The Non-intermediacy of Benzo[1,2-*d*:2,3-*d'*]bistriazole During the Diazotization of a 4-Aminobenzotriazole

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Labeling studies with ^{15}N demonstrate that a diazonium ion prepared from a 4-aminobenzotriazole does not cyclize to a tricyclic intermediate.

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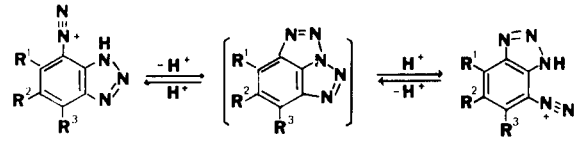
Nitrosation (diazotization) of *o*-phenylenediamines (1,2-benzenediamines) results in immediate cyclization to benzotriazoles [1]. Consideration of a homologous situation, diazotization of a 4-aminobenzotriazole, posed the question of whether cyclization of the resulting diazonium ion **2a** (Figure 1) could occur to form the tricyclic system **1**. The literature contains a few reports of diazotizations of 4-aminobenzotriazoles; in all cases the reported products were those expected from normal aromatic diazonium ions. Several examples [2-4] described dye-forming coupling reactions, but there were also at least two replacement reactions by which 4-aminobenzotriazole was converted to 4-chlorobenzotriazole [5] and to 4-hydroxybenzotriazole [6]. The latter two examples would not have tested the intermediacy of **1** because of symmetry ($R^1 = R^3 = H$, Figure 1), but at least two of the dye precursors (R^1 or $R^3 = NO_2$ [2,3]) could have formed unsymmetrical **1** derivatives which might have opened to either rearranged benzotriazoles or to mixtures of products. No unexpected products were reported, but there was no indication that the possibility was addressed.

As a result of an earlier study [7,8] on microbiological transformation of herbicide metabolites, a sample of 3-nitro-5-(trifluoromethyl)benzene-1,2-diamine **3** [9] was on hand. This was converted to the benzotriazole **4a** (Scheme 1) and to the 2-^{15}N-analog **4b**, whereupon hydrogenation converted **4a** and **4b** to the 4-aminobenzotriazoles **5a** and **5b**, respectively.

To convert diazonium ions **6a** and **6b** into conveniently assayable products, we chose the simple reaction with potassium iodide [9]. Sequential treatment of acidified **5a** with aqueous sodium nitrite and (after 5 minutes) a saturated solution of potassium iodide smoothly provided 4-iodo-6-(trifluoromethyl)benzotriazole **7a**. The same basic reaction was then repeated twice: once with **5a** and Na-$^{15}NO_2$ and again with **5b** and sodium nitrite. If the diazobenzotriazoles deprotonated and cyclized to the tricyclic system **1**, the same ^{15}N-labeled species **1b** should have been formed in each sequence.

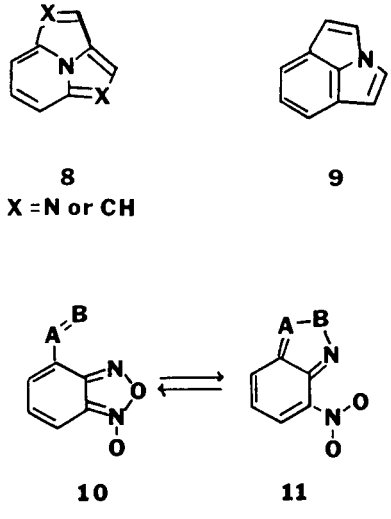
Mass spectra of the iodobenzotriazoles **7a** and **7b** clearly demonstrated that **1b** was *not* formed. Within detectable limits, no ^{15}N had been incorporated into **7a**, and no ^{15}N had been lost during the formation of **7b**.



