Didehydroazepines from the Photolysis of Phenyl Azide and 3- and 4-Substituted Phenyl Azides isolated in Low-temperature Matrices

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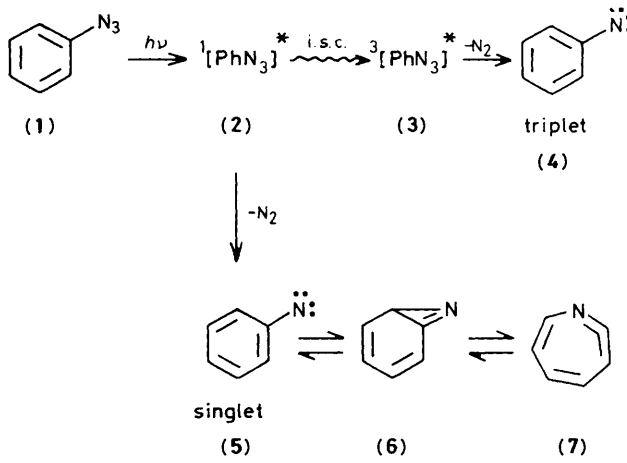
Phenyl azide, its ^{15}N-labelled derivative ($Ph^{15}NNN$), and a series of 3- and 4-substituted phenyl azides have been photolysed in N_2 and Ar matrices at 12 K. In all cases, the major decomposition pathways yield didehydroazepines with characteristic i.r. absorptions at *ca.* 1 890 cm^{-1}. Neither the reaction pathway nor the characteristic group frequency of the didehydroazepines seem much affected by variation of the substituents.

Studies of the photochemical decomposition of aryl azides in solution have formed in recent years a large and expanding body of knowledge. Reviews of the field[1] have pointed out applications of azides as synthetic precursors, as photoresists, and in photoaffinity labelling, and have also discussed the numerous mechanistic investigations. Part of the accrued understanding of the mechanism of aryl azide photolysis is illustrated in Scheme 1 for the simplest case of phenyl azide (**1**). In this description of the processes, loss of nitrogen from the initial singlet excited state (**2**) competes with intersystem crossing to the triplet state (**3**). Thus both the triplet nitrene (**4**) and the singlet nitrene (**5**) may result. The former reacts by abstraction of hydrogen atoms, yielding aniline, or by dimerization to azobenzene. The singlet nitrene, on the other hand, appears to exist in equilibrium with benzazirine (**6**) and didehydroazepine (**7**), and in the presence of suitable nucleophiles, azepines derived from (**6**) or (**7**) are the ultimate products. Additional equilibria between (**6**), (**7**), and, for example, pyridyl carbenes have also been discovered, so that the full reaction scheme is fairly complex. Moreover, substituents, solvents, external nucleophiles, and the use of sensitizers can all influence the nature of the products. An equally complex picture has emerged from flash vapour thermolysis studies of aryl azides.[2]

Amongst the experimental techniques that have been used to further this work, matrix isolation has played an important part.[3] The principal contribution made by matrix experiments has been the detection and characterization of representatives of each of the different types of ground state intermediate shown in Scheme 1. Thus triplet aryl nitrenes, including phenyl nitrene, have been observed by e.s.r.[4] and u.v. absorption[5] at 4—77 K, but the most important impact of the mechanistic understanding of these reactions has come from i.r. studies. In 1978, Chapman and Le Roux[6] reported the identification of didehydroazepine (**7**) as the apparent major product from the photolysis of phenyl azide in Ar at 8 K. A little later, naphthazirines, analogous to (**6**), were detected in the matrix photolysis of both 1- and 2-azidonaphthalene, and these were shown to undergo secondary photolysis to the corresponding didehydrobenzazepines.[7] In Ar and N_2 matrices, triplet nitrene formation appears to be a minor pathway, but in the case of pentafluorophenyl azide, nitrene rearrangement is suppressed, and the i.r. spectrum of pentafluorophenyl nitrene, presumably in the triplet ground state, has been recorded.[8] Despite these successes, the full range of intermediates, nitrene, benzazirine, and didehydroazepine, has not yet been followed through by i.r. spectroscopy in a single molecular system. Positive correlations of u.v., i.r., and e.s.r. spectra have also been lacking. These two objectives remain as worthwhile challenges to matrix chemists.



Scheme 1.

