

2-Pyridylnitrene—1,3-Diazacyclohepta-1,2,4,6-tetraene Rearrangements in the Trifluoromethyl-2-pyridyl Azide Series^{1a}

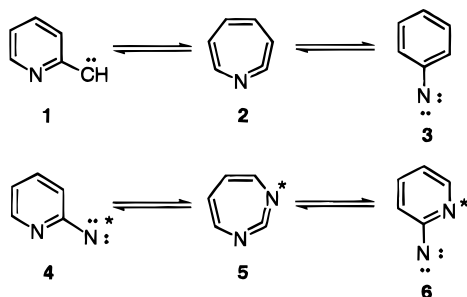
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Abstract: Photolysis of Ar matrix isolated trifluoromethyl-substituted 2-pyridyl azides/tetrazolo[1,5-*a*]pyridines at 12–18 K causes rapid and mostly clean conversion to the corresponding 1,3-diazacyclohepta-1,2,4,6-tetraenes (**4D**, **5D**, **5,6D**, and **4,6D**) absorbing near 2000 cm⁻¹ in the IR. In the latter case, the intermediate 3,5-bis(trifluoromethyl)-2-pyridylnitrene (**4,6N**) was observed by both ESR and IR spectroscopy and converted to the diazacycloheptatetraene **4,6D** in the course of 90 min of UV irradiation. The 2-pyridylnitrenes were generally observable by ESR spectroscopy ($|D/hc| \sim 1.05\text{--}1.10$; $|E/hc| \sim 0.0\text{ cm}^{-1}$) following both photochemical and thermal (FVP) generation from the 2-azidopyridines. Irradiation of the Ar matrix isolated mixtures of nitrenes and diazacycloheptatetraenes also caused development of weak carbene transitions ($|D/hc| \sim 0.40\text{--}0.45$; $|E/hc| \sim 0.006\text{ cm}^{-1}$) in the ESR spectra.

The ring expansion of 2-pyridylcarbenes^{2,3} (**1**) to azacycloheptatetraene **2**, the interconversion of **1**, **2**, and phenylnitrene **3**, and the related 2-pyridylnitrene automerization⁴ (**4** \rightleftharpoons **5** \rightleftharpoons **6**) were the first examples of the fascinating rearrangements of carbenes and nitrenes.⁵



In the early publications, the seven-membered ring intermediates were thought to be carbenes (**7** and **8**) rather than the cumulenes **2** and **5**.^{2,3} Photolysis of an Ar matrix containing the triplet nitrene ³**4** as well as **5** produces a carbene, observed by ESR spectroscopy and tentatively identified as carbene **8**.⁶ The existence of a phenyl derivative of **7** in equilibrium with ¹**3** (and **2**) is suggested from solution trapping experiments.⁷

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(1) (a) Hetarylnitrenes, Part X. For Part IX, see ref 1b. For Part VIII, see ref 9. (b) Evans, R. A.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1062. (c) Present address: CSIRO, Division of Chemicals and Polymers, Clayton, Victoria 3169, Australia.

(2) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1968**, 6149.

(3) Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1969**, 1386.

(4) Wentrup, C.; Crow, W. D. *J. Chem. Soc., Chem. Commun.* **1969**, 1387.

(5) (a) Wentrup, C. *Top. Curr. Chem.* **1976**, 62, 175–251. (b) Chapman, O. L. *Pure Appl. Chem.* **1979**, 51, 331–339. (c) Jones, W. M. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Chapter 3. (d) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 4. (e) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, 28, 233–361. (f) Wentrup, C. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: New York 1984; Chapter 8, pp 395–432. (g) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; Chapter 4.

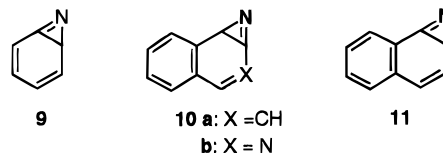
(6) Wentrup, C.; Kuzaj, M.; Lüerssen, H. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 480.

(7) Murata, S.; Sugawara, T.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1198. Cf. Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, 107, 6317.

However, IR spectroscopic observations of **2**⁸ and **5**⁹ in cryogenic matrices and of **2** in solution¹⁰ make it clear that the long-lived species are the cumulenic forms shown.



Laser flash photolytic (LFP) and product studies in solution at room temperature were also interpreted in terms of 1-azacyclohepta-1,2,4,6-tetraene (1,2-didehydroazepine) (**2**) in equilibrium with the singlet nitrene ¹**3**.^{10,11} The bicyclic azirine **9**, predicted¹² to lie on the reaction coordinate from ¹**3** to **2** but of higher energy than **2**, has neither been observed directly nor trapped in reactions of phenyl azide. There is, however, some trapping evidence for the bicyclic azirine in the photolysis of a substituted phenyl azide.¹³ In contrast, in the photolysis of naphthyl and pyrenyl azides, it is the tricyclic azirines that are being trapped (e.g., **10a** and **11** from 2- and 1-naphthyl nitrenes, respectively) to the exclusion of the dehydroazepines.^{11,14} There



(8) Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, 100, 282. Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *ibid.* **1978**, 100, 6245. *Recl. Trav. Chim. Pays-Bas.* **1979**, 98, 334.

(9) Wentrup, C.; Winter, H.-W. *J. Am. Chem. Soc.* **1980**, 102, 6159.

(10) (a) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, 110, 8092. (b) Marcinek, A.; Leyva, E.; White, D.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, 115, 8609.

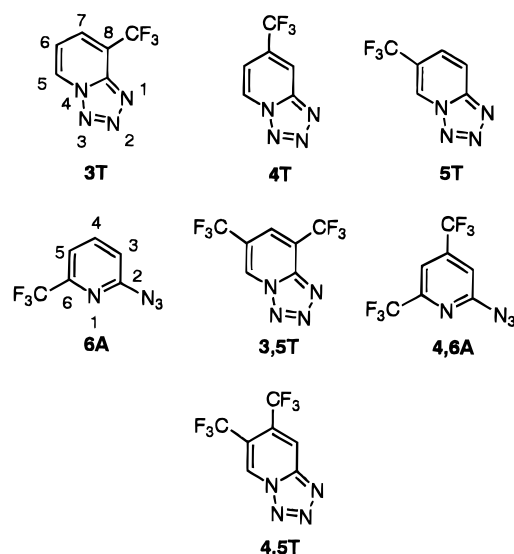
(11) Schuster, G. B.; Platz, M. S. *Adv. Photochem.* **1992**, 117, 69–143.

(12) For MNDO calculations of the C₆H₅N potential energy surface, see ref 10a. For CNDO/2 and Extended Hückel calculations, see: Gleiter, R.; Rettig, W.; Wentrup, C. *Helv. Chim. Acta* **1974**, 57, 2111. For thermochemical calculations, see: Wentrup, C. *Tetrahedron* **1974**, 30, 1301. For MINDO/2 and INDO calculations, see: Shillady, D. D.; Trindle, C. *Theor. Chim. Acta* **1976**, 43, 137. For force field–SCF calculations, see: Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. J. *Tetrahedron* **1985**, 41, 1601.

(13) Younger, C. G.; Bell, R. A. *J. Chem. Soc., Chem. Commun.* **1992**, 1359.

(14) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, 106, 5234.

Chart 1



is IR spectroscopic evidence for both the tricyclic azirines and the benzodehydrodiazepines from Ar matrix photolysis of the naphthyl azides,¹⁵ but neither could be detected by time resolved IR spectroscopy in solution on the μs time scale.¹⁰ The UV active transients observed in LFP experiments were assigned to **10a** and **11**.¹⁴ Azirino[2,3-*c*]isoquinoline (**10b**) has been observed by Ar matrix IR spectroscopy following photolysis of 3-isouquinolyl azide.^{5f}

The first-formed intermediates in all these studies, the singlet nitrenes (e.g., **13**) have not been observed. Triplet nitrenes are observable under quite different conditions by ESR spectroscopy in crystals, organic glasses at 77 K, or Ar matrices at ≤ 15 K^{6,8,16,17} but are not usually observed by IR spectroscopy. In the original matrix photolysis work on phenyl azide, only dehydroazepine **2** was observed, not the nitrene **3**.⁸ However, Hayes and Sheridan¹⁸ were able to observe **33** directly by IR spectroscopy, using 334 nm irradiation of phenyl azide. The nitrene was converted to **2** on irradiation at 485 nm.

Here we wish to report full details of our studies of trifluoromethyl-substituted 2-pyridyl azides.^{1b} These compounds are of particular interest due to their considerable synthetic potential, being excellent precursors for high-yielding preparations of stable 1*H*- and 5*H*-1,3-diazepines.¹⁹ We also describe an example of the direct IR spectroscopic observation of a 2-pyridyl nitrene (**3,5N**)²⁰ and its photoisomerization to a didehydrodiazepine (**4,6D**).²⁰

Results and Discussion

1. Synthesis. The 2-azidopyridines/tetrazolo[1,5-*a*]pyridines used in this study (Chart 1)²⁰ were prepared from the corresponding 2-chloropyridines by two methods: (i) direct nucleophilic substitution with NaN_3 in DMF or (ii) conversion to the

(15) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499.

(16) Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319. Platz, M. S. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: New York, 1984; Chapter 7.

(17) Leyva, E.; Munoz, D.; Platz, M. S. *J. Org. Chem.* **1989**, *54*, 5938. Mahé, L.; Izuoha, A.; Sugawara, T. *J. Am. Chem. Soc.* **1992**, *114*, 7904.

(18) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5881.

(19) (a) Reisinger, A.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1996**, in press. (b) Reisinger, A.; Wentrup, C. Unpublished results.

(20) Formulas are numbered according to the following system: **4A** is 4-trifluoromethyl-2-azidopyridine. **4T** is the corresponding tetrazolo[1,5-*a*]pyridine, and **4N** is the corresponding 2-pyridyl nitrene; **34N** is the triplet nitrene; **5D** is 5-trifluoromethyl-1,3-diazacyclohepta-1,2,4,6-tetraene, etc.

