Electronic Control of Stereoselectivity. 5. Stereochemistry of Singlet Oxygen Capture by Cyclopentadiene Rings Fused to Norbornyl and Norbornenyl Frameworks[1]

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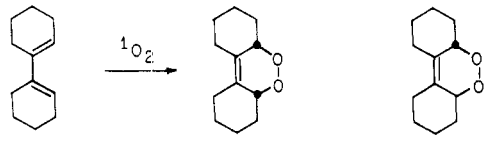
The stereochemistry of the photooxygenation of tricyclo[5.2.1.$0^{2,6}$]deca-2,5-diene (**5**) and tricyclo[5.2.1.$0^{2,6}$]-deca-2,5,8-triene (**6**) has been investigated. For characterization purposes, the initially formed endo peroxides were thermally isomerized to diepoxides. The products were separated and fully characterized by ^{1}H and ^{13}C NMR. When these techniques failed to generate unambiguous stereochemical assignments and other chemical transformations proved equally inconclusive, the three-dimensional features of **11** were established by X-ray crystallography. The oxygenations are shown to proceed only with moderate endo stereoselectivity, in contrast to the behavior of a wide range of dienophiles. The unusual facets of $^1O_2$ behavior during (4 + 2)π cycloaddition are reviewed and placed in proper mechanistic and energetic perspectives. Ultimately, the loss of stereochemical control is attributed to energetic factors arising from the ionization potential of $^1O_2$ (16.12 eV) which differs considerably from that of the π_1(S) energies of normal dienophiles (10.5–11.5 eV) and the π_1(S) energies of the diene substrates (9.6–10.0 eV). The disparate nature of singlet oxygen's energy beclouds the ability of the reagent to distinguish between the advantages of endo attack relative to exo bonding.

The endoperoxidation of cisoid 1,3-dienes with singlet oxygen[2-5] has been developed to the point where the reaction is presently regarded as an important and reliable synthetic procedure.[6-12] Because of the obvious similarities to the familiar Diels–Alder reaction, a direct mechanistic parallel was immediately drawn between the two processes. In a systematic study of the effect of temperature on the rate of reaction of $^1O_2$ with a variety of dienes, Koch showed that rather small activation energies (0–6 kcal/mol) were involved.[13] The deduction followed that endoperoxidation is a symmetry-allowed reaction as earlier forecasted by Kearns.[4,14] Interestingly, the supposed concerted nature of singlet oxygen capture appears to rest upon a single piece of stereochemical data, viz., the stereospecific endoperoxidation of 1,1′-bicyclohexenyl (**1**).[15] In view of the fact that **2** is formed exclusively, a nonconcerted two-step mechanism involving an intermediate biradical was considered ruled out.



1 **2** **3**

More recent theoretical considerations by Dewar and Thiel have justifiably reopened the question of the operability of synchronous pericyclic bonding during endoperoxidation.[16] Their MINDO/3 calculations led to the conclusion that reactant-like perepoxides such as **4** (cis or

4

trans stereochemistry at the O–O bond) are likely involved, such intermediates subsequently rearranging easily to the cyclic peroxides. The stereospecificity observed in the conversion of **1** to **2** was attributed to hindered rotation about either the exocyclic double bond or the C–C bond in the perepoxide rings.

Clearly, the availability of additional experimentally based insight into the peroxidation reaction would be highly desirable. For this reason, we were drawn to examine the responses of **5** and **6** to the action of singlet

5 **6**

oxygen. Earlier results obtained in The Ohio State University laboratories[1,17] and at the hands of Sugimoto, Kobuke, and Furukawa[18] have revealed that both cyclo-

† Cornell University.

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(2) Arbuzov, R. A. *Russ. Chem. Rev. (Engl. Transl.)* **1965**, *34*, 558.
(3) (a) Gollnick, K.; Schenk, G. O. In "1,4 Cycloaddition Reactions"; Hamer, J., Ed.; Academic Press: New York, 1967; p 255 ff. (b) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1.
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(5) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133.
(6) Review: Adam, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 619.
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(10) (a) Matsumoto, M.; Kondo, K. *J. Org. Chem.* **1975**, *40*, 2259. (b) Demole, E.; Demole, C.; Berthet, D. *Helv. Chim. Acta* **1972**, *56*, 265. (c) Kondo, K.; Matsumoto, M. *Tetrahedron Lett.* **1976**, 391. (d) Harirchian, B.; Magnus, P. D. *Synth. Commun.* **1977**, *7*, 119. (e) Sasaoka, M.; Hart, H. *J. Org. Chem.* **1979**, *44*, 368 and references cited therein.
(11) Corey, E. J.; Taylor, W. C. *J. Am. Chem. Soc.* **1964**, *86*, 3881.
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(13) Koch, E. *Tetrahedron* **1968**, *24*, 6295.
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(15) Schulte-Elte, K. H. Dissertation, University of Gottingen, 1961 (as cited in ref 3a).
(16) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 2338.
(17) (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.*, accompanying paper in this issue.

