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Nitrile Imines and Nitrile Ylides: Rearrangements of Benzonitrile *N*-Methylimine and Benzonitrile Dimethylmethylide to Azabutadienes, Carbodiimides, and Ketenimines. Chemical Activation in Thermolysis of Azirenes, Tetrazoles, Oxazolones, Isoxazolones, and Oxadiazolones

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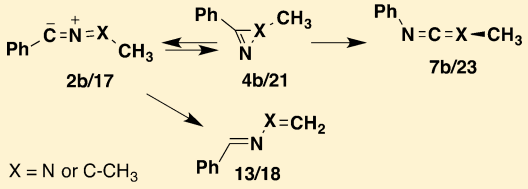
Supporting Information

ABSTRACT: Flash vacuum thermolysis (FVT) of 1-methyl-5-phenyltetrazole (**5b**), 2-methyl-5-phenyltetrazole (**1b**), and 3-methyl-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (**3b**) affords the nitrile imine (**2b**), which rearranges in part to *N*-methyl-*N*′-phenylcarbodiimide (**7b**). Another part of **2b** undergoes a 1,4-H shift to the diazabutadiene (**13**). **13** undergoes two chemically activated decompositions, to benzonitrile and $CH_2{=}NH$ and to styrene and N_2. FVT of 2,2-dimethyl-4-phenyl-oxazol-5(2*H*)-one (**16**) at 400 °C yields 3-methyl-1-phenyl-2-azabutadiene (**18**) in high yield. In contrast, FVT of 3,3-dimethyl-2-phenyl-1-azirene (**21**) at 600 °C or 4,4-dimethyl-3-phenyl-isoxazolone (**20**) at 600 °C affords only a low yield of azabutadiene (**18**) due to chemically activated decomposition of **18** to styrene and acetonitrile. There are two reaction paths from azirene (**21**): one (path a) leading to nitrile ylide (**17**) and the major products styrene and acetonitrile and the other (path b) leading to the vinylnitrene (**22**) and ketenimine (**23**). The nitrile ylide $PhC^-{=}N^+{=}C(CH_3)_2$ (**17**) is implicated as the immediate precursor of azabutadiene (**18**). FVT of either 3-phenylisoxazol-5(4*H*)one (**25**) or 2-phenylazirene (**26**) at 600 °C affords *N*-phenylketenimine (**28**). The nitrile ylide $PhC^-{=}N^+{=}CH_2$ (**30**) is postulated as a reversibly formed intermediate. *N*-Phenylketenimine (**28**) undergoes chemically activated free radical rearrangement to benzyl cyanide. The mechanistic interpretations are supported by calculations of the energies of key intermediates and transition states.



INTRODUCTION

Nitrile imines (nitrilimines) and nitrile ylides are important synthetic intermediates,[1] and their structures and reactivities are of ongoing, fundamental interest.[2] Recently, we described the formation and direct spectroscopic observation of several nitrile imines, including **2a−d**, formed by matrix photolysis and/or flash vacuum thermolysis (FVT) of 2,5-disubstituted tetrazoles (**1a−d**) as well as the oxadiazolone (**3a**) (Scheme 1).[3] Moreover, both thermal and photochemical rearrangements of nitrile imines to carbodiimides (**7**) were observed,[2b,3−5] and this is believed to take place via the 1*H*-diazirene (**4**) and the imidoylnitrene (**6**). 1*H*-Diazirenes are little-known compounds, but Fausto and co-workers have reported the direct observation of a few such species in low-temperature matrixes.[6]

Benzonitrile imine (**2a**) has been generated in an Ar matrix by photolysis of 5-phenyltetrazole (**1a**) at 254 nm.[3] The fundamental, antisymmetric IR stretching vibration of the cumulene moiety at 2073 cm^{-1} is in accord with the allenic structure of **2a** shown in Scheme 1, whereas the corresponding propargylic form $Ph{-}C{\equiv}N^+{-}N^-H$ is a transition state. The nitrile imine rearranges to *N*-phenylcarbodiimide (**7a**) on further photolysis as well as on FVT at 700−800 °C. Carbodiimide (**7a**) is also formed by matrix photolysis of 3-phenylsydnone, and the energetics involved in the interconversions **2a** ⇄ **4a** ⇄ **6a** ⇄ **7a** have been evaluated at the B3LYP/6-31+G** and QCISD(T) levels of theory.[7] The carbodiimide lies ca. 48 kcal/mol below the nitrile imine, the barrier for cyclization of the nitrile imine (**2a**) to diazirene (**4a**) is also ca. 48 kcal/mol, and the onward barrier to carbodimide (**7**) is ca. 9 kcal/mol. Barriers of this magnitude are readily accessible under FVT conditions.

