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Intermolecular triplet-sensitized photolysis of alkyl azides Trapping of triplet alkyl nitrenes

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Abstract

We report the first observation that the intermolecular triplet sensitization of alkyl azides leads to bimolecular reactivity, by forming triplet alkyl nitrenes. The intermolecular triplet-sensitized photolysis of 1-azidoadamantane with acetone, acetophenone and benzophenone leads to the formation of di-(adamantan-1-yl)-1,2-diazene as the major product via dimerization of triplet adamantan-1-yl nitrene. The triplet alkyl nitrene also abstracts a H-atom from the solvent to form adamantan-1-yl amine, adamantan-1-yl-benzyl amine and adamantan-1-yl benzylidene amine. The rates of the energy transfer from acetophenone and benzophenone to 1-azidodamantane are 1×10^8 and $5 \times 10^6\ M^{-1}\ s^{-1}$, respectively. Triplet-sensitized photolysis of benzyl azide with acetophenone gave methylene phenyl amine, dibenzyl amine and tribenzyl amine as the major products. Thus triplet benzyl nitrene abstracts a H-atom from the solvent to form dibenzyl amine and tribenzyl amine and rearranges to form methylene phenyl amine. The energy transfer rate between acetophenone and benzyl azide is diffusion controlled, or $2 \times 10^9\ M^{-1}\ s^{-1}$. Sensitized photolysis of benzyl azide with benzophenone yielded only benzylideneamine. Presumably, benzophenone abstracts a H-atom from benzyl azide and the resulting radical rearranges into benzylideneamine. The rate of the chemical quenching of benzophenone with benzyl azide is $5 \times 10^7\ M^{-1}\ s^{-1}$.

Keywords: Alkyl azides; Triplet-sensitized photolysis; Alkyl nitrenes

1. Introduction

The formation of aryl nitrenes from aryl azides has been studied extensively for the last several decades [1]. Since aryl nitrenes undergo bimolecular reactions they have been used for photoaffinity labeling bio-organic molecules and in several industrial processes such as microlithography. There is a distinct difference between the reactivities of aryl and alkyl azides. Alkyl azides rearrange and lose nitrogen to form imine derivatives when irradiated or thermally activated (Scheme 1). This rearrangement can be concerted from the excited state of the alkyl azide, or can proceed stepwise through alkyl nitrene intermediates. Since thermal decomposition and direct photolysis of alkyl azides rarely leads to products that can be assigned to trapped alkyl nitrene intermediates [2], the conclusion was reached that this rearrangement is concerted [3]. However, triplet methyl nitrene derivatives have been detected in the gas phase and in matrices at low temperature [4–9]. We have demonstrated that the photolysis of azido aryl ketones, which have intramolecular triplet sensitizers, leads to products that come from trapping triplet alkyl nitrene intermediates [10]. Thus, we were curious as to whether intermolecular triplet sensitization would also lead to formation of triplet alkyl nitrenes. If so, then a variety of triplet alkyl nitrenes would readily become available.

There are only a few examples of intermolecular triplet-sensitized photolysis of alkyl azides that unambiguously give rise to triplet energy transfer [11,12]. In these studies, although it was shown that sensitized photolysis leads to azide decomposition, the reaction products were not characterized. For example, Lewis and Saunders showed that the excited state of various ketones and aromatics can be quenched by alkyl azides [11], and in the absence of product studies suggested that it was possible that some of the reactivity was through singlet rather than triplet sensitization [12]. We decided to extend these investigations and determine the products formed upon triplet sensitization of alkyl azides **1** (see Scheme 2) and **2** (see Scheme 3) to determine if the products could be attributed to formation of triplet alkyl nitrenes. We also set out to measure the rate of energy transfer from the triplet sensitizer to the alkyl azides.

The direct photochemistry of azides **1** and **2** was studied extensively some time ago [3b,5,13]. Direct photolysis of azide **1** yields imine **3**, which is not a stable product [5,13].

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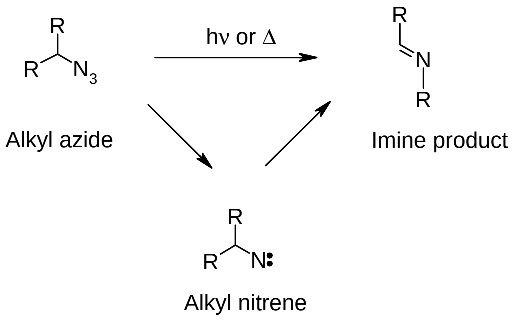
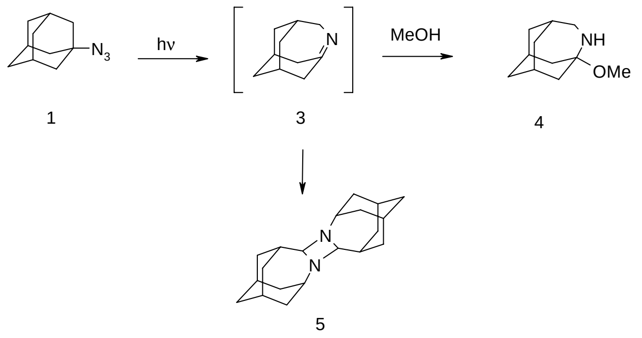
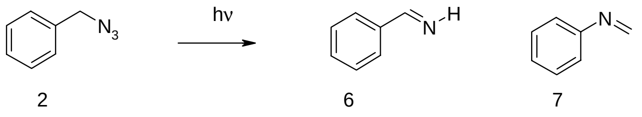


Scheme 1.



