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The mechanism of photolysis of aromatic azides

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ABSTRACT. A survey has been made of data published in recent years on the nature, spectra and reactivity of intermediates obtained on photolysis of aromatic azides. Aspects requiring further investigations have been highlighted.

The bibliography includes 147 references.

Contents

I. Introduction 500
II. The structure, electronic spectra and properties of azides 500
III. The nature and properties of key intermediates 503
IV. The reactivity of intermediate singlet species 507
V. Reactions of triplet aromatic nitrenes 509
VI. Quantum chemical calculations on the properties of intermediates 513
VII. Conclusions 514

I. Introduction

The photochemical reactions of organic azides have been a focus of study for more than 60 years, and interest in this field is in no way declining. This is principally because these compounds have many practical applications, e.g. in polymer chemistry, in photolithography, and as light-sensitive agents for use in photographic processes which are not based on silver salts.[1–3] Aryl and heteroaryl azides are also used as reactive reagents in the photoaffinity modification of biopolymers.[4,5] Interest in the photochemistry of organic azides has also developed from mechanistic considerations, many of which are complex and unresolved.

It was towards the end of the 1950s, with the advent of new analytical methods, that exhaustive studies were first made on the structure and reactivity of the intermediates obtained on photolysis of organic azides. The results obtained up to 1983 have been reviewed[6,7] and presented as monographs.[8–10] In the Soviet literature of 1975, there is also a review on the photochemistry of organic azides,[11] together with a number of short surveys published as monographs.[1,2] However, in spite of the enormous interest in the photochemistry of organic azides, many mechanistic details remain unclear, and certain data from a number of authors are contradictory.[10] Significant progress has been made during the last 5–6 years as a result of using new methods[12–14] and applying traditional methods in a more sophisticated way.[15–17]

II. The structure, electronic spectra and properties of azides

1. Structure and electronic spectra of azides

Azides are a class of compound with the general formula, RN_3. The three atoms of nitrogen are linear.[18–21] The atom of nitrogen bonded to substituent R is sp^2-hybridised (the R–N–N angle being close to 120°).[18–22] In aryl azides all three nitrogen atoms are involved in conjugation with the aromatic system, although such interaction is weak.[22] As a consequence there is a similarity between the absorption spectra of azides and those of the corresponding aromatic hydrocarbon.

Table 1. Electronic spectral absorption of phenyl azide derivatives.

Substituent	Solvent	T, K	λ_{max}, nm (lg ε, l(mol)$^{-1}$ cm)	Refs.
H	EPA	77	247(3.9), 278 (3.3), 315(1.9)*	[22]
	EtOH	77	252(4.06)	[23]
	EtOH	298	249(4.06), 285(3.22)	[24]
p-Me	EtOH	77	254(4.18)	[23]
	EtOH	298	251(4.12), 291(3.23)	[24]
	hexane	300	250(4.18), 283(3.45), 292(3.34)	[25]
p-NH_2	EtOH	77	280(4.17)	[23]
	hexane	300	267(4.23), 303(3.51)	[25]
p-MeO	EtOH	77	253(4.13)	[23]
p-NO_2	EtOH	77	322(4.18)	[23]
	hexane	300	220(4.08), 299(4.30), 318(4.00)	[25]
p-MeCO	EtOH	77	288(4.35)	[23]
p-Ph	EtOH	77	280(4.31)	[23]
m-Ph	EPA	77	246(4.2), 292(3.5), 320(2.3)*	[22]
o-Ph	EPA	77	267(4.1), 296(3.3), 315(2.2)*	[22]
p,*o*′,*p*-Me_3	EPA	77	213(3.8), 247(3.4), 286(2.8), 300(2.1)*	[22]

* $n\pi^*$-region.

The principal bands in the absorption spectra of aromatic azides have been assigned to $\pi\pi^*$ transitions in the aromatic system. There is also absorption, thought to correspond with $n\pi^*$-type transitions,[22–24] which is not evident in the spectra of the corresponding hydrocarbon. The values of these absorption maxima are approximate because they appear as shoulders on the

absorptions due to the more intense ππ*-transitions. These weak absorptions are not a consequence of complex formation or associations,[26] nor due to impurities.[27] Recently, it was proposed that the extended asymmetric tail in the absorption spectra of aromatic azides is due to their transition into dissociated singlet states.[27] Spectral data for a number of substituted phenyl azides are given in Table 1.

2. Quantum yields for the photo-decomposition of aromatic azides

Azides are unstable compounds, decomposing with elimination of N_2 to form nitrenes on photolysis and thermolysis[6–11]

$$ArN_3 \xrightarrow{h\nu} ArN + N_2.$$

Table 2. Quantum yields (φ) for the photolysis for phenyl azide derivatives on irradiation at 254 nm.

Substituent	Concentration ArN_3, mol/l	Solvent	φ at 298 K	φ at 77 K	Refs.
H		hexane	0.53		[28]
	10^{-5}—10^{-4}	acetonitrile	0.72		[29]
	10^{-4}	acetonitrile	0.56		[30]
		Mcy-Ip*		0.52	[28]
	10^{-4}	3-methylpentane		0.49	[31]
p-Me		ethanol	0.59		[24]
p-MeCO		hexane	1.00**		[28]
		Mcy-Ip*		1.00**	[28]
p-NO_2	10^{-4}	acetonitrile	0.54		[30]
	10^{-3}—10^{-1}	acetonitrile	0.7		[32]
p-NH_2	$4 \cdot 10^{-5}$—$2 \cdot 10^{-4}$	toluene	0.96***		[33, 34]
		toluene-THF		0.8***	[33, 34]
p-Br	10^{-4}	acetonitrile	0.80		[30]
o, *o*', *p*-Me_3		hexane	0.96		[28]
		Mcy-Ip*		0.98	[28]
o, *o*', *p*-Br_3	10^{-4}	acetonitrile	0.16		[30]
m-Ph		hexane	0.37		[28]
		Mcy-Ip*		0.36	[28]
o-Ph		hexane	0.46		[28]
		Mcy-Ip*		0.43	[28]

* Mixture of methylcyclohexane and isopentane (1 : 1).
** Irradiation at 280 nm.
*** Irradiation at 313 nm.

The quantum yields for the photolysis of aromatic azides, presented in Tables 2 and 3, are a consequence of excitation in the ππ*-transition. The values of the quantum yield are not dependent on the temperature. It can be seen that the quantum yields for the photolysis of polynuclear aromatic azides are higher than those for PhN_3 and its derivatives. Quantum yields are also available for the photolysis of di-, tri- and tetra-azides.[24,28] Photo-decomposition of PhN_3 and its derivatives on irradiation with visible light ($\lambda < 430$ nm) has also been observed.[23]

Table 3. Quantum yields for the photolysis of poly-condensed aromatic azides.[28]

Compound	λ_{irr}, nm	φ at 298 K	φ at 77 K
1-Azidonaphthalene	303	1.00±0.02	0.95±0.05
3-Azidoquinoline	303	0.84±0.05	0.87±0.05
1-Azidoanthracene	365	1.00±0.03	1.02±0.05

For quenching of triplet nitrenes by reaction with an azide molecule [Eqn. (1)],

$$^3ArN + ArN_3 \rightarrow ArN{=}NAr + N_2, \quad (1)$$

the quantum yield may exceed 1 (but not 2).[35,36] However, Waddell and Lee Go have found that the quantum yield for the photolysis of PhN_3 in acetonitrile can reach $\simeq 300$.[31] In subsequent work devoted to more detailed studies of the photolysis of PhN_3 and certain of its derivatives, even higher quantum yields (up to 15 300) were recorded, consistent with the following chain mechanism:[29,30,37–39]

$$^3ArN + ArN_3 \rightarrow 2\,^3ArN + N_2. \quad (2)$$

Apart from information reported by Waddell et al.,[29,30,37–39] there are no other data in the literature on the effect of concentration on the quantum yield for the photolysis of aromatic azides, and no other references to quantum yields greater than unity have been reported. The quantum yield for the photolysis of 1-azidonaphthalene does not depend on the concentration of the azide in the range 10^{-5} to 10^{-2} M and is equal to 1.[28] Schuster and Liang[32] were unable to reproduce the results of Waddell et al. for the photolysis of *p*-nitrophenyl azide.[30] According to the latter authors, the quantum yield increased from 0.54, at an azide concentration of 10^{-4} M, to 434 at 10^{-1} M.[32] However, according to Schuster et al., the value is independent of concentration in the interval 10^{-3} to 10^{-1} M, the quantum yield being 0.7 under these conditions. Thus, there are contradictory data on the photolysis of PhN_3 and its derivatives.

3. Initial processes in direct and sensitised photolysis

It is generally accepted that singlet nitrenes are the species obtained initially on dissociation of azides in the excited singlet state, while triplet nitrenes are predominantly formed from azides in the excited triplet state.[10–14,40–42] For all aryl azides which have been studied thus far, the main excited state is the triplet one.[40] This has been verified from the ESR characteristics of the triplet species formed on azide photolysis in glass matrices[43–48] or as single crystals[49–50] at 77 or 4 K.

Mechanistic information on the role of triplet azides and nitrenes has been gained by studying the sensitised photolysis of aromatic azides.[15–17,26–28,41,51–54] Leyshon and Reiser[26] found that PhN_3 and 1-$C_{10}H_7N_3$ quench both the singlet and triplet states of the sensitiser. In kinetic experiments, the rate constants for quenching the triplet state of the sensitiser [$k_q(T)$] have been calculated. Based on the relationship between $k_q(T)$ and the position of the triplet level of the sensitiser, it has been proposed that quenching involves

transfer of energy to a thermally populated non-linear azide [ground] state. It is thus considered that in the excited triplet state the non-linear configuration of the azide has the minimum energy.[26] Quantum chemical calculations have in fact shown that distortion of the terminal nitrogen from the plane of the azido group leads to a decrease in the energy of the lower excited triplet state.[51,55]

It has been established that aromatic ketones (benzophenone, acetophenone) function as triplet sensitisers in the photolysis of PhN_3 and 1-$C_{10}H_7N_3$.[15,53] However, the $k_q(T)$ value for quenching the triplet excited state of benzophenone by phenyl azide was found to be 2×10^9 l/mol/s,[15] which is significantly different from the value reports by Leyshon et al.[26] [$k_q(T) = 1.8 \times 10^6$ l/mol/s]. With such a discrepancy, it would be difficult to draw meaningful conclusions.[26]

The quantum yield (φ) for the sensitised decomposition of *o*-azidobiphenyl in the presence of acetophenone is 0.3 [52] (for PhN_3 $\varphi < 0.1$ [15]). In the triplet-sensitised photolysis of *p*-dimethylaminophenyl azide, the quantum yield is very small (in direct photolysis $\varphi \approx 1$).[14] In the sensitised decomposition of 1-$C_{10}H_7N_3$ with benzophenone[53] and of 1-azidopyrene with biacetyl,[42] quenching of the triplet state of the sensitiser is accompanied by the appearance of the corresponding triplet nitrene. The spectrum of ^{3}PhN was not recorded during the sensitised photolysis of PhN_3.[16] There was no sensitised decomposition of *p*-dimethylaminophenyl azide in the presence of 2-acetonaphthone.[27]

