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3-Pyridazinylnitrenes and 2-Pyrimidinylnitrenes

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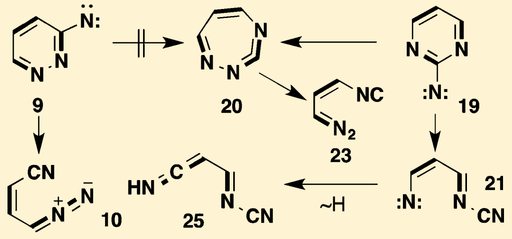
Supporting Information

ABSTRACT: Mild flash vacuum thermolysis of tetrazolo[1,5-*b*]pyridazines **8T** generates small amounts of 3-azidopyridazines **8A** (**8aA**, IR 2145, 2118 cm^{-1}; **8bA**, 2142 cm^{-1}). Photolysis of the tetrazoles/azides **8T**/**8A** in Ar matrix generates 3-pyridazinylnitrenes **9**, detected by ESR spectroscopy (**9a**: D/hc = 1.006; E/hc = 0.003 cm^{-1}). Cyanovinylcarbenes **11**, derived from 4-diazobut-2-enenitriles **10**, are also detected by ESR spectroscopy (**11a**: D/hc = 0.362; E/hc = 0.021 cm^{-1}). Carbenes **11** rearrange to cyanoallenes **12** and 3-cyanocyclopropenes **13**. Triazacycloheptatetraenes **20** were not observed in the photolyses of **8**. Photolysis of tetrazolo[1,5-*a*]pyrimidines/2-azidopyridmidines **18T**/**18A** in Ar matrices at 254 nm yields 2-pyrimidinylnitrenes **19**, observable by ESR, UV, and IR spectroscopy (**19a**: ESR: D/hc = 1.217; E/hc = 0.0052 cm^{-1}). Excellent agreement with the calculated IR spectrum identifies the 1,2,4-triazacyclohepta-1,2,4,6-tetraenes **20** (**20a**, 1969 cm^{-1}; **20b**, 1979 cm^{-1}). Compounds **20** undergo photochemical ring-opening to 1-isocyano-3-diazopropenes **23**. Further irradiation also causes Type II ring-opening of pyrimidinylnitrenes **19** to 2-(cyanimino)vinylnitrenes **21** (**21a**: D/hc = 0.875; E/hc = 0.00 cm^{-1}), isomerization to cyaniminoketenimine **25** (2044 cm^{-1}), and cyclization to 1-cyanopyrazoles **22**. The reaction mechanisms are discussed and supported by DFT calculations on key intermediates and pathways. There is no evidence for the interconversion of 3-pyridazinylnitrenes **9** and 2-pyrimidinylnitrenes **19**.



INTRODUCTION

In recent papers, we have demonstrated the occurrence of two types of ring-opening reactions of (hetero)aromatic nitrenes and carbenes: Type I causing ring-opening to nitrile ylides, exemplified by 3-pyridylcarbene **1a**,[1] 3-pyridylnitrene **1b**,[1] and 2-pyrazinylnitrene **1c**[2] (Scheme 1); and Type II causing ring-opening to diradicals, nitrenes, or carbenes, exemplified by the formation of vinylnitrene **6** and ketenimine **7** on photolysis, and glutacononitrile on flash vacuum thermolysis (FVT) of 2-pyridylnitrene **4** and its isomer 3-pyridazinylcarbene, as well as similar reactions of 1-isoquinolylnitrene and 2-quinoxalinylnitrene (Scheme 1).[1]

There have been previous reports on 3-pyridazinylnitrene.[3−5] Flash vacuum thermolysis (FVT) of tetrazolo[1,5-*b*]pyridazine **8aT** at 305−380 °C produced diazobutenenitrile **10a** and the products of N_2 elimination, viz., cyanoallene **12a** and 3-cyanocyclopropene **13a**, which, particularly in the higher temperature regime, rearrange partially to propargyl cyanide **14a** and tetrolonitrile **15a**; these four products were isolated in a combined yield of 99% (Scheme 2).[3] The first two products, **12a** and **13a**, were also obtained on matrix photolysis.[4,5a] As we will show, similar products are obtained from the dimethyl derivative **8b**, but, in addition, isomerization to the conjugated nitriles **16** and **17** becomes possible. We now report the direct detection of 3-azidopyridazine and 3-pyridazinylnitrene **9a**, its ring-opening reaction and ensuing chemistry, and its relationship with 2-pyrimidinylnitrene **19a** (Scheme 3). These two nitrenes, **9a** and **19a**, undergo Type I and Type II ring-opening, respectively.

RESULTS AND DISCUSSION

1. 3-Pyridazinylnitrenes. Tetrazolopyridazines exist exclusively in the tetrazole forms **8T** (**8aT**, R = H; **8bT**, R = CH_3, Scheme 2) in the solid state at room temperature. Codeposition of the unsubstituted **8a** with Ar at 25 K also produced largely the unchanged tetrazole **8aT**, but a small amount of the azide valence tautomer **8aA** (2145, 2118, 1585, 1431, 1293 cm^{-1}) is formed on gentle FVT at 250 °C (Figure 1). The calculated energy difference between the tetrazole and the azide is 5.5 kcal/mol (see below). Therefore, if equilibrium was attained at 250 °C there would only be ca. 0.5% azide present; at 400 °C there would be ca. 2% azide. FVT at higher temperatures, up to 400 °C, clearly produces more of the azide, but the pyrolysis products now start to form also, primarily cyanoallene **12a** (1976 and 2229 cm^{-1}) and 3-cyanocyclopropene (cyclopropene-3-carbonitrile) **13a** (2241 and 1664 cm^{-1}) (Figure S1). The azide **8aA** was not observed previously[4] because FVT was not used. As described below, the ring-opening of tetrazolo[1,5-*a*]pyrimidines to the azides is much more favorable.

For the purpose of ESR spectroscopy, a mixture of tetrazole and azide **8aT**/**8aA** was generated by FVT at 250 °C as above and deposited in an Ar matrix. Subsequent photolysis at 222 or 254 nm caused formation of the nitrene **9a** as revealed by ESR spectroscopy (D/hc = 1.006; E/hc = 0.003 cm^{-1}; Figure 2). The D value fits our correlation with calculated spin densities ($D-\rho$ correlation).[6] The nitrene disappeared after further photolysis of the matrix at 289 nm for 45 min. We were able to

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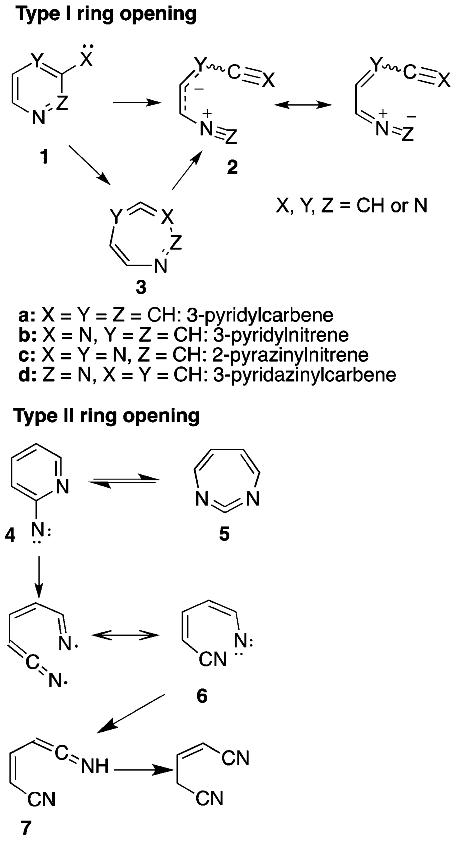
Scheme 1. Type I and Type II Ring-Opening Reactions

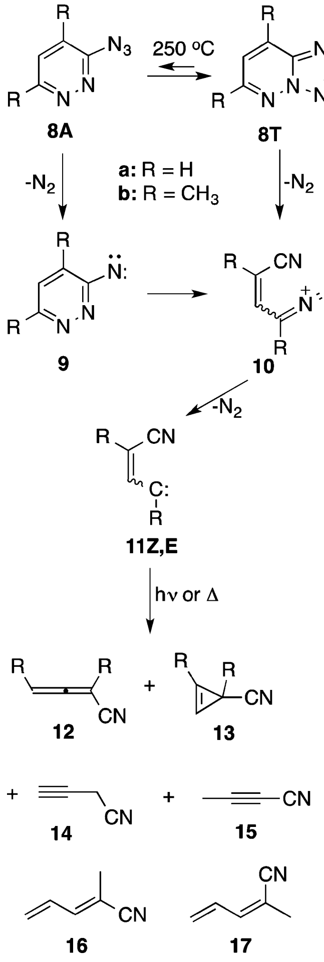


see nitrene **9a** by ESR (and likewise nitrene **9b** as described below), because we used FVT of the tetrazoles to produce enough of the azides, which then photolyzed to the nitrenes. Hill and Platz[4] did not use FVT and therefore saw neither azides nor nitrenes.

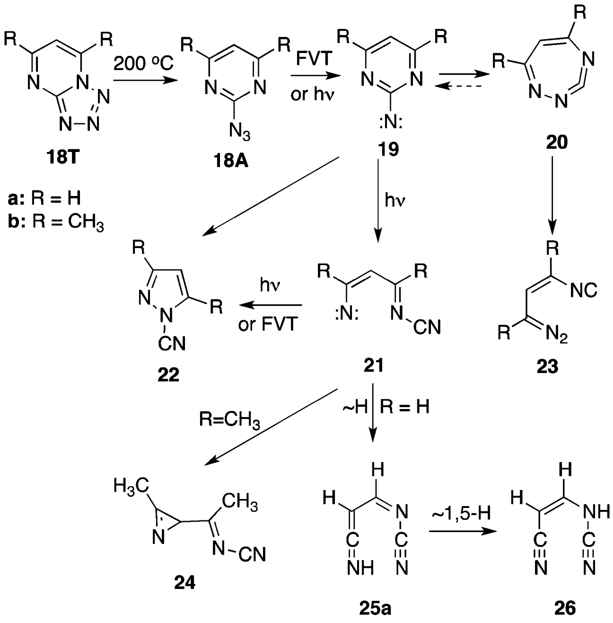
It is seen in Figure 2 that an additional, strong signal is present at 5962 G. As reported previously, the same or a very similar signal is formed from 1,2,3-triazolo[1,5-*a*]pyridazine, and we assigned it to propargylene, HCCCH, formed by elimination of $2N_2$ + HCN.[7] In the present case, it is formed on matrix photolysis as well as FVT; on FVT at 500 °C with isolation of the product in Ar matrix, it is the only species observable by ESR spectroscopy. This signal remains after further photolysis of the matrix in Figure 2 at 289 nm for 45 min, whereas nitrene **9a** disappears under these conditions.

In the IR spectrum, two conformers of diazo compound **10Z,E** are observed at 2086 and 2072 cm^{-1} within the first few minutes of irradiation (Figure S2) in agreement with previous observations.[4] Difference spectra clearly show that the azide peaks diminish as the diazo peaks grow (Figure S1). When the azide has been depleted, the diazo compound starts to disappear also due to photoreactions forming more cyanoallene **12a** (1976, 2229 cm^{-1}) and cyclopropenecarbonitrile **13a** (2241, 1664 cm^{-1}) (Figure S1). When no azide is present in the original matrix due to deposition at room temperature, photolysis still causes formation of the diazo compound and depletion of the tetrazole without any azide being observed. It is possible that the tetrazole undergoes photochemical ring-opening to the azide, which photolyzes as fast as it is formed, or that the tetrazole affords the diazo compound directly (see Mechanism section below). When both azide and tetrazole are present in the matrix, the azide is depleted first.

