

# Chemical Activation in Azide and Nitrene Chemistry: Methyl Azide, Phenyl Azide, Naphthyl Azides, Pyridyl Azides, Benzotriazoles, and Triazolopyridines

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Chemical activation (the formation of ‘hot’ molecules due to chemical reactions) is ubiquitous in flash vacuum thermolysis (FVT) reactions, and awareness of this phenomenon is indispensable when designing synthetically useful gas-phase reactions. Chemical activation is particularly prevalent in azide chemistry because the interesting singlet nitrenes are high-energy intermediates, and their reactions are highly exothermic. Consequently, chemical activation is observed in the isomerization of methylnitrene  $\text{CH}_3\text{N}$  to methylenimine (methanimine)  $\text{CH}_2=\text{NH}$ , facilitating the elimination of hydrogen to form HCN or HNC. Rearrangements of phenylnitrene, 1- and 2-naphthyl nitrenes, and 2-, 3- and 4-pyridyl nitrenes afford cyanocyclopentadiene, 3- and 2-cyanoindenes, and 2- and 3-cyanopyrroles, all showing the effects of chemical activation by undergoing facile interconversion of isomers. Chemical activation can often be reduced or removed entirely by increasing the pressure, thereby promoting collisional deactivation. Larger molecules having more degrees of freedom are better able to dissipate excess energy; therefore the effects of chemical activation are less pronounced or completely absent in the formation of 3-cyanoindole and 1-cyanobenzimidazoles from 3- and 4-quinolyl nitrenes and 4-quinazolinyl nitrenes, respectively. In compounds possessing nitro groups, chemical activation can cause the loss of the nitro group at nominal temperatures far below those normally needed to cleave the C-NO<sub>2</sub> bond.

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## Introduction

Chemical activation (CA) is the phenomenon of acceleration of chemical reactions due to excess thermal energy carried over from preceding reaction steps.<sup>[1]</sup> In other words the ‘hot’ molecules formed in exothermic reactions may contain sufficient vibrational energy to overcome the activation barrier for the next step(s) at temperatures where the reactions would not usually occur. Not only the exothermicity, but the energy difference between the preceding transition state and the ground state of the newly formed hot molecule can be used in this way. The phenomenon is most important for small molecules, because larger molecules have many more vibrational modes over which the excess energy can be redistributed.

Chemical activation is usually only observed for reactions in the gas-phase at low pressure, because collisions with other molecules will help deactivate the hot molecules. Thus, it can be expected in many flash vacuum thermolysis (FVT) reactions. It is important to consider this possibility, because so-called ‘control experiments’ prove nothing if CA is involved in the reaction under investigation but not in the control. In practise, the unactivated process may take place at temperatures several hundred degrees above that of the chemically activated one.

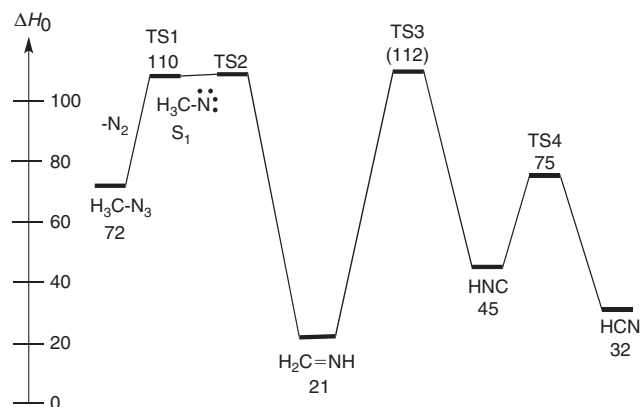
It is also noted that reactions in crossed molecular beams can lead to vibrationally excited molecules and radicals, which can therefore undergo secondary isomerizations. The exact collision energies and available excess energies in the observed reaction channels can often be determined in such experiments.<sup>[2]</sup>

In a thermal reaction such as FVT at low pressure, molecules are activated by collisions with the wall rather than with other molecules. But collisions can also serve to deactivate hot molecules. Thus, performing an FVT reaction at a higher pressure, for example in a stream of Ar or N<sub>2</sub>, may deactivate chemically activated molecules sufficiently, so that the ‘unactivated’ chemistry is observed. A change from e.g. 10<sup>−3</sup> hPa to 1 hPa can be sufficient. Examples will be presented below.

Although CA is typically a low-pressure gas-phase phenomenon, there are occasional suggestions of chemical activation in solution. The case of an unusually reactive benzyne derivative was reported recently.<sup>[3]</sup> The aryne was formed in an intramolecular [2+4] cycloaddition reaction of a triyne and estimated to be exothermic by ~50 kcal mol<sup>−1</sup> (1 kcal mol<sup>−1</sup> = 4.186 kJ mol<sup>−1</sup>), and it is suggested that this excess energy is the reason for the increased reactivity.<sup>[4]</sup>

## Methyl Azide – Methylnitrene – Methanimine – HCN + H<sub>2</sub>

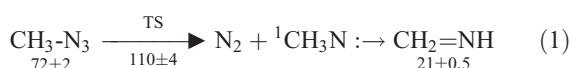
Methylnitrene has a triplet ground state and a singlet–triplet energy splitting of ~31 kcal mol<sup>−1</sup>, and the singlet is an extremely fleeting intermediate.<sup>[5–7]</sup> The thermal and photochemical decomposition of methyl azide  $\text{CH}_3\text{N}_3$  **1** has been investigated since 1933, but the early studies, particularly as regards the possible formation of methylnitrene  $\text{CH}_3\text{N}$  and methylenimine  $\text{CH}_2=\text{NH}$  (methanimine; formaldimine) gave



**Fig. 1.** Thermolysis of methyl azide **1**. Experimental enthalpies of formation of **1**,  $\text{CH}_2=\text{NH}$ , HNC and HCN and activation energies for denitrogenation of  $\text{CH}_3\text{N}_3$  and isomerization of HNC to HCN in  $\text{kcal mol}^{-1}$  (error limits  $\pm 2$  for **1**,  $\pm 4$  for TS1,  $\pm 1$  for  $\text{CH}_2\text{NH}$ , HNC, HCN, and TS4). A small barrier is assumed for the 1,2-H shift (TS2) in singlet  $\text{CH}_3\text{N}$  (see text).

contradictory and inconclusive results. Leermakers and others postulated the formation of methylenimine, but it was not directly identified.<sup>[8]</sup> Darwent and others denied the formation of  $\text{CH}_2=\text{NH}$  altogether.<sup>[9]</sup> However, 1,2-shifts of H and substituents are ubiquitous in carbene and nitrene chemistry,<sup>[10,11]</sup> so it would be expected that methylenimine  $\text{CH}_2=\text{NH}$  was a primary product of methyl azide decomposition.

