Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 9455–9464

TETRAHEDRON

Gas-phase thermolysis of benzotriazole derivatives. Part 2: Synthesis of benzimidazo[1,2-*b*]cinnolines, a novel heterocyclic ring system, by pyrolysis of benzotriazole derivatives. Kinetic and mechanistic study

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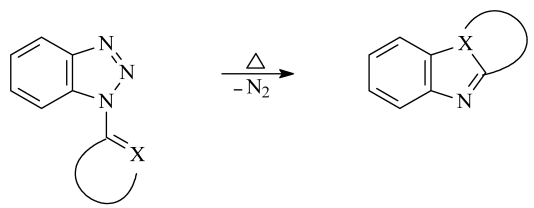
Received 7 April 2003; revised 11 August 2003; accepted 4 September 2003

Abstract—Gas-phase pyrolysis of benzotriazolyl ketones and their arylhydrazones gave indole, benzimidazole and benzimidazo[1,2-*b*]-cinnoline derivatives via interesting novel routes. The homogeneous first-order gas-phase pyrolysis of 10 arylhydrazono derivatives of α-benzotriazol-1-yl ketones was investigated over the temperature range 420–530 K. Five of these substrates were 2-(arylhydrazono)-2-(benzotriazol-1-yl)-1-phenylethanone derivatives (Series 1), and the remaining five were the corresponding acetone analogues (Series 2). The values of the Arrhenius frequency factor (log A/s^{-1}) for the pyrolysis of the compounds of Series 1 and 2 were, respectively, 12.27±1.44 and 9.07±1.20, while the values of the Arrhenius activation energy (E_a/kJ mol^{-1}) were 132.8±8.4 and 123.2±23.0, respectively. Besides, reaction pathways are offered to rationalize the kinetic results and to account for the products of pyrolysis of the substrates under study, namely: (i) extrusion of N_2 and formation of a 1,3-biradical reactive intermediate leading to substituted imidazoles (Series 1); (ii) intramolecular nucleophilic addition, cyclization and subsequent fragmentation with or without loss of H_2O/N_2 fragments (Series 1 and 2).

1. Introduction

Many derivatives of benzotriazole (BT) have been shown to undergo pyrolytic transformation mainly through initial loss of N_2 and subsequent intramolecular cyclization leading to facile clean synthesis of a wide range of heterocyclic compounds.[1,2] Thus, substituted benzotriazoles of the general formula **A** were reported to pyrolyse into the corresponding condensed heterocyclic system **B**.



A **B**

In this way, several derivatives of indole,[1,3] carbazole,[4] isomeric pyridoindoles,[4d,5] pyrido[1,2-*a*]benzimidazoles,[5] benzimidazo[1,2-*a*]pyrimidines,[6] benzimidazo[1,2-*b*]pyridazines,[6] benzimidazo[2,1-*a*]isoquinolines,[7] benzimidazo-[2,1-*b*]benzothiazoles,[8] phenanthridines,[9] benzoxazoles,[7,10] and quinolines[11] as well as other heterocyclic systems became readily available.

In the present work, we wish to report further synthetic application and novel pyrolytic products of benzotriazole derivatives, and to complement our earlier kinetic and mechanistic study on the gas-phase thermolysis of α-benzotriazol-1-yl ketones,[1] by providing data related to the effect of the arylhydrazono substituent on reactivity, and its influence on the course of the thermal gas-phase elimination reaction of these ketones. The 10 arylhydrazono α-benzotriazol-1-yl ketones under consideration (Scheme 1) include five 2-arylhydrazono-1-phenylethanone derivatives (Series **1a–e**) and five acetone analogues (Series **2f–j**).

2. Results and discussion

2.1. Synthesis

Compounds **1a–e** and **2f–j** were prepared by coupling 1-(benzotriazol-1-yl)-acetophenone and 1-(benzotriazol-1-yl)-acetone with the appropriate aryldiazonium chloride in basic ethanolic media. Good yields (≥55%) of **1a–e**, **2i** and

Keywords: benzotriazole ketones; arylhydrazono group; pyrolysis; kinetics; mechanism.
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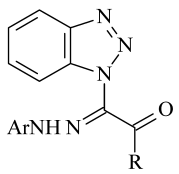
doi:10.1016/j.tet.2003.09.009

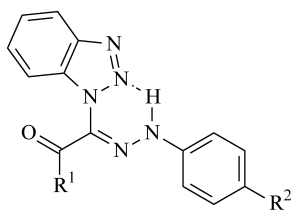


	Ar	R
1a	C_6H_5	C_6H_5
1b	*p*-$CH_3OC_6H_4$	C_6H_5
1c	*p*-$CH_3C_6H_4$	C_6H_5
1d	*p*-ClC_6H_4	C_6H_5
1e	*p*-$NO_2C_6H_4$	C_6H_5
2f	C_6H_5	CH_3
2g	*p*-$CH_3OC_6H_4$	CH_3
2h	*p*-$CH_3C_6H_4$	CH_3
2i	*p*-ClC_6H_4	CH_3
2j	*p*-$NO_2C_6H_4$	CH_3

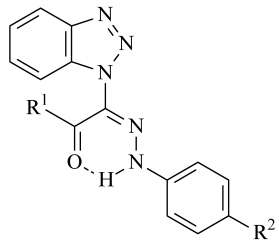
Scheme 1. 2-Arylhydrazone-2-(benzotriazol-1-yl)-1-phenylethanone (**1a–e**) and their acetone analogues (**2f–j**).

2j were obtained using ethanolic sodium hydroxide solution. Synthesis of **2f–h** and **2j** was achieved using sodium acetate in lieu of NaOH. Attempts to prepare **2f–h** using ethanolic sodium hydroxide gave a mixture of products, from which (in the case of **2h**) the formazan **3c** was isolated in pure form. Formazan (**3c**), prepared for the first time in the present work, was identified by its MS: $M^{+\cdot}$ at m/z=369, ^{1}H NMR ($CDCl_3$): signals at δ=2.43 (s, 6H, $2CH_3$), 7.29 (d, J=7.1 Hz, 4H, ArH), 7.47 (t, J=7.5 Hz, 1H, ArH), 7.60 (m, 5H, ArH), 7.91 (d, J=8.4 Hz, 1H, ArH), 8.19 (d, J=8.3 Hz, 1H, ArH), 14.80 (br s, 1H, NH); and ^{13}C NMR ($CDCl_3$): signals at δ=21.77, 112.26, 119.44, 120.33, 124.69, 128.61, 130.64, 133.03, 136.83, 139.37, 145.34, 146.13. The presence of 12 carbon signals in the ^{13}C NMR indicates the existence of **3c** in an equilibrium state of the strongly H-bonded structures **I** and **II** whereby the two aryl groups appear equivalent in the NMR spectrum. It appears that in the case of these compounds (**2f–h**), the presence of strong base led to further azo-coupling of the Japp–Klingemann type in which the acetyl group is replaced by the *p*-substituted arylhydrazone.[12,13]

NMR spectra of the substrates **1a–e** and **2f–j** in $CDCl_3$ show dynamic flux over time until a *syn*/*anti* isomeric equilibrium is reached. At equilibrium the ratio of the two isomers in the NMR spectra vary from one substrate to another. For example, the equilibrium ratio (*syn*/*anti*) is 5:1 and 5:2 in the case of **1b** and **2g**, respectively. These results could be explained on the basis of an equilibrium being established between the *syn* and *anti* isomers under the influence of the solvent ($CDCl_3$), and the relative strength of the hydrogen bonds between the NH group and the nitrogen of benzotriazole for the *syn* isomer, and the bond between the hydrogen of the NH group and the carbonyl oxygen for the *anti* isomer. ^{13}C NMR spectra show a larger downfield shift of the carbonyl signal in the case of *anti* than for *syn*.



