Gas-phase Thermolysis of Benzotriazole Derivatives. Part 4. Pyrolysis of 1-Acylbenzotriazole phenylhydrazones. Interesting Direct Routes Towards *N*-Aminobenzimidazoles

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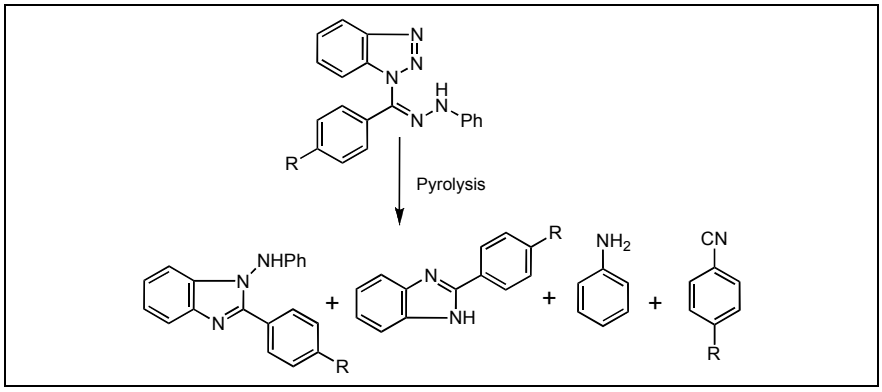
Received May 20, 2007



Flash vacuum pyrolysis (FVP) of 1-acylbenzotriazole phenylhydrazones gave benzonitriles, aniline and 2-arylbenzimidazole derivatives. Static pyrolysis of the same substrates at 180 °C gave exclusively the corresponding *N*-anilino-2-arylbenzimidazole derivatives. Pyrolysis of the isomeric 2-acylbenzotriazole phenylhydrazones gave similar products.

J. Heterocyclic Chem., **45**, 723 (2008).

INTRODUCTION

We have recently studied kinetically and mechanistically the pyrolytic behavior of a number of substituted benzotriazole derivatives [1]. We also reported the products obtained under different pyrolytic techniques including mainly static and flash vacuum conditions. These reactions offer some advantageous synthetic approach to many interesting heterocyclic systems, which have been reviewed in our previous publications [1d]. These pyrolytic reactions have been extensively used for the preparation of many interesting heterocyclic systems [1,2-11]. The primary step in the pyrolysis of these compounds involves mainly N_2 elimination, yielding the corresponding diradical intermediates followed by intramolecular cyclization.

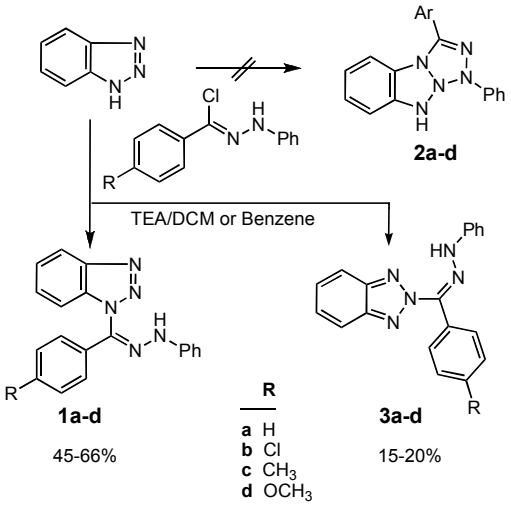
The present work describes the pyrolytic behavior of 1-acylbenzotriazole phenylhydrazone derivatives **1a-d** together with suggested mechanism for this pyrolytic reaction in comparison with the analogous benzotriazole derivatives.