In 1979, Fischer, Wentrup, and Winnewisser (FWW) investigated the FVT of methyl azide **1** by real-time, online millimeterwave spectroscopy.<sup>[12–14]</sup> The azide was pyrolyzed in the temperature range 500–900°C at  $10^{-2}$  hPa, and the products were led directly into the evacuated and continuously pumped  $250 \times 10$  cm glass cell of the millimeterwave spectrometer.<sup>[15]</sup> Methylenimine was unambiguously identified as a product by monitoring characteristic frequencies,<sup>[16]</sup>  $J = 6_{1,5} \leftarrow 6_{1,6}$ ;  $F = 5 \leftarrow 5$ ,  $F = 7 \leftarrow 7$  (110896.94 (25) MHz) and  $J = 6_{1,5} \leftarrow 6_{1,6}$ ;  $F = 6 \leftarrow 6$  (110899.28(25) MHz). The intensities of the methylenimine signals increased over the temperature range 500–900°C. Moreover, signals due to HCN were also present,<sup>[17]</sup> weakly at 500°C, but strongly at 900°C. FWW interpreted this in terms of chemical activation of the methylenimine by  $89 \pm 5 \text{ kcal mol}^{-1}$  arising from the activation energy for denitrogenation of azido-methane<sup>[18]</sup>  $\sim 38 \pm 2 \text{ kcal mol}^{-1}$  plus the exothermicity of the reaction  $\sim 51 \pm 3 \text{ kcal mol}^{-1}$ <sup>[19,20]</sup> (Eqns 1 and 2 and Fig. 1). This amount of CA is hardly enough by itself for the elimination of  $\text{H}_2$ , but the additional thermal energy available on FVT at 500–900°C allows the decomposition to take place.<sup>[12–14]</sup> Temperatures above 1000°C are required to decompose the unactivated methylenimine to HCN under these conditions.<sup>[21]</sup>

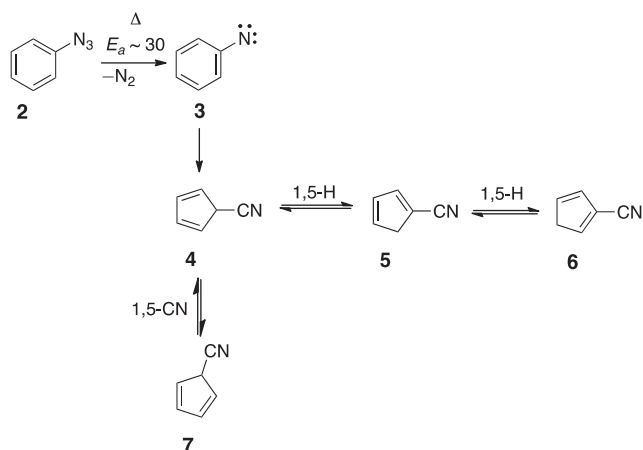


This thermochemical estimate is in excellent agreement with a CASPT2 calculation, giving an energy difference of  $82.9 \text{ kcal mol}^{-1}$  between  ${}^1\text{CH}_3\text{N}$  and  $\text{CH}_2\text{NH}$  and a low barrier of  $2.5 \pm 1 \text{ kcal mol}^{-1}$  for the 1,2-H shift in the singlet nitrene.<sup>[6]</sup>

The microwave spectrum of methylenimine generated by pyrolysis of methyl azide at 490°C (and of aminoacetonitrile at 740°C) was also reported by Brown, Godfrey, and Winkler.<sup>[22]</sup> Formation of methylenimine by pyrolysis of methyl azide and its chemically activated decomposition to HCN and  $\text{H}_2$  was confirmed by photoelectron spectroscopy in detailed studies by Bock and Dammel and others,<sup>[23]</sup> and more recently by cavity ring down spectroscopy by Dagdigian et al.<sup>[24]</sup> However, on the basis of semiempirical calculations, Bock and Dammel concluded that methylnitrene (singlet or triplet) was not an intermediate, i.e. that the formation of methylenimine was concerted with  $\text{N}_2$  loss from methyl azide, and this was supported by early *ab initio* calculations.<sup>[25]</sup> More recently, multiconfigurational *ab initio* calculations (CASSCF and CAS/MP2) have revealed that methylnitrene (singlet and/or triplet) is indeed an intermediate, which undergoes isomerization to methylenimine via a very low barrier ( $1.4 \text{ kcal mol}^{-1}$ ), and a second reaction channel leads directly from singlet methylnitrene to  $\text{HCN} + \text{H}_2$  (barrier  $19.4 \text{ kcal mol}^{-1}$ ).<sup>[26]</sup> The methylenimine can undergo chemically activated decomposition to HCN and  $\text{H}_2$  as well. The calculated barrier is  $107 \text{ kcal mol}^{-1}$ , so in the absence of CA this reaction will be extremely slow at temperatures below 1000°C. The decomposition of methylenimine to HNC and  $\text{H}_2$  (Eqn 3) has a much smaller calculated activation barrier of  $91 \text{ kcal mol}^{-1}$  — close to the amount of chemical activation available ( $89 \pm 5 \text{ kcal mol}^{-1}$ ; see Fig. 1) — which raises the question why HNC has not been observed.<sup>[26,27]</sup> In fact, it has long been known that matrix photolysis of methylenimine at 4 K affords mainly HNC with little HCN.<sup>[28]</sup> A likely explanation is that HNC is in fact formed in the FVT reactions, but it too is chemically activated and rearranges rapidly to HCN.<sup>[27,29]</sup> The barrier for this process (Eqn 4) is  $\sim 30 \text{ kcal mol}^{-1}$ ,<sup>[30]</sup> and the enthalpy of formation difference between HNC and HCN is close to  $14 \text{ kcal mol}^{-1}$ .<sup>[30,31]</sup> This means that the thermal decomposition of methyl azide under FVT conditions can yield chemically activated  $\text{CH}_2=\text{NH}$  and chemically activated HNC, which finally isomerizes to HCN (Eqns 1–4). The tautomerization of HNC to HCN will also be facilitated by collisions with the walls of the pyrolysis tube in FVT experiments. For the same reason all our attempts to observe the millimeterwave spectrum of some other unstable and easily tautomerizable molecules such as HOCN and  $\text{H}_2\text{N-C}\equiv\text{C-H}$  failed because of wall-catalyzed isomerization to HNCO and  $\text{HN}=\text{C}=\text{CH}_2/\text{CH}_3\text{CN}$ ,<sup>[32]</sup> respectively.