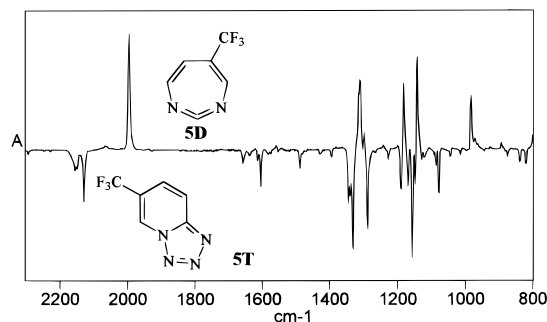


Figure 1. Difference FTIR spectrum of **5D** (positive peaks) generated by Ar matrix photolysis of **5A/5T** (negative peaks).

2-hydrazinopyridines with hydrazine hydrate, followed by diazotization. 2-Azido-6-trifluoromethyl-pyridine (**6A**) could only be obtained by method (ii). The hydrazinopyridines are unstable solids that can be purified by sublimation but discolor even on storage at -20 °C. Compounds **4T**, **6A**, and **4,6A** have been discussed in a patent,²¹ but few data were reported. **6A** and **4,6A** exist as azides in the neat liquid state at room temperature. However, all the azide-to-tetrazole isomerizations are exothermic, with the enthalpies of the azides being higher than those of the tetrazoles ($\Delta H^\circ_{\text{isom}} = -13$ to -30 kJ mol⁻¹; $\Delta S^\circ_{\text{isom}} = -50$ to -59 ± 8 J mol⁻¹ K⁻¹), as determined by variable temperature ¹H NMR spectroscopy in DMSO-*d*₆ or CDCl₃ solution.^{1b,22} Thus, the existence of the azides is an entropic effect. For those compounds that exist as azides in the liquid state, the tetrazole isomers were detectable by ¹H and ¹³C NMR spectroscopy in DMSO solution. Conversely, the ring opened azide forms of **5T**, **3,5T**, and **4,5T** were detectable by IR spectroscopy in CHCl₃ solution. The azide corresponding to **5T** was detectable by ¹H NMR in TFA-*d* solution (**5T:5A** = 4.9:1 at 22 °C), and for **3,5T** and **4,5T** the azide forms were also observed in CDCl₃ solution by ¹³C NMR spectroscopy (see Experimental Section). Sublimation of the tetrazoles, usually at 40–50 °C, caused significant ring opening to the azides as revealed by the IR spectra of the Ar matrix isolated materials, except in the case of **4T** which only showed weak azide bands in the 2100 cm⁻¹ region under these conditions (see spectra below). This conversion to azides facilitated the subsequent matrix photolysis, but the tetrazole forms also photolyzed with elimination of N₂.

2. 1,3-Diaza-5-trifluoromethylcyclohepta-1,2,4,6-tetraene (5D). Tetrazole **5T** was sublimed at 40–50 °C and deposited with Ar at 15 K on a BaF₂ disk. The infrared spectrum (Figure 1, negative peaks) demonstrated partial ring opening to the azide **5A** (2155, 2128 cm⁻¹). Photolysis for 6 min with the unfiltered light of a 1000 W high pressure Hg-Xe lamp caused complete consumption of the **5A/5T** mixture and formation of a new compound absorbing strongly at 1997 cm⁻¹ and assigned as the cyclic carbodiimide **5D** (Figure 1, positive peaks, and Scheme 1). This is some 135–160 cm⁻¹ below the normal value for linear carbodiimides.²³ The assignment is based on comparison with previously reported 1,3-diazacyclohepta-1,2,4,6-tetraenes^{9,24} as well as B3LYP/6-31G* calculations, which reproduces the experimental spectra extremely well (Table 1).²⁵

(21) Rogers, R. B.; Gerwick, B. C.; Egli, E. A. US Patent 4,474,599 (1984); *Chem. Abstr.* **1985**, *102*, P45956g.

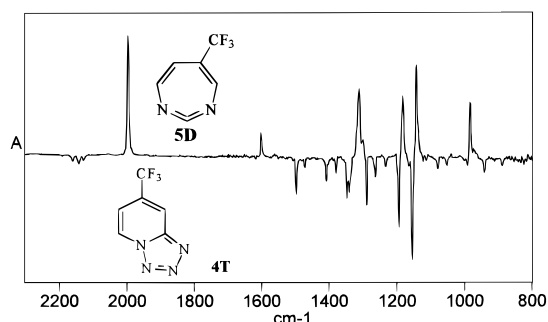
(22) Evans, R. A. PhD Thesis, The University of Queensland, 1992.

(23) IR of open chain carbodiimides: Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*; McGraw-Hill: London, 1995. Palomo, C.; Mestres, R. *Synthesis* **1981**, *5*, 373. Cyclic carbodiimides: Richter, R.; Tucker, B.; Ulrich, H. *J. Org. Chem.* **1983**, *48*, 1694. Molina, P.; Alajarin, M.; Sanchez-Andrada, P.; Elguero, J.; Jimeno, M. L. *J. Org. Chem.* **1994**, *59*, 7306, and references therein.

Table 1. Calculated (B3LYP/6-31G*) and Experimental IR Spectra of **5D**, **4D**, **6D** and Triplet **3,5N**^{a,b}

5D			4D			4,6D			3,5N		
expt freq	calc freq	calc inten	expt freq	calc freq	calc inten	expt freq	calc freq	calc inten	expt freq	calc freq	calc inten
	3119	2		3101	10		3123	1		3121	1
	3103	9		3094	2		3104	2		3073	5
	3078	0		3068	2	2000 s	1991	372		1564	12
1997 s	1987	353	1992 s	1984	357		1619	9		1472	61
	1588	7		1611	7		1558	28		1429	7
	1550	22		1552	9	1337 w	1334	27		1362	3
	1364	10		1354	16		1289	105	1338 w	1321	146
	1286	21	1319 m	1283	18		1288	35		1283	11
1311 m	1278	289	1294 m	1276	242	1280 s	1247	490	1276 s	1241	508
						1277 ^e s					
	1237	35		1229	20		1225	15	1208 m	1196	106
	1177	4	1192 s	1177	202	1200 s	1182	234		1185	79
1184 m	1170	181		1166	11	1190 m	1174	184	1182 m	1167	143
						1186 ^c m					
1143 s	1137	256	1164 s	1158	244	1170 s	1162	227	(1171) ^d m	1164	278
	1021	15	1040 m	1013	128	1150 m	1142	237	1159 m	1152	209
985 m	966	113	1006 w	989	62		1041	12		1141	66
	956	45		922	5	1041 m	1014	143	1075 w-m	1056	64
	919	4		916	12	985 w	968	87	1029 w-m	1008	108
	886	12		880	10		895	2		939	2
	849 ^e	1		831 ^f	3		876 ^g	27		916 ^h	30

^a Frequency in cm^{-1} and intensity in km mol^{-1} . ^b Calculated frequencies scaled by 0.9613 (ref 30). ^c These bands may be due to matrix sites. ^d **3,5A** and **4,6D** both have bands at 1171 cm^{-1} , thus making the assignment of a band at 1171 cm^{-1} for **3,5N** uncertain. ^e No calculated band with intensity $>28 \text{ km mol}^{-1}$ below 849 cm^{-1} . ^f No calculated band with intensity $>33 \text{ km mol}^{-1}$ below 831 cm^{-1} . ^g No calculated band with intensity $>27 \text{ km mol}^{-1}$ below 876 cm^{-1} . ^h No calculated band with intensity $>30 \text{ km mol}^{-1}$ below 916 cm^{-1} .

**Figure 2.** Difference FTIR spectrum (15 K) of **5D** (positive peaks) generated by Ar matrix photolysis of **4T** (negative peaks).

Other prominent bands in the IR spectrum of **5D** are at 1311 m, 1184 m, 1143 s (ν_{CF_3}), and 985 m cm^{-1} .

The same carbodiimide (**5D**) was generated by 20 min broad-band photolysis of tetrazole **4T** (Figure 2). This tetrazole only gave a small amount of azide **4A** on sublimation (Figure 2, negative peaks). The IR spectra of **5D** from the two sources (**5A** and **4T**) were identical, as required by the chemistry depicted in Scheme 1.

Prolonged irradiation of carbodiimide **5D** (30–60 min) resulted in the growth of a small peak at 2066 cm^{-1} concurrent with decomposition of **5D**. The 2066 cm^{-1} signal always remained weak to medium, and no other peak could be correlated with it. On further irradiation with the full light of a 75 W low pressure Hg lamp, a nitrile absorption developed at 2235 cm^{-1} .^{19b} The carrier of the 2066 cm^{-1} signal may be a ketenimine. We have seen such signals in several other cases (see also **4D** and **4,6D** below). The carrier of the 2235 cm^{-1} signal may be a cyanopyrrole in analogy with the results of FVP experiments.^{1b} These secondary photolyses are under further investigation.

3. 1,3-Diaza-4-trifluoromethylcyclohepta-1,2,4,6-tetraene (4D). This compound was again produced from two isomeric

precursors, the azide **6A** and the tetrazole **3T**, the latter tautomerizing in part to **3A** on sublimation/deposition (Scheme 2 and Figures 3 and 4). **6A** was converted completely to **4D** after 12 min of irradiation, giving major bands at 1992 s, 1319 m, 1294 m, 1192 s, 1164 vs (ν_{CF_3}), 1040 m, and 1006 w cm^{-1} (the band at 1294 cm^{-1} is not seen in the difference spectrum, Figure 3, as it is coincident with a stronger band due to the azide **6A**). Again, there is good agreement with B3LYP/6-31G* calculations (Table 1).

4D was likewise obtained from **3T/3A** in 2 min (Figure 4). The same seven bands as above were clearly identified, although the reaction in this case was less clean. Unidentified bands appeared at 1310 m, 1208 m, 1175 m, and 1150 m cm^{-1} on complete conversion of **3T/3A**. They must arise from a reaction of **3T/3A** or the related nitrene or azirine and not from the carbodiimide **4D** since they are not formed from the clean sample of **4D** described above (Figure 3), and they stop developing once **3T/3A** have been fully consumed. A weak signal at 2041 cm^{-1} also appeared, but this grew more slowly and was unrelated to the other species. Except for this case, all the azides/tetrazoles were cleanly and virtually quantitatively converted to cyclic carbodiimides.

Comparison of the four spectra of carbodiimides makes it clear that one carbodiimide is generated from the two precursors in Scheme 1; a different carbodiimide is generated from the two precursors in Scheme 2.

