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Flash Vacuum Pyrolysis over Solid Catalysts. 1. Pyrazoles over Zeolites†

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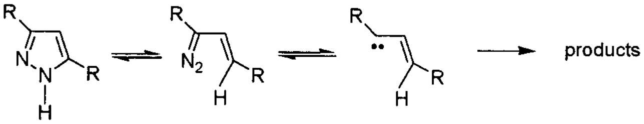
Flash vacuum pyrolysis (fvp) reactions of 1*H*-pyrazole (**1**), 3,5-dimethylpyrazole (**2**), and 3,5-diphenylpyrazole (**3**) were carried out over zeolites. Reactions were performed using ZCOY-7, NH_4-Y, and Na-Y zeolites. Reaction temperatures of heterogeneous reactions were lower than the corresponding temperatures in the homogeneous system, showing a catalytic effect of the zeolites. Compounds **1**−**3** afforded nitrogen extrusion in homogeneous fvp reactions while in the heterogeneous ones different reactions were present. Compounds **1** and **2** also afforded nitrogen extrusion; products arising from ring fragmentation were found in reactions of **2** and **3** while an isomeric imidazole was isolated in reactions of **3**. Isomerization of **3** is attributed to a transition-state selectivity by the catalyst due to the relation between the size of the molecule and the cavity of the zeolite. This isomerization reaction was present only when zeolites with active Brönsted sites were used.

Introduction

For several years, we have been engaged in the study of flash vacuum pyrolysis (fvp) of nitrogen heterocycles, pyrazoles being one of our targets. These reactions proved to be very interesting from both mechanistic and synthetic points of view.[1,2] In general terms, pyrazoles afford two main types of reactions depending on substitution at N1: loss of nitrogen in N1-unsubstituted compounds and different reactions in N1-substituted pyrazoles. Isomerizations, homolytic cleavages, and eliminations take place depending on the nature of this substituent.[1] Nitrogen extrusion reactions take place by a unique mechanism that involves two isomerization steps and nitrogen extrusion from a vinyldiazomethane intermediate to give a vinylcarbene[2] as shown in Scheme 1. These reactions seem to be interesting from a mechanistic point of view, since they give information on vinylcarbene reactivity but are not useful as a synthetic tool because they have large energies of activation and should be carried out at high temperatures. We decided to study the possibility of lowering their energy of activation and therefore reaction temperatures without changing the type of reaction and chose the use of solid catalysts, zeolites in this paper, as an alternative.

Scheme 1



There are natural and synthetic zeolites. Natural zeolites are alumino-silicate structures containing water or other cations having the general formula[3]

$$x[(M^{I}\cdot M^{II}{}_{1/2})\cdot Al_2O_3]\cdot ySiO_2\cdot zH_2O$$

where M^{I} = Li, Na, K, etc. and M^{II} = Mg, Ca, Sr, Ba, etc.

All zeolites have a characteristic aluminosilicate framework composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ that are linked together through oxygen bridges. Zeolites A and X/Y have the sodalite cage, a truncated octahedron that has eight hexagonal and six square faces, as their basic structure. In zeolites X and Y (faujasites), the spherical internal cavity generated when eight sodalite cages are joined is about 13 Å diameter and is called the α cage. The entrance of this cavity is about 7−8 Å wide (Figure 1). Due to their size, several organic molecules can enter the cavity. Most of the reactions take place inside the cavity of the zeolites, and this is the main characteristic of their activity as catalysts when compared with others that present only surface catalysis. Zeolites have Brönsted and Lewis acid sites, so they are acid catalysts. It is possible to inhibit Brönsted sites by changing H by a cation to study the type of catalysis present. The shape selectivity observed in zeolite catalysts has been categorized in three

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† Dedicated to Prof. Dr. José Elguero.

