

Supplementary Material

Chemical Activation in Azide and Nitrene Chemistry

(Methyl Azide, Phenyl Azide, Pyridyl Azides, Naphthyl Azides, Benzotriazole and Triazolopyridines)

Curt Wentrup

School of Chemistry and Molecular Biosciences
The University of Queensland, Brisbane, Qld 4072, Australia
wentrup@uq.edu.au

Details of computational methods:

Energies were calculated at the (U)B3LYP/6-31G*, CAS(8,8)/6-31G* and CASPT2//CAS(8,8)/6-31G* levels as detailed below:

Closed-shell species were calculated at the B3LYP/6-31G* level and open-shell species at the UB3LYP/6-31G* level using Gaussian 03.¹ In cases where $\langle S^2 \rangle \approx 1$ (e.g. open-shell singlet nitrenes S_1), the energy was corrected using the sum method of Cramer and Ziegler²: “The energy is computed as $E(S_1) = 2 E(50:50) - E(T_0)$ where $E(50:50)$ is the energy of the broken symmetry unrestricted DFT wave function having an expectation value of 1 for the $\langle S^2 \rangle$ operator applied to a Slater determinant formed from the DFT orbitals (i.e., the exact wave function for the non-interacting Kohn–Sham reference system), and $E(T_0)$ is the energy of the triplet”.

The singlet-triplet energy splittings (S_1-T_0) in phenylnitrene and 2-pyridylnitrene as well as the activation barriers for ring opening/ring contraction of the S_1 open-shell singlet nitrenes were also calculated at the CASPT2//CAS(8,8)/6-31G* level using MOLCAS.³

Previous calculations on the 1- and 2-naphthyl nitrenes showed good agreement between CASPT2 and (U)B3LYP calculations.⁴

Experimental

General Experimental Procedures have been described previously.⁵

All FVT reactions were carried out using unpacked quartz tubes, 20 x 2 cm for preparative reactions and 10 x 0.8 cm I.D. for matrix-isolation experiments. Vacuum was maintained using turbomolecular or oil diffusion pumps and were usually ca. 10^4 - 10^{-3} hPa. When N_2 or Ar was used as a carrier gas, it was introduced through a needle valve or a capillary so that the desired pressure was maintained (e.g. 0.1 – 1 hPa) while still pumping continuously.

Methyl azide. This was pyrolyzed at 400-900 °C using a 25 x 1 cm preparative FVT tube in an oven directly attached to the continuously pumped millimeterwave spectrometer flow tube.⁶

Phenyl and 4-pyridyl azides

In order to achieve good yields of ring contraction of phenylnitrene and 4-pyridylnitrene to cyanocyclopentadiene and cyanopyrroles, respectively, it is necessary to perform the reaction under “violent pyrolysis” conditions, whereby the azide is heated rapidly to ca. 100 °C in a sample reservoir directly attached to the continuously pumped pyrolysis tube. The ensuing rapid evaporation causes the formation of a shock wave, which evaporates the bulk of the azide instantaneously. Thus, temperatures far higher than the nominal temperatures (400-500 °C) are achieved. This is necessary because otherwise these nitrenes undergo intersystem crossing to the ground state triplets, which do not undergo ring contraction, forming arylamines and azo compounds instead.

Other azides, tetrazoles and triazoles

The other compounds investigated here do not require “violent pyrolysis”. They were pyrolyzed under normal conditions, i.e. generally 350-900 °C/10⁻⁴-10⁻³ hPa, and the starting materials were sublimed into the FVT tubes at temperatures below their melting points.

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03, Revision E.01*; Gaussian, Inc., Wallingford CT, 2004.

(2) Johnson, W. T. G.; Sullivan, M. B.; Cramer, C. J. *Int. J. Quant. Chem.* **2001**, *85*, 492.

(3) Andersson, K.; Barysz, M.; Bernhardsson, A.; Blomberg, M. R. A.; Carissan, Y.; Cooper, D. L.; Cossi, M.; Devarajan, A.; Fülscher, M. P.; Gaenko, A.; Gagliardi, L.; de Graaf, C.; Hess, B. A.; Hagberg, D.; Karlström, G.; Krogh, J. W.; Lindh, R.; Malmqvist, P.-Å.; Nakajima, T.; Neogrády, P.; Olsen, J.; Pedersen, T. B.; Raab, J.; Roos, B. O.; Ryde, U.; Schimmelpfennig, B.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Stålring, J.; Thorsteinsson, T.; Veryazov, V.; Widmark, P.-O. *MOLCAS*, version 7.2, University of Lund: Sweden, 2008.

(4) Maltsev, T. Bally, M.-L. Tsao, M. S. Platz, A. Kuhn, M. Vosswinkel and C Wentrup, *J. Am. Chem. Soc.* **2004**, *126*, 237.

(5) Wentrup, C.; Kvaskoff, D. *Aust. J. Chem.* **2013**, *66*, 286 (Supplementary Material). Wentrup, C.; Lan, N. M.; Lukosch, A.; Bednarek, P.; Kvaskoff, D. *Beilstein J. Org. Chem.* **2013**, *9*, 743. Wentrup, C.; Reisinger, A.; Kvaskoff, D. *Beilstein J. Org. Chem.* **2013**, *9*, 754. Kvaskoff,

D.; Bednarek, P.; Wentrup, C. *J. Org. Chem.* **2010**, *75*, 1600. Kvaskoff, D.; Mitschke, U.; Addicott, C.; Bednarek, P.; Finnerty, J.; Wentrup, C. *Aust. J. Chem.* **2009**, *62*, 275. Lan, N. M.; Burgard, R.; Wentrup, C. *J. Org. Chem.* **2004**, *69*, 2033.

(6) Winnewisser, M.; Winnewisser, B. P. *Z. Naturforsch. A* **1974**, *29a*, 633.