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1*H*-1,3-Diazepines and Ketenimines from Cyanotetrazolopyridines*

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Cyano-substituted tetrazolo[1,5-*a*]pyridines/2-azidopyridines **8T** and **15T** undergo thermal ring opening to the azides **8A** and **15A**. Solution photolysis causes nitrogen elimination and ring expansion to 1,3-diazacyclohepta-1,2,4,6-tetraenes **10** and **17**, which react with alcohols to afford 2-alkoxy-1*H*-1,3-diazepines, with secondary amines to 2-dialkylamino-5*H*-1,3-diazepines, and with water to 1,3-diazepin-2-ones (**12**–**14**, **19**, **21**). Argon matrix photolysis of the azides affords the diazacycloheptatetraenes **10** and **17** as principal products together with ring-opened dicyanovinylketenimines **11** and **18**. The matrix-isolated species were identified on the basis of comparison of the infrared spectra with those calculated at the *B3LYP/6−31+G** level.

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Introduction

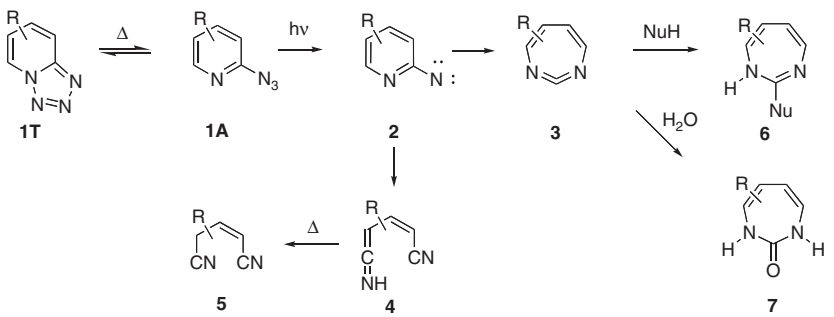
1,4-Diazepines are well known for their many pharmaceutical properties. In contrast, 1,3-diazepines are relatively little known.[1] Some 1,3-diazepin-2-ones and other cyclic ureas have received considerable attention recently as potential anti-AIDS drugs.[2] In previous publications, we have described the photolysis of variously substituted tetrazolo[1,5-*a*]pyridines **1T**/2-azidopyridines **1A** as a convenient method of synthesis of 1,3-diazepines **6** and diazepinones **7**.[3,4] The reaction proceeds via ring expansion of the first-formed 2-pyridylnitrenes **2** to 1,3-diazacyclohepta-1,2,4,6-tetraenes **3**, which in several cases have been characterized by matrix-isolation infrared (IR) spectroscopy (Scheme 1).[3,5]

In several cases, the additional appearance of IR bands near 2040 cm^{-1} has been ascribed to formation of ketenimines **4** formed in a side reaction in the low-temperature matrix photolyses.[3] Flash vacuum thermolysis (FVT) reactions of tetrazolo/azidopyridines also produce 1,3-diazacyclohepta-1,2,4,6-tetraenes **3**, and here glutacononitriles **5** are often isolated as minor by-products in yields of the order of 10%.[5] These products, **4** and **5**, are believed to be formed via cleavage of the N_1–C_2 bond in the 2-pyridylnitrenes to generate ring-opened, transient cyanovinylnitrenes; an H-shift then generates ketenimines **4**, which tautomerize to the glutacononitriles **5** at elevated temperatures. However, a detailed spectroscopic description of the ketenimines and their rates of formation relative to **3** has been lacking. Here we report the direct observation of cyclic carbodiimides **3** and ring-opened ketenimines **4** as well as the synthesis of 1,3-diazepines in the cyano-substituted series.

Results and Discussion

6-Cyanotetrazolo[1,5-*a*]pyridine exists in the tetrazole form **8T** in the solid state, but NMR spectroscopy demonstrated that this tetrazole and the azide **8A** coexist in a ratio of ~2.2:1 in $CDCl_3$ solution at room temperature. However, in [D_6]DMSO only the tetrazole form **8T** was detectable in the ^{1}H NMR spectrum. This solvent effect on the azide–tetrazole equilibrium is common.[6]

Photolysis of tetrazole/azide **8T**/**8A** in 1,4-dioxan solution containing diisopropylamine afforded the 1*H*-1,3-diazepine **12a** (Nu = NPr^i_2) as a red solid in 35% yield after chromatography



Scheme 1. Overview of 2-pyridylnitrene chemistry.

* This paper is *Diazepines Part IV*. For Part III, see A. Reisinger, R. Koch, P. V. Bernhardt, C. Wentrup, *Org. Biomol. Chem.* **2004**, 2, 1227. doi:10.1039/B317099C

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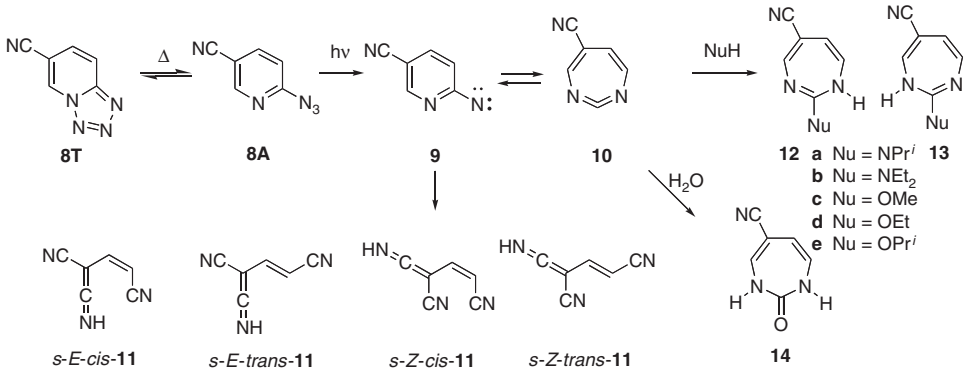
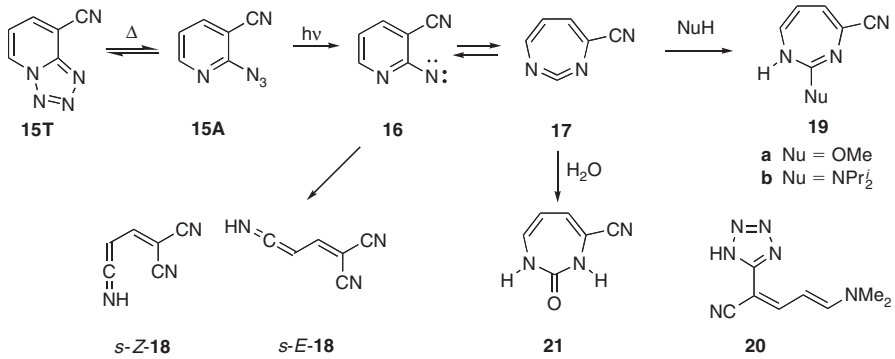


Scheme 2. Reactions of 5-cyano-2-pyridylnitrene.



