Improved Process for the Preparation of Tetrabutylammonium Anthracenesulfonate, a Precursor to Anthracenesulfonyl Chloride

Peter G. M. Wuts*

Chemical Process Research and Development, 7000 Portage Road, 1500-91-2, Pharmacia and Upjohn Inc., Kalamazoo, Michigan 49001

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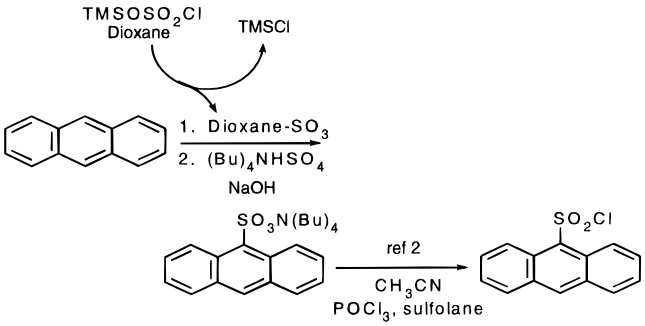
The anthracenesulfonyl group has considerable potential as an amine protecting group[1] as well as a ligand modifier for the development of chiral catalysts.[2] This group has not seen its full potential because the literature preparations are not very user friendly. We now wish to describe a procedure for the preparation of tetrabutylammonium anthracenesulfonate, which can be converted to the corresponding sulfonyl chloride with excellent efficiency.[3]

Robinson and Wyatt[3] reported an improved preparation of anthracenesulfonyl chloride that uses chlorosulfonic acid as the sulfonating agent, but we have found aspects of the isolation to be quite cumbersome and the yields were quite variable. The significant improvement in their process was the isolation of the anthracenesulfonate as its $(n\text{-Bu})_4N$ salt rather than the Na salt.

It is also known that anthracene can be sulfonated with the dioxane$-SO_3$ complex.[4] The disadvantage of this reagent is that its preparation from SO_3 is quite messy due to the fact that adding SO_3 to dioxane is quite exothermic and difficult to control, and additionally, dioxane freezes at 11 °C. To develop a simple and reasonably efficient process for the synthesis of tetrabutylammonium anthracenesulfonate, we have taken advantage of the little-known process that converts trimethylsilyl chlorosulfonate ($TMSOSO_2Cl$) to dioxane$-SO_3$ + trimethylsilyl chloride (TMSCl) simply by mixing dioxane and $TMSOSO_2Cl$ together at room temperature followed by removal of TMSCl via distillation.[5] The distinct advantage here over addition of SO_3 to dioxane is that this is a nearly thermoneutral reaction. Anthracene is then added to the resulting dioxane$-SO_3$ slurry, and the mixture is stirred for 2−3 h at room temperature. (The anthracene never goes completely in solution, and attempts to improve the yield by heating to 40 °C only results in more color formation.) Isolation is achieved by pouring the mixture onto ice, neutralizing with NaOH, treating with $(n\text{-Bu})_4NHSO_4$, and extracting with CH_2Cl_2 to afford a viscous oil after solvent removal. After the material is concentrated to an oil it is dissolved in hot ethyl acetate and crystallized. The yield for the reaction is typically 64% using 25.0 g of anthracene. Conversion to sulfonyl chloride is done using the reported procedure, which works very well.[3]

The original preparation of the tetrabutylammmonium salt by Robinson and Wyatt used tetrabutylammonium hydroxide, which is considerably more expensive and offers no advantage in the isolation. We have found no problems using $(n\text{-Bu})_4NHSO_4$ or the bromide salt, which works equally well in the isolation.

Overall, this is a very simple and reliable process that should make anthracenesulfonyl chloride much more available for routine use as a protecting group and as a ligand modifier in catalyst design.



Experimental Section

To a 250 mL flask was added 75 mL of dry dioxane and 25 mL of $TMSOSO_2Cl$. The clear solution was stirred for 5 min, and then the TMSCl was removed by vacuum distillation (27 in Hg) while keeping the pot temperature <40 °C. When the distillation was complete, 25.0 g of anthracene was added, and the slurry, which turned yellow, was stirred for 2 h at rt. The reaction mixture was filtered through a medium porosity sintered-glass funnel, and the filtrate was then poured onto about 200 mL of crushed ice/water, treated with 30 mL of 50% NaOH and 47.8 g of $(n\text{-Bu})_4HSO_4$, and extracted with 200 mL of CH_2Cl_2. After drying, the CH_2Cl_2 solution was washed 2× with 100 mL of water. The CH_2Cl_2 solution was concentrated to a viscous oil, which was dissolved in 110 mL of ethyl acetate preheated to 65 °C and allowed to cool to rt with slow stirring. If crystals did not form, the solution was seeded, which resulted in rapid crystal formation. The slurry was cooled to 0 °C, stirred for 10 min, and filtered to give a pale yellow solid. The solids were washed with ethyl acetate and then methyl *tert*-butyl ether. Drying afforded 44.6 g (64%) of the salt, which was used in the sulfonyl chloride preparation. We have found that the reaction works if the TMSCl is not removed, but the yields are not as consistent. ^1H NMR ($CDCl_3$, 300 MHz): 9.77 (d, 0.03 Hz); 8.35 (s); 7.85 (d, 0.03 Hz); 7.37 (m); 2.76 (m); 1.18 (m); 0.97 (sextet, 0.02 Hz), 0.71 (t, 0.02 Hz) ppm. ^{13}C NMR ($CDCl_3$): 140.21, 131.60, 129.74, 129.09, 128.77, 128.07, 125.45, 124.57, 57.89, 23.53, 19.30, 13.51 ppm.

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* To whom correspondence should be addressed. Tel.: (616) 833-4351. Fax: (616) 833-9158. E-mail: peter.gm.wuts@am.pnu.com.

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