Benzonitrile *N*-methylimine (**2b**) has been generated in a similar manner by photolysis of 2-methyl-5-phenyltetrazole (**1b**) in Ar matrix.[3] The IR stretching vibration at 2032 cm^{-1} again indicates that **2b** exists in the allenic form shown in

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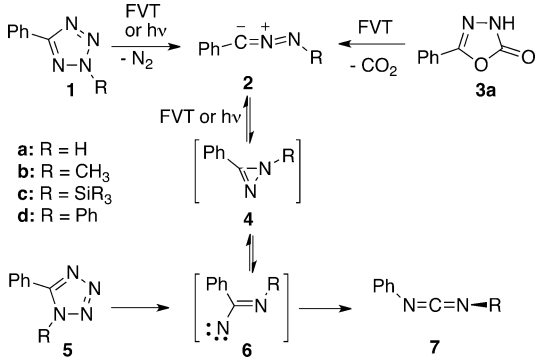
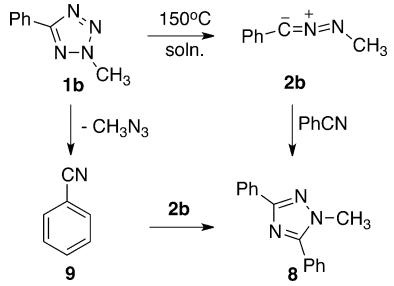
Scheme 1. Thermal and Photochemical Formation of Nitrile Imines



Scheme 1, and the corresponding propargylic form Ph—C≡N$^+$—N$^-$Me is a transition state. The nitrile imine rearranges rapidly to *N*-methyl-*N*′-phenylcarbodiimide (**7b**) on photolysis at 254 nm. FVT of either **1b** (420−600 °C) or 1-methyl-5-phenyltetrazole (**5b**) at 430−600 °C with Ar matrix isolation of the product at 12 K also produced the carbodiimide (**7b**).[3]

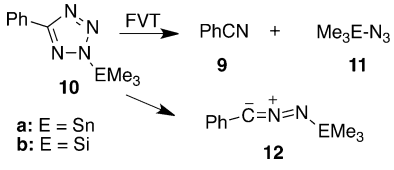
The benzonitrile *N*-methylimine (**2b**) has also been generated in solution by thermolysis of **1b** and found to undergo 1,3-dipolar cycloaddition, inter alia with nitriles to furnish 1,2,4-triazoles.[8] Surprisingly, thermolysis of **1b** at 150 °C without any added benzonitrile still generated the 1,2,4-triazole (**8**). Accordingly, it was postulated that the tetrazole undergoes a competing 1,3-dipolar cycloreversion to benzonitrile (**9**) and methyl azide, CH_3-N_3. The benzonitrile so-formed then undergoes a 1,3-dipolar cycloaddition with the nitrile imine (**2b**) (Scheme 2).

Scheme 2. Postulated Mechanism of Formation of Triazole (8) from Tetrazole (1b)[8]



The idea seemed reasonable: mild FVT of 5-phenyltetrazole (**1a**) gives rise to small amounts of HN_3 and benzonitrile (**9**) formed by 1,3-dipolar cycloreversion.[3] An attempt to generate the phenyl(stannyl) nitrile imine (**12a**) by FVT of the tetrazole (**10a**) led to quantitative cycloreversion to the stannyl azide (**11a**) and benzonitrile (**9**) (Scheme 3),[9] whereas the corresponding phenyl(silyl) nitrile imine (**12b**) was obtained readily on both FVT and photolysis of **10b** (Scheme 3).[3] Nevertheless, as we will show, the presumptive mechanism presented in Scheme 2 is not responsible for the formation of benzonitrile from **1b**.

Scheme 3. Formation of *C*-Phenyl *N*-Trimethylsilyl Nitrile Imine (12b), Formation of 11a, and Absence of Formation of *N*-Trimethylstannyl Nitrile Imine (12a) on FVT of 10



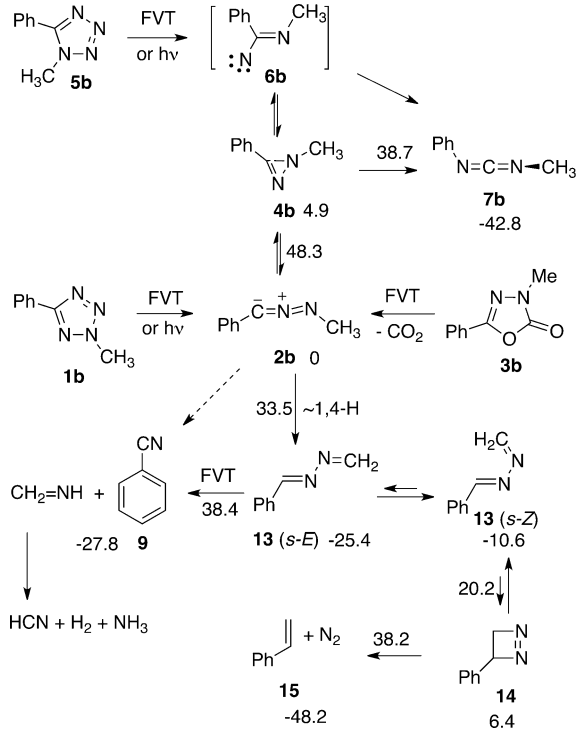
In this paper, we wish to report a detailed study of the thermal rearrangements of nitrile imines and nitrile ylides.