Scheme 3. Reactions of 3-cyano-2-pyridylnitrene.

(Scheme 2). Similar photolysis in 1,4-dioxan/diethylamine afforded the 1*H*-diazepine **12b** (Nu = NEt_2) in 47% yield. 1,3-Diazepines can potentially exist in 1*H* and 5*H* forms; the 1*H* forms are favoured thermodynamically for 2-alkoxy-1,3-diazepines, and the 5*H* forms for 2-amino-1,3-diazepines, but the 1*H* forms are always formed first and are isolable in both the alkoxy- and the amino-substituted series.[3,4a] Furthermore, unsymmetrical 1,3-diazepines can exist in interconverting 1*H* and 3*H* forms.[3] The 3*H*-isomers **13a**,**b** were not observed by NMR spectroscopy in the present work.

Irradiation of a methanol/1,4-dioxan solution of **8T**/**8A** for 2.5 h followed by chromatography furnished the 2-methoxy derivative **12c** (Nu = OMe) as a red solid in 35% yield. Here, both the 1*H* form **12c** and the 3*H* form **13c** were present, in an ~3:1 ratio as determined from the ^{1}H and ^{13}C NMR spectra. Using ethanol under similar reaction conditions afforded a mixture of **12d** and **13d** (Nu = OEt) in 50% yield. The isopropyl derivatives **12e**/**13e** (Nu = OPr^i) were prepared by photolysis of **8T** in 1,4-dioxan/isopropyl alcohol. Again, the NMR spectra demonstrated the presence of both the 1*H*-isomer **12e** and the 3*H*-isomer **13e**, in a ratio of ~2:1. The alkoxydiazepines **12**/**13** are red solids, which can be stored below 0°C. They are easily purified by sublimation.

Photolysis of **8T** in water/1,4-dioxan followed by chromatography on alumina afforded a yellow solid insoluble in $CDCl_3$ and identified as the cyclic urea **14** by its spectroscopic and microanalytical data.

Photolysis of the isomeric tetrazole **15T** in methanol/dioxan afforded the 1*H*-2-methoxy-1,3-diazepine **19a** (Scheme 3). It was clear from the ^{1}H NMR spectrum in $CDCl_3$ that the 3*H* isomer of **19a** was absent. The 2-diisopropylamino-1,3-diazepine **19b** was obtained with diisopropylamine, but the more nucleophilic dimethylamine caused ring-opening of the pyridine ring in a reaction in the dark at room temperature to afford the dienyltetrazole **20**.[7]

4-Cyano-1,3-diazepin-2-one **21** was prepared by photolyzing **15T** in wet acetonitrile. Column chromatography and sublimation yielded the yellow compound **21** in 20% yield.

For the characterization of the diazepines by NMR spectroscopy, it is advantageous to use [D_6]acetone and especially [D_6]DMSO, where signals are better resolved (although still somewhat broad) and coupling information can be obtained. This is attributed to their higher polarity helping to disrupt hydrogen bonding between diazepine molecules. Such disruption prevents formation of a diazepine molecular network with intermolecular hydrogen exchange responsible for line broadening in NMR spectra.

Matrix Isolation

Argon matrix isolation studies were carried out in order to identify the 1,3-diazacyclohepta-1,2,4,6-tetraene intermediates. For this purpose, **8T** was sublimed at 70°C in a steady stream of Ar and condensed onto a CsI deposition window maintained at 25 K to form a matrix. After cooling of the matrix to 7 K, the IR spectrum showed absorptions assigned to the azide **8A**, the strongest of which were the azide symmetrical (1288 cm^{-1}) and antisymmetrical (2126, 2136, 2153, and 2164 cm^{-1}) bond stretches (see Fig. S1 in the Accessory Publication). The simplicity of the spectrum suggested that **8T** was not present, and this was confirmed by co-subliming **8T** with Ar through an oven held at ~300°C, which resulted in the exclusive deposition of **8A**. The experimental spectrum of **8A** so obtained matches the calculated spectrum very accurately (see Fig. S1). Comparison with the IR spectrum

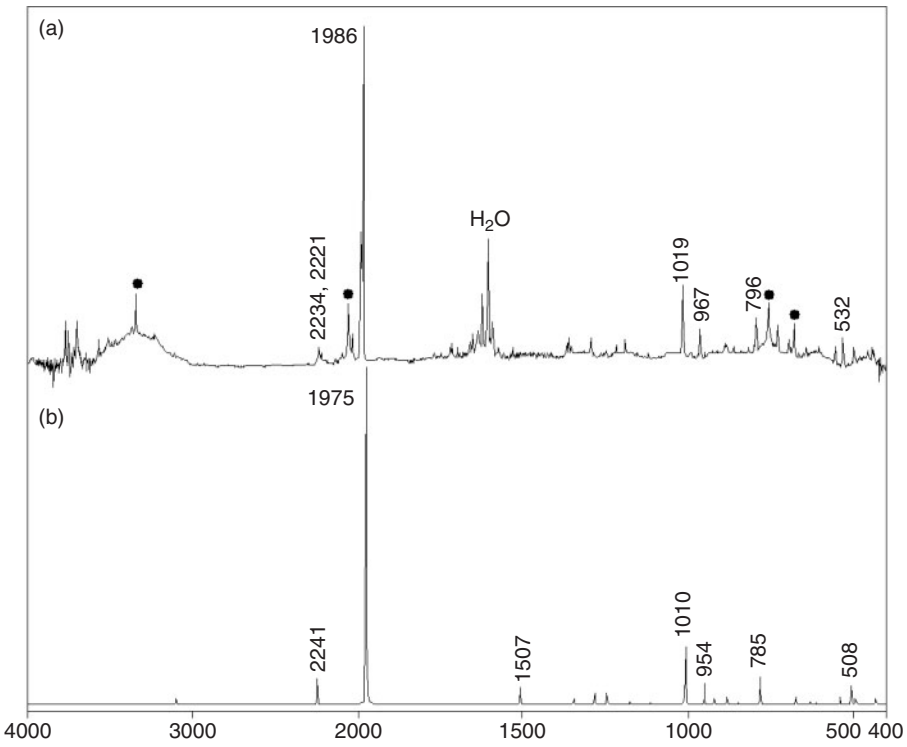


Fig. 1. (a) Infrared (IR) spectrum obtained after 3 min of UV irradiation of **8A** (abscissa in wavenumbers, ordinate in arbitrary absorbance units). The bands marked with wavenumbers are assigned to **10**. Additional bands at 3350, 2060, 2041, 757, and 683 cm^{-1} are marked with black dots and assigned (in part) to ketenimine **11**. (b) Calculated IR spectrum of **10** at the *B3LYP/6−31+G** level (wavenumbers scaled by 0.9613).

of solid tetrazole **8T** (see Experimental) confirmed the absence of this compound. The nitrile group absorptions of **8A** (2238, 2244 cm^{-1}) were very weak. A weak overtone/combination band at 2285 cm^{-1} accompanied them.