Scheme 2. Formation and Reaction of 3-Pyridazinylnitrenes 9



Scheme 3. Formation and Reactions of 2-Pyrimidinylnitrenes



When the diazo compound is photolyzed in the ESR cryostat, signals ascribed to cyanovinylcarbenes **11a** are rapidly

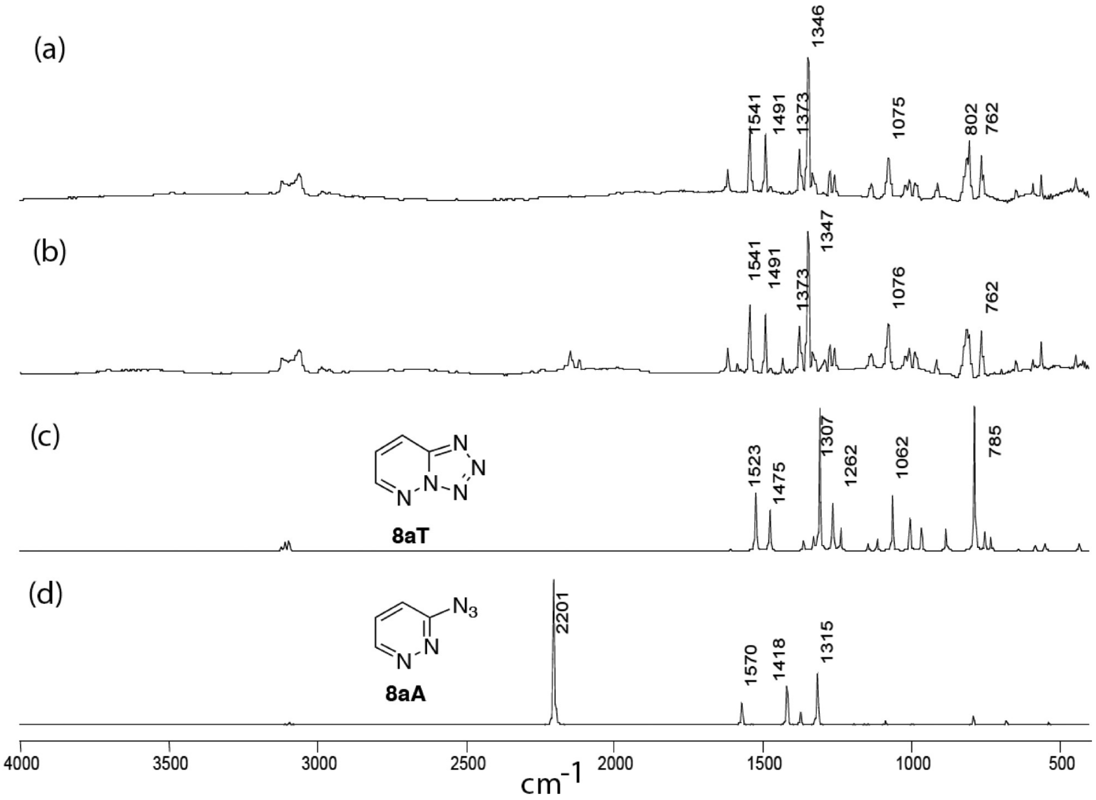


Figure 1. IR spectra following deposition of tetrazolo[1,5-*b*]pyridazine **8a** in Ar matrices. (a) FVT at 100 °C (only tetrazole **2aT** present). (b) FVT of **2aT** at 250 °C (small amount of azide **8aA** formed (2141, 2118 cm^{-1})). (c) Calculated IR spectrum of tetrazolo[1,5-*b*]pyridazine **8aT**. (d) Calculated spectrum of 3-azidopyridazine **8aA** (all calculations at the B3LYP/6-31G* level with wavenumbers scaled by a factor 0.9613).

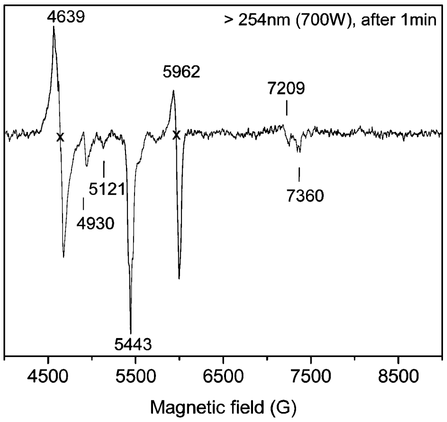


Figure 2. ESR spectrum (Ar, 20 K) of 3-pyridazinylnitrene **9a** resulting from photolysis of **8aT**/**8aA** in Ar matrix at $\lambda \geq 254$ nm for 1 min. The mixture of **8aT**/**8aA** was prepared by FVT of **8aT** at 250 °C in a stream of Ar at 10^{-4} h Pa. **9a**: 7209, 7360 G; $D/hc = 1.060$; $E/hc = 0.0030$ cm^{-1}. Also present is carbene **11a** (4639, 5443 G; $D/hc = 0.3616$; $E/hc = 0.0209$ cm^{-1}) derived from diazo compound **10a**. The field positions used to calculate D/hc and E/hc are marked with an x. The signal at 5962 G is due to a different species (see text). $H_o = 3471.1$ G.

detected in the ESR spectrum ($D/hc = 0.362$; $E/hc = 0.021$ cm^{-1}; Figure 2). In the UV spectrum, the diazo compound gives rise to an absorption at ca. 300−355 nm (Figure S3). Continued photolysis at 313 nm causes the diazo bands in the IR to disappear in concert with the 300−355 nm UV band. At the same time, the usual photolysis products, cyanoallene **12a** (1976, 2227 cm^{-1}) and 3-cyanocyclopropene **13a** (1664, 2241 cm^{-1}), are formed (Figure S4; see also Figure 3).

The presence of cyanoallene (1976 cm^{-1}) was not considered in the previous work,[4] where a very weak absorption at 1981 cm^{-1} was assigned to the seven-membered ring **20a.**[4,8] This species, 1,3,4-triazacyclohepta-1,2,4,6-tetraene (**20a**, see Scheme 3), was not observed as a product of either photolysis or thermolysis of **8a** in our work, nor were the photolysis products arising from **20a**, which are described in Section 2. 20a *is* formed and observed at 1969 cm^{-1} in the isomeric 2-pyrimidinylnitrene (**19**) system described in Section 2 below.

FVT of **8a** at 400−600 °C with Ar matrix isolation of the products confirmed the previously reported results from preparative FVT:[3] **12a**, **14**, and **15** are the principal products, with only little 3-cyanocyclopropene **13a** surviving under these conditions (Figure 3 and Figure S5).

The dimethyl derivative **8bT** behaved in a manner very similar to that of **8a**, forming a trace of the azide **8bA** (2142 cm^{-1}) on mild FVT at 200−250 °C (Figure S6). One minute's photolysis at 254 or 222 nm caused the formation of nitrene **9b** (7081 G; $D/hc = 1.036$; $E/hc = 0.0025$ cm^{-1}) and carbene **11b** (4576 and 5320 G; $D/hc = 0.341$; $E/hc = 0.020$ cm^{-1}) as observed by ESR spectroscopy (Figure 4). The signals of both species diminish on further photolysis and have all but disappeared after 45 min (Figure S7 and Scheme S1, Supporting Information). This compound cannot easily form HC_3H, and the major signal near 6000 G in Figure 2 is, therefore, strongly reduced in Figure 4. Minor, unidentified signals are present at 4788 and 5995 G.

In the IR spectrum, diminution of the tetrazole bands and formation of diazo compound **10b** (2046, 2207, 1464, 1330, 1032 cm^{-1}) were observed (Figure S8). A band at 325 nm in the UV spectrum is also assigned to the diazo compound

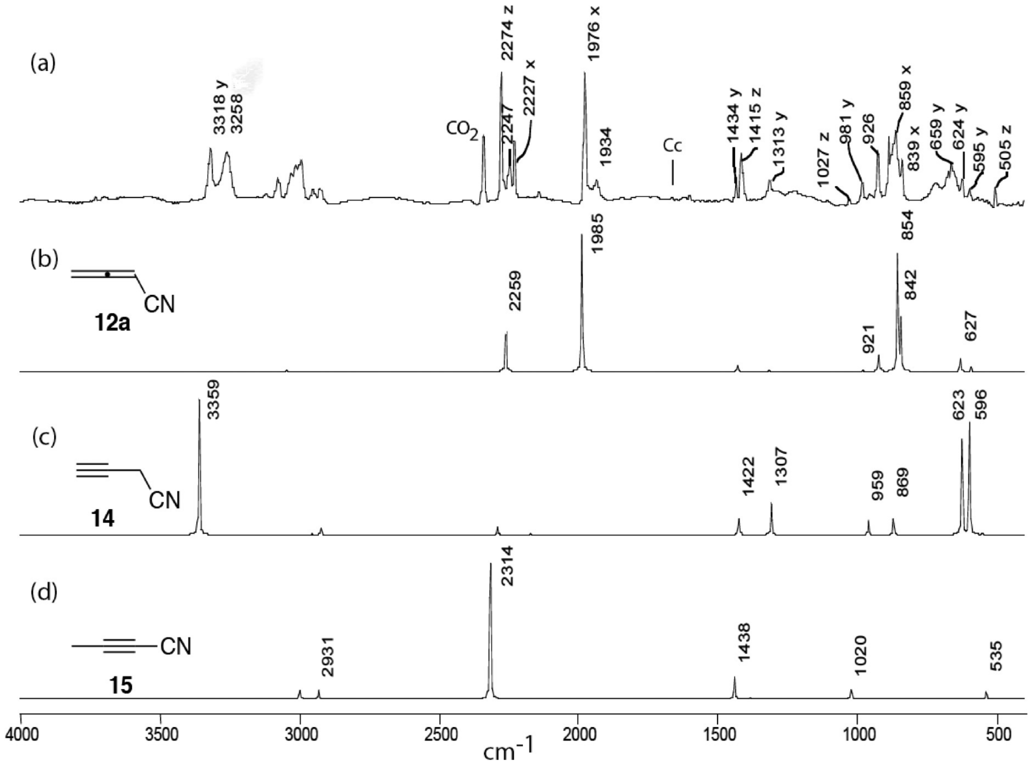


Figure 3. (a) Products of flash vacuum thermolysis (FVT) of **8aT** at 600 °C with isolation of the thermolysate in Ar matrix at 20 K; bands marked with an x belong to cyanoallene **12a**, those with an y to but-3-ynenitrile **14**, and those with a z to but-2-ynenitrile **15**; (b) calculated spectrum of **12a**; (c) calculated spectrum of **14**; (d) calculated spectrum of **15** (B3LYP/6-31G*, wavenumbers scaled by a factor 0.9613). Very little 3-cyanocyclopropene **13a** (labeled *Cc*,1664 cm^{-1}) survives under these FVT conditions (compare Figures S4 and S5).

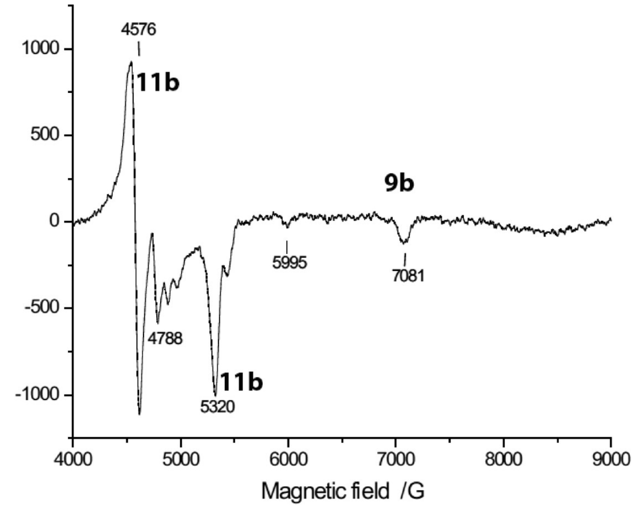


Figure 4. ESR spectrum 4,6-dimethyl-2-pyrazinylnitrene **9b** (7081 G; D/hc = 1.036; E/hc = 0.0025 cm^{-1}) and 4-cyano-3-penten-2-ylidene **11b** (4576 and 5320 G; D/hc = 0.341; E/hc = 0.020 cm^{-1}) (Ar, 20 K). H_o = 3471.2 G. Ordinate: intensities in arbitrary units. For the temporal evolution of the spectrum, see Figure S7 in Supporting Information.

