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Intermolecular Radical Displacement Reactions of Heteroaromatic Aryl Sulphones

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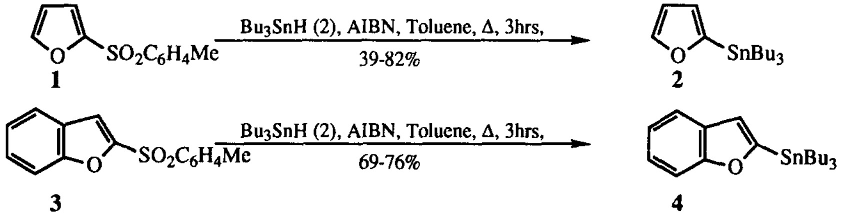
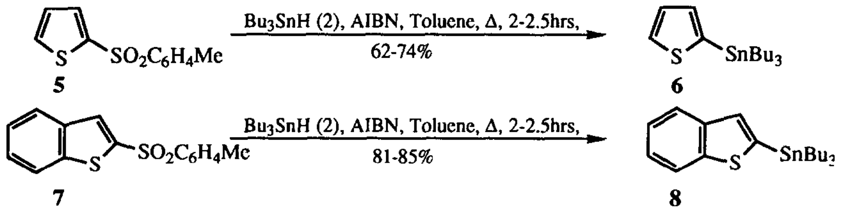
Abstract: Heteroaromatic aryl sulphones undergo intermolecular radical substitution to provide heteroaromatic stannanes in good yield.

The efficiency of free radical reactions has made them attractive for the construction of carbon-carbon bonds[1]. As part of an interest in the development of free radical based methodologies we have been examining substitution reactions of aryl sulphones[2]. We have recently demonstrated that nitrogen containing heteroaromatic aryl sulphones undergo free radical substitution reactions[3]. In this letter we detail our recent results which demonstrate the generality and further application of this substitution process for the synthesis of oxygen and sulphur containing heteroaromatic stannanes.

Our initial investigations concentrated on examining the reactions of the 4-(methyl)phenylsulphone substituted furan and benzofuran derivatives **1**[4,5] and **3**[4,5]. Treatment of a solution of sulphones **1** or **3** in toluene at reflux, with tri-*n*-butyltin hydride (2 equiv.) and AIBN, led, after chromatographic purification on alumina, to the isolation of stannanes **2**[5] and **4**[5] in moderate to good yield.

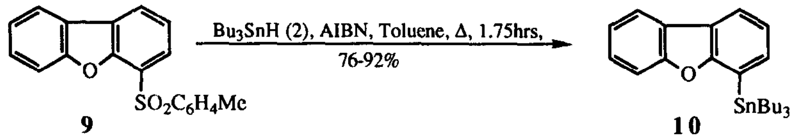


We decided to investigate the process in the thiophene series; treatment of the thiophene sulphone **5**[4,5] with tri-*n*-butyltin hydride under the conditions described above led to the formation of stannane **6**[4,5] in 62-74% yield. The 2-tri-*n*-butylstannyl benzothiophene **8**[4,5] could also be readily obtained in 81-85% yield from sulphone **7**[4,5].



In order to further extend this methodology we investigated a closely related displacement in which the sulphone is β to a heteroatom.

We were pleased to find that dibenzofuran sulphone **9**[4,5] underwent an analogous regioselective substitution with tri-*n*-butyltin hydride to provide **10**[4,5] in good yield.



9 **10**

In conclusion, we have demonstrated that a range of aryl sulphone substituted heterocycles undergo regioselective substitution reactions with tri-*n*-butyltin hydride. These recent results show that both oxygen and sulphur substituents are tolerated under the reaction conditions; further the displacement process does not appear to be limited to α heteroatom substituted aryl sulphones. The variety of useful transformations which organostannanes can undergo[6] provides a strong impetus for the development of mild methodologies for their preparation. We believe this substitution process may be of synthetic value, particularly in more elaborate systems and we are currently investigating the generality of this method by variation of the radical source and by using more remotely substituted aryl sulphones.

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References and Notes

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2. For interesting examples of related intermolecular radical additions see Watanabe, Y.; Ueno, Y.; Araki, T.; Endo, T.; Okuwara, M. *Tetrahedron Lett.*, **1986**, *27,* 215. McCarthy, J. R.; Matthews, D. P.; Stemerick, D. M.; Huber, E. W.; Bey, P.; B. J. Lippert, B. J.; Snyder, R. D.; Sunkara, P. S. *J. Am. Chem. Soc.*, **1991**, *113,* 7439. Russel, G. A.; Tashtoush, H.; Ngoviwatchai, P.; *J. Am. Chem. Soc.* **1984**, *106*, 4622. Hollingworth, G. J.; Sweeney, J. B.; *Tetrahedron Lett.*, **1992**, *46*, 7049. For other examples of intramolecular radical addition to aromatic sulphone systems see: **Alkyl radical addition;** Clive, D. L. J.; Boivin, T. L. B.; *J. Org. Chem.*, **1989**, *54*, 1997; **Vinyl radical addition;** Motherwell, W. B.; Pennell, A. M. K.; Ujjainwalla, F.; *J. Chem. Soc., Chem., Commun.*, **1992**, 1067; **Aryl radical addition;** Motherwell, W. B.; Pennell, A. M. K.; *J. Chem. Soc., Chem., Commun.*, **1992**, 1068.

3. Caddick, S.; Joshi, S.; *Synlett,* **1992**, 805; Caddick, S.; Aboutayab, K. A.; West, R. A.; *Synlett,* **1993**, 231

4. We are currently investigating a number of methods for the synthesis of these sulphones but for the purposes of this investigation they could be conveniently prepared *via* standard lithiation procedures (ref 5) followed by sulphonation with 4-(methyl)benzenesulphonyl fluoride.

5. All compounds gave spectroscopic data (i.r., ^{1}H, NMR, ^{13}C NMR, M.S) in accordance with their structure. For a recent report relating to the synthesis of these organostannanes see Liebeskind, L. S.; Wang, J.; *J. Org. Chem.*, **1993**, *58*, 3550

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