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Diazotization of 6-Amino-2-phenyl-7-chloro-2*H*-benzotriazole-4-carboxylic Acid and Transformations of the Resulting Diazo Compounds

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Abstract—6-Amino-2-phenyl-7-chloro-2*H*-benzotriazole-4-carboxylic acid was prepared by oxidation of 2,5-diamino-4-chloro-2-phenylazobenzoic acid, and its diazotization and subsequent transformations of the diazo compounds were studied. 7-Hydroxy-2-phenyl-2*H*-benzotriazole-4-carboxylic acid was prepared.

The chemical properties of 2*H*-benzotriazoles containing several substituents in the benzene moiety are studied insufficiently [1, 2] because of limited availability of di- and trisubstituted *m*-phenylenediamines required for their preparation. In this connection, starting from 4-chloro-3,5-diaminobenzoic acid, we prepared by the known scheme [3] 6-amino-2-phenyl-7-chloro-2*H*-benzotriazole-4-carboxylic acid **I** and performed with it certain chemical transformations.

Amino compound **I** is diazotized in HCl difficultly because of its poor solubility and low basicity of the amino group caused by the electron-withdrawing properties of the triazole moiety [4]. After prolonged standing at room temperature, the reaction mixture contains, according to TLC, the starting compound exhibiting strong blue luminescence. When the diazotization was performed with addition of acetic acid, in which compound **I** is readily soluble, the reaction was complete in 1 h. The resulting diazonium salt **II** entered into further transformations without complications only in acid solution: Its reaction with *N*,*N*-diethylaniline yielded azo compound **III**, and the reaction with a solution of SO_2 in acetic acid in the presence of HCl yielded benzotriazolesulfonyl chloride **IV** and 6,7-dichloro-2-phenyl-2*H*-benzotriazole-4-carboxylic acid **V**. At the same time, attempted azo coupling of diazonium salt **II** with 2-naphthol in alkaline solution failed because of tarring of the reaction mixture, probably caused by instability of **II** under these conditions.

