Direct Conversion of Alkylthiols to the Corresponding Sulfonyl Fluorides

Ch. Comninellis, Ph. Javet, and E. Plattner

Institut de Génie chimique, Ecole Polytechnique Fédérale de Lausanne, 140 rue du Centre, CH-1025 St.-Sulpice, Switzerland

Aliphatic sulfonyl fluorides have found application as starting products of diverse surfactants[1]. They were traditionally prepared by oxidation of the corresponding thiol to the sulfonic acid, conversion to the sulfonyl chloride, and replacement of chlorine with fluorine e.g. by treatment with potassium fluoride[2].

The present method is the first example of a simple, one-step preparation of sulfonyl fluorides by the oxidation of thiols with nitrogen dioxide in aqueous hydrogen fluoride.

$$R{-}SH + 3\,NO_2 + HF \longrightarrow R{-}SO_2{-}F + 3\,NO + H_2O$$

This equation is simplified; actually at the beginning of the reaction, N_2O is probably formed, as the gaseous educt does not turn brown when brought into contact with air.

The oxidation of a suspension of *n*-octanethiol in 83% hydrogen fluoride with nitrogen dioxide produces the corresponding sulfonyl fluoride in a yield of 80–85%[3]. Cyclic thiols (e.g. cyclohexanethiol) react to give a yield of 60–70% if only 30–40% of the thiol is allowed to react. Tertiary thiols (e.g. *t*-nonanethiol) react to give low yields, e.g. 30%. Aromatic thiols react to give resinous products and reactions of heterocyclic thiols (e.g. 4-pyridinethiol) give the disulfides in yields of 80%.

The success of the reaction depends on the concentration of hydrogen fluoride in the aqueous solution, which must not be allowed to sink below 65%. With more dilute acid concentrations, the sulfonic acid is obtained.

Table. Preparation of Alkanesulfonyl Fluorides

R	Yield(%)	Reaction conditions	Physical Data
n-C_8H_{17}	85	as in text	N.M.R., I.R.
c-C_6H_{11}	60–70	30–40% of thiol reacted	—[a]
	35–40	all the thiol reacted but not the intermediate disulfide	
	traces	all the thiol and all the disulfide reacted	
t-C_9H_{19}	30	as in text	—[a]

[a] Product identified by G. C. and comparison with literature references.

Preparation of *n*-Octanesulfonyl Fluoride:

A suspension of *n*-octanethiol (192 g, 1.31 mol) in 83% aqueous hydrogen fluoride (600 g) was stirred in a polyethylene beaker fitted with a steel reflux condenser, a metal thermometer, and a gas inlet tube passing below the liquid surface. The temperature was maintained at 25° by external ice/water cooling. Gaseous nitrogen dioxide (225 g, 4.85 mol, 22% excess) was bubbled through the reaction mixture at 25° for 4–5 h (~300 ml/min).

The gaseous educt is colourless at the beginning and the vigorous reaction must be slowed by intensive cooling. After 2 h, the reaction proceeds more slowly and the outlet gas, although colourless, turns brown on contact with air ($NO \rightarrow NO_2$). After 5 h, there was no more evolution of heat and the gas in the outlet tube was brown. This is an indication for the end of the reaction.

The organic layer (230 g) was separated from the hydrogen fluoride layer. The hydrogen fluoride layer was extracted with *n*-heptane and, after evaporation of the *n*-heptane, 23 g product were obtained and added to the main fraction. Chromatographic analysis (Chromosorb G. phenyl silicone 14%) showed that the purity of the total crude product was 87%; impurites were compounds with a carbonyl function and unreacted thiol (in ratio 10:1); molar yield: 85%.

Distillation of the crude product gave a pure sample of *n*-octanesulfonyl fluoride; yield: 225 g (85%); b.p. 120–125°/20 torr (Lit. 115/12 torr).

I.R. (liquid) $\nu_{max} = 2915, 2840, 1400, 1200\,cm^{-1}$.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 0.9$ (t, 3H, CH_3), 1.0–1.8 (m, 12H, $-(CH_2)_6-$), 3.3 ppm (m, 2H, $-CH_2-SO_2-F$).

Received: August 31, 1974

---

[1] E. Plattner, Ch. Comninellis, Ph. Javet, *Swiss Patent Application* No. 13026/73 of 11. 9. 73.

[2] W. Davies, J. H. Dick, *J. Chem. Soc.* **1932**, 483.

[3] E. Plattner, Ch. Comninellis, Ph. Javet, *Swiss Patent Application* No. 13025/73 of 11. 9. 73

Downloaded by: Collections and Technical Services Department. Copyrighted material.