

Modified Methods for the Synthesis of Triazinyl Fluorescent Brightener Intermediates

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Abstract: The production of triazinyl fluorescent brightener intermediates in high yields is described. The method involves a simplified work-up for the preparation of 4-nitrotoluene-2-sulfonic acid and the use of diethylene glycol instead of water in the preparation of 4,4'-dinitrostilbene-2,2'-disulfonic acid.

Keywords: Triazinyl Fluorescent Brighteners; Sulfonation; Direct Separation.

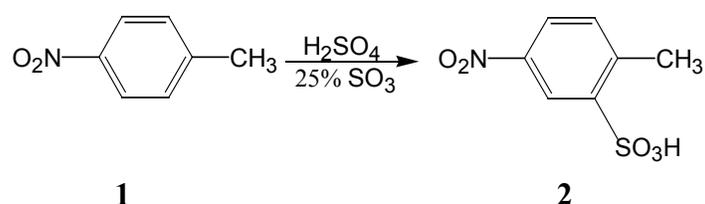
Introduction

4-Nitrotoluene-2-sulfonic acid (**2**) and 4,4'-dinitrostilbene-2,2'-disulfonic acid (**3**) are the key intermediates for the synthesis of triazinyl fluorescent brighteners [1]. Although there are many reports of preparations of these compounds, they all have problems in the work-up of compound **2** and they also report low yields and long reaction times in the preparation of 4,4'-dinitrostilbene-2,2'-disulfonic acid (**3**) [2-8]. Herein we report a modification of the common procedures to produce compounds **2** and **3** which involves simple work-ups, short reaction times and also affords high product yields.

Results and Discussion

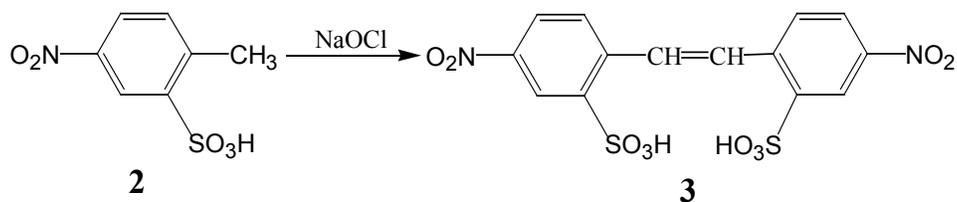
In the common procedures for the separation of **2** after the sulfonation of 4-nitrotoluene (**1**) (Scheme 1), compound **2** is converted into the corresponding salt. Subsequently it is extracted from the reaction mixture and ultimately the salt is acidified [2-4]. These methods involve many steps for the work-up of the product. This problem was solved by the use of a mixture of acetone-benzene as the solvent for the direct separation of product. In this alternative method the product was crystallized directly from the sulfonation mixture using that solvent system. The advantages of this method are the fewer separation steps and the high yield (96%) {lit[2] yield 95-96%}.

Scheme 1



Previous methods for the self-oxidation of **2** by sodium hypochlorite (Scheme 2) in aqueous solutions suffer from low yields and long reaction times [5-8]. By the use of diethylene glycol instead of water in this reaction we both increased the yield (from 86 to 93%) and reduced the reaction time.

Scheme 2



The above intermediate **3** can be converted into the triazinyl fluorescent brighteners **6** through the reduction of nitro groups to give **4**, subsequent reaction with cyanuric chloride (**5**) and amines or alcohols (Scheme 3) [9,10].

Conclusions

A convenient method has been developed for the synthesis of 4-nitrotoluene-2-sulfonic acid and 4,4'-dinitrostilbene-2,2'-disulfonic acid as fluorescent brightener intermediates. Simple and clean work-ups, high yields and also short reaction times make this procedure an attractive method for the possible commercial synthesis of these products.

cream colored solid melting at 133°C {lit. [2] mp 132-133°C}. yield: 19.0 g (96%); ¹H-NMR δ(ppm): 2.7 (s; 3H); 7.5 (d; 1H); 8.1 (d; 1H); 8.5 (s; 1H). MS (EI): m/z: 217 (M⁺); 200; 182; 135; 105; 89; 30.

Preparation of 4,4'-dinitrostilbene-2,2'-disulfonic acid (3) using diethylene glycol as the solvent.

A mixture of sodium hypochlorite (50 mL, 5% available chlorine) and a solution of sodium hydroxide (6g) in water (8 mL) was slowly added with stirring to a warm (40-45°C) solution of compound **2** (5g) in diethylene glycol (30 mL). Stirring was continued and the temperature raised to 85°C. After about ten minutes the reaction was complete (as indicated by starch-iodide paper). Upon cooling and filtration the sodium salt of 4,4'-dinitrostilbene-2,2'-disulfonic acid (5.6 g) was obtained. Treatment of this salt with hydrochloric acid afforded the free acid **3** (5.1 g, 93% yield), m.p. 266°C (lit. [6] m.p. 266°C); ¹H-NMR δ (ppm): 7.9 (d; 1H); 8.3 (d; 1H); 8.4 (s; 2H); 8.6 (s; 1H); FTIR (cm⁻¹): 2800, 3400, 1475, 1590, 1350, 1520, 1140, 1200; MS (EI): m/z: 430 (M⁺); 349; 214; 165; 75.

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Sample Availability: Samples of compounds **2** and **3** are available from the authors.