

Syn and Anti Cycloaddition of Singlet Oxygen to Bisdialinet

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Singlet oxygen undergoes cycloaddition to bisdialine **1** to afford predominantly the *anti* adduct **2**, while the expected *syn* product **3** is formed only in low yield.

One of the most adamant principles in organic chemistry is that the stereoselectivity of the Diels–Alder reaction is rigorously *syn* due to its concerted mechanistic nature.¹ Contrary to this expectation, we observed that singlet oxygen reacts with bisdialine **1**† to afford predominantly the *anti* cycloadduct **2**, while the normal, expected [4 + 2] *syn* cycloadduct **3** was formed only in low yield.‡ The reaction was carried out by passing oxygen gas through a dichloromethane or deuteriochloroform (NMR tube) solution of **1**, which contained tetraphenylporphine (H₂tpp) as sensitizer while irradiating with a standard 200 W halogen lamp. Column chromatography on silica gel afforded the two pure endoperoxides **2** (mp 168–170 °C from CH₂Cl₂–MeOH) and **3** (mp 112–114 °C from CH₂Cl₂–hexane) in 70 and 15% yields.

The structure of the two cycloadducts could not be inferred by spectroscopic means§ and an X-ray analysis of both compounds¶ was necessary for a definitive structure proof. Fig. 1 shows the perspective drawings of the two endoperoxides as defined by the X-ray determination.

The two endoperoxides **2** and **3** do not interconvert. On heating a benzene solution of the *anti* adduct **2** [in the presence or in the absence of Co(tpp)], clean rearrangement into the *anti* bisepoxide **4** (mp 167–168 °C from CH₂Cl₂–EtOH) was observed³ as confirmed by an X-ray structure determination.¶ The latter bisepoxide **4** on standing in chloroform solution or under the action of silica gel or a Lewis acid (BF₃–ether) converted rapidly into the furan **5**¶ (mp 225–228 °C from CH₂Cl₂–Et₂O).

The *syn* adduct **3** exhibits different behaviour when heated in benzene. The NMR spectrum shows the transient formation of at least two compounds, both of which convert into the furan **5** with such ease that their separation and purification proved difficult. Although we may suspect that at least one of these two labile intermediates is the *syn* bisepoxide **6**, definite proof to support its structure is not yet available.

The present reaction is of mechanistic importance in the establishment of concerted *versus* stepwise mechanism. Indeed, precedent studies on the endoperoxidation of the closely related 1,1'-bicyclohexenyl⁴ supported a concerted cycloaddition mechanism because the reaction was shown to occur strictly

syn. The unexpected observation that bisdialine **1** gives mainly the *anti* adduct may be due to its inability to acquire a planar conformation (unlike bicyclohexenyl) due to steric repulsion of the *peri* hydrogens. Such an hypothesis supports a stepwise mechanism with the perepoxide **7**⁵ as intermediate, which opens up to the zwitterions **8** and **9** and leads respectively to the

