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Gas-phase pyrolysis of benzimidazole derivatives: novel route to condensed heterocycles

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ABSTRACT

Gas-phase pyrolysis of *N*-(1*H*-benzimidazol-2-yl)-*N*′-arylidenehydrazines **1a–e** gave the corresponding arylnitriles **2a–e**, 2-aminobenzimidazole **3**, 2,4,5-triphenylimidazole **4**, 1,3-diphenyl-8*H*-2,3a,8-triazacyclopenta[a]indene **5**, and 5,11-diphenyl-6*H*,12*H*-dibenzimidazo[1,2-*a*];1′,2′-*d*]pyrazine **6**. The kinetics and analysis of the products of reaction are reported and used to elucidate the mechanism of the elimination process.

1. Introduction

Gas-phase pyrolysis is a useful alternative synthetic strategy offering an important route for the preparation of novel condensed heterocycles. Many valuable heterocyclic compounds of synthetic importance and potential biological, pharmaceutical and industrial application have been prepared using the two major gas-phase pyrolysis methodologies: static (sealed-tube) pyrolysis (STP) and flash vacuum pyrolysis (FVP).[1–7] Both processes are conducted at low pressure, while FVP is further characterized by relatively short (millisecond) substrate residence time.[2,5,8] Our pioneering use of STP in the study of the kinetics of gas-phase pyrolysis reactions gave extensive data on thermal reactivity, which was used in combination with product analysis to provide added support for proposed mechanisms of thermal gas-phase elimination reactions.[3–5] It is to be noted that no reagents, solvents or catalysts are used in these reactions, and hence these reactions: (a) are deemed reasonably economic and environmentally benign;[8,9] (b) are increasingly being employed as models for theoretical investigations of thermal gas-phase reactivity, transition states and reaction mechanisms.[10–13]

Earlier, we have used *N*-substituted cyclic amides, thioamides, and related nitrogen heterocycles as substrates in thermal gas-phase elimination reactions to prepare condensed heterocyclic compounds, in which the reactions of *N*-arylidenaminoheterocycles were found to proceed via a six-membered transition state (TS) with elimination of arylnitriles.[14–17] However, the rates and products of the reaction were affected by structural factors and the nature of the heterocyclic ring. Here, we report the results of a kinetic and mechanistic investigation of the FVP and STP reactions of substituted benzimidazolylarylidinehydrazine compounds in which the arylidene diaza substituent is on a ring carbon atom of the nitrogen heterocycle. This feature and the nature of the benzimidazole ring account for the interesting condensed heterocyclic compounds obtained in the elimination process.

2. Results and discussion

2.1. Products and mechanism

Reaction products from the complete gas-phase pyrolysis of *N*-(1*H*-benzimidazol-2-yl)-*N*′-arylidenehydrazines **1a–e** were obtained at optimal STP reaction conditions of temperature, pressure (0.045 Torr), and substrate residence time (ca. 900 s) compatible with ≥98% reaction as evidenced by HPLC analysis of the pyrolysate in kinetic runs. The products of FVP of **1a–e** at 700 °C and 0.02 Torr

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pressure (ca. 10 ms residence time) were separated and directly collected in a U-shaped trap cooled in liquid nitrogen, and analyzed by ^{1}H NMR spectroscopy and LCMS. The elimination products from FVP consist of arylnitriles **2a–e** and 2-aminobenzimidazole **3** in yields of ca. 75% and 80% (±10%), respectively (Table 1). A plausible mechanism to explain the elimination products of FVP is shown in Scheme 1. It is suggested that the amine tautomer (**A**, **B**) of the substrates **1a–e** pyrolyzes to give the two major elimination fragments via a six-membered TS, suggested earlier for the FVP of compatible heterocycles.[3] An alternative pathway involves the fragmentation at the N–N bond of the amine tautomer to give reactive radical intermediates, which exchange hydrogen atoms and form the elimination fragments.[3–5] This pathway is evident from analysis of the mechanism proposed for the STP process and the results of both the kinetic and products of pyrolysis. Besides, formation of radicals during FVP has been reported for a wide range of reactions.[3,6,10,17,18]

Table 1
Products of FVP of **1a–e**, STP of **1a** and **16**, and % yield

Substrate	X	Condition	% Yield of pyrolysis products							
			2a–e	**3**	**4**	**5**	**6**	**17**	**18**	**2a**
1a	H	[a]	78	73	—	—	—	—	—	—
1a	H	[b]	15	20	21	15	18	—	—	—
1b	OCH_3	[a]	85	78	—	—	—	—	—	—
1c	CH_3	[a]	86	85	—	—	—	—	—	—
1d	Cl	[a]	65	67	—	—	—	—	—	—
1e	NO_2	[a]	58	65	—	—	—	—	—	10
16	H	[b]	—	—	—	—	—	48	38	—

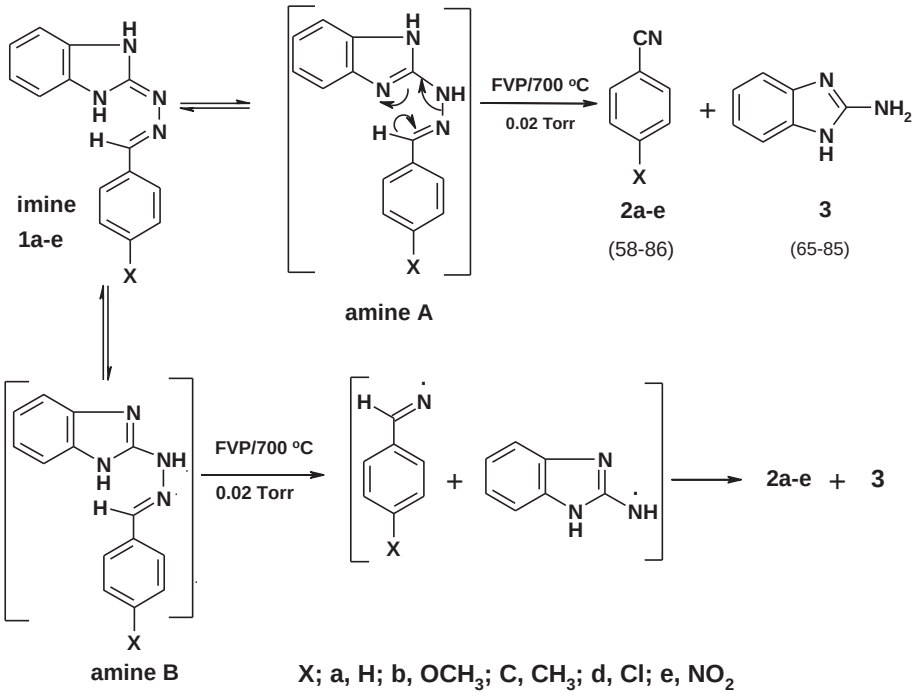
[a] FVP, 700 °C, 0.02 Torr.
[b] STP, 280 °C, 0.045 Torr, 15 min.