4. 5,6-Bis(trifluoromethyl)-1,3-diazacyclohepta-1,2,4,6-tetraene (5,6D). The tetrazole/azide mixture **4,5T/4,5A** (Scheme 3) was converted after 2 min of broad-band photolysis to the carbodiimide **5,6D** (Figure 5). The latter absorbed at 2010 m , 1336 s , 1307 s , 1183 s , 1167 s (ν_{CF_3}), 991 m , 970 w , and 875 w cm^{-1} . For symmetry reasons, there is only one azide/tetrazole precursor to this molecule.

5. 4,6-Bis(trifluoromethyl)-1,3-diazacyclohepta-1,2,4,6-tetraene (4,6D) and 3,5-bis(trifluoromethyl)-2-pyridylnitrene (3,5N). The carbodiimide **4,6D** was obtainable from two precursors, **4,6A** and **3,5T** (Scheme 4). **4,6A** underwent clean

(24) Wentrup, C.; Thétaz, C.; Tagliaferri, E.; Lindner, H. J.; Kitschke, B.; Winter, H.-W.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 566.

(25) Further calculations on the $\text{C}_5\text{H}_4\text{N}_2$ energy surface and substituted species will be published by Wong, M. W.; Wentrup, C.

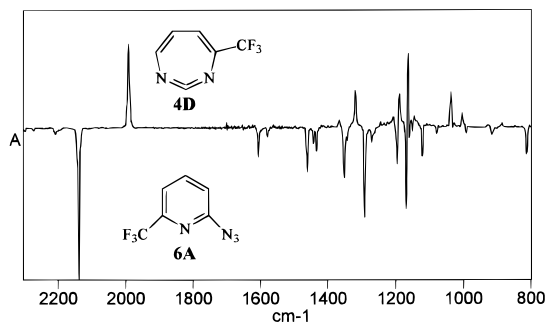


Figure 3. Difference FTIR spectrum (15 K) of **4D** (positive peaks) generated by Ar matrix photolysis of **6A** (negative peaks).

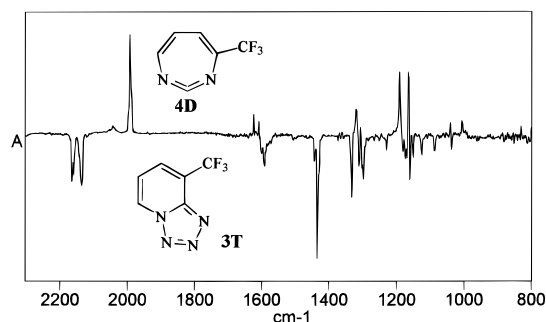
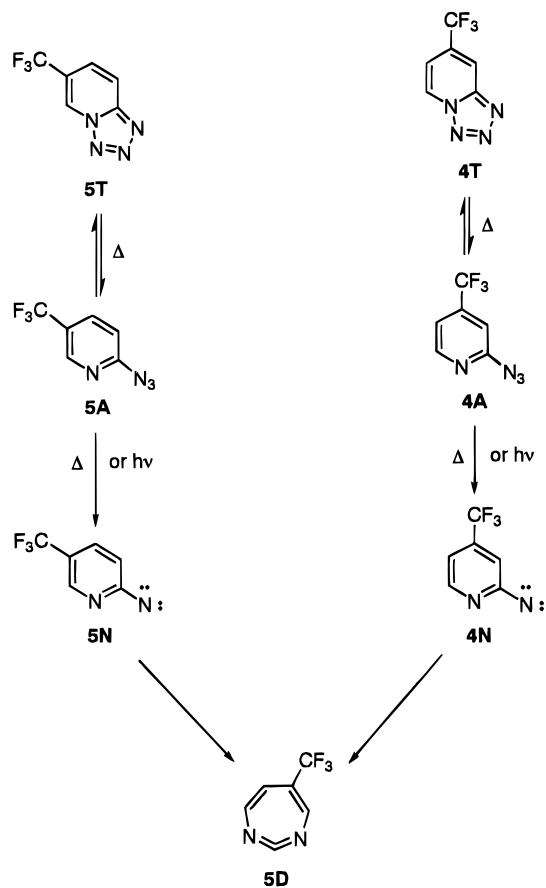


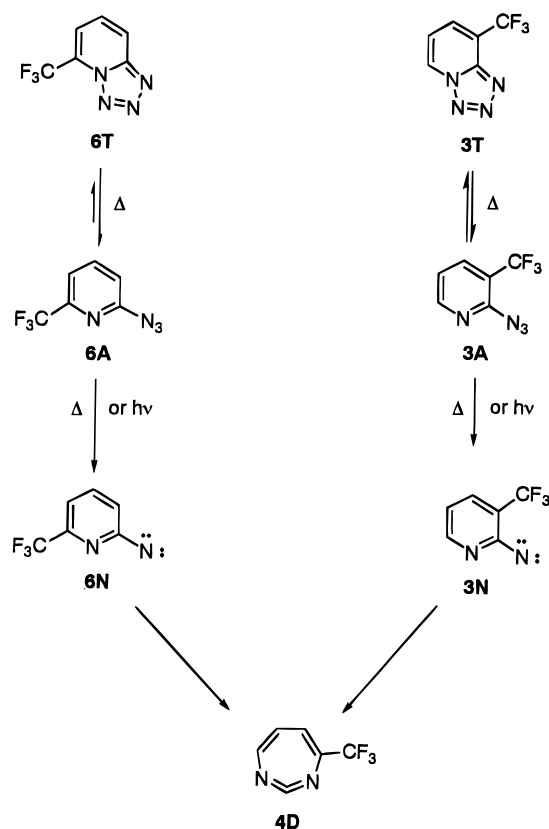
Figure 4. Difference FTIR spectrum (15 K) of **4D** (positive peaks) generated by Ar matrix photolysis of **3A/3T** (negative peaks).

Scheme 1



and complete conversion to the carbodiimide **4,6D** during 6 min of photolysis. This product absorbs at 2000 s, 1279 s, 1277 s, 1200 s, 1190 w, 1186 m, 1171 s, 1151 m (this and four preceding bands ν_{CF}), 1041 m, and 985 w cm^{-1} (Figure 6). The experimental and calculated values are in good agreement (Table 1).

Scheme 2



Scheme 3

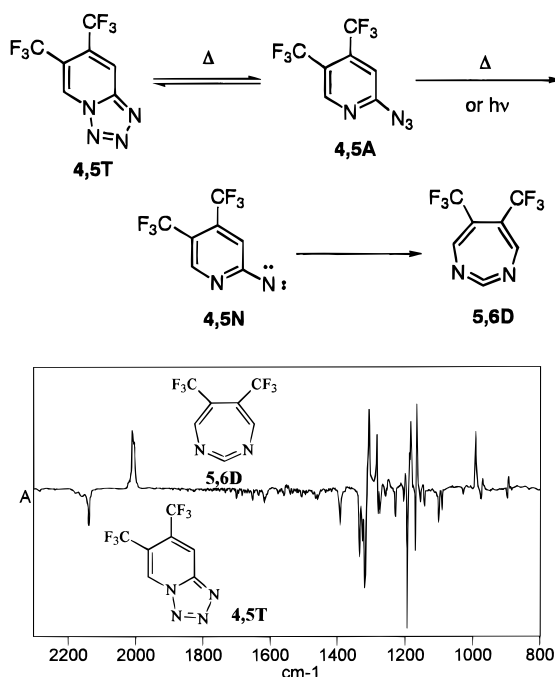


Figure 5. Difference FTIR spectrum (15 K) of **5,6D** (positive peaks) generated by Ar matrix photolysis of **4,5T/4,5A** (negative peaks).

Tetrazole **3,5T** underwent ring opening to azide **3,5A** on sublimation/deposition (Figure 7). Photolysis converted it to the same carbodiimide as above (**4,6D**), but a distinct intermediate was obtained in this process (bands marked B in Figure 7). Continuous broad-band irradiation for 85 min converted the intermediate B fully to the carbodiimide **4,6D** (bands marked C in Figure 7). All the azide/tetrazole **4,6A/4,6T** had been consumed within the first 10–12 min of photolysis, and the

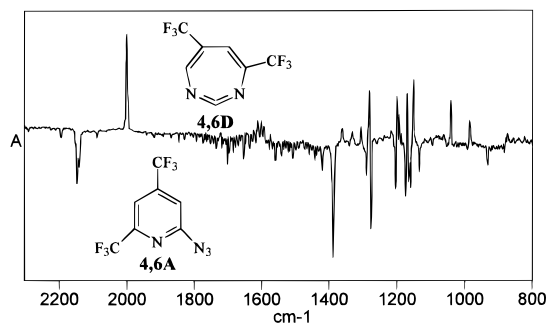
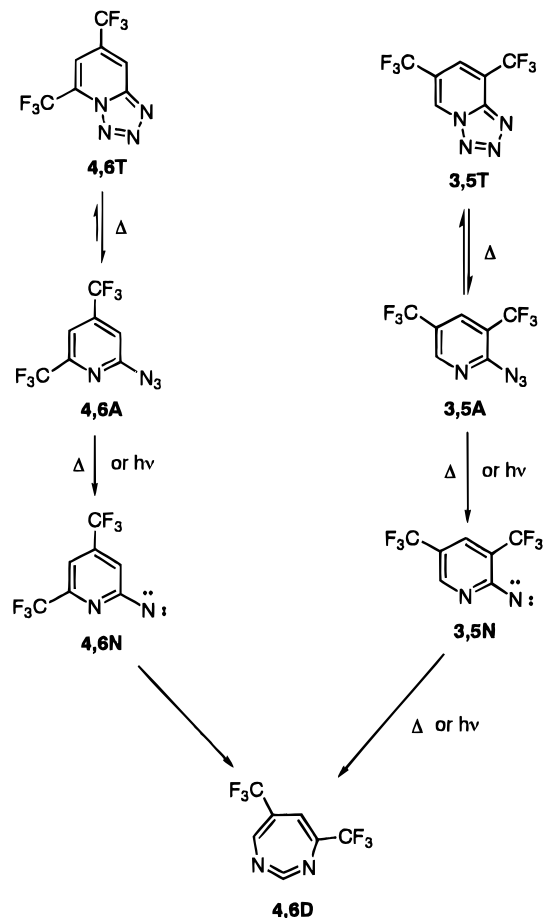


Figure 6. Difference FTIR spectrum (15 K) of **4,6D** (positive peaks) generated by Ar matrix photolysis of **4,6A** (negative peaks).

