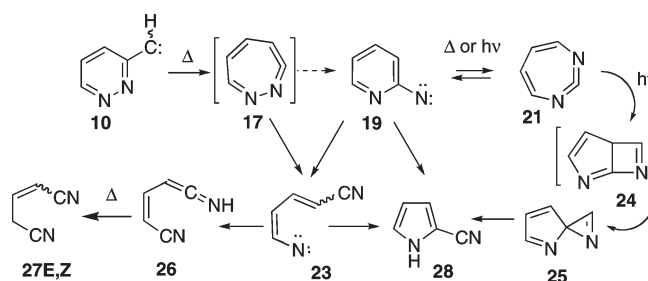


2-Pyridylnitrene and 3-Pyridazylcarbene and Their Relationship via Ring-Expansion, Ring-Opening, Ring-Contraction, and Fragmentation

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Photolysis of triazolo[1,5-*b*]pyridazine **8** isolated in Ar matrix generates diazomethylpyridazines **9Z** and **9E** and diazopentenynes **11Z** and **11E** as detected by IR spectroscopy. ESR spectroscopy detected the 3-pyridazylcarbene **10** as well as pent-2-en-3-yn-1-ylidene **12** formed by loss of one and two molecules of N₂, respectively. Further photolysis caused rearrangement of the carbenes to 1,2-pentadien-4-yne **13** and 3-ethynylcyclopropene **14**. Flash vacuum thermolysis (FVT) of **8** at 400–500 °C with Ar matrix isolation of the products yielded **13**, **14**, and 1,4-pentadiyne **15**. At higher temperatures, glutacononitriles **27Z** and **27E** were formed as well together with minor amounts of 2- and 3-cyanopyrroles **28** and **29**. Tetrazolo[1,5-*a*]pyridine/2-azidopyridine **22T/22A** yields 2-pyridylnitrene **19** as well as the novel open-chain cyanodienylnitrene **23** and the ring-expanded 1,3-diazacyclohepta-1,2,4,6-tetraene **21** on short wavelength photolysis. Nitrenes **19** and **23** were detected by ESR spectroscopy, and cumulene **21** by IR and UV spectroscopy. FVT of **22T/22A** also affords 2-pyridylnitrene **19** and diazacycloheptatetraene **21**, as well as glutacononitriles **27Z,E** and 2- and 3-cyanopyrroles **28** and **29**. Photolysis of **21** above 300 nm yields the novel spiroazirene **25**, identified by its matrix IR spectrum. The reaction pathways connecting the four carbenes (**10Z,E** and **12Z,E**) and three nitrenes (**19**, **23EZ**, and **23ZZ**) in their open-shell singlet and triplet states are elucidated with the aid of theoretical calculations at DFT, CASSCF, and CASPT2 levels. Three possible mechanisms of ring-contraction in aryl nitrenes are identified: (i) via ring-opening to dienylnitrenes, (ii) concerted ring-contraction, and (iii) via spiroazirenes **25**, whereby (i) is the energetically most favorable.

Introduction

In recent papers we have demonstrated the occurrence of two types of ring-opening reactions of (hetero)aromatic nitrenes and carbenes, Type I and Type II (Scheme 1).

Type I ring-opening generates nitrile ylides exemplified by 3-pyridylcarbene, 3-pyridylnitrene,¹ and 2-pyrazinylnitrene/4-pyrimidylnitrene.² Pyridazinylnitrene **2**, generated from

tetrazolo[1,5-*a*]pyridazine/3-azidopyridazine **1T/1A**, undergoes an analogous ring-opening to a diazonium ylide, viz. the diazo compound **3**, under both thermal and photochemical conditions. Flash vacuum thermolysis (FVT) of **1** produced **3** and the products of N₂ elimination (Scheme 2).³ The same products were also obtained on matrix photolysis,^{4,5} and a weak signal ascribed to nitrene **2** was detected by ESR

(1) Bednarek, P.; Wentrup, C. *J. Am. Chem. Soc.* **2003**, *125*, 9083.

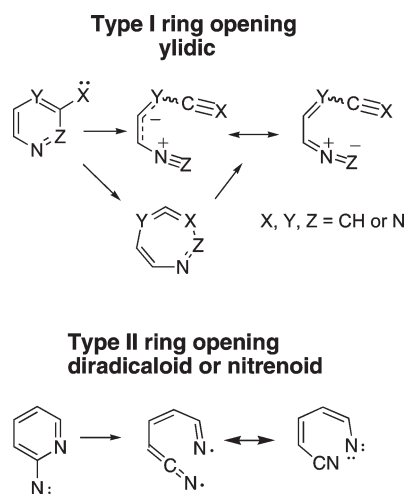
(2) Addicott, C.; Wong, M. W.; Wentrup, C. *J. Org. Chem.* **2002**, *67*, 8538.

(3) Wentrup, C.; Crow, W. D. *Tetrahedron* **1970**, *26*, 4915.

(4) Hill, B. T.; Platz, M. S. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1051.

(5) Torker, S. Diploma Thesis, The University of Queensland (Australia) and Technical University of Graz (Austria), **2003**.

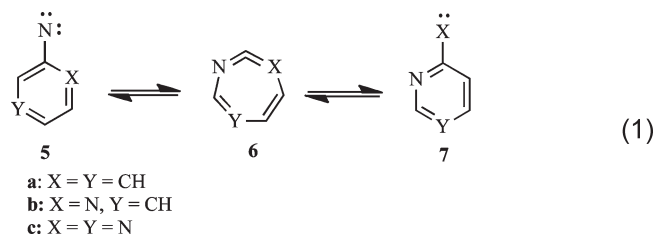
SCHEME 1. Type I and Type II Ring-Openings



spectroscopy of Ar matrices.⁶ The formation of diazo compound **3** can be described as a Type I ring-opening reaction of the nitrene **2**.

Type II ring-opening generates diradicals or vinylnitrenes (Scheme 1). The ring-opening of 2-pyridylnitrene is the subject of detailed discussion in this paper. Type II ring-openings in 2-quinoxalynitrene and 1-isoquinolynitrene have been reported previously.^{6,7}

Phenylnitrene **5a** and 2-pyridylcarbene **7a** can interconvert via 1-azacyclohepta-1,2,4,6-tetraene **6a** (eq 1).⁸ 2-Pyridylnitrene **5b/7b** undergoes a degenerate interconversion with 1,3-diazacyclohepta-1,2,4,6-tetraene **6b**,⁹ and 2-pyrazinylnitrene **5c** and 4-pyrimidylnitrene **7c** interconvert via ring-expansion to 1,3,5-triazacycloheptatetraene **6c** (eq 1).²

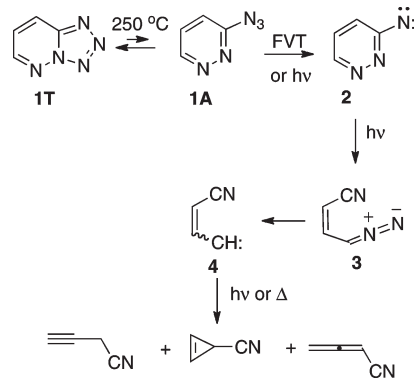


These reactions motivated us to investigate the potential interconversion of 3-pyridazylcarbene **10** and 2-pyridylnitrene **19**. The results are described herein.