The formation of singlet methylnitrene and its isomerization to methylenimine were revealed in an investigation of the collision-free photolysis of azidomethane.<sup>[33]</sup> The hot methylenimine underwent two distinct decay reactions, one to HNC via 1,1- $\text{H}_2$  elimination, and one to HCN via sequential elimination of H atoms, first from the NH function. Much more energy is available in these photochemical reactions, and elimination of H atoms is not likely to be competitive under FVT conditions. Also, the observation of distinct pathways for HNC and HCN formation in the photolysis does not preclude the very favourable  $\text{HNC} \rightarrow \text{HCN}$  isomerization under FVT conditions (Eqn 4).

*Ab initio* trajectory calculations also predicted  $\text{H}_2$  elimination to produce HNC and both molecular ( $\text{H}_2$  elimination) and radical (H atom elimination) routes to HCN.<sup>[34]</sup>



Scheme 1.

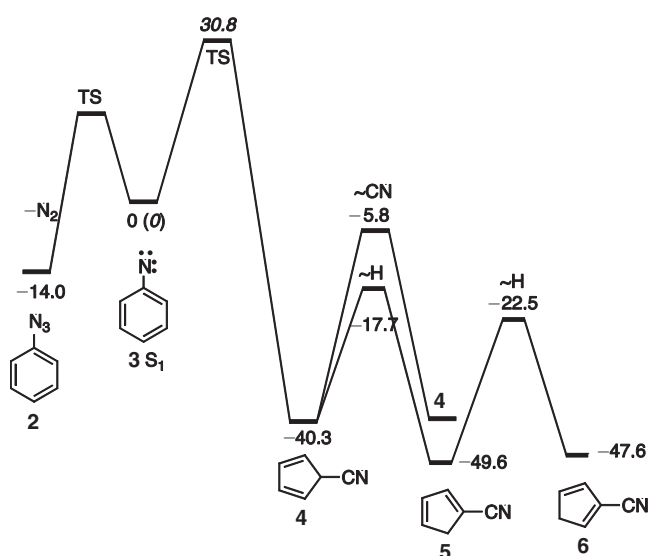


Fig. 2. Relative energies in kcal mol<sup>-1</sup>: B3LYP/6-31G\* + ZPVE (normal font) and CASSCF(8,8)/CASPT (italics).

### Phenyl Azide – Phenyl Nitrene – Cyanocyclopentadiene

The open-shell singlet phenyl nitrene  $S_1$  **3** has been characterized spectroscopically.<sup>[35]</sup> It lies  $\sim 15$  kcal mol<sup>-1</sup> above the ground state triplet  $T_0$  **3**.<sup>[36]</sup> FVT of phenyl azide **2** at high temperatures affords cyanocyclopentadiene **5**; high temperature is necessary because under milder conditions the nitrene is deactivated to the triplet ground state, which yields azobenzene and aniline as the major products.<sup>[37]</sup> The activation energy for denitrogenation of phenyl azide in solution has been reported as 32.6<sup>[38]</sup> or 30.0<sup>[39]</sup> kcal mol<sup>-1</sup>. The activation barrier for ring contraction of the open shell singlet  $S_1$  phenyl nitrene in the gas-phase is calculated as 32 kcal mol<sup>-1</sup> at the CASPT2 level (see Scheme 1 and Fig. 2).<sup>[40]</sup>

The 5-cyano-5H-cyclopentadiene **4** initially formed lies  $\sim 40$  kcal mol<sup>-1</sup> below the  $S_1$  nitrene and  $\sim 71$  kcal mol<sup>-1</sup> below the transition state for ring contraction. Therefore **4** can be activated by as much as 71 kcal mol<sup>-1</sup>. This is far more than the energy required for cycloperambulation in the cyanocyclopentadiene (23–27 kcal mol<sup>-1</sup> for H-shifts and  $\sim 34$  kcal mol<sup>-1</sup> for CN-shifts calculated at the B3LYP/6-31G\* level) (see Scheme 1 and Fig. 2). Labelling experiments have demonstrated that, in

fact, all ring carbon atoms in cyanocyclopentadiene become completely scrambled due to these rapid sigmatropic shifts of H and CN.<sup>[41]</sup>

### Naphthyl Azides – Naphthyl Nitrenes

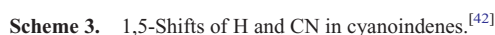
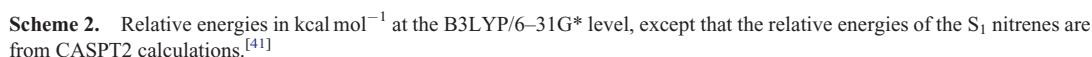
A mixture of 2- and 3-cyanoindenes **17** and **16** is obtained on FVT of 1- and 2-naphthyl azides **8** and **22** as well as the triazoles and tetrazoles **10**, **11**, **21**, and **24** at 340–400°C (Scheme 2). The triazoles and tetrazoles have been shown to be precursors of quinolyl- and isoquinolylcarbenes, which rearrange to the 1- and 2-naphthyl nitrenes via ring expansion to cyclic carbodiimides **12** and **19**.<sup>[42]</sup> The nitrenes finally undergo ring contraction to the cyanoindenes (Scheme 2).

Experiments at different temperatures and pressures reveal that the product ratios are strongly affected by chemical activation. The calculated energies of 3- and 2-cyanoindene **16** and **17** are 36 and 38 kcal mol<sup>-1</sup> below the cyclic ketenimine **12**, respectively (B3LYP/6-31+G\* energies).<sup>[43]</sup> With calculated activation energies for ring contraction of 32–38 kcal mol<sup>-1</sup> for the two nitrenes, the initially formed 3-cyano-3H-indene **15** may be activated by as much as 75 kcal mol<sup>-1</sup> and the 3-cyanoindene itself by 81 kcal mol<sup>-1</sup> (see Scheme 3), regardless whether they are generated from the azides, the triazoles, or the tetrazoles. This CA will cause interconversion of the cyanoindenes by means of sigmatropic shifts of H and CN (Scheme 3). The highest activation barrier in this scheme,  $\sim 53$  kcal mol<sup>-1</sup> above the energy of 3-cyanoindene **16**, corresponds to the 1,5-shift of CN, from C3 to C2, so even at this transition state there are still at least 25 kcal mol<sup>-1</sup> of excess energy available. 2-Cyanoindene **17** is a little lower in energy than 3-cyanoindene, so under conditions of reversibility, 2-cyanoindene will be the major product, and this is exactly what is found experimentally, from all precursors, on FVT at 10<sup>-3</sup> hPa. However, when N<sub>2</sub> is used as a carrier gas at 1 Torr, 3-cyanoindene becomes the principal ring contraction product in all cases due to collisional deactivation, so it can be concluded that 3-cyanoindene is the primary product. Since the cyanoindenes have more degrees of freedom than cyanocyclopentadiene **5** (3N – 6 = 48 and 30 vibrational modes, respectively), they are able to distribute some excess energy more readily; consequently it becomes easier to deactivate the cyanoindenes than cyanocyclopentadiene collisionally. Furthermore, the isomerization of the cyanoindenes has to go through non-aromatic *ortho*-quinonoid intermediates (Scheme 3, Fig. 3), which raise the activation barriers compared with cyanocyclopentadiene. When pure, isolated samples of 2- or 3-cyanoindenes are subjected to FVT (i.e. in the absence of chemical activation), their interconversion requires much higher temperatures (800–1000°C).<sup>[44,45]</sup>

