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Are Aroylnitrenes Ground-State Singlets? Photochemistry of β-Naphthoyl Azide

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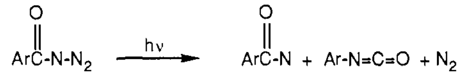
Abstract: Both direct-irradiation and triplet-sensitized photolyses of β-naphthoyl azide (BNA) give nitrene-derived products indicative of reaction only from the singlet state of β-naphthoylnitrene (BNN). The triplet nitrene is not detected in chemical trapping or spectroscopic experiments, which readily reveal related intermediates. The results require that the energy of singlet BNN be very close to or below the energy of triplet BNN. The data are most consistent with a singlet ground state for BNN. A qualitative perturbation molecular orbital approach is used to account for this surprising finding.

It has appeared for some time that the basic tenets of acyl- and aroylnitrene chemistry are well understood and adequately documented by experiment and theory.[1] Generally, photolysis of a precursor azide gives the nitrene and Curtius rearrangement to an isocyanate (eq 1). Nitrenes may exist either in an electron-paired singlet state or in a radical-like state with triplet spin multiplicity. All alkyl-, aryl-, and acylnitrenes[2] that have been investigated to date are believed to be triplets in their ground state.



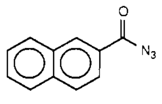
$$\mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-N-N_2} \xrightarrow{h\nu} \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-N} + \mathrm{Ar-N{=}C{=}O} + \mathrm{N_2} \qquad (1)$$

A matter of some importance and interest is the magnitude of the energy gap separating triplet and singlet nitrene states (ΔG_{st}). An estimate of this value has been obtained experimentally in only two cases. Spectroscopic measurements on the simplest nitrene, imidogen (HN:), yield a value of 35 kcal/mol.[3] Recent electron photodetachment experiments by Drzaic and Brauman on phenylnitrene (C_6H_5N:) indicate that its triplet is 4.3 kcal/mol below the lowest singlet state.[4] A considerable effort has been made to obtain estimates of ΔG_{st} for nitrenes by computational methods. Of most relevance to the present report are calculations for formylnitrene (HCON:).[5-10] In these studies the triplet is predicted to be the ground state, and the lowest energy singlet is estimated to be 10–35 kcal/mol above this level. This energy difference is expected to be relatively insensitive to replacement of the hydrogen atom bound to carbon by other groups.[9]

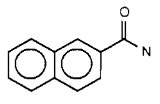
Experimental investigations of the chemical properties of acylnitrenes have generally revealed properties consistent with the predicted behavior.[1] The singlet state is a powerful electrophile capable of inserting into unactivated carbon–hydrogen bonds, of adding to olefins to form aziridines, and of combining with nucleophiles such as alcohols. On the other hand, triplet acylnitrenes are generally thought to react as radicals that abstract hydrogen atoms and add to olefins to form 1,3-biradicals. For the particular cases of (ethoxycarbonyl)nitrene[11] (EtOCON:) and benzoylnitrene[12-15] (PhCON:), existing experimental results have been interpreted to support the prediction of triplet ground states.

Two observations exist in counterpoint to the neat package of experimental and computational results outlined briefly above. First, despite ready measurement of characteristic ESR spectra for triplet (ethoxycarbonyl)nitrene and for aryl-substituted nitrenes (ArN:) in general, Wasserman and co-workers were unable to observe a spectrum for benzoylnitrene.[16] Second, recent experiments by Inagaki and co-workers have shown that both direct photolysis and triplet sensitization of benzoyl azide in *cis-* or *trans-*1,4-dimethylcyclohexane give exclusively insertion products characteristic of the singlet nitrene.[17] This behavior seems inconsistent with the theoretical predictions of ΔG_{st}.

We chose to study the chemical properties of β-naphthoyl azide (BNA) and β-naphthoylnitrene (BNN) in an attempt to resolve this apparent inconsistency. The naphthyl-substituted example was selected to overcome problems previous workers encountered with azides that absorb light only in the deep-UV spectral region, to facilitate triplet energy transfer, and to permit laser transient absorption experiments. We assumed that changing the phenyl substituent to naphthyl would only minimally affect the properties of the nitrene.



BNA



BNN

To our considerable surprise, all experiments carried out to test the spin multiplicity of ground-state BNN indicate that it is a singlet. It is important to recognize before considering these experiments that it is not possible to confirm unambiguously a singlet ground state for a transient intermediate. There exist no experiments analogous to the Curie law test, which certifies a triplet ground state from the behavior of an ESR spectrum. In contrast, the experimental case supporting a singlet ground state for an intermediate can only consist of circumstantial evidence.

Results

1. Optical Spectroscopy. Shown in Figure 1 are the absorption and emission spectra of BNA at room temperature in cyclohexane and at 77 K in a frozen methylcyclohexane glass, respectively. The absorption spectrum is unremarkable, but the emission spectra provide important information about the excited states of the azide.

The emission bands centered at ca. 380 nm are identified as fluorescence of BNA^{*1} from its lifetime (<2 ns at room temperature and 13 ns at 77 K), the excitation spectrum that matches

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(1) Lwowski, W. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: New York, 1984; Chapter 4.

(2) We use the term acyl in a generic sense, which includes acyl-; aroyl-; and (carboalkoxy)nitrenes.

(3) Okabe, H. *Photochemistry of Small Molecules*; Wiley: New York, 1978.

(4) Drzaic, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443. Drzaic, P. S.; Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 5285.

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(17) Inagaki, M.; Shingaki, T.; Nagai, T. *Chem. Lett.* **1981**, 1419. Inagaki, M.; Shingaki, T.; Nagai, T. *Chem. Lett.* **1982**, 9.

