Synthesis of Sulfonic Esters under Phase-Transfer Catalysed Conditions

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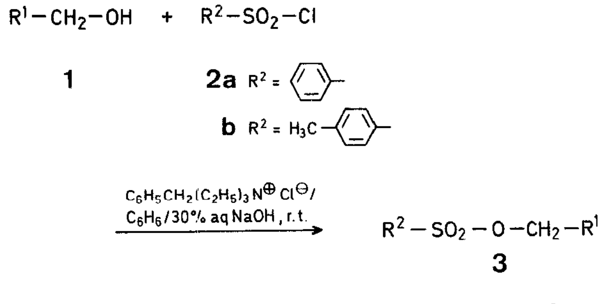
Sulfonic esters constitute an important and versatile class of compounds for potential application in synthesis[1]. For this reason various methods for preparing these compounds have been investigated[2]. In the conventional methods, esters are prepared according to the Schotten-Baumann procedure[3] or by utilising pyridine as a condensing agent.

The usual preparative procedures, however, are unsatisfactory when applied to benzyl sulfonates[1]. A method consisting of the sulfonylation of a suspension of sodium phenylmethoxide, prepared by refluxing an etheral solution of the alcohol with sodium hydride has been described[5]. Although in this method the yields are high, it requires an expensive hydride. The phase-transfer catalysed method (PTC method) is presently the most convenient procedure for a number of nucleophilic substitution reactions[6]. This method is also very suitable for the preparation of amidosulfonyl esters of phenols[7].

We now report that good to excellent yields of benzenesulfonates **3** ($R^2 = C_6H_5$) or *p*-toluenesulfonates **3** ($R^2 = 4\text{-}H_3C\text{—}C_6H_4$) can be obtained if the reaction of alcohols **1** with benzenesulfonyl chloride (**2a**) or *p*-toluenesulfonyl chloride (**2b**) is carried out under PTC conditions.

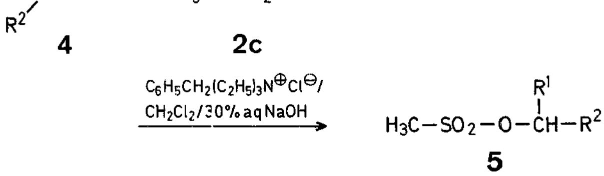


Thus, the sulfonyl chloride is added to a stirred, heterogenous mixture of alcohol **1** in an organic solvent, benzyltriethylammonium chloride, and aqueous sodium hydroxide solution. The reaction is exothermic and better yields are obtained when the reaction mixture is cooled to maintain room temperature. The reaction of arenesulfonyl chlorides with alcohols usually is complete within a few hours.

The utility of the PTC method depends to a large extent on the nature of the solvent used. Thus, when a solution of alcohol **1a** or **1b** in benzene, dichloromethane, or carbon tetrachloride was treated with **2a** good yields of the corresponding esters were obtained. Our attempts, however, to prepare these compounds using the more hydrophilic solvent tetrahydrofuran were only partly successful. In this case, the hydrolysis of the sulfonyl chloride predominated, yielding esters only as minor by-products.

The versality of the proposed procedure is particularly well demonstrated by the conversion of benzyl alcohol into the benzenesulfonate and *p*-toluenesulfonate. Although the reaction is carried out in an aqueous medium, only a minor fraction of the formed esters and sulfonyl chloride is hydrolysed. The major advantages of our approach in comparison with the previous one[5] are the less laborious procedure, the lower cost because of the use of common, very cheap reagents, and the higher yield of the products.

To demonstrate further the utility of PTC procedure, we applied it for synthesis of methanesulfonates **5** of primary and secondary alcohols **4**.



We have also obtained good yields of esters from this special water-sensitive sulfonyl chloride. In this case an excess of chloride was used and the reaction was performed at a lower temperature. As expected, **2c** is much more reactive and within a few minutes of its addition the reaction is complete. The experimental results of the conversion of alcohols into sulfonates are listed in the Table. The examples reported herein prove that synthesis of sulfonic esters under PTC conditions compares well with alternative methods.

