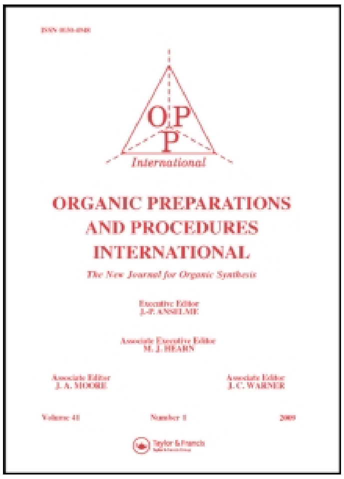

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IMPROVED SYNTHESIS OF *O*-BENZENEDISULFONIMIDE

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IMPROVED SYNTHESIS OF *o*-BENZENEDISULFONIMIDE

Submitted by
(08/05/97)

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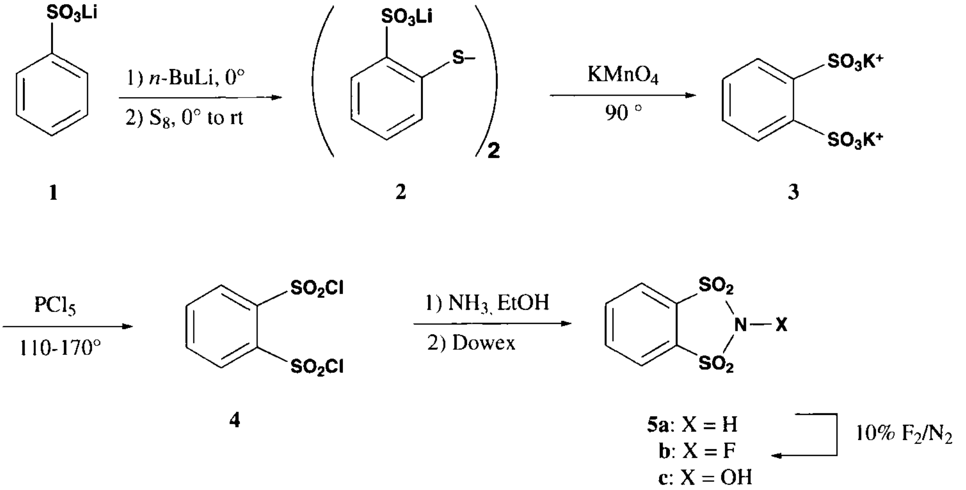
N-Fluoro-*o*-benzenedisulfonimide (NFOBS, **5b**) is an important electrophilic source of fluorine which efficiently monofluorinates carbanions and enolates.[1] This reagent is prepared in >90% yield by treatment of *o*-benzenedisulfonimide (**5a**) with 10% F_2/N_2.[1b] N-Hydroxy-*o*-benzenedisulfonimide (NHOBS, **5c**) is a selective oxidizing reagent for the oxidation of thiols to disulfides, sulfides to sulfoxides and benzyl alcohols to aldehydes.[2] It is prepared from *o*-benzenedisulfonyl chloride by reduction with sodium sulfite, followed by nitrosation.[3] The key intermediate in both these syntheses is *o*-benzenedisulfonyl chloride (**4**) which can be prepared from the disulfonic acid **3**[4] or from a 1,2-benzenedithiol derivative.[5] However, the necessity for preparing **4** from anthranilic acid[5] or aniline-2-sulfonic acid[5,6] *via* diazonium salts is inefficient and limits the scale on which NFOBS **5b** and NHOBS **5c** can be synthesized. This paper describes an efficient four-step synthesis of *o*-benzenedisulfonimide (**5a**) in 50% overall yield, from lithium benzenesulfonate (**1**).[7]



Our synthesis of **5a** relies on the *ortho* lithiation of lithium benzenesulfonate (**1**) with *n*-butyllithium first reported by Figuly and Martin.[7] Thus, treatment of a suspension of **1** at 0° in THF with 1.1 equivalents of *n*-butyllithium rapidly generated the *ortho* lithio species as indicated by the formation of a yellow colored, homogenous solution. Addition of 2 equivalents of elemental sulfur to the dilithio intermediate afforded, after quenching with 3 N HCl and removal of the solvent, a pale yellow solid (Scheme 1). The ^1H NMR indicated that it was an 88:12 mixture of the disulfide **2** and the starting material **1**. The two sets of protons in **1**, appearing as multiplets at δ 7.5 and 7.75, are clearly distinguishable from the protons in **2**. Since separation of **2** from the lithium sulfonate **1** proved impractical the mixture was used without purification and oxidized at 90° with potassium permanganate ($KMnO_4$). Removal of the aqueous solvent gave the crude sulfonic acid salt **3** which was dried under vacuum and heated at 110-170°, as previously described, with PCl_5 to give the disulfonyl chloride **4**.[1b] Treatment of **4** with $EtOH/NH_3$ afforded **5a** in 49% overall yield, following purification, from the lithium sulfonate **1**. Since none of the intermediates were purified until the end, this represents a highly efficient, safe synthesis of *o*-benzenedisulfonimide (**5a**).