Scheme 4



bands of intermediate B reached maximum intensity within the first 8–10 min of photolysis. The additional amount of carbodiimide formed during the 85 min of photolysis must therefore come from intermediate B. Difference spectra clearly revealed the disappearance of B in concert with formation of **4,6D**. In addition, the long term irradiation also caused formation of new bands marked X in Figure 7, due to secondary reaction of either B or **4,6D**.

Intermediate B cannot be an azirine of type **9** as such compounds are expected to have IR absorptions in the vicinity of 1750 cm^{-1} .^{5f,15} The nitrene **3,5N** is a likely candidate in analogy with the experiment of Hayes and Sheridan on phenylnitrene.¹⁸ This was confirmed by observation of the ESR spectrum of triplet **3,5N**. For this purpose, **3,5T/3,5A** was deposited at 20 K with Ar on the Cu rod target of an ESR cryostat. Photolysis as above generated a typical aryl nitrene XY_2 signal centered at 7335.5 G (midpoint) ($|D/hc| = 1.108\text{ cm}^{-1}$; $E/hc \approx 0.00$) within the first 5 min of photolysis (see

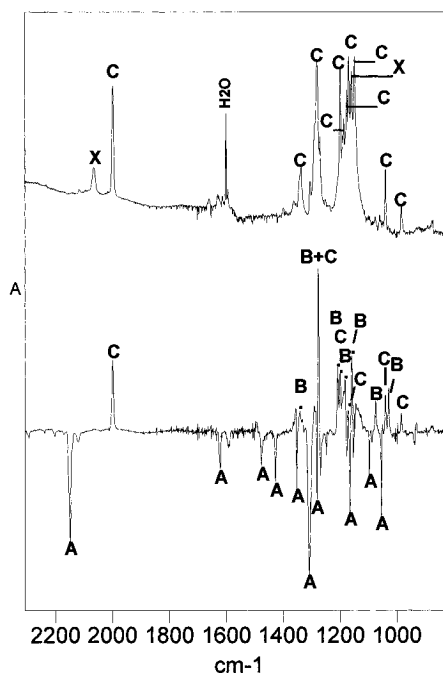


Figure 7. Lower trace: Difference spectrum showing **3,5T/3,5A** (negative peaks, marked A) and a mixture of nitrene **3,5N** (peaks marked B) and **4,6D** (peaks marked C), produced by 5 min photolysis (Ar, 15 K). Upper trace: After 85 min of photolysis; X = unidentified product; C = **4,6D**.

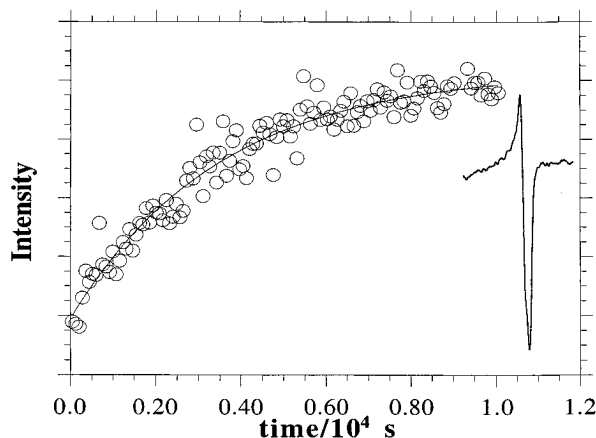


Figure 8. First order decay toward zero intensity of the negative XY_2 ESR signal of **3,5N** during continuous irradiation at 20 K. Inset: the XY_2 signal at 7395.3 G (microwave frequency 9.72779 MHz).

inset in Figure 8). Continuous broad-band irradiation within the ESR cavity caused this signal to decay over a 90 min period, i.e., a time scale very close to that observed for intermediate B by IR spectroscopy under the same conditions. The decay obeyed a first-order rate law with $k \approx 2 \times 10^{-4}\text{ s}^{-1}$ (Figure 8).

The close correspondence between IR and ESR spectroscopic behavior virtually identifies the intermediate B as the triplet nitrene, **3,5N**. Furthermore, the observed IR spectrum is in very good agreement with B3LYP/6-31G* calculated data (Table 1). We assume that the ring expansion **3,5N** \rightarrow **4,6D** takes place on the singlet energy surface and hence it requires intersystem crossing (ISC) to the (not observed) singlet nitrene. It is possible that the ring expansion of singlet **3,5N** is slightly retarded because of steric hindrance by the neighboring CF_3 group, thus making ISC to the triplet ground state more competitive with ring expansion. However, a similar effect was not observed for **3N**.

6. Thermally Produced Nitrenes and Diazacycloheptatetraenes. All the nitrenes described in this study (Schemes 1–4)

Table 2. Zero Field Splitting Parameters of Nitrenes^a

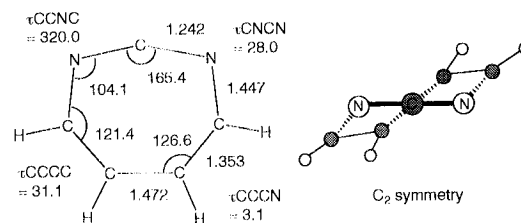
nitrene	$ D/hc $	E/hc
3N	1.0768	0.00
4N	1.0826	0.00
5N	1.0865	0.00
6N	1.0575	0.00
3,5N	1.1080	0.00

^a Ar matrix, 20 K. D/hc and E/hc in cm^{-1} .

have been observed by ESR spectroscopy by irradiation of Ar matrices of the deposited azides/tetrazoles, and they are therefore expected to have triplet ground states. Moreover, the same nitrenes were also generated by flash vacuum thermolysis (FVT) (200–400 °C) of the azides/tetrazoles, deposited in Ar matrices, and observed by ESR spectroscopy. Some D and E values are collected in Table 2. The cyclic carbodiimides **4D**, **5D**, **4,6D**, and **5,6D** were also observed by Ar matrix IR spectroscopy following FVP at 360–410 °C, giving spectra identical with the ones reported above. At FVP temperatures above 450 °C, the carbodiimides were replaced by trifluoromethyl-substituted cyanopyrroles. Details of these rearrangements^{1b} will be the subject of a separate publication.

7. Photochemically Produced Carbenes. From the IR and ESR experiments described above, we know that photolysis produces 1,3-diazacycloheptatetraenes within a few minutes, and triplet nitrenes are formed at the same time. Both of these species are also formed on FVP. Photolysis of the thermally deposited Ar matrices containing a mixture of the triplet nitrenes and the diazacycloheptatetraenes in the cavity of the ESR spectrometer caused development of very weak signals typical of carbenes in some cases. These signals were usually too weak for accurate measurement and assignment but resemble those previously reported for **8** and other 1,3-diazacycloheptatrienylidenes.⁶ For example, photolysis of a matrix containing **3,6N** (observed by ESR) and **4D** (observed by IR in separate experiments) gave weak signals for which zero field splitting parameters $|D/hc| = 0.4501 \text{ cm}^{-1}$ and $|E/hc| = 0.0059 \text{ cm}^{-1}$ were derived. These values are similar to those of **8** and of cycloheptatrienylidene itself and unlikely to be due to pyridyl- or pyrimidylcarbenes.^{6,26} We speculate that the carbenes are the 1,3-diazacycloheptatrienylidenes, generated either by excitation of the singlet 1,3-diazacycloheptatetraenes to the triplet states or by photochemical rearrangement of the triplet nitrene, although further experimentation will be necessary.

8. Computational Results. In order to gain some insight into the structures of the seven-membered ring carbodiimides and the relative energies of the intermediates, ab initio calculations were carried out at the B3LYP/6-31G* level of theory. As with the carbon analogue (1,2,4,6-cycloheptatetraene),²⁷ the

**Figure 9.** Computed structure of 1,3-diazacyclohepta-1,2,4,6-tetraene (**5**) (B3LYP/6-31G*).

cyclic carbodiimide **5** (1,3-diazacyclohepta-1,2,4,6-tetraene) is predicted to have a chiral equilibrium geometry, with C_2 symmetry (Figure 9). The $\text{N}=\text{C}=\text{N}$ bond angle deviates from linearity by just 15° and the CNC angle is rather acute (104°). The corresponding bond angles in the allene moiety of 1,2,4,6-cycloheptatetraene are 146° and 114° , respectively (B3LYP/6-31G*). This suggests that the nitrogen atoms in **5** aid in alleviating the considerably strained cumulenonic bonds. Introduction of one or two CF_3 substituents in **5** (i.e., compounds **4D**, **5D**, **4,6D**, and **5,6D**) leads to small changes in the molecular geometry (see supporting information).

The parent 2-pyridylnitrene (**4**) is predicted to have a triplet ground state and a substantial singlet triplet gap. The bicyclic azirine is calculated to be a stable equilibrium structure, *ca.* 53 kJ mol^{-1} above the cyclic carbodiimide **5**, but the barrier toward ring opening to **5** is only *ca.* 14 kJ mol^{-1} , thus making this azirine virtually unobservable. **5** lies slightly below the triplet nitrene. For the CF_3 -substituted systems, the carbodiimides are also calculated to be the most stable species. For instance, the bis- CF_3 -substituted carbodiimide **4,6D** is predicted to lie 19 kJ mol^{-1} below the triplet nitrene **3,5N**.²⁵ Finally, we note that the calculated B3LYP/6-31G* IR spectra for the carbodiimides and nitrene (Table 1) are in very good agreement with experiment. In particular, the calculated B3LYP frequencies for the triplet nitrene **3,5N** are significantly better than those predicted at the UHF/6-31G* level.

