

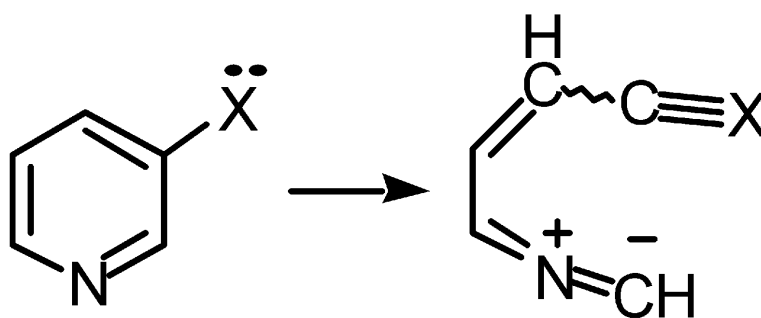
Article

## 3-Pyridylcarbene and 3-Pyridylnitrene: Ring Opening to Nitrile Ylides

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### 3-Pyridylcarbene and 3-Pyridylnitrene: Ring Opening to Nitrile Ylides

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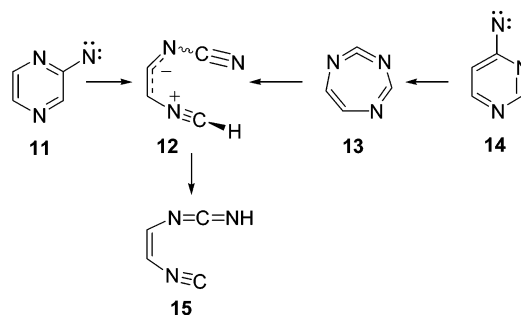
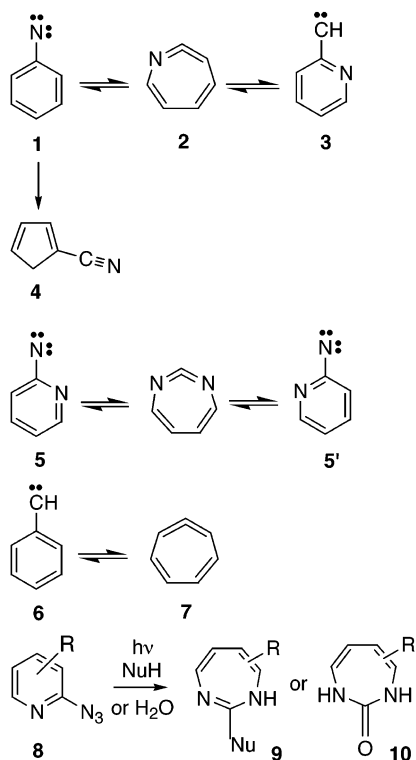
**Abstract:** Photolysis of 3-pyridyldiazomethane in an Ar matrix at 7–10 K gives 3-pyridylcarbene. Further photolysis causes ring opening to nitrile ylide **26** (formonitrile pent-2-en-4-ynylide) as the major reaction together with a minor amount of ring expansion to 1-azacyclohepta-1,3,4,6-tetraene, **27**. Matrix photolysis of 3-azidopyridine leads to ring opening to formonitrile *N*-cyanovinylmethylide, **33**.

#### Introduction

The interconversions of phenylnitrene **1** and 2-pyridylcarbene<sup>1,2</sup> **3**, 2-pyridylnitrenes<sup>3</sup> **5**, and phenylcarbenes<sup>4</sup> **6** via ring-expanded cumulenes are basic reactions in nitrene and carbene chemistry. The understanding of carbene and nitrene rearrangements is important for a wide range of subjects, from synthetic organic chemistry to chemistry in interstellar clouds.<sup>5</sup> However, despite extensive reviews<sup>1,6,7</sup> and recent theoretical calculations,<sup>8</sup> there is still little understanding of the factors governing these rearrangements. Why is it that sometimes ring contraction and sometimes ring expansion is observed? The question is important because the ring expansion reaction is a very useful method of synthesis of azepines and diazepines: the solution photolysis of tetrazolo/azidopyridines **8** in the presence of suitable trapping

agents affords diazepines **9** and diazepinones **10** in excellent yields.<sup>9</sup> These compounds are difficult to prepare by other means, and consequently their chemical and biological properties are little known.<sup>10</sup>

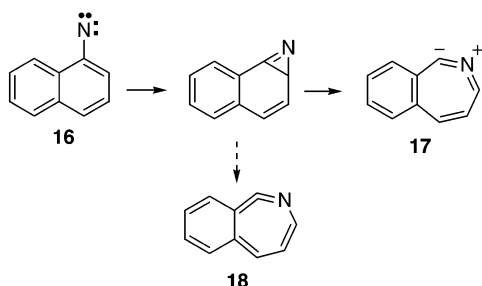
During the last year we have discovered two new and fundamental phenomena in carbene and nitrene rearrangement chemistry: (i) a new ring cleavage to open-chain ylide intermediates such as **12**, which takes place on matrix photolysis of pyrazinylnitrene **11** and 4-pyrimidylnitrene **14**,<sup>11</sup> and (ii) a