Note also that, as usual,<sup>[37,46]</sup> the singlet carbenes are of higher energy than the isomeric, open-shell singlet nitrenes (by 20–26 kcal mol<sup>-1</sup> in Scheme 3).

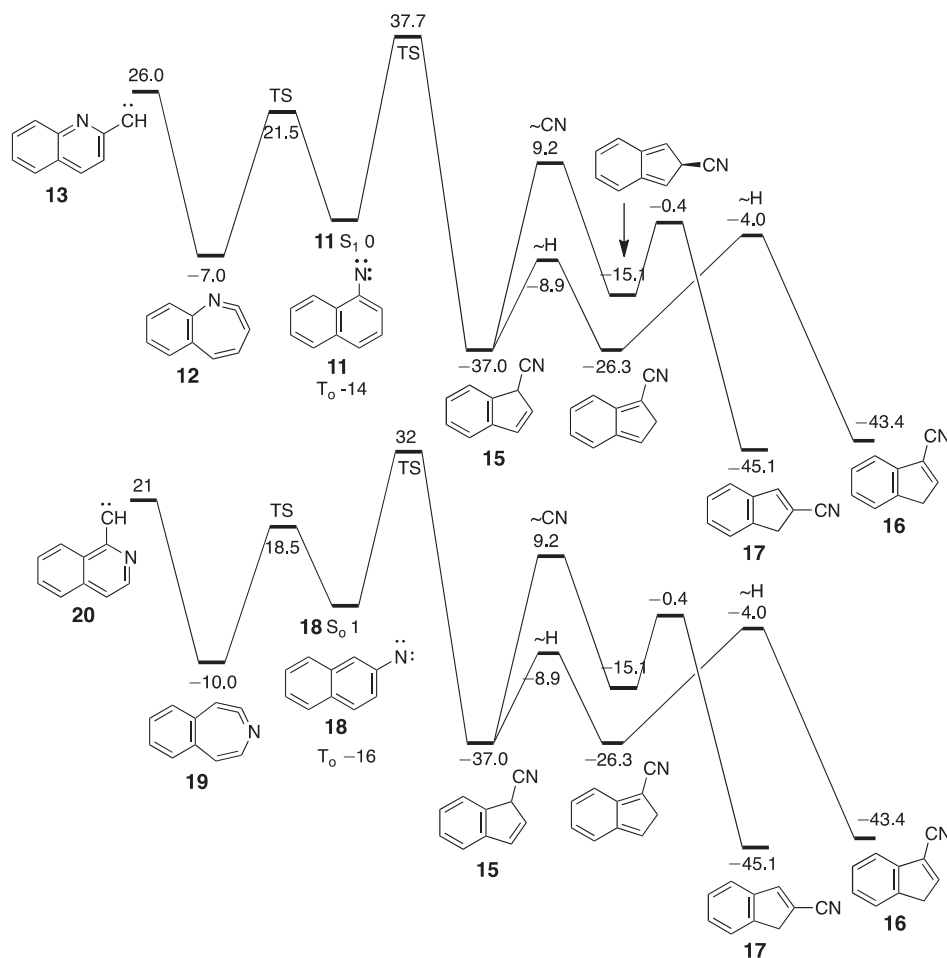
### 3-Pyridyl Nitrene – 2- and 4-Pyrimidinylcarbenes – Cyanopyrroles

FVT of 3-azidopyridine **25** affords a mixture of 3- and 2-cyanopyrroles **30** and **31**, with the 3-cyanopyrrole isomer dominating.<sup>[45,47]</sup> For the  $S_1$  3-pyridyl nitrene **26** the lowest energy route to ring contraction is via ring opening to the nitrile ylide **28**,<sup>[48]</sup> which has been observed directly (Scheme 4, Fig. 4).<sup>[49]</sup> Ylide **28** may be formed either directly from the nitrene or via the cyclic ketenimine **27** (Scheme 4). There is only a small, calculated barrier of 14–16 kcal mol<sup>-1</sup> for the ring

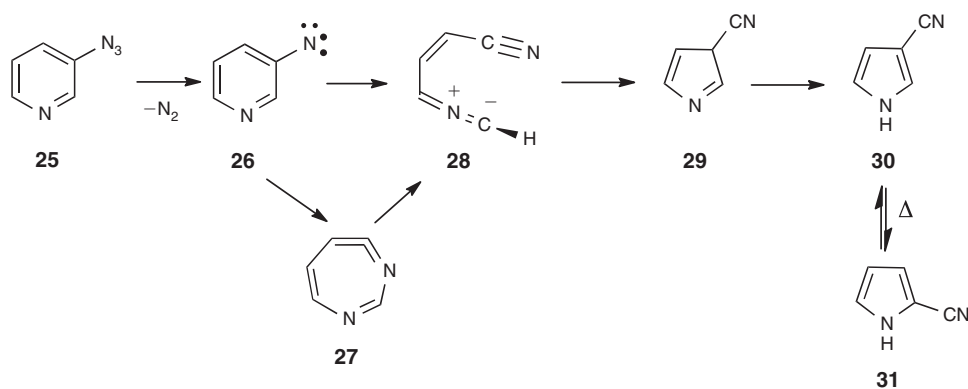


FVT of 2-(5-tetrazolyl)pyrimidine **34** also affords a mixture of 2- and 3-cyanopyrroles (**Scheme 6**). Similarly, the tetrazoles

