Infrared Evidence for Tricyclic Azirines and Didehydrobenzazepines in the Matrix Photolysis of Azidonaphthalenes

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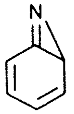
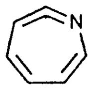
Summary U.v. irradiation of 1- and 2-azidonaphthalene in N_2 or Ar matrices at 12 K leads to the formation of didehydrobenzazepines *via* photolabile precursors which are assigned tricyclic azirine structures.

PHOTOLYSIS of phenyl azide (PhN_3) in the presence of nucleophiles results in a ring-expansion to give azepines.[1,2] Previous workers have proposed either the azirine (**1**) or the didehydroazepine (**2**) as intermediates. Of the two, the



(1)



(2)

azirine was originally preferred on the basis of MO calculations[3] and other arguments.[1] When Chapman and coworkers[4] studied the photolysis of PhN_3 in an argon matrix at 8 K, however, they detected a strong i.r. absorption at 1895 cm^{-1}, which was reasonably attributed to the didehydroazepine (**2**). This molecule thus became a credible alternative to the azirine (**1**) as the postulated intermediate in the solution photolysis of PhN_3, although its actual intermediacy is questioned.[5] Without more discriminatory results, the solution photolysis of PhN_3 is consistent with the preliminary formation of either (**1**) or (**2**).

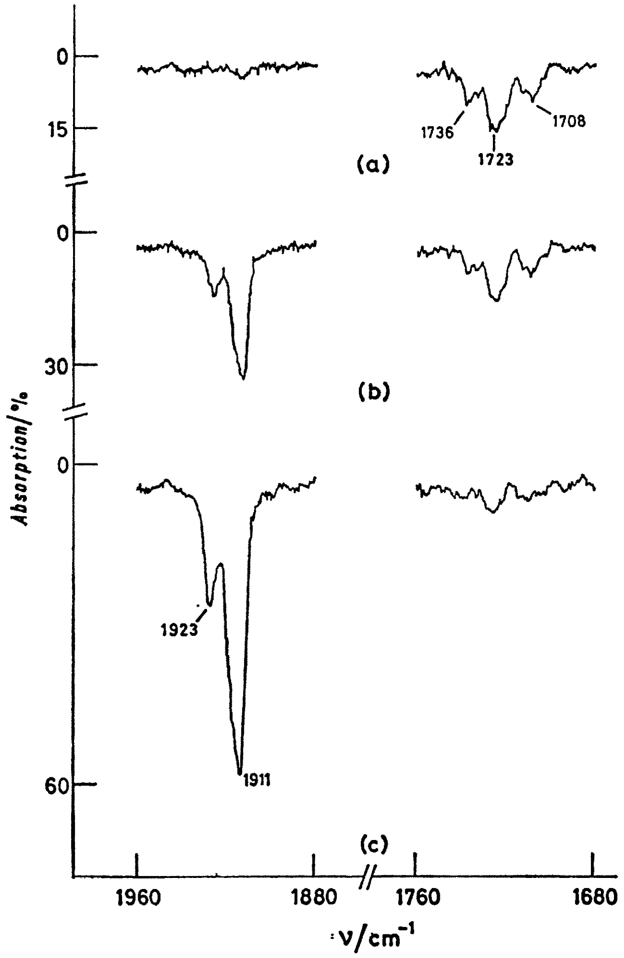


FIGURE. I.r. spectra obtained after photolysis of (**9**) in N_2 at 12 K (200 W Hg arc). (a) After 20 min ($\lambda > 330$ nm, water filter); at this stage, the original ν_{NNN} bands of (**9**) were reduced from 92 to 2% absorption. (b) After a further 30 min ($\lambda > 300$ nm, water filter). (c) After a further 50 min (water filter only).

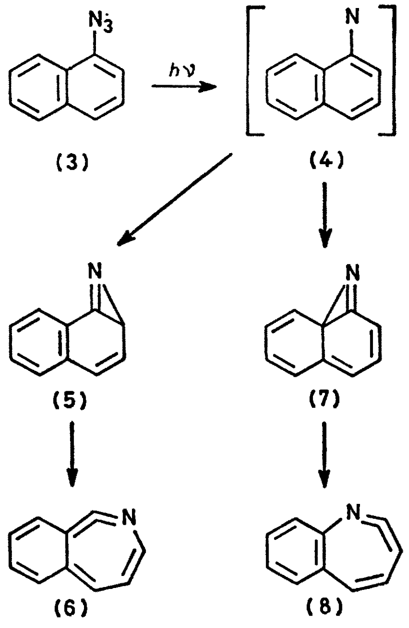
Products from the photolysis of 1- and 2-azidonaphthalene [(**3**) and (**9**)], on the other hand, cannot be easily reconciled with intermediate didehydrobenzazepines [(**6**), (**8**), (**12**), or (**14**)], but seem to require tricyclic azirine intermediates [(**5**), (**7**), (**11**), or (**13**)].[2,6]

TABLE. I.r. bands (cm^{-1}) observed during the photolysis of azidonaphthalenes in N_2 at 12 K.