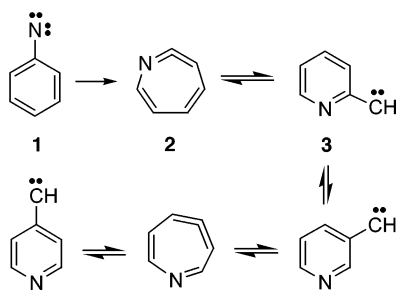
new ring expansion of nitrenes such as **16** to seven-membered cyclic nitrile ylide type species (e.g., **17**). This mode of ring expansion was discovered computationally<sup>12,13</sup> for 4-quinolylnitrene and the 1- and 2-naphthylnitrenes (e.g., **16**), and subsequent experimental evidence for its occurrence in the naphthylnitrenes will be published.<sup>14</sup> Both **17** and **18** are calculated energy

- (1) Review: Gritsan, N. P.; Platz, M. S. *Adv. Phys. Org. Chem.* **2001**, *36*, 255.
- (2) Review: Karney, W. L.; Borden, W. T. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 2001; Vol. 3, p 205.
- (3) Evans, R. A.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 4009, and references therein.
- (4) See, e.g.: Geise, C. M.; Hadad, C. M. *J. Org. Chem.* **2002**, *67*, 2532, and references therein.
- (5) Kaiser, R. L.; Aswany, O.; Lee, Y. T. *Planet. Space Sci.* **2000**, *48*, 483.
- (6) (a) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173. (b) Wentrup, C. In *Houben-Weyl: Methoden der Organischen Chemie*; Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 824–976.
- (7) Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.
- (8) Kemnitz, C. R.; Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 3499.
- (9) Reisinger, A.; Koch, R.; Wentrup, C. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2247.

minima, but the gain in aromatic resonance energy makes the ylide **17** the most stable isomer.



The photochemical interconversion of the pyridylcarbenes has never been well understood. While 2-pyridylcarbene and phenylnitrene interconvert, and the 4- and 3-pyridylcarbenes likewise interconvert, the connection between the 3- and 2-pyridylcarbenes is enigmatic.<sup>15</sup>

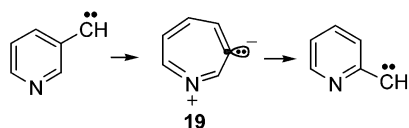


We now report that a major new reaction intervenes in this process, namely, the ring opening of 3-pyridylcarbene to afford the nitrile ylide **26**.

## Results

**3-Pyridylcarbene.** We will describe the results with respect to Scheme 1. 3-Pyridyldiazomethane **22** was isolated in an Ar matrix and photolyzed at 7 K under a variety of conditions.

- (10) Le Count, D. J. *Comprehensive Heterocyclic Chemistry II*; Elsevier: New York, 1996; Vol. 9, p 139.  
 (11) Addicott, C.; Wong, M. W.; Wentrup, C. *J. Org. Chem.* **2002**, *67*, 8538.  
 (12) Kuhn, A.; Vosswinkel, M.; Wentrup, C. *J. Org. Chem.* **2002**, *67*, 9023.  
 (13) The parent seven-membered ring ylide corresponding to **17** was described computationally by: Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 1378, but this system is significantly higher in energy than the cyclic ketenimine **2**.  
 (14) Maltsev, A.; Bally, T.; Kuhn, A.; Vosswinkel, M.; Wentrup, C.; Tsao, M.-L.; Platz, M. S. To be submitted for publication.  
 (15) (a) Chapman, Sheridan, and LeRoux postulated that the link between 3- and 2-pyridylcarbenes

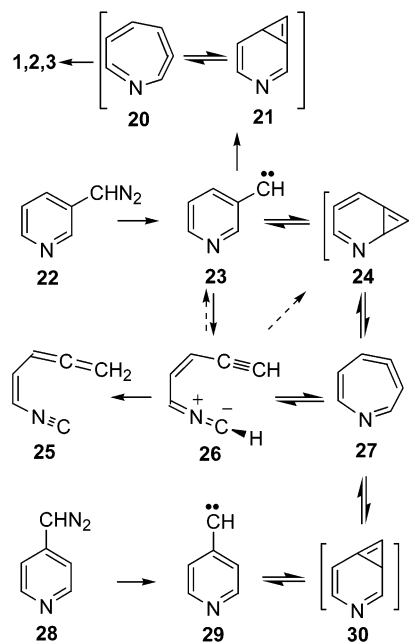


was the seven-membered ring ylidic cumulene **19** on the basis of IR spectroscopic evidence, in particular an absorption at 1935  $\text{cm}^{-1}$ , and the result of a deuterium labeling experiment.<sup>15b,c</sup> However, unstrained 2-azaallene ions have IR stretching frequencies similar to those of allenes, in the 1900  $\text{cm}^{-1}$  range.<sup>15d</sup> Analogy with other strained seven-membered ring cumulenes suggests a lowering of the frequency to the 1700–1800  $\text{cm}^{-1}$  range. DFT calculations<sup>12</sup> on several ylidic compounds similar to **17** also predict cumulenic absorptions in the 1700  $\text{cm}^{-1}$  range. At the B3LYP/6-31G\* level of theory we were not able to locate an energy minimum for **19**. As detailed below, the “1935  $\text{cm}^{-1}$  species” (**19**) should now be replaced by the nitrile ylide **26**. (b) Chapman, O. L.; Sheridan, R. S.; LeRoux, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 3690. (c) Chapman, O. L.; Sheridan, R. S.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 6245. (d) Böttger, G.; Geisler, A.; Fröhlich, R.; Würthwein, E.-U. *J. Org. Chem.* **1997**, *62*, 6407.

