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Short Note

3-(2-Hydroxyethyl)-2-methylbenzothiazolium Bromide

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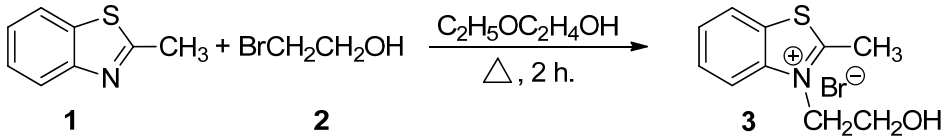
Abstract: A novel method for the preparation of 3-(2-hydroxyethyl)-2-methylbenzothiazolium bromide was developed. It consists of heating of 2-methylbenzothiazole, 2-bromoethanol and ethoxyethanol for 2 h. On the next day the precipitate was filtered and air dried.

Keywords: 2-methylbenzothiazole; 2-bromoethanol; 3-(2-hydroxyethyl)-2-methylbenzo-thiazoli-um bromide

1. Introduction

Very few papers in English were found in the literature that deal with the synthesis of 3-(2-hydroxyethyl)-2-methylbenzothiazolium bromide **3** or iodide [1,2]. The rest of the references found were in Chinese or Japanese [3–5] or related to the patent literature [6–8] and thus were relatively inaccessible. The preparation of **3** with a reaction time of less than 2 h has only been reported once, but in that reference the proposed method required special conditions and MW system [1]. 3-(2-Hydroxyeth-yl)-2-methylbenzothiazolium bromide is a useful compound. It has been shown that this derivative, which incorporates a benzothiazole subunit, exhibits very high static first hyperpolarizability values in the acido-generated form [2]. This compound is a typical intermediate for the preparation of cyanine dyes [1,2,8] which have different applications in the preparation of, for example, styryl dyes [2], or squaraine dyes [5,6]. The usual synthetic method requires heating for up to 18 h [8]. However, we have found that **3** can be obtained in a shorter time by heating for only 2 h (Scheme 1).



Scheme 1. Preparation of 3-(2-hydroxyethyl)-2-methylbenzothiazolium bromide **3** by quaternization with 2-bromoethanol **2**.

The structure of 3-(2-hydroxyethyl)-2-methylbenzothiazolium bromide was confirmed by NMR spectra (See Supplementary Materials).

2. Experimental Section

2.1. Materials

Unless otherwise stated, all reagents and solvents used in the synthesis and analysis were obtained from Sigma-Aldrich (St. Louis, MO, USA), Alfa-Aesar (Haverhill, MA, USA), as commercial products of analytical grade, and used without further purification.

2.2. Instrumentation

^{1}H-NMR spectrum were recorded on a Bruker Avance III 500 MHz (Rheinstetten, Germany) using DMSO-d_6 at room temperature. Chemical shifts (δ) are reported in ppm and referenced indirectly to the corresponding shift of the deuterated solvent peak. The melting point temperatures were determined on a Kofler bench apparatus (DDR, Berlin, Germany) and are uncorrected.

2.3. Experimental Procedure for the Preparation of 3-(2-hydroxyethyl)-2-methylbenzothiazolium Bromid

A 250 mL Erlenmeyer flask was charged with 2-methylbenzothiazole **1** (12.70 mL, 0.1 mol), 2-bromoethanol **2** (10.00 mL, 0.14 mol), and 15 mL ethoxyethanol. The reaction mixture was heated under reflux and stirred for 120 min. The reaction mixture was cooled down to room temperature and left at room temperature for 24 h. On the next day the precipitate of **3** was filtered off and air dried. The compound was recrystallized from methanol/ethylacetate with charcoal. The crude yield of **3** was 80%. The pure product for 3-(2-hydroxy-ethyl)-2-methylbenzothiazolium bromide had a melting point 166–168 °C (methanol/ethyl acetate)— lit. m.p.178 °C [2].

3-(2-Hydroxyethyl)-2-methylbenzothiazolium Bromide **5** ^{1}H-NMR (DMSO-d_6) δ (ppm): 3.24 (s, 3H, C**H**$_3$); 3.89 (t, 2H, C**H**$_2$OH, *J* = 5.0 Hz); 4.87 (t, 2H, C**H**$_2$N, *J* = 5.0 Hz); 5.23 (br.s, 1H, O**H**); 7.80 (t, 1H, **H**-Ph, *J* = 7.6 Hz); 7.87 (t, 1H, **H**-Ph, *J* = 7.6 Hz); 8.34 (d, 1H, **H**-Ph, *J* = 8.3 Hz); 8.47 (d, 1H, **H**-Ph, *J* = 8.3 Hz); ^{13}C-NMR (DMSO-d_6) δ (ppm): 17.41 (1C, **C**H$_3$); 51.99 (1C, **C**H$_2$N); 58.53 (1C, **C**H$_2$OH); 117.13 (1C, Ph); 124.61 (1C, Ph); 128.03 (1C, Ph); 129.01 (1C, Ph); 129.22 (1C, Ph); 141.11 (1C, Ph); 178.03 (1C, N**C**S).

Supplementary Materials: The following are available online at www.mdpi.com/1422-8599/2016/4/M920.

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Conflicts of Interest: The authors declare no conflict of interest.

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