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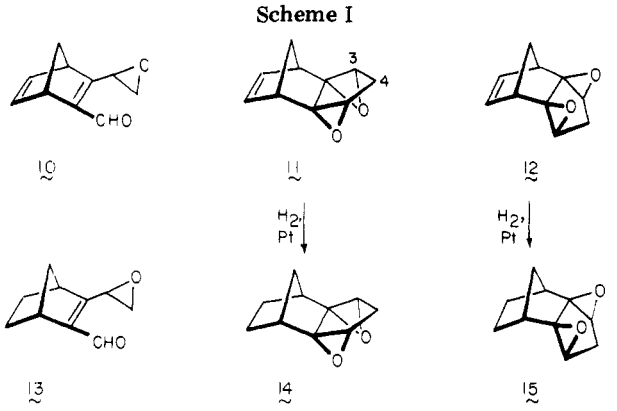
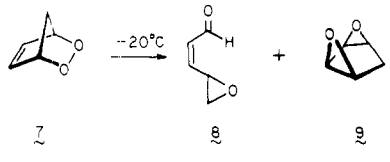
Scheme I



pentadiene systems enter into stereospecific Diels–Alder reaction with a wide range of dienophiles to form products arising exclusively or predominantly from endo bond formation. This stereochemical behavior is considered to arise from suitable mixing of the norbornyl and norbornenyl σ electrons with the diene π_S orbital with resultant disrotatory π orbital tilting.[17] Accordingly, to the extent that singlet oxygen capture is mechanistically related to the (4 + 2) cycloaddition of a host of dienophiles, full endo stereospecificity should be observed. However, if an alternative pathway is followed, comparable electronic forces need not intervene, and loss of stereoelectronic control could develop. In actuality, the latter course of events does transpire, and this present paper details our findings in this area.

Results

Oxygenation Experiments. The possibility that the directionality of singlet oxygen capture by **5** and **6** could be obscured in whole or in part by a stereoselectivity nondiagnostic rearrangement[19] was recognized at the outset. In 1969, Ohloff and his co-workers reported that the endo peroxide **7** derived from cyclopentadiene is rapidly converted at −20 °C under neutral conditions chiefly to 4,5-epoxy-*cis*-pentenal (**8**) and to a lesser extent to *cis*-diepoxide **9**. The monomethylated cyclopentadienes behave in a similar manner. Fortunately, however, the more highly substituted endo peroxides derived from **5** and **6** are not as prone to ring cleavage.[20]



Methylene blue sensitized photooxygenation of **6** in 1,2-dichloroethane solution during 1.25 h at room temperature gave a mixture of endo peroxides which was directly isomerized by subsequent heating of the reaction mixture at the reflux temperature for 20 min. After careful silica gel chromatography, three products were isolated in 26%, 42%, and 23% yields. Thus, better than 90% of the product mixture is accounted for, indicating that the process is a rather clean and well-defined one. The more rapidly eluted substance exhibited a singlet aldehydic resonance of area 1 at δ 9.88, a two-proton olefinic multiplet centered at δ 6.70, and methine proton signals at δ 3.43 (m, 1 H) and 3.12–2.47 (m, 2 H), which clearly established it to be **10** (see Scheme I). This point is critical, since it reflects the fact that only approximately one-fourth of the possible endo peroxide rearrangement options are channeled into the least-desired manifold.[19] The remaining two products were clearly diepoxides; their structural assignments are discussed in the next section.

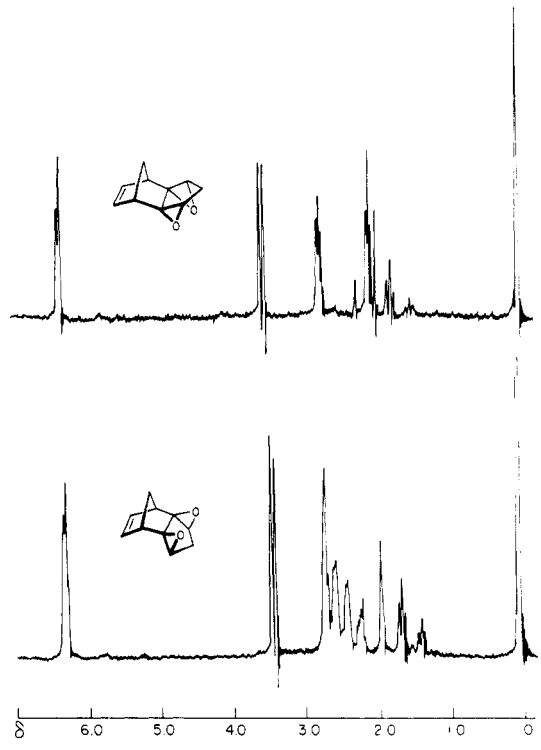


Figure 1. ^{1}H NMR spectra (60 MHz, $CDCl_3$) of **11** (top) and **12** (bottom).