The matrix was photolyzed at $\lambda > 260$ nm and monitored by periodically recording IR spectra. After 1 min, a new band at 1986 cm^{-1} (with shoulder at 1994 cm^{-1}) appeared, whose intensity increased on further irradiation. This absorption was assigned to carbodiimide **10** (Scheme 2). A total of 3 min of irradiation caused complete destruction of **8A** and left a matrix composed largely of **10** (Fig. 1). Cyclic carbodiimides isolated in Ar matrices are known to absorb strongly near 2000 cm^{-1}.[3–5] The calculated IR spectrum of **10** at the *B3LYP/6−31+G** level is in very good agreement with the experimental spectrum, leaving little doubt that this is the main product of photolysis (Fig. 1). The strongest calculated bands at 2241, 1975, 1010, 954, 785, and 508 cm^{-1} correlate well with the experimental values at 2221, 2234, 1986, 1019, 967, and 532 cm^{-1}. The experimental spectrum in Fig. 1 also reveals that one or more additional photoproducts are formed, with principal absorptions at 3350, 2060, 2041, 757, and 683 cm^{-1}. Absorptions in the 3350 and 2040 cm^{-1} regions are indicative of a ketenimine moiety, C=C=NH. This product or product mixture formed more slowly than **10**, as documented by plotting the intensities of all peaks as a function of time (see Figs S1–S4 in the Accessory Publication). Moreover, extensive photolysis of the matrix for 60 min at 7 K resulted in the complete disappearance of **10** and development of additional bands in the NH, CN, and CCN regions (2249, 2245, 2070, 2054, 2047, and 2041 cm^{-1}) and in the fingerprint region (several bands between 830 and 698 cm^{-1}) (Fig. S3). The appearance of new ketenimine bands may be due to either the formation of new conformers of ketenimine **11** or the creation of new photo-induced matrix sites.

The slow formation of ketenimine products and the disappearance of **10** can be interpreted in terms of ring-opening of nitrene **9**, which is expected to exist in photoequilibrium with **10**.[8,9] Several other such ring-opening reactions have been reported recently,[3,9] and are particularly well documented in the 1-isoquinolylnitrene[9] and 2-quinazolylnitrene systems.[10] The occurrence of unassigned bands in the 2040 cm^{-1} region in the matrix photolyses of other pyridylnitrenes[5a] can be explained analogously. Thus, the ring opening of nitrene **9** can give rise to several conformers of the dicyanovinylketenimine **11** (Scheme 2). The calculated IR spectra of the conformers of **11** are all very similar, and it is not possible to determine which conformers are present (see Fig. S2 in the Accessory Publication). The general appearance of these spectra is similar to those of other, related cumulenes.[9,11]

The matrix isolation of 8-cyanotetrazolo[1,5-*a*]pyridine/2-azidopyridine **15T**/**15A** proceeded in a similar manner. Sublimation at 100°C in a stream of Ar and deposition on the CsI window at 25 K resulted in a mixture of **15T** and **15A**. The azide photolyzed more rapidly than the tetrazole, thus allowing an assignment of IR bands to each compound (Fig. S5). Sublimation of **15T** through the FVT oven maintained at 290°C afforded exclusively the azide **15A**, which exhibits strong IR absorptions at 1425 (symmetrical N_3 stretch), 2140, and 2153 cm^{-1} (antisymmetric N_3 stretches), a weak CN band at 2234 cm^{-1} and a weak overtone/combination band at 2289 cm^{-1}.

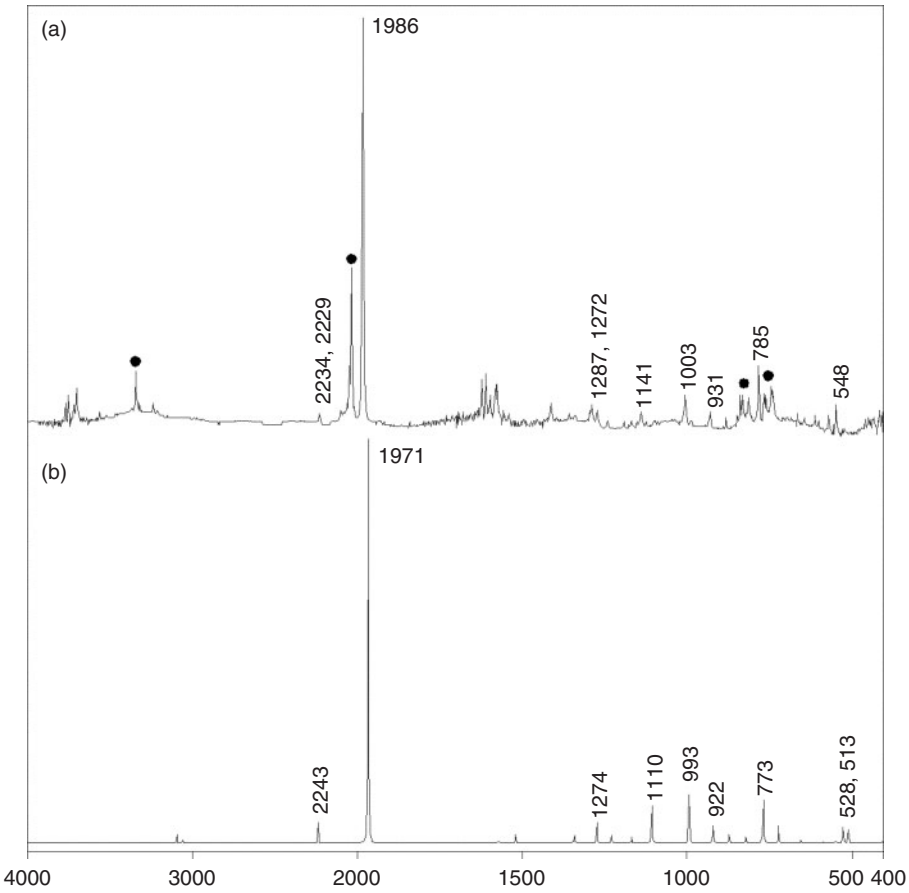


Fig. 2. (a) Infrared (IR) spectrum obtained after 7.5 min of UV irradiation of **15A** (abscissa in wavenumbers; ordinate in arbitrary absorbance units). The bands marked with wavenumbers are assigned to **17**. Additional bands at 2042, 2052, 2229, 3326, and 3349 cm^{-1} marked with black dots are assigned (in part) to ketenimine **18**. (b) Calculated IR spectrum of **17** at the *B3LYP/6−31+G** level (wavenumbers scaled by 0.9613).

