

A Synthon for C₂ Polycyclic 1,4,5,8-Tetrahydronaphthalenes via Double Diels–Alder Cycloaddition

Ottorino De Lucchi*^a and Sergio Cossu^b

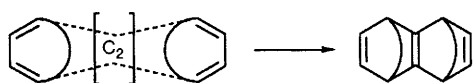
^a Dipartimento di Chimica, Università di Venezia, Dorsoduro 2137, I-30123 Venezia, Italy

^b Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari, Italy

2-Chloro-1,4-benzodithiin-*S,S'*-tetroxide **1** is a synthon for C₂ because its Diels–Alder adducts, after dehydrochlorination, react further with another molecule of diene and the resulting product can be desulfonylated into the same hydrocarbons that would have formed from C₂.

The recent intense research on the fullerenes has sparked interest into the synthesis of other highly unsaturated polycyclic hydrocarbons with potential for defining new synthetic tools applicable to large-scale preparations of complex, unsaturated molecules. In this context, synthons of diatomic carbon, which, unlike the actual C₂ molecule,¹ react in a fully controlled fashion in cycloadditions, are of interest. For example, if C₂ could react with two moles of a diene in a Diels–Alder cycloaddition, it would furnish substituted 1,4,5,8-tetrahydronaphthalenes (Scheme 1). With cyclic dienes, the method would constitute a simple entry into hitherto unknown or inaccessible polycyclic molecules some of which may exhibit hyperstable character.²

Reagents able to perform this synthetic target are still unknown. In principle, they could be acetylenes substituted with activating and removable functionalities such as carboxy,³ cyano,⁴ or arylsulfonyl groups.⁵ Unfortunately, the former two are difficult to remove while the latter are too sterically hindered to provide sufficient activation. Here, we report on the utility of 2-chloro-1,4-benzodithiin *S,S'*-tetroxide **1** as a synthon for C₂ in cycloaddition reactions. As shown

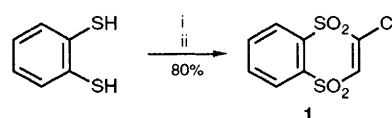


Scheme 1

by molecular models, the *cis*-locked configuration leads to a favourable conformation of the sulfonyl groups for Diels–Alder cycloadditions. Indeed, the higher reactivity of the unsubstituted 1,4-benzodithiin-*S,S'*-tetroxide with respect to the bis(phenylsulfonyl)ethylenes has been reported recently.⁶

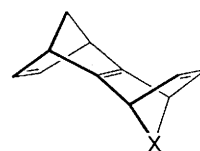
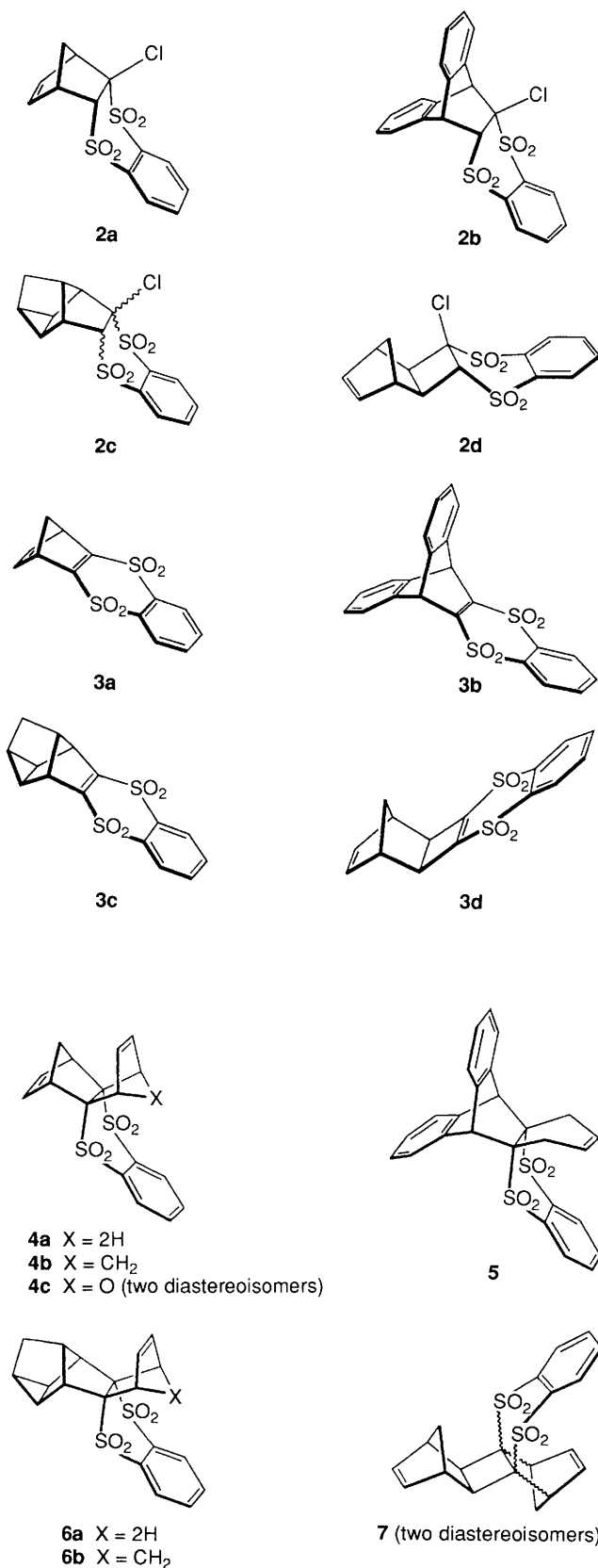
Reaction of the disodium salt of benzene-1,2-dithiol with trichloroethylene provided quantitative yields of 2-chloro-1,4-benzodithiin that was oxidized in *ca.* 80% to the crystalline tetroxide **1** (m.p. 175–177 °C), Scheme 2.

