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Triazoloazine – Diazomethylazine Valence Isomerization. [1,2,3]Triazolo[1,5-*a*]pyridines and 2-Diazomethylpyridines

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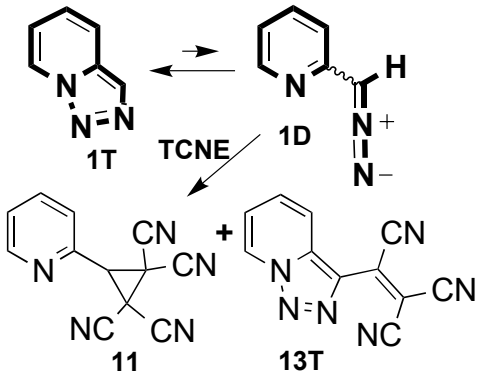


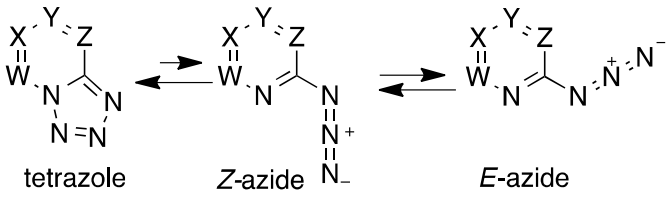
Abstract. 2-Diazomethylpyridines **1D** and **6D**, the valence isomers of [1,2,3]triazolo[1,5-*a*]pyridines **1T** and **6T**, have been observed directly at ~2080 cm^{-1} by a combination of mild flash vacuum pyrolysis (FVP) at 200-600 ^{o}C with low temperature IR spectroscopy. Calculations confirm a ca. 17 kcal/mol barrier for the formation of 2-diazomethylpyridine **1D** from [1,2,3]triazolo[1,5-*a*]pyridine **1T**, the diazo compound lying ca. 5 kcal/mol above the triazole. In

the higher temperature range (400-600 °C) 2-diazomethylpyridine **1D** eliminates N_2 with formation of 2-pyridylcarbene **2** and rearrangement to 1-cyanocyclopentadiene **4**. 2-Diazomethylpyridine **1D** undergoes 1,3-dipolar cycloaddition with tetracyanoethylene (TCNE) at 20-90 °C to yield 3-(2-pyridyl)cyclopropanetetracarbonitrile **11** and 3-(tricyanovinyl)-[1,2,3]triazolo[1,5-*a*]pyridine **13T** via unobserved pyrazolines **10** and **12**. FVP of triazole **13T** affords an IR absorption at 2080 cm^{-1} ascribed to the corresponding diazo compound **13D**.

Introduction

The tetrazole – azide valence tautomerization, e.g. in tetrazoloazines (Scheme 1) is well-known,[1,2,3] and it is usually possible to observe both the tetrazole and the azide valence isomer. The tetrazoles are usually of lower enthalpy, but because the enthalpy differences are small, positive entropies of azide formation make the azide forms accessible or even dominating, at mildly increased temperatures.[3,4]

Scheme 1. Tetrazole – Azide Valence Isomerization[a]

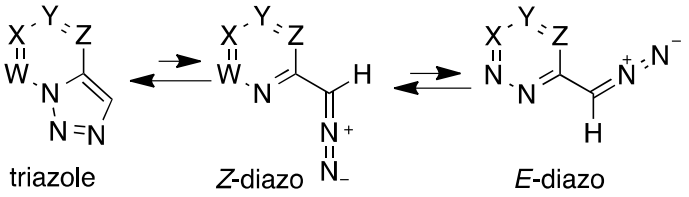


[a]In this paper *Z* and *E* are used to denote s-*Z* and s-*E* conformers.

The corresponding triazoloazine – diazomethylazine valence tautomerization (Scheme 2) is much less well known. Calculations indicate an enthalpy difference of 6-10 kcal/mol between the triazole and the diazo compound, with the triazole at the lowest enthalpy, and an activation barrier around 20 kcal/mol for the ring opening of the triazoles

(see details below).[5,6] This makes it difficult to observe the diazo valence isomers directly in solution, and only a few cases, in the [1,2,3]triazolo[1,5-*a*]pyrimidine series (ΔG^{o} =18±2 kcal/mol by ^{1}H NMR spectroscopy), have been reported.[7]