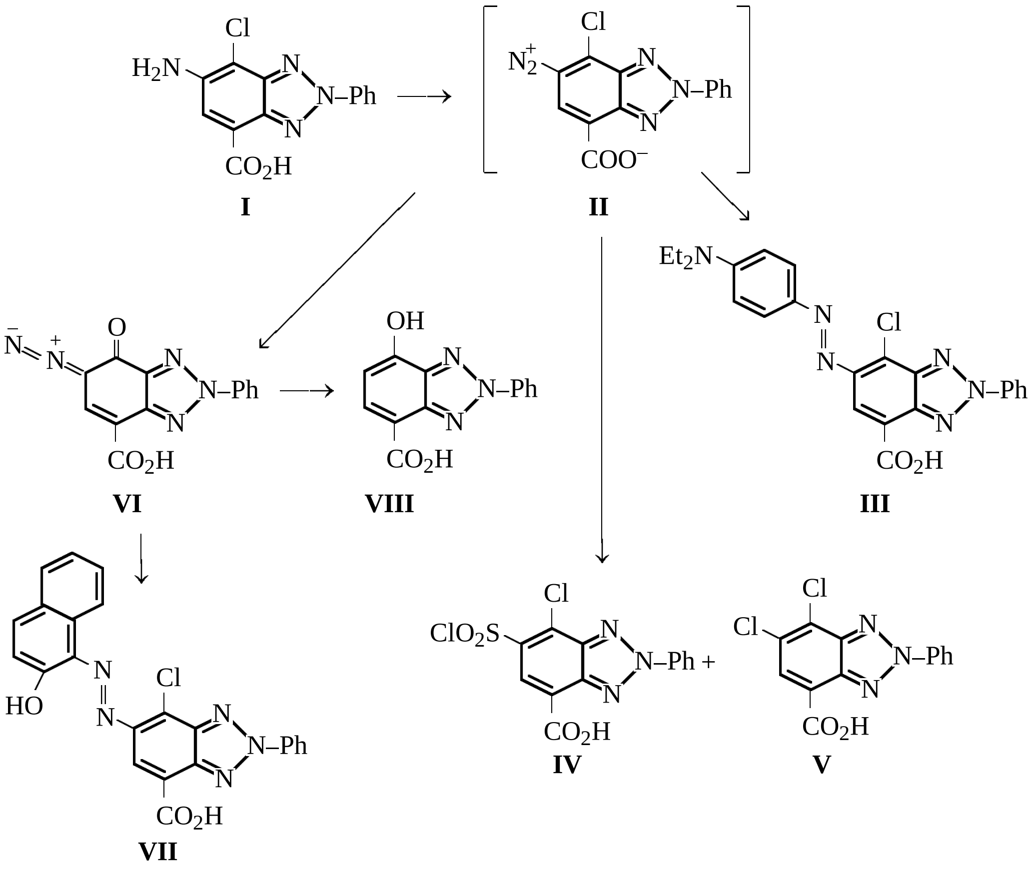
We believe that the specific features of the diazo compound obtained from **I** are confirmed by the results of diazotization in aqueous sulfuric acid at elevated temperature. The diazo compound isolated from the reaction was characterized by ^{1}H NMR, mass, and IR spectra, which indicate that the compound exists in the form of quinone diazide **VI**. This compound was also prepared by treatment of a solution of diazonium salt **II** in acetic acid with sodium carbonate. The presence in **VI** of the diazo function in the form of diazo rather than diazonium group is confirmed by a strong narrow band in the IR spectrum at 2180 cm^{-1} [5–7]. Formation of **VI** is apparently due to lability of the chlorine atom in the molecule of **II**; this atom is replaced by the hydroxy group under the action of water, which is followed by the tautomeric transformation into the diazonium salt of hydroxybenzotriazole. Diazo compound **VI** is highly stable, so that we detected a molecular ion in its mass spectrum.

Quinone diazide **VI** is formed in a high yield and is stable in storage. It reacts with 2-naphthol in alkaline solution to form 2,2-diaryl hydroxy azo compound **VII** and undergoes nitrogen substitution in a strongly acidic or strongly alkaline solution, i.e., under the conditions facilitating the transformation of the quinone diazide into the diazo compound salt [8].

Prolonged heating of **VI** in ethanol in the presence of copper(II) sulfate resulted in substitution of the diazo group with hydrogen and formation of 7-hydroxy-2-phenyl-2*H*-benzotriazole-4-carboxylic acid **VIII**. In refluxing ethanolic solution of NaOH, compound **VIII** is formed from **VI** considerably faster.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrophotometer (mulls in mineral oil). The ^{1}H NMR spectra were taken on a Bruker WP-200 spectrometer (200 MHz) in DMSO-d_6 at 40°C, internal reference TMS. The mass spectra were recorded on a Kratos MS-39 spectrometer (ionizing electron ener-



gy 70 eV, ionization chamber temperature 220°C, direct sample inlet).

6-Amino-2-phenyl-7-chloro-2*H*-benzotriazole-4-carboxylic acid I. A 13-g portion of 3,5-diamino-4-chloro-2-phenylazobenzoic acid was suspended in 150 ml of isopropyl alcohol, and the mixture was heated to 50°C. A copper ammine solution prepared from 63 g of $CuSO_4 \cdot 5H_2O$, 150 ml of 25% aqueous ammonia, and 70 ml of water was added with stirring. The mixture was heated to reflux. After 6 h, the cooled mixture was acidified with 10% HCl to strongly acidic reaction. The precipitate was filtered off, washed with water, dried, and recrystallized from glacial acetic acid. Yield of **I** 14.3 g (69%), mp 283–284°C. IR spectrum (mineral oil), ν, cm^{-1}: 3400, 3460 (NH_2), 1700 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.17 d (2H, $H^{2',6'}$, 8.0), 7.82 s (1H, H^5), 7.58–7.46 m (3H, $H^{3',4',5'}$), 6.12 br.s (2H, NH_2). Found, %: C 54.17; H 3.09; N 19.53. *M* 288. $C_{13}H_9ClN_4O_2$. Calculated, %: C 54.09; H 3.14; N 19.41. *M* 288.

