HETEROCYCLES, Vol. 55, No. 9, pp. 1703 - 1710, Received, 28th May, 2001

α-BENZOTRIAZOLYLPYRIDINES AND THEIR *N*-OXIDES

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Abstract - α-Benzotriazolyl-substituted pyridines, -quinolines and -isoquinolines have been prepared by reactions of pyridine, quinoline and isoquinoline *N*-oxides with 1-tosylbenzotriazole in the presence of triethylamine. Treatment of α-benzotriazolylpyridines, -quinolines and -isoquinolines with hydrogen peroxide in glacial acetic acid afforded *N*-oxides, the structures of which were determined by X-Ray crystallography. Reactions of 1-(2-pyridinyl)-benzotriazole with alkyl halides or tosylates led to the corresponding *N*-alkylpyridinium salts.

α-Benzotriazolyl-substituted pyridines have previously been prepared from halopyridines and benzotriazole by nucleophilic displacement without[1a-d] or with transition metal catalysis,[1e] and some of their reactions have been investigated.[1b] We now report that α-benzotriazolyl-pyridines (**2a-d**), -quinoline (**8**) and -isoquinoline (**11**) can be prepared in 58-92% isolated yields by reactions of 1-tosylbenzotriazole (**13**) with pyridine, quinoline and isoquinoline *N*-oxides (**1a-d**, **7**, and **10**), respectively, in the presence of a stiochiometric amount of triethylamine on heating in toluene or xylene (Schemes 1 and 2). α-Substituted derivatives require harsher reaction conditions, e.g. reflux in xylene for 48 h in the case of **2d**. When the reagents are heated neat, a strong exothermic reaction provides the products in somewhat lower yields.

RESULTS AND DISCUSSION

Formation of *N*-oxides. We investigated the reactions of compounds (**2a-d, 8,** and **11**) with peracetic acid, which is known to convert pyridines readily into their *N*-oxides.[2] Previously known benzotriazole *N*-oxides have generally been obtained by ring closure reactions;[3a] only recently have examples of the direct conversion of benzotriazoles into their *N*-oxides been reported.[3b] Surprisingly, the reactions of α-benzotriazolylpyridines (**2a-d**) with hydrogen peroxide in glacial acetic acid generally afforded three products; (i) pyridine *N*-oxides (**4a-d**), (ii) benzotriazole 3-*N*-oxides (**5a-d**) and (iii) the corresponding bis-*N*-oxides (**6a,b,d**) (Table 1).

The structures of 2-(benzotriazol-1-yl)-4-methylpyridine *N*-oxide (**4b**) and 1-(2-pyridyl)benzotriazole 3-*N*-oxide **(5a)** were determined by X-Ray crystallography (Figures 1 and 2). In the solid state the two heterocyclic rings of **4b** are inclined at an angle of 46.7 ^{o} for steric reasons, whereas in **5a** the two rings systems are approximately coplanar, the corresponding angles being 3.8 ^{o} and 3.0 ^{o} for the two

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independent molecules in the unit cell. The structures of **4a,c,d** and of **5b,c,d** were determined by comparing their spectra with those of **4b** and **5a**, respectively.

Scheme 1

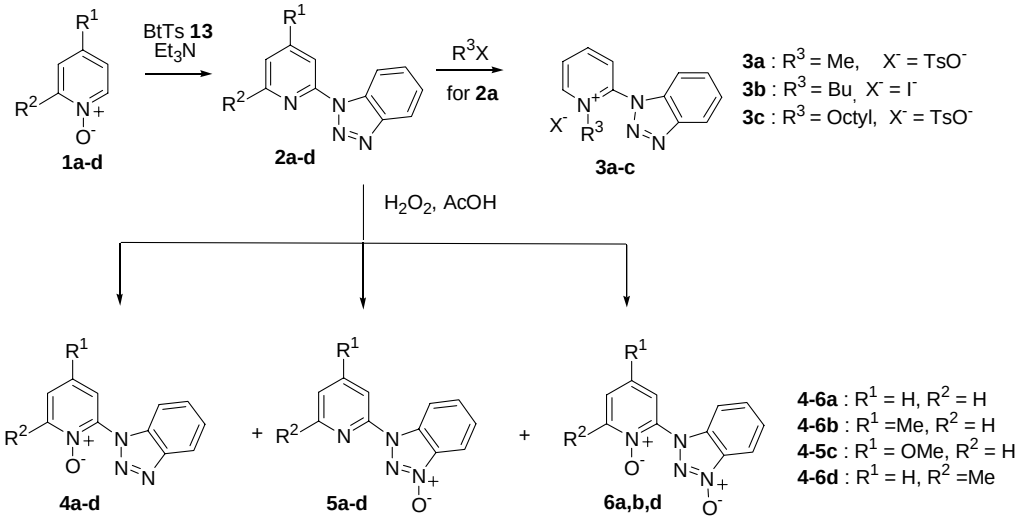
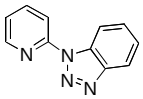
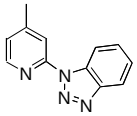
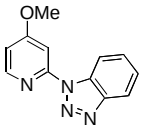
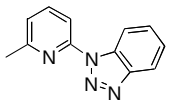
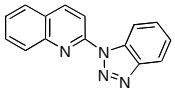
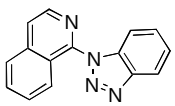


Table 1. Preparation of α-benzotriazolyl-pyridines, -quinoline and –isoquinoline (2a-d,8,11), benzotriazole 3-*N*-oxides (5a-d,9), pyridine-*N*-oxides (4a-d) and –isoquinoline-*N*-oxide (12), and bis-*N*-oxides (6a,b,d).