RESULTS AND DISCUSSION

1. *C*-Phenyl-*N*-methyl Nitrile Imine (2b) and Methyl(phenyl)carbodiimide (7b). Preparative FVT of 1-methyl-5-phenyltetrazole (**5b**) at 600 °C (5×10^{-4} hPa) afforded an 85% yield of methyl(phenyl)carbodiimide (**7b**), which has been completely characterized spectroscopically;[4] it is amenable to gas chromatographic assay but polymerizes rapidly at room temperature.

Preparative FVT of 2-methyl-5-phenyltetrazole (**1b**) at 550−960 °C/~10^{-4} hPa afforded a much lower yield of the carbodiimide (**7b**) (up to 9% yield). Instead, benzonitrile (**9**) (up to 50%), styrene (**15**) (up to 10%), HCN (up to 33%), and NH_3 (up to 14%) were formed as determined by GC, IR, and ^{1}H NMR spectroscopy (Scheme 4).

Scheme 4. *C*-Phenyl-*N*-methyl Nitrile Imine (2b) and Its Isomers[a]



[a]Numbers in normal font are energies calculated at the B3LYP/6-31G* level in kcal/mol relative to **2b**.

FVT of the oxadiazolone (**3b**) gave essentially the same products as described for **1b** except that an equivalent of CO_2 was also formed. By analogy with the chemistry of **3a** and **1b**, it is assumed nitrile imine (**2b**) was formed and rearranged to the diazabutadiene (**13**) (Scheme 4).

While benzonitrile and methyl azide cannot, of course, be formed by cycloreversion from **3b**, benzonitrile and methylnitrene CH_3N could still be formed by cleavage of the N−N bond in nitrile imine (**2b**). There is strong evidence that nitrile

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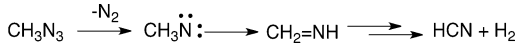
imines can cleave to nitriles and nitrenes photochemically[3,10] and also in the mass spectrometer.[11] The formation of benzonitrile was observed in the matrix photolysis of **2b**.[3] If methylnitrene CH_3N were formed, then methanimine (methylenimine) CH_2=NH would necessarily be a thermal product,[12] and as we have described in detail recently, this in turn would undergo rapid decomposition to HCN and H_2 under FVT conditions, accelerated by chemical activation stemming from the exothermicity of the reaction (Scheme 5).[12]

Scheme 5. Decomposition of Methyl Azide to Methylnitrene, Methanimine, and HCN



The ammonia observed as a product from both **1b** and **3b** is likely to arise from the oligomerization of CH_2=NH to hexamethylenetetramine, which takes place above −80 °C with evolution of ammonia.[13]

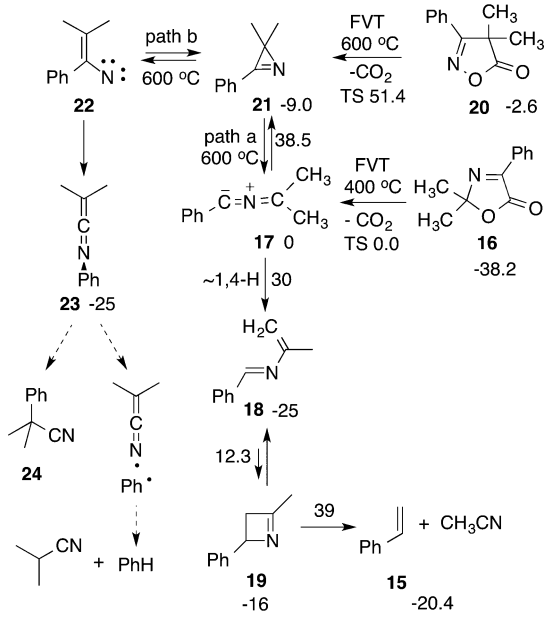
However, the most likely source of benzonitrile (**9**) and CH_2=NH in the present reaction is the cleavage of the diazabutadiene (**13**), itself formed by rearrangement of the nitrile imine (**2b**) (Scheme 4). In fact, FVT of **13** itself yielded substantial amounts of benzonitrile (up to 60% isolated yield) and HCN (up to 48% isolated yield) together with styrene (10−16%) and ca. 1% of carbodiimide (**7b**) at temperatures of 840 °C and above, but not at 550 °C. Azines are known to form nitriles on FVT via homolysis of the N—N bond.[14] Therefore, a free radical route to PhCN + CH_2=NH is possible. However, we also found an intramolecular route from **13** (*s-E*) to **9** + CH_2=NH with an activation barrier of 63.8 kcal/mol (see calculated energies at the B3LYP/6-31G* level in Scheme 4). This is virtually identical with the N—N bond dissociation energy in hydrazine (63 ± 3 kcal/mol).[15] Such barriers are achievable under FVT at 840 °C. Moreover, as detailed below, when compound **13** is generated from **2b**, it will carry substantial chemical activation, thereby facilitating its fragmentation.