Photolysis of the matrix of **15A** with light of $\lambda > 260$ nm resulted in the disappearance of the IR bands of **15A** in the course of 7.5 min to be replaced with two medium to strong bands at 1986 and 2042 cm^{-1} (Fig. 2a). The 1986 cm^{-1} band is assigned to carbodiimide **17**, and the bands at 2234, 1272, 1141, 1003, 931, 785, 548, and 528 cm^{-1} also belong to this species. There is very good agreement with the calculated bands at 2243, 1971, 1110, 993, 922, and 773, 528, and 513 cm^{-1} (Fig. 2b). Another group of bands at 2042, 2052, 2229, 3326, and 3349 cm^{-1} as well as two clusters of bands at 740–775 cm^{-1} and 805–850 cm^{-1} belong to different photoproducts that form more slowly according to the kinetic monitoring of the growth of all bands (Figs S6–S9). These bands are assigned to the conformers of the ring-opened ketenimine **18** because of the good agreement with the calculated IR spectra (Fig. S7).

When the matrix was irradiated further, carbodiimide **17** slowly disappeared. The bands assigned to ketenimine **18** initially maintained their intensities, and then slowly decreased. A new nitrile band at 2240 cm^{-1} grew during this time. In the fingerprint region, some new, weak bands appeared between 680 and 710 cm^{-1} (Fig. S8). The deterioration of the matrix on extensive photolysis due to line broadening and a decreased signal to noise ratio made a structural assignment of the secondary products impossible, but because it is known that *NH*-ketenimines rearrange very easily to nitriles,[11] and glutacononitriles (2-propene-1,3-dicarbonitriles **5**) are formed as byproducts in the thermal reactions of 2-pyridylnitrenes,[5] the disappearance of the ketenimine and appearance of a new nitrile function is not surprising.

Conclusions

The 6- and 8-cyanotetrazolo[1,5-*a*]pyridines **8T** and **15T** undergo valence tautomerization to the corresponding azides **8A** and **15A** on mild thermolysis (FVT at 100–250°C). The azides photolyze to 2-pyridylnitrenes **9** and **16**, which undergo efficient ring expansion to 1,3-diazacyclohepta-1,2,4,6-tetraenes **10** and **17**. The latter are readily observable by matrix-isolation IR spectroscopy and trappable in solution with nucleophiles to produce 1*H*-1,3-diazepines **12**, **13**, and **19** and 1,3-diazepin-2-ones **14** and **21**. Slower-forming photolysis products are assigned as the various conformers of the open-chain ketenimines **11** and **18**, which are assumed to be formed by ring opening of the 2-pyridylnitrenes in photoequilibrium with the 1,3-diazacyclohepta-1,2,4,6-tetraenes.

Computational Method

The *GAUSSIAN 98* suite of programs was used to simulate IR spectra.[12] Geometry optimizations were performed at either *B3LYP/6−31+G** or *B3LYP/6−311++G*** levels. The *B3LYP* formulation of density functional theory corresponds

to Becke's three-parameter exchange functional in combination with the Lee–Yang–Parr correctional functional.[13] A frequency scaling factor of 0.9613 was used for both *B3LYP/6−31G** and *B3LYP/6−31+G**.[14] Frequencies calculated at the *B3LYP/6−311++G*** level were scaled by 0.97.[15] The temperature used was 298 K. Standard orientations, energies, and IR spectra are presented in the Accessory Publication.

Experimental

General procedures for matrix isolation experiments have been published.[5,9,10] Ar matrices were deposited onto a CsI disk, usually at 25 K, and IR spectra were recorded at 7–10 K. Ar was ultra high purity grade (99.999%). The Ar flow rate was maintained at 100 Pa. In all matrix experiments, a bed of Ar (200–300 Pa) was laid on the deposition window before sublimation of the desired tetrazole. On completion of sublimation, another 200–300 Pa Ar was used to coat the matrix. Photolyses were performed using either a Gräntzel (Karlsruhe) 350 W low-pressure Hg lamp (λ 200–254 nm) or a Hanovia 1000 W high-pressure broadband Hg–Xe lamp (λ > 260 nm) equipped with a water filter. IR spectra were recorded at 1-cm^{-1} resolution.

All solution trapping experiments used the aforementioned 1000 W high-pressure Hg–Xe lamp. Reactions were conducted in quartz vessels with magnetic stirring. Photolysis solvents were distilled over appropriate drying agents, except acetonitrile, which was distilled once from Na_2CO_3. Before photolysis, solutions were purged with N_2 for ∼2 h. Reaction progress was mainly monitored by gas chromatography-mass spectrometry and TLC. Alumina 90 (Merck) for column chromatography of diazepines was deactivated before use by stirring in a 1:1 methanol/water solution overnight, then drying on a Büchner funnel. Silica gel 100 (Merck) was used as supplied. TLC was performed on silica gel 60 or neutral alumina plates.

6-Cyanotetrazolo[1,5-a]pyridine ***8T***

2-Chloro-5-cyanopyridine (3.18 g, 23 mmol) was added to 66% aqueous ethanol (37 mL) and the mixture combined with a suspension of sodium azide (3.06 g, 47 mmol) in 50% aqueous ethanol (17 mL). Aqueous HCl (10%, 12 mL) was added, and the solution was refluxed for 24 h. Cooling the solution to room temperature and then in a refrigerator (2°C) for several hours afforded crystals of the crude tetrazole, which were collected on a Büchner funnel. The light brown **8T** so obtained was purified by sublimation (13 Pa, oil bath 90°C). Yield 2.29 g (69%). Mp 96–98°C [lit.[16] 90°C]. *m/z* 145 ($M^{+\bullet}$), 117 (–N_2), 90 (–N_2 and HCN), 63 (–N_2 and 2HCN). ν_{max}(KBr)/cm^{-1} 3140m, 3090s, 3043m, 2248s, 1761w, 1658w, 1634vs, 1505vs, 1490vs, 1426s, 1361m, 1334s, 1260s, 1203s, 1149s, 1106m, 1065s, 991s, 885s, 828vs, 751m, 612vs. δ_H ($CDCl_3$, 400 MHz) tetrazole 7.79 (dd, ^3J 9.4, ^4J 1.5, 1H, H7), 8.2 (dd, ^3J 9.4, ^5J 1.2, 1H, H8), 9.28 (t, average ^4J, ^5J 1.2, 1H, H5); azide 6.87 (dd, ^3J 8.5, ^5J 0.8, 1H, H8), 7.83 (dd, ^3J 8.5, ^4J 2.3, 1H, H7), 8.60 (dd, ^4J 2.3, ^5J 0.80, 1H, H5), ratio tetrazole:azide 2.26:1. δ_C ($CDCl_3$, 100 MHz) 103.6, 105.5, 114.1, 114.2, 116.5, 117.5, 131.4, 132.2, 141.4, 148.3, 152.5, 158.2. δ_H ([D_6]DMSO, 400 MHz) 8.14 (d, ^3J 9.2, 1H, H7, or H8), 8.38 (d, ^3J 9.2, 1H, H8, or H7), 10.24 (s, 1H, H5). δ_C ([D_6]DMSO, 100 MHz) 102.5 (C6), 115.4 (CN), 116.4, 133.4, 134.1, 148.3 (C8a).

