

DIAZOTISATION OF 5,6-DIAMINO-1*H*-BENZIMIDAZOLE

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Abstract

The synthesis of the bis(diazonium) salt derived from 5,6-diamino-1*H*-benzimidazole and subsequent coupling with β -naphthol are reported. The coupling reaction gives an imidazo-benzotriazole derivative when the diazotization is performed with nitrosyl hydrogen sulfate and a mono-azo compound when coupling is done in the presence of concentrated HCl.

Introduction

Research carried out on the reduction of 5,6-dinitro-1*H*-benzimidazole is limited in literature ^(1,2) and the diazotization and the coupling reactions of the reduction product 5,6-diamino-1*H*-benzimidazole have not yet been studied.

In the present study, a well-known synthesis of benzotriazoles using o-diamines as starting materials ^(3,4) was employed for 5,6-diamino-1*H*-benzimidazole. In recent years, many analogues of 2-(2*H*-1,2,3-benzotriazol-2-yl) naphthol have been intensively studied because of their ultraviolet absorber activity protecting the natural and synthetic materials against light ⁽⁵⁻⁷⁾. As an extension of these investigations, the synthesis a new ring system 1,7-dihydroimidazo[4,5-*f*] [1,2,3] benzotriazole which may also form ultraviolet absorber agen is reported. On the other hand, by the hydroxy-dediazoniation reaction, a mono-azo compound was also obtained depending on the experimental conditions.

Experimental

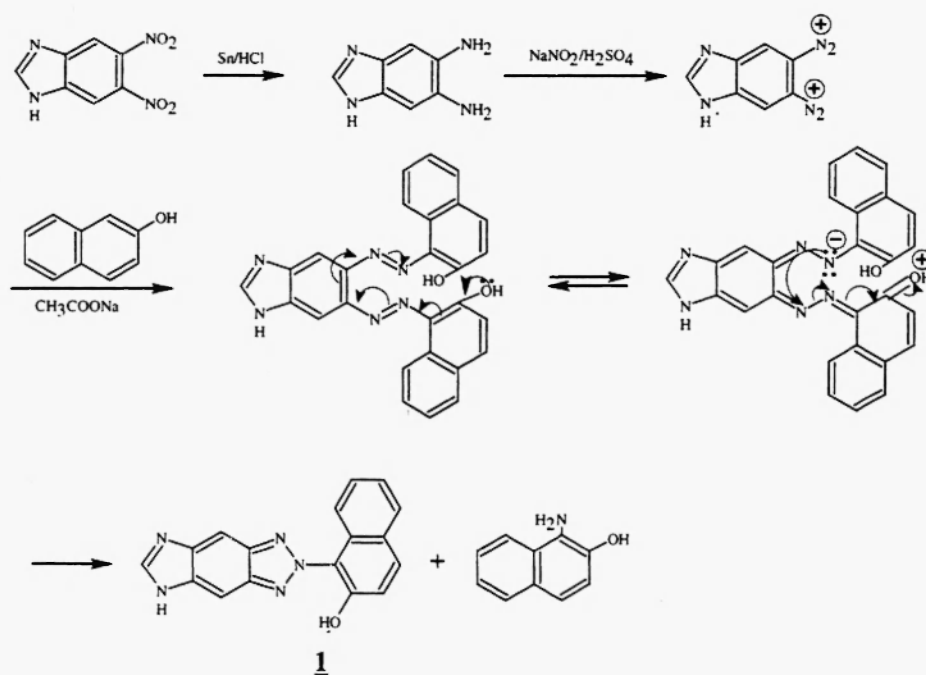
Melting points were obtained on a Gallenkamp apparatus (uncorrected). IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr discs. ¹H and ¹³C NMR spectra were obtained with a Bruker DPX-400 spectrometer in hexadeuteriodimethylsulfoxide. Mass spectra were recorded on a Agilent GC-MSD spectrophotometer. Elemental analyses were carried out an a LECO-932 C, H, N analyser.

5,6-Dinitro-1*H*-benzimidazole was obtained employing the method described in literature ⁽⁸⁾ and used as a starting material to synthesize the desired benzimidazole derivatives.

