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# 1,2,4-Triazolo[1,2-*a*]benzotriazoles: first examples of a novel ring system

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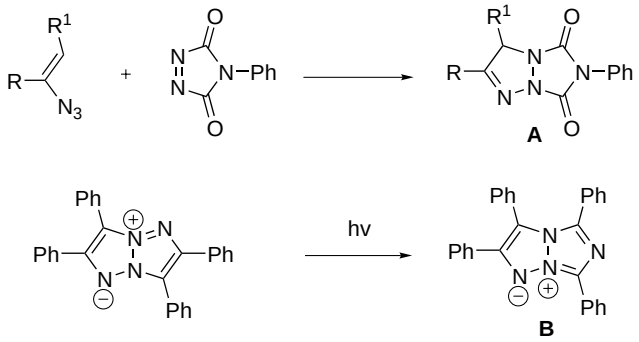
**Abstract**—α-Benzotriazolylamides **6a–d** afforded *N*-(benzotriazol-1-ylmethyl)arylimidoyl chlorides (**4a–d**), which reacted in situ with potassium *tert*-butoxide to form 3-aryl-1,2,4-triazolo[1,2-*a*]benzotriazoles (**7a–d**) (44–68%), representatives of a novel heterocyclic system. The structure of **7a** was confirmed by single crystal X-ray analysis. © 2001 Elsevier Science Ltd. All rights reserved.

1,2,4-Triazolo[1,2-*a*]benzotriazoles represent, to the best of our knowledge, a previously unreported non-classical tricyclic ring system. The few known bicyclic 1,2,4-triazolo[1,2-*a*]-1,2,3-triazoles (Scheme 1) were prepared: (i) by cycloaddition of 4-phenyl-1,2,4-triazoline-3,5-dione and vinyl azides to give **A**,[1] and (ii) by photoisomerization of 1,2,3-triazolo[1,2-*b*]-1,2,3-triazoles to give **B**.[2] We now disclose the first syntheses of 1,2,4-triazolo[1,2-*a*]benzotriazoles (**7a–d**).

*N*-(Benzotriazol-1-ylmethyl)arylimidates, **2** and **4**, are versatile synthetic building blocks: **2** cyclizes to give pyrroles (**1**)[3a,b] and imidazoles (**3**),[3b] while **4** produces pyrroles (**1**)[3c] or rearranges into 1,2,4-triazolo[1,5-*a*]quinoxalines (**5**)[3c] (Scheme 2).




**Scheme 1.**

In further exploration of their synthetic utility, *N*-(benzotriazol-1-ylmethyl)arylimidoyl chlorides (**4a–d**), (prepared in situ from the corresponding α-benzotriazolyl amides **6a–d**,[4a,b,c]) were reacted with potassium *tert*-butoxide. We now report that this gives 2-aryl-1,2,4-triazolo[1,2-*a*]benzotriazoles **7a–d** (44–68%) (Scheme 3).

The transformations of **4a–d** into **7a–d** (Scheme 3) probably involve proton abstraction to furnish carbanion **9**, which eliminates chloride to form nitrile ylide **10**. Intramolecular 8-electron electrocyclic rearrangement of **10** gives 1,2,4-triazolo[1,2-*a*]benzotriazoles **7a–d**. Nitrile ylide species are known to be formed on addition of a carbene to acetonitriles[5a] or on photo-rearrangement of 2H-azirines.[5b]

Structure **7a** was confirmed by X-ray crystallography[6] (Fig. 1) and is compatible with the $^{1}H$ and $^{13}C$ NMR spectra.[7] The structures of compounds **7b–d**[7] were assigned by analogy and by spectroscopic data comparisons. Inspection of the bond lengths shown in Fig. 1, reveals that these compounds should not be represented by a single resonance contributor, and that there is an important contribution from resonance structures **8a–d** (Scheme 3). The crystal structure determination shows that the 1,2,4-triazolo[1,2-*a*]benzotriazole ring system is planar [average deviation from the plane = 0.011 Å]. Interestingly, the attached phenyl ring is almost coplanar with the triazolobenzotriazole ring system [angle between meanplanes = 6.2°].

*Keywords*: benzotriazole; heterocyclic betaines; crystal structure.