Formation of the diazabutadiene (**13**) from the nitrile imine (**2b**) can take place via a 1,4-H shift with a modest calculated barrier of 33.5 kcal/mol (Scheme 4). Compound **13** will be chemically activated by the sum of the activation energy plus the exothermicity of its formation, by as much as 73 kcal/mol when formed from **5b** and ∼59 kcal/mol when formed from **2b** (Scheme 4). The lowest energy minimum of **13** is the *s-E* conformer (**13** *s-E*); the *s-Z* conformer has one imaginary frequency and is a rotational transition state lying 14.8 kcal/mol above **13** *s-E*. The chemically activated **13** will thus be able to cross the activation barrier toward 4-π electrocyclization to diazetine (**14**), which lies 30.8 kcal/mol above **13** *s-Z*. This is another example of a reaction with two consecutive transition states,[16] the first one being a rotational TS.[17] The diazetine (**14**) can now fragment to N_2 and styrene (**15**). 1,2-Diazetines are known to eliminate nitrogen with activation energies of ca. 32 kcal/mol,[18] and indeed, we calculate a barrier of 31.8 kcal/mol. Importantly, the diazabutadiene (**13**) was isolable when the FVT temperature was kept low (10% yield at 500 °C; 1.5% at 800 °C). Thus, the diazabutadiene (**13**) emerges as the immediate precursor of benzonitrile, styrene, and methanimine CH_2=NH, the latter decomposing to HCN, H_2, and NH_3 (Scheme 4).

It is interesting to note that the carbodiimide (**7b**) is obtained not only from the imidoylnitrene precursor (**5b**) (as expected) but also, in small amount, from the nitrile imine precursors **1b** and **3b**. The calculated energy barrier for the rearrangement of Ph—CNNCH$_3$ (**2b**) to Ph—N=C=N—CH$_3$ (**7b**) is 48 kcal/mol (Scheme 4). The same barrier (48 kcal/mol) was obtained for the rearrangement of *N*-phenylnitrile imine to *N*-phenylcarbodiimide, PhNNCH → PhN=C=NH.[7] While this is a substantial barrier, it is readily accessible under the FVT conditions employed here.

2. Benzonitrile Methylide (17) and Ketenimine (23). Analogous chemistry is observed for the benzonitrile *methylide* (**17**) (Scheme 6). 3-Methyl-1-phenyl-2-azabutadiene (**18**) is

Scheme 6. Benzonitrile Methylide (17) and Its Isomers[a]



[a]Numbers in normal font are energies calculated at the B3LYP/6-31G* level in kcal/mol relative to **17**.

formed in high yield on FVT of 2,2-dimethyl-4-phenyl-oxazol-5(2*H*)-one (**16**) at 400 °C and above.[19] Compound **18** is also formed on FVT of 3,3-dimethyl-2-phenyl-1-azirene (**21**) but in much lower yield—only traces at 600−650 °C—due to decomposition as described below.

FVT of the isoxazolone (**20**) at 600 °C and above results in elimination of CO_2 and formation of azirene (**21**) together with the products of thermolysis of **21**. The thermolysis of **20** is initiated by N−O bond breakage,[20] and the calculated barrier **20** → **21** is 54 kcal/mol (Scheme 6). Oxazolones like **16** eliminate CO_2 with significantly lower activation barriers, so that these reactions take place already in solution.[18] Compound **16** is thermodynamically much more stable than **20**, but its activation barrier toward cycloreversion to CO_2 and nitrile ylide (**17**) is lower, calculated as only 38 kcal/mol (Scheme 6). There is essentially no barrier for the reverse reaction, the cycloaddition of CO_2 to **17** to form **16**.

The differences between the outcomes of FVT of the three precursors **16**, **20**, and **21** can be understood in terms of chemical activation of azabutadiene (**18**) arising from the activation energies for its formation and the exothermicities of the reactions. Azabutadiene (**18**) can be chemically activated by as much as 64−75 kcal/mol when generated from **21** or **20** but only by ca. 55 kcal/mol when generated from **16** (see computational data in Scheme 6). The resulting "hot"

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azabutadiene decomposes to styrene (**15**) and acetonitrile via ring closure to **19** and subsequent [2 + 2] cycloreversion. This becomes the near-exclusive reaction at 700 °C. The chemical activation can be removed in part by collisional deactivation by using N_2 as a carrier gas at 1 hPa, which leads to the isolation of **18** in 10% yield from azirene (**21**); at the same time, the ketenimine (**23**), previously only detectable in trace amounts, becomes clearly observable by ^{1}H NMR and IR spectroscopy.

Thus, in summary, there are two reaction paths from azirene (**21**): one (path a) leading to nitrile ylide (**17**) and the major products styrene (**15**) and acetonitrile and the other (path b) leading to the vinylnitrene (**22**) and ketenimine (**23**). The ketenimine disappears on FVT at 700 °C, not by rearrangement to the dimethylbenzyl cyanide (**24**) (α-methylphenylacetonitrile) but rather by free radical decomposition leading to benzene and 2-methylpropionitrile. There has been much discussion about the mechanism of rearrangement of ketenimines to nitriles, but it is clear from product studies that a free-radical mechanism is common.[21] This is discussed further below.

