

6,7-Dimethylene-3-thiabicyclo[3.2.0]heptane-3,3-dioxide, a Masked Form of [4]Dendralene and Conjunctive Reagent for Tandem Annulations

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Previous limitations of highly reactive [4]dendralene [3,4-dimethylenehexa-1,5-diene (1)] as a tandem annelating reagent in Diels–Alder reactions are overcome by use of its masked form, 6,7-dimethylene-3-thiabicyclo[3.2.0]heptane-3,3-dioxide (2), and subsequent extrusion of SO₂ under flash vacuum pyrolytic conditions.

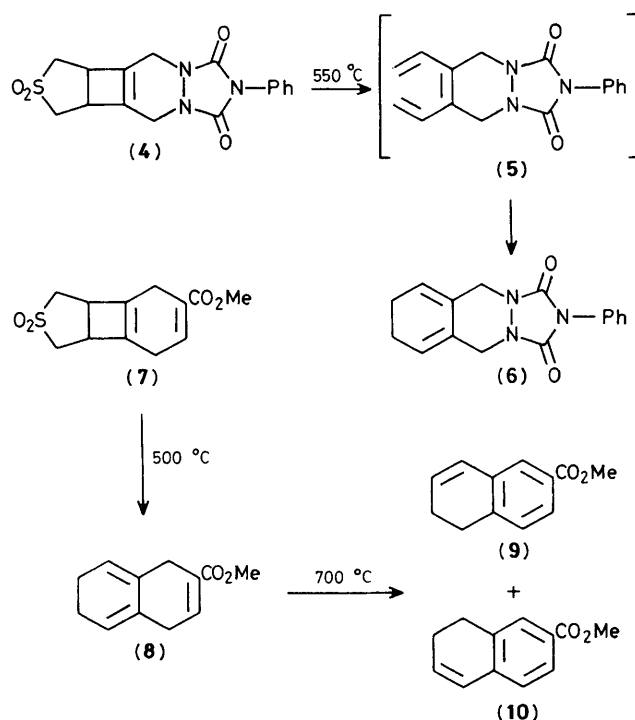
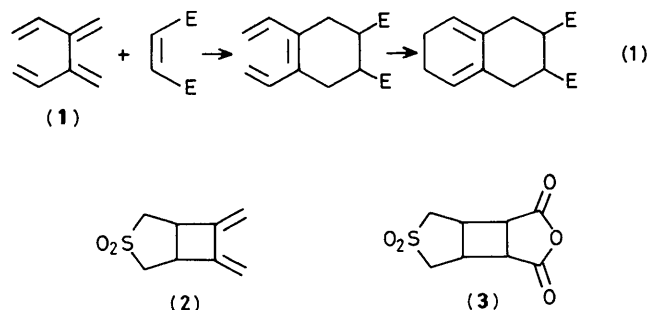
[4]Dendralene [3,4-dimethylenehexa-1,5-diene (1)], having two overlapping cross-conjugated diene systems,¹ is a fascinating yet little studied compound not least since it is difficult to prepare in the pure state² and is very prone to polymerisation.³ These difficulties are further compounded from a synthetic viewpoint by its indiscriminate reactivity in Diels–Alder reactions^{2,4} which prevent its direct use in a tandem annelation scheme as symbolized by equation (1). We now describe a straightforward experimental means of achieving this end by use of the novel bicyclic sulphone (2) which in reality is a masked form of pure [4]dendralene (1).

