Synthesis and Diels–Alder Reactions of Electron Deficient 2,3-Ethylenedisulphonyl-1,3-butadiene

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The title compound undergoes [4 + 2] Diels–Alder reactions with a number of dienophiles to provide the corresponding cycloadducts.

Recently, hetero-substituted dienes have been widely used in the synthesis of functionalized ring systems *via* Diels–Alder reactions.[1] The introduction of hetero substituents has a significant influence on the reactivity and regioselectivity of the diene.[2] Since the chemistry of 2,3-dihetero-substituted 1,3-dienes may be more complicated and more interesting, we designed a convenient preparation of these compounds based on the concept of butadienyl cation equivalents and carried out their Diels-Alder reactions.[3] Electron-deficient 2,3-dihetero-substituted 1,3-dienes (**1**)—(**4**) have been prepared by different routes.[4] Although diene (**3**) has been used as a bis-dienophile with cyclopentadiene[5] as well as a good precursor to 2,5-dihydropyrroles,[6] compounds (**1**)—(**4**) could not be used as four-electron components in Diels–Alder reactions. This may be due to either the lowered HOMO energy level caused by the two electron-withdrawing groups or to the *transoid* conformation of these dienes caused by the steric bulk of the vicinal substituents. We now report the preparation of the rigid, electron deficient diene (**5**) and the Diels–Alder reactions of the diene with a number of dienophiles.

The substitution reaction of the known 4-bromo-3-chloro-2-sulpholene (**6**)[7] with the sodium salt of ethane-1,2-dithiol gave a mixture of 3,4-ethylenedithio-2-sulpholene (**7**) and 3,4-ethylenedithio-3-sulpholene (**8**) in 50% yield.[8] The mixture was not separated and was directly oxidized with peracetic acid at 50 °C for 70 h to give the disulphonyl products (**9**) and (**10**) (37%). Thermolysis of the solution of the mixture of (**9**) and (**10**) in acetone in the presence of pyridine at 130 °C in a sealed tube for 12 h gave compound (**5**) (80%). The diene (**5**) underwent Diels–Alder reactions in dichloromethane with several dienophiles in a sealed tube. The conditions and results† are shown in Table 1.

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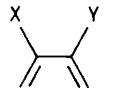
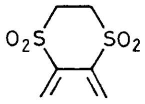
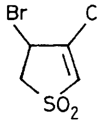
† All new compounds gave correct spectral data (i.r., n.m.r., and mass) consistent with the proposed structures.



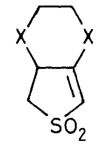
(1) X = Y = SOPh
(2) X = SOPh, Y = SO_2Ph
(3) X = Y = SO_2Ph
(4) X = Y = $POPh_2$



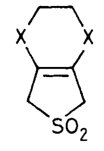
(5)



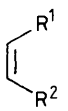
(6)



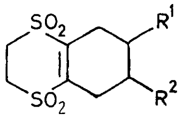
(7) X = S
(9) X = SO_2



(8) X = S
(10) X = SO_2

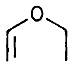
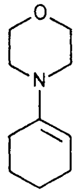
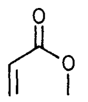
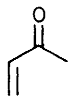
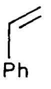
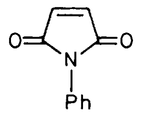


(A)



(B)

Table 1. Diels–Alder reactions of diene (5); conditions and results.

Entry	Dienophile (A) (equiv.)	Conditions	H.p.l.c. isolated yield, %, of adduct (B)
1	 (235)	60 °C, 45 h	45
2	 (10)	room temp., 2 h	80
3	 (210)	60 °C, 45 h	84
4	 (215)	60 °C, 45 h	77
5	 (30)	60 °C, 87 h	85[a]
6	 (30)	70 °C, 180 h	26
7	 (5)	150 °C, 10 h	28[b]

[a] The spectral and chromatographic data indicate that this compound exists as only one stereoisomer. However, the stereochemistry was not determined. [b] The mixture of compounds (9) and (10) was used as the diene precursor instead of diene (5) and the reaction solvent was benzene.

The steric and electronic environments of the diene unit of (5) appear to be quite similar to those of (3). The sharp contrast of their behaviour in the Diels–Alder reactions clearly indicates that the reluctance of (3) to undertake [4 + 2] cycloaddition reactions is due not to its electronic-deficient nature but to the instability of its *cisoid* conformation. It is also important to note that (5) may react well with a wide variety of alkenes ranging from electron-poor (*e.g.* entries 3, 4 and 7 of Table 1) to electron-rich dienophiles (*e.g.* entries 1 and 2 of Table 1). This dual behaviour, coupled with the fact that its cycloadducts all contain a versatile vinyl disulphone functionality,[9] makes (5) a useful reagent in the construction of bi- and multi-cyclic molecules. A similar dual behaviour of 2-(phenylsulphonyl)-1,3-dienes in Diels–Alder reactions has been observed recently.[10]

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