First, the pyrimidinylcarbenes generated by double N<sub>2</sub> loss from the tetrazoles rearrange to 3-pyridylnitrenes **42** and **46** via ring expansion to cyclic carbodiimides **41** and **45** (Scheme 7). Second, the pyridylnitrenes and/or the seven-membered ring carbodiimides undergo ring contraction. As before, the lowest energy pathways proceed via the nitrile ylides **43** and **48** (Scheme 7). The initially formed 3-cyano-3*H*-pyrroles **44** and **49** can be activated by ~46 kcal mol<sup>-1</sup>, but, in addition, because the carbenes are higher in energy than the nitrene,<sup>[37,46]</sup> the reactions are easier when starting from the tetrazoles and afford good yields of the pyrroles at 400°C/10<sup>-3</sup> hPa. Mixtures of **37**, **38**, and **39** are invariably obtained from both tetrazole precursors under these conditions due to the sigmatropic shifts of H, CN, and CH<sub>3</sub>. However, already a pressure increase to 1 hPa N<sub>2</sub> leads to more distinct product mixtures, with dimethylcyanopyrrole **37** as the primary reaction product of **35**, and the isomeric



**Fig. 3.** Energy diagram for 2-quinolyl- and 1-isoquinolylcarbenes, 1- and 2-naphthyl nitrenes, and ring contraction to cyanoindenes. Note that azirine intermediates<sup>[42]</sup> have been omitted for clarity. Relative energies in kcal mol<sup>-1</sup> at the B3LYP/6-31G\* level.



**Scheme 4.** Ring opening–ring contraction in 3-pyridyl nitrene.<sup>[48,49]</sup>

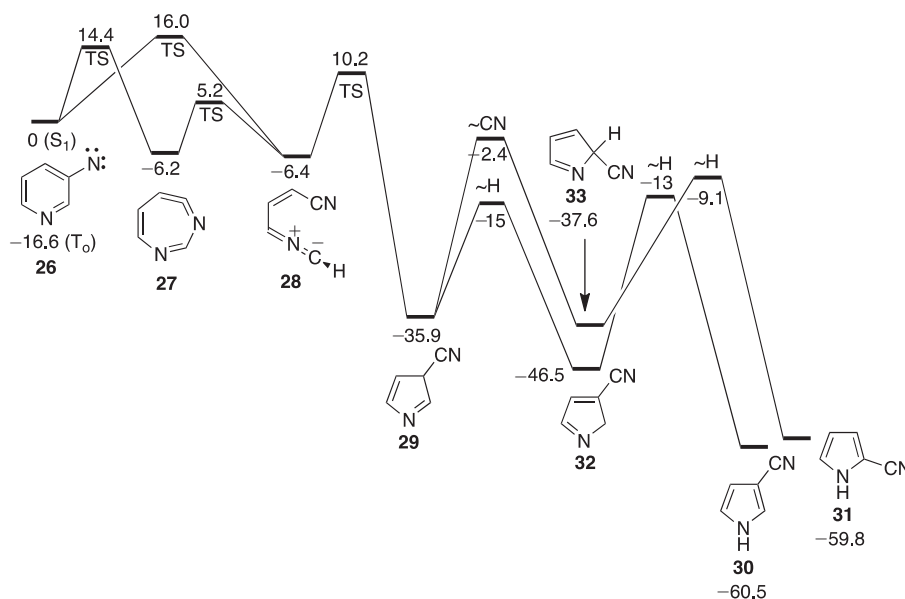
dimethylcyanopyrroles **38** and **39** as the primary products from **36**. FVT of the individual dimethylcyanopyrroles **37** and **38** requires a temperature of 800°C for isomerization to occur (see section on benzotriazoles below).<sup>[51,52]</sup>

#### Tetrazolo[1,5-*a*]pyridine – 2-Azidopyridine – 2-Pyridyl Nitrene

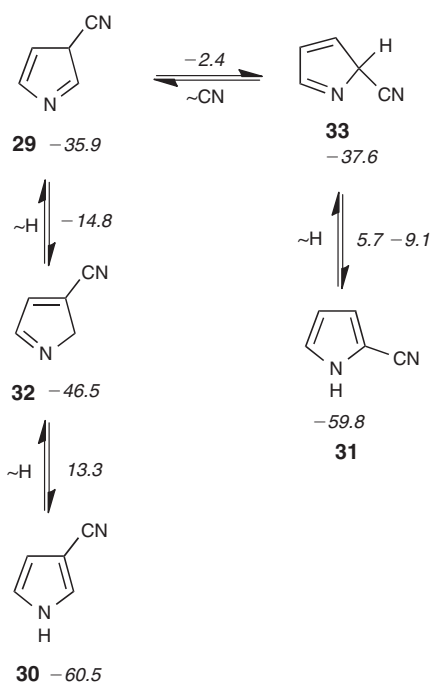
Tetrazolo[1,5-*a*]pyridine **50** is calculated to be 4 kcal mol<sup>-1</sup> lower in energy than the *anti*-2-azidopyridine **51** and 0.4 kcal

mol<sup>-1</sup> below the *syn*-2-azidopyridine **52**. The azide forms cannot be detected in solution at room temperature but are readily formed on mild FVT at 100–200°C and isolated at low temperatures.<sup>[53]</sup> The azide cyclizes back to the tetrazole at ~-10°C. FVT of the tetrazole/azide mixture at 370–500°C causes decomposition to the open-shell singlet S<sub>1</sub> 2-pyridyl nitrene **53** (Scheme 8). By analogy with phenyl azide and 3-pyridyl azide (see above), the activation energy for decomposition of the azide is expected to be 30–32 kcal mol<sup>-1</sup>.



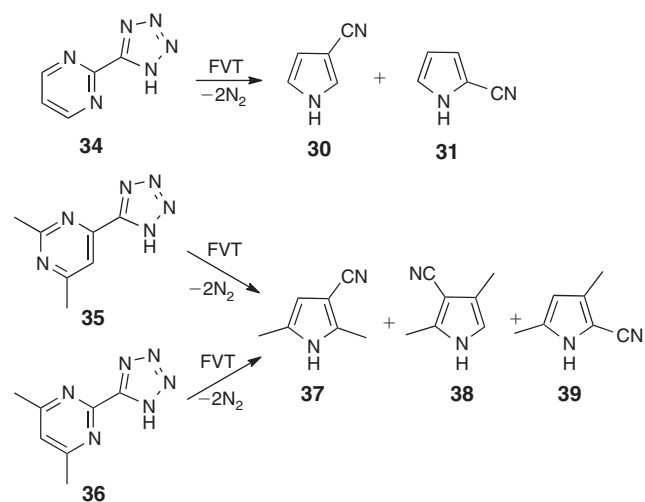


**Fig. 4.** The 3-pyridylnitrene – cyanopyrrole energy surface. Energies in  $\text{kcal mol}^{-1}$  relative to  $S_1$  3-pyridylnitrene **26** at the B3LYP/6–31G\* level.<sup>[45,49,50]</sup>