Benzene- and *p*-Toluenesulfonic Esters 3; General Procedure:
A solution of benzenesulfonyl chloride (**2a**; 19.4 g, 0.11 mol) or *p*-toluenesulfonyl chloride (**2b**; 21.0 g, 0.11 mol) in benzene (50 ml) is added dropwise to a stirred, heterogenous mixture of benzene (100 ml), the alcohol **1** (0.10 mol), benzyltriethylammonium chloride (0.91 g, 0.004 mol), and 30% aqueous sodium hydroxide solution, maintained at 20–25°. The reaction is terminated when the odour of sulfonyl chloride disappears (5–8 h). Then, the organic layer is separated, washed with water until neutral, and dried with anhydrous sodium sulfate. After evaporation of the solvent, the product is purified by distillation or crystallisation from petroleum ether or chloroform/petroleum ether.

Methanesulfonic Esters 5; General Procedure:
A solution of the alcohol **1** (0.1 mol) and benzyltriethylammonium chloride (0.23 g, 0.001 mol) in dichloromethane (100 ml is stirred with

Table. Sulfonic Esters **3** and **5** Prepared Under PTC Conditions

R^1	Yield [%]	b.p./torr or m.p. (solvent)	Lit. b.p./torr or m.p.
Benzenesulfonates **3** ($R^2 = C_6H_5$):			
n-C_3H_7	81	134–136°/2	147–149°/4[10]
n-C_4H_9	85	136–138°/1	136–138°/1[10]
n-C_5H_{11}	82	139–140°/1	135–136°/0.5[10]
n-$C_{13}H_{27}$	85	25° (PE)	25–25.5°[10]
C_6H_5	85 (92)	58–59° (PE/$CHCl_3$)[b]	59°[11]
H_2C CH	88	121–122°/1	120–122°/1[11]
p-*Toluenesulfonates* **3** ($R^2 = 4\text{-}H_3C{-}C_6H_4$):			
n-C_3H_7	82	146–147°/2	170°/10[3]
n-$C_{11}H_{23}$	88	29–30° (PE)	28–30°[4]
n-$C_{13}H_{27}$	81 (94)	35° (PE)[c]	35°[4]
C_6H_5	82 (95)	58° (PE/$CHCl_3$)[d]	58.5–58.9°[5]

R^1	R^2	Yield [%]	b.p./torr	Lit. b.p./torr
Methanesulfonates **5**:				
n-C_3H_7	H	74	77–79°/2	77–79°/2[8]
n-C_4H_9	H	81	81–83°/2	81–83°/2[8]
n-C_5H_{11}	H	76	89–92°/2	89–92°/2[8]
i-C_3H_7	H	72	59–60°/2	53°/1[9]
C_2H_5	CH_3	68	55–56°/2	49°/1[9]

[a] Yield of purified product; values in brackets refer to crude products; purity of liquids ⩾97% as determined by G.L.C. (5% SE 30, Chromosorb W HMDS).

[b] m.p. of crude product: 57–58°; mixture m.p. 58–59°.

[c] m.p. of crude product: 33–34°; mixture m.p. 35°.

[d] m.p. of crude product: 57–58°; mixture m.p. 58°.

a 30% aqueous sodium hydroxide solution (50 ml). The heterogenous mixture is cooled to −5° and a solution of methanesulfonyl chloride (**2c**; 17.1 g, 0.15 mol) in dichloromethane (50 ml) is added dropwise at a rate to maintain a temperature below 0°. The reaction mixture is stirred for an additional 10 min. Then, the organic layer is separated, washed with water until neutral, and dried with anhydrous sodium sulfate. After evaporation of the solvent, the ester is purified by distillation under reduced pressure (see Table).

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