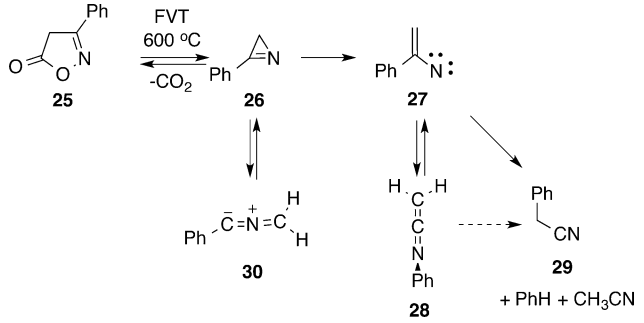
Path a has been observed previously by Wendling and Bergmann,[22−24] but path b (formation of ketenimine (**23**)) has not. The conditions used by these authors were not FVT; instead, the reactions were carried out at atmospheric pressure using helium as a carrier gas and residence times of ca. 10 s. This causes efficient deactivation of any "hot" molecules, and the phenomenon of chemical activation of the products was not observed. Instead, the long contact time and high pressure cause collisional activation.

The nitrile ylide (**17**) is not observed directly in any of these FVT reactions, but several nitrile ylides generated by FVT have been observed by matrix isolation.[25] Like nitrile imines,[2,3,5] nitrile ylides can exist in either allenic or propargylic forms. Consequently, the cumulenic IR absorptions of nitrile ylides span a very wide range, from the 1900s to near 2300 cm^{-1}.[1,2b,26] Calculations demonstrate that compound **17** has the allenic structure indicated in Scheme 6 with a harmonic vibrational frequency of 1968 cm^{-1}; the corresponding propargylic form Ph—C≡N$^+$—C$^-$(CH$_3$)$_2$ is a transition state. The calculated energy of **17** is ca. 25 kcal/mol above the ketenimine (**23**), and the barrier for the 1,4-H shift to **18** is 30 kcal/mol. The barrier for cyclization of **18** to azetine (**19**) is only 12 kcal/mol relative to **17**. The final fragmentation to styrene (**15**) and acetonitrile requires an overall barrier of 39 kcal/mol. These reactions will be very facile under FVT conditions.

3. 2-Phenylazirene (26) and *N*-Phenylketenimine (28). FVT of either 3-phenylisoxazol-5(4*H*)-one (**25**) or 2-phenylazirene (**26**) at or above 600 °C gave rise to *N*-phenylketenimine (**28**). Like other isoxazolones, **25** is expected to undergo elimination of CO_2 with an activation barrier of the order of 55 kcal/mol[20] on FVT. The azirene itself was observed as a product of FVT of **25** at 600 °C. Both **26** and **28** were isolated and characterized by comparison of IR and NMR data with data for authentic samples. However, ketenimine (**28**) was isolated in only 7% yield on FVT of **26** at 700 °C, and it disappeared from the thermolyzate on FVT above 850 °C. The low yield of ketenimine (**28**) can be ascribed to a rearrangement to benzyl cyanide (**29**); the ratio of yields **28**:**29** was 1:3 at 700 °C (24% yield of **29**). The easy formation of **29** can again be ascribed to chemical activation of the ketenimine (see below), because FVT of the pure, isolated ketenimine at the same temperature (700 °C) led to only 8% rearrangement to benzyl cyanide. The formation of benzyl cyanide (**29**) is not necessarily due to a 1,3-phenyl shift in ketenimine (**28**) but rather a free-radical cleavage[21] of **28** to Ph• and •CH$_2$CN radicals, because benzene and acetonitrile are also formed. This is discussed further below. The vinylnitrene (**27**) can also in principle rearrange to **29** by means of a 1,2-phenyl shift.[27]

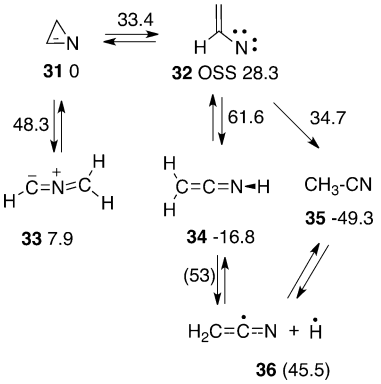
Although the nitrile ylide (**30**) has not been observed directly under these reaction conditions, analogy with the processes depicted in Scheme 6 suggests that **30** is formed reversibly as an intermediate (Scheme 7). **30** is observed on matrix photolysis of **26**.[26b,c] There is no obvious escape route for **30** under FVT conditions—the thermal cleavage to benzonitrile and methylene is not likely. Instead, the high temperature and chemical activation will ensure that the most stable products, **28** and **29**, are formed.

Scheme 7. Rearrangements of 2-Phenylazirene (26) and *N*-Phenylketenimine (28)



The lowest electronic singlet state of vinylnitrenes has an open-shell structure (OSS).[28,29] Therefore, multiconfigurational calculations are necessary in order to obtain reliable energies of the associated transition states. We carried out CASPT2 calculations for the relevant reactions of 1-azirene itself with the results shown in Scheme 8.

Scheme 8. CASPT2 Calculations Based on CASSCF(6,5) 2σ + 3π Geometries[a]



[a]Energies in kcal/mol relative to 1-azirene (**31**). The values in parentheses are derived from thermochemical kinetics (see text).