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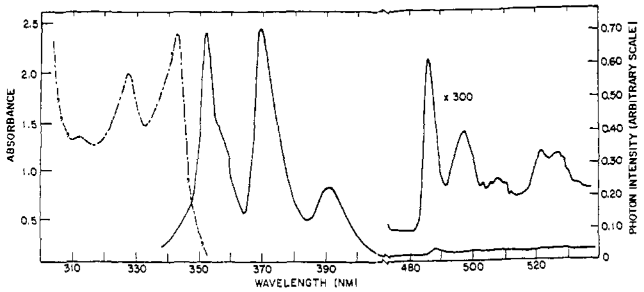

Figure 1. Absorption (dotted) and emission spectra of BNA. The absorption spectrum was recorded in cyclohexane solution at room temperature. The emission spectra were recorded in methylcyclohexane at 77 K.

the absorption spectrum of BNA, and the observation that this emission disappears as BNA is consumed by irradiating the sample. The emission centered ca. 500 nm is likewise identified as the phosphorescence of BNA^{*3}. This emission cannot be observed in spectra run at room temperature. At 77 K its excitation spectrum parallels the absorption spectrum of BNA and it has a decay lifetime of 2.3 s. Evidence that the 500-nm emission originates with BNA and not with a photoproduct or an impurity similarly comes from the observation that it decreases and eventually disappears entirely as the azide is consumed by irradiation.

Calculations from the fluorescence and phosphorescence emissions of BNA place the lowest singlet and triplet excited states of the azide at 82 and 59 kcal/mol, respectively. The fluorescence of the azide is not quenched by the reagents used to trap the nitrene (see below). This finding eliminates possible confusion arising from the intervention of reactions that might originate with the singlet excited azide but give products usually thought to be characteristic of the nitrene.

Irradiation of BNA at 77 K leads to the formation of characteristic nitrene-derived products (see below). This observation ensures that an excited state of BNA does lose nitrogen at this temperature. We are not able to detect a metastable intermediate under these conditions by optical absorption or emission spectroscopy that might be associated with a nitrene. However, if the frozen solution of the azide is irradiated with a pulsed light source, a transient species with an apparent absorption maximum at 450 nm is detected. This species has the same decay lifetime as that measured for the phosphorescence of BNA^{*3} and is thus assigned to this state. Further evidence in support of this assignment comes from transient absorption measurements made at room temperature.

Photolysis of BNA in cyclohexane at room temperature with the output of a nitrogen laser (13 ns, 337 nm, 7 mJ) generates the same transient species with maximum at 450 nm as is detected in the low-temperature experiment (Figure 2). This spectrum is similar to the triplet-triplet absorption of other naphthalene derivatives that have been recorded.[18] The detected species is formed within the rise time of the laser and decays following a first-order kinetic law with a lifetime of ca. 17 μs. The decay rate is unaffected by the olefins or alcohols that efficiently trap BNN (see below). The transient species is quenched at a diffusion-limited rate by known naphthalene triplet quenchers such as 1,3-cyclohexadiene and O_2. Significantly, the products of reaction are unchanged by the presence of sufficient diene to quench all of the transient. When O_2 is the quencher, no oxygen-containing products are formed. These findings show that both O_2 and the diene are physical rather than chemical quenchers of the detected transient intermediate. All of the evidence points to assignment of the detected transient as BNA^{*3}. While this was not the hoped for result, it does eliminate possible confusion arising from the intervention of reactions that might originate with the triplet azide but give products commonly thought to be characteristic of the nitrene.

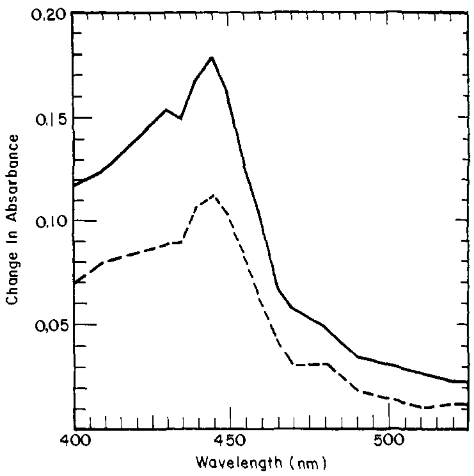

Figure 2. Transient absorption spectra recorded immediately (solid) and ca. 1 μs (broken) after irradiation of BNA in cyclohexane at room temperature.

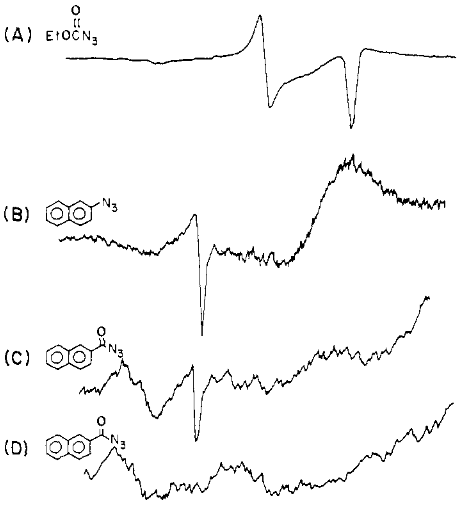

Figure 3. ESR spectra from photolysis of azides (5000–11 000 G): (A) irradiation of ethoxycarbonyl azide at 77 K, recorded at 8 K in Fluorolube; (B) irradiation of β-naphthyl azide at 77 K, recorded at 8 K in Fluorolube; (C) irradiation of BNA at 77 K, recorded at 8 K in Fluorolube; (D) after warming sample C to room temperature and refreezing at 8 K.

2. Electron Spin Resonance (ESR) Spectroscopy. Observation of a characteristic ESR spectrum at low temperature is the most certain way to identify a triplet intermediate.[19] The ESR spectra of many triplet nitrenes have been observed readily under standard conditions.[16] We attempted to measure the ESR spectrum of BNN; the results are summarized in Figure 3.

A solution of BNA was prepared in Fluorolube at room temperature, cooled to 77 K, and then irradiated in the cavity of an ESR spectrometer. No signals that could be assigned to BNN were detected. Prolonged irradiation of the sample does generate a triplet nitrene spectrum, but it is readily assigned to β-naphthylnitrene formed from secondary photolysis of β-naphthyl isocyanate (a product of photolysis of BNA; see below). Similar findings were reported by Wasserman for benzoyl azide.[16] As a control experiment, ethoxycarbonyl azide was irradiated under these conditions. (Ethoxycarbonyl)nitrene is known to have a triplet ground state, and its singlet is thought to be more reactive than those of aroylnitrenes.[11] The ESR spectrum of (ethoxycarbonyl)nitrene was easily observed and is shown on Figure 3.