	2 (or **8, 11**)	Yield (%)	Yield (%)			
			4a-d or **(12)**	**5a-d** or **(9)**	**6a,b,d**	Recovered SM
2a		84	20	26	5	22
2b		67	21	28	4	20
2c		64	14	29	-	25
2d		58	21	31	2	21
8		77	-	27	-	25
11		92	12	-	-	4

The structures of the bis-*N*-oxides (**6a,b,d**) were based on ^{1}H, ^{13}C NMR spectra and CHN analysis. The chemical shifts of the α-protons in the pyridine ring and H-4 protons in the benzotriazole ring were assigned by homonuclear decoupling experiments. Oxidation at the pyridine nitrogen and at the benzotriazole *N*-3 position causes upfield shifts of the α-protons in the pyridine ring and the H-4 protons in the benzotriazole ring of compounds (**6a,b,d**), respectively. For example, the α-proton in the pyridine ring is shifted upfield from 8.62 ppm (ddd, J = 0.9, 1.8, 5.0 Hz, 1H) in the starting material (**2a**) to 8.43 ppm (m, 1H) in the bis-*N*-oxide (**6a**). The benzotriazole H-4 proton at 8.66 ppm (dt, J = 8.5, 0.9 Hz, 1H) in **2a** is shifted upfield to 8.05 (d, J = 8.8 Hz, 1H) in **6a**.

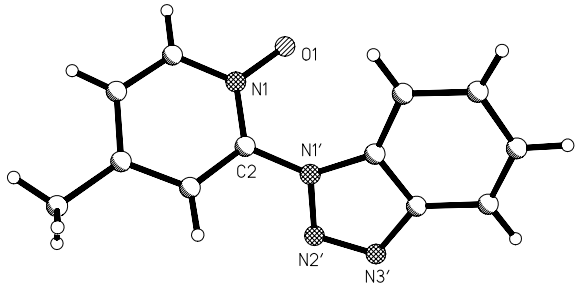


Figure 1. Perspective view of the X-Ray crystal structure of **4b**.

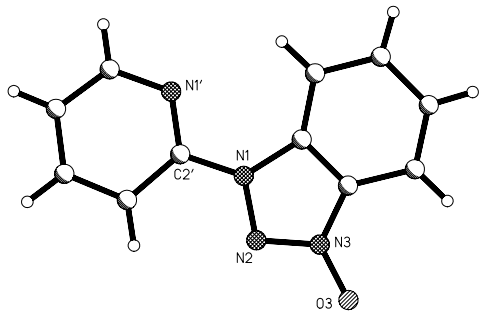
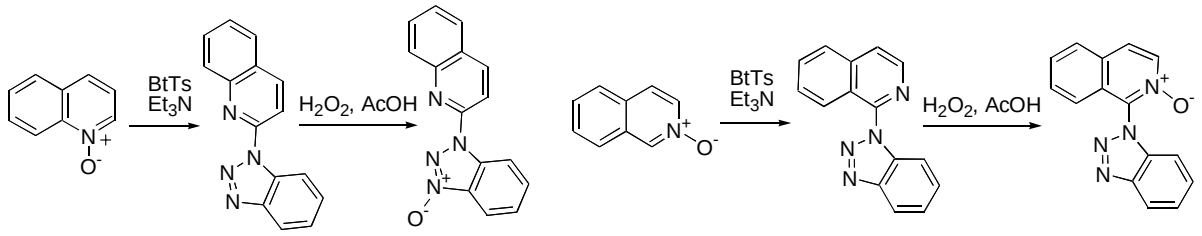


Figure 2. Perspective view of the X-Ray crystal structure of **5a**.



7 **8** **9** **10** **11** **12**

Scheme 2

In contrast to the behavior of **2a-d**, the reactions of 2-benzotriazolylquinoline (**8**) and 1-benzotriazolylisoquinoline (**11**) with hydrogen peroxide in glacial acetic acid led only to a single product the benzotriazole *N*-3-oxide (**9**) or the isoquinoline 2-oxide (**12**) (Scheme 2). While 1-(2-quinolinyl)-1*H*-1,2,3-benzotriazole 3-*N*-oxide (**9**) was formed from **8** in 27% yield**,** the corresponding reaction of **11** gave a complex mixture from which only 12% of 1-(1*H*-1,2,3-benzotriazol-1-yl)-isoquinoline-*N*-oxide (**12**) was isolated. Once again the benzotriazole *N*-3-oxide (**9**) (Figure 3) has the two ring systems approximately coplanar (12.8 ^{o}), whereas the isoquinoline *N*-oxide (**12**) (Figure 4) has the rings inclined at an angle of 46.7 ^{o}, in order to minimize steric interactions.

