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A medium effect in the photolysis of phenyl azide in low-temperature matrices

Ian R. Dunkin *, Michael A. Lynch, Fiona McAlpine, Denis Sweeney

Department of Pure and Applied Chemistry, The University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, UK

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Abstract

Measurements have been made of the relative rates of formation of azacyclohepta-1,2,4,6-tetraene and disappearance of the starting material in the photolysis of phenyl azide in Ar, CH_4 and 3-methylpentane matrices. With narrow band light ($\lambda = 280 \pm 5$ nm), formation of the ring expanded product lagged behind the decomposition of the azide by a distinct and reproducible amount in the early stages of the photolyses in CH_4 and 3-methylpentane. Full arc photolysis ($\lambda > 200$ nm), on the other hand, resulted in a linear relationship between growth of product and disappearance of starting azide. No similar wavelength dependence was observed for the photolysis in argon. This is clear evidence that the photolysis in the hydrocarbon matrices proceeds in part to triplet phenylnitrene, which can subsequently absorb a second photon to give the azacycloheptatetraene. Vibrational coupling between the initially formed singlet phenylnitrene and the host material, which should be much more efficient in CH_4 and 3-methylpentane than in the monatomic argon, is proposed to account for the observed difference in behaviour in the matrix hosts.

Keywords: Photolysis; Phenyl azide; Matrix hosts; Vibrational coupling

1. Introduction

1.1. History

The photolysis and thermolysis of phenyl azide (PhN_3) and its derivatives and analogues have been studied for many years [1,2]. The reactions have been investigated in the gas phase, in liquid solutions and in frozen matrices. For such an apparently simple system, a surprising amount of controversy has been generated. For the photolysis of PhN_3 in solution, one group [3] has claimed that an autocatalytic chain dissociation occurs at concentrations above about 2×10^{-4} M, with quantum yields for the disappearance of PhN_3 rising to the order of 1000. This has been contested [4–7], but a modelling study, taking into account light intensity, mass transfer and sampling time, seems to have reconciled the apparently contradictory results from the various laboratories [8].

Investigations of the photolysis of phenyl azide in frozen matrices were originally intended to help in the understanding of the processes in fluid media, by allowing the spectroscopic characterization and identification of key reactive intermediates. Even these, however, provided apparently contradictory results. The first of such experiments were carried out by Reiser et al. [9–12], who photolysed a number of aryl azides, including PhN_3, in organic glassy matrices at 77 K. These workers found that the primary photoproducts were stabilized under these conditions, and recorded their UV-visible absorption spectra. The spectra were independent of the solvent and disappeared when the matrices were softened at 90 K or above. They were assigned to the corresponding nitrenes (cf. **2**). At about the same time, ESR studies indicated that aryl nitrenes had triplet ground states [13], although photolysis of the azides probably first generated singlet excited nitrenes [14].

Some years later, Chapman and Le Roux [15] photolysed phenyl azide in Ar matrices at 8 K, and were able to record the IR spectrum of the major photoproduct, which had a strong band at 1895 cm^{-1}. There were several possibilities for the matrix photoproduct of PhN_3 (see Scheme 1): the singlet or triplet nitrenes (S-**2**, T-**2**), the bicyclic azirine **3**, and the azacycloheptatetraene (or didehydroazepine) **4**. Of these, only **4**, with its strained ketenimine structure, could account for the 1895 cm^{-1} IR band. In our laboratory, similar azacycloheptatetraenes were subsequently observed as the major photoproducts from a series of matrix isolated 3- and 4-substituted phenyl azides, and the presence of a nitrogen

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* Corresponding author. Tel: +44 141 552 4400, ext. 2276. Fax: +44 141 552 5664.

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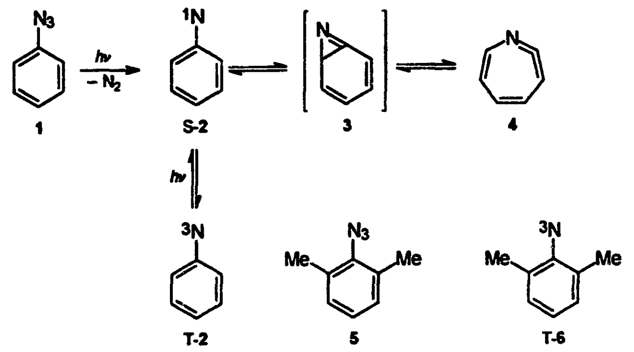

Scheme 1.

atom in the functional group giving rise to the 1895 cm^{-1} band was confirmed by ^{15}N labelling [16].