The products of complete pyrolysis from the STP reaction of the substrates under study were collected and separated by column chromatography using silica gel and ethyl acetate/petroleum ether (60–80) as eluent (5–25% ethyl acetate). The pyrolysates were analyzed qualitatively and quantitatively by GC–MS, LCMS, ^{1}H and ^{13}C NMR and 2D NMR spectroscopy. Thus, substrate **1a** pyrolyzed to give (Table 1): benzonitrile **2a** (15%), 2-aminobenzimidazole **3** (20%), 2,4,5-triphenylimidazole **4** (21%), 1,3-diphenyl-8*H*-2,3-a,8-triazacyclopenta[*a*]indene **5** (15%), and 5,11-diphenyl-6*H*,12*H*-dibenzimidazo[1,2-*a*];1',2'-*d*]pyrazine **6** (18%), as shown in Scheme 2.

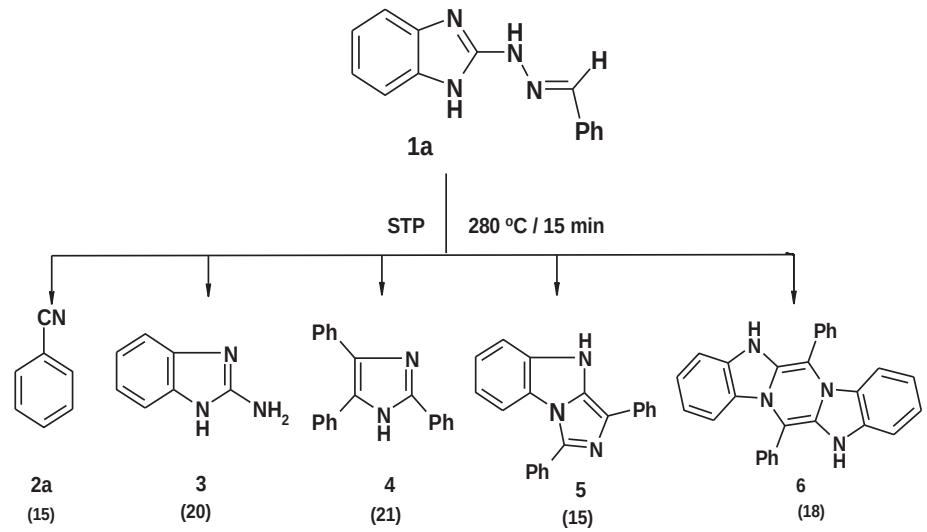
Assignment of the heterocyclic ring protons and carbons of compound **5** are shown in Figure 1. These assignments were made based on ^{1}H, H-COSY, HMQC, HMBC, and HSQC experiments. The numbering used and the important HMBC correlation of the heterocyclic proton/carbon cross peaks: H^9 at 7.25 correlates with C^7, C^{11} at 136.5, 123.4; H^{10} at 7.04 correlates with C^8, C^{12} at 125.6, 112.5; H^{11} at 7.28 correlates with C^7, C^9 at 136.5, 111.6; H^{12} at 7.43 correlates with C^8, C^{10} at 125.6, 119.6; H^{14} at δ 7.68 correlates with C^1, C^{16} at δ 118.2, 128.36; H^{15} at 7.36 correlates with C^{13} at 134.8; H^{16} at δ 7.49 correlates with C^{14} at δ 130.4; H^{18} at 7.72 correlates with C^3, C^{20} at δ 137.8, 127.0; H^{19} at δ 7.54 correlates with C^{17} at δ 130.6, and H^{20} at δ 7.30 correlates with C^{18} at δ 127.5.

Scheme 3 illustrates plausible mechanistic routes to explain the formation of the products of pyrolysis (**2**–**6**) in the STP reaction of compound **1a**. It has already been shown in Scheme 1 that the amine tautomer **B** of substrates **1a** pyrolyzes into radical intermediates **10** and **11** (as labeled in Scheme 3), which undergo intermolecular H exchange to give the observed fragmentation products **2** and **3**, respectively. On the other hand, elimination of H_2 and extrusion of molecular nitrogen from the substrate **1a** under the conditions of pyrolysis yield intermediate **8** followed by the diradical **9**. This diradical reacts further with the benzonitrile **2a** present in the reaction mixture to produce the condensed heterocycle **5**. Besides, colligation of two units of the diradical **9** leads to the formation of the heterocycle **6**.

Evidence for the mechanism was obtained in part from the STP reaction (280 °C/15 min) of the substrate **1a** in the presence of *p*-tolunitrile. Analysis of the pyrolysate using LCMS confirmed the presence of a methyl substituent in the aryl derivative **5**, while compound **6** remained unchanged. On the other hand, when compound **6** was pyrolyzed at higher temperature (310 °C) and



Scheme 1. Pathway of FVP of benzimidazolylarylidenehydrazine **1a–e**.