The independent catalytic hydrogenation of **11** and **12** afforded pure samples of **14** and **15**. As matters turned out, **5** was transformed under analogous photooxygenation conditions to a mixture of **13** (23%), **14** (44%), and **15** (16%). The parallelism in yields is particularly striking. Once again, therefore, the additional double bond in **6** is seen not to perturb stereoselection.[1,17]

The effects of differing sensitizer and solvent were briefly investigated in the case of **6**. With methylene blue in acetonitrile, there was obtained a mixture of **10**, **11**, and **12** in isolated yields of 18%, 32%, and 24%. Tetraphenylporphyrin in benzene gave similar results: **10** (27%), **11** (35%), **12** (27%). Therefore, as expected from the fact that these sensitizers all possess triplet energies adequately high to produce $^1\Delta_g$ oxygen via an exothermic energy transfer process, the product distributions show no correlation within experimental error with triplet energies. Solvent effects also appear to have no impact on the relative ratios of **10**–**12**.

Spectral Characterization of the Diepoxides. The ^{1}H NMR spectrum of the less polar unsaturated diepoxide **12** is shown in Figure 1 (top). While its α-epoxy protons (H_3, H_5) appear as a narrow doublet (J = 2.8 Hz) at δ 3.40, H_{4exo} is seen as a doublet (J = 17 Hz) at δ 2.01, and H_{4endo} consists of a doublet of triplets (J = 17 and 2.8 Hz) at δ 1.50. More significant is the observation that H_{10anti} and

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(20) This property appears to be shared by the endo peroxide of 2,3-dimethylenenorbornene, thermolysis of which (130 °C, 6 h) gives 57–70% of *trans*-diepoxide, <15% of γ-hydroxy-α,β-unsatutated aldehyde, and a furan (<1%): Hagenbuch, J.-P.; Vogel, P. *Tetrahedron Lett.* **1979**, 561.

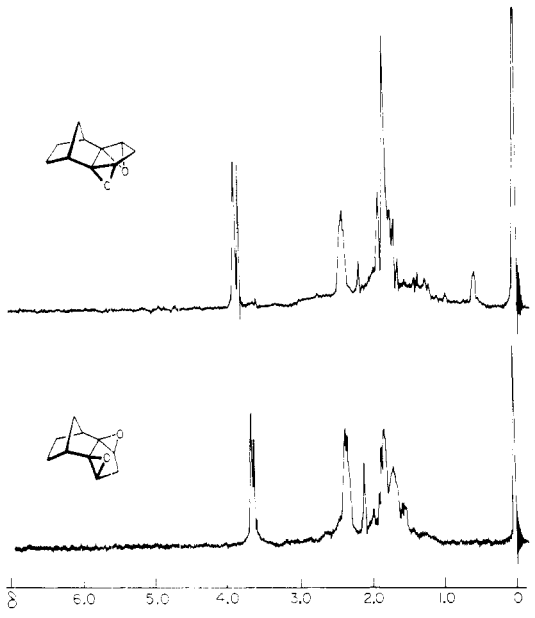


Figure 2. ^{1}H NMR spectra (60 MHz, $CDCl_3$) of **14** (top) and **15** (bottom).

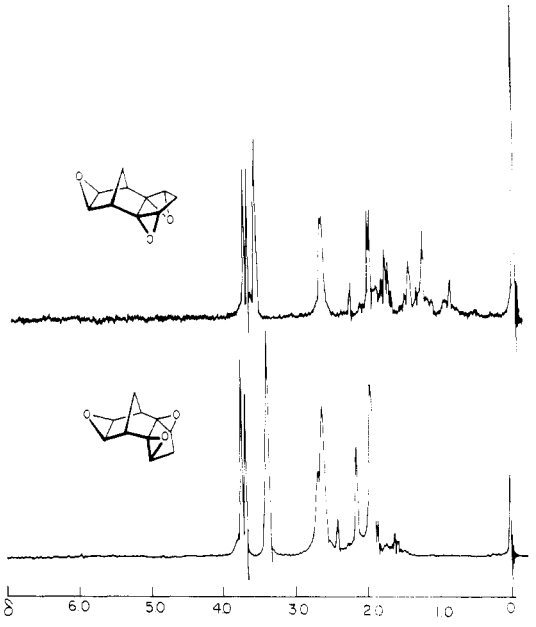


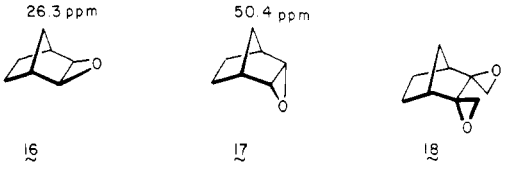
Figure 3. ^{1}H NMR spectra (60 MHz, $CDCl_3$) of **20** (top) and **21** (bottom).