Reiser's group had not been mistaken in identifying their reactive species as nitrenes, however. It was discovered that phenyl azides with two *ortho* substituents—pentafluorophenyl azide and 2,6-dimethylphenyl azide (**5**)—did not give azacycloheptatetraenes as the main products when photolysed in Ar or N_2 matrices [17]. Instead, the trapped photoproducts had no very distinctive IR absorptions, could be made to react with CO to give the corresponding phenyl isocyanates, and were thus identified as the ground-state triplet nitrenes, e.g. **T-6**. Making use of this fact, Leyva et al. [4] examined the photolysis of PhN_3 and a number of di-*ortho*-substituted derivatives in EPA solution at 77 K, and showed that in these conditions the triplet nitrenes and not the azacycloheptatetraenes are the major products, even in the case of phenyl azide.

This work led to a surprising conclusion for the photolysis of phenyl azide: that in solutions at ambient temperature, the only trappable intermediate is the azacycloheptatetraene **4**; that in frozen solvents at 77 K, the major photoproduct is the triplet nitrene **T-2**; and that in Ar or N_2 matrices at 8–20 K, it is the azacycloheptatetraene which again predominates. Hayes and Sheridan went some way towards resolving this paradox, by showing that careful selection of photolysis wavelength allows the triplet nitrene to build up in even in Ar and N_2 matrices [18]. They were able to assign the IR spectrum of matrix isolated **T-2**, and follow its secondary photolysis at long wavelengths ($\lambda > 450$ nm) to give **4**. They proposed that, on excitation, **T-2** could regain the singlet manifold via upper triplet levels and thus isomerize to **4** via **S-2**. They also suggested that, in most previous matrix experiments, the conditions of photolysis would have ensured that all **T-2** generated would have undergone this secondary photolysis. These findings still left open the question why Reiser et al., with unfiltered Hg arcs of various kinds and quite short photolysis times, were able to generate nitrenes in organic glasses at 77 K, apparently as the major products of azide photolysis.

Azirines similar to **3** have been observed in the matrix photolysis [19] and solution flash photolysis [20] of naphthyl azides, and in solution for pyrenyl azides also [20]. Such azirines have apparently never been observed following photolysis of monocyclic aryl azides, so there is uncertainty whether **3** is an energy minimum or energy maximum on the pathway from **S-2** to **4**.

Platz has recently made a convincing attempt to combine most of the experimental results so far obtained to give an overall understanding of both the photolysis and thermolysis of phenyl azide [2]. Nevertheless, in the previous papers dealing with the problems related to phenyl azide photolysis, the possibility that the chemical nature of the solvent or matrix host might significantly influence the reaction pathway seems unresolved. This has prompted us to report the findings which are presented in this paper.

1.2. The influence of matrix host material

When excited state PhN_3 loses N_2, the nitrene formed is initially in the excited singlet state (**S-2**) with a considerable amount of excess vibrational energy. If this vibrational energy is not quickly dissipated into the surrounding medium, the singlet nitrene will have plenty of activation energy to surmount any energy barriers on the singlet surface connecting **S-2**, **3** and **4**. In these circumstances, the ring expanded product **4** is likely to be favoured. On the other hand, if the excess vibrational energy of the singlet nitrene is rapidly transferred to the reaction medium, the lifetime of **S-2** will be prolonged and intersystem crossing to the ground-state triplet nitrene (**T-2**) will become competitive.

Vibrational coupling between an excited guest species and a matrix host is likely to be much more efficient if the host material is a molecular species, with its own numerous vibrational levels, than if the host is a monatomic species such as Ar. On this argument, it would be expected that, independent of temperature, frozen organic glasses, such as those used by Reiser et al. [9–12], would favour the formation of **T-2**, while solid Ar, as used by later workers [15,16], would favour the direct formation of **4**, in accord with observation. This matrix effect has been proposed by Leyva et al. [4], and investigated by Hayes and Sheridan [18] in a comparison of the 334 nm photolysis of PhN_3 in Ar, N_2 and 2-methylbutane matrices. With 334 nm light, **T-2** was found to be the major primary photoproduct in all three matrices, and no medium effect was detected. The results we present in this paper, which arise from a comparison of the 280 nm photolysis of PhN_3, do now provide experimental support for the postulated effect.