Scheme 2. Products of STP of substrate **1a**.

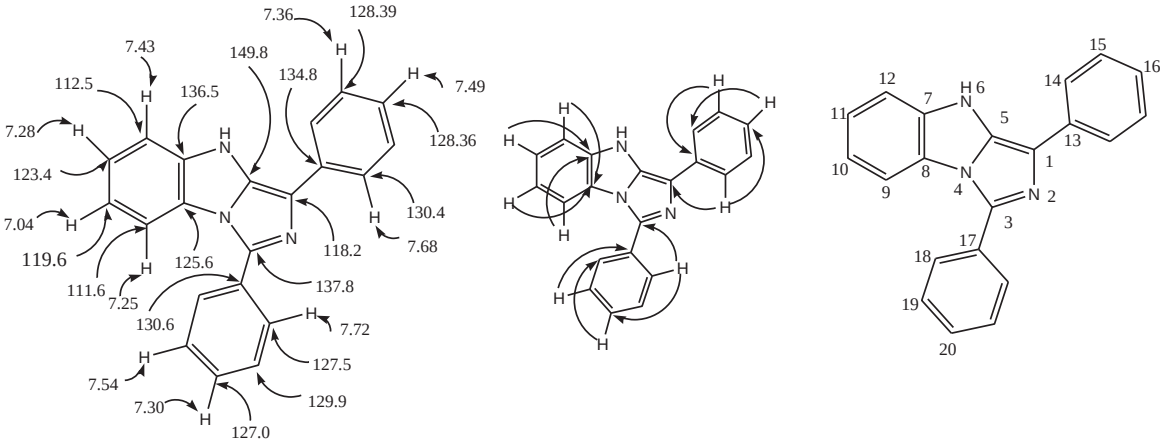


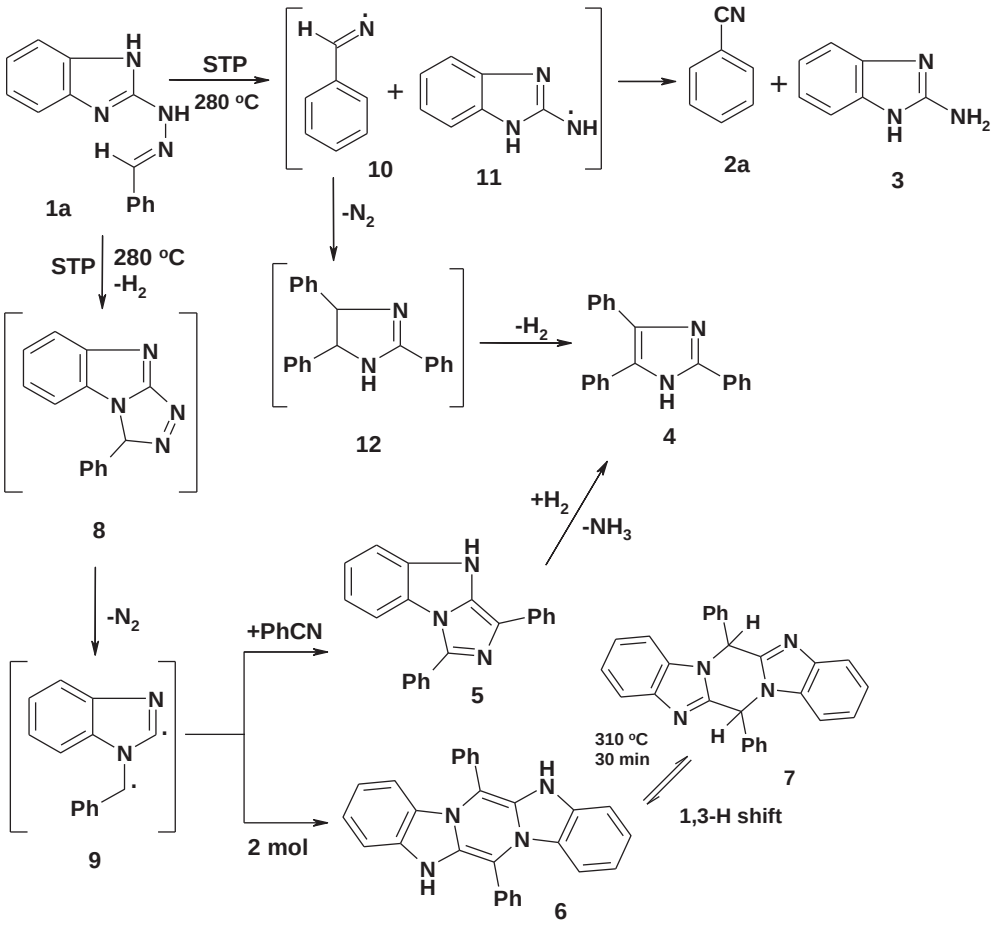
Figure 1. Assignment of heterocyclic protons and carbons of compound **5**.

longer residence time (30 min), to ascertain the route of formation of **5**, it was found that compound **6** had isomerized by 1,3-H shift to yield the 5*H*, 11*H*-dihydroderivative **7**. The LCMS data of these two compounds were, respectively, 412 at R_t 5.5 and R_t 9.5. Besides, compound **5** when heated at higher temperature (310 °C) and longer time (30 min) it remained unchanged.

