

THE TEMPERATURE DEPENDENT PHOTOCHEMISTRY  
OF PHENYL AZIDE IN DIETHYLAMINE

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**Summary:** The photochemistry of phenylazide in diethylamine changes from products consistent with electrophilic singlet intermediates to products consistent with triplet nitrenes as the temperature is lowered from 273 to 77K.

The photochemistry of phenylazide 1 has been studied by chemical and physical methods and has been shown to be highly complex. In 1966 Doering and Odum discovered that the photolysis of 1 in diethylamine leads to the formation of 3H azepine 5 in good yield.<sup>2</sup> This chemistry is best rationalized by the intermediacy of an electrophilic singlet species such as 3 and/or 4. The products expected for the reaction of triplet nitrene 2T with solvent [anilines 8 and 9, azobenzene 6] were formed in only trace amounts.

Low temperature spectroscopic methods have been applied extensively to aryl azides but a full understanding of azide photochemistry is lacking.<sup>3</sup> In 1962 Wasserman photolyzed phenylazide at 77K in a variety of glasses and obtained the EPR spectrum of triplet phenylnitrene.<sup>4</sup> A few years later Reiser<sup>5</sup> and coworkers followed the photolysis of phenylazide at 77K by UV spectroscopy. Irradiation of 1 with 313 nm light in an ether-pentane-alcohol glass led to the disappearance of the azide spectrum and the appearance of a new UV spectrum. The latter spectrum was assigned to the nitrene 2T partly on the basis of Wasserman's EPR study. In 1978 Chapman<sup>6</sup> studied the photochemistry of 1 in argon at 10K by infrared spectroscopy and observed an intense band at 1895 cm<sup>-1</sup> which was assigned to azacyclooctatetraene 3. In later work Dunkin and Thompson<sup>7</sup> observed the IR spectra of both azacyclooctatetraenes and azirines derived from photolysis of 1 and 2 naphthylazide. Based upon the IR work of Chapman and LeRoux it is not clear what species (2T or 3) is predominantly formed upon photolysis of phenylazide at 77K. It is not clear what specie(s) is responsible for Reiser's UV spectrum. Flash photolysis studies have given contradictory results and interpretations.<sup>8</sup> The most recent study prefers to assign Reiser's spectrum as due to 3.

To shed further light on the identity(ies) of the specie(s) formed upon photolysis of 1 at low temperature we have studied the matrix chemistry of phenylazide. The results are listed in the Table, as usual the percent conversion of the starting material is much lower in a polycrystalline solid than in solution (the m.p. of diethyl amine is 227K).

The data clearly shows that there is a change in product distribution with temperature. At 273 and 195K the only significant product observed is azepine 5. At 173 and 153K considerable amounts of azobenzene are formed relative to azepine 5. Upon further cooling to 77K the yield of azepine drops to zero! Photolysis of phenylazide in frozen diethylamine at 77K does not produce 3 or 4 as trapable species but leads instead to very high yields (~73%) of triplet nitrene derived products. The reactions of triplet nitrene 2T probably do not occur at 77K but at a higher temperature as the EPR signal of 2T is stable at 77K. Triplet phenylnitrene is stable in solid diethylamine even at 100K, but decays slowly (over many minutes) at 120K. It decays very rapidly at 140K ( $\tau_{1/2} < 1$  min) as measured by EPR. Samples which were photolyzed at 77K were kept frozen at 195K for 24 hours prior to thawing and chemical analysis. This insured that all of the chemistry of triplet phenyl nitrene occurred at a temperature below the melting point of diethylamine. It is possible that electrophilic species are formed upon photolysis of 1 at 77K but are chemically inert in the matrix. Any 3 or 4 that is formed at 77K must irreversibly intersystem cross to triplet phenylnitrene prior to warming to 195K as direct photolysis of phenylazide at the higher temperature gives almost entirely azepine 5. The dramatic dependence of the product distribution with temperature reported herein is similar to work with carbenes reported by Moss<sup>8</sup> and Tomioka.<sup>9</sup> These workers found that low temperature matrix conditions enhance triplet carbene chemistry relative to singlet chemistry.

Table 1. The distribution of products formed upon photolysis of phenylazide in diethylamine as a function of temperature.