(Figure S9). In the IR spectrum, weak bands due to 1,3-dimethyl-3-cyanocyclopropene **13b** can be seen to form at 2226 and 1793 cm^{-1} already during the initial photolysis at 222 nm. These bands grew together with bands due to dimethylcyanoallene (2-methyl-2,3-pentadienenitrile) **12b** on further photolysis at 254 or 222 nm (Figure S10). In this case, the cyanocyclopropene **13b** is the principal product, with only a little of the dimethylcyanoallene **12b** forming.

FVT of **8bT** at 450−700 °C afforded dimethylcyanoallene **12b** and dimethylcyanocyclopropene **13b**, as well as a mixture of nitriles identified as the *s*-*E*- and *s*-*Z*-2-methylpentadienenitriles **16** and **17** on the basis of comparison with the calculated IR spectra (Figure S11).

2. 2-Pyrimidinylnitrenes. In contrast to tetrazolopyridazines, tetrazolo[1,5-*a*]pyrimidines **18T** undergo easy ring-opening to the azides **18A** already on sublimation at 60−70 °C. The azide−tetrazole equilibria of these and related compounds have been the subject of detailed NMR studies.[9] These compounds exist in the tetrazole forms in the solid state, but entropy-dominated tautomerization to the azides takes over above room temperature. However, B3LYP calculations erroneously predict the azides to be of lower energy than the tetrazoles. Sublimation of **18aT** through the FVT tube held at 200 °C and deposition of the vapor in an Ar matrix affords the essentially pure azide **18aA** (Scheme 3; Figure 5).

2-Pyrimidinylnitrenes **19** are obtained under both FVT and photolysis conditions and directly observed by ESR spectroscopy (**19a**:[10] D/hc = 1.217; E/hc = 0.0052 cm^{-1}; **19b**: D/hc = 1.2; E/hc = 0.0) (Figure 6). For this purpose, the starting materials **18a** and **18b** are either deposited in an Ar matrix and then photolyzed to generate **19**, or **18** is subjected to FVT in order to generate more of the azides **18aA** and **18bA**, which then decomposes thermally to the nitrenes **19a** and **19b**. The latter are then isolated in Ar matrixes, and the ESR spectra are recorded.

The *D* values of **19a** and **19b** fit our correlation with calculated spin densities.[6] The triplet nitrene **19a** is also observed in the matrix UV spectrum, where it features a typical vibrational progression at 390−422 nm (Figure 7) in agreement with the previous report.[8] The absorptions around 331 nm present in

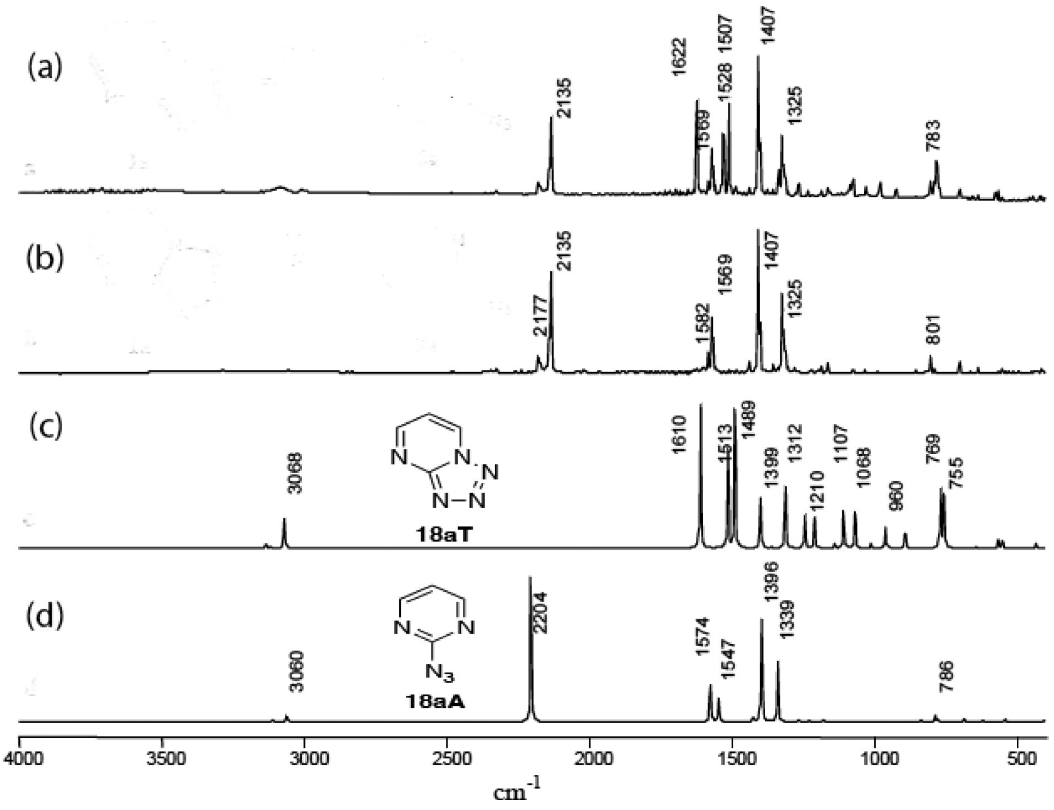


Figure 5. Ar matrix depositions of tetrazolo[1,5-*a*]pyrimidine **18a** through the FVT oven. (a) FVT oven at 70 °C (tetrazole **18aT** is in equilibrium with azide **18aA**); (b) FVT oven at 200 °C (equilibrium almost completely on the side of azide **18aA**); (c) calculated spectrum of tetrazolo-[1,5-*a*]pyrimidine **18aT** (B3LYP/6-31G*, wavenumbers scaled by a factor 0.9613); (d) calculated spectrum of 2-azidopyrimidine **18aA**.

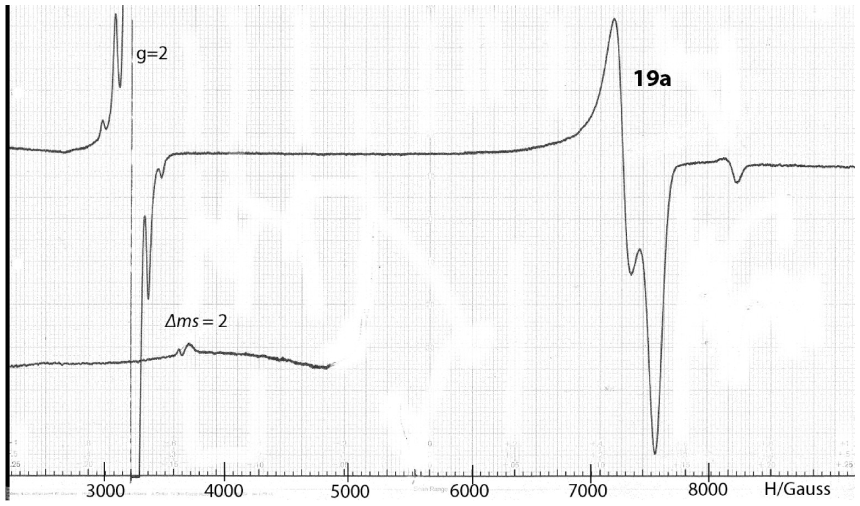


Figure 6. ESR spectrum resulting from FVT of tetrazolo[1,5-*a*]pyrimidine/2-zidopyrimidine **18aT**/**18aA** at 500 °C with Ar matrix-isolation of the resulting 2-pyrimidinylnitrene **19a**: X_2 7326 G; Y_2 7597 G. Half-field signal 1683 G (inset: 0–3000 G). H_o = 3374.7 G. Strong signals around g = 2 (3375 G) are ascribed to adventitious doublet radicals and H atoms. The origin of the weak signal at 8137 G is unknown.

Figure 7 are ascribed to diazo compound **23a** as discussed below.

By knowing the conditions for observation of 2-pyrimidinylnitrene by ESR and UV spectroscopy, its IR spectrum[8] can also be assigned. It is observed following brief photolysis at either 254 or 222 nm (Figure 8). Most interestingly, a weak IR band at 1969 cm^{-1}, which formed at the same time, is in excellent agreement with the calculated cumulenic stretch of the seven-membered-ring carbodiimide **20a**: 1967 cm^{-1} at the B3LYP/6-31G* level (Figure 8). Note that the benzo-analog, 2-quinazolinylnitrene, also affords only a very weak band due to the seven-membered ring carbodiimide, 1,2,4-triazabenzo[e]-cyclohepta-2,3,5,7-tetraene **27a**, but this compound becomes very prominent when a phenyl group is added (**27b**) (eq 1).[6] Bucher et al. have reported the ring expansion of an *s*-triazinylnitrene to the corresponding tetraazacycloheptatetraene.[11] The band reported by Platz et al.[4,8] at 1970 cm^{-1} is most likely identical with our band at 1969 cm^{-1} assigned to **20a**, but their band reported at 2045 cm^{-1} is assigned to the open-chain ketenimine **25a** (Scheme 3) as described below.

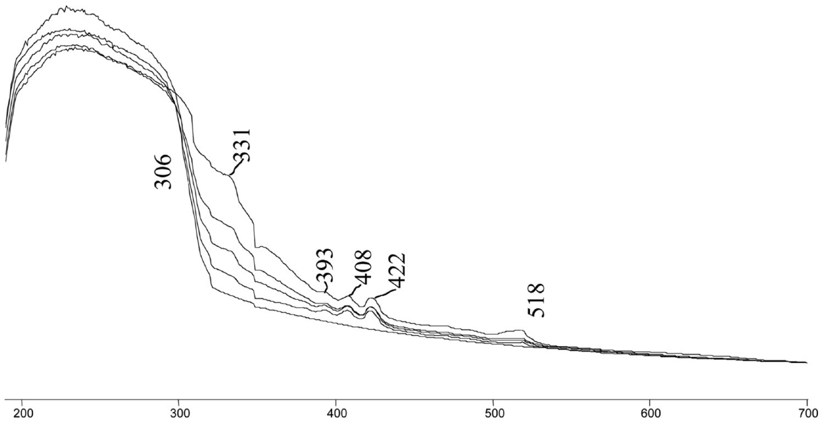


Figure 7. Ar matrix UV absorption spectra during photolysis of 2-azidopyrimidine **18aA**/tetrazole **18aT** at 254 nm at 8 K – not background corrected; spectrum 1 (bottom): directly after deposition (70 °C), azide **18aA** + tetrazole **18aT** show absorption <306 nm; spectra 2, 3, and 4 from bottom: after 15 min, 45 min, and 2.5 h photolysis at 254 nm; and spectrum 5 (top) after additional photolysis at 222 nm for 18 min. The structured band at 393–422 nm is assigned to 2-pyrimidinylnitrene **19a**. A band at ca. 331 nm may be ascribed to diazo compound **23a**. Abscissa in nm.