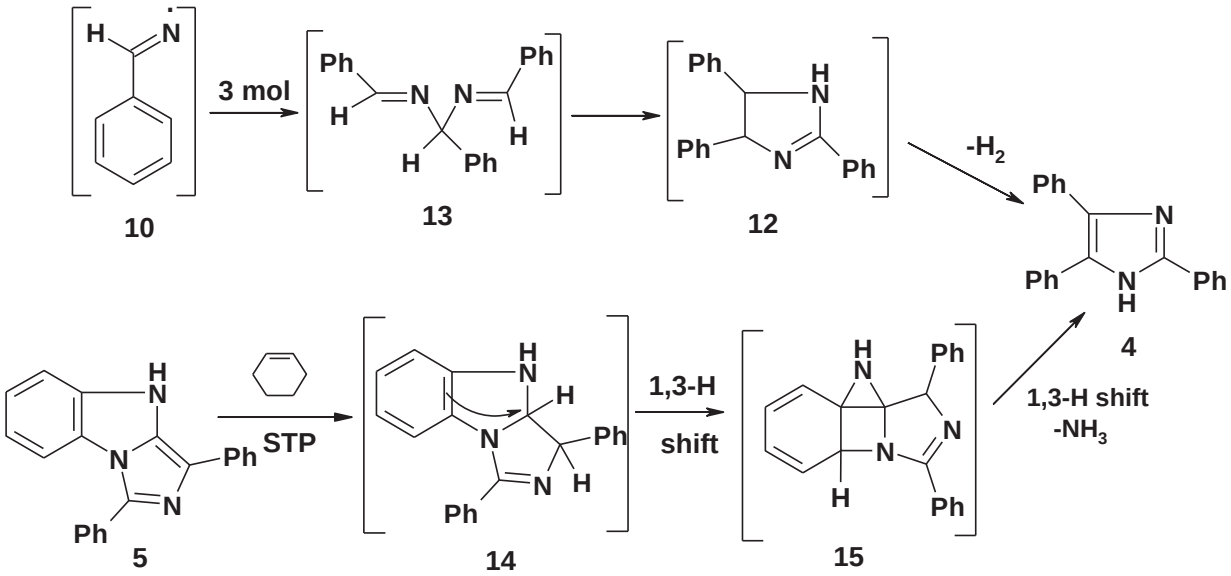
The STP reaction mechanism (Scheme 3) shows two routes open for the formation of 2,4,5-triphenylimidazole **4**, a feature, which indicates a convergence of the reaction pathways and thus an added confirmation of the mechanism suggested for the pyrolysis of the substrate under study. According to one route (Scheme 4), conversion of radical **10** into the amarine derivative **12** proceeds through intermediate **13**. Formally, the reaction involving three moles of **10** yields one mole of **13** in addition to nitrogen, and the generation of two molecules of **13** would be associated with the extrusion of molecular nitrogen. Subsequent dehydrogenation of **12** gives compound **4**. It is noteworthy that reaction of the radical intermediate **10** with hydrogen leads to the formation of the corresponding arylimine, which has been reported to yield **13** by elimination of ammonia.[19]

The alternative route to **4** involves the pyrolysis of compound **5** obtained from the diradical intermediate **9**. It is argued that during STP, compound **5** reacts with H_2 to yield intermediate **14**, which in turn undergoes consecutive 1,3-H shifts to yield **15**; and the latter by 1,3-H shift and loss of an NH_3 unit yields the 2,4,5-triphenylimidazole **4** (Scheme 4). This argument is supported by the results of two experiments. In one experiment, compound **5** was reacted under the conditions of STP in the presence of hydrogen from an external source (cyclohexene); the result was the formation of 2,4,5-triphenylimidazole **4**. In a separate experiment, substrate **1a** was pyrolyzed after reaction with methyl iodide (to remove imidazole hydrogen from the substrate molecule), as a consequence of which neither compound **4** nor any of the other condensed heterocycles (**5**, **6**) could be obtained. Instead, STP of **16** at the same reaction conditions (280 °C, 15 min.) gave only 3-phenyl-9*H*-benzo[4,5]imidazo[2,1-*c*][1,2,4]triazole **17**, and 9-methyl-3-phenyl-9*H*-benzo[2,1-*c*][1,2,4]triazole **18** as the major products of reaction (Scheme 5). Further, it is of interest to note that the data shown in Table 1 seem to provide additional support for the proposed mechanism, in that the formation of compounds **4**–**6** appears to come at the expense of the elimination fragments **2** and **3**.

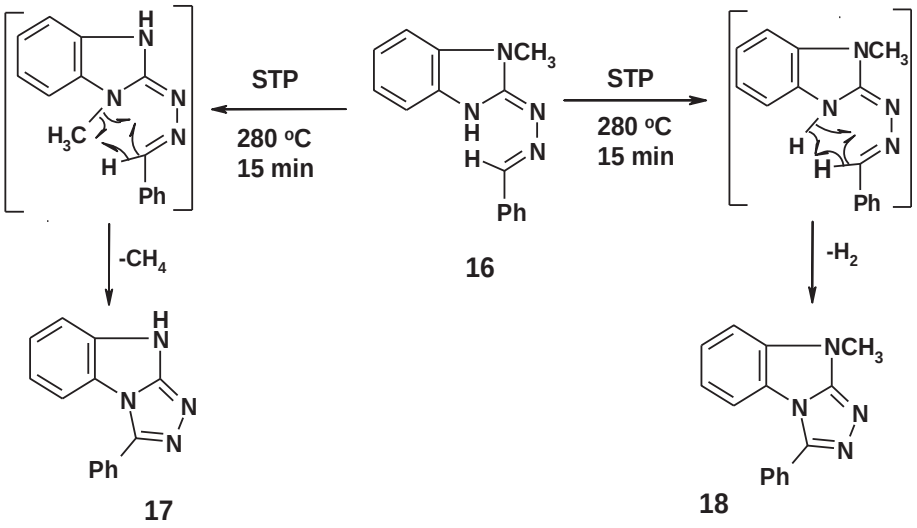
From Table 1, it is evident that FVP of substrate **1a** gave similar products to those obtained from STP except for compounds **4**, **5**, **6**. This could be explained by further fragmentation during the longer residence time of the STP reaction (15 min, 280 °C compared with 10 ms and 700 °C for FVP).



Scheme 3. Mechanism and STP products of **1a**.



Scheme 4. Two routes to compound **4**.



Scheme 5. STP reaction products of **16**.