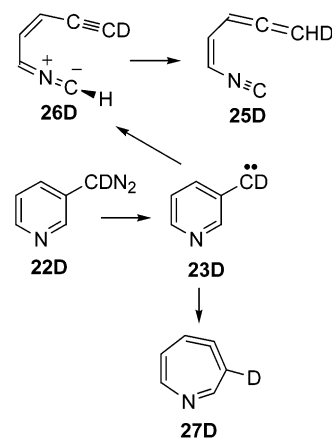
The carbene **23** was generated and observed by photolysis of the diazo compound **22** at  $\lambda > 480$  nm for 60 h as previously reported.<sup>15b</sup> Further photolysis at  $\lambda > 410$  nm produced a new species absorbing at 1930  $\text{cm}^{-1}$  in the IR and at 352 nm in the UV spectrum (Figures 1 and 2).

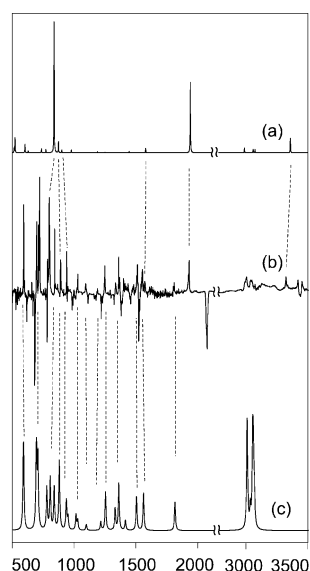
The IR spectrum is complicated due to the fact that two species are formed, ylide **26** and allene **27**. Since **27** is also formed from 4-pyridyldiazomethane **28** (see below), its bands

## Scheme 1

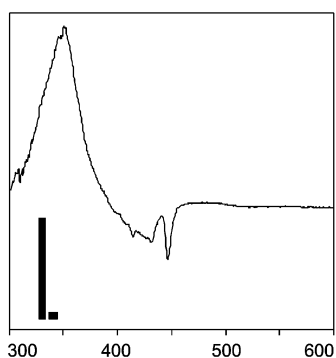


can be identified. The allenic absorption is weak and gives rise to a double band at 1810 and 1800  $\text{cm}^{-1}$ . 3-Deuteriodiazomethylpyridine **22D** produces a clearer IR spectrum (Figure 3), which is almost devoid of the ring-expanded allene **27D**; that is, there appears to be a differential kinetic isotope effect disfavoring the ring expansion reaction. The excellent agreement with the calculated spectra as well as the deuterium isotope shifts in the IR spectrum clearly identify the major species as the acetylenic nitrile ylide **26** (Scheme 1). The very weak acetylenic CC triple bond vibration of **26** is hidden under the strong diazo band of 3-pyridyldiazomethane in Figure 1, but it is visible at 1988  $\text{cm}^{-1}$  in the deuterated compound **26D**. The acetylenic C–H stretching vibration moves from 3319 to 2591  $\text{cm}^{-1}$  on deuteration (see the Supporting Information).



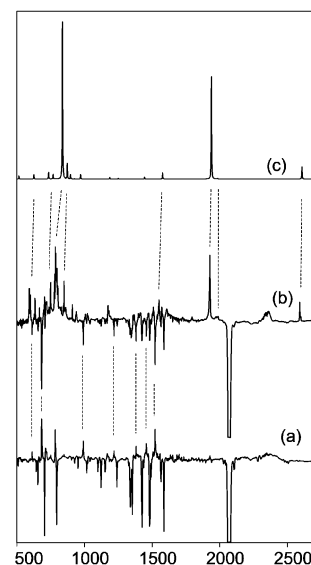


**Figure 1.** (a) Calculated IR spectrum of nitrile ylide **26**. (b) IR difference spectrum after irradiation of 3-pyridyldiazomethane **22** in Ar at 7 K at  $\lambda > 480$  nm for 60 h followed by  $\lambda > 410$  nm for 15 min; negative peaks due to carbene **23**: 1522, 1457, 991, 985, 784, 684  $\text{cm}^{-1}$ ; positive peaks: 3319, 1930, 800, 786  $\text{cm}^{-1}$  due to nitrile ylide **26**, and 1810, 1800, 1361, 1248, 892, 844, 722, 698, 593  $\text{cm}^{-1}$  due to **27**. (c) Calculated IR spectrum for compound **27**. Calculated spectra at the B3LYP/6-31G\* level with abscissa in wavenumbers scaled by 0.9613.



**Figure 2.** UV-vis difference spectrum of product formed on irradiation of 3-pyridyldiazomethane **22** in Ar at 7 K, first at  $\lambda > 480$  nm (negative spectrum), at  $\lambda = 480$  nm (positive spectrum). The band forming at 352 nm is ascribed to nitrile ylide **26**, and the diminishing band at 446 nm to 3-pyridylcarbene **23**. Heavy bars represent CAPT2 predicted excitations for ylide **26**.

