

Short Note

2,2'-Thio-bis[(4-methylphenyl)-2-aminobenzoate]

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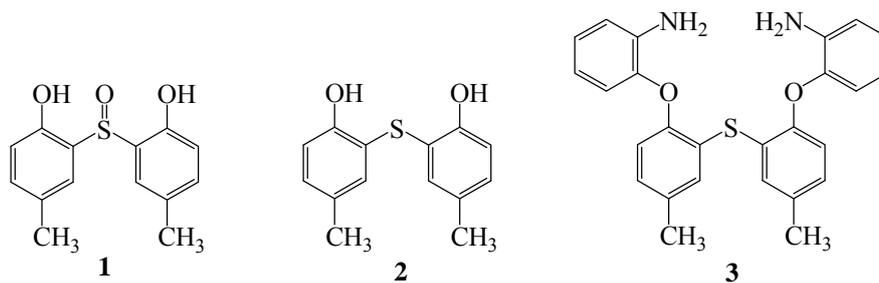
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Abstract: A novel symmetrical bisamine derivative (**4**) was synthesized by condensation reaction of 2,2'-thio-bis[4-methylphenol] (**1**) and isatoic anhydride in acetonitrile as solvent in the presence of K₂CO₃ under reflux conditions. The structure of the title compound was established on the basis of elemental analysis, FT-IR, ¹H-NMR, ¹³C-NMR and mass spectral data.

Keywords: isatoic anhydride; 2,2'-thio-bis[4-methylphenol]; 2,2'-thio-bis[(4-methylphenyl)-2-aminobenzoate]

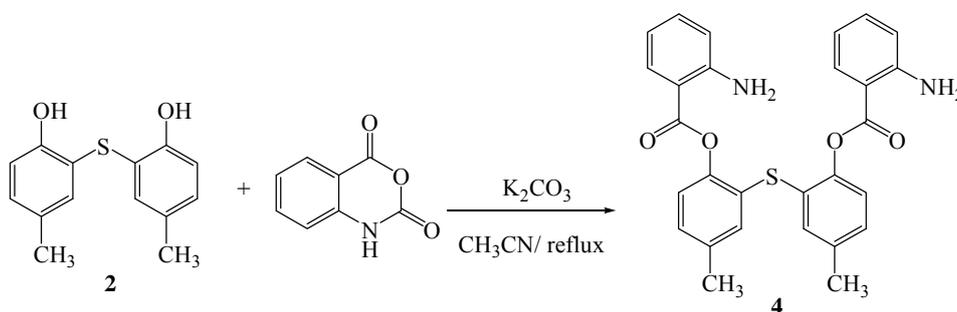
Introduction

Symmetric diaryl sulfides and their sulfoxides have been synthesized by many groups using different conditions [1–3]. The Friedel-Crafts method is generally used for the synthesis of these compounds. Treatment of *p*-cresol with thionyl chloride and anhydrous aluminum chloride in dichloromethane afforded 2,2'-sulfinyl-bis-(4-methylphenol) (**1**). The reduction of sulfoxide (**1**) to 2,2'-thio-bis-(4-methylphenol) (**2**) under different conditions has been reported [4–7]. Also, dibenzosulfide (**2**) was synthesized based on a reported procedure in 65% yield [8]. Treatment of the dibenzosulfide **2** with 1-fluoro-2-nitrobenzene and then reduction with NH₄Cl/Zn afforded 2,2'-thio-bis-(4-methyl (2-aminophenoxy)phenyl ether) (**3**) in 90% yield (Figure 1) [9].

Figure 1. Examples of sulfoxides and diaryl sulfides.

In addition, the preparation of macrocyclic compounds from dibenzosulfide (**2**) and diamine (**3**) have attracted much attention recently, because of their significant metal ion complexing ability as well as being valuable intermediates for the synthesis of aza-crown ethers and related compounds.

In our previous work, we have described the synthesis of new bis-Betti bases [10] and new multibenzo oxygen-sulfur donor macrocycles containing lactams [11] from dibenzosulfide (**2**) and diamine (**3**), respectively. In the present study, we report the synthesis of a new bisamine containing a dibenzosulfide moiety. The title compound (**4**) was synthesized as presented in Scheme 1 by condensation of compound (**2**) with 2 equivalents of isatoic anhydride in acetonitrile as solvent in the presence of K_2CO_3 at reflux conditions.

Scheme 1. Synthetic route to the title compound **4**.

Mechanistically, we assume that when dibenzosulfide **2** is treated with 2 equivalents of K_2CO_3 , a thio-bis [4-methyl potassium phenoxide] intermediate is formed which is attacked by 2 equivalents of isatoic anhydride, followed by liberation of 2 equivalents of CO_2 to give the title product. The latter can be used for metal ion complexing, synthesis of new aza-crown ethers and related compounds. Identification of product **4** was carried out on the basis of spectroscopic information.

Experimental

All commercially available chemicals and reagents were used without further purification. The melting point was determined with an Electrothermal model 9100 apparatus and is uncorrected. The IR spectrum was recorded on a Shimadzu 4300 spectrophotometer. The 1H and ^{13}C -NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-500 Avance spectrometer. Chemical shifts (δ) are reported in parts per million and are referenced to the NMR solvent. The mass spectrum of the product was

obtained with a HP (Agilent technologies) 5937 mass selective detector. Elemental analyses were carried out by a CHN–O–Rapid Heraeus elemental analyzer (Wellesley, MA).

Synthesis of 2,2'-thio-bis[(4-methylphenyl)-2-aminobenzoate (**4**): A mixture of 2,2'-thio-bis[4-methylphenol] (1 mmol), isatoic anhydride (2 mmol) and K_2CO_3 (2 mmol) in acetonitrile (10 mL) was refluxed for 12 h. After completion, the reaction mixture was cooled to room temperature and 10% aqueous KOH (40 mL) was added to the mixture. The white precipitate that formed was filtered, washed with H_2O and dried. The product thus obtained was found to be pure upon TLC examination. Yield: 85%; m.p.: 194–196 °C; IR (KBr): 3480 (NH_2), 3370 (NH_2), 3023, 2913, 1695 (C=O), 1611, 1480, 1240, 1033, 870 cm^{-1} ; 1H -NMR (500 MHz, $CDCl_3$): (δ) 2.22 (s, 6H, CH_3), 5.65 (s, 4H, NH_2), 6.59–7.81 (m, 14H, Ar-H) ppm; ^{13}C -NMR (125 MHz, $CDCl_3$): (δ) 20.69, 109.53, 116.27, 116.46, 123.04, 127.43, 129.36, 131.91, 133.85, 134.65, 136.22, 147.91, 151.11, 166.08 ppm; EI-MS: $m/z = 484 (M^+)$, 365, 246, 146, 120, 108, 92; Anal. calcd. for $C_{28}H_{24}N_2O_4S$: C, 69.42; H, 4.96; N, 5.78. Found: C, 69.53; H, 4.84; N, 5.81.

Acknowledgments

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