JOC Article

Different Behavior of Nitrenes and Carbenes on Photolysis and Thermolysis: Formation of Azirine, Ylidic Cumulene, and Cyclic Ketenimine and the Rearrangement of 6-Phenanthridylcarbene to 9-Phenanthrylnitrene

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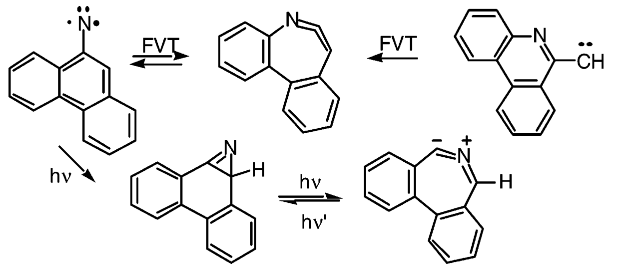
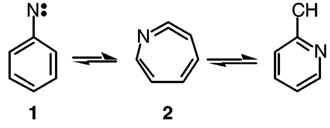


Flash vacuum thermolysis (FVT) of 9-azidophenanthrene **8**, 6-(5-tetrazolyl)phenanthridine **18**, and [1,2,3]triazolo[1,5-*f*]phenanthridine **19** yields 9-cyanofluorene **12** as the principal product and 4-cyanofluorene as a minor product. In all cases, when the product is condensed at or below 77 K, the seven-membered ring ketenimine **24** is detectable by IR spectroscopy (1932 cm^{-1}) up to 200 K. Photolysis of Ar matrix isolated **8** at $\lambda = 308$ or 313 nm generates at first the azirine **26**, rapidly followed by the ylidic cumulene **27**. The latter reverts to azirine **26** at $\lambda > 405$ nm, and the azirine reverts to the ylidic cumulene at 313 nm. Nitrene **9** is observed by ESR spectroscopy following FVT of either azide **8**, tetrazole **18**, or triazole **19** with Ar matrix isolation of the products. Nitrene **9** and carbene **21** are observed by ESR spectroscopy in the Ar matrix photolyses of azide **8** and triazole **19**, respectively.

Introduction

The rearrangements and interconversions of aromatic carbenes and nitrenes, e.g., phenylnitrene **1** and 2-pyridylcarbene (eq 1), have been the subject of intense interest.[1] Recently, DFT calculations[2] revealed that annelated derivatives of the cyclic ketenimine **2** may exist in an ylidic (zwitterionic) form **6** rather than the classical *o*-quinoid ketenimine form **7**. The cost of charge separation in the ylide is compensated by the recovery of the resonance energy of the benzene ring. 4-Quinolylnitrene and 1-naphthylnitrene **3** can in principle undergo ring expansion in two directions, either via the high energy azirine **4a** (which is a transition state) or the lower



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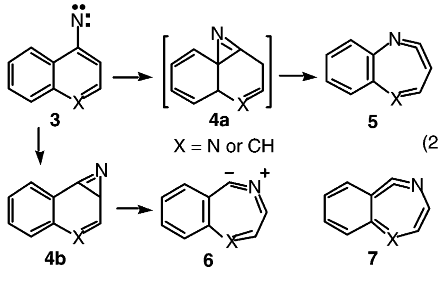

(2)

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(1) (a) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173. (b) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*. 232. (c) Gritsan, N. P.; Platz, M. S. *Adv. Phys. Org. Chem.* **2001**, *36*, 255. (d) Karney, W. L.; Borden, W. T. *Adv. Carbene Chem.* **2001**, *3*, 205.

(2) Kuhn, A.; Vosswinkel, M.; Wentrup, C. *J. Org. Chem.* **2002**, *67*, 9023.

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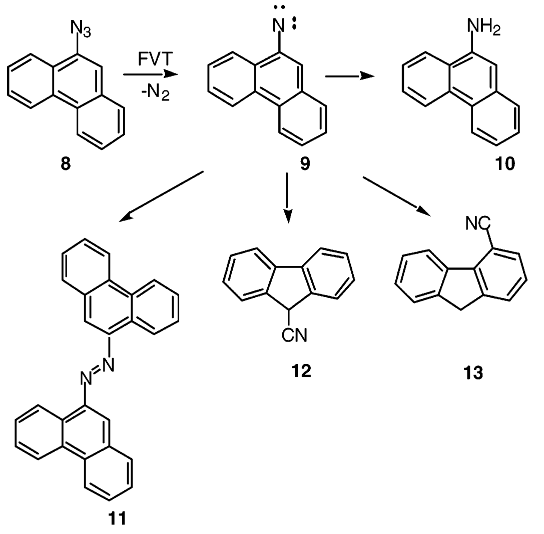
energy azirine **4b**, to afford ketenimines **5** and/or **6/7** (eq 2). Calculations indicated that all three cumulenes (**5**, **6**, and **7**) can exist as separate energy minima,[2,3] and a similar choice exists for 2-naphthylnitrene. Recent experiments have demonstrated that the ylides such as **6** formed from 1- and 2-naphthylnitrenes are indeed spectroscopically observable.[3] Here we report that different cumulenes are obtained from 9-phenanthrylnitrene under thermal and photochemical conditions. Furthermore, the rearrangement of 6-phenanthridylcarbene to 9-phenanthrylnitrene is demonstrated.

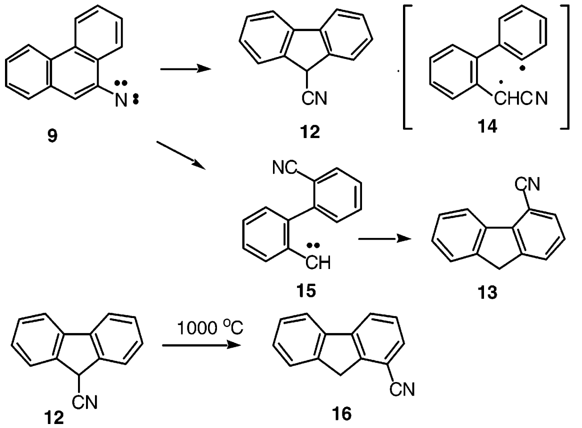
Results and Discussion

FVT. 9-Azidophenanthrene **8** was subjected to flash vacuum thermolysis (FVT) at temperatures between 450 and 600 °C (no significant reaction took place at lower temperatures). The following products were isolated and identified from the FVT reaction at 500 °C: 9-cyanofluorene **12** (73%), phenanthrene (7%), 9,9′-azophenanthrene **11** (10%), and 9-aminophenanthrene **10** (10%). Compounds **10** and **11** are the typical triplet arylnitrene products, and their formation demonstrates that some intermolecular reaction take place under FVT conditions. Compound **12** is the expected product of ring contraction.[1a,4]



Closer inspection of the Ar matrix IR spectra and GC/MS analyses of the crude thermolysis products revealed that minor amounts of 4-cyanofluorene **13** and 1-cyanofluorene **16** were also present (2.5% of each at 500 °C; 6.7% of **13** and 3.7% of **16** at 600 °C by GC).[5] These compounds were identified by direct comparison with synthetic samples. Because it is known that cyano groups can undergo migrations in aromatic systems at high temperatures, and such shifts can be accelerated strongly by chemical activation,[6] it was necessary to check the FVT of 9-cyanofluorene **12**. FVT of **12** at 600−800 °C did not result in any isomerization. At 1000 °C a 5% rearrangement to 1-cyanofluorene **16** took place; 4-cyanofluorene was not detectable. A 1% yield of fluorene was also obtained, which indicates the occurrence of a free radical pathway. Therefore, in any FVT reaction where 9-cyanofluorene **12** is formed at elevated temperature, and/or in strongly exothermic reactions, where chemical activation is likely, minor amounts of 1-cyanofluorene **16** may be expected as a byproduct.