Synthesis of 1-imidazo[4,5-*f*][1,2,3]benzotriazol-2(5*H*)-yl-2-naphthol **1**

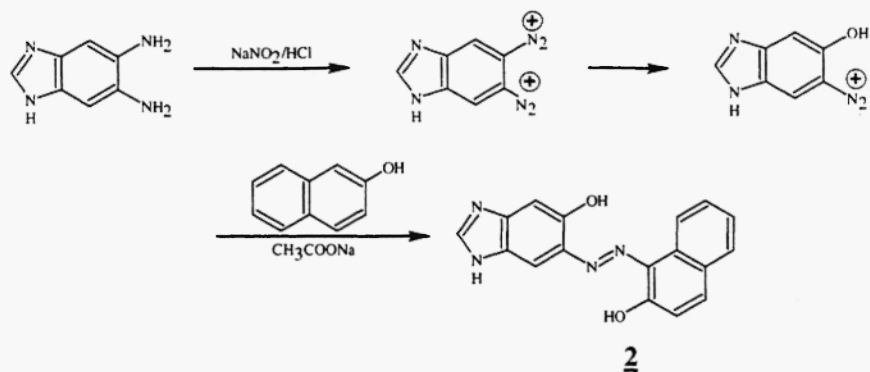
5,6-Diamino-1*H*-benzimidazole: Reduction of 5,6-dinitro-1*H*-benzimidazole (5.0 g, 2.4×10^{-2} mol) with tin (16.0 g) and concentrated hydrochloric acid (50.0 mL) gave 5,6-diamino-1*H*-benzimidazole dihydrochloride salt. According to literature procedure ⁽¹⁾, treatment with ammonia and recrystallisation from water afforded 5,6-diamino-1*H*-benzimidazole as colourless needles, mp 213-214 °C (2.9 g, 84 %).

Ring closure of 5,6-diamino-1*H*-benzimidazole: Nitrosylsulfuric acid was prepared by adding sodium nitrite (1.5 g) to sulfuric acid (98 %, 15.0 mL) at 20-30 °C, heating to 60-65 °C over 10 minutes with stirring and maintaining this temperature for 5 minutes to ensure complete dissolution. After cooling, a solution of 5,6-diamino-1*H*-benzimidazole (0.3 g, 2×10^{-3} mol) in concentrated sulfuric acid was added over for 30 minutes below 5 °C. When the diazotisation was completed, the bis(diazonium) salt solution was used immediately for the coupling reaction. The solution of β -naphthol in sodium hydroxide (5 % in 2*N* NaOH) was slowly added at 5-10 °C maintaining the pH at 5-6 by addition of aqueous solution of sodium acetate (40 %). The obtained precipitate was filtered off, washed with water and air-dried. The crude product (0.43 g, 72 %) was purified by a combination of column chromatography (silicagel, 230-400 mesh ASTM / toluene: ethyl acetate, 95:5) and recrystallisation (aqueous ethanol). The pure product is a light red powder with melting point 263-265 °C. The yield is 0.41 g (68 %). Found, %: C 67.12; H 3.41; N 23.18. $C_{17}H_{11}N_5O$. Calculated, %: C 67.78; H 3.66; N 23.26. MS; m/z : 301 [M^+], 286, 272, 222, 192.



Synthesis of 6-[(2-hydroxy-1-naphthyl)diazenyl]-1*H*-benzimidazol-5-ol **2**

5,6-Diamino-1*H*-benzimidazole (0.3 g, 2×10^{-3} mol) was dissolved in concentrated hydrochloric acid (10.0 mL) and cooled at 0-5 °C. A solution of sodium nitrite (0.2 g) in ice-water (1.0 mL) was added over for 30 minutes, maintaining the temperature at 0-5 °C. The mixture was stirred for a further 15 minutes during which time the temperature was allowed to rise at 40-45 °C. When the evolution of the N_2 gas was completed, the pH was adjusted to 6-7 by addition of aqueous solution of sodium acetate then the solution of β -naphthol in sodium hydroxide was added until the precipitation of the reaction product ceased. Recrystallisation from ethanol gave the pure **2**, red powder (0.32 g, 53 %). The melting point is 209-211 °C. Found, %: C 67.35; H 3.60; N 18.31. $C_{17}H_{12}N_4O_2$. Calculated, %: C 67.11; H 3.95; N 18.42. MS; m/z : 304 [M^+], 272, 244, 144.



Results and discussion

Ring closure reaction. According to the literature ⁽¹⁰⁾, the method of the diazotization in which a solution of the diamine in concentrated sulfuric acid is mixed with nitrosyl sulfuric acid was employed successfully for the preparation of bis(diazonium) salt derived from 5,6-diamino-1H-benzimidazole. The coupling with β -naphthol give 1-imidazo[4,5-f][1,2,3]benzotriazol-2(5H)-yl-2-naphthol in good yield.