H_{10syn} in **12** have dissimilar chemical shifts (δ 2.57 and 2.32, respectively). Both form doublets (J = 9.0 Hz) which are further split due to long-range coupling. This behavior contrasts with that seen for the more popular isomer **11** whose methano bridge protons appear as a quite narrow multiplet at δ 2.05 (Figure 1, bottom).

Although epoxide rings were first believed to exert magnetic anisotropy effects comparable to those of their cyclopropane congeners, this assumption was subsequently shown to be incorrect.[21] Ensuing investigations produced the working hypothesis that shielding can be expected above and below the plane of an epoxide ring except when the proton in question is in close proximity to the oxygen atom, in which case deshielding results.[22] Recently, however, a note of caution was introduced by Paquette and co-workers, who showed that slight changes in epoxide ring geometry can generate key alterations in shielding patterns, the magnitudes of which may not be recognized in the absence of proper conformational analysis and analogue intercorrelation.[23] Complications appear to result because the available anisotropy models are too simple and/or are inadequately detailed. In this connection, it is entirely likely that the screening effects emanating from the rear side of an epoxide ring are dependent not only on distance (the result of shielding contours) but also on group anisotropy contributions which have a $\cos^2$ angular dependence.

Dreiding molecular models leave little doubt that **11** and **12** are reasonably rigid molecules. Can one now distinguish the two stereoisomers on the basis of the obviously different shieldings of the C_{10} protons? Are the combined anisotropic effects of the C=C and the syn and exo epoxide rings adequate to cause H_{10syn} and H_{10anti} to become distinctly separated and downfield shifted? Or do these two effects act to cause the bridge protons to overlap with each other? No unambiguous, decisive answer can seemingly be advanced. Nor is additional conclusive evidence available from the hydrogenation products **14** and **15**. The ^{1}H NMR spectra of these reduced diepoxides take on added complexity and provide no new or diagnostic recognition patterns (Figure 2).

The long-range effects of epoxide rings on ^{13}C chemical shifts can sometimes be quite marked,[24,25] particularly where epoxynorbornanes are concerned.[25,26] In systems of the latter type, C_7 in the exo isomer **16** is more than 20 ppm upfield of its counterpart in the endo isomer (**17**). Depending on one's viewpoint, this striking feature may be the result of a significant deshielding caused by the endo-oriented oxirane ring or the result of intense shielding by the *exo*-epoxy substituent. Trans diepoxide **18**, which has an oxygen atom geometry more closely aligned to those found in **11**, **12**, **14**, and **15**, exhibits carbon signals for C_5, C_6, C_7 at 36.2, 26.2, 23.8 ppm (not individually distinguished).[19]



16 **17** **18**

The chemical shifts of C_{10} in **11** (47.9 ppm) and **12** (54.2 ppm) are indeed distinctly different, but much less so. The same relative ordering is manifested by **14** (36.3 ppm) and **15** (42.7 ppm). Although these comparisons are informative, they must be considered as less than confirmatory of stereochemistry in the absence of additional data. That the situation is indeed complicated can be seen by the remarkably high shift of the bridge carbon in **19**.[27]

In an effort to obtain a chemical proof of structure for **11** and **12**, these diepoxides were further oxidized with *m*-chloroperbenzoic acid and converted to the triepoxides **20** and **21**. Interestingly, whereas the polarity responses

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(22) (a) Herz, W.; Hall, A. L. *J. Org. Chem.* **1974**, *39*, 11. (b) Cross, A. D. *J. Am. Chem. Soc.* **1962**, *84*, 3206. (c) Jefford, C. W.; Medary, R. T. *Tetrahedron* **1967**, *23*, 4123. (d) Meklati, B.; Bessière-Chrétien, Y. *Bull. Soc. Chim. Fr.* **1972**, 3133.

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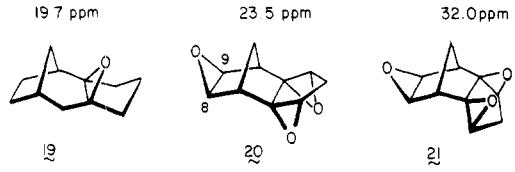

of the precursor molecules to silica gel fell in the order **11** > **12** and **14** ≈ **15**, the responses of **20** and **21** were reversed (**21** > **20**). The ^{1}H NMR spectra of the triepoxides are illustrated in Figure 3. Clearly, a return to a rather sharply defined spectrum has materialized in the case of **20**, whereas H_{10syn} and H_{10anti} in **21** have once again become sharply differentiated. While this finding was encouraging, we were really seeking to observe appreciable variation in the shielding levels of H_8 and H_9 in **20** and **21**. These protons are necessarily endo oriented in both instances and, as a result, are expected not to couple to the bridgehead protons and to appear as well-defined singlets in both cases. Moreover, in one instance they would find themselves proximate to a pair of endo epoxide oxygen atoms and to the rear side of the oxirane C–C bonds in the other. While singlets were indeed observed in both examples, no definitive stereochemical deduction could be arrived at due to the unexpected similarity of the chemical shifts in question: δ 3.57 for **20** and δ 3.38 for **21**.

