Effect of Wavelength on the Photolysis of *p*-Cyanophenyl Azide in Dimethylamine

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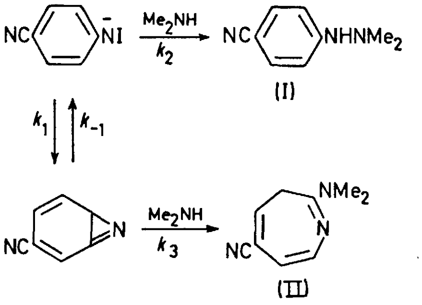
Summary The ratio of products, 2-(4-cyanophenyl)-1,1-dimethylhydrazine (I) and 5-cyano-2-dimethyl-3*H*-azepine (II), which is obtained from the photolysis of *p*-cyanophenyl azide in dimethylamine is wavelength dependent; this wavelength effect is rationalized in terms of excess of excitation energy producing a hot nitrene.

There are few studies of photolysis of aryl azides with varying wavelengths. D'Amore and Odum found that wavelength did not alter the relative rates of formation of 2-dimethylamino-3-methyl-3*H*-azepine and *o*-methylaniline on photolysing *o*-methyphenyl azide in dimethylamine, but wavelength was an important factor in synthesis since the azepine was preferentially destroyed by light in the region where the azide absorbed weakly.[1] Reiser and Marley investigated the effect of wavelength on the quantum yield for disappearance of 1-azidonaphthalene and reported that it increased as wavelength was decreased until it reached unity and remained constant.[2] We report a change in product yields on changing wavelength when photolysing *p*-cyanophenyl azide in dimethylamine.

Irradiation of *p*-cyanophenyl azide in dimethylamine yields compounds (I) and (II). The data supporting the assignment of structure to (I) appear elsewhere[3] and (II) was characterized by elemental analysis and i.r. and n.m.r. spectra which are similar to those of the 2-amino-3*H*-azepines obtained in photoreactions of other azides and amines.[3,4] Both products arise from singlet species,[3,5] and are accounted for by the mechanism shown in the Scheme.



Scheme

When a solution of *p*-cyanophenyl azide (0·015m) in dimethylamine under reflux is irradiated in a Rayonet photochemical reactor with 350 nm RPR lamps, the yields of (I) and (II) are 88 and 12%, respectively. A similar reaction differing only in the use of 253·7 nm RPR lamps produces 56% of (I) and 46% of (II). When solutions of *p*-cyanophenyl azide and dimethylamine in tetrahydrofuran, an inert solvent, are photolysed the ratio of (I) to (II) decreases as the amine concentration is decreased at either wavelength. The effect of varying the amine concentration on the product ratio requires that each arise from different species reacting with dimethylamine. The possibility, that (I) is formed by photolysis of a complex of amine and azide, is excluded since a comparison of the u.v. spectra of the azide in a range of solvents including solutions of the amine reveals no such complex. However, the effect of amine concentration is in accord with the mechanism in the Scheme if k_1 is not much larger than k_2.

There is doubt about the primary process in the photochemistry of aryl azides. Arguments supporting the hypothesis that they decompose in a hot ground state were advanced in 1968,[2] and more recently Reiser and Wagner suggested that decomposition occurs in the $n\pi^*$ state.[6] In any case, vibrational equilibration in the excited state must be slower than internal conversion or decomposition in order to account for the dependence of quantum yield on wavelength which was reported for 1-azidonaphthalene. This excess of energy can be carried over to bond rupture and result in a hot nitrene. This hot nitrene will have a different $k_2 : k_1$ ratio than a thermally equilibrated nitrene, thus changing the product composition.

A change in wavelength may alter the product distribution in this way provided there are competitive reaction pathways for the nitrene. Evidence that the two pathways of nitrene disappearance are competitive, is provided by the fact that the (I) : (II) product ratio can be decreased by a decrease in dimethylamine concentration. There are many reactions in which an aryl nitrene appears to react competitively in two or more ways. Thus, although this is the first report of such an effect, wavelength may be an important variable in other photoreactions of aryl azides.

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