Table 4. Excitation energies for the singlet state E_s and rate constants [k_q(S)] for fluorescence quenching of sensitisers by phenyl and 1-naphthyl azide.[26]

Sensitiser	E_S, kcal/mol	k_q(S), l.mol^{-1} s^{-1}	
		PhN_3	$C_{10}H_7N_3$
Phenanthrene	81.7	$1.3 \cdot 10^{10}$	$1.4 \cdot 10^{10}$
Anthracene	75.1	$6.6 \cdot 10^9$	$1.0 \cdot 10^{10}$
9,10-Dimethylanthracene	70.2	$2.5 \cdot 10^9$	$5.4 \cdot 10^9$
Perylene	64.9	$3.4 \cdot 10^8$	$2.7 \cdot 10^9$
Tetracene	60.0	$2.3 \cdot 10^7$	$3.5 \cdot 10^8$
Rubrene	51.1	$1.0 \cdot 10^5$	$5.5 \cdot 10^6$

The efficiency of singlet sensitisation has been studied by determining the fluorescence quenching of the sensitiser (Table 4). The authors[26] came to the following conclusions:

1) singlet sensitisation is more effective in promoting azide decomposition than triplet sensitisation if the energy of the sensitiser is the same;

2) sensitisation is observed well below the estimated acceptor level of the azide;

3) singlet sensitisation of aryl azides is effected by two competing processes: a) S–S-transfer of energy; and b) transfer of an electron [from the azide to the excited hydrocarbon (sensitiser) molecule]. The latter conclusion was based on indirect information [namely the dependence of the rate constant for quenching $k_q(S)$ on the free energy of the electron transfer (ΔG_{ET}) in accordance with the Rehm–Weller equation[56]].

In studying the sensitised photolysis of *p*-dimethylaminophenyl azide in the presence of a series of aromatic hydrocarbons (pyrene, 1-acetamidopyrene, 9-acetamidoacridine),[27] the authors came to the same conclusion as Leyshon et al.,[26] i.e. that two mechanisms of singlet sensitisation, a) and b) were operative. However, in contradiction to Reiser et al.,[26] Schuster et al. consider that the electron transfer takes place from the excited hydrocarbon to the azide.[27] This is supported by the appearance of absorption corresponding to the pyrene cation. It is thought that the electron transfer may take place on the azide molecule in a dissociated state.[27] Such energy transfer to singlet and triplet repulsive states of organic peroxides has already been reported.[57]

4. The mechanism of photo-dissociation of aromatic azides

Aromatic azides have proved interesting as model compounds for studying photo-dissociative processes. In order to gain information on the initial processes, it is necessary to apply highly sensitive methods to measure the very short relaxation times. Basic information on the mechanism of dissociation can be derived by determining the spatial and energy distribution of the resulting molecular fragments.[58–61] In a picosecond time-resolved study of the flash photolysis of aromatic azides, it was shown that photo-dissociation of *p*-dimethylaminophenyl azide in toluene at room temperature proceeds in the singlet excited state within < 6 ps.[14]

In order to ascertain mechanistic details, it is important to measure quantum yields as a function of the excitation wavelength.[58] Reiser and Marley[28] considered three possible mechanisms operative in the preliminary stage:

1) uncoupling of the spin of the electrons forming in the N–N σ-bonds (repulsive state T_{σ^*});

2) transfer into dissociated and pre-dissociated states;

3) supply of kinetic energy in excess of the bond energy to a critical vibrational mode (collapse from a principal "hot" electron state).

The first pathway can be discounted because, on this basis, either an aromatic nitrene or a molecule of nitrogen would be found in the triplet state;[28] as has been demonstrated, dissociation of singlet-excited azides results in the formation of *singlet* nitrenes.[9–14,40–42] The formation of a triplet-excited molecule of nitrogen is also unlikely because the energy of the $^3\Sigma_u^+$ state for nitrogen is 6.224 eV.[19,62] Furthermore, triplet-excited nitrogen has not been detected experimentally.[63]

According to Reiser and Marley, the mechanism of azide photo-dissociation involves a collapse of a vibrationally-excited electron state.[28] In our opinion and those of other authors,[24,55,64,65] this is also unlikely. From an analysis of the relationship between the quantum yield for the photolysis of *p*-azidomalachite green and both wavelength and temperature, it has been concluded that dissociation proceeds from an electronically-excited state.[24,64] Two mechanisms are possible:[24] a non-adiabatic dissociation and a pre-dissociation.[66] It is considered that the latter is more likely.[24,64]

Having analysed absorption spectra and performed quantum chemical calculations, Kondratenko and Shrubovich[65] came to the same conclusion as Shields et al.,[27] namely that the long wavelength absorption in the spectra of aromatic azides was a result of a transfer into a dissociated state ($\pi\sigma^*$-type). In their view, the initial mechanism of photolysis is a dissociative one, although they do not exclude a contribution due to pre-dissociation on excitation to higher electronic states.

From semi-empirical quantum chemical calculations, Tsuda et al. came to the conclusion that the motive forces behind the dissociative process of phenyl azides are involved with the displacement of the terminal nitrogen atom from the plane of the other atoms, which leads to a lowering of the activation barrier.[55] A distortion of the terminal nitrogen atom also leads to a shifting of the lower excited states $^1n\pi^*$ and $^1\pi\pi^*$, excitation of which precedes the dissociation. For aromatic azides it is considered that all the excitation energy is concentrated on the azido group, while the aromatic ring functions as an antenna for the photoabsorption.[55]

III. The nature and properties of key intermediates

The formation of nitrenes on photolysis and thermolysis of azides was first postulated on the evidence of product analyses.[6–11] It was not until 1962 that Wasserman et al. provided, through ESR studies, the first spectroscopic indication of the existence of triplet nitrenes.[46] This was based on the observation of a $\Delta m = 2$ transition in a moderate field and a $\Delta m = 1$ transition in a weak field (at 1620 and 6701 G, respectively, for ^{3}PhN).

1. ESR spectroscopy of aromatic nitrenes

The ESR spectroscopic characteristics of triplet molecules are determined by the spin-spin dipole interaction of unpaired electrons. In the absence of a magnetic field, this leads to a splitting of the triplet levels, as described by the spin Hamiltonian:[67]

$$H_{SS} = D(S_z^2 - {}^1/_3S^2) + E(S_x^2 - S_y^2). \quad (3)$$

The splitting parameters in a zero field, D and E, are given by:

$$D = \left\langle \Phi_k \left| \frac{3g^2\beta^2}{4} \frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5} \right| \Phi_k \right\rangle, \quad (4)$$

$$E = \left\langle \Phi_k \left| \frac{3g^2\beta^2}{4} \frac{y_{12}^2 - x_{12}^2}{r_{12}^5} \right| \Phi_k \right\rangle, \quad (5)$$

where Φ_k is the coordinated part of the wave function of unpaired electrons in the triplet state; g is the g-factor, equal to ~ 2; β is the Bohr magneton; and r_{12} is the inter-electronic distance. The spin Hamiltonian takes the form (3) for a specific system of coordinates relative to the axes of the molecule, which, for high symmetry, coincides with the axes of symmetry.[67]

In an external magnetic field, the spin Hamiltonian becomes:

$$H = g\beta HS + H_{SS}. \quad (6)$$

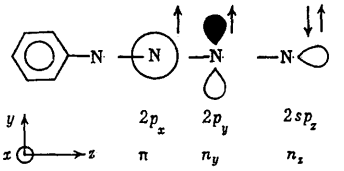
When the applied field is oriented to align with one of the molecular axes, the spin Hamiltonian, as defined by Eqn. (6), can be readily determined.

In the general case, the value of the applied magnetic field strength at absorption depends on the orientation of the field relative to the axes of the molecule. The intensity of the signals in a glass matrix and in the semicrystalline state is noticeably lower than that registered for single-crystals possessing the same number of oriented triplets.[45] The experimentally observed resonances in glass matrices and in the semi-crystalline state are due to the relatively few molecules in which one of the three magnetic axes is approximately aligned with the direction of the applied magnetic field.[45]

For arylnitrenes the main axis z coincides with the C–N bond; the axes x and y are equivalent so that $E \approx 0$.[45,47] The ESR spectra of triplet nitrenes are characterised by a D value which is significantly greater than the microwave quantum of energy.[43,46] From a calculation of the values of the resonance fields for allowed transition with $\Delta m = 1$ when the applied field is oriented to align with one of the axes (using ESR spectrometers where $H < 10\,000$ G), it can be concluded that the recorded signals correspond to an orientation of the applied magnetic field parallel to the plane xy.[45,46] The value of the resonance field can be determined from the equation:

$$H^2 = H_0(H_0 + D), \quad (7)$$

where H_0 is the resonance field for the isolated doublet state, and H is the resonance field for the triplet nitrene (assuming that E = 0).



Mapping of the orbitals of phenylnitrene.[16]

Table 5. Splitting parameters in a zero field (D) for triplet aromatic nitrenes (^{3}RN).