SCHEME 1



Formation of 9-cyanofluorene **12** could proceed via ring opening to diradical **14** (Scheme 1), but calculations reported below indicate that there is a lower energy transition state for the concerted ring contraction, **9** → **12**. CASPT2/CASSCF(8,8) calculations with the cc-PVDZ-Dunning basis set for phenylnitrene **1 OSS** (open-shell singlet) give an activation energy of 31 kcal/mol for the concerted ring contraction to 5-cyanocyclopentadiene. This is further discussed in the Calculations section.

The mechanism of formation of 4-cyanofluorene **13** is thought to involve ring opening to the carbene **15** (Scheme 1). Calculations reported below show that this carbene can cyclize to **13** in a highly exothermic reaction (∼92 kcal/mol). The cyclization of 2-biphenylylcarbene to fluorene takes place via "isofluorene" (9a*H*-fluorene) and has a very small calculated barrier.[7]

When the FVT of **8** was carried out with isolation of the products on a KBr target, either as a neat solid film at 77 K or with Ar at 20 K for IR spectroscopic monitoring, a new species absorbing strongly at 1932 cm^{-1} was observed together with 9-cyanofluorene, which has characteristic strong bands at 1451, 759, and 742 cm^{-1} and CN stretching vibrations at 2262 and 2234 cm^{-1} (Figure 1).

The 1932 cm^{-1} signal disappeared on warming between 150 and 200 K and is ascribed to the dibenzo[*d,f*]-1-azacycloheptatraene **24** (Scheme 2). No discrete product was identified as a result of the warming, but dimerization analogous to that of the carbodiimide (dibenzo[*d,f*]-1,3-diazacycloheptatetraene) analog[5b] is a possibility. Compound **24** is the first seven-membered ring keten-

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

(4) (a) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1967**, 4379. (b) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol 1, Chapter 4, p 263f. (c) Wentrup, C. In *Azides and Nitrenes*; Scrivcn, E. F. V., Ed.; Academic Press: New York, 1984; Chapter 8, p 395 f.

(5) The thermal ring contractions of 9-phenanthridylnitrene to a mixture of 9- and 4-cyanocarbazoles, its ring expansion to dibenzo-[*d,f*]-1,3-diazcycloheptatetraene, and the dimerization of the latter to a stable 2,4-diimino-1,2-diazetidine derivative have been reported: (a) Wentrup, C.; Thetaz, C.; Mayor, C. *Helv. Chim. Acta* **1972**, *55*, 2633. (b) Wentrup, C.; Winter, H.-W. *J. Am. Chem. Soc.* **1980**, *102*, 6159.

(6) (a) Lan, N. M.; Burgard, R.; Wentrup, C. *J. Org. Chem.* **2004**, *69*, 3022. (b) Wentrup, C.; Crow, W. D. *Tetrahedron* **1970**, *26*, 3965.

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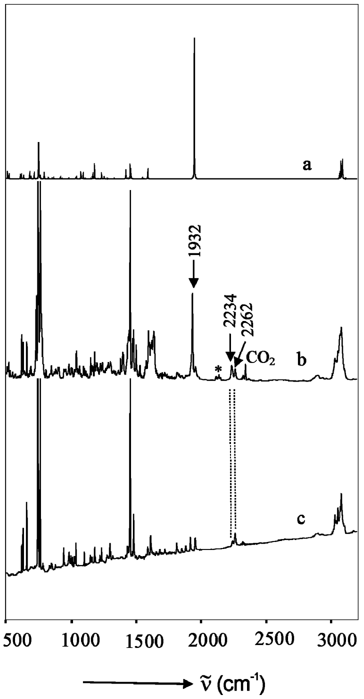
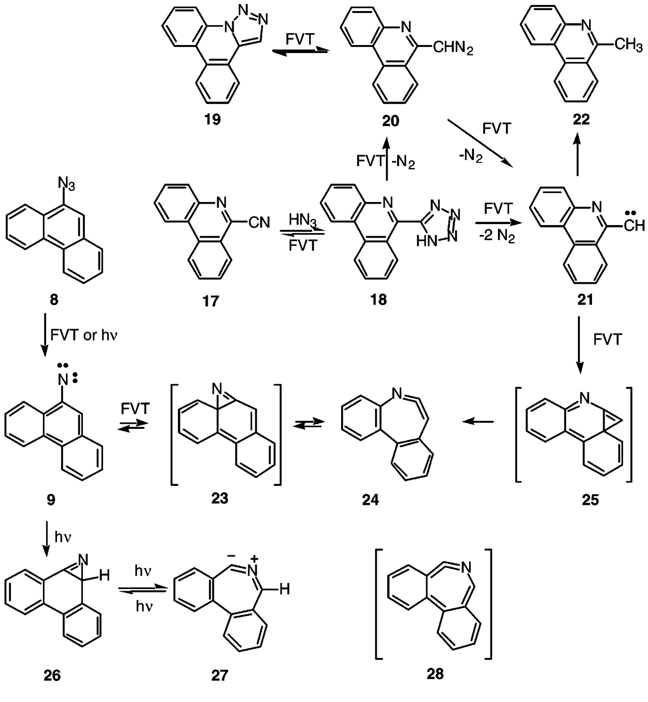


FIGURE 1. (a) Calculated IR spectrum of dibenzoazacycloheptatraene **24** (B3LYP/6-31G* level with a scaling factor of 0.9613 for wavenumbers). (b) IR spectrum after FVT of 9-azidophenanthrene **8**. A strong ketenimine band at 1932 cm^{-1} is assigned to species **24**; bands belonging to 9-cyanofluorene **12** are at 2262, 2234, 1451, 759, and 742 cm^{-1}; the increased intensity at 2234 cm^{-1} is due to 4-cyanofluorene **13**; the asterisk depicts a trace of the precursor, **8**. (c) IR spectrum of matrix-isolated 9-cyanofluorene **12** with characteristic bands at 2262, 2234, 1455, 1451, 759, 742 cm^{-1}. The abscissa is in wavenumbers.

SCHEME 2

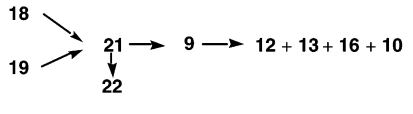


imine to be stable enough to be detected in an FVT experiment without recourse to matrix isolation photochemistry. In other words, this is the first direct proof that arylnitrenes actually undergo ring expansion to azacycloheptatetraenes in the gas phase under thermal conditions. The two benzo rings confer considerable stability to the molecule, just as is the case for the cyclic carbodiimide analogue.[5] Nevertheless, **24** is a delicate compound. It was observable only when an "internal" oven was used, consisting of a 10 cm long, 0.7 cm i.d., electrically heated quartz tube suspended in a vacuum chamber directly flanged onto the cryostat cold head so that the FVT products can travel to the cold KBr target without any wall collisions occurring. If an "external" oven was used, consisting of a similar quartz tube but with a 5 cm unheated length connecting it to the cold head, no trace of the 1932 cm^{-1} absorption was detectable.