Scheme 2. Triazole – Diazomethane Valence Isomerization



However, once again, positive entropies make the ring-opened isomers relatively more stable at elevated temperatures, and several α-diazomethylazines have in fact been observed spectroscopically by low-temperature isolation of the products of flash vacuum pyrolysis (FVP) of triazoles at temperatures below or near the temperatures needed for decomposition by N_2 loss. Thus, 9-dizomethylphenanthridine[8] and 2-diazomethylpyrazine[9] were observed by IR spectroscopy, albeit as the minor constituents in the presence of unchanged triazole. Photolysis may also generate diazo isomers from triazoles, but this of course does not say anything about the thermochemistry, and the *Z/E* ratios obtained for the diazo isomers on photolysis are not necessarily the thermodynamic ratios. Calculations indicate that the *Z*-isomers of 2-azidoazines and 2-diazomethylazines are of lower energy than the *E*-isomers[6] (Schemes 1 and 2). IR absorptions of photochemically generated 2-diazomethylpyridine,[10] 2-diazomethylpyrazine,[9] 2-diazomethylquinoline,[11] 1-diazomethylisoquinoline,[11] 2-diazomethylquinoxaline,[12] and 4-diazomethylquinazoline[13] have been reported, but even under these conditions, it can sometimes be difficult to observe appreciable amounts, and the triazoles may photolyze very sluggishly.[8,11]

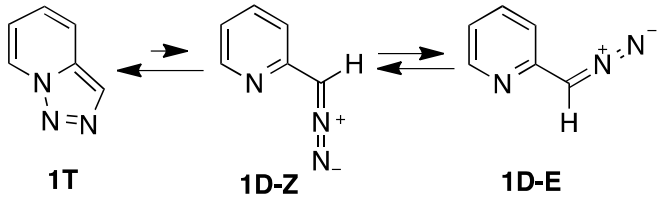
Results and Discussion

1. Direct observation of 2-Diazomethylpyridine

FVP was carried out in quartz tubes consisting of a sublimation zone and a pyrolysis zone, each 10 cm x 0.8 cm I.D., housed in a vacuum chamber in an apparatus allowing the deposition of thermolysis products at 77 K on a KBr target attached to a liquid nitrogen cryostat.[14] The distance from the exit of the pyrolysis tube to the cold KBr target was 2.5 cm. Vacuum was maintained at $\sim 10^{-4}$ hPa with a turbomolecular pump. Using this apparatus, [1,2,3]triazolo[1,5-*a*]pyridine **1T** (Scheme 3) did not undergo any reaction at temperatures below 200 °C. At higher temperatures 2-diazomethylpyridine **1D** was formed, with a maximal intensity of its 2080 cm^{-1} absorption at 400 °C (Figure 1a).

On subsequent warming of the cold pyrolyzate, the diazo absorption disappeared rapidily above -40 °C (Figure 1b). The end spectrum was identical with that of the starting material **1T**. The observation of a single, sharp absorption at 2080 cm^{1} suggests that the *Z* form, **1D-Z**, is being observed because this is calculated to be of lower energy[6] (cf. Figure 2), although it is possible that the absorptions of the two isomers cannot be resolved in the 77 K IR spectrum. The same thermodynamic considerations do not apply under photolysis conditions, where both **1D-Z** and **1D-E** may be formed, as indicated by a double absorption at 2075 and 2095 cm^{-1} in the Ar-matrix IR spectrum.[10] Similarly, in the case of 2-diazomethylpyrazine, a double absorption at 2092 and 2076 cm^{-1} was observed for the photochemically generated compound in Ar matrix,[9] but we observe a single absorption at 2080 cm^{-1} at 77 K under the FVP conditions described here.

Scheme 3. [1,2,3]Triazolo[1,5-*a*]pyridine – 2-Diazomethylpyridine Valence Isomerization



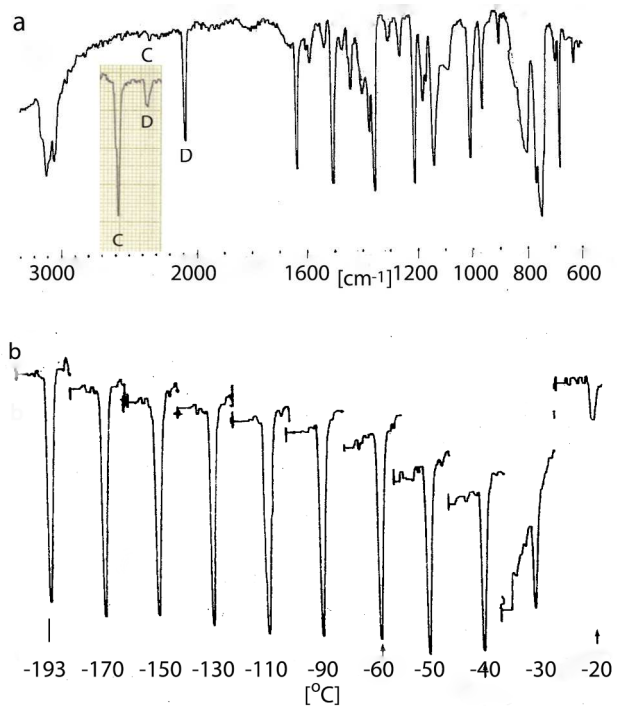
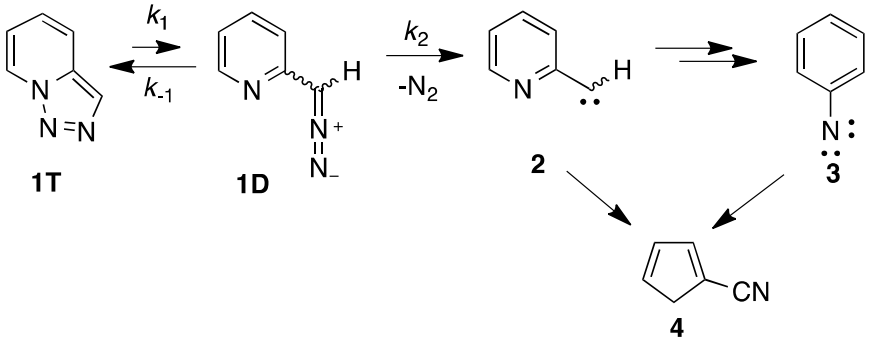