R	D, cm^{-1}
Phenyl	0.998 [47]; 1.003 [68]; 0.999 [48, 49]
Substituted phenyl	0.871—1.065 [47, 48,50,69]
1-Naphthyl	0.789 [47]; 0.798 [68]; 0.79 [71]
2-Naphthyl	1.008 [47]
1-Anthryl	0.663 [47]; 0.65 [72]
2-Anthryl	0.778 [47]; 0.75 [72]
1-Pyrenyl	0.73 [70]

For the simple nitrene, :NH, $D = 1.863$ cm^{-1} (the contribution of spin-spin interaction being 1.595 cm^{-1}, and the contribution of spin-orbital interaction being 0.268 cm^{-1}).[67] The parameter D for various alkylnitrenes lies in the region 1.57–1.66 cm^{-1}.[46] For aromatic nitrenes one of the unpaired electrons is localised in a p_y-orbital of the nitrogen atom (see above), while a second occupies a delocalised π-orbital. Delocalisation leads to a decrease in the spin density at the atom of nitrogen and, correspondingly, to a decrease in the value of D for aromatic nitrenes relative to alkyl nitrenes (Table 5). The following equation may be used for determining the approximate value of the spin density of a π-type unpaired electron on the nitrogen atom:

$$\rho_\pi^N \approx D/D_0 \ , \quad (8)$$

where D is the parameter for an aromatic nitrene, and D_0 for alkyl nitrenes (D_0 = 1.6 cm^{-1}). For arylnitrenes the value ρ_π^N lies in the region of 0.42–0.64.[46]

From ESR spectroscopic data for a series of fourteen para-substituted phenyl azides, recorded under identical conditions hyperfine splitting at the nitrogen nuclei was detected in five instances (a_N = 17 ± 1 G), as well as at the fluorine nucleus (a_F = 17.5 G) and at iodine (a_I = 85 G) in the para-position.[48] The value of D for para-substituted phenylnitrenes lies in the region 0.874–1.008 cm^{-1}, the spin density at the nitrogen nucleus being sensibly independent of the nature of the substituent.[48] Consequently, the simplified Eqn. (8) gives only a rough assessment of the ρ_π^N value. To obtain a quantitative correlation with experimental findings, it is necessary to consider more accurately the effects of delocalisation. The effect of substituents on the value of the parameter D has been studied for 8-substituted 1-naphthylnitrenes[71] and for variously substituted 9-anthracenylnitrenes.[72]

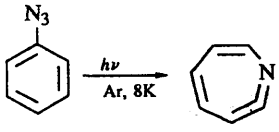
Constrasting with alkyl- and aryl-nitrenes, for which the triplet state predominates, aroylnitrenes fail to provide recordable ESR spectra.[47,73,74] Furthermore, the products obtained by both direct and triplet-sensitised photolysis of aroyl azides ($ArCON_3$) are typical of those obtainable from singlet nitrenes.[73–76] On the basis of these data, one can assume that aroylnitrenes (ArCON) exist principally in the singlet state.[73,74] These are potentially electrophilic, being readily and effectively inserted even into non-activated CH-bonds. Thus, aroyl azides may be used for photo-affinity modification of the lipophilic residues of biopolymers.[77,78]

2. The nature and optical spectra of intermediates

Shortly after the ESR spectra of triplet nitrenes were recorded, Reiser et al. studied the electronic absorption spectra of the species obtained by photolysis of a number of aromatic azides under the same conditions (in oranic glass matrices at 77 K).[22,79,80] They came to the conclusion that the recorded spectra were due to nitrenes in the triplet state. This was based on the following: firstly, the conditions under which the spectra were recorded were the same as those under which the ESR spectra were taken; and, secondly, there was a close similarity between the electronic absorption spectra of [presumed] triplet nitrenes and those of radicals having an unpaired π-electron. For example, the spectrum of ^{3}PhN (λ = 314 and 402 nm) is similar to that of $^2PhCH_2$ (λ = 318 and 463 nm) and, more strikingly, to those of ^{2}PhO (λ = 300 and 403 nm) and ^{2}PhNH (λ = 309 and 403 nm).[22] These results were later reproduced, and low-temperature absorption spectra were recorded for the species obtained from other aromatic azides. Here, too, absorption was assigned to triplet aromatic nitrenes[23,24,40,70,72,81,82] (see Table 6).

a) Photolysis of phenyl azides and its derivatives

In 1978, Chapman et al. showed that 1-aza-1,2,4,6-cycloheptatetraene (1,2-didehydroazepine) was the major intermediate formed on irradiation on PhN_3 in an argon matrix at 8 K.[83] This assumption was based on the appearance of an absorption band at 1895 cm^{-1}, in the IR spectrum, which was characteristic of an intermediate having a cumulene structure.[83]



Similar results were obtained for the photolysis of 3- and 4-substituted phenyl azides.[84] The participation of didehydroazepines and/or azirines in the photochemical conversions of aryl azides had already been suggested on the evidence of product analyses for photolytic reactions in the presence of amines (primary and secondary)[10,85–87] or other nucleophiles.[10,88–91]

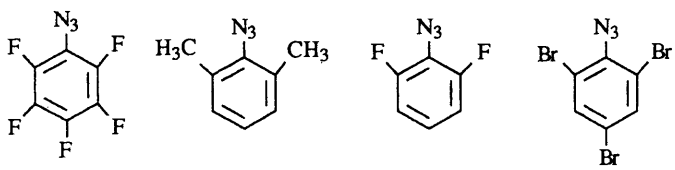
Table 6. Electronic absorption spectra for triplet aromatic nitrenes (^{3}RN) in EPA [22] and ethanol[23] at 77 K.

R	λ_{max}(lg ε, l.mol^{-1} s^{-1})	Refs.
Phenyl	241(3.7), 303(2.8), 368(2.5)	[22]
	243(3.93), 304(3.34), 383(2.93)	[23]
p-Tolyl	250(4.06), 315(3.75), 385(3.04)	—
p-Aminophenyl	309(4.03), 356(3.32), 437(3.48)	—
p-Methoxyphenyl	271(4.21), 330(3.88), 388(3.34)	—
p-Nitrophenyl	312(4.14), 380(2.85), 500(2.57)	—
p-Acetylphenyl	276(4.21), 410(2.94), 508(2.62)	—
p-Biphenylyl	320(4.24), 478(3.04)	—
Mesityl	255(3.7), 320(3.4), 391(2.4)	[22]
m-Biphenylyl	242(4.8), 330(3.5), 393(3.1)	—
o-Biphenylyl	343(3.7), 373(3.0)	—
1-Naphthyl	223(4.5), 321(4.0), 536(3.2)	—
3-Quinolyl	390(3.4), 550(2.3)	[22]
1-Anthryl	240(5.3), 448(4.1), 697(3.2)	—

According to IR spectroscopic data, neither didehydroazepine nor benzazirine intermediates are formed on irradiation of pentafluorophenyl azide[92] or 2,6-dimethylphenyl azide[93] in an argon or nitrogen matrix at 12 K. Here, triplet nitrenes are the key intermediates; however, prolonged irradiation of 2,6-dimethylphenyl azide affords only small amounts of didehydroazepine (ν = 1898 cm^{-1}), presumably as a result of secondary photolysis.[94] An ESR spectroscopy study indicated that irradiation of PhN_3 in an argon matrix at 12 K yields both 1,2-didehydroazepine and ^{3}PhN, while prolonged irradiation affords 2-pyridylmethylene.[94]

After the publications of Chapman et al.[83,94] and Dunkin et al.,[84] some doubts were raised about the authors interpretation of the electronic absorption spectra of azides recorded at 77 K in a glass matrix.[15,16] As a consequence, Platz et al. reproduced the earlier results of low-temperature photolysis (77 K) of PhN_3 and some of its derivatives.[16,95] In this context, low-temperature UV spectra were recorded, and an analysis was made of the product obtained on warming the photolysate to room temperature. The temperature of the photolyses was in the range from room temperature to 77 K. Platz found that, on irradiation of PhN_3 in diethylaniline, the yield of 3*H*-azepine fell from 80% at 273 K to 3% at 153 K and to 0% at 77 K.[95] Irradiation of PhN_3 at 77 K afforded azobenzene and aniline,[95] both of which would be anticipated if photolysis proceeds through triplet nitrenes.[10] There is also reference to the absorption spectra of the products obtained by photolysis of PhN_3 and azides (I–IV) at 77 K, as well as fluorescence spectra and excitation

fluoresecence spectra of the products obtained by photolysis of PhN_3 and azides (I) and (II).[16]



(I) (II) (III) (IV)

The similarity between the absorption spectra and the excitation spectra confirms that the same species is formed.[16] An analysis of results obtained by flash photolysis of PhN_3 in the presence of DEA in a wide temperature interval, [16] as well as the data obtained by Leyva et al.,[95] indicate that the efficiency of didehydroazepine formation decreases as the temperature is reduced, and that ^{3}PhN is the principal species formed on photolysis of PhN_3 at 77 K in a glass matrix.[16] Thus, the electronic spectroscopic interpretations made by Reiser and others are correct.[22–24,40,70–72] (see Table 6).

It should be pointed out that triplet aromatic nitrenes are unstable on prolonged irradiation at 77 K,[16,22,23,79,96,97] which may be associated with the formation of an aniline-solvent radical pair. Recombination of the latter in the gaseous state leads to a substituted amine.[23,96,97] Prolonged photolysis of ^{3}PhN leads to the formation of didehydroazepine.[16] The photochemical reactions of triplet nitrenes also complicate the interpretation of their absorption spectra and make it difficult to determine extinction coefficients (Table 6).

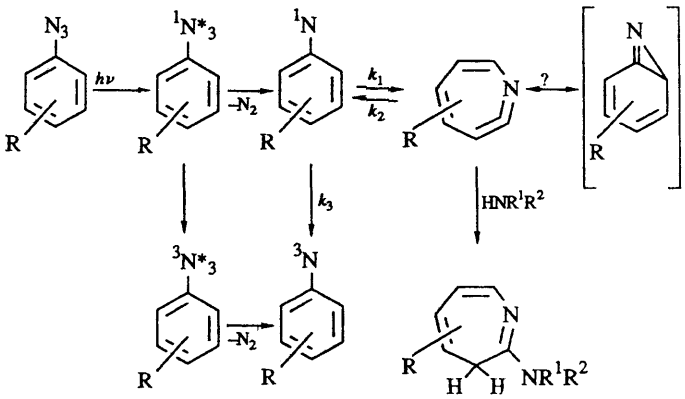
In order to explain why the products obtained by photolysis of aromatic azides at 10 K in an inert gas matrix are different from those obtained in a glass matrix at 77 K, Platz et al.,[16] advanced the hypothesis that at 10 K, in an inert gas matrix, secondary photolysis of the triplet nitrenes takes place to give a didehydroazepine; it is also considered that high-temperature chemistry is manifested in locally heated areas. In recent work, it has been shown that ^{3}PhN is the principal product obtained by photolysis of PhN_3 in a hydrocarbon glass matrix (3-methylbutane at 45 K) and in an inert gas matrix (N_2 or Ar at 12 K).[98] Didehydroazepine has even been detected as the primary species formed on photolysis of ^{3}PhN.[83,84] Hayes et al. argued that didehydroazepine, which had always been formed in small amounts (~20%) on photolysis of ^{3}PhN in a number of matrices, is the result of isomerisation of a vibrationally- or electronically-excited singlet nitrene state, ^{1}PhN.[98]

At present, there are around 20 publications devoted to systematic kinetic studies of the photo-reactions of aryl azides.[12–17,27,32,34,36,42,53,70,82,99–107] In the majority of these, electronic absorption spectra of intermediates were recorded, and, in two instances,[12,13] IR absorption data for the intermediates are available. Essentially, the electronic spectra of the intermediates were interpreted in terms of triplet aromatic nitrene absorption because of the similarity with the absorption spectra of the products obtained by low-temperature photolysis.[36,42,70,99–101]

