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# Unexpected valence bond isomerization of [1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazines under flash vacuum pyrolytic (fvp) conditions

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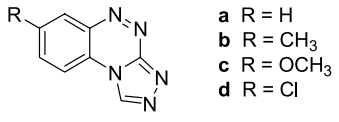
**Abstract**—Flash vacuum pyrolysis (fvp) of some substituted [1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine derivatives (**1a–d**) has been studied between 450 and 600 °C. The only transformation observed up to 525 °C was the unexpected valence bond isomerization of the angularly fused starting compounds to the isomeric linearly fused [1,2,4]triazolo[4,3-*b*][1,2,4]benzotriazine derivatives (**9a–d**), whereas at higher temperatures fragmentation products such as aromatic nitriles were also formed. Kinetic measurements revealed negative entropies of activation in the isomerization process, which suggest a concerted ring closure reaction to an intermediate antiaromatic diazirine. Reversibiblity of the title isomerization reaction was also proved by FVP experiments.


## 1. Introduction

Flash vacuum pyrolysis (fvp) of nitrogen containing heterocycles has been the focus of our studies for many years as reflected by a recently published review.[1] In the course of these investigations, heteroaromatic rings involving the N–N moiety in the ring seemed of special interest due to the possibility of nitrogen extrusion and formation of diradicals or vinylcarbenes.[1,2] From this point of view, interesting results have been obtained by comparison of the behavior of [1,2,3]- and [1,2,4]-benzotriazines: while most of [1,2,3]-benzotriazines afforded reaction products via benzazetes,[3] no evidence for these intermediates was found in fvp of 1-deoxy or 1-oxy derivatives of [1,2,4]-benzotriazines and, instead, benzonitriles and biphenylene were found as final products. Furthermore, in the case of 3-methylsulfanyl derivatives of these compounds, a competing radical reaction was also found in fvp due to the lability of the C–S bond.[4]

As a continuation of these studies we report here, on flash vacuum pyrolysis of some [1,2,4]triazolo[3,4-*c*]benzotriazines (**1a–d**, Scheme 1). These model compounds have the special structural feature that they contain two N–N parts in the ring and, in principle, two kinds of nitrogen elimination could occur under fvp conditions.




**1**

**Scheme 1.**

Five-membered compounds with an N=N moiety in the ring can undergo nitrogen elimination under thermal and photochemical conditions. Thus, 1-arylbenzotriazoles are convenient precursors of carbazoles by thermal extrusion of nitrogen, which is known as the Graebe-Ullman synthesis. The reaction mechanism was confirmed to involve cyclisation of a diradical or iminocarbene to 4*H*-carbazole which isomerizes to substituted aromatic carbazoles by a hydrogen shift.[5]

Some [1,2,4]-triazoles with alkyl[6] or acyl[7] groups attached to a ring atom afforded migration of these substituents followed by further transformations. In the former case, isomeric 1,2,4-triazoles were formed, whereas in the second case nitrogen extrusion took place to result in a ring transformation of the starting compound (Scheme 2).

*Keywords*: Flash vacuum pyrolysis; Valence bond isomerisation; Sigmatropic rearrangement; Enthropy of activation; Azirine intermediate.
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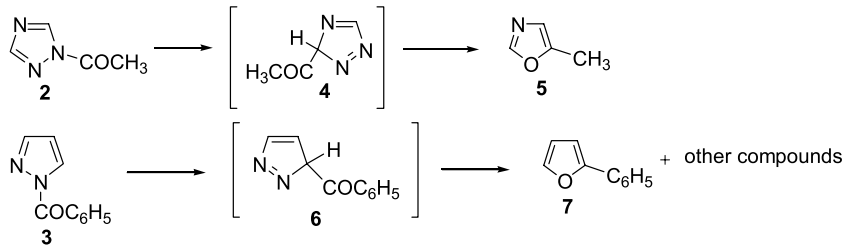


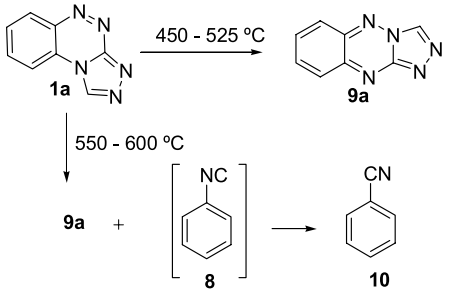

**Scheme 2.**

Thus, 1-acetyl-1*H*-1,2,4-triazole (**2**) underwent an N–C acyl migration, and the resulting intermediate (**4**) lost one molecule of nitrogen to yield 5-methyloxazole (**5**). A similar transformation was observed with 1-benzoyl-1*H*-pyrazole (**3**), where formation of 2-phenylfurane (**7**) via intermediate **6** was reported.[8] Unfortunately, no references on reactions of fused 1,2,4-triazoles were found.

## 2. Results and discussion

### 2.1. Fvp of [1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (1a)

Reactions of **1a** were carried out between 450 and 600 °C, with pressures of $\sim 10^{-2}$ Torr and contact times of $\sim 10^{-2}$ s. The reaction was clean affording one single product up to 525 °C identified as [1,2,4]triazolo[4,3-*b*][1,2,4] benzotriazine (**9a**) (Scheme 3). Over 550 °C small amounts of benzonitrile (**10**) and a carbonaceous residue were formed from decomposition (Scheme 3). The relative amounts of **1a** and **9a** calculated from the $^1$H NMR spectra are summarized in Table 1.




**Scheme 3.**

**Table 1**. Fvp reactions of **1a** and **1b**

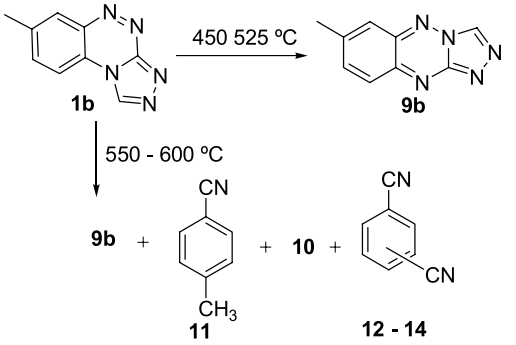
| *T* (°C) | | % **1** | % **9** | Other products |
|---|---|---|---|---|
| 450 | **1a** | 95.3 | 4.7 | — |
| | **1b** | 94.2 | 5.8 | — |
| 475 | **1a** | 90.6 | 9.4 | — |
| | **1b** | 90.4 | 9.6 | — |
| 500 | **1a** | 82.5 | 17.5 | — |
| | **1b** | 82.4 | 17.6 | — |
| 525 | **1a** | 74.8 | 25.2 | — |
| | **1b** | 71.8 | 28.2 | — |
| 550 | **1a** | 72.7 | 27.3 | **10**[a] |
| | **1b** | 69.5 | 30.5 | **11**[a] |
| 575 | **1a** | 72.7 | 27.3 | **10**[a] |
| | **1b** | 62.5 | 37.5 | **9**, **11**[a] |
| 600 | **1a** | 79.2 | 20.8 | **10**[a] |
| | **1b** | 64.9 | 35.1 | **10**, **12–14**[a] |
| 625 | **1a** | — | — | — |
| | **1b** | 76.2 | 23.8 | **10**, **12–14**[a] |

[a] Detected by GC/MS, not quantified.