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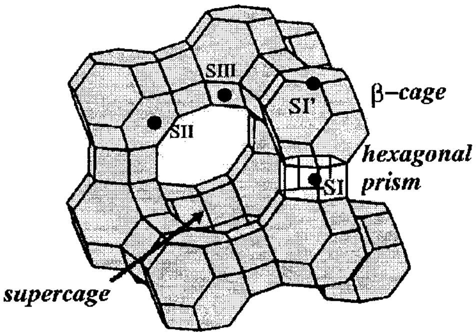


Figure 1. Schematic representation of faujasite (Y type zeolite) (from http://drake.che.udel.edu/~group/feuerstein.html with permission from the author.)

Table 1. Reactions of 1*H*-pyrazole (1)

T (°C)	catalyst	% **1**
450	none	100
450	Na-Y	19
450	NH_4-Y	16
450	ZCOY-7	13
560	none	100
560	Na-Y	8
560	NH_4-Y	6
560	ZCOY-7	3
660	none	100
660	Na-Y	7
660	NH_4-Y	3
660	ZCOY-7	0

types:[4] (1) reactant selectivity (only reactants with the appropriate dimensions can enter the cavity); (2) product selectivity (only products with the appropriate dimensions can leave the cavity); and (3) transition-state selectivity (only transition states with the appropriate dimensions can be formed at reasonable rates inside the cavity).

Thus, zeolites can control the selectivity of a certain chemical transformation with good yields.

Although zeolites are used in organic synthesis, there are only a few reports of their utilization in fvp reactions,[5] and there are also some reports of fvp reactions over silica−alumina and clay as catalysts.[6]

Here we report our results of flash vacuum pyrolysis of 1*H*-pyrazole (**1**), 3,5-dimethylpyrazole (**2**), and 3,5-diphenylpyrazole (**3**) over ZCOY-7, NH_4-Y, and Na-Y catalysts, all of them faujasites. ZCOY-7 is a cracking catalyst with 25% of zeolite Y while NH_4Y is a protonic zeolite and NaY is a zeolite without protons, both of them are pure zeolite Y.

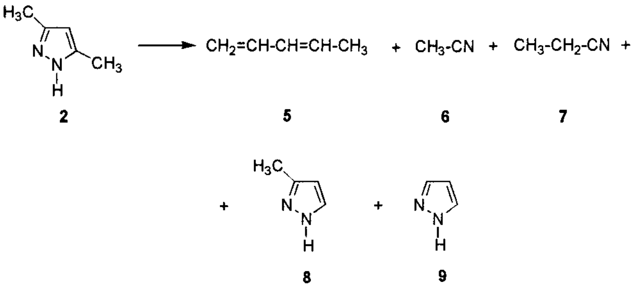
Results and Discussion

Flash Vacuum Pyrolysis of 1*H*-Pyrazole (1). Reactions were carried out between 450 and 660 °C using zeolites ZCOY-7, NH_4-Y, and Na-Y as catalysts. As shown in Table 1, the only reaction product is propyne (**4**), which agrees with previously reported results carried out in a homogeneous system.[7] Results show that reaction temperatures are lower than the ones described in the homogeneous system and that there is no change in product composition when Na-Y zeolite was used, which shows that the reaction is catalyzed, but not by protons as this zeolite has no Brönsted acid sites. It is also clear that ZCOY-7 catalyst is the most effective of the three, which is not surprising as it is an ultrastable catalyst. As reactions here described have the same pattern as the ones carried out in the homogeneous fvp system and there is not a proton-catalyzed reaction (see results with Na-Y zeolite in Table 1), there is no reason to think in a different mechanism so we propose that this extrusion reaction takes place by the mechanism depicted in Scheme 1 (R = H), which is the same one described for fvp reactions of **1** in the homogeneous system.