Figure 1. (a) IR spectrum (-196 °C) of the product of FVP of **1T** at 400 °C. The product consists of a mixture of triazolopyridine **1T** and 2-diazomethylpyridine **1D**, with the diazo peak (D) at 2080 cm^{-1}. A very weak absorption at 2215 cm^{-1} (C) is ascribed to cyanocyclopentadiene **4**. Inset: peaks D and C resulting from FVP at 620 °C. (b) Repetitive scanning of the 2080 cm^{-1} peak during warm-up from -193 °C towards room temperature. The heating rate is 10 °C per minute.

The intensity of the diazo absorption of **1D** increased further at an FVP temperature of 500 °C, but now cyanocyclopentadiene **4** (2215 cm^{-1}) was formed as well owing to the elimination of N_2 and rearrangement of the so-formed 2-pyridylcarbene **2** to phenylnitrene **3** and **4** (Scheme 4) as shown in Figures S1a-b (Supplementary Material). The mechanism of this reaction was described recently.[15] At 620 °C the diazo absorption of **1D** at 2280 cm^{-1} was still visible, but **4** was now the major product (see Inset in Figure 1a and further details in Figure S1).

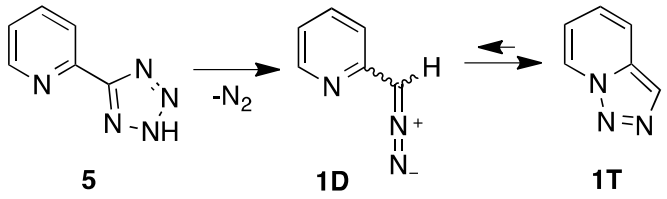
Scheme 4. Formation of 2-Pyridylcarbene 2, Phenylnitrene 3, and Cyanocyclopentadiene 4[a]



[a]Wiggly bonds denote undefined stereochemistry.

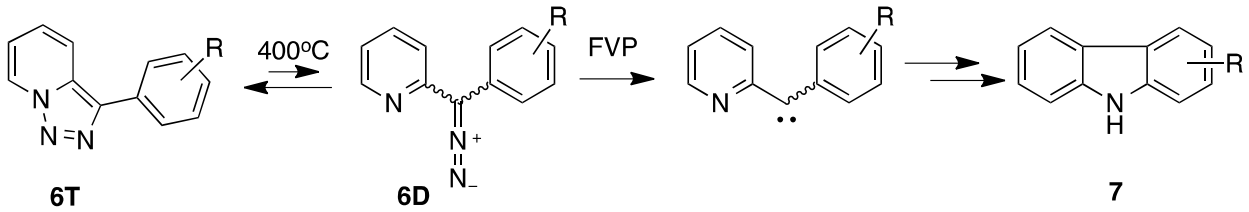
Diazo compound **1D** is also formed on FVP of 2-(5-tetrazolyl)pyridine **5** (Scheme 5).[16] **1D** either cyclizes to **1T** or decomposes to **2**, but the diazo absorption at 2080 cm^{-1} can again be observed in the IR spectrum following pyrolysis of **5** at 400-500 °C analogous to the experiment reported for **1T** above.