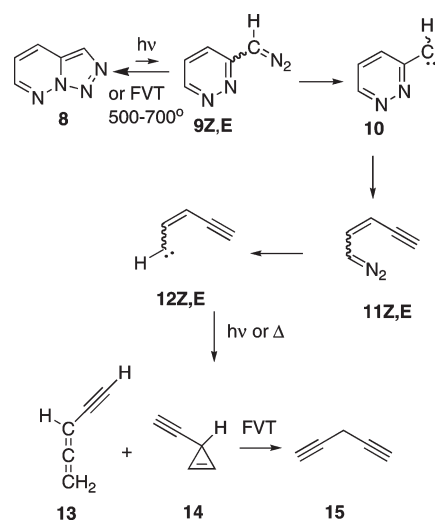
Results and Discussion

3-Pyridazylcarbene by Photolysis of Triazolo[1,5-*b*]pyridazine. We first describe the formation of diazo compounds and carbenes (Scheme 3). Triazole **8** was prepared by oxidation of the hydrazone of 3-pyridazinecarboxaldehyde with active MnO₂. The compound exists exclusively in the triazole form in the solid state at room temperature, and codeposition with Ar at 25 K also produced very largely the

SCHEME 2. 3-Pyridazylnitrene and Its Reactions



SCHEME 3. 3-Pyridazylcarbene Ring-Opening and Fragmentation on Photolysis and Thermolysis



unchanged triazole (Figure S1 in the Supporting Information shows the IR and UV spectra), but a small amount of the diazo valence tautomer **9Z,E** is formed on gentle FVT at 500 °C (see below). Photolysis of the matrix-isolated triazole **8** at 222 or 254 nm resulted in ring-opening to the diazo compound **9** with a UV maximum at ca. 460 nm and IR peaks at 2094 (vs), 1586 (m), 1446 (s), 1373 (w), 1222 (vw), 801 (w), and 671 (w) cm⁻¹ (Figure 1). Further photolysis resulted in increased intensity of an additional peak at 2097 cm⁻¹ as well as a smaller doublet at 2070–2075 cm⁻¹ accompanied by a C–H stretching band at 3321 cm⁻¹. The double peak at 2094 (2093)–2097 cm⁻¹ is ascribed to the *s*-*Z* and *s*-*E* conformers of **9**. The new peaks at 2070–2075 and 3321 cm⁻¹ indicate the presence of a second, acetylenic, diazo compound, viz. diazopentenynes **11Z** and **11E** (Figure 2). Good agreement with the calculated IR spectra (Figure 2) supports the assignments. Difference spectra show that, as **9** is photolyzed, **11** is formed (Scheme 3 and in the Supporting Information Figure S2).

Photolysis of an Ar matrix of triazolopyridazine **8** in the ESR spectrometer gave rise to three sets of carbene signals (Figure 3), which are ascribed to pyridazylcarbene **10** and the *s*-*E* and *s*-*Z* conformers of pentenylnitrene, **12E** and **12Z**, on the basis of their zero field splitting (ZFS) parameters. After 45 s of photolysis at 308 nm only **10** and one conformer of **12**

(6) Kvaskoff, D.; Bednarek, P.; George, L.; Waich, K.; Wentrup, C. *J. Org. Chem.* **2006**, 71, 4049.

(7) Addicott, C.; Reisinger, A.; Wentrup, C. *J. Org. Chem.* **2003**, 68, 1470.

(8) (a) Wentrup, C. *Top. Curr. Chem.* **1976**, 62, 175. (b) Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, 100, 6245.

(9) (a) Winter, H.-W.; Wentrup, C. *J. Am. Chem. Soc.* **1980**, 102, 6159. (b) McCluskey, A.; Wentrup, C. *J. Org. Chem.* **2008**, 73, 6265.

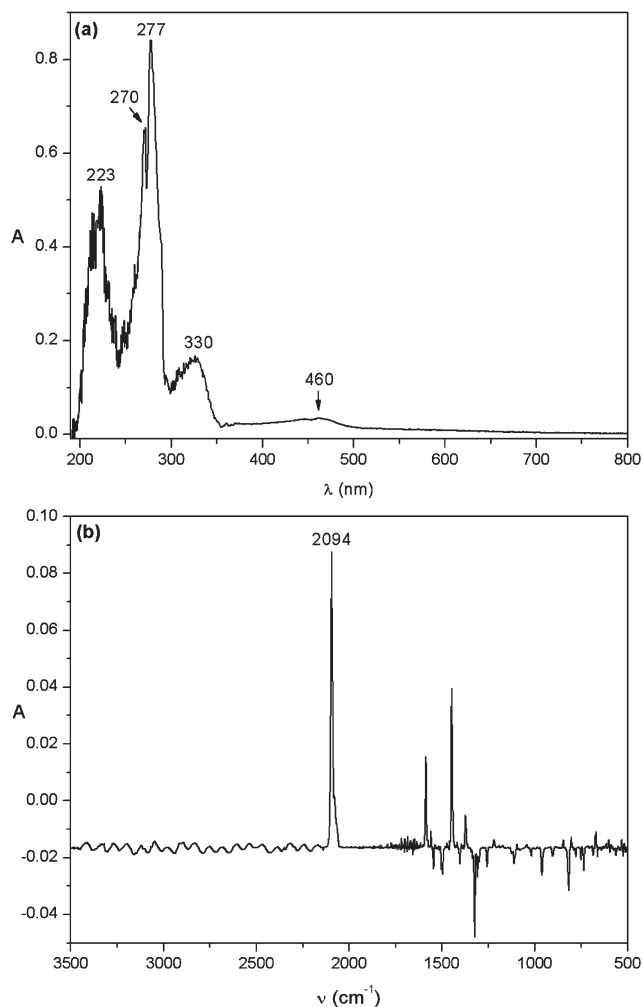


FIGURE 1. (a) UV difference spectrum of 3-pyridazylidomethane **9** (major conformer at 2094 cm^{-1}) in Ar matrix, obtained by photolysis of **8** in Ar matrix at 254 nm for 1 min (200 mA, 50 W low-pressure Hg lamp). (b) The corresponding IR spectrum. (For the matrix UV and IR spectra of **8**, see Figure S1 in the Supporting Information)

(**12E**) were detectable (Figure S3, SI). After 60 s at 308 nm all three species were obtained (Figure 3). Only one conformer of **10** was detected at all times. The spectra become more intense but also more complicated at longer photolysis times with small amounts of other, unidentified triplet species being formed (see below). ZFS parameters for **10**: $D/hc = 0.5440 \text{ cm}^{-1}$; $E/hc = 0.0254 \text{ cm}^{-1}$. This D value fits the correlation with calculated natural spin densities on the carbene carbon in aryl- and heteroarylcarbenes.¹⁰ Vinylcarbenes have significantly smaller D values. ZFS parameters for **12E**: $D/hc = 0.3360 \text{ cm}^{-1}$, $E/hc = 0.0208 \text{ cm}^{-1}$, $E/D = 0.0619$; **12Z**: $D/hc = 0.3798 \text{ cm}^{-1}$, $E/hc = 0.0162 \text{ cm}^{-1}$, $E/D = 0.0427$. For comparison, the ZFS parameters for the parent vinylcarbene in MTHF solution at 6 K are the following:¹¹ (*s-E*)-vinylcarbene: $D/hc = 0.4093 \text{ cm}^{-1}$, $E/hc = 0.0224 \text{ cm}^{-1}$, $E/D = 0.0547$; (*s-Z*)-vinylcarbene: $D/hc = 0.4578 \text{ cm}^{-1}$, $E/hc = 0.0193 \text{ cm}^{-1}$, $E/D = 0.0422$. The lower D values for **12Z,E** are

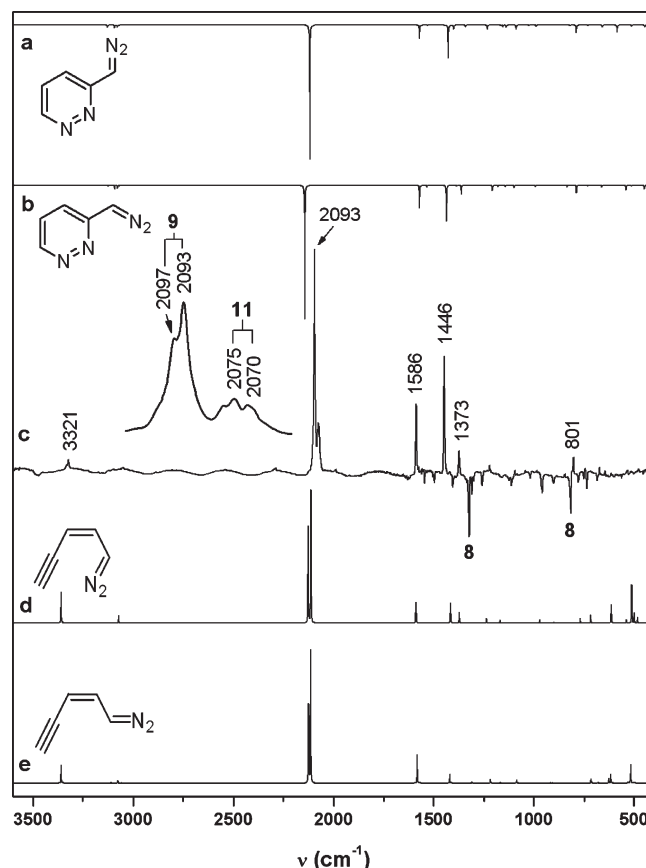


FIGURE 2. IR spectrum of triazolopyridazine **8** in Ar matrix after photolysis at 254 nm for 2 min, showing peaks of diazo compounds **9** and **11** (**9Z**, **9E** and **11Z**, **11E**). (a) Calculated spectrum of diazo compound **9E**. (b) Calculated spectrum of diazo compound **9Z**; (c) photolysis at 254 nm, 2 min (the negative peaks are the spectrum of **8** before photolysis). (d) Calculated spectrum of diazo compound **11Z**. (e) Calculated spectrum of diazo compound **11E**. The shoulders indicating the presence of the *s-Z* and *s-E* geometrical isomers of **9** and **11** are shown in the inset. All calculations are at the B3LYP/6-311G** level, with wavenumbers scaled by a factor of 0.967.

