A Simplified Synthesis of Benzo[1,2-*d*:4,5-*d'*]bistriazole[1]

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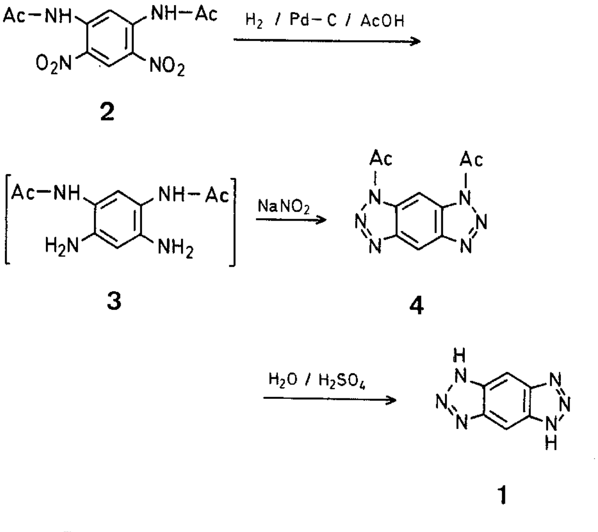
The only synthesis thus far reported for benzo[1,2-*d*:4,5-*d'*]bistriazole (**1**) is a tedious, five-step process starting with *m*-phenylenediamine[2]. We wish to report a more convenient route to **1** starting with 1,5-bis[acetylamino]-2,4-dinitrobenzene (**2**), which is easily obtained by acetylation of commercially available 1,5-diamino-2,4-dinitrobenzene. Hydrogenation of **2** in acetic acid gave a solution of 1,5-bis[acetylamino]-2,4-diaminobenzene(**3**), which was treated *in situ* with sodium nitrite to yield 1,7-diacetylbenzo[1,2-*d*:4,5-*d'*]bistriazole (**4**). Hydrolysis of **4** provided **1** in quantitative yield. Both **1** and **4** were obtained analytically pure directly from their reaction mixtures. Several attempts to obtain **1** by treating 1,2,4,5-tetraaminobenzene with nitrous acid failed.



1,5-Bis[acetylamino]-2,4-dinitrobenzene (2):

A mixture of 1,5-diamino-2,4-dinitrobenzene (5.0 g, 0.0025 mol), acetic anhydride (50 ml), and concentrated sulfuric acid (2 drops) was gradually heated to reflux. After refluxing for 5 min the clear soluting was cooled to 25° and poured into water (300 ml) with stirring. After the excess acetic anhydride had hydrolyzed, the solid was collected by filtration, washed with water, and dried at 100° to give crude **2**; yield: 6.4 g (91%). Recrystallization from acetic acid gave an analytically pure product; m.p. 228° [lit.[3] m.p. 228°].

$C_{10}H_{10}N_4O_6$	calc.	C 42.56	H 3.57	N 19.85
(282.21)	found	42.48	3.37	19.92

1,7-Diacetylbenzo[1,2-*d*:4,5-*d'*]bistriazole (4):

Compound **2** (2.82 g, 0.01 mol) was hydrogenated in acetic acid (100 ml) over 5% palladium on charcoal under 3.3 atmospheres of hydrogen for 1 h. The catalyst was removed by filtration, and the filtrate was treated with a solution of sodium nitrite (5.0 g, 0.07 mol) in water (15 ml) at 25°. The mixture was stirred at 25° for 30 min, then it was diluted with water (150 ml). The product was collected by filtration, washed with water, and dried at 100° to give pure **4**; yield: 1.47 g (60%); m.p. 239°.

$C_{10}H_8N_6O_2$	calc.	C 49.18	H 3.30	N 34.41
(244.21)	found	48.91	3.56	34.79

^{1}H-N.M.R. (DMSO-d_6): $\delta = 3.02$ (s, 6H), 8.74 (d, 1H, $J = 0.5$ Hz), 9.19 (d, 1H, $J = 0.5$ Hz).

Benzo[1,2-*d*:4,5-*d'*]bistriazole (1):

A mixture of **4** (0.73 g, 0.003 mol), 50% aqueous ethanol (100 ml), and concentrated sulfuric acid (1 ml) was heated under reflux for 1 h, then the reflux condenser was removed, and most of the ethanol was allowed to evaporate. The resultant mixture was chilled and filtered to remove the product, which was washed with water and dried at 100° to give pure **1**; yield: 0.46 g (96%); explosion temperature 370° when heated at 20°/min.

$C_6H_4N_6$	calc.	C 45.00	H 2.52	N 52.48
(160.14)	found	45.00	2.62	52.20

^{1}H-N.M.R. (DMSO-d_6): $\delta = 8.50$ (s, 2H), 15.53 (broad s, 2H).

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[3] R. Nietzki, E. Hagenbach, *Ber. dtsch. chem. Ges.* **20**, 334 (1887).