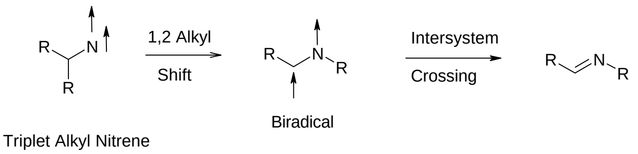
Scheme 2.



Scheme 3.

Imine **3** can be trapped with methanol to form **4**, whereas in the absence of trapping agents imine **3** dimerizes to form **5**. Similarly, direct irradiation of **2** yields imines **6** and **7** in a 3:1 ratio [3b].

Ellison et al. have shown that triplet methyl nitrene is 31 kcal/mol lower in energy than singlet methyl nitrene and thus triplet alkyl nitrenes must be the ground state [14]. Singlet nitrenes can rearrange to the imine products directly, whereas migration in triplet nitrenes leads to the formation of biradicals that have to undergo intersystem crossing in order to form the corresponding imine products (see Scheme 4). Thus, we anticipated that the triplet alkyl nitrene intermediates formed from triplet-sensitized photolysis of azides **1** and **2** would not lead to imine products but, rather, could be trapped in bimolecular reactions. Additionally, we did not expect triplet-sensitized photolysis of azide **2** to yield imine **6** since it must be formed through a 1,2-H shift which is not allowed in the triplet manifold.



Scheme 4.

Lewis and Saunders estimated the triplet energy of simple alkyl azides to be between 75 and 80 kcal/mol [11a]. Thus, we selected acetone and acetophenone as our triplet sensitizers, since their triplet energies are 77 and 74 kcal/mol, respectively [15]. We also decided to use benzophenone as a triplet sensitizer even though it has a triplet energy of 69 kcal/mol [15], in order to explore whether the triplet energy transfer would take place when there is an activation barrier of more than 6 kcal/mol.

2. Experimental

2.1. General procedures

Photolyses were done with a 450 W ACE glass mercury arc lamp. The lamp was housed in a borosilicate glass immersion well. We used a Pyrex filter for photolysis in acetones, whereas photolysis in all other solvents were done through a Schott colored glass filter (Model #GG 385, cut on wavelength 385 nm) from ORIEL Instruments. Toluene, acetone and methanol were dried and distilled before use. Hexadecane (Aldrich) was used as received as an internal standard in photolytic product studies.

2.2. Laser flash photolysis

Laser flash photolysis was done with a lambda physik excimer laser (308 nm, 17 ns). The system has been described in detail elsewhere [16].

2.3. Quenching experiments

Solutions of benzophenone and acetophenone in dichloromethane were prepared and transferred to several volumetric flasks. To each volumetric flask was added a specific amount of azide **1** or azide **2** and the flask filled to the mark with dichloromethane. The absorbance at 308 nm was 0.5 for these solutions. The transient spectra of triplet acetophenone and benzophenone have been described previously [17]. We measured the absorbance of the triplet state of acetophenone at 340 nm as a function of time. Upon adding alkyl azide **1** the lifetime of the triplet state of acetophenone became shorter. The rate of decay of the sensitizer was measured at least twice for each concentration of azide **1**. Plotting the rate of decay of the triplet excited state of the acetophenone versus the concentration of alkyl azide **1** yields a straight line. The slope of the line is the rate constant for the quenching of the excited state of acetophenone with alkyl azide **1**. The rate for quenching the excited state of acetophenone with alkyl azide **2** was measured similarly. The rate of quenching the triplet excited state of benzophenone with alkyl azides **1** and **2** was measured using the same strategy. However, the absorbance of the triplet excited state of benzophenone was followed at 520 nm.

2.4. *Starting material*

Adamantan-1-yl azide (**1**) and benzyl azide (**2**) are commercially available and were used as received.

2.5. *Characterization of photoproducts*

The formation of photoproducts adamantan-1-yl amine (**11**), adamantan-1-yl-benzyl amine (**12**), adamantan-1-yl-benzylidene-amine (**13**), dibenzylamine (**17**), tribenzyl amine (**18**), benzyl amine (**19**) and *N*-benzylidenebenzylamine (**20**) were verified by authentic samples on GC and GC/MS. These compounds are all commercially available.

Di-(adamantan-1-yl)-1,2-diazene (**10**), was synthesized following the procedure by Stetter and Smulders [18].

