A Convenient Synthesis of Aryl Sulfamates

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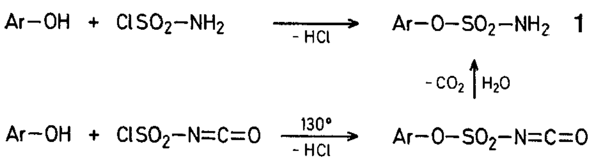
During the past few years, a number of aryl sulfamates (**1**, aryl esters of sulfamic acid) have been synthesized. These esters exhibit some interesting properties[1,2,3]. The two general methods for their synthesis hitherto described consist of the reaction of phenols with sulfamoyl chloride[4] or chlorosulfonyl isocyanate[5,6]. Both reagents are highly toxic and their manipulation is difficult.



$$Ar{-}OH + ClSO_2{-}NH_2 \xrightarrow[-HCl]{} Ar{-}O{-}SO_2{-}NH_2 \quad \mathbf{1}$$

$$Ar{-}OH + ClSO_2{-}N{=}C{=}O \xrightarrow[-HCl]{130°} Ar{-}O{-}SO_2{-}N{=}C{=}O \xrightarrow{H_2O,\ -CO_2} \mathbf{1}$$

Table. Aryl Sulfamates (**1**) from Aryloxysulfonyl Azides[a] (**2**)

1	R	Yield[b] [%]	m.p.	Lit.[5] m.p. or Molecular Formula[c]	I.R. (KBr) ν_{max} [cm^{-1}]	
					ν_{NH_2}	ν_{SO_2}
a	H	75	85°	86°	3310, 3290	1360, 1170
b	2-CH_3	70	80°	$C_7H_9NO_3S$ (187.2)	3370, 3270	1345, 1170
c	4-CH_3	75	80°	80°	3380, 3250	1350, 1170
d	2,6-di-CH_3	70	115°	110°	3350, 3260	1345, 1185
e	2-C_6H_5	50	87°	$C_{12}H_{11}NO_3S$ (249.3)	3350, 3270	1360, 1170
f	4-C_6H_5	65	165°	165°	3420, 3330	1365, 1175
g	4-Cl	72	104°	105°	3380, 3260	1355, 1185

[a] The aryloxysulfonyl azides **2a, c, f, g** were prepared by the general procedure reported in Ref.[7]. The new aryloxysulfonyl azides were prepared using the same procedure and were purified by chromatography on alumina using ether as eluent.

2b; yield: 95 %; oil; $C_7H_7N_3O_3S$ (213.2).

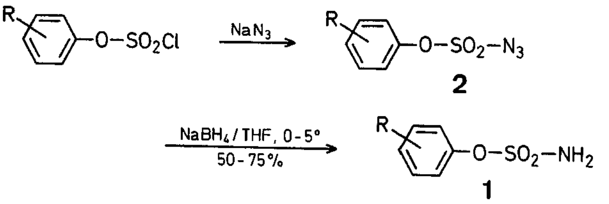
2d; yield: 50 %; oil; $C_8H_9N_3O_3S$ (227.3)

2e; yield: 94 %; m.p. 70°; $C_{12}H_9N_3O_3S$ (175.3).

[b] Yield of isolated product.

[c] All compounds gave satisfactory microanalyses: C, ±0.20 %; H, ±0.35 %; N, ±0.30 %.

In a previous paper[7], we reported that aryloxysulfonyl azides (**2**, aryl azidosulfates) can be reduced to aryl sulfamates (**1**) by means of copper/methanol. We now describe a convenient method for the synthesis of aryl sulfamates (**1**) by reduction of **2** with sodium borohydride under mild conditions.



The present procedure provides a simple method for the preparation of **1** in good yields. Cleavage of the O—SO_2 bond as in the reduction of **2** with lithium alanate is not observed[7].

Aryl Sulfamates (1) from Aryloxysulfonyl Azides (2); General Procedure:

To a stirred suspension of sodium borohydride (1 g, 26 mmol) in anhydrous tetrahydrofuran (30 ml) at 0–5°, a solution of the aryloxysulfonyl azide (**2**; 25 mmol) in tetrahydrofuran (50 ml) is added dropwise. After the mild exothermic reaction is finished, stirring is continued for 15 h at room temperature. The mixture is then poured into 10 % hydrochloric acid (100 ml) and extracted with ether. The extract is washed with water, dried with sodium sulfate, and the solvent removed in vacuo. The resultant colorless residue is recrystallized from carbon tetrachloride.

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