Flash photolysis of PhN_3 [13,15,16,102,106] and certain of its derivatives[12–14,16,32,102,104–107] has been widely reported. In an early study of azide photolysis in the presence of amines, only the absorption of 1*H*-azepine was detected.[102] Later, the absorption of an intermediate, presumed to be ^{3}PhN, was detected in the absence of an amine.[82,105] However, this was subsequently disputed.[15] A detailed comparison of the absorption spectrum of ^{3}PhN at 77 K with that of the intermediate formed at room temperature showed that the similarity was far from exact. For example, the well-defined splitting in the spectrum of ^{3}PhN with maxima at 490, 382 and 303 nm was absent in the absorption spectrum of the intermediate, which exhibited a broad, poorly-defined band with a maximum at ~350 nm.[16] Only with compound (IV) was there a complete superposition of the spectrum obtained by flash photolysis with that obtained at low temperature. The spectra of compounds (I) and (III) were consistent with absorption of triplet nitrenes, exhibiting a poorly-defined maximum in the region ~340–350 nm.[16] A similar low-intensity absorption in the region 320–380 nm was registered for PhN_3 (λ_{max} ~ 340 nm) [15] and for *p*-dimethylaminophenyl azide (λ_{max} ~ 360 nm).[12] On pulsed excitation of 4,4′-diazidobiphenyl in cyclohexane, an intermediate absorption with λ_{max} = 380 nm ($\Delta\lambda$ = 50 nm) and a life-time of 19 ± 2 ns was detected.[107] This was assigned to a singlet intermediate (a singlet mononitrene or a didehydroazepine).[107]

The IR spectroscopic absorption at 1887 cm^{-1} (and that at 1877 cm^{-1} for the ^{15}N isotope), registered during the photolysis of PhN_3 and its derivatives, provided further evidence that reaction proceeds via didehydroazepines (azacycloheptatetraenes), formed by dehydrogenation of the corresponding 1*H*-azepine;[12,13] this was also consistent with product analyses from photolyses in the presence of amines. The IR spectra of intermediates obtained by pulsed excitation of PhN_3 and its derivatives did not exhibit absorption corresponding to benzazirines. Thus, the following scheme may be proposed for the photolysis of PhN_3 and its derivatives:[10,12–16,40]

Scheme 1



b) Spectral characteristics of intermediates

The electronic spectra absorptions of ^{3}PhN and its derivatives are given in Table 6.[22,23] The data relate only to $\pi\pi^*$-transitions. There is a long-wavelength absorption for ^{3}PhN, but it does not correspond with a specific transition.[23] The absorptions for ^{3}PhN and its derivatives were recorded with the following characteristics: $\lambda_{max} \approx 500$ ($\lg\varepsilon \sim 2.5$); ~400 (~3); ~320 (~3.5), and ~240 nm ($\lg\varepsilon \approx 4$).[16] It is considered that the long-wavelength absorption of ^{3}PhN (λ_{oo} = 489 nm) corresponds with transitions of the type $n_y \rightarrow \pi^*$ and $\pi \rightarrow n_y$, while $\pi\pi^*$ transitions are primarily responsible for the other absorptions. It is possible that the first absorption peak is due, in part, to a transition of the type $n_z \rightarrow n_y$.

Luminescence is characteristic of triplet aromatic nitrenes which possess neutral or donor substituents. This has been classified as $T_1 \rightarrow T_0$ fluorescence.[16,23,42,108] The fluorescence quantum yield for *p*-tolylnitrene is 0.01 ± 0.02 [24] and for *p*-aminophenylnitrene it is 0.10 ± 0.02.[34]

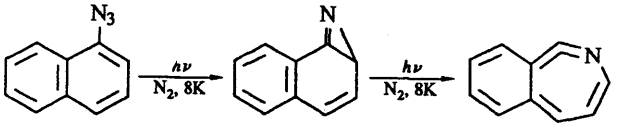
The absorption spectrum of ^{1}PhN is unknown at present. It cannot be ruled out that the broad absorption in the region 400–480 nm, obtained on flash photolysis of *p*-dimethylaminophenyl azide, is due to the presence of singlet *p*-dimethylaminophenylnitrene.[14] It is not clear which singlet species (a didehydroazepine or a singlet mononitrene) is responsible for the absorption at λ_{nm} = 380 nm, recorded on impulse excitation of 4,4′-diazidobiphenyl.[107]

The IR spectra of didehydroazepines (azacycloheptatetraenes) are characterised by absorption with $\nu_{max} \sim 1990$ cm^{-1}; there is also weak, poorly-defined, absorption in the near UV region with a maximum at 340–360 nm. 1*H*-Azepines—the products obtained by addition of primary and secondary amines to didehydroazepines—show significantly higher absorption in this region ($\lambda_{max} \approx 360$ nm). 3*H*-Azepines, formed by subsequent photo-conversion of 1*H*-azepines, absorb in a shorter wavlength region.[15,102]

c. Photolysis of polynuclear aromatic azides

Annelation of azidobenzenes to other aromatic ring systems has a profound effect on the chemical behaviour of the intermediate nitrenes and other species obtained on photolysis.[10] Thus, contrasting with the photolytic behaviour of PhN_3 and its derivatives, the photolysis of polynuclear aromatic azides in the presence of primary and secondary amines leads to aromatic dialkylamines rather than 3*H*-azepines.[10,53,109–111] These products would be anticipated for photolysis via azirines.

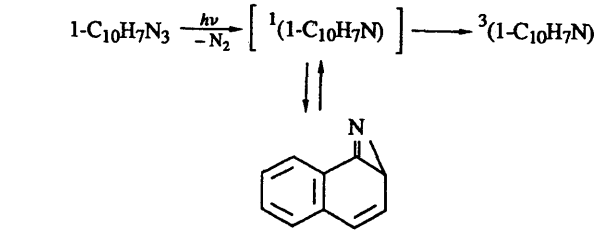
The IR spectra of the products obtained by irradiation of 1- and 2-naphthyl azide in an argon or N_2 matrix at 8 K are characterised by a cluster of absorption bands (typical of tricyclic azirines (1708–1736 cm^{-1}).[112] On prolonged irradiation they disappear and are replaced by a new cluster of bands (1910–1930 cm^{-1}) which possibly correspond to the intermediate didehydroazepines:



However, triplet ^{3}(1-$C_{10}H_7N$) is formed on irradiation of 1-$C_{10}H_7N_3$ in a glass matrix at 77 K.[113]

There are only a few references to flash photolysis of polycondensed azides.[36,42,53,70] Reiser et al. were first to record the absorption of intermediates obtained on flash photolysis of 1-azidonaphthalene and 1-azidoanthracene, and concluded that triplet nitrenes were responsible.[36] Sumitani et al. showed that excitation of 1-azidopyrene using a laser pulse of less than 15 ns produces a species with an absorption maximum in the region 455 n.[42] This was supported later by Schrock et al.[53] After a period of 22 ns at room temperature and 34 ns at 77 K, this species is converted into another with a maximum at 420 nm.[42,53] The latter species was also formed on triplet sensitisation and had an absorption spectrum identical to that of ^{3}(1-PyN) at 77 K. Under the conditions of laser excitation it disappeared in a second-order process to give 1,1′-azopyrene. The Japanese authors assigned the absorption maximm at 420 nm to ^{3}(1-PyN), and that in the region of 455 nm to ^{1}(1-PyN).[42] However, Schrock et al. did not exclude the possibility that the latter absorption was due to the corresponding azirine.[53]

The photolysis of 1-azidonaphthalenes in benzene leads to the formation of 1,1′-azonaphthalene, but in diethylamine a significant amount of 1-aminonaphthalene is formed.[53,109] No absorption was detected in the region 350–650 nm directly after 13 ns laser impulse excitation at this azide in benzene. However, the intensity of the absorption in the near UV region, with a maximum at 370 nm, increased exponentially with time over a period of 2.8 ± 0.2 μs. The species absorbing at 370 nm would appear to be ^{3}(1-$C_{10}H_7N$). It disappeared in a second-order process to give 1,1′-azonaphthalene. The precursor of ^{3}(1-$C_{10}H_7N$), having a lifetime of 2.8 μs, is presumed to be an azirine.[53]

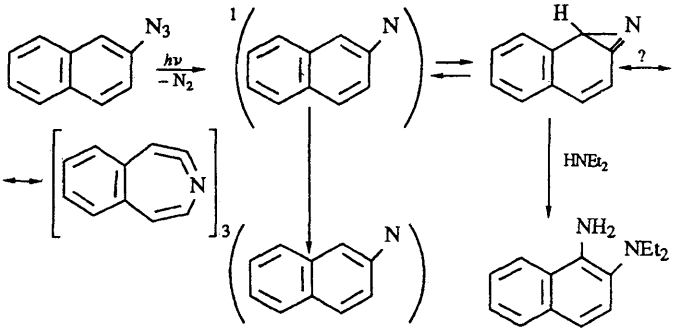


Azo compounds were isolated on irradiation of 2-azidonaphthalene and 2-azidopyrene in benzene, whereas, in the presence of diethylamine, the products were 2-diethylamino-1-naphthylamine and 2-diethylamino-1-pyrenylamine, respectively.[53,113] The triplet-sensitised photolysis of 2-$C_{10}H_7N_3$ in the presence of diethylamine does not lead to the formation of diamines.[53] There was absorption in the region 350–650 nm immediately after laser excitation of 2-$C_{10}H_7N_3$. Then, with a time frame of ~1 ms, azonaphthalene was formed in a second-order process. In the presence of benzophenone as triplet sensitiser, ^{3}(2-$C_{10}H_7N$) was formed with an absorption maximum in the near UV region at 365 nm. This disappeared in a second-order process, more rapidly by direct photolysis, to give azonaphthalene.[53] No novel intermediate species were detected in the presence of diethylamine. However, the yield of azonaphthalene was much lower. The differences in the photochemical behaviour of 1- and 2-azidonaphthalene are evidently associated with the fact that the life-time of the azirine intermediate is significantly longer in the latter case.[53]

After laser pulse irradiation of 2-azidopyrene, an absorption was detected with a maximum at 420 nm, this being assigned to ^{3}(2-PyN_3). The same absorption was evident in diethylamine as solvent. This disappeared after 2.5 μs with the formation of 2-diethylamino-1-pyrenylamine, absorbing in the region 445 nm. Schuster et al. proposed that the conversion of singlet 2-PyN to the triplet form was reversible.[53]

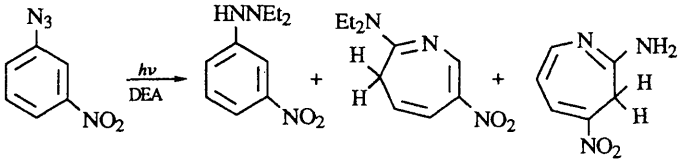
The primary processes involved in the photolysis of polycondensed azides are exemplified by the photo-conversion of 2-azidonaphthalene, as shown below:

Scheme 2

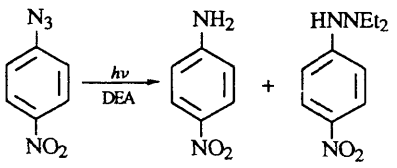


IV. The reactivity of intermediate singlet species

Singlet aromatic nitrenes are not dispersed to insert into C–H bonds or add across double bonds.[10] Compounds which, formally, are products of C–H bond insertion are often obtained as a result of cleavage of hydrogen by triplet nitrenes.[114,115] There are several references to N–H insertion by singlet arylnitrenes having acceptor substituents.[32,116–118] Thus, hydrazine compounds are formed together with 3*H*-azepines by irradiation of 4-cyanophenyl azide in dimethylamine[116,117] and of 3-nitrophenyl azide in diethylamine:[118]



Furthermore, irradiation of 4-nitrophenyl azide in diethylamine affords a mixture of 4-nitroaniline and *N*-(4-nitrophenyl)-*N'*,*N'*-diethylhydrazine (9%):[32]



The yield of the hyrazine falls significantly on triplet sensitisation,[117] and the variation in the yield of hydrazine and azepines,[116,117] or aniline and hydrazine,[32] as a function of the concentration of amine confirms the fact that a singlet nitrene is the precursor of the hydrazine.