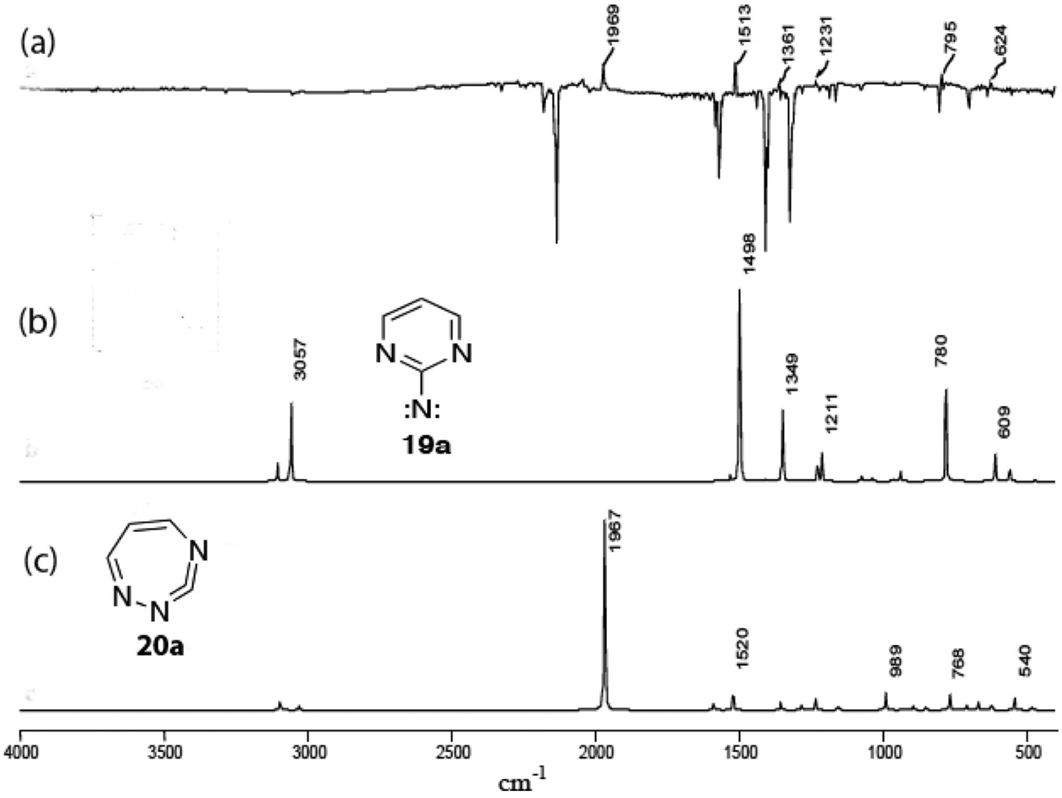
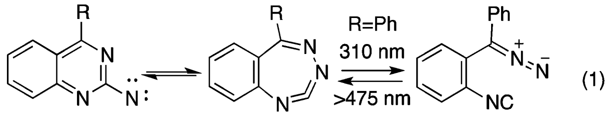


Figure 8. Result of matrix photolysis of 2-azidopyrimidine **18aA** for 5 min at 254 nm. (a) Difference spectrum showing the depletion of 2-azidopyrimidine (negative peaks) and formation of triplet 2-pyrimidinylnitrene **19a** (positive bands) and of 1,2,4-triaza-cyclohepta-1,2,4,6-tetraene **20a** (positive bands); (b) calculated spectrum of triplet 2-pyrimidinylnitrene **19a**; (c) calculated spectrum of 1,2,4-triaza-cyclohepta-2,3,5,7-tetraene **20a** (B3LYP/6-31G*, wavenumbers scaled by a factor 0.9613).



a: R = H. **b:** R = Ph **27** **28**

Another two important bands develop at 2044 and 2135 cm^{-1} after a few minutes of photolysis of **18aA** (Figures 9 and S12). The first, at 2044 cm^{-1}, is assigned to the ketenimine **25a**, formed in a Type II ring-opening (**25a**: 2044, 2187, 2203, 3429, 3416 cm^{-1}; calc 2058, 2199, 3386 cm^{-1} (B3LYP/6-31G*)) (Scheme 3). The intensity of the 1969 cm^{-1} band of **20a** (actually a double band at 1969 and 1972 cm^{-1}) first increases, then decreases again after 15 min photolysis at 254 nm. The 2044 cm^{-1} band (**25a**) increases more slowly, then also disappears after 2 h of photolysis. All the while, the 2269 cm^{-1} band (**22a**) increases slowly (Figure S13).

The other prominent band at 2135 cm^{-1} (Figure 9) is ascribed to 3-diazo-1-isocyanopropene **23a**. The UV–vis absorption centered at ca. 331 nm (Figure 7) may also be ascribed to **23a**. The IR spectrum of **23a** changes in the course of further photolysis at 313 nm (Figures S12 and S13) by forming new

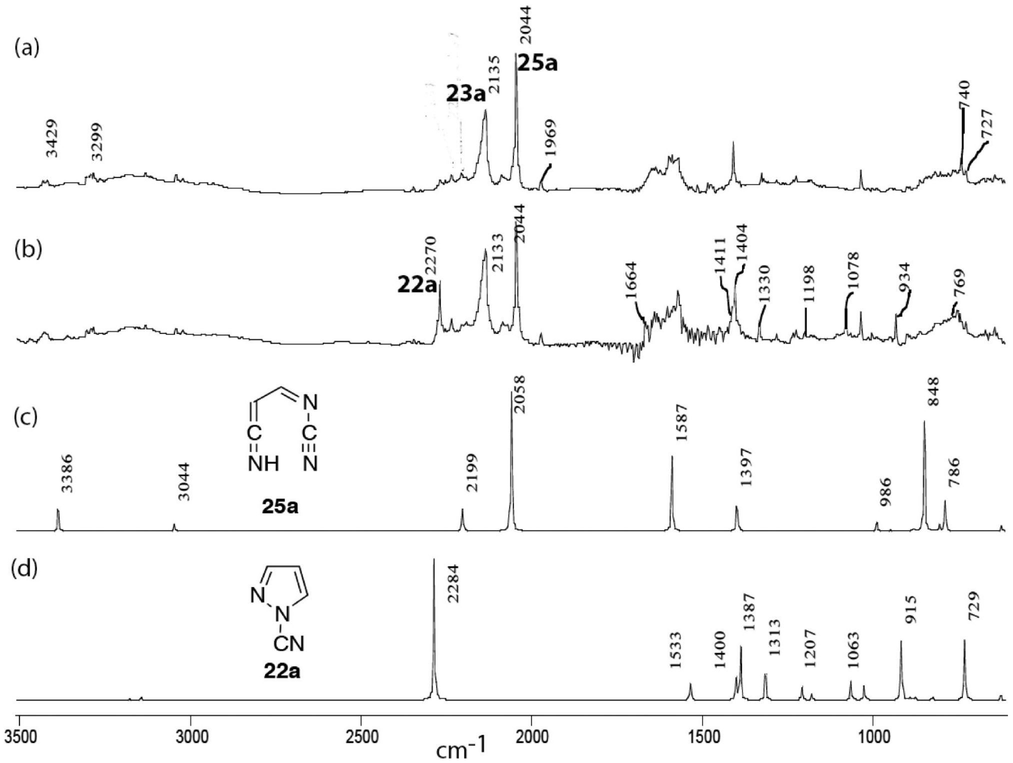


Figure 9. IR spectrum (a) after 1 h photolysis of azide **18a** with 222 nm (20 K); (b) after 2.5 h photolysis of azide **18a** at 254 nm (20 K). (c) Calculated spectrum of cyanimino-ketenimine **25a** (B3LYP/6-31G*). (d) Calculated spectrum of 1-cyanopyrazole **22a** (B3LYP/6-31G*, wavenumbers scaled by a factor 0.9613). Interpretations: 1969 cm^{-1} band = **20a**; 2044 cm^{-1} = **25a**; 2270 cm^{-1} = **22a**. The broad band at 2135/2133 cm^{-1} is ascribed to diazo-isocyanide **23a**.

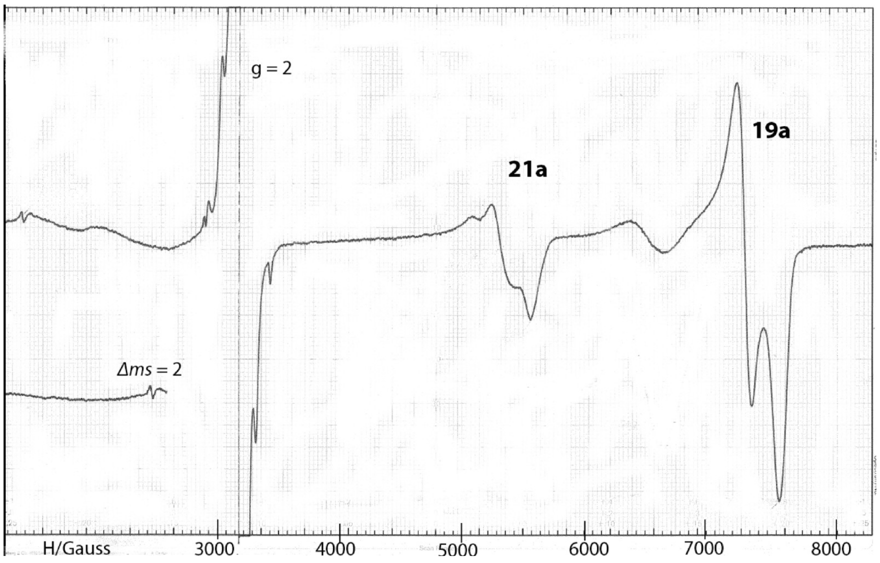


Figure 10. ESR spectrum resulting from 2 h UV photolysis of the 2-pyrimidinylnitrene **19a** isolated in Ar matrix. 2-Pyrimidinylnitrene **19a**: X_2 7326 G. Y_2 7597 G. Half-field signal 1683 G. 4-Cyano-4-azabutadien-1-ylnitrene **21a**: X_2 5408 G. Y_2 5648 G. The signals of nitrene **21a** are already clearly present after 5 min of photolysis. The strong band at $g = 2$ (ca. 3375 G) is due to adventitious monoradicals. The origin of the broad signal at 6551 G, which grows as a function of photolysis time, is unknown. Inset 600−1950 G range. H_o = 3374.5 G.

absorptions on the high-frequency side of the band. First, compound **23** can exist in several conformeric forms. Second, photochemical decomposition of the diazo compound is expected to form products such as isocyanopropadiene, isocyanocyclopropene, and so forth, all absorbing near 2135 cm^{-1}. We postulate that isocyanides **23** are formed by photochemical ring-opening of the triazacycloheptatetraenes, **20** → **23** (Scheme 3), which is analogous to eq 1. This is discussed further in the context of the dimethyl derivative **23b** below.