2. Results and discussion

2.1. Matrix hosts

In order to investigate the influence of matrix host material on the photolysis of PhN_3, we decided to compare the rate of appearance of the characteristic $\nu(C{=}C{=}N)$ band of **4** with the rate of disappearance of the $\nu(N_3)_{as}$ band of the azide in Ar, CH_4, 3-methylpentane (3-MP) and other organic matrices at 12 K—the base temperature of our low temperature cell. Whereas Ar, CH_4 and 3-MP formed glassy matrices with acceptable optical quality when condensed at 12 K, other organic solvents tried—*n*-pentane, *n*-hexane, *n*-heptane, cyclohexane, methylcyclohexane, 2,2,4-trimethylpentane, THF, and *t*-butyl chloride—all gave microcrystalline matrices of very poor optical quality. Our experiments were therefore confined to the first three matrix hosts.

2.2. *Irradiation wavelength*

The irradiation wavelength was chosen so as to maximize the chance of the triplet phenylnitrene (T-**2**) accumulating in the matrices. The optimum wavelength for the experiments would thus be one at which PhN_3 photolysed rapidly but at which T-**2** had little or no absorption. PhN_3 has λ_{max} at about 250 nm, with structured absorption to about 350 nm [10]. In the conditions of our matrix experiments, we have found that photolysis of PhN_3 is unacceptably slow with $\lambda > 320$ nm, and, indeed, the previously reported photolysis with 334 nm light [18] seems to have involved very long irradiation times (e.g. 40 h.). We thus needed an estimate of the region of smallest absorption by T-**2** in the range 250–320 nm.

Fig. 1(a) shows the UV–visible absorption spectrum of the photoproduct of PhN_3 in an Ar matrix at 12 K. The spectrum has sharp features at 231 and 235 nm, a broad shoulder at about 255 nm, but little significant absorption at longer wavelengths. In these conditions, the major photoproduct is known to be **4** [15,16], and the twisted nature of this molecule accounts for the short wavelength λ_{max} observed. In contrast, photolysis of 2,6-dimethylphenyl azide (**5**) in Ar or N_2 matrices yields predominantly 2,6-dimethylphenylnitrene (T-**6**) [17]; the UV–visible spectrum of **6** in Ar at 12 K is shown in Fig. 1(b). This has a strong absorption at 246 nm, and structured absorptions with maxima at 290, 302, 384 and 516 nm. In the region between 270 and 600 nm, to which the earlier experiments were confined, these absorptions closely resemble those already reported for triplet 2,6-dimethylphenylnitrene (T-**6**) trapped in glasses at 77 K [4]. There is also a close resemblance in the region 220–410 nm to the spectrum reported by Reiser for triplet phenylnitrene (T-**2**) [10]. The spectrum of Fig. 1(b) can thus be confidently assigned to T-**6**, and is the most complete electronic absorption spectrum of this species so far reported. It has been shown that the UV–visible absorptions of T-**6** and T-**2**, in the region 270–600 nm, are very similar when these species are generated in EPA at 77 K [4]. We therefore conclude that the UV–visible absorptions of T-**2** in Ar matrices will be very similar to those of T-**6**.

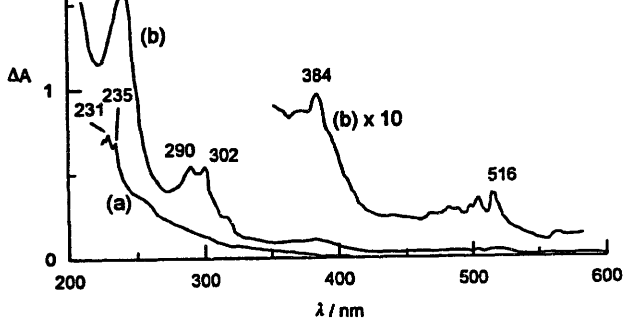

Fig. 1. UV–visible absorption spectra (background subtracted) of Ar matrices at 12 K: (a) azacycloheptatetraene **4** from complete photolysis of PhN_3 ($Ar/PhN_3 = 1000$) with $\lambda > 200$ nm (31 min); (b) triplet 2,6-dimethylphenylnitrene (T-**6**) from complete photolysis of **5** (matrix ratio not determined) with $\lambda > 200$ nm (4 min).