7-Chloro-6-(4''-*N*,*N*-diethylanilinophenylazo)-2-phenyl-2*H*-benzotriazole-4-carboxylic acid III. A 1-g portion of 6-amino-2-phenyl-7-chloro-2*H*-benzotriazole-4-carboxylic acid was dissolved with heating in 80 ml of glacial acetic acid. The solution was cooled, and 15 ml of concentrated HCl and a solution of 0.28 g of sodium nitrite in 7 ml of water were added. After 1 h, a solution of 0.5 g of *N*,*N*-diethylaniline in 10 ml of absolute ethanol was added to the resulting diazo salt solution. The mixture was neutralized to weakly acidic reaction with a saturated solution of sodium acetate and allowed to stand for 1 h. The precipitate was filtered off, reprecipitated from acetone, recrystallized from ethanol, and dried. Yield of **III** 0.6 g (13%), mp 267–268°C. IR spectrum (mineral oil), ν, cm^{-1}: 1700 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.55 s (1H, H^5), 8.35 d (2H, $H^{2',6'}$, 8.0), 7.72 d (2H, $H^{2'',6''}$, 10.0), 7.61–7.55 m (3H, $H^{3',4',5'}$), 6.85 d (2H, $H^{3'',5''}$, 10.0), 3.50 d (4H, $2CH_2$, 6.9), 1.18 t (6H, $2CH_3$, 6.9). Found, %: C 61.33; H 4.70; N 18.56. *M* 448. $C_{23}H_{21}ClN_6O_2$. Calculated, %: C 61.54; H 4.72; N 18.72. *M* 448.

7-Chloro-6-chlorosulfonyl-2-phenyl-2*H*-benzotriazole-4-carboxylic acid IV and 6,7-dichloro-2-phenyl-2*H*-benzotriazole-4-carboxylic acid V. A 1-g portion of 6-amino-2-phenyl-7-chloro-2*H*-benzotriazole-4-carboxylic acid was dissolved with heating in 80 ml of glacial acetic acid. The solution was cooled, and 15 ml of concentrated HCl and a solution of 0.28 ml of sodium nitrite in 7 ml of water were added.

After keeping for 1 h, the solution of the diazo salt was added to 20 ml of a 30% solution of SO_2 in glacial acetic acid, and a concentrated aqueous solution of 0.1 g of $CuCl_2 \cdot 2H_2O$ was added. Warming of the mixture was prevented by cooling with ice-cold water. The reaction was complete in 10 min. The mixture was diluted with water and filtered; the precipitate was dried and recrystallized from glacial acetic acid. A mixture of **IV** and **V** (0.7 g) was obtained. Compound **IV**, M^+ 372; compound **V**, M^+ 308. IR spectrum (mineral oil), ν, cm^{-1}: 1180, 1380 (SO_2Cl), 1700 (C=O). Compound **IV**: ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.69 s (1H, H^5), 8.33 d (2H, $H^{2',6'}$, 8.0), 7.74–7.59 m (3H, $H^{3',4',5'}$). Compound **V**: ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.33 d (2H, $H^{2',6'}$, 8.0), 8.15 s (1H, H^5), 7.74–7.59 m ($H^{3',4',5'}$). As judged from the ratio of the integral intensities of the H^5 signals, the relative content of **IV** and **V** in the mixture is 65 and 35%, respectively.