The ^{13}C chemical shifts of the methano bridge carbons in **20** and **21** are expectedly shielded relative to those of the precursor olefins (see formulas). Internal consistency is seen in the fact that the resonance of the relevant carbon atom in **20** appears upfield of that in **21**. As before, however, no distinction between the isomers could be made beyond a reasonable doubt. A resolution of the stereochemical question was deemed important for at least two reasons: (a) specifically, to unravel unambiguously the stereoselection favored by **5** and **6** in their capture of singlet oxygen, and (b) more generally, to develop added appreciation of the anisotropic effects of oxirane rings on ^{1}H and ^{13}C chemical shifts. To this end, **11** was subjected to three-dimensional X-ray crystal structure analysis.

X-ray Analysis of 11. Preliminary X-ray photographs of **11** showed monoclinic symmetry. Accurate cell constants, determined by a least-squares fit of 15 moderate 2θ values, were a = 6.425 (3) Å, b = 7.712 (3) Å, c = 15.972 (7) Å and β = 86.44 (3)°. The systematic extinctions were uniquely accommodated by the common space group $P2_1/c$, and density considerations (1.36 g/cm^3 for Z = 4) indicated one molecule of $C_{10}H_{10}O_2$ per asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were surveyed on a computer-controlled four-circle diffractometer using Ni-filtered Cu Kα radiation (1.541 78 Å), a variable speed, and a 1° ω span. Of the 1089 reflections examined, a total of 1046 (96%) were judged observed ($|F_o| \geq 3\sigma(F_o)$) after correction for Lorentz, polarization and background effects.

A phasing model was achieved by permuting the signs of five variable reflections and expanding these initial sets into sign indications for the 100 largest E values.[28] The most consistent set was used to calculate an E synthesis which revealed all of the nonhydrogen atoms. These positions were refined in block-diagonal and full-matrix least-squares refinements. Hydrogen atoms were located in a subsequent ΔF synthesis which revealed no abnormally high residual electron density, and no short intermolecular contacts were observed. Additional crystallographic details can be found in the supplementary material described at the end of this paper.

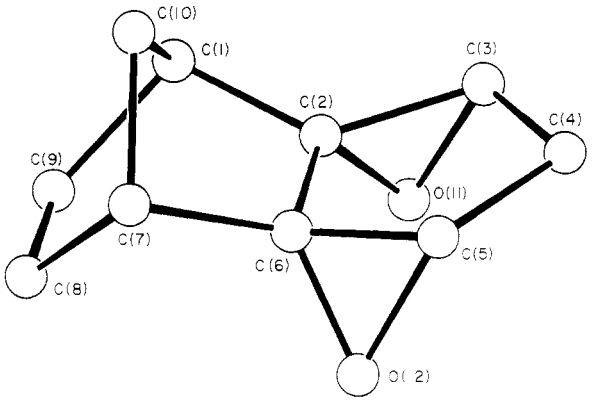

Figure 4. Computer-generated perspective drawing of the final X-ray model of diepoxide **11**. Hydrogens are omitted for clarity.

Figure 4 is a computer-generated perspective drawing of the final X-ray model of diepoxide **11**. The most important structural feature is the stereochemistry of the oxirane rings. As can be seen, the oxygen atoms are syn to the etheno and anti to the methano bridge. The cyclopentane ring containing the diepoxide network is planar with an average deviation of 0.02 Å from the best plane. The other cyclopentane ring is in an envelope conformation with C_{10} as the flap which is 0.91 Å from the best four-atom plane. The cyclopentane ring is also an envelope with C_{10} at 0.83 Å from the best four-atom plane. These two four-atom planes form a 67° angle. In general, bond distances and angles agree well with anticipated values, and the molecule has noncrystallograpic mirror symmetry.

Discussion

Steric approach control customarily plays a decisive role in determining the stereochemistry of addition reactions to polycyclic bridged compounds. When anomalies have appeared, interpretative arguments based upon the concept of product development control have generally been advanced. Only recently has attention been paid to the control of stereoselection by remote electronic effects.[1,17,18,28-31] The overwhelming kinetic preference of dienophiles for endo attack on **5** and **6** cannot be attributed to steric factors because the relevant carbons of the cyclopentadiene rings are too remote from either bridge.[1,17] Moreover, if such effects were invoked, the behavior of **5**, and probably **6** as well, would necessarily be contrasteric. Accordingly, steric approach control arguments become implausible in this instance.