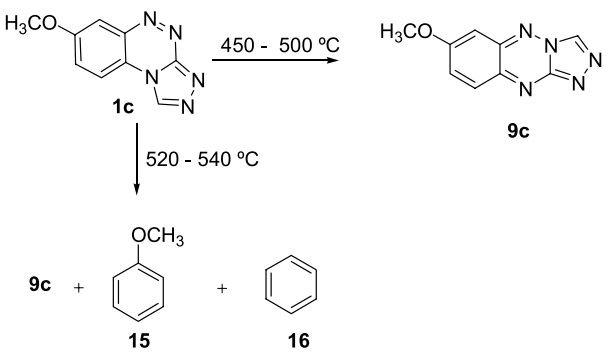
Compound **10** may be formed from **1a** or from **9a** by nitrogen extrusion or by fragmentation to benzeneisocyanide (**8**) and subsequent isomerization to **10** via a well known pathway.[9]

### 2.2. Fvp of 7-methyl-[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (1b)

Reactions of **1b** were carried out between 450 and 625 °C, with pressures of $\sim 10^{-2}$ Torr and contact times of $\sim 10^{-2}$ s. The only product up to 525 °C was 7-methyl-[1,2,4]triazolo[4,3-*b*][1,2,4]benzotriazine (**9b**); over this temperature **10**, *p*-tolunitrile (**11**) and a mixture of dicyanobenzenes (**12–14**) were also formed from decomposition of **1b** and/or **9b** (Scheme 4, Table 1). Relative quantification of **1b** and **9b** was carried out by the help of $^1$H NMR spectra. It is important to note that 100% conversion could not be achieved and over 600 °C, coke was also formed. Compounds **10** and **12–14** can be formed by pyrolysis of **11** as already reported.[10]




**Scheme 4.**




**Scheme 5.**

### 2.3. Fvp of 7-methoxy [1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (1c)

Reactions of **1c** were carried out between 440 and 540 °C, with pressures of $\sim 10^{-2}$ Torr and contact times of $\sim 10^{-2}$ s. Up to 520 °C the only product was 7-methoxy-[1,2,4]triazolo[4,3-*b*][1,2,4]benzotriazine (**9c**), over this temperature, anisole (**15**), benzene (**16**) and coke were also formed (Scheme 5 and Table 2). Relative quantification of **1c** and **9c** was performed by $^1$H NMR.

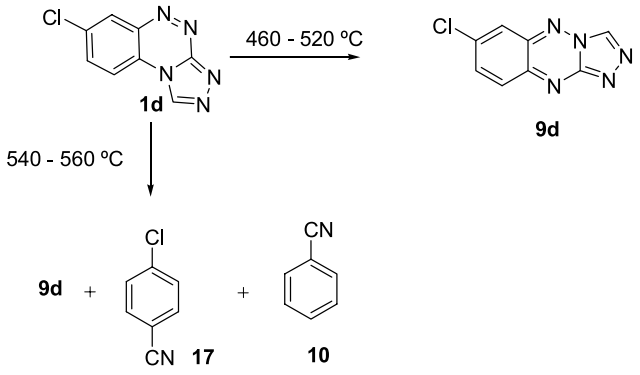
**Table 2**. Fvp reactions of **1c** and **1d**

| *T* (°C) | | % **1** | % **9** | Other products |
|---|---|---|---|---|
| 440 | **1c** | 100 | — | — |
| | **1d** | — | — | — |
| 460 | **1c** | 97.7 | 12.3 | — |
| | **1d** | 85.6 | 14.4 | — |
| 480 | **1c** | 78.7 | 21.3 | — |
| | **1d** | 80.5 | 19.5 | — |
| 500 | **1c** | 69.2 | 30.8 | — |
| | **1d** | 74.7 | 25.3 | — |
| 520 | **1c** | 58.8 | 41.2 | — |
| | **1d** | 69.7 | 30.3 | — |
| 540 | **1c** | 61.1 | 38.9 | **15**, **16**[a] |
| | **1d** | 64.4 | 35.6 | **17**[a] |
| 560 | **1c** | — | — | — |
| | **1d** | 64.9 | 35.1 | **10**, **17**[a] |

[a] Detected by GC/MS, not quantified.

### 2.4. Fvp of 7-chloro [1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (1d)

Reactions of **1d** were carried out between 460 and 560 °C with pressures of $\sim 10^{-2}$ Torr and contact times of $\sim 10^{-2}$ s. As in reactions of **1a–c**, only one product was formed up to 520 °C, identified as 7-chloro[1,2,4]triazolo[4,3-*b*][1,2,4]-benzotriazine (**9d**), at higher temperatures, 4-chlorobenzonitrile (**17**) and benzonitrile (**10**) as well as coke were also formed (Scheme 6, Table 2). Relative quantification of **1d** and **9d** was performed by the help of $^1$H NMR spectra.



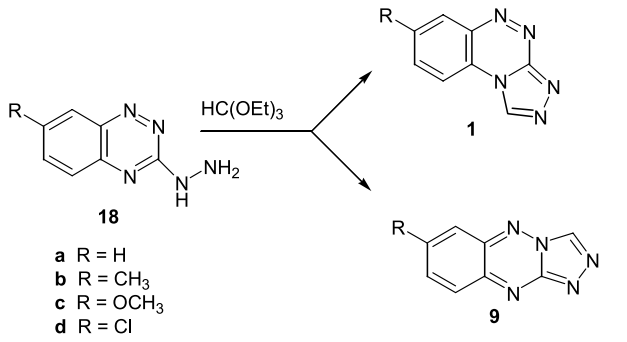

**Scheme 6.**

Although, spectral analyses of the main products of these FVP transformations suggested that derivatives of the the linearly fused ring system [1,2,4]triazolo[3,4-*c*]benzo[1,2,4] triazine (**9a–d**) were formed, preparative evidence for this asignment seemed also desirable. To this end, we repeated the ring closure reactions to **1a–d** according to the described literature procedure[27]—that is, treatment of substituted 3-hydrazinobenzo[1,2,4]triazines (**18**) with ethyl orthoformiate—and carried out thorough analyses of the mother liquors of these reaction mixtures to learn whether the isomeric linearly fused compounds **9a–d** had also been formed in small amounts in these transformations (Scheme 7).

