The Unexpected Regio- and Stereo-specific Diels–Alder Reaction between Cyclopentadiene and 2-Benzenesulphonyl-3-trimethylsilylbicyclo[2.2.1]hepta-2,5-diene

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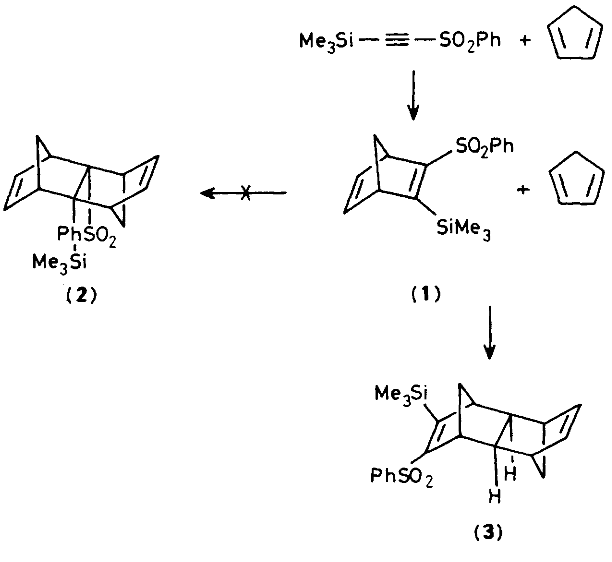
The title reaction exhibits remarkable specificity as only one of the eight possible regio- and stereo-isomers is obtained in 98% yield; the structure of this single adduct is elucidated by chemical degradation.

As part of a study towards the synthesis of the *anti*-sesquinorbornyl nucleus, the Diels–Alder addition between 2-benzenesulphonyl-3-trimethylsilylbicyclo[2.2.1]hepta-2,5-diene (**1**)† and cyclopentadiene was examined. It was anticipated that addition would occur at the electronically activated double bond with the well precedented *exo* attack leading to the *anti*-sesquinorbornadiene (**2**).[2] Cycloaddition proceeded smoothly to give a single adduct in 98% yield. However this adduct exhibited only two olefinic protons in the ^1H n.m.r. spectrum immediately precluding the possibility of it being (**2**). Mass, ^{13}C, and ^1H n.m.r.[3] spectra were consistent with the structure of this adduct being (**3**), which is in agreement with the stereoselectivity exhibited in cycloadditions to simple norbornenes.[2] However the alternative products resulting from addition of cyclopentadiene to the sterically less encumbered double bond cannot be excluded from consideration.

Structural proof of adduct (**3**) was obtained by elaboration to the known hydrocarbon (**4**).[4] Hydrogenation of (**3**) gave norbornene (**5**) in good yield. Upon treatment with 3 equivalents of lithium aluminium hydride at ambient temperature for 1 h, further reduction resulted and (**5**) cleanly gave the desired β-silylsulphone (**6**), most likely with the stereochemistry shown (the assignment is based upon the ^1H n.m.r. spectrum). Fluoride ion treatment[5] gave (**7**), clearly isomeric (by g.c.–mass spectrometry) with the known hydrocarbon (**8**).[2a,3] Both (**7**) and (**8**) gave the same product (**4**) upon hydrogenation clearly demonstrating that the adduct has the *anti*-sesquinorbornyl framework.

Only adduct (**3**) would yield (**7**) upon reduction and fluoride ion treatment. The alternate *anti* adduct resulting from *endo* attack on diene (**1**) would give the isomeric olefin (**8**) identical to the authentic sample prepared by addition of cyclopentadiene to norbornene. Thus it is unambiguously established that the single addition product between cyclopentadiene and diene (**1**) is sulphone (**3**).



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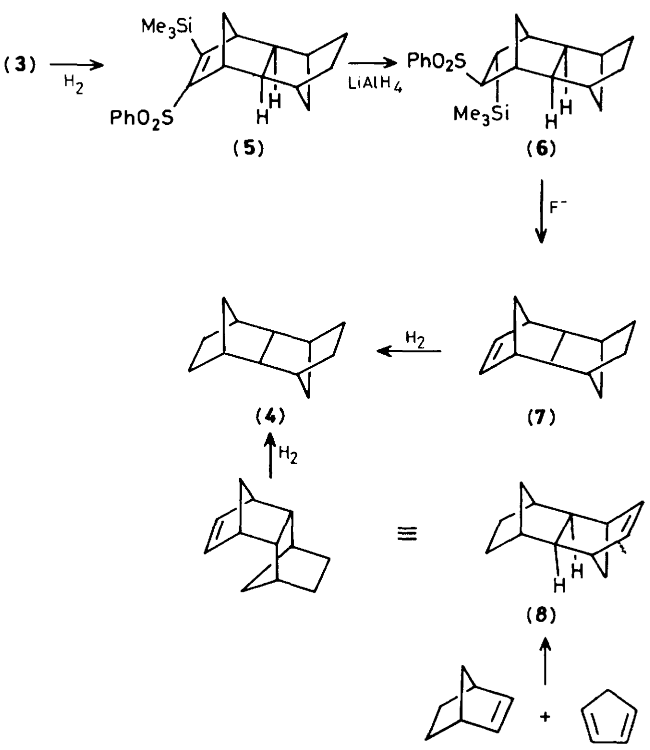
† Compound (**1**) was obtained in 93% yield from the ambient temperature cycloaddition of cyclopentadiene and 1-benzenesulphonyl-2-trimethylsilylacetylene, which was prepared by the method of Walton (ref. 1).



De Lucchi[6] has observed the same stereochemical outcome in the cycloaddition of cyclopentadiene to 2,3-bis(benzenesulphonyl)bicyclo[2.2.1]hepta-2,5-diene where again regiospecific addition occurs at the unsubstituted double bond. The present work confirms De Lucchi's stereochemical assignments, which are based on spectral parameters.

Currently this study is being extended to establish 1-benzenesulphonyl-2-trimethylsilylacetylene as a versatile and very reactive acetylene equivalent for the Diels–Alder reaction. Obviously cycloaddition with $Me_3SiC{\equiv}CSO_2Ph$ followed by lithium aluminium hydride and fluoride ion treatment is equivalent to the corresponding unlikely addition of acetylene.

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