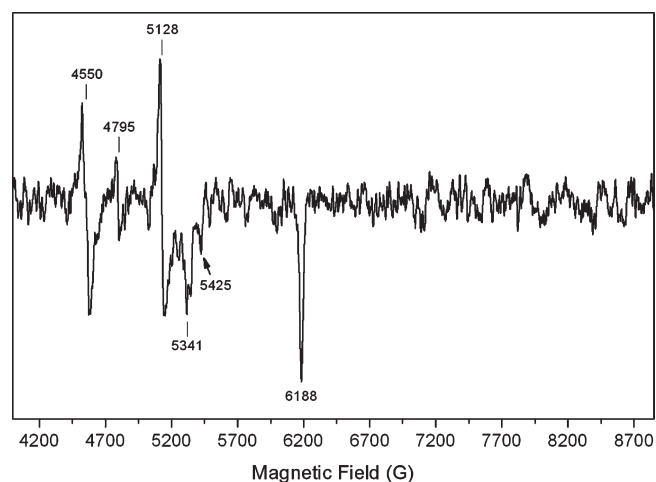


FIGURE 3. ESR spectrum showing three carbenes after photolysis of **8** at 308 nm for 60 s. **10**: $D/hc = 0.5440 \text{ cm}^{-1}$; $E/hc = 0.0254 \text{ cm}^{-1}$; $Z_1 = 2330 \text{ G}$; $X_2 = 5128 \text{ G}$; $Y_2 = 6188 \text{ G}$; $Z_2 = 9243 \text{ G}$. **E-12**: $D/hc = 0.3360 \text{ cm}^{-1}$; $E/hc = 0.0208 \text{ cm}^{-1}$; $X_2 = 4550 \text{ G}$; $Y_2 = 5341 \text{ G}$. **Z-12**: $D/hc = 0.3798 \text{ cm}^{-1}$; $E/hc = 0.0162 \text{ cm}^{-1}$; $X_2 = 4795 \text{ G}$; $Y_2 = 5425 \text{ G}$. Microwave frequency 9.7278 GHz. $H_0 = 3471 \text{ G}$.

(10) Kvaskoff, D.; Bednarek, P.; George, L.; Pankajakshan, S.; Wentrup, C. *J. Org. Chem.* **2005**, *70*, 7947.

(11) Hutton, R. S.; Manion, M. L.; Roth, H. D.; Wasserman, E. *J. Am. Chem. Soc.* **1974**, *96*, 4680.

in accord with the extended conjugation, and the E/D ratios for **12Z,E** follow the same trend as those for the parent vinylcarbenes.

In addition to the carbene signals described above, two triplet species are formed in the matrix photolyses of **8**, particularly at 222 nm (Figure S4, Supporting Information). The strongest of these signals ($D = 0.636 \text{ cm}^{-1}$; $E = 0.0007 \text{ cm}^{-1}$) is indicative of a highly conjugated nitrene or an (almost) linear carbene. None of these unassigned signals match the cyanovinyl nitrene **23**, which is formed from 2-pyridyl nitrene as described below. Some candidates for one or more of the unassigned triplet species are indicated in Scheme S1 in the Supporting Information. The same triplet signal is also obtained on photolysis or pyrolysis (FVT) of the isosteric tetrazolo[1,5-*a*]pyridazine **1T** ($D = 0.637 \text{ cm}^{-1}$, $E = 0.0009 \text{ cm}^{-1}$). The signal looks very much like that of propynylidene, HCCCH ,¹² but it is too weak for a secure identification.

Photolysis of **8** at 254 or 222 nm in the IR cryostat gave, in addition to the peaks due to the diazo compounds **9** and **11** described above, new peaks at 3333 (m), 1955 (w), 889 (m), 852 (m), and 644 (m) cm^{-1} and another set at 3338 (w), 2125 (vw), 1661 (m), 986 (s), 945 (m), 613 (s), 605 (vw), and 516 (m) cm^{-1} , as well as a single, weak peak at 1988 cm^{-1} not belonging to any of the other sets of peaks (Figure 4 and in the Supporting Information Figures S5–S7). The resulting IR spectrum is interpreted as a composite of two secondary photolysis products, derived from the carbene **12** (Scheme 3; Figure 4). The first set of absorptions is assigned to 1,2-pentadien-4-yne **13**, and the second set to 3-ethynylcyclopropene **14**. The peaks due to **13** appeared first. Compounds **13** and **14** were identified by comparison with literature data¹³ and with the calculated spectra shown in the Supporting Information (see Figure S7). IR difference spectra show that **9** photolyzes to **11**, **13**, and **14** at 222 and 254 nm (Figures S2 and S5). Both **9** and **11** photolyze to **13** and **14** at 281 nm (Figure S6, Supporting Information). Compounds **13** and **14** were also isolated from the preparative FVT described below.

Photolysis of the matrix containing the mixture of diazo compounds at $\lambda > 405 \text{ nm}$ caused the intensities of the triazole peaks to *increase*, thereby indicating that a portion of the diazo compounds **9Z,E** reverted back to triazole **8**, while another portion was converted to products **13** and **14**.

Additional weak peaks appeared during the photolysis at 254 nm; the weak, single peak at 1988 cm^{-1} (Figure 4 and in the Supporting Information Figure S5 and S7) does not belong to either **12** or **13**. The most likely assignment is the 1,3-diazacycloheptatetraene **21** (see Scheme 4 and the discussion below), but the weakness prevented the observation of any other peaks belonging to **21**; therefore, any assignment of the carrier must remain tentative.

A signal labeled K at 2042 cm^{-1} in Figure 4 may be due to cyanovinylketenimine **26**, one of the possible precursors of

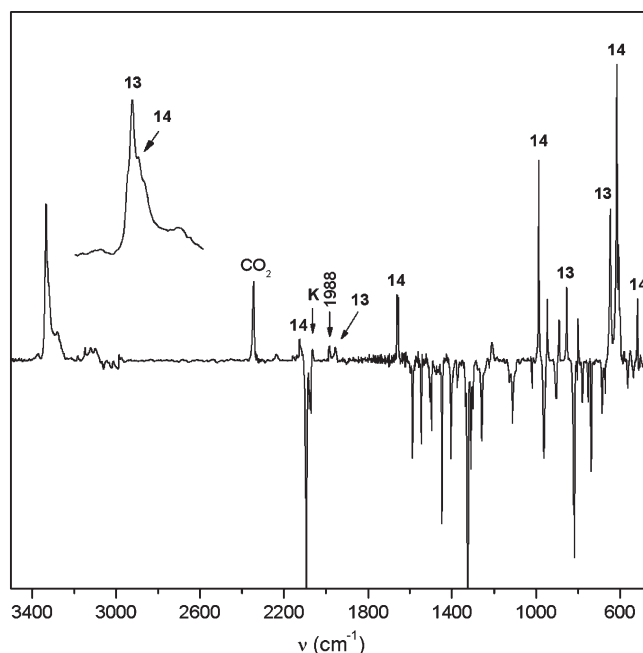


FIGURE 4. IR difference spectrum showing the characteristic absorptions of the final photoproducts 1,2-pentadien-4-yne **13** and 3-ethynylcyclopropene **14** after continued photolysis in Ar matrix at 254 nm for 120 min. Negative peaks are due to the spectrum obtained at 254 nm for 60 min (mainly a mixture of **8**, **9Z,E**, and **11Z,E**). The acetylenic C–H stretching region at 3325–3333 cm^{-1} is shown in the inset. Allene **13** appears at 1955 cm^{-1} . For the peaks at 1988 and 2042 (K) cm^{-1} see the text.

glutacononitriles **27Z,E**, which are formed on FVT (see below). The ketenimine **39** described below is another possibility, but this compound should not form at 254 nm.