There are several reasons why the ESR spectrum of a triplet intermediate might be difficult or impossible to observe. First, under the conditions of the experiment the triplet might not be

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Table I. Irradiation of BNA in Cyclohexane Containing Various Nitrene Trapping Reagents

	product yields (absolute %)					
				aziridine		
trapping reagent, M	BNI	amide **1**	β-naphthamide (**2**)	**3**	**4**	**5**
none						
N_2 saturated	54	44	trace[a]			
O_2 saturated	54	45	trace			
laser irradiation	58	41	trace			
cyclohexene						
0.3	53	trace	trace	36		
0.03	49	22	trace	26		
0.003	52	44	trace	8		
cis-4-methyl-2-pentene						
0.2	52	trace	ND[b]		46	ND
0.05	54	16	ND		32	ND
0.01	52	34	ND		17	ND
0.01 (O_2 saturated)	52	33	ND		16	ND
trans-4-methyl-2-pentene						
0.67	53	9			ND	36
0.05	53	39	1		ND	4

[a] Trace means that a peak with the proper retention volume was observed by HPLC, but represents a yield of <1%. [b] ND means no peak with the proper retention volume is detected.

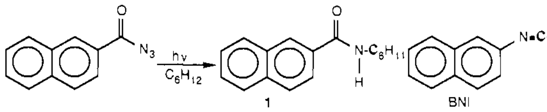
formed. In the present case, for example, it is possible that excited BNA does not give the nitrene at 77 K. However, this concern is readily eliminated since products characteristic of BNN are formed from photolyses conducted at 77 K. Similarly, it is possible that singlet BNN is consumed in chemical reactions before it can intersystem cross to the detectable triplet nitrene. We attempted to reduce the chance that this complication prevented our detection of the ESR spectrum for BNN. Irradiation of BNA at 3 K in a 2-methyltetrahydrofuran glass failed to give an ESR spectrum for BNN under conditions where arylnitrenes were readily detected. Also, irradiation of BNA in a CO_2 host (which is expected to be particularly inert) at 77 K does not yield appropriate signals.[20] Finally, attempts to bypass the singlet state completely by triplet sensitization with a glass formed from acetophenone and benzaldehyde also did not yield the hoped for ESR spectrum.

A second general reason why the ESR spectrum might be difficult to detect is that the triplet nitrene is thermally or photochemically unstable. The experiments described above designed to inhibit reaction of the singlet should simultaneously have solved the problem of a thermally reactive triplet nitrene. We attempted to reduce the chance that secondary photolysis of BNN causes its rapid destruction by varying the wavelength and time of irradiation. Photolysis at 254 nm, where the azide absorbs very strongly and thus will help protect the nitrene from photodestruction, does not give the spectrum of BNN, but β-naphthylnitrene (secondary photolysis) is eventually detected.

A third possibility is that the nitrene signals might be particularly weak, or broad, or in a unexamined region of the spectrum. The first two possibilities were probed with (ethoxycarbonyl)nitrne as a model. Cooling samples of this nitrene that had been formed by irradiation at 77 K (where it is certain that BNN is formed) to 8 K results in an 8-fold enhancement of the signal. When the same procedure is applied to irradiated samples of BNA, there are still no signals detected that can be assigned to BNN. Finally, to examine the remote possibility that BNN has an unusually large *D* value, we searched in vain for signals to 12000 G.

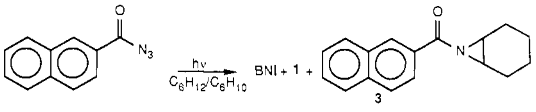
All attempts to measure the ESR spectrum of BNN failed. This negative result has two possible interpretations. Either the triplet is not the ground state for this nitrene or we did not perform the correct experiment to detect this particular triplet. The body of chemical evidence we have gathered is consistent with the first explanation.

3. Photochemistry of β-Naphthoyl Azide. Irradiation of BNA in cyclohexane at room temperature gives β-naphthyl isocyanate (BNI, 50%), *N*-cyclohexyl-β-naphthamide (**1**, 45%), and a trace (<1%) of β-naphthamide (**2**) (eq 2 and Table I). The products are not affected by saturation of the solution before photolysis with either N_2 or O_2. The quantum efficiency for consumption of BNA under these conditions is 0.5.



(2)

Irradiation of BNA in cyclohexane solutions containing cyclohexene gives BNI, insertion product **1**, and aziridine **3** (eq 3 and Table I). As the concentration of cyclohexene is raised, the



(3)

yield of **1** decreases, that of **3** increases, but the yield of BNI remains unchanged. This behavior has been observed previously in the photolysis of benzoyl azide.[12] It signals the existence of at least two reactive intermediates. The first undergoes the Curtius rearrangement to give the isocyanate, the second either is trapped by cyclohexene to give aziridine **3** or reacts with cyclohexane to give **1**. The trappable intermediate is routinely identified as the nitrene.[1] In the present case, this assignment is additionally supported by the observation that cyclohexene does not quench the fluorescence of BNA. The untrappable intermediate may be an excited state of the azide or an upper singlet state of the nitrene.[7] Irradiation of BNA in a frozen glassy solution of cyclohexene (8 M) in methylcyclohexane at 77 K similarly gives BNI and aziridine **3**. This obervation confirms nitrene formation under the low-temperature conditions.

It is generally recognized that "insertion" products such as **1** are characteristic of reactions originating with singlet nitrenes.[11] However, the most certain traditional test of nitrene multiplicity is based on the Skell–Woodworth hypothesis developed for carbenes.[21] For example, (ethoxycarbonyl)nitrene, which is certified by ESR spectroscopy as having a triplet ground state, gives both the *cis*- and *trans*-aziridines from reaction with *cis*-4-methyl-2-pentene.[1,11] In contrast, nitrogen- and sulfur-substituted nitrenes (R_2NN: and RSN:), which are believed to have singlet ground states, add to olefins with retention of stereochemistry.[22] Irradiation of BNA in cyclohexane solutions containing either *cis*- or *trans*-4-methyl-2-pentene gives the expected

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[20] The azide was dissolved in liquid CO_2 and then frozen at 77 K. Great care must be taken in this procedure to prevent rupture of the sealed ESR tubes during the dissolution.

[21] Woodworth, R. C.; Skell, P. S. *J. Am. Chem. Soc.* **1959**, *81*, 3383.

