

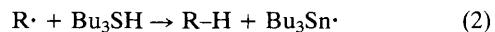
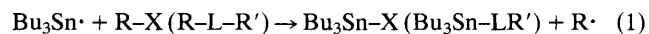
Generation of Alkoxy Radicals from *O*-Alkyl Benzenesulphenates

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Representative examples (**1**, **2**, and **3**) of primary, secondary, and tertiary alkyl benzenesulphenates, when treated with tributylstannane, generate alkoxy radicals which undergo characteristic β -scission or intramolecular addition reactions; the rate constants of these processes have been determined.

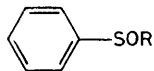
A common means of generating alkyl radicals is through the reaction of tributylstannane (Bu_3SnH) with either alkyl halides (RX ; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) or dialkylchalcogenides (R-L-R ; $\text{L} = \text{S}, \text{Se}, \text{Te}$).¹ These reactions proceed by radical chain mechanisms with $\text{S}_{\text{H}}2$ displacement of the alkyl radical by $\text{Bu}_3\text{Sn}^\cdot$ (equation 1) and hydrogen atom abstraction from Bu_3SnH by the alkyl radical (equation 2) as the chain carrying steps. This approach is not limited to alkyl radicals. For example, the reaction of Bu_3SnH with dialkyl dichalcogenides (RL-LR ; $\text{L} = \text{S}, \text{Se}, \text{Te}$) affords alkane-thiyl, -selenyl, and -telluryl radicals.² We report here investigations of the reaction of Bu_3SnH with *O*-alkyl benzenesulphenates (**1**–**3**), which demonstrate that $\text{Bu}_3\text{Sn}^\cdot$ is also able to effect the $\text{S}_{\text{H}}2$ displacement of alkoxy radicals from sulphur.



Compounds (**1**)–(**3**) were selected for initial study since they contain alkoxy groups which serve as mechanistic probes, *i.e.*, $\text{S}_{\text{H}}2$ displacement by $\text{Bu}_3\text{Sn}^\cdot$ upon these substrates would liberate alkoxy radicals known to undergo rapid, characteris-

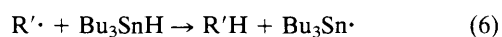
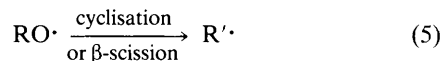
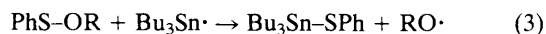
tic intramolecular reactions. The detection of products which result from such intramolecular reactions provides direct evidence for the intermediacy of alkoxy radicals. The required compounds were prepared in 60–70% yield by the addition of benzenesulphenyl chloride to 1 molar equiv. of the appropriate lithium alkoxide in tetrahydrofuran (THF) and were purified by fractional distillation.³ When a solution containing (**1**), (**2**), or (**3**), (0.030 M), Bu_3SnH (0.30 M), and azoisobutyronitrile (AIBN) (0.003 M) in *t*-butylbenzene was heated under nitrogen at 80 °C, the reaction was complete within 30 min. The products were as follows (g.l.c.): pent-4-en-1-ol (26%) and 2-methyltetrahydrofuran (73%) from (**1**); cyclopentanol (18%) and pentanal (79%) from (**2**); and 1,1,2,2-tetramethylpropan-1-ol (4%) and acetone (95%) from (**3**).

These products are consistent with a chain mechanism (equations 3–6) where alkoxy radical intermediates either abstract a hydrogen atom from Bu_3SnH to afford alcohol or undergo expected intramolecular reactions. Thus, the formation of 2-methyltetrahydrofuran from (**1**) accords with the known propensity of pent-4-enyl-1-oxy radicals to undergo rapid *exo* cyclization.⁴ Similarly, the formation of pentanal from (**2**) and acetone from (**3**) is consistent with the characteristic, facile β -scissions of the cyclopentyloxy radical⁵



- (1) R = (CH₂)₃CH=CH₂
 (2) R = cyclopentyl
 (3) R = CMe₂CMe₃

and the 1,1,2,2-tetramethyl-1-propyloxy radical.⁶ It is noteworthy that the formation of such products cannot reasonably be reconciled with any polar mechanism or with the formation of ionic intermediates.



In previous studies of *N*-alkoxy-pyridine-2-thiones,^{5,7} we have demonstrated this type of reaction manifold (equations 3—6) to be ideally suited for the investigation of the kinetics of rapid alkoxy radical reactions. The current results indicate that *O*-alkyl benzenesulphenates can also be used in such kinetic studies. For example, the results obtained for the pent-4-enyloxy radical yield a k_C/k_H ratio of 0.80 mol dm⁻³,[†] where k_C is the rate constant for cyclization and k_H is that for hydrogen atom transfer from Bu₃SnH. If it is assumed that k_H for the pent-4-enyloxy radical is similar to that for the *t*-butoxy radical ($6.6 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 80 °C),[‡] then $k_C = 5.2 \times$

[†] This ratio was calculated from the following equation: $k_C/k_H \approx [\text{Bu}_3\text{SnH}]_{\text{av.}} \times [\text{2-methyltetrahydrofuran}]/[\text{pent-4-en-1-ol}]$, where $[\text{Bu}_3\text{SnH}]_{\text{av.}} = ([\text{Bu}_3\text{SnH}]_{\text{initial}} + [\text{Bu}_3\text{SnH}]_{\text{final}})/2 = 0.285 \text{ mol dm}^{-3}$.

[‡] This value of k_d was calculated using the Arrhenius parameters: $-\log A/\text{mol dm}^{-3} \text{ s}^{-1} = 9.5 \pm 0.1$ and $E_a = 1.1 \pm 0.1 \text{ kcal mol}^{-1}$ (personal communication with Dr. J. Lusztyk) (kcal = 4.184 kJ).

10^8 s^{-1} . Similar treatment yields 80 °C β -scission rate constants of $8.3 \times 10^8 \text{ s}^{-1}$ for the cyclopentyloxy radical[§] and $4.5 \times 10^9 \text{ s}^{-1}$ for the 1,1,2,2-tetramethylpropyl-1-oxy radical.

Since primary, secondary, and tertiary *O*-alkyl benzenesulphenates can readily be prepared in reasonable yield, these compounds also promise to be useful precursors of alkoxy radicals for synthetic work. This is an advantage over the *N*-alkoxy-pyridine-2-thiones which can only be prepared in poor or modest yields (e.g. 30—40% for primary, 40—60% for secondary, and $\leq 5\%$ for tertiary alkyl groups) even under carefully selected and controlled conditions.⁸

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[§] While the β -scission of the cyclopentyloxy radical has been shown to be reversible, the back reaction is negligible at $[\text{Bu}_3\text{SnH}] \leq 0.3 \text{ M}$.⁵ The 80 °C k_β/k_H ratio of 1.25 mol dm⁻³ obtained from the reaction of (2) is in excellent agreement with the previously measured value of 1.28 mol dm⁻³.⁵