FVT of Triazolo[1,5-*b*]pyridazine. Triazolopyridazine **8** was subjected to FVT at 500–700 °C, with the products being deposited together with Ar at 25 K to form a matrix. The IR spectrum recorded at 10 K showed that, at an FVT temperature of 500 °C much unchanged triazole was recovered. At 700 °C the conversion to products was nearly complete.

Throughout the temperature range 600–700 °C, peaks corresponding to the two photoproducts described above, 1,2-pentadien-4-yne **13** and 3-ethynylcyclopropene **14**, were observed, as well as new absorptions at 3319 (s), 2140 (w), 1417 (m), 1300 (w), and 605 (w) (Figure S8, Supporting Information). The new species was identified as 1,4-pentadiyne **15**, formed by thermal rearrangement of **14** and/or **13** (Scheme 3);¹⁴ the same three products were isolated in preparative FVT experiments and identified by ¹H NMR spectroscopy.

In addition to the peaks due to the three products **13**, **14**, and **15**, new peaks were observed at 2275, 2235, and 2260 cm^{-1} in the products of FVT at 600–700 °C (Figure S9, Supporting Information). Absorptions in this region are typical of nitriles, and these absorptions were readily assigned to the known *Z*- and *E*-glutacononitriles^{9,15} **27Z,E** (2275 and 2235 cm^{-1}), 2-cyanopyrrole⁹ **28** (2235 cm^{-1}), and

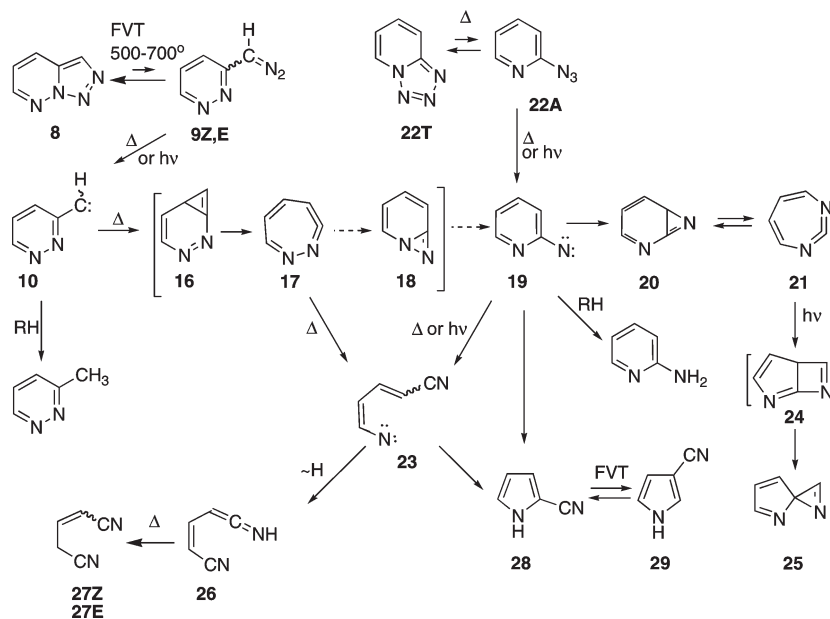
(12) (a) Bernheim, R. A.; Kempf, R. J.; Gramas, J. V.; Skell, P. S. *J. Chem. Phys.* **1965**, *43*, 196. (b) Seburg, R. A.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **2009**, *131*, 9442. The matrix site effects reported by these authors were not observed. The weak Z_1 and Z_2 transitions in our spectra is very similar to that described in: DePinto, J. T. Ph.D. Thesis, University of Wisconsin, **1993**.

(13) (a) Maier, G.; Endres, J. *J. Mol. Struct.* **2000**, *556*, 179. (b) Jones, E. R. H.; Lee, H. H.; Whiting, M. C. *J. Chem. Soc.* **1960**, 341.

(14) Haley, M. M.; Biggs, B.; Looney, W. A.; Gilbertson, R. D. *Tetrahedron Lett.* **1995**, *36*, 3457.

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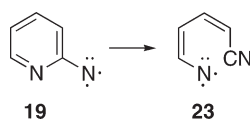
SCHEME 4. Further Rearrangements of 3-Pyridazylcarbene 10 and 2-Pyridylnitrene 19



3-cyanopyrrole⁹ **29** (2260 cm^{-1}) (Scheme 4 and in the Supporting Information Figure S9). The presence of these compounds was confirmed by GC-MS and ^1H NMR spectroscopy and comparison with samples prepared from tetrazolo[1,5-*a*]pyridine **22T** (see below).⁹ Very weak peaks due to **27Z,E** were visible in the ^1H NMR spectrum already at $500\text{ }^\circ\text{C}$, along with **13–15** as the main products, but the cyanopyrroles were not detectable at this temperature.

2-Pyridylnitrene. The formation and photochemistry of 2-pyridylnitrene are now described. 2-Pyridylnitrene **19** is easily detected by its Ar matrix ESR spectrum when generated by FVT of tetrazolo[1,5-*a*]pyridine/2-azidopyridine **22T/22A** (see Scheme 4).^{9b} Photolysis of matrix-isolated 2-azidopyridine **22A** at 254 nm also affords a strong ESR signal due to triplet 2-pyridylnitrene **19** (Figure 5). However, a second signal at ca. 5000 G has the typical appearance of the X_2Y_2 transition of a strongly delocalized nitrene with a nonzero E value ($D/hc = 0.425\text{ cm}^{-1}$; $E/hc = 0.006\text{ cm}^{-1}$) (Figure 5).

The D value of 0.425 cm^{-1} is too low to be due to an aliphatic or aromatic nitrene but would fit a conjugated vinylnitrene. This signal is ascribed to the ring-opened cyanodienylnitrene **23**.



This assignment is supported by the calculated natural spin density ρ on the nitrene-N in **23** (1.2486), which makes this nitrene fit very well on our $D-\rho$ correlation diagram⁶ (see Figure S10, Supporting Information). Nitrene **23** is the expected precursor of glutakonitriles **27Z,E** described below. The formation of open-chain ketenimines has been

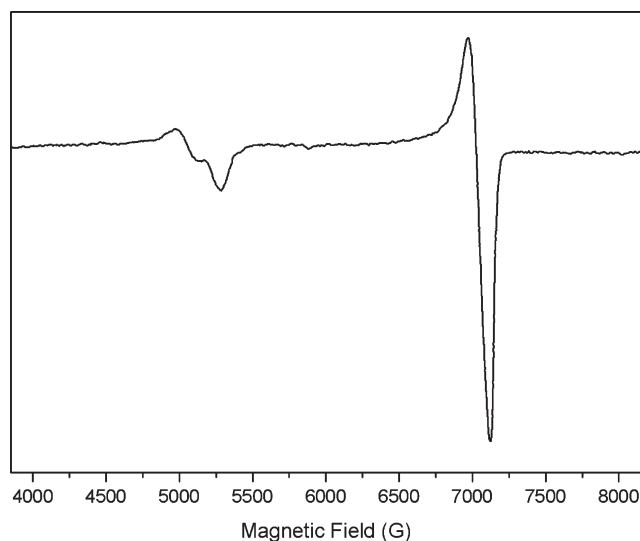


FIGURE 5. ESR spectrum obtained after mild FVT of tetrazolopyridine **22T** at $200\text{ }^\circ\text{C}$ to generate 2-azidopyridine **22A**, isolation of the products in Ar matrix at 15 K , and photolysis at 254 nm . Signal at $X_2 = 7025\text{ G}$, $Y_2 = 7126\text{ G}$; $D/hc = 1.073\text{ cm}^{-1}$; $E/hc = 0.002\text{ cm}^{-1}$ (assigned to 2-pyridylnitrene **19**). Signal at $X_2 = 5055\text{ G}$, $Y_2 = 5281\text{ G}$; $D/hc = 0.425\text{ cm}^{-1}$; $E/hc = 0.006\text{ cm}^{-1}$ (assigned to **23**).