Table 2. Reactions of 3,5-Dimethylpyrazole (2)

T (°C)	catalyst	% **2**	products
330	none	100	
330	Na-Y	25	**6**, **7**
330	NH_4	32	**6**, **7**
330	ZCOY-7	27	**6**, **7**
450	none	100	
450	Na-Y	7	**5**, **6**, **7**
450	NH_4-Y	11	**6**, **7**
450	ZCOY-7	97	**5**, **6**, **7**
560	none	100	
560	Na-Y	15	**5**, **6**, **7**, **8**, **9**
560	NH_4-Y	20	**5**, **6**, **7**, **8**, **9**
560	ZCOY-7	0	**5**, **6**, **7**
660	none	100	
660	Na-Y	10	**5**, **6**, **7**, **8**, **9**
660	NH_4-Y	9	**5**, **6**, **7**, **9**
660	ZCOY-7	0	**5**, **6**, **7**

Scheme 2



Flash Vacuum Pyrolysis of 3,5-Dimethylpyrazole (2). Reactions were carried out between 330 and 660 °C using ZCOY-7, NH_4-Y, and Na-Y as catalysts. Results of these experiments as well as the ones reported earlier for the homogeneous system[7] are depicted in Table 2. Product composition can only be explained by three different reactions: nitrogen extrusion (as in the non-catalyzed fvp) affording 1,3-pentadiene (**5**), ring fragmentation to acetonitrile (**6**) and propionitrile (**7**), and a radical reaction for the formation of 3-(5)-methylpyrazole (**8**) and pyrazole (**9**) (Scheme 2). Ring fragmentation reaction may be analogous to cracking reactions of hydrocarbons,[8] one of the most common reactions catalyzed by zeolites. Besides, the fact that **8** and **9** arise from a radical reaction, is demonstrated by the formation of bibenzyl in reactions when toluene was used as carrier gas. It is worth to remember that this is a well-known test of the presence of radicals.

Flash Vacuum Pyrolysis of 3,5-Diphenylpyrazole (3). Reactions were carried out between 330 and 660 °C, and results are shown in Table 3 where it can be seen that different reactions take place when using these solid catalysts, i.e., isomerization and ring fragmentation. Products formed in the fragmentation reaction are benzonitrile (**10**) and phenylacetonitrile (**11**), while 2,5-diphenylimidazole (**12**) is the isomeric product. At higher temperatures, closer to the ones of the homogeneous system,[2] 2-phenylindene (**13**) and 3-phenylindene (**14**) are formed. These results, summarized in Scheme 3, suggest that there is no catalysis for nitrogen extrusion reaction and that ring fragmentation and isomerization are cat-

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[4] Sen, S. E.; Smith, S. M.; Sullivan, K. A. *Tetrahedron* **1999**, 12657.

[5] (a) Banciu, M. D.; Cira, O.; Petride, A.; Banciu, A.; Draghici, C. *J. Anal. Appl. Pyrol.* **1997**, 42, 177. (b) Banciu, M. D.; Cira, O.; Petride, A.; Banciu, A. *Rev. Roumanie Chim.* **1997**, *42*(11), 1093.

[6] See, for example: van der Waals, A.; Klundeer, A. J. H.; van Buren, F. R.; Zwanenburg, B. *J. Mol. Catal. A: Chem.* **1998**, 134, 179.

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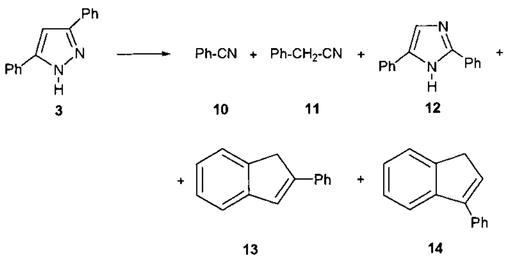
[8] See for example: Zhang, W.; Smirnotis, P. G. *J. Catal.* **1999**, *182*, 400.

