Effect of substitution on the yield of high-spin nitrenes in the photolysis of 2,6-diazidopyridines

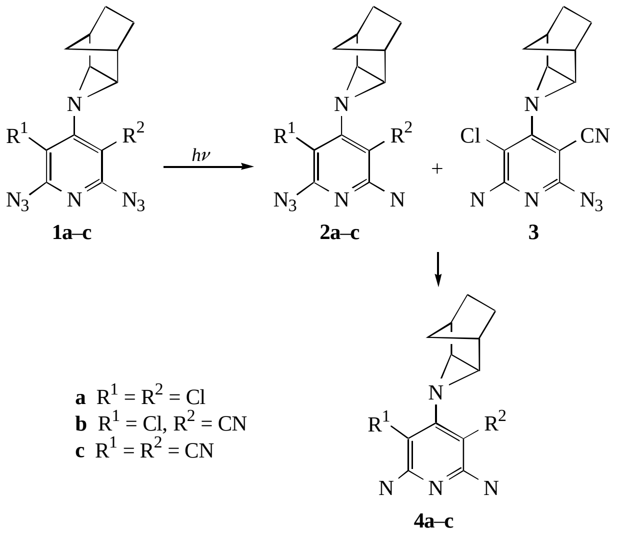
Sergei V. Chapyshev,*[a] Richard Walton[b] and Paul M. Lahti*[b]

[a] *Institute for Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 096 515 3588; e-mail: chap@icp.ac.ru*
[b] *Department of Chemistry, University of Massachusetts, Amherst, MA 01003-4510, USA. Fax: +1 413 545 4490; e-mail: lahti@grond.chem.umass.edu*

10.1070/MC2000v010n03ABEH001281

The effect of substitution on the yield of high-spin nitrenes in the photolysis of 3-(2,6-diazidopyridin-4-yl)-3-azatricyclo[3.2.1.0^{2,4}]-octane derivatives at a cryogenic temperature in inert matrices is described.

In recent years, there has been considerable progress in the study of high-spin nitrenes as models for molecular electronic behaviour.[1] The attention was focused on the exploration of the effects of geometry and bond connectivity in nitrenes on their spin states and EPR characteristics.[2] At the same time, almost nothing is known about the effect of substituents on the yield of high-spin nitrenes in the photolysis of polysubstituted aryl azides. Such azides do not undergo undesirable ring expansions[3] upon irradiation and therefore can be considered as the most promising precursors of high-spin nitrenes. This work deals with an EPR study of open-shell products formed by photolysis of diazides **1a–c** in a cryogenic marix.



The synthesis of diazides **1a–c** was described earlier.[4] The irradiation of diazide **1a** in a degassed frozen 2-methyltetrahydrofuran (MTHF) solution for 5 min with a xenon arc lamp (Pyrex filtered, > 300 nm) at 77 K led to the appearance of an EPR spectrum (Figure 1). By analogy with previously studied pyridylnitrenes,[5–7] a strong signal at 6900 G can be assigned to triplet 2-nitrenopyridine **2a** with the zero field splitting (zfs) parameters $|D/hc| = 1.02$ cm^{-1} and $|E/hc| = 0.003$ cm^{-1}.

The other signals in the spectrum are attributable to quintet dinitrene **4a** with the following zfs parameters assigned by an eigenfield[8] simulation: $S = 2$, $|D/hc| = 0.257$ cm^{-1} and $|E/hc| = 0.052$ cm^{-1}. For aromatic *m*-dinitrenes, the quintet zfs *D*-value typically is significantly smaller, with a major peak at about 3000 G rather than the peak at about 3300 G, just upfield of a radical peak at $g \sim 2$.[9] The higher *D*-value for **4a** is apparently due to the effect of the pyridine nitrogen on the intramolecular exchange interaction between electrons in two nitrene units. Figures 1(*a*) and 1(*b*) show the simulated and experimental EPR spectra, respectively.

Diazides **1b**,**c** were irradiated under the same conditions as in the case of **1a**. Only a very weak EPR signal of triplet nitrene **2c** at about $|D/hc| = 1.05$ cm^{-1} was detected from **1c** [Figure 1(*c*)]. The higher *D*-value for **2c** compared to that for **2a** is explained by the effect of the two strong electron-withdrawing CN groups. Similar effects were observed earlier for other triplet pyridyl-2-nitrenes.[6(*b*)] Interestingly, there is no indication of the quintet dinitrene formation from **2c**. This shows that the formation of **4c** is inefficient in this case. B3LYP/6-31G* computations[†] indicate that the ground state of **4c** should still be a quintet by about 29 kJ mol^{-1}, so the lack of a quintet spectrum is presumably not due to a change in the ground state spin multiplicity going from **4a** to **4c**. The EPR spectrum of **1b** [Figure 1(*d*)] represents an intermediate behaviour between that of **1a** and **1c**, since it contains a broad upfield peak from presumed nitrenes **2b** and **3**, as well as weak signals at 1047 and 3233 G attributable to quintet dinitrene **4b**. The appearance of the upfield peak is similar to an analogous peak observed in the photolysis of **1a**. Presumably, only small amounts of the nitrene *ortho* to the CN group are formed, but enough to give the observed small quintet peak.