The lack of stereospecificity seemingly cannot be attributed to product development control of concerted endoperoxidation either. MINDO/3 calculations of the heats of formation of endo peroxides **22**–**25** reflect a reversal in relative stability order with **23** > **22** and **24** > **25**.[32] Yet,

(28) The following library of crystallographic programs was used: Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. B* **1970**, *B24*, 274 (MULTAN); Hubbard, C. R.; Quicksall, C. O.; Jacobson, R. A. USAEC Report 1S-2625; Institute for Atomic Research, Iowa State University: Ames, Iowa, 1971; Busing, W. R.; Martin, K. O.; Levy, H. A. USAEC Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1965; Johnson, C. USAEC Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

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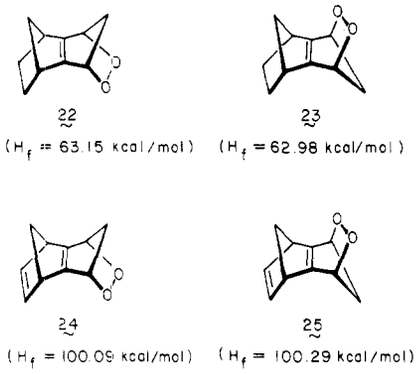
(30) (a) Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1978**, *100*, 6509. (b) Okada, K.; Mukai, T. *Tetrahedron Lett.* **1979**, 3429. (c) Hoffmann, R. W.; Hauel, N. *Ibid.* **1979**, 4959.

(31) Malpass, J. R.; Walter, M. P. *J. Chem. Soc., Chem. Commun.* **1979**, 585.

(32) The MINDO/3 results were provided to us by Professor Rolf Gleiter, whom we thank.



as we have seen, the diepoxide product distributions from **5** and **6** are very similar.

In a recent kinetic study, Gorman, Lovering, and Rodgers demonstrated that the dienophilic reactivity of singlet oxygen toward cyclopentadiene is chiefly entropy controlled, i.e., $\Delta H^{\ddagger} = 0$ kcal/mol and $\Delta S^{\ddagger} = -25.9$ eu.[33] The close structural similarity of **5** and **6** to cyclopentadiene leads one to believe that they probably also conform to this general trend. Such data argue either for a single entropy-controlled cycloaddition which gives rise directly to an endo peroxide or for the formation in a rate-determining entropy-controlled step of an intermediate which rapidly isomerizes to product.

It now becomes useful to call attention to the fact that "normal" concerted Diels–Alder reactions have early transition states. As the result of such timing, the activated complex closely resembles a two-plane orientation of the reactants. Enthalpy changes of zero or approaching zero are not typical of Diels–Alder reactions involving cyclopentadiene; in benzene solution, for example, its (4 + 2) cycloadditions to various dienophiles are characterized by $\Delta H^{\ddagger}$'s which fall into the 10–18-kcal/mol range.[34] The essentially zero $\Delta H^{\ddagger}$ terms for capture of $^1\Delta_g$ singlet oxygen by dienes are plausibly attributable to the electronically excited nature of the reagent and, in particular, the energy of its LUMO. Nonetheless, stereoselection between the top and bottom faces of **5** and **6** must be dependent on a difference in the $\Delta H^{\ddagger}$ terms for the two processes (a relatively small number of calories per mole), since it is rather unlikely that dissimilar entropy factors are associated with the competing endoperoxidation reactions.

An important consequence of the highly negative entropies of activation is to limit significantly our interpretation of the degrees of freedom available in these transition states. Either the activated complexes themselves are highly ordered or substantial solvent reorganization is required. However, as we have shown earlier for **6**, changes in solvent and sensitizer do not greatly affect isomer distribution. The inference is that stepwise processes involving zwitterionic intermediates do not gain significance. The same restrictions do not apply to the more highly structured perepoxide-like (end-on approach of $^1O_2$) or endo peroxide-like (parallel approach) biradicaloid structures **26** and **27** which are similar in character

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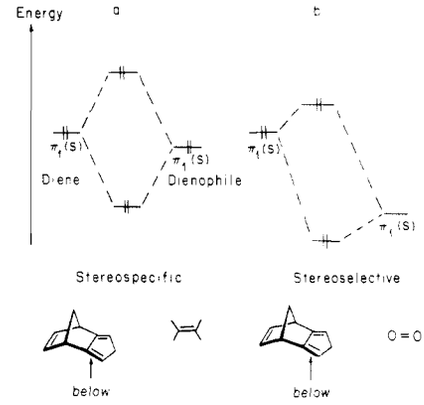

Figure 5. Qualitative diagram of the interaction between (a) π_1(S) of **5** (or **6**) and a dienophile and (b) π_1(S) of **5** (or **6**) and singlet oxygen.

to the perepoxide[16,35,36] and biradical species[37,38] favored by theoreticians.

It is not our intention to view **26** and **27** as biradicals or to impose additional activation energy requirements for their further reaction.[39] In cyclic compounds of this type, the vibrational amplitude may be so great that while exceedingly strong overlap or C–O bonding may characterize the compressional side, little overlap or bonding may characterize the extensional side. At these distances, the possibility of concertedness or control by first-order orbital overlap becomes vanishingly small.