Table 3. Reactions of 3,5-Diphenylpyrazole (3)

T (°C)	catalyst	% **3**	% **10**	% **11**	% **12**	% **13**	% **14**	% others[a]
330	none	100						
330	Na-Y	1	99					
330	NH_4-Y	100						
330	ZCOY-7	95	5					
450	none	100						
450	Na-Y	2	98					
450	NH_4-Y	66	8	2	24			
450	ZCOY-7	48	10	1	38			3
560	none	100						
560	Na-Y	12	88					
560	NH_4-Y	3	83	13	1			
560	ZCOY-7	4	96					
660	none	47				53		
660	Na-Y	8	22			19	19	32
660	NH_4-Y	6	87		2			5
660	ZCOY-7	26				64	9	1

[a] Benzene, anthracene, phenanthrene, and other aromatic compounds.

Scheme 3

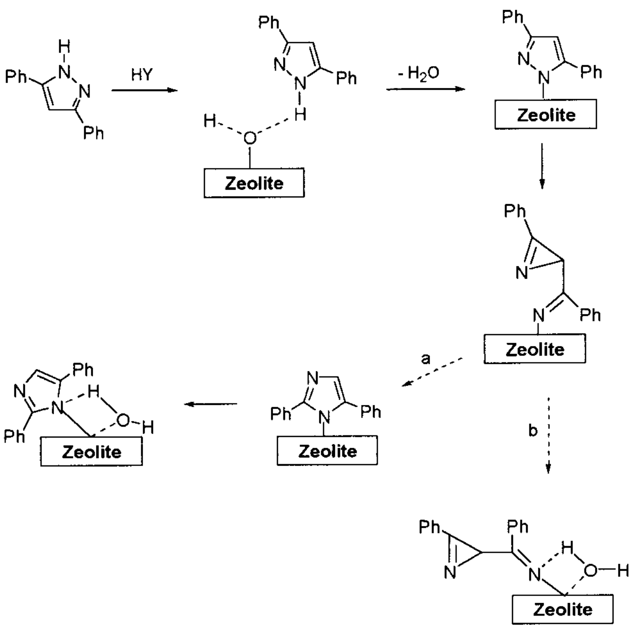


alized reactions. Fragmentation reactions should lead to the same amounts of **10** and **11** (Scheme 4) but, as can be seen in Table 3, this is not the case. Compound **11** is only found in minor quantities than **10**, so we supposed that **11** may decompose under reaction conditions. To check this, we carried out reactions of 2,2-diphenylacetonitrile (with a similar structure of **11**) at 400 °C and found that this compound gave rise to benzene and condensed aromatic compounds which may be considered as evidence that **11** has the same reaction.

From the results described above for reactions of **1**−**3**, it is clear that there is an effective catalysis when different zeolites are used in fvp of NH-pyrazoles, although the final products depend on ring substitution and in some cases on the type of zeolite employed. It is also clear from experimental results (see Tables 1−3) that there is a decrease in the yield of conversion in reactions at high temperatures (above 640 °C). This effect is more evident in reactions of **3**. To check if the catalyst was losing its activity, we carried out a reaction of **3** with wet air as carrier gas, which is the way to recover the catalyst, and found 100% conversion and some other products arising from reaction with O_2. This experiment suggests that the catalyst gets poisoned at high temperatures, but can be recovered, and that this poisoning is stronger in reactions of **3** than in the corresponding of **1** or **2**.

Concerning reaction products, it was found that in reactions of **1** only nitrogen extrusion product, i.e., propyne, is formed and no products arising from competing reactions were detected. It is worth to remember here that propyne is the only product in homogeneous fvp reactions. On the other hand, reactions of **2** and **3** have different pathways: nitrogen extrusion at lower temperatures than in the classic fvp,[9] ring fragmentation and homolytic cleavage in reactions of **2** while reactions of **3** show isomerization and ring fragmentation. It is surprising that there is no catalysis for nitrogen extrusion in reactions of **3** and, instead of this, isomeric **12** is formed.

