

***cis*-1,2-Bis(phenylsulphonyl)ethylene: a Novel, Convenient Acetylene Synthon in Diels–Alder Reactions**

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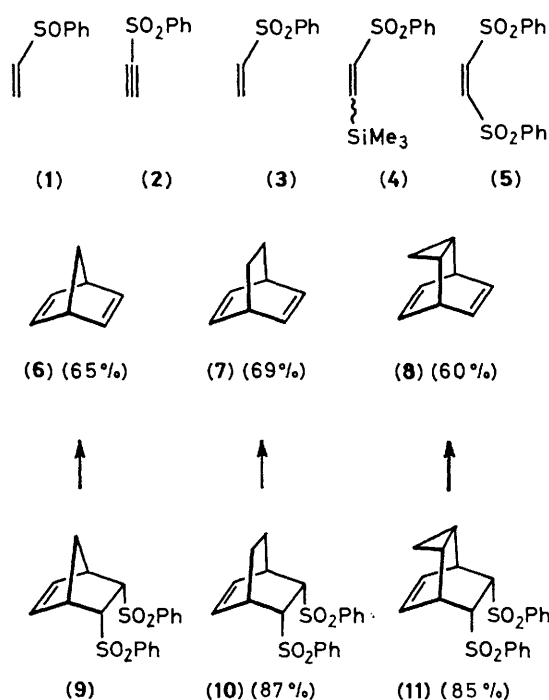
cis-1,2-Bis(phenylsulphonyl)ethylene (**5**) is found to be a reactive acetylene synthon in Diels–Alder reactions since, after cycloaddition to cyclopentadiene, cyclohexadiene, and cycloheptatriene, and reduction with sodium amalgam, the corresponding bicyclodienes (**6**)—(**8**) are obtained in good yields.

The search for new, reactive acetylene synthons for Diels–Alder reactions has recently received much attention. This synthetic effort is justified by the lack of reactivity of acetylene itself for [4 + 2]-cycloadditions and by the safety hazards in handling acetylene at the high temperatures and pressures that are otherwise required. Among the reagents which are more amenable to such reactions are sulphur-containing olefins with various oxidation states at sulphur. For example, the vinyl sulphoxide¹ (**1**) has been shown to be an acetylene equivalent in a number of cases, and the ethynylsulphone² (**2**) can also be used with some reactive substrates. The drawback of these systems is the low dienophilic reactivity of (**1**), associated with the poor electron withdrawing activity of sulphoxides, and for (**2**) the well-known poor dienophilicity of the triple bond. On the other hand the more reactive vinyl sulphone³ (**3**) gives adducts from which the desired olefin-forming elimination proceeds with difficulty.⁴ To overcome these problems β -

silylsulphones (**4**) have been tested; however, their dienophilicity is still rather poor.⁵

The higher reactivity in Diels–Alder reactions of 1,2-disulphonylethylenes (which is expected owing to the combined effect of the two sulphonyl groups) has been verified in some test reactions,⁶ but has not yet been fully exploited in the synthesis of polycyclic systems because of the lack of an easy method for the olefin-forming elimination. We report a novel method of synthesis of the hydrocarbons norbornadiene (**6**), bicyclo[2.2.2]octa-2,5-diene (**7**), and tricyclo[3.2.2.0^{3,4}]nona-6,8-diene (**8**) *via* addition of *cis*-1,2-bis(phenylsulphonyl)ethylene (**5**) to cyclopentadiene,⁶ cyclohexadiene, and cycloheptatriene followed by reductive elimination of the resulting disulphones.

The cycloadducts (**10**) and (**11**) (m.p. 304–306 and 269–271 °C, respectively, with partial decomposition), that are formed in good yields on heating the reagents (*ca.* 20% excess



of diene) at 130 °C for 24 h in toluene, were identified by their ^1H n.m.r. and i.r. spectra and by elemental combustion analysis. The spectral data compare well with those reported for other similar adducts of the same substrates.†

To our knowledge, the reductive elimination of β -disulphones has not so far been reported, although related reactions such as the elimination of β -hydroxy-, silyl-, and nitro-sulphones have been accomplished.⁷ We observed that such reactions can easily be carried out by reduction using 2% sodium amalgam in methanol, buffered with sodium dihydrogenphosphate at room temperature. Thus, a mixture of the disulphone (9)—(11) (2.5 mmol) and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (5 g) in ca. 40 ml of dry methanol was stirred overnight at room temperature in the presence of freshly prepared sodium amalgam (Na ca. 0.4 g,

17 mmol). Extraction with pentane and usual work-up afforded the corresponding dienes (6)—(8) in the reported yields.

We emphasize that the hydrocarbons (6)—(8) have been obtained in 62, 60, and 51% overall yields in a two-step synthesis which has to be compared with the reported routes and which, particularly for (7) and (8), gives lower yields through more cumbersome multistep reactions.⁸ The advantage of this procedure is two-fold: the high reactivity of disulphonyl ethylenes gives good yields of adducts even with relatively poor dienes [cyclohexadiene and cycloheptatriene are not reported to react with (1), (2), and (4)], and the easy reductive elimination of the β -sulphonyl group which is not accompanied, at least in the cases so far studied, by side reactions or skeletal rearrangements.

Received, 23rd April 1982; Com. 458

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† The stereochemical assignment is tentative but is consistent with previous reports and with the coupling constant in the ^1H n.m.r. spectrum.