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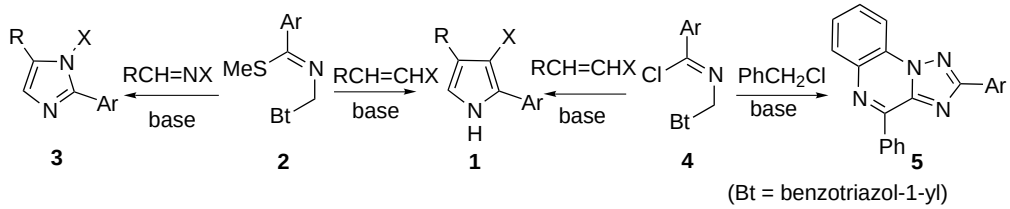
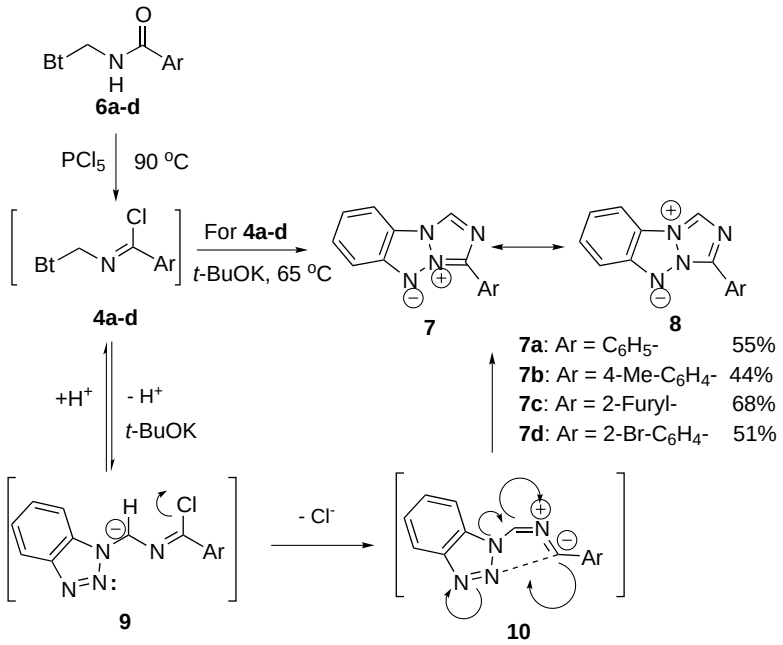



**Scheme 2.**




**Scheme 3.**

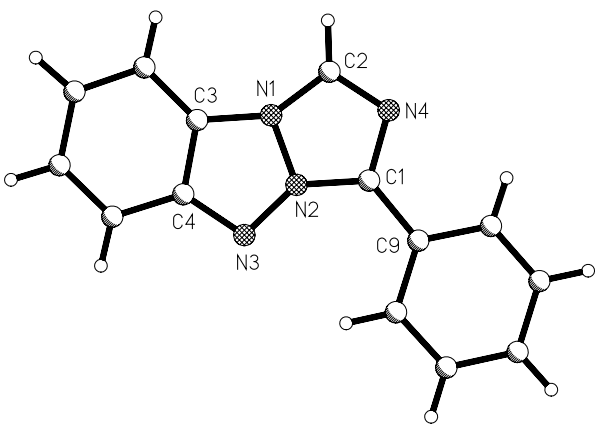



**Figure 1.** Perspective view and partial atom labeling of the X-ray crystal structure of **7a**. Selected bond distances (Å): N(1)–C(2) 1.354(2); N(1)–N(2) 1.381(2); N(1)–C(3) 1.384(2); N(2)–N(3) 1.354(2); N(2)–C(1) 1.354(2); N(3)–C(4) 1.373(2); N(4)–C(2) 1.315(2); N(4)–C(1) 1.356(2); C(1)–C(9) 1.449(2); C(3)–C(4) 1.409(2).

The nature of the Ar substituent in the starting amide (**6**) influences the reaction significantly: in **6c** (Ar = 2-furyl), the isolated yield of **7c** is 68%, compared with 44% for the *para*-tolyl derivative **7b**.

In conclusion: we have disclosed the first synthesis of 3-aryl-1,2,4-triazolo[1,2-*a*]benzotriazoles (**7a**–**d**) via a novel electrocyclic rearrangement in a one-pot protocol utilizing readily available starting materials.