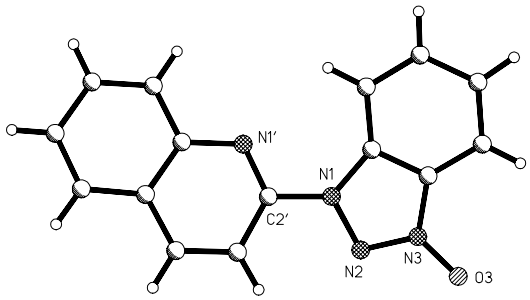


Figure 3. Perspective view of the X-Ray crystal structure of **9**.

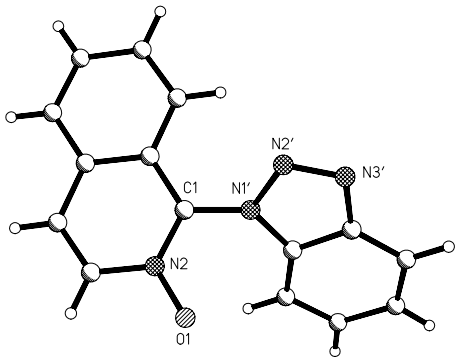


Figure 4. Perspective view of the X-Ray crystal structure of **12**.

***N*-Alkylation.** Compound (**2a**) was converted into pyridinium salts (**3a-c**) by treatment with the corresponding alkyl halides or tosylates in 45-82% yields.[4b] Tosylates turned out to be superior alkylating agents to the corresponding halides. For example **3a** was prepared from **2a** and methyl *p*-toluenesulfonate at 140 ºC in 82% yield, while the analogous iodide was obtained in only 7% from **2a** and methyl iodide. Prolonged reaction with butyl iodide in refluxing acetonitrile afforded **3b** in 45% yield. The alkylation of **2a** with octyl bromide even in the presence of NaI afforded only traces of pyridinium salt (**3c**). However, **3c** was prepared using octyl *p*-toluenesulfonate in 55% yield. The structure of **3a** was determined on the basis of NOE experiments which indicated that the methyl group was located on the pyridine nitrogen instead of benzotriazole. For example, the interaction between *N*-CH_3 group and the α-proton (δ 8.66, d, J = 4.7 Hz) of the pyridine ring was displayed when the *N*-methyl protons at δ 4.88 (s) ppm were irradiated. The structures of **3b** and **3c** were assigned by comparing their NMR spectra with those of **3a**, **2b** and **2c,** respectively.

In summary, α-benzotriazolylpyridines, -quinoline and –isoquinoline were prepared by reactions of pyridine-, quinoline-, and isoquinoline *N*-oxides with 1-tosylbenzotriazole (**13**)[5] in the presence of triethylamine in 58-92% yields. Reactions of α-benzotriazolylpyridines with peracetic acid afforded pyridine *N*-oxides (**4a-d**), benzotriazole 3-*N*-oxides (**5a-d**) and the bis-*N*-oxides (**6a,b,d**). Treatment of 2-(benzotriazol-1-yl)quinoline (**8**) and 1-(benzotriazol-1-yl)isoquinoline (**11**) with hydrogen peroxide in glacial acetic acid under similar conditions led to 1-(2-quinolinyl)-1*H*-1,2,3-benzotriazole 3-*N*-oxide (**9**) and 1-(1*H*-1,2,3-benzotriazol-1-yl)isoquinoline *N*-oxide (**12**), respectively. The structures of **4b, 5a**, **9** and **12** were determined by X-Ray crystallography. *N*-Alkylation of α-benzotriazolylpyridines by alkyl halides or tosylates yielded the corresponding α-benzotriazolyl *N*-alkylpyridinium salts (**3a-c**)**.**

EXPERIMENTAL

General Methods. Melting points were determined on a MEL-TEMP capillary melting point apparatus equipped with a Fluke 51 digital thermometer. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with tetramethylsilane as the internal standard for ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR. All reactions with air-sensitive compounds were carried out under argon atmosphere. Octyl *p*-toluenesulfonate was synthesized according to a literature procedure.[4c] 1-Tosylbenzotriazole (**13**)[5] was prepared according to a modified procedure.

Modified Procedure for the Preparation of 1-Tosylbenzotriazole (13). To an ice-cold solution of benzotriazole (23.8 g, 0.20 mol) and triethylamine (22.3 g, 0.22 mol) in dry dichloromethane (350 mL), a solution of *p*-toluenesulfonyl chloride (38.1 g, 0.2 mol) in dichloromethane (150 mL) was added dropwise. The mixture was stirred overnight at rt and then heated under reflux for 2 h. The organic layer was

washed with water and dried over anhydrous $MgSO_4$. Removal of the solvents *in vacuo* gave a solid, which was recrystallized from dichloromethane / hexane to afford 1-tosylbenzotriazole (**13**) (44.8 g, 82%) as colorless prisms: mp 133-135 °C (lit.,[5] 134-135 °C).