**Scheme 5.** Sigmatropic shifts of H and CN interconverting the cyanopyrroles (energies in  $\text{kcal mol}^{-1}$  at the B3LYP/6–31G\* level).<sup>[50]</sup>

Three different routes to cyanopyrroles from 2-pyridylnitrene **53** have been identified,<sup>[50]</sup> whereby the overall lowest energy path proceeds via ring opening to the biradical/vinylnitrene **56** (Scheme 9). Depending on the route and the method of calculation (B3LYP and CASPT2), CA will be present to the extent of at least  $52 \text{ kcal mol}^{-1}$  in the initially formed 2-cyano-2H-pyrrole **33**, or  $\sim 74 \text{ kcal mol}^{-1}$  in the 2-cyanopyrrole **31** itself (Scheme 9).<sup>[50]</sup> Not surprisingly therefore, the principal reaction product is again a mixture of 2- and 3-cyanopyrroles, even under the mildest possible conditions ( $400\text{--}500^\circ\text{C}/10^{-3} \text{ hPa}$ ) (Scheme 9).<sup>[50,54]</sup>

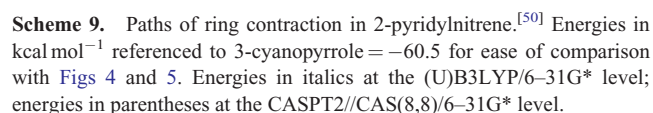
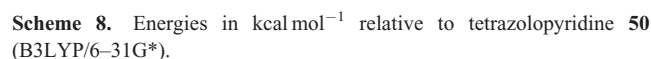


**Scheme 6.** Cyanopyrroles from tetrazole precursors of pyrimidinylcarbenes.<sup>[45]</sup>

### 6-Nitrotetrazolo[1,5-a]pyridine – 2-Azido-5-nitropyridine – 5-Nitro-2-pyridylnitrene

The C–NO<sub>2</sub> bond dissociation energy in nitrobenzene has been determined as  $70 \pm 3 \text{ kcal mol}^{-1}$  ( $\log A = 17.0 \pm 0.5$ ),<sup>[55]</sup> and this has been supported by a laser-powered homogeneous pyrolysis experiment<sup>[56]</sup> and by calculations using several different methods.<sup>[57]</sup> Fields and Meyerson generated phenyl radicals by pyrolysis of nitrobenzene at  $600^\circ\text{C}$ ,<sup>[58]</sup> but this was in a flow reactor with contact times of the order of 2–30 s (typically 9 s), which are  $\sim 1000$  times longer than those typically used in FVT experiments. Therefore, one does not expect the C–NO<sub>2</sub> bond to break under FVT conditions below  $700\text{--}1000^\circ\text{C}$ .

In agreement with this, FVT of 3-(*p*-nitrobenzyl)benzo[*c*]cinnoline at  $900^\circ\text{C}/0.02 \text{ hPa}$  (contact time  $\sim 10 \text{ ms}$ ) only gave products resulting from loss of the NO<sub>2</sub> group (phenanthrene, anthracene, and phenylacetylene).<sup>[59]</sup> In contrast, FVT of



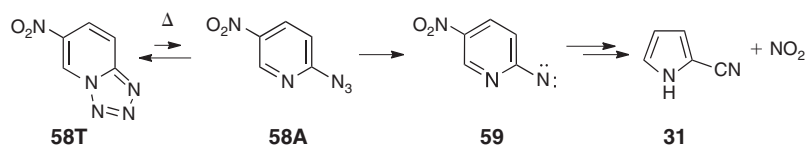
4-nitro-2,5-dimethylisoxazole in N<sub>2</sub> flow at 400°C (0.1 hPa) afforded 1-cyano-1-nitroacetone in quantitative yield, i.e. without any loss of the NO<sub>2</sub> group.<sup>[60]</sup>

In contrast to tetrazolo[1,5-*a*]pyridine **50** (Scheme 8), 6-nitrotetrazolo[1,5-*a*]pyridine **58T** exists in equilibrium with a small amount of the azide valence isomer **58A** at room temperature.<sup>[61]</sup> Chollet observed that the FVT of this material at 400°C/10<sup>-3</sup> hPa afforded a 15–20% yield of 2-cyanopyrrole **31** as well as NO<sub>2</sub> as the only low molecular weight products (Scheme 10).<sup>[62]</sup> NO<sub>2</sub> was identified by its IR spectrum<sup>[63]</sup> in the gas-phase. Loss of NO<sub>2</sub> is not expected at such a low temperature under FVT conditions. Therefore, the loss of NO<sub>2</sub> and the fact that only 2-cyanopyrrole – not 3-cyanopyrrole – was identified, suggest that CA caused the breaking of the C–NO<sub>2</sub> bond to form a 2-cyanopyrrolyl radical, which by hydrogen abstraction afforded the observed product. The 2-cyanopyrrole so formed will no longer be chemically activated and therefore does not undergo isomerization to 3-cyanopyrrole.

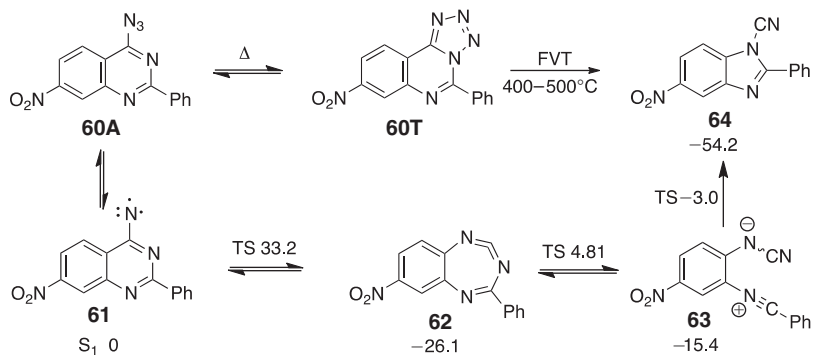
In contrast, the nitro group remains intact on FVT of 4-azido-7-nitro-2-phenylquinazoline/ 8-nitro-5-phenyltetrazolo[1,5-*c*]quinazoline **60A/60T** at 400–500°C to yield 5-nitro-2-phenylbenzimidazole-1-carbonitrile **64** quantitatively (Scheme 11).<sup>[64]</sup> The large molecule with 78 fundamental vibrational modes allows for more efficient redistribution of the excess energy and hence no apparent effect of CA, even though the reaction product will carry some 70 kcal mol<sup>-1</sup> of excess energy originating from the ring expansion of the S<sub>1</sub> nitrene **61**. The reaction also takes place photochemically, where it has been shown to proceed via the directly observed and spectroscopically characterized intermediates **62** and **63** (Scheme 11).