The wavenumber of the ketenimine function in **24** is in line with expectations; 1895 cm^{-1} for **2**; 1902−1909 for **5** (X = N)[2] and 1913−1926 for **5** (X = CH).[3,6,8] The calculated IR spectrum of **24** (Figure 1a) predicts the cumulenic stretching vibration at 1947 cm^{-1} at the B3LYP/6-31G* level. At the B3LYP/6-31+G* level it is at 1934 cm^{-1}. The *o*-quinoid ketenimine "bond-shift" isomer **28** (Scheme 2) is not an energy minimum, and hence its IR spectrum was not calculated. However, judging from our computational experience with the ring expansion products of the quinolyl- and naphthylnitrenes,[2,3] *o*-quinoid ketenimines of this type, e.g., **7** (eq 2), should absorb strongly around 1800 cm^{-1}, i.e., in between the aromatic ketenimines such as **5** and **24** and ylidic cumulenes such as **6** and **27** (see below).

We have reported the aromatic carbene−nitrene rearrangement (eq 1)[9] and demonstrated that nitrenes are inherently more stable than the isomeric carbenes.[1a] Thus, 2-pyridylcarbene rearranges thermally to phenylnitrene **1**. Modern calculations have confirmed this.[10] Arylcarbenes can be generated by FVT of 5-aryltetrazoles by consecutive loss of two nitrogen molecules, a reaction leading to aryldiazomethanes initially.[6a,11] The same aryldiazomethanes may be formed by reversible ring opening of triazoloazines.[6a,11] Therefore, to generate carbene **21**, tetrazole **18** was prepared by addition of HN_3 to phenanthridine-6-carbonitrile **17**, and triazole **19** by oxidation of the hydrazone of phenanthridine-6-carboxaldehyde with MnO_2.

Preparative FVT of tetrazole **18** at 600 °C resulted in partial cycloreversion to nitrile **17** (3−10%), but the main product was 9-cyanofluorene **12** (isolated in 68% yield), which suggests that a very efficient carbene−nitrene rearrangement (**21** → **9**) is taking place. 6-Methylphenanthridine **22** and small amounts of 4-cyanofluorene **13**, 1-cyanofluorene **16**, and 9-aminophenanthrene **10** were also formed (eq 3). The former product (**22**) suggests


(3)

$$\begin{tikzcd}
\mathbf{18} \arrow[dr] & & & \\
& \mathbf{21} \arrow[r] \arrow[d] & \mathbf{9} \arrow[r] & \mathbf{12}+\mathbf{13}+\mathbf{16}+\mathbf{10} \\
\mathbf{19} \arrow[ur] & \mathbf{22} & &
\end{tikzcd} \qquad (3)$$

H-abstraction by 6-phenanthridylcarbene **21**, again revealing the occurrence of intermolecular reactions under

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(8) Dunkin, I.; Thomson, P. C. P. *Chem. Commun.* **1980**, 499.

(9) (a) Wentrup, C. *Chem. Commun.* **1969**, 1386. (b) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1968**, 6149.

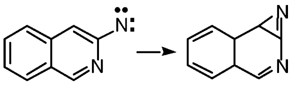
(10) Kemnitz, C. R.; Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 3499.

(11) Wentrup, C. *Helv. Chim. Acta* **1978**, *61*, 1755.

FVT conditions. The presence of a small amount of 9-aminophenanthrene is important evidence for the formation of nitrene **9**. When this reaction was carried out at 600 °C using the internal oven with product isolation at 20 K for IR spectroscopy, 9-cyanofluorene **12** (2262, 742 cm^{-1}), 4-cyanofluorene (2235 cm^{-1}), and the cyclic ketenimine **24** (1932 cm^{-1}; observable until 200 K on warm up without Ar) were recorded (the IR spectrum is shown as Figure S1 in the Supporting Information). GC/MS of the thermolysate also revealed the formation of substantial amounts of triazolophenanthridine **19**, formed by loss of N_2 from the tetrazole **18** and recyclization of the diazo compound **20** so produced.

Similarly, FVT of triazole **19** at 600−750 °C followed by GC/MS analysis afforded 9-cyanofluorene **12**, 6-methylphenanthridine, and small amounts of 1- and 4-cyanofluorenes and 9-aminophenanthrene. FVT at 550 °C using the internal oven and Ar matrix isolation of the products at 12 K allowed the detection of the cyclic ketenimine **24** (1932 cm^{-1}) and 9-cyanofluorene **12** (2262, 742 cm^{-1}) by IR spectroscopy.

Photolysis. The matrix photolysis of azide **8** was quite different. The ketenimine **24** was not observed at all. Instead, brief photolysis of **8** (Ar, 7 K, 313 nm, 30 s) resulted in a new species absorbing at 1742 cm^{-1}. In the course of further photolysis another new species rapidly grew in at 1702 cm^{-1}, and this was the main species after 14 h, i.e., the time required to fully destroy the azide. Photolysis of the 1702 cm^{-1} species at $\lambda > 405$ nm regenerated the 1742 cm^{-1} species, which could again be converted to the 1702 cm^{-1} species at 313 nm. It was possible to cycle between these two species several times. Suitable spectral subtraction generated the spectra of the individual compounds, and the good agreement with the DFT-calculated spectra identify them as azirine **26** ($\nu_{C=N} = 1742$ cm^{-1}) and ylidic cumulene **27** (1702 cm^{-1}), respectively (Scheme 2 and Figure 2). The corresponding azirine **4b** derived from 1-naphthylnitrene **3** (eq 2; $X =$ CH) has $\nu_{C=N} \sim 1730$ cm^{-1}, and the ylidic cumulene **6** absorbs at ca. 1700 cm^{-1}.[3] The analogous azirine and ylidic cumulene from 2-naphthylnitrene absorb at ca. 1725−1730 and 1680 cm^{-1}, respectively.[3] The azirine **29** formed by cyclization of 3-isoquinolylnitrene has $\nu_{C=N} =$ 1725 cm^{-1} in an Ar matrix.[4c]



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As explained above, the *o*-quinoid ketenimine "bond-shift" isomer **28** (Scheme 2) is not a calculated energy minimum, but it would be expected to absorb in the 1800 cm^{-1} range in the IR spectrum.[2,3]

Similar matrix photolysis with UV−vis detection revealed a yellow intermediate with an absorption maximum at 450 nm, which is assigned to the ylidic cumulene **27** (Figure 3). This absorption disappeared again on bleaching at $\lambda > 405$ nm. The initial UV spectrum shows fine structure in the 325−360 nm region due to azide **8**. New, weak, fine structure grows in on photolysis, and by analogy with other arylnitrenes,[3] this may be due to the presence of nitrene **9T**. More substantial evidence for the nitrene is given by the ESR spectrum below.

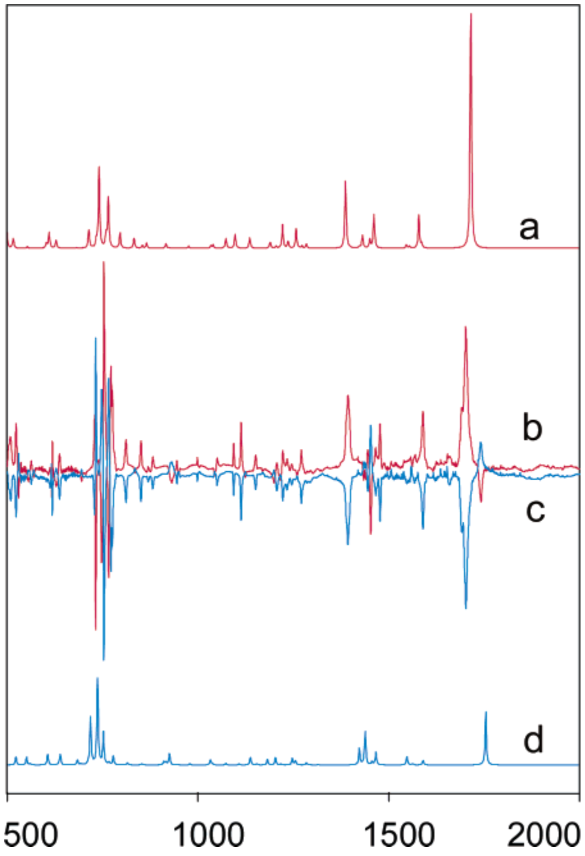

FIGURE 2. (a) Calculated IR spectrum of ylidic cumulene **27** (B3LYP/6-31G* with a scaling factor of 0.9613 for wavenumbers). (b) Difference IR spectrum after photolysis at $\lambda =$ 313 nm (monochromator) showing the formation of cumulene **27** and disappearance of azirine **26**. (c) Difference IR spectrum after photolysis at $\lambda > 405$ nm showing the formation of azirine **26** and vanishing of ylidic cumulene **27**. Spectra b and c are mirror images and show reversible interconversion of **26** and **27**. (d) Calculated IR spectrum of azirine **26** (B3LYP/6-31G* level with a scaling factor of 0.9613 for wavenumbers). The abscissa is in wavenumbers.