General Procedure for the Preparation of Compounds (2a-d, 8 and 11). 1-Tosylbenzotriazole (**13**) (328 mg, 1.2 mmol) was heated under reflux with the appropriate *N*-oxide (1 mmol) in toluene (20 mL) in the presence of a stoichiometric amount of triethylamine. After 24 h, the reaction mixture was washed with water, dried and concentrated to yield a greenish solid. Recrystallization (from toluene in the case of **2a**, otherwise over diethyl ether / hexane) afforded the desired products as white solids. In the cases of **2d** and **10**, the reaction mixture was purified by flash chromatography with methylene chloride as an eluent.

1-(2-Pyridinyl)benzotriazole (**2a**). White microprisms from toluene (84%), mp 106–108 °C (lit.,[1c] 108-110 °C); ^{1}H NMR δ 7.33 (ddd, *J* = 1.2, 5.0, 7.6 Hz, 1H), 7.45 (ddd, *J* = 1.0, 7.0, 8.2 Hz, 1H), 7.61 (ddd, *J* = 1.1, 7.0, 8.2 Hz, 1H), 7.94 (ddd, *J* = 2.1, 7.6, 8.5 Hz, 1H), 8.13 (dt, *J* = 1.0, 8.3 Hz, 1H), 8.30 (dt, *J* = 1.1, 8.3 Hz, 1H), 8.62 (ddd, *J* = 0.9, 1.8, 5.0 Hz, 1H), 8.66 (dt, *J* = 0.9, 8.5 Hz, 1H); ^{13}C NMR δ 114.4, 114.8, 119.7, 122.2, 124.8, 128.7, 131.4, 138.8, 146.7, 148.3, 151.6; Anal. Calcd for $C_{11}H_8N_4$: C, 67.33; H, 4.12; N, 28.55; Found: C, 67.20; H, 4.00; N, 28.79.

1-(4-Methyl-2-pyridinyl)benzotriazole (**2b**). White needles from ether / hexane (67%), mp 112–114 °C (lit.,[6] 118-119.5 °C); ^{1}H NMR δ 2.23 (s, 3H), 6.83 (d, *J* = 4.9 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.86 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 8.17 (d, *J* = 4.9 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR δ 21.0, 114.3, 114.8, 119.3, 123.1, 124.5, 128.4, 131.3, 146.4, 147.6, 150.0, 151.4. Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.55; H, 4.80; N, 26.66; Found: C, 68.48; H, 4.60; N, 26.49.

1-(4-Methoxy-2-pyridyl)benzotriazole (**2c**). White needles from ether / hexane (64%), mp 120–121 °C; ^{1}H NMR δ 3.99 (s, 3H), 6.86 (dd, *J* = 2.2, 5.7 Hz, 1H), 7.45 (ddd, *J* = 1.1, 7.2, 8.2 Hz, 1H), 7. 60 (ddd, *J* = 1.0, 7.3, 8.3 Hz, 1H), 7.82 (d, *J* = 2.2 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 4.4 Hz, 1H), 8.66 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR δ 55.7, 98.9, 110.3, 115.0, 119.7, 124.8, 128.7, 131.7, 146.8, 149.2, 153.3, 167.6; Anal. Calcd for $C_{12}H_{10}N_4O$: C, 63.71; H, 4.46; N, 24.76. Found: C, 63.69; H, 4.46; N, 24.81.

1-(6-Methyl-2-pyridinyl)benzotriazole (**2d**). White microprisms from ether / hexane (54%), mp 83–84 °C (lit.,[6] 84-85 °C); ^{1}H NMR δ 2.73 (s, 3H), 7.19–7.22 (m, 1H), 7.53–7.55 (m, 1H), 7.67–7.69 (m, 1H), 7.85–7.88 (m, 1H), 8.14–8.22 (m, 2H), 8.75 (t, *J* = 5.3 Hz, 1H); ^{13}C NMR δ 22.5, 110.9, 114.9, 119.5, 121.4, 124.6, 128.4, 131.4, 138.8, 146.6, 150.9, 157.6; Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.55; H, 4.80; N, 26.66; Found: C, 68.39; H, 4.74; N, 26.29.

2-(Benzotriazol-1-yl)quinoline (**8**). White microprisms from ether / hexane (77%), mp 143–144 °C (lit.,[7] 145-146 °C); ^{1}H NMR δ 7.48 (ddd, *J* = 1.0, 7.0, 8.2 Hz, 1H), 7.54 (ddd, *J* = 1.2, 7.0, 8.1 Hz, 1H), 7.65 (ddd, *J* = 1.1, 7.0, 8.4 Hz, 1H), 7.75 (ddd, *J* = 1.4, 7.0, 8.4 Hz, 1H), 7.84 (dd, *J* = 0.9, 8.1 Hz, 1H), 8.11 (dd, *J* = 0.9, 7.8 Hz, 1H), 8.14 (dd, *J* = 0.8, 8.4 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 8.8 Hz, 1H), 8.92 (dd, *J* = 1.0, 8.4 Hz, 1H); ^{13}C NMR δ 113.3, 115.4, 119.8, 125.1, 126.6, 127.0, 127.7, 128.7, 128.9, 130.4, 131.6, 139.1, 146.4, 146.9, 150.4; Anal. Calcd for $C_{15}H_{10}N_4$: C, 73.16; H, 4.09; N, 22.75; Found: C, 73.30; H, 4.08; N, 22.80.

