

AN UNUSUAL HOMO-DIELS-ALDER CYCLOADDITION REACTION BETWEEN
1,2-DEHYDROBENZENE AND BIS(ETHENYL)SULPHONE

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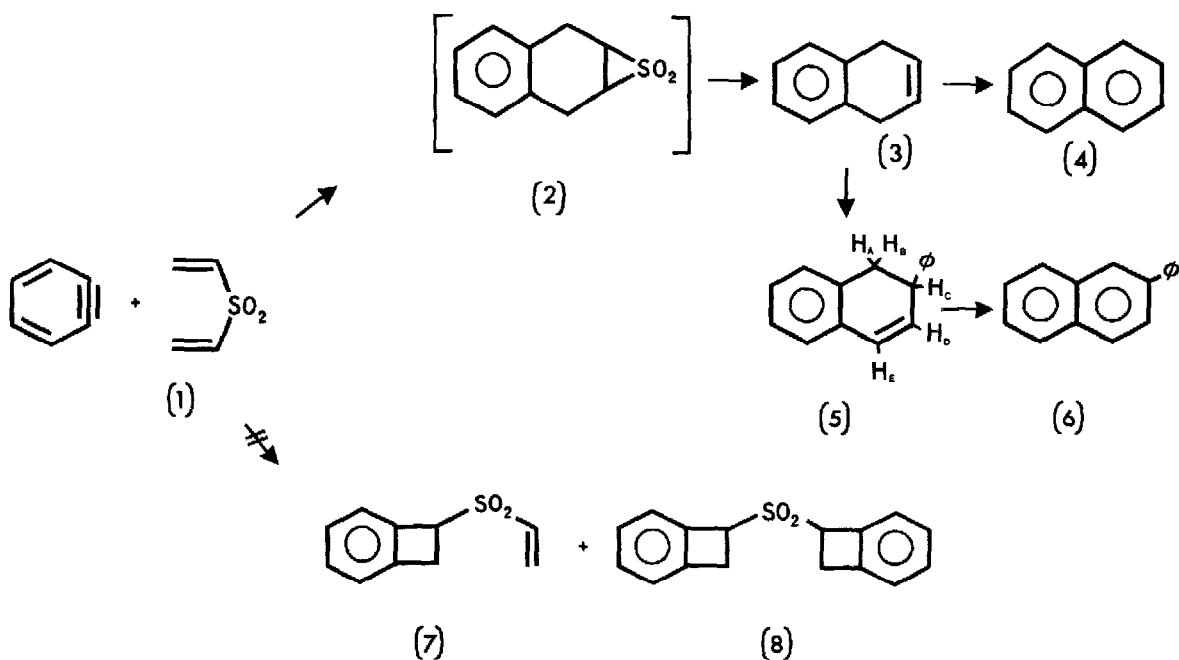
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1,2-Dehydrobenzene has been shown to give $(2+2)\pi$ cycloadducts in high yield with olefins activated by ring strain¹ or electron-donating substituents,² and in rather lower yield with simple olefins bearing electron-withdrawing substituents.³ In the reaction of 1,2-dehydrobenzene with conjugated dienes, Diels-Alder adducts and/or $(2+2)\pi$ adducts may be formed, the proportion of each depending on the ability of the diene to adopt the *s-cis* conformation required for the concerted $(4+2)\pi$ process.⁴ Reactions of 1,2-dehydrobenzenes with non-conjugated dienes have been observed only with bicyclo(2,2,1)-heptadiene, with which $(2+2)\pi$ adduct formation competes favourably with homo-Diels-Alder cycloaddition (ratio typically 3:1).⁵ It is here reported that (electron-deficient*) bis(ethenyl)sulphone (1) undergoes a cycloaddition reaction with 1,2-dehydrobenzene which gives in good yield a series of products which appears to be derived exclusively from the homo-Diels-Alder adduct (2).