Under diazotization conditions reported in literature, the formation of the unsubstituted triazole ring is prevented and consequently 1,7-dihydroimidazo [4,5-f] [1,2,3] benzotriazole was not obtained. However, by raising the pH to 5-6, the coupling reaction with β -naphthol takes place very easily and the ring closure followed. The resulting N-substituted N-azo group forms part of the fused triazole ring of 1,7-dihydroimidazo [4,5-f][1,2,3] benzotriazole.

Hydroxy-dediazoniation reaction. 5,6-Diamino-1H-benzimidazole was dissolved in concentrated hydrochloric acid and sodium nitrite solution in water was added 0-5 °C. The whole reaction mixture was maintained at 40-45 °C with stirring to ensure the evolution of N₂ gas. Adjusting the pH to 6-7 and coupling with β -naphthol, 6-[(2-hydroxy-1-naphthyl)diazonyl]-1H-benzimidazol-5-ol was obtained.

According to the literature, it is not possible to diazotise one amino group of the 5,6-diamino-1H-benzimidazole on treatment with acid ⁽¹⁰⁾. Also a ring closure reaction was not observed under these experimental conditions. Both amino groups were diazotised in acid. However, one of N₂⁺ groups was replaced by water in an ordinary substitution reaction. The imidazole ring, which is an electron-supplying group, increases the double bond character of the C-N bond in the diazonium cation and the cleavage of this bond in the latter diazonium group was hindered ⁽¹¹⁾.

Spectroscopic properties

The structures of the compounds **1** and **2** were examined by ¹H and ¹³C NMR and infrared spectroscopies. The elemental analysis results agree with the structures determined.

IR spectroscopy was used to distinguish between two benzimidazole derivatives. The compound **1** displayed an absorption band in the region 3200-2900cm⁻¹ having markedly lowered intensity, whereas the compound **2** showed a broad band near 3600-3500cm⁻¹. The compound **1** displayed an absorption band, (O-H stretching vibration) at lower values depending on the intramolecular hydrogen bonding ⁽¹²⁾. However the compound **2** cannot form an intramolecular hydrogen bond.

For ¹H NMR measurements, the samples were dissolved in hexadeuteriodimethylsulfoxide. In all cases, the aromatic regions were characteristic indicating the presence of the 2-hydroxy-1-naphthyl group. Doublets at δ 7.09, 7.89, 8.03, 8.73 ppm and triplets at δ 7.50 and 7.68 ppm were assigned to aromatic protons in the compound **1**. These assignments were observed at δ 7.43, 7.96, 8.08, 8.97 and δ 7.69 and 7.88 ppm respectively in the compound **2**.

Singlets at δ 8.19 and 8.49 ppm were assigned to 4-H and 7-H in the benzimidazole ring of **2**, whereas a singlet at δ 8.31 ppm is due to the same protons in **1**. The appearance of a singlet at δ 8.53 ppm, indicating one proton, confirmed the presence of the hydroxyl group in the compound **2**. The compounds **1** and **2** displayed one singlet corresponding to 2-H at δ 8.27 and 8.21 ppm respectively.

The signal observed at δ 15.47 ppm proved the azo-hydrazone tautomerism in solution for the compound **2** ⁽¹³⁾.

The ^{13}C NMR spectra in hexadeuteriodimethylsulfoxide showed seventeen aromatic carbon signals in the region 112.18 – 159.59 ppm. The 2-hydroxy-1-naphthyl group provided ten ^{13}C NMR signals. C-2 was observed at δ 159.59 ppm. C-1 was assigned at δ 129.49 ppm. C-3, C-4, C-7, C-8 and C-8a were assigned at δ 125.78, 144.28, 122.35, 122.25 and 133.34 ppm respectively while C-4a, C-5 and C-6 peaks appeared in the region of 128.72-129.71 ppm. The benzimidazole carbon ring signals were observed at δ 147.73, 144.72, 137.54, 116.27 and 112.18 ppm for C-5, C-2, C-4a, C-7a, C-4(7) and C-6 respectively for the compound **2** whilst for the compound **1** ^{13}C chemical shifts were not significantly distinguishable.

Conclusion

1-Imidazo[4,5-f][1,2,3]benzotriazol-2(5H)-yl-2-naphthol and 6-[(2-hydroxy-1-naphthyl)diazenyl]-1H-benzimidazol-5-ol were prepared in good yields by the diazotisation and the coupling reactions of 5,6-diamino-1H-benzimidazole.

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