Azacycloheptatetraene **27** is the link between the 3- and 4-pyridylcarbenes **29** and **23** (Scheme 1), and the same species **27** is also obtained on photolysis of 4-pyridyldiazomethane **28** (see the Supporting Information). Moreover, a smaller amount of the nitrile ylide **26** is also formed from **28**. The calculated IR spectra of the azacycloheptatetraenes **20** and **27** are very similar. It cannot be excluded that a small amount of the isomeric azacycloheptatetraene **20** is present, but the IR spectrum (Figure 1) is in best agreement with **27**. The nitrile ylide **26** can be bleached selectively with extended irradiation at  $\lambda > 410$  nm (see the Supporting Information). The bleaching of **26** resulted in new bands in the IR spectrum. Due to their weakness, a rigorous assignment is not possible, but the analogy with 3-pyridylnitrene described below and pyrazinylnitrene described previously<sup>11</sup> makes it likely that a 1,7-hydrogen shift to afford the allene **25** (isocyanide band at 2122  $\text{cm}^{-1}$ ) is

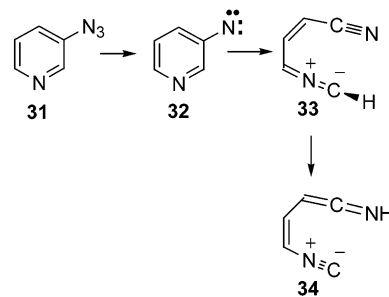


**Figure 3.** (a) IR difference spectrum after irradiation of diazo compound **22D** in Ar at 7 K at  $\lambda > 480$  nm. Negative peaks: 2069, 1589, 1485, 1427, 1355, 1340, 795, 705  $\text{cm}^{-1}$ , **22D**; positive peaks: 1522, 1457, 1382, 1219, 993, 784, 683  $\text{cm}^{-1}$  due to formation of carbene **23D**. (b) IR difference spectrum after subsequent irradiation at  $\lambda > 410$  nm; positive peaks: 2591, 1988 (vw), 1928, 796, 785  $\text{cm}^{-1}$  due to formation of nitrile ylide **26D**. (c) Calculated IR spectrum of compound **26D** (B3LYP/6-31G\* with abscissa in wavenumbers scaled by 0.9613).

involved. The deuterated compound **24D** underwent analogous bleaching to afford new bands at 2122 and 1943  $\text{cm}^{-1}$  ascribed to **25D**.

**3-Pyridylnitrene.** Photolysis of 3-azidopyridine **31**, matrix isolated in Ar at 7 K at 222 nm for 5 min, resulted in the IR and UV spectra shown in Figures 4 and 5.

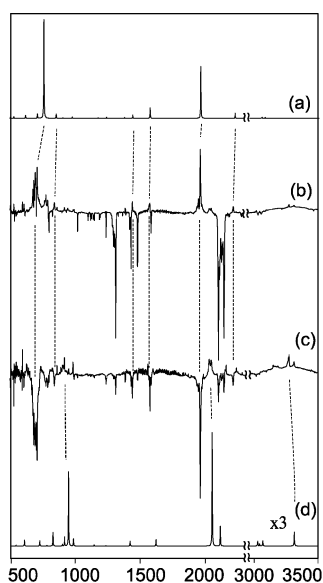
The excellent agreement with the calculated spectra identifies the new compound as the cyanovinyl nitrile ylide **33** (2212, 1961, and a broad band with maxima at 683, 693, 703, and 710  $\text{cm}^{-1}$ ). At longer photolysis times a second rotamer of **33** is observed with bands at 2216 and 1947  $\text{cm}^{-1}$  and a splitting of the broad band around  $\sim 700$   $\text{cm}^{-1}$ . At the same time, rearrangement of **33** to a compound exhibiting isocyanide and ketenimine absorptions is observed. This is again ascribed to the 1,7-H



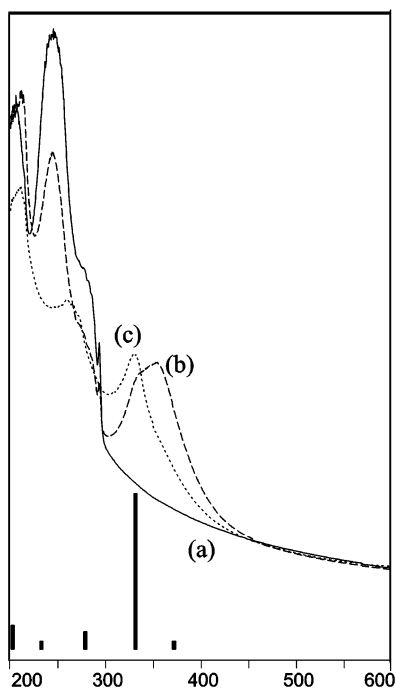
shift<sup>11</sup> to afford the ketenimine **34** in two rotameric forms (918, 984, 2029, 2043, 2158, 3279, 3316  $\text{cm}^{-1}$ ).

## Discussion

The spectroscopic evidence clearly identifies the product of photolysis of 3-pyridylcarbene **23** as the nitrile ylide **26**. In particular, the deuteration experiment allowed the identification of the acetylenic C–H (C–D) stretch as well as the very weak CC triple bond vibration. A minor amount of the ring-expanded



**Figure 4.** (a) Calculated IR spectrum of nitrile ylide **33**. (b) IR difference spectrum after irradiation of 3-azidopyridine **31** in Ar at 7 K at  $\lambda = 222$  nm; negative peaks: 2142, 2101, 1482, 1477, 1430, 1311, 1237, 801, 703  $\text{cm}^{-1}$  **31**; positive peaks: 2212, 1961, 1575, 710, 693  $\text{cm}^{-1}$  due to formation of **33**. (c) IR difference spectrum after additional irradiation at  $\lambda = 222$  nm; positive peaks: 3279, 2158, 2043, 2029, 984, 918  $\text{cm}^{-1}$  due to formation of ketenimine **34**. (d) Calculated IR spectrum of compound **34**. Calculated spectra at the B3LYP/6-31G\* level with abscissa in wavenumbers scaled by 0.9613.