A second possibility which deserves serious consideration is electron transfer between $^1O_2$ and the diene in a highly ordered "exciplex" structure. This process, which could be facilitated as the result of the relatively large diene HOMO–$^1O_2$ LUMO gap, could also vitiate orbital symmetry control during C–O bond making.[40]

The stereochemical findings described here do not appear to follow directly from compression of the exo/endo reaction profiles in accord with the Hammond postulate.[41] Benzyne and *N*-methyltriazolinedione, two highly reactive dienophiles, undergo exclusive endo attack in reactions which are equally, if not more, rapid.[1,17] Rather, the loss of stereochemical control appears to be due to energetic factors. In those instances where π_1(S) of the diene and π_1(S) of the dienophile have comparable energies (see Figure 5a), the interaction between both is large. Consequently, cycloadditions of this type are stereospecific since the energy difference between topside and bottomside approach is considerable. In the case of $^1O_2$, the energy difference between π_1 of the diene and π_1 (symmetric) of the singlet oxygen is sizable, and thus the mutual interaction of these orbitals is lessened significantly (see Figure 5b). As a corollary, the difference in the two avenues of approach is not very large. The π_1 ionization of $^1O_2$ is

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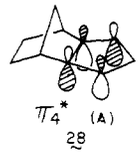
found at 16.12 eV while π_1 of the dienes falls in the range of 9.6–10.0 eV.[32] In contrast, the ionization potentials (π_1) of the dienophiles earlier examined are found at approximately 10.5–11.5 eV.

One final point deserves mention. Singlet oxygen has two degenerate orbitals, one occupied and one empty. Therefore, the $\pi_A(O_2)$ acceptor–$\pi_2(A)$ donor interaction can be expected to be dominant. According to calculations by Gleiter, Böhm, and Schang,[32] the interaction of π_A (donor) of $^1O_2$ with $\pi_4(A)$ of the diene remains considerable. The latter empty orbital ($\pi^*_4(A)$) is polarized due to considerable 2s character at the carbon atoms as shown in **28**. Thus, addition from below remains favored due to this $\pi g/\pi^*_4$ interaction.



28

We have anticipated that this phenomenon is hardly restricted to **5** and **6** but is of more widespread occurrence. The ensuing paper describes our assessment of the stereochemistry of the photooxygenation of bicyclic fused dimethoxynaphthalene systems.[42]

Experimental Section

Proton magnetic resonance spectra were obtained with a Varian T-60 spectrometer; apparent splittings are given in all cases. ^{13}C NMR spectra were recorded on a Bruker WP-80 spectrometer, and infrared spectra were determined on a Perkin-Elmer Model 467 instrument. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory.

Photooxygenation of 6. In 130 mL of 1,2-dichloroethane (freshly distilled from potassium carbonate) were dissolved 30 mg of methylene blue and 3.4 g (26.2 mmol) of tricyclo-[5.2.1.$0^{2,6}$]deca-2,5,8-triene (**6**).[17,43] The solution was irradiated with a Sylvania 500-W tungsten halogen lamp while a stream of oxygen was vigorously bubbled through the system. Three additional 30-mg portions of methylene blue in 45 mL of the same solvent were introduced at 15-min time intervals. After a total irradiation time of 1.25 h, the photooxygenate was transferred to a one-necked round-bottomed flask and heated at reflux for 20 min. The cooled solution was filtered through Celite, and the solvent was removed in vacuo. The dark residue was chromatographed on silica gel (60 g) with 30% ethyl acetate in hexane as eluent. First to elute was epoxy aldehyde **10** (1.12 g, 26.4%) which was obtained as a yellow oil which darkened upon standing overnight at room temperature: ^1H NMR ($CDCl_3$) δ 9.88 (s, 1 H), 6.70 (m, 2 H), 3.95 (m, 2 H), 3.43 (m, 1 H), 3.12–2.47 (m, 2 H), 1.98 (m, 2 H); mass spectrum, m/e calcd 162.0681, obsd 162.0684.

Further elution with 50% ethyl acetate in hexane gave 2.7 g (64%) of a 35:65 (^1H NMR analysis) mixture of **11** and **12** as a viscous oil. Separation of the exo and endo diepoxides was achieved by preparative layer chromatography under comparable conditions. The less polar band was found to consist of **12**, sublimation of which at 70 °C and 0.1 torr afforded waxy white needles. Recrystallization of this material from ether–hexane (1:5) gave the analytical sample as a transparent solid: mp 66.5–68 °C; ν_{max} (CCl_4) 3060, 2990, 2940, 2870, 1448, 940, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.26 (m, 2 H), 3.40 (d, J = 2.8 Hz, 2 H), 2.68 (m, 2 H), 2.57 (d with further splitting, J = 9.0 Hz, 1 H), 2.32 (d with further splitting, J = 9.0 Hz, 1 H), 2.01 (d, J = 17 Hz, 1 H), 1.52 (dt, J = 17 and 2.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 137.1 (d, J = 172 Hz), 72.3 (s), 64.1 (d, J = 179 Hz), 54.2 (t, J = 134 Hz), 41.7 (d, J = 145 Hz), 32.2 ppm (t, J = 134 Hz); mass spectrum, m/e calcd 162.0681, obsd 162.0684.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.10; H, 6.23.