It is apparent from Fig. 1(b) that a suitable wavelength for reasonably rapid photolysis of PhN_3, which must lie in the range 250–320 nm, cannot be chosen for a region where T-**2** does not absorb significantly. The optimum choice seems to be at about 270–280 nm, where there is a minimum in the absorption of T-**6** and, by inference, T-**2**. We therefore selected the line at 280 nm in the output of the high pressure Hg arc for our photolyses, with a monochromator slit setting of ±5 nm.

2.3. *Photolysis of PhN_3 in Ar, CH_4 and 3-MP matrices*

PhN_3 was isolated in Ar, 3-MP and CH_4 matrices at 12 K and photolysed with light of $\lambda = 280 \pm 5$ nm. The progress of the reaction was followed by monitoring the growth of the characteristic IR band of **4** at 1893 (Ar) or 1890 cm^{-1} (3-MP and CH_4) and the disappearance of the strongest component of the asymmetric azide stretch at 2137 (Ar), 2131 (3-MP) or 2134 cm^{-1} (CH_4). In a separate set of experiments, similar photolyses were carried out with the full Hg arc ($\lambda > 200$ nm).

Fig. 2 shows IR spectra recorded during the photolysis of PhN_3 in 3-MP at 12 K, and Fig. 3 shows the quantitative results from two typical experiments with PhN_3 in 3-MP matrices with narrow band and full arc irradiation. The splitting of the $\nu(N_3)_{as}$ band into at least three components at 2131, 2100 and 2085 cm^{-1}, as shown in Fig. 2(a), is due mainly to Fermi resonance [21]. Matrix site effects are small: for example, these three components of $\nu(N_3)_{as}$ of PhN_3 are found at 2134, 2103 and 2090 cm^{-1} in CH_4 matrices, and at 2137, 2101 and 2087 cm^{-1} in N_2 [22]. Fig. 3(a) shows that photolysis with the full arc ($\lambda > 200$ nm) resulted in a linear relationship between growth of product and disappearance of the azide, indicating that no significant build up of an intermediate such as T-**2** occurred. Photolysis with narrow band light ($\lambda = 280 \pm 5$ nm), however, resulted in a definite lag in the formation of **4**, shown as a downward curvature of the plot in Fig. 3(b). These experiments were repeated several times, with consistent results. It is concluded, therefore, that, with narrow band 280 nm light, photolysis of PhN_3 in 3-MP matrices gives both the azacycloheptatetraene **4** and an intermediate, probably T-**2**. Similar results were obtained with CH_4 matrices; Fig. 4 shows typical results.

With Ar matrices, experiments conducted in the same way showed no significant difference between the photolyses with unfiltered or narrow band light. In both sets of photolysis conditions and in repeated experiments, only a linear rela-

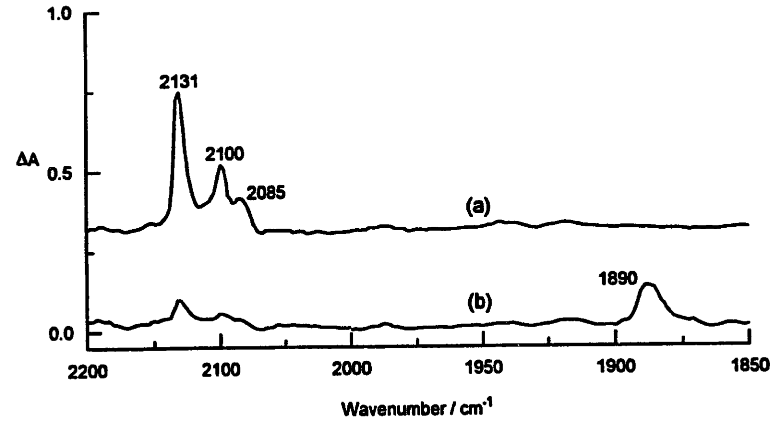

Fig. 2. IR absorptions (background subtracted) in the region 2200–1850 cm^{-1} for 3-MP matrices at 12 K containing PhN_3 (3-MP/PhN_3 = 1000): (a) before photolysis; (b) after 25 min photolysis with $\lambda > 200$ nm. For clarity, spectrum (a) is offset by 0.3*A*.