Continued photolysis of the matrices derived from **18a** and **18b** at 254 or 313 nm caused increased development of bands readily assigned to the 1-cyanopyrazoles **22a** (2270 cm^{-1}; Figure 9) and **22b** (2259 cm^{-1}), respectively, by comparison with the cyanopyrazoles formed by FVT.[3]

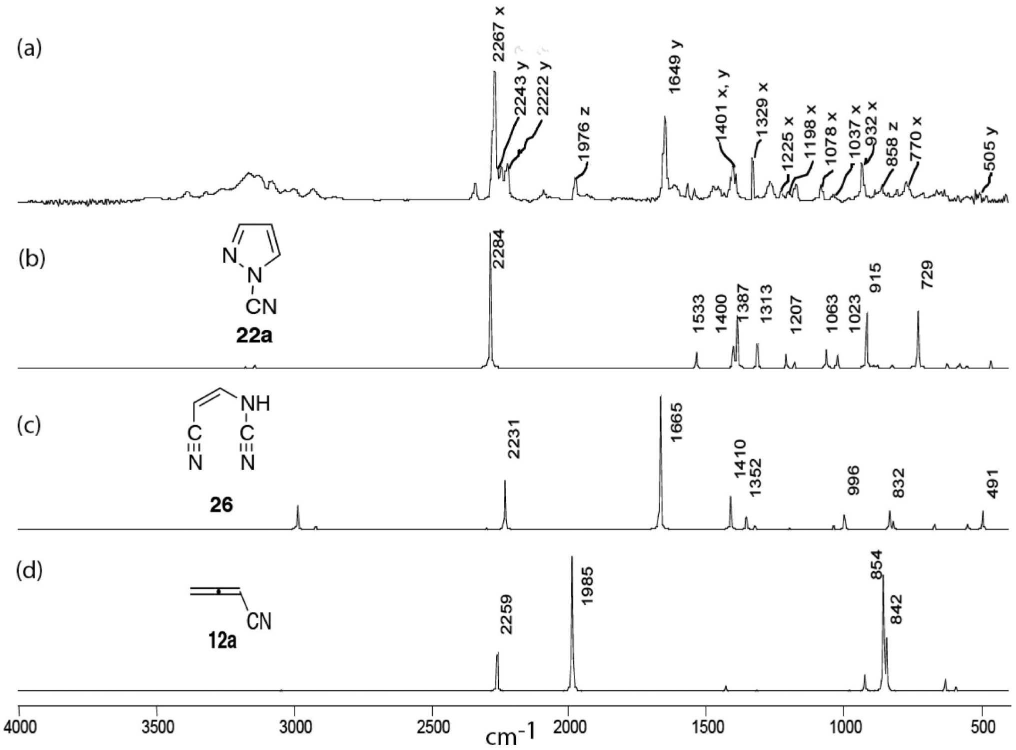


Figure 11. (a) Flash vacuum thermolysis of tetrazolo[1,5-*a*]pyrimidine/2-azidopyrimidine **18a** at 700 °C and subsequent isolation in an Ar matrix at 20 K; bands marked with an x belong to 1-cyanopyrazole **22a**, those with an y are assigned to (2-cyanovinyl)cyanamide **26**, and those with a z to cyanoallene **12a**; (b) calculated spectrum of 1-cyanopyrazole **22a** (B3LYP/6-31G*, wavenumbers scaled by a factor 0.9613); (c) calculated spectrum of (2-cyanovinyl)cyanamide **26**; (d) calculated spectrum of cyanoallene **12a** (pyrolysis product of **22a**). Note that 2-aminopyrimidine is not formed under these FVT conditions.

Moreover, a second nitrene is formed on UV photolysis of **18aT**/**18aA** and observed in the ESR spectrum (Figure 10). Its ZFS parameters are in good agreement with expectations for the open-chain vinylnitrene **21a** ($D/hc = 0.542$, $E/hc = 0.0056$ cm^{-1}) and very similar to those of the isomeric nitrene NC—CH═N—CH═CH—N formed by ring-opening of 2-pyrazinylnitrene.[12] The D value fits very well on the D–ρ correlation.[12] A D value of 0.5 is much too low to be associated with an aromatic or heteroaromatic nitrene. This nitrene, **21a**, is a likely precursor of both ketenimine **25a** and 1-cyanopyrazole **22a**, whereby **22a** may also form directly from nitrene **19a** in a concerted ring contraction (Scheme 3).[7,13]

FVT of **18aT**/**18aA** at 700 °C with isolation of the products in Ar matrix affords 1-cyanopyrazole **22a**[3] together with new absorptions at 2243, 2222, and 1649 cm^{-1}, which are assigned to *N*-(cyanovinyl)cyanamide **26**, i.e., a tautomer of ketenimine **25a** (Scheme 3 and Figure 11). This is analogous to the formation of glutacononitriles from 2-pyridylnitrenes (Scheme 1).[1] Cyanoallene **12a** is also formed in this FVT reaction (Figure 11); this is due to a secondary pyrolysis of 1-cyanopyrazole[14] **22a** and has nothing to do with the pyridazinylnitrene reactions in Scheme 2. 2-Aminopyrimidine is formed in the preparative FVT reaction of **18aT**/**18aA** due to hydrogen abstraction by the triplet nitrene,[3] but it is not formed under the high vacuum conditions of the present FVT experiments in the presence of argon as a carrier gas.

The 2,6-dimethylpyrimidinyl azide **18bA** is formed by mild FVT of the tetrazole **18bT** (Figure S14). The nitrene **19b** is observed by IR, UV, and ESR spectroscopy (Figures 12 and S15–S17). A weak signal ascribed to triazacycloheptatetraene **20b** is observed at 1979 cm^{-1} (Figures 12 and S15).

Prolonged photolysis caused the formation of 1-cyano-3,5-dimethylpyrazole **22b** (Figure S18), which is also the product of FVT.[3] Formation of a ketenimine **25b** from the vinylnitrene **21b** is unlikely, as it would require a 1,2-shift of a methyl group. While not impossible, such a reaction undoubtedly has higher activation energy than the formation of azirene **24b**. The closure of open-shell singlet vinylnitrene to 1-azirene is said to be barrierless,[15] but we calculate, in fact, a small barrier of 5 kcal/mol, at the CASPT2 level. Azirenes are sometimes observed in the matrix photolysis of vinyl azides.[16] Furthermore, singlet (2-acyl)vinylnitrenes are found to cyclize to azirenes.[17] The development of weak bands at 2212, 2202, 1628, and 1244 cm^{-1} in the photolysis of **18b** at 313 nm for 2 h may be ascribed to azirene **24b** (calculated C≡N and C═N absorptions 2202, 1629, and 1222 cm^{-1}), but this compound was not investigated in detail (Figures S19–S20).

Another prominent band at 2099 cm^{-1} develops on photolysis of **18b** at 254 nm and decreases again on photolysis at 313 nm (Figures S19–S21). In analogy with the similar observation of **23a**, this is assigned to the diazo isocyanide **23b** formed by ring-opening of the triazacycloheptatetraene **20b** (1979 cm^{-1}) (Scheme 3). Compound **23b** has a calculated IR absorption at 2089 cm^{-1} as the only strong band in the IR spectrum (Figure S21). A corresponding maximum at 322 nm was observed in the UV spectrum (Figure S16). When **18bA** was photolyzed at 313 nm from the beginning, neither the diazo band at 2099 cm^{-1} nor the UV band at 322 nm formed; instead, the bands tentatively ascribed to azirene **24b** developed immediately. There is good precedence for ring-opening reactions of the type **20** → **23**: 5-phenyl-1,3,4-triazabenzocyclohepta-1,2,4,6-tetraene

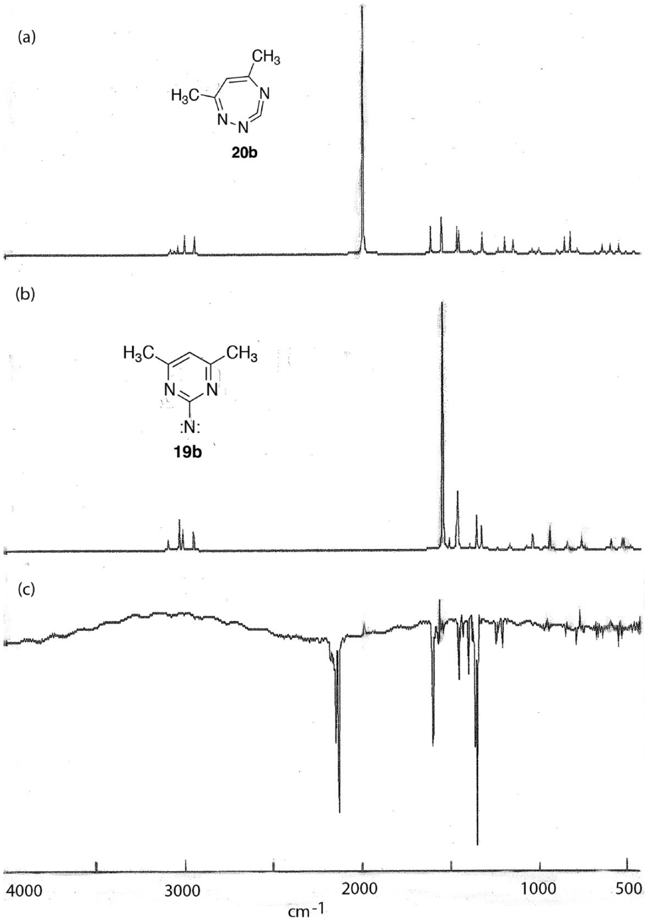
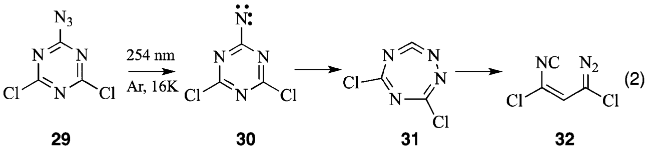


Figure 12. (a) Calculated IR spectrum of 5,7-dimethyl-1,2,4-triazacyclohepta-2,3,5,7-tetraene **20b**. (b) Calculated spectrum of triplet 4,6-dimethyl-2-pyrimidinylnitrene **19b** (all calculations B3LYP/6-31G*, wavenumbers scaled by a factor 0.9613). (c) IR spectrum of the products of photolysis of 2-azido-4,6-dimethylpyrimidine **18bA** with 254 nm for 1 min at 20 K. Positive peaks: triplet 4,6-dimethyl-2-pyrimidylnitrene **19b** and 5,7-dimethyl-1,2,4-triazacyclohepta-2,3,5,7-tetraene **20b** (1979 cm^{-1}); the negative peaks are due to the consumed 4,6-dimethyl-2-azidopyrimidine **18bA**. For more details see Figure S15.

27b undergoes reversible ring-opening to *o*-isocyanophenyl-(phenyl)diazomethane **28b** (eq 1).[6]

Furthermore, Chapyshev has investigated the matrix photolysis of azido-*s*-triazine **29** and suggested the ring-opening of tetraazacycloheptatetraene **31** (1951 cm^{-1}) to the isocyano diazo compound **32** (2087 cm^{-1}) (eq 2).[18]



3. Mechanism. Thermal reaction paths were explored by calculating the relative energies of some of the species of interest at the (U)B3LYP/6-31G* level of theory. Energies of open-shell singlet nitrenes (S_1, $^1A''$) were estimated using the Cramer-Ziegler method.[19] The relevant data for the 'a' series (unsubstituted compounds) are collected in Scheme 4. Very similar relative energies apply to the dimethyl ('b') series. Hill and Platz[4] have already carried out detailed calculations on the nitrenes, azirines, and seven-membered rings as well as the transition states connecting them at B3LYP/6-31G* and CASPT2(8,8)//CASSCF(8,8)6-31G* levels of theory and demonstrated that the trends of the two types of calculation are in broad agreement.

The calculations demonstrate that the interconversion of all the molecules in the top row of Scheme 4 is possible in principle, but our experimental results clearly show that the interconversion of the nitrenes **9** and **19** does not happen. Part of the reason can be found in the relative activation barriers. The ring-opening of triplet 2-pyrimidinylnitrene **19** to the observed triplet iminovinylnitrene **21** is a very favorable process with a modest activation energy (32 kcal/mol). The triazacycloheptatetraene **20** must necessarily be a singlet. Its formation has a somewhat higher overall barrier because of the higher barrier toward the diazirene **33** (43 kcal/mol), which may be ascribed to lone pair−lone pair repulsion in the transition state as well as potential antiaromaticity of the diazirene. When **20** does form, it too could undergo ring-opening to **21**, but the activation barrier of 53 kcal/mol is much higher than that for the nitrene **19**. A barrier of 42 kcal/mol between **34a** and **9a** also prevents the interconversion of **19a** and **9a**.

The ring-opening of **20** to 1-isocyanodiazopropene **23** also has a high calculated barrier, *ca.* 54 kcal/mol, but it must be kept in mind that the calculations are for the ground-state reactions, whereas this reaction is in fact photochemical. In the case of 2-quinazolinylnitrene, the analogous interconversion of triazacycloheptatetraene **27** and isocyano-diazo compound **28** (eq 1) was clearly demonstrated to be a photochemical process—[6]not surprisingly, since a formal double bond is broken.

