Tri-n-butylstannyl Radical Induced Rearrangement of Homopropargyl (But-3-ynyl) Arenesulfonates: A Route to Novel 4-Aryl-5,6-dihydro-1,2-oxathiin 2,2-Dioxides

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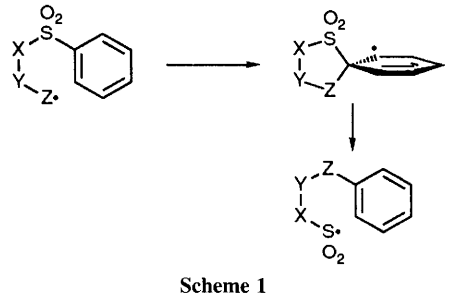
Addition of a tri-n-butylstannyl radical to arenesulfonate esters of the homopropargyl alcohol **1**, leads, *via ipso*-substitution and subsequent 6-*endo* addition–elimination, to the title derivatives **5**.

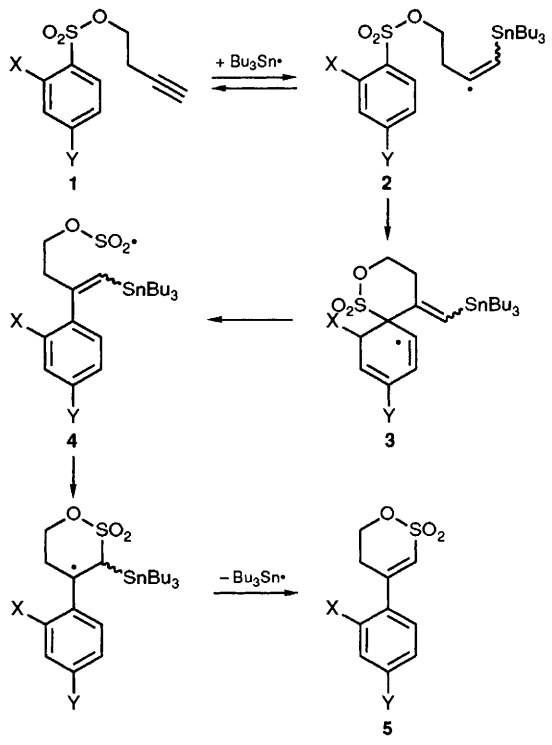
We have recently outlined a general route to biaryl derivatives based on intramolecular free radical *ipso*-substitution[1] of a variety of sulfonyl substituted aromatic derivatives by a second *ortho*-substituted aryl radical.[2] The essential requirement for successful implementation of this approach, as depicted in generalised form in Scheme 1 (Z = *ortho*-substituted aryl radical) was to discover the number and electronic nature of the atoms (X, Y) in the tethering chain, such that formation of a spirocyclic intermediate capable of rearomatisation was ensured.

It was therefore of interest to examine the behaviour of vinyl radicals in such systems (Z = vinyl radical) in order to determine their potential for the construction of substituted styrenes.

Accordingly, we elected to study radicals **2** (Scheme 2) generated by reversible addition of tri-n-butylstannyl radicals[3] to a series of readily available arenesulfonate esters of the homopropargyl alcohol **1**. Based on our experience with aryl radicals,[2] we considered that [1,6] *ipso*-substitution would



Scheme 1



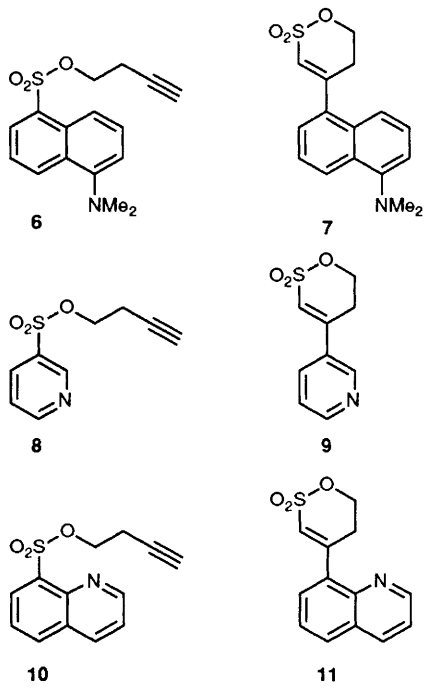
Scheme 2

Table 1 Tri-n-butylstannyl radical rearrangement of homopropargyl arenesulfonates

Substrate	Substituents	Product	Yield (%)
1	X = CO_2Me, Y = H	**5**	61
1	X = H, Y = Me	**5**	35
1	X = Y = F	**5**	39
1	X = H, Y = OMe	**5**	8
1	X = H, Y = N(Me)COMe	**5**	19
6		**7**	53

predominate over the alternative [1,7] addition and that subsequent loss of sulfur dioxide would furnish functionalised vinylstannanes. In the event however, the major product derived from a reaction involving slow addition of tri-n-butylstannane containing azoisobutyronitrile (AIBN) as initiator to a benzene solution of the sulfonate **1** (X = CO_2Me, Y = H) was revealed by a combination of spectroscopic data, microanalyses and X-ray crystallographic determination to be the cyclic α,β-unsaturated sultone **5** (X = CO_2Me, Y = H). To the best of our knowledge, only two examples of this unusual oxathiin unit at such an oxidation level have been reported,[4] and neither of these feature the β-aryl residue present in **5**. From the mechanistic standpoint, we consider that the loss of sulfur dioxide from intermediate **4**, derived *via* spirocycle **3**, is therefore sufficiently slow to permit an alternative 6-*endo* addition–elimination sequence with resultant expulsion of a potentially catalytic tri-n-butylstannyl radical as the chain carrier (Scheme 2). Some support for the above pathway comes from elegant studies by Walton,[5] who observed preferential 6-*endo* cyclisation of the archetype pentenesulfonyl radical.

Examination of the results in Table 1 reveals that the above process provides a general route to this class of compounds. As in the case of biaryl syntheses *via ipso*-substitution,[1] the reaction tolerates a wide variety of aromatic substituents. The isolated yields, however, presumably reflect the fact that the initial spirocyclic ring closure is facilitated by appropriately sited electron-withdrawing groups. We have also conducted a preliminary study using the heterocyclic derivatives **8** and **10** which afforded sultones **9** (24%) and **11** (57%) respectively. The major competing reaction (in all cases) involves simple hydrostannylation of the alkyne, although we have made every effort in practical terms to minimise this outcome by slow motor-driven syringe addition of tri-n-butylstannane containing up to 1 mol. equiv. of AIBN to the substrate. Clearly, the rearrangement sequence, although potentially catalytic with respect to the tri-n-butylstannyl radical, is rather inefficient in terms of chain propagation.



In summary, the present methodology has demonstrated the potential for the construction of a vinylic carbon–carbon bond, to aromatic and heteroaromatic systems, under neutral conditions, using free radical *ipso*-substitution at a sulfonyl substituted aromatic carbon atom.

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