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Table II. Relative Rates of Reaction of BNN with Trapping Reagents

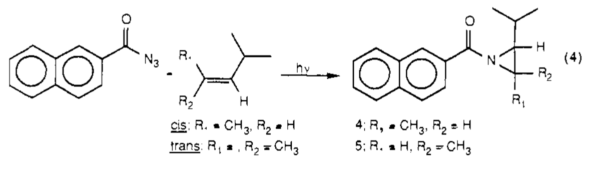
excitation	trap	rel rate
direct	cyclohexane	1.00
direct	*trans*-4-methyl-2-pentene	60
direct	cyclohexene	170
direct	α-methylstyrene	250
direct	*cis*-4-methyl-2-pentene	500
direct	ethanol	1000
sensitized	*trans*-4-methyl-2-pentene	75
sensitized	*cis*-4-methyl-2-pentene	450

Table III. Triplet-Sensitized Irradiation of BNA in Cyclohexane Containing Nitrene Trapping Reagents

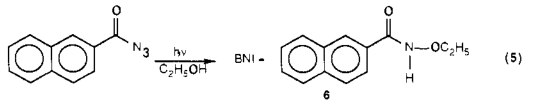
[BNA], M	product yields (absolute %) BNI	amide 1	aziridine 4	aziridine 5	β-naphthamide (2)
	No Trapping Reagent				
4.4×10^{-4}	5	63			25
	0.66 M *cis*-4-Methyl-2-pentene Trap				
3.3×10^{-3}	2	3	90	ND	6
1.7×10^{-3}	trace	trace[a]	86	ND	8
8.5×10^{-4}	ND[b]	trace	82	ND	15
3.3×10^{-4}	ND	ND	71	ND	23
	0.66 M *trans*-4-Methyl-2-pentene Trap				
5.3×10^{-3}	5	6	ND	30	44
1.6×10^{-3}	trace	5	ND	34	66
5.7×10^{-4}	ND	trace	ND	9	74
5.4×10^{-4}	ND	ND	ND	6	86

[a] Trace means that a peak with the proper retention volume was observed by HPLC, but represents a yield of less than 1%. [b] ND means no peak with the proper retention volume is detected.

aziridines (**4** and **5**) with complete (>98%, the experimental limit) retention of olefin stereochemistry, (Table I and eq 4).



Stereospecific aziridine formation by itself may be taken as evidence that the reacting nitrene state is a singlet, but it offers very little guidance about the multiplicity of the ground-state nitrene. For example, the singlet nitrene may be so reactive that it combines with the olefin before intersystem crossing to the lower energy triplet occurs. To reduce the likelihood that this phenomenon is complicating our results, the stereochemistry of aziridine formation was measured at low (0.01 M) olefin concentration. Under these conditions the major nitrene-derived product is amide **1**, but aziridine formation remains stereospecific (Table I). This result gains added significance from competition reactions (Table II) which show that formation of hydroxamate **6** from ethyl alcohol (eq 5) is the fastest reaction of the nitrene we found. In comparison, insertion into cyclohexane occurs ca. 1000 times more slowly.



A second, more certain way to test for reaction from the singlet nitrene before it intersystem crosses is by triplet sensitization of the azide. We chose 2-isopropylthioxanthone (ITX) as the sensitizer. The triplet energy of ITX (65 kcal/mol)[23] is above that of BNA, and laser spectroscopy confirms a diffusion-limited quenching rate. Irradiation of a cyclohexane solution of BNA containing ITX with light >385 nm (ITX absorbs >95% of the light) gives insertion product **1** (63%), amide **2** (25%), and BNI (5%) (Table III). The yield of isocyanate is of special significance since it is formed only on direct irradiation of BNA and thus provides an internal confirmation of triplet sensitization. The quantum efficiency for reaction of BNA by triplet sensitization is <10% of the direct irradiation value. Thus, light absorbed directly by the azide much more effectively initiates loss of N_2. The reduced yield of BNI in the triplet-sensitized experiment shows that no more than 10% of the BNA is reacting by the direct route and that 90% of the products are formed by reactions that start with the triplet azide. This result is confirmed by experiments run in the presence of isoprene, which, as a quencher of ITX^{3*}, appropriately slows the sensitization reaction.

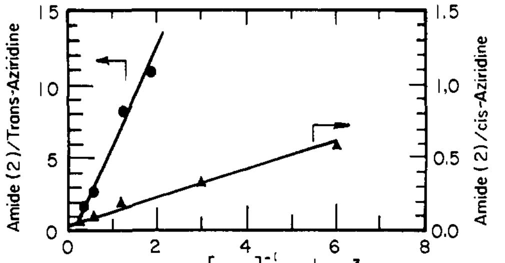
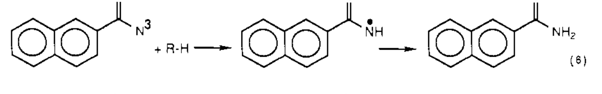
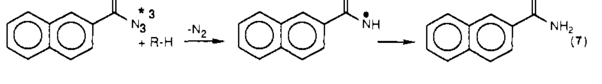


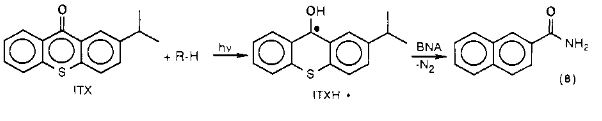
Figure 4. Plots of amide **2** to aziridine yields against the reciprocal of BNA concentration for triplet sensitization with ITX. The left-hand axis is for 0.66 M *trans*-4-methyl-2-pentene. The right-hand axis is for 0.66 M *cis*-4-methyl-2-pentene.

Triplet sensitization of BNA by ITX in cyclohexane solutions containing *cis*- and *trans*-4-methyl-2-pentene (Table III) gives a small amount of BNI by unavoidable direct irradiation, solvent insertion product **1**, amide **2**, and the expected aziridines **4** and **5**. The relative yields of these products vary sensibly in response to changes in concentration (see below), and the aziridines are formed with complete retention of the olefin stereochemistry under all conditions examined. Additionally, competition experiments show that the nitrene trapped by the pentenes in the triplet-sensitized experiment exhibits the same selectivity for the *cis*- and *trans*-pentene isomers as is observed in the direct irradiation of BNA (Table II).

