The Intermediates in Direct Photolysis of Alkyl Azides[1]

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Abstract: The lack of selectivity shown in migration aptitudes in triarylmethyl azide photolysis, and the formation of triphenylmethylamine in photolysis of triphenylmethyl azide in the presence of efficient hydrogen donors support the existence of a discrete nitrene intermediate. While the occurrence of a triplet-sensitized decomposition shows that a triplet azide, and presumably a triplet nitrene, can be involved, efforts to detect triplet azide in the direct photolysis by quenching experiments failed. This failure, and the high quantum yields, indicate that part or all of the direct photolysis may occur *via* a singlet azide and a singlet nitrene.

We have shown that migration aptitudes in the direct[3] and sensitized[4] photolytic rearrangements of triarylmethyl azides are all close to unity regardless of the electronic nature of the migrating aryl group, while migration aptitudes in the thermal rearrangement are increased by electron-repelling, and decreased by electron-withdrawing substituents.[5] We took this evidence not only to suggest concerted loss of nitrogen and phenyl participation for the thermal reaction but also adiscrete nitrene intermediate in the photolysis. The present work was prompted by the desirability of providing further evidence to test this hypothesis and of deciding whether singlet or triplet excited azide (or both) is the precursor of the nitrene in the direct photolysis.

One worrisome problem remained in the migration aptitudes. While they were all within experimental error of unity for the triarylmethyl azides and 2-phenyl-2-propyl azide, the Ph–Me migration aptitude for 1,1-diphenylethyl azide ranged from 1.87 to 2.45[3] in three separate experiments. The poor precision and the clearly nonstatistical results prompted us to repeat the experiment using direct analysis of the product mixture by glpc to minimize error. The results in Table I make it clear that selective loss, presumably by photodecomposition, of the benzophenone methylimine is occurring, for the migration aptitude is within experimental error of unity at the lowest conversion. Since the previous results[3] are higher for equivalent conversions than the present ones, a systematic error in the analytical method appears to have been present as well. There is now no exception to the rule that alkyl and aryl migration aptitudes are invariant in the photolytic rearrangement.

Table I. Migration Aptitudes in Photolytic Rearrangement of 1,1-Diphenylethyl Azide

Duration of photolysis, hr	Reaction, %[a]	Migration aptitude, Ph–Me[b]
1	11	0.94 ± 0.10
2	19	1.23 ± 0.02
4	30	1.44 ± 0.07

[a] By nitrogen evolution. [b] Corrected for the statistical preference for Ph.

A second line of evidence for a discrete nitrene was obtained from trapping experiments. Photolysis of triphenylmethyl azide in hexane solution in the presence of tri-*n*-butyltin hydride gave 5–7% triphenylmethylamine after correction for a slight dark reaction. Photolysis in *sec*-butyl mercaptan as solvent gave 3–4% amine. These results are most easily explained by the assumption that triphenylmethyl nitrene is formed, but rearranges about 20 times as fast as it is trapped. Unfortunately, the evidence for a discrete nitrene is not rigorous, for one cannot exclude the possibility that electronically excited azide would be reactive toward hydrogen donors.

Although the occurrence of sensitized photolyses of triarylmethyl[4] and other alkyl[6] azides indicates that triplet excited azide molecules can undergo decomposition to triplet nitrenes, the direct photolysis need not necessarily involve the same intermediates. The singlet excited azide formed by light absorption could either decompose directly to singlet nitrene, or undergo intersystem crossing to triplet azide which would then give triplet nitrene.

The triplet energies of alkyl azides have been found to be in the range 75–80 kcal/mol.[6] Consequently, quenching by *cis*-piperylene (E_T = 57 kcal/mol[7]) should occur at the diffusion-controlled rate. Photolyses of triphenylmethyl and isobutyl azides gave the same quantum yields of nitrogen in the presence as in the absence of *cis*-piperylene. That no energy transfer was occurring was also shown by the lack of isomerization of the *cis*-piperylene. Photolysis of triphenylmethyl azide in hexane under 1 atm of oxygen and in a thoroughly degassed solution gave the same quantum yields. Either no triplet excited azide is formed in direct photolysis, or it loses nitrogen much faster than it undergoes collisions with other solute molecules. For the latter to be true, the rate constant for nitrogen loss must be at least 10^{11} sec^{-1}. While this is not impossibly high for a unimolecular reaction, there is another reason for doubting the involvement of a triplet azide.

