions can be expected to be important. The lifetime of the upper state responsible for the photocleavage will of course be a factor; unfortunately, we know little about this subject and any discussion would be mere speculation. A considerable amount is known about other types of chromophores (azulene, thiones)[25] and a similar degree of understanding would be desirable in the case of naphthalenes. The other aspect relates to the singlet state characteristics. Undoubtedly, excited singlets will be good candidates for two-photon one-laser reactions, and indeed there is some indication that in the case of benzil such processes play a role.[24] In the case of BNP (Table II) one-photon cleavage of the singlet is inefficient, reflecting the localization of the energy in the carbonyl chromophore. Two-photon processes may play a minor role in the one-laser (308 nm) cleavage of BNP.

Experiment Section

Materials and General Techniques. The synthesis of 1,3-bis(1-naphthyl)-2-propanone has been reported in an earlier publication.[3] Dibenzyl ketone and benzophenone were recrystallized before use. 1,3-Cyclohexadiene was vacuum distilled. Other reagents and solvents (Aldrich Gold Label) were used as received. Aberchrome-540 was purchased from Aberchromics Ltd. (Cardiff).

Fluorescence and phosphorescence spectra were recorded on a Perkin-Elmer LS-5 fluorescence spectrometer. Fluorescence lifetimes were measured on a PRA instrument. GC analyses were done on a Perkin-Elmer 8320 gas chromatograph with a 12-m BPI on vitreous silica capillary column. GC/MS spectra were recorded on a Hewlett Packard 5995 instrument equipped with a 10-m Ultra I (OV-101) capillary column. HPLC analyses were done on a Varian instrument equipped with a reverse-phase column and with methanol/water mixtures as eluent. Preparative separations were done on a Perkin-Elmer 10 liquid chromatograph with a Lobar Silica Gel 60 prepacked column.

Laser Photolysis. The laser photolysis facility and recent modifications required for two-laser experiments have been described in earlier publications.[26,27] 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 BNP triplets and a Candela flash pumped dye laser (Stilbene 420 dye in 50% aqueous methanol; 100-200 mJ/pulse; ~250 ns pulse width) for excitation of the triplet. The benzophenone sensitization experiments were carried out with use of a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, ≤9mJ/pulse) for excitation.

Samples of BNP (0.2 mM in benzene) were contained in 7 × 7 mm^2 quartz cells and were degassed by nitrogen purging.

Lamp Irradiations. Samples of BNP in the appropriate solvent were degassed by nitrogen purging and irradiated with RPR 3000 lamps. Products were identified by comparison of GC, GC/MS, and HPLC traces to those of authentic samples. Quantitative product analysis was done by HPLC with 9-phenylanthracene as an internal standard (added after irradiation) and with a standard mixture of ketone plus products for calibration.

For quantum yield measurements, samples of BNP and valerophenone in benzene with matched optical densities at 313 nm were degassed by nitrogen purging and irradiated in a merry-go-round with a Hanovia 200 W mercury/xenon arc lamp and a potassium chromate filter to isolate the 313-nm line. Quantitative product analysis for BNP samples was done by HPLC, as above. The valerophenone actinometer samples were analyzed for acetophenone production ($\phi = 0.3$)[12] by GC with hexadecane as an internal standard.

Laser Product Studies. Samples of BNP in benzene (3 mL; 0.5 mM) were purged with nitrogen and irradiated with (i) 500-308-nm laser shots, (ii) 500 pairs of 308- and 430-nm pulses with a 500-ns delay between the two pulses, and (iii) 500 pairs of shots as in (ii) but with the laser sequence reversed. The samples were continuously purged with nitrogen during the laser irradiations to provide sample mixing. Continuous mixing is essential for the comparison of one-laser, two-laser, and reverse-sequence experiments to be valid. Quantitative analysis was done by HPLC.

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Registry No. 1,3-Bis(1-naphthyl)-2-propanone, 51042-38-7.

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Biradical Reversion in the Intramolecular Photochemistry of Carbonyl-Substituted 1,5-Hexadienes

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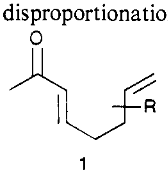
Abstract: We have studied the intramolecular photochemistry of dienones **10a,b**–**12a,b**. The initial rate of loss of alkene stereochemistry in recovered starting ketone provides a measure of the rate of reversion (k_r) of the biradical intermediate (Scheme I) relative to its conversion to products (k_p). Results are presented in Table I along with quantum yields for products (Φ_p) and for reversion (Φ_r) and the fraction of absorbed light not accounted for by these processes (Φ_{dif}). Both 1-acyl (**10a,b**) and 2-acyl (**11a,b**) hexadienes yield freely reverting biradicals. In these series both Φ_p and Φ_r increase on replacement of hydrogen by methyl at C(6), providing evidence for the postulated exciplex. The 3-keto hexadienes **12a,b** are quite different: (1) the biradical does not revert to starting ketone (<1%); (2) substitution of methyl for hydrogen at C(6) causes a decrease in Φ_p; and (3) initial bonding in the biradical is at C(β) of the enone. An explanation for the regiochemistry and relative Φ_p's of the three series is offered.

In previous studies we have investigated the role of structural features in control of the regiochemistry of intramolecular photochemical reactions of the carbonyl-substituted 1,5-hexadienes generalized as **1**–**3**.[1] These studies have led to rules predicting whether cyclization of the diene **4** leads to biradical **5** (crossed, 1,5 or 2,6 closure) or **6** (straight, 1,6 closure) or both. Collapse or disproportionation of these biradicals then leads to the observed



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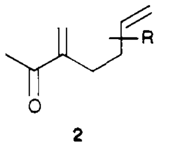

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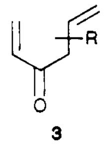

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[1] (a) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1291. (b) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1299. (c) Matlin, A. R.; Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1983**, *24*, 2961.

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