N-Brom-1-aminadamantan, was synthesized from 1-adamantanamine-hydrochloride (Aldrich) following the literature [18]. IR (KBr): 3124, 2934, 2904, 2848, 601 cm^{-1}.

Di-(adamantan-1-yl)-1,2-diazene (**10**), was prepared from *N*-brom-1-aminadamantan via the literature [18]. IR (neat): 2909, 2850, 2155, 1453, 1103, 813 cm^{-1}. MS (EI) m/z 299 ($M + 1$), 298 (M^+), 136, 135, 102.

2.6. *Photolysis of azide **1***

A solution of azide **1** (0.1 M), acetophenone (0.1 M) and hexadecane (0.02 M) in toluene was bubbled with argon and photolyzed for 4 h through a 385 nm filter. GC analysis of the reaction mixture at 1, 3, and 4 h showed formation of **5**, **10**, **12**, and **13**. GC analysis of the reaction mixture also indicated some minor photoreduction of acetophenone.

A solution of azide **1** (0.04 M), acetophenone (0.04 M), and hexadecane (0.001 M) in methanol was bubbled with argon and photolyzed for 60 min through a 385 nm filter. GC analysis of the reaction mixture at 5, 10, 15, 30, and 60 min showed two major products, **10** and **11**, and a small amount of **4**. The GC analysis demonstrated that some of the acetophenone had undergone the expected photoreduction.

A solution of azide **1** (0.01 M) and hexadecane (0.002 M) in acetone was bubbled with argon and photolyzed for 25 min through a Pyrex filter. GC analysis of the reaction mixture at 10, 15 and, 25 min showed that **5**, **10**, and **11** were formed.

A solution of azide **1** (0.1 M), benzophenone (0.1 M), and hexadecane (0.003 M) in toluene was bubbled with argon and photolyzed for 2 h through a 385 nm filter. GC analysis of the reaction mixture after 0.5, 1 and 2 h irradiation showed the presence of **5**, **10**, **11**, **12**, and **13**, and some photoreduction of benzophenone.

2.7. *Photolysis of azide **2***

A solution of azide **2** (0.015 M), acetophenone (0.041 M), and hexadecane (0.002 M) in toluene was bubbled with argon and photolyzed for 7 h total through a 385 nm filter. At 4, 5, and 7 h irradiation the reaction mixture was analyzed with GC, which showed formation of **7**, **17**, **18**, **19**, and **20** and that some of the acetophenone had undergone photoreduction as well.

A solution of azide **2** (0.01 M) and hexadecane (0.008) in acetone was bubbled with argon and photolyzed for 90 min. GC analysis of the reaction mixture after 20, 40, and 90 min of irradiation showed only formation of products **6** and **7**.

A solution of azide **2** (0.02 M), benzophenone (0.02 M), and hexadecane (0.005) in toluene was photolyzed for 7 h. GC analysis of the reaction mixture after 2, 4, and 7 h irradiation showed formation of only imine **6** and that some of the benzophenone had been photoreduced.

3. Results

3.1. *UV-Vis absorbance spectra of azides **1** and **2***

The UV-Vis absorbance spectra of 0.1 M azides **1** and **2** in hexane are shown in Fig. 1. For comparison we also show the UV-Vis absorbance spectra of 0.1 M acetone, acetophenone and benzophenone in hexane. By using a 385 nm, filter we can ensure that only the benzophenone and acetophenone absorb the light and not the azides. It is, however, not possible to use filters to separate the absorption by acetone and azides **1** and **2**, but in dilute solutions most of the light above 300 nm will be absorbed by acetone.

3.2. *Product formation*

Scheme 5 depicts the photoproducts formed by the sensitized photolysis of azide **1** and the product ratios are in Table 1. In Fig. 2 are displayed product ratios as a function of the conversion of azide **1**. Since the product ratio varied at higher conversion when azide **1** was photolyzed in methanol with acetophenone as a triplet sensitizer, we concentrated on product studies at low conversion. The photoproducts formed by the sensitized photolysis of azide **2** are shown in Scheme 6, and the product ratios are in Table 2. Fig. 3 displays the product ratio from azide **2** as a function of conversion of the starting material.