Scheme 5. Formation of 1D and 1T by FVP of Tetrazolylpyridine 5



Similar pyrolyses of substituted [1,2,3]triazolo[1,5-*a*]pyridines **6T** also resulted in the formation of absorptions at ~2080 cm^{-1} ascribed to the diazo isomers **6D** (Scheme 6), although the absorptions were weak to very weak in all cases. The best result were obtained for the 3-*m*-nitrophenyl, 3-*p*-nitrophenyl, 3-*p*-cyanophenyl and 3-*p*-methoxyphenyl derivatives **6Db-e** in the 200-400 °C range (see Figure S2, Supplementary Material, for the *m*-nitrophenyl derivative **6Dc**). At higher temperatures substituted carbazoles **7** were formed due to the well-established carbene-nitrene rearrangement of the phenyl(2-pyridyl)carbenes.[17]

Scheme 6. Substituted Triazolopyridines 6T Giving Rise to Weak Absorptions at ~2080 cm^{-1} Ascribed to the Diazo Valence Isomers 6D on FVP at 400 °C[a]



[a]**a**: R = H; **b**: R = *p*-MeO-C_6H_4; **c**: R = *m*-NO_2-C_6H_4; **d**: R = *p*-O_2N-C_6H_4; **e**: R = *p*-NC-C_6H_4. At higher temperatures carbazoles **7** are formed via carbene-nitrene rarrangement.[17]

2. Thermochemistry

We calculated the relative enthalpies and free energies for **1T**, **1DZ**, and **1DE** and the transition states connecting them at the B3LYP/6-31G* level of theory (Table 1), which has proved to be adequate for calculations on these and related systems.[5,6] The free energies are plotted in Figure 2.

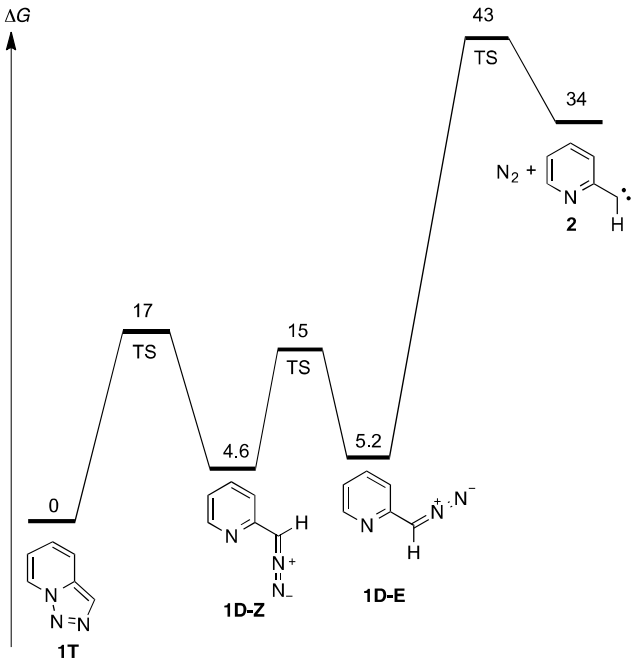


Figure 2. Free energy diagram (relative values of ΔG in kcal/mol) for triazolo/diazomethylpyridine **1T** and **1D** and their dissociation to 2-pyridylcarbene **2** and N_2 and the transition states connecting them at the B3LYP/6-31G* level. The corresponding values of ΔH are 0, 17.5, 6.7, 16, 7.3, 48 and 47 kcal/mol.

The calculated entropy change ΔS for the ring opening **1T → 1D-Z** is 7.02 e.u. at this level. Therefore, at room temperature (298 K) the $T\Delta S$ term contributes to a lowering of ΔG by ca. 2 kcal/mol. At 400 and 500 °C $T\Delta S$ is 4.7 and 5.4 kcal/mol, respectively. The

corresponding equilibrium constant at room temperature, K_{298} is ~10^{-4}. If thermodynamic equilibrium was attained – which is usually not guaranteed under FVP conditions – then the equilibrium constants calculated from the van't Hoff equation at 400 and 500 °C are K_{673} = 0.2 and K_{773} = 0.5 at the B3LYP level. In other words, there is no chance of observing the diazo compound **1D** at room temperature, but thanks to the strength of the diazo absorption in the IR, it is very feasible at elevated temperatures as long as the diazo compound does not decompose. Since it does decompose to form **4** above 400 °C, the optimal temperature for observing **1D** is close to 400 °C.

The thermal decomposition of **1T** was also monitored in diphenyl ether, where it followed first order kinetics[18] as measured by the volume of N_2 evolution in the temperature range 180-220 °C; e.g. at 180.5 °C: $k_{453.5}$ = 3.62 × 10^{-6} s^{-1}. The Arrhenius parameters were evaluated as log A_{obs} = 16; $E_{a(obs)}$ = 43.5±1 kcal/mol, from which we obtain the experimental enthalpy of activation ΔH^* = 42±1 kcal/mol, ΔS^* = 12 cal·$K^{-1}$$mol^{-1}$ and ΔG^* = 37±1 kcal/mol at 180 °C. The consistency of the experimental with the calculated data can be probed by considering the free energy of activation for 2-pyridylcarbene formation, which will be dominated by the step **1D-E → 2** = 38 kcal/mol at 298 K according to Figure 2. At 453 K (180 °C) this value becomes 36 kcal/mol in good agreement with the experimental value of 37 ± 1 kcal/mol, seeing that the calculations (Figure 2) refer to the gas phase, and the measurements to diphenyl ether solution.