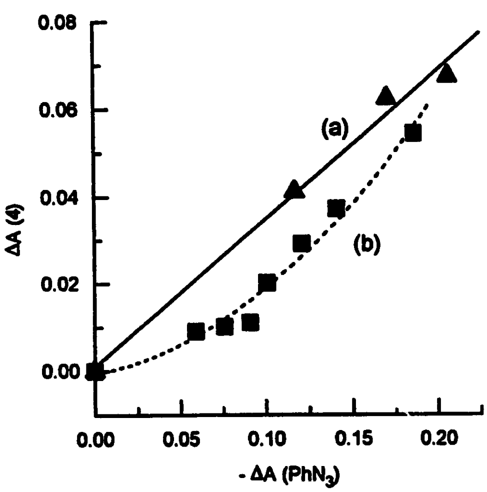

Fig. 3. Increase in absorbance of ν(C=C=N) of 4 at 1890 cm^{-1} (ΔA(4)) against decrease of absorbance of $\nu(N_3)_{as}$ of PhN_3 at 2131 cm^{-1} ($-\Delta A$(PhN_3)) during photolysis of PhN_3 in 3-MP at12 K (3-MP/PhN_3 = 1000): (a) photolysis with $\lambda > 200$ nm; (b) photolysis with $\lambda = 280 \pm 5$ nm.

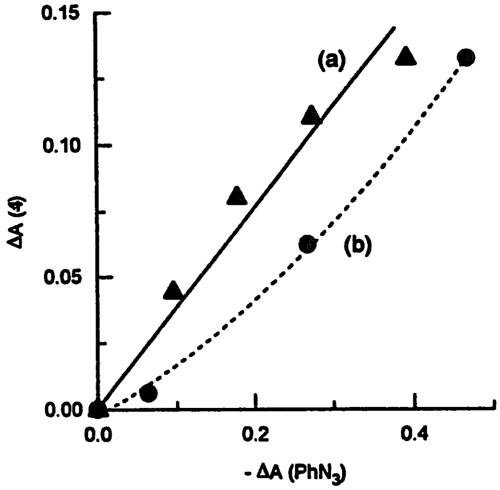

Fig. 4. Increase in absorbance of ν(C=C=N) of 4 at 1890 cm^{-1} (ΔA(4)) against decrease of absorbance of $\nu(N_3)_{as}$ of PhN_3 at 2134 cm^{-1} ($-\Delta A$(PhN_3)) during photolysis of PhN_3 in CH_4 at 12 K (CH_4/PhN_3 = 1000): (a) photolysis with $\lambda > 200$ nm; (b) photolysis with $\lambda = 280 \pm 5$ nm.

tionship between appearance of 4 and disappearance of PhN_3 resulted. Thus, for the matrix photolysis of PhN_3, a distinct difference has been established for the medium effect of Ar, on one hand, and 3-MP and CH_4, on the other. This difference is in accord with what was expected from considerations of vibrational coupling between the initially formed, vibrationally excited, singlet nitrene S-2 and the surrounding matrix medium (see above).

The effect is unlikely to be due solely to the rigidity of the matrix host, since Ar and CH_4 have similar melting points (83.3 and 90.7 K, respectively) and softening points (35 and 45 K, respectively) [23], while 3-MP melts at the much higher temperature of 267 K. If matrix rigidity were the main factor, Ar and CH_4 would be expected to show similar matrix effects with 3-MP considerably different.

It is probably significant that this matrix effect has been detected in the photolysis of PhN_3 with 280 nm but not with 334 nm light. The higher photon energy of the former may produce S-2 with a critically larger amount of vibrational energy, thus revealing the effects of the different matrix hosts. Notorious 'specific laboratory effects' cannot, however, be completely ruled out. These can include (i) variations in matrix deposition methods, influencing the properties of the matrices, such as light scattering and the state of aggregation of the 'isolated' molecules, (ii) lamp ageing, resulting in ostensibly similar light sources having significantly different spectral distributions, and (iii) window quality, giving rise to varying filtering effects. We have sought to minimize the chance that these are determining factors in the differences observed in our experiments and those carried out in other laboratories: a genuine medium effect seems to have been observed.

