A Convenient Synthesis of *p*-Toluenesulphinic Esters

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The standard method for the preparation of sulphinic esters is the reaction of an alcohol with a sulphinyl chloride[1]. The common sulphinyl halides are liquids of limited stability and the preparation of pure samples is relatively tedious[2,3]. There

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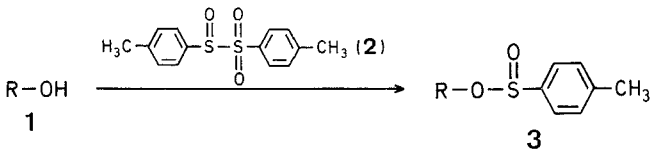
has been a report of an explosion occurring during the attempted distillation of *p*-toluenesulphinyl chloride[3]. With these difficulties in mind, several alternative methods for the conversion of an alcohol into the sulphinate have been described[4-7].

With a few special exceptions, dehydration of a sulphinic acid leads not to the corresponding sulphinic anhydride (R—SO—O—SO—R) but to the thermodynamically more stable sulphinyl sulphone[8] (R—SO—SO_2—R, disulphide *S,S,S'*-trioxide). Whilst the kinetics of the hydrolysis of sulphinyl sulphones has been extensively studied (see, in particular, Ref.[9]), the use of these compounds for the preparative sulphinylation of, for example, alcohols does not appear to have been exploited. We now report that *p*-toluenesulphinyl *p*-tolyl sulphone **(2)** is an efficient and highly convenient reagent for the preparation of *p*-toluenesulphinates **(3)** of alcohols.

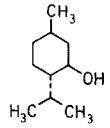
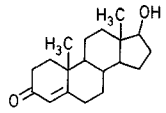
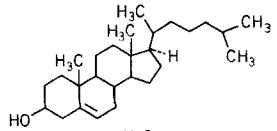
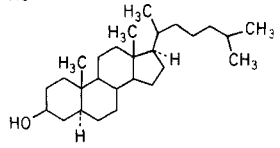
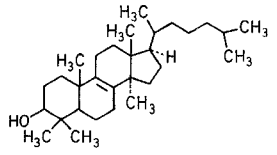
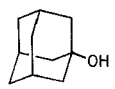


p-Toluenesulphinyl *p*-tolyl sulphone **(2)** is relatively unstable but material of adequate purity can be simply and rapidly prepared from the stable (and commercially available) sodium *p*-toluenesulphinate[10,11]. Representative results are summarised in the Table. Reactions were typically complete within 1–2 h at room temperature. In contrast to some alternative methods, yields of the sulphinic esters were uniformly good, even for tertiary and/or sterically hindered alcohols.

***p*-Toluenesulphinyl *p*-Tolyl Sulphone (2):**

A saturated solution of sodium *p*-toluenesulphinate in water is treated dropwise with 2 molar sulphuric acid until maximum precipitation is achieved. The *p*-toluenesulphinic acid is filtered off, washed with ice-cold water, and dissolved in ether. The ether layer is dried with magnesium sulphate and then evaporated to dryness under reduced pressure. Dicyclohexylcarbodiimide (200 mg, 1 mmol) is added to *p*-toluenesulphinic acid (312 mg, 2 mmol) in dichloromethane (5 ml). After 20 min, the mixture is filtered and the filtrate is evaporated under reduced pressure to a volume of ~ 1 ml. Gradual addition of hexane (5 ml) causes the crystallisation of *p*-toluenesulphinyl *p*-tolyl sulphone **(2)**; yield: 230 mg (78%); m.p. 86–88 °C (Ref.[12], m.p. 87 °C). This product is of adequate purity for the subsequent preparation of *p*-toluenesulphinic esters.

Table. *p*-Toluenesulphinic Esters **(3)** prepared

Alcohol **1**	*O*-(*p*-Toluenesulphinyl) Derivative **3**			
	Yield[a] [%]	m.p. [°C][b] (solvent)	Molecular formula[c] or Lit. m.p. [°C]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
a 	82	102–106° (aqueous acetone)	108–109°[11]	2.41 (s, 3H); 3.95–4.35 (m, 1H); 7.31, 7.63 (each d, 2H, J=8 Hz)
b 	83	169–175° (chloroform/methanol)	$C_{26}H_{34}O_3S$ (426.6)	2.43 (s, 3H); 4.14 (m, 1H); 5.74 (s, 1H); 7.34, 7.61 (each d, 2H, J=8 Hz)
c 	74	132–135° (chloroform/methanol)	$C_{34}H_{52}O_2S$ (524.8)	2.41 (s, 3H); 4.0–4.4 (m, 1H); 5.28, 5.42 (each br d, ~½H); 7.32, 7.62 (each d, 2H, J=8 Hz)
d 	85	121–123° (chloroform/methanol)	$C_{34}H_{54}O_2S$ (526.9)	2.41 (s, 3H); 4.05–4.45 (m, 1H); 7.31, 7.61 (each d, 2H, J=8 Hz)
e 	90	150–155° (chloroform/methanol)	$C_{37}H_{58}O_2S$ (566.9)	2.41 (s, 3H); 3.8–4.15 (m, 1H); 7.31 (d, 2H, J=8 Hz); 7.63, 7.66 (each d, ~1H, J=8 Hz)
f 	79	80–82° (ethyl acetate/hexane)	$C_{17}H_{22}O_2S$ (290.4)	1.69 (m, 6H); 2.13 (m, 6H); 2.24 (br m, 3H); 2.39 (s, 3H); 7.30, 7.60 (each d, 2H, J=8 Hz)
g t-C_4H_9–OH	62	oil	oil[6]	1.54 (s, 9H); 2.38 (s, 3H); 7.28, 7.58 (each d, 2H, J=8 Hz)

[a] Yield of pure, isolated product. Mixture of epimers at sulphur.

[b] Not corrected.

[c] The microanalyses showed the following maximum deviations from the calculated values: C, ±0.40; H, ±0.29; S, ±0.22. Exception: **3d**; S, −0.42.

I.R. (nujol) of all esters **3**: ν = 1130–1140 cm^{-1}.

1-Adamantanyl *p*-Toluenesulphinate (3f); Typical Procedure:
Freshly prepared *p*-toluenesulphinyl *p*-tolyl sulphone (**2**; 773 mg, 4 mol equiv) is added to 1-adamantanol (100 mg, 1 mol equiv) and pyridine (400 mg, 8 mol equiv) in dichloromethane (5 ml). The mixture is left at room temperature until T.L.C. (silica gel, 10% ethyl acetate in light petroleum b.p. 60–80 °C as eluent) indicates that no 1-adamantanol has remained (~ 1 h). The mixture is poured into water (10 ml) and extracted with dichloromethane (3 × 10 ml). The combined organic layers are washed with 10% aqueous sodium carbonate (10 ml) and saturated aqueous sodium chloride (10 ml), dried with magnesium sulphate, and evaporated under reduced pressure. The oily residue is subjected to column chromatography on silica gel (eluent 10% ethyl acetate in light petroleum b.p. 60–80 °C) to afford *S*-(*p*-tolyl) *p*-toluenethiosulphonate, m.p. 76–78 °C (Ref.[13], m.p. 76–77 °C), and 1-adamantanyl *p*-toluenesulphinate **(3f)**; yield: 151 mg (79%); m.p. 80–82 °C.

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