Benzenediazonium 2-carboxylate was prepared from anthranilic acid (34.2 g) by the usual procedure⁷ and added as a slurry in 1,2-dichloroethane

* Bis(ethenyl)sulphone behaves as an electron-deficient dienophile in its reactions with simple electron-rich dienes which yield normal Diels-Alder adducts.⁶



to a refluxing solution of the sulphone⁸ (1) (8.9 g) in the same solvent. After removal of a considerable quantity of polymeric material by precipitation from 1,2-dichloroethane/light petroleum, fractional distillation gave fractions A (4.4 g) b.p. 56-65°/2 mm, B (1.1 g) b.p. 78-83°/0.3 mm, C (2.6 g) b.p. 90-120°/0.3 mm and a residue D (1.5 g).

Fraction A on further work-up yielded unchanged bis(ethenyl)sulphone (2.1 g) and a 5:2 mixture of 1,4-dihydronaphthalene (3) and naphthalene (2.3 g, 26.8%).⁹ These two hydrocarbons were not separated, the mixture being treated with DDQ to dehydrogenate the dihydrocompound, and the resulting naphthalene being identified as its picrate (m.p. 148-149°).

Fraction B was found to consist largely of biphenylene (0.6 g), presumably formed by dimerisation of 1,2-dehydrobenzene, together with smaller amounts of the components of fractions A and C and traces of very minor products which were not identified.¹⁰

Fraction C contained biphenylene (0.1 g) and a compound $C_{16}H_{14}$,¹¹ m.p. 35-37°, identified as 1,2-dihydro-2-phenyl-naphthalene (5) (2.5 g, 11.2%⁹), principally on the basis of its 1H n.m.r. spectrum [(CCl_4 , δ p.p.m.) 2.93 (1H, d, H_A); 3.07 (1H, s, H_B); 3.75 (1H, m, H_C); 6.03 (1H, dd, olefinic H_D); 6.60 (1H, dd, olefinic H_E); 6.9-7.3 (9H, m, aromatic protons); coupling constants: J_{AC} 3.3.Hz; $J_{BC} \approx 0$ Hz; J_{CD} 3.1 Hz; J_{CE} 2.0 Hz and J_{DE} 10.0 Hz] and its dehydrogenation by DDQ to 2-phenylnaphthalene (1,3,5-trinitrobenzene derivative m.p. 112-113°).

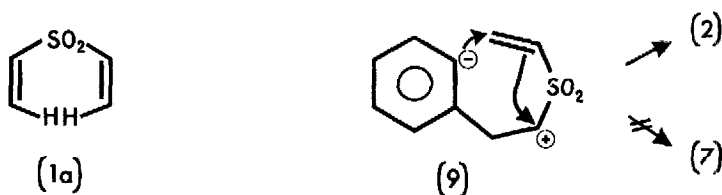
Fraction D was largely intractable, but a small quantity of 2-phénylnaphthalene (0.06 g, 0.5%) was isolated by silica chromatography.

Compounds (7) and (8), or products which might be derived from these (2+2) π adducts, were not found.

There is little doubt that the naphthalene (4) and 2-phenylnaphthalene (6) are formed by dehydrogenation of their respective dihydrocompounds (3) and (5), and that (5) is derived from (3) by a hydrogen abstraction - allylic phenylation ('ene') reaction. Similar dehydrogenations have been observed in other dihydroaromatic systems.¹²

Direct formation of 1,4-dihydronaphthalene (3) from 1,2-dehydrobenzene and the sulphone by closure of the carbocyclic ring in concert with sulphur dioxide elimination seems unlikely. On the other hand, the known instability of thiirane 1,1-dioxides¹³ makes the intermediacy of the homo-Diels-Alder cycloaddition product (2) most likely indeed. The clear preference for (2+2+2) π cycloaddition is surprising since models indicate that in the planar cis conformation of the sulphone (1a) necessary for concerted cycloaddition, the two internal ethenyl hydrogen atoms are severely eclipsed.

It would seem therefore that the cycloaddition is not concerted, but proceeds through the Zwitterionic intermediate⁵ (9) whose geometry is such that ring closure to (2) is more favourable than closure to (7).



It is hoped that further studies will permit amplification of the mechanistic and synthetic aspects of this reaction.

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