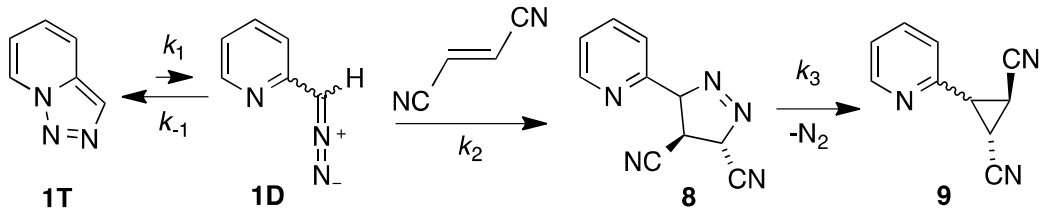
5-(2-Pyridyl)tetrazole **5** also underwent first-order decomposition with N_2 evolution in diphenyl ether solution at 180-220°C (log A = 15.2; $E_{a(obs)}$ = 41.5±1 kcal/mol, or ΔH^* = 40.5±1 kcal/mol).[19] This value is typical for tetrazoles, which are reported to decompose with activation barriers of 36-44 kcal/mol.[20] As shown above and supported by

other work,[15] **5** eliminates one molecule of N_2 to form **1D**, which then cyclizes to **1T**. Therefore, the further decomposition of **5** in solution will be that of **1T/1D** according to Figure 2.

3. Reactions of the Diazo Valence Isomer in Solution

Although the diazo compound **1D** is a reactive intermediate, which can only be observed directly under special conditions due to its low equilibrium concentration, it should nevertheless be generated rapidly in thermal equilibrium with **1T**, and this allows its trapping with dipolarophiles. We have reported the trapping with fumaronitrile, resulting in the formation of the 1-pyrazoline **8**.[18] However, 1-pyrazolines formed from diazo compound decompose very easily, often at room temperature, with the formation of cyclopropanes.[21] Therefore, under our reaction conditions (130-150°C in diphenyl ether) **8** undergoes fast elimination of N_2 to yield the cyclopropylpyridine **9** (Scheme 7).[19]

Scheme 7. Reaction of 1T/1D with Fumaronitrile (F)



The rate of N_2 evolution from **1T/1D** in the presence of a large excess excess of fumaronitrile (F) was measured previously and found to be ca. 100 times faster than the value given above in the absence of fumaronitrile, e.g. at 150 °C k_{obs} = 3.61 x 10^{-4} s^{-1}; $E_{a(obs)}$ ~ 17±2, or ΔH^* ~16±2 kcal/mol.[18] Here, the steady-state approximation, assuming k_3 is not rate determining, yielded $k_{obs} \sim k_1k_2[F]/(k_{-1}+ k_2[F])$ ([F] = 0.167 mol/L).[18] Assuming the

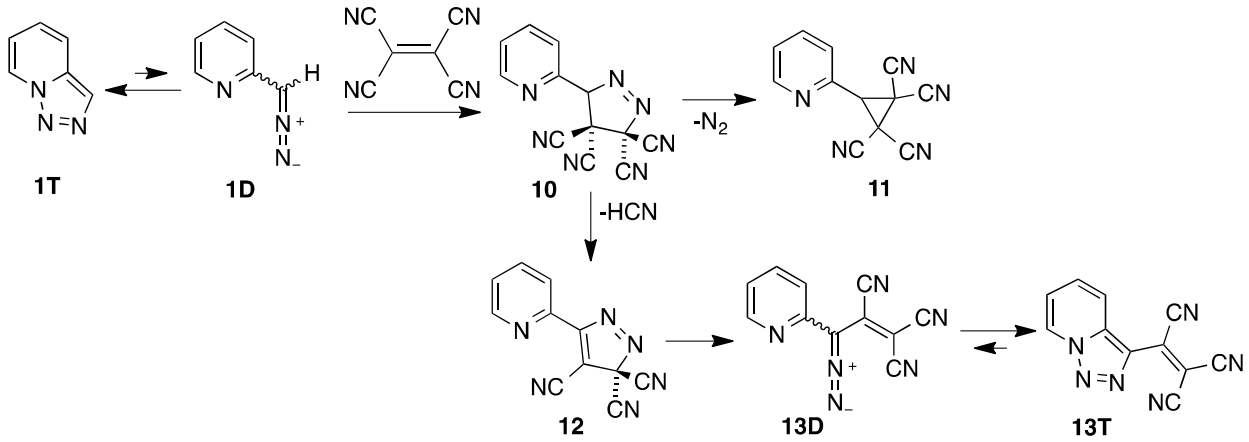
activation enthalpy for reaction of **1D** with fumaronitrile is 8 kcal/mol[22] and using $\Delta H^*_{obs} = \Delta H^*_1 - \Delta H^*_{-1} + \Delta H^*_2$ with the calculated enthalpy values from Figure 2, we get $\Delta H^* = 17.5 - 10.8 + 8 = 15$ kcal/mol in good agreement with the experimental value of 16 ± 2 kcal/mol.