2a **1** **2b**

Figure 1

The reasons for non-formation of **1b** are not known. The existence [11] of cycl[3.2.2]azines such as **8** and the pyrrolo[3,2,1-*h,i*]indole **9** [12] (Figure 2) argue against prohibitive strain being a major factor; in fact, the aromaticities of these systems have been evaluated and discussed [13]. Interconversions of ortho-substituted benzofuroxans (**10** → **11** [14], Figure 2) are well known, although formal tricyclic intermediates need not be involved in these cases. Linearity of the diazo group or protonation of the benzotriazole at the relatively low *p*H's employed also seem to be unlikely factors inasmuch as they do not deter benzotriazole formation from (the more basic) *o*-phenylenediamines under the same conditions.

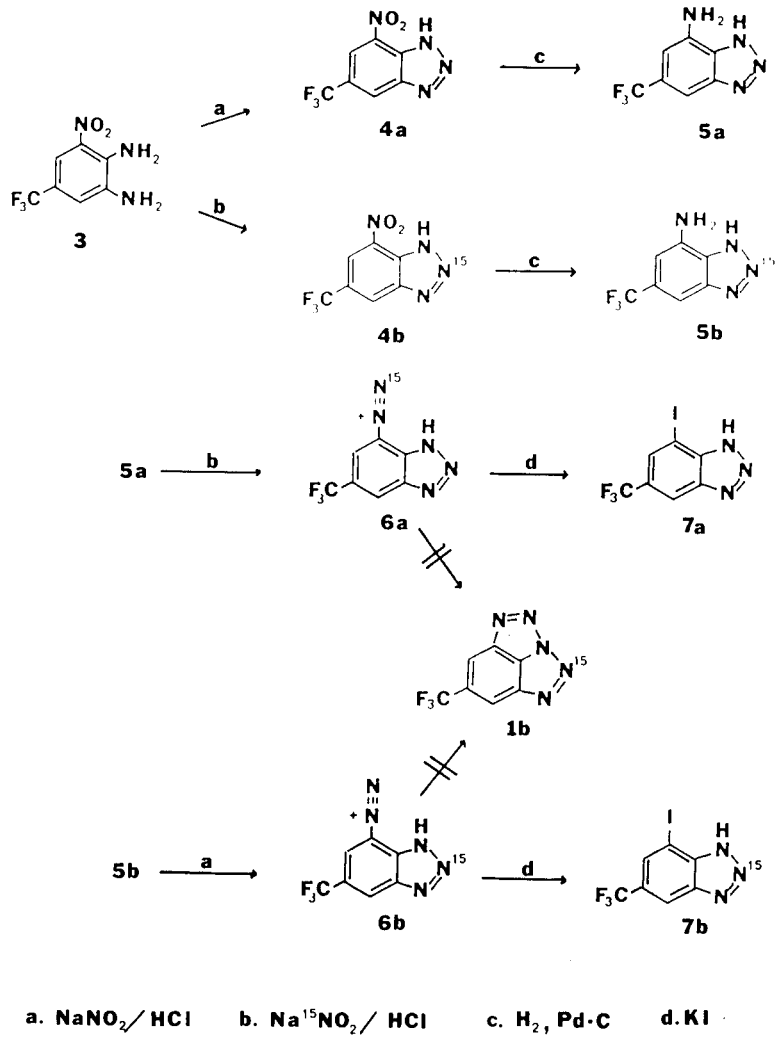


8 **9**

X = N or CH

10 **11**

Figure 2



Scheme 1

EXPERIMENTAL [15]

Mass spectra were obtained from a Finnigan Model 4510 GC-MS-DS fitted with a 30 m × 0.32 mm i.d. DB-1 fused silica column. Sodium nitrite-^{15}N (99% ^{15}N) was purchases from Stohler Isotope Chemicals. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

4-Nitro-6-(trifluoromethyl)-1*H*-benzotriazole (**4a**).