The reaction of the latter with dienes led to the expected Diels–Alder adducts **2**[†] which were readily dehydrochlorinated with triethylamine to dienes **3**. The products shown are representative of different types of cycloadditions (*i.e.* [4 + 2], homo-[4 + 2] and cycloaddition to strained σ bonds) and derive from cyclopentadiene [adduct **2a** (m.p. 271–272 °C)], anthracene [adduct **2b** (spontaneously dehydrochlorinates to

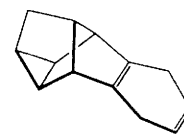


Scheme 2 Reagents: i, Cl₂=CHCl; ii, *m*-CPBA

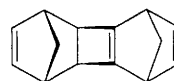
[†] The structures of the adducts (except **10**) are drawn on the basis of MM2 calculations.



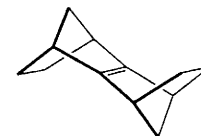
8a X = 2H
8b X = CH₂



9



10 (two diastereoisomers)



11

compounds **3** is reactive toward several dienes affording the double Diels–Alder adducts **4**–**7**. For example, **3a** (m.p. 184–185 °C) reacted smoothly with buta-1,3-diene (as delivered by 3-sulfolene at 70 °C), cyclopentadiene and furan to afford cycloadducts **4a** (m.p. 247–249 °C), **4b** (m.p. 256–258 °C), and **4c** (two diastereoisomers), respectively. In a similar way, bis-adduct **5** (m.p. >320 °C) was obtained from **3b** and 3-sulfolene, while adducts **6a** (m.p. 316–318 °C) and **6b** (m.p. 278–279 °C) were obtained from **3d** and 3-sulfolene or cyclopentadiene. Finally, compound **7** was obtained as a mixture of two diastereoisomers from **3c** and cyclopentadiene. The stereochemistry of the adducts has been assigned on the basis of the ¹H NMR spectra plus NOE experiments.

Because the diene has to be introduced in two steps it is possible to control the reaction in order to produce symmetric or non-symmetric compounds.

Reduction of the bis adducts with 6% sodium amalgam in buffered (NaH₂PO₄) methanol produced the hydrocarbons in high purity and yields. Representative examples are the ready synthesis of the dihydrobenzonorbornadiene **8a**,⁴ of the sesquinorbornadiene **8b**⁷ and of the hitherto unknown dienes **9** and **10**.

The preparation of these new molecules testify the potential of this synthetic method. It bears also mentioning that sodium amalgam reduction of hydrogenated **4b** led in over 80% yield to sesquinorbornene **11**. This preparation is in our opinion the most rapid and high yielding synthesis of sesquinorbornene so far reported.⁴

This work was supported by CNR (Rome).

Received, 18th May 1992; Com. 2102586H

References

- 1 P. S. Skell, L. M. Jackman, S. Ahmed, M. L. McKee and P. B. Shevlin, *J. Am. Chem. Soc.*, 1989, **111**, 4422 and references cited therein.
- 2 A. B. McEwen and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1986, **108**, 3951.
- 3 O. De Lucchi and G. Modena, *Tetrahedron*, 1984, **40**, 2585.
- 4 O. De Lucchi, N. Piccolrovazzi and G. Modena, *Tetrahedron Lett.*, 1986, **27**, 4347; O. De Lucchi, N. Piccolrovazzi, G. Licini, G. Modena and G. Valle, *Gazz. Chim. Ital.*, 1987, **117**, 401.
- 5 L. Pasquato, O. De Lucchi and L. Krotz, *Tetrahedron Lett.*, 1991, **32**, 2177; U. Azzena, S. Cossu, O. De Lucchi and G. Melloni, *Gazz. Chim. Ital.*, 1989, **119**, 357; S. Cossu and O. De Lucchi, *Gazz. Chim. Ital.*, 1990, **120**, 569.
- 6 E. Wenkert and C. A. Broka, *Finn. Chem. Lett.*, 1984, 126; J. Nakayama, Y. Nakamura and M. Hoshino, *Heterocycles*, 1985, **23**, 1119.
- 7 O. De Lucchi, G. Licini and L. Pasquato, *J. Chem. Soc., Chem. Commun.*, 1985, 418; L. A. Paquette, H. Künzer, K. E. Green, O. De Lucchi, G. Licini, L. Pasquato and G. Valle, *J. Am. Chem. Soc.*, 1986, **108**, 3453.

3b], norbornadiene [adduct **2c** (6:4 mixture of *endo-exo* isomers)] and quadricyclane [adduct **2d** (m.p. 210–212 °C)].

The preparation of compounds **3** could be conveniently carried out in a 'one pot' operation, without isolation of cycloadducts **2**. The bis-sulfonyl activated double bond of