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A NOVEL SYNTHESIS OF ALKYL PHENYLSULFINATES

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Summary Alkyl phenylsulfinates (Ph-SO-OR) were prepared from thiophenol (or diphenyldisulfide) by electrolysis in acetic acid with alcohols and sodium acetate in satisfactory yields.

Sulfinates seem to play an important role in the synthesis of sulfones[1] and sulfoxides[2] which are key intermediates of organic synthesis. Ordinally, sulfinic ester is prepared from sulfinyl chloride which is derived from sulfonyl chloride via sulfinic acid as shown eq.-1.[3]

$$RSO_2Cl \xrightarrow[Na_2CO_3]{Zn} RSO_2Na \xrightarrow{H^+} RSO_2H \xrightarrow{SOCl_2} RSOCl \xrightarrow[Py.]{R'OH} RSO\text{-}OR' \qquad \text{eq.-1}$$

In this communication we describe a novel synthesis of alkyl phenylsulfinate from thiophenol or diphenyldisulfide.

Thiophenol(2 g, 18 mmol) was dissolved in acetic acid(8 ml) with corresponding alcohol(3-4 ml) and sodium acetate(0.35 g, 4.5 mmol). The mixture was electrolyzed in an undivided cell by using two platinum electrodes at 15-45°C. After passing about 6 F/mol of electricity at 0.01-0.04 A/cm^2 of current density (applied voltage ~30 V), the solvent was removed and the residue was washed with aqueous sodium carbonate and extracted with ether. Distillation of the extract under reduced pressure gave the pure alkyl phenylsulfinate. The yields are summarized in Table 1.

$$\begin{matrix} PhSH \\ (\text{or } PhSSPh) \end{matrix} \xrightarrow[\text{in } CH_3COOH]{\text{electrolysis, 6 F/mol(S)}} PhSO\text{-}OR$$

$$ROH,\ CH_3COONa$$

Table 1 Electrolysis of PhSH (or PhSSPh) in acetic acid with ROH in the presence of sodium acetate

ROH R=	Electricity F/mol(sulfur)	Reaction Temp.(°C)	PhSO-OR[a] Yield(%)
CH_3	6	25	95
	(2)	(15-20)	(24)
	(5)	(25)	(74)
CH_3CH_2	6	25	83
	(2)	(25)	(31)
$(CH_3)_2CH$	6	30-45	85[b]
	(2)	(40)	(49)

a) The structure agreed with the authentic sample prepared by the method shown eq.-1.[3]

b) MS m/e(rel%) 184(13) 143(17) 142(58) 125(46) 97(12) 94(17) 78(100) 77(70).

References and Notes

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