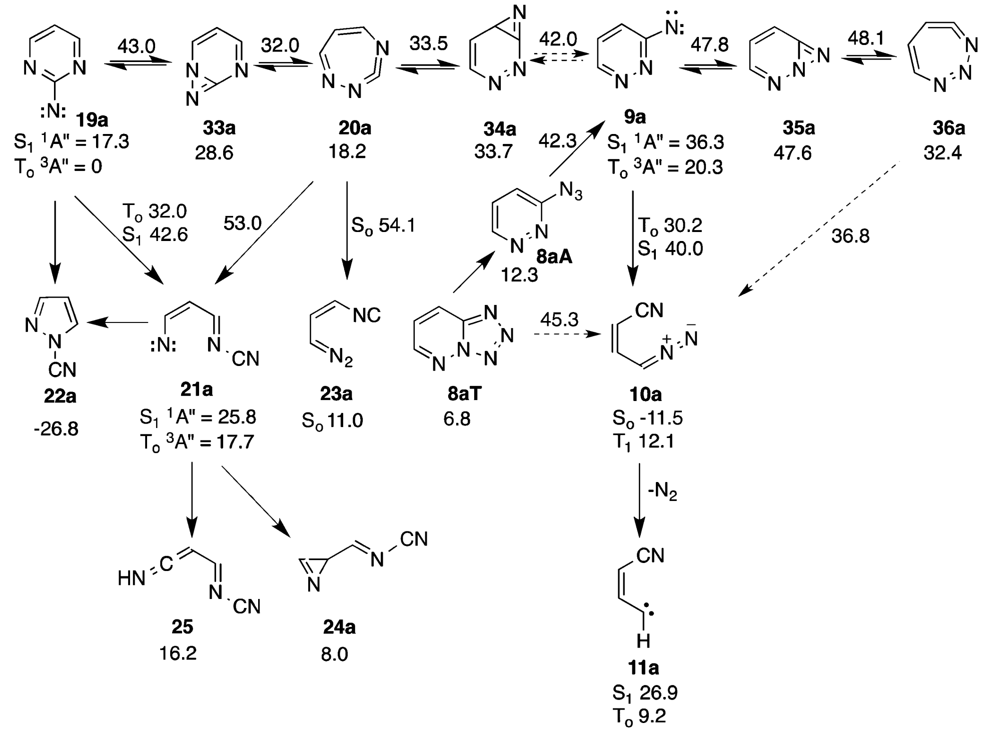
For 3-pyridazinylnitrene **9a**, ring-opening to diazo compound **10a** is very feasible for both the singlet and the triplet states. The thermal activation barriers are 4 and 10 kcal/mol, respectively, with respect to the singlet and triplet states of nitrene **9** (Scheme 4). The tetrazole **8aT** may also photolyze directly to **10a** in a process with concerted ring-opening and N_2 elimination. The calculated thermal barrier is 45 kcal/mol, but again, the reaction is photochemical. The internal reaction coordinate calculation for the singlet ground-state reaction **8aT** → **10a** features an inflection point, which corresponds roughly to the nitrene (see Supporting Information).

Thermal ring expansion of 3-pyridazinylnitrene **9** to the 1,2,4-triazacycloheptatetraene **20** is potentially feasible, but not observed. It would require an activation energy of *ca.* 42 kcal/mol for the open-shell singlet state. The potential ring expansion in the other direction, to the 1,2,3-triazacycloheptatetraene **36**, would require a substantially higher barrier, 48 kcal/mol. If **36** did form, it would exist in a very shallow minimum with a low barrier toward ring-opening to **10**.[8] There is no evidence for the formation of **36**. As described above, the final products in the two systems can be understood in terms of rearrangements of cyanovinylcarbene **11** (to cyanoallene **12**, cyanocyclopropene **13**, propargyl cyanide **14**, and tetrolonitrile **15**), isocyanodiazopropene **23** (to unidentified isocyanides, e.g., isocyanoallene and isocyanocyclopropene), and (cyanimino)-vinylnitrene **21** (to 1-cyanopyrazole **22**, ketenimine **25**, cyanamide **26**, and azirene **24**).

■ CONCLUSION

Mild flash vacuum thermolysis (FVT) of tetrazolopyridazines **8T** generates a small amount of the azide valence tautomers **8A**. Both matrix photolysis and FVT of **8T**/**8A** give rise to

Scheme 4. Calculated Reaction Paths[a]



[a]Energies of minima and transition structures relative to **19a** T$_0$ at the (U)B3LYP/6-31G* level (ZPVE corrected) in kcal/mol.

3-pyridazinylnitrenes **9**, which were detected by ESR spectroscopy in the photolysis reaction. Neither the azides nor the nitrenes have been observed previously. Matrix photolysis with IR observation reveals ring-opening of the nitrenes to diazovinyl cyanides **10**, which again lose N_2 to generate (cyanovinyl)carbenes **11**. The carbenes **11** were also detected by ESR spectroscopy. These vinylcarbenes rearrange primarily to cyanoallenes **12** and 3-cyanocyclopropenes **13**.

Tetrazolo[1,5-*a*]pyrimidines **18T** easily ring open to the azide valence tautomers **18A**; both photolysis and FVT generate 2-pyrimidinylnitrenes **19**, which were observed by Ar matrix ESR, UV, and IR spectroscopies. A second nitrene, interpreted as the ring-opened vinylnitrene **21a**, is formed rapidly on photolysis of matrix-isolated **19a**, and this is the logical precursor of (cyanimino)ketenimine **25a**, which is observed in the IR spectrum. Another photolysis end product is 1-cyanopyrazoles **22**, which is also formed on FVT. Azirene **24** is suggested as a photolysis product from **18b**. Weak IR absorptions are ascribed to 1,2,4-triazacyclohepta-2,3,5,7-tetraenes **20a** and **20b** (1969 and 1979 cm^{-1}, respectively). The development of strong bands in the 2100 cm^{-1} region on extended photolysis is in accord with ring-opening of **20** to (isocyanovinyl)diazomethanes **23**.

An interconversion of 3-pyridazinylnitrenes **9** and 2-pyrimidinylnitrenes **19** is, in principle, energetically possible, but other reactions described above are more favorable, with the consequence that the interconversion is not observed by either ESR or IR spectroscopy. In the case of the related isomeric pair, 3-pyridazinylcarbene **1d** and 2-pyridylnitrene **4**, there was also very tenuous evidence for interconversion.[7] This is in contrast to the well-established interconversion of phenylnitrene and 2-pyridylcarbene, which takes place both thermally[1] and photochemically.[20] The reason can be found in the fact that ring-opening reactions are much more facile in heterocyclic than in carbocyclic carbenes and nitrenes.[1,12] This is true especially for Type I ring-openings, which dominate the reactions of 3-pyridazinylcarbenes and -nitrenes, whereas they are not possible at all in carbocyclic systems.

■ COMPUTATIONAL METHOD

The energies and vibrational frequencies of the various species were calculated at theB3LYP/6-31G* level of theory using the *Gaussian 09* suite of programs.[21] Reported energies include zero-point vibrational energy corrections. The vibrational frequencies were scaled by a factor 0.9613.[22] Further details are given in the Supporting Information.

■ EXPERIMENTAL SECTION

Matrix isolation experiments employed an apparatus consisting of an FVT oven containing 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 cold head of a closed cycle liquid He cryostat with a wall-free flight path of ca. 3 cm between the exit of the quartz tube and the cold target (10−25 K).[12] The quartz tube was unpacked and not chemically treated or seasoned. The cold target was KBr for IR spectroscopy, quartz or KBr for UV−vis spectroscopy, and a Cu rod for ESR spectroscopy.[12] Tetrazolo[1,5-*b*]pyridazines **8a,b** and tetrazolo[1,5-*a*]pyrimidines **18a,b** were sublimed at 60−90 °C in a stream of Ar, passing the vapor through the FVT oven, either at room temperature or at the indicated temperature before depositing the material on the cold target, usually at 20 K, to form a matrix. Afterward, the target was cooled to 8−10 K. IR spectra were recorded with 1 cm^{-1} resolution. The deposited compounds were photolyzed with different wavelength, usually starting with 254 nm. Photolysis was carried out using a 75 W low pressure Hg lamp (254 nm), a 1000 W high pressure Xe/Hg lamp equipped with a monochromator and appropriate cutoff filters, or excimer laser lamps operating at 222 nm (25 mW/cm^2) and 308 nm (50 mW/cm^2). In FVT experiments, the tetrazoles/azides were pyrolyzed at 400−700 °C, and the products were isolated in Ar matrixes as above.

Tetrazoles **8aT**, **18aT**, and **18bT** were prepared according to literature procedures.[3,9a]

Azidoyridazines **8aA** and **8bA** were only observed following mild FVT of the tetrazoles (up to 400 °C). Consequently, ESR spectra of pyridazinylnitrenes **9a** and **9b** were best observed by photolysis of the matrix-isolated thermolyzates, where azides were detectable by IR spectroscopy. *D*/*hc* and *E*/*hc* values were calculated from ESR spectra using Wasserman's equations and method of defining field positions.[23]

5,7-Dimethyltetrazolo[1,5-*b*]pyridazine 8bT. A solution of 1.59 g (11.15 mmol) 3-chloro-4,6-dimethyl-pyridazine[24] and 1.45 g (22.3 mmol) sodium azide in 20 mL 10% EtOH containing 11.2 mmol HCl was refluxed for 1 h. After cooling to 0 °C, the crystals formed were filtered off and purified by sublimation at 115−120 °C/0.005 hPa, yielding 1.38 g **8bT** (83%), mp 136−138 °C. The substance recrystallizes from EtOH/water 9/1, mp 135−138 °C. ^{1}H NMR (CDCl$_3$) δ 7.15 (s, 1 H), 2.76 (s, 3 H), 2.68 (s, 3 H). ^{13}C NMR (CDCl$_3$) δ 156.9, 143.2, 136.7, 125.1, 21.4, 16.5; IR (KBr) 3058 m, 2965 w, 2928 w, 1606 m,1575 s, 1564 m, 1483 s, 1437 s, 1428 s, 1418 m, 1397 w, 1382 s, 1359 m, 1343 s, 1336 w, 1267 s, 1211 m, 1166 m, 1130 s, 1080 w, 1064 s, 1043 m, 1037 m, 1025 w, 995 s, 949 m, 903 s, 826 m, 766 m, 709 w, 638 s, 529 s, 515 w, 487 s cm^{-1}; MS (EI) *m*/*z* 149 (M$^+$, 1%), 92 (19), 78 (8), 66 (100), 51 (27). Anal. Calcd for $C_6H_7N_5$: C 48.32, H 4.73, N 46.96. Found: C 48.03, H 4.65, N 46.94.

Matrix Isolation Experiments, IR Peak Listings, and Calculated Vibrational Wavenumbers. (B3LYP/6-31G*).[21] All calculated wavenumbers in this document are scaled by 0.9613. Calculated relative peak intensities are normalized to 100.

Tetrazolo[1,5-*b*]pyridazine 8aT and 3-Azidopyridazine 8aA. **8aT** was sublimed at 60 °C in an Ar stream and deposited on a KBr window at 20 K. An IR spectrum of pure tetrazole was recorded. IR (Ar, 20 K) tetrazole **8aT** λ^{-1}/cm^{-1} 3117 m, 3102 w, 3086 w, 3061 m, 1619 w, 1542 m, 1492 m, 1474 w, 1373 m, 1347 s, 1334 w, 1324 w, 1272 w, 1256 w, 1133 w, 1076 w, 1019 w, 1006 w, 985 w, 913 w, 812 m, 802 m, 762 m, 754 w, 648 w, 588 w, 563 w, 444 w; calc. (B3LYP/6-31G*) 3107 (6), 3095 (7), 1524 (41), 1476 (29), 1363 (7), 1326 (10), 1308 (99), 1262 (33), 1238 (15), 1144 (5), 1113 (7), 1063 (39), 1002 (23), 965 (16), 880 (15), 786 (100), 752 (13), 730 (9), 581 (4), 548 (5), 433 (4).

