New Ketene Equivalents for the Diels–Alder Reaction. Vinyl Sulphoxide Cycloadditions

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1-Phenylsulphinyl-1-trimethylsilylethene and phenyl vinyl sulphoxide have been shown to be effective ketene equivalents for the Diels–Alder reaction.

It is well known that ketenes do not undergo satisfactory [4 + 2] cycloadditions, the [2 + 2] mode being observed generally.[1] To obtain the highly desirable [4 + 2] products several dienophilic equivalents of ketene have been developed.[2] None of these equivalents is ideal. They all tend to suffer from one or more of the following disadvantages: low dienophilicity, instability of the equivalent, high toxicity, and harsh non-specific conditions for elaboration to the desired ketone functionality. We felt that 1-phenylsulphinyl-1-trimethylsilylethene (**1**) would serve as an excellent ketene equivalent and

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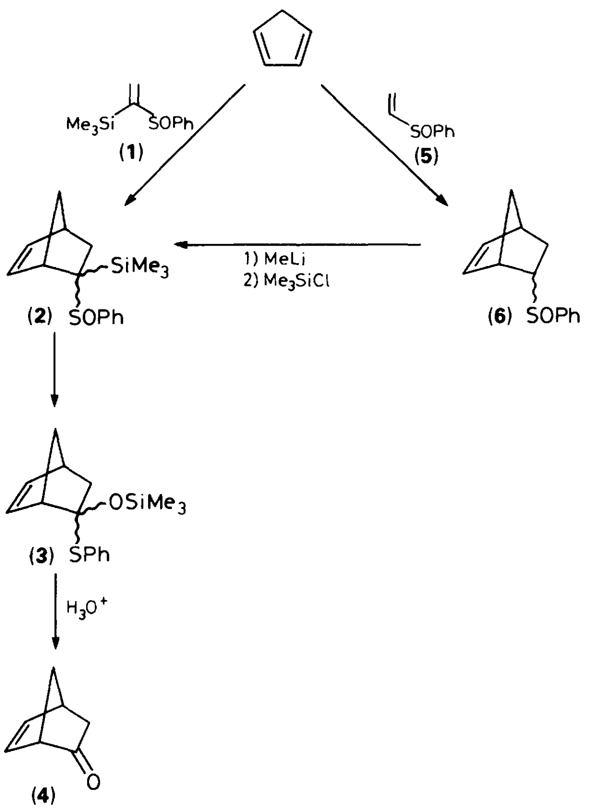

also circumvent the major problems associated with other such equivalents. An additional anticipated advantage of (**1**) is the potential for considerable asymmetric induction[3,6–8] through the use of a single enantiomer of the chiral sulphoxide. Vinyl sulphoxides are known to function as effective dienophiles in the Diels–Alder reaction,[3,9,10] although their dienophilicity is improved upon substitution with an additional electron withdrawing group.[8] It was anticipated that the adduct (**2**) would undergo the facile sila-Pummerer rearrangement[11,12] to give the thioketal (**3**) which upon hydrolysis would give the desired ketone (**4**).

To establish the feasibility of this scheme the readily available phenyl vinyl sulphoxide (**5**)[13] in benzene solution was heated under reflux with excess cyclopentadiene (2.5 equiv.) for 20 h to give a quantitative yield of the eight isomeric sulphoxides (**6**).[‡] Previously, we had established rigorously the structure of each racemic pair of diastereoisomers of (**6**) by *X*-ray analysis and correlated their NMR spectra with their structural features.[9] Treatment of the mixture, or an individual racemate, with methyl-lithium at −78 °C followed by quenching of the anion with excess chlorotrimethylsilane (TMSCl) gave the desired ketone (**4**) directly upon aqueous work up (see Scheme 1).[§]

Presumably the intermediate silylsulphoxide (**2**) underwent thermolysis at ambient temperature to the thioketal (**3**) which upon aqueous acidic (HCl resulting from hydrolysis of the excess TMSCl) work up hydrolysed to the ketone (**4**). The yield of ketone (**4**) was improved to 80—85% by a modified work up of the reaction mixture; acid wash (dilute HCl), to ensure complete hydrolysis, followed by dilute aqueous sodium hydroxide wash (to remove the resultant benzenethiol). The reported yields, which were not optimised, were obtained by interpolation from the yield of the 2,4-dinitrophenylhydrazone derivative. Isolated yields (bulb to bulb distillation) were somewhat lower (approximately 50%) owing to the high volatility of ketone (**4**).

Having demonstrated the effectiveness of this methodology we turned our attention to the dienophile (**1**). We prepared (**1**) in 67% yield[‖] by the buffered (NaHCO$_3$) *m*-chloroperbenzoic acid oxidation of 1-phenylthio-1-trimethylsilylethene.[14] Cycloaddition proceeded smoothly under reflux in benzene with excess (2.5 equiv.) cyclopentadiene once again to yield directly the ketone (**4**) in 61% yield after the usual work up.

The current work clearly indicates the potential for 1-phenysulphinyl-1-trimethylsilylethene (**1**) and phenyl vinyl sulphoxide (**5**) to function as ketene equivalents in the Diels–Alder reaction. Raphael[3] had previously shown that a vinyl sulphoxide could behave as a ketene equivalent, although in his case the elaboration of the intermediate sulphoxide adduct to a ketone required rather severe conditions and was only achieved in moderate yield.

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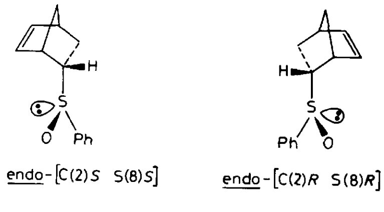
[‡] The ratio of the four racemic pairs of diastereoisomers could be controlled to some extent by the choice of kinetic or thermodynamic conditions and by the use of Lewis acid catalysis. The best yield resulted from the conditions described, in which racemic (**6**) compound III (the third component to elute upon chromatography) *endo*-(2*SR*,8*SR*)-bicyclo[2.2.1]hept-5-en-2-yl phenyl sulphoxide dominated (I, 8%; II, 26%; III, 55%; IV, 11%).



Stereochemistry of the racemic pair of (**6**) compound III.

[§] Ketone (**4**) gave NMR and IR spectra identical to those described in the literature[5] and a 2,4-dinitrophenylhydrazone of m.p. 168—170 °C (lit.[5] 170—172 °C).

[‖] All new compounds gave satisfactory NMR, IR, and mass spectra and elemental analyses.