Syn

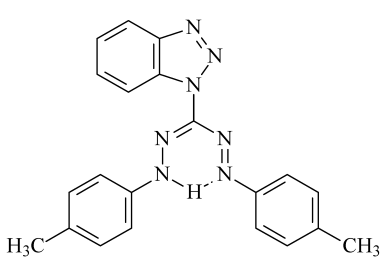


Anti

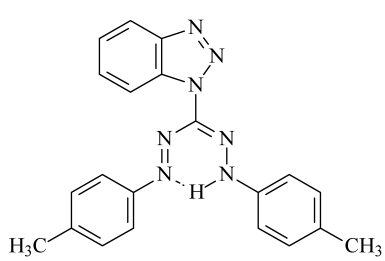
2.2. Pyrolysates and mechanism of pyrolytic reactions

Reaction products from complete gas-phase pyrolysis of substrates **1a–e** (Scheme 2) and **2f–j** (Scheme 3) were obtained at optimal reactor conditions of temperature, pressure (0.06 mbar) and substrate residence time compatible with >98% reaction established for kinetic runs. The pyrolysates were carefully analyzed and their constituents fully characterized using preparative thin layer chromatography (PLC), GC/MS/MS, ^{1}H and ^{13}C NMR techniques.

The pyrolysates from the gas-phase elimination reaction of the arylhydrazonophenylethanone α-benzotriazol-1-yl ketones **1a–e** included products whose MS showed $M^{\cdot+}$ peaks corresponding to a lost fragment of 28 mass units indicating extrusion of molecular nitrogen from the ketone substrates. Based on MS, ^{1}H and ^{13}C NMR analyses, these products were identified as the (1-anilino-1*H*-benzimidazol-2-yl)phenylmethanone compounds **4a–e** (Scheme 2). The pyrolysates also contained 2-benzoylbenzimidazole (**5**),[14] aniline and *p*-substituted anilines (**6a–e**).[15] Typically, spectral characterization of compound **4d** (Scheme 2) showed ^{1}H NMR signals at δ=6.52 (d, J=8.7 Hz, 2H, H^{10}), 7.14 (d, J=8.7 Hz, 2H, H^{11}), 7.47 (t, J=7.9 Hz, 1H, H^5), 7.51–7.54 (m, 3H, $H^{6,15}$), 7.61 (d, J=7.9 Hz, 1H, H^7), 7.66 (t, J=7.4 Hz, 1H, H^{16}), 8.00 (d, J=8.1 Hz, 1H, H^4), 8.11 (br s, 1H, NH), 8.37 (d, J=8.1 Hz, 2H, H^{14}); NOE difference spectra by irradiation at δ=8.11 showed enhancement at δ=6.52 corresponding to H^{10}. From H,H-COSY experiment, H^{11} was readily assigned by examining the cross-peak with H^{10}. ^{1}H NMR of the sample, after adding D_2O, indicated disappearance of the NH peak