1. Isomerisation of singlet aromatic nitrenes

Isomerisation into didehydroazepines (Scheme 1) or into tricyclic azirines (Scheme 2) are the most characteristic reaction of singlet aromatic nitrenes. It is known that these isomerisations take place within 10 ns (the period of the laser pulse).[12–16] The isomerisation is activated thermally, the rate constant for the isomerisation of ^{1}PhN at room temperature being approximately $10^{11\pm1}$ s^{-1}.[16] 3*H*-Azepines were not formed on irradiation of the following aromatic azides in the presence of amines: *p*-nitro=, *o*- and *p*-cyano-, *o*-chloro-, *p*-amino- and *p*-dimethylaminophenyl azide.[10,13,32,119,120]

In contrast to the above-mentioned azides, PhN_3 and the majority of its derivatives are converted into 3*H*-azepines in high yield in the presence of amines.[10,13] The efficiency of formation of the intermediate didehydroazepines was assessed from IR absorption in the region 1887 cm^{-1} relative to that obtained for *p*-chlorophenyl azide[13] (Table 7).

The effect of a heavy halogen atom (Cl, Br, I) on the yield of didehydroazepine is thought to be associated with enhancement of inter-system crossing (ISC) into the initial azide.[13] In our opinion, introduction of a nitro group into the 3- and 4-position of the azidoarene ring has a significant effect on ISC into the azide and is responsible for the low yield of didehydroazepine. With 2-dimethylaminophenyl azide, the efficiency of isomerisation is assumed to be low, as is confirmed by MDNO calculations for the potential barrier to reaction.[13]

Table 7. Relative values for the optical density of the IR absorption of intermediates at 1887 cm^{-1} (ΔD_{rel}) on impulse excitation of para-substituted phenyl azides (p-$XC_6H_4N_3$), and the values of rate constant (k_4) for the reaction of 5-substituted 1,2-didehydroazepines with diethylamine in cyclohexane.[13]

X	ΔD_{rel}	k_4, l.mol^{-1} s^{-1}
H	0.83	$6.5 \cdot 10^6$
Ph		$3.6 \cdot 10^5$ ($1.4 \cdot 10^4$)*
SMe		$1.6 \cdot 10^5$
OMe	0.48	$2.5 \cdot 10^4$
CO_2H		$3.0 \cdot 10^7$
$CONMe_2$		$4.4 \cdot 10^7$
COMe		$2.8 \cdot 10^8$
NO_2	< 0.05 (0.12**)	
Cl	1.00	$1.3 \cdot 10^8$
Br	1.14	$1.7 \cdot 10^8$
I	0.22	$2.7 \cdot 10^8$

* The rate constant for the reaction of *N*,*N*-diisopropylamine.
** ΔD_{rel} for X = *m*-NO_2.

Table 8. Activation parameters for the effective rate constant $\tilde{k}$ for the conversion of 5-methyl-1,2-didehydroazepine into triplet tolynitrene.[17,25]

Solvent	$\tilde{k}$ (298 K), s^{-1}	lg $\tilde{k}_0$, s^{-1}	E_{act}, kcal/mol
Hexane	92	9.5±0.2	10.3±0.4
Acetonitrile	$8 \cdot 10^2$	9.6±0.2	9.1±0.3
Ethanol	$5 \cdot 10^3$	8.0±0.1	5.9±0.2

2. Reactions of 1,2-didehydroazepines

It has been shown that the rate of 1,2-didehydroazepine conversion increases with the concentration of PhN_3, the pseudo-first-order rate constant being linearly proportional to the concentration.[13] The bimolecular rate constant for the reaction of didehydroazepine with PhN_3 in heptane at room temperature is 7.5×10^4 l/mol/s.[13] Evidently, this reaction leads to the formation of unidentified polymeric products on both photolysis and thermolysis of PhN_3 as well as its derivatives.[10] The reaction of didehydroazepines with azides may lead to an increase in the quantum yield of azide photolysis as the concentration is increased.[29–31]

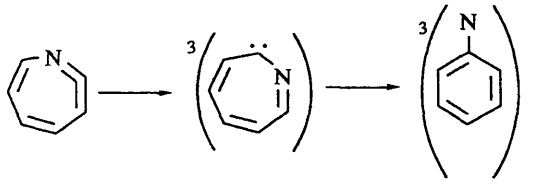
On extrapolation to zero concentration of the azide, the life-time of 1,2-didehydroazepine in heptane at room temperature was found to be 4.8 ms.[13] The life-time (τ) of the 1,2-didehydroazepine formed on impulse photolysis of *p*-tolyl azide was measured in different solvents in the temperature range to 13–60 °C.[17,25] This study of *p*-tolyl azide was undertaken at very low concentration ($< 5 \times 10^{-5}$ M) so that its reaction with the intermediate didehydroazepine does not make a contribution to the measured life-time. The

activation parameters ($\tilde{k}_0$ and E) relating to the effective rate constant for the irreversible conversion of the didehydroazepine into triplet nitene ($\tilde{k} = 1/\tau$) are given in Table 8. The effective constant $\tilde{k}$ is expressed in terms of the rate constants for the individual steps (see Scheme 1) as follows:

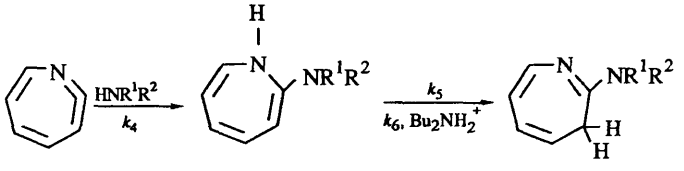
$$\tilde{k} = k_3k_2/(k_1 + k_3) \approx k_3k_2/k_1. \quad (9)$$

Since the rate constant for ISC (k_3) does not normally depend on the temperature, the value of E will equate to the enthalpy of isomerisation of *p*-tolylnitrene into the corresponding didehydroazepine. On conducting the reaction in ethanol, since it was not established whether the didehydroazepine reacts with ethanol under these conditions, it cannot be excluded that the decrease in the value of E is associated with the occurrence of this side-reaction.

Constrasting with the outlined scheme for the irreversible conversion of 1,2-didehydroazepines into triplet nitrenes via singlet nitrenes (Scheme 1),[9,16] an alternative pathway has been proposed on the basis of MNDO calculations:[13]



The reaction of didehydroazepines with amines leads to 1*H*-azepine derivatives which then isomerise into stable 3*H*-azepine derivates.[12,13,15,88,102]



The 1*H*-azepines obtained from a number of ortho-substituted phenyl azides are relatively stable, and their formation has been detected by NMR spectroscopy.[88]

The nature of the solvent and substitution of the phenyl ring affects the rate of formation of 1*H*-azepines (Table 9).[102] When the concentration of the amine is above 3 M the rate of formation of 1*H*-azepine becomes independent of the concentration and nature of the amine.[15] The negative activation energy (Table 9) and the non-linear dependence of the rate on the concentration of amine would suggest that the reaction with amines involves two intermediates.[102]

The rate constant k_4 has been determined by measuring the rate of disappearance of the IR absorption for the intermediate didehydroazepines.[13] It was found that the value of k_4 changes by more than two orders of magnitude on varying the substituent in the 5-position of the 1,2-didehydroazepine (see Table 7) and increases with the electron-accepting properties of the substituent. A reasonable linear dependence (Hammett plot) was found for $\lg k_4$ against the σ-substituent constant.[13]

The rate of isomerisation of 1*H*-azepines to the corresponding stable 3*H*-azepine does not depend on the concentration of the amine and increases significantly in the presence of dibutylammonium ion.[102] The activation parameters relating to the rate constants for the monomolecular and $Bu_2NH_2^+$-catalysed isomerisation of 1*H*-azepines to 3*H*-azepines are given in Table 10.

Table 9. Activation parameters and values of the rate constant for the reaction of didehydroazepines (formed on impulse excitation of derivatives of PhN_3) with dibutylamine (k_4); and the values of the rate constants for the unimolecular (k_5) and $Bu_2NH_2^+$-catalysed (k_6) isomerisation of 1*H*-azepines into 3*H*-azepines in acetonitrile at 21.7 ± 0.3 °C.[102]

Substituent in phenylazide	k_4, l.mol^{-1} s^{-1}	k_4^2, l.mol^{-1} s^{-1}	E_4, kcal/mol	$-k_5$, s^{-1}	k_6, l.mol^{-1} s^{-1}
H	$3.5 \cdot 10^7$			11	$3.1 \cdot 10^6$
H*	$9.7 \cdot 10^5$	$(4.2\pm1.4) \cdot 10^4$	−1.8±0.2	0.11	
o-Me	$7.5 \cdot 10^4$	$(5.9\pm1.3) \cdot 10^5$	1.1±0.2	$\sim 10^{-4}$**	72
o-Et	$2.9 \cdot 10^4$			$\sim 10^{-4}$**	
o-CF_3	$7.8 \cdot 10^8$			$\sim 2 \cdot 10^{-3}$	250
p-Me***	$1.6 \cdot 10^6$				

* The value of k and E in hexane.

** k_5 measured in dioxane.

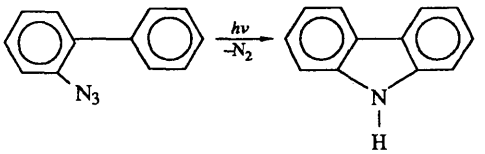
*** The rate constant refers to the reaction with tert-$BuNH_2$ in ethanol.[17]

Table 10. Activation parameters for the rate constants for the monomolecular (k_5) and $Bu_2NH_2^+$-catalysed (k_6) isomerisation of 1*H*-azepines into 3*H*-azepines.[102]

Azide	Solvent	k_5^2, s^{-1}	E_5, kcal/mol	k_6^2, l.mol^{-1} s^{-1}	E_6, kcal/mol
Phenyl azide	hexane	0.7±0.3	1.1±0.4		
	acetonitrile	$(4.2\pm1.0) \cdot 10^2$	2.0±0.2	$(3.8\pm0.7) \cdot 10^8$	2.6±0.2
o-Tolylazide	acetonitrile			$(5.5\pm0.8) \cdot 10^9$	9.9±0.5

3. Cyclisation of ortho-substituted aromatic azides

A large number of photochemical and thermal cyclisation of ortho-substituted aryl azides are known.[10] Only the photochemical cyclisation of *o*-azidobiphenyl (*o*-AB) to carbazole will be examined in this review.