The thermal activation energy for formation of the nitrile ylide (**33**) is higher than that for formation of the nitrene (**32**), but the ylide has a lower ground state energy. The closed-shell singlet (CSS) state of the vinylnitrene S_2 is 25.3 kcal/mol above the open-shell (OSS) S_1.

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The nitrile ylide (**33**) can be chemically activated by ca. 40 kcal/mol when formed by FVT of the azirene (the activation energy minus the energy of the product). In the reactions of the substituted azirene (**21**) in Scheme 6, this excess energy was carried over in the subsequent exothermic rearrangement to the azabutadiene (**18**), thereby facilitating its cyclization to **19** and cleavage to **15**.

The ketenimine (**34**) can be chemically activated by as much as 78 kcal/mol due to the high barrier for its formation and the very exothermic reaction. This excess energy facilitates the observed rearrangement to acetonitrile. However, this is probably not a direct 1,3-shift of hydrogen, which will have a high activation barrier. The chemically activated ketenimine may return to the vinylnitrene (**32**), which can now undergo a 1,2-H shift with a low barrier of only ca. 7 kcal/mol. Furthermore, given such a high level of chemical activation (78 kcal/mol), the rearrangement of ketenimines $R_2C{=}C{=}N{-}R'$ to nitriles $R'R_2C{-}CN$ via cleavage to free radicals $R_2C{=}C{=}N\bullet + \bullet R'$ followed by recombination becomes perfectly feasible. The occurrence of free radical decomposition of ketenimines under FVT conditions has been demonstrated previously.[21a] The average C—N bond dissociation energy is only 73 kcal/mol, and the experimental activation energy for the thermal gas-phase rearrangement of ketenimine $CH_2{=}C{=}NH$ to acetonitrile $CH_3{-}CN$ is 70 ± 3 kcal/mol in a shock tube extrapolated to the high-pressure limit.[30] Using this value in Scheme 8 gives a transition state energy of 53 kcal/mol for the $H_2C{=}C{=}N\bullet + \bullet H$ reaction, and this is the easiest route for isomerization of $CH_2{=}C{=}NH$ to CH_3CN. Moreover, the reverse reaction, $CH_3CN \rightarrow H_2C{=}C{=}N\bullet + \bullet H \rightarrow CH_2{=}C{=}NH$ is equally possible as a source of the ketenimine (**34**) in Scheme 8.

The best experimental heat of formation of the CH_2CN radical is 60.4 kcal/mol.[31] Adding the heat of formation of a hydrogen atom (52.1 kcal/mol[32]) gives $\Delta_fH°(H_2CCN\bullet + \bullet H)$ = 112.5 kcal/mol, or 94.8 kcal/mol above CH_3CN (17.7 kcal/mol[32]). Thus, $\Delta_fH°(H_2CCN\bullet + \bullet H)$ = 45.5 kcal/mol on the scale of Scheme 8.

We did not locate a transition state for the direct 1,3-shift **34** → **35** at the CASSCF level. However, a barrier of 67.4 kcal/mol for the homolysis **34** → $H_2CCN\bullet + \bullet H$ (**36**) was calculated at ab initio levels up to MP4(SDTQ)/6-31G*//MP2(FU)/6-31G* in good agreement with the shock tube value of 70 ± 3 kcal/mol. Thus, by this calculation, the energy of the radical pair is 50 kcal/mol relative to azirene (**31**) on the scale of Scheme 8 in reasonably good agreement with the experimental value of 45.5 kcal/mol derived above.

CONCLUSION

C-Phenyl-*N*-methylnitrile imine (**2b**) is generated by FVT of tetrazole (**1b**) and 1,3,4-oxadiazolone (**3b**). **2b** undergoes a 1,4-H shift to the azabutadiene (**13**) with a calculated activation barrier of 33.5 kcal/mol. Furthermore, compound **13** decomposes to styrene, N_2, benzonitrile, and $CH_2{=}NH$ due to chemical activation under the low-pressure conditions of its formation. B3LYP calculations indicate that the decomposition to styrene and N_2 takes place via 4-electron electrocyclization to diazetine (**14**) with an overall activation barrier of 38 kcal/mol.

Isoxazolone (**20**), azirene (**21**), and oxazolone (**16**) all afford benzonitrile dimethylmethylide (**17**) on FVT. However, **17** is chemicaly activated by as much as 51 kcal/mol when generated from **20**. This causes the 1,4-H shift to azabutadiene (**18**) with an activation barrier of only 30 kcal/mol. Azabutadiene (**18**) is also chemically activated, by 64−75 kcal/mol when generated from **20** or **21**, and consequently undergoes cyclization to azetine (**19**) and finally fragmentation to styrene and acetonitrile with an overall barrier of 64 kcal/mol. A lower heat of formation of oxazolone (**16**) and a lower barrier for its fragmentation to nitrile ylide (**17**) and CO_2 mean that the nitrile ylide (**17**) generated this way carries much less chemical activation (38 kcal/mol). The ylide (**17**) still isomerizes to azabutadiene (**18**), but this compound is now isolable in much better yield.