The tetrazole **18** was photochemically inert, and the triazole **19** photolyzed extremely sluggishly. Such behavior has been observed for other triazoloazines.[6a] A diazo compound (**20**) was observed at 2080−2097 cm^{-1} on photolysis at 222 nm, but the intensities of subsequent photoproducts in the matrix IR spectrum were too weak for a clear-cut demonstration of the rearrangement of carbene **21** to nitrene **9** (via **25**, **24**, and **23**, Scheme 2). However, this rearrangement was revealed by ESR spectroscopy, which is more sensitive than IR.

ESR Spectroscopy. Photolysis of triazole **19** in an Ar matrix at 15 K using a 308 nm lamp afforded the carbene **21** (Figure 4a; $D = 0.5161$ cm^{-1}; $E = 0.0257$ cm^{-1}). In contrast, FVT of either tetrazole **18** or triazole **19** at 550 °C with Ar matrix isolation at 15 K afforded the ESR spectrum of the *nitrene* **9** (Figure 4b and Figures S2 and S4 in the Supporting Information; $D = 0.8110$ cm^{-1}; $E \leq 0.0023$ cm^{-1}; averages of several measurements) (the carbene was not detectable under FVT conditions). The thermolysate from the tetrazole was recovered from the cryostat, and examination by GC/MS revealed triazolophenanthridine **19**, 9-cyanofluorene **12**, 4-cyanofluorene

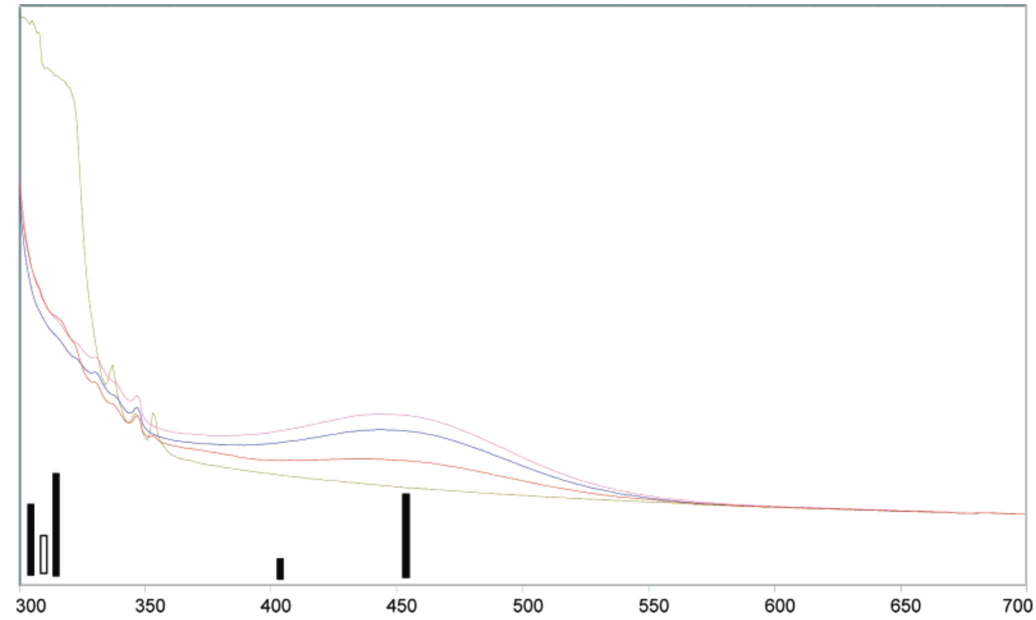

FIGURE 3. UV−vis spectra resulting from the photolysis of 9-azidophenanthrene **8** at $\lambda = 313$ nm showing formation of ylide **27** with an absorption maximum at 450 nm. The heavy bars represent the calculated optical spectrum of ylide **27**. The open bar is for azirine **26** (time-dependent B3LYP/6-31G*). The abscissa is in nanometers; the ordinate is in arbitrary intensity units.

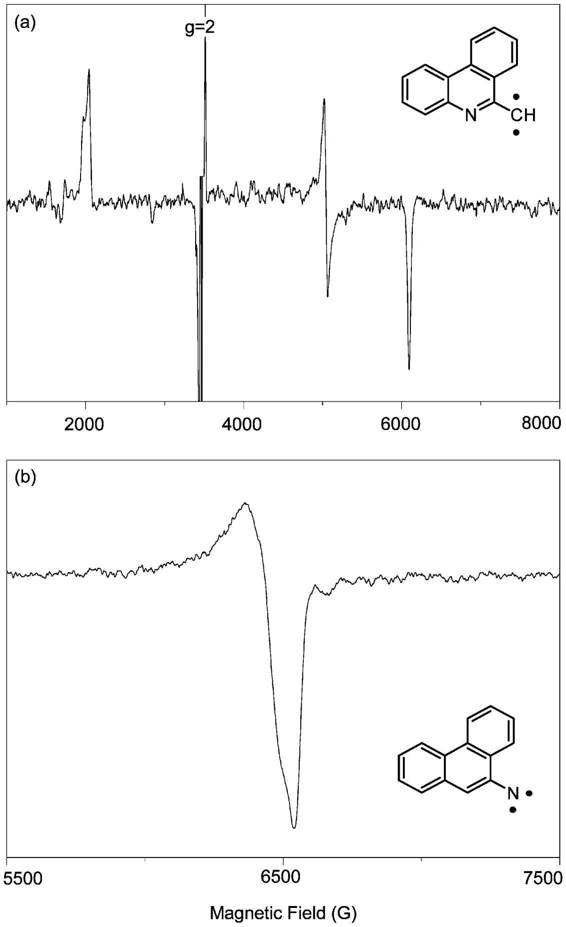

FIGURE 4. (a) ESR spectrum of carbene **21** obtained after a 45 min photolysis of **19** at 308 nm. (b) ESR spectrum of nitrene **9** obtained by FVT of **19** at 550 °C.

13, 1-cyanofluorene **16**, 6-methylphenanthridine **22**, and 9-aminophenanthrene **10**.

Photolysis of azide **8** in an Ar matrix at 15 K at 308 nm also afforded the ESR spectrum of nitrene **9**, and thermolysis of this azide in a stream of Ar at 550 °C using the internal oven and condensation of the product to form an Ar matrix at 15 K afforded the ESR spectrum of nitrene **9** (Figure S3 in the Supporting Information).