3. Conclusions

For the photolysis of PhN_3 with 280 nm light, our results show that, as matrix host materials, 3-MP and CH_4 favour formation of triplet phenylnitrene (T-**2**) more than Ar at the same temperature. The most likely explanation of this effect has been proposed previously [4], and is that molecular matrix materials, with their own numerous vibrational levels, couple more strongly than monatomic hosts like Ar with the vibrationally excited singlet phenylnitrene (S-**2**) that is formed immediately upon N_2 loss from electronically excited PhN_3. Thus in 3-MP and CH_4, vibrational deactivation of vibrationally excited S-**2** will be significantly faster than in Ar, reducing the chance of this species surmounting energy barriers on the singlet surface leading to **3** and **4**, and increasing the probability of intersystem crossing to the ground-state triplet nitrene T-**2**.

3-MP and CH_4 are non-polar molecules, and coupling between vibrationally excited S-**2** and the matrix host is likely to be even more effective for polar hosts such as EPA, where dipole–dipole interactions and H-bonding can enhance vibrational energy transfer from the guest species to its surroundings. We therefore conclude that the efficiency of vibrational deactivation of S-**2** should not be neglected as a factor in determining the reaction pathway in the photolysis of phenyl azide.

4. Experimental details

4.1. Materials

Research grade Ar ($\geq 99.9997\%$) and CH_4 ($\geq 99.995\%$) were obtained from BOC Ltd. and used without further purification. 3-Methylpentane (3-MP) (Aldrich, >99%) was redistilled by vacuum transfer into cooled ampoules (liquid N_2), and degassed by several freeze–pump–thaw cycles. At room temperature, 3-MP was found to have a vapour pressure of about 130 mbar, and could therefore be used to make up gas mixtures with PhN_3 by standard manometric techniques.

Phenyl azide (**1**) was prepared by diazotization of phenylhydrazine [24], and 2,6-dimethylphenyl azide (**5**) by diazotization of 2,6-dimethylaniline followed by treatment with NaN_3 [25,26]. Both azides were stored in a freezer until needed for the matrix experiments.

4.2. Equipment

The matrix isolation cold cell has been described in detail previously [27]. It consisted of a CsBr window enclosed in a vacuum shroud and cooled by an Air Products Displex, model CSA-202, closed cycle helium refrigerator. The vacuum shroud was fitted with external KBr windows and was pumped to about 10^{-6} mbar. Temperatures were measured by means of (i) a hydrogen vapour bulb and (ii) a Chromel–Au–0.07 at.% Fe thermocouple connected to an Air Products APD-B temperature controller. The base temperature of the cell was 12 K.

IR spectra were recorded on a Perkin–Elmer model 684 grating instrument interfaced to a Perkin–Elmer 3600 data station. Maximum (16-fold) signal averaging was employed for the quantitative absorbance measurements. UV–visible spectra were recorded on a Shimadzu UV250 double monochromator instrument, which had a modified sample compartment to accommodate the cold cell.

Photolysis was achieved with an Oriel 200 W high pressure Hg arc. This was equipped either with a water filter with quartz windows (13 cm pathlength), to eliminate IR radiation and give light of $\lambda > 200$ nm, or with an Applied Photophysics high radiance *f*/3.4 monochromator set to isolate light of 280 ± 5 nm.

4.3. Matrix deposition

Phenyl azide (**1**) was sufficiently volatile at room temperature to be premixed with the host materials by standard manometric techniques. A matrix ratio (host/guest) of 1000 was adopted for all the experiments reported in this study. The gas mixture was deposited on the cold window at 12 K, by admitting it into the vacuum shroud of the cold cell through a fine needle valve. 2,6-Dimethylphenyl azide (**5**) was insufficiently volatile for this procedure, so it was sublimed onto the cold window from a glass side-arm, fitted with a vacuum valve and attached to the vacuum shroud, while host gas was separately but simultaneously deposited. In these circumstances, matrix ratios could not be determined, but appropriate adjustments to the flows of both host gas and azide ensured good matrix isolation was achieved.

Acknowledgements

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References

[1] For early reviews, see B. Iddon, O. Meth-Cohn, E.F.V. Scriven, H. Suschitsky and P.T. Gallagher, *Angew. Chem. Int., Ed. Engl., 18* (1979) 900; C. Wentrup, *Top. Curr. Chem., 62* (1979) 173; W. Lwowski in M. Jones, Jr., and R.A. Moss (eds.), *Reactive Intermediates*, Vol. 2, Wiley, New York, 1981, p. 315; E.V.F. Scriven, in R.A. Abramovitch (ed.), *Reactive Intermediates*, Vol. 2, Plenum, New York, 1982, p. 1; E.F.V. Scriven (ed.), *Azides and Nitrenes*, Academic Press, Orlando, FL, 1984; C. Wentrup, *Reactive Molecules*, Wiley, New York, 1984, Chapter 4; M.P. Budyka, M.M. Kantor and M.B. Alfimov, *Usp. Khim., 61* (1992) 48.