2.2. Kinetic analysis and thermal reactivity

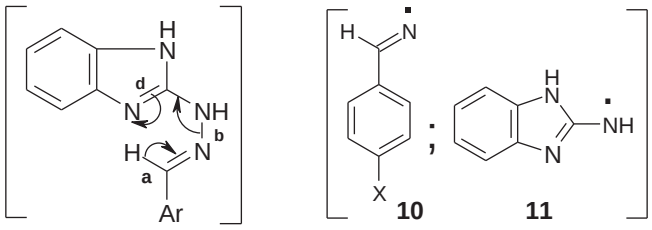
The rates of pyrolysis of the substrates under study **1a–e** shown in Table 2 were measured over a temperature range of 57±8 K between 453 and 558 K, a condition deemed necessary for reliable kinetic analysis of thermal gas-phase elimination reactions.[3,5b,11] The rate constant at each reaction temperature is an average from at least three kinetic runs in agreement to within ±2% rate spread. Rate is obtained by monitoring the disappearance of the substrate during the reaction, and using the relation for a first-order rate equation: $\log k = \log A - E_a/4.57\,T$. The values of the Arrhenius $\log A/s^{-1}$ and energy of activation (E_a/kJ mol^{-1}) also shown in Table 2 were obtained from Arrhenius plots that were strictly linear over ≥92% reaction and with correlation coefficients of the order of 0.997±0.002. The limits of error in the table represent the correlation statistical values. The rate constant data used for comparing the thermal reactivity of the substrates were calculated at 500 K for two valid reasons: (i) this temperature lies within the range over which the kinetic measurements were made; (ii) rates calculated at this temperature allow comparisons to be made with data for other compatible heterocycles.[3,4,6,7,14–17]

The kinetic data in Table 2 show all the substituted compounds under investigation to be more reactive than the parent heterocycle **1a**. The relative rates (k=3±0.03) of **1b–d** though moderate are nevertheless significant, while k_{rel} of the nitro compound **1e** is six-fold higher. Both the electron-withdrawing and the electron-donating groups in these substrates appear to enhance the molecular reactivity of compounds **1b–e** in their thermal gas-phase elimination reactions. This pattern of substituent effect associated with the arylidinehydrazine group has been observed, and the different behaviour of the nitro group in gas-phase pyrolysis has also been reported.[3,5] The present kinetic results support a reaction mechanism in which both a six-membered transition (TS) and radical reactive intermediate pathways (Schemes 1 and 3) contribute

Table 2
Rate constant (k/s^{-1}), Arrhenius log A, and E_a, and rate constant at 500 K of gas-phase pyrolysis of compounds (**1a–e**)

Cpd	X	T/K	$10^4 k$/s^{-1}	log A/s^{-1}	E_a/kJ mol^{-1}	$10^4 k_{500K}$/s^{-1}
1a	H	502.05	1.087	12.6±0.62	159.0±6.3	1.01
		516.25	3.619			
		530.10	8.933			
		544.25	25.73			
		558.15	48.11			
1b	OCH_3	489.95	1.691	6.97±0.23	100.7±2.3	2.80
		513.85	5.389			
		525.75	9.658			
		537.75	14.41			
		549.65	25.47			
1c	CH_3	487.95	1.911	6.23±0.08	93.00±0.85	3.29
		503.05	3.783			
		518.05	7.019			
		553.25	28.62			
1d	Cl	497.75	2.573	9.90±0.54	128.9±5.3	2.76
		507.75	4.481			
		517.75	7.099			
		537.75	23.23			
		547.55	44.43			
1e	NO_2	453.25	3.574	4.42±0.31	68.50±2.9	18.6
		466.45	5.275			
		479.15	8.989			
		492.10	15.06			
		504.95	21.60			

to the observed overall thermal gas-phase reactivity of compounds **1a–e**. The three molecular sites in the TS (Fig. 2) leading to its development are bonds **a**, **b**, and **d**.[8,11] An electron-withdrawing group (x) in the arylidinehydrazine moiety would enhance reactivity by an effect on the protophilic character of the hydrogen of bond (**a**) and the polarization of the (N–N) bond (**b**), and through the stabilization of any partial negative charge being developed at the incipient cyano moiety.



Six-membered TS Free radical intermediates

Figure 2.

The radical pathway is initiated by the thermolysis of the polar (N–N) bond (**b**). The important electronic effect associated with this pathway would be the resonance stabilization of radical (**11**) due to the conjugative interaction of the nitrogen free radical centre with the benzimidazole ring system.[3,20] The electron-donating substituents could exert their observed moderate effect by stabilizing the arylnitrile fragment (**10**).

3. Conclusion

The present study offers interesting new routes towards heterocyclic compounds, some of which are novel. The study also provides comparison between FVP and static pyrolysis of arylhydrazinobenzimidazole, which shows that FVP gave similar products to those obtained from static pyrolysis (STP), except for products of further pyrolysis arising from longer residence time in STP.

4. Experimental

4.1. General

Melting points were recorded on a Gallenkamp apparatus. IR spectra in KBr were recorded on a Perkin–Elmer System 2000 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX 400, 600 MHz super-conducting NMR spectrometers. LCMS were measured using an Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Mass spectra were recorded on VG Auto-spec-Q (high resolution, high performance, tri-sector GC/MS/MS). Microanalyses were performed on LECO CH NS-932 Elemental Analyzer.

4.2. Preparation of starting compounds 1a–e

General procedure: A mixture of 2-hydrazinobenzimidazole[21a,b] (1.48 g, 10 mmol), the appropriate aromatic aldehyde (12.0 mmol), and sodium acetate (1.2 g, 15 mmol) in glacial acetic acid (20.0 mL) was heated under reflux for 1 h. After cooling, ice water (50 mL) was added to the reaction mixture; the precipitate so formed was collected by filtration and crystallized from the proper solvent to give **1a–e**.