EXPERIMENTAL SECTION

Benzenesulfonic acid and *n*-butyllithium were purchased from Aldrich Chemical Co. Evaporations were carried out on a rotary evaporator using an aspirator.

CAUTION: Phosphorus pentachloride is toxic. All operations were conducted in a good fume hood.

***o*-Benzenesulfonic Acid Disulfide (2)**.- To a cold (0°) suspension of dry lithium benzenesulfonate[7] (**2**; 1.64 g, 10 mmol) in dry THF (100 mL) under an inert atmosphere was added *n*-BuLi (3.7 mL of 3M hexane solution, 11 mmol) dropwise over 5 min. The pale yellow suspension became homogeneous in about 10 min. and after stirring for 5 min. elemental sulfur (0.64 g, 20 mmol) was added *via* a solid addition funnel in one portion. The brown reaction mixture was allowed to warm to rt and stirred for 15 h. The clear brown solution was quenched with 3N HCl (50 mL). The solution was concentrated, H_2O (50 mL) was added to the syrupy residue and the mixture was extracted with ether (3 x 75 mL). The organic phase was washed with 3N HCl (30 mL). The combined aqueous phases were concentrated and dried under vacuum to afford 2.4 g of **2** as a hygroscopic, pale yellow solid contaminated with **1** in a ratio of 88:12. ^1H NMR (500 MHz, D_2O): δ 7.82 (dd, 1H, J = 7.7 and 1.5 Hz); 7.43 (dd, 1H, J = 7.7 and 1.1 Hz); 7.34 (dt, 1H, J = 7.7 and 1.5 Hz); 7.24 (dt, 1H, J = 7.7 and 1.1 Hz)

***o*-Benzenedisulfonimide (5a)**.- To a hot (90°) aqueous solution (30 mL) of the crude disulfide **2** was added saturated aqueous $KMnO_4$ (10 mL) until a pale pink color persisted in the reaction mixture. After 10 min. at 90°, the excess permanganate was destroyed by addition of *i*-PrOH (2-3 mL). The reaction mixture was cooled to rt, the brown solid was removed by filtration and rinsed with H_2O (3 x 10 mL). The aqueous solution was concentrated to give a white solid which was dried under vacuum for 48 h. The crude disulfonic acid salt **3** was heated, as previously described,[1b] with PCl_5 (5.12 g, 25 mmol) first at 110° and than at 170° to give the crude disulfonyl chloride **4** which was treated with ammonia (3.1 g in 50 mL of EtOH) at 0° followed by purification of the aqueous extract by ion exchange (Dowex resin 50 x 8-100) to afford 1.08 g (49%) of **5a** as a white solid. mp. 190-192°, lit.[1b] 192-194°.

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1-ALKYLIDENE(ARYLIDENE)AMINO-2-AMINOETHANES AND THEIR TAUTOMERIZATION TO IMIDAZOLIDINES

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In theory, the interaction of ethylenediamine (**1**) with aldehydes and ketones could lead to the corresponding mono-imines (**2**). In practice, however, the *bis*-imines are actually obtained with aromatic[1-4] and aliphatic aldehydes,[4] aliphatic ketones,[2,5] acetophenone[2] and benzophenone.[2] The mono-imines have been isolated only with cyclohexanone and its homologues. The formation of mono-mines has been claimed with formaldehyde[9] and acetone[6] but no products were isolated. The instability of these mono-imines has been ascribed to their tendency toward hydrolysis and polymerization. Chromatographic methods and vacuum distillation are not useful for isolation because of the decomposition of these substances on the adsorbent surface, even at relatively low temperatures.[5]

We carried out several PMR-monitored experiments of the reaction mixtures of diamine **1** with typical carbonyl compounds, such as benzaldehyde and acetone, in order to devise a synthetic path to 1-monoalkylidene derivatives **2**. The *bis*-derivative **3a** predominates in the reaction mixture of benzaldehyde with ethylenediamine in a 1:1 proportion. Although 1-arylideneamino-2-aminoethane (**2e**) is present in less than 10%, it becomes the only product when the proportion