## 4-Azidopyridines and 4-Pyridylnitrenes

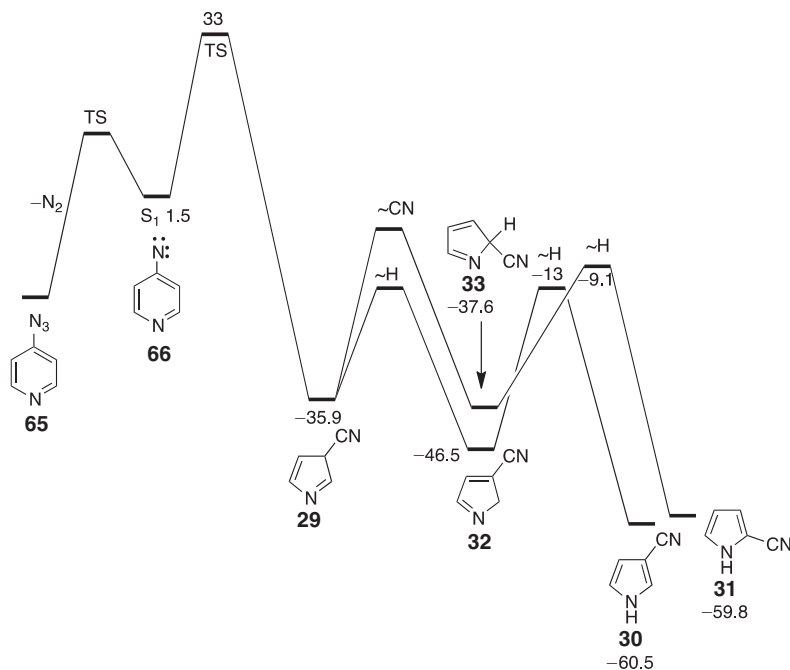
FVT of 4-azidopyridine **65** also affords a mixture of 3- and 2-cyanopyrroles **30** and **31** (Fig. 5). Here, the 3-isomer is expected to be the first-formed, but CA of  $\sim 68 \text{ kcal mol}^{-1}$  ensures that a mixture is obtained.<sup>[65]</sup> The concerted mechanism for ring contraction (Fig. 5) is analogous to that proposed for phenylnitrene above, and the calculated amount of CA is also very similar (compare Figs. 2 and 5). Note that much less CA is generated in the reaction of 3-pyridylnitrene **26** ( $\sim 51 \text{ kcal mol}^{-1}$ , Fig. 4) because this nitrene has an especially favourable pathway open, namely the ring opening to the nitrile ylide, which can only take place when there is a *meta*-relationship between a nitrene or carbene centre and a ring nitrogen atom.<sup>[48]</sup>



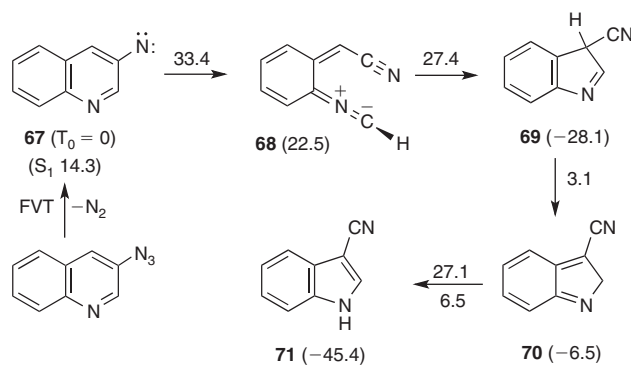
**Scheme 10.** 6-Nitrotetrazolo[1,5-*a*]pyridine – 5-nitro-2-pyridyl nitrene – 2-cyanopyrrole.<sup>[62]</sup>



**Scheme 11.** Relative energies in kcal mol<sup>-1</sup> at the BLYP/6-31G\* level.<sup>[64]</sup>



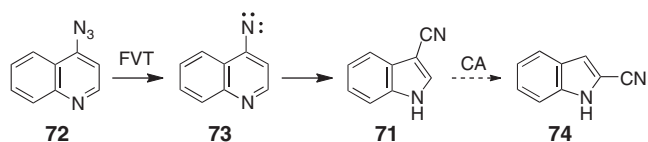
**Fig. 5.** The 4-pyridyl nitrene energy surface. Relative energies in kcal mol<sup>-1</sup> at the B3LYP/6-31G\* level on the same scale as Fig. 4.



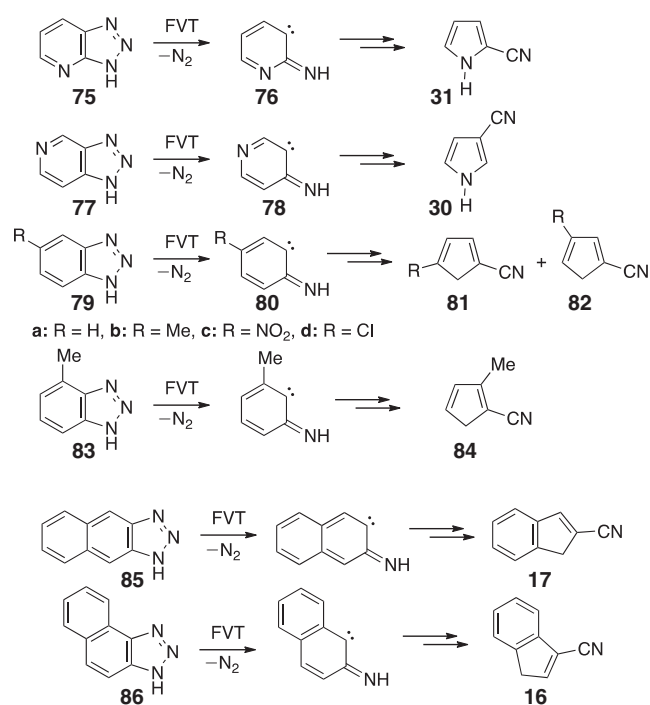
**Scheme 12.** Rearrangement of 3-quinolyl nitrene to 3-cyanoindole.<sup>[66]</sup>