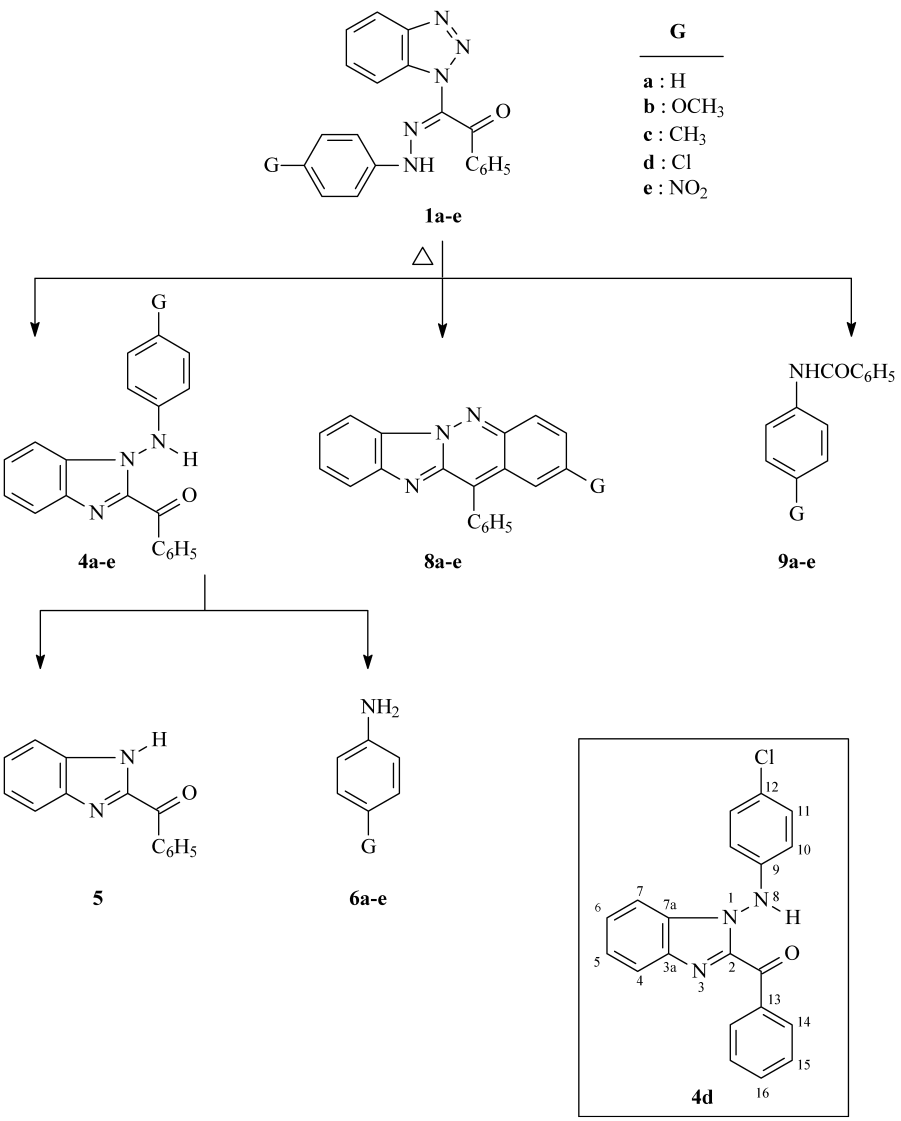


I

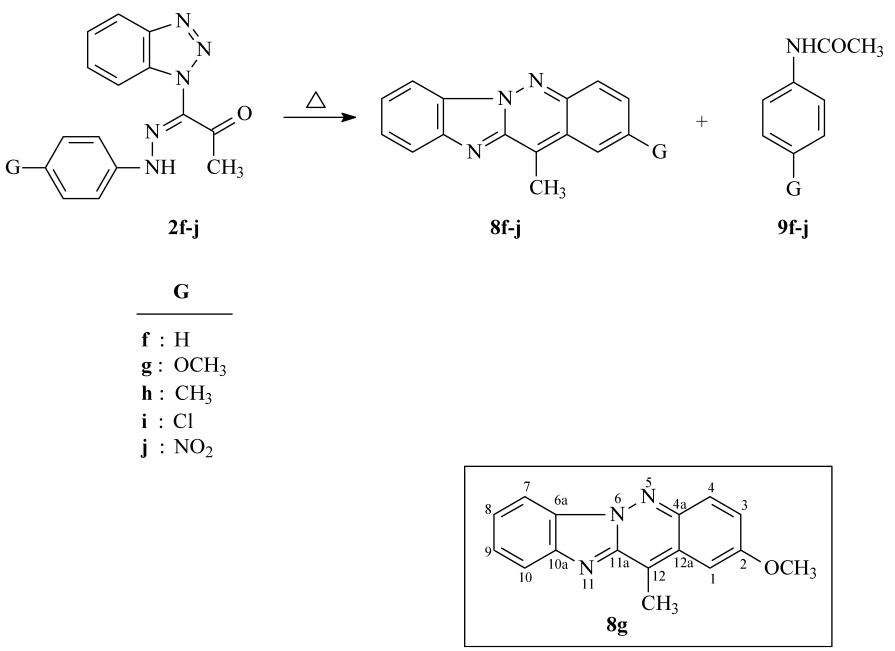


II

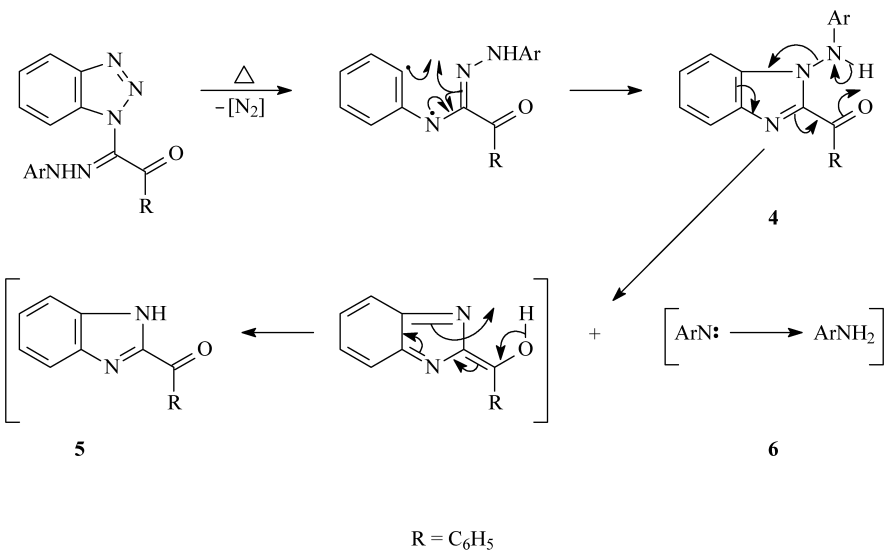
(3c)



Scheme 2. Gas-phase pyrolysis (0.06 mbar) of 2-arylhydrazono-2-(benzotriazol-1-yl)-1-phenylethanone (**1a**–**e**).



Scheme 3. Gas-phase pyrolysis (0.06 mbar) of 2-arylhydrazono-1-(benzotriazol-1-yl)-propan-2-one (**2f**–**j**).

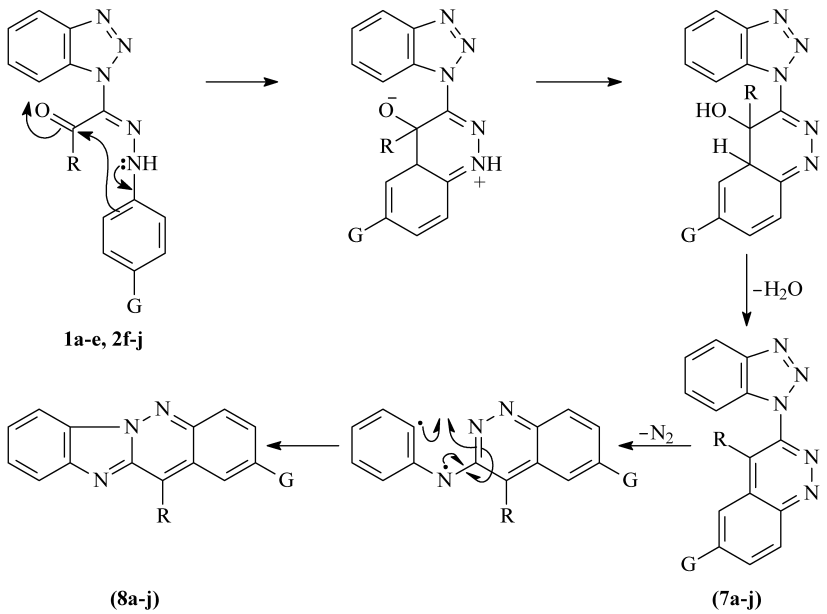


Scheme 4. Pyrolytic reaction pathway involving 1,3-biradical reactive intermediate.

confirming the presence of the exchangeable NH proton. From ^{13}C, HMBC and HMQC experiments, the different carbon signals of **4d** were assigned at δ=111.24 (C^7), 115.53 (C^{10}), 122.79 (C^4), 124.94 (C^5), 127.51 (C^6), 127.85 (C^{12}), 128.92 (C^{15}), 129.85 (C^{11}), 131.58 (C^{14}), 134.51 (C^{16}), 135.67 (C^{7a}), 135.97 (C^{13}), 139.53 (C^{3a}), 144.84 (C^2), 146.18 (C^9), 185.95 (C=O). MS spectrometry of **4d** gave [$M^{\cdot+}$] at *m*/*z*=347/349 (35/15%), base peak at 105, and major fragment ions at 77 and 91.

A plausible mechanism is outlined in Scheme 4 to account for the presence of compounds **4a–e**, **5** and **6a–e** among the products of pyrolysis of substrates **1a–e**. It includes extrusion of a stable N_2 molecule, formation of a 1,3-biradical reactive intermediate and subsequent cyclization and fragmentation processes. Besides, and to confirm **4a–e** as the likely precursors of **5** and **6a–e** (Schemes 2 and 4), the former set of compounds (**4a–e**) were isolated from their pyrolysates and then subjected to further pyrolysis. In each case, **5** and the corresponding substituted aniline (**6**) constituted the products of reaction. It is instructive to note that a similar 1,3-biradical pathway has also been postulated for the thermal gas-phase elimination reaction of the parent α-benzotriazol-1-yl ketones without an arylhydrazono substituent,[1] and a range of other BT compounds.[16] The noteworthy observation in the present mechanistic investigation is that no reaction products corresponding to **4f–j**, **5** or **6f–j** (Schemes 2 and 4, R=CH_3) were detected in the pyrolysates of the arylhydrazone α-benzotriazol-1-yl ketones **2f–j**. In this case a complete departure from the 1,3-biradical pathway has occurred.

