4-Hydroxybenzenesulfonyl Chloride

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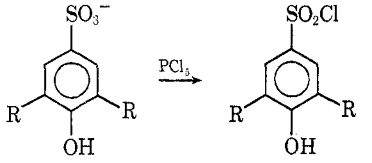
Received October 16, 1972

A variety of 3,5-disubstituted 4-hydroxybenzenesulfonyl chlorides have been reported in the literature.[1–4] They were obtained either from the reaction of the corresponding sulfonate salt with a chlorinating agent or by direct chlorosulfonation of the corresponding phenol. The parent compound, 4-hydroxybenzenesulfonyl chloride (I), apparently resisted synthesis because of the reactive, unhindered phenolic group. Anschutz[5] reported in 1908 that treatment of potassium 4-hydroxybenzenesulfonate with phosphorus pentachloride yielded the dichlorophosphate ester of I.



R = CH_3, Cl, Br

We have reinvestigated this reaction and found that sodium 4-hydroxybenzenesulfonate (II) treated with phosphorus pentachloride under a variety of conditions gave product mixtures showing no hydroxyl absorption in the infrared. Reactions of chlorosulfonic acid with II or phenol gave complex reaction mixtures which failed to yield the desired sulfonyl chloride. When II was treated with thionyl chloride using dimethylformamide as solvent, small amounts of intractable oils were obtained which showed very little hydroxyl absorption.

We have found, however, that, if II is suspended in a substantial excess of thionyl chloride containing a catalytic amount of dimethylformamide for several hours at 60°, an 80–90% yield of I is obtained, mp 68–70°. A complicating feature of the work-up is the fact that this material absorbs sufficient water to form an oily layer when poured over ice, making filtration impossible. Extraction techniques result in a partitioning of the dimethylformamide between the aqueous and organic phases. The low melting point of I contributes to purification difficulties. Unsuccessful attempts were made to isolate I by sublimation, distillation, and conventional recrystallization. A technique[6] found to be useful for converting the oily reaction product to a more easily handled solid is to dissolve it in benzene, freeze the dry benzene solution, add hexane to the frozen solution, and collect the white precipitate produced as the mixture warms to room temperature. The hydroxysulfonyl chloride is then easily recrystallized from methylene chloride.

This material was found to be quite stable when stored at 0° under a nitrogen atmosphere. If all traces of dimethylformamide are removed, I is stable at room temperature when protected from atmospheric moisture. Conditions have been found[7a,b] for conversion of I into high molecular weight polymer.

A brief examination of other catalysts has shown[8] that some organophosphorus compounds (*e.g.*, triphenylphosphine, triphenylphosphine oxide, and hexamethylphosphoramide) can be used for the production of I. These reagents do not give as high conversions under the same conditions as dimethylformamide.

In 1965 King and Smith[9] published an article dealing with the sulfur–chlorine stretching band in sulfonyl chlorides. They reported the preparation of I from the reaction of phosphorus pentachloride and II. The similarity of their reported melting behavior (mp 90–92°) with that of Anschutz (mp 87–88°) combined with our observation that I has bands at 375 and 338 cm^{-1} compared with King's report of bands at 377, 354, and 343 cm^{-1}, has led us to believe that their product was incorrectly identified.[10]

Experimental Section

4-Hydroxybenzenesulfonyl Chloride (I).—A solution of 300 g (2.5 mol) of thionyl chloride and 3.0 g of dimethylformamide was quickly added to 98.1 g (0.5 mol) of sodium 4-hydroxybenzenesulfonate. The resulting mixture was stirred at 60° for 3.5 hr. At the end of this time, the mobile, nearly homogeneous reaction mixture was poured over 800 g of ice with vigorous stirring. An oily lower layer was produced and was dissolved in 300 ml of methylene chloride. The aqueous layer was extracted with 2 × 200 ml of methylene chloride and the combined organic solutions were washed with 200 ml of ice water. The organic solution was dried over $MgSO_4$ and solvent was removed *in vacuo*. The oil remaining was dissolved in 300 ml of benzene and dried over $MgSO_4$ and the solution was frozen. Hexane was added and the solution was allowed to warm to room temperature. The white precipitate was removed as it formed (3 × 30 ml of hexane used). The product was dried in a vacuum desiccator, yielding 80.7 g (84%) of crude I, mp 63–69°. Recrystallization from methylene chloride at −70° and twice at 0° yielded I: mp 68–70°; ir (Nujol mull) OH at 2.9 μ, SO_2 at 7.4 and 8.6 μ; nmr ($CDCl_3$) δ 6.70 (1 H, s, OH), 7.04 (2 H, d, J = 9 Hz, protons ortho to OH), 7.94 (2 H, d, J = 9 Hz, protons ortho to SO_2Cl). *Anal.* Calcd for $C_6H_5ClO_3S$: C, 37.5; H, 2.6; S, 16.7; Cl, 18.4. Found: C, 37.4; H, 2.7; S, 16.7; Cl, 18.4.

Registry No.—I, 4025-67-6; sodium 4-hydroxybenzenesulfonate, 825-90-1.

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(7) (a) R. W. Campbell, U. S. Patent 3,549,595, issued to Phillips Petroleum Co., 1970; (b) R. W. Campbell and H. Wayne Hill, Jr., U. S. Patent 3,565,862, issued to Phillips Petroleum Co., 1971.

(8) H. Wayne Hill, Jr., and R. W. Campbell, U. S. Patent 3,673,247, issued to Phillips Petroleum Co., 1972.

(9) J. F. King and D. J. H. Smith, *Can. J. Chem.*, **43**, 1870 (1965).

(10) After this note was submitted for publication, it was learned by the authors *via* private communication that King had independently arrived at the same conclusion.

The Reaction of (Carbethoxymethylene)triphenylphosphorane with ω-Nitrostyrenes and Isatoic Anhydrides

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Received October 12, 1972

Our continuing interest in the reactions of phosphonium ylides for the production of novel, syntheti-