We easily prepared the key compound (2) in 25% overall yield from the photoadduct (3) of 2,5-dihydrothiophene 1,1-dioxide with maleic anhydride⁵ by successive esterification, reduction to the diol, conversion into the bis(toluene-*p*-sulphonate), and elimination with potassium *t*-butoxide in dimethyl sulphoxide (DMSO). It is a colourless crystalline solid (m.p. 90–92 °C decomp.) which can be handled without special precautions although it does show a tendency to polymerize on standing and is best stored admixed with a free radical inhibitor such as galvinoxyl (<5% w/w). The structure of (2) was established by elemental analysis and complementary spectral data† and its behaviour when subjected to flash vacuum pyrolysis (f.v.p.) at 550 °C and 10^{–3} mmHg. Under these conditions, it loses SO₂ to produce [4]dendralene (1)‡ as the sole product in virtually quantitative yield. This result demonstrated the nature of (2) as a masked equivalent of [4]dendralene (1). It is also an excellent diene for Diels–Alder cycloadditions and by combining this reaction with subsequent unmasking, we have developed a new methodology for the construction of annelated six-membered rings.

In a typical annelation sequence, the conjunctive reagent (2) was reacted with *N*-phenyl-3*H*-1,2,4-triazoline-3,5-dione in dry diethyl ether at room temperature to give the adduct (4)

(91%) as a colourless crystalline solid, m.p. 235–236 °C [¹H n.m.r. ([²H₆]DMSO) 7.49–7.36 (5H, m), 4.25–4.07 (4H, m), 3.83–3.80 (2H, m), and 3.37–3.11 (4H, m)]. Removal of SO₂ by f.v.p. of (4) at 500 °C and 10^{–3} mmHg then gave the novel tetrahydrophthalazine derivative [(6); m.p. 141–142 °C; ¹H n.m.r. (CDCl₃) 7.53–7.34 (5H, m), 5.83 (2H, br.s), 4.32 (4H, d, *J* 1.2 Hz), and 2.19 (4H, d, *J* 2.0 Hz)] in 56% yield. Formation of (6) is envisaged as occurring by electrocyclicization of the intermediate (5) and is in marked contrast to the equivalent reaction of [4]dendralene (1) with *N*-phenyl-3*H*-1,2,4-triazoline-3,5-dione and other dienophiles in which bis- and tris-Diels–Alder adducts are formed.

Similar pyrolyses of other cycloadducts obtained from the diene (2) and a variety of dienophiles, including maleic anhydride (77%), dimethyl acetylenedicarboxylate (53%), tetracyanoethylene (91%), maleimide (78%), 1,2-disulphonylphenylethene (49%), and methyl propiolate (52%), generated tetra- and hexa-hydronaphthalene derivatives in good-to-excellent yields. In the case of methyl propiolate, pyrolysis of the adduct (7) at 500 °C gave mainly the tetrahydro-compound (8). At the higher temperature of 700 °C, a 1:1 mixture of the dihydro-isomers (9) and (10) was formed from (8) by 1,5-hydrogen shifts and loss of hydrogen. The structures of (9) and (10) followed from their



† All new compounds gave analytical and spectral data in agreement with their assigned structures: (2) ¹H n.m.r. (CDCl₃) δ 5.39 (2H, s), 4.96 (2H, s), 3.83–3.65 (2H, m), and 3.50–2.98 (4H, m); ¹³C n.m.r. (CDCl₃) δ 147.94, 106.92, 53.33, and 38.85.

‡ We are indebted to Professor Roth for a copy of the ¹H n.m.r. spectrum of (1) (see ref. 4).

spectroscopic properties and essentially quantitative conversion into methyl 2-naphthoate (m.p. 77–78 °C; lit.⁶ 76 °C) with 2,3,5,6-dichlorodicyanobenzoquinone (DDQ) in benzene at room temperature.

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References

- 1 For a review of cross-conjugated molecules of the dendralene type, see H. Hopf, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 948.
- 2 [4]Dendralene (**1**) was first prepared by W. J. Bailey and N. A. Nielsen, *J. Org. Chem.*, 1962, **27**, 3088 as part of a complex mixture of at least twenty products from the pyrolysis of the tetra-acetate of butane-1,2,3,4-tetracarboxylic acid. Other methods for its preparation are reviewed in ref. 1, but a similar lack of specificity and the synthetic effort required to make the different precursors renders them essentially useless for practical purposes.
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