# One-pot Access to Benzosulfolenes (1,3-Dihydrobenzo[*c*]thiophene *S,S*-Dioxides) *via* Allenyl Furfuryl (2-Furylmethyl) Sulfone Intramolecular Cycloaddition Strategy

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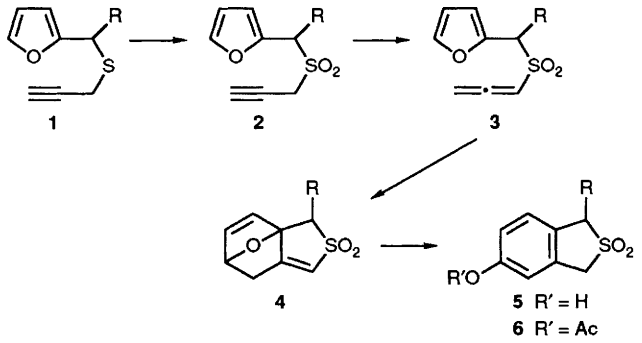
Benzosulfolene and its derivatives are ready obtained by the intramolecular cycloaddition of allenyl furfuryl sulfone in the presence of base.

Benzosulfolenes are key precursors of *o*-quinodimethanes (*o*-QDM)[1] which are useful synthetic key intermediates for many natural products such as steroids and lignans. Oppolzer[2] achieved the total synthesis of optically pure estradiol *via* the intramolecular Diels–Alder (IMDA) reaction of an *o*-QDM generated by cheletropic elimination of sulfur dioxide. Durst,[3] Charlton[4] and Mann[5] also synthesized podophyllotoxin derivatives by using the *o*-QDM derived from benzosulfolene. Generally, the preparations of benzosulfolene[6] employed by Charlton and Durst[3] have involved the reversible trapping of an *o*-QDM by sulfur dioxide. Previously we have developed the furan ring transfer[7] (FRT) reaction: a facile method for the construction of fused furans and synthetically useful isobenzofurans. Linde[8] has prepared benzo[*c*]thiophene *via* the intramolecular cycloaddition of allenyl furfuryl sulfide in an analogue of the FRT reaction.[7] We now describe the IMDA reaction of an allenyl furfuryl sulfone leading to a one-pot synthesis of benzosulfolenes.

The requisite furfuryl propynyl sulfone **2a** was prepared from the readily available furfuryl thiol by propynylation ($Et_3N$, propynyl bromide, $CH_2Cl_2$, 0 °C; 82%) followed by oxidation with *m*-chloroperbenzoic acid (MCPBA) (99%).

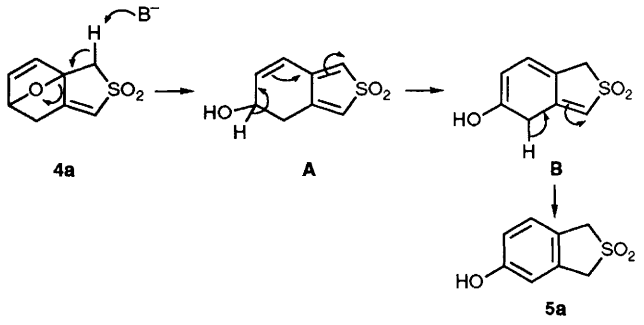



a; R = H
b; R = Me

**Scheme 1**

When furfuryl propynyl sulfone **2a** was stirred with a catalytic amount of aluminium oxide in dichloromethane for 4 h at room temperature, allenyl furfuryl sulfone **3a** was obtained in 33% yield together with a cycloadduct **4a** in 29% yield. This mixture was heated under reflux in toluene, and the cycloadduct **4a** was obtained as the sole product in 89% yield. The sulfone **2a** was converted into the cycloadduct **4a** by heating in refluxing toluene in 57% yield. This cycloadduct **4a** was converted into 5-hydroxybenzosulfolene **5a** *via* fragmentation and subsequent aromatization by refluxing with potassium *tert*-butoxide in *tert*-butyl alcohol in 80% yield. The aromatization (Scheme 2) probably took place *via* 1,5-H migration in the conjugated alkene **A** followed by 1,3-H migration **B** caused by the electron-attracting sulfone, because of the non-aromaticity of the dihydrothiophene dioxide nucleus. This result is quite different from that of the FRT reaction of allenyl furfuryl ethers[7] and allenyl furfuryl sulfide,[8] since their products were aromatized in the hetero rings and substituted by the allylic alcohol.

Finally the 5-hydroxy benzosulfolene **5a** was easily isolated in one pot from furfuryl propynyl sulfone **2a** under basic conditions in moderate yield. The structure of **5a** was confirmed by spectral data [m.p. 174–179 °C; IR $\nu_{max}/cm^{-1}$ (KBr) 3400, 1320 and 1120; $^1H$ NMR ($CDCl_3$) δ 6.91–6.75 (m, 3H), 5.70 (br s, 1H) and 4.30 (s, 4H); *m/z* (electron impact, 30 eV), 184 ($M^+$, 1.3%) and 120 ($M^+ - SO_2$, 18.9)]. Compound **5a** was also characterized by conversion into 5-acetylbenzosulfolene **6a**.




**Scheme 2**

Similarly, treatment of the methyl derivative **3b**† with potassium *tert*-butoxide in *tert*-butyl alcohol afforded the 5-hydroxy-1-methylbenzosulfolene **5b** in high yield.

This synthetic methodology allows ready access to benzosulfolenes with potential as intermediates for the synthesis, *via* inter- and intra-molecular thermal Diels–Alder reactions of multiply fused ring systems.

*Received, 31st December 1991; Com. 1/06515G*

## References

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† The starting material was the readily available furfuryl aldehyde (furfural); α-methylfurfuryl alcohol was obtained *via* alkylation by treatment with methyllithium in 90% yield. Rappoport's method[9] provided α-methylfurfuryl thioacetate in 94% yield. Hydrolysis and propynylation gave α-methylfurfuryl propynyl sulfide **1b** in 53% yield.