documented in the matrix photolyses of several substituted tetrazolo/azidopyridines.^{7,16}

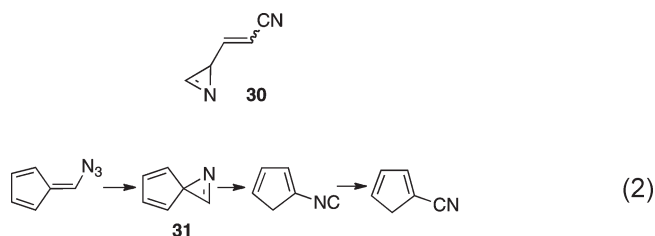
2-Pyridylnitrene undergoes facile ring-expansion to the cyclic carbodiimide **21** on both photolysis and FVT as observed by IR spectroscopy.⁹ Thus photolysis of **22T/22A** in an Ar matrix at 254 nm affords a very clean IR spectrum of **21** in very good agreement with the calculated spectrum (Figure 6): 1989 (vs) , 1318 (m) , 978 (m) , 975 (m) , 747 (m) , 551 (m) cm^{-1} . The UV spectrum of **21** has a maximum at 328 nm (Figures S11–S12, Supporting Information), and the compound therefore undergoes secondary photolysis in the $300\text{--}400\text{ nm}$ range.

(16) Addicott, C.; Wentrup, C. *Aust. J. Chem.* **2008**, *61*, 592.

Most interestingly, further photolysis of **21** at 308 or 365 nm (using a 310–390 nm interference filter) leads to a new compound, the IR spectrum of which agrees very well with the calculated spectrum of the spiroazirene **25** (Scheme 4, Figure 7, and in the Supporting Information Figure S13).

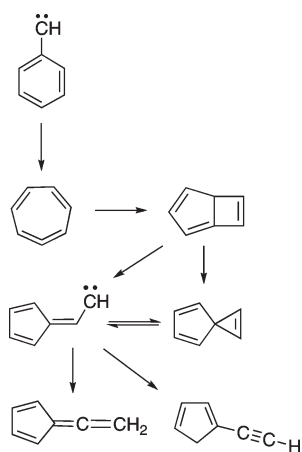
In contrast, very poor agreement was found with the calculated IR spectra of a number of alternative structures, including cyanovinylazirenes **30** and isocyanovinylazirenes.

The C=N stretching vibration of spiroazirene **25** appears at 1688 cm^{-1} . 1-Azaspiro[2.4]hepta-1,4,6-triene **31** (eq 2) has been prepared by photolysis of 6-azidofulvene



and is reported to absorb at 1676 cm^{-1} in CCl_4 solution.¹⁷ The formation of spiroazirene **25** has precedent in the all-carbon series, where the analogous spirocyclopropene is postulated as a key intermediate in the *thermal* carbon scrambling in phenylcarbene (Scheme 5).¹⁸ Such a spirocyclopropene can actually be isolated in the indene series.¹⁹ The *photochemical* formation of **25** would be a logical consequence of an electrocyclic process yielding **24** (Scheme 4).

SCHEME 5. Phenylcarbene Rearrangements¹⁸



Either a concerted 1,5-shift or ring-opening to a vinylnitrene and reclosure leads to **25**. This process is considered further in the Computational Method section below. The weak absorption at 2042 cm^{-1} in Figure 7 and in the Supporting Information Figure S13 may be due to the ketenimine **26** (Schemes 4 and 6) or **39** (Scheme 7, described below). The weakness of this signal does not permit a distinction.

FVT of **22T/22A** affords the cyclic carbodiimide **21** as the main product at temperatures below ca. $500\text{ }^\circ\text{C}$.⁹ At higher temperatures, **21** gradually disappears, to be replaced by 2- and 3-cyanopyrroles **28** and **29** along with minor amounts

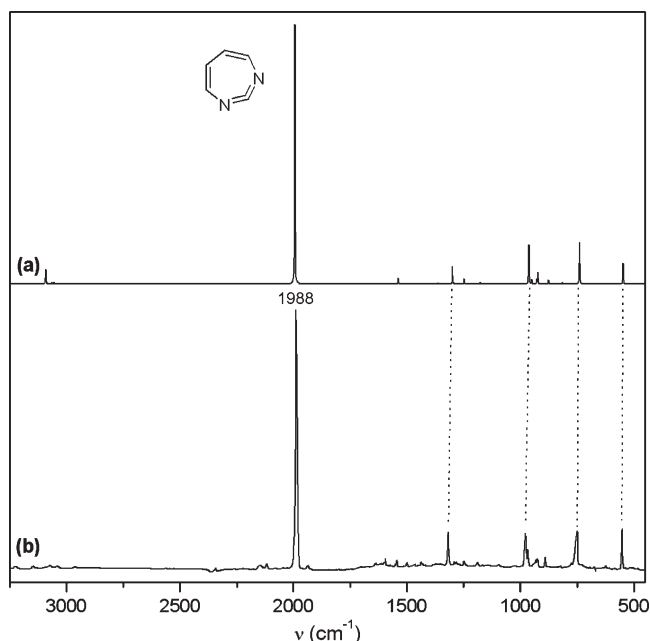


FIGURE 6. (a) Calculated IR spectrum of carbodiimide **21** at the B3LYP/6-311G** level, wavenumbers scaled by 0.967, and (b) Ar matrix IR spectrum resulting from photolysis of tetrazolopyridine/2-azidopyridine **22T/22A** at 222 nm for 30 min. Peaks due to **21**: 1989 (vs), 1318 (m), 978 (m), 975 (m), 925 (w), 890 (w), 747 (m), 551 (m) cm^{-1} . The same spectrum is obtained on photolysis of **22T/22A** at 254 nm.

of 2-aminopyridine (formed from triplet 2-pyridylnitrene by H-abstraction, in yields of 1–10% depending on conditions) and *Z*- and *E*-glutacononitriles **27Z,E** (ca. 10%).⁹ 2-Cyanopyrrole **28** appears first, but since 2- and 3-cyanopyrroles interconvert by means of a series of 1,5-H and 1,5-CN shifts, a mixture of **28** and **29** inevitably forms at elevated temperatures.⁹ The cyclization of dienylnitrene **23** and a concerted ring-contraction of 2-pyridylnitrene **19** are attractive mechanisms of formation of the cyanopyrroles (see several routes to cyanopyrroles in Schemes 4, 6, and 7). Although spiroazirene **25** is a photochemical product, and the cyanopyrroles are not obtained in any significant quantities on photolysis, the question has to be asked whether **25** could be a precursor of the cyanopyrroles in FVT reactions. The analogous spiroazirene **31** (eq 2) rearranges to isocyanocyclopentadiene on both photolysis and thermolysis, and on FVT above $420\text{ }^\circ\text{C}$ only cyanocyclopentadiene was obtained.¹⁷ A similar reaction could be the source of weak isocyanide absorptions seen at $2127\text{--}2133\text{ cm}^{-1}$ in IR spectra of the photolyses of **22**. The question of involvement of **25** in cyanopyrrole formation will be considered in the Computational Method section.

