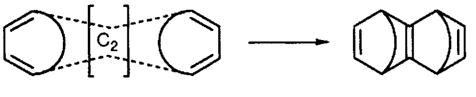
A Synthon for C_2 Polycyclic 1,4,5,8-Tetrahydronaphthalenes *via* Double Diels–Alder Cycloaddition

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 C_2 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 C_2.

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 C_2 molecule,[1] react in a fully controlled fashion in cycloadditions, are of interest. For example, if C_2 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]

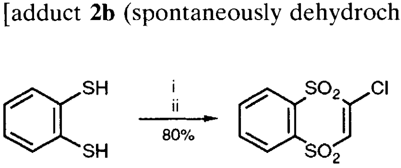


Scheme 1

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 C_2 in cycloaddition reactions. As shown 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



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Scheme 2 *Reagents*: i, Cl_2=CHCl; ii, *m*-CPBA

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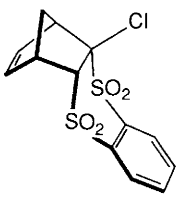
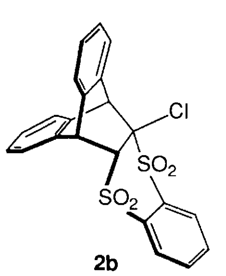
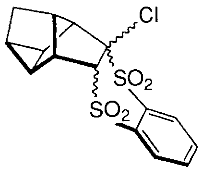
† The structures of the adducts (except **10**) are drawn on the basis of MM2 calculations.



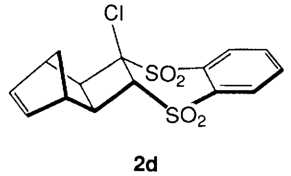
2a



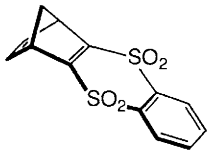
2b



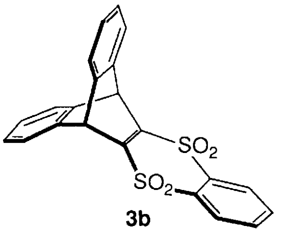
2c



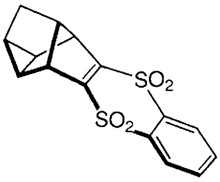
2d



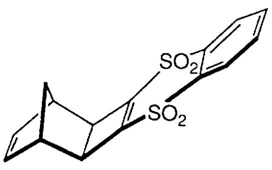
3a



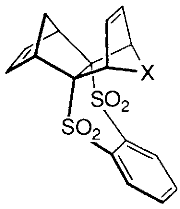
3b



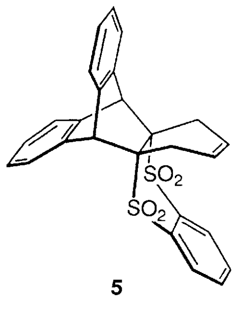
3c



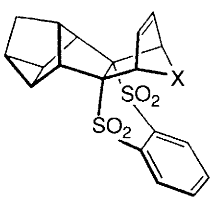
3d



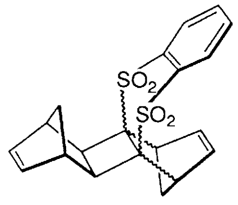
4a X = 2H
4b X = CH_2
4c X = O (two diastereoisomers)



5



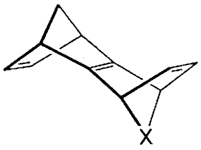
6a X = 2H
6b X = CH_2



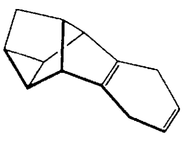
7 (two diastereoisomers)

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

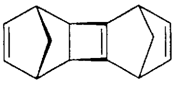
The preparation of compounds **3** could be conveniently carried out in a 'one pot' operation, without isolation of cycloadducts **2**. The bis-sulfonyl activated double bond of compounds **3** is reactive toward several dienes affording the double Diels–Alder adducts **4–7**. For example, **3a** (m.p. 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.



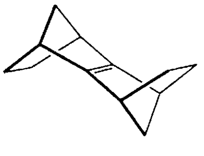
8a X = 2H
8b X = CH_2



9



10 (two diastereoisomers)



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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 (NaH_2PO_4) 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]

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