After mild FVT at 250 °C small amounts of 3-azidopyridazine **8aA** were observed as well. IR (Ar, 20K) azide **8aA** λ^{-1}/cm^{-1} 2163, 2145, 2118, 1585, 1431, 1293, 696; calc. (B3LYP/6-31G*) 3093 (2), 3080 (1), 2202 (100), 1570 (16), 1418 (27), 1373 (10), 1316 (37), 1087 (3), 995 (1), 791 (6), 678 (3), 536 (2).

Photolysis of the matrix-isolated tetrazole **8aT** with 254 nm light for 2 min at 20 K produced a strong double peak at 2086/2072 cm^{-1} which is assigned to the stretching vibration of the diazo group of 4-diazobut-2-enenitrile **10a**: IR (Ar, 20 K) λ^{-1}/cm^{-1} 2214 w, 2086 s, 2072 s, 1592 m, 1582 m, 1417 m, 1362 m, 1236 m, 1164 w, 789 w, 703 w, 495 w; calc. (B3LYP/6-31G*) 3089 (1), 3072 (1), 2232 (8), 2133 (100), 1589 (24), 1417 (12), 1365 (10), 1232 (5), 1163 (1), 970 (1), 768 (3), 698 (7), 579 (4), 548 (1), 503 (11).

Further photolysis at 222, 254, or 313 nm gave rise to several new peaks, which are assigned to 3-cyanocyclopropene **13a** and buta-2,3-dienenitrile (cyanoallene) **12a**. The ratio of these two products changes with the wavelength. Irradiation at 254 nm produces distinctively stronger bands at 2227 and 1976 cm^{-1} (cyanoallene) compared to bands 2241 and 1664 cm^{-1} (cyanocyclopropene). IR (Ar, 20 K) 3-cyanocyclopropene **13a** λ^{-1}/cm^{-1} 2995 m, 2241 m, 1664 m, 1352 w, 986 s, 949 w, 888 m, 623 s, 543 m; calc. (B3LYP/6-31G*) 3162 (5), 2990 (37), 2261 (22), 1691 (33), 1331 (8), 1113 (6), 1011 (8), 974 (77), 932 (11), 876 (21), 800 (2), 619 (100), 554 (8), 535 (29); cyanoallene **12a** λ^{-1}/cm^{-1} 2227 w, 1976 s, 858 s, 843m; calc. (B3LYP/6-31G*) 3043 (1), 2259 (28), 1985 (100), 1428 (3), 1315 (1), 976 (1), 922 (12), 854 (85), 842 (40), 628 (9).

6,8-Dimethyltetrazolo[1,5-*b*]pyridazine 8bT and 2-Azido-4,6-dimethylpyridazine 8bA. Compound **8bT** was sublimed at 65 °C in an Ar stream, and was deposited on a KBr window at 20 K. An IR spectrum then showed almost pure tetrazole **8bT**: IR (Ar, 20 K) λ^{-1}/cm^{-1} 3066 w, 3049 w, 3103 w, 2974 w, 2936 w, 2927 w, 1612 m, 1579 s, 1569 m, 1490 s, 1460 w, 1444 s, 1431 s, 1418 w, 1396 m, 1383 m, 1367 m, 1342 m, 1334 w, 1309 w, 1276 m, 1211 w, 1168 w, 1127 m, 1076 w, 1054 m, 1039 m, 1019 w, 986 m, 947 m, 901 w, 875 m, 826 w, 766 w, 709 w, 634 m, 528 m, 513 w, 485 m, 472 w; calc. (B3LYP/6-31G*) 3045 (8), 3027 (24), 2997 (10), 2990 (21), 2938 (24), 1598 (33), 1553 (100), 1482 (50), 1451 (38), 1442 (21), 1431 (50), 1386 (17), 1343 (25), 1321 (27), 1317 (28), 1267 (33), 1195 (4), 1151 (8), 1111 (30), 1039 (23), 1033 (16), 1002 (10), 976 (19), 965 (10), 928 (6), 861 (20), 809 (10), 738 (1), 689 (1), 619 (4), 609 (0), 548 (1), 521 (7), 502 (6), 472 (8), 362 (7), 284 (1), 240 (4), 218 (0), 174 (0), 147 (1), 109 (1).

Mild FVT at 250 °C caused formation of a small amount of the azide **8bA**, which is only identified by its strongest band, λ^{-1}/cm^{-1} 2142; calc. (B3LYP/6-31G*) 2201 (100), 1582 (3), 1532 (6), 1460 (7), 1447 (2), 1394 (12), 1385 (5), 1374 (27), 1353 (2), 1306 (23), 1223 (2), 1175 (1), 1157 (1), 1107 (1), 1033 (1), 1002 (1), 970 (1), 945 (1), 883 (1), 802 (1), 611 (2), 578 (1).

After a few minutes of photolysis at either 254 or 222 nm a strong band assigned to 4-diazo-2-methyl-pent-2-enenitrile **10b** was observed. IR (Ar, 20 K) **10b** λ^{-1}/cm^{-1} 2935 w, 2207 w, 2046 s, 1603 w, 1465 w, 1320 w, 1032 w; calc. (B3LYP/6-31G*) 3021 (1), 3011 (3), 2979 (7), 2926 (13), 2227 (8), 2103 (100), 1600 (14), 1472 (7), 1451 (2), 1445 (2), 1389 (2), 1352 (4), 1345 (13), 1207 (1), 1038 (1), 1022 (6), 980 (1), 871 (1), 821 (1), 759 (2), 637 (1), 598 (2), 577 (1).

Further photolysis at either 254 or 222 nm caused appearance of new bands, which are assigned to 1,2-dimethyl-cycloprop-2-enecarbonitrile **13b** and 2-methyl-penta-2,3-dienenitrile **12b**. In the following, bands labeled with an x belong to **13b**, those with an y to **12b**, and those with no label may belong to both: IR (Ar, 20 K) **12b** + **13b** λ^{-1}/cm^{-1} 2988, 2936, 2226, 1968 y, 1793 x, 1453, 1376, 1206, 1153, 1090 x, 1069 x, 1002, 958 x, 918 x, 790 y, 719 x, 704 x, 607 y, 501 y, 473 y, 439 x. calc. (B3LYP/6-31G*) for **13b** 3167 (3), 3010 (70), 2992 (57), 2986 (27), 2930 (100), 2249 (55), 1807 (43), 1467 (15), 1457 (16), 1449 (36), 1446 (40), 1380 (7), 1195 (9), 1132 (51), 1080 (41), 1058 (9), 1024 (5), 982 (19), 939 (15), 901 (16), 711 (52), 699 (62), 640 (11), 566 (3), 555 (4), 423 (24); calc. (B3LYP/6-31G*) for **12b** 3030 (61), 3009 (6), 2995 (41), 2982 (53), 2938 (69), 2930 (100), 2248 (70), 1984 (61), 1472 (12), 1461 (25), 1453 (28), 1450 (28), 1389 (4), 1375 (24), 1207 (55), 1146 (17), 1065 (4), 1032 (2), 1025 (2), 985 (55), 888 (7), 784 (49), 674 (11), 603 (18), 578 (6), 497 (25), 472 (7).

FVT of Tetrazolo[1,5-*b*]pyridazine 8a. FVT of tetrazolo[1,5-*b*]pyridazine **8aT** was carried out at 600 °C, and three major products were identified after isolation in an Ar matrix, namely, cyanoallene **12a**, 3-butynenitrile (propargyl cyanide) **14** and 2-butynenitrile (tetrolonitrile) **15**. Very little 3-cyanocyclopropene **13a** is formed under these conditions, but it is identifiable by its absorption at 1664 cm^{-1}. Other products may form as well, since not all IR bands are assigned. IR (Ar, 20 K) cyanoallene **12a** λ^{-1}/cm^{-1} 2227 m, 1976 s, 859 s, 840 m (this band appears at 843 upon photolysis, probably due to different deposition conditions); 3-cyanocyclopropene **13a** λ^{-1}/cm^{-1} 1664 vw; 3-butynenitrile **14** λ^{-1}/cm^{-1} 3318 s, 1434 w, 1313 m, 981 w, 660 s, 624 m, 595 w; calc. (B3LYP/6-31G*) 3359 (100), 2953 (1), 2922 (5), 2288 (5), 2170 (1), 1422 (12), 1307 (24), 959 (11), 870 (12), 624 (70), 596 (83), 352 (3), 342 (9), 302 (8), 134 (5); 2-butynenitrile **15** λ^{-1}/cm^{-1} 2274 s, 1415 m, 1027 w, 505 w; calc. (B3LYP/6-31G*) 2997 (6), 2931 (7), 2315 (100), 1438 (15), 1382 (1), 1020 (7), 536 (5).

FVT of 6,8-Dimethyltetrazolo[1,5-*b*]pyridazine 8bT. FVT with Ar matrix isolation of the products was performed at temperatures ranging from 450 to 700 °C in intervals of 50 °C. Three major products were identified by comparison with the calculated spectra: 1,2-dimethylcycloprop-2-enecarbonitrile **13b**, 2-methylpenta-2,3-dienenitrile **12b**, and the *s*-*Z* and *s*-*E*-isomers of 2-methylpenta-2,4-dienenitrile **16** and **17**. The ratio of **12b** and **13b** changes with increasing temperature in favor of the cyanoallene (**12b**). In Figure S11, bands marked with an x belong to 1,2-dimethylcycloprop-2-enecarbonitrile **13b**, and those with an y to 2-methylpenta-2,3-dienenitrile **12b**. Bands assigned to **16** and **17**: IR (Ar, 20 K) λ^{-1}/cm^{-1} 3122 m, 3024 w, 2986 m, 2969 m, 2935 m, 2225 s, 1656 m, 1635 w, 1595 m, 1451 s, 1441 s, 1420 s, 1391 w, 1382 m, 1321 w, 1301 w, 1033 m, 1110 s, 995 s, 926 s, 770 w, 675 w, 549 w; calc. (B3LYP/6-31G*) for **16**: 3129 (32), 3068

(45), 3053 (7), 3046 (14), 3038 (25), 2987 (29), 2938 (37), 2239 (100), 1642 (14), 1597 (15), 1461 (17), 1449 (21), 1418 (23), 1391 (12), 1328 (7), 1288 (5), 1199 (5), 1130 (3), 1037 (1), 993 (80), 920 (90), 904 (21), 776 (3), 657 (17), 573 (3), 552 (26); calc. (B3LYP/6-31G*) for **17**: 3128 (27), 3060 (14), 3046 (31), 3019 (28), 2984 (34), 2931 (48), 2240 (72), 1644 (5), 1598 (17), 1464 (15), 1445 (19), 1418 (20), 1386 (6), 1315 (5), 1286 (7), 1203 (3), 1110 (3), 1040 (17), 1019 (50), 1002 (36), 915 (100), 892 (3), 757 (1), 673 (25), 605 (7), 567 (2).