Scheme 4



Thermal isomerization reaction has previously been described for *N*-phenylpyrazoles,[1a] *N*-benzoylpyrazole,[1c] and *N*-adamantylpyrazoles,[1d] but this is the first time this reaction is described for an N-unsubstituted pyrazole. Photochemical isomerizations of N-substituted[10] and N-unsubstituted[11] pyrazoles to imidazoles has also been reported. The mechanism of thermal and photochemical isomerizations involves the formation of a 1-azirine (not detected in these reactions) and then a ring opening reaction of the three- membered ring to afford the corresponding imidazole. We have no reason to suppose that reactions of **3** take place by a different mechanism. It is clear that this reaction is only present when zeolites with Brönsted acid sites are used (see Table 3), which strongly suggests that protons catalyze this reaction, which is not surprising since pyrazoles have a basic nitrogen in the ring. We propose the mechanism depicted in Scheme 4 with the participation of zeolite's protons. In this mechanism, pyrazole is bonded to the zeolite through a H-bond and after loss of water it is covalently bonded to the active site. At this point, isomerization to the 1-azirine takes place, and at this stage of the mechanism there are two possibilities: (a) isomerization to imidazole and then leaving of the active site with participation of a molecule of water or (b) the 1-azirine leaves the active site with the participation of water and then it isomerizes to the imidazole. We believe that this last option is better because the N atom in the 1-azirine is more free to interact with a molecule of water than the N atom of the imidazole.

Ring fragmentation is a competitive reaction in fvp of **2** and **3**. It was discussed by Rademacher in his review on fragmentations of five-membered rings.[12] This author

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[9] Pérez J. D.; Yranzo, G. I. *Bull. Soc. Chim. Fr.* **1986**, 473.

[10] (a) Beak, P.; Messer, W. *Tetrahedron* **1969**, 25, 3287. (b) Pavlik, J. W. In *Organic Photochemistry*; Ramamaurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1997; Vol. 1, 57.

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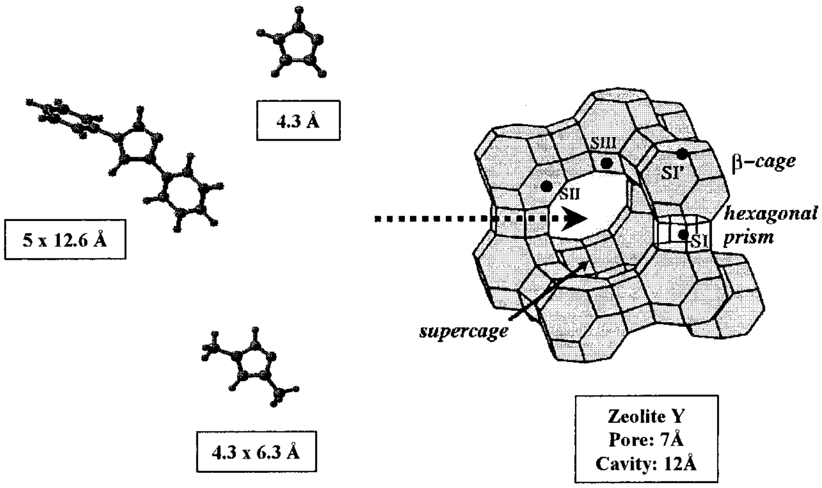
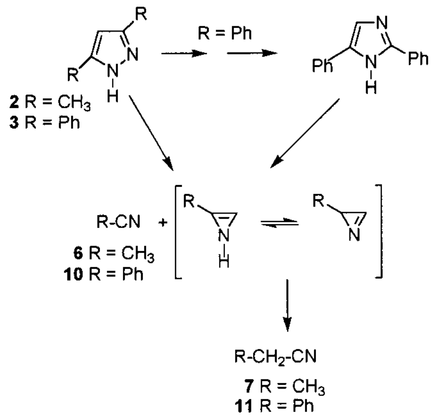


Figure 2. Comparative sizes of **1**, **2**, and **3** with faujasite.