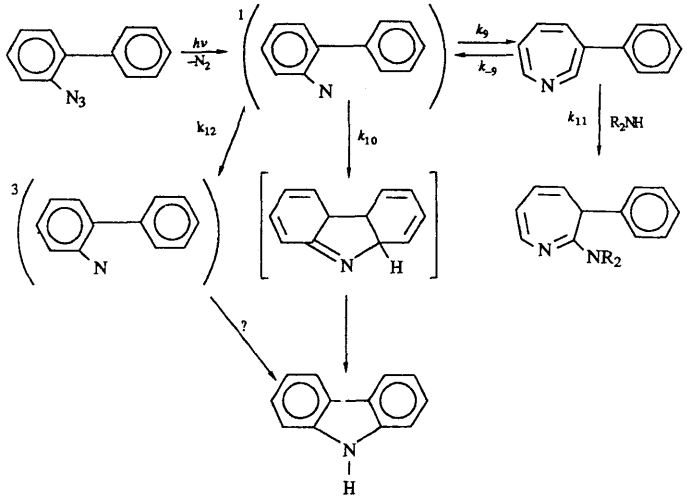
Swenton et al. isolated carbazole (68−74%) and 2,2′-azobiphenyl (8−12%) as a result of photolysis of *o*-AB at a concentration of 10^{-2} M.[52] Triplet quenchers (dienes, pyrene, oxygen) decreased, and triplet sensitisers (benzophenone, acetophenone) increased, the yield

of the azo compound (to 39–49%).[52] A 3*H*-azepine was obtained in addition to carbazole on irradiating *o*-AB in the presence of diethylamine.[101,103,121] The yield of carbazole derivatives was significant on photolysis of *o*-AB and its 2′,3′-disubstituted analogues, even in pure diethylamine (49% for *o*-AB). As the concentration of diethylamine increases the relative proportion of carbazole and 3*H*-azepine begins to fall and then remains sensibly constant.[103]

A kinetic study has been made of carbazole formation (λ_{max} = 289 nm) and of the decay of the intermediate (absorbing at λ_{max} = 342 nm), assumed by the authors to be a triplet nitrene.[100] The rate constant for carbazole formation (k_7) and decay of the intermediate (k_8) in cyclohexane agreed with a factor of 2. On this basis, the authors concluded that a triplet nitrene was a precursor of the carbazole.[100] Later, Sundberg reproduced the results and found that the rate constants k_7 and k_8 in hexane differed by a factor of 2, whereas in other solvents the difference was two orders of magnitude.[101] The intermediate formed during the course of the reaction was not converted into carbazole in significant amount. A kinetic study of the photolysis of 2′,4′,6′-trideuterio-3′,5′-dimethyl- and 3′,5′-bis(trifluoromethyl)-derivatives of *o*-AB (Table 11) has also been undertaken, as a result of which three hypothetical mechanisms were proposed for the formation of carbazole.[101]

The following mechanism for carbazole formation (Scheme 3) may be proposed on the basis of the results obtained for the photolysis of *o*-AB,[52,101,103,121,122] with reference to the conversions of other aryl azides (Scheme 3):

Scheme 3



The reactions of triplet nitrene may lead to the formation of azo compounds.[52] However, it cannot be excluded that a small amount of carbazole is also formed via these species.

The effective rate constant k_7, assuming that k_{12} is negligible, is given by Eqn. (10):

$$k_7 = k_{10}k_{-9}/(k_9 + k_{10}). \quad (10)$$

In the presence of an amine the proportion of carbazole can be expressed by the ratio:

$$\Phi_{min} = k_{10}/(k_{10} + k_9).$$

For *o*-AB, $\Phi_{min} \approx 0.5$, so that $k_{10} \approx k_9$. The activation energy for carbazole formation is evidently close in value to the enthalpy of isomerisation of the intermediate singlet nitrene to didehydroazepine. In cyclohexane, the calculated value of the activation energy (11.5 kcal/mol [100]) is close to the value of that relating to the rate constant ($\tilde{k}$) for the conversion of 5-methyl-1,2-didehydroazepine to triplet tolylnitrene (10.3 kcal/mol [17,25]). The increase in k_7 on passing from hexane to acetonitrile and methanol (see Table 11) coincides with a similar variation in the value of $\tilde{k}$ (see Table 8). The proposed mechanism outlined in Scheme 3 is in reasonable accord with experimental findings, but the nature of the intermediate absorbing in the region $\lambda_{max} \approx 340$ nm has not been established.

Table 11. The values of the effective rate constant for the formation of carbazole (k_7) and the decay of the intermediate (k_8) for the reaction of *o*-azidobiphenyl and its derivatives at 20 ± 1 °C.[101]

Substituent	Solvent	k_7, s^{-1}	k_8, s^{-1}
H	hexane	980	490
	cyclohexane	960*	—
	THF	$5.0 \cdot 10^3$	27
	acetonitrile	$9.8 \cdot 10^3$	—
	methanol	$19.6 \cdot 10^3$	9.9
2,4,6-D_3	cyclohexane	$1.0 \cdot 10^3$*	260*
	THF	$4.9 \cdot 10^3$	11.3
3,5-Me_2	hexane	$1.3 \cdot 10^3$	390
	THF	$6.7 \cdot 10^3$	12.4
	acetonitrile	$7.5 \cdot 10^3$	12.6
3,5-$(CF_3)_2$	hexane	140	~140
	THF	830	—
	acetonitrile	$1.6 \cdot 10^3$	—

* Value at 18 °C.

V. Reactions of triplet aromatic nitrenes

1. Formation of azo compounds

There are two mechanisms by which azo compounds are formed.[32,36,53,70,106]

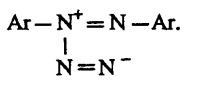
$$^3ArN + Ar'N_3 \xrightarrow{k_{13}} [ArN_4Ar'] \rightarrow ArN{=}NAr' + N_2, \quad (11)$$

$$^3ArN + {}^3ArN \xrightarrow{k_{14}} ArN{=}NAr. \quad (12)$$

The existence of pathway (11) is substantiated by the formation of unsymmetrical azo compounds on irradiation of 1- or 2-azidonaphthalene in the presence of PhN_3.[53] However, no (4-nitrophenyl)azobenzene was detected on photolysis of *p*-nitrophenyl azide

in the presence of PhN_3.[32] Reaction (11) was observed on flash photolysis of 1-azidoanthracene (k_{13} = 0.5 × 10^9 l mol^{-1} s^{-1}) in ethanol.[36]

The yield of azonaphthalene, formed on irradiation of 1-azidonaphthalene with a non-laser source, increases after a few hours in the dark from 22 to 46% (for 2-azidonaphthalene, the increase is from 22 to 45%).[53] This confirms the existence of a relatively stable intermediate adduct. A tetrazene structure, Ar–N=N–N=N–Ar, has been proposed for this compound.[53] It is also possible that it has a 1,2-tetrazene structure:[9,10]



The yield of azobenzene from PhN_3 does not increase when irradiation has been ceased.[15]

The rate of reaction (12) is controlled by diffusion,[36] the approximate value of the rate constant k_{14} being just under the theoretical limit for a diffusion-controlled process (Table 12).

Table 12. Values for the rate constant for recombination (k_{14}) of triplet aromatic nitrenes (^{3}ArN).

Ar	Solvent	$k_{14}.10^{-9}$, l.mol^{-1} s^{-1}	Refs.
1-Naphthyl	hexane	0.55±0.05	[36]
	benzene	0.45	—
	ethanol	0.40	—
	liq. paraffin	0.09	—
1-Pyrenyl	benzene	2.1±0.2	[70]
4-Nitrophenyl	"	1.0	[32]

A third pathway for the formation of azo compounds was examined in Smith's review:[9] dimerisation of aminyl radicals formed by abstraction of an atom of hydrogen from the solvent, substrate or product by a triplet nitrene, followed by dehydrogenation of the resulting hydrazo compound.

2. Abstraction of a hydrogen atom

Amines are often formed together with azo compounds via triplet aromatic nitrenes.[10,36]

$$^3ArN + RH \xrightarrow{k_{15}} Ar\dot{N}H + \dot{R}, \quad (13)$$

$$Ar\dot{N}H + \dot{R} \rightarrow ArNHR, \quad (14)$$

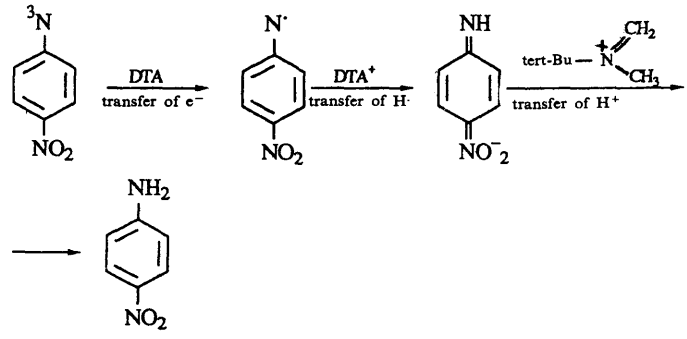
$$Ar\dot{N}H + RH \rightarrow ArNH_2 + \dot{R}. \quad (15)$$

Reaction (13) does not compete with reaction (12) on pulsed irradiation, so that the amount of information on this step is limited. The value of the rate constants for the abstraction of hydrogen from hexane by triplet ^{3}(1-$C_{10}H_7N$) and from ethanol by 4,4′-dinitrobiphenyl† have been evaluated at 2.6 × 10^2 l/mol/s.[36] It is thought that abstraction of hydrogen from the aromatic ring of the azide or the nitrene leads to a polymeric product.[36]

The contribution of pathway (13) predominates in a polymeric matrix, under which conditions amines (principally primary amines) are the main product.