Further, the pyrolysates from the thermolysis of the



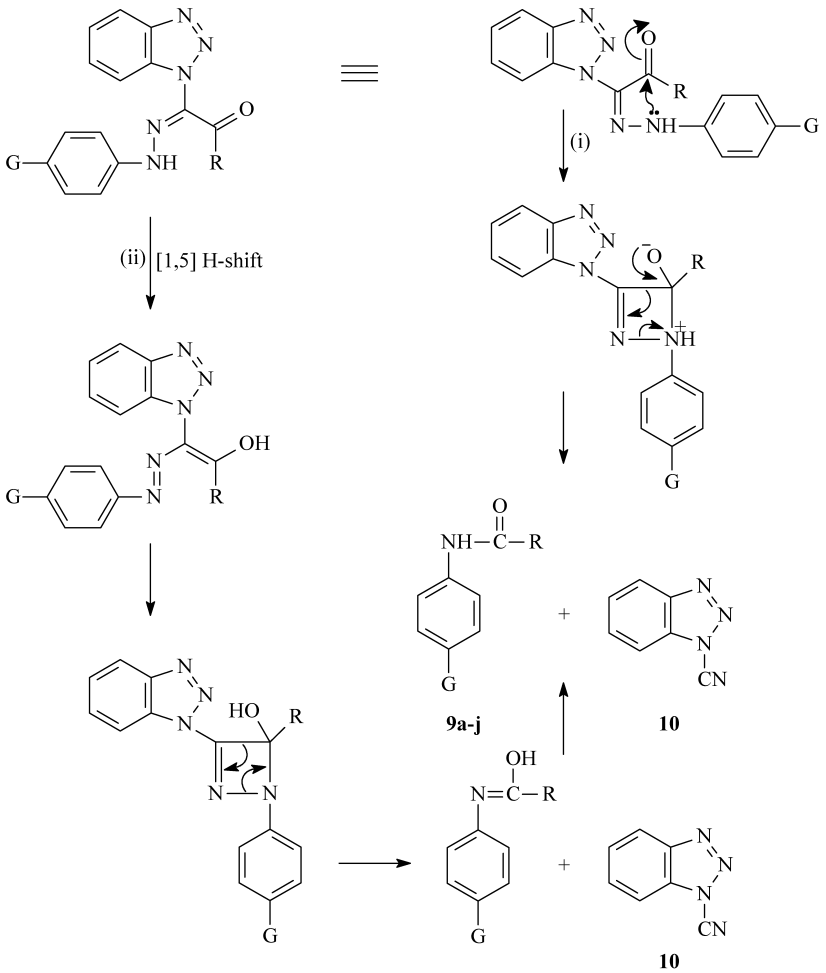
Scheme 5. Mechanism of cinnoline (**8a–j**) formation.

substrates of both series **1a–e** and **2f–j** contained reaction products that gave MS spectra indicating loss of 46 mass units attributed to loss of H_2O and N_2. These products were established to be the phenyl- and methyl-4*b*,5,11-triazabenzo[*b*]fluorene (i.e. benzimidazo[1,2-*b*]cinnoline) **8a–j** derivatives (Scheme 5). The structure of this novel ring system was confirmed by full proton and carbon signal assignment of compound **8g** (Scheme 3) as a representative example, based on ^{1}H NMR, ^{13}C NMR, NOE-difference spectra, the 2-D H,H-COSY, HMQC and HMBC of **8g**. Thus, NOE difference spectra (by irradiation at the CH_3 signal at δ=3.06) showed enhancement at δ=7.94 corresponding to H^1. From coupling constants in the ^{1}H NMR spectra and the cross-peaks in the H,H-COSY experiment, all the protons were assigned at δ=3.06 (s, 3H, CH_3), 4.07 (s, 3H, OCH_3), 7.19 (dd, ^4J=2.5 Hz, ^3J=8.9 Hz, 1H, H^3), 7.61–7.68 (m, 2H, H$^{8 \text{ and } 9}$), 7.94 (d, J=2.5 Hz, 1H, H^1), 8.05 (d, J=8.9 Hz, 1H, H^4), 8.17 (d, J=7.2 Hz, 1H, H^7), 8.38 (d, J=7.2 Hz, 1H, H^{10}). From ^{13}C NMR, HMBC and HMQC experiments the different carbon signals of **8g** were assigned at δ=21.89 (CH_3), 56.37 (OCH_3), 99.89 (C^1), 112.64 (C^3), 114.54 (C^7), 122.28 (C^{10}), 124.84 (C^9), 125.86 (C^8), 130.38 (C^{4a}), 130.76 (C^{6a}), 131.65 (C^4), 142.08 (C^{11a}), 144.48 (C^{10a}), 151.73 (C^{12a}), 160.30 (C^{2,12}). MS analysis gave [M$^{\cdot+}$] at m/z=263.

It is to be noted that the yields of the cinnoline compounds from **1a–e** were noticeably lower than those from **2f–j**, probably due to competition from the 1,3-biradical pathway which operates only for the substrates of series **1a–e**.

The formation of the cinnolines (**8a–j**) during the pyrolysis of the substrates of both series **1a–e** and **2f–j** follows the mechanism proposed in Scheme 5. In this mechanism, intramolecular nucleophilic addition involving the arylhydrazono group and the ketone carbonyl moiety is followed by cyclization and subsequent fragmentation in which (H_2O) and (N_2) molecular species are lost, in that order. Initial threshold loss of (N_2) was ruled out, since, as noted earlier, no reaction products indicative of a 1,3-biradical mechanism were observed in the case of the compounds of series **2f–j**. It was, however, not possible to isolate the intermediates **7a–j** suggested in the present mechanism. The tendency of the arylhydrazono (ArNHN=) group to cause a switch in the mechanism of thermal gas-phase elimination reactions has been reported for the gas-phase thermolysis of derivatives and analogues of 3-arylhydrazono-pentan-2,4-diones.[17,18]

Further, analysis of the pyrolysates from **1a–e** and **2f–j** has established the formation of the anilide and *p*-substituted



R = C_6H_5, CH_3; G = H, CH_3, CH_3O, Cl, NO_2

Scheme 6. Mechanism of anilide (**9a–j**) formation.

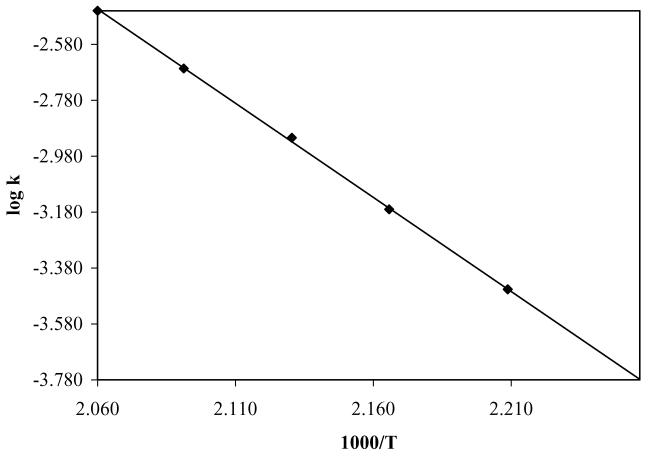


Figure 1. Arrhenius plot for pyrolysis of 2-(benzotriazol-1-yl)-1-phenyl-2-(phenyl-hydrazono)ethanone (**1a**).