Consideration of the published results has led us into a more methodical investigation of the photolysis of aryl azides in low-temperature matrices. As a first step, we have studied the photolysis of phenyl azide, its ^{15}N-labelled derivative, $Ph^{15}NNN$, and a series of 3- and 4-substituted phenyl azides in Ar and N_2 matrices at 12 K. The work had three principal aims: (i) to determine if substituents would in any way alter the reaction pathway, (ii) to assess the influence of substituents and matrix effects on the frequency of the characteristic ν(C=C=N) band of didehydroazepines occurring at *ca.* 1 890 cm^{-1}, and (iii) to see if it would be possible to detect two isomeric didehydroazepines, (**16**) and (**17**), derived from the 3-substituted phenyl azides (**12**). We now report our results.

Experimental

Equipment.—The matrix isolation cold cell has been described in detail previously.[9] It consisted of a CsBr or CsI window in a metal holder enclosed in a vacuum shroud and cooled by means of an Air Products Displex, model CSA-202, closed-cycle helium refrigerator. Temperature measurements were made by means of (i) a hydrogen vapour bulb and (ii) a Chromel–Au–0.07 atom-% Fe thermocouple connected to an Air Products, model APD-B, temperature controller. The base temperature of the cell was 12 K. I.r. spectra, in the range 4 000—400 cm^{-1}, were recorded on JASCO model IRA-2 or Perkin-Elmer model 684 spectrometers. The latter was interfaced to a Perkin-Elmer model 3 600 Data Station. Spectra

were calibrated against polystyrene film, and quoted frequencies are accurate to $\pm 2\,cm^{-1}$. U.v. radiation was produced by an Oriel 200 W high-pressure Hg arc. A water-cooled water-filter (13 cm pathlength) with quartz windows was placed in the beam at all times, in order to remove i.r. radiation. The lamp was mounted on a small trolley, and both sides of the matrix could be irradiated.

Matrix Gases and Azides.—Research grade N_2 (<99.994%) and Ar (<99.9997%) were obtained from BOC Ltd., and were used without further purification.

Phenyl azide was prepared by diazotization of phenylhydrazine.[10] ^{15}N-Labelled phenyl azide, $Ph^{15}NNN$ (50 atom-% ^{15}N), was prepared by diazotization of a mixture of 99 atom-% ^{15}N-labelled aniline (Merck, Sharp and Dohme) (0.5 g) and freshly distilled unlabelled aniline (0.5 g), followed by treatment of the diazonium salt with sodium azide.[11] All the other azides used in this work (**8**; X = F, Cl, CN, Me, OMe) and (**12**; X = F, Cl, CN, Me, OMe) were prepared from the corresponding amines by diazotization and treatment with sodium azide, following established procedures.[12] They were generally purified by Kugelrohr distillations and in all cases the spectroscopic properties confirmed the identity of the azides.

Matrix Deposition.—Phenyl azide or its ^{15}N-labelled isotope were mixed with the appropriate matrix host gas on a preparative vacuum line, using standard manometric techniques. The resulting gas mixture was then allowed to condense on the cold window at 12 K at a rate controlled by a needle valve. Most of the substituted phenyl azides were insufficiently volatile for this procedure. So as to adopt a uniform deposition technique, all the substituted azides were deposited by direct evaporation or sublimation from a side-arm attached to the vacuum shroud of the cold cell. The matrix host gas was deposited simultaneously. In these cases, matrix ratios could not be estimated.

Results and Discussion

Phenyl Azide (**1**) *and* ^{15}N-*Labelled Phenyl Azide.*—Irradiation of phenyl azide in N_2 matrices (matrix ratio 1:1 000) at 12 K with light from a high-pressure Hg arc (water filter only) results in decomposition of the azide. I.r. spectra of the resulting matrices are always very complex and it is usually easy to find 40 or more new absorptions with intensities that are distinctly above the noise threshold. By far the strongest of the new bands is one at 1 891 cm^{-1} corresponding closely to an absorption at 1 895 cm^{-1} which was observed previously by Chapman and Le Roux[6] after Ar matrix photolysis of (**1**) and assigned by them to the ν(C=C=N) mode of the didehydroazepine (**7**). The remaining bands cannot all belong to the same species (**7**), since there are too many for a 12-atom molecule, and also some of the relative intensities can vary with experimental conditions. After numerous repetitions of the matrix photolysis of phenyl azide, we can assign 11 i.r. bands to species (**7**) with reasonable confidence. These are presented in Table 1. In view of the differences in experimental conditions and the complexity of the spectra, there is good agreement between our data for (**7**) in N_2 matrices and that reported previously for Ar matrices.[6] We have also photolysed (**1**) in Ar matrices at 12 K, with results that confirm the earlier work.