The results clearly indicate that the progressive introduction of cyano groups into the 3- and 5-positions of 2,6-diazidopyridines disfavours the preparation of high-spin products. This effect most probably results from an enhanced photolability of intermediates **2b**,**c** and **3**, which more readily undergo fragmentation[‡] of the pyridine ring rather than produce quintet dinitrenes **4b**,**c**. Similar problems have recently been observed on an attempt to prepare high-spin products from cyanuric triazide.[11] Obviously, the higher the percentage of nitrogen atoms in the molecules of nitrenes, the lower the stability. At the same time, the high yield of quintet dinitrene **4a** from **1a** [Figure 1(*b*)] demonstrates that readily available chlorine-substituted aromatic polyazides can be successfully used for the synthesis of novel magnetic organic materials.

This work was supported by the National Science Foundation (grant nos. CHE-951595 and CHE-9740401).

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[†] Computations were carried out using the B3LYP density functional with the 6-31G* basis set, optimising the quintet and triplet states separately with the program Gaussian-98 for Silicon Graphics computer.[10]

[‡] According to an FTIR study[6(c)] of the photolysis of **1c** in argon at 7 K, this diazide forms nitrene **2c** in < 1% yield. This is obviously the reason for the low intensity of the EPR signal of **2c** [Figure 1(*c*)].

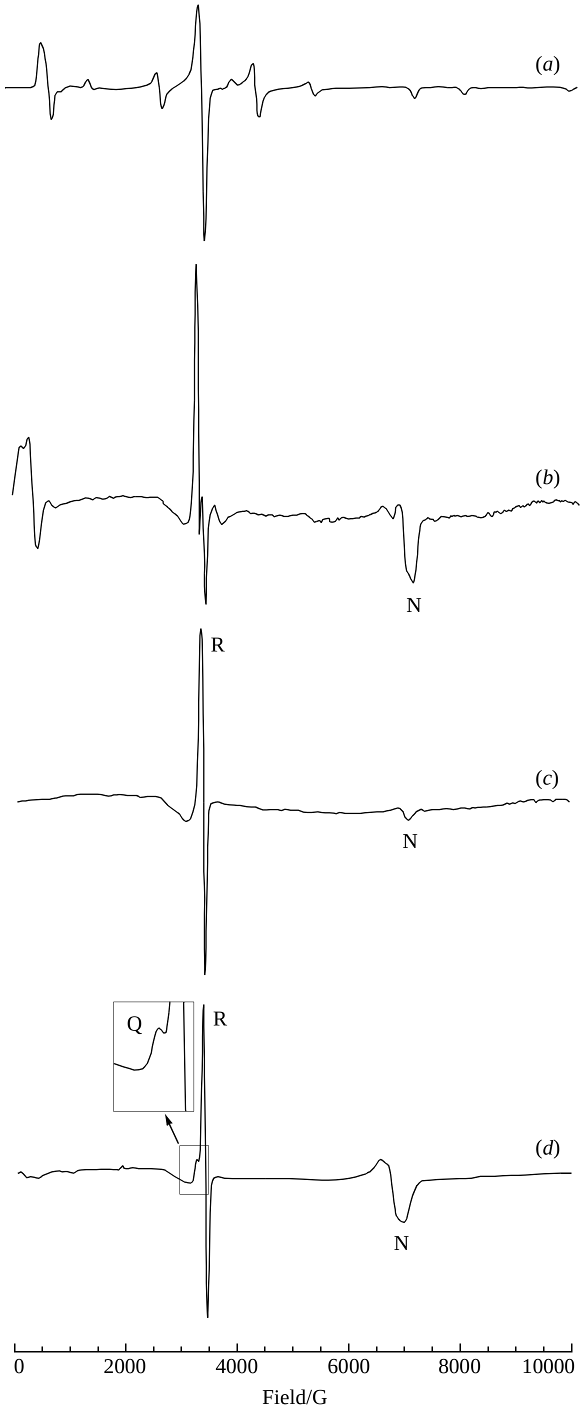

Figure 1 (*a*) Simulated[8] EPR spectrum for a randomly oriented system with $S = 2$, $|D/hc| = 0.257\ \text{cm}^{-1}$, $|E/hc| = 0.052\ \text{cm}^{-1}$; (*b*) EPR spectrum from the photolysis of diazide **1a** ($\nu_0 = 9.562$ GHz) at 77 K in a 2-methyltetrahydrofuran glass; (*c*) EPR spectrum from the photolysis of diazide **1c** ($\nu_0 = 9.562$ GHz) at 77 K in a 2-methyltetrahydrofuran glass; (*d*) EPR spectrum from the photolysis of diazide **1b** ($\nu_0 = 9.569$ GHz) at 77 K in a 2-methyltetrahydrofuran glass. The arrow indicates the quintet peak in the inset for 3000–3500 G. N is the triplet nitrene peak, Q is the quintet dinitrene peak and R is the radical peak.

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Received: 11th February 2000; Com. 00/1607