4.2.1. N-1H-Benzimidazol-2-yl-N′-benzylidenehydrazine ***1a***. Yield (2.0 g, 85%) as a colourless solid from DMF, mp 286–287 °C (lit.[22a,b] mp 290 °C). IR: 3432, 3056, 1657, 1589, 1523, 1461, 1433, 1351, 1269, 1136, 932, 733. LCMS: m/z=237 (M+1). MS: m/z=236 (M^+, 25%), 133 (20%). ^{1}H NMR (DMSO-d_6) δ 11.61 (br, 2H, 2NH), 8.03 (s, 1H), 7.81 (d, 2H, J 7.8 Hz), 7.44 (t, 2H, J 7.6 Hz), 7.36 (t, 1H, J 7.8 Hz), 7.25 (m, 2H), 6.97 (m, 2H). ^{13}C NMR (DMSO-d_6) δ 153.4, 140.6, 135.2, 128.8, 128.6, 126.4, 119.9, 113.4, 109.4. Anal. Calcd for $C_{14}H_{12}N_4$ (236.3): C, 71.17; H, 5.12; N, 23.71. Found: C, 71.01; H, 5.21; N, 23.73.

4.2.2. N-1H-Benzimidazol-2-yl-N′-p-methoxybenzylidenehydrazine ***1b***. Yield (2.0 g, 75%) as a colorless solid from DMF, mp 210–212 °C (lit.[22b] mp 212 °C). IR: 3395, 3061, 2981, 1656, 1609, 1510, 1460, 1247, 1168, 1163, 1106, 1027, 733. LCMS: m/z=267 (M+1). MS: m/z=266 (M^+, 75%), 133 (100%). ^{1}H NMR (DMSO-d_6) δ 11.45 (br, 2H, 2NH), 7.99 (s, 1H), 7.75 (d, 2H, J 8.8 Hz), 7.24 (m, 2H), 7.00 (d, 2H, J 8.8 Hz), 6.97 (m, 2H), 3.81 (s, 3H, OCH_3). ^{13}C NMR (DMSO-d_6) δ 160.0, 153.4, 140.7, 136.4, 127.9, 127.7, 119.6, 114.1, 112.4, 55.2. Anal. Calcd for $C_{15}H_{14}N_4O$ (266.3): C, 67.65; H, 5.30; N, 21.04. Found: C, 67.59; H, 5.21; N, 21.03.

4.2.3. N-1H-Benzimidazol-2-yl-N′-p-methylbenzylidenehydrazine ***1c***. Yield (2.0 g, 80%) as a colorless solid from DMF mp 275–276 °C (lit.[22b] mp 277 °C). IR: 3445, 3060, 2916, 1654, 1586, 1517, 1460, 1267, 1129, 1034, 809, 737. LCMS: m/z=251 (M+1). MS: m/z=250 (M^+, 85%), 221 (20%), 133 (100%). ^{1}H NMR (DMSO-d_6) δ 11.52 (br, 1H, NH), 11.42 (br, 1H, NH), 8.0 (s, 1H), 7.70 (d, 2H, J 7.6 Hz), 7.24 (m, 4H), 6.96 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 153.5, 140.7, 138.4, 132.4, 129.2, 126.4, 119.3, 114.9, 109.4, 21.0. Anal. Calcd for $C_{15}H_{14}N_4$ (250.3): C, 71.98; H, 5.64; N, 22.38. Found: C, 71.91; H, 5.52; N, 22.30.

4.2.4. N-1H-Benzimidazol-2-yl-N′-p-chlorobenzylidenehydrazine ***1d***. Yield (2.3 g, 85%) as colorless crystals from DMF, mp 267–69 °C. (lit.[22b] 270 °C). IR: 3432, 3053, 1651, 1585, 1516, 1491, 1268, 1087, 1013, 826, 738. LCMS: m/z=273 (M+2), 271 (M+1). MS: m/z=270 (M^+, 100%), 241 (10%), 133 (100%). ^{1}H NMR (DMSO-d_6) δ 11.65 (br, 2H, 2NH), 8.03 (s, 1H), 7.85 (d, 2H, J 8.4 Hz), 7.50 (d, 2H, J 8.4 Hz), 7.27 (m, 2H), 7.00 (m, 2H). ^{13}C NMR (DMSO-d_6) δ 153.0, 140.0, 137.2, 134.1, 133.2, 128.7, 128.1, 120.3, 112.2. Anal. Calcd for $C_{14}H_{11}ClN_4$ (270.7): C, 62.11; H, 4.10; N, 20.70. Found: C, 62.09; H, 4.21; N, 20.63.

4.2.5. N-1H-Benzimidazol-2-yl-N′-p-nitrobenzylidenehydrazine ***1e***. Yield (2.5 g, 89%) as red crystals from DMF, mp 280–82 °C. (lit.[22b] 283 °C). IR: 3417, 3060, 1641, 1586, 1508, 1333, 1267, 1149, 1107, 826, 738. MS: m/z=281 (M^+, 100%), 252 (10%), 133 (70%). ^{1}H NMR (DMSO-d_6) δ 11.79 (br, 2H, 2NH), 8.26 (d, 2H, J 8.8 Hz), 8.13 (s, 1H), 8.06 (d, 2H, J 8.8 Hz), 7.25 (m, 2H), 7.01 (m, 2H). ^{13}C NMR (DMSO-d_6) δ 153.8, 146.6, 142.1, 138.7, 132.9, 120.9, 119.9, 114.4, 109.5. Anal. Calcd for $C_{14}H_{11}N_5O_2$ (281.3): C, 59.78; H, 3.94; N, 24.90. Found: C, 59.69; H, 3.91; N, 24.83.