If **1T** □ **1D** represents a fast pre-equilibrium, a better dipolarophile will result in a larger k_2, faster displacement of the equilibrium, and faster consumption of **1T**. From kinetic data for phenyl and diphenyldiazomethane[21,22] we can estimate an enthalpy of activation for cycloaddition of **1D** to tetracyanoethylene (TCNE) as ~7.5 kcal/mol. In fact, we have now determined that the reaction of **1T** with TCNE proceeds at 50 °C in toluene solution to yield two products, **11** and **13T** as well as a red, insoluble and unsublimable solid. The reaction even took place slowly at 20 °C in the course of 3 weeks with formation of the same two products and the red polymer. The reaction is interpreted in terms of initial formation of the 1-pyrazoline **10**, which could not be isolated (Scheme 8). Even at room temperature it decomposes with evolution of both N_2 and HCN. The product **11**, the expected tetracyanocyclopropane derivative, precipitated together with the red solid and was isolated by sublimation. The soluble compound **13T**, which was the major product, was isolated by chromatography. The amount of polymer increased as a function of thermolysis time. Furthermore, separate thermolysis of the isolated compound **11** in acetone solution at 50 °C also afforded the red solid. Thus, the low isolated yield of **11** (11%) is undoubtedly due to its instability under the reaction conditions.

The reactions are interpreted in Scheme 8 in terms of two competing reactions of the 1-pyrazoline **10**, (i) loss of N_2 to form **11**, and (ii) loss of HCN to form the 3*H*-pyrazole **12**. The latter decomposes further by ring opening to the 2-diazomethylpyridine **13D**, which then ring closes to **13T**. Compound **11** decomposes to the red solid, which features

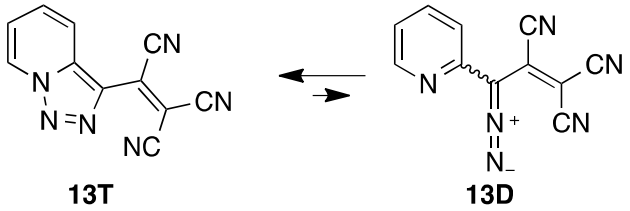
nitrile absorptions at 2200 and 2230 cm^{-1}; NMR and mass spectra could not be obtained. The red solid was not examined in detail because of its insolubility, but it is known that tetracyanocyclopropanes undergo both acid- and base-catalyzed ring opening,[23] as well as nucleophile-induced ring opening[24] and polymerization,[25] and recent calculations indicate that nucleophiles attack the "σ-hole" in the weakened bond between the two $C(CN)_2$ moieties.[26]

Scheme 8. Reaction of 1T/1D with Tetracyanoethylene



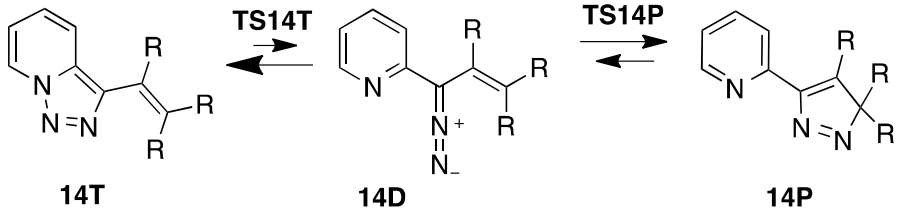
In contrast to **11**, the major product **13T** was stable under the thermolysis conditions and remained stable after heating at 95 °C in acetone solution in a closed system for 8 days. However, since **13T** is a [1,2,3]triazolo[1,5-*a*]pyridine, it should be capable of ring-opening to diazo compound **13D**. We subjected **13T** to FVP under the conditions described for **1T** above. No change took place up to a temperature of 330 °C, but after FVP at 430 °C, the low temperature IR spectrum featured a weak-to-medium absorption at 2080 cm^{-1}, which we ascribe to the 2-diazomethylpyridine **13D**. This absorption disappeared on warming of the pyrolyzate above -70 °C, and the resulting IR spectrum was identical with that of **13T** (Scheme 9 and Figure S3).