**Figure 5.** (a) UV-vis spectrum of 3-azidopyridine **31** in Ar at 7 K. (b) Product formed on irradiation of **31** at  $\lambda = 222$  nm; formation of nitrile ylide **33** with absorption band at 360 nm. (c) Additional irradiation at  $\lambda = 222$  nm; formation of **34** and disappearance of **33**. Heavy bars represent CASPT2 predicted excitations for species **33**.

cumulene **27** is also formed, and this is identical to the product formed from 4-pyridyldiazomethane **28**. The alternate ring-expanded cumulene **20** either has not been observed or is present only as a minor component. The simplest explanation for this nonobservation is that the stationary concentration of **20** is simply not high enough. The calculated energy of **20** ( $-12.5$

kcal/mol) is higher than those of **27** ( $-16.6$  kcal/mol) and **2** ( $-20.1$  kcal/mol at the B3LYP/6-31G\* level) (Figure 6 and Table S1). It must be kept in mind that the reactions are photochemical, whereas the calculations are restricted to the lowest singlet state energy surface. For clarity, the ring expansion reactions are depicted as proceeding via bicyclic cyclopropene intermediates **21**, **24**, and **30** in Scheme 1, but none of these have been observed.

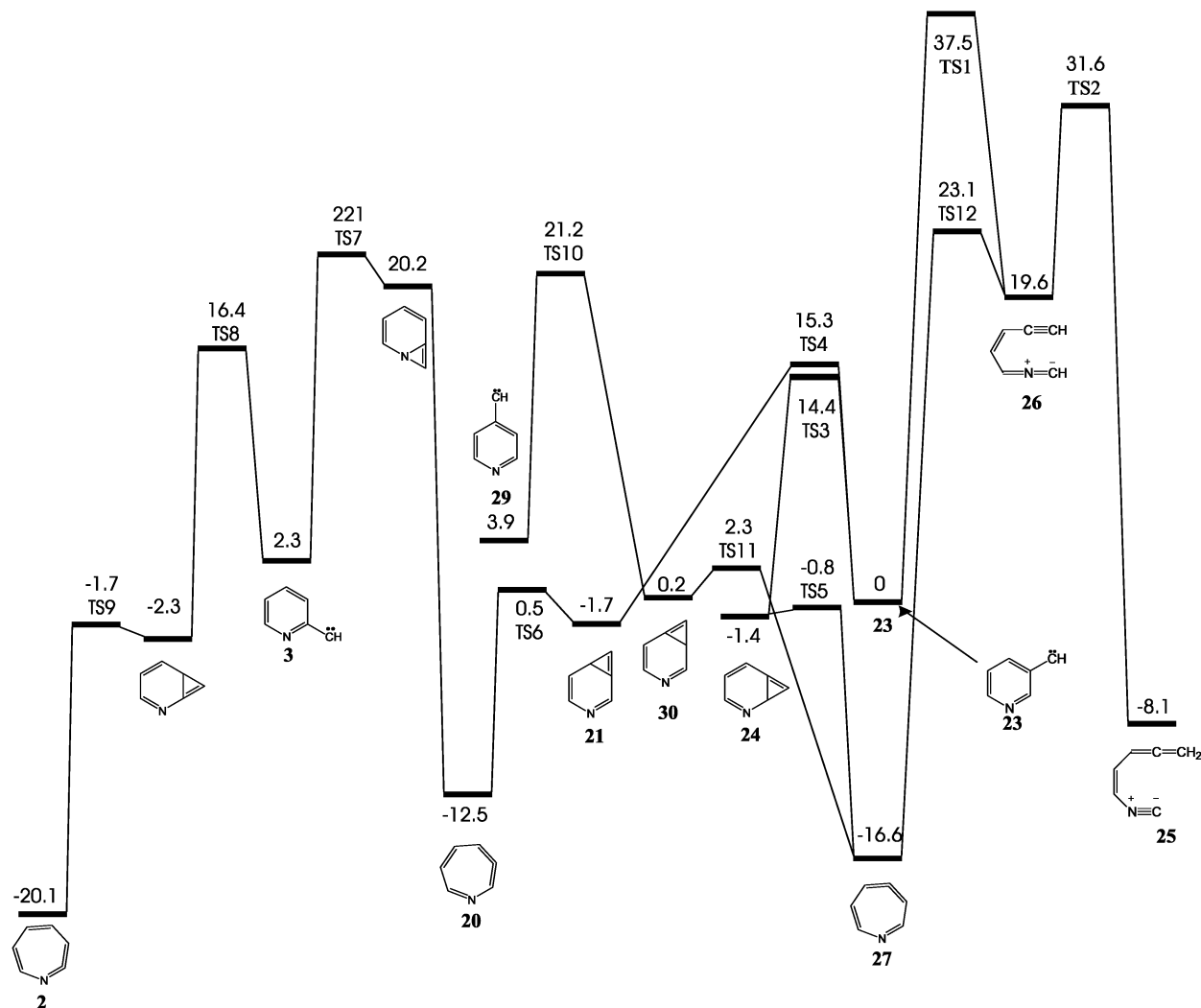
The analogous ring expansion **6**  $\rightarrow$  **7** has been the subject of extensive theoretical calculations,<sup>4,16</sup> and there is general agreement that the bicyclic cyclopropene resides in a shallow high-energy well, which makes its detection extremely difficult. This is also true of the cyclopropenes **21**, **24**, and **30** connecting **29**, **23**, and **2** (Figure 6).