TLC of all four reaction mixtures indicated that besides the intense spots for the main products (**1a–d**), a well defined other spot is also present. Separation of these fractions by column chromatography gave rise to the isolation of **9a–d** which proved to be entirely identical (mp, TLC, IR NMR-spectra) with the samples obtained by FVP. It is interesting to note that the **1/9** ratios in the reaction mixtures obtained from **18a–d** proved to be very different, the isolated yields are shown in Table 3 (Scheme 7).[27]

**Table 3**. Yields of **1a–d** and **9a–d** starting from **18a–d**

| | **1** (%) | **9** (%) |
|---|---|---|
| **a** | 78.0 | 3.9 |
| **b** | 70.6 | 2.9 |
| **c** | 86.1 | 1.8 |
| **d** | 78.0 | 3.4 |

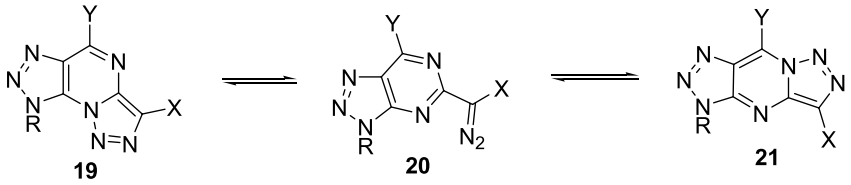



**Scheme 7.**

This finding that **9** can be formed from **1** under fvp conditions raises the interesting question of a possible mechanism for this transformation. Similar analoguous valence bond isomerizations have been reported in the literature. Four such cases for comparison should be recalled here.

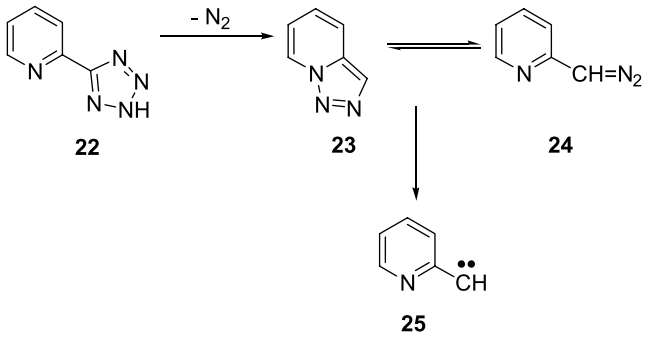
An example structurally related to the title compounds is the behavior of bis[1,2,3]triazolopyrimidines where an equilibrium between the angular (**19**) and the linear structure (**21**) is established through an open chain diazo form (**20**); this reaction is described to take place in the presence of a strong base. It is important to mention that the diazo form was detected by spectral methods and the equilibrium between the angular and the linear isomer is strongly dependent on the substituents X and Y (Scheme 8).[11] The introduction of an additional nitrogen atom into the fused azine ring facilitates triazole cleavage and potential rearrangements. Thus, [1,2,3]triazolo[5,1-*c*][1,2,4]triazine isomerized spontaneously to the thermodynamically more stable 1,2,3-triazolo[1,5-*b*]triazine during its preparation.[12]

A similar reaction was found in the pyrolysis of 2-(5-tetrazolyl)pyridine (**22**), where the first nitrogen extrusion




**Scheme 8.**

reaction afforded [1,2,3]triazolo[1,5-*a*]pyridine (**23**) in equilibrium with 2-pyridyldiazomethane (**24**). At higher temperatures [1,2,3]triazolo[1,5-*a*]pyridine (**23**) also afforded nitrogen loss to form pyridylcarbene (**25**) (Scheme 9).[13]

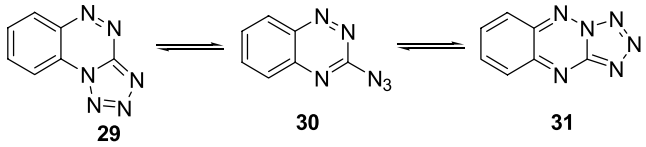



**Scheme 9.**

The same kind of isomerization, through an open chain compound, is described with several fused tetrazoles. Thus, the existence of an equilibrium between two isomeric tetrazolopyrimidones (**26** and **28**) through an azido intermediate (**27**) as well as Arrhenius parameters has been reported (Scheme 10).[14]

Angularly fused tetrazolo[5,1-*c*]benzo[1,2,4]triazines (**29**) and the linearly fused isomers tetrazolo[1,5-*b*]benzotriazines (**31**) were reported to be in equilibrium with an open chain azide (**30**) (Scheme 11) in DMSO, while **29** is stable in the crystalline form.[15] The relative amounts of **29**, **30** and **31** are strongly dependent on solvent and on substitution as was demonstrated in $^1$H NMR experiments.[16]

It is important to note that in all these literature cases the isomerisation of the angularly fused ring to the linearly fused isomer (or the reverse reaction) proceeds via a well defined and relatively stable intermediate (i.e., via a heteroaromatic azide or diazomethane). An analysis of our present results described here, however, seemed more complicated because if the transformation of **1** to **9** proceeds in a pathway analogous to these cited reactions, an N–C bond cleavage would be anticipated to yield **32** and/or **33** as possible intermediates (Scheme 12).




**Scheme 11.**

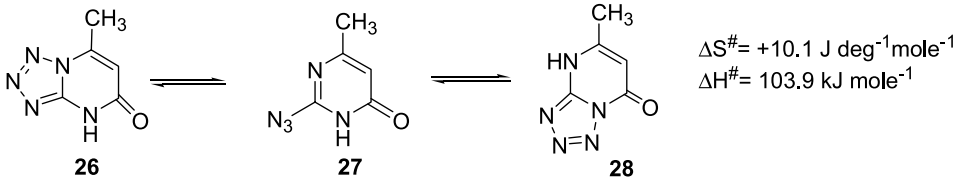
As formation of either **32** or **33** seemed rather unlikely, more detailed considerations concerning the acting mechanism involving reactive intermediates or concerted reactions seemed straightforward as depicted in Scheme 13.

Route a involves diradicals with an imine group, isomerization of these imines would lead to the final product by cyclization, which is a known stereoisomeric isomerization of imines.[17] Pathway b is a concerted [1,5] sigmatropic shift with rotation of a C–N bond partially doubly bonded and, finally, route c is a [1,3] sigmatropic shift with a ring contraction to form antiaromatic diazirine **34**, too unstable to be isolated, which by a concerted [1,3] shift (pathway d) or by ring opening affording **32** and/or **33** would lead to the final products.