1-(Benzotriazol-1-yl)isoquinoline (**11**). White micro-prisms (92%) from diethyl ether / hexane, mp 158–159 °C (lit.,[8] 159-160 °C); ^{1}H NMR δ 7.48 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.60 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.69 (dd, *J* = 7.6, 7.9 Hz, 1H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 5.9 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 5.6 Hz, 1H), 8.60 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR δ 112.8, 119.8, 121.9, 122.8, 124.8, 126.2, 126.9, 128.6, 128.7, 131.1, 133.3, 138.8, 140.6, 145.8, 148.1. HRMS (FAB) $[M+H]^+$ Calcd for $C_{15}H_{11}N_{14}$: 247.0948. Found: 247.0964.

General Procedure for the Preparation of Compounds (3a,c). 1-(2-Pyridinyl)-1*H*-1,2,3-benzotriazole (**2a)** (980 mg, 5 mmol) was heated neat with the appropriate alkyl *p*-toluenesulfonate (5 mmol) for 24 h at 140 °C. The reaction mixture was purified by flash chromatography with acetone as an eluent. Concentration of the acetone eluate yielded the corresponding *N*-alkylpyridinium salt.

2-(Benzotriazol-1-yl)-1-methylpyridinium *p*-toluenesulfonate (**3a**). White microprisms from 2-propanol / ether (82%), mp 132–133 °C; ^{1}H NMR δ 2.17 (s, 3H), 4.88 (s, 3H), 6.86 (d, *J* = 7.8 Hz, 2H),

7.46 (d, *J* = 7.9 Hz, 2H), 7.60 (dd, *J* = 5.0, 7.5 Hz, 1H), 7.80–7.90 (m, 2H), 8.09 (t, *J* = 7.9 Hz, 1H), 8.25 (d, *J* = 7.9 Hz, 1H), 8.42 (d, *J* = 7.8 Hz, 1H), 8.66 (d, *J* = 4.7 Hz, 1H), 8.75 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR δ 21.0, 39.4, 114.8, 116.7, 116.8, 125.6, 126.2, 128.0, 131.4, 132.4, 132.9, 136.2, 138.3, 140.4, 144.0, 148.7, 148.8; Anal. Calcd for $C_{19}H_{18}N_4O_3S$: C, 59.67; H, 4.74; N, 14.65; Found: C, 59.27; H, 4.74; N, 14.26.

2-(Benzotriazol-1-yl)-1-octylpyridinium *p*-toluenesulfonate (**3c**). White microprisms from 2-propanol / ether (55%), mp 65 °C; ^{1}H NMR δ 0.84 (t, *J* = 6.1 Hz, 3H), 1.22–1.35 (m, 10H), 2.10–2.21 (m, 2H), 2.22 (s, 3H), 5.30 (t, *J* = 6.8 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.65 (dd, *J* = 5.0, 7.3 Hz, 1H), 7.85–7.94 (m, 2H), 8.15 (dd, *J* = 7.6, 8.1 Hz, 1H), 8.29 (d, *J* = 8.1 Hz, 1H), 8.51 (d, *J* = 8.8 Hz, 1H), 8.71 (d, *J* = 4.5 Hz, 1H), 8.81 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR δ 13.9, 21.0, 22.4, 26.2, 28.7, 28.8, 29.0, 31.5, 53.3, 114.8, 116.8, 116.9, 125.7, 126.3, 128.0, 131.6, 132.6, 133.0, 135.6, 138.3, 140.5, 144.1, 148.8; HRMS (FAB) $[M-H]^+$ Calcd for $C_{19}H_{25}N_4$ (2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-octylpyridinium): 309.2079. Found: 309.2096.

Procedure for the Preparation of Compound 3b. 1-(2-Pyridinyl)-1*H*-1,2,3-benzotriazole (**2a)** (196 mg, 1 mmol) was heated under reflux with iodobutane (202 mg, 1.1 mmol) in acetonitrile (5 mL) for 48 h. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography with acetone as an eluent. Concentration of the acetone solution yielded the corresponding *N*-butyl pyridinium salt.

2-(Benzotriazol-1-yl)-1-butylpyridinium iodide (**3b**). Black prisms from 2-propanol / ether (45%), mp 87–89 °C; ^{1}H NMR δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.75–1.83 (m, 2H), 2.46–2.54 (m, 2H), 5.38 (t, *J* = 7.4 Hz, 2H), 7.89–7.93 (m, 1H), 8.24–8.39 (m, 2H), 8.35–8.51 (m, 2H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.99 (d, *J* = 4.4 Hz, 1H), 9.26 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR δ 13.4, 19.7, 30.7, 53.4, 113.6, 116.6, 118.1, 126.4, 132.2, 133.0, 133.1, 135.3, 140.4, 148.5, 149.0; HRMS (FAB) $[M+H]^+$ Calcd for $C_{15}H_{17}N_4$: 253.1453. Found: 253.1457.