3.3. *Quenching rates*

We used laser flash photolysis to measure quenching rates of the excited states of acetophenone and benzophenone with azides **1** and **2**. We used dichloromethane as the solvent for the laser flash photolysis rather than toluene, methanol or acetone as in the product studies. Since, the triplet alkyl nitrene intermediates can abstract hydrogen atoms from toluene, methanol and acetone, these solvents are good for product studies. Whereas, product studies in

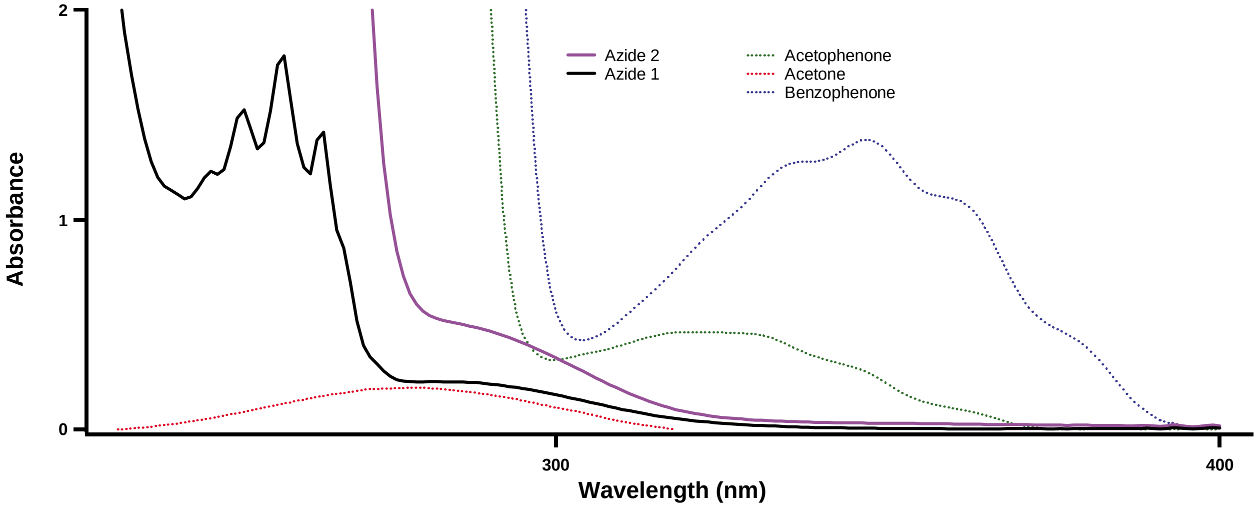
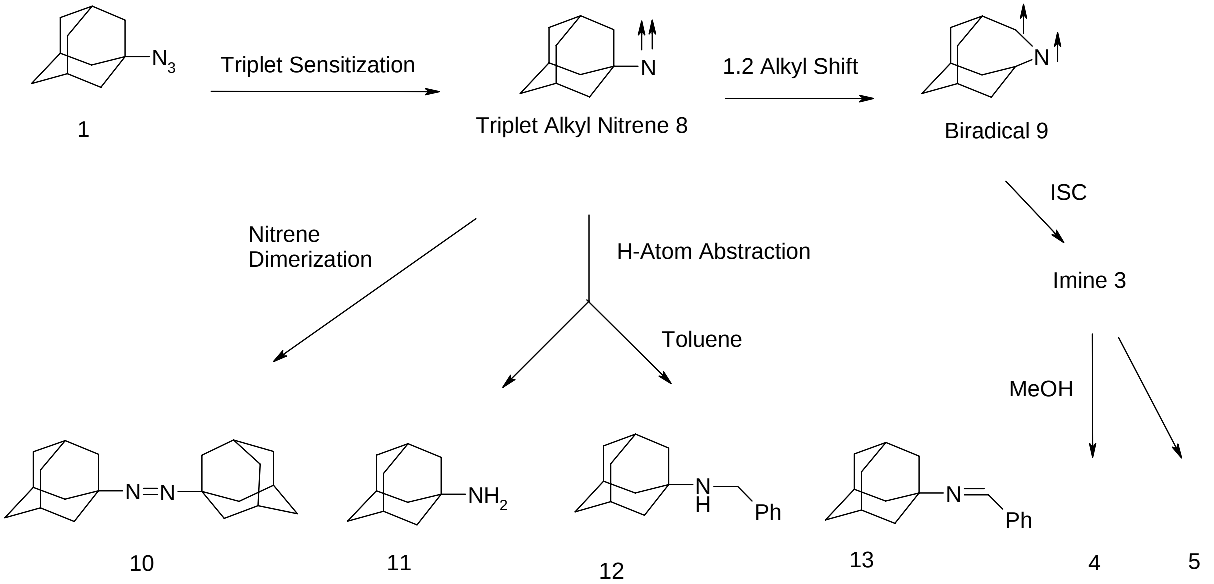


Fig. 1. UV spectra of azides **1** and **2** in *n*-hexane.



Scheme 5.

Table 1
Product ratios from the triplet-sensitized photolysis of azide **1**

Sensitizer	Filter	Solvent	**10**	**11**	**12**	**13**	**4**	**5**	Conversion (%)
Acetophenone	385 nm	Toluene	48		23	20		9	13
Acetophenone	385 nm	Methanol	49	44			7		43
Acetone	Pyrex	Acetone	76	6				18	23
Benzophenone	385 nm	Toluene	76	17	1	1		5	11

Table 2
Product ratios from the triplet-sensitized photolysis of azide **2**

Sensitizer	Filter	Solvent	**6**	**7**	**17**	**18**	**19**	**20**	Conversion (%)
Acetophenone	385 nm	Toluene		49	25	12	1	14	55
Acetone	Pyrex	Acetone	66	34					10[a]
Benzophenone	385 nm	Toluene	100						11[b]

[a] The product ratio are unaffected up to 10% conversion.