Quantum yields for nitrogen evolution from a number of alkyl azides were determined in various solvents

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Table II. Quantum Yields in the Direct Photolysis of Alkyl Azides

R in RN_3	λ, Å	Solvent	ϕ^a
C_2H_5	2537	MeOH	0.88
	3130	MeOH	0.88
	3130	Et_2O	0.89
n-C_3H_7	3130	MeOH	0.83
	3130	C_7H_{16}	0.79
n-C_4H_9	3130	C_6H_{14}	0.79
i-C_4H_9	3130	C_7H_{16}	0.79
n-C_6H_{13}	2537	MeOH	0.86
	3130	MeOH	0.71
	3130	Et_2O	0.71
	3130	C_7H_{16}	0.69
c-C_6H_{11}	3130	Heptane	0.68
$(C_6H_5)_3C$	3130	MeOH	0.80^b

[a] Each value is the average of two or more determinations. Reproducibility ±3% or better. [b] Estimated from initial rate of nitrogen evolution. Reproducibility *ca.* ±0.05.

using light of two different wavelengths. The results are given in Table II. There is no appreciable dependence of quantum yield on wavelength or solvent. The values are all high, but tend to be somewhat lower the larger the alkyl group. Quantum yields near 1.0 are reported for the solution-phase photolysis of ethyl azide.[8]

If nitrogen loss in the direct photolysis occurs from a triplet azide, the quantum yield for intersystem crossing (ϕ_{ST}) must be at least 0.7–0.9. Kasha[9] has suggested that the rates of radiationless processes such as intersystem crossing should be inversely proportional to the energy difference between the two electronic states involved. Lamola and Hammond[10] have indeed observed a rough correlation between ΔE_{ST} and ϕ_{ST}. For our alkyl azides, ΔE_{ST} is 20–25 kcal/mol. Some systems with comparable ΔE_{ST} values are chrysene, 22 kcal/mol, $\phi_{ST} = 0.67$; fluorene, 27 kcal/mol, 0.31; diphenylamine, 17 kcal/mol, 0.38; 1-naphthylamine, 28 kcal/mol, 0.15. Although the correlation is not sufficiently precise to be conclusive evidence, it does strongly suggest that the quantum yields we observe are higher than expected for the value of ΔE_{ST}.

Even if the precursor of the nitrene could be proved to be a singlet, it would not necessarily follow that the nitrene rearranged as a singlet, for it could also undergo intersystem crossing to a triplet. Since the organic products of the direct and sensitized photolyses are the same both qualitatively and quantitatively, we cannot distinguish singlet from triplet nitrenes by their chemical behavior. It has been reported that carbonyl nitrenes[11] and cyanonitrene[12] are initially formed as singlets in the direct photolysis of their precursor azides. These reports lend additional weight to our conclusion that the most reasonable path in direct photolysis of alkyl azides involves decomposition of a singlet excited azide to a singlet nitrene. Given the fact that our nitrenes rearrange considerably faster than they can be trapped (see above), it seems likely that rearrangement would also be faster than intersystem crossing to the triplet.

Experimental Section

Preparation of Azides. Alkyl azides were prepared and purified as described by Lewis and Saunders.[6] Triphenylmethyl azide was obtained by the method of Saunders and Ware.[5] 1,1-Diphenylethyl azide was obtained by the method of Gudmundsen and McEwen.[13]

Preparation of Imines. Benzophenone methylimine was obtained by the method of Curtin and Hausser.[14] Acetophenone phenylimine was prepared by the method of Saunders and Caress.[3]

Kinetics of Nitrogen Evolution. A solution containing 0.08–0.24 *M* azide in purified hexane (50 ml) was placed in a 100-ml Pyrex tube attached to a gas buret by a short length of Tygon tubing. The tubes were wrapped with aluminum foil and placed in a Rayonet type RS reactor equipped with 2537-Å lamps. After thermal equilibrium was attained the foil was removed and gas evolution followed over a period of several hours. For the alkyl azides, a plot of log $(v_0/(v_0 - v_t))$ *vs.* t was linear over at least the first 20% of reaction. For triphenylmethyl azide, curvature of the plot began at about 5% reaction.