Inspection of Table III reveals that the triplet-sensitized reactions of BNA can give a high yield of β-naphthamide. This is an important observation since a similar finding for benzoylnitrene was used to support postulation of a triplet ground state in this case.[12] It is critical to the interpretation of the sensitization experiments to identify the route for formation of the naphthamide. We considered three candidate mechanisms for this process. In the first, triplet nitrene abstracts hydrogen from the olefin to form an amidyl radical that ultimately gives the amide (eq 6). The second route starts with hydrogen abstraction by the triplet azide; loss of N_2 gives the amidyl radical, which again forms the amide (eq 7). The final mechanism considered begins with hydrogen abstraction by triplet ITX to give the ketyl radical (ITXH•), which serves as a hydrogen donor to BNA; following loss of N_2 gives the amidyl radical, which goes on to the amide (eq 8). This latter route has been shown to be the mechanism for benzamide formation in the of benzophenone-sensitized reactions of benzoyl azide.[24]







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The routes for formation of naphthamide **2** shown in eq 6 and 7 may be readily distinguished from the path outlined in eq 8. If either triplet nitrene or triplet azide is the precursor of the β-naphthamide, then increasing the efficiency of energy transfer by increasing the concentration of the azide will give a greater yield of amide. On the other hand, if triplet ITX is the precursor to amide, then increasing the energy-transfer efficiency will reduce the yield of β-naphthamide. The results are shown in Figure 4 in the form of plots of naphthamide to aziridine yields against the reciprocal of BNA concentration at fixed olefin concentration for the *cis*- and *trans*-pentenes. It is clear that the yield of naphthamide decreases as the concentration of BNA is raised and energy transfer becomes more efficient. Moreover, at extrapolated infinite BNA concentration, where energy transfer should be 100% efficient, the experiment shows a predicted yield for β-naphthamide of approximately zero. Additional support for the mechanism outlined in eq 8 comes from confirmation by laser spectroscopy that ITX^{*3} reacts with the pentenes to form the ketyl radical, and $ITXH^{\bullet}$ was observed to react with BNA with a rate constant of $1.3 \times 10^8\ M^{-1}\ s^{-1}$.

The significant points from the triplet sensitization experiments are that the products characteristic of a singlet nitrene originate from a triplet precursor and that there is no evidence for reactions involving the triplet nitrene. These results help to exclude the possibility that the chemical behavior observed in the direct irradiation of BNA is a consequence of reaction from the singlet nitrene before it intersystem crosses, but they still do not eliminate the possibility that the ground state of the nitrene is a triplet. It could be that the reactive singlet state is formed reversibly from a nearby, lower energy, unreactive reservoir of triplet states.

An "unreactive" triplet ground state would be revealed if it could be coaxed to react in some characteristic way. For example, triplet (ethoxycarbonyl)nitrene is known to react with α-methylstyrene very rapidly to give a distinctive amide product.[11] But, we find that photolysis of BNA in cyclohexane containing α-methylstyrene gives only one nitrene-derived product, the expected aziridine. Moreover, when this experiment is carried out with (*E*)-β-deuterio-α-methylstyrene, the aziridine that results is formed with complete retention of olefin configuration. This finding is particularly significant since the two aziridine isomers in this case differ only in the position of deuterium substitution, and the 1,3-diradical that would be formed by addition of the triplet nitrene to the olefin is especially stabilized.

Similarly, it is well-known that triplet intermediates generally react rapidly with O_2.[25,26] Nitrenes may prove to be an exception to this rule, but triplet (*p*-nitrophenyl)nitrene[27], for example, is scavenged effectively in O_2 saturated solutions. In contrast, O_2 saturation before irradiation has no effect on any of the reactions of BNA we have examined.

Finally, dimerization of triplet nitrenes to form azo compounds occurs with a rate limited only by spin statistics (i.e., ca. one-ninth diffusion control).[28] As a consequence, irradiation of azides with high-power pulsed lasers gives a high instantaneous triplet nitrene concentration, which leads to an increased yield of the nitrene dimers. However, we find that irradiation of BNA in cyclohexane with a 1-MW nitrogen laser gives precisely the same products as does the low-power photolysis in a Rayonet photoreactor (Table I). In particular, no dinaphthoyldiazine dimers of BNN could be detected under any reaction conditions.

Discussion

The central issue of this investigation is identification of the spin multiplicity for the ground state of BNN. We employed spectroscopic and chemical probes in the attempt to settle this question. The results lead to two possible conclusions. First, the ground state of this nitrene is a singlet. Or second, BNN has a triplet ground state whose properties are unlike those of other nitrenes, and the singlet of BNN is only barely above the ground triplet state. We will consider the second hypothesis first.

It is clear that only the singlet state of BNN is detected in all of the trapping experiments reported above. With this constraint, one of two possible sets of conditions must be met in order for the ground state of BNN to be a triplet. These are (1) either the triplet is never formed because the singlet nitrene reacts so rapidly, or (2) the triplet is formed, but its sole reaction is intersystem crossing to the higher energy, reactive singlet state.

The hypothesis that the nitrene is consumed before the triplet is formed requires an unreasonably long-lived upper singlet state. The relative rates of reaction of BNN with various traps revealed in the competition studies (Table II) show that ethanol reacts with the nitrene ca. 1000 times faster than does cyclohexane. The fastest any reagent can trap BNN is the diffusion-limited rate ($k_{\text{diff}} \sim 1 \times 10^{10}\ M^{-1}\ s^{-1}$). Thus, the greatest possible rate constant for reaction of the singlet nitrene with cyclohexane (k_s) is ca. $10^7\ M^{-1}\ s^{-1}$. Since only singlet nitrene derived products are detected (>95%) in this experiment, these considerations allow estimation of a maximum value for the rate constant of intersystem crossing from the singlet to the hypothetical ground-state triplet nitrene (k_{st}). According to calculation from eq 9, k_{st} must be less than

$$k_{st} \leq \left[\frac{\text{triplet product}}{\text{singlet product}}\right] k_s = 5 \times 10^6\ s^{-1} \tag{9}$$

$5 \times 10^6\ s^{-1}$, which corresponds to a lifetime of more than 200 ns for the upper singlet state in the absence of a trapping reagent. This is an unreasonably long lifetime, especially when compared with the lifetimes of related carbenes, whose upper singlet states have lifetimes ca. 1000 times less than this limit.[29]

The results of the triplet sensitization experiments exclude with certainty the possibility that direct irradiation of BNA gives products that arise from the singlet nitrene before the triplet is formed. In these experiments all nitrene-derived products are characteristic of singlet BNN. However, the singlet nitrene must have a triplet precursor. It is unreasonable and unprecedented to propose that its immediate precursor is the triplet azide. This route would require simultaneous spin inversion and nitrogen loss. The only conceivable triplet precursor to singlet BNN is the triplet nitrene. Formation of the singlet in this way requires it to be accessible from the triplet. This will certainly be the case if the singlet is the ground state. If, on the other hand, triplet BNN is the ground state, then the rate of intersystem crossing from the triplet to the singlet (k_{ts}) must be much greater than the rate of all reactions that consume the triplet nitrene. This, in essence, is the second condition mentioned above that will permit a triplet ground state for BNN to be consistent with the data. This condition can only be met if the upper singlet state can be populated thermally from the ground state and if no reactions exist that consume the triplet nitrene.