anilides **9a–j** (Scheme 6). MS spectrometric and spectrophotometric characterization of these products is in agreement with literature data.[19–23] The mechanism offered to account for the formation of the anilides is presented in Scheme 6, and is in accord with feasible mechanisms reported for the pyrolysis of α-acylhydrazones.[24,25] The proposed reaction pathway proceeds either through a polar intermediate (route i), or through a thermally-allowed 1,5-H shift followed by electrocyclization (route ii). Route (i) involves intramolecular nucleophilic addition between the arylhydrazono group and the ketone carbonyl function. Both routes suggest the formation of 1-cyanobenzotriazole (**10**), which could not, however, be detected in the product of reaction. As a result, 1-cyanobenzotriazole (**10**) was prepared following literature procedures[26] and subjected to both kinetic and preparative pyrolytic investigation.[1] 1-Cyanobenzotriazole was found to pyrolyse faster than any of the substrates under study to give charred and as yet non-identifiable products. However, kinetic observations serve to explain the secondary decomposition of 1-cyanobenzotriazole under the conditions of pyrolysis of compounds **1a–e**, **2f–j**.

Table 1. Rate coefficients (k/s^{-1}) and Arrhenius parameters at 500 K of substrates **1a–e**

Substrate	T/K	10^4k/s^{-1}	log A/s^{-1}	E_a/kJ mol^{-1}	$10^4k_{500\ K}$/s^{-1}
1a	443.15	1.660	11.49±0.13	139.5±1.13	90.68
	452.75	3.501			
	461.75	6.769			
	469.40	12.20			
	478.20	21.56			
	485.45	34.70			
1b	419.75	1.351	13.71±0.43	141.2±3.64	915.4
	428.35	3.352			
	438.15	7.367			
	447.85	16.32			
	457.65	41.52			
1c	433.35	1.062	12.23±0.18	134.4±1.72	153.9
	443.25	2.400			
	453.05	5.636			
	463.15	11.54			
	472.85	23.94			
1d	424.95	0.414	12.12±0.09	134.4±0.753	121.1
	434.55	0.918			
	445.95	2.330			
	455.35	5.066			
	463.75	9.795			
	473.45	19.62			
	483.55	40.92			
1e	438.45	1.046	10.83±0.42	124.4±3.64	68.75
	448.05	2.391			
	459.45	4.266			
	470.05	8.999			
	481.25	22.50			
	492.25	46.28			

Table 2. Rate coefficients (k/s^{-1}) and Arrhenius parameters at 500 K of substrates **2f–j**

Substrate	T/K	10^4k/s^{-1}	log A /s^{-1}	E_a/kJ mol^{-1}	$10^4k_{500\ K}$/s^{-1}
2f	486.45	1.483	11.87±0.15	146.2±1.55	3.947
	495.35	2.926			
	504.15	5.093			
	513.25	9.632			
	522.15	17.68			
	530.85	30.83			
2g	444.60	1.176	7.842±0.14	100.2±1.21	23.84
	457.25	2.516			
	470.65	5.291			
	484.15	11.25			
	497.55	20.58			
2h	470.75	1.670	8.110±0.33	107.3±3.10	7.958
	481.85	2.833			
	494.50	6.229			
	506.95	10.79			
	518.25	20.52			
2i	464.35	1.053	9.351±0.09	118.5±0.962	9.307
	475.25	2.112			
	499.15	8.686			
	510.65	16.60			
	522.75	33.03			
2j	450.35	1.687	8.203±0.04	103.3±0.377	26.07
	462.15	3.422			
	473.55	6.445			
	486.05	12.87			
	497.70	23.21			

2.3. Kinetic analysis

Pyrolysis of the present substrates (**1a–e**, **2f–j**) is a homogeneous, first-order gas-phase elimination reaction free of reactor surface effects. The temperature range over which the substrates were studied was 420–530 K. The internal standard used in the chromatographic analysis of the kinetic runs was either chlorobenzene for (**1c**, **2i**), 1,3-dichlorobenzene for (**1d**, **2g**, **2h**), or 1,2,4-trichlorobenzene for the remaining five substrates. The solvent used was acetonitrile which was also used in aqueous solution as eluent for HPLC analysis, and the wavelength used for HPLC monitoring was 256 nm. The substrates behaved well kinetically, gave reproducible rate coefficients, and Arrhenius plots which were linear for up to ≥90% reaction with high correlation coefficients (0.998±0.001). A representative Arrhenius plot is given in Figure 1 for 2-(benzotriazol-1-yl)-1-phenyl-2-(phenylhydrazono)ethanone (**1a**). The kinetic data and the values of the Arrhenius log A/s^{-1} and E_a/kJ mol^{-1}, and the rate coefficients at 500 K of the 10 substrates under study are summarized in Table 1 (Series **1a–e**) and Table 2 (Series **2f–j**). The Arrhenius parameters are in the range expected for thermal gas-phase first-order reactions.[27]

Although the reaction pathways (Schemes 4–6) offered earlier to account for product formation in the pyrolysis of the present arylhydrazono α-benzotriazol-1-yl ketones (**1a–e** and **2f–j**) and their ketone analogues[1] appear elaborate and complex, the results of the kinetic investigation of these compounds are, on the other hand, both informative and simple to rationalize. The arylhydrazono group, when substituted in place of the α-methylene hydrogens of the α-benzotriazolyl phenylethanone and acetone compounds, produces a dramatic change in mechanism from a 1,3-biradical pathway either partially or completely to a mechanism involving intramolecular nucleophilic addition, followed by cyclization with or without fragmentation. Incorporation of the arylhydrazono group into the BT ketones also leads to very large rate enhancement. For example, 2-(benzotriazol-1-yl)-1-phenyl-2-(phenylhydrazono)ethanone (**1a**) is ca. 10^3-fold more reactive than the unsubstituted 2-(benzotriazol-1-yl)-1-phenylethanone.[1] The rate enhancement factor for the acetone counterpart is 8.6×10^2. It has already been noted that substitution of the arylhydrazono (ArNHN=) group at the 3-position of the 2,4-pentandione produces not only a change-over in the mechanism of gas-phase pyrolysis but also leads to ca. 257-fold increase in reactivity.[17,18] The arylhydrazonophenylethanone BT ketones (**1a–e**) are more reactive than their acetone analogues (**2f–j**) by factors ranging between ca. 3–38. Similar rate differences have been observed for the unsubstituted phenylethanone and acetone BT ketones.[1] In both cases, the origin of this order of reactivity is related to the effect of the electron-withdrawing phenyl group in the phenylethanone BT ketones vis-à-vis the electron-donating methyl moiety of the acetone counterparts. It is of interest to note that there seems to be no opposing substituent effect from the *para* position of the aryl moiety of the arylhydrazono group consistent with the electron-donating character of the methyl and methoxy substituents and the electron-withdrawing character of the chloro and nitro substituents. In fact all these substituents promote reactivity albeit by a modest rate factor of 1.34–10.1. It is conceivable that the effects of these substituents on the reactivity of the present substrates combine ground-state and long-range electronic effects.[1]

3. Conclusion

Replacement of methylene hydrogen atoms by an arylhydrazono group at the α-position of ketone moieties substituted at the N(1) position of BT led to a substantial increase in rates of pyrolysis of BT and a change-over in the mechanism of the thermal gas-phase elimination reaction. In addition, this structural modification also made it possible to obtain novel condensed heterocyclic ring systems by an essentially clean and environmentally friendly gas-phase elimination process.