Azide	Primary products[a]	Secondary products[b]
(3)	1730 m[c]	1926 m 1912 w
(9)	1736 w 1723 m 1708 w	1923 w 1911 m

[a] Formed on initial photolysis ($\lambda > 330$ nm). [b] Formed on continued photolysis, as bands of the primary products diminished. [c] m medium, w weak.

We have examined, by i.r. absorption spectroscopy, the u.v. photolyses of (**3**) and (**9**) in N_2 and Ar matrices at 12 K.[7] The critical i.r. bands observed with N_2 matrices are summarized in the Table, and typical spectra are shown in the Figure. (Similar results were obtained with Ar matrices.)†



SCHEME 1.

The results may be interpreted by means of Schemes 1 and 2. In each case, irradiation ($\lambda > 330$ nm) produced new i.r. bands, the strongest being in the region 1708—1736 cm^{-1}. On continued irradiation (with or without a cut-off filter)

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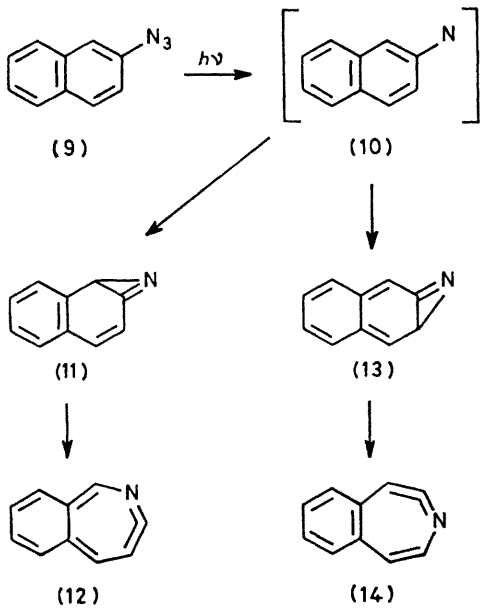
† Matrices were prepared by sublimation of the azide on a CsBr window at 20 K, with simultaneous deposition of N_2 or Ar (B.O.C., Grade X). Matrix ratios are therefore undetermined. I.r. spectra were recorded on a JASCO IRA-2 i.r. spectrometer. U.v. irradiation was produced by 125 W medium pressure or 200 W high pressure Hg-arcs, with water filtration at all times.



Scheme 2.

these bands diminished in intensity and a second set of bands at *ca.* 1910—1930 cm^{-1} appeared. Following Chapman,[4] we attribute the latter bands to the didehydrobenzazepines [(**6**) and/or (**8**) from (**3**), (**12**) and/or (**14**) from (**9**)]. The presence of two i.r. bands at 1910—1930 cm^{-1} may indicate the formation of two didehydroazepines for each azide, but may be due merely to matrix splitting. The i.r. bands at 1708—1736 cm^{-1} clearly belong to precursors of the didehydroazepines. We assign these bands to the tricyclic azirines [(**5**) and/or (**7**) from (**3**), (**11**) and/or (**13**) from (**9**)],‡ rather than the nitrenes [(**4**) and (**10**)], which would not be expected to have a strong absorption in this region.

Thus, for the photolysis of naphthyl azides (and, by extension, possibly also phenyl azide) the azirine intermediates are accessible and do have finite lifetimes.

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‡ *Cf.* 2-Phenylazirine, γ(C=N) 1755 cm^{-1} in an argon matrix (ref. 4a).

[1] B. A. DeGraff, D. W. Gillespie, and R. J. Sundberg, *J. Am. Chem. Soc.*, 1974, **96**, 7491.
[2] S. E. Carroll, B. Nay, E. F. V. Scriven, and H. Suschitzky, *Tetrahedron Lett.*, 1977, 943.
[3] D. D. Shillady and C. Trindle, *Theor. Chim. Acta*, 1976, **43**, 137.
[4] (a) O. L. Chapman and J. P. LeRoux, *J. Am. Chem. Soc.*, 1978, **100**, 282. (b) O. L. Chapman, R. S. Sheridan, and J. P. LeRoux, *Rec. Trav. Chim. Pays-Bas*, 1979, **98**, 334.
[5] J. Rigaudy, C. Igier, and J. Barcelo, *Tetrahedron Lett*, 1979, 1837.
[6] J. Rigaudy, C. Igier, and J. Barcelo, *Tetrahedron Lett.*, 1975, 3845.
[7] Azides (**3**) and (**9**) were prepared by the method of G. Boshev, L. K. Dyall, and P. R. Sadler, *Aust. J. Chem.*, 1972, **25**, 599.