8-Cyanotetrazolo[1,5-a]pyridine ***15T***

2-Chloro-3-cyanopyridine (7.43 g, 0.054 mol) was added to 66% aqueous ethanol (87 mL) and the mixture combined with a suspension of sodium azide (7.06 g, 0.109 mol) in 50% aqueous ethanol (38 mL). Aqueous HCl (10%, 27 mL) was added, and the solution was refluxed for 24 h. Cooling the solution to room temperature afforded crystals of crude **15T** that were collected on a Büchner funnel and purified by sublimation (13 Pa, oil bath 140°C). Yield 6.33 g (81%). Mp 185–188°C (dec.) [lit.[17] 183°C]. *m/z* 145 ($M^{+\bullet}$), 117 (–N_2), 90 (–N_2, –HCN), 63 (–N_2, –2HCN). ν_{max}(KBr)/cm^{-1} 3123m, 3103s, 3087s, 3046m, 2237s, 1623vs, 1568m, 1498vs, 1422m, 1373vs, 1347s, 1281m, 1245m, 1161m, 1109m, 1098m, 1059m, 1020s, 997s, 883s, 817s, 805s, 764vs, 663s, 639w. δ_H ([D_6]DMSO, 400 MHz) 7.59 (t, ^3J 7.2, 1H, H6), 8.58 (dd, ^3J 7.2, ^4J 0.94, 1H, H7, or H5), 9.61 (dd, ^3J 7.0, ^4J 0.9, 1H, H5, or H7). δ_H ([D_6]DMSO, 100 MHz) 99.5 (C8), 113.7 (CN), 116.9 (C6 or C7), 131.4 (C7 or C6), 141.2 (C5), 147.3 (C8a).

Solution Photolysis and Trapping Studies

5-Cyano-2-diisopropylamino-1H-1,3-diazepine ***12a***

A solution of **8T** (0.15 g, 1.03 mmol) in 1,4-dioxan (100 mL) containing diisopropylamine (15 mL) was irradiated for 4.5 h. The solution turned dark red-brown. Evaporation of excess solvent gave a red oil, which was chromatographed on neutral alumina with 1:1 diethyl ether/hexane. A red-brown band was eluted, which on evaporation of the solvent gave the red solid diazepine. This was recrystallized by dissolving in ether and then adding hexane dropwise until precipitation commenced. Yield 80 mg (35%). Mp 126–127°C. Calc. for $C_{12}H_{18}N_4$: C 66.0, H 8.3, N 25.7. Found: C 66.2, H 8.6, N 25.5%. *m/z* 218 ($M^{+\bullet}$), 203 (–Me), 175 (–propyl radical), 148, 132. ν_{max}(KBr)/cm^{-1} 3418m, 2979w, 2196s, 1665w, 1544vs, 1458w, 1396w, 1371w, 1341m, 1315w, 1274m, 1161w, 1123w, 1008w, 958w, 845w, 750w, 713w. δ_H ($CDCl_3$, 400 MHz) 1.25 (d, ^3J 6.9, 12H, 4 Me), 4.01 (br d, ^3J 5.2, 1H, H1), 4.10 (septet, ^3J 6.9, 2H, Pr^i), 5.41 (t, ^3J 6.3, 1H, H7), 5.5 (d, ^3J 6.68, 1H, H6), 7.22 (s, 1H, H4). δ_C ($CDCl_3$, 100 MHz) 21.0 (Me), 47.5 (Pr^i), 94.8 (C5), 118.1 (C6), 121.1 (CN), 126.2 (C7), 151.5 (C2), 154.8 (C4). δ_H ([D_6]acetone, 400 MHz) 1.27 (d, ^3J 6.9, 12H, 4 Me), 4.09 (septet, ^3J 6.8, 2H, Pr^i), 5.17 (d, ^3J 7.0, 1H, H6), 5.58 (br d, ^3J 5.0, 1H, H7), 5.60 (br s, 1H, H1), 7.05 (s, 1H, H4). δ_C ([D_6]acetone, 100 MHz) 21.1 (Me), 48.3 (Pr^i), 96.2 (C5), 114.7 (C6), 121.4 (CN), 130.5 (C7), 154.4 (C2), 156.2 (C4).

5-Cyano-2-diethylamino-1H-1,3-diazepine ***12b***

A solution of diethylamine (2 mL) in 1,4-dioxan (100 mL) was purged with N_2 for 0.5 h. Tetrazole **8T** (0.13 g, 0.90 mmol) was added and irradiation commenced immediately at room temperature. Photolysis was continued for 4.5 h. Evaporation of excess solvent gave a red-brown oil, which was chromatographed on neutral alumina with 1:1 diethyl ether/hexane. An orange band was eluted, which on evaporation of the solvent gave the orange, solid diazepine. Yield 0.08 g (47%). Recrystallization from diethyl ether/hexane gave analytically pure red needles. Mp 109–110°C. Calc. for $C_{10}H_{14}N_4$: C 63.1, H 7.4, N 29.5. Found: C 63.2, H 7.6, N 29.3%. *m/z* 190 ($M^{+\bullet}$), 175 (–Me), 161 (–Et), 134, 118, 106, 93. ν_{max}(KBr)/cm^{-1} 3362s, 2979m, 2936m, 2198vs, 1652m, 1582vs, 1539vs, 1464m, 1436m, 1418m, 1394s, 1359s, 1333vs, 1317s, 1280s, 1266m, 1227w, 1178m, 1080m, 1013m, 925m, 883m, 786w, 752w, 704m, 650w, 550w, 513w. δ_H ([D_6]acetone, 400 MHz) 1.16 (t, ^3J 7.1, 6H, 2 Me), 3.42 (q, ^3J 7.1, 4H, 2 –CH_2–), 4.98 (d, ^3J 7.4, 1H, H6), 5.52 (br d, ^3J 5.6, 1H, H7), 6.16 (br s, 1H, H1), 6.94 (s, 1H, H4). δ_C ([D_6]acetone, 100 MHz)

13.6 (Me), 44.0 (CH_2), 96.0 (C5), 112.6 (C6), 121.4 (CN), 130.7 (C7), 155.8 (C2), 156.7 (C4).

