1-Benzenesulfonyl-2-trimethylsilylacetylene: a New Acetylene Equivalent for the Diels–Alder Reaction

Richard Vaughan Williams,* Kamlesh Chauhan and Vijay R. Gadgil
Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA

1-Benzenesulfonyl-2-trimethylsilylacetylene has been shown to be an effective acetylene equivalent for the Diels–Alder reaction.

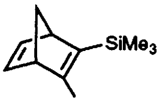
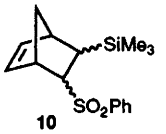
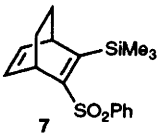
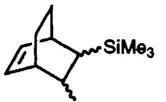
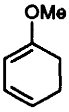
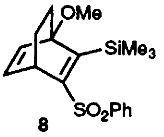
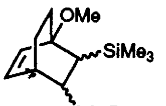
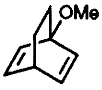
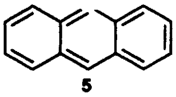
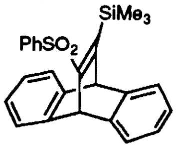
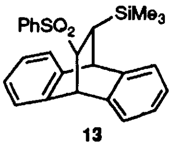
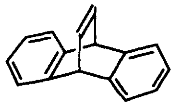
Owing to the low dienophilicity of acetylene and the hazards associated with its use at elevated temperatures and high pressures, equivalents for acetylene in the Diels–Alder reaction are essential.[1] Recently there has been much interest in developing new dienophilic equivalents of acetylene for the Diels–Alder reaction.[2] While all of these equivalents are effective, in the main, they tend to be dienophiles of relatively low reactivity and yield intermediates that require harsh non-specific conditions for elaboration to the desired cyclohexa-1,4-dienes. Earlier studies, by us,[3] Kloek,[4] and Whitham,[5] clearly demonstrated the dienophilicity of 1-arylsulfonyl-2-trimethylsilylacetylenes. We also noted the potential of 1-benzenesulfonyl-2-trimethylsilylacetylene **1** as an acetylene equivalent for the Diels–Alder reaction.[3] Here, we report our results demonstrating the realization of this potential.

1-Benzenesulfonyl-2-trimethylsilylacetylene proved to be a most efficient dienophile reacting readily, and in high yield, with a range of cyclic 1,3-dienes **2–5**.† The resulting bicyclic vinyl sulfones **6–9** underwent facile conjugate reduction with lithium aluminium hydride to give the corresponding β-silylsulfones **10–13**. The well-known fluoride ion mediated elimination proceeded smoothly giving the desired cyclohexa-1,4-dienes **14–17**, the formal Diels–Alder adducts from the addition of acetylene to the dienes **2–5**, (Table 1).

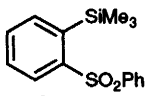
It is interesting to note that in the cycloaddition of **1** with methoxycyclohexadiene **4**, only regioisomer **8** is produced, and contrary to expectations,[6] the trimethylsilyl group controlled the regiochemistry. The lithium aluminium hydride reduction of vinyl sulfone **6** leads to an easily separable mixture of stereoisomers. Reduction of the other adducts **7–9** gives only one stereoisomer in each case. Fluoride ion treatment was carried out directly on the purified mixed β-silylsulfones **10**. Essentially identical results were obtained with the individual single isomers of **10**. Caution must be exercised in handling the compounds from cyclohexa-1,3-diene **3** and 1-methoxycyclohexa-1,3-diene **4**, as upon heating to temperatures greater than 60–65 °C facile retro-Diels–Alder reactions ensue resulting in the formation of the aromatic species such as **18** and **19**.

Table 1 Diels–Alder reaction results

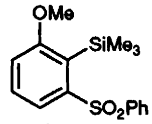
1 **2–5** **6–9** **10–13** **14–17**

Diene	Conditions[a] (yield)	Adduct	Conditions[b] (yield)	β-Silylsulfone	Conditions[c] (yield)	Cyclohexa-1,4-diene
 **2**	Methanol 0 °C → Ambient 2 h (100%)	 **6**	THF, reflux 3 h (92%)	 **10**	THF, reflux 7–18 h[d] (90–100%)[7,8]	 **14**
 **3**	Benzene 60 °C 8 h (96%)	 **7**	THF, 65 °C 3 h (94%)	 **11**	THF, reflux 8 h (76%)[e]	 **15**
 **4**	Benzene 55 °C 72 h (71%)	 **8**	THF, 65 °C 6 h (90%)	 **12**	THF, 55 °C 6 h (quantitative)[f]	 **16**
 **5**	Toluene 110 °C 10 h (92%)	 **9**	THF, 65 °C 3 h (90%)	 **13**	THF, reflux 1 h (96%)	 **17**

[a] The mol ratio of dienes: **1** varied between 1:1 and 3:1. [b] The mol ratio of vinyl sulfones:$LiAlH_4$ varied between 1:0.8 and 1:2. [c] Commercial (Aldrich Chemical Company) 1 mol dm^{-3} solutions of tetrabutylammonium fluoride were used as reagent and solvent (large excess). [d] After 7 h at reflux all of **10** was consumed (by TLC). However, the yield could not be determined accurately due to the volatility of this product. The reported yield is extrapolated from the elimination on the diphenylisobenzofuran adducts.[7,8] [e] The reported yield was obtained *via* preparative gas chromatography, the actual yield is probably higher. [f] The reported yield was estimated by NMR. Compound **16** could not be purified by preparative gas chromatography, at all oven temperatures used retro-Diels–Alder reaction resulted yielding anisole.



18



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1-Benzenesulfonyl-2-trimethylsilylacetylene **1** has proved to be an excellent equivalent of acetylene in the Diels–Alder reaction giving cyclohexa-1,4-dienes in 64–90% overall yield from **1**. Analogy with earlier studies suggests that **1** will also function as an equivalent for various substituted acetylenes by generation of the α-sulfonyl anions from compounds **10–13** followed by electrophilic quench and the usual fluoride ion treatment.[7,8] Similarly if the lithium aluminium hydride reduction step is replaced by a nucleophilic conjugate addition, then nucleophilic substituents may also be introduced.

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Footnote

† All new compounds were fully characterised except for **16** which is extremely labile and has, to date, defied isolation in a completely pure state.