On prolonged photolysis in N_2 at 12 K, (**7**) itself undergoes decomposition. While the 11 i.r. bands of (**7**) decrease in intensity, a further ten bands grow, and these may therefore be identified as belonging to the secondary photoproduct or products. These bands occur at 1 679, 1 657, 1 169, 1 046, 978, 877, 854, 814, 743, and 630 cm^{-1}, in close agreement with the published i.r. spectrum of the secondary products in Ar matrices.[6] The photolysis of (**7**) does not appear to yield benzazirine (**6**), since a new band at 1 700—1 750 cm^{-1}, which is expected[6,7] for this species, does not arise in the process. Thus the identities of the photoproducts of (**7**) remain to be established, and assignment of all the i.r. bands observed during matrix photolyses of (**1**) seems even more distant.

Table 1. I.r. bands assigned to (**7**), observed after photolysis of phenyl azide (**1**) in N_2 at 12 K (matrix ratio 1:1 000)

$\tilde{\nu}/cm^{-1}$	Relative intensity	$\tilde{\nu}/cm^{-1}$	Relative intensity
3 024	0.05	691	0.35
1 891 (^{15}N: 1 876)	1.0	664	0.25
1 346	0.15	655	0.1
1 110	0.1	585	0.15
1 100 (^{15}N: 1 092?)	0.1	516	0.1
978	*		

* This band overlaps with a band of a photoproduct of (**7**) and is of variable relative intensity.

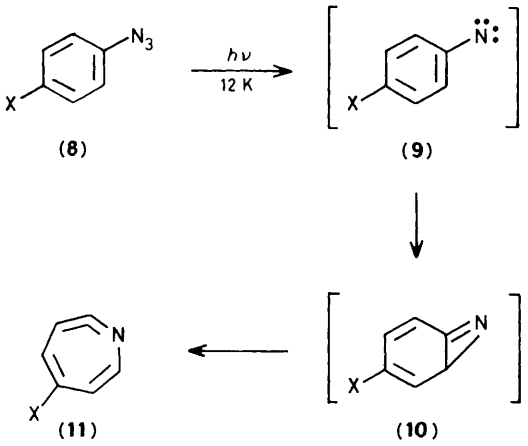
The identification of the major primary photoproduct of phenyl azide as the didehydroazepine (**7**) is given further support by our experiments with the specifically labelled ^{15}N-isotope, $Ph^{15}NNN$. Irradiation of a 1:1 mixture of PhN_3 and $Ph^{15}NNN$ in N_2 at 12 K (matrix ratio 1:1 000) was carried out as described above for the unlabelled azide, and a very similar product i.r. spectrum was obtained. A clear ^{15}N-isotope shift was observed for the ν(C=C=N) band of (**7**), which in this experiment was split into two approximately equally strong bands at 1 891 and 1 876 cm^{-1}. Because of the complexity of the spectrum, however, unequivocal recognition of other isotope splittings in the bands of (**7**) was not possible. Nevertheless, an absorption at 1 092 cm^{-1} had both the required intensity and position to be reasonably attributed to a coalescence of two bands of ^{15}N-labelled (**7**), corresponding to the bands at 1 110 and 1 100 cm^{-1} of the unlabelled molecule (Table 1). The vibrations at these frequencies may thus be assumed to have substantial ν(C–N) character. ^{15}N-Labelled (**7**) has previously been generated from a different precursor in diethyl ether–isopentane–ethanol and poly(vinyl chloride) matrices at 85 K and in PVC at 10 K.[13] In these experiments a ^{15}N-isotope shift of $-12\,cm^{-1}$ was observed for the ν(C=C=N) band, but solvent absorptions obscured the entire region below 1 500 cm^{-1}.

Substituted Phenyl Azides (**8**) *and* (**12**).—A series of five 4-substituted phenyl azides (**8**) and five 3-substituted phenyl azides (**12**) were photolysed in both N_2 and Ar matrices at 12 K. As with phenyl azide itself, the resulting i.r. spectra were complex, containing many weak bands, but in each case the strongest product band occurred at *ca.* 1 890 cm^{-1} and was assigned to the ν(C=C=N) vibration of the corresponding didehydroazepine, (**11**) (Scheme 2) or (**16**) and (**17**) (Scheme 3). The observed ν(C=C=N) frequencies are presented in Table 2. The following points arise from the data.