RESULTS AND DISCUSSION

Literature shows that compounds **1a,c** have been obtained with another isomeric products assigned as **2a,c** [12]. The latter structures have been corrected by Elguero *etal*. as 2-benzoylbenzotriazole phenylhydrazones **3a,c** [13]. In the present investigation we prepared the required starting materials **1a-d** as the main products (45-66%) along with their isomeric products **3a-d** as minor by-product (15-20%) by reacting benzotriazole with the appropriate *N*-phenylbenzohydrazonoyl chloride derivatives. The reaction was performed either at room temperature for 24 hrs in dichlromethane (DCM) in the presence of triethyl amine (TEA) or by reflux for 3 hrs in benzene in the presence of TEA (Scheme 1). The symmetry of the benztriazole ring of **3a-d** confirmed their structures over **2a-d** as found mainly from ^{13}C NMR spectra which displayed two less carbon signals than is expected for **2a-d**.

FVP of each of **1a-d** at 700 °C and 0.01 Torr gave the corresponding 2-arylbenzimidazoles **5a-d**, aniline **6** and benzonitrile derivatives **7a-d**. On the other hand, gas phase pyrolysis of **1a-d** at 250 °C and 0.045 Torr gave aniline and compounds **5a-d**. Since these pyrolytic conditions did not give the anticipated products **4a-d** but a secondary thermolysis product we tried other conditions. Finally compounds **4a-d** have been obtained as the sole reaction products in good yields (70-78%) by heating the corresponding starting materials **1a-d** in an oil bath at 180-190 °C for 10 minutes. The pyrolyzates were qualitatively and quantitatively determined by HPLC (Table 1) and by ^1H NMR spectroscopy. Scheme 2 and Table 1 summarize the pyrolysis products under different pyrolytic conditions.

Scheme 1



for Bt derivatives containing RCO instead of the Ar moieties in the present study). The formation of the nitriles **7** results from fragmentation of the starting compounds **1a-d** into BtH and ArCNNPh. The latter under FVP gave **7** and aniline. Under static conditions (250 °C, 0.045 Torr) compounds **5a-d** and aniline were the only observed products which indicate that the fragmentation to ArCN required the more drastic conditions of FVP. By lowering the pyrolytic temperature to 180-190 °C we have been able to obtain exclusively the primary expected pyrolysis products **4a-d** in excellent yields. The formation of **5a-d** from **4a-d** was confirmed by subjecting compounds **4a-d** to the same static pyrolytic conditions (250 °C, 0.045 Torr) where this led to the formation of **5a-d** and aniline (Table 1).

Similar attempts to pyrolyze the isomeric derivatives **3a-d** was only successful under the static conditions at

Table 1

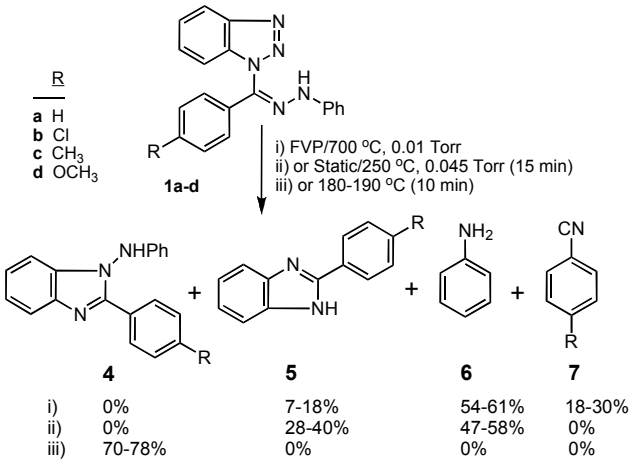
Pyrolysis products of **1a-d, 3a-d, 4a-d** under different pyrolytic conditions.

substrate	Condition	% yield of pyrolysis products			
		Compound **4a-d**	Compound **5a-d**	Compound **6**	Compound **7a-d**
1a	i	-	18	54	29
	ii	-	34	58	-
	iii	78	-	-	-
1b	i	-	5	43	26 (5)[iv]
	ii	-	45	55	-
	iii	75	-	-	-
1c	i	-	7	61	27 (4)[iv]
	ii	-	28	49	-
	iii	76	-	-	-
1d	i	-	3	58	10 (8)[iv]
	ii	-	40	47	-
	iii	70	-	-	-
3a	ii	-	20	41	-
3b	ii	-	31	42	-
3c	ii	-	22	33	-
3d	ii	-	21	35	-
4a	ii	-	34	28	-
4b	ii	-	46	43	-
4c	ii	-	43	39	
4d	ii	-	56	39	