Nitrenes that have been previously studied are consumed readily by reactions from their triplet states.[1] We attempted to force the reaction of triplet BNN in three independent ways. The first relies on the Skell hypothesis. If the triplet reacts with an olefin to form an aziridine, then loss of stereochemistry is the expected outcome. The most sensitive test of this sort we could imagine, deuteriated α-methylstyrene, shows no detectable contribution from triplet BNN. Similarly, the inability of O_2 to inhibit or divert even the relatively slow reaction of BNN with cyclohexane signals the absence of a contribution from the triplet nitrene. And lastly, the inability of BNN to form dimers under high-power irradiation is inconsistent with a role from the triplet nitrene. In short, there is no evidence for the presence of triplet BNN under conditions where other triplet nitrenes are readily revealed by their reactions.

The data require that the energy of singlet BNN be very close to or below the energy of triplet BNN. The data are most consistent with a singlet ground state for BNN. If the triplet is the

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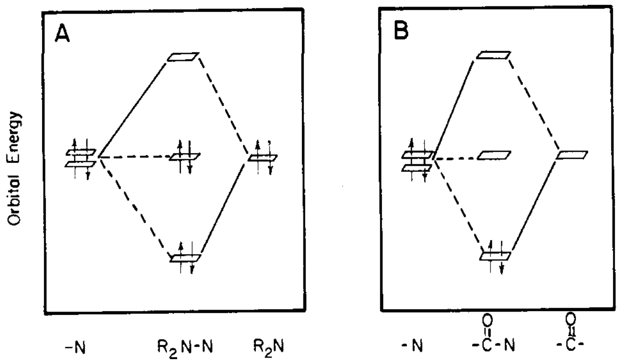

Figure 5. Qualitative molecular orbital perturbation diagram showing the effect of (A) mixing a high-lying occupied orbital with a nitrene and (B) mixing a low-lying unoccupied orbital with a nitrene.

ground state, then it must be uniquely unreactive and simultaneously uniquely undetectable by ESR spectroscopy. These two requirements seem mutually exclusive. In the absence of the development of evidence to the contrary, it seems prudent to favor a singlet ground state for BNN.

There is good reason to expect that ΔG_{st} for acylnitrenes should be smaller than it is for imidogen or arylnitrenes. This is easily illustrated by a qualitative perturbation MO approach.[30] Recall first that the frontier orbitals of an unperturbed (cylindrical symmetry) nitrene are degenerate 2p orbitals.[3,6] In this case ΔG_{st} is at its maximum value, which is set by the increased repulsion of two electrons in a single orbital.

The degeneracy of the nitrene frontier orbitals can be broken by substituents. For example, some nitrogen-substituted nitrenes (1,1-diazines) are stable, isolable compounds with demonstrable singlet ground states.[31] This can be envisioned as a consequence of the perturbation of the LUMO of the nitrene by the nonbonding orbital (HOMO) of the donor nitrogen substituent (Figure 5A). In the perturbed nitrene, ΔG_{st} is set by the electron–electron repulsion energy minus the energy difference between the HOMO and LUMO. If the perturbation is large, this difference can be negative and the singlet becomes the ground state. Precisely analogous arguments can be made for perturbation of a nitrene by an electron-withdrawing carbonyl group. In this case, however, it is likely to be the π^* LUMO of the substituent that perturbs the nitrene to break the degeneracy (Figure 5B). If the perturbation is large enough, the ground state of the acylnitrene will be a singlet.

One of the attractive aspects of the perturbation model is that it can account for the different properties of (ethoxycarbonyl)nitrene and BNN. Perturbation of the nitrene by the oxycarbonyl group will be less than that of the carbonyl group because the donor oxygen pushes the LUMO of the former to higher energy. A smaller perturbation gives a relatively larger ΔG_{st} and thus the ground state of (ethoxycarbonyl)nitrene remains a triplet. We are planning additional tests of the predictive value of this model.

Experimental Section

General. Proton magnetic resonance spectra were recorded on a Varian Associates XL-200 or a General Electric QE-300 spectrometer. Infrared spectra were measured on an IBM Instruments Inc. IR/32 FTIR spectrometer. High-resolution mass spectra were obtained with a Finnigan MAT 731 mass spectrometer. Electron paramagnetic resonance spectra at 77 K were recorded on a Varian Associates E-4 spectrometer, at 8 K on a Bruker ER-220D spectrometer, and at 4 K on a Bruker ER-200D spectrometer. High-preformance liquid chromatography (reverse phase, water/acetonitrile, C-18 column) was performed on an IBM Instruments Inc. LC/9560 ternary gradient liquid chromatograph with a perkin-Elmer LC-75 detector. Melting points (uncorrected) were determined with a Büchi apparatus. Steady-state UV-vis absorption spectra were measured on a Perkin-Elmer Model 552 spectrophotometer. The nanosecond spectrometer has been previously described.[32] Direct irradiation of BNA for product studies was performed in a Rayonet photoreactor equipped with 350-nm lamps at ambient temperature (350-nm irradiation). Triplet-sensitized irradiation with ITX was carried out at wavelengths >385 nm with a 450-W Hanovia medium-pressure mercury lamp filtered through a solution of ferric chloride.