Relationship between 3-Pyridazylcarbene and 2-Pyridylnitrene. The high-temperature formation of compounds **27–29** from **8** could suggest the possible isomerization of 3-pyridazylcarbene to 2-pyridylnitrene as illustrated in Scheme 4. This reaction would have to pass through molecules or transition structures resembling the cyclopropene **16**, the seven-membered ring ketenimine **17** (a ketene hydrazone; not observed experimentally; see Figure S14 in the Supporting Information), and the formally antiaromatic diazirene **18** (Scheme 4). The 2-pyridylnitrene energy surface

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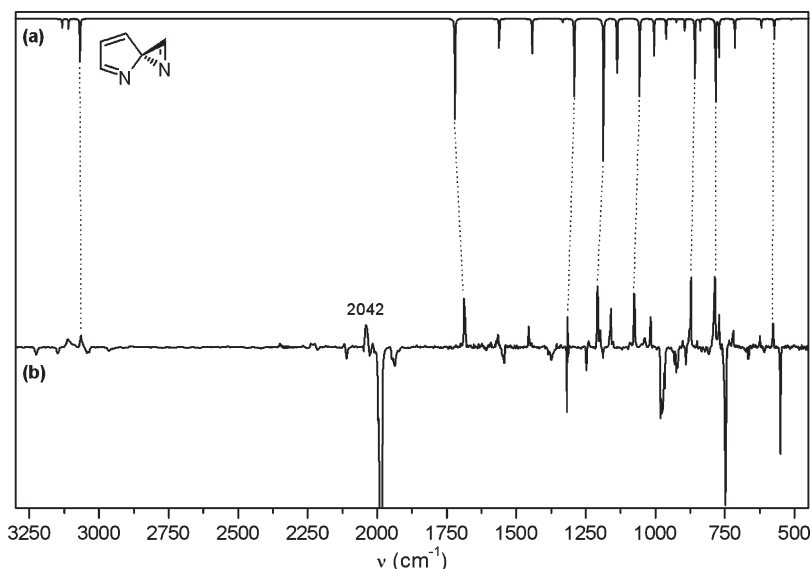


FIGURE 7. (a) Calculated spectrum of spiroazirene **25** at the B3LYP/6-311G** level, wavenumbers scaled by 0.967, and (b) difference IR spectrum obtained after photolysis of tetrazolopyridine **22T** at 222 nm for 30 min to generate **21** (negative spectrum), followed by 308 nm for 30 min to generate **25** (positive spectrum). The weak signal at 2042 cm^{-1} may be due to ketenimine **26** or **39**.

is usually accessed from tetrazolopyridine/2-azidopyridine **22T/22A**.⁹ However, the ratio of yields of glutakonitriles **27E,Z** and cyanopyrroles **28** and **29**, [**27E,Z**]:[**28** + **29**] is much higher from **8** than from **22** (ratio $\sim 6:1$ from triazole **8** at $600\text{ }^{\circ}\text{C}$; ratio $\sim 1:7$ from tetrazole **22T**). This suggests that the unobserved seven-membered-ring ketenimine **17** can undergo Type II ring-opening to cyanodienylnitrene **23**, thus leading to an excess of glutakonitriles when proceeding from the pyridazine side (see Scheme 4). Moreover, no 2-aminopyridine was detectable by either GC-MS or NMR spectroscopy of the products of FVT of **8**, whereas this compound is always formed as a minor product (1–10%, depending on conditions) from (triplet) 2-pyridylnitrene.⁹ Instead, 3-methylpyridazine was formed on FVT of **8**, a characteristic (triplet) carbene H-abstraction product.¹⁰ Conversely, when 2-pyridylnitrene is generated from **22**, there is no formation of either 3-methylpyridazine or the low molecular weight compounds derived from triazolopyridazine, viz. **13–15**. 2-Pyridylnitrene **19** is easily detected by its Ar matrix ESR spectrum when generated by FVT^{9b} of **22**, but FVT of **8** with Ar matrix isolation in the ESR cryostat affords at best a trace of a triplet ESR signal, which may be due to 2-pyridylnitrene **19**, but it is too weak to assign it with any degree of certainty. As described above, 2-pyridylnitrene undergoes facile ring-expansion to the cyclic carbodiimide **21** on both photolysis and FVT; **21** is detectable by its strong absorption at $1988\text{--}1989\text{ cm}^{-1}$ in the IR spectrum (Figure 6). A weak band was observed at 1988 cm^{-1} in the photolyses of **8** (Figure 4 and in the Supporting Information Figures S5 and S14), but it was too weak for any secure assignment; none of the other absorptions belonging to **21** were detectable. Thus, if 3-pyridazylcarbene rearranges to 2-pyridylnitrene, this leads at best to trace amounts of nitrene **19** and carbodiimide **21** being observable.

There was no direct spectroscopic evidence for the cyclic 7-membered-ring ketenimine **17** in the photolyses or thermolyses of **8**. The calculated frequency for this compound at the B3LYP/6-31G* level of theory is 1898 cm^{-1} ; no matching

peak was observable in the experimental spectra (see Figure S14, Supporting Information). A rearrangement of **17** to 2-pyridylnitrene **19** would be possible via the diazirene **18** as an intermediate or transition state (see the Computational Method section below). Rearrangements via 1,3-diazirenes have been invoked in other, similar ring-expansions of hetarylnitrenes such as 2-pyrimidyl-,⁵ 2-quinazolyl-,⁶ and *s*-triazolylnitrenes.²⁰

When the reaction proceeds from 2-pyridylnitrene **19**, type II ring-opening to **26** and **27** is a minor process under both thermal^{9,21} and photochemical^{16,22} conditions, whereas formation of the cyanopyrroles **28** and **29** is the major process under FVT conditions.^{9,21} FVT of 3-azidopyridine also leads to a mixture of 2- and 3-cyanopyrroles as end products, but no glutakonitrile is formed. Here, 3-cyanopyrrole is probably formed via the open-chain nitrile ylide in a Type I ring-opening–ring-closure.¹ The reaction paths will now be discussed in more detail in light of theoretical calculations.

Calculations. For further insight, the thermal reaction paths were explored by calculating the relative energies of most of the species of interest at the B3LYP/6-31G* level of theory. The ground state of 2-pyridylnitrene **19** is the triplet ($^3A''$), which is the reference point for all the energies in Scheme 6. It is now well-known that singlet nitrenes have an open shell electronic structure;²³ therefore a detailed exploration of the reaction path **18** \rightarrow **19** requires CASSCF and CASPT2 calculations, the results of which are reported in Scheme 6. It is possible to make reasonable estimates for open-shell singlet species at the B3LYP/6-31G* level with use of the Cramer–Ziegler sum method.²⁴ The latest value

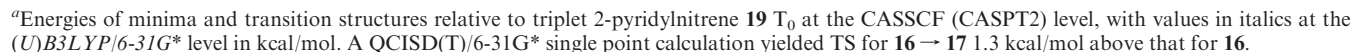
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approximately thermoneutral or modestly endothermic. Diazirene **18** was optimized as an energy minimum at the B3LYP level, but it is a transition state for the reaction $17 \rightarrow 19$ at the CASSCF level. The ring-opening of **18** to **19** (OSS) has a calculated barrier of ca. 2 kcal/mol at the B3LYP/6-31G* level. The cyclic carbodiimide **21** has been the subject of prior calculations, and its energy is close to that of the triplet nitrene **19**.²⁶ The bicyclic azirene **20** lies 10–13 kcal/mol above **21**.

The ring-opened species **23** may be described as a resonance hybrid of a nitrene (**23N**) and a diradical (**23R**). The calculated bond lengths indicate that the dienylnitrene canonical structure **23N** has higher weight than the diradical structure **23R** in agreement with the experimental observation that the species is a nitrene. Note, however, that suitable benzannulation can cause the diradical character to predominate.²⁷



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2-pyridylnitrene **19**, but not with ring-contraction via cyanodienylnitrenes **23** (Scheme 6). The activation energy for the first step, **21** → **24**, is high (ca. 47 kcal/mol), but the reaction would be achievable under high-temperature FVT conditions.