(i) FVP, 700°C (0.02 Torr); (ii) Static pyrrolysis 250°C (0.045 Torr)/15 min; (iii) static pyrrolysis (oil bath) 180-190°C/10 min; (iv) benzonitrile formed in FVP from substituted benzonitrile by pyrolysis of the initial formed substituted benzonitriles.[14]

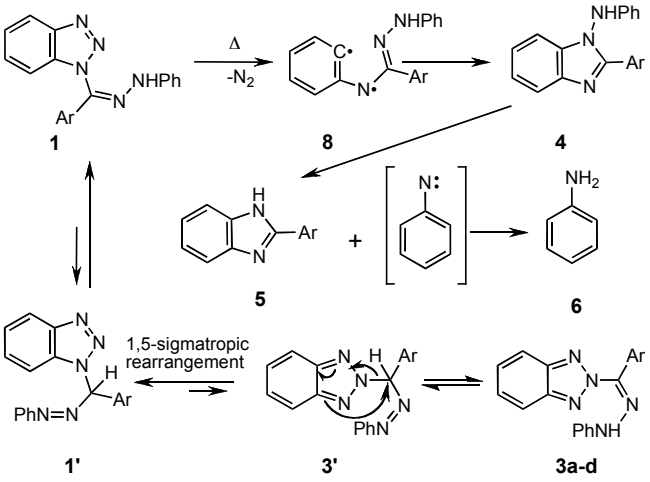
Scheme 3 illustrates possible mechanistic routes explaining the formation of the products **4a-d** and **5a-d** obtained in the present pyrolytic study. The reaction starts by extrusion of N_2 to give the diradicals **8a-d** which then undergo intramolecular cyclization to give the corresponding 1-anilinobenzimidazoles **4a-d**. The latter undergo further fragmentation under FVP conditions to give the corresponding benzimidazole derivatives **5a-d** and aniline (similar mechanism [1a] has been suggested 250 °C, 0.045 Torr for 15 min. This was found to give also the corresponding benzimidazoles **5a-d** (20-31%) and aniline **6** (33-42%) (Table 1). The reaction presumably proceeds *via* first 1,5-sigmatropic shift (most probably *via* the azo tautomers **3'**) to give the corresponding isomeric 1-substituted Bt derivatives **1a-d** followed by the same mechanistic pyrolysis proposed in Scheme 3. Such 1,5-sigmatropic shifts have also been reported for other 2-substituted Bt derivatives [1b].

Scheme 2



In conclusion different pyrolytic studies on 1-acylbenzotriazole phenylhydrazones gave direct easy efficient synthesis of *N*-anilino-2-arylbenzimidazole derivatives, which are otherwise difficult to synthesize. Combined with interesting diverse biological activity of benzimidazole derivatives, [16] this synthetic route can be used in strategic synthesis of biologically active compounds containing this ring system.

Scheme 3



EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded in KBr disks using Perkin Elmer System 2000 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400, 400 MHz super-conducting NMR spectrometer. LCMS were measured using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Microanalyses were performed on LECO CHNS-932 Elemental Analyzer. The starting *N*-phenylbenzohydrazonoyl chloride derivatives were prepared from the corresponding *N*-aroyl-*N*'-phenylhydrazine derivatives [15] by stirring at room temperature with CCl_4 and Ph_3P in acetonitrile at room temperature overnight following reported procedure [17].

Preparation of starting compounds 1a-d and 3a-d.