Quantum Yield Determinations. Photolyses at 2537 Å utilized a Hanovia SC 2537 low-pressure mercury lamp or a Rayonet type RS reactor equipped with low-pressure mercury lamps. Photolyses at 3130 Å utilized a Hanovia 67A medium-pressure mercury lamp, the 3130-Å line being isolated by a Corning 7-54 filter plus a 2.0-cm thickness of 7.0×10^{-4} *M* potassium chromate in 1% aqueous potassium carbonate. A "merry-go-round" apparatus[7] was used to ensure equal illumination of sample and actinometer. A uranyl oxalate actinometer[15] was used.

Photolysis tubes were made of 15-mm o.d. Pyrex, Vycor, or quartz tubing equipped with high-vacuum stopcocks. Solutions of the azides (0.2–2.0 *M*) were degassed and photolyzed and the nitrogen yield was determined in the manner described elsewhere.[6]

Attempted Quenching of Azide Triplets. Photolysis of a hexane solution 0.5 *M* in isobutyl azide and 0.5 *M* in *cis*-piperylene resulted in no decrease in the quantum yield of nitrogen and no isomerization of the *cis*-piperylene. Photolysis of a pentane solution 0.033 *M* in triphenylmethyl azide and 0.059 *M* in *cis*-piperylene for 24 hr (Hanovia medium-pressure lamp) also gave no isomerization of the *cis*-piperylene. The solution was analyzed by glpc using a 20 ft × 0.125 in. column of 25% adiponitrile on Chromosorb P at room temperature. In a control experiment, a tube containing 0.024 *M* benzophenone and 0.059 *M* *cis*-piperylene in pentane was irradiated at the same time as the azide solution. The solution contained 45% *trans*-piperylene after photolysis. In another attempted quenching experiment, photolysis of 0.057 *M* triphenylmethyl azide in hexane under 1 atm of oxygen gave the same quantum yield of nitrogen as a thoroughly degassed solution irradiated simultaneously.

Photolysis of 1,1-Diphenylethyl Azide. Solutions containing 0.05 g (0.23 *M*) of 1,1-diphenylethyl azide in 10 ml of hexane were degassed and photolyzed in Vycor tubes with the Hanovia medium-pressure lamp. Separate samples were analyzed after 1, 2, and 4 hr by glpc on a 5 ft × 0.125 in. column of Apiezon L on Chromosorb G at 155°. Identification was by comparison of retention times with those of authentic samples, and unreacted azide and product imines were shown to be stable to the conditions of the analysis.

Trapping of Triphenylmethyl Nitrene. A solution containing 4.5 g (0.016 mol) of triphenylmethyl azide and 23.2 g (0.08 mol) of tri-*n*-butyltin hydride[16] in 150 ml of hexane was photolyzed for 40 hr with the low-pressure Hanovia lamp. The solution was treated with dry hydrogen chloride, and the resulting precipitate collected and extracted with water. The aqueous solution was made alkaline with 20% sodium hydroxide and extracted with ether. The ether layer was dried and the ether removed to give 0.90 g of brown oil, from which colorless plates separated after several hours; melting point and mixture melting point were identical with authentic triphenylmethylamine.[17] Analysis of the oil by glpc (5 ft × 1/8 in. 3% Aprezon L on Chromosorb G at *ca.* 230°) showed two components, the one corresponding in retention time to triphenylmethylamine constituting 65% of the mixture, or 12% yield based on starting material. The second component was assumed to be N-

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phenyldiphenylmethylamine from photoreduction of benzophenone phenylimine.[18] Reaction of triphenylmethyl azide with tri-*n*-butyltin hydride in the dark gave 3–5% triphenylmethylamine, so that the net yield in the photolysis was 5–7%.

A solution of 0.17 g (0.06 mol) of triphenylmethyl azide in 10 ml of *sec*-butyl mercaptan was photolyzed for 48 hr with the Hanovia medium-pressure lamp. Analysis of the reaction mixture by glpc showed 3–4% yield of material with the same retention time as triphenylmethylamine.