General Procedure for the Preparation of Compounds (4, 5, 6, 9 and 12). A solution of **2a-d, 8** or **11** (10 mmol) in a mixture of 30% hydrogen peroxide (7.5 mL, 66 mmol) and glacial acetic acid (5 mL) was heated under reflux over 30 h. The reaction mixture was concentrated and extracted with methylene chloride. The organic layer was washed with saturated sodium bicarbonate solution, dried and concentrated again. The resulting residue was purified by flash chromatography using methylene chloride, ethyl acetate, and acetone as eluents. Recrystallization from the appropriate solvent afforded the corresponding products.

2-(Benzotriazol-1-yl)pyridine *N*-oxide (**4a**). White needles from ethyl acetate / acetone (20%), mp 178–179 °C; ^{1}H NMR δ 7.44–7.49 (m, 3H,), 7.59 (t, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 4.6 Hz, 1H,), 8.14 (d, *J* = 8.2 Hz, 1H), 8.46 (dd, *J* = 4.4, 3.4 Hz, 1H); ^{13}C NMR δ 113.5, 120.1, 124.7, 125.7, 128.6, 133.1, 140.5, 143.2, 145.9; Anal. Calcd for $C_{11}H_8N_4O$: C, 62.26; H, 3.80; N, 26.40. Found: C, 62.41; H, 3.78; N, 26.48.

2-(Benzotriazol-1-yl)-4-methylpyridine *N*-oxide (**4b**). White needles from ethyl acetate / acetone (21%), mp 182 °C; ^{1}H NMR δ 2.46 (s, 3H), 7.25 (dd, *J* = 2.4, 6.7 Hz, 1H), 7.45 (ddd, *J* = 1.1, 8.3, 7.0 Hz, 1H), 7.57 (ddd, *J* = 0.9, 8.1, 7.3 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 6.7 Hz, 1H); ^{13}C NMR δ 20.6, 113.9, 120.3, 124.9, 125.4, 127.0, 128.9, 133.5, 138.3, 139.9, 142.5, 146.2; Anal. Calcd for $C_{12}H_{10}N_4O$: C, 63.71; H, 4.46; N, 24.76. Found: C, 63.55; H, 4.43; N, 24.66.

Crystal data for 4b: $C_{12}H_{10}N_4O$, MW 226.24, orthorhombic, space group $P2_12_12_1$, *a* = 7.592(6), *b* = 11.741(9), *c* = 12.236(9) Å, V = 1091(1) Å^3, F(000) = 472, Z = 4, T = -105 ^{o}C, μ (MoKα) = 0.094 mm^{-1}, D_{calcd} = 1.378 g.cm^{-3}, $2\theta_{max}$ 46^o (CCD area detector, MoKα radiation), GOF = 1.05, wR(F^2) = 0.1868 (all 1513 data), R = 0.0693 (1107 data with I > 2σI). Selected bonding geometry: O1-N1, 1.312(5); N1-C2, 1.353(6); C2-N1', 1.406(6); N1'-N2', 1.399(6); N2'-N3', 1.301(6) Å; O1-N1-C2, 121.4(4); N1-C2-N1', 118.9(4); C2-N1'-N2', 117.8(4); N1'-N2'-N3', 108.6(4) ^{o}; N1-C2-N1'-N2', 132.9(4) ^{o}.

2-(Benzotriazol-1-yl)-4-methoxypyridine *N*-oxide (**4c**). Pale yellow needles from ethyl acetate / acetone (14%), mp 185 °C; ^{1}H NMR (DMSO-d_6) δ 3.94 (s, 3H), 7.32–7.36 (m, 1H), 7.50–7.55 (m, 1H),

7.61–7.65 (m, 2H), 7.70 (d, *J* = 3.3 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.48 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 55.9, 111.0, 113.0, 114.1, 119.5, 124.7, 128.5, 133.1, 140.7, 141.5, 144.9, 156.6; Anal. Calcd for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13. Found: C, 59.36; H, 3.98; N, 23.05.

2-(Benzotriazol-1-yl)-6-methylpyridine *N*-oxide (**4d**). White needles from ethyl acetate / acetone (21%), mp 214 °C; ^{1}H NMR δ 2.65 (s, 3H), 7.35 (dd, *J* = 7.8, 7.9 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.56 (dd, *J* = 6.9, 8.0 Hz, 1H), 7.61 (s, 1H), 7.66 (dd, *J* = 7.9. 7.1 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR δ 18.0, 113.4, 120.1, 122.2, 124.5, 124.6, 126.1, 128.5, 133.3, 143.1, 145.5, 150.7; Anal. Calcd for $C_{12}H_{10}N_4O_2$: C, 63.71; H, 4.46; N, 24.76. Found: C, 63.89; H, 4.71; N, 24.80.

1-(Benzotriazol-1-yl)isoquinoline *N*-oxide (**12**). Yellow prisms from ethyl acetate / acetone (12%), mp 185 °C; ^{1}H NMR (DMSO-d_6) δ 7.33 (d, *J* = 8.2 Hz, 1H), 7.69–7.92 (m, 5H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 7.3 Hz, 2H), 8.81 (d, *J* =7.3 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 111.6, 119.8, 121.4, 124.9, 126.0, 127.2, 127.6, 128.7, 129.0, 131.0, 133.5, 136.2, 137.4, 144.9; HRMS (FAB) $[M+H]^+$ Calcd for $C_{15}H_{11}N_4O$: 263.0932. Found: 263.0928.