General procedure

Method A. To a mixture of benzotriazole (1.19 gm, 10 mmol) in DCM (40 mL) and TEA (3 mL) was added dropwise with stirring at room temp. the appropriate *N*-phenylbenzohydrazonoyl chloride derivatives (10 mmol). The mixture was then stirred overnight. The solvent was then removed *in vacuo* and the residue was washed with water and recrystallized from the proper solvent to give yellow crystals of **1a-d** and **3a-d**.

Method B. To a mixture of benzotriazole (1.19 gm, 10 mmol) in benzene (40 mL) and TEA (3 mL) was added dropwise with string at room temp. the appropriate *N*-phenylbenzohydrazonoyl chloride derivatives (10 mmol). The reaction mixture was then heated under reflux for 3 hrs. The solvent was then removed *in vacuo* and the residue was washed with water and recrystallized from the proper solvent to give yellow crystals of **1a-d** and **3a-d**.

1-Benzoylbenzotriazole phenylhydrazone (1a). Yellow crystals from ethanol, yield 45% (A), 45% (B), mp 193-94 °C (lit.12 mp 194 °C). MS; *m/z*: 313 (M^+, 10 %), 285 (100%), 194 (60%). ^{1}H NMR ($CDCl_3$): δ 8.68 (br, 1H, NH), 8.22 (m, 1H), 7.49 (m, 2H), 7.45-7.39 (m, 5H), 7.32 (t, *J* 7.4 Hz, 2H), 7.20 (d, *J* 7.7 Hz, 2H), 7.14 (m, 1H), 6.97 (t, *J* 7.4 Hz, 1H).

1-*p*-Chlorobenzoylbenzotriazole phenylhydrazone (1b). Yellow crystals from ethanol, yield 48% (A), 66% (B), mp 185-87 °C. MS; *m/z*: 349 (M + 2, 5%), 347 (M + 1, 15%), 319 (100%), 284 (70%), 228 (42%). IR (KBr) 3440, 3289, 3237, 3057, 1594, 1517, 1493, 1255, 1171, 1091, 1070, 951, 832, 747, 692. ^{1}H NMR ($CDCl_3$): δ 8.61(br, 1H, NH), 8.23 (m, 1H), 7.54-7.49 (m, 2H), 7.37-7.28 (m, 6H), 7.19 (d, *J* 8.2 Hz, 2H), 7.14 (m, 1H), 6.98 (t, *J* 7.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 145.2 (C), 143.0 (C), 135.2 (C), 132.1 (C), 131.4 (C), 129.4 (2CH), 129.1 (CH), 129.0 (2CH), 127.2 (2CH), 127.0 (C), 125.2 (CH), 121.8 (CH), 120.4 (CH), 113.7 (2CH), 111.1 (CH). *Anal.* Calcd for $C_{19}H_{14}ClN_5$ (347.8): C 65.61; H 4.06; N 20.14. Found: C 65.49; H 4.31; N 20.17.

1-*p*-Toluoylbenzotriazole phenylhydrazone (1c). Yellow crystals from DMF / EtOH, yield 63% (A), 55% (B), mp 182-83 °C (lit. [12] mp 180 °C). MS; *m/z*: 327 (M^+, 10%), 299 (90%), 284 (100%), 208 (55%), 194 (45%). IR (KBr): 3443, 3284, 3055, 3031, 3004, 2918, 1602, 1583, 1497, 1447, 1269, 1252, 1171, 1069, 821, 783, 747, 693. ^{1}H NMR ($CDCl_3$): δ 8.60 (br, 1H, NH), 8.23 (m, 1H), 7.47 (m, 2H), 7.34-7.28 (m, 4H), 7.20 (m, 4H), 7.13 (m, 1H), 6.95 (t, *J* 7.4 Hz, 1H), 2.41 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 145.2 (C), 143.5 (C), 139.6 (C), 132.3 (C), 130.1 (C), 129.5 (2CH), 129.3 (2CH), 128.8 (CH), 128.3 (C), 126.2 (2CH), 125.0 (CH), 121.3 (CH), 120.3 (CH), 113.5 (2CH), 111.4 (CH), 21.4 (CH_3). *Anal.* Calcd for $C_{20}H_{17}N_5$ (327.4): C 73.37; H 5.23; N 21.39. Found: C 73.03; H 5.40; N 21.47.