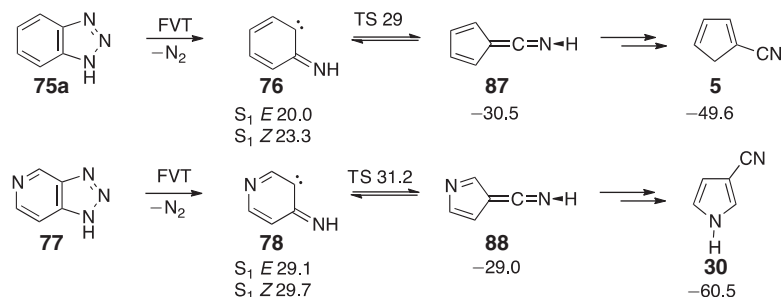
It is noteworthy that 3-azidoquinoline affords 3-cyanoindole **71** cleanly and in high yield without any appreciable isomerization to 2-cyanoindole.<sup>[66]</sup> The reaction mechanism (Scheme 12) has been elucidated under matrix-isolation photolysis conditions, and the same mechanism is expected to apply under FVT conditions. The calculated energies indicate that there would be enough energy available for isomerization, namely  $\sim 60 \text{ kcal mol}^{-1}$  for the 3-cyano-3*H*-indole **69** arising from ring opening/ring contraction in 3-quinolynitrene **67** (Scheme 12). The



**Scheme 13.** Rearrangement of 4-quinolynitrene to 3-cyanoindole (and chemically activated rearrangement to 2-cyanoindole).<sup>[67]</sup>



**Scheme 14.** Cyanopyrroles, -cyclopentadienes, and -indenes from triazoloarenes.<sup>[52]</sup>



**Scheme 15.** Ring contraction in benzotriazole and triazolo[4,5-c]pyridine. Relative energies are referenced to **5** =  $-49.6$  and **30** =  $-60.5 \text{ kcal mol}^{-1}$  in order to facilitate comparison with Figs 2, 4 and 5. For simplicity, only one of the two possible triazole tautomers is shown in each case. The other tautomer of **77** will generate isomers of **78** with very similar energies.

indoles have many more degrees of freedom than the pyrroles over which to dissipate the excess vibrational energy, with the result that the effects of CA are not apparent.

Similarly, 4-quinolynitrene **73** yields nearly pure 3-cyanoindole **71** on FVT with matrix isolation of the product, but partial rearrangement to 2-cyanoindole **74** is observed under preparative FVT conditions (Scheme 13). The mechanism is similar to that described for 1-naphthyl nitrene **11** and 4-pyridyl nitrene **66** above (Figs. 3 and 5). The CA causing partial isomerization to 2-cyanoindole can again be removed by increasing the pressure.<sup>[67]</sup>

## Triazolopyridines and Benzotriazoles

Interestingly, and synthetically usefully, the pure, unisomerized 2- and 3-cyanopyrroles **31** and **30** can be obtained in nearly quantitative yields by FVT of triazolopyridines **75** and **77**, respectively, at 600°C (Scheme 14).<sup>[52]</sup> Benzotriazole (**79a**) similarly gives cyanocyclopentadiene **81a** in virtually quantitative yield (Scheme 14).

Unisomerized methylcyanocyclopentadienes **81b** and **84** are obtained from the corresponding 4- and 5-methylbenzotriazoles **79b** and **83** at 500°C (a small amount of the tautomer **82b** accompanies **81b**) under mild conditions (500°C) and with a low degree of conversion, but interconversion of the nitriles takes place at 600–700°C.<sup>[52]</sup> Naphtho[4,5-*a*]- and naphtho[4,5-*b*] triazoles **85** and **86** yield the respective cyanindenes **17** and **16** on FVT at 500–600°C (Scheme 14), but interconversion of these nitriles does take place on FVT at 700–1000°C due to thermally activated substituent migration.<sup>[52]</sup> All these reactions are highly exothermic; the initially formed ketenimine can carry  $\sim 50 \text{ kcal mol}^{-1}$  excess energy in the benzotriazole case, and  $60 \text{ kcal mol}^{-1}$  in the triazolopyridine case as illustrated in Scheme 15. The final products, cyanocyclopentadiene **5** and 3-cyanopyrrole **30** are even more highly activated, by 70 and 90 kcal mol<sup>-1</sup>, respectively. As clearly revealed in the examples described above, this would be more than sufficient to isomerize a cyanopyrrole or cyanocyclopentadiene. The apparent absence of CA under mild FVT conditions is ascribed to the fact that the initial products are not nitriles but ketenimines **87** and **88**, formed in a Wolff-type rearrangement.<sup>[68]</sup> The ketenimines cannot easily undergo any sigmatropic rearrangements. The tautomerization to cyanopyrroles is likely to take place during workup and/or during collisions with the walls of the pyrolysis tube, which would help dissipate the excess energy.

That chemical activation is nevertheless present is revealed by the nitro-group effect: FVT of the NO<sub>2</sub>-substituted benzotriazole

(79c) leads to loss of the NO<sub>2</sub> group, and even in the case of the chloro-substituted benzotriazole (79d) there is a 20 % loss of Cl under the mildest possible conditions for reaction to occur (550°C/0.1 hPa). In contrast, the stronger F–C bond stays intact.<sup>[52]</sup>

## Conclusion

Chemical activation (CA) is ubiquitous in azide gas-phase chemistry because the nitrenes are high-energy intermediates, and their reactions are highly exothermic. Whereas the nitrenes usually have triplet ground states (T<sub>0</sub>), preparatively interesting rearrangements take place in the singlet nitrenes (S<sub>1</sub>). The effects of CA is observed in the isomerization of methylnitrene CH<sub>3</sub>N to methylenimine (methanimine) CH<sub>2</sub>=NH, where it causes elimination of hydrogen to form HCN or HNC already at FVT temperatures above 500°C, whereas a temperature above 1000°C is required in the absence of CA. FVT of the relevant aryl azides at 400–500°C generates phenylnitrene, 1- and 2-naphthyl nitrenes, and 2-, 3-, and 4-pyridyl nitrenes, which undergo ring contraction to cyanocyclopentadiene, 3- and 2-cyanoindenes, and 2- and 3-cyanopyrroles, respectively; CA causes facile interconversion of isomers by means of sigma-tropic shifts of both H and CN (and CH<sub>3</sub> when present), so that mixtures of nitriles are invariably obtained in each case. However, CA can be reduced or removed entirely by increasing the pressure, thereby promoting collisional deactivation. Using N<sub>2</sub> or Ar as carrier gas at a pressure of 1 hPa is usually sufficient to remove most of the CA. Because larger molecules have more degrees of freedom, they are better able to dissipate the excess energy, with the result that chemical activation is less apparent or completely absent in the formation of 3-cyanoindole and 1-cyanobenzimidazoles from 3- and 4-quinolyl nitrenes and 4-quinazolinylnitrenes, respectively. In compounds possessing nitro groups, chemical activation can cause the loss of the nitro group at nominal temperatures far below those normally needed to cleave the C–NO<sub>2</sub> bond, as seen in the example of 5-nitro-2-pyridyl nitrene.

## Supplementary Material

Details of the computational methods used and general experimental procedures are available on the Journal's website.

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