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NOVEL SYNTHESIS FOR 4-HYDROXY-2-PHENYL-2H-BENZOTRIAZOLES

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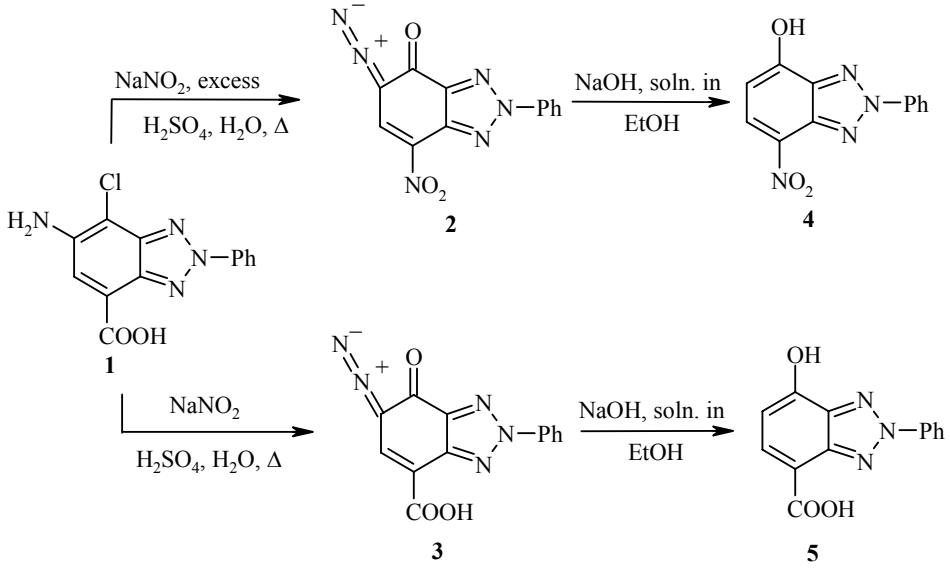
We have established that in diazotization of 6-amino-2-phenyl-7-chloro-2H-benzotriazole-4-carboxylic acid (**1**) in aqueous sulfuric acid using a large excess of $NaNO_2$, followed by holding the mixture at the boiling point, the compound 5-diazo-7-nitro-2-phenyl-2H-benzotriazol-4-one (**2**) is formed. In diazotization with an equimolar amount of $NaNO_2$, from compound **1** we obtain 6-diazo-7-oxy-2-phenyl-2H-benzotriazole-4-carboxylic acid (**3**). When quinonediazides **2** and **3** are treated with sodium hydroxide in aqueous ethanol, respectively 7-nitro-2-phenyl-2H-benzotriazol-4-ol (**4**) and 7-hydroxy-2-phenyl-2H-benzotriazole-4-carboxylic acid (**5**) are formed.

For compound **4**, the signals in the ^1H and ^{13}C spectra were assigned using the two-dimensional heteronuclear techniques HSQC and HMBC.



The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 (500 MHz and 125 MHz respectively) in DMSO-d_6 at 30°C. Two-dimensional HSQC and HMBC spectra were obtained using the gradient technique.

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5-Diazo-7-nitro-2-phenyl-2H-benzotriazol-4-one (2). A solution of sodium nitrite (4.00 g, 58 mmol) in water (20 ml) was poured in portions into a suspension (cooled down to 20°C) of 6-amino-7-chloro-2-phenyl-2H-benzotriazole-4-carboxylic acid **1** (1.00 g, 3.47 mmol) in water (16 ml) and 95% sulfuric acid (20 ml); the reaction was monitored to make sure that nitrogen oxides were not evolved too vigorously. After 15 min, the reaction mass was brought to the boiling point, held there for 1.5 h, cooled, and poured over ice. The precipitate was filtered out and recrystallized from ethanol. Yield 0.31 g (32%); mp 220-222°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 2160 ($=N^+=N^-$); 1540, 1344 (NO_2). ^1H NMR spectrum, δ, ppm: 9.11 (1H, s, 6-H); 8.20 (2H, m, 2'-, 6'-H); 7.61 (3H, m, 3'-,4'-, 5'-H). Mass spectrum, *m/z*: $[M]^+$ 282. Found, %: C 51.03; H 2.19; N 29.74. $C_{12}H_6N_6O_3$. Calculated, %: C 51.07; H 2.14; N 29.78.

