

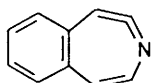
Pentafluorophenyl Nitrene: a Matrix Isolated Aryl Nitrene that Does Not Undergo Ring Expansion

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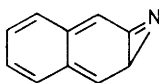
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Photolysis of pentafluorophenyl azide or pentafluorophenyl isocyanate in low-temperature matrices gives pentafluorophenyl nitrene which, in the presence of CO, may react photochemically but not thermally to give the isocyanate.

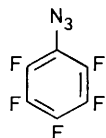
Numerous photolyses of aryl azides in a variety of rigid media at low temperatures have permitted the observation of electronic or e.s.r. spectra of the corresponding nitrenes.¹ On the other hand, i.r. studies of the photolysis of phenyl azide² in Ar matrices and naphthyl azides³ in N₂ and Ar matrices indicate that the major products are ring-expanded dehydroazepines, *e.g.* (1), that may arise *via* intermediate bicyclic or tricyclic azirines, *e.g.* (2). The conclusion, therefore, is that triplet nitrenes are minor products under these conditions.



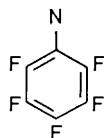
(1)



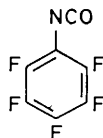
(2)



(3)



(4)



(5)

Azepine products are commonly obtained from both thermal and photochemical decomposition of aryl azides in solution. Pentafluorophenyl azide (3), however, generally yields nitrene-derived products.⁴ Only when it has been passed through a platinum tube at 280–300 °C has pentafluorophenyl azide given a ring-expanded product, and then only in low yield.⁵ Hence we chose this azide as a likely precursor of an aryl nitrene that would be reluctant to form either azirine or dehydroazepine secondary products, when photolysed in low-temperature matrices.

U.v. irradiation (240 min, $\lambda > 300$ nm) of (3) in N₂ or Ar matrices at 12 K (matrix ratio 1:400–500) led to the disappearance of its i.r. bands and the appearance of a new i.r. spectrum.^{†‡} The photoproduct had no i.r. bands in the

[†] Matrix gas mixtures were prepared monometrically and deposited on a CsBr window at 20 K. I.r. spectra were recorded on a JASCO IRA-2 i.r. spectrometer. The photolysis source was a 200 W high-pressure Hg arc.

[‡] I.r. bands (cm⁻¹) arising upon photolysis of (3) in N₂ matrices at 12 K: 1575 m, 1565 m, 1502 vs, 1462 vs, 1454 vs, 1359 s, 1284 m, 1204 w, 1149 w, 1029 vs, 1007 s, 990 m, and 981 vs (w = weak, m = medium, s = strong, vs = very strong). For Ar and CO matrices, similar bands arose at frequencies within 4 cm⁻¹ of those quoted.

regions characteristic of dehydroazepines ($1800\text{--}2000\text{ cm}^{-1}$) or azirine intermediates ($1650\text{--}1800\text{ cm}^{-1}$), and was stable towards further irradiation and annealing at 35 K. A bright orange colour developed, however, when the matrices were boiled off (70 K). The photoproduct was thus most probably the nitrene (4).

When (3) was photolysed in CO matrices or N_2 matrices doped with 12% CO (matrix ratio 1:500—700), both the nitrene and pentafluorophenyl isocyanate (5) were formed; the latter being identified by spectral comparison with an authentic sample. Annealing of these matrices to 35 K did not, however, result in further growth of the i.r. bands of (5) or diminution of those of (4). In N_2 matrices doped with only 2—3% CO (matrix ratio 1:500), nearly all the azide could be photolysed, with very little initial formation of the isocyanate. As before, annealing to 35 K caused no growth of the isocyanate bands, but further irradiation ($\lambda > 330\text{ nm}$) following annealing resulted in formation of the isocyanate at the expense of the nitrene. Thus the nitrene may react photochemically with CO but not thermally.

Perhaps it is not surprising that the triplet nitrene does not react thermally with CO at such low temperatures, since the direct formation of ground state isocyanate is spin-forbidden. It should be noted, however, that in similar matrices, cyclopentadienylidene, a triplet carbene, reacts readily with CO at 25—30 K, yielding the corresponding keten.⁸ Nitrene (4) is therefore much less reactive than cyclopentadienylidene. The most straightforward interpretation of our results for the reaction between (4) and CO assumes (i) that the ground state triplet nitrene is unreactive towards CO at 35 K, (ii) that annealing matrices containing triplet-(4) and CO merely allows diffusion of CO, and (iii) that after such diffusion newly formed cage-pairs of (4) and CO molecules may react photochemically *via* an excited state of (4). This would probably be the first singlet state, attained by intersystem crossing from the first excited triplet state. Isocyanate produced during initial photolysis of (3) probably derives largely from cage-pairs of (3) and CO that are formed in the matrix upon deposition.

The isocyanate (5) was only slowly photolysed in N_2 matrices, but irradiation with an unfiltered Hg arc (100 min) resulted in partial decomposition of (5) to CO and the nitrene (4). Our assignment of the nitrene structure (4) to the matrix photoproduct of azide (3) is thus supported by its formation from both the azide and the isocyanate, and by its reaction with CO.

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References

- 1 See for example: A. Reiser, G. Bowes, and R. J. Horne, *Trans. Faraday Soc.*, 1966, **62**, 3162; S. B. Brichkin, V. A. Smirnov, M. V. Alifimov, T. P. Naidenova, and L. F. Avramenko, *Khim. Vys. Energ.*, 1980, **14**, 23; G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, 1962, **84**, 3220; E. Wasserman, G. Smolinsky, and W. A. Yager, *ibid.*, 1964, **86**, 3166; J. A. R. Coope, J. B. Farmer, C. L. Gardner, and C. A. McDowell, *J. Chem. Phys.*, 1965, **42**, 54; R. M. Moriarty, M. Rahman, and J. G. King, *J. Am. Chem. Soc.*, 1966, **88**, 842; E. Wasserman, *Prog. Phys. Org. Chem.*, 1971, **8**, 319; O. L. Chapman, R. S. Sheridan, and J.-P. LeRoux, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 334.
- 2 O. L. Chapman and J.-P. LeRoux, *J. Am. Chem. Soc.*, 1978, **100**, 282.
- 3 I. R. Dunkin, and P. C. P. Thomson, *J. Chem. Soc., Chem. Commun.*, 1980, 499.
- 4 R. A. Abramovitch and S. R. Challand, *J. Chem. Soc., Chem. Commun.*, 1972, 1160; R. A. Abramovitch, S. R. Challand, and Y. Yamada, *J. Org. Chem.*, 1975, **40**, 1541; R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Am. Chem. Soc.*, 1972, **94**, 1374; R. E. Banks and A. Prakash, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1365.
- 5 R. E. Banks, N. D. Venayak, and T. A. Hamor, *J. Chem. Soc., Chem. Commun.*, 1980, 900.
- 6 M. S. Baird, I. R. Dunkin, N. Hacker, M. Poliakoff, and J. J. Turner, *J. Am. Chem. Soc.*, 1981, **103**, 5190.