[b] Imine **6** is the only product observed up to 11% conversion.

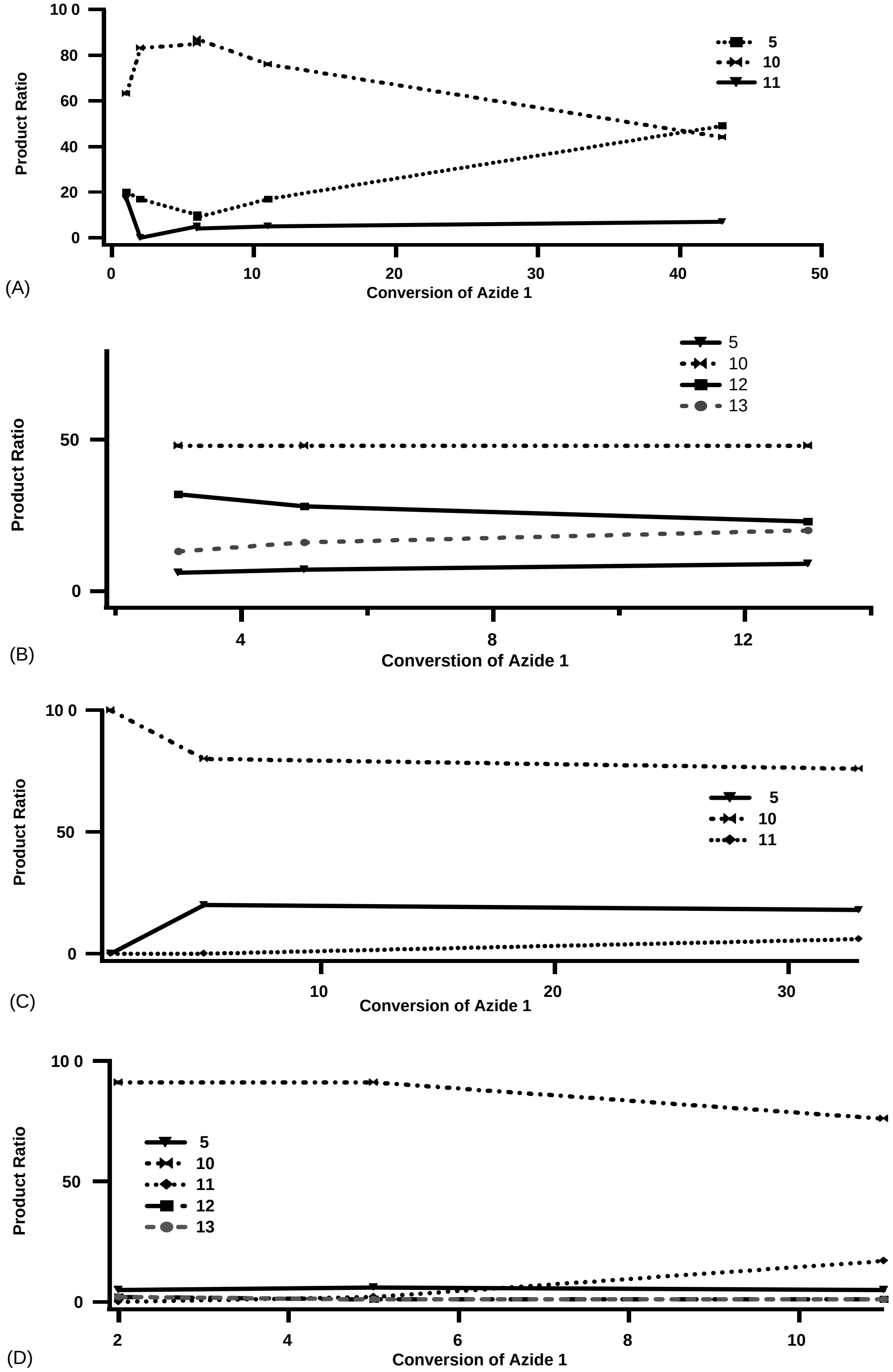
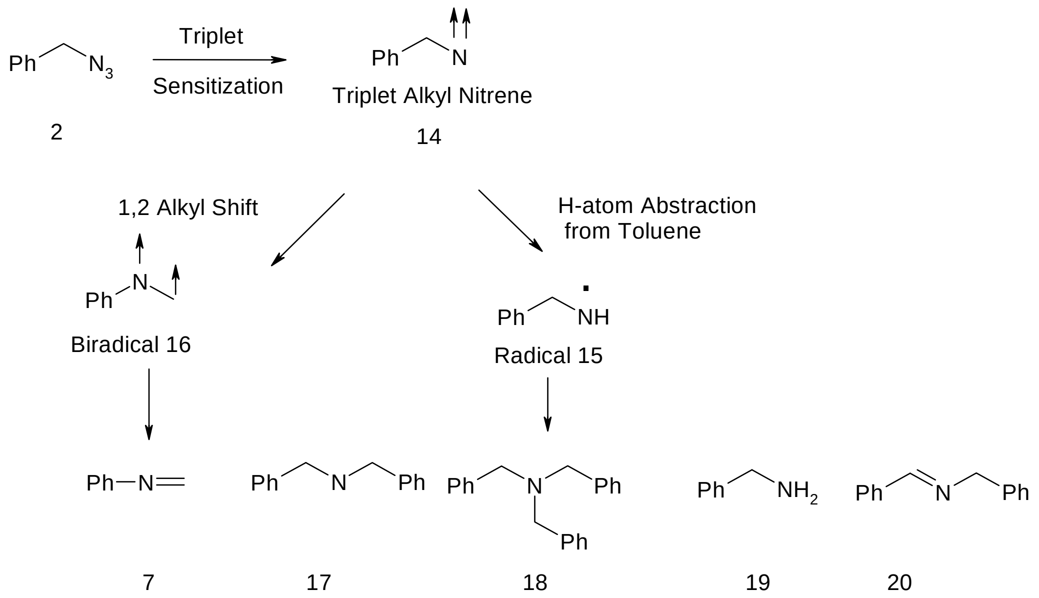