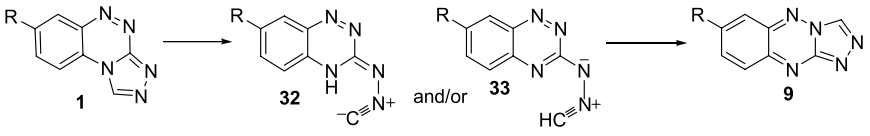
Isomerizations of fused tetrazoles through azides afforded positive entropies of activation ($\Delta S^{\#}$ of $+10.1$ J deg$^{-1}$ mol$^{-1}$ and $\Delta H^{\#}$ of $+103.9$ kJ mol$^{-1}$) (Scheme 10), with this reference for comparison, kinetic measurements of the reactions described here would give valuable information on the mechanism.

## 2.5. Kinetics

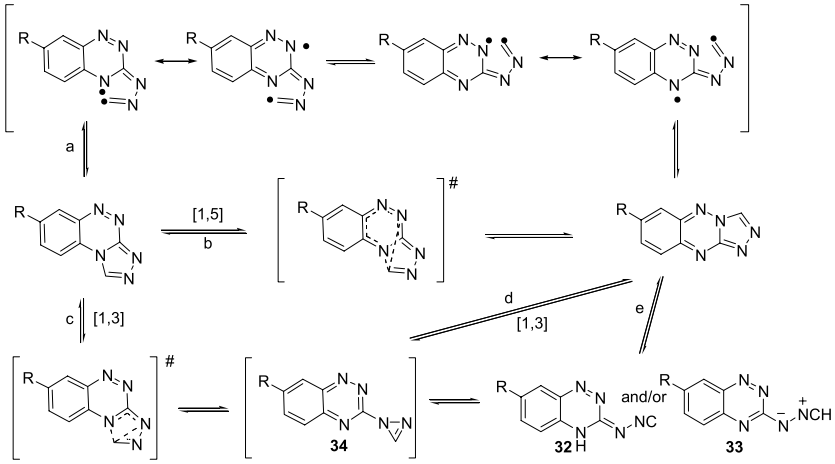
Reaction constants were measured at each temperature with the relative concentrations of starting materials and products determined by $^1$H NMR and averaged over at least three determinations. Reaction times were calculated as $V_0/\mu$ being $V_0$ the volume of the reaction tube inside the hot zone and $\mu$ the carrier gas flow. Arrhenius parameters were calculated by the classical equation ($\ln k$ vs $1/T$) with data for at least four different temperatures. To check the system, kinetic parameters of ethylacetate pyrolysis were measured in the fvp system and compared with those reported for a static system, these results as well as a detailed description of the methodology have already been described.[18]




**Scheme 10.**




**Scheme 12.**




**Scheme 13.**

**Table 4**. Kinetics of fvp of **1a**

| $T$ (K) | $C/C_0$ | $t$ ($10^{-2}$) s | $k$ ($s^{-1}$) |
|---|---|---|---|
| 723.15 | 0.953 | 2.2 | $2.2\pm0.2^a$ |
| 748.15 | 0.906 | 2.1 | $4.7\pm0.2^a$ |
| 773.15 | 0.825 | 2.0 | $9.2\pm0.2^b$ |
| 798.15 | 0.748 | 2.0 | $14.7\pm0.6^b$ |

[a] Average of three determinations.
[b] Average of four determinations.

**Table 5**. Kinetics of fvp of **1b**

| $T$ (K) | $C/C_0$ | $t$ ($10^{-2}$) s | $k$ ($s^{-1}$) |
|---|---|---|---|
| 723.15 | 0.942 | 2.2 | $2.7\pm0.4^a$ |
| 748.15 | 0.907 | 2.1 | $4.7\pm0.2^b$ |
| 773.15 | 0.824 | 2.0 | $9.5\pm0.9^b$ |
| 798.15 | 0.718 | 2.0 | $16.8\pm0.9^b$ |

[a] Average of three determinations.
[b] Average of four determinations.

**Table 6**. Kinetics of fvp of **1c**

| $T$ (K) | $C/C_0$ | $t$ ($10^{-2}$) s | $k$ ($s^{-1}$) |
|---|---|---|---|
| 733.15 | 0.888 | 2.2 | $5.4\pm0.6^a$ |
| 753.15 | 0.787 | 2.1 | $11.2\pm0.9^a$ |
| 773.15 | 0.692 | 2.1 | $17.8\pm0.9^b$ |
| 793.15 | 0.588 | 2.0 | $26.1\pm0.9^b$ |

[a] Averaged of three determinations.
[b] Averaged of four determinations.

**Table 7**. Kinetics of fvp of **1d**

| $T$ (K) | $C/C_0$ | $t$ ($10^{-2}$) s | $k$ ($s^{-1}$) |
|---|---|---|---|
| 733.15 | 0.856 | 2.2 | $7.1\pm0.9^a$ |
| 753.15 | 0.805 | 2.2 | $10.1\pm0.8^b$ |
| 773.15 | 0.747 | 2.1 | $13.9\pm0.9^b$ |
| 793.15 | 0.697 | 2.0 | $17.9\pm0.8^b$ |
| 813.15 | 0.644 | 2.0 | $22.1\pm0.9^b$ |

[a] Averaged of three determinations.
[b] Averaged of four determinations.

Reactions are first order, rate constants for reactions of compounds **1a–d** are depicted in Tables 4–7 and Arrhenius parameters in Table 8.

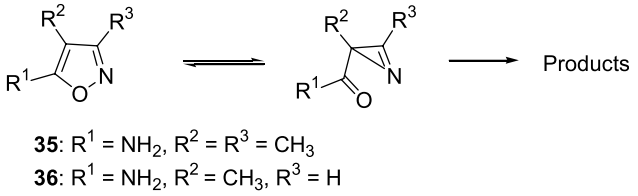
From all this information, the most important data are the negative entropies of activation, which preclude path a in Scheme 13: this is a ring opening reaction that should have a positive value and it is not expected for a ring closure reaction of a diradical to be the rate determining step. Paths b and c are concerted reactions where the better movement of the atoms is in the supra-supra mode as they are all bonded and a supra-antara situation should have steric impediments. Path b is a concerted [1,5] sigmatropic shift, although, this reaction is allowed by the Woodward-Hoffmann's rules,[19] it has strong steric impediments as the C=N bond (Fig. 1) of triazole ring should rotate 90° to allow a bonding interaction between all the atoms involved in the transition state.

