

***anti*-1,4,5,8-Tetrahydro-1,4;5,8-dimethanonaphthalene† (Sesquinorbornadiene), a Molecule with Three Parallel, Coplanar, and Interacting Double Bonds**

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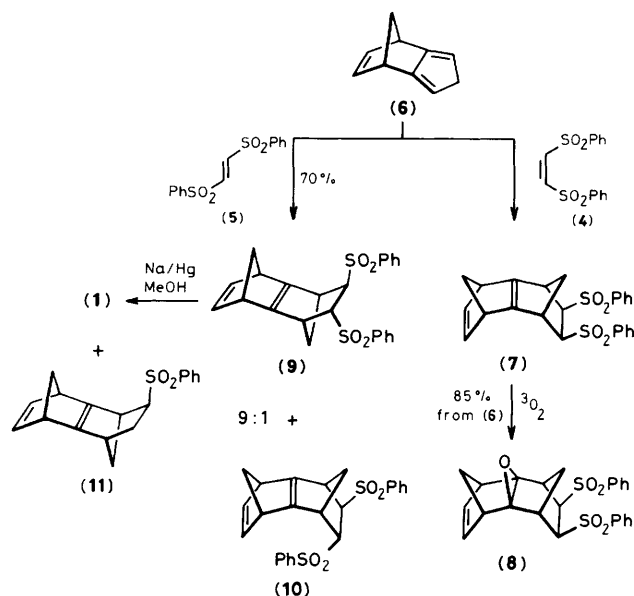
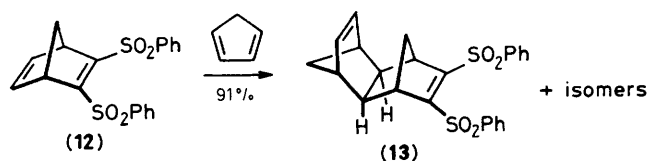
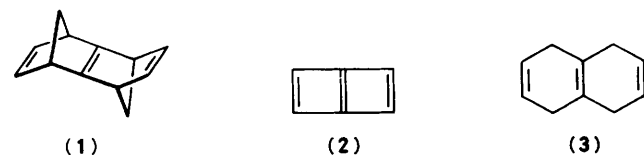
Anti-1,4,5,8-Tetrahydro-1,4;5,8-dimethanonaphthalene (sesquinorbornadiene) (**1**), a molecule possessing six electrons distributed in three parallel double bonds set in one plane and within an interacting through-space distance, has been synthesized.

The hitherto unknown *anti*-1,4,5,8-tetrahydro-1,4;5,8-dimethanonaphthalene† (sesquinorbornadiene) (**1**), contains three parallel and coplanar double bonds which, by virtue of the geometry imposed by the two methano bridges, are set at a distance at which through-space interaction is possible. This

particular electronic arrangement is also found in related hydrocarbons such as butalene (**2**) or 1,4,5,8-tetrahydronaphthalene (**3**), but the first has been shown by theoretical calculations¹ and experiments² to be extremely unstable and the second exhibits no through-space interactions.^{3‡}

† I.U.P.A.C. extended von Baeyer name: tetracyclo-[6.2.1.1^{3,6}0.2⁷]dodeca-2(7),4,9-triene. The trivial name sesquinorbornadiene has been attributed by analogy with 1,2,3,4,5,6,7,8-octahydro-1,4;5,8-dimethanonaphthalene already known as sesquinorbornene; see for example ref. 6b.

‡ In other words, there should operate among the three molecules (**1**)—(**3**) a relationship analogous to that of norbornadiene with cyclobutadiene and cyclohexa-1,4-diene, but with the possibility of extra stabilization due to the presence of six electrons.



The synthesis of (1) reported now derives from the cycloaddition of the recently reported acetylene synthetic equivalents (4) and (5)⁴ to dehydroisodicyclopentadiene (6). The results obtained were *a priori* unexpected as cycloaddition to this dienic substrate should lead to the undesired *syn*-adducts.⁵ Indeed (*Z*)-1,2-bis(phenylsulphonyl)ethylene (4) affords the *syn*-adduct (7) which, as for related molecules,⁵ reacts readily with atmospheric oxygen to give the epoxide (8) (m.p. 204 °C), as unambiguously determined by *X*-ray structure analysis.[§] The cycloaddition of (*E*)-1,2-bis(phenylsulphonyl)ethylene (5) proceeds at a much slower rate than that of the (*Z*)-isomer (4), in contrast with the reactivity observed towards other dienes.⁴ More importantly the reaction affords a mixture of two adducts in which the *anti*-isomer (9) (m.p. 163–164 °C) predominates (*ca.* 9:1), as determined by ¹H n.m.r. spectral data and confirmed by *X*-ray structure determinations.[§] The minor product, *i.e.*, the *syn* isomer (10) (m.p. 169–171 °C), is remarkably stable towards atmospheric oxygen, although the *X*-ray structure analysis shows a deviation of 16° from planarity for the central double bond. This dissimilarity compared with the related isomer (7) may be attributed to the steric hindrance that would be exerted by the *endo* phenylsulphonyl group against a further pyramidalization of the central carbon atoms resulting from a hybridization change from sp² to sp³ on epoxidation.

§ The *X*-ray structure analyses were performed by Dr. G. Valle and will be published elsewhere.

The *anti*-isomer (9), on reduction with sodium amalgam in buffered methanol affords a hydrocarbon (30–60% yield by n.m.r.) together with variable amounts of a side product (m.p. 111–113 °C) still containing a phenylsulphonyl group. Structure (11) was assigned to the latter compound on the basis of its n.m.r. data and especially nuclear Overhauser effect (n.O.e.) experiments. Structure (1) was assigned to the hydrocarbon on the basis of its unequivocal ¹H n.m.r. spectrum.[¶] Sesquinorbornadiene (1) is oxygen-sensitive; in the absence of air at room temperature it forms as yet unidentified products with an half-life of *ca.* 5 h. These preliminary experiments point to a rather low stability for (1) and suggest that a conformation which may be stabilized by the six coplanar π electrons is not obtained, probably owing to steric constraints.

The present method is of particular interest as (1) cannot be obtained by the cycloaddition of cyclopentadiene to compound (12) (m.p. 128–130 °C), a reaction which *a priori* should proceed with the correct stereochemistry⁶ and enable the crucial, central double bond to be introduced as the last step. In fact, although cyclopentadiene reacts readily with (12), it cycloadds to the unsubstituted side affording predominantly the undesired cycloadducts (13) (m.p. 184–186 °C) whose stereochemistry was assigned from n.O.e. experiments.

The present preparation of (1) provides an example of the utilization of bis(phenylsulphonyl)ethylenes as synthetic equivalents of acetylene in cycloaddition reactions when other derivatives cannot be used because of the incompatibility of the product with the methods for removing the activating groups.

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- For related examples see: (a) J. R. Edman and H. E. Simmons, *J. Org. Chem.*, 1968, **33**, 3808; (b) P. D. Bartlett, A. J. Blakeney, M. Kimura, and W. H. Watson, *J. Am. Chem. Soc.*, 1980, **102**, 1383.

¶ ¹H N.m.r. (200 MHz in CDCl₃): δ 2.02 (2H, dm, *J* 5.5 Hz), 2.27 (2H, dm), 3.52. (4H, m), and 6.82 (4H, t, *J* 1.8 Hz).