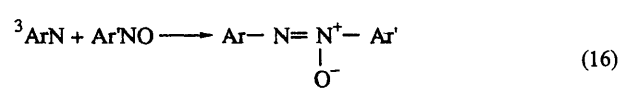
The kinetics of the decay of ^{3}ArN in polymeric matrices cannot be described by a simple kinetic equation.[36] The kinetic curves are characterised by three points in time: τ_0, the estimated time after which the curve starts to slope $\tau_{1/2}$, when the concentration of ^{3}ArN falls by half; and τ_1, the period of the entire process. Time $\tau_{1/2}$ varies between 10^{-3} s in weak polymeric matrices (polystyrene, plasticised toluene) to 0.1–2 s in hard polymeric matrices. The limiting factor in the reaction would appear to be the nature of the surroundings (configurational diffusion). Electron-accepting substituents increase the rate of hydrogen abstraction, the logarithm of the half-life time ($\lg\tau$) being −0.2 (for *p*-morpholinophenylnitrene), −0.8 (for 2,4,6-trimethylphenylnitrene), and −1.5 (for *p*-acetylphenylnitrene).[99]

An alternative pathway for the formation of amine has been proposed for the conversion of *p*-nitrophenyl azide in the presence of *N,N*-dimethyl-tert-butylamine (DTA):[32,106]



3. Photochemical oxidation of aromatic azides

Reiser et al. were first to study the reactions of triplet aromatic nitrenes with oxygen.[22] At 77 K, the reaction is limited by the mobility of oxygen and is associated with the formation of compounds absorbing in the region 400–650 nm. This disappears on thawing the matrix. For a long time, it was thought that nitro compounds were the principal oxygen-containing products formed on photolysis of aromatic azides.[69,70,104,123,124] However, azoxy compounds, arising by interaction of triplet nitrenes with nitroso compounds, have also been detected.[32,124,125]



(16)

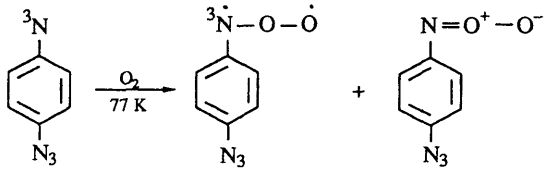
It has been shown that nitrobenzene ($PhNO_2$) is the main product from the oxidative photolysis of PhN_3 in acetonitrile at a high concentration of the azide (1.2 × 10^{-2} M). However, on decreasing the concentration to 10^{-4} M, nitrosobenzene (PhNO) becomes the sole product.[29] The authors propose that PhNO is the initial product, and that $PhNO_2$ is formed therefrom in a secondary photolytic process (a mechanism for formation of PhNO was not proposed).

Shortly after, it was demonstrated that irradiation of *p*-azidoaniline in oxygen-saturated aprotic solvents affords *p*-nitroso- and *p*-nitro-aniline.[126] However, the latter was not considered to arise

† According to Miura et al., pulsed excitation of 4,4′-diazidobiphenyl produces a triplet mononitrene.[107]

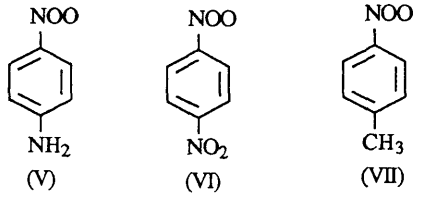
by secondary photolysis. A number of authors reported the simultaneous formation of nitro- and nitroso-compounds on photolysis of PhN_3 and its derivatives.[25,32–34,125] Sawaki et al. also argued that $PhNO_2$ was not formed by secondary photolysis of PhNO.[127]

It has been shown that triplet *p*-azidophenylnitrene reacts in a glass matrix at 77 K with dissolved oxygen to give two types of product: a paramagnetic compound, characterised by ESR spectroscopy (D = 0.11 cm^{-1}) as a triplet species; and a diamagnetic compound, absorbing intensely in the visible region (400–500 nm).[69] By analogy with carbene chemistry, it was proposed that these species are, respectively, a *p*-azidophenylaminodioxide biradical and a bipolar nitroso oxide.



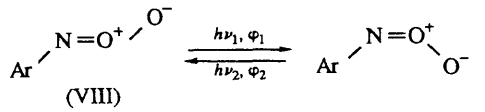
The formation of a paramagnetic adduct has also been recorded in the reaction of O_2 with 4,4′-dinitrenoazobenzene.[69] The reaction of ^{3}PhN and its *p*-nitro-, *p*-methoxy-, *p*-amino- and *p*-dimethylamino-derivatives with oxygen leads to coloured diamagnetic adducts, paramagnetic adducts not being recorded.[25,34,69] Evidently, the simultaneous formation of diamagnetic and paramagnetic adducts is more an exception than a rule.

Quantum chemical calculations by the AM1 method have shown that adducts (V–VII) can exist as two geometric isomers (*cis* and *trans*).[25]

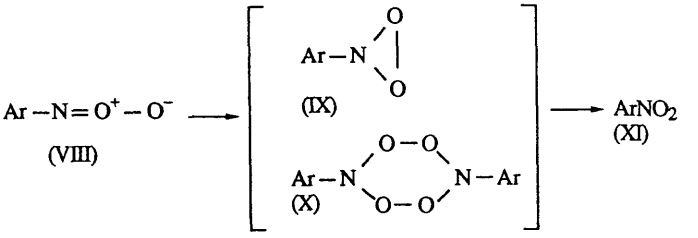


The *cis*-isomers exist principally in the singlet state (the triplet state being higher by 8–10 kcal/mol). Calculations for the *trans*-isomers point to effectively degenerate singlet and triplet states. Thus, diamagnetic and paramagnetic adducts not only have different electronic states, but also exist in isomeric forms. As a result, relaxation into the more stable adduct is not observed.[69]

Two diamagnetic adducts (λ_{max} = 495 and 588 nm), presumed to be *cis*- and *trans*-forms of (V), are produced by reaction of triplet *p*-aminophenylnitrene with O_2 at 95 K. The more stable form, absorbing at λ_{max} = 495 nm, is the sole product at 100 K. It is possible that a reversible equilibrium between the two forms is established on exposure to light ($\varphi_1 + \varphi_2 \sim 1$).[17,25]



In the thermal conversion of nitroso oxides, Brinen et al. proposed the intermediate formation of compounds (IX) or (X),[69] by analogy with carbene chemistry.[127,128]



In practice, warming compound (V) to 115 K produces a species exhibiting an absorption maximum in the region 336 nm (in methylcyclohexane) and at 318 nm (in toluene/THF). On freezing the matrix, *p*-nitro- (XII) and *p*-nitroso-aniline (XIII) are formed in comparable amounts.[17,25] The simultaneous formation of nitro and nitroso compounds would be consistent with the intermediate formation of compound (X).

Compound (V) has been detected at room temperature:

$$^3ArN + O_2 \xrightarrow{k_{16}} \underset{(V)}{ArNOO} \quad . \qquad (17)$$

$Ar = NH_2C_6H_4$.

By measuring the absorption against time, the kinetics of the decay of (V) was found to be of the second order [as would be anticipated if (X) is the initial reaction product]

$$(V) + (V) \xrightarrow{k_{17}} (X). \qquad (18)$$

In toluene, the rate constant k_{17} is (1.4 ± 0.4) × 10^9 l mol^{-1} s^{-1} and (0.72 ± 0.2) × 10^{10} l mol^{-1} s^{-1} in hexane.[34,130]

The dimeric peroxide (X) decomposes in two ways (Table 13):

$$(X) \xrightarrow{k_{18}} 2(XII), \qquad (19)$$

$$(X) \xrightarrow{k_{19}} 2(XIII) + O_2 \ . \qquad (20)$$

Table 13. Activation parameters for the rate constants for the formation of *p*-nitro- (k_{18}) and *p*-nitroso-aniline (k_{19}).[33,34]

Solvent	k_{18} (298 K), s^{-1}	$\lg k^{\circ}_{18}$	k_{19} (298 K), s^{-1}	$\lg k^{\circ}_{19}$	$E_{18} = E_{19}$, kJ/mol
Hexane	1.9	15.8±0.8	0.8	15.4±0.8	88.5±4.6
Toluene	0.8	12.9±0.6	1.0	13.1±0.6	74.5±3.8

Thus, the mechanism of the photo-conversion of *p*-azidoaniline (XIV) in the presence of O_2 can be described as follows:[17,33,34]

Scheme 4

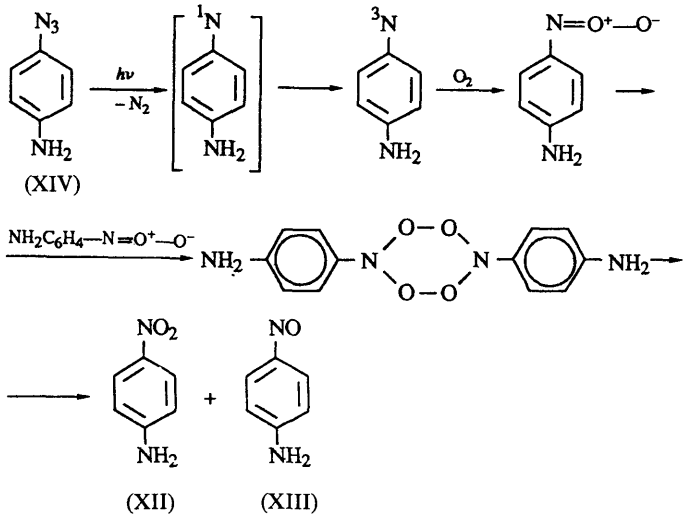


Table 14. Experimental and theoretical values for the long-wavelength maxima in the spectra of phenylnitroso oxide derivatives.[17,25]

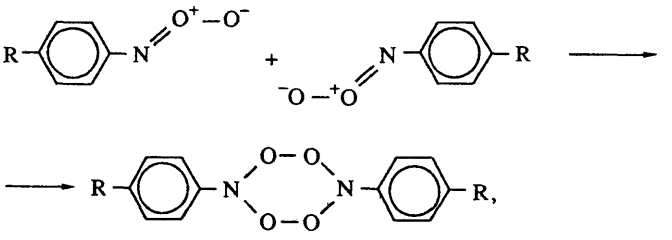
Substituent	λ_{max}^{exp} (77 K), nm	λ_{max}^{exp} (300 K), nm	λ_{max}^{theor}, nm	
			cis	*trans*
p-NH_2	495 and 588	440±5	406	430
p-NO_2	388	380±5	381	393
p-Me	400	395±5	393	415

Table 15. Values of the rate constants (k_{16}) for the reaction of triplet aromatic nitrenes (^{3}ArN) with oxygen.[17,25]

Ar	Solvent	*T*, K	$k_{16}.10^{-6}$, l.mol^{-1} s^{-1}
p-Aminophenyl	hexane	285	4.5±1.2
	toluene	—	8.0±2.0
p-Nitrophenyl	hexane	293	0.8±0.1
	ethanol	290	1.1±0.1
p-Tolyl*	acetonitrile	290	1.9±0.2
1-Pyrenyl**	benzene	—	0.9±0.1**

* The photolysis of *p*-tolyl azide was sensitised by benzophenone.
** The value of k_{16} was determined by Yamaoka et al.[70]

The formation of nitroso oxides has also been detected on low-temperature and flash photolysis of *p*-nitro- and *p*-methyl-phenyl azide (Table 14). However, intermediate species with structure (IX) and (X) were not evident. Kinetic data for the decomposition of (VII), based on absorption measurements, are in accord with a first order process, the rate constant being 0.2 s^{-1} in hexane at 20 °C. The kinetic curve for the decay of (VI) was not exponential, nor corresponded to a second order process ($\tau_{1/2} \approx 0.2$ s).[25] One may assume that the photo-conversion of *p*-nitro- and *p*-methyl-phenyl azide proceeds by a mechanism other than that described by Scheme 4, although the experimental observations are in accord with the process in outline. It is possible that the dimeric peroxide is formed by the cycloaddition of two *trans*-arylnitroso oxide molecules:



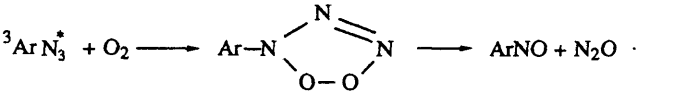
R = NO_2, Me.

