

Short Note

Barium 5-(*tert*-butyl)-2,3-dihydroxybenzenesulfonate

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Abstract: Catechols and their derivatives attract great scientific interest due to the broad spectrum of their functional properties, including complexation, redox behavior, association ability and antioxidant activity. Because of the low molecular mass and two-electron redox process, they are considered to be a promising energy storage compound in different types of electrochemical power sources, such as metal-ion batteries or redox flow batteries. Herein, we report a preparation of the sterically hindered sulfonated catechol, namely the barium salt of 5-(*tert*-butyl)-2,3-dihydroxybenzenesulfonic acid, by the direct sulfonation of 4-*tert*-butylcatechol, by concentrated sulfuric acid. The proposed procedure is green and atom-economic, providing the desired product in high yield after simple purification. The solvent-free procedure is inexpensive and highly scalable, which enables direct industrial production of the title product. The resulting product was characterized by the ^1H and ^{13}C nuclear magnetic resonance (NMR) and ESI-high resolution mass spectrometry (ESI-HRMS).

Keywords: catechol; sulfonate; sulfonation; green; solvent-free



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1. Introduction

Catechols are known for the vast variety of their functional properties, as follows: they can act as the chelators for transition metals [1], antioxidants and radical scavengers [2], redox-mediators [3], polymerization inhibitors [4] and adhesives [5]. Catechol functionality may be found in different natural compounds; for example, in dopamine or mussel foot proteins [6]. In the last few decades, catechols have attracted increased attention, as promising electrochemical energy storage material, due to its outstanding redox properties. Catechols can undergo reversible two-electron oxidation, which delivers high energy density to be accumulated.

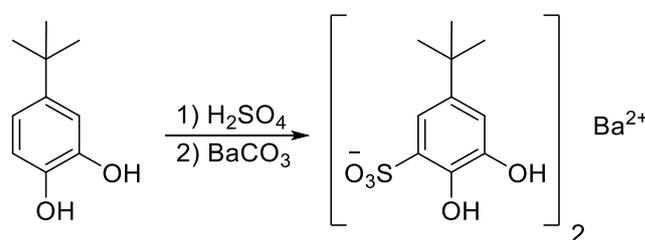
Natural and synthetic polymeric catechols meet their application as cathode materials or binders in accumulators [7,8] and supercapacitors [9,10], while the molecular catechols, for example, 3,5-pyrocatecholdisulfonate (Tiron), are considered as promising catholytes for organic flow batteries [11]. The presence of anionic fragments is helpful in both cases, providing sufficient solubility for in-solution applications or as an anchoring group, while using with conductive polymers [12]. Considering this, the novel sterically hindered sulfonated catechol may be useful for the development of the redox flow batteries or as a model compound for the investigation of polymeric sulfocatechol materials for energy storage.

Herein, we report the synthesis of the barium salt of 5-(*tert*-butyl)-2,3-dihydroxybenzenesulfonic acid by sulfonation of the 4-*tert*-butylcatechol. The sulfonation of the catechols may be impeded by competitive reactions of sulfation, excessive sulfonation and, while using concentrated sulfuric acid or oleum as a sulfonating agent, by oxidation [13]. In case of the sulfonation of *tert*-butyl catechol with strongly acidic agents, the acid-promoted cleavage of the *tert*-butyl group is also possible. Another issue was how to purify the resulting sulfonic acid from the inorganic salts. However, we finally obtained the product, which was then characterized with nuclear magnetic resonance (NMR) spectroscopy and high-resolution mass spectrometry (HRMS).

2. Results

First, we attempted to prepare the desired product by the sulfonation of the 4-*tert*-butylcatechol with the chlorosulfonic acid, using the procedure we described earlier for the sulfonation of the polycatechol [14]. However, we failed to isolate the desired product from the complex reaction mixture, which is formed due to the excessive sulfonation. Treatment of the 4-*tert*-butylcatechol with the 80% sulfuric acid, analogous to the procedure described in the literature [13], left the starting material intact. This result is discouraging, since 4-*tert*-butylcatechol is more active in electrophilic reactions, compared with the catechol employed in the abovementioned study, but may be explained by insufficient solubility in the starting material, in 80% sulfuric acid.