The long-wavelength photolysis ( $\lambda > 410$  nm) of the nitrile ylide **26** affords the azacycloheptatetraene **27**.<sup>15b</sup> This can in principle take place as a direct cyclization, via the cyclopropene **24** and/or via reversion to 3-pyridylcarbene **23** (see Scheme 1). The slow conversion of **27** to **2** (absorbing at 1895  $\text{cm}^{-1}$ ) at  $\lambda > 410$  nm is expected to take place via the nonobserved intermediates **24**, **21**, and **20**. The nonobservation of intermediates is presumably a question of reaction rates. Furthermore, the conversion of **27** to **3**, **2**, and **1** appears to be a very inefficient process, probably because the main reaction channel leads to the nitrile ylide **26**. Although **1** and **3** were observed by ESR spectroscopy,<sup>15c</sup> only a small amount of **2** is obtained by photolysis of the matrix containing **26** and **27** at  $\lambda > 410$  nm, where isomerization to the open-chain allene **25** is believed to take place. Apparently, in the excited state, there is a much higher probability of 3-pyridylcarbene **23** undergoing the ring opening reaction to nitrile ylide **26** than rearrangement to **3** and **2**. Ylide **26** can return, in part, to carbene **23** and hence eventually to **2**.

4-Pyridylcarbene **29** gives rise to the same nitrile ylide **26**, but interestingly with a higher ratio of ring expansion to ring opening (**27**:**26**) than does 3-pyridylcarbene **23**. Starting from 4-pyridylcarbene **29**, the ring-expanded allene **27** has to be formed before **26** can form (Scheme 1). This indicates that cleavage of **27** is not the only route to ylide **26**; ring cleavage of 3-pyridylcarbene **23** to **26** must also play a role. Furthermore, the deuterated diazo compound **22D** gives mostly the nitrile ylide **26D** and very little of the allene **27D**. Therefore, again, it is most likely that the carbene **23D** is the main species undergoing ring opening to the nitrile ylide. Computationally, it is found that both 3-pyridylcarbene **23** and the seven-membered ring allene **27** can undergo ring opening to ylide **26**. The barriers for these two processes are virtually identical (Figure 6).

It should be noted that there is nothing to prevent a photochemical process from giving a product that is of higher energy than the starting material, e.g., in this case ring opening of 3-pyridylcarbene to ylide **26**, which is of higher calculated energy than both the carbene and its potential ring expansion products **27** and **20** (Scheme 1 and Figure 6). Such a process

(16) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535. Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022. Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Bordon, W. T.; Hamilton, T. P.; Schaefer, H. F., III. *J. Org. Chem.* **1996**, *61*, 7030.



**Figure 6.** Potential energy diagram for the pyridylcarbene isomers, including transition states, at the B3LYP/6-31G\* level of theory. Energies in kcal/mol normalized to closed shell  $1A'$  singlet carbene.

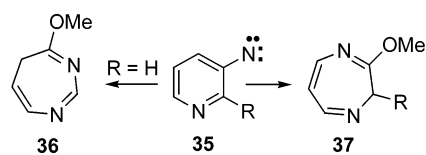
occurs in the ring opening reaction of pyridine in its  $S_1$  state by C–N bond scission to form a diradical on photolysis at 267 nm.<sup>17</sup>

The calculated energy profile of 3-pyridylcarbene and its isomers (Figure 6) pertain to the carbene **23** in its closed shell singlet state ( $1A'$ ). At our best computational level (CASPT2//CAS(8,8)/cc-pVDZ) the triplet ground state carbene ( $3A''$ ) is 12.5 kcal/mol below and the open shell singlet ( $1A''$ ) is 8.8 kcal/mol above the closed shell singlet. For phenylnitrene the lowest singlet is known to be open shell ( $1A''$ ), which lies ca. 18 kcal/mol above the ground state triplet ( $3A''$ ).<sup>2</sup> Similarly for 3-pyridylnitrene, the lowest singlet is the open shell **23**, which is the reference point in Figure 7. It lies 19.4 kcal/mol above the ground state triplet and 17.8 kcal/mol below the closed shell singlet ( $1A'$ ) at the CASPT2//CAS(8,8)/cc-pVDZ level of theory (see Tables S1 and S2 in the Supporting Information for details of CAS(8,8), CASPT2, CCSD(T), and B3LYP calculations).

In the case of 3-pyridylnitrene **32**, the only primary reaction observed is the ring opening to the nitrile ylide **33**. The calculated energy profile (Figure 7 and Table S2) suggests that here the nitrile ylide is of lower energy than the nitrene, and it

is protected from rearrangement by high energy barriers. The barrier to form the ylide from the nitrene (18.6 kcal/mol) is also smaller than the barrier for the analogous 3-pyridylcarbene ring opening (37.5 kcal/mol; Figure 6), in agreement with the experimental observation that **33** is very easily formed. It is likely that the unobserved cyclic ketenimine **39** can also undergo ring opening to ylide **33**.