The third possibility shown is Scheme 13 (path c) is a [1,3] sigmatropic shift; according to Woodward–Hoffmann′s rules it should be a supra-antara process that has strong steric impediment. But, it is possible to consider a supra-supra transition state, with lower steric requeriments, formally forbidden. This incompatibility can be over-compensated if the Migrating Group (MG) and the Migrating Framework (MF) differ in their electron releasing–electron withdrawing ability.[20] The difference $I_D-A_A$ ($I_D$=ionization potential of the donor partner; $A_A$= electron affinity of the acceptor partner), affords an index of the activation energy of a sigmatropic shift with the reaction barrier becoming lower as $I_D-A_A$ decreases.[21] These arguments, supported by molecular orbital calculations, were used in fvp isomerizations of isoxazoles,[22] which have similar entropies of activation values to the ones reported in this article suggesting a common reaction pathway. Recently, some theoretical calculations carried out by

**Table 8**. Arrhenius parameters of fvp of **1a–d** and of some isoxazoles*

| | $k$ ($s^{-1}$) (500 °C) | $E_a$ (kJ $mol^{-1}$) | log $A$ ($s^{-1}$) | $\Delta S^{\#}$ (eu) | $\Delta H^{\#}$ (kJ $mol^{-1}$) | $\Delta G^{\#}$ (kJ $mol^{-1}$) | $r$ |
|---|---|---|---|---|---|---|---|
| **1a** | 9.2±0.2 | 123±3 | 9.2±0.5 | −18.2±0.4 | 116±3 | 176±4 | −0.997 |
| **1b** | 9.5±0.9 | 118±3 | 9.0±0.3 | −19.4±0.3 | 112±3 | 176±4 | −0.998 |
| **1c** | 17.8±0.9 | 125±4 | 9.7±0.8 | −16.0±0.8 | 119±4 | 172±8 | −0.992 |
| **1d** | 13.9±0.9 | 71±2 | 5.9±0.2 | −33.5±0.2 | 64±2 | 172±4 | −0.997 |
| 35[a] | | 108±1 | 9.00 | | | | |
| 36[b] | | 109±1 | 9.00 | | | | |

[a] From Ref. 17.
[b] From Ref. 22.




**Scheme 14.**

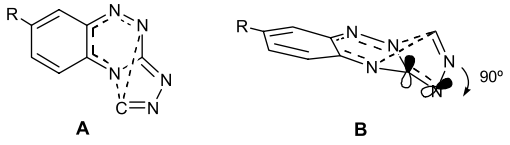



**Figure 1.** Steric representation of [1,5]sigmatropic shift of A via transition state B.

Davico[22] supported the mechanism proposed by some of us 20 years ago on a kinetic basis.[18,23] The author demonstrated that the rate limiting step is a concerted ring closure to the isomeric azirine in a similar reaction as described here. Arrhenius parameters for fvp isomerization reactions of 5-amino-3,4-dimethylisoxazole (**35**)[18] and 5-amino-4-methylisoxazole (**36**)[23] (Scheme 14) were compared with the ones of **1a–d** and reported in Table 8.

It should be mentioned that some of the azirines obtained from isoxazoles are stable enough to be isolated or detected by spectroscopy, which is not the case of the diazirines proposed as intermediates in the reactions here reported. These diazirines are antiaromatic and this is the reason why they are not detected nor isolated, similar antiaromatic compounds, such as the 1*H*-azirines were proposed as intermediates in reactions of *N*-substituted 1,2,3-triazoles and benzotriazoles[24] and in reactions of 1-phthalimido-1,2,3-triazoles.[25]

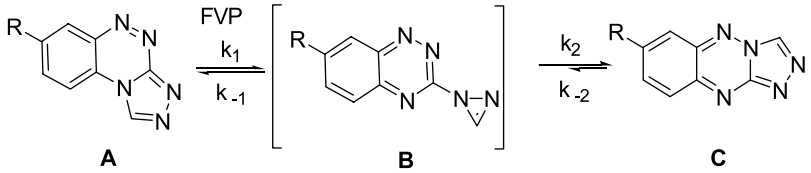
With the kinetic evidence reported here (large negative entropies of activation), it is possible to propose path c of Scheme 13 as the one taking place in these reactions. As formation of the diazirine is the rate determining step, with these results it is not possible to distinguish how the diazirine ring opens, as a concerted reaction (way d) or through an open chain isomer (way e).

The other point that was checked is the reversibility of the reaction: if the angular isomer is also formed from the linear one under the same fvp conditions. In order to study this possibility, fvp reactions of **9b** were carried out at 480 °C. As expected, **1b** (26.3%) was found to be the reaction product as well as unreacted **9b** (73.7%), confirming the reversibility of the reaction. These results also show that the system is not in equilibrium, probably because this is a flow system with short contact times, since the yields starting from **9a** and from **9b** are different. These results may bring clarity to the whole mechanism taking into account the microscopic reversibility principle. Thus, it was demonstrated that the angular compounds form the diazirine with negative entropies of activation. If the linear compounds also afford isomerization to the angular one, the reaction should proceed through the diazirine. If this is so, the open chain intermediates (**32** and **33**) postulated in path c–e (Scheme 13) cannot be present, as the angular compounds can be formed directly from these intermediates without cyclization to the diazirine. With this in mind, path c–d seems more possible (Scheme 15, Fig. 2) as the actual mechanism in accordance with the microscopic reversibility principle. As the linear isomer has an unfavorable *ortho* quinoid arrangement it is expected to be less stable than the linear isomer (as naphthalene and phenanthrene), so the qualitative energy profile of the reaction in Figure 2 could be a suitable representation of these reactions.

The kinetic expression for this reaction (assuming stationary state for B) is:

$$k = k_1 + (k_{-1}k_{-2}/k_2) \quad (1)$$

An analysis of the relative expected values of the different rate constants show that $k_2$ should be larger than $k_{-1}$ as the reaction goes to products; $k_{-2}$ should have a smaller value than $k_2$ but larger than $k_1$ as this reaction starts from the thermodynamically less stable isomer. These assumptions make the second term of the rate constant expression (Eq. 1) negligible, so the measured rate constant $k_{obs} \sim k_1$, which is




**Scheme 15.**

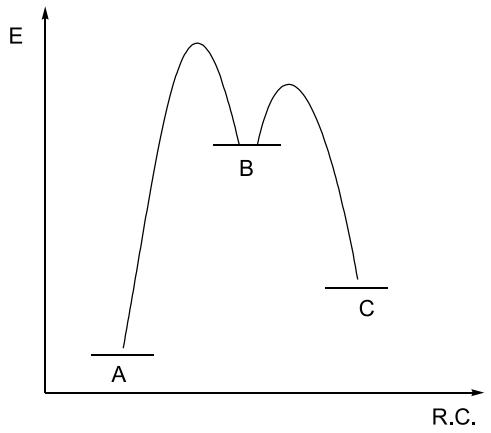



**Figure 2.** Qualitative representation of reaction coordinate for reactions of **1a–d**. A: initial angularly fused triazole **1**, B: azirine intermediate, C: linearly fused triazole product.

in accordance with the negative entropy of activation for a ring contraction reaction.