Conclusion

1,3-Diazacyclohepta-1,2,4,6-tetraenes **4D**, **5D**, **5,6D**, and **4,6D** are formed very efficiently and rapidly on UV photolysis of the corresponding azide and/or tetrazole precursors. The corresponding triplet nitrenes are observable by ESR spectroscopy both under matrix photolysis and under flash vacuum thermolysis conditions (**4N**, **5N**, **6N**, **3N**, and **3,5N**). Nitrene **3,5N** was also observed by IR spectroscopy; it decayed in the course of *ca.* 90 min on broad-band UV irradiation with concomitant formation of the diazacycloheptatetraene **4,6D** as observed by IR spectroscopy. The nitrene decay took place in the same time interval when monitored under the same photochemical conditions by ESR spectroscopy ($k \cong 2 \times 10^{-4} \text{ s}^{-1}$). Photolysis of the mixtures of triplet nitrenes and diazacycloheptatetraenes also produced very weak carbene signals in the ESR spectra, tentatively assigned to 1,3-diazacycloheptatrienylidenes.

(26) (a) It has been shown that the ESR spectrum reported by Chapman and McMahon^{26b} was incorrectly assigned to cycloheptatrienylidene.^{26c,d} Although treatment of tropone tosylhydrazone with *n*-BuLi, followed by thermolysis, yields an isolable diazo compound,^{26b} it is now clear that the diazo compound is *not* diazocycloheptatriene. The material obtained by reaction of tropone tosylhydrazone with *n*-BuLi does not regenerate tropone tosylhydrazone on hydrolysis, nor does it produce an appreciable quantity of heptafulvalene on thermolysis or photolysis.^{26c} In contrast, the tropone tosylhydrazone salts prepared with NaH or LiH indeed regenerate tropone tosylhydrazone on hydrolysis and produce heptafulvalene on thermolysis and photolysis.^{26c} Thermolysis/matrix deposition of these Na or Li salts directly onto the ESR cold tip, followed by photolysis, provided Kuzaj, Lüerssen, and Wentrup with triplet cycloheptatrienylidene.⁶ (b) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1986**, *108*, 1713. (c) Blanch, R. J. Ph.D. Thesis, The University of Queensland, Brisbane, 1991. Blanch, R. J.; Wentrup, C. To be published. (d) Chapman, O. L. Personal communication, 1989. McMahon, R. J. Personal communication, 1995.

(27) For example, see: (a) Waali, E. E. *J. Am. Chem. Soc.* **1981**, *103*, 3604. (b) Radom, L.; Schaefer, H. F.; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411. (c) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535. (d) Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* Submitted. Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* Submitted.

Experimental and Computational Section

Calculations. Density functional calculations were carried out using the Gaussian 92/DFT series of programs.²⁸ Geometry optimizations were performed at the B3LYP/6-31G* level.^{29,30} The B3LYP formulation³⁰ of density functional theory corresponds to Becke's three-parameter exchange functional^{30a} in combination with the Lee–Yang–Parr correctional functional.^{30b} Harmonic frequencies and infrared intensities were determined at these optimized geometries. The directly calculated frequencies were scaled by a factor of 0.9613 to account for the overestimation of vibrational frequencies at this level of theory.³¹ Improved relative energies were obtained through B3LYP/6-311+G** calculations,^{29,30} based on the B3LYP/6-31G* optimized geometries.

General Experimental Apparatus. ¹H and ¹³C NMR spectra were recorded on a JEOL GX-400, mass spectra on a Kratos MS25RFA, ESR spectra on a Bruker ER2000, UV spectra on a Varian Cary 1, and FTIR spectra on a Perkin Elmer 1720X spectrometer, the latter with 1 cm⁻¹ resolution. Photolyses were carried out using a Hanovia 1000 W high-pressure Xe-Hg lamp equipped with a 150 mm water filter and a monochromator or cutoff filters if required. Matrix isolation used Ar (99.999%) and an Air Products Displex DE202 cryostat for ESR or IR spectroscopy. A Leybold-Heraeus ROK 10-300 cryostat was also used for IR spectroscopy. FVP equipment was as previously described.³² The 1,3-diazacycloheptatetraenes were stable enough for direct isolation at 77 K, without any matrix host, and a liquid N₂ cooled cryostat equipped with BaF₂ windows was used for this purpose. The inner targets for matrix deposition were BaF₂ for all IR spectra and electrolytically refined Cu for ESR spectroscopy. Ar matrices were deposited at temperatures between 12 and 23 K, and spectra were recorded at the lowest accessible temperature (10–14 K).

General Procedure for the Synthesis of 2-Hydrazinopyridines. The appropriate mono- or bis(trifluoromethyl)-2-chloropyridine (Ishihara Sangyo Kaisha, Tokyo, or Maybridge, UK) (ca. 0.08 mol) was added to a large excess of hydrazine hydrate (Ajax Chemicals) (ca. 70 mL), and the mixture was gently heated. Enough ethanol (40 mL) was added to make the solution homogeneous and the solution was gently refluxed (2–3 h) until TLC analysis (silica gel/chloroform) showed none of the starting 2-chloropyridine remained. When the reaction was complete, the heat was removed, and as much water and excess hydrazine was removed in vacuo as possible. The resultant slurry was cooled and extracted with ether (3 × 150 mL). The combined ether extracts were dried (MgSO₄) and evaporated to give a solid, the crude 2-hydrazinopyridine. The 2-hydrazinopyridines were purified by gentle sublimation (ca. 40 °C, 10⁻⁴ mbar). They were all unstable compounds and readily discolored in a few hours after purification. Refrigeration at -20 °C slowed decomposition/decoloration but did not prevent it.

Caution: The 2-hydrazinopyridines have significant vapor pressure at atmospheric pressure and may be toxic. Inhalation of their vapor may cause nausea for some hours. 2-Hydrazino-4-trifluoromethylpyridine was particularly potent.

2-Hydrazino-5-trifluoromethylpyridine: wax-like white solid; yield 88%; mp 62–63 °C. ¹H NMR (CDCl₃) δ 8.32 (br s, 1H, H(C-6)), 7.59 (dd, ³J = 8.9 Hz, ⁴J = 2.4 Hz, 1H, H(C-3/4)), 6.95 (br s, 1H, NH), 6.74 (d, ³J = 8.9 Hz, 1H, H(C-4/3)), 3.79 (br s, 2H, NH₂); ¹³C NMR (CDCl₃, H coupled), δ 162.9 (br s, C2), 145.5 (dq, ¹J(CH) = 181.0 Hz, ³J(CF) = 4.0 Hz, C6), 134.5 (dq, ¹J(CH) = 166.0 Hz, ³J(CF) = 3.4 Hz, C4), 124.4 (q, ¹J(CF) = 270.2 Hz, C7), 116.6 (q, ²J(CF) = 32.9 Hz, C5), 105.9 (d, ¹J(CH) = 168.1 Hz, C3); IR (KBr) 3303 m,

br, 1625 s, 1577 w, 1526 m, 1332 vs, 1193, 1110 s, 1077 m, 1003 w, 936 m, 822 s sh, 507 w cm⁻¹; HRMS *m/z* 177.0516 (C₆H₆F₃N₃ requires 177.05138).

2-Hydrazino-4-trifluoromethylpyridine: This compound was particularly unstable and decomposed even when stored at -30 °C: wax-like white solid; yield 70%; mp 38 °C. ¹H NMR (CDCl₃) δ 8.24 (d, ³J = 5.4 Hz, 1H, H6), 7.01 (br s, 1H, H3), 6.84 (dm, ³J = 5.39 Hz, 1H, H5), 6.27 (br s, 1H, NH), 3.84 (br s, 2H, NH₂); ¹³C NMR (CDCl₃) δ 161.7 (C2), 148.9 (C6), 139.8 (q, ²J(CF) = 33.6 Hz, C4), 123.0 (q, ¹J(CF) = 273.0 Hz, C7), 109.3 (q, ³J(CF) = 3.7 Hz, C5), 102.6 (q, ³J(CF) = 4.3 Hz, C3); IR (KBr) 3316 m br, 1620 m, 1575 m, 1449 m, 1337 s, 1129 vs, 1083 m, 984 w, 882 m, 816 m, 670 sh m cm⁻¹; HRMS *m/z* 177.0535 (C₆H₆F₃N₃ requires 177.05138).

2-Hydrazino-6-trifluoromethylpyridine: wax-like white solid; yield 65%; mp 53 °C. ¹H NMR (CDCl₃) δ 7.56 (apparent t, *J* = ca. 7–8 Hz, 1H, H4), 6.98 (d, ³J = 7.0 Hz, 1H, H5), 6.90 (d, ³J = 8.6 Hz, 1H, H3), 6.40 (br s, 1H, NH), 3.86 (br s, NH₂); ¹³C NMR (CDCl₃) δ 161.2 (C2), 146.0 (q, ²J(CF) = 31.6 Hz, C6), 138.2 (C4), 121.6 (q, ¹J(CF) = 273.6 Hz, C7), 110.4 (q, ³J(CF) = 3.4 Hz, C5), 110.4 (q, ³J(CF) = 1.3 Hz, C3); IR (KBr) 3377 m sh, 3275 m, 1648 m, 1608 m, 1470 m, 1363 s, 1277 s, 1190 s, 1130 vs, 1099 s, 1073 m, 986 m, 932 w, 886 w, 804 s cm⁻¹. HRMS *m/z* 177.0514 (C₆H₆F₃N₃ requires 177.05138).

2-Hydrazino-3-trifluoromethylpyridine: wax-like white solid; yield 64%; mp 71–73 °C. ¹H NMR (CDCl₃) δ 8.32 (br d, ³J = 4.8 Hz, 1H, H6), 7.58 (dm, ³J = 7.7 Hz, 1H, H4), 6.61 (ddm, ³J(H5,H4) = 7.5 Hz, ³J(H5,H6) = 4.8 Hz, 1H, H5), 6.51 (br s, 1H, NH), 4.03 (br s, 2H, NH₂); ¹³C NMR (CDCl₃) δ 156.3 (q, ³J(CF) = 1.4 Hz, C2), 151.1 (C6), 134.9 (q, ³J(CF) = 4.7 Hz, C4), 123.9 (q, ¹J(CF) = 271.6 Hz, C7), 112.5 (C5), 108.4 (q, ²J(CF) = 32.3 Hz, C3); IR (KBr) 3303 br m, 1613 m, 1583 m, 1508 m, 1471 s, 1435 m, 1309 s, 1151 m, 1110 vs, 1030 s, 767 m, 488 w cm⁻¹; HRMS *m/z* 177.0516 (C₆H₆F₃N₃ requires 177.05138).