Thus, in summary, we have identified three potential routes to cyanopyrroles: (i) ring-opening–ring-closure via dienylnitrene **23** (Scheme 6); (ii) concerted ring-contraction of 2-pyridylnitrene **19** to 2-cyano-2*H*-pyrrole **32** (Scheme 6; not likely here, but possible in other aryl nitrenes); and (iii) electrocyclic rearrangement of diazacycloheptatetraene **21** via spiroazirene **25** (Scheme 7). The latter pathway is actually followed in the phenylcarbene rearrangement.¹⁸ While we have no experimental evidence for the spiroazirene route to cyanopyrroles (Scheme 7), it will be necessary to consider it in future work. It may well be that different routes of ring-contraction will be followed in different systems. Strong evidence for the ring-opening–ring-closure pathway has been adduced for other systems.^{2,6,27,29} The existence of several potential pathways can also provide an explanation for the different product ratios obtained from pyridazine **8** and pyridine **22**. The ring-opening–ring-closure mechanism (i) is fully consistent with the results of ¹⁵N- and substituent labeling of 2-pyridylnitrenes.³⁰ The spiroazirene mechanism (iii) can explain the products obtained from 6-substituted tetrazolo[1,5-*a*]pyridine, but does not explain the major product obtained from 8-substituted tetrazolo[1,5-*a*]pyridine.³⁰

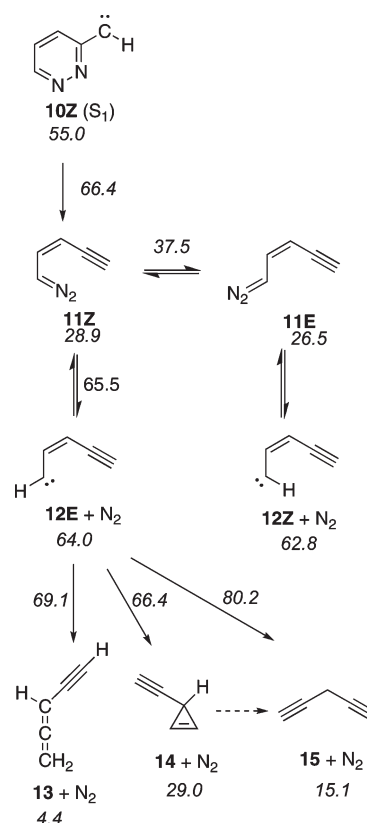
The potential formation of the azafulvenylnitrene **38** (Scheme 7) as a rearrangement product of diazacycloheptatetraene **21** makes it necessary to consider this nitrene as an alternative to the cyanodienylnitrene **23** as carrier of the low-field nitrene signal (5000–5300 G) in the ESR spectrum (Figure 5). This ESR spectrum was obtained by photolysis of tetrazole/azide **22T/22A** at 254 nm. Under the same photolysis conditions, diazacycloheptatetraene **21** is formed cleanly as observed by IR spectroscopy (Figure 6). Compound **21** is stable at this wavelength and rearranges to **25** on irradiation at 308 or 365 nm. Thus, nitrene **38** should not be formed at 254 nm. Hence, the evidence supports cyanodienylnitrene **23** as the carrier of the low-field triplet ESR signal.

Further Reactions of the Pyridazylcarbenes. We will now consider the remaining reactions of the pyridazylcarbenes **10** (Schemes 8 and 9). The barriers for isomerization of carbene **12E** to allene **13** and cyclopropene **14** are only ca. 4 and 2 kcal/mol, respectively. These are the first reactions to take place on FVT. The isomerization of ethynylcyclopropene **14** to pentadiene **15** is exothermic by ca. 14 kcal/mol, but that of pentadienyne **13** to pentadiene **15** would be endothermic by ca. 11 kcal/mol (Scheme 8).

The alternative cyclization of carbene **10Z** to azirene **42** has a calculated barrier of 14 kcal/mol, and **10E** can form the same product with a barrier of ca. 11 kcal/mol. The seven-membered ring allene **43** is ca. 12 kcal/mol higher in energy than the cyclic ketenimine **17**, and ca. 37 kcal/mol above cyclic carbodiimide **21**. There was no experimental evidence for the formation of **43** (Scheme 9 and in the Supporting Information Figure S14).

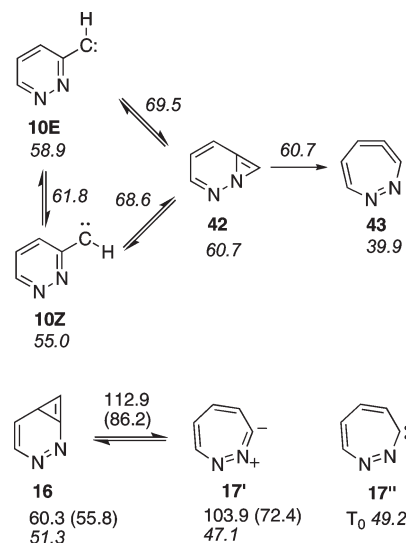
Two isomers of **17**, viz. the cyclic nitrile ylide **17'** and diazacycloheptatrienyliene **17''**, were also considered (Scheme 9). There was no experimental evidence for these

SCHEME 8. Calculated Energies for Ring-Opening and Fragmentation of 3-Pyridazylcarbene^a



^aB3LYP/6-31G* in kcal/mol relative to **19** *T*₀ = 0.

SCHEME 9. Unobserved Ring-Expansions of 3-Pyridazylcarbene **10**^a



^aCalculations at the CASSCF (CASPT2) and B3LYP/6-31G* levels in kcal/mol relative to **19** *T*₀ = 0.

species. The calculated energy of **17'** and the activation barrier for the reaction **16** → **17'** are too high for their likely involvement.

Conclusion

The isomeric 3-pyridazylcarbene **10** and 2-pyridylnitrene **19** were investigated. There is little evidence for interconversion of these two isomers, but each has a rich chemistry. Mild FVT of triazolopyridazine **8** generates the diazomethyl valence tautomer **9**, which on either matrix photolysis or flash vacuum thermolysis (FVT) gives rise to 3-pyridazylcarbene **10**. The carbene was detected by ESR spectroscopy in the photolysis reaction. Matrix photolysis with IR observation reveals ring-opening of the carbene to diazoalkenyne **11**, which again loses N₂ to generate a new carbene, pent-2-en-4-yn-1-ylidene **12**; this too was detected by ESR spectroscopy, and it rearranges to pentadienyne **13**, ethynylcyclopropene **14**, and, at elevated temperatures, 1,4-pentadiyne **15**.

Photolysis of matrix-isolated tetrazolo[1,5-*a*]pyridine/2-azidopyridine **22T/22A** yields both triplet 2-pyridylnitrene **19** and its ring-opened isomer, the cyanodienylnitrene **23**, which are detected by ESR spectroscopy. 1,3-Diazacycloheptatetraene **21** is formed cleanly on matrix photolysis as observed by IR spectroscopy. It is also a major product of FVT of **22T/22A** under mild conditions. Photolysis of **21** above 300 nm causes its rearrangement to the spiroazirene **25**, identified by its Ar-matrix IR spectrum.

FVT of **8/9** causes formation of *Z*- and *E*-glutacononitriles **27Z,E** and minor amounts of 2- and 3-cyanopyrroles **28** and **29** in addition to **13–15**. FVT of tetrazolopyridine/2-azidopyridine **22T/22A** also affords compounds **27–29**, but the ratios of yields of these products are very different in the two systems.

Calculations support the postulate that both 3-pyridazylcarbene (via 1,7-diazacycloheptatetraene **17**) and 2-pyridylnitrene **19** can undergo ring-opening to vinylnitrene **23**, but they can lead to different conformers of **23**; one, **23EZ**, is predominantly a precursor of glutacononitriles **27**; the other, **23ZZ**, is a precursor of 2- and 3-cyanopyrroles via 2-cyano-2*H*-pyrrole **32**. Another potential route to cyanopyrroles proceeds via electrocyclization of 1,3-diazacycloheptatetraene **21** to diazabicyclo[3.2.0]heptatriene **24** and spiroazirene **25**. The ring-opening–reclosure reaction via dienylnitrene **23** emerges as the energetically most favorable mechanism of ring-contraction in 2-pyridylnitrenes.

Computational Method

Calculations of all species were performed with the B3LYP method,³¹ as implemented in the Gaussian 03 suite of programs,³² with the 6-31G* basis set for geometry and transition state optimizations. Energies of open-shell S₁ nitrenes at the (U)B3LYP/6-31G* level were estimated with use of the Cramer–Ziegler method.²⁴ Reported energies include zero-point vibrational energy corrections. All transition states were confirmed by intrinsic reaction coordinate calculations. Harmonic vibrational frequencies were computed with use of the 6-311G** basis set, and a scaling factor of 0.967 was applied.³³ Additional

CASSCF³⁴ optimizations and single-point CASPT2 calculations³⁵ were performed for open-shell and related systems, and were carried out with the MOLCAS suite of programs,³⁶ using the 6-31G* basis set. The CASSCF calculations used an 8-electron, 8-orbital active space, e.g. for **19**: 3 π , 3 π^* , and the 2 p-AOs on the nitrene-N atom. The reference weights of the CASSCF wave function remained stable in the range 77–80%. Cartesian coordinates, energies, vibrational frequencies, and details of the correlated orbitals in the CASSCF active space are listed in the Supporting Information.