*5-Cyano-2-methoxy-1*H-*1,3-diazepine* **12c**/ *5-Cyano-2-methoxy-3*H-*1,3-diazepine* **13c**

A solution of tetrazole **8T** (0.11 g, 0.76 mmol), 1,4-dioxan (70 mL), and methanol (10 mL) was irradiated for 2.5 h while cooling with ice–water. Evaporation of excess solvent gave a red-brown oil, which was chromatographed on neutral alumina with 1:1 ether/hexane. The red solid diazepine was collected and dried under vacuum. Yield 0.04 g (35%). Mp 79–80°C. Calc. for $C_7H_7N_3O$: C 56.4, H 4.7, N 28.2. Found: C 56.4, H 4.7, N 28.0%. *m*/*z* 149 ($M^{+\bullet}$), 134 (–Me), 106, 92. ν_{max}(KBr)/cm^{-1} 3326s, 3053w, 2949m, 2525w, 2296w, 2211s, 2048w, 1675s, 1618s, 1587s, 1461s, 1414s, 1344s, 1259s, 1226s, 1172m, 1068s, 986s, 939m, 925m, 906s, 782m, 715s, 666w. δ_H ($CDCl_3$, 400 MHz) 1*H* isomer **12c** 3.72 (s, 3H, OMe), 4.75 (br s, 1H, H1), 4.88 (ddd, ^3J 7.7, ^4J 1.7, ^4J 1.1, 1H, H6), 5.36 (ddd, ^3J 7.7, ^3J 6.5, ^5J 1.1, 1H, H7), 6.75 (t, average ^4J, ^5J 1.1, 1H, H4); 3*H* isomer **13c** 3.7 (s, 3H, OMe), 5.02 (br s, 1H, H3), 5.05 (d, ^3J 8.28, 1H, H6), 6.03 (dd, ^3J 8.5, ^5J 0.9, 1H, H7), 6.05 (dd, ^3J 7.2, ^5J 0.9, 1H, H4); ratio 1*H* isomer to 3*H* isomer was ~3:1. δ_C ($CDCl_3$, 100 MHz) 1*H* isomer **12c** 56.6 (OMe), 103.0 (C5), 109.5 (C6), 118.7 (CN), 132.2 (C7), 152.6 (C4), 158.2 (C2); 3*H* isomer **13c** 56.3 (OMe), 98.2 (C5), 113.3 (C6), 117.8 (CN), 139.8 (C4 or C7), 144.3 (C7 or C4), 153.6 (C2).

*5-Cyano-2-ethoxy-1*H-*1,3-diazepine* **12d**/ *5-Cyano-2-ethoxy-3*H-*1,3-diazepine* **13d**

These compounds were prepared in the same manner as **12c**/**13c** and obtained as a red oil, which solidified after drying on a vacuum pump and storing overnight in a freezer. Sublimation (13 Pa, oil bath 50°C) gave analytically pure product. Yield 0.03 g (50%). Mp 59–60°C. Calc. for $C_8H_9N_3O$: C 58.9, H 5.6, N 25.8. Found: C 58.8, H 5.6, N 25.8%. *m*/*z* 163 ($M^{+\bullet}$), 148 (–Me), 135, 120, 107, 93, 80. ν_{max}(KBr)/cm^{-1} 3300s, 2994w, 2983w, 2210s, 1813w, 1678s, 1615s, 1585, 1469s, 1416m, 1393m, 1367w, 1342s, 1262s, 1231m, 1154w, 1069m, 1015m, 942w, 923w, 909w, 886m, 797m, 753m, 726m, 715m, 565w, 519w. δ_H ($CDCl_3$, 400 MHz) 1*H* isomer **12d** 1.22 (t, ^3J 7.1, 3H, Me), 4.12 (q, ^3J 7.1, 2H, –CH_2–), 4.82 (br s, 1H, H1), 4.86 (ddd, ^3J 7.8, ^4J 1.68, ^4J 1.1, 1H, H6), 5.35 (ddd, ^3J 7.8, ^3J 6.5, ^5J 0.8, 1H, H7), 6.73 (t, average ^4J, ^5J 1.0, 1H, H4), 3*H* isomer **13d** 1.21 (t, ^3J 7.2, 3H, Me), 4.07 (q, ^3J 7.1, 2H, –CH_2–), 5.02 (d, ^3J 8.2, 1H, H6), 5.17 (br s, 1H, H3), 6.01 (d, ^3J 8.2, 1H, H7), 6.05 (d, ^3J 7.2, 1H, H4); ratio 1*H* isomer to 3*H* isomer was ~3:1. δ_C ($CDCl_3$, 100 MHz) 1*H* isomer **12d** 14.0 (Me), 65.8 (CH_2), 102.6 (C5), 109.3 (C6), 118.8 (CN), 132.3 (C7), 152.8 (C4), 157.6 (C2); 3*H* isomer **13d** 14.0 (Me), 65.3 (CH_2), 97.8 (C5), 113.1 (C6), 117.9 (CN), 140.0 (C4 or C7), 144.6 (C7 or C4), 153.0 (C2).

*5-Cyano-2-isopropoxy-1*H-*1,3-diazepine* **12e**/ *5-Cyano-2-isopropoxy-3*H-*1,3-diazepine* **13e**

A mixture of **8T** (0.05 g, 0.34 mmol), 1,4-dioxan (45 mL), and isopropyl alcohol (5 mL) was irradiated for 1.5 h at room temperature. Evaporation of excess solvent left a brown oil, which was chromatographed on neutral alumina with 1:1 ether/hexane to afford the product as a red oil, which solidified after drying on a vacuum pump. Sublimation (13 Pa, oil bath 52°C) afforded an orange solid, yield 0.04 g (65%). Mp 70–71°C. Calc. for $C_9H_{11}N_3O$: C 61.0, H 6.3, N 23.7. Found: C 60.9, H 6.3, N 23.7%. *m*/*z* 177 ($M^{+\bullet}$), 162, 148, 135, 118, 107, 93. ν_{max}(KBr)/cm^{-1} 3329s, 2992m, 2215s, 1663s, 1607s, 1574s, 1470m, 1436m, 1415m, 1385w, 1373w, 1353m, 1336m, 1273s, 1247s, 1221s, 1176m, 1141w, 1103m, 945m, 924w, 914m, 905w, 844m, 795m, 734m, 714m, 664w, 563w, 521w. δ_H ([D_6]DMSO, 400 MHz) 1*H* isomer **12e** 1.19 (d, ^3J 6.2, 6H, 2 Me), 4.76 (d, ^3J 7.9, 1H, H6), 4.81 (septet, ^3J 6.2, 1H, Pr^i), 5.33 (t, ^3J 7.1, 1H, H7), 6.71 (s, 1H, H4), 7.23 (d, ^3J 5.2, 1H, H1); 3*H* isomer **13e** (isopropyl group signals masked) 4.90 (d, ^3J 7.4, 1H, H6), 5.87 (d, ^3J 7.5, 1H, H7), 6.17 (d, ^3J 5.9, 1H, H4), 7.71 (d, ^3J 4.4, 1H, H3); ratio of 1*H* isomer to 3*H* isomer was ~2–2.5:1. δ_C ([D_6]DMSO, 100 MHz) 1*H* isomer **12e** 21.3 (Me), 72.3 (Pr^i), 101.7 (C5), 107.5 (C6), 118.9 (CN), 134.7 (C7), 153.4 (C4), 158.8 (C2); 3*H* isomer **13e** 21.3 (Me), 71.6 (Pr^i), 94.9 (C5), 112.8 (C6), 118.4 (CN), 139.8 (7), 148.1 (C4), 153.9 (C2).