Scheme 9. 3-(Tricyanovinyl)-[1,2,3]triazolo[1,5*a*]pyridine – (2-Pyridyl)(tricyanovinyl)diazomethane Valence Isomerization



We examined the energetics of the interconversion of triazole **14T**, diazo compound **14D**, and 3*H*-pyrazole **14P** (Scheme 10) at the B3LYP/6-31G* computational level.

Scheme 10. Vinyltriazole – Vinyldiazo – 3*H*-Pyrazole Interconversion



The results for **14T** and **14D** are very similar to those for **1T** and **1D** at this level: the relative free energies ΔG for **14Ta**, **TS14Ta**, **14Da**, **TS14Pa**, and **14Pa** (R = H) are 0, 17, 6, 32, and 3 kcal/mol, respectively. For the tricyano-substituted compounds **14Tb**, **TS14Tb**, **14Db**, **TS14Pb**, and **14Pb** (R = CN) the corresponding values of ΔG are 0, 14, 10, 37, and 20 kcal/mol. Thus, the CN groups make the triazole **14Tb** (= **13T**) ca. 20 kcal/mol more stable than the pyrazole **14Pb** (= **12**) in agreement with the actual isolation of **13T**. Activation free energies for cyclization of other vinyldiazo compounds to pyrazoles are of the order of 27±2 kcal/mol.[27]

Conclusion

The valence isomerization [1,2,3]triazolo[1,5-*a*]pyridine **1T** – 2-diazomethylpyridine **2D** is endothermic by ~ 5 kcal/mol and has a free energy of activation of ~ 17 kcal/mol. This makes the diazomethylpyridine isomers unobservable at ambient temperatures, but they become observable by low-temperature IR spectroscopy following FVP at ~400 ^{o}C. At higher pyrolysis temperatures the diazo compounds decompose by elimination of N_2, rearrangement of the 2-pyridylcarbene **2** so formed to phenylnitrene **3** and ultimately cyanocyclopentadiene **4**. Aryl(2-pyridyl)diazomethanes **6D** were observed analogously. 2-Diazomethylpyridine **2D** is trapped in 1,3-dipolar cycloaddition reactions in solution. The pyrazoline **10** so formed with tetracyanoethylene eliminates N_2 to yield 3-(2-pyridyl)cyclopropanetetracarbonitrile **11** but also undergoes elimination of HCN to afford 3-vinyl-[1,2,3]triazolo[1,5-*a*]pyridine-1',2',2'-tricarbonitrile **13T**.

Experimental Section

The apparatus and methods for flash vacuum pyrolysis (FVP) have been described.[14] The apparatus illustrated in Figure 5 in ref. 14 was used. Vacuum was maintained at ~10^{-4} hPa using a high performance turbomolecular pump. Starting materials were sublimed into the pyrolysis tube at 40 ^{o}C, and pyrolyses were carried out at the temperatures given in the text. Pyrolysis products were isolated on KBr targets convectively cooled with liq. N_2 for IR spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded at 100.0 and 25.1 MHz, respectively. Mass spectra were recorded on a conventional sector instrument using electron ionization at 70 eV.

[1,2,3]Triazolo[1,5-*a*]pyridine 1T

This compound was prepared from **5** as described previously and obtained as white crystals, mp 38-40°C.[19] ^{1}H NMR (DMSO-d_6) 8.8 (d, J = 7 Hz, 1H), 7.9 (s, 1H), 7.7 (d, J = 9 Hz, 1H), 7.2 (dd, J = 9 and 6.5 Hz, 1H), 7.0 (dd, J = 6.5 and 7 Hz, 1H), see Figure S5. ^{13}C NMR (DMSO-d_6) 133.3 (C4), 125.6 (C8), 125.3 (C3), 117.9 (C5), 115.6 (C6, C7). For the decoupled and ^{1}H-coupled spectra and assignments, see Figures S6 and S7). IR (KBr) 1635 m, 1505 s, 1355 s, 1210 s, 1140 s, 1010 s, 800 vs, 750 vs, 680 s cm^{-1}. MS *m/z* (%), 119 ([$M^{\cdot+}$], 62), 92 (9), 91 (100), 65 (14), 64 (40), 63 (34), 52 (12), 51 (10), 50 (6), 45.5 ([M-N_2]$^{2+}$, 9), 44.5 (7).

2-Diazomethylpyridine 1D

For FVP of **1T** at 400 °C and IR spectrum (77 K) of 2-diazomethylpyridine **1D** (2080 cm^{-1}), see Figure 1. For FVP of **1T** at 330, 500 and 620 °C showing IR absorptions (77 K) of 2-diazomethylpyridine **1D** (2080 cm^{-1}) and cyanocyclopentadiene **4** (2215 cm^{-1}), see Figure S1.