Crystal data for 12: $C_{15}H_{10}N_4O$, MW 262.27, orthorhombic, space group $Pca2_1$, *a* = 25.664(19), *b* = 3.964(3), *c* = 11.546(8) Å, V = 1175(2) Å^3, F(000) = 544, Z = 4, T = -105 ^{o}C, μ (MoKα) = 0.099 mm^{-1}, D_{calcd} = 1.483 g.cm^{-3}, $2\theta_{max}$ 53^o (CCD area detector, MoKα radiation), GOF = 1.09, wR(F^2) = 0.1297 (all 1747 data), R = 0.0528 (1465 data with I > 2σI). Selected bonding geometry: O1-N2, 1.301(4); N2-C1, 1.350(5); C1-N1', 1.403(4); N1'-N2', 1.393(4); N2'-N3', 1.283(4) Å; O1-N2-C1, 121.6(3); N2-C1-N1', 115.9(3); C1-N1'-N2', 120.7(3); N1'-N2'-N3', 108.7(3) ^{o}; N1-C2-N1'-N2', 126.7(3) ^{o}.

1-(2-Pyridyl)-benzotriazole 3-*N*-oxide (**5a**). White microprisms from ethyl acetate (26%), mp 172–173 °C; ^{1}H NMR δ 7.29 (ddd, *J* = 1.6, 5.0, 6.6 Hz 1H,), 7.50 (dt, *J* = 0.6, 7.2 Hz, 1H), 7.72 (dt, *J* = 1.0, 7.2 Hz, 1H), 7.86-7.94 (m, 2H), 8.04 (d, *J* = 8.5 Hz, 1H), 8.55 (d, *J* = 4.7 Hz, 1H), 8.81 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR 113.0, 115.1, 116.4, 121.8, 125.4, 131.5, 131.8, 132.4, 139.0, 148.0, 150.3; Anal. Calcd for $C_{11}H_8N_4O$: C, 62.26; H, 3.80; N, 26.40. Found: C, 62.42; H, 3.81; N, 26.49.

Crystal data for 5a: $C_{11}H_8N_4O$, MW 212.21, orthorhombic, space group $Pca2_1$, *a* = 7.312(4), *b* = 12.442(7), *c* = 21.003(12) Å, V = 1911(2) Å^3, F(000) = 880, Z = 8, T = -110 ^{o}C, μ (MoKα) = 0.101 mm^{-1}, D_{calcd} = 1.475 g.cm^{-3}, $2\theta_{max}$ 50^o (CCD area detector, MoKα radiation), GOF = 0.95, wR(F^2) = 0.1719 (all 3359 data), R = 0.0587 (2097 data with I > 2σI). Selected bonding geometry [and for the other independent molecule]: O3-N3, 1.295(6) [1.284(6)]; N1-N2, 1.362(6) [1.370(6)]; N2-N3, 1.317(6) [1.327(7)]; N1-C2', 1.391(10) [1.477(10)]; N1'-C2', 1.316(6) [1.326(6)] Å; O3-N3-N2, 121.2(4) [121.7(5)]; N1-N2-N3, 105.0(4) [104.5(4)]; N2-N1-C2', 119.8(4)[118.0(4)]; N1-C2'-N1', 117.1(7) [112.1(7)] ^{o}; N2-N1-C2'-N1', 177.4(5) [176.6(5)] ^{o}.

1-(4-Methyl-2-pyridyl)benzotriazole 3-*N*-oxide (**5b**). White microprisims from ethyl acetate / acetone (28%), mp 198–200°C; ^{1}H NMR δ 2.47 (s, 3H), 7.10 (d, *J* = 5.1 Hz, 1H), 7.51 (dt, *J* = 0.9, 7.4 Hz, 1H), 7.71 (dt, *J* = 1.1, 7.4 Hz, 1H), 7.78 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 4.9 Hz, 1H), 8.80 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR δ 21.6, 113.9, 115.4, 116.8, 123.3, 125.6, 131.8, 132.1, 132.9, 148.0, 150.8, 151.0; Anal. Calcd for $C_{12}H_{10}N_4O$: C, 63.71; H, 4.46; N, 24.76. Found: C, 63.64; H, 4.22; N, 24.74.

1-(4-Methoxy-2-pyridyl)benzotriazole 3-*N*-oxide (**5c**). White microprisims from ethyl acetate / acetone (29%), mp 194 °C; ^{1}H NMR δ 3.94 (s, 3H), 6.79 (dd, *J* = 2.2, 5.7 Hz, 1H), 7.42 (d, *J* = 2.2 Hz, 1H), 7.48 (dt, *J* = 0.9, 7.1 Hz, 1H), 7.70 (ddd, *J* = 1.1, 7.1, 8.4 Hz, 1H), 8.01 (td, *J* = 0.9, 8.5 Hz, 1H), 8.30 (d, *J* = 5.7 Hz, 1H), 8.78 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR δ 55.7, 97.5, 110.5, 115.1, 116.6, 125.4, 131.5, 131.8, 132.7, 148.9, 151.9, 167.7; HRMS (FAB) Calcd for $C_{12}H_{11}N_4O_2$: $[M+H]^+$ 243.0882. Found: 243.0882.