Tetrazolo[1,5-*a*]pyrimidine 18aT and 2-Azidopyrimidine 18aA. Tetrazole **19aT** was sublimed at 60 °C in a stream of Ar and deposited on a KBr target at 22 K. The matrix was then cooled to 8 K and an IR spectrum of the mixture of tetrazole **18aT** and azide **18aA** was recorded. After mild FVT up to 250 °C, only azide **18aA** was observed in the matrix. The following bands are assigned: IR (Ar, 8 K) tetrazole **18aT** λ^{-1}/cm^{-1} 3108 w, 3086 w, 1623 s, 1529 m, 1508 s, 1486 w, 1457 w, 1375 w, 1340 w, 1337 w, 1333 m, 1331 m, 1267 w, 1263 w, 1231 w, 1117 w, 1084 w, 1075 w, 977 w, 924 w, 789 w, 784 m, 780 m, 773 w, 576 w, 565 w, 458 w, 444 w, 419 w; calc. (B3LYP/6-31G*) 3118 (1), 3068 (20), 1610 (100), 1514 (69), 1489 (96), 1399 (35), 1359 (1), 1312 (43), 1245 (24), 1210 (22), 1139 (3), 1108 (25), 1068 (24), 1012 (3), 960 (15), 945 (1), 925 (0), 892 (10), 769 (42), 755 (38), 680 (0), 642 (1), 566 (5), 551 (5), 434 (3); IR (Ar, 20 K). Azide **18aA** 3058 w, 3052 w, 2178 w, 2136 s, 1583 w, 1569 s, 1565 m, 1557 w, 1440 w, 1407 s, 1401 m, 1356 w, 1340 w, 1325 s, 1317 m, 1303 w, 1281 w, 1221 w, 1185 w, 1164 w, 1076 w, 1033 w, 858 w, 801 w, 792 w, 701 w, 635 w, 554 w, 495 w, 413 w; calc. (B3LYP/6-31G*) 3060 (5), 2204 (100), 1574 (26), 1547 (17), 1424 (3), 1396 (71), 1340 (43), 1264 (1), 1230(1), 1180 (1), 1056 (0), 838 (1), 787 (5), 777 (2), 686 (2), 620 (1), 542 (2), 405 (1).

Photolysis of the azide **18aA** for a few minutes at either 222 or 254 nm caused the azide to disappear, and two intermediate species were formed. By comparison with the calculated IR spectra (B3LYP/6-31G*), they were identified as the 2-pyrimidinylnitrene **19a** and 1,2,4-triaza-cyclohepta-2,3,5,7-tetraene **20a**. IR (Ar, 20 K) nitrene **19a** λ^{-1}/cm^{-1} 3018 w, 1531 s, 1361 m, 1231 m, 795 m, 624 m; calc. (B3LYP/6-31G*) 3058 (41), 1531 (4), 1498 (100), 1405 (1), 1349 (37), 1227 (8), 1212 (15), 1073 (2), 1038 (2), 961 (1), 938 (5), 848 (0), 781 (49), 759 (1), 610 (15), 558 (6).

Because of its low concentration, only the strongest band of the triazacycloheptatetraene **20a** is assigned: λ^{-1}/cm^{-1} 1969 s; calc. (B3LYP/6-31G*) 1968 (100), 1587 (3), 1520 (8), 1356 (4), 1284 (3), 1233 (6), 1154 (1), 990 (10), 936 (1), 919 (1), 896 (2), 848 (1), 768 (9), 708 (3), 667 (4), 623 (2), 541 (7).

After photolysis of azide **18aA** at 222 nm for 2 h at least two new products were formed. The following bands are assigned to cyaniminoketenimine **25a** (conformer(s) unspecified): IR (Ar, 20 K) **25a** λ^{-1}/cm^{-1} N–H: 3299 w, 3289 w; NCN: 2203 w, 2187 w; C=C=N: 2044 s; 740 m, 727 w; calc. (B3LYP/6-31G*) 3386 (15), 3045 (4), 2200 (16), 2058 (100), 1587 (53), 1398 (18), 1138 (0), 987 (7), 947 (1), 880 (2), 848 (78), 804 (6), 787 (22), 620 (4), 515 (6). The peak ascribed to 1,2,4-triazacyclohepta-2,3,5,7-tetraene **20a** at 1969 cm^{-1} is still present after this photolysis. A strong, broad band at 2135 cm^{-1} is ascribed to 3-diazo-1-isocyanopropene **23a**; calc. (B3LYP/6-31G*) λ^{-1}/cm^{-1} 3116 (1), 3101 (2), 3081 (1), 2127 (100) (CNN), 2098 (17) (NC), 1611 (8), 1417 (12), 1365 (4), 1242 (3), 1177 (2), 982 (3), 782 (1), 700 (5), 553 (4).

After photolysis of azide **18aA** at 254 nm for 2.5 h further bands were formed, which are assigned to 1-cyanopyrazole **22a**: IR (Ar, 20 K) λ^{-1}/cm^{-1} 2270 s, 1411 m, 1404 s, 1330 m, 1198 w, 1078 w, 934 m, 769 m. The spectrum was identical with that of the previously characterized 1-cyanopyrazole.[3]

Further photolysis of the matrices at 313 nm caused growth of bands at 2269 (**22a**), 2130–2140 cm^{-1} (ascribed to isocyanides derived from **23a**), while bands at 2203, 2187, 2044 (**25a**) and 1969 cm^{-1} (**20a**) decreased.

5,7-Dimethyltetrazolo[1,5-*a*]pyrimidine 18bT and Azide 18bA. Compound **18bT** was sublimed at 60 °C in an Ar stream and subjected to mild FVT at 200 °C with deposition of the products on a KBr target at 20 K. The IR spectrum of the resulting matrix showed only azide **18bA**: IR (Ar, 20 K) λ^{-1}/cm^{-1} 3009 w, 3002 w, 2979 w, 2937 w, 2171 w, 2159 w, 2142 s, 2123 s, 1638 w, 1593 s, 1561 m, 1555 m, 1546 w, 1535 w, 1447 m, 1439 w, 1436 w, 1424 w, 1392 m, 1373 w, 1353 s, 1344 s, 1321 w, 1235 m, 1223 w, 1200 m, 1175 w, 1096 w, 1034 w, 991 w, 964 w, 935 w, 840 w, 782 w, 742 w, 632 w, 567 w, 545 w; calc. (B3LYP/6-31G*) 3024 (5), 3001 (2), 2942 (3), 2201 (100), 1570 (47), 1543 (33), 1454 (17), 1446 (3), 1416 (2), 1387 (6), 1377 (3), 1356 (71), 1328 (28), 1249 (3), 1220 (1), 1160 (1), 1028 (2), 1019 (1), 971 (1), 944 (2), 920 (2), 827 (1), 767 (2), 723 (1), 622 (1), 547 (1), 542 (1), 528 (1).

After photolysis at 254 nm for a few minutes at 20 K the azide **18bA** was disappearing, and new bands appearing were assigned to triplet 4,6-dimethyl-2-pyrimidylnitrene **19b** and 5,7-dimethyl-1,2,4-triazacyclohepta-2,3,5,7-tetraene **20b**. IR (Ar, 20 K) 4,6-dimethyl-2-pyrimidylnitrene **19b**: λ^{-1}/cm^{-1} 1555 s, 949 w, 837 w, 763 w, 586 w, 533 w (values for bands between 1555 and 949 cm^{-1} cannot be given due to overlapping (negative) peaks of the azide); calc. (B3LYP/6-31G*) 3024 (12), 3004 (6), 2944 (7), 1535 (100), 1498 (3), 1455 (12), 1451 (23), 1446 (10), 1382 (2), 1343 (14), 1317 (9), 1157 (2), 1061 (1), 1028 (6), 957 (1), 930 (7), 918 (1), 830 (3), 753 (5), 608 (0), 583 (3), 522 (3), 514 (3). Again, because of its low concentration, only the strongest band is assigned to the 5,7-dimethyl-1,2,4-triazacyclohepta-2,3,5,7-tetraene **20b**: λ^{-1}/cm^{-1} 1979; calc. (B3LYP/6-31G*) 3047 (2), 3027 (3), 2988 (6), 2934 (6), 1981 (100), 1597 (11), 1538 (15), 1451 (8), 1439 (8), 1382 (2), 1372 (1), 1308 (6), 1216 (2), 1181 (5), 1132 (4), 1036 (1), 1024 (2), 986 (2), 884 (1), 842 (5), 809 (6), 771 (2), 670 (0), 627 (3), 584 (2), 538 (2).

After 2 h of photolysis at 254 nm no azide was left in the matrix, and new bands had formed. 1-Cyano-3,5-dimethylpyrazole **22b** was identified by comparison with previously reported data.[3] IR (Ar, 20 K) λ^{-1}/cm^{-1} 3008 w, 2974 w, 2937 w, 2259 s, 1354 m, 1107 m, 964 m, 799 m, 784 w, 479 w; calc. (B3LYP/6-31G*) 3146 (1), 3031 (7), 2988 (14), 2937 (20), 2275 (100), 1583 (33), 1481 (1), 1460 (6), 1453 (6), 1449 (8), 1441 (7), 1402 (23), 1377 (11), 1340 (65), 1215 (1), 1140 (1), 1082 (15), 1036 (3), 1010 (3), 970 (2), 949 (15), 784 (13), 761 (4), 643 (0), 605 (1), 592 (1), 562 (1), 541 (1), 467 (5). A band at 2099 cm^{-1} is assigned to 4-diazo-2-isocyano-2-pentene **23b**; calc. (B3LYP/6-31G*) λ^{-1}/cm^{-1} 3067 (2), 3019 (4), 2975 (6), 2923 (11), 2098 (100) (C=N$_2$), 2091 (21) (NC), 1626 (4), 1473 (6), 1466 (2), 1450 (2), 1442 (2), 1388 (1), 1351 (10), 1337 (3), 1213 (1), 1127 (1), 1038 (1), 1025 (5), 978 (1), 844 (2), 822 (1), 784 (1), 636 (1), 564 (1), 539 (1), 499 (1); 5,7-dimethyl-1,2,4-triaza-cyclohepta-2,3,5,7-tetraene **20b** is still present after this photolysis (1979 cm^{-1}). Some unidentified peaks were present in the nitrile/isonitrile region at 2200, 2191, 2175, 2155, and 2035 cm^{-1}, and between 1600 and 1350 cm^{-1}.

Further photolysis at 313 nm (2.5 h) caused bands at 2099 and 1979 cm^{-1} to disappear. New peaks growing in their place were attributed to 1-(2-methyl-3*H*-aziren-3-yl)ethylidenecyanamide **24b**: IR (Ar, 20 K) λ^{-1}/cm^{-1} 2212 s, 2202 s, 1806 w, 1628 s, 1244 s; calc. (B3LYP/6-31G*) 3053 (5), 3031 (4), 3021 (19), 2979 (5), 2945 (6), 2930 (3), 2202 (55), 1807 (15), 1629 (100), 1445 (19), 1439 (22), 1374 (22), 1371 (16), 1353 (22), 1222 (92), 1194 (8), 953 (11), 940 (12), 874 (6), 819 (7), 584 (5), 508 (5). Further bands appearing in the isocyanide region at 2083 and 2073 cm^{-1} could belong to compounds derived from **23b** such as 3-isocyano-1,3-dimethyl-cyclopropene and 2-isocyanopenta-2,3-diene; calc. (B3LYP/6-31G*) 3-isocyano-1,3-dimethyl-cyclopropene: λ^{-1}/cm^{-1} 3017 (18), 3012 (13), 2995 (14), 2987 (7), 2934 (18), 2931 (17), 2119 (100), 1793 (13), 1467 (2), 1455 (5), 1449 (11), 1447 (11), 1381 (3), 1377 (2), 1232 (12), 1107 (28), 1098 (23), 1063 (3), 1024 (3), 988 (6), 951 (4), 881 (11), 725 (20), 712 (11), 646 (6), 525 (4); calc. (B3LYP/6-31G*) 2-isocyanopenta-2,3-diene: λ^{-1}/cm^{-1} 3036 (8), 3028 (13), 3003 (3), 2991 (9), 2979 (11), 2935 (14), 2928 (21), 2114 (100), 1993 (1), 1474 (3), 1459 (4), 1453 (5), 1446 (5), 1376 (4), 1214 (25), 1141 (22), 1067 (1), 1034 (1), 987 (8), 890 (7), 792 (9), 679 (3), 585 (8).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional Ar matrix IR, UV and ESR spectra, NMR spectra of **8bT**, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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