5-Cyano-2,3-dihydro-1,3-diazepin-2-one **14**

A solution of tetrazole **8T** (0.05 g, 0.34 mmol), 1,4-dioxan (40 mL), and water (10 mL) was irradiated for 1.5 h at room temperature. The yellow solution was evaporated, and the dark residue was chromatographed on neutral alumina using 2.5% methanol/dichloromethane to elute a yellow band. The resulting yellow solid was purified by sublimation (13 Pa, oil bath 80–110°C). Yield 5 mg (11%). Mp 138–140°C (dec.). Calc. for $C_6H_5N_3O$: C 53.3, H 3.7, N 31.1. Found: C 53.2, H 3.8, N 31.1%. *m*/*z* 135 ($M^{+\bullet}$), 119, 107, 93, 80. ν_{max}(KBr)/cm^{-1} 3569m, 3498m, 3287s, 3181m, 3009m, 2230m, 2216s, 1707vs, 1673vs, 1646vs, 1507w, 1473w, 1437w, 1392m, 1304m, 1258s, 1237s, 1222s, 1215s, 1115w, 1076w, 898w, 766m, 649w. δ_H ([D_6]DMSO, 400 MHz) 4.76 (dt, ^3J 8.9, ^4J 1.1, 1H, H6), 5.45 (ddd, ^3J 8.9, ^3J 6.0, ^5J 0.6, 1H, H7), 6.26 (dt, ^3J 7.0, average ^4J, ^5J 0.8, 1H, H4), 8.10 (br d, ^3J 4.9, 1H, H1, or H3), 8.53 (br d, ^3J 6.0, 1H, H3, or H1). δ_C ([D_6]DMSO, 100 MHz) 92.5 (C5), 104.5 (C6), 119.1 (CN), 127.3 (C7), 139.7 (C4), 159.0 (C2).

*4-Cyano-2-methoxy-1*H-*1,3-diazepine* **19a**

A solution of tetrazole **15T** (0.15 g, 1.03 mmol) in methanol (100 mL) was photolyzed under N_2 at room temperature for 3 h. Evaporation of the red-brown solution left a brown solid, which was chromatographed on neutral alumina with 25% hexane/ether. The brown band was collected, and the solvent was removed to give an orange solid further purified by sublimation (13 Pa, oil bath 60°C). A red solid was obtained; yield 15 mg (10%). Mp 85–86°C. Calc. for $C_7H_7N_3O$: C 56.4, H 4.7, N 28.2. Found: C 56.5, H 4.8, N 28.2%. *m*/*z* 149 ($M^{+\bullet}$), 134 (–Me), 120, 106, 92, 79. ν_{max}(KBr)/cm^{-1} 3338s, 3045w, 3008w, 2960m, 2223m, 1854w, 1684s, 1635s, 1589m, 1456s, 1405m, 1361m, 1275s, 1251s, 1197m, 1159m, 1116m, 1018m, 1000w, 971m, 892m, 860m, 835m, 740m, 720m, 688m, 636m, 599w, 551w, 539w. δ_H ($CDCl_3$, 400 MHz) 3.70 (s, 3H, OMe), 4.72 (br s, 1H, H1), 4.84 (ddd, ^3J 7.9, ^3J 6.1, ^4J 1.7, 1H, H6), 5.47 (dd, ^3J 8.1, ^3J 6.6, 1H, H7), 5.87 (d, ^3J 6.1, 1H, H5). δ_C ($CDCl_3$, 100 MHz) 56.6 (OMe), 109.9 (C6), 118.6 (C4 or CN), 123.7 (CN or C4), 130.0 (C5), 135.8 (C7), 158.4 (C2).

4-Cyano-1,3-dihydro-1,3-diazepin-2-one **21**

A solution of tetrazole **15T** (0.11 g, 0.76 mmol) in acetonitrile (90 mL) was irradiated under N_2 at room temperature for 3 h. The solvent was removed, and the solid material was subjected to column chromatography on silica gel. The crude product was eluted with 2.5% methanol/dichloromethane and then chromatographed once more on silica gel, with dichloromethane

as eluent. The orange-yellow band was slowly eluted, and evaporation yielded a yellow-orange solid (40 mg). After sublimation (13 Pa, oil bath 90–110°C) a yellow solid was obtained, yield 0.02 g (20%). Mp 175–180°C (dec.). Calc. for $C_6H_5N_3O$: C 53.3, H 3.7, N 31.1. Found: C 53.3, H 3.7, N 30.9%. *m/z* 135 ($M^{+\bullet}$), 107, 92, 80. ν_{max}(KBr)/cm^{-1} 3268s, 3153s, 3016m, 2973m, 2214s, 1723s, 1659m, 1625s, 1501w, 1476w, 1425m, 1383m, 1317m, 1258m, 1162m, 1122w, 1015w, 922w, 871w, 848w, 776s, 617m, 602m, 580m, 538w, 500w. δ_H ([D$_6$]DMSO, 400 MHz) 5.05 (ddd, ^3J 8.6, ^3J 6.3, ^4J 1.1, 1H, H6), 5.86 (dd, ^3J 8.6, ^3J 6.3, 1H, H7), 6.09 (dd, ^3J 6.1, ^4J 1.5, 1H, H5), 8.28 (br d, ^3J 4.3, 1H, H1), 8.47 (br s, 1H, H3). δ_C ([D$_6$]DMSO, 100 MHz) 107.0 (C6), 108.7 (C4 or CN), 116.3 (CN or C4), 127.5 (C5), 133.7 (C7), 163.0 (C2).