Scheme 5



describes [5 → 3 + 2] fragmentations of different heterocycles such as furanes, pyrroles, thiophenes, pyrazoles, and isoxazoles in concerted or stepwise mechanisms. It is worth to mention here that nitrogen extrusion reactions of pyrazoles may be considered as this type of fragmentations, where the molecular nitrogen is the two-atoms fragment. In the present case, we report a different fragmentation pattern of pyrazole ring when solid acid catalysts are used. This fragmentation corresponds to N–N and C3–C4 bond fission (see Scheme 5), which were reported in shock tube reactions of isoxazole[13] and flash vacuum pyrolysis of 3,6-diphenyl-1,4,2,5-dioxadiazine.[14] It is not probable that reactions of **2** and **3** are concerted, since the final products are formed by migrations of H and R (CH_3 or C_6H_5), and this may probably occur through three-membered ring intermediates.

To check if **10** and **11** were formed from fragmentation of **12** as well as from **3**, we carried out some reactions of **12** under the same conditions of **3**. Compounds **10** and **11** were found along with some other products (aromatic compounds); with this evidence we cannot discard the pathway in Scheme 5.

Now the absence of nitrogen extrusion in reactions of **3** should be discussed. To find an explanation to this fact, we calculated the size of compounds **1**–**3** to be compared with the pore and the cavity sizes of zeolite Y. Results are shown in Figure 2. As is clear, compounds **1** and **2** are small enough to enter the cavity, and the transition states and intermediate compounds to the corresponding vinylcarbenes can be held inside the zeolite. On the other hand, dimensions of **3** are very close to the dimensions of the cavity, so a ring expansion reaction is unlikely to happen. Instead of this, a ring contraction reaction to the isomeric 1-azirine has more chances to take place. These events may be interpreted as a transition state selectivity by zeolite Y.

As a summary of results described in this paper, it is important to point out that zeolites catalyze fvp reactions of pyrazoles. When these results are compared with the ones obtained in homogeneous fvp reactions of the same compounds,[2a,7] it is found that some different reactions are produced along with nitrogen extrusion in ring substituted compounds provided that the transition state has enough capacity inside zeolite's cavity. As a continuation of this work, reactions of NH-pyrazoles over different solid catalysts are being carried out and will be published soon.

Conclusions

Some important conclusions may be drawn from the above results: (1) It is possible to carry out flash vacuum pyrolysis over solid catalysts. (2) Zeolites are good catalysts for this purpose, although in the case of pyrazoles they derive to different competing reactions. (3) When the size of the reacting pyrazole is very similar to the size of the zeolite cavity, the molecule can enter the catalyst, but an isomerization via a ring contraction reaction is preferred. This isomerization may be of higher energy than nitrogen extrusion as this reaction is not found in small compounds where this last reaction is found.

Experimental Section

General Methods. Reactions were carried out in Vycor glass fvp equipment using a Thermolyne 21100 tube furnace with a temperature controller device. Oxygen-free dry nitrogen or a mixture of nitrogen/toluene was used as carrier gas. Samples to be pyrolyzed were 30–50 mg. Contact times were around 10^{-2} s, and pressures of 0.2–0.1 Torr were measured with a Mc'Leod manometer. In a typical run, 0.75–1.50 g of fractured catalyst was placed along the reactor (30 cm length, 1 cm diameter) using ceramic wool fiber as inert support.

