New Allene Equivalents for the Diels–Alder Reaction: Vinyl Sulphoxide Cycloadditions

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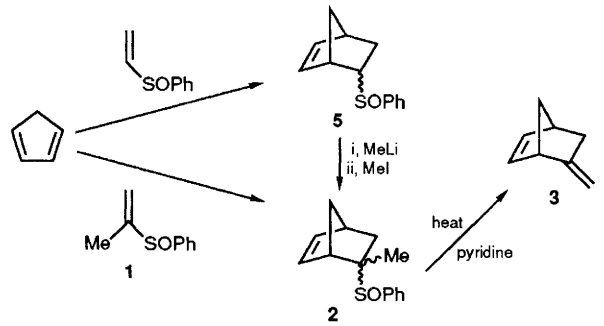
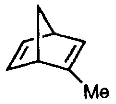
2-Phenylsulphinylpropene and phenyl vinyl sulphoxide have been shown to be effective allene equivalents for the Diels–Alder reaction.

Allene, as well as being difficult to handle, is a poor dienophile in the Diels–Alder reaction.[1] It undergoes [2 + 2] in addition to the desired [4 + 2] cycloadditions.[2] The mechanism of allene cycloadditions has been suggested to be stepwise proceeding through radical intermediates which often result in extensive side reactions, poor yields, and a low stereoselectivity.[2] However, highly strained allenes and those substituted with powerful electron[4] withdrawing groups are effective dienophiles.[3] Little effort has been directed towards the development of dienophilic equivalents of allene, although





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such methodology would find widespread applications in synthesis.[4,5] Instead, the general approach adopted would seem to be the indirect method of ketone formation followed by conversion of this functionality into the required exomethylene moiety.[5]

As a continuation of our investigations of the scope and utility of vinyl sulphoxide cycloadditions[6] we examined 2-phenylsulphinylpropene **1** as a potential allene equivalent. Vinyl sulphoxides are known to be effective dienophiles in the Diels–Alder reaction[6,7] and we reasoned that sulphoxides **2** would undergo the well known *syn* elimination[8] to give the desired exomethylene **3**. We predicted that the elimination would proceed in favour of **3** rather than the alternative norbornadiene **4** owing to the much greater ring strain present in **4**.[9]

We had previously prepared the eight isomeric adducts **5** in quantitative yield from cyclopentadiene and racemic phenyl vinyl sulphoxide.[6] To establish the effectiveness of the methodology proposed herein, the adducts **5** in dry tetrahydrofuran were treated with 1.1 equiv. of methyllithium at −78 °C. The resulting anion was quenched with methyl iodide to give **2** as a mixture of isomers (98%).† Thermolysis of **2**‡ in pyridine resulted in a 78% yield of the desired **3**.§ The isomeric mix of sulphoxides **2** could be prepared directly (59%) by reaction of 2-phenylsulphinylpropene **1**¶ with cyclopentadiene in benzene under reflux. The latter method has the advantage of avoiding treatment of the intermediate cycloadduct with strong base; thus in the presence of base-sensitive functionality side reaction is avoided. This methodology also has the potential for considerably asymmetric induction through the use of a single enantiomer of the chiral sulphoxides.[6]

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† All new compounds were fully characterised.

‡ The various isomers of **2** could be separated by column chromatography and individually thermolysed to **3** all in essentially the same yield as the thermolysis of the mixture of isomers.

§ Compound **3** produced in the above sequence gave NMR and IR spectra identical to those described in the literature.[10]

¶ Compound **1** was prepared in 69% yield by buffered ($NaHCO_3$)—chloroperbenzoic acid oxidation of the known isopropenyl phenyl sulphide.[11]