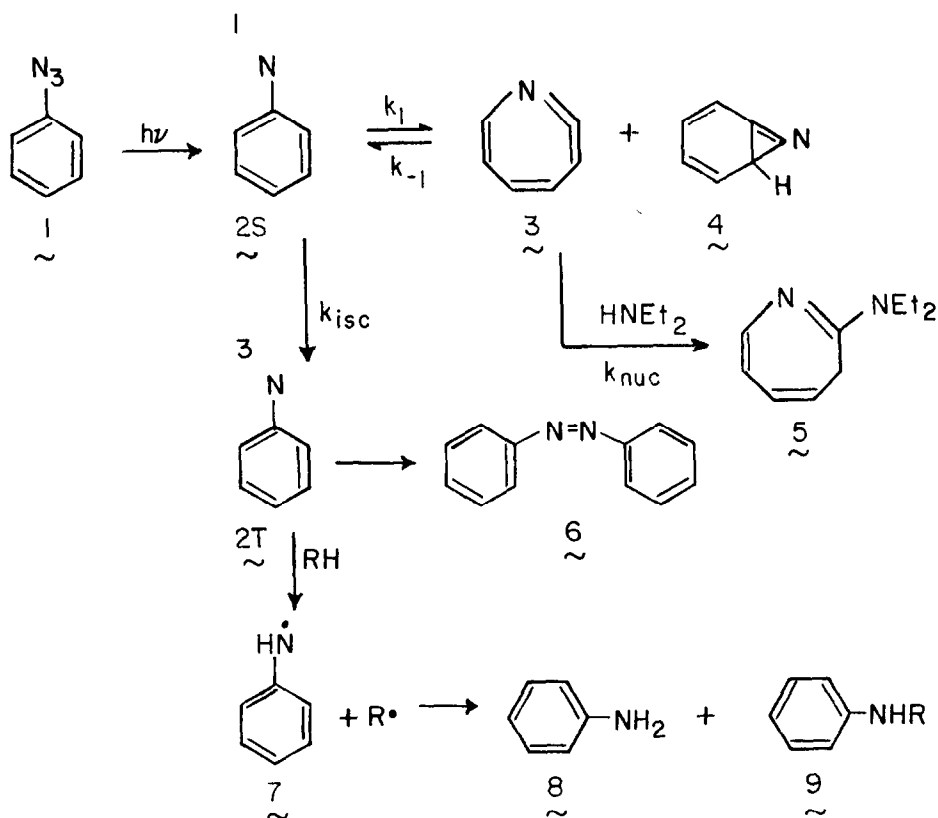
<u>Temp (K)</u> <sup>11</sup>	<u>Phenylazide 1</u>	<u>Aniline 9</u>	<u>Azepine 5</u>	<u>Azobenzene 6</u>
273 <sup>a</sup>	-	-	80%	-
195 <sup>b</sup>	5%	7%	76%	1-3%
173 <sup>c</sup>	67%	-	9%	3%
153 <sup>c</sup>	78%	-	3%	7%
77 <sup>d,e</sup>	21%	22%	-	35%

(a) 2 hours photolysis at 3500Å, rayonet reactor; (b) 4 hours photolysis; (c) 3.5 hours photolysis; (d) 5 hours photolysis. Note the product ratios are insensitive to the length of the photolysis; (e) After 5 hours photolysis the sample was warmed to 195K where it was kept at these temperatures for 24 hours before thawing.

These results can be interpreted in several ways in terms of Scheme 1. (Note this scheme has been proposed earlier, see references 6 and 8 and references therein.) Photolysis of 1 leads to singlet phenylnitrene 2S which partitions between valance tautomerism ( $k_1$ ) and irreversible intersystem crossing to the triplet 2T which is lower in energy than

2S, 3 and 4. It is possible that 3 (or 4) is formed at 77K in the diethylamine matrix but can not react with nucleophiles under these conditions ( $k_{\text{nuc}} \sim 0$ ). On the long timescale of the matrix experiment 3 will eventually convert to the ground state triplet nitrene, at some temperature between 77 and 195K. The triplet nitrene will then ultimately give the observed products. Alternatively the ratio of  $k_{\text{isc}}/k_1$  may be temperature dependent and increase as the temperature is lowered. It is even possible that the partitioning of singlet phenylnitrene is different in diethylamine than in the less reactive matrices used in IR and UV spectroscopy. Experiments are currently in progress to distinguish these possibilities.

Scheme 1



### References

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11. All analyses were performed on a Hewlett Packard 5830A GC using a 6' SE-30 column. The products were identified by coinjection with authentic samples and GC-MS. The error is  $\pm 3\%$ .

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