Valuable conclusions can be drawn by analysis of the effect of substituents reflected in the Arrhenius parameters. In NMR studies of the equilibrium between the angular and the linear structures of tetrazolo-benzo-*as*-triazines through the isomeric azide (Scheme 11) the authors demonstrated that substituents attached to C7 have a strong influence on the position of the ternary equilibrium.[16,26] Looking at the data reported in Table 8, it is clear that all the free energies of activation are almost the same, but, the entropic and enthalpic data are quite different, as well as reaction constants measured at the same temperature. The more electron donating the substituent (methoxy in this case) the faster the reaction. Chlorine has a lower rate constant than methoxy but faster than hydrogen and methyl. Hydrogen and methyl have almost the same values within the experimental errors. Thus, the rate constant values follow the electronic effect of the substituents while the entropies of activation have a different sequence. The large negative value for chlorine can be interpreted as a more concerted character of the reaction probably due to a combination of inductive (electron withdrawing) and electronic (electron donor) effects or an isokinetic relation, $\Delta H^*$ is very low, as all compounds have similar $\Delta G^*$ confirming that they react by the same mechanism.

Finally, with the above described results it can be concluded that these reactions could be included in types I or III AX of Epioti′s classification. Theoretical calculations should be made to determine, which are the donor and the acceptor partners with the lower energy difference for HOMO–LUMO interaction.

Some additional remarks on formation of aromatic compunds at higher temperatures should be made concerning the analysis of these reactions. As it was stated above, **1a** afforded benzonitrile (**10**) as well as **9a** over 550 °C; **1b** afforded *p*-methylbenzonitrile (**11**), dicyanobenzenes (**12–14**) and **9b** over 550 °C; **1c** afforded anisole (**15**), benzene (**16**) and **9c** over 520 °C and **1d** afforded *p*-chlorobenzonitrile (**17**), benzonitrile (**10**) and **9d**. In all of these reactions also, a carbonaceous residue was obtained at higher temperatures. These results are not surprising and were also found in reactions of 2-substituted 1,2,4-benzotriazines described in a previous paper.[4] It is common for aromatic hydrocarbons to lose a substituent by radical reactions, so products from radical combination are also formed as well as coke.

The striking point is that in reactions of **1b** and **1c** the cyano group is maintained while it is lost in reactions of **1c**. In order to rationalise this finding, some calculations on bond length have been carried out by using Hyperchem™ programme [A semi-empirical method (AM1) with algorithm Polak-Ribiere (Conjugate Gradient)]. Results showed that the C–CN bond is of 1.42 Å for **10**, **11**, **17**, and *p*-methoxybenzonitrile while the C–$CH_3$ in **11** bond is of 1.48 Å, the C–Cl bond in **17** is of 1.70 Å and the C–$OCH_3$ in *p*-methoxybenzonitrile is of 1.38 Å. These data show that C–CN is the weaker bond in *p*-methoxybenzonitrile and this may be the reason why anisole is the product formed by the radical scission reaction.

## 3. Conclusions

Reactions described here support that the isomerization equilibrium between [1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazines (**1**) and [1,2,4]triazolo[4,3-*b*][1,2,4]benzotriazines (**9**) goes through antiaromatic diazirines. Formation of these intermediates is the rate-limiting step with large negative entropies of activation. It was proved that electron-donating substituents diminish the concerted character reflected in a less negative entropy of activation and larger reaction rate constant. All the studied compounds have almost the same free energy of activation values, which suggests that all of them react by the same mechanism. Reactions described here show that the mechanism of isomerization is different from those described for similar compounds with 1,2,3-triazoles and tetrazoles where open chain intermediates were isolated or detected by spectroscopy.

## 4. Experimental

### 4.1. General

Flash vacuum pyrolysis reactions were carried out in a vycor glass reactor using a Thermolyne 21100 tube furnace with a temperature controller device. Oxygen-free dry nitrogen was used as carrier gas. Samples to be pyrolyzed were of ~40 mg. Contact times were around $10^{-2}$ s and pressures of 0.02 Torr were used. Products were trapped at the liquid air temperature, extracted with solvent and submitted to different analysis or separation techniques. Gas chromatography/mass spectrometry (GC/MS) analysis were performed with a SE-30 column, using helium as eluent at a flow rate of 1 mL/min, the heating rate was different for each compound or mixture of compounds. Mass spectra were obtained in the electron impact mode (EI) using 70 eV as ionization energy. $^1$H NMR and $^{13}$C NMR spectra were carried out in $CDCl_3$ with a Bruker 200 FT spectrometer (at 200 MHz) and in DMSO with Varian UNITY INOVA spectrometer (200 and 400 MHz for $^1$H and 100 MHz for $^{13}$C). Chemical shifts are reported in ppm

downfield from TMS. The IR spectra were recorded with a Thermo Nicolet AVATAR 320 FT-IR spectrophotometer. Column and thin layer chromatographies were performed on silica gel. Solvents were analytical grade. Recovery of material was >90% in all fvp experiments. Melting Points were determined by a Büchi apparatus and are uncorrected.

### 4.2. Synthesis of starting materials

Compounds **1a** and **1d** were prepared by a previously described procedure.[27]

**4.2.1. 7-Methyl[1,2,4]triazolo[3,4-*c*]benzo[1,2,4]triazine (1b).** This compound was prepared by the same procedure as described for **1a** and **1d** starting from 3-hydrazino-7-methyl[1,2,4]benzotriazine[26] (1.0 g, 5.7 mmol). It was mixed with triethyl orthoformate (10.0 g, 11.2 mL, 67.5 mmol) and refluxed for 10 h (oil bath temperature 130–140 °C). The reaction mixture was cooled down to room temperature and the precipitated solid was filtered off. The crude product was recrystallized from DMF to give the product (0.746 g, 70.6%): mp 289–290 °C; IR (KBr) $\nu_{max}$ 3107, 1579, 1524, 1477, 1360, 1316, 1216, 1227, 1191, 1124, 1030, 957, 825, 772, 662, 636, 600, 552, 424 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$ 400 MHz) $\delta$ 2.6 (s, 3H, H–$CH_3$), 7.95 (dd, 1H, $J=2.0$, 8.4 Hz, H-8), 8.34 (d, 1H, $J=8.4$ Hz, H-9), 8.48 (d, 1H, $J=2.0$ Hz, H-6), 10.5 (s, 1H, H-1); $^{13}C$ NMR (DMSO-$d_6$) $\delta$ 21.3 (C–$CH_3$), 117.0 (C-9), 120.8 (C-9a), 131.4 (C-6), 135.7 (C-1), 138.0 (C-8), 138.4 (C-5a), 139.2 (C-7), 153.5 (C-3a). Anal. Calcd for $C_9H_7N_5$ (185.19): C, 58.37; H, 3.81; N, 37.82. Found: C, 58.36; H, 3.67; N, 37.52.