4. Experimental

General. Experimental techniques and instrumentation were described in Part 1,[1] and the procedures for conducting kinetic runs and data analysis were reported in earlier communications.[28]

Synthesis. The hydrazones **2f–h, j** were prepared according to a modified literature procedure using sodium acetate instead of sodium hydroxide as base for the synthesis of compounds **2f–h**.[29,30]

4.1. General procedure for synthesis of 1a–e, 2i

To a cold solution of each of 1-(benzotriazol-1-yl)acetone and 1-(benzotriazol-1-yl)acetophenone (0.01 mol) in ethanol (100 ml) was added sodium hydroxide (2.0 g) for the preparation of **1a–e**, and sodium acetate (4.0 g) for the preparation of **2i**. The mixture was then treated gradually with stirring at room temperature with a solution of the aryldiazonium salt (prepared from 0.01 mol of the arylamine and the appropriate quantities of hydrochloric acid and sodium nitrite). The product, which separated on standing, was collected by filtration and crystallized from ethanol.

4.1.1. 2-(Benzotriazol-1-yl)-1-phenyl-2-(phenylhydrazono)-ethanone, 1a. The title compound was obtained as yellow crystals in 60% yield, mp 200°C. MS: m/z=341 ($M^{+\cdot}$). IR (KBr): $\tilde{\nu}$ 3434 (NH), 1626 cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ=7.10 (t, J=7.2 Hz, 1H, Ar-H); 7.24 (d, J=8 Hz, 2H, Ar-H), 7.36 (t, J=7.6, 8 Hz, 2H, Ar-H), 7.43 (d, J=8.4 Hz, 1H, Ar-H), 7.47 (d, J=7.6 Hz, 1H, Ar-H), 7.57 (t, J=7.6 Hz, 1H, Ar-H), 7.62 (d, J=7.6 Hz, 2H, Ar-H), 7.70 (t, J=7.6, 7.2 Hz, 1H, Ar-H), 8.09 (d, J=8.4 Hz, 1H, Ar-H), 8.22 (d, J=7.2 Hz, 2H, Ar-H), 10.48 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ=112.45, 115.52, 120.41, 124.33, 125.51, 126.46, 128.59, 129.37, 130.02, 131.06, 132.72, 133.14, 137.08, 142.14, 145.31, 184.66. $C_{20}H_{15}N_5O$ (341.4): calcd C 70.37, H 4.43, N 20.52; found C 70.60, H 4.42, N 20.40.

4.1.2. 2-(Benzotriazol-1-yl)-2-[(4-methoxyphenyl)hydrazono]-1-phenylethanone, 1b. The title compound was obtained as orange crystals in 55% yield, mp 156°C. MS: m/z=371 ($M^{+\cdot}$). IR (KBr): $\tilde{\nu}$ 3434 (NH), 1631 cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ=3.80 (s, 3H, MeO), 6.90 (d, J=8.8 Hz, 2H, Ar-H), 7.25 (d, J=8.8 Hz, 2H, Ar-H), 7.36 (t, J=7.6 Hz, 1H, Ar-H), 7.43 (d, J=8.4 Hz, 1H, Ar-H), 7.54 (t, J=7.6 Hz, 2H, Ar-H), 7.59 (d, J=7.2, 7.6 Hz, 1H, Ar-H), 7.68 (t, J=7.6, 8.4 Hz, 1H, Ar-H), 7.85 (d, J=8 Hz, 1H, Ar-H), 8.20 (d, J=7.6 Hz, 2H, Ar-H), 10.62 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ=55.99, 111.93, 115.29, 117.05, 119.74, 125.31, 125.74, 128.50, 129.14, 131.00, 132.81, 133.02, 136.15, 137.42, 145.12, 156.91, 184.75. $C_{21}H_{17}N_5O_2$ (371.4): calcd C 67.92, H 4.61, N 18.86; found C 68.19, H 4.62, N 18.73.

4.1.3. 2-(Benzotriazol-1-yl)-1-phenyl-2-(*p*-tolylhydrazono)-ethanone, 1c. The title compound was obtained as reddish brown crystals in 60% yield, mp 171°C. MS: m/z=355 ($M^{+\cdot}$). IR (KBr): $\tilde{\nu}$ 3432 (NH), 1630 cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ=2.34 (s, 3H, CH_3), 7.14 (d, J=8.8 Hz, 2H, Ar-H), 7.15 (t, J=8.8 Hz, 2H, Ar-H), 7.43 (d, J=8.4 Hz, 1H, Ar-H), 7.47 (d, J=8 Hz, 1H, Ar-H), 7.56 (d, J=8 Hz, 1H, Ar-H), 7.59 (t, J=8.4, 7.6 Hz, 2H, Ar-H), 7.69 (t, J=7.2, 7.6 Hz, 1H, Ar-H), 8.10 (d, J=8.4 Hz, 1H, Ar-H), 8.21 (d, J=7.2 Hz, 2H, Ar-H), 10.38 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ=21.25, 112.25, 115.60, 120.15, 125.41, 126.07,

Table 3. Analytical pyrolysis temperature (*T*/K) and pyrolysate composition

Cpd	*T*/K	Pyrolysates and yields (%)				
1a	498	**4a** (50%)	**5**[14] (~1%)	**6a**[15] (~1%)	**8a** (5%)	**9a**[21] (18%)
1b	478	**4b** (27%)	**5**[14] (~1%)	**6b**[15] (~1%)	**8b** (~1%)	**9b**[19,20] (12%)
1c	468	**4c** (35%)	**5**[14] (~1%)	**6c**[15] (~1%)	**8c** (~1%)	**9c**[19] (11%)
1d	488	**4d** (48%)	**5**[14] (~1%)	**6d**[15] (~1%)	**8d** (~1%)	**9d**[19,20] (4%)
1e	498	**4e** (42%)	**5**[14] (~1%)	**6e**[15] (~1%)	**8e** (~1%)	**9e**[19,20] (23%)
2f	538				**8f** (12%)	**9f**[21] (21%)
2g	523				**8g** (48%)	**9g**[22] (28%)
2h	528				**8h** (14%)	**9h**[19,23] (29%)
2i	533				**8i** (5%)	**9i**[19,23] (30%)
2j	523				**8j** (5%)	**9j**[22] (5%)

128.53, 129.25, 130.54, 131.06, 132.85, 132.97, 134.13, 137.24, 139.93, 145.24, 184.68. $C_{21}H_{17}N_5O$ (355.4): calcd C 70.97, H 4.82, N 19.71; found C 71.27, H 4.77, N 19.72.