2-Hydrazino-4,6-bis(trifluoromethyl)pyridine: wax-like white solid; yield 80%; mp 79–80 °C. ¹H NMR (CDCl₃) δ 7.34 (s, 1H, H5), 7.31 (br s, 1H, NH), 7.15 (s, 1H, H3), 3.95 (br s, 2H, NH₂); ¹³C NMR (CDCl₃, H coupled) δ 162.0 (d, ²J(CH) = 6.0 Hz, C2); 147.5 (q, ²J(CF) = 35.0 Hz, C6), 141.0 (q, ²J(CF) = 34.3 Hz, C4); 122.4 (qt, ¹J(CF) = 272.9 Hz, ³J(CH) = 4.0 Hz, C7), 121.0 (qd ¹J(CF) = 273.6 Hz, ³J(CH) = 3.0 Hz, C8), 106.4 (dq, ¹J(CH) = 168.7 Hz, ³J(CF) = 3.4 Hz, C3), 105.6 (d of sept, ¹J(CH) = 172.1 Hz, ³J(CF) = 3.4 Hz, C5); IR (KBr) 3265 br m, 1660 m, 1587 w, 1465 m, 1396 m, 1297 m, 1278 vs, 1185 vs, 1149 s, 1112 s, 952 m, 931 m, 896 m, 856 m, 846 m, 685 s cm⁻¹; HRMS *m/z* 245.0389 (C₇H₅F₆N₃ requires 245.03877).

General Procedure for the Synthesis of Tetrazolo[1,5-*a*]pyridines/2-Azidopyridines from 2-Hydrazinopyridines. The appropriate mono- or bis(trifluoromethyl)-2-hydrazinopyridine (ca. 0.034 mol) was added to 20 mL of water, and enough concentrated hydrochloric acid (ca. 5 mL) was added to give the solution of pH of ca. 1. The solution was then cooled to 0–5 °C and a precooled solution of 2.5 g (0.036 mol) of sodium nitrite in 10 mL of water was added dropwise. Mild frothing generally occurred on the addition of each drop.

The tetrazoles **5T**, **4T**, and **3T** precipitated from the solutions as formed. The precipitate was collected, dried, and readily purified by sublimation.

The 2-azidopyridines **6A** and **4,6A** separated as oils. After the complete addition of the sodium nitrite solution, the reaction mixture was extracted with ether (3 × 20 mL). The extracts were dried and evaporated to give the crude 2-azidopyridines. These were purified by vacuum distillation using a Büchi Kugelrohr apparatus.

6-Trifluoromethyltetrazolo[1,5-*a*]pyridine (5T/5A): white solid; purified by sublimation (90 °C (melt), 0.05 mbar); yield 61%, mp 67 °C. ¹H NMR (CDCl₃) δ 9.29 (br s, 1H, H5), 8.25 (apparent d, ³J(H8,H7) = 10.2 Hz, 1H, H8), 7.90 (dd, ³J(H7,H8) = 10.0 Hz, ⁴J(H7,H5) = 1.9 Hz, 1H, H7); ¹H NMR (TFA-*d*), tetrazole isomer **5T**: δ 9.26 (1H, H5), 8.32 (d, ³J(H8,H7) = 8.72 Hz, 1H, H8), 8.07 (d, ³J(H7,H8) = 8.72 Hz, 1H, H7); azide isomer **5A**: δ 8.63 (s, 1H, H6), 8.56 (d ³J(HH) = 8 Hz, 1H), 7.84 (d, ³J(HH) = 8 Hz, 1H); ratio tetrazole:azide **5T:5A** (22 °C) = 4.9:1. ¹³C NMR (CDCl₃) δ 148.8 (C8a), 128.3 (q, ³J(CF) = 24 Hz, C7), 124.7 (q, ³J(CF) = 5.5 Hz, C5), 122.1 (q, ¹J(CF) = 272.2 Hz, C9), 117.2 (C8). Selected irradiation

(28) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92/DFT, Gaussian Inc.: Pittsburgh, PA, 1993.

(30) (a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(31) Wong, M. W. *Chem. Phys. Lett.* Submitted.

(32) Kappe, C. O.; Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1995**, *60*, 1686.

of H7 (δ 7.90) in the proton coupled ^{13}C NMR spectrum revealed (i) no $^1\text{J}(\text{CH})$ coupling for $^3\text{J}(\text{CF})$ quartet at δ 128.8 (C7); (ii) $^1\text{J}(\text{CH})$ coupling for $^3\text{J}(\text{CF})$ quartet at δ 124.7 (C5), and (iii) $^1\text{J}(\text{CH})$ coupling for singlet at 117.2 (C8); ^{13}C NMR (TFA-*d*), tetrazole isomer 5T: δ 150.5 (C8a), 135.5 br s, C7), 128.7 (q, $^3\text{J}(\text{CF}) = 5.4$ Hz, C5), 127.4 (q, $^2\text{J}(\text{CF}) = 37.0$ Hz, C6), 124.9 (q, $^1\text{J}(\text{CF}) = 272.2$ Hz, C9), 117.2 (C8); azide isomer 5A: δ 158.6 (s, C2), 148.3 (q $^3\text{J}(\text{CF}) = 2.7$ Hz, C6), 141.2 (br s, C4?), 121.4 (s, C3), other C not observed above baseline noise; IR (KBr) 3091 w, 3034 m, 1650 m, 1552 w, 1333 vs, 1293 m, 1186 s, 1169 s, 1150 s, 839 m, 683 m, 583 cm^{-1} ; mass spectrum (E.I.) m/z 188 (43%, M^+), 160 (100, $\text{M}^+ - \text{N}_2$), 141 (32), 140 (41), 113 (10), 91 (14), 69 (41), 64 (32); HRMS m/z 188.0313. ($\text{C}_6\text{H}_3\text{F}_3\text{N}_4$ requires 188.03098). Anal. Calc. for $\text{C}_6\text{H}_3\text{F}_3\text{N}_4$: C, 38.30; H, 1.60; N, 29.80. Found: C, 38.08; H, 1.51; N, 30.19.

7-Trifluoromethyltetrazolo[1,5-*a*]pyridine (4T): white solid; purified by sublimation (50 °C, 0.05 mbar); yield 83%; mp 56 °C. ^1H NMR (CDCl_3) δ 9.07 (d, $^3\text{J}(\text{H}_5, \text{H}_6) = 7.3$ Hz, 1H, H5), 8.41 (br s, 1H, H8), 7.49 (dd, $^3\text{J}(\text{H}_6, \text{H}_5) = 7.3$ Hz, $^4\text{J}(\text{H}_6, \text{H}_8) = 1.6$ Hz, 1H, H6); ^{13}C NMR (CDCl_3) δ 147.7 (s, C8a), 134.0 (q, $^2\text{J}(\text{CF}) = 35.4$ Hz, C7), 127.0 (C5), 121.8 (q, $^1\text{J}(\text{CF}) = 273.4$ Hz, C9), 114.1 (q, $^3\text{J}(\text{CF}) = 4.9$ Hz, C8), 112.7 (q, $^3\text{J}(\text{CF}) = 2.7$ Hz, C5); selected irradiation of H6 (δ 7.49) in the proton coupled ^{13}C NMR spectrum revealed (i) $^1\text{J}(\text{CH})$ coupled for singlet at δ 127.0 (C5), (ii) $^1\text{J}(\text{CH})$ coupling for $^3\text{J}(\text{CF})$ quartet at δ 114.1 (C8), and (iii) no $^1\text{J}(\text{CH})$ coupling for quartet at δ 112.7 (C6); IR (KBr) 3091 m, 3034 m, 1650 m, 1551 w, 1333 vs, 1186 vs, 1094 m, 1055 m, 839 m, 683 m, 583 m, 456 cm^{-1} ; mass spectrum (E.I.) m/z 188 (48%, M^+), 169 (6, $\text{M}^+ - \text{F}$), 160 (100, $\text{M}^+ - \text{N}_2$), 141 (18, $\text{M}^+ - \text{N}_2 - \text{F}$), 140 (26), 133 (8), 91 (13), 69 (32), 64 (28); HRMS m/z 188.0318 ($\text{C}_6\text{H}_3\text{F}_3\text{N}_4$ requires 188.03098). Anal. Calc for $\text{C}_6\text{H}_3\text{F}_3\text{N}_4$: C, 38.30; H, 1.60; N, 29.80. Found: C, 37.98; H, 1.44; N, 30.13.