**4.2.2. 7-Methoxy[1,2,4]triazolo[3,4-*c*]benzo[1,2,4]triazine (1c).** This compound was prepared by the same procedure as described for **1a** and **1d** starting from 3-hydrazino-7-methoxy[1,2,4]benzotriazine[26] (1.0 g, 5.2 mmol). It was mixed with triethyl orthoformate (10.0 g, 11.2 mL, 67.5 mmol) and refluxed for 10 h (oil bath temperature 130–140 °C). The reaction mixture was cooled down to room temperature and the precipitated solid was filtered off. The crude product was recrystallized from DMF to give the product (0.905 g, 86.1%): mp 298–299 °C; IR (KBr) $\nu_{max}$ 3111, 1616, 1582, 1520, 1458, 1389, 1364, 1327, 1253, 1156, 1116, 1038, 1009, 945, 847, 770, 650, 631, 529 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$ 400 MHz) $\delta$ 4.0 (s, 3H, H–$OCH_3$), 7.77 (dd, 1H, $J=9.0$, 2.8 Hz, H-8), 8.18 (d, 1H, $J=2.8$ Hz, H-6), 8.42 (d, 1H, $J=9.0$ Hz, H-9), 10.06 (s, 1H, H-1); $^{13}C$ NMR (DMSO-$d_6$) $\delta$ 57.1 (C–MeO), 111.9 (C-6), 117.7 (C-9a), 118 (C-9), 126.2 (C-8), 136.2 (C-1), 139.3 (C-5a), 153.7 (C-3a), 159.6 (C-7). Anal. Calcd for $C_9H_7N_5O$ (201.18): C, 53.73; H, 3.51; N, 34.81. Found: C, 53.69; H, 3.27; N, 34.41.

### 4.3. General procedure for isolation of [1,2,4]triazolo-[4,3-*b*]benzo[1,2,4]triazines (9a–d)

Reaction mixtures obtained with the synthesis of **1a–d** starting from 3-hydrazinobenzo[1,2,4]triazines (**18a–d**, 5 mmol) were worked up as follows. The main product (**1**) was removed by filtration, the mother liquor was evaporated and the residue was subjected to column chromatography on silica. Besides the main product a well defined yellow fraction with a higher $R_f$ value appeared in all cases which was separated, evaporated, and the residue recrystallized from the given solvent.

**4.3.1. [1,2,4]Triazolo[4,3-*b*]benzo[1,2,4]triazine (9a).** Synthesis of **1a**[27] was carried out starting from 3-hydrazinobenzo[1,2,4]triazine[26] (**18a**, 0.806 g, 5 mmol). Work up of the reaction mixture (column chromatography with eluent hexane/ethyl acetate 3:7) yielded, besides **1a**, **9a** as brown crystals (0.033 g, 3.86%): mp 207–209 °C; IR (KBr) $\nu_{max}$ 3091, 1505, 1381, 1290, 1140, 1023, 932, 783, 760, 729, 708, 607, 421 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$ 400 MHz) $\delta$ 7.74–7.86 (m, 2H, H-7, H-8), 7.86 (d, 1H, $J=9.5$ Hz, H-9), 7.92 (d, 1H, $J=9.5$ Hz, H-6), 10.08 (s, 1H, H-3); $^{13}C$ NMR (DMSO-$d_6$) $\delta$ 127.4 (C-9), 129.6 (C-8), 133.7 (C-7), 136.0 (C-6), 137.3 (C-3), 142.0 (C-5a), 145.2 (C-9a), 147.4 (C-10a); HRMS calcd for $C_8H_5N_5$ 171.0545, found 171.0544. Anal. Calcd for $C_8H_5N_5$ (171.1625): C, 56.14; H, 2.94; N, 40.92. Found C, 56.50; H, 2.76; N, 40.62.

**4.3.2. 7-Methyl[1,2,4]triazolo[4,3-*b*]benzo[1,2,4]triazine (9b).** Synthesis of **1b** was carried out starting from 7-methyl-3-hydrazinobenzo[1,2,4]triazine[26] (**18b**, 0.876 g, 5 mmol). Work up of the reaction mixture yielded, besides **1b**, **9b** as ocher crystals (0.026 g, 2.89%): mp 240–241 °C; UV $\lambda$ (nm) log $\varepsilon$ in acetonitrile: 352 (3.645), 444 (3.379); IR (KBr) $\nu_{max}$ 3109, 1540, 1373, 1296, 1150, 1029, 1009, 939, 814, 728, 709, 659, 567, 424 $cm^{-1}$; $^1H$ NMR ($CDCl_3$ 200 MHz) $\delta$ 2.58 (s, 3H, H–$CH_3$), 7.60 (s, 1H, H-6), 7.59 (d, 1H, $J=9.5$ Hz, H-8), 7.84 (d, 1H, $J=9.5$ Hz, H-9), 9.43 (s, 1H, H-3); $^{13}C$ NMR ($CDCl_3$) $\delta$ 22.52 (C–$CH_3$), 123.7 (C-6), 129.2 (C-9), 135.9 (C-8), 138.5 (C-7), 138.9 (C-3), 142.0 (C-9a), 144.3 (C-5a), 147.2 (C-10a); HRMS calcd for $C_9H_7N_5$ 185.0701, found 185.0696. Anal. Calcd for $C_9H_7N_5$ (185.19): C, 58.37; H, 3.81; N, 37.82. Found C, 58.26; H, 3.75; N, 37.48.