4.1.4. 2-(Benzotriazol-1-yl)-2-[(4-chlorophenyl)hydrazono]-1-phenylethanone, 1d. The title compound was obtained as reddish brown crystals in 55% yield, mp 190°C. MS: *m*/*z*=375/377 ($M^{+\cdot}$) (20/11%). IR (KBr): $\tilde{\nu}$ 3434 (NH), 1629 cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ=7.17 (d, *J*=8.8 Hz, 2H, Ar-H), 7.32 (d, *J*=8.8 Hz, 2H, Ar-H), 7.42 (d, *J*=8.4 Hz, 2H, Ar-H), 7.47 (t, *J*=7.6 Hz, 1H, Ar-H), 7.57 (t, *J*=7.6 Hz, 1H, Ar-H), 7.61 (t, *J*=7.6 Hz, 1H, Ar-H), 7.71 (t, *J*=7.6 Hz, 1H, Ar-H), 8.10 (d, *J*=8.4 Hz, 1H, Ar-H), 8.19 (d, *J*=8.4 Hz, 2H, Ar-H), 10.59 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ=112.51, 116.64, 117.23, 120.42, 125.62, 126.68, 128.65, 128.91, 129.26, 129.48, 130.06, 131.02, 133.33, 136.92, 140.88, 184.59. $C_{20}H_{14}ClN_5O$ (375.8): calcd C 63.92, H 3.75, N 18.63; found C 63.92, H 3.83, N 18.32.

4.1.5. 2-(Benzotriazol-1-yl)-2-[(4-nitrophenyl)hydrazono]-1-phenylethanone, 1e. The title compound was obtained as brown crystals in 50% yield, mp 217°C. MS: *m*/*z*=386 ($M^{+\cdot}$). IR (KBr): $\tilde{\nu}$ 3434 (NH), 1655 cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ=7.30 (d, *J*=7.2 Hz, 2H, Ar-H), 7.40 (d, *J*=8.4 Hz, 1H, Ar-H), δ=7.52 (t, *J*=7.6 Hz, 1H, Ar-H),7.59 (d, *J*=7.6 Hz, 1H, Ar-H), 7.64 (t, *J*=7.6, 8 Hz, 2H, Ar-H), 7.77 (t, *J*=7.6, 7.2 Hz, 1H, Ar-H), 8.16 (d, *J*=8 Hz, 1H, Ar-H), 8.21 (d, *J*=8.4 Hz, 2H, Ar-H), 8.26 (d, *J*=7.6 Hz, 2H, Ar-H), 11.15 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ=112.46, 115.06, 120.44, 125.96, 126.34, 128.07, 128.91, 129.85, 131.10, 132.31, 134.01, 136.32, 143.53, 145.11, 147.62, 184.62. $C_{20}H_{14}N_6O_3$ (386.4): calcd C 62.17, H 3.65, N 21.75; found C 62.40, H 3.76, N 21.63.

4.1.6. 1-(Benzotriazol-1-yl)-1-[(4-chlorophenyl)hydrazono]propan-2-one, 2i. The title compound was obtained as yellow crystals in 55% yield, mp 186°C. MS: *m*/*z*=313/315 ($M^{+\cdot}$) (20/8%). IR (KBr): $\tilde{\nu}$ 3433 (NH), 1659 cm^{-1} (CO). ^1H NMR ($CDCl_3$): δ=2.78 (s, 3H, Me), 7.30 (d, *J*=7.2 Hz, 2H, Ar-H), 7.36 (d, *J*=7.2 Hz, 2H, Ar-H), 7.41 (t, *J*=8 Hz, 2H, Ar-H), 7.56 (t, *J*=8, 7.2 Hz, 1H, Ar-H), 7.95 (d, *J*=8.4 Hz, 1H, Ar-H), 10.22 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ=25.65, 112.08, 116.72, 119.77, 125.42, 127.46, 129.32, 129.51, 130.02, 133.05, 140.81, 145.13, 190.22. $C_{15}H_{12}ClN_5O$ (313.8): calcd C 57.42, H 3.86, N 22.32; found C 57.61, H 3.91, N 22.26.

4.1.7. 1-Cyanobenzotriazole, 10. The title compound was prepared according to procedures published earlier in the literature.[26]

4.2. General procedure for pyrolysis of 1a–e, 2f–j and 4a–e

Each of the substrates (0.2 g) was introduced in the reaction tube (1.5×12 cm Pyrex), cooled in liquid nitrogen, sealed under vacuum (0.06 mbar) and placed in the pyrolyser for 900 s at a temperature comparable to that used for complete pyrolysis in the kinetic studies. The pyrolysate was then separated into its constituents by preparative TLC (MERCK,12 PSC-Platten 20×20 cm, Silica gel 60 F_{254} 2 mm) using chloroform: petroleum ether (40:60) in 80:20 ratio as eluent, and each constituent was collected, analyzed and characterized. The techniques used include ^1H NMR, ^{13}C NMR and GC/MS.

Temperatures of analytical pyrolysis, constituents of pyrolysates and percentage yield of substrates **1a–e** and **2f–j**, and of further pyrolysis of compounds **4a–e** are given in Table 3. This table also includes useful references for characterization data.

4.3. MS and NMR characterization

4.3.1. 1-Anilino-2-benzoylimidazole, 4a. MS: *m*/*z*=313 ($M^{+\cdot}$). ^1H NMR ($CDCl_3$): δ=6.58 (d, *J*=7.6 Hz, 2H), 6.93 (t, *J*=7.2, 7.6 Hz, 1H), 7.19 (t, *J*=7.6 Hz, 2H), 7.44–7.66 (m, 6H), 8.00 (d, *J*=8 Hz, 1H), 8.14 (br s, 1H, NH), 8.36 (d, *J*=8.4 Hz, 2H).

4.3.2. 1-*p*-Toluedino-2-benzoylimidazole, 4c. MS: *m*/*z*=327 ($M^{+\cdot}$). ^1H NMR ($CDCl_3$): δ=2.22 (s, 3H, CH_3), 6.49 (d, *J*=8.4 Hz, 2H, H^{10}), 6.98 (d, *J*=8.4 Hz, 2H, H^{11}), 7.46–7.65 (m, 2H, $6H^{5,6,(4\text{ or }7),15,16}$), 7.99 (d, *J*=8 Hz, 1H, $H^{4\text{ or }7}$), 8.10 (br s, 1H, NH), 8.35 (d, *J*=8.4 Hz, 2H, H^{14}).

4.3.3. 1-*p*-Chloroaniline-2-benzoylimidazole, 4d. MS: *m*/*z*=347/349 ($M^{+\cdot}$) (35/15%), base peak at 105, and major fragment ions at 77 and 91. ^1H NMR ($CDCl_3$): δ=6.52 (d, *J*=8.7 Hz, 2H, H^{10}), 7.14 (d, *J*=8.7 Hz, 2H, H^{11}), 7.47 (t, *J*=7.9 Hz, 1H, H^5), 7.52–7.54 (m, 3H, $H^{6,15}$), 7.61 (d, *J*=7.9 Hz, 1H, H^7), 7.66 (t, *J*=7.4 Hz, 1H, H^{16}), 8.00 (d, *J*=8.1 Hz, 1H, H^4), 8.11 (br s, 1H, NH), 8.37 (d, *J*=8.1 Hz, 2H, H^{14}). ^{13}C NMR ($CDCl_3$): δ=111.24 (C^7), 115.53 (C^{10}), 122.79 (C^4), 124.94 (C^5), 127.51 (C^6), 127.85 (C^{12}), 128.92 (C^{15}), 129.85 (C^{11}), 131.58 (C^{14}), 134.51 (C^{16}), 135.67 (C^{7a}), 135.97 (C^{13}), 139.53 (C^{3a}), 144.84 (C^2), 146.18 (C^9), 185.95 (C=O).