Fig. 2. Product ratio from triplet-sensitized photolysis of azide **1**: (A) acetophenone in methanol; (B) acetophenone in toluene; (C) acetone; and (D) benzophenone in toluene.



Scheme 6.

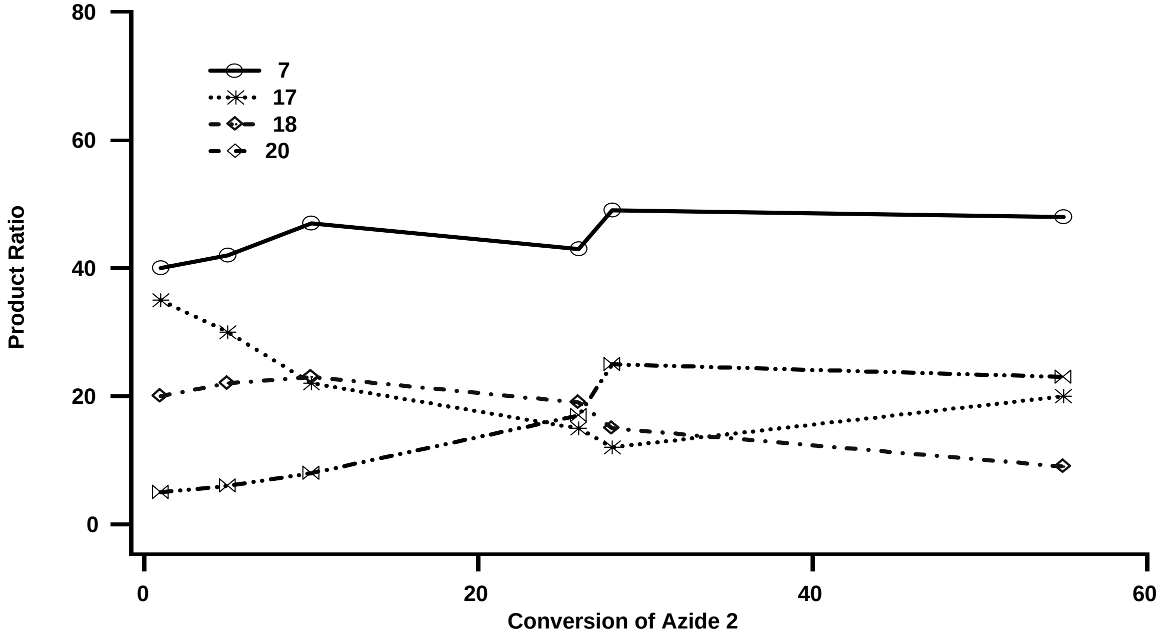


Fig. 3. Product ratio for triplet-sensitized photolysis of azide **2** with acetophenone.

dichloromethane are complicated by formation of polymers, since its H-atom can not be easily abstracted. In contrast dichloromethane is a good solvent for laser flash photolysis studies, since acetophenone and benzophenone do not abstract a H-atom from it to form the corresponding ketyl radical. The triplet excited state of benzophenone and its ketyl radical have similar UV absorbance which makes it complicated to resolve the decay of the triplet excited state of benzophenone. For comparison, we did the laser flash experiments of acetophenone in dichloromethane. It was not practical to do the same experiment with acetone. In Fig. 4 are plotted the rate of decay of the sensitizers versus the concentrations of azides **1** and **2**. The slopes of the lines obtained in Fig. 2 give the rate of quenching of the triplet excited state of acetophenone and benzophenone with azides **1** and **2** (see Table 3).