Finally, the desired product was obtained by heating the 4-*tert*-butylcatechol in concentrated sulfuric acid. Contrary to the concerns of acid-promoted cleavage of the *tert*-butyl group at elevated temperatures, the resulting product was obtained as a solution in sulfuric acid. To remove the sulfate ion, it was precipitated with BaCO₃, while the target product remained in solution as a barium salt, which was then isolated by lyophilization in high yield (Scheme 1).



Scheme 1. Reaction conditions for the sulfonation of the 4-*tert*-butylcatechol with concentrated sulfuric acid.

Since the solubility of the BaCO₃ in water is 24 mg L⁻¹, the contamination of the resulting product is negligible while using moderate amounts of water to dilute the reaction mixture. However, to remove the contaminant, the product can be passed through the cation exchange resin in H⁺ form, which yield the free acid of the title product free of inorganic salts.

The ¹H-NMR spectrum of the product (Figure S1) shows two 1H doublets at 7.08 and 7.15 ppm, which are coupled with ⁴J = 2.3 Hz and 9H singlet of the *tert*-butyl group at 1.30 ppm. The -OH protons freely exchange with the D₂O and, thus, cannot be detected. The ¹³C-NMR spectrum (Figure S2), obtained at 333 K, contains two aliphatic signals at 34.0 and 30.8 ppm, as well as six aromatic signals at 144.6, 144.4, 139.6, 127.9, 116.9 and 115.3 ppm. The exact mass of the [M]⁻ ion, determined by ESI-HRMS (Figure S3), was found to be 245.0482 (245.0489 as calcd. for C₁₀H₁₃O₅S⁻). The barium content was estimated by an XRF spectroscopy (Figure S4).

Herein, we report the synthesis of the barium 5-(*tert*-butyl)-2,3-dihydroxybenzenesulfonate. The synthesis may be considered as green, since it is solvent-free, atom-economic and utilizes only water as a solvent on a purification step. The low cost and scalability of the procedure makes it possible to produce the title product, even on an industrial scale. Due to the catechol functionality and the presence of both hydrophilic and hydrophobic fragments, the title molecule may be of interest as a phase-transition chelating agent or redox-mediator.

3. Materials and Methods

3.1. General Consideration

Reagents of “reagent grade” purity were purchased from local suppliers. ¹H and ¹³C-NMR spectra were acquired on a Bruker Avance 400 spectrometer (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) at 400 and 101 MHz, respectively, in D₂O. HRMS spectrum was recorded using electrospray ionization on a Shimadzu Nexera X2 LCMS-9030 (Shimadzu Europa GmbH, Kyoto, Japan) in negative mode. XRF spectra were recorded using Shimadzu XRF-1800 apparatus (Shimadzu Europa GmbH, Kyoto, Japan).

3.2. Synthesis of Barium 5-(tert-butyl)-2,3-dihydroxybenzenesulfonate

To a 0.25 mL of concentrated sulfuric acid ($d\ 1.84\ \text{g cm}^{-3}$), placed in a screw vial, powdered 4-tert-butylcatechol (499 mg, 3 mmol) was added. The vial was sealed and heated at 45 °C for 4 h with the TLC control (SiO_2 , DCM:CH₃OH 10:1). After the disappearance of the starting material, the reaction mixture was poured in water, extracted with DCM and basified with BaCO₃ to pH 5–6. The precipitate was filtered off, and the filtrate was lyophilized to obtain the product as an opaque solid (754 mg, 1.2 mmol, 80%).

¹H-NMR (400 MHz, D₂O) δ , ppm: 7.15 (d, $J = 2.3\ \text{Hz}$, 1H), 7.08 (d, $J = 2.3\ \text{Hz}$, 1H), 1.30 (s, 9H), ¹³C-NMR (101 MHz, D₂O) δ , ppm: 160.9, 148.8, 142.9, 126.5, 116.5, 112.2, 33.6, 30.6. HRMS (ESI) m/z [M][−] calcd for C₁₀H₁₃O₅S[−] 245.0489, found 245.0482.

Supplementary Materials: The following are available online: ¹H and ¹³C-NMR spectra, HRMS and XRF data for barium 5-(tert-butyl)-2,3-dihydroxybenzenesulfonate.

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