1-(6-Methyl-2-pyridyl)benzotriazole 3-*N*-oxide (**5d**). White microprisms from ethyl acetate / acetone (31%), mp 178 °C; ^{1}H NMR (DMSO-d_6) δ 2.61 (s, 3H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.55–7.63 (m, 2H), 7.83 (t, *J* = 8.2 Hz, 1H), 7.91–8.01 (m, 2H), 8.72 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 23.7, 109.6, 114.9, 116.1, 121.4, 125.6, 131.3, 131.9, 140.0, 149.1, 157.5; Anal. Calcd for $C_{12}H_{10}N_4O_2$: C, 63.71; H, 4.46; N, 24.76. Found: C, 64.01; H, 4.75; N, 24.75.

1-(2-Quinolinyl)-benzotriazole 3-*N*-oxide (**9**). Red prisms from ethyl acetate / acetone (28%), mp 216 °C; ^{1}H NMR δ 7.66–7.74 (m, 2H), 7.90–8.00 (m, 3H), 8.12–8.23 (m, 3H), 8.46 (d, *J* = 9.0 Hz, 1H),

9.21 (d, = 8.6 Hz, 1H); ^{13}C NMR δ 112.2, 1153, 116.9, 125.7, 126.6, 126.7, 127.8, 128.3, 130.7, 131.7, 132.2, 132.7, 139.5, 146.2, 149.0; Anal. Calcd for $C_{15}H_{10}N_4O$: C, 68.69; H, 3.84; N, 21.36. Found: C, 68.32; H, 3.60; N, 21.32.

Crystal data for 9: $C_{15}H_{10}N_4O$, MW 262.27, monoclinic, space group C2/c, *a* = 11.887(4), *b* = 9.442(3), *c* = 21.993(7) Å, *β* = 98.234(5) ^{o}, V = 2443(1) Å^3, F(000) = 1088, Z = 8, T = -110 ^{o}C, μ (MoKα) = 0.095 mm^{-1}, D_{calcd} = 1.426 g.cm^{-3}, $2\theta_{max}$ 53^o (CCD area detector, MoKα radiation), GOF = 1.06, wR(F^2) = 0.1124 (all 2474 data), R = 0.0408 (1965 data with I > 2σI). Selected bonding geometry: O3-N3, 1.281(2); N1-N2, 1.373(2); N2-N3, 1.311(2); N1-C2', 1.418(2); N1'-C2', 1.313(2) Å; O3-N3-N2, 122.5(1); N1-N2-N3, 105.5(1); N2-N1-C2', 118.7(1); N1-C2'-N1', 115.0(1) ^{o}; N2-N1-C2'-N1', 171.1(1).

3-(1-Oxido-2-pyridiniumyl)-3*H*-1,2,3-benzotriazol-1-ium-1-olate (6a). White microprisms from acetone (5%), mp 237 °C; ^{1}H NMR δ 7.43–7.53 (m, 3H,), 7.68–7.70 (m, 2H), 7.74–7.77 (m, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 8.41–8.44 (dd, *J* = 2.1, 5.4 Hz, 1H); ^{13}C NMR δ 115.8, 116.3, 124.8, 125.6, 125.8, 126.8, 127.0, 131.5, 132.0, 135.1, 141.0; Anal. Calcd for $C_{11}H_8N_4O_2$: C, 57.89; H, 3.53; N, 24.55. Found: C, 57.56; H, 3.50; N, 24.27.

3-(4-Methyl-1-oxido-2-pyridiniumyl)-3*H*-1,2,3-benzotriazol-1-ium-1-olate (6b). White microprisms from acetone (4%), mp 240 °C; ^{1}H NMR δ 2.46 (s, 3H), 7.23 (d, *J* = 6.5 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.56 (s, 1H), 7.64–7.74 (m, 2H), 8.03 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 6.7 Hz, 1H); ^{13}C NMR δ 20.6, 115.4, 116.1, 124.7, 125.1, 126.2, 131.0, 131.7, 134.8, 138.2, 139.8, 141.2; Anal. Calcd for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13. Found: C, 59.27; H, 4.17; N, 22.90.

3-(6-Methyl-1-oxido-2-pyridiniumyl)-3*H*-1,2,3-benzotriazol-1-ium-1-olate (6d). White microprisms from acetone (2%), mp 235 °C; ^{1}H NMR δ 2.65 (s, 3H), 7.34 (dd, J = 7.9, 8.0 Hz, 1H), 7.42–7.51 (m, 2H), 7.61–7.70 (m, 3H), 8.04 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR δ 18.0, 115.5, 116.0, 122.0, 124.8, 125.0, 125.8, 130.9, 131.7, 134.9, 142.0, 150.9; HRMS (FAB) Calcd for $C_{12}H_{10}N_4O_2$: 243.0882. Found: 243.0892.

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