The zero-field splitting parameters *D* for both the nitrene **9T** and the carbene **21T** are in very good agreement with expectations based on correlations with natural (or Mulliken) spin densities calculated with the UB3LYP/EPR−II program within Gaussian 03. Smolinsky et al. were the first to report a correlation between *D* values and HMO spin densities in arylnitrenes.[12] We have found excellent linear correlations between the measured values of *D* (cm^{-1}) and the calculated natural and Mulliken spin densities on the nitrene nitrogen (ρ) in a wide range of aryl- and heteroarylnitrenes, and similarly between *D* and the spin density on the carbene carbon in aryl- and heteroarylcarbenes.[13]

Calculations. It is now well established that for arylnitrenes (unlike the corresponding carbenes) the open-shell singlet (OSS) states have lower energies than the closed-shell singlets (CSS).[14] It is not possible to calculate the open-shell singlet nitrene **9 OSS** using DFT

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(12) Smolinsky, G.; Snyder. L. C.; Wasserman, E. *Rev. Mod. Phys.* **1963**, *35*, 576.

(13) (a) Bednarek, P.; Kvaskoff, D.; Wentrup, C. The University of Queensland, Brisbane, Australia. Unpublished results, 2004−2005. (b) Kvaskoff, D. Ph.D. Thesis, The University of Queensland, Brisbane, Australia, 2005. (c) Selected examples of (D,ρ) values for several nitrenes: 2-pyrimidyl (1.217, 1.703), 4-pyridyl (1.107, 1.6312), 3-pyridazinyl (1.066, 1.6374), 2-pyridyl (1.051, 1.6393), phenyl (0.998, 1.5993), 2-naphthyl (0.925, 1.5605), 9-phenanthryl **9T** (0.811, 1.4567), 1-naphthyl (0.793, 1.4891), 1-anthryl (0.65, 1.3919), 9-anthryl (0.470, 1.2837). Selected examples of (D,ρ) values for several carbenes: 2-pyrimidyl (0.565, 1.7373), 4-pyrimidyl (0.555, 1.7312 (*Z*)), 3-pyridazinyl (0.544, 1.7066 (*E*), 1.7180 (*Z*)), 2-pyridyl (0.537, 1.7000 (*E*), 1.7230 (*Z*)), 4-quinazolyl (0.5253, 1.6737 (*Z*)), phenyl (0.517, 1.6841), 6-phenanthridyl **21T** (0.5161, 1.6575 (*E*), 1.6581 (*Z*)), (*E*)-2-naphthyl (0.4926, 1.6538), (*E*)-1-naphthyl (0.4347, 1.5973), 9-anthryl (0.3008, 1.4592).

(14) Karney. W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 1378.

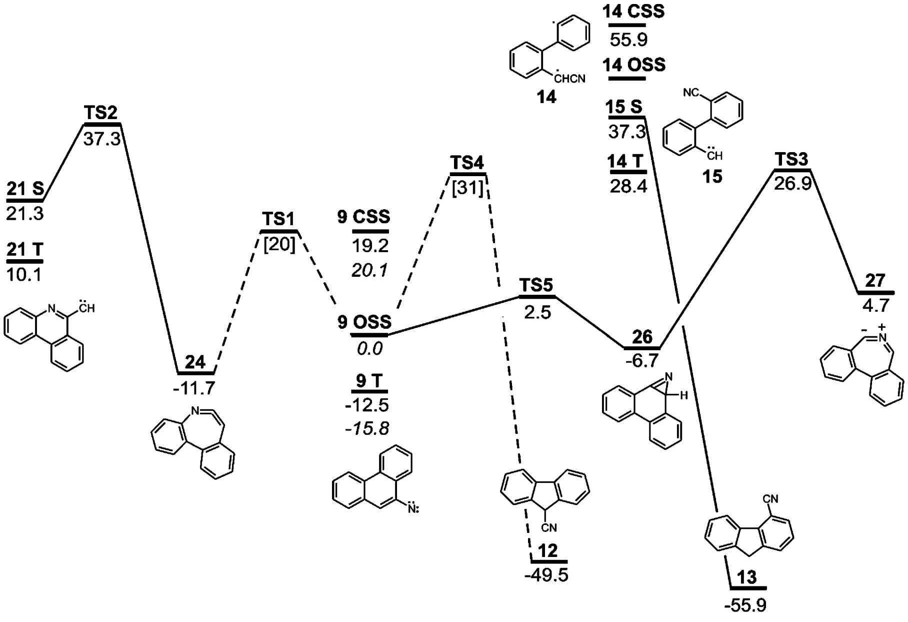
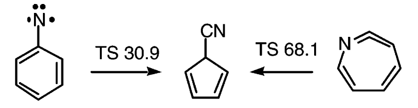


FIGURE 5. Potential energy diagram for phenanthrylnitrene **9**, its rearrangement products, and the corresponding transition states. The energies are in kcal/mol relative to **9 OSS**. The numbers in italics are CASPT2/CASSCF(8,8) calculations. All other energies are normalized to triplet $^3A''$ phenanthrylnitrene **9T** + S−T gap from the CASPT2 calculation (15.8 kcal/mol); the roman numbers are B3LYP/6-31G* except **TS5**, which is from a UB3LYP/6-31G* calculation; numbers in brackets are estimates, see text. **OSS** = open-shell ($^1A''$) singlet; **CSS** = closed-shell singlet.

methods. An approximation described by Cramer[15] was used to estimate the energy of **9 OSS** at the B3LYP/6-31G* level in Figure 5. This places **9 OSS** 19.2 kcal/mol below **9 CSS** and 12.5 kcal/mol above **9T**. A CASPT2/CASSCF(8,8) calculation with the ANO basis set places **9 OSS** 20.1 kcal/mol below **9 CSS** and 15.8 kcal/mol above **9T** (Figure 5). We have used the latter value for the singlet−triplet (S−T) gap in **9**. To calculate the transition states connecting **9 OSS** with the interesting products **12**, **24**, and **26**, CASSCF calculations would be required, but this would be beyond our current computing resources. DFT calculations of the transition states **TS1** (27 kcal/mol) and **TS4** (32 kcal/mol on the energy scale of Figure 5) connecting **12** and **24** with the *closed-shell singlet*, **9 CSS**, have been performed, but these energy values can be expected to be too high. In the case of the open-shell naphthylnitrenes, it was found that UB3LYP calculations gave transition state energies for the cyclization to azirines which were in good agreement with CASPT2 calculations.[3] The CASPT2//CASSCF(12,12)/6-31G* calculations on the open-shell 1- and 2-naphthylnitrenes gave barriers of 3−7 kcal/mol for cyclization to azirines analogous to **26**, e.g., **4b** (eq 2).[3] A UB3LYP/6-31G* calculation of **TS5** connecting **9 OSS** and **26** gives a value of 2.5 kcal/mol (Figure 5) with a spin contamination factor $\langle S^2 \rangle$ of 0.26. Thus, estimates based on the naphthylnitrenes seem justified. For comparison, activation barriers of 6−9 kcal/mol were found for cyclizations of 2-biphenylnitrene to azirines at CASPT2/CASSCF and CASPT2/DFT levels of theory[16] and 4−8 kcal/mol for cyclization of 2,6-dialkylphenylnitrenes[17] and the parent phenylnitrene at the DFT/CASPT2 level. Cyclization to nonaromatic azirines such as **4a** (eq 2) and **23** (Scheme 2) have much higher activation energies due to the loss of the resonance energy of a second benzene ring. On the basis of the comparison with the naphthylnitrenes,[2,3] **TS1** connecting **9 OSS** and ketenimine **24** is estimated as ca. 20 kcal/mol (Figure 5). This nonaromatic transition state **TS1** has the structure of azirine **23** in Scheme 2, and this azirine is not found to be a minimum at the DFT level. Since CASPT2 calculations may overestimate the stability of open-shell singlet nitrenes relative to azirines,[3,14] the true energies of **TS1** and **TS5** may be a few kcal/mol lower. This would make the cyclization of **9 OSS** to azirine **26** virtually barrierless.