[2] For the most recent review, see M.S. Platz, *Acc. Chem. Res., 28* (1995) 487.

[3] C.H. Lee Go and W.H. Waddell, *J. Am. Chem. Soc., 106* (1984) 715; J.P. Costantino, H.W. Richter, C.H. Lee Go and W.H. Waddell, *J. Am. Chem. Soc., 107* (1985) 1744.

[4] E. Leyva, M.S. Platz, G. Persy and J. Wirz, *J. Am. Chem. Soc., 108* (1986) 3783.

[5] T.-Y. Liang and G.B. Schuster, *J. Am. Chem. Soc., 109* (1987) 7803.

[6] Y.-Z. Li, J.P. Kirby, M.W. George, M. Poliakoff and G.B. Schuster, *J. Am. Chem. Soc., 110* (1988) 8092.

[7] M.F. Budyka, M.M. Kantor and M.V. Alfimov, *Bull. Russ. Acad. Sci., Div. Chem. Sci., 41* (1992) 590.

[8] G. Terrones and A.J. Pearlstein, *J. Am. Chem. Soc.*, *113* (1991) 2132.

[9] A. Reiser and V. Fraser, *Nature (London)*, *208* (1965) 682.

[10] A. Reiser, G. Bowes and R.J. Horne, *Trans. Faraday Soc.*, *62* (1966) 3162.

[11] A. Reiser, H.M. Wagner, R. Marley and G. Bowes, *Trans. Faraday Soc.*, *63* (1967) 2403.

[12] A. Reiser and R. Marley, *Trans. Faraday Soc.*, *64* (1968) 1806.

[13] G. Smolinksy, E. Wasserman and W.A. Yager, *J. Am. Chem. Soc.*, *84* (1962) 3220; J.A.R. Coope, J.B. Farmer, C.L. Gardner and C.A. McDowell, *J. Chem. Phys.*, *42* (1965) 54; R.M. Moriarty, M. Rahman and J.G. King, *J. Am. Chem. Soc.*, *84* (1966) 842; E. Wasserman, *Progr. Phys. Org. Chem.*, *8* (1971) 319.

[14] A. Reiser and L.J. Leyshon, *J. Am. Chem. Soc.*, *93* (1971) 4051.

[15] O.L. Chapman and J.-P. Le Roux, *J. Am. Chem. Soc.*, *100* (1978) 282.

[16] T. Donnelly, I.R. Dunkin, D.S.D. Norwood, A. Prentice, C.J. Shields and P.C.P. Thomson, *J. Chem. Soc., Perkin Trans. 2*, (1985) 307.

[17] I.R. Dunkin and P.C.P. Thomson, *J. Chem. Soc., Chem. Commun.*, (1982) 1192; I.R. Dunkin, T. Donnelly and T.S. Lockhart, *Tetrahedron Lett.*, *26* (1985) 359.

[18] J.C. Hayes and R.S. Sheridan, *J. Am. Chem. Soc.*, *112* (1990) 5879.

[19] I.R. Dunkin and P.C.P. Thomson, *J. Chem. Soc., Chem. Commun.*, (1980) 499.

[20] A.K. Schrock and G.B. Schuster, *J. Am. Chem. Soc.*, *106* (1984) 5234.

[21] A. Treinin, in S. Patai (ed.), *The Chemistry of the Azido Group*, Interscience, London, 1971, Chapter 1.

[22] I.R. Dunkin, *Spectrochim. Acta, Part A*, *42* (1986) 649.

[23] H.E. Hallam and G.F. Scrimshaw, in H.E. Hallam (ed.), *Vibrational Spectroscopy of Trapped Species*, Wiley, London, 1973, Chapter 1.

[24] R.O. Lindsay and C.F.H. Allen, *Org. Synth., Coll. Vol.*, *3* (1955) 710.

[25] G. Smolinsky, *J. Org. Chem.*, *26* (1961) 4108.

[26] P.A.S. Smith and B.B. Brown, *J. Am. Chem. Soc.*, *73* (1951) 2438.

[27] I.R. Dunkin and J.G. MacDonald, *J. Chem. Soc., Perkin Trans. 2*, (1984) 2079.