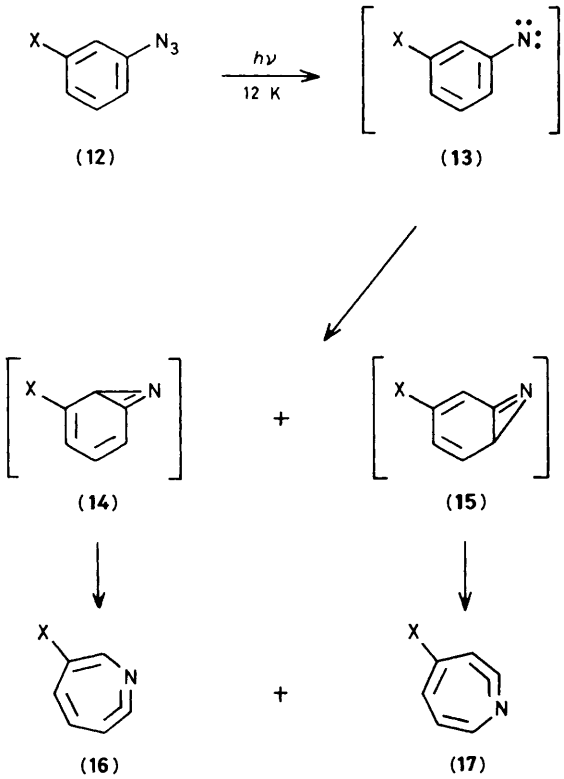
(1) In all the photolyses, didehydroazepines appear to be the major primary products. Thus electron-withdrawing (*e.g.* CN) and electron-releasing substituents (Me and MeO) in the 3- and 4-position neither inhibit the rearrangement of the nitrene nor promote an alternative pathway.

(2) All the observed ν(C=C=N) bands lie in the range 1 883—1 906 cm^{-1} so that the frequency of this vibration in molecules such as (**11**), (**16**), and (**17**) is relatively insensitive to variation of the substituent.

(3) Unless hydrogen migration or wholesale rearrangement takes place (see below) a 4-substituted azide (**8**) can yield only one didehydroazepine (**11**) (Scheme 2). Despite this, more than



Scheme 2.



Scheme 3.

one ν(C=C=N) band is present in most of the product spectra of this series, particularly with Ar matrices. Where the band splitting varies between N_2 and Ar matrices, it can be attributed to matrix site-effects. This is obvious with (**8**; X = Cl and CN), for example. In other cases (**8**; X = F and Me) where spectra are similar in both types of matrix, the splitting may be an intrinsic feature of the molecule.

(4) With 3-substituted azides (**12**), two didehydroazepines (**16**) and (**17**) will probably be formed from each precursor (Scheme 3). Since the decompositions of 3-substituted phenyl azides in solution have been found to lead to the two expected azepines,[14] it is reasonable to suppose that both (**16**) and (**17**) are produced under matrix conditions. Unfortunately, the insensitivity of the ν(C=C=N) frequency to substituent type and location, and the splitting of bands by site-effects and other

Table 2. Frequencies for ν(C=C=N) bands of didehydroazepines*

Precursor	X	$\tilde{\nu}$(C=C=N)/cm^{-1} N_2 Matrices	Ar Matrices
(**8**)	H	1 891	1 893†
	F	1 906, 1 903, 1 895	1 904, 1 901, 1 895
	Cl	1 895	1 894, 1 891
	CN	1 897	1 895, 1 893
	Me	1 893, 1 890	1 892, 1 886
	MeO	1 893	1 894
(**12**)	F	1 902, 1 890	1 889
	Cl	1 892	1 892, 1 883
	CN	1 901, 1 888	1 899, 1 887
	Me	1 891	1 890
	MeO	1 889	1 892, 1 888

* All the observed bands were distinctly asymmetrical and many possessed additional shoulders not included in the Table. † This frequency from our experiments compares with a value of 1 895 cm^{-1} from ref. 6.

factors, have prevented any demonstration of the presence of the two didehydroazepines. Indeed, there is no correlation at all between the number of observed ν(C=C=N) bands and the expected number of these products.

(5) The possibility that the multiple bands in the 1 890 cm^{-1} region are due to rearrangements and the formation in each case of several isomeric didehydroazepines merits consideration. Such isomerizations are known to occur at high temperatures *via* nitrogen and hydrogen migrations in nitrenes,[2] and in our experiments would give mixtures of (**11**), (**16**), (**17**), and two other isomers from both (**8**) and (**12**), rather than a single product (Scheme 2) or two products (Scheme 3). The data of Table 2, however, do not support this interpretation. If such scrambling were complete, then for a given X-substituent and a given matrix host, the same set of bands would be observed after photolysis of (**8**) or (**12**). This is clearly not the case, but even incomplete scrambling is also inconsistent with the data. For instance, any such isomerization occurring during photolysis of a 4-substituted azide (**8**) would be expected to give at least one of the products, (**17**), obtained from the 3-substituted azide (**12**) with the same substituent. While for some of the azides this might seem to be true, for others it is definitely not. Photolysis of (**8**; X = F) in Ar, for example, gives a product with three bands near 1 900 cm^{-1}, non of which corresponds to the single band observed after Ar matrix photolysis of (**12**; X = F). Table 2 provides other similar comparisons. While such scrambling may occur to a minor extent in our experiments, all attempts to relate i.r. bands near 1 890 cm^{-1} to individual species on a 1:1 basis seem to fail. Matrix splittings combined with other factors, such as Fermi resonance, seem the most likely cause of the multiple bands.