Materials. Cyclohexane (Baker Analyzed Reagent) and benzene (Burdick and Jackson, Distilled-in-Glass) were washed with sulfuric acid until the washes were colorless and then with water until the washes were neutral, and the washes were dried with calcium hydride. The benzene was distilled under nitrogen from sodium paraffin, and the cyclohexane was distilled under nitrogen from calcium hydride. Cyclohexene (Aldrich) was purified by passing it through basic alumina and then distillation under nitrogen from LAH. Methyltetrahydrofuran (Aldrich) was purified by distillation under nitrogen from sodium paraffin. α-Methylstyrene (Aldrich) was distilled before use. Methylcyclohexane (spectrograde, Kodak), *cis*- and *trans*-4-methyl-2-pentene (Wiley), and Flurolube Oil LG-160 (Fisher Scientific) were used without further purification. 2-Isopropylthioxanthone (a gift from Mead Corp.) was purified by recrystallization from methanol.

BNA was prepared from β-naphthoic acid and diphenylphosphoryl azide by the procedure of Kitagawa[33] and recrystallized from ether: 90%, mp 75–76 °C, (lit.[33] mp 76–77 °C). BNI was prepared by Vittenet's procedure[34] from β-naphthylamine and phosgene in 88% yield. Sublimation gave white crystals, mp 54–55 °C (lit.[34] mp 55–56 °C). Analysis of BNI in photolysis mixtures was facilitated by its quantitative conversion to β-naphthylethyl carbamate with ethanol; mp 70–71 °C (lit.[34] mp 69–70 °C). Amides **1** and **2** were prepared by Schotten–Baumann syntheses from the acid chloride and cyclohexylamine to give **2**: 79% recrystallized from CCl_4, mp 181–182 °C (lit.[35] mp 183–184 °C). Amide **1** was prepared from aqueous ammonia: 48%, mp 170–171 °C (lit.[36] mp 171–172 °C).

Attempted Detection of BNN by ESR Spectroscopy. (A) Direct Irradiation. Three samples were prepared: the first contained BNA (1×10^{-2} M) in methylcyclohexane; the second, BNA in 2-methyltetrahydrofuran (MTHF); and the third, 2 mg of BNA in 2 g of Fluorolube. The samples were frozen at 77 K in a long-necked quartz Dewar. ESR spectra (X-band, 9.11 MHz) were recorded (0–9000 G) after 30 s, 90 s, 3 min, 5 min, 10 min, 15 min, and 30 min of irradiation (254 or 350 nm in a Rayonet photoreactor). No signals attributable to BNN were detected. However, a signal at 6850 G (β-naphthylnitrene) was observed in samples irradiated for more than 10 min.

Suspensions of BNA in Fluorolube frozen at 77 K were irradiated (30 s to 30 min, 254 nm) and quickly transferred to the cavity of the Bruker ESR spectrometer (X-band, 9.35 MHz), which had been cooled to 8 K. The spectrum was scanned from 0 to 12 000 G. Irradiation for more than 5 min gave a signal for β-naphthylnitrene, but no signals attributable to BNN could be detected. Irradiation of ethoxycarbonyl azide or β-naphthyl azide under the conditions described above gave the expected ESR signals after 3 min of irradiation. These signals were 8 times more intense in the 8 K experiment than at 77 K.

A solution of BNA (1×10^{-2} M) in MTHF in a standard ESR tube was cooled to 8 K in the cavity of a Bruker ESR 220D spectrometer and irradiated with a mercury lamp through the grating of the cavity. The spectrum was recorded after 3, 30, and 40 min of irradiation. No signals attributable to BNN were observed, but β-naphthylnitrene was detected after 30 min of irradiation.

Gaseous CO_2 was condensed on a solid 2-mg sample of BNA in a thick-walled (4-mm o.d., 2.8-mm i.d.) quartz tube immersed in liquid nitrogen. The tube was sealed and transferred to a dry ice/2-propanol bath (−80 °C). At this temperature the CO_2 liquefied and the BNA dissolved. The solution was frozen at 77 K in the ESR Dewar, and the spectra were recorded (Varian, X-band, 9.11 MHz) after 30 s, 90 s, 3 min, 5 min, and 15 min of irradiation at 254 nm. No signals characteristic of BNN could be detected. *Cautionary Note!* The pressure above the liquid CO_2 at −80 °C is relatively high. Because of occasional tube explosion, all preparations should be done behind a blast shield.

(B) Triplet Sensitization. Two samples were prepared: the first contained BNA (10^{-2} M) in a (50/50 (v/v)) solution of acetophenone and benzaldehyde and the second contained BNA (10^{-3} M) in methylcyclohexane and ITX (0.1 M). Irradiation times up to 45 min did not produce signals attributable to triplet species.

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Direct Irradiation of BNA in Cyclohexane. Solutions of BNA (7.5×10^{-4} M) in cyclohexane were purged with N_2 or O_2 for 20 min and then irradiated at 350 nm (Rayonet) for 12 min. A 50-μL portion of ethanol was added to each sample, and the solutions were analyzed by HPLC. Both samples gave identical products: carbamate (from BNI) (54%), and amide **1** (44%). No additional products could be detected in the oxygen-saturated sample.

Triplet-Sensitized (ITX) Irradiation of BNA in Cyclohexane. A N_2-purged solution of BNA (4.4×10^{-4} M) in cyclohexane containing ITX (1.6×10^{-3} M) was prepared in a Pyrex cell equipped with a magnetic stir bar and a Teflon stopcock. The sample was irradiated (>385 nm) for 105 min, and then 50 μL of ethanol was added. HPLC analysis showed amide **1** (63%), β-naphthamide **2** (25%), and carbamate (from BNI) (5%).

Direct Irradiation of BNA in Solutions Containing Cyclohexene. A solution of BNA (2.3×10^{-3} M) in cyclohexane containing cyclohexene (1 M) was purged with N_2 and irradiated at 350 nm (Rayonet) for 12 min. After addition of ethanol, the products were analyzed by HPLC: carbamate (from BNI) (52%) and aziridine **3** (42%) were detected. Authentic **3** was prepared from β-naphthoyl chloride and cyclohexenimine in 21% yield after recrystallization from cyclohexane/benzene (6/1 (v/v)): white crystals, mp 88–89 °C; IR ($CHCl_3$) 1672, 1285 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.3 (m, 8 H), 2.92 (d, 2 H), 7.5–8.5 (m, 8 H); mass spectrum (high resolution), calcd for $C_{17}H_{17}NO$, 251.1310; found, 251.1314.