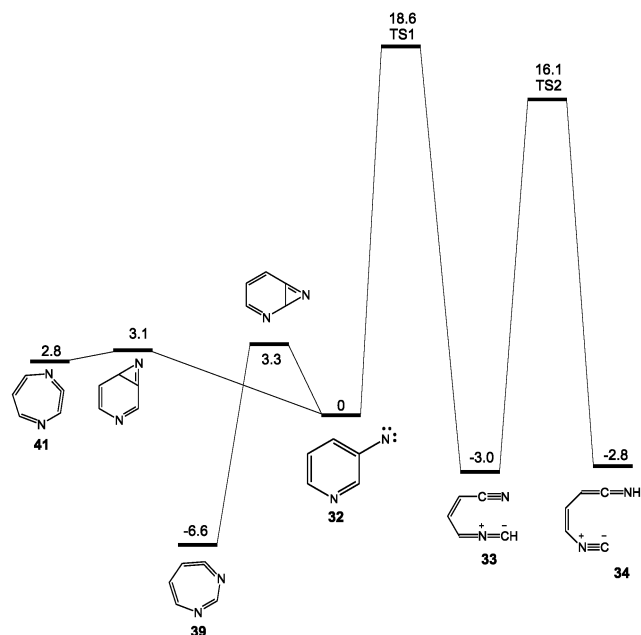
Ring expansion to diazacycloheptatetraene **39** or **41** (Figure 7) was not observed in the matrix photolyses of 3-pyridyl azide **31**. However, such species have been trapped by methoxide ion in solution.<sup>18</sup> This is a further example to demonstrate that the



same intermediates are not necessarily observed in matrix and solution photolyses.<sup>12</sup> The preferred formation of **36** in solution trapping is in agreement with the lower calculated energy of

(17) Lobastov, V. A.; Srinivasen, R.; Goodson, B. M.; Ruan, C.-Y.; Feenstra, J. S.; Zewail, A. H. *J. Phys. Chem. A* **2001**, *105*, 11159.

(18) Sawanishi, H.; Tajima, K.; Tsuchiya, T. *Chem. Pharm. Bull.* **1987**, *35*, 4101.



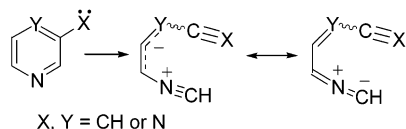
**Figure 7.** Potential energy diagram for the pyridylnitrene isomers, including transition states, at the B3LYP/6-31G\* level of theory. Energy values are referenced to the open shell 1A'' singlet nitrene **32**.

**39** (Figure 7). Presumably, under matrix photolysis conditions the equilibrium concentration of **39** is too low to permit its observation; but under solution photolysis conditions the concentration is high enough to allow its trapping, and hence drive the whole reaction in the direction of **36** or, when the 2-position in nitrene **35** is blocked, **37**.

The outcomes of thermal reactions of the pyridylcarbenes and -nitrenes are quite different. Under flash vacuum thermolysis (FVT) conditions, all the pyridylcarbenes rearrange efficiently to phenylnitrene and then to cyanocyclopentadiene **4**. Similarly, FVT of both 4- and 3-azidopyridine and tetrazolo[1,5-*a*]pyridine affords mixtures of 2- and 3-cyanopyrroles.<sup>19</sup>

## Conclusion

Heteroarylcarbenes and -nitrenes having a substitution pattern as in 3-pyridylcarbene and 3-pyridylnitrene undergo photochemical ring opening to nitrile ylides. This is now seen to be a general process, also taking place in pyrazinylnitrenes,<sup>11</sup> 3-quinolylnitrene,<sup>20</sup> and 2-quinoxalylnitrene.<sup>21</sup> The ring cleavage reaction may take place in either the carbene or nitrene or in the seven-membered ring cumulene intermediate, which is not always observed. A different type of ring opening of het-



eroarylnitrenes to vinylnitrenes takes place when structural constraints prevent the formation of the nitrile ylides.<sup>22</sup>

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## Computational Details

The energies of the relevant molecules were calculated at the B3LYP/6-31G\* and CASPT2//CAS(8,8)/cc-pVDZ levels of theory using the Gaussian 98 suite of programs<sup>23</sup> and MOLCAS.<sup>24</sup> Additionally CCSD-(T)/cc-pVDZ single-point energies were calculated for CASSCF(8,8)/cc-pVDZ optimized geometries. The full data are presented in the Supporting Information. The B3LYP energies of the open shell singlet carbene **23** and nitrene **32** were estimated using a method described by Cramer.<sup>25</sup> The calculated energy profiles for all the pyridylcarbene isomers in Scheme 1 and the corresponding 3-pyridylnitrene isomers are presented in Figures 6 and 7.

The CASSCF calculations used an eight-electron/eight-orbital (8,8) active space to calculate all species of interest. In  $C_s$  symmetry the active space was composed of 1A' and 3A'' occupied and 4A'' virtual orbitals. Dynamic correlation of electrons was determined by single-point CASPT2 energies at CASSCF(8,8)/cc-pVDZ optimized geometries. Dunning's correlation-consistent valence basis set cc-pVDZ was used. Excited state calculations were performed using the same active space, and to ensure orthogonality, the CASSCF wave functions were averaged over all excited states of the same symmetry. The CASPT2 wave functions are described to 65–70% by the CASSCF wave function for all excited states. Transition moments were calculated on the basis of these wave functions, using CASPT2 energy differences in the denominator.

