

오르토 벤젠디술포염의 새로운 합성법

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A New Method for the Synthesis of *o*-Benzenedisulfonate

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o-Benzenedisulfonic acid has long been known and it was characterized by transforming to the corresponding sulfonate or sulfonyl chloride because it was very hygroscopic. Principal synthetic method of *o*-benzenedisulfonic acid by far consists of the reaction of sodium *o*-halobenzenesulfonate with sodium sulfite in the presence of cupric sulfate at reflux temperature^{1,2}. For example, yield from sodium *o*-chlorobenzenesulfonate was reported to be 48.7%, which was higher than that from the analogous bromo and iodo compounds.² The *o*-halobenzenesulfonates are, however, not readily available and thus synthesized generally from orthonilic acid³ which is commercially available or must be prepared from other commercially accessible compounds.^{2,4}

Other method reported by H. Cerfontain and co-worker⁵ involved direct sulfonation of benzenesulfonic acid using 101-104% or 115% sulfuric acid at 25°C. This method is, however, no useful because only 0.5% of the products was the desired product.

Hydrolysis of the recrystallized sulfonic anhydrides was utilized to prepare specific anhydrous sulfonic acids but *o*-benzenedisulfonic acid could not be prepared from benzenesulfonic anhydride.⁶

Oxidation of 2-nitrobenzo-1,4-dithiadine with alkaline KMnO₄ afforded the desired compound. This method may not be a promising route because the starting material must be synthesized through four steps from 1,2-dithiophenol which is not available readily and 2-bromoacetaldehyde diethylacetal.⁷

Recently⁸, photodecomposition of thianthrene cation radical perchlorate was described in the previous paper.¹ Although a large amount of dry acetonitrile (ca. 500 ml) was used as a solvent, no thianthrene-5-oxide which was believed to be formed from the reaction with moisture remained in the solvent was not detected. This result prompted us to investigate photochemistry of thianthrene and thianthrene-5-oxide. We have found that thianthrene and thianthrene-5-oxide underwent photochemical oxidations in the presence of oxygen to afford *o*-benzenedisulfonic acid. Progress of the reactions was found to be dependent on the reaction time and the initial concentrations of the reactant. It seems likely that the disulfonic acid is converted to its salt on silicagel column. Here a typical experimental procedure with an optimum reaction time is described: thianthrene (1.112 g, 5.140 mmol) and a stirring magnet were placed in a reaction

vessel constructed of borosilicate glass with one angle joint connected to the oxygen tank, one vertical joint equipped with a condenser with drying tube. The center mouth was accommodated by a double-walled quartz immersion well with inlet and outlet tubes for cooling. Distilled water used for the coolant was maintained at 10°C by a constant temperature circulator.

Thianthrene was dissolved in 500 ml of dry acetonitrile and the stirred solution was purged with dried oxygen through the reaction. The solution was irradiated for 8 h with a Hanovia 450 W mercury-vapor lamp. Solvent of the reaction mixture was very acidic in view of color change of litmas paper. After the yellow solvent was removed using a rotary evaporator, the residue was chromatographed on a silica gel column (13 × 2.5 cm, Merck Art. 7734, 70-325 ASTM mesh, 0.05-0.2 mm). Elution with benzene gave two kinds of unknown compounds (39 mg, 52 mg). Elution next with ethyl ether afforded 497 mg and 371 mg of compounds, which have not been identified. Finally, elution with methanol gave 1454 mg of brown sticky material which was decolorized with charcoal, followed by crystallization using a mixture of methanol and acetone containing a few drops of ethyl ether. Thus formed solid was very hygroscopic and became immediately sticky material. So, small amount of acetone was added to methanolic solution, which was stored in a refrigerator. White needle type crystals were obtained: mp > 300°C; IR^{3,9} (KBr) 3350 (OH

stretch), 1650 (OH bend), 1200 (SO asym), 1120, 1080, 1045 (SO sym), 1000, 770 cm⁻¹; ¹H NMR (D₂O) δ 7.45-8.15 (m, aromatic); UV^{10,11} λ_{max}^{MeOH} 220, 262, 269, 275 nm. This compound was assigned to be a hydrate form of *o*-benzenedisulfonate.

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