A second thermal pathway from oxazolone (**20**) involves ring-opening of azirene (**21**) to vinylnitrene (**22**); the latter isomerizes to *N*-phenylketenimine (**23**).

FVT of the isoxazolone (**25**) causes loss of CO_2 and formation of 2-phenylazirene (**26**). Further thermolysis of **26** yields *N*-phenylketenimine (**28**), probably via vinylnitrene (**27**). The *N*-phenylketenimine (**28**) is again chemically activated by ca. 78 kcal/mol and therefore rearranges to phenylacetonitrile, most probably via a free radical fragmentation and recombination.

CASPT2 calculations on the unsubstituted azirene (**31**) indicate that the two thermal ring-opening reactions, to vinylnitrene (**32**) and nitrile ylide (**33**), have activation barriers of 33 and 48 kcal/mol, respectively. Thus, under ordinary reaction conditions, vinylnitrene formation will be energetically preferred, but both pathways become possible under high-temperature FVT conditions.

COMPUTATIONAL METHODS

Structures of ground and transition states were investigated by DFT theory at the B3LYP/6-31G* level using the Gaussian 09 suite of programs.[33] Energies of open-shell singlet nitrenes were estimated using the Cramer−Ziegler method.[34] For the reactions in Scheme 8, the energies were also calculated at the CASPT2 level based on CASSCF(6,5) $2\sigma + 3\pi$ geometries. Where applicable, calculated wavenumbers were scaled by a factor of 0.9613.[35]

EXPERIMENTAL SECTION

FVT reactions were carried out in unpacked quartz tubes (20 × 2 cm I.D.), usually in dynamic vacua of 10^{-4}−10^{-3} hPa maintained by using high capacity oil diffusion pumps, except when N_2 was used as a carrier gas in order to achieve collisional deactivation, usually at 1 hPa under continuous pumping. Products were collected in liquid-N_2-cooled traps or on liquid-N_2-cooled cold fingers. Further details have been reported.[12] After the end of each FVT experiment, the HCN/NH_3 mixture was volatilized by warming the cold finger/cold trap to ca. −20 °C, collected in an evacuated IR gas cell, and assayed by IR spectroscopy by comparison with gas mixtures of known composition. Higher boiling liquids and solids were collected after equalizing the system pressure. Product mixtures were assayed by gas chromatography on SE30, SE50, or Carbowax columns as well as ^{1}H NMR spectroscopy, and known compunds were identified by coinjection and by comparison of their spectroscopic data with those of authentic materials.

MATERIALS

2-Methyl-5-phenyltetrazole[3,36] (mp 50 °C), 3-methyl-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one[37] (mp 105 °C), benzaldehyde methylenehydrazone (2,3-diaza-1-phenylbuta-1,3-diene)[38] (mp (decomp.) 146 °C), 2,2-dimethyl-4-phenyloxazol-5(2*H*)-one[39] (mp 36 °C, bp 90−100 °C/10^{-2} hPa), 3-phenylisoxazol-5-(4*H*)-one[40] (mp 148 °C), 2-phenyl-1-azirene[41] (bp 64 °C/5 hPa), 3,3-dimethyl-2-phenyl-1-azirene[42] (bp 94 °C/15 hPa), 3-ethyl-1-phenyl-2-azabuta-1,3-diene,[13] *N*-methyl-*N*′-phenylcarbodiimide (by FVT of 1-methyl-5-phenyltetrazole at 600 °C),[3] *N*-phenylketenimine (by FVT of 4-(*N*-anilinomethylidene)-3-

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methylisoxazol-5(4*H*)-one at 650 °C),[43] and *N*-phenyl-3,3-dimethylketenimin[44] were synthesized according to the cited literature procedures.

FVT of 2-Methyl-5-phenyltetrazole (1b). Portions of 150 mg (0.9 mmol) were subjected to FVT at temperatures between 550 and 960 °C (5×10^{-4} hPa). The sublimation temperature was 45 °C. More than 95% of the unchanged starting material was recoved at FVT temperatures below 500 °C. The product compositions and yields, determined by GC (IR spectroscopy for HCN and NH_3), at various temperatures are collected in Table 1.

Table 1. Yields of Products from the FVT of 2-Methyl-5-phenyltetrazole (1b)

yield/FVT temp (°C)	550	800	900	960
styrene	9	6	0.5	1
benzonitrile	44	49	32	42
diazabutadiene (**13**)	10	1.5	0	0
carbodiimide (**7b**)	1.5	6.5	7	9
HCN	24	31	32	31
NH_3	10	13	14	13

FVT of 3-Methyl-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3b). Portions of 200 mg (1.14 mmol) were subjected to FVT at temperatures between 700 and 980 °C at a sublimation temperature of 70 °C. The product composition and yields are given in Table 2. The gas mixtures consisted of HCN/NH_3 in the usual molar ratio of 70:30 together with substantial amounts of CO_2.