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Products were trapped at the liquid air temperature, extracted with solvent, and submitted to different analyses or separation techniques. Gas chromatography/mass spectrometry (GC/MS) analyses were performed in a Perkin-Elmer Q-Mass 910 spectrometer equipped with an SE-30 column, using helium as eluent gas at a flow rate of 1 mL/min and a heating rate of 40 °C for 5 min and 40−280 °C for 35−40 min. 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 Cl_3CD in a Bruker 200 FT spectrometer (at 200 MHz). Chemical shifts are reported in parts per million (ppm) downfield from TMS. Column and thin-layer chromatography were performed on silica gel. Recovery of material was >90% in all in fvp experiments. In reactions of **1** and **2**, quantification of starting material was performed by ^{1}H NMR using 2−3 μL of nitromethane as internal standard. There is no information of quantities of reaction products because some of them are volatile. In reactions of **3** starting material and reaction products were quantified by ^{1}H NMR using 2−3 μL of nitromethane as internal standard. Calculations were performed using the Hyperchem program using AM1 for geometrical optimization.

Catalytic Material. Zeolites Na-Y (Si/Al = 4.61; Al/Na = 1.0) NH_4-Y (Si/Al = 8.77), and ZCOY-7 (Si/Al = 6.5, matrix area: 52m^2/g, zeolite area: 144m^2/g, aO: 24.46 Å, La_2O_3: 0.27%, CeO_2: 0.55%, Al_2O_3: 41.3%) were kindly donated by Prof. Eduardo Herrero from CITeQ-UTN (Córdoba, Argentina). All zeolites were preactivated in air at 500−550 °C for 4 h (including heating, 100 °/h) before each reaction. The catalysts were pressed, fractured, sieved to the desired particle size fraction of 12−20 mesh, and stored under ambient atmosphere.

FVP of 1. Compound **1** was commercially available from SIGMA and purified by sublimation in vacuo. After the fvp experiment, the reaction crude contained a solid identified as **1** and a gaseous product. Compound **1** was compared with commercial sample and the gaseous product was dissolved in Cl_3CD and analyzed by ^{1}H NMR. The spectrum showed only one signal at δ = 1.85 ppm, attributed to **4** as reported previously.[7]

FVP of 2. Compound **2** was synthesized by a modification of the synthesis of 3,5-dimethylisoxazole using 2,4-pentanedione and hydrazine instead of hydroxylamine and then purified by sublimation in vacuo.[15] After the fvp experience, the reaction crude was submitted to radial and thin-layer chromatography using chloroform/benzene, 50:50 as solvents), and the isolated products were analyzed by ^{1}H and ^{13}C NMR and GC/MS. In all cases, **2** as well as **5**−**9** were detected in different amounts depending on reaction temperature. The identity of compounds **6** and **9** were established by comparison with commercial samples while **5** was compared with the product obtained in a fvp reaction of **2** in the homogeneous system. The NMR and MS data of **7** and **8** were identical to those published previously.[16a,b]

FVP of 3. Compound **3** was prepared as described in the literature from 1,3-diphenyl-1,3-propanedione and hydrazine.[17] After fvp reactions, products were extracted from the cold trap and separated by column chromatography using benzene: methanol (90:10) as solvents. The identity of **10** was established by comparison with a commercial sample, while **13** and **14** were identified by comparison with samples obtained from fvp reactions of **3** in homogenoeus fvp experiments as described elsewhere.[2a] Nitrile **11** was identified by its ^{1}H and ^{13}C NMR spectra and GC/MS analysis, which were in agreement with previous observations.[18] Isomer **12** was isolated from the reaction crude and characterized by ^{1}H NMR, ^{13}C NMR, and GC/MS. Spectral data: ^{1}H NMR ($CDCl_3$) δ (ppm) 3.81 (1H, broad signal), 7.05−7.76 (7H, m), 7.80−8.51 (4H, m); ^{13}CNMR (acetone-d_6) δ (ppm) 123.5, 124.8, 126.0, 128.3, 129.5, 130.2, 131.2, 133.0, 157.0; GC/MS m/z 220 (100), 205 (9), 191 (8), 165 (27), 96 (19), 89 (38), 77 (31), 63 (39), 51 (61), 39 (46); retention time 26.34 ± 0.02 min.

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