A proper description of the ring contraction of nitrene **9** to 9-cyanofluorene **12** via **TS4** again requires CASSCF calculations. We have investigated the analogous ring contraction in phenylnitrene **1 OSS** using CASPT2//CASSCF(8,8) calculations and found a transition state for the concerted ring contraction to 5-cyanocyclopentadiene **30** with a barrier of 30.9 kcal/mol (eq 4).[18] Assuming a similar barrier for phenanthrylnitrene **9 OSS**, this places **TS4** at ca. 31 kcal/mol (Figure 5). Ring contraction to 5-cyanocyclopentadiene can also take place from the seven-membered ring ketenimine **2**, albeit with a drastically higher calculated activation energy (68 kcal/mol; eq



(4)

1 OSS **30** (-40.3 kcal/mol) **2** (-2.6 kcal/mol)

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4). Thus, starting from the carbene side, **21**, it is possible that ketenimine **24** may undergo some direct ring contraction to 9-cyanofluorene **12**. The diradical **14** could form by ring opening of either **9** or **24**, and it would also be able to ring close to **12**. The triplet state **14T** is calculated to be 44.2 kcal/mol above **9T** (28.4 kcal/mol above **9 OSS**), and **14 CSS** is 55.9 kcal/mol above **9 OSS** (Figure 5). The energy of **14 OSS** cannot be calculated directly using DFT methods, but its energy is estimated as ca. 45 kcal/mol using Cramer's method,[15] whereby it is necessary to constrain the molecule to planarity.

The formation of 4-cyanofluorene **13** can take place via ring opening to the singlet 2-(2-cyanophenyl)phenylcarbene **15S**, which in its s-trans conformation (43 degrees twist between phenyl rings) is a minimum at ca. 37.3 kcal/mol above **9 OSS** (the s-cis conformation is not a minimum; it ring closes to **13**). **TS4** lies significantly below **15S** in agreement with the observation that **12** is the major thermal product even though **13** has a lower absolute energy.

TS2 (37.3 kcal/mol) connects the closed-shell singlet phenanthridylcarbene **21S** with cyclic ketenimine **24** and has a structure corresponding to the nonaromatic and nonobserved cyclopropene **25** (Scheme 2). The ketenimine **24** is calculated to be the global minimum among the isomeric singlet species in Scheme 2 prior to ring contraction to cyanofluorenes. This molecule (**24**) preserves two aromatic rings and has no charge separation.

TS3 (26.9 kcal/mol) connects azirine **26** and the ylidic cumulene **27**. The azirine **26** is calculated to be 11.4 kcal/mol lower in energy than the ylide **27** (Figure 5). The *o*-quinoid ketenimine **28** (Scheme 2) was not observed in any of the experiments (it would be expected to absorb in the 1800 cm^{-1} range in the IR spectrum; see above[2]). It is not an energy minimum at the DFT computational level, but at the Hartree−Fock level it is ca. 10 kcal/mol less stable than **27** and thus not energetically competitive with the observed cumulenes **24** and **27**.

Under FVT conditions, all the (singlet) species can be expected to be in thermal equilibrium, including **24**, **26**, and **27** (and perhaps even **28**), but the thermodynamically preferred and observable intermediate **24** will dominate prior to ring contraction to the cyanofluorenes **12** and **13**. The latter are thermodynamic sinks, and under preparative FVT conditions they become the exclusive rearrangement products.

Conclusion

Both 9-phenanthrylnitrene **9** and 6-phenanthridylcarbene **21** undergo ring expansion in the gas phase under thermal conditions to give dibenzoazacycloheptatetraene **24** (ν_{max} 1932 cm^{-1}). In sharp contrast, under matrix photochemical conditions, the nitrene cyclizes to the azirine **26** ($\nu_{C=N}$ 1742 cm^{-1}), which can be photochemically interconverted with the novel ylidic cumulene **27** (ν_{max} 1702 cm^{-1}, λ_{max} 450 nm). DFT calculations indicate that **24** is the product of thermodynamic control. Under FVT conditions it is likely that all the intermediates, **24**, **26**, and **27** can form, but thermochemistry will favor the former. Although the barrier for ring contraction of 9-phenanthrylnitrene **9** to 9-cyanofluorene **12** is higher than that for ring expansion to ketenimine **24**, **12** is the thermodynamic sink, and it cannot be avoided that it is formed under FVT conditions.

6-Phenanthridylcarbene **21** is observed by ESR spectroscopy when photochemically generated ($D = 0.5161$ cm^{-1}; $E = 0.0257$ cm^{-1}), and it rearranges thermally to 9-phenanthrylnitene **9**, which is also observed by ESR spectroscopy ($D = 0.8110$ cm^{-1}; $E \leq 0.0023$ cm^{-1}); thermal rearrangement to ketenimine **24** is observed by IR spectroscopy, and 9-cyanofluorene **12** is a major product of preparative FVT.

Computational Methods

The energies of the relevant species isomeric with phenanthrylnitrene were calculated at the B3LYP/6-31G* level of theory using the Gaussian 98 suite of programs.[19] The energies, together with those of the triplet nitrene (**9T**), the closed-shell singlet nitrene (**9 CSS**), and the open-shell singlet nitrene (**9 OSS**) are depicted in Figure 5. The energy of the open-shell singlet nitrene was estimated using the method of Cramer.[15] The energies of the open-shell singlet and triplet nitrenes were also calculated at the CASPT2 level using the MOLCAS[20] suite of programs. According to CASPT2/CASSCF(8,8) with the ANO basis set, the triplet is 15.8 kcal/mol more stable than the open-shell singlet. The active space for CASSCF and CASPT2 calculations was constructed from 8 orbitals, 3 $\pi(A'')$, 1 $p(\sigma)$-(A') on N, and 4 $\pi^*(A'')$, with 8 electrons. All reference weights were above 0.6, which is assumed as enough reference weight for the CASSCF wave function in CASPT2 for this size of molecule.

The geometry was optimized with CASSCF(8,8)/ANO, and the single-point CASPT2 energy was obtained for this geometry (the description of states is included in the Supporting Information).

The UV−vis spectra were predicted using density functional theory based on time-dependent (TD) response theory.[21] We used the TD-DFT implementation in Gaussian 98 as described recently by Stratmann et al.[22]

Mulliken and natural spin densities in nitrenes and carbenes were calculated using UB3LYP/EPR-II within Gaussian 03, revision C.01. Zero-field splitting parameters of nitrenes and carbenes were calculated using Wasserman's equations.[23]