6-Diazo-7-oxo-2-phenyl-2*H*-benzotriazole-4-carboxylic acid VI. *a*. A 1-g portion of **I** was suspended in 20 ml of 96% sulfuric acid and 15 ml of water. A solution of 0.48 g of sodium nitrite in 10 ml of water was added in portions. Diazotization was performed with stirring at 60°C, until the starting compound disappeared. After cooling, the mixture was poured into 10% NaOH; the precipitate was filtered off, washed with water, and dried. Yield of **VI** 0.74 g (76%).

b. A 1-g portion of **I** was dissolved with heating in 80 ml of glacial acetic acid. The solution was cooled, and 5 ml of concentrated HCl was added. A solution of 0.28 g of sodium nitrite in 20 ml of water was added dropwise at room temperature. After 1 h, excess acetic acid was distilled off on a rotary evaporator, the solution was neutralized with 10% sodium carbonate to pH 6, the mixture was diluted with water, and the precipitate was filtered off, washed with water, and dried in air. Yield of **VI** 0.65 g (67%), mp 200–201°C. IR spectrum (mineral oil), ν, cm^{-1}: 2180 ($=N^+=N^-$), 1690 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.45 s (1H, H^5), 8.20 d (2H, $H^{2',6'}$, 7.4), 7.61 m (3H, $H^{3',4',5'}$). Found, %: C 55.56; H 2.54; N 24.74. *M* 281. $C_{13}H_7N_5O_3$. Calculated, %: C 55.52; H 2.51; N 24.90. *M* 281.

7-Hydroxy-6-(2-hydroxynaphthyl-1-azo)-2-phenyl-2*H*-benzotriazole-4-carboxylic acid VII. A suspension of 2 g of 6-diazo-7-oxo-2-phenyl-2*H*-benzotriazole-4-carboxylic acid **VI** in 30 ml of water was added to a solution of 1 g of 2-naphthol and 2 g of NaOH in 100 ml of water at room temperature. The mixture was heated for 2 h at 60°C. The precipitate was filtered off, washed with water, dried, and recrystallized two times from ethanol. Yield of **VII** 1.10 g (37%), mp 246–247°C. IR spectrum (mineral oil), ν, cm^{-1}: 1700 (C=O). Found, %: C 61.33; H 4.70; N 18.56. *M* 425. $C_{23}H_{15}N_5O_4$. Calculated, %: C 64.94; H 3.55; N 16.46. *M* 425.

7-Hydroxy-2-phenyl-2*H*-benzotriazole-4-carboxylic acid VIII. *a*. A 0.2-g portion of 6-diazo-7-oxo-2-phenyl-2*H*-benzotriazole-4-carboxylic acid **VI** was dissolved in 50 ml of ethanol, and 0.10 g of $CuSO_4 \cdot 5H_2O$ was added. The mixture was refluxed for 6 h, cooled, brought to a weakly acidic reaction, and filtered. The reaction product crystallized from the filtrate; it was filtered off and dried in air. Yield of **VIII** 0.04 g (22%).

b. To a suspension of 1 g of **VI** in 100 ml of ethanol, 5 ml of a 50% NaOH solution was added, and the mixture was refluxed for 1 h. After cooling, the mixture was acidified with 10% HCl to a weakly acidic reaction. The precipitate was filtered off, washed with water, dried in air, and recrystallized from 80% aqueous acetic acid. Yield of **VIII** 0.3 g (33%), mp 203–204°C. IR spectrum (mineral oil), ν, cm^{-1}: 3600, 3400 (OH), 1690 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 11.60 br.s (1H, OH), 8.32 d (2H, $H^{2',6'}$, 7.4), 8.04 d (1H, H^6, 8.32), 7.73–7.57 m (3H, $H^{3',4',5'}$), 6.81 d (1H, H^5, 8.32). Found, %: C 61.23; H 3.48; N 16.43. M^+ 255. $C_{13}H_9N_3O_3$. Calculated, %: C 61.18; H 3.55; N 16.46. M^+ 255.

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