1-*p*-Methoxybenzoylbenzotriazole phenylhydrazone (1d). Yellow crystals from ethanol yield 50% (A), 54% (B), mp 166-168 °C. MS; *m/z*: 343 (M^+, 10%), 315 (100%), 224 (60%). IR (KBr): 3443, 3287, 3060, 3006, 2919, 2834, 1603, 1503, 1446, 1305, 1247, 1169, 1069, 1030, 831, 750. ^{1}H NMR ($CDCl_3$): δ 8.51 (br, 1H, NH), 8.24 (m, 1H), 7.50 (m, 2H), 7.37 (d, *J* 8.0 Hz, 2H), 7.29 (t, *J* 8.0 Hz, 2H), 7.17 (d, *J* 8.0 Hz, 2H), 7.14 (m, 1H), 6.94 (t, *J* 7.6 Hz, 1H), 6.91 (d, *J* 8.2 Hz, 2H), 3.86 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 160.6 (C), 145.2 (C), 143.6 (C), 132.3 (C), 129.3 (2CH), 128.8 (CH), 128.2 (C), 127.8 (2CH),

125.5 (C), 125.0 (CH), 121.2 (CH), 120.3 (CH), 114.2 (2CH), 113.5 (2CH), 111.4 (CH), 55.4 (OCH_3). *Anal.* Calcd for $C_{20}H_{17}N_5O$ (343.4): C 69.96; H 4.99; N 20.39. Found: C 69.73; H 4.90; N 20.32.

2-Benzoylbenzotriazole phenylhydrazone (3a). Yellow crystals from dilute ethanol, m.p. 173-175 °C (lit. [12] mp 175 °C), yield 18% (A), 20% (B). IR (KBr): 3450, 3310, 3056, 3032, 1598, 1579, 1497, 1487, 1266, 1253, 1151, 1093, 1071, 831, 746, 692. ^{1}H NMR ($CDCl_3$): δ 11.10 (br, s, 1H, NH), 8.01 (m, 2H), 7.94 (dd, *J* 8.0, 1.3 Hz, 2H), 7.75 (m, 2H), 7.48-7.41 (m, 2H), 7.35-7.19 (m, 3H), 7.20 (d, *J* 8.0 Hz, 2H), 6.97 (t, *J* 7.8 Hz, 1H).

2-*p*-Chlorobenzoylbenzotriazole phenylhydrazone (3b). Yellow crystals from petroleum ether 60-80, yield 18% (A), 15% (B), mp 188-89 °C. IR (KBr): 3436, 3241, 3063, 1588,1514, 1494, 1262, 1146, 1087, 951, 830, 747, 692. ^{1}H NMR ($CDCl_3$): δ 11.24 (br, 1H, NH), 8.02 (m, 2H), 7.73 (d, *J* 8.5 Hz, 2H), 7.56 (m, 2H), 7.45 (d, *J* 8.5 Hz, 2H), 7.38 (t, *J* 7.2 Hz, 2H), 7.31 (d, *J* 7.5 Hz, 2H), 7.00 (t, *J* 7.12 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 143.3 (C), 143.2 (C), 134.9 (C), 131.8 (C), 129.5 (2CH), 129.3 (2CH), 128.4 (2CH), 128.3 (2CH), 128.1 (C), 121.6 (CH), 118.3 (2CH), 113.7 (2CH). *Anal.* Calcd for $C_{19}H_{14}ClN_5$ (347.8): C 65.61; H 4.06; N 20.14. Found: C 65.58; H 4.19; N 19.95.