Direct Irradiation of BNA with *cis*- and *trans*-4-Methyl-2-pentene. A stirred, N_2-saturated solution of BNA (50 mg) in 25 mL of cyclohexane containing 0.67 M of the *trans*-pentene was irradiated at 350 nm (Rayonet) for 2 h. After addition of 0.5 mL of ethanol, the solvent and unreacted olefin were removed by evaporation, and the residue was analyzed by ^1H NMR spectroscopy. The products were ethyl carbamate (from BNI) (53%), *trans*-aziridine **5** (36%), and amide **1** (9%). Adduct **5** was isolated by chromatography on silica gel (Chromatotron), eluting with ether/petroleum ether (1/7 (v/v)) in 22% yield as a viscous oil: ^1H NMR ($CDCl_3$) δ 1.07 (m, 9 H), δ 1.66 (m, 1 H), δ 2.03 (d of d, 1 H), δ 2.80 (m, 1 H), δ 7.5–8.5 (m, 7 H); IR ($CHCl_3$) 1661 cm^{-1}; mass spectrum (high resolution), calcd for $C_{17}H_{19}NO$, 253.14655; found, 253.14689.

The experiment was repeated with *cis*-4-methyl-2-pentene. The ^1H NMR spectrum in this case showed ethyl carbamate (54%), *cis*-aziridine **4** (43%), and amide **1** (2%). The *cis*-aziridine was isolated as above, and after recrystallization from ether gave 18 mg (28%): mp 89–90 °C; IR ($CHCl_3$) 1669 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06, 1.23 (two d, 6 H), 1.53 (d, 3 H), 1.65 (m, 1 H), 2.49 (m, 2 H), 7.5–8.5 (m, 7 H). Anal. Calcd for $C_{17}H_{19}NO$: C, 80.59; H, 7.56; N, 5.53. Found: C, 80.89; H, 7.59; N, 5.50.

Triplet-Sensitized (ITX) Irradiation of BNA with *cis*- and *trans*-4-Methyl-2-pentene. Nitrogen-purged, stirred cyclohexane solutions of BNA (5×10^{-3} to 3×10^{-4} M; see Table III) containing either the *trans*- or *cis*-pentene (0.66 M) and ITX (1.36×10^{-3} M) were irradiated for 4 h (>385 nm) in Pyrex cuvettes. The precipitated β-naphthamide that formed during the irradiation dissolved when 50 μL of ethanol was added to convert BNI to the carbamate. The solutions were analyzed by HPLC; the results are summarized in Table III and on Figure 4.

Direct Irradiation of BNA with Ethanol. A N_2-purged cyclohexane solution of BNA (2.35×10^{-3} M) containing ethanol (1 M) was irradiated at 350 nm (Rayonet) for 15 min. The products, analyzed by HPLC, were the ethyl carbamate (from BNI) (54%), hydroxamate **6** (42%), and amide **1** (3%). Hydroxamate **6** was isolated from a preparative-scale experiment (BNA, 100 mg in 35 mL of ethanol irradiated at 350 nm for 90 min) by chromatography on silica gel (Chromatotron). Recrystallization from cyclohexane/$CHCl_3$ yields 10 mg of white crystals (26% based on BNA consumed): mp 124–125 °C; IR ($CHCl_3$) 3405, 1686 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, 3 H), 4.3 (q, 2 H), 7.5–8.5 (m, 7 H). Anal. Calcd for $C_{12}H_{12}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.36; H, 6.13; N, 6.49.

Direct Irradiation of BNA in α-Methylstyrene. A solution of BNA (5.1×10^{-3} M) in cyclohexane containing the styrene (0.15 M) was purged with nitrogen and irradiated for 20 min at 350 nm. The products, determined by ^1H NMR spectroscopy were carbamate from BNI (54%) and the expected aziridine (40%). The experiment was repeated with (*E*)-deuterio-α-methylstyrene (0.15 M) to determine the stereochemistry of addition. The products were carbamate (55%) and the deuteriated aziridine (40%); only one isomer of the aziridine could be detected. ^1H NMR ($CDCl_3$) δ 1.55 (s, 3 H), 2.56 (s, 1 H), 2.86 (s, 1 H), 7.2–8.25 (m, ArH). The NMR spectrum of the aziridine from the deuteriated styrene was identical except that the absorption in the aziridine at δ 2.86 was reduced to the level of residual hydrogen in the *E* position of the styrene. The aziridine could not be separated from the ethyl carbamate without decomposition. It was converted to *N*-(2-methoxy-2-phenylpropyl)-β-naphthamide for characterization: ^1H NMR ($CDCl_3$) δ 1.66 (s, 3 H), 3.10 (s, 3 H), 3.61 (d of d, 1 H), 3.91 (d of d, 1 H), 6.64 (bs, 1 H), 7.2–8.2 (m, 12 H); mass spectrum (high resolution), Calcd for $C_{21}H_{21}NO_2$, 319.15719; found, 319.15712.

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Do the Organocopper Conjugate Additions to α,β-Unsaturated Esters Proceed in a 1,4- or 1,2-Fashion?

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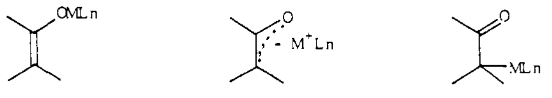
Abstract: The organocopper conjugate addition to methyl tiglate (**4**) and methyl angelate (**6**) followed by protonolysis at −78 °C produced the syn (**8**) and anti (**9**) adducts in the same isomer ratio (73:27). Further, the conjugate addition to **4** and **6** followed by treatment with acetone-d_6 at −78 °C gave the syn (**12**) and anti (**13**) adducts, again in the same isomer ratio (2:1). These results clearly indicate the intermediacy of the copper–oxygen-bonded enolate (**1a**) rather than α-cupriocarbonyl derivative (**3a**).

Conjugate addition reactions of organocopper reagents to α,β-unsaturated carbonyl compounds produce enolate anions, which are protonated or further reacted with electrophiles. This process is now a very important synthetic procedure in modern organic chemistry.[1] Mechanistically, important unanswered questions remain concerning the enolate structure.[2] Most of the literature adopts the copper–oxygen-bonded enolate **1a** (see Chart I) without any convincing evidence. On the other hand, the α-cupriocarbonyl

Chart I



1a; M = Cu
b: M = SnPh$_3$

2a; M = Cu

3a; M = Cu
b; M = SnPh$_3$

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