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Experimental Section

The apparatus and procedures for preparative FVT,[24] for isolation at 77 K,[24] and for Ar matrix isolation[25] were as previously described. The internal oven employed a 10 cm long, 0.7 cm i.d., electrically heated quartz tube suspended in a vacuum chamber directly flanged to the cryostat cold head, with a wall-free flight path of ca. 3 cm between the exit of the quartz tube and the cold target (KBr or CsI for IR spectroscopy, quartz for UV spectroscopy, and Cu for ESR spectroscopy). The external oven consisted of a 20 cm (0.7 cm i.d.) quartz tube ending in a quartz flange directly flanged to the cryostat cold head; this tube was heated on a 10 cm length and had a ca. 5 cm unheated length connecting it to the cold head. For matrix isolation and FVT/matrix isolation, ca. 10 mg of the compounds were sublimed in a stream or Ar at 60−100 °C (azide **8**), 70−250 °C (tetrazole **18**), 90−110 °C (triazole **19**), and 120 °C (9-cyanofluorene **12**). FVT products were isolated in liquid nitrogen (77 K) in the preparative thermolyses, at 12−20 K with Ar for matrix isolation IR and UV experiments, and at 15 K with Ar for ESR experiments. Photolysis experiments were carried out in Ar matrixes at 7 K for **8** and at 25 K for **19**. A 1000 W high-pressure Xe/Hg lamp equipped with a monochromator and appropriate filters, a 75 W low-pressure Hg lamp (254 nm), and excimer lamps operating at 222 nm (25 mW/cm^2) and 308 nm (50 mW/cm^2) were used for the photolyses. IR spectra were recorded with a resolution of 1 cm^{-1}. GC for GC/MS analysis was performed on a 30 m capillary column, with an injector port temperature of 200 °C and a temperature program of 100 °C for 2 min, then 16 °C/min to 270 °C. 9-Aminophenanthrene **10** and 6-methylphenanthridine **22** were commercial samples. 9,9′-Azophenenthrene **11** was prepared according to Schmidt and Strobel[26] and had a mp of 270−275 °C (literature value,[26] 270 °C (dec without melting completely)), and 6-phenanthridinecarbonitrile 17 was prepared in 85% yield from the N-oxide according to the method of Fife[27a] and had a mp of 136 °C (literature value,[27b] 135 °C). Melting points are uncorrected.

Fluorene-9-carbonitrile 12.[6b,28] This compound was prepared by literature methods; mp 152.5−153 °C (literature value,[6b,28] 152−153°C); GC/MS R_t 10.94 min; m/z 191.

Fluorene-2-carbonitrile.[29] This compound was prepared by literature methods; mp 90 °C (literature value,[29] 92 °C); GC/MS R_t 11.63 min; m/z 191.

Fluorene-4-carbonitrile 13. To fluorene-4-carboxylic acid (50 mg; tech grade, 90%, 0.21 mmol) in dry CH_2Cl_2 (15 mL) was added chlorosulfonyl isocyanate[30] (23 mL, 0.26 mmol) during 5 min at 0 °C, and the mixture was then stirred at 20 °C for 15 h. Triethylamine (34 mL, 0.25 mmol) was then added at 0 °C over 5 min, and the resulting mixture was stirred for 3 h at room temperature. The reaction mixture was poured into water (10 mL), and the product was extracted with CH_2Cl_2 (10 mL). The extract was dried over $MgSO_4$, filtered, and evaporated to yield a crude solid (66 mg). This was purified by flash silica gel chromatography (eluent CH_2Cl_2) to afford a white solid (30 mg, 73%; or 95% based on recovered fluorene-4-carboxylic acid (10 mg, 22%)); mp 77 °C (literature value,[31] 77−78 °C); GC/MS R_t 11.18 min; m/z 191, 163, 95, 81; ^{1}H NMR (200 MHz, $CDCl_3$) 3.89 (s, 2H), 7.30−7.46 (m, 3H), 7.58 (d, 1H, $J = 7.8$ Hz), 7.62 (d, 1H, $J = 7.8$ Hz), 7.72 (d, 1H, $J = 7.6$ Hz), 8.42 (d, 1H, $J = 7.6$ Hz).

Fluorene-1-carbonitrile 16. This was prepared analogously to **13** from 210 mg (1 mmol) of fluorene-1-carboxylic acid with chlorosulfonyl isocyanate to yield 121 mg (63%); mp 92 °C (literature value,[31] 94−94.5 °C); GC/MS R_t 10.97 min; m/z 191.

9-Azidophenanthrene 8. This was initially prepared by lithiation of 9-bromophenanthrene in ether with butyllithium in hexane at reflux followed by addition to tosyl azide in ether at 0 °C by adaptation of literature procedures.[32] However, this procedure affords as a byproduct a butylated azidophenanthrene which, if not removed completely, gives rise to some butylated cyanofluorene on FVT (detected by GC/MS and IR but not examined further).

Pure 9-azidophenanthrene was prepared as follows: 9-aminophenanthrene (0.525 g, 2.7 mmol) was dissolved in a warm (60 °C) solution of concentrated sulfuric acid (3 mL) in water (18 mL) and diazotized with sodium nitrite (0.225 g, 3.3 mmol) in water (12 mL) at 0 °C. After stirring for 30 min, active charcoal (0.3 g) was added, and the mixture was stirred for another 10 min at 0 °C. The cold yellow solution of diazonium salt was filtered on Celite by suction. Sodium azide (0.300 g, 4.6 mmol) in water (10 mL) was added dropwise to the filtrate at 0 °C. After 3 h, the precipitated azide was collected and recrystallized from methanol/water (20:1) to yield 9-azidophenanthrene as white shiny needles (0.356 g, 60%); mp 112−113°C (literature value,[33a] 112−113 °C; literature value,[33b] 115−116 °C); sublimes at 80−100 °C (10^{-3} mbar). The substance is extremely light sensitive and should be kept in the dark. ^{1}H NMR ($CDCl_3$) δ 8.65 (dd, $J = 9.3$ and 1.1 Hz, 1H), 8.62−8.60 (m, 1H), 8.18 (dd, $J = 9.2$ and 1.2 Hz, 1H), 7.82.-7.80 (m, 1H), 7.70 (ddd, $J = 15.3$, 8.4 and 1.4 Hz, 1H), 7.64−7.57 (m, 3H), 7.46 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 135.1, 131.6, 131.1, 128.2, 127.5, 127.3, 127.1, 126.7, 126.5, 126.1, 126.0, 123.1, 122.6, 113.4 ppm; IR (KBr) 2217(w), 2157(w), 2114, 2103(s), 2070(m), 1395(m), 1314(m), 1267(s), 764(m), 747(m), 725(s) cm^{-1}; UV (CH_3CN) λ_{max} 318 (sh), 310, 262, 256 (sh), 246 nm (cf. ref 33b). Anal. Calcd for $C_{14}H_9N_3$: C, 76.70; H, 4.14; N, 19.16. Found: C, 76.71; H, 4.05; N, 19.18.

6-(5-Tetrazolyl)phenanthridine 18. A mixture of 1 g (5 mmol) of 6-cyanophenanthridine, 3.25 g (50 mmol) of NaN_3, and 2.65 g (50 mmol) of NH_4Cl was suspended in 50 mL of DMF and refluxed for 6 h. The solvent vas removed in vacuo, and the residue was taken up in 50 mL of H_2O and brought to pH 2 with concentrated HCl. The product thus precipitated was filtered and recrystallized from EtOH to give 0.7 g (63%) of **18** as white needles, mp 203−206 °C. ^{13}C NMR (DMSO-d_6) δ 154.8, 144.2, 142.3, 132.8, 131.7, 129.8, 129.4, 128.8, 128.4, 127.5, 124.0, 123.3, 122.8, 122.6 ppm. Anal. Calcd for $C_{14}H_9N_5$: C, 68.01; H, 3.67; N, 28.32. Found: C, 67.60; H, 3.53; N, 28.36.

[1,2,3]Triazolo[1,5-f]phenanthridine 19. Phenanthridine-6-carboxaldehyde[34] (3.0 g; 14.2.mmol) was dissolved in 250 mL of warm ethanol (60 °C). Concentrated sulfuric acid (6 mL) and hydrazine hydrate (36 mL) were added with stirring. The mixture was allowed to stir at 60 °C for 3 h, cooled to room temperature, and evaporated in vacuo. Water (50 mL) was added, and the solution was extracted with 400 mL of $CHCl_3$. Drying over $MgSO_4$, filtering, and removal of the solvent in vacuo afforded 2.5 g (79%) of the hydrazone, mp 119−121 °C, which was used immediately by dissolving it in 125 mL of $CHCl_3$ and adding 20 g of activated MnO_2 in small portions while stirring. After stirring for 3 h, the mixture was filtered over Celite, and the filtrate was concentrated in vacuo to yield

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1750 mg (70%) of colorless crystals of **19**, mp 185−186 °C (literature value,[35] 187−188 °C); sublimes at 90 °C (10^{-3} mbar).

