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GENERATION OF SULPHONYL RADICALS FROM SULPHONATE ESTERS

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Abstract. Alkane alkylsulphonates and arylsulphonates are useful sources of sulphonyl radicals on treatment with organotin radicals. EPR spectra of the adduct radicals from $CH_3SO_2^{\bullet}$ and alkenes containing donor substituents were observed.

Sulphonyl radicals, $RSO_2^{\bullet}$, figure in a variety of organosulphur reactions, some of which are synthetically useful[1]. The radicals have been generated for spectroscopic work by hydrogen abstraction from sulphinic acids[2,3] and by oxidation of thiols, disulphides and sulphoxides[4], but sulphonyl chlorides have been almost the only precursors used in synthesis[1,5-7].

It seemed to us that sulphonate esters would have advantages as radical precursors because of the ease with which they can be handled. We decided to investigate their radical reactions by means of EPR spectroscopy and product analysis.

The sulphonate esters **1-3** were made by the conventional route from the alcohol ROH and the

CH_3SO_2OR	Pr^iSO_2OR	CCl_3SO_2OR
1	**2**	**3**

	a	b	c	d
R	n-C_6H_{13}	Pr^i	Bu^t	$PhCH_2$

appropriate sulphonyl chloride. Solutions of the ester, hexamethylditin and a trace of peroxide in t-butylbenzene solvent, when photolysed with UV light, gave rise to strong EPR spectra of $CH_3SO_2^{\bullet}$, $Pr^iSO_2^{\bullet}$

or $CCl_3SO_2^\bullet$ radicals. In most cases purification of the ester was unnecessary. Excellent signals were obtained for esters of primary, secondary, tertiary and benzyl alcohols (**1** a-d). Aryl esters, $ArSO_2OR$ gave poor spectra, possibly because the aryl groups absorbed too much UV light; product analysis showed, however, that $ArSO_2^\bullet$ radicals were formed.

It seems possible that S_H2 attack of the tin-centred radical on the ester gives the sulphonyl radical together with the organotin alkoxide (equ.1)

$$Bu^tOOBu^t \xrightarrow{hv} 2Bu^tO^\bullet$$

$$Bu^tO^\bullet + Me_3SnSnMe_3 \longrightarrow Bu^tOSnMe_3 + Me_3Sn^\bullet$$

$$Me_3Sn^\bullet + R'SO_2OR \longrightarrow R'SO_2^\bullet + Me_3SnOR \quad (1)$$

The reaction can be carried out on a preparative scale using tri-n-butyltin hydride as the tin radical source and UV light as the initiator. Under these conditions the main product from isopropyl toluene sulphonate was the sulphinic acid $4\text{–}CH_3C_6H_4SO_2H$ formed when the $R'SO_2^\bullet$ radicals [equ. (1) R' = Ar] abstract hydrogen from the Bu_3SnH.

Free radical addition of sulphonyl chlorides to alkenes is a well known synthetic procedure[5,6]. We found that a sulphonate ester, in conjunction with an organotin radical, can be used as an alternative. For example, when isopropyl methane sulphonate was used as the source of $CH_3SO_2^\bullet$ radicals; the adduct radicals with various alkenes **4** were detected by EPR spectroscopy.

$$Me_3Sn^\bullet + CH_3SO_2OPr^i \longrightarrow CH_3SO_2^\bullet + Me_3SnOPr^i$$

4

R = OMe, OBu, SPh, SiMe3, alkyl.

The best spectra were obtained with alkenes carrying electron-releasing substituents (OR, SR, $SiMe_3$). This is probably because there is a favourable polar effect in the transition state for addition of the electrophilic $CH_3SO_2^\bullet$ radical to the electron rich alkene, which increases the addition rate. The spectrum obtained for n-butyl vinyl ether (**4**, R = OBu^n) is shown in the figure.

This particular reaction shows the advantage of using sulphonate esters rather than sulphonyl chlorides because when this alkene was added to CH_3SO_2Cl a black tar was produced in seconds.

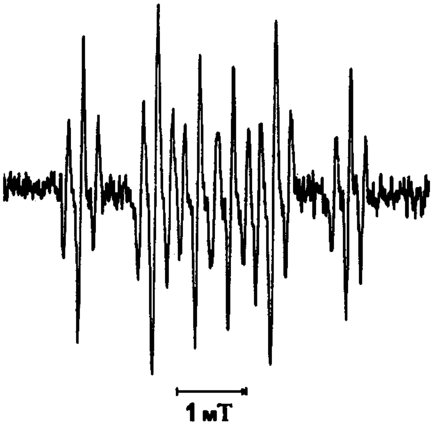
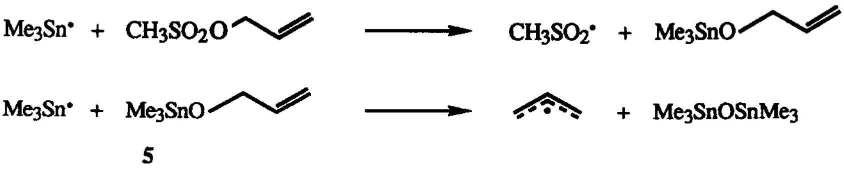


Figure: EPR spectrum of radical (4, R = OBu^n) in $PhBu^t$ at 230 K.

The EPR spectrum obtained from the reaction of trimethyltin radicals with allyl methanesulphonate showed initially a weak spectrum of $CH_3SO_2^{\bullet}$ radicals which was rapidly replaced by that of allyl radicals. The propynyl $(HC{=}C{-}CH_2)$ and pentadienyl radicals were obtained from the propynyl and penta-1,4-dienyl esters. However, this process was not simply controlled by the thermodynamic stability of the product radical because the benzyl ester gave only the $CH_3SO_2^{\bullet}$ radical.

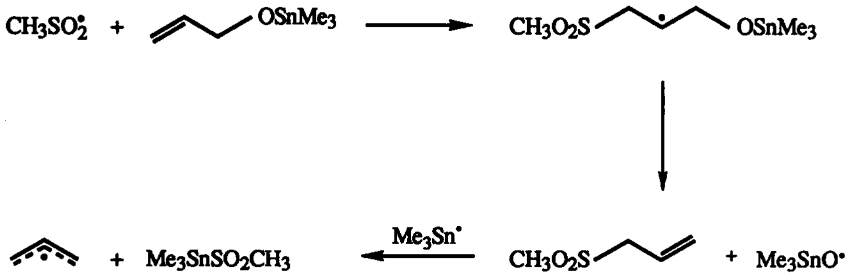
Direct displacement of the delocalised radical from the ester seemed unlikely, especially as the benzyl derivative failed to give benzyl radicals. One mechanistic possibility was displacement of the allyl radical from the first formed organotin alkoxide, 5, equ. (2).



(2)

However, authentic 5 did not produce any detectable allyl radicals on treatment with $Me_3Sn^{\bullet}$ radicals or on direct photolysis or thermolysis. We observed, however, that 5 did give allyl radicals when treated with $CH_3SO_2^{\bullet}$ radicals derived from 1b. A second possibility therefore involves addition of $CH_3SO_2^{\bullet}$ radicals to 5 followed by ß-scission to the sulphone 6 and subsequent displacement.

Reactions of sulphones going via alkyl radical intermediates are known[4,8]. This process would also explain the non-production of benzyl radicals by 1d, or 2d, because the addition step cannot occur. Further work to confirm or disprove this sequence is in progress.



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