4.3.4. 2-Methoxy-12-phenylbenzimidazo[1,2-*b*]cinnoline, 8b. MS: *m*/*z*=325 ($M^{+\cdot}$). ^{1}H NMR ($CDCl_3$): δ=4.10 (s, 3H, OCH_3), 7.23 (dd, ^3J=8.8 Hz, ^4J=2.4 Hz, 1H, H^3), 7.47–7.53 (m, 2H, $H^{8,9}$), 7.58 (d, *J*=6.8 Hz, 1H, H^{16}), 7.63 (t, *J*=6.8 Hz, 2H, H^{15}), 8.01 (d, ^4J=2.4 Hz, 1H, H^1), 8.20 (d, *J*=8.8 Hz, 1H, H^4), 8.22 (d, *J*=6.8 Hz, 1H, $H^{7 \text{ or } 10}$), 8.44 (d, *J*=6.8 Hz, 1H, $H^{7 \text{ or } 10}$), 8.71 (d, *J*=7.2 Hz, 2H, H^{14}).

4.3.5. 2-Methyl-12-phenylbenzimidazo[1,2-*b*]cinnoline, 8c. MS: *m*/*z*=309 ($M^{+\cdot}$). ^{1}H NMR ($CDCl_3$): δ=2.72 (s, 3H, CH_3), 7.25 (d, *J*=8 Hz, 2H, H^3), 7.45 (t, *J*=8.8 Hz, 2H, H^{15}), 7.54 (t, *J*=7.6 Hz, 1H, H^{16}), 7.58–7.62 (m, 3H, $H^{8 \text{ or } 9 \text{ and } 14}$), 7.85–7.87 (m, 1H, $H^{8 \text{ or } 9}$), 8.01 (d, *J*=8.4 Hz, 1H, $H^{7 \text{ or } 10}$), 8.17 (s, 1H, H^1), 8.63 (d, *J*=8.4 Hz, 1H, $H^{7 \text{ or } 10}$).

4.3.6. 2-Chloro-12-phenylbenzimidazo[1,2-*b*]cinnoline, 8d. MS: *m*/*z*=329 ($M^{+\cdot}$) (60%), 331 (M+2) (43%). ^{1}H NMR ($CDCl_3$): δ=7.54–7.62 (m, 5H, $H^{3,4,8,9}$), 6.93 (d, *J*=7.6 Hz, 2H, H^{15}), 8.03 (d, *J*=8.4 Hz, 1H, $H^{7 \text{ or } 10}$), 8.05 (t, *J*=7.2 Hz, 1H, H^{16}), 8.24 (d, *J*=8 Hz, 1H, H^{14}), 8.38 (d, *J*=1.2 Hz, 1H, H^1), 8.36 (d, *J*=8.4 Hz, 1H, $H^{8 \text{ or } 9}$).

4.3.7. 2-Methoxyl-12-methylbenzimidazo[1,2-*b*]cinnoline, 8g. MS: *m*/*z*=263 ($M^{+\cdot}$). ^{1}H NMR ($CDCl_3$): δ=3.06 (s, 3H, CH_3), 4.07 (s, 3H, OCH_3), 7.19 (dd, ^4J=2.5 Hz, ^3J=8.9 Hz, 1H, H^3), 7.61–7.68 (m, 2H, $H^{8 \text{ and } 9}$), 7.94 (d, *J*=2.5 Hz, 1H, H^1), 8.05 (d, *J*=8.9 Hz, 1H, H^4), 8.17 (d, *J*=7.2 Hz, 1H, H^7), 8.38 (d, *J*=7.2 Hz, 1H, H^{10}). ^{13}C NMR ($CDCl_3$): δ=21.89 (CH_3), 56.37 (OCH_3), 99.89 (C^1), 112.64 (C^3), 114.54 (C^7), 122.28 (C^{10}), 124.84 (C^9), 125.86 (C^8), 130.38 (C^{4a}), 130.76 (C^{6a}), 131.65 (C^4), 142.08 (C^{11a}), 144.48 (C^{10a}), 151.73 (C^{12a}), 160.30 ($C^{2,12}$).

4.3.8. 2,12-Dimethylbenzimidazo[1,2-*b*]cinnoline, 8h. MS: *m*/*z*=247 ($M^{+\cdot}$). ^{1}H NMR ($CDCl_3$): δ=2.71 (s, 3H, CH_3), 3.09 (s, 3H, CH_3), 7.25 (d, ^3J=8.4 Hz, 1H, H^3), 7.63–7.66 (m, 2H, $H^{8 \text{ and } 9}$), 8.03 (d, *J*=8.4 Hz, 1H, H^4), 8.19 (d, *J*=6.8 Hz, 1H, $H^{7 \text{ or } 10}$), 8.32 (s, 1H, H^1), 8.48 (d, *J*=6.8 Hz, 1H, $H^{7 \text{ or } 10}$).

4.4. MS characterization

The following compounds could not be separated in pure form. GC/MS of the mixture obtained showed mass peaks corresponding to the molecular mass of the substrates as follows: compound **4b**, MS: *m*/*z*=343; **4e**, MS: *m*/*z*=358; **8a**, MS: *m*/*z*=295; **8e**, MS: *m*/*z*=340; **8f**, MS: *m*/*z*=233; **8i**, MS: *m*/*z*=267/269 ($M^{+\cdot}$) (50/20%); **8j**, MS: *m*/*z*=278.

4.5. Kinetic runs and data analysis

Stock solution (7 ml) was prepared by dissolving 6–10 mg of the substrate in acetonitrile as solvent to give a concentration of 1000–2000 ppm. Internal standard was then added, the amount of which was adjusted to give the desired peak area ratio of substrate to standard (2.5:1). The solvent and the internal standard are selected because both are stable under the conditions of pyrolysis, and because they do not react with either substrate or product. The internal standards used in this study were chlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. Each solution was filtered to ensure that a homogeneous solution was obtained.

The weight ratio of the substrate with respect to the internal standard was calculated from the ratio of the substrate peak area to the peak area of the internal standard. The kinetic rate was obtained by tracing the rate of disappearance of the substrate with respect to the internal standard as follows.

An aliquot (0.2 ml) of each solution containing the substrate and the internal standard was pipetted into the reaction tube which was then cooled sufficiently (liquid nitrogen) sealed and placed in the pyrolyzer for 6 min under non-pyrolytic conditions. A sample was then analyzed using the HPLC probe with the UV detector at wavelength of 256 nm, and the standardization value (A_o) was then calculated. Several HPLC measurements were obtained with an accuracy of ≥2%. The temperature of the pyrolysis block was then raised until approximately 10% pyrolysis was deemed to occur over 900 s. This process was repeated after each 10–15°C rise in the temperature of the pyrolyzer until ≥90% pyrolysis takes place. The relative ratio of the integration values of the sample and the internal standard (A) at the pyrolysis temperature was then calculated. A minimum of three kinetic runs were carried out at each 10–15°C rise in the temperature of the pyrolyzer to ensure reproducible values of (A). Treatment of the kinetic data has been detailed elsewhere.[31–33]

Acknowledgements

This work was supported by Kuwait University through research grant # SC01/99 and ANALAB and SAF grants # GS01/01 and GS03/01.

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