Table 3
Rate of quenching of the triplet excited states of acetophenone and benzophenone with azides **1** and **2**

Azide	Benzophenone ($M^{-1}\,s^{-1}$)	Acetophenone ($M^{-1}\,s^{-1}$)
1	5×10^{6}	1×10^{8}
2	5×10^{7}	2×10^{9}

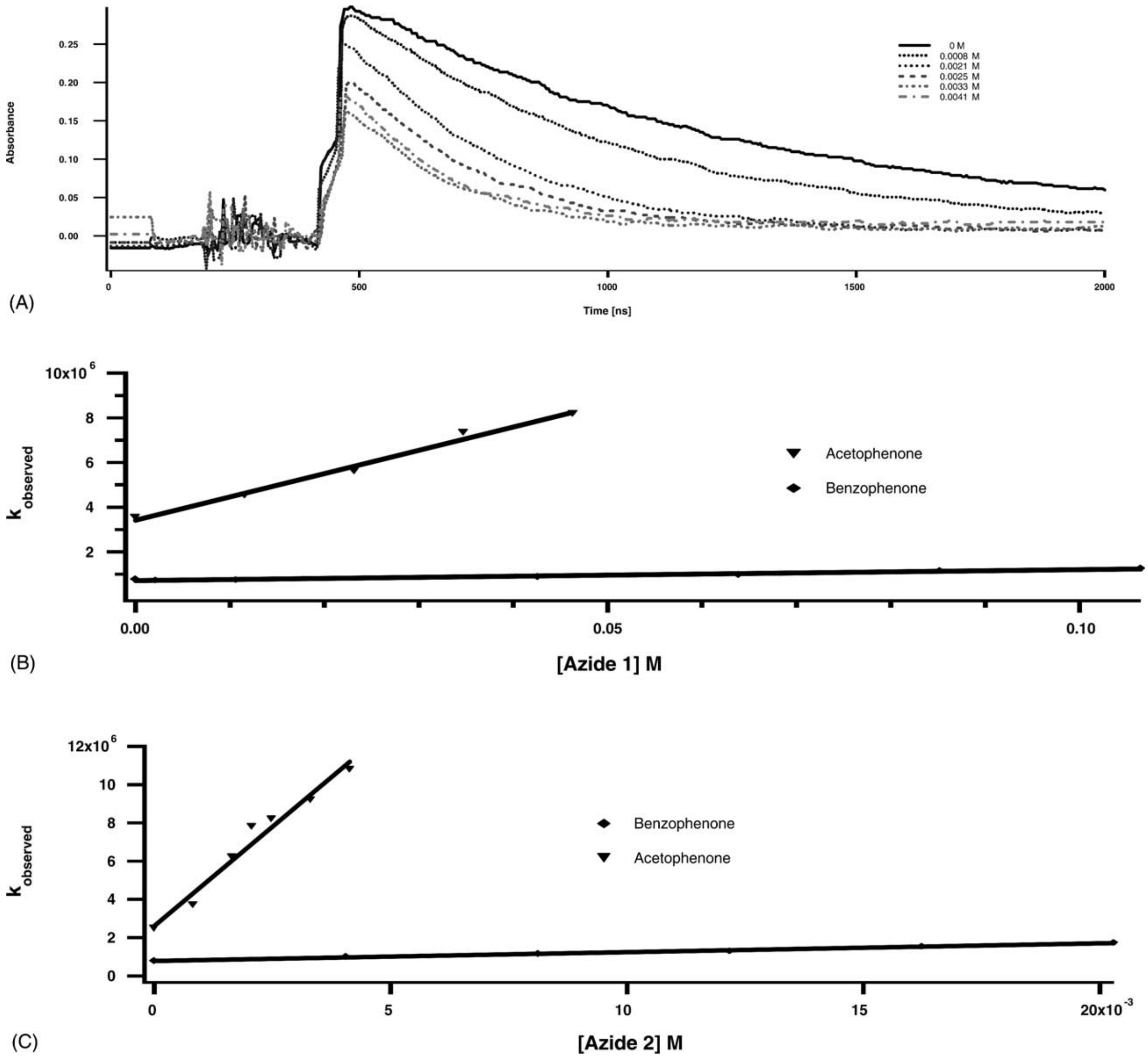


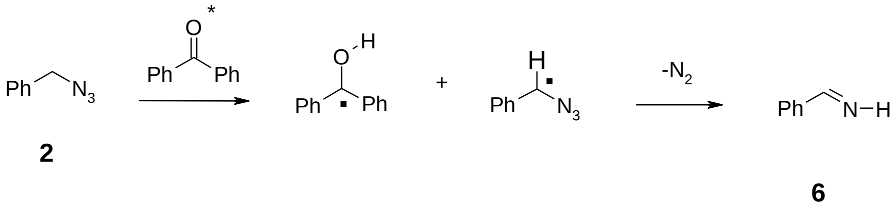
Fig. 4. (A) Decay of the triplet excited state of acetophenone at various concentration of azide **1**. Rates of quenching the triplet excited state of benzophenone and acetophenone as a function of concentration of (B) azide **1** and (C) azide **2**.