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6. **Crystal Data for 7a**: $C_{14}H_{10}N_4$, $M_w$ 234.26, orthorhombic, space group $Pca2_1$, $a=17.278(5)$, $b=5.217(2)$, $c=12.286(4)$ Å, $V=1107.4(6)$ Å$^3$, $F(000)=488$, $Z=4$, $T=-105$°C, $\mu$ (Mo K$\alpha$) $=0.089$ mm$^{-1}$, $D_{calcd}=1.405$ g cm$^{-3}$, $2\theta_{max}$ 50° (CCD area detector, Mo K$\alpha$ radiation, 99.4% completeness), GOF $=1.039$, $wR(F^2)=0.0675$ (all 1934 data), $R=0.0261$ (1846 data with $I>2\sigma I$).
7. **Typical data for compounds 7a–d**. General procedure for the preparation of 3-aryl-1,2,4-triazolo[1,2-*a*]benzotriazoles (**7a–d**) from *N*-(benzotriazolylmethyl)arylamides (**6a–d**): *N*-(benzotriazol-1-ylmethyl)arylcarboxamide[4] (**6a–d**, 5 mmol) was dissolved in toluene (100 mL) and treated with phosphorus pentachloride (1.25 g, 6 mmol). The reaction mixture was heated at 90–100°C for 3 h, then it was filtered while hot, and the solvent and $POCl_3$ were removed under reduced pressure. The crude imidoyl chloride (**4a–d**) obtained was used in the subsequent reaction without additional purification. A mixture of crude imidoyl chloride (**4a–d**, 0.83 g, 3 mmol) in dry tetrahydrofuran (30 mL) was treated with potassium *tert*-butoxide (1.12 g, 10 mmol). The reaction mixture was stirred for 0.5 h at room temperature, heated under reflux for an additional 6 h, allowed to cool down and filtered. The residue obtained after solvent evaporation was purified by column chromatography (eluting with hexane/EtOAc = 6/1) to give the corresponding 3-aryl-1,2,4-triazolo[1,2-*a*]benzotriazoles (**7a–d**) as yellow needles. **3-Phenyl-1,2,4-triazolo[1,2-*a*]benzotriazole (7a)**: yellow needles (55%), mp 179–180°C; $^1$H NMR ($CDCl_3$): $\delta$ 6.99 (t, $J=7.5$ Hz, 1H), 7.32–7.42 (m, 2H), 7.48–7.59 (m, 3H), 7.65 (d, $J=8.2$ Hz, 1H), 8.36 (s, 1H), 8.47 (d, $J=7.4$ Hz, 2H); $^{13}$C NMR: $\delta$ 110.6, 114.4, 116.9, 118.0, 118.2, 125.1, 126.7, 126.9, 127.9, 128.4, 128.9, 149.3. Anal. calcd for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.86; H, 4.30; N, 23.87. **3-(4-Methylphenyl)-1,2,4-triazolo[1,2-*a*]-benzotriazole (7b)**: yellow needles (44%), mp 208–209°C; $^1$H NMR ($CDCl_3$): $\delta$ 2.42 (s, 3H), 7.03 (t, $J=7.7$ Hz, 1H), 7.34 (d, $J=8.1$ Hz, 2H), 7.43 (t, $J=7.8$ Hz, 1H), 7.60 (d, $J=7.8$ Hz, 1H), 7.70 (d, $J=8.1$ Hz, 1H), 8.39 (d, $J=8.4$ Hz, 2H), 8.41 (s, 1H); $^{13}$C NMR: $\delta$ 21.7, 110.7, 114.4, 117.0, 117.9, 118.2, 124.2, 125.2, 127.2, 128.0, 129.7, 138.6, 149.5. Anal. calcd for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57. Found: C, 72.51; H, 5.00; N, 22.62. **3-(2-Furyl)-1,2,4-triazolo[1,2-*a*]benzotriazole (7c)**: yellow needles (68%), mp 212–213°C; $^1$H NMR ($CDCl_3$): $\delta$ 6.66 (dd, $J=3.3$, 1.8 Hz, 1H), 7.10 (t, $J=7.8$ Hz, 1H), 7.31 (d, $J=3.3$ Hz, 1H), 7.48 (t, $J=8.1$ Hz, 1H), 7.66–7.64 (m, 2H), 7.77 (d, $J=8.1$ Hz, 1H), 8.46 (s, 1H); $^{13}$C NMR: $\delta$ 109.5, 110.9, 112.1, 114.8, 117.5, 118.3, 118.5, 120.6, 128.2, 142.1, 143.5, 149.6. Anal. calcd for $C_{12}H_8N_4O$: C, 64.28; H, 3.60; N, 25.00. Found: C, 64.54; H, 3.30; N, 25.04. **3-(2-Bromophenyl)-1,2,4-triazolo[1,2-*a*]benzotriazole (7d)**: yellow needles (51%), mp 192–193°C; $^1$H NMR ($CDCl_3$): $\delta$ 7.11 (t, $J=7.2$ Hz, 1H), 7.32 (t, $J=7.8$ Hz, 1H), 7.46–7.55 (m, 2H), 7.62 (d, $J=7.8$ Hz, 1H), 7.80 (t, $J=7.4$ Hz, 2H), 8.24 (d, $J=7.8$ Hz, 1H), 8.57 (s, 1H); $^{13}$C NMR: $\delta$ 110.9, 114.7, 117.4, 117.8, 118.4, 121.9, 125.1, 127.7, 127.8, 128.2, 130.6, 130.7, 134.6, 149.1. Anal. calcd for $C_{14}H_9BrN_4$: C, 53.70; H, 2.90; N, 17.89. Found: C, 53.73; H, 2.85; N, 17.50.