The cyclodimerisation of *cis*-arylnitroso oxides would be sterically inhibited. Thus, it would appear that the adduct (V) is either formed in the *trans*-configuration or is readily converted into this form prior to dimerisation into (X) at a rate approximating to that of diffusion. If *cis*-(VI) and *cis*-(VII) are primary intermediates formed on reaction of *p*-nitro- and *p*-methyl-phenylnitrene, respectively, in the presence of oxygen, and if *cis*–*trans* isomerisation is a limiting step, then the decay of (VI) and (VII) would not follow second order kinetics.[25]

In order for reaction (17) to become dominant, a low concentration of azide and intermediate species is required. The desired conditions would also exist in polymeric matrices.[25,36,131–133] It has not been possible to detect reaction (17) on laser excitation in solution. Only the upper limit of the rate constant has been determined: $k_{16} \leqslant 10^6$ l mol^{-1} s^{-1} for 2,4,6-tribromophenylnitrene[16] and $k_{16} \leqslant 2 \times 10^5$ l mol^{-1} s^{-1} for *p*-nitrophenylnitrene.[32] The rate constants k_{16} obtained by flash photolysis are given in Table 15.[17,25,70] As can be seen, the values of k_{16} are significantly lower than that for a diffusion-controlled process and there is effectively no dependence on the nature of the aromatic nitrene. It should be noted that the rate constant for the reaction of oxygen with triplet carbenes[134–136] is significantly higher, being $(1-5) \times 10^9$ l mol^{-1} s^{-1} (1.9×10^8 l mol^{-1} s^{-1} for dimesitylcarbene[137]):

$$^3(R^1R^2C) + O_2 \rightarrow R^1R^2COO$$

A small propotion (~20%) of *p*-nitrosobenzene is formed without the involvement of triplet nitrenes, possibly by the route:[32,124]



Ar = $NO_2C_6H_4$. (21)

Recently, attempts were made to study the reactivity of PhNOO,[127] which, in the opinion of the authors, is a biradical. Irradiation of PhN_3 in the presence of diphenyl sulphide, diphenyl sulphoxide or *p*-chloronitrosobenzene results in oxidation of the additive. It is thought that oxidation takes place by interaction of the additive with PhNOO, as shown below with a nitrosoarene.

$$PhNOO + ArNO \longrightarrow Ph-\dot{N}-O-O-\underset{\underset{O\cdot}{|}}{N}-Ar \longrightarrow$$

$$\longrightarrow PhNO + ArNO_2 \qquad (22)$$

The following order of reactivity has been established

$$PhNO >> Ph_2S > Ph_2SO > PhH \quad \text{(Ref.127)}.$$

The observed increase in the yield of $PhNO_2$ on increasing the concentration of azide could be explained by the intervention of reaction (22).[29]

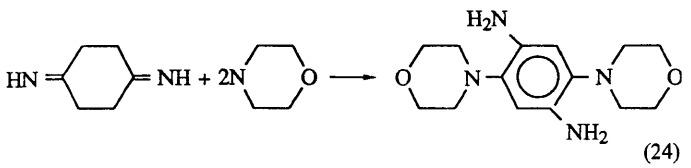
The photoconversion depicted in Scheme 4 proceeds only on irradiation of *p*-azidoaniline (XIV) in aprotic media. *p*-Benzoquinone diimine (XV) is formed on photolysis of (XIV) in water or in hexane containing an alcohol, amine, or a mercaptan at a concentration of 10^{-2} to 10^{-1} M. Presumably this takes place by the reaction:[25,120]



(23)

(XV)

Compound (XV) readily reacts with nucleophiles, as exemplified below.[120]



(24)

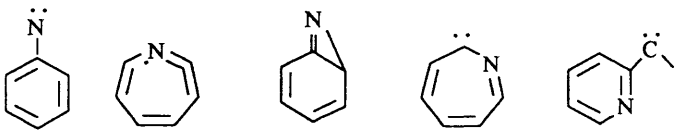
Derivatives of (XIV), e.g. nucleoside-5′-triphosphate γ-*p*-azidoanilides,[138,139] are used in the photo-affinity modification of proteins. It cannot be excluded that in such protein modification an intermediate *p*-benzoquinone diimine is implicated in a nucleophilic addition process.[140]

VI. Quantum chemical calculations on the properties of intermediates

The first quantum chemical calculations on the properties of triplet aromatic nitrenes were carried out by π-electron approximation.[44,81,141] Later, INDO calculations were made in order to interpret the ESR spectra of aromatic nitrenes.[48,50]

Information on the properties of singlet aromatic nitrenes is limited. From the photo-electron spectrum of the NH^- anion in the gas phase, a measurement was made of the splitting between the primary ($^3\Sigma^-$) state and the first excited ($^1\Delta$) state of nitrene itself (NH). This was found to be 34.6 ± 0.4 kcal/mol.[142] For a long time, it was only possible to deduce information on singlet-triplet splitting in PhN by quantum chemical calculations.[143] It was not until 1984 that experimental states of PhN in the gas phase (4.3 ± 0.4 and 8.8 ± 0.5 kcal/mol).[144,145]

Shillady et al.[143] applied the MINDO/2 method to calculate the geometry of all the possible intermediates in the photolysis and thermolysis of PhN_3:



(PhN) (A) (B) (C) (D)

The relative energies of these species were calculated by the MINDO/2 and INDO/P method (of Pople), and an assessment of the multi-configurational character of the electronic states of the intermediates was made by the INDO/P/INO method. The long-wavelength maxima in the spectrum of ^{3}PhN, as calculated by the INDO/S method, were assigned to $n_z \rightarrow \pi$ (380 nm) and $n_z \rightarrow n_y$ (330 nm) transitions,[143] although earlier it has been reported that the ^{3}PhN spectrum corresponds essentially to ππ*-type transitions. The long-wavelength transition with λ_{00} = 489 nm was not reproduced by calculation.

Table 16. Calculated values for the relative energy (E_{rel}) and absorption spectra of hypothetical intermediates from the photolysis of phenyl azide.[143]

Species	E_{rel}, kcal/mol			λ, nm (strength of the oscillator)
	MINDO/2	INDO/P	INDO/P/INO	
^{1}PhN	0	0	0	354(0.17), 307(0.03), 250(0.13)
^{3}PhN	—	-18.4	-15	380, 330, 297, 274, 222
^{1}A	6.9	—	—	—
^{1}B	-19	-68.2	-64.6	398(0.03), 313(0.02), 252(0.10)
^{3}B	—	11.3	—	382, 358, 315, 301, 284, 275
^{3}C	1.2	58.3	60.6	422(0.08), 354(0.10), 262(1.03)
^{1}D	6.3	—	—	—

It has been suggested that ^{1}PhN is formed in a configuration with seven π-electrons ($n_z^2 n_y^1 \pi^1$).[143] However, it is not known whether the singlet-triplet splitting (15–18 kcal/mol) corresponds essentially to this state or to a state with six π-electrons ($n_z^2 n_y^2$) (according to the INDO calculations of Pople et al.,[146] the latter is a lower singlet state). It has been calculated (Table 16)[143] that the bicyclic azirine (B) is a stable intermediate species, a fact which is not borne out experimentally.[12,13]

Schuster et al. calculated the heat of formation of all the considered intermediates by the MINDO method,[147] although the electronic configuration of ^{1}PhN was not specified. By comparison with other data,[17,25] it would appear that this configuration involves six π-electrons ($n_z^2 n_y^2$) (Table 17). According to these data[17,25] and the results obtained by *ab initio* 3−21G calculations,[145] the lower singlet state of ^{1}PhN is in the $n_z^2 n_y^1 \pi^1$ configuration. More detailed *ab initio* calculations on a broader basis are required in order to ascertain the exact electronic structure of singlet aromatic nitrenes.

Table 17. Results from calculations of the enthalpy of formation of intermediates (MNDO method).

Species	ΔH, kcal/mol		
	(Ref.13)	(Refs.17, 25)	MNDO+KB (2×2)
^{1}PhN	120	121 ($n_z^2 n_y^2$)	118
	—	105 ($n_z^2 n_y^1 \pi^1$)	
^{3}PhN	99	98($n_z^2 n_y^1 \pi^1$)	
^{1}A	100	—	
^{1}B	110	—	
^{3}C	103	—	

The MNDO calculations (Table 17) are roughly in accord with experimental data: the calculated singlet-triplet splitting (7 kcal/mol) is close to that measured experimentally,[144,145] and the calculated energy difference between ^{1}(PhN) and ^{1}(A) (5 kcal/mol) accords with the experimental value (5−10 kcal/mol) obtained in different solvents[17,25] (see Table 8). It follows that a didehydroazepine (^{1}A) is the most likely intermediate species formed on impulse photolysis of PhN_3, AM1, MNDO and MNDOC calculations are essentially in agreement in that acceptor (*p*-NO_2) and donor (*p*-NH_2) substituents lead to a small (1−2 kcal/mol) decrease in the singlet−triplet splitting in ArN.[17,25]

VII. Conclusions

From the material examined, it is evident that the mechanism of photolysis of azides is understood in broad outline. However, the possibility of parallel reaction pathways, involving key intermediate species (nitrenes didehydroazepines and/or azirines, etc.), adds to the overall complexity, and specific variations may simply be substrate-dependent. The precise course of the reaction may also depend on the concentration of the reactants, the temperature and presence of impurities. Thus the results obtained under different experimental conditions may differ significantly. The precise structure of the intermediate species, and their involvement in a particular pathway of azide photo-decomposition, has not been established in each instance, and more extensive kinetic data are required to obtain further information in this respect. This is particularly true for the initial processes involving singlet intermediate species. As there are no data on the rate of isomerisation of singlet aromatic nitrenes into didehydroazpines (and/or azirines), it is not possible to ascertain the effect of substitution on the formation of isomers.

Significantly more studies have been made on the reactions of triplet aromatic nitrenes, although quantitative data is still lacking. For example, the rate constant for reaction (11) has only been established under one set of conditions. Our understanding of the mechanism of azide photolysis in the presence of oxygen is limited, and contradictory results have been reported on the photo-decomposition of azides by chain propagation. In practice, when studying the reactions of aromatic azides, it is important to consider a large number of competing processes and the effect of experimental conditions on them.

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