A solution of 0.66 g of 3-nitro-5-(trifluoromethyl)benzene-1,2-diamine [9] in acetic acid (6 ml) was treated with 0.3 ml concentrated hydrochloric acid, then was cooled and stirred while a solution of sodium nitrite (0.3 g) in water (2 ml) was added slowly. After a few minutes the mixture was diluted with water and 0.54 g of **4a** was collected by filtration. Recrystallization from benzene gave a light tan solid, mp 166-167.5°; ms: m/z 232 (M^{+}), 100%, 204 (M^{+}-N_2), 20%, 131, 20%.

Anal. Calcd. for $C_7H_3F_3N_4O_2$: C, 36.22; H, 1.30. Found: C, 35.99; H, 1.20.

6-(Trifluoromethyl)-1*H*-benzotriazol-4-amine (**5a**).

Hydrogenation of **4a** in a Parr apparatus (50 psi) with 10% palladium on carbon in absolute ethanol gave **5a**, mp 192.5-193° after recrystallization from benzene or toluene; ms: m/z 202 (M^{+}), 100%, 184 (M^{+}-HF), 8%, 174 (M^{+}-N_2), 25%, 173, 20%, 147, 22%.

Anal. Calcd. for $C_7H_5F_3N_4$: C, 41.59; H, 2.49. Found: C, 41.59; H, 2.39.

6-(Trifluoromethyl)-1*H*-benzotriazol-4-amine-2-^{15}N (**5b**).

A sample of **3** was converted to 4-nitro-6-(trifluoromethyl)benzotriazole-2-^{15}N (**4b**) as described for the preparation of **4a** but using sodium nitrite-^{15}N. The product was not purified but rather was hydrogenated as described for the **4a**, **5a** conversion to give **4b**. A small amount of a high-melting (mp > 300°) solid was removed by crystallization from methanol-water, and the more soluble **5b** was recovered from the filtrate and crystallized from benzene; ms: m/z 203 (M^{+}), 100%, 183 (M^{+}-HF), 8%, the remainder of the spectrum was identical to that of **5a** (illustrating that N_2-loss preceeds all other fragmentation).

4-Iodo-6-(trifluoromethyl)-1*H*-benzotriazole (**7a**).

A suspension of 25 mg of **5a** in 100 $\mu\ell$ of water, 40 $\mu\ell$ concentrated hydrochloric acid and 100 $\mu\ell$ of acetic acid was stirred and cooled (ice/methanol), then a solution of 19 mg of sodium nitrite in 50 $\mu\ell$ of water was added in 10 $\mu\ell$ portions. A dark yellow solution resulted. After 5 minutes, several drops of saturated potassium iodide were added, and the resulting dark mixture was gently warmed for 10 minutes. After cooling, it was

neutralized with 1*N* sodium bicarbonate and extracted with ether. The ether was washed with aqueous sodium bisulfite then with brine, dried and evaporated to give a yellow solid that was recrystallized from benzene to give 14 mg of **7a**, mp 235-244° (slow decomposition); ms: m/z 232 ($M^{+\cdot}$), 100%, 285 ($M^{+\cdot}$-N_2), 80%, 158 ($M^{+\cdot}$-N_2-I), 40%, 138 ($M^{+\cdot}$-N_2-I-HF), 33%. An analytical sample was similarly prepared. Passing a dichloromethane solution through a silica extraction cartridge removed a small amount of an orange or red contaminent to give a light yellow sample that was recrystallized from benzene.

Anal. Calcd. for $C_7H_3F_3N_3I_3$: C, 26.86; H, 0.97. Found: C, 26.97; H, 0.92.

Diazotizations of **5a** with $Na^{15}NO_2$/hydrochloric acid of **5b** with sodium nitrite/hydrochloric acid were performed as described above. The mass spectrum of the iodobenzotriazole from **5a** and $Na^{15}NO_2$ was indistinguishable from that of **7a** described above. The mass spectrum of **7b**, obtained from **5b** and sodium nitrite, had m/z 314 ($M^{+\cdot}$), 100%, 285 ($M^{+\cdot}$-$^{15}N{=}N$), 80%; the remainder of the spectrum was identical to that of **7a**.

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