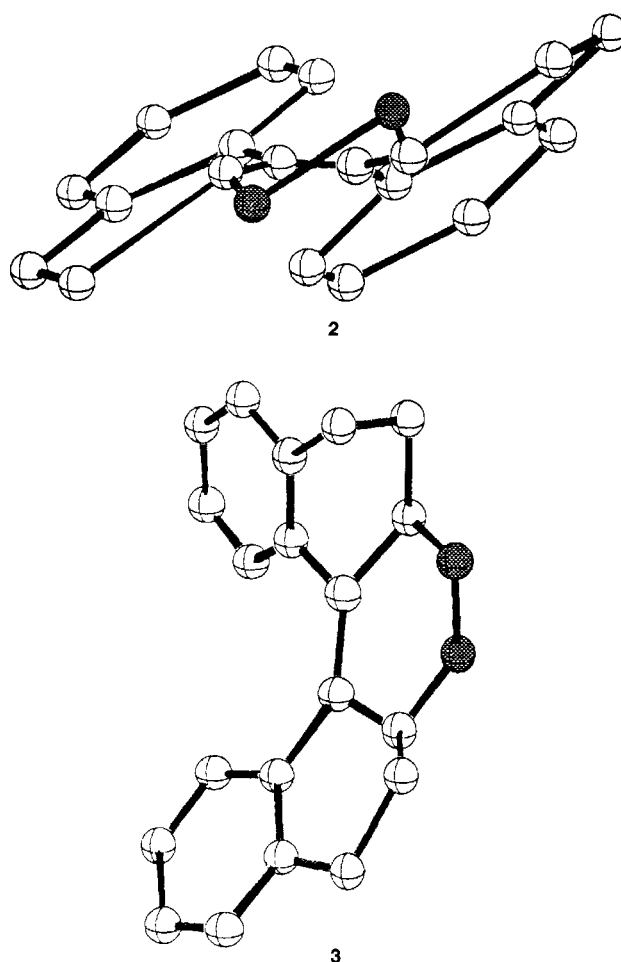
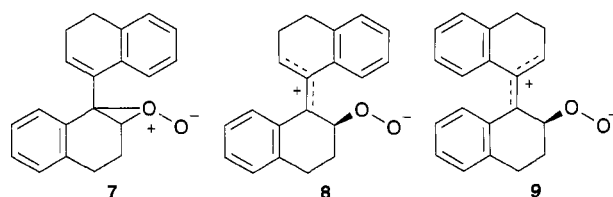
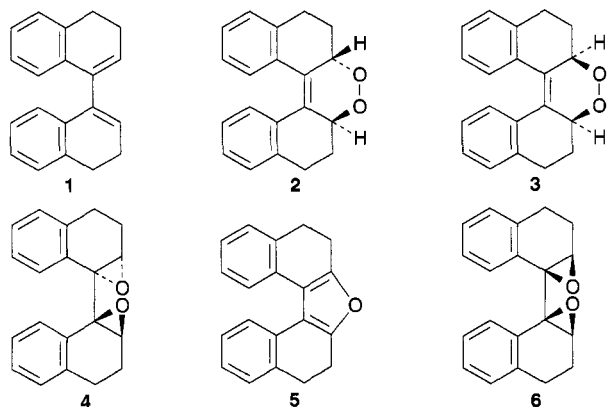


Fig. 1 Perspective drawings of the endoperoxides **2** and **3** as determined by the X-ray structure analysis



endoperoxides **2** and **3**. The intervention of diradical instead of the dipolar species **8** and **9** cannot be ruled out because theory predicts that charge separation in the perepoxyde **7** is quite low.⁶

Finally, cycloaddition of bisdialine with other dienophiles such as maleic anhydride, *N*-phenylmaleimide and benzo-1,4-dithiine tetroxide⁷ gave the standard *syn* cycloadducts. Even triazolindiones, which are also capable of polar cycloadditions,⁸ afforded *syn* addition products.¶ Although there are described in the literature other cases of nonstereospecific cycloaddition of singlet oxygen,⁹ the photooxygenation described here constitutes the first and only *anti* cycloaddition so far reported.

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Footnotes

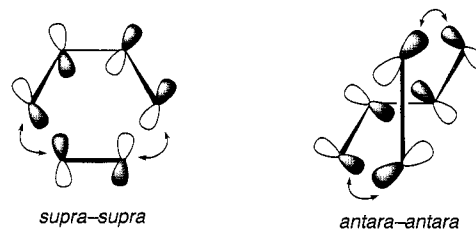
† IUPAC name: 3,3',4,4'-tetrahydro-1,1'-binaphthalene. Bisdialine is a trivial name suggested in ref. 2.

‡ Prior to this report a few Diels–Alder reactions on bisdialine were reported but no stereochemistry was described.²

§ It should be noted that two sets of signals in the NMR spectrum of the *syn* adducts were expected because, at variance with the *anti* adducts that possess C_2 symmetry, the *syn* adducts lack of all elements of symmetry. Since in all cases the spectra consisted of a number of lines in accordance with very symmetrical structures (even at temperatures as low as $-70\text{ }^\circ\text{C}$), it was necessary to resort to X-ray analysis to define the structure of the cycloadduct.

¶ X-Ray data for **2**, **3**, **4** and **5** as well as for the adducts of bisdialine to *N*-phenylmaleimide, benzo-1,4-dithiine *S,S*-tetroxide and 4-methyl-1,2,4-triazolin-3,5-dione will be reported elsewhere.

|| Alternatively, the attractive possibility of a still concerted *antara-antara* instead of the 'normal' *supra-supra* cycloaddition cannot be ruled out and we are planning new dienic systems to test this hypothesis. (We thank Professor W. Adam, University of Würzburg, BRD for this suggestion).



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