4.2.6. N-Benzylidene-N′-1-methylbenzimidazol-2-yl-hydrazine ***16***. General procedure: A mixture of 1-methylbenzimidazole-2-yl-hydrazine[23] (1.62 g, 10 mmol), benzaldehyde (1.27 g, 12.0 mmol), and sodium acetate (1.2 g, 15 mmol) in glacial acetic acid (20.0 mL) was heated under reflux for 2 h. After cooling, ice water (50 mL) was added to the reaction mixture; the precipitate so formed was collected by filtration and crystallized from DMF to give **16** (2.1 g, 75%) as a colorless solid, mp 283–85 °C (lit.[24] mp 280–282 °C). IR: 3428, 3055, 1660, 1560, 1488, 1381, 1239, 1116, 1089, 953, 743. LCMS: m/z=251 (M+1). MS: m/z=250 (M^+, 100%), 1147 (30%). ^{1}H NMR (DMSO-d_6) δ 12.08 (br, 1H, NH), 8.33 (s, 1H), 7.89 (dd, 2H, J 8.4, 1.2 Hz), 7.49–7.40 (m, 4H), 7.32 (m, 1H), 7.20 (m, 2H), 3.60 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ 151.8, 147.7, 134.8, 132.2, 130.2, 129.5, 128.6, 127.1, 122.4, 122.1, 110.4, 109.0, 28.9. Anal. Calcd for $C_{15}H_{14}N_4$ (250.3): C, 71.98; H, 5.64; N, 22.38. Found: C, 71.79; H, 5.51; N, 22.23.

4.3. Pyrolysis product

4.3.1. Flash vacuum pyrolysis of ***1a–e***. The apparatus used was similar to the one, which has been described in our recent

publications.[25a–c] The substrate was volatilized from a tube in a Büchi Kugelrohr oven through a 30×2.5 cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A to a temperature of 700 °C, the temperature being monitored by a Pt/Pt-13%Rh thermocouple situated at the center of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 010^{-2} Torr by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the cold trap and pump. Under these conditions the contact time in the hot zone was estimated to be ca. 10 ms. The different fractions of the product collected in the U-shaped trap were analyzed by ^{1}H, ^{13}C NMR spectroscopy, IR, and GC–MS. Relative and percent yields were determined from NMR.[25c]

4.3.2. Static pyrolysis of ***1a***, ***16***. A sample of the substrate (1 mmol), was introduced in the reaction tube (1.5×12 cm Pyrex), cooled in liquid nitrogen, sealed under vacuum (0.045 Torr) and placed in the pyrolyzer for 15 min at 280 °C, a temperature that is required for complete pyrolysis of the substrate as indicated by preliminary HPLC studies. The reaction products were separated by column chromatography using Merck Al-silica gel 60 F_{254} with ethyl acetate/petroleum ether (60–80) to give successively **2**, **3**, **4**, **5**, and **6** from substrate **1a** and give **17**, **18** from **16**. The static sealed-tube (STP) pyrolysis was conducted in a custom-made Chemical Data System (CDS) pyrolyser consisting of an aluminum block with a groove to accommodate the Pyrex sealed-tube reactor, and fitted with a platinum-resistance thermometer and thermocouple connected to a Comark microprocessor thermometer. The block temperature was controlled by a Eurothem 093 precision temperature regulator. Aluminum was chosen for its low temperature gradient and resistance to elevated temperatures. Maximum pyrolysis for product analysis was conducted at temperatures equal to or exceeding those recorded for complete pyrolysis during kinetic runs.

4.3.3. Benzonitrile ***2a***. LCMS: m/z=104 (M+1). ^{1}H NMR spectroscopic data identical to that reported in the literature.[26a]

4.3.4. p-Methoxybenzonitrile ***2b***. LCMS: m/z=134 (M+1). ^{1}H NMR spectroscopic data identical to that reported in the literature.[26b]

4.3.5. p-Tolunitrile ***2c***. LCMS: m/z=118 (M+1). ^{1}H NMR spectroscopic data identical to that reported in the literature.[27]

4.3.6. p-Chlorobenzonitrile ***2d***. LCMS: m/z=139, 138 (M+2, M+1). ^{1}H NMR spectroscopic data identical to that reported in the literature.[26c]

4.3.7. p-Nitrobenzonitrile ***2e***. LCMS: m/z=149 (M^+1). ^{1}H NMR spectroscopic data identical to that reported in the literature.[26d]

4.3.8. 2-Aminobenzimidazole ***3***. Colourless crystals from ethanol, yield static (48 mg, 20%), FVP (65–85%, Table 1), mp 222–24 °C (lit.[28] mp 225 °C). IR: 3431, 1651, 1567, 1463, 1049, 1025, 1002, 826, 764. LCMS m/z=134 (M+1). MS: m/z=133 (M^+, 100%), 105 (30%). ^{1}H NMR (DMSO-d_6) δ 7.10 (m, 2H), 6.88 (m, 2H), 6.11 (br, 3H, NH, NH_2). ^{13}C NMR (DMSO-d_6) δ 155.1, 136.4, 119.2, 111.5. Anal. Calcd for $C_7H_7N_3$ (133.2): C, 63.14; H, 5.30; N, 31.56. Found: C, 63.09; H, 5.21; N, 31.43.

4.3.9. 2,4,5-Triphenylimidazole ***4***. Yield (50 mg, 21%), white crystals from ethyl acetate, mp 274–276 °C (lit.[19] mp 274–75). LCMS: m/z=297 (M+1). MS: m/z=296 (M^+, 100%), 190 (10%), 165 (85%). IR: 3395, 3061, 2928, 1756, 1639, 1503, 1435, 1240, 1148, 1034, 736. ^{1}H NMR (DMSO-d_6) δ 12.68 (br, 1H, NH), 8.08 (dd, 2H, J 8.4, 1.2 Hz), 7.55 (dd, 2H, J 8.4, 1.6 Hz), 7.50 (dt, 2H, J 7.4, 1.2 Hz), 7.45 (d, 2H, J 7.8 Hz), 7.43 (d, 2H, J 7.8 Hz), 7.38 (dt, 2H, J 7.8, 1.2 Hz), 7.30 (t, 2H, J 7.8 Hz), 7.22 (t, 1H, J 7.2 Hz). ^{13}C NMR (DMSO-d_6) δ 145.9, 137.5, 135.6, 131.5, 130.8, 129.2, 129.1, 128.9, 128.73, 128.71, 128.6, 128.3, 127.5, 126.9, 125.6. Anal. Calcd for $C_{21}H_{16}N_2$ (296.4): C, 85.11; H, 5.44; N, 9.45. Found: C, 85.09; H, 5.31; N, 9.45.