2-*p*-Toluoylbenzotriazole phenylhydrazone (3c). Yellow crystals from hexane, yield 15% (A), 18% (B), mp 141-143 °C (lit. [12] 145 °C), IR (KBr): 3440, 2919, 1630, 1593, 1504, 1383, 1262, 1147, 952, 819, 748. ^{1}H NMR ($CDCl_3$): δ 11.09 (br, 1H, NH), 8.01 (m, 2H), 7.64 (d, *J* 8.1 Hz, 2H), 7.55 (m, 2H), 7.37-7.28 (m, 6H), 6.98 (t, *J* 7.0 Hz, 1H), 2.45 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 143.8 (C), 143.4 (C), 139.3 (C), 130.6 (C), 129.5 (C) 129.4 (2CH), 129.1 (2CH), 128.3 (2CH), 128.1 (2CH), 121.3 (CH), 118.5 (2CH), 113.7 (2CH), 21.5 (CH_3).

2-*p*-Methoxybenzoylbenzotriazole phenylhydrzone (3d). Yellow crystals from petroleum ether, yield 16% (A), 20% (B), mp 146-48 °C. MS; *m/z*: 343 (M^+, 10%), 315 (100%), 300 (15%), 284 (30%), 224 (55%). ^{1}H NMR ($CDCl_3$): δ 11.03 (br, 1H, NH), 8.01 (m, 2H), 7.70 (d, *J* 8.8 Hz, 2H), 7.54 (m, 2H), 7.38-7.28 (m, 4H), 7.00 (d, *J* 8.8 Hz, 2H), 6.95 (t, *J* 8.4 Hz, 1H), 3.89 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 160.4 (C), 143.8 (C), 143.3 (C), 129.7 (2CH), 129.3 (2CH), 128.8 (C), 128.1 (2CH), 125.9 (C), 121.1 (CH), 118.4 (2CH), 113.7 (2CH), 113.6 (2CH), 55.4 (OCH_3). *Anal.* Calcd for $C_{20}H_{17}N_5O$ (343.4): C 69.96; H 4.99; N 20.39. Found: C 69.68; H 4.98; N 20.33.

Pyrolysis of 1a-d, 3a-d, 4a-d.

General Procedures.

A) Flash Vacuum Pyrolysis. The apparatus used was similar to the one that has been publications [1]. The sample was volatilized from a tube in a Büchi Kugelrohr oven through a 30x2.5 cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A to a temperature of 500 °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 10^{-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 the pump. Under these conditions the contact time in the hot zone was estimated to be ≅ 10 ms. The different zones of the products collected in the U-shaped trap were analyzed by ^{1}H, ^{13}C NMR, IR and GC-MS. Relative and percent yields were determined from ^{1}H NMR. described in our recent.

(B) Static Pyrolysis. Each substrate (0.2 g) was introduced in the reaction tube (1.5 x 12 cm Pyrex), cooled in liquid nitrogen, sealed under vacuum of 0.045 Torr and placed in the pyrolyser for 15 min at 250 °C. The products were analyzed by ^{1}H, ^{13}C NMR, IR and GC-MS. Relative and percent yields were determined from ^{1}H NMR.

(C) Pyrolysis in an oil bath of 1a-d. Each substrate (0.2 g) was introduced in a test tube which was placed in an oil bath for 10 min at 180-190 °C. The product was crystallized from benzene/petroleum ether (60-80) to give compounds **4a-d**.

Reaction products from complete gas-phase pyrolysis of substrates 1a-d, 3a-d and 4a-d.