2-Azido-6-trifluoromethylpyridine (6A)/(6T): clear oil; purified by Kugelrohr distillation (50 °C, 0.01 mbar); yield 31%; ^1H NMR (CDCl_3) δ 7.8 (apparent t, $^3\text{J}(\text{HH}) = 7.9$ Hz, 1H, H4), 7.42 (d, $^3\text{J}(\text{H}_5, \text{H}_4) = 7.3$ Hz, 1H, H5), 6.98 (d, $^3\text{J}(\text{H}_3, \text{H}_4) = 7.9$ Hz, 1H, H3); ^1H NMR ($\text{DMSO-}d_6$), tetrazole isomer 6T; δ 8.57 (dd, $^3\text{J}(\text{H}_8, \text{H}_7) = 8.9$ Hz, $^4\text{J}(\text{H}_8, \text{H}_6) = 0.6$ Hz, H8), 8.05 (m, obscured by azide isomer, H7?), 7.99 (d?, obscured by azide isomer, H6); azide isomer 6A: δ 8.05 (apparent t, obscured by tetrazole isomer, H4), 7.65 (d, $^3\text{J}(\text{H}_5, \text{H}_4) = 7.6$ Hz, 1H, H5), 7.24 (d, $^3\text{J}(\text{H}_3, \text{H}_4) = 8.3$ Hz, 1H, H3); ratio tetrazole: azide 6T:6A (22 °C) = 1:2.3; ^{13}C NMR (CDCl_3), azide isomer 6A: δ 155.3 (C2), 147.4 (q, $^2\text{J}(\text{CF}) = 35.0$ Hz, C6), 139.8 (C4), 121.0 ($^1\text{J}(\text{CF}) = 273.6$ Hz, C7), 117.1 (C3), 116.4 (q, $^3\text{J}(\text{CF}) = 3.4$ Hz, C5); selected irradiation of H3 (δ 6.98) in proton coupled ^{13}C NMR spectrum revealed (i) $^1\text{J}(\text{CH})$ coupling for singlet (C4), (ii) no $^1\text{J}(\text{CH})$ for singlet at δ 117.1 (C3), and (iii) $^1\text{J}(\text{CH})$ coupling for $^3\text{J}(\text{CF})$ quartet at δ 116.4 (C5). ^{13}C NMR ($\text{DMSO-}d_6$), tetrazole isomer 6T: δ 149.0 (C8a), 132.5 (C7), 124.6 (q, $^2\text{J}(\text{CF}) = 39.0$ Hz, C5), 120.2 (C8), 119.4 (q, $^1\text{J}(\text{CF}) = 272.9$ Hz, C9), 117.9 (q, $^3\text{J}(\text{CF}) = 4.7$ Hz, C6); azide isomer 6A: δ 154.3 (C2), 145.6 (q, $^2\text{J}(\text{CF}) = 35.0$ Hz, C6), 141.5 (s, C4), 121.0 (q, $^1\text{J}(\text{CF}) = 274.1$ Hz, C7), 117.9 C3; 117.2 (q, $^3\text{J}(\text{CF}) = 2.7$ Hz, C5); selected irradiation of H8 (δ 8.57, tetrazole isomer) in coupled ^{13}C NMR spectrum revealed (omitting azide isomer) (i) $^1\text{J}(\text{CH})$ coupling for singlet at δ 132.5 (C7), (ii) no $^1\text{J}(\text{CH})$ for singlet at δ 120.2 (C8), and (iii) $^1\text{J}(\text{CH})$ coupling for $^3\text{J}(\text{CF})$ quartet at 117.9 (C6); IR (CHCl_3) 2135 vs, 1603 m, 1459 m, 1347 m, 1288 s, 1216 vs, 1193 m, 1150 m, 813 w cm^{-1} ; IR (KBr) 2198 w, 2133 vs, 1604 m cm^{-1} ; mass spectrum (E.I.) m/z 188 (38%, M^+), 160 (100, $\text{M}^+ - \text{N}_2$), 141 (21, $\text{M}^+ - \text{N}_2 - \text{F}$), 140 (20), 131 (13), 113 (11), 69 (100); HRMS m/z 188.0309 ($\text{C}_6\text{H}_3\text{F}_3\text{N}_4$ requires 188.03098).

8-Trifluoromethyltetrazolo[1,5-*a*]pyridine (3T): white solid; purified by sublimation (90 °C, 0.05 mbar); yield 85%; mp 99 °C; ^1H NMR (CDCl_3) δ 9.10 (d, $^3\text{J}(\text{H}_5, \text{H}_6) = 6.6$ Hz, 1H, H5), 8.10 (dm, $^3\text{J}(\text{H}_7, \text{H}_6) = 7.3$ Hz, 1H, H7), 7.47 (apparent t, $^3\text{J}(\text{HH}) = 7.0$ Hz, 1H, H6); ^{13}C NMR (CDCl_3) δ 145.2 (C8a), 130.6 (q, $^3\text{J}(\text{CF}) = 4.7$ Hz, C7), 128.8 (C5), 121.4 (q, $^1\text{J}(\text{CF}) = 272.2$ Hz, C9), 119.0 (q, $^2\text{J}(\text{CF}) = 37.0$ Hz, C8), 115.6 (C6); IR (KBr) 3129 m, 3057 m, 1634 m, 1583 m, 1496 m, 1428 m, 1364 s, 1321 s, 1249 m, 1239 m, 1187 m, 1164 m, 1139 vs, 1096 s, 1047 m, 1002 m, 990 m, 984 m, 959 m, 809 w cm^{-1} ; mass spectrum (E.I.) m/z 188 (55%, M^+), 160 (100, $\text{M}^+ - \text{N}_2$), 141 (17, $\text{M}^+ - \text{N}_2 - \text{F}$), 140 (18), 113 (7), 91 (7), 69 (41); HRMS m/z 188.0310 ($\text{C}_6\text{H}_3\text{F}_3\text{N}_4$ requires 188.03098).

2-Azido-4,6-bis(trifluoromethyl)pyridine (4,6A)/(4,6T): clear oil; purified by Kugelrohr distillation (50 °C, 0.15 mbar); yield 49%; ^1H NMR (CDCl_3) δ 7.60 (s, 1H, H5), 7.20 (s, 1H, H3); ^1H NMR ($\text{DMSO-}d_6$), tetrazole isomer 4,6T: δ 9.29 (s, 1H, H8), 8.40 (s, 1H, H6); azide isomer 4,6A: δ 8.00 (s, 1H, H5), 7.70 (s, 1H, H3), ratio tetrazole: azide 4,6T:4,6A (22 °C) 1:9.8; ^{13}C NMR (CDCl_3), tetrazole isomer 4,6A: δ 156.9 (C2); 149.0 (q, $^2\text{J}(\text{CF}) = 36.3$ Hz, C6), 142.7 (q, $^2\text{J}(\text{CF}) = 35.0$ Hz, C4), 121.8 (q, $^1\text{J}(\text{CF}) = 273.6$ Hz, C8), 120.4 (q, $^1\text{J}(\text{CF}) = 274.9$ Hz, C7), 113.4 (q, $^3\text{J}(\text{CF}) = 3.0$ Hz, C3), 112.3 (sept., $^3\text{J}(\text{CF}) = 3.4$ Hz, C5); selected irradiation of H3 (δ 7.25) in proton coupled ^{13}C NMR spectrum revealed (i) no $^1\text{J}(\text{CH})$ coupling for $^3\text{J}(\text{CF})$ quartet at δ 113.4 (C3), and (ii) $^1\text{J}(\text{CH})$ coupling for $^3\text{J}(\text{CF})$ septet at 112.3 (C5). ^{13}C NMR ($\text{DMSO-}d_6$), tetrazole isomer 4,6T: δ 149.0 (C8a), 132.2 (q, $^2\text{J}(\text{CF}) = 35.6$ Hz, C7), 126.3 (q, $^2\text{J}(\text{CF}) = 39.7$ Hz, C5), 122.0 (q, $^1\text{J}(\text{CF}) = 272.9$ Hz, C9), 121.9 (q, $^1\text{J}(\text{CF}) = 258.1$ Hz, C10), 119.8 (q, $^3\text{J}(\text{CF}) = 4.7$ Hz, C8), 113.9 (br s, C6); azide isomer 4,6A: δ 156.1 (C2), 147.2 (q, $^2\text{J}(\text{CF}) = 35.6$ Hz, C6), 141.5 (q, $^2\text{J}(\text{CF}) = 34.3$ Hz, C4), 121.7 (q, $^1\text{J}(\text{CF}) = 273.6$ Hz, C8) (q, $^1\text{J}(\text{CF}) = 274.3$ Hz, C7), 114.7 (q, $^3\text{J}(\text{CF}) = 3.0$ Hz, C3), 113.1 (br s, C5); selected irradiation of H8 (δ 9.29) of the tetrazole isomer 4,6T in proton coupled ^{13}C NMR spectrum revealed no $^1\text{J}(\text{CH})$ coupling for the $^3\text{J}(\text{CF})$ coupled quartet at δ 119.8, thus confirming ^1H NMR assignments. IR (KBr) 2187 w and 2142 s, 1624 m, 1585 w, 1440 m, 1380 vs, 1286 s, 1274 s, 1274 s, 1149 s, 1096 m, 989 m, 930 m, 885 m, 845 m, 713 m, 686 m, sh cm^{-1} ; IR (CHCl_3) 2187 m, 2141 vs, 1623 m, 1585 m, 1450 m, 1439 m, 1417 m, 1383 vs, 1275 vs, 1096 m, 1047 m, 989 m, 930 s, 885 s, 848 m cm^{-1} . Sample was too volatile to allow standard E.I. mass spectrum to be obtained. GC-mass spectrum (E.I.) m/z 256 (8, M^+), 228 (27, $\text{M}^+ - \text{N}_2$), 209 (4), 189 (17), 159 (8), 69 (100).

General Procedure for the Bis(Synthesis of the Bis(trifluoromethyl)tetrazolo[1,5-*a*]pyridines/2-Azidopyridines. The appropriate 2-chlorobis(trifluoromethyl)pyridine (*ca* 9.2 g; 0.037 mol) was dissolved in 36 mL of DMF (AR grade, Ajax Chemicals) and 2 \times 3 g (total 0.09 mol) of sodium azide was added slowly over 1 h. The mixture was stirred overnight at 70 °C. The solution was then cooled and slowly added, with vigorous stirring, to 150 mL of ice-cold water. The resultant precipitate was collected and washed thoroughly with water, air dried, and further purified by sublimation.

6,8-Bis(trifluoromethyl)tetrazolo[1,5-*a*]pyridine (3,5T)/(3,5A): white solid, purified by sublimation (100 °C (melt), 0.1 mbar); yield 48%; mp 97–98 °C; ^1H NMR (CDCl_3), tetrazole isomer 3,5T: δ 9.40 (s, 1H, H5), 8.13 (s, 1H, H7); azide isomer 3,5A: δ 8.71 (s, 1H, H6), 8.08 (s, 1H, H4) ratio tetrazole: azide (22 °C) 3.2:1.