4. Discussion

Triplet-sensitized photolysis of **1** with all three sensitizers yielded **10** as the major product, which is formed by dimerization of two triplet alkyl nitrenes **8** or nitrene **8** reacting with azide **1**. This is similar to what has been observed for triplet phenyl nitrenes, which mainly decay by dimerization rather than abstracting a H-atom from the solvent [19,20]. In addition to dimerization nitrene **8**, also decays by H-atom abstraction from the solvent. For example, in toluene, nitrene **8** abstracts a H-atom to form a benzyl radical and adamantan-1-yl aminyl radical, and then these radicals recombine to form amine **12**. Similarly, **13** must be formed from the reaction of nitrene **8** with a benzyl radical. In methanol, nitrene **8** abstracts a H-atom to form amine **11**.

Triplet-sensitized photolysis of azide **1** with acetophenone and benzophenone did yield small amounts of products **5** in toluene and **4** in methanol. We assume that these products are formed from triplet nitrene **8** undergoing a 1,2-alkyl shift to form biradical **9**, since azide **1** does not absorb light directly above 385 nm. Acetone-sensitized photolysis of azide **1** using Pyrex filter yielded more of **5** than the other sensitizers, since azide **1** absorbs some of the light directly and thus reacts from its singlet excited state as well as undergoing triplet sensitization.

Acetophenone-sensitized photolysis of azide **2** in toluene gives mainly **7** and **17**. Most importantly, we observed no formation of imine **6**, which, can only form in the singlet manifold of the reaction. This allows us to suggest that imine **7** arises from the rearrangement of nitrene **14** into imine **7**.



Scheme 7.

Nitrene **14** must also abstract a H-atom from toluene to form a benzyl radical and **15**. Radical **15** then reacts with benzyl radicals to form **17** and **18**. Nitrene **14** also undergoes a 1,2-alkyl shift to form biradical **16**, which then intersystem crosses to form imine **7**. Imine **20** comes from the initial trapping of nitrene **14** with a benzyl radical. We observed no azo dimer from photolysis of azide **2**, suggesting that the triplet nitrene **14** abstracts a H-atom better than nitrene **8**.

Photolysis of a 0.01 M solution of azide **2** in acetone through Pyrex gave no triplet reactivity, since most of the light was absorbed directly by azide **2**, which reacts then from its singlet manifold. From Fig. 1 it can be seen that azide **2** has a much large absorption coefficient above 300 nm than azide **1** which explains why acetone can be used as a triplet-sensitizer for azide **1** and not azide **2**.

Benzophenone-sensitized photolysis of azide **2** yielded only imine **6**. Our hypothesis then is that imine **6** is formed by the triplet-excited benzophenone abstracting a H-atom from azide **2**, and the resulting radical then rearranges into imine **6** (see Scheme 7). Thus, benzophenone is quenched chemically rather than physically with alkyl azide **2**.

The rate of the energy transfer from acetophenone to azide **2** is a diffusion controlled process but slower for azide **1**. Presumably, the steric bulkiness of azide **1** makes it less effective in quenching the triplet excited state of acetophenone than azide **2**. Thus, the triplet energy of azides **1** and **2** must be similar to the triplet energy of acetophenone. This is in agreement with Lewis and Saunders who, estimated that the triplet energy of alkyl azides is between 75 and 80 kcal/mol [11]. As expected, the quenching rates of benzophenone with **1** and **2** are slower than for acetophenone, which has higher triplet energy. Interestingly, energy transfer does take place between azide **1** and benzophenone even though this is an activated process of at least 6 kcal/mol. Product studies on the other hand demonstrate that benzophenone does not transfer its triplet energy to azide **2** but abstracts a H-atom from it instead. The H-atom abstraction from azide **2** must be more efficient than from azide **1**, since the resulting radical will be stabilized by both the phenyl and the azide groups [21].

4.1. Conclusion

We have successfully shown that intermolecular triplet-sensitized photolysis of alkyl azides **1** and **2** leads to products that can be attributed to the formation of triplet alkyl nitrene intermediates. The triplet alkyl nitrenes are not highly reactive, since they decay mainly by dimerization and by abstracting H-atoms from the solvent. The rate of the energy transfer from the triplet sensitizer to the azide depends on the triplet energy of the sensitizer. For example, the triplet energy transfer from acetophenone to azide **2** is diffusion controlled, which indicates that the triplet energy of the azido group is similar to the triplet energy of acetophenone. Presumably, steric effects make the energy transfer from acetophenone to azide **1** less efficient. In spite of the low triplet energy of benzophenone it can be used as a triplet-sensitizer for azide **1**, whereas benzophenone abstracts a H-atom from azide **2**.

Acknowledgements

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