6-Diazo-7-oxy-2-phenyl-2H-benzotriazole-4-carboxylic Acid (3). A solution of (0.24 g, 3.47 mmol) sodium nitrite in water (20 ml) was poured in portions into a suspension (cooled down to 20°C) of compound **1** (1.00 g, 3.47 mmol) in water (16 ml) and 95% sulfuric acid (20 ml). After 15 min, the reaction mass was brought to 60°C, held there for 1.5 h, and poured over ice. The precipitate was filtered out and recrystallized from ethanol. Yield 0.50 g (52%); mp 185-186°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 2148 ($=N^+=N^-$); 1700 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 8.45 (1H, s, 5-H); 8.20 (2H, m, 2'-, 6'-H); 7.61 (3H, m, 3'-, 4'-, 5'-H). ^{13}C NMR spectrum, δ, ppm: 172.0 (7-C); 164.6 (COOH); 148.0 (8-C); 141.8 (9-C); 140.0 (1'-C); 132.7 (5-C); 130.9 (3'-, 5'-C); 130.6 (4'-C); 121.0 (2'-, 6'-C); 109.9 (4-C); 84.4 (6-C). Mass spectrum, *m/z*: $[M]^+$ 281. Found, %: C 55.56; H 2.54; N 24.74. $C_{13}H_7N_5O_3$. Calculated, %: C 55.52; H 2.51; N 24.90.

4-Hydroxy-7-nitro-2-phenyl-2H-benzotriazole (4). A 50% NaOH solution (5 ml) was added to a solution of compound **2** (0.50 g, 1.77 mmol) in ethyl alcohol (100 ml), and the mixture was heated to the boiling point. After 15 min, the reaction mass was cooled and then made slightly acidic with 10% HCl. The precipitate obtained was filtered out and recrystallized from ethanol. Yield 0.17 g (38%); mp 211-212°C. IR spectrum (KBr), ν, cm^{-1}: 3616, 3428 (OH); 1530, 1356 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.45 (1H, d, J = 7.0, 6-H); 8.32 (2H, m, 2'-H, 6'-H); 7.63 (3H, m, 3'-,4'-, 5'-H); 6.85 (1H, d, J = 7.0, 5-H). ^{13}C NMR spectrum, δ, ppm: 157.2 (4-C); 139.9 (9-C); 139.2 (1'-C); 138.2 (8-C); 131.3 (6-, 4'-C); 130.1 (3'-, 5'-C); 128.6 (7-C); 120.7 (2'-, 6'-C); 107.4 (5-C). Mass spectrum, *m/z*: $[M]^+$ 256. Found, %: C 56.13; H 3.08; N 21.81. $C_{12}H_8N_4O_3$. Calculated, %: C 56.25; H 3.15; N 21.87.

7-Hydroxy-2-phenyl-2H-benzotriazole-4-carboxylic Acid (5). Obtained as for compound **4**, from compound **3** (0.5 g, 1.78 mmol) in ethyl alcohol (100 ml) and 50% NaOH (5 ml). The compound was recrystallized from dilute acetic acid. Yield 0.15 g (33%); mp 203-204°C. IR spectrum (KBr), ν, cm^{-1}: 1685 (C=O). ^1H NMR spectrum, δ, ppm (*J,* Hz): 11.60 (1H, br. s, OH); 8.32 (2H, m, 2'-, 6'-H); 8.04 (1H, d, J = 7.8, 5-H); 7.65 (3H, m, 3'-, 4'-, 5'-H); 6.81 (1H, d, J = 7.8, 6-H). Mass spectrum, *m/z*: $[M]^+$ 255. Found, %: C 61.23; H 3.48; N 16.43. $C_{13}H_9N_3O_3$. Calculated, %: C 61.18; H 3.55; N 16.46.