Conclusions

The formation of didehydroazepines, previously reported for phenyl azide[6] and the naphthyl azides,[7] has now been shown to be a general pathway in the matrix photolysis of 3- and 4-substituted phenyl azides.

Neither electron-attracting nor -releasing substituents seem to inhibit the reaction. Didehydroazepines exhibit very characteristic, intense i.r. absorptions in the neighbourhood of 1 890 cm^{-1}, which are little affected by variations in the substituent, but which are prone to band splitting, especially by site-effects. Although the didehydroazepines are not the only photoproducts derived from the azides, it has proved impossible so far to use the i.r. spectra to identify any of the others.

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References

1 B. Iddon, O. Meth-Cohn, E. F. V. Scriven, H. Suschitzky, and P. T. Gallagher, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 900; W. Lwowski in 'Reactive Intermediates,' eds. M. Jones, Jr., and R. A. Moss, Wiley, New York, 1981, vol. 2, p. 315; E. F. V. Scriven in 'Reactive Intermediates,' ed. R. A. Abramovitch, Plenum, New York, 1982, vol. 2, p. 1.

2 C. Wentrup, *Top. Curr. Chem.*, 1979, **62**, 173.

3 For a general review of this technique and its applications to organic chemistry see I. R. Dunkin, *Chem. Soc. Rev.*, 1980, **9**, 1.

4 G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, 1962, **84**, 3220; R. M. Moriarty, M. Rahman, and J. G. King, *ibid.*, 1966, **88**, 842; J. A. R. Coope, J. B. Farmer, C. L. Gardner, and C. A. McDowell, *J. Chem. Phys.*, 1965, **42**, 54; E. Wasserman, *Prog. Phys. Org. Chem.*, 1971, **8**, 319; O. L. Chapman, R. S. Sheridan, and J.-P. Le Roux, *J. Am. Chem. Soc.*, 1978, **100**, 6245.

5 A. Reiser, G. Bowes, and R. J. Horne, *Trans. Faraday Soc.*, 1966, **62**, 3162; S. B. Brichkin, V. A. Smirnov, M. V. Alfimov, T. P. Naidenova, and L. F. Avramenko, *Khim. Vys. Energ.*, 1980, **14**, 23 (*Chem. Abstr*, 1980, **93**, 34878c).

6 O. L. Chapman and J.-P. Le Roux, *J. Am. Chem. Soc.*, 1978, **100**, 282.

7 I. R. Dunkin and P. C. P. Thomson, *J. Chem. Soc., Chem. Commun.*, 1980, 499.

8 I. R. Dunkin and P. C. P. Thomson, *J. Chem. Soc., Chem Commun.*, 1982, 1192.

9 I. R. Dunkin and J. G. MacDonald, *J. Chem. Soc., Perkin Trans. 2*, 1984, 2079; J. G. MacDonald, Ph.D. Thesis, Strathclyde University, 1980.

10 R. O. Lindsay and C. F. H. Allen, *Org. Synth.*, 1955, Coll. Vol. 3, 710.

11 K. Clusius and H. Hürzeler, *Helv. Chim. Acta*, 1954, **37**, 798.

12 E. Noelting and O. Michel, *Ber.*, 1893, **26**, 86; H. O. Spauschus and J. M. Scott, *J. Am. Chem. Soc.*, 1951, **73**, 208; J. E. Leffler and R. D. Temple, *ibid.*, 1967, **89**, 5235; V. A. Gilyarov and M. I. Katachnik, *Zh. Obshch. Khim.*, 1966, **36**, 282.

13 N. H. Toubro and A. Holm, *J. Am. Chem. Soc.*, 1980, **102**, 2093.

14 T. deBoer, J. I. G. Cadogan, H. M. McWilliam, and A. G. Rowley, *J. Chem. Soc., Perkin Trans. 2*, 1975, 554.

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