4.3.10. 1,3-Diphenyl-8H-2,3a,8-triazacyclopenta[a]indene ***5***. Yield (36 mg, 15%), white crystals from ethyl acetate, mp 310–312 °C. LCMS: m/z=310 (M+1). MS: m/z=309 (M^+, 100%), 281 (10%), 165 (20%). IR: 3395, 3061, 1656, 1609, 1510, 1460, 1247, 1168, 1027, 733. ^{1}H NMR ($CDCl_3$) δ 7.72 (dd, 2H, J 7.4, 1.2 Hz), 7.68 (dd, 2H, J 7.6, 1.6 Hz), 7.54 (tt, 2H, J 7.2, 1.2 Hz), 7.49 (tt, 1H, J 7.6, 1.5 Hz), 7.43 (dd, 1H, J 7.2, 0.8 Hz), 7.36 (t, 2H, J 7.8 Hz), 7.30 (tt, 1H, J 7.2, 1.2 Hz), 7.28 (tt, 1H, J 7.2, 1.2 Hz), 7.25 (dd, 1H, J 7.2, 1.2 Hz), 7.04 (dt, 1H, J 7.2, 1.2 Hz), 3.31 (br, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 149.8, 137.8, 136.5, 134.8, 130.6, 130.4, 129.0, 128.39, 128.36, 127.5, 127.0, 125.6, 123.4, 119.6, 118.2, 112.5, 111.6. Anal. Calcd for $C_{21}H_{15}N_3$ (309.4): C, 81.53; H, 4.89; N, 13.58. Found: C, 81.49; H, 4.81; N, 13.45. HRMS=309.1261 ($C_{21}H_{15}N_3$ requires 309.1260).

*4.3.11. 5,11-diphenyl-6H,12H-dibenzimidazo[1,2-a];1',2'-d]pyrazine (****6****); 5,11-diphenyl-5H,11H-dibenzimidazo[1,2-a;1',2'-d]pyrazine (****7****).* Yield (43 mg, 18%), white crystals from ethyl acetate, mp 301–303 °C (lit.[29a,b] mp 301 °C). LCMS: m/z=413 (M+1). MS: m/z=412 (M^+, 100%), 308 (10%), 205 (20%). IR: 3059, 3032, 2955, 2928, 2857, 1725, 1584, 1540, 1341, 1370, 1272, 1124, 1070, 916, 739. ^{1}H NMR (DMSO-d_6) δ 13.21 (br, 2H, 2NH), 7.84 (m, 2H), 7.69 (m, 2H), 7.55–7.24 (m, 14H). ^{13}C NMR (DMSO-d_6) δ 152, 142.2, 136.9, 130.1, 128.6, 128.2, 123.9, 123.4, 119.5, 111.1. Anal. Calcd for $C_{28}H_{20}N_4$ (412.5): C, 81.53; H, 4.89; N, 13.58. Found: C, 81.50; H, 5.00; N, 13.50. HRMS=412.1682 ($C_{28}H_{20}N_4$ requires 412.1682).

4.3.12. 3-Phenyl-9H-benzo[4,5]imidazo[2,1-c][1,2,4]triazole ***17***. Colourless crystals from ethanol/water, yield (120 mg, 48%), mp 267–268 °C (lit.[22b] mp 270 °C). LCMS m/z=235 (M+1). MS: m/z=234 (M^+, 100%), 205 (10%), 104 (25%). ^{1}H NMR (DMSO-d_6) δ 7.95 (dd, 2H, J 7.8, 1.6 Hz), 7.71 (d, 1H, J 8.0 Hz), 7.68 (t, 2H J 7.6 Hz), 7.61 (t, 1H, J 7.8), 7.51 (d, 1H, J 8.0 Hz), 7.42 (dt, 1H, J 8.0, 1.2 Hz), 7.21 (dt, 1H, J 8.0, 1.2 Hz), 3.4 (br, 1H, NH). ^{13}C N MR (DMSO-d_6) δ 155.8, 142.7, 130.1, 129.3, 127.4, 127.0, 125.4, 122.9, 120.3, 113.4, 112.6, 112.4. Anal. Calcd for $C_{14}H_{10}N_4$ (234.3): C, 71.78; H, 4.30; N, 23.92. Found: C, 71.69; H, 4.21; N, 23.93.

4.3.13. 9-Methyl-3-phenyl-9H-benzo[4,5]imidazo[2,1-c][1,2,4]triazole ***18***. Colourless crystals from ethanol, yield (96 mg, 38%), mp 202–204 °C. IR: 3060, 2930, 1705, 1599, 1492, 1447, 1170, 1112, 914. LCMS: m/z=249 (M+1). MS: m/z=248 (M^+, 100%), 105 (30%). ^{1}H NMR ($CDCl_3$) δ 7.98 (dd, 2H, J 8.0, 1.6 Hz), 7.86 (d, 1H, J 8.4 Hz), 7.68 (t, 3H, J 7.4 Hz), 7.56 (t, 1H, J 8.0 Hz), 7.41 (m, 2H), 3.73 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 157.1, 144.9, 138.9, 133.2, 129.9, 129.1, 128.4, 127.6, 125.6, 120.6, 112.8, 109.9, 53.4. Anal. Calcd for $C_{15}H_{12}N_4$ (248.3): C, 72.56; H, 4.87; N, 22.57. Found: C, 72.49; H, 4.81, N, 22.56. HRMS=248.1056 ($C_{15}H_{12}N_4$ requires 248.1056).

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