5-(2-Pyridyl)tetrazole 5 was prepared as described previously.[19] FVP of this compound at 400-500 °C gave rise to an absorption at 2080 cm^{-1} in the 77 K IR spectrum, which is ascribed to the diazo compound **1D**.

***m*-Nitrophenyl)(2-pyridyl)diazomethane 6Dc**

m-Nitrophenyl)(2-pyridyl)diazomethane **6Dc** is formed by slow sublimation of 3-(*m*-nitrophenyl)-[1,2,3]triazolo[1,5-*a*]pyridine **6Tc** and FVP of the vapor at 210 °C. The IR spectrum of the neat pyrolyzate at 77 K features a diazo absorption at 2080 cm^{-1} (see Figure S2). This

absorption disappears on warming to -30 °C (see Figure S2). FVP of **6cT/6Dc** at 400 °C results in formation of the carbene and rearrangement to a mixture of 1- and 3-nitrocarbazoles **7**.[17]

3-(2-Pyridyl)cyclopropane-1,1,2,2-tetracarbonitrile 11.

A mixture of [1,2,3]triazolo[1,5-*a*]pyridine **1T** (119 mg, 1 mmol) and 1280 mg (10 mmol) of TCNE in 66 mL of toluene was heated with stirring at 50 °C for 24 h. The resulting precipitate was filtered, washed with toluene, and vacuum dried over $CaCl_2$ to yield 58 mg of crude product, which was sublimed at 130 °C/3 hPa to yield 25 mg (11%) of **11**, mp 160-161 °C. ^{1}H NMR (DMSO-d_6) 8.63 (m 1H), 7.91 (m, 2H), 7.51 (m 1H), 5.28 (s, 1H), see Figure S9. ^{13}C NMR 148.9, 146.3, 137.6, 126.5, 125.1, 111.3, 108.9, 41.1, 22.3, see Figures S10 and S11. IR (KBr) 3070 m, 3060 s, 2260 s, 1600 s, 1580 s, 1480 s, 1405 s, 1140 m, 1000 s, 790 s, 750 s cm^{-1}. MS *m/z* (%) 220 (7), 219 ($M^{\bullet+}$, 50), 193 (45), 104 (17), 78 (100). Anal. Calcd for $C_{12}N_5H_5$: C, 65.76; H, 2.30; N, 31.94. Found: C, 65.43; H, 2.25; N, 31.75.

3-Vinyl-[1,2,3]triazolo[1,5-*a*]pyridine-1', 2',2'-tricarbonitrile 13T

The toluene was distilled in high vacuum from the filtrate from the above thermolysis experiment, and the remaining substance was dissolved in ethyl acetate (5 mL per 100 mg) and purified by preparative layer chromatography on silica gel 60, PF_{254}, eluting with ethyl acetate. The main component with an RF value of 0.6 was isolated by extraction with acetone and analyzed as **13T** (1.23 g; 56%), mp 219-220 °C. ^{1}H NMR (DMSO-d_6) 9.52 (d, 1H), 8.29 (d, 1H), 8.08 (m, 1H), 7.63 (m, 1H), see Figure S14. ^{13}C NMR (DMSO-d_6) 134.4, 133.2, 128.6, 128.1, 127.9, 127.8, 119.0. 117.5, 113.2, 113.1, 112.1, see Figure S15. MS *m/z* (%) 221 (4), 220 ($M^{\bullet+}$,

28), 193 (12), 192 (100), 165 (21), 140 (62), 78 (100), see Figure S16. Anal. Calcd for $C_{11}H_4N_6$: C, 60.01; H, 1.83; N, 38.16. Found: C, 59.79; H, 1.80; N, 37.91.

FVP of this compound at 430 ^{o}C gave rise to a weak absorption at 2080 cm^{-1} ascribed to the diazo compound **13D** as well as cyano group absorptions at 2220-2260 cm^{-1} (see Figure S3).

Computational Details

All calculations were performed using the Gaussian 03 suite of programs.[28] Reported energies (298.15 K) include zero-point vibrational energy corrections. Enthalpies, entropies and free energies for all calculated compounds and imaginary frequencies for transition state structures are reported in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Partial IR spectra of **1T**, **1D** and **4**, 3-(*m*-nitrophenyl)-[1,2,3]triazolo[1,5-*a*]pyridine **6Tc** and the corresponding diazo compound **6Dc**, and **13D**; IR, ^{1}H and ^{13}C NMR spectra of **1T**, **11** and **13T**, mass spectra of **11** and **13T**, and computational data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc….

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Notes

The authors declare no competing financial interest.

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