Table 2. Yields of Products from the FVT of 3-Methyl-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (3b)

yield/FVT temp (°C)	700	900	960
styrene	8	12	6
benzonitrile	71	75	63
diazabutadiene (**13**)	0	0	0.2
carbodiimide (**7b**)	1	1.5	9
HCN	18	34	
NH_3	8	14	

FVT of 2,3-Diaza-1-phenylbuta-1,3-diene (Benzaldehyde Methylenehydrazone) (13). A sample of 50 mg (0.38 mmol) was subjected to FVT between 550 and 960 °C with a sublimation temperature of 100−120 °C. The products were analyzed as described above, and the results are collected in Table 3.

Table 3. Yields of Products from the FVT of 2,3-Diaza-1-phenylbuta-1,3-diene (13)

yield/FVT temp (°C)	550	840	900	980
styrene	9	16	10	12
benzonitrile	32	59	55	60
diazabutadiene (**13**)	45	0	0	0
carbodiimide (**7b**)	1	1	1	0.5
HCN		48	45	46
NH_3		31	29	30

FVT of 2,2-Dimethyl-4-phenyloxazol-5(2*H*)-one (16). FVT of samples of 250 mg (1.3 mmol) was carried out at 400 and 600 °C. At 400 °C, a ca. 1:1 mixture of the unchanged starting material and 1-phenyl-3-methyl-2-azabuta-1,3-diene (**18**) was obtained. At 600 °C, **18** (170 mg) was obtained as the only discrete product in 87% yield.

FVT of 3,3-Dimethyl-2-phenyl-1-azirene (21). Portions of 500 mg were pyrolyzed. At 500 °C, the starting material was recovered unchanged. (a) At 600 °C, a mixture of starting material (33%), acetonitrile (30%), and styrene (35%) was obtained together with ca. 2% of azabutadiene (**18**). (b) At 650 °C, a mixture of starting material (10%), acetonitrile (40%), styrene (40%), and benzonitrile (ca. 5%) was obtained together with ca. 1% percent of 1-phenyl-3-methyl-2-azabuta-1,3-diene (**18**). (c) At 700 °C, the starting material was almost completely consumed. The product consisted of a 1:1 mixture of acetonitrile and styrene, and the azabutadiene (**18**) was no longer detectable. (d) The pyrolysis was repeated at 600 °C with N_2 as carrier gas at a pressure of 1 hPa under continuous pumping. The product mixture consisted of starting material (4%), acetonitrile (35%), styrene (51%), azabutadiene (**18**) (10%), and the ketenimine (**23**) (ca. 1%). The trapping of the volatile acetonitrile may be incomplete under these conditiions.

FVT of 4,4-Dimethyl-3-phenylisoxazol-5-(4*H*)-one (20). (a) Preparative pyrolysis of this compound was carried out at 600 °C with isolation of the products in a liquid-N_2 cold trap to yield starting material (**20**) (6%), azirene (**21**) (44%), styrene (**15**) (16%), acetonitrile (14%), azabutadiene (**18**) (4%), and keteniminene (**23**) (1%). (b) When the pyrolysis products were condensed on a KBr target in a liquid-N_2-cooled cryostat, the formation of acetonitrile (2252 cm^{-1}), *N*-phenyl-3,3-dimethylketenimine (**23**) (2016 cm^{-1}), and 3,3-dimethyl-2-phenylazirene (**21**) (1735 cm^{-1}) was confirmed by the IR absorptions.

FVT of 3-Phenylisoxazol-5-(4*H*)-one (25). Compound **25** (500 mg portions) was pyrolyzed at 600 and 700 °C with a sublimation temperature of 120 °C. At 600 °C, a mixture of the unchanged starting material, benzonitrile, and 2-phenyl-1-azirene (**26**) was obtained, the latter two in a ca. 1:1 ratio. At 700 °C, the starting material was completely consumed, and benzonitrile, 2-phenyl-1-azirene (**26**), *N*-phenylketenimine (**28**), and benzyl cyanide (**29**) were obtained in ratios of ca. 5:5:1:4.

FVT of 2-Phenyl-1-azirene (26). Portions of 500 mg were pyrolyzed at 700−900 °C. At 700 °C, a large proportion of the starting material remained unchanged. Benzonitrile, 2-phenyl-1-azirene (**26**), *N*-phenylketenimine (**28**), and benzyl cyanide (**29**) were obtained in ratios of ca. 2:5:1:2. At 800 °C, benzonitrile, 2-phenyl-1-azirene, *N*-phenylketenimine, and benzyl cyanide were obatined in ratios of ca. 5:1:0:4. At 850 °C, no azirene remained in the product. Benzonitrile and benzyl cyanide were obtained in a ratio of ca. 1:1. *N*-Phenylketenimine (IR 2030 cm^{-1}) was not detectable at 800 and 850 °C. Pyrolysis at 900 °C gave virtually the same result as that at 850 °C.

FVT of *N*-Phenylketenimine (28). Complete pyrolysis of this compund was not achieved because a part of the compound invariably polymerized in the sample flask prior to pyrolysis. At 700 °C, a conversion to 8% benzyl cyanide was obtained. At 800 °C, ca. 34% conversion to benzyl cyanide was achieved. The formation of benzene and acetonitrile was confirmed by GC in each case.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational details for the calculated species in Schemes 4, 6, and 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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