Experimental Section

General procedures have been published.^{16,27,29} In matrix isolation for IR spectroscopy, Ar gas and sample vapor were codeposited on a CsI target maintained at 25 K. The Ar flow rate was maintained at ca. 4 mbar per min to obtain a thin, transparent matrix. After depositing the matrix for ca. 30 min, the CsI target was cooled to 10 K, and IR spectra were recorded with 1 cm^{−1} resolution. For ESR spectroscopy a similar cryostat was used, where the sample and Ar were condensed on a Cu rod at ca. 15 K. Photolyses were carried out with use of a 1000 W high-pressure Xe/Hg lamp equipped with a monochromator and appropriate cutoff and interference filters, a 75 W low pressure Hg lamp (254 nm), or excimer lamps operating at 222 (25 mW/cm²) and 308 nm (50 mW/cm²).

FVT experiments with matrix isolation employed a 10 cm long, 0.7 cm i.d. electrically heated quartz tube suspended in a vacuum chamber (2.0 × 10^{−6} mbar) 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 CsI or Cu targets. The temperatures used for FVT experiments ranged from 500 to 700 °C.

In preparative FVT experiments, the sample was placed in a sublimation tube and sublimed into a 20 × 2 cm quartz pyrolysis tube. The FVT unit was evacuated with an oil diffusion pump capable of a vacuum of 10^{−5}–10^{−4} mbar. The pyrolysis products were collected on a coldfinger cooled with liquid nitrogen (ca. 77 K). After the end of the experiment, the collected product was dissolved in CDCl₃, and NMR and GC-MS analyses were carried out.

GC-MS analysis used a ZB-5 Zebron GC column (30 m, 0.32 mm i.d., 0.25 μ m film thickness), He carrier gas at a flow rate of 3.7 mL/min, column head pressure 100 kPa, inlet temperature 200 °C, and GC-MS interface 250 °C. The temperature program started at 85 °C for 2 min, followed by a ramp of 12 deg/min up to 250 °C.

[1,2,3]Triazolo[1,5-*b*]pyridazine **8**. 3-Pyridazinecarboxaldehyde³⁷ was synthesized from furfuryl acetate³⁸ and converted to its hydrazone.³⁹ The hydrazone (500 mg, 4 mmol) was dissolved in 50 mL of chloroform, and activated manganese dioxide (460 mg, 8 mmol, Fluka) was added slowly. The solution was stirred for 3 h at rt and filtered over Celite, then the solvent was removed in vacuum. The solid so obtained was purified by sublimation (70–75 °C, 4 × 10^{−5} mbar) to yield colorless crystals, 348 mg (71%), mp 132–133 °C (lit.³⁹ mp 132–133 °C); ¹H NMR (CDCl₃) 8.47 (dd, *J* = 4.3, 1.8 Hz, 1 H), 8.18 (s, 1 H), 8.14 (dd, *J* = 9.0, 1.8 Hz, 1 H), 7.12 (dd, *J* = 9.0, 4.3 Hz, 1 H).

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Anal. Calcd for $C_5H_4N_4$: C, 50.00; H, 3.36; N, 46.65. Found: C, 50.25; H, 3.33; N, 46.56.

Matrix Isolation and Photolysis of Triazolo[1,5-*b*]pyridazine. Triazolo[1,5-*b*]pyridazine **8** was sublimed at 65–70 °C under vacuum (2.0×10^{-6} mbar) and codeposited with Ar on a CsI target at 25 K. The IR spectrum recorded at ca. 10 K showed the main triazole peaks at 1544 (m), 1494 (m), 1403 (m), 1321 (s), 1307 (m), 1256 (m), 957 (m), 815 (s), and 734 (m) cm^{-1} (see Figure S1 in the Supporting Information for the IR and UV spectra).

Preparative FVT of Triazolopyridazine. Preparative FVT of **8** (150 mg) was carried out at 500–700 °C. The collected products were examined by 1H NMR ($CDCl_3$; 500 MHz) and GC-MS. Data are presented below.

2-Ethynylcyclopropene 14:^{13a,14} IR (Ar, 10 K) 3338 (w), 2125 (vw), 1661 (m), 986 (s), 945 (m), 613 (s), 605 (vw), and 516 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) 7.10 (dd, 2H, $J = 1.65$ and 0.3 Hz), 1.95 (dt, 1H, $J = 1.65$ and 1.35 Hz), 1.65 (d, 1H, $J = 1.35$ Hz) (unresolved coupling, ca. 0.3 Hz also present).

Penta-1,2-dien-4-yne 13:¹³ IR (Ar, 10 K) 3333 (m), 1955 (w), 889 (m), 852 (m), 644 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) 5.35 (td, 1H, $J = 7.0$ and 2.6 Hz), 5.02 (dd, 2H, $J = 7.0$ and 1.6 Hz), 2.87 (dt, 1H, $J = 2.6$ and 1.6 Hz).

1,4-Pentadiyne 15:^{14,40} IR (Ar, 10 K) 3319 (s), 2140 (w), 1417 (m), 1300 (w), and 605 (w); 1H NMR ($CDCl_3$, 500 MHz) 3.15 (t, 1H, $J = 2.75$, 2.07 Hz).

Z-Glutacononitrile 26Z:^{9,15} 1H NMR ($CDCl_3$, 500 MHz) 6.47 (dt, 1H, $J = 7.0$ and 10.8 Hz), 5.65 (dt, 1H, $J = 10.3$ and 1.7 Hz), 3.35 (dd, 1H, $J = 6.8$ and 1.7 Hz); ^{13}C NMR ($CDCl_3$) (mixture of *Z* and *E* isomers) 141.1, 140.7, 115.4, 114.2, 105.4, 104.9, 21.2, 19.6; IR (Ar, 10 K) 2275 and 2235 cm^{-1} (mixture of *Z* and *E* isomers).

E-Glutacononitrile 26E:^{9,15} 1H NMR ($CDCl_3$, 500 MHz) 6.59 (dt, 1H, $J = 5.0$ and 16.25 Hz), 5.80 (dt, 1H, $J = 16.25$ and 2.1 Hz), 3.50 (dd, 2H, $J = 6.7$ and 1.65 Hz); ^{13}C NMR ($CDCl_3$) see data for mixture under *Z*-glutacononitrile.

2-Cyanopyrrole 27:^{9,41} IR (Ar, 10 K) 2235 cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) 9.37 (br, 1H), 6.94 (m, 1H, apparent $J = 3.5$, 2.7, and 1.4 Hz), 6.84 (m, 1H, apparent $J = 3.8$, 2.5, and 1.4 Hz), 6.25 (dt, 1H, $J = 3.8$ and 2.7 Hz); ^{13}C NMR ($CDCl_3$) 123.9, 120.1, 114.8, 109.8, 100.1.

3-Cyanopyrrole 28:^{9,42} IR (Ar, 10 K) 2260 cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) 8.96 (br, 1H), 7.30 (m, 1H, apparent $J = 3.3$ and 1.9 Hz), 6.78 (m, 1H, apparent $J = 2.7$, 2.1, and 0.7 Hz), 6.47 (m, 1H, apparent $J = 2.6$ and 1.3 Hz).

Ratios of 13, 14, 15, 26Z, 26E, 27, and 28 formed by FVT of triazolopyridazine 8 and determined by GC and NMR. GC retention times $R_t = 3.1$, 4.2, 5.6, and 8.3 min. Ratio **13:14:15:26Z:26E:27:28** at 500 °C: 12:40:40:3.5:3.5:0:0 (**27** and **28** not detectable). Ratio **13:14:15:26Z:26E:27:28** at 600 °C: 31:20:22:12.5:10:2:2. Triazole **8** was recovered in ca. 20% yield, and 3-methylpyridazine was formed in ca. 4% yield. Ratio **13:14:15:26Z:26E:27:28** at 700 °C: 18:15:35:12:12:4:4.

Ratios of Z- and E-Glutacononitriles 26Z, 26E, 27, and 28 formed by FVT of tetrazolo[1,5-*a*]pyridine 19T. Ratio **26Z:26E:27:28** at 500 °C: 6:4:38:35. Ratio **26Z:26E:27:28** at 600 °C: 6:4:45:41. Ratio at 700 °C: 9:9:41:38.

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