^{13}C NMR (CDCl_3) tetrazole isomer 3,5T: δ 145.5 (C8a), 127.9 (q, $^3\text{J}(\text{CF}) = 5.4$ Hz, C5); 127.0 (m, C7), 121.6 (q, $^1\text{J}(\text{CF}) = 272.9$ Hz, C10/C9), 120.7 (q, $^1\text{J}(\text{CF}) = 273.6$ Hz, C9/C10), 120.6 ($^2\text{J}(\text{CF}) = 37.7$ Hz, C8/C6), 120.5 ($^2\text{J}(\text{CF}) = 37.7$ Hz, C6/C8); azide isomer 3,5A: δ 155.8 (C2), 149.0 (q, $^2\text{J}(\text{CF}) = 4.0$ Hz, C6), 133.8 (C4), 122.8 (q, $^1\text{J}(\text{CF}) = 271.6$ Hz, C7/C8), 122.6 (q, $^2\text{J}(\text{CF}) = 35.0$ Hz, C5), 121.4 (q, $^1\text{J}(\text{CF}) = 271.0$ Hz, C8/C7), 115.9 (q, $^2\text{J}(\text{CF}) = 4.3$ Hz, C3); IR (KBr) 3109 m, 3073 w, 1657 m, 1591 m, 1386 m, 1360 m, 1339 m, 1279 vs, 1139 s, 1074 s, 974 m, 898 m, 779 m, 733 m, 704 m, 657 m cm^{-1} ; IR (CHCl_3) 2145 m, 1655 m, 1618 w, 1583 m, 1513 m, 1470 m, 1425 w, 1382 w, 1361 m, 1350 m, 1333 s, 1304 s, 1282 vs, 1161 vs, 1123 m, 1095 m, 1098 m, 1053 m, 970 m, 924 m, 886 m cm^{-1} ; mass spectrum (E.I.) m/z 256 (16, M^+), 228 (43, $\text{M}^+ - \text{N}_2$), 209 (16), 189 (11), 69 (100); HRMS m/z 256.0180 ($\text{C}_7\text{H}_2\text{F}_6\text{N}_4$ requires 256.01837).

6,7-Bis(trifluoromethyl)tetrazolo[1,5-*a*]pyridine (4,5T)/(4,5A): white solid; purified by Kugelrohr distillation (75–80 °C, 0.1 mbar); yield 56%; mp 46–47 °C; ^1H NMR (CDCl_3), tetrazole isomer (4,5T); δ 9.40 (s, 1H, H5), 8.62 (s, 1H, H8); azide isomer (4,5A): δ 8.80 (s, 1H, H6), 7.18 (s, 1H, H3); ratio tetrazole: azide 4,5T:4,5A (22 °C) = 2.2:1; ^{13}C NMR (CDCl_3), tetrazole isomer (4,5T) δ 147.8 (C8a), 131.0 (q, $^2\text{J}(\text{CF}) = 36.3$ Hz, C7), 128.0 (q, $^3\text{J}(\text{CF}) = 8.1$ Hz, C5), 121.3 (q, $^1\text{J}(\text{CF}) = 274.6$ Hz, C9), 121.0 (q, $^1\text{J}(\text{CF}) = 274.3$ Hz, C10), 117.7 (q, $^2\text{J}(\text{CF}) = 36.0$ Hz, C6), 117.5 ($^2\text{J}(\text{CF}) = 7.1$ Hz, C8); selective decoupling of H5 (δ 9.40) of the tetrazole isomer in the proton coupled ^{13}C NMR spectrum revealed (i) no $^1\text{J}(\text{CH})$ coupling for the $^3\text{J}(\text{CF})$ coupled quartet at δ 128.0 (C5), and (ii) $^1\text{J}(\text{CH})$ coupling for $^3\text{J}(\text{CF})$ coupled quartet at δ 117.5 (C8); azide isomer (4,5A): δ 159.7 (C2), 148.9 (q, $^3\text{J}(\text{CF}) = 6.7$ Hz, C6), 138.6 (qm, $^2\text{J}(\text{CF}) = 35.6$ Hz, C4),

122.3 (1J (CF) = 273.0 Hz, C8), 121.1 (q, 1J (CF) = 274.6 Hz, C7), 118.6 (qm, 2J (CF) = 34.0 Hz, C5), 112.0 (q, 3J (CF) = 6.1 Hz, C3); selective decoupling of H3 (δ 7.18) of the azide isomer in the proton coupled ^{13}C NMR spectrum revealed (i) 1J (CH) coupling for the 3J (CF) coupled quartet at δ 148.9 (C6), and (ii) no 1J (CH) coupling for the 3J (CF) coupled quartet at δ 112.0; IR (KBr) 3083 w, 1661 m, 1540 w, 1459 m, 1335 s, 1317 s, 1276 s, 1264 s, 1170 vs, 1130 m, 1095 m, 1069 w, 996 m, 981 m, 889 m, 759 m, 715 m, 632 m, 625 w cm^{-1} ; IR (CHCl_3), 2135 s (ν_{azide}), 1657 m, 1611 m, 1559 w, 1535 w, 1457 m, 1387 s, 1316 s, 1274 s, 1093 m, 1028 m, 978 m, 895 m cm^{-1} ; mass spectrum (EI.) m/z 256 (46, $\text{M}^{+\cdot}$), 228 (100, $\text{M}^{+\cdot} - \text{N}_2$), 209 (48), 189 (17), 159 (25), 139 (26), 69 (40); HRMS m/z 256.0184 ($\text{C}_7\text{H}_2\text{F}_6\text{N}_4$ requires 256.01837). Anal. Calcd for $\text{C}_7\text{H}_2\text{F}_6\text{N}_4$ C, 32.80; H, 0.78; N, 21.80. Found C, 32.21; H, 0.82; N, 21.81.

Matrix Isolation. Solid samples (ca 10 mg) were sublimed at ca. 40–50 °C from a Knudsen cell and deposited with Ar at 20 K and ca. 10^{-4} mbar in the course of ca. 50 min. Liquids were admitted through a needle valve.

5T containing a smaller amount of **5A** had the following IR (Ar, 15 K): 2155 m, 2118 m (ν_{azide}), 1659 m, 1605 m, 1689 m, 1346 s, 1334 s, 1289 s, 1187 s, 1170 m, 1158 vs (ν_{CF}), 1147 w, 1087 m, 1079 m, 821 w cm^{-1} .

Six minutes of broadband irradiation caused complete conversion of the precursor to give exclusively **5D** as described in section 2. Thirty-six minutes of irradiation caused ca. 40% destruction of **5D** to unknown products. No significant new peak appeared except a band at 2066 cm^{-1} .

4T underwent ring opening to a very small amount of **4A** (2135 cm^{-1}) under analogous conditions. **4T**, IR (Ar, 18 K): 1498 m, 1379 m, 1346 s, 1340 m, 1288 s, 1262 m, 1234 w, 1194 vs, 1656 vvs (ν_{CF}), 1122 w, 1077 w, 1051 w, 989 w, 941 w, 891 w cm^{-1} .

Twenty minutes broadband irradiation caused complete and exclusive conversion to **5D** as described in section 2. An additional 90 min of irradiation caused almost complete destruction of **5D**, with only a weak band at 2066 and a broad feature at 1180 cm^{-1} appearing.

The use of monochromatic irradiation ($\lambda = 268$ nm, which is the λ_{max} of **4T** in EtOH) gave the same result, with formation of **5D** from **4T** in 20 min. No intermediate was observed.

6A was matrix isolated in 25 min and had IR (Ar, 15 K): 2137 vvs, 1606 m, 1578 w, 1461 m, 1443 w, 1434 m, 1351 s, 1342 w, 1291 s, 1262 w, 1195 m, 1169 vs, 1160 m, 1149 w, 1121 m, 1079 w, 1033 w, 992 w, 916 w, 863 m cm^{-1} . It was converted fully to **4D** during 12 min of broadband irradiation, as described section 3. **4D** underwent ca. 30% decomposition in the course of an additional 16 min of irradiation, causing development of a weak band at 2065 cm^{-1} .

3T had IR (Ar, 15 K): 2163 m, 2157 m, 2136 m (ν_{azide}), 1624 m, 1443 w, 1435 s, 1368 m, 1334 m, 1310 s, 1299 m, 1231 m, 1180 m, 1173 vs, 1160 s, 1150 m, 1123 m, 1087 m, 1037 m, 953 m cm^{-1} .

Complete conversion to **4D** was achieved in 5 min of broad-band irradiation. The formation of byproducts is described in section 3.

4,5T had IR (Ar, 20 K): 2138 m (ν_{azide}), 1393 m, 1335 s, 1321 m, 1391 s, 1281 m, 1273 m, 1229 m, 1205 m, 1192 vs, 1185 m, 1170 s, 1154 w, 1141 w, 1101 w, 1091 w, 975 w, 898 w cm^{-1} . It was converted completely to **5,6D** during 3 min of broad-band irradiation, as described in section 4.

4,6A had IR (Ar, 15 K): 2146 s, 1441 w, 1420 w, 1389 vs, 1362 m, 1290 m, 1277 vs, 1216 m, 1203 m, 1186 m, 1173 s, 1165 m, 1159 m, 1132 m, 933 m, 882 m, 758 cm^{-1} . It was converted completely to **4,6D** in 6 min of irradiation. An additional 90 min of irradiation appeared to cause ca. 30% destruction of **4,6D** with no specific new absorptions appearing.

3,5T underwent significant ring opening to the azide (**3,5A**) during deposition. IR (Ar, 18 K): 2148 s, 1623 m, 1592 m, 1475 m, 1427 m, 1353 m, 1306 vs, 1279 vs, 1268 m, 1248 w, 1171 m, 1166 m, 1154 m, 1097 w, 1054 m, 938 w, 781 w cm^{-1} . Five minutes of broad-band irradiation caused complete conversion of the precursor to carbodiimide **4,6D** together with an intermediate B as described in section 5. B had IR (Ar, 11 K): 1337 m, 1276 s, 1208 m, 1182 s, 1159 m, 1075 m, 1029 m cm^{-1} . The bands due to species B disappeared during a further 80 min of irradiation, with concomitant increase in the peaks due to carbodiimide **4,6D**. Unknown decomposition products (X) were formed during this time as well: 2065 w, 1271 m, 1199 m, 1176 w, 1161 m cm^{-1} . The carbodiimide **4,6D** had IR (Ar, 18 K): 2000 s, 1280 s, 1200 s, 1190 w, 1186 m, 1171 s, 1151 m, 1041 m, 985 w cm^{-1} . After a total of 16 h of irradiation, complete destruction of all the species had occurred, with only weak bands in the ν_{CF} region of the IR spectrum remaining (1285, 1213, 1181 cm^{-1}).

Repetition of this experiment with monochromatic light (267 nm which is λ_{max} of **3,5T** in EtOH) had the same outcome, but the reaction was slower.

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Supporting Information Available: Calculated structures (BLYP/6-31G*) of **4D**, **5D**, **4,6D**, and **5,6D** (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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