Matrix Isolation and Photolysis

*2-Azido-5-cyanopyridine **8A***

Tetrazole **8T** was co-sublimed at 70°C in a stream of Ar for 20 min, and the vapour was condensed onto a CsI window held at 25 K. The Ar matrix so obtained was then cooled to 7 K. The IR spectrum showed absorptions of **8A**: ν_{max}(Ar)/cm^{-1} 2424w, 2285w, 2280w, 2244w, 2238w, 2177w, 2169w, 2164w, 2153m, 2136s, 2126m, 1596m, 1566w, 1557w, 1474m, 1443w, 1425w, 1391w, 1384w, 1382w, 1375w, 1373w, 1362w, 1317w, 1309w, 1302w, 1288s, 1271w, 1254w, 1246w, 1242w, 1239w, 1217w, 1209w, 1195w, 1154w, 1144w, 1128w, 1022w, 943w, 940w, 862w, 849w, 846w, 840w, 837w, 823w, 820w, 768w, 751w, 599w, 545w. Broadband UV irradiation (3 min) caused loss of **8A** and generation of carbodiimide **10** and other photoproducts assigned as the conformers of **11**: ν_{max}(Ar)/cm^{-1} (7 K) 3350w, 2234w, 2221w, 2097w, 2060w, 2041w, 1994m, 1986s, 1597w, 1593w, 1531w, 1328w, 1323w, 1318w, 1298w, 1265w, 1262w, 1187w, 1152w, 1122w, 1019w, 1017w, 1015w, 998w, 994w, 974w, 967w, 954w, 951w, 928w, 924w, 913w, 887w, 883w, 863w, 818w, 802w, 800w, 796w, 757w, 740w, 737w, 732w, 729w, 698w, 695w, 692w, 683w, 556w, 554w, 532w, 530w, 500w. Prolonged irradiation caused the loss of **10** (see Figs S3 and S4). The IR spectrum showed that some bands generated after 3 min of photolysis grew stronger after 60 min of irradiation. There were also some new bands: ν_{max}(Ar)/cm^{-1} (7 K) 3475w, 3469w, 3370w, 2249w, 2245w, 2237w, 2150w, 2138w, 2129w, 2122w, 2116w, 2094w, 2079w, 2070w, 2054w, 2047w, 2041w, 1410w, 1173w, 1135w, 1085w, 1073w, 972w, 947w, 923w, 865w, 837w, 830w, 819w, 752w, 703w, 698w, 695w, 689w, 677w, 664w, 657w, 644w, 629w, 606w, 589w, 575w, 574w, 569w, 563w, 482w, 455w. After 14 h of irradiation, the following weak bands were present: ν_{max}(Ar)/cm^{-1} (7 K) 2249w, 2245w, 1476w, 1452w, 1412w, 1368w, 1316w, 1302w, 1282w, 1236w, 1217w, 1189w, 1174w, 1135w, 1105w, 1085w, 972w, 957w, 906w, 865w, 851w, 844w, 835w, 830w, 818w, 815w, 811w, 809w, 758w, 752w, 747w, 745w, 743w, 740w, 727w, 677w, 668w, 657w, 634w, 589w, 563w, 498w, 496w.

Kinetic Monitoring of the Photolysis of 2-Azido-5-cyanopyridine 8A in Ar at 7 K

Tetrazole **8T** was co-sublimed with Ar at 71–72°C for 30 min onto a deposition window at 25 K. The temperature of the Ar matrix of **8A** so obtained was then lowered to 7 K. Broadband irradiation was commenced and IR spectra were recorded every 20 s for 5 min, then at 30-s intervals during the next 5 min. The distance between the light source and matrix was kept constant. The time interval was increased to 1 min between several spectra and later to 5, 20, and 30 min. The area of many bands were integrated and plotted against time (see Fig. S4). This analysis identified four groups of absorptions according to their rate of formation: (i) **10** was the fastest formed, 500w, 532w, 554w, 556w, 796w, 967w, 1015w, 1017w, 1019w, 1986s, 1994m, 2234w cm^{-1}; (ii) conformers of **11**, 683w, 729w, 732w, 757w, 1187w, 2041w, 2060w, 2221w, 3349w cm^{-1}; (iii) 483w, 629w, 688w, 695w, 698w, 703w, 923w, 1410w, 2047w, 2054w, 2070w, 3370w cm^{-1}; (iv) after 17 h of irradiation, 589w, 657w, 830w, 972w, 2249w cm^{-1}.

*2-Azido-3-cyanopyridine **15A***

Tetrazole **15T** was co-sublimed at 90–100°C in a stream of Ar through a 10-cm FVT quartz tube held at 290°C for 25 min, and the vapours were condensed onto a KBr window held at 25 K. The matrix was then cooled to 10 K. The IR spectrum showed absorptions of **15A** only: ν_{max}(Ar)/cm^{-1} (10 K) 2289w, 2234w, 2183w, 2177w, 2153m, 2140s, 2130w, 1587w, 1573w, 1568w, 1455w, 1446w, 1425s, 1319w, 1314w, 1310w, 1292m, 1281w, 1271w, 1248w, 1194w, 1145w, 1098w, 862w, 802w, 800w, 797w, 761w, 651w, 583w, 547w. When **15T** was sublimed under the same conditions in the absence of the FVT oven, the IR spectrum of the resulting matrix exhibited a mixture of **15T** and **15A**. Thus, bands for **15T** were identified: ν_{max}(Ar)/cm^{-1} (10 K) 1626m, 1508w, 1500s, 1497s, 1372m, 1369m, 1349w, 1342w, 1265w, 1238w, 1151w, 1103w, 1053w, 1049w, 1008w, 987m, 983m, 883w, 789w, 758s, 757s, 663w, 591w, 451w. The matrix containing **15A** only was photolyzed with broadband UV light for 7.5 min. This resulted in almost complete conversion to carbodiimide **17** and other photoproducts assigned as the conformers of **18**: ν_{max}(Ar)/cm^{-1} (10 K) 3349w, 3326w, 2234w, 2229w, 2222w, 2218w, 2104w, 2066w, 2052w, 2042m, 1989m, 1986s, 1581w, 1575w, 1416w, 1293w, 1287w, 1272w, 1242w, 1195w, 1171w, 1151w, 1141w, 1126w, 1005w, 1003w, 931w, 893w, 884w, 869w, 857w, 849w, 845w, 840w, 833w, 823w, 817w, 814w, 807w, 785w, 779w, 770w, 765w, 761w, 759w, 757w, 748w, 746w, 714w, 707w, 693w, 684w, 647w, 618w, 613w, 605w, 574w, 557w, 548w, 465w, 456w, 451w, 442w. After 2.5 h of irradiation, **17** had nearly disappeared. Some of the minor photoproduct **18** remained. New bands were observed: ν_{max}(Ar)/cm^{-1} (10 K) 3470w, 3461w, 3455w, 2240w, 2124w, 2066w, 2025w, 1398w, 1343w, 1249w, 1190w, 1187w, 1184w, 1179w, 1167w, 1050w, 935w, 795w, 792w, 708w, 696w, 663w, 644w, 625w, 465w.

Kinetic Monitoring of the Photolysis of 2-Azido-3-cyanopyridine 15A

Tetrazole **15T** was co-sublimed with Ar at 100°C through a quartz FVT tube (300°C) for 23 min, and the vapours were condensed on a CsI deposition window at 25 K. This resulted in an Ar matrix of **15A**. The matrix temperature was lowered to 7 K. Broadband irradiation of **15A** was commenced, and IR spectra were recorded every 30 s for 6 min, then at 1-min intervals for the next 5 min. Spectra were then recorded after 13, 16, and 20 min of photolysis. All significant bands were integrated and plotted against time (see Fig. S9). Two groups of bands were characterized (cm^{-1}): (i) **17**, 746w, 785w, 884w, 931w, 1003w, 1141w, 1242w, 1986s; and (ii) conformers of **18**, 748w, 765w, 770w, 807w, 814w, 817w, 823w, 833w, 840w, 849w, 2042m, 2052w, 3349w.

Accessory Publication

Electronic supplementary information is available showing Ar matrix IR spectra (Figs S1–S6) and computational data (Cartesian coordinates, absolute energies, IR, ^{1}H, and ^{13}C NMR spectra) from the author or, until August 2013, the *Australian Journal of Chemistry*.

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