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Sensitized Photolysis of Organic Azides. A Possible Case of Nonclassical Energy Transfer[1]

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Abstract: Quantum yields for nitrogen evolution were determined in sensitized photolyses of several alkyl azides, phenyl azide, and ethyl azidoformate. Determination of the quantum yield as a function of azide concentration, along with data from the literature on the sensitizers, permitted the calculation of rates of triplet energy transfer from sensitizers to azide. These rates were closely similar for any given sensitizer with *n*-hexyl, cyclohexyl, and isobutyl azides, but were larger for phenyl azide and smaller for ethyl azidoformate. The energy transfer to the alkyl azides approaches the diffusion-controlled rate only as the sensitizer triplet energy approaches 75–80 kcal/mol, suggesting a triplet energy in this range for the azides. Sensitizers with lower triplet energies are considerably more effective than expected for a classical endothermic energy transfer. It is suggested that the energy transfer is accompanied by bending of the N–N–N bond angle from its normal 180°, resulting in a "nonspectroscopic" triplet. Extended Hückel theory calculations on methyl azide support the hypothesis that the molecule is more stable with a bent than a linear configuration of the azide group in the first excited state.

Recently we reported that the loss of nitrogen and rearrangement to benzophenone phenylimines of triarylmethyl azides could be effected by various triplet sensitizers.[3] Sensitizers as low in triplet energy as pyrene (48.7 kcal/mol) gave appreciable reaction, which led us to suggest that the triplet energy of the azide was below 48 kcal/mol. Efforts to confirm this estimate by emission studies failed when no emission spectrum could be observed from the azide in a 3-methylpentane glass at 77°K. Attempts to observe singlet–triplet absorption in ethyl iodide solution[4] also failed.

In the absence of confirming evidence, our estimate of the triplet energy remained a nagging problem. It requires a very large difference between the lowest triplet and lowest singlet, for the latter is in the vicinity of 100 kcal/mol for alkyl azides.[5] Consequently, we sought other means of determining the triplet energies of the azides.

Determination of the rate of energy transfer as a function of the triplet energy of the sensitizer seemed a promising approach. As long as the triplet energy of the sensitizer is greater than that of the acceptor, the energy transfer should occur at the diffusion-controlled rate. When the triplet energy of the sensitizer becomes less than that of the acceptor the rate of energy transfer falls very rapidly, for the energy deficiency must be supplied as a thermal activation energy.[6] By determining the region in which the fall off begins, then, one can estimate the triplet energy of the acceptor within a few kcalories/mole.

Because we lacked the equipment for determining the rate of energy transfer by flash spectroscopy,[6] we chose an indirect method. Degassed solutions of sensitizer and azide, prepared so that the sensitizer absorbed >99% of the incident light, were photolyzed, and the quantum yield of nitrogen evolution determined as a function of azide concentration. A plot of $1/\phi$ *vs.* $1/[\mathrm{A}]$ was found to be linear. This, and our other experimental observations are accommodated by the following mechanism, where S = sensitizer, S_1^* = singlet excited sensitizer, S_3^* = triplet excited sensitizer, A = azide, and A_3^* = triplet excited azide.

$$\mathrm{S} \xrightarrow{h\nu} \mathrm{S_1}^* \tag{1}$$

$$\mathrm{S_1}^* \xrightarrow{\mathrm{ISC}} \mathrm{S_3}^* \tag{2}$$

$$\mathrm{S_3}^* \xrightarrow{k_\mathrm{d}} \mathrm{S} \tag{3}$$

$$\mathrm{S_3}^* + \mathrm{A} \xrightarrow{k_\mathrm{q}} \mathrm{A_3}^* + \mathrm{S} \tag{4}$$

$$\mathrm{A_3}^* \xrightarrow{k_\mathrm{p}} \text{products} \tag{5}$$

$$\mathrm{A_3}^* \xrightarrow{k_\mathrm{o}} \mathrm{A} \tag{6}$$

The over-all quantum yield of azide decomposition may then be expressed as follows.

$$\frac{1}{\phi} = \frac{1}{\phi_{\mathrm{ST}}}\left(1 + \frac{k_\mathrm{d}}{k_\mathrm{q}[\mathrm{A}]}\right)\frac{k_\mathrm{o} + k_\mathrm{p}}{k_\mathrm{p}} \tag{7}$$

Here ϕ_{ST} is the quantum yield for intersystem crossing

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