IR spectra were calculated at the B3LYP/6-31G\* level, and a scaling factor of 0.9613 was used for frequencies.<sup>26</sup>

## Experimental Section

The starting materials **22**,<sup>27</sup> **28**,<sup>27</sup> and **31**<sup>28</sup> were prepared according to the literature. 3-(Deuteriodiazomethyl)pyridine **22D** was prepared by exchange of **22** with a 100-fold excess of D<sub>2</sub>O in the presence of a catalytic amount of NaOMe.<sup>15b</sup> The apparatus and procedure for matrix isolation were as previously described.<sup>29</sup> A 1000 W high-pressure Xe/Hg lamp equipped with a monochromator and appropriate filters and an excimer lamp operating at 222 nm (25 mW/cm<sup>2</sup>) were used for the photolyses.

**3-Diazomethylpyridine 22** was deposited with Ar (ca 1:1000) at 22 K. IR (Ar, 7 K): 2070, 1591, 1483, 1437, 1389, 1379, 1249, 1219, 1185, 1123, 1021, 1017, 796, 767, 671, 661, 553 cm<sup>-1</sup>.

Photolysis of **22** at  $\lambda > 480$  nm for 60 h produced 3-pyridylcarbene **23** with the following characteristic bands: IR (Ar, 7K): 1522, 1457, 991, 985, 784, 684 cm<sup>-1</sup>; UV (Ar, 7 K)  $\lambda_{\max}$  446, 431, 414 nm.

Further photolysis at  $\lambda > 410$  nm for 15 min produced two new species: **26**: IR (Ar, 7 K) 3319, 1930, 800, 786 cm<sup>-1</sup>; UV (Ar, 7 K)

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$\lambda_{\max}$  352 nm. **27**: IR (Ar, 7 K) 1810, 1800, 1361, 1248, 892, 844, 722, 698, 593  $\text{cm}^{-1}$ .

Further photolysis at 410 nm for 1 h resulted in selective destruction of **26** with formation of new band at 2122  $\text{cm}^{-1}$ .

**3-Deuteriodiazomethylpyridine 22D** was deposited and photolyzed analogously.

IR (**22D**, Ar, 7 K): 2069, 1589, 1485, 1427, 1355, 1340, 795, 705  $\text{cm}^{-1}$ .

IR (**23D**, Ar 7 K): 1522, 1457, 1382, 1219, 993, 784, 683  $\text{cm}^{-1}$ .

IR (**26D**, Ar, 7 K): 2591, 1988 (vw), 1928, 796, 785  $\text{cm}^{-1}$ .

IR (**27D**, Ar, 7 K): 1802, 1795  $\text{cm}^{-1}$ .

Bleaching of **26D** at 410 nm for 80 min resulted in new bands at 2122 and 1943  $\text{cm}^{-1}$  ascribed to **25D**.

**4-Pyridyldiazomethane 28** was deposited with Ar as above. IR (Ar, 7 K): 2076, 2070, 1596, 1386, 1222, 1206, 988, 809, 644  $\text{cm}^{-1}$ . Photolysis at 480 nm for 48 h followed by 410 nm for 3 min produced **26** and **27** with IR absorptions identical with those described above, but with a larger proportion of **27**. A spectrum is shown in the Supporting Information.

**3-Azidopyridine 31** was deposited with Ar (ca 1:1000): IR (Ar, 7 K) 2142, 2101, 1482, 1477, 1430, 1311, 1237, 801, 703  $\text{cm}^{-1}$ ; UV (Ar, 7 K)  $\lambda_{\max}$  245 nm with sidebands at 278, 294. Photolysis at 222 nm for 5 min afforded cyanovinyl nitrile ylide **33**: IR (Ar, 7 K) 2212, 1961, 683, 693, 703, and 710  $\text{cm}^{-1}$ ; UV (Ar, 7 K)  $\lambda_{\max}$  360 nm. At longer photolysis times a second rotamer of **33** appears with bands at 2216 and 1947  $\text{cm}^{-1}$  and a splitting of the broad band around  $\sim 700$

$\text{cm}^{-1}$ . At the same time, **33** rearranges to a compound exhibiting isocyanide and ketenimine absorptions attributed to the rotamers of ketenimine **34**: IR (Ar, 7 K) 918, 984, 2029, 2043, 2158, 3279, 3316  $\text{cm}^{-1}$ ; UV (Ar, 7 K)  $\lambda_{\max}$  332 nm.

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**Supporting Information Available:** Tables of the energies of the ground state triplets and closed and open shell singlet states of 3-pyridylcarbene and 3-pyridylnitrene, and energies of the singlet ground states for all the relevant isomers in Figures 6 and 7, including transition states for the pyridylcarbene interconversions and ring opening at the B3LYP/6-31G\*, CAS-(8,8)/cc-pVDZ, CASPT2//CAS(8,8)/cc-pVDZ, and CCSD(T)/cc-pVDZ//CAS(8,8)/cc-pVDZ levels of theory; IR spectra showing the formation of carbene **23D** and ylide **26D**; the photolysis of 4-pyridyldiazomethane to **26** and **27**; excited state calculation (CASPT2) for structures **26** and **33** (used in Figures 2 and 5), and tables of Cartesian coordinates for all species of interest with thermochemical data and frequencies at the B3LYP/6-31G\* and CASPT2//CAS(8,8)/cc-pVDZ level (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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