Preparative FVT of 9-Azidophenanthrene 8. A 150 mg (0.6 mmol) portion of **8** was sublimed at 80 °C and thermolyzed at 450 °C at a vacuum of 10^{-4}–10^{-3} mbar in the course of 3 h. The products were isolated on a coldfinger cooled with liquid nitrogen. After the end of the thermolysis, the products were taken up in acetone and separated by chromatography on silica gel and eluted with $CHCl_3$ to afford phenanthrene (30%), 9-cyanofluorene **12** (40%), 9,9′-azophenanthrene **11** (10%), and 9-aminophenanthrene **10** (ca. 10%), all of which were identified by spectroscopic comparison with authentic materials. For GC/MS analysis similar FVT was carried out at 500 and 600 °C at a vacuum of 10^{-5}–10^{-4}. The following results are derived from uncorrected GC integrations of the products of FVT at 500 (600) °C: fluorene 0.5 (0.5)%, phenanthrene 7 (5)%, 9-cyanofluorene **12** 71 (74)%; 4-cyanofluorene **13** 2.7 (6.4)%, 1-cyanofluorene **16** 0.1 (1.5)%, and 9-aminophenanthrene **10** 11 (5)%

Preparative FVT of 9-Cyanofluorene 12. 9-Cyanofluorene (60 mg) was subjected to preparative FVT at 600−1000 °C at a vacuum of 10^{-5} mbar, and the products were examined by GC/MS. At 600 (800) °C **12** was recovered unchanged in 99.9 (99.0)% yield, together with a 0.1 (1.0)% yield of fluorene. At 1000 °C the following results were obtained: fluorene, 1.2%; 9-cyanofluorene, 95.9%; 1-cyanofluorene, 2.9% (uncorrected GC integration). 1-Cyanofluorene was isolated by sublimation (85 °C, 10^{-3} mbar) and recrystallization from petroleum ether (bp 60−80 °C) and had a mp of 92−94 °C (literature value,[31] 94−94.5 °C), and its IR and UV spectra were identical with those reported.[31] The 2-, 3- and 4-cyanofluorenes were not detectable in this experiment.

Preparative FVT of 6-(5-Tetrazolyl)phenanthridine 18. A 0.1 g (0.4 mmol) portion of **13** was sublimed at 180 °C and thermolyzed at 600 °C/10^{-3} mbar in the course of 5 h. The product was isolated on a liquid nitrogen coldfinger. TLC of the product indicated one major compound and only very minor additional spots. The major component was isolated by column chromatography (silica gel/$CHCl_3$) and identified as 9-cyanofluorene **12** (52 mg; 68%). In some of the FVT reactions 6-cyanophenanthridine **17** was isolated in 3−10% yield.

For GC/MS analysis FVT was carried out at 450 (550) °C at a vacuum of 10^{-6} mbar with Ar matrix isolation on a Cu rod for ESR spectroscopy. After the end of the ESR experiment the products was rinsed from the Cu rod with CH_2Cl_2 and examined by GC/MS with the following results: fluorene 0 (0.5)%, phenanthrene 0 (1.0)%, phenanthridine 0.9 (9.0)%, 9-cyanofluorene **12** 0.5 (7.6)%, 4-cyanofluorene **13** 0 (4.2)%, 1-cyanofluorene **16** 0 (0.5)%, 6-methylphenanthridine **22** 0 (13.5)%, 6-cyanophenanthridine **17** 3.4 (8.4)%, 9-aminophenanthrene 0 (6.1)%, and triazolophenanthridine **19** 80 (36)%.

Preparative FVT of triazolophenanthridine 19. For GC/MS analysis FVT was carried out at 750 °C at a vacuum of 10^{-5} mbar with the following results: fluorene 0.1%, phenanthrene 2.3%, phenanthridine 10.8%, 9-cyanofluorene **12** 40.2%, 4-cyanofluorene **13** 6.3%, 1-cyanofluorene **16** 12.4%, 6-methylphenanthridine **22** 6.6%, and 9-aminophenanthrene 2.7%.

ESR Spectra. These were recorded on an X-band spectrometer. Zero-field splitting parameters D and E were evaluated using Wasserman's method.[23] For the observation of thermally produced nitrenes, 10 mg of the precursor was subjected to FVT in the internal oven described above, in a vacuum of ca. 10^{-6} mbar, and the products were codeposited with Ar on a Cu rod (7 cm long, 1.5 mm i.d.) at 15 K.

9-Azidophenanthrene **8** was sublimed at 60 °C, codeposited with Ar, and photolyzed at 308 nm for 2 min at 15 K using the excimer lamp. The ESR spectrum of the nitrene **9** was recorded at a microwave frequency of 9.728230 GHz (H_0 3471.4 G). $X_2 = 6436.5$ G, $Y_2 = 6543.4$ G. $D = 0.8098$ cm^{-1}; $E \leq 0.0023$ cm^{-1}.

9-Azidophenanthrene **8** was sublimed at 60 °C and thermolyzed at 550 °C. The ESR spectrum of the nitrene **9** was recorded at a microwave frequency of 9.728229 GHz (H_0 3471.3 G). $X_2 = 6461.0$ G, $Y_2 = 6551.5$ G. $D = 0.8108$ cm^{-1}; $E \leq 0.0020$ cm^{-1}.

Tetrazolylphenanthridine **18** was sublimed over the temperature interval 70−250 °C and thermolyzed at 550 °C. The ESR spectrum of the nitrene **9** was recorded at a microwave frequency of 9.727944 GHz (H_0 3471.2 G). $X_2 = 6434.1$ G, $Y_2 = 6541.1$ G. $D = 0.8093$ cm^{-1}; $E \leq 0.0024$ cm^{-1}.

Triazolophenanthridine **19** was sublimed through the internal oven at 110 °C, codeposited with Ar, and photolyzed at 308 nm using the excimer lamp. The ESR spectrum of carbene **21** was recorded at a microwave frequency of 9.728155 GHz (H_0 3471.2 G). Resonance fields: $Z_1 = 2035$ G, $X_2 = 5043$ G, $Y_2 = 6100$ G, $Z_2 = 8986$ G. $D = 0.5161$ cm^{-1}; $E = 0.0257$ cm^{-1} (Figure 4a).

Triazolophenanthridine **19** was sublimed at 110 °C and thermolyzed at 550 °C. The ESR spectrum of the nitrene **9** was recorded at a microwave frequency of 9.728211 GHz (H_0 3471.3 G). $X_2 = 6434.4$ G, $Y_2 = 6538.9$ G. $D = 0.8090$ cm^{-1}; $E \leq 0.0023$ cm^{-1} (Figure 4b).

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Supporting Information Available: IR spectra of the FVT products from **18**; ESR spectra of nitrene **9T** formed from **8**, **18**, and **19**; Cartesian coordinates, absolute energies, frequencies, and structures of compounds and transition states calculated at the (U)B3LYP/6-31G* level of theory (for nitrene **9**, also at the CASPT2/CASSCF(8,8) level); time-dependent B3LYP/6-31G* calculations of UV−vis spectra; UB3LYP/EPR-II optimized geometries and spin densities for nitrene **9T** and carbene **21T**. This material is available free of charge via the Internet at http://pubs.acs.org.

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