1-Anilino-2-phenylbenzimidazole (4a). Colorless crystals from aq. ethanol, yield (Table 1), mp 210-12 °C (lit. [18] mp 211-13). MS; *m/z*: 285 ($M^{+\cdot}$ 100 %), 193 (45%). 1H NMR (CDCl3): δ 8.07 (m, 2H), 7.87 (d, *J* 8.0 Hz, 1H), 7.45 (m, 3H), 7.34 (t, *J* 7.8 Hz, 1H), 7.31-7.25 (m, 3H), 7.21 (t, *J* 8.4 Hz, 1H), 7.01 (t, *J* 7.4 Hz, 1H), 6.80 (br, 1H, NH), 6.72 (d, *J* 7.8Hz, 2H). ^{13}C NMR (CDCl3): δ 152.6 (C), 145.6 (C), 141.1 (C), 134.7 (C), 130.1 (CH), 129.7 (2CH), 129.0 (2CH), 128.9 (C), 128.5 (2CH), 123.4 (CH), 123.3 (CH), 122.0 (CH), 120.4 (CH), 113.0 (2CH), 109.8 (CH). *Anal.* Calcd for $C_{19}H_{15}N_3$ (285.4): C 79.98; H 5.30; N 14.73. Found: C 79.96; H 5.21; N 14.75.

1-Anilino-2-*p*-chlorophenylbenzimidazole (4b). Colorless crystals from benzene/petroleum ether 60-80, yield (Table 1), mp 232-34 °C. MS; *m/z*: 321 (M + 2, 27%) 319 (M^+, 85%), 227 (100 %). IR (KBr): 3437, 3165, 3108, 3022, 10602, 1492, 1326, 1093, 1013, 829, 745, 696. ^{1}H NMR ($CDCl_3$): δ 8.05 (d, *J* 8.6 Hz, 2H), 7.85 (d, *J* 8.4 Hz, 1H), 7.41 (d, *J* 8.4 Hz, 2H), 7.38-7.22 (m, 4H), 7.16 (d, *J* 8.4 Hz, 1H), 7.02 (t, *J* 8.0 Hz, 1H), 6.89 (br, 1H, NH), 6.69 (d, *J* 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 151.4 (C), 145.3 (C), 140.9 (C), 136.4 (C), 134.7 (C), 130.2 (2CH), 129.8 (2CH), 128.8 (2CH), 127.2 (C), 123.7 (CH), 123.5 (CH), 122.2 (CH), 120.4 (CH), 113.1 (2CH), 109.9 (CH). *Anal.* Calcd for $C_{19}H_{14}N_3Cl$ (319.8): C 71.36; H 4.41; N 13.14. Found: C 71.30; H 4.30; N 13.01.

1-Anilino-2-*p*-tolylbenzimidazole (4c). Colorless crystals from benzene/petroleum ether, yield (Table 1), mp 234-36 °C. MS; *m/z*: 299 (M^+, 100 %), 207 (70%). IR (KBr): 3434, 3168, 3108, 3060, 3022, 2997, 2917, 1602, 1495, 1451, 1392, 1324, 1255, 1180, 820, 743. ^{1}H NMR ($CDCl_3$): δ 7.96 (d, *J* 7.9 Hz, 2H), 7.85 (d, *J* 8.0 Hz, 1H), 7.35-7.28 (m, 6H), 7.18 (t, *J* 7.9 Hz, 1H), 7.0 (t, *J* 7.8 Hz, 1H), 6.83 (br, 1H, NH), 6.70 (d, 2H, *J* = 8.0 Hz), 2.41 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 152.8 (C), 145.7 (C), 141.0 (C), 140.4 (C), 134.8 (C), 129.7 (2CH), 129.3 (2CH), 128.9 (2CH), 126.0 (C), 123.5 (CH), 123.2 (CH), 121.9 (CH), 120.2 (CH), 113.0 (2CH), 109.8 (CH), 21.5 (CH_3). *Anal.* Calcd for $C_{20}H_{17}N_3$ (299.4): C 80.24; H 5.72; N 14.04. Found: C 80.20; H 5.65; N 14.01.