**4.3.3. 7-Methoxy[1,2,4]triazolo[4,3-*b*]benzo[1,2,4]triazine (9c).** Synthesis of **1c** was carried out starting from 7-methoxy-3-hydrazinobenzo[1,2,4]triazine[26] (**18c**, 0.956 g, 5 mmol). Work up of the reaction mixture yielded, besides **1c**, **9c** as yellow crystals (0.0179 g, 1.77%): mp 216–218 °C; UV $\lambda$ (nm) log $\varepsilon$ in acetonitrile: 368 (3.564), 439 (2.992); IR (KBr) $\nu_{max}$ 3094, 1626, 1548, 1535, 1450, 1428, 1383, 1300, 1249, 1213, 1180, 1132, 1034, 998, 944, 828, 738, 709, 660, 622, 557, 406 $cm^{-1}$; $^1H$ NMR ($CDCl_3$ 400 MHz) $\delta$ 4.00 (s, 3H, H–$OCH_3$), 6.90 (s, 1H, H-6), 7.44 (d, 1H, $J=9.9$ Hz, H-8), 7.80 (d, 1H, $J=9.9$ Hz, H-9), 9.34 (s, 1H, H-3); $^{13}C$ NMR ($CDCl_3$) $\delta$ 56.6 (C–$OCH_3$), 99.2 (C-6), 130.78 (C-9), 132.8 (C-8), 135.9 (C-3), 143.4 (C-9a), 143.5 (C-5a), 147.2 (C-7), 162.6 (C-10a); HRMS calcd for $C_9H_7N_5O$ 201.065, found 201.0642. Anal. Calcd for $C_9H_7N_5O$ (201.18): C, 53.73; H, 3.51; N, 34.81. Found C, 53.47; H, 3.35; N, 34.70.

**4.3.4. 7-Chloro[1,2,4]triazolo[4,3-*b*]benzo[1,2,4]triazine (9d).** Synthesis of **1d** was carried out starting from 7-chloro-3-hydrazinobenzo[1,2,4]triazine[26] (**18d**, 0.978 g, 5 mmol). Work up of the reaction mixture yielded, besides **1d**, **9d** as yellow crystals (0.035 g, 3.40%): mp 295–299 °C; UV $\lambda$ (nm) log $\varepsilon$ in acetonitrile: 354 (3.672), 444 (3.352); IR (KBr) $\nu_{max}$ 3122, 3066, 1611, 1505, 1435, 1296, 1248, 1149, 1056, 1022, 935, 877, 834, 799, 712, 615, 579, 522, 423 $cm^{-1}$; $^1H$ NMR ($CDCl_3$ 200 MHz) $\delta$ 7.68 (d, 1H, $J=$

9.7 Hz, H-8), 7.91 (s, 1H, H-6), 7.94 (d, 1H, $J=9.7$ Hz, H-9), 9.49 (s, 1H, H-3); $^{13}$C NMR ($CDCl_3$) $\delta$ 118.3 (C-6), 124.4 (C-9), 131.1 (C-8), 131.7 (C-7), 136.2 (C-9a), 136.6 (C-5a), 140.0 (C-3), 141.6 (C-10a); HRMS calcd for $C_8H_4N_5Cl$ ($^{35}Cl$) 205.01552, found 205.01550. Anal. Calcd for $C_8H_4N_5Cl$ (205.60): C, 46.73; H, 1.96, N, 34.06. Found C, 46.76, H, 1.96, N, 33.76.

### 4.4. Flash vacuum pyrolysis of 1a

Reactions of **1a** were carried out between 450 and 600 °C, with pressures of $\sim 10^{-2}$ Torr and contact times of $\sim 10^{-2}$ s. The reaction was clean affording a single product up to 525 °C identified as [1,2,4]triazolo[4,3-*b*][1,2,4]benzotriazine (**9a**) (Scheme 6). Over 550 °C small amounts of **10** and a carbonaceous residue were formed from decomposition. The relative amounts of **1a** and **9a** were calculated by $^1$H NMR. The structure of **9a** was confirmed by comparison with authentic sample prepared from **18a**. Data for at least three reactions were averaged for the kinetic measurements.

*Benzonitrile* (**10**). Mass Spectrum: more than 90% match with NIST database. CAS No. 100-47-0.

### 4.5. Flash vacuum pyrolysis of 1b

Reactions of **1b** were carried out between 450 and 600 °C, with pressures of $\sim 10^{-2}$ Torr and contact times of $\sim 10^{-2}$ s. The reaction was clean affording a single product up to 525 °C identified as [1,2,4]triazolo[4,3-*b*][1,2,4]benzotriazine (**9b**) (Scheme 8). Over 550 °C small amounts of **10**, *p*-methylbenzonitrile (**11**) and a mixture of dicyanobenzenes (**12–14**) were also formed from decomposition of **1b** and/or **9b** (Scheme 8). The structure of **9b** was confirmed by comparison with authentic sample prepared from **18b**. Relative quantification of **1b** and **9b** was performed by $^1$H NMR. It is important to mention that 100% conversion could not be achieved and that over 600 °C coke was also formed. Compounds **10** and **12–14** are formed from pyrolysis of **11**. Data for at least three reactions were averaged for the kinetic measurements.

*p-Methylbenzonitrile* (**11**). Mass Spectrum: more than 90% match with NIST database. CAS No. 100-47-0.

*Dicyanobenzenes* (**12–14**). Mass Spectrum: (1,2) More than 90% match with NIST database CAS No. 91-15-6. Mass Spectrum: (1,3) More than 90% match with NIST database. CAS No. 626-17-5. Mass Spectrum: (1,4) more than 90% match with NIST database. CAS No. 623-26-7.

### 4.6. Flash vacuum pyrolysis of 1c

Reactions of **1c** were carried out between 440 and 540 °C, with pressures of $\sim 10^{-2}$ Torr and contact times of $\sim 10^{-2}$ s. Up to 520 °C the only product was 7-methoxy-[1,2,4]triazolo[4,3-*b*][1,2,4]benzotriazine (**9c**), over this temperature anisole (**15**), benzene (**18**) and coke were also formed (Scheme 9). The structure of **9c** was confirmed by comparison with authentic sample prepared from **18c**. Relative quantification of **1c** and **9c** were performed by $^1$H NMR. Data for at least three reactions were averaged for the kinetic measurements.

*Methoxybenzene (anisole)* (**15**). Mass Spectrum: more than 90% match with NIST database. CAS No. 100-66-3.

*Benzene* (**16**). Mass Spectrum: more than 90% match with NIST database. CAS No. 71-43-2.

### 4.7. Flash vacuum pyrolysis of 1d

Reactions of **1d** were carried out between 460 and 560 °C with pressures of $\sim 10^{-2}$ Torr and contact times of $\sim 10^{-2}$ s. As in reactions of **1a–c** only one product was formed up to 520 °C, identified as 7-chloro[1,2,4]triazolo[4,3-*b*][1,2,4]-benzotriazine (**9d**), at higher temperatures 4-chlorobenzonitrile (**17**) and **10** as well as coke were also formed (Scheme 10). The structure of **9d** was confirmed by comparison with authentic sample prepared from **18d**. Relative quantification of **1d** and **9d** was performed by $^1$H NMR. Data for at least three reactions were averaged for the kinetic measurements.

4-*Chlorobenzonitrile* (**17**). Mass Spectrum: more than 90% match with NIST database. CAS No. 623-03-0.

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