1-Anilino-2-*p*-methoxyphenylbenzimidazole (4d). Colorless crystals from benzene/petroleum ether 60-80, yield (Table 1), mp 228-30 °C. MS; *m/z*: 315 (M^+, 40 %), 224 (100 %). IR (KBr): 3435, 3172, 3110, 3001, 2932, 1605, 1496, 1478, 1323, 1256, 1179, 1027, 832, 746. ^{1}H NMR ($CDCl_3$): δ 8.04 (d, *J* 8.8 Hz, 2H), 7.82 (d, *J* 8.0 Hz, 1H), 7.33-7.24 (m, 3H), 7.21 (t, *J* 7.8 Hz, 1H), 7.15 (t, *J* 8.0 Hz, 1H), 7.00 (t, *J* 7.8 Hz, 1H), 6.95 (d, *J* 8.8 Hz, 2H), 6.86 (br, 1H, NH), 6.71 (d, *J* 8.0 Hz, 2H), 3.85 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 161.3 (C), 152.5 (C), 145.6 (C), 141.1 (C), 134.7 (C), 130.5 (2CH), 129.8 (2CH), 123.2 (2

overlapped CH), 121.9 (CH), 121.3 (C), 120.0 (CH), 114.0 (2CH), 113.0 (2CH), 109.7 (CH), 55.3 (OCH_3). *Anal*. Calcd for $C_{20}H_{17}N_3O$ (315.1): C 76.19; H 5.39; N 13.33. Found: C 76.10; H 5.22; N 13.26.

2-Phenyl-1*H*-benzimidazole (5a). White crystals, mp 289-290°C (lit. [19,20] 286-289 °C). LCMS; *m/z*: 266 (M + 1). ^{1}H NMR ($CDCl_3$): δ 7.29 (m, 3H), 7.45 (m, 3H), 7.68 (m, 2H), 8.12 (m, 2H).

2-*p*-Chlorophenyl-1*H*-benzimidazole (5b). White crystals, mp 289-290 °C (lit. [21] 290-292 °C). LCMS; *m/z*: 231 (M + 3), 229 (M + 1). ^{1}H NMR (DMSO-d_6): δ 7.19 (m, 2H), 7.57 (m, 2H), 7.58 (d, *J* 8.4 Hz, 2H), 8.18 (d, *J* 8.4Hz, 2H), 12.98 (br, 1H, NH).

2-*p*-Tolyl-1*H*-benzimidazole (5c). Colorless crystals, mp 269-270 °C (lit. [21] 270-272 °C). LCMS; *m/z*: 209 (M + 1). ^{1}H NMR (DMSO-d_6): δ 2.33 (s, 3H, CH_3), 7.16 (m, 2H), 7.32 (d, *J* 8.0 Hz, 2H), 7.56 (m, 2H), 8.05 (d, *J* 8.0 Hz, 2H), 12.80 (br, 1H, NH).

2-*p*-Methoxyphenyl-1*H*-benzimidazole (5d). White crystals, mp 223-224 °C (lit. [21] 222-225 °C). LCMS; *m/z*: 225 (M + 1). ^{1}H NMR ($CDCl_3$): δ 3.84 (s, 3H, OCH_3), 7.24 (d, *J* 8.8 Hz, 2H), 7.48 (m, 2H), 7.74 (m, 2H), 8.08 (d, *J* 8.8 Hz, 2H), 12.80 (br, 1H, NH).

Aniline (6). ^{1}H NMR spectroscopic data identical to that reported in the literature [22a].

Benzonitrile 7a. LCMS: *m/z* = 104 (M + 1). ^{1}H NMR spectroscopic data identical to that reported in the literature [22b].

***p*-Chlorobenzonitrile 7b.** ^{1}H NMR spectroscopic data identical to that reported in the literature [22c].

***p*-Tolunitrile 7b.** LCMS; *m/z*: 118 (M + 1). ^{1}H NMR spectroscopic data identical to that reported in the literature [23].

***p*-Methoxybenzonitrile 7d.** LCMS; *m/z*: 134 (M + 1). ^{1}H NMR spectroscopic data identical to that reported in the literature [22d].

Acknowledgment. The support of the University of Kuwait received through research grant no. SC04/05 and the facilities of ANALAB and SAF (grants no. GS01/01, GS03/01) are gratefully acknowledged.

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