The more polar band consisting of **11** was initially isolated as a colorless viscous liquid which crystallized from ether–hexane (1:6) to give a transparent solid: mp 66–67 °C; ν_{max} (neat) 3070, 2995, 2940, 2870, 1448, 940, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.34 (m, 2 H), 3.55 (d, J = 3.0 Hz, 2 H), 2.72 (m, 2 H), 2.08 (d, J = 17 Hz, 1 H), 2.05 (pseudo s, 2 H), 1.68 (dt, J = 17, 3.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 136.8 (d, J = 175 Hz), 66.8 (d, J = 187 Hz), 47.9 (t, J = 140 Hz), 41.9 (d, J = 147 Hz), 32.2 (t, J = 137 Hz), 74.2 ppm (s); mass spectrum, m/e calcd 162.0681, obsd 162.0684.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.91; H, 6.20.

Hydrogenation of 11. To a slurry of prereduced platinum oxide (8 mg) in ethyl acetate (1 mL) was added 27 mg (0.167 mmol) of **11** dissolved in 4 mL of the same solvent. Hydrogenation at atmospheric pressure was carried out during 20 min, and the reaction mixture was filtered through Celite. Evaporation of the filtrate left 22 mg (80.4%) of **14** as a colorless oil: ν_{max} (neat) 3010, 2965, 1438, 928, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (d, J = 3.0 Hz, 2 H), 2.38 (m, 2 H), 1.98 (d, J = 15.5 Hz, 1 H), 1.82 (pseudo s, 4 H), 1.88–1.17 (series of m, 3 H); ^{13}C NMR ($CDCl_3$) 71.2, 36.7, 36.3, 30.1, 23.5 ppm; mass spectrum, m/e calcd 164.0837, obsd 164.0841.

Hydrogenation of 12. A 34-mg (0.21 mmol) sample was hydrogenated in the predescribed manner to give 24 mg (69.7%) of **14** after purification by preparative layer chromatography (elution with ethyl acetate–hexane, 1:1). Spectral data for the colorless liquid include the following: ν_{max} (neat) 3010, 2960, 1435, 968, 922, 892, 813 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.60 (d, J = 2.8 Hz, 2 H), 2.35 (m, 2 H), 2.65–1.35 (series of m, 8 H); ^{13}C NMR ($CDCl_3$) 64.1, 42.7, 37.4, 32.3, 26.4 ppm; mass spectrum, m/e (relative intensity) 164 (M^+, 13), 148 (38), 136 (114).

Photooxygenation of 5. In a manner identical with that employed for **6**, 2.4 g (18.2 mmol) of **5** was photooxygenated in 1,2-dichloroethane solution with methylene blue (80 mg total) as sensitizer. The total irradiation time was 50 min. After the reaction mixture had been heated at reflux and the solvent had been evaporated, the crude product mixture was chromatographed on silica gel (140 g, elution with 30% ethyl acetate in hexane) to furnish 680 mg (23%) of **13** as a pale yellow oil: ν_{max} (neat) 2721, 1660, 1610, 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.88 (s, 1 H), 3.88 (dd, J = 4.5, 2.5 Hz, 1 H), 3.28 (m, 1 H), 2.92 (m, 3 H), 1.92–0.96 (series of m, 6 H); mass spectrum, m/e calcd 164.0837, obsd 164.0841.

Further elution with 50% ethyl acetate in hexane afforded 1.78 g (59.7%) of a 73:27 mixture (^1H NMR analysis of the δ 4.0–3.5 region) of **14** and **15**. Attempts to separate this mixture by preparative layer chromatography were unsuccessful.

Epoxidation of 11. To a stirred solution of **11** (183 mg, 1.13 mmol) in dichloromethane (3 mL) under an argon atmosphere was added dropwise a solution of 85% *m*-chloroperbenzoic acid in 8 mL of the solvent. The mixture was stirred at room temperature for 8 h, washed successively with 10% sodium bicarbonate solution, water, and brine, dried, and evaporated. The resulting colorless oil was purified by preparative layer chromatography on silica gel (elution with ethyl acetate–hexane, 4:1) to give 112 mg (56%) of **20** as a colorless crystalline solid: mp 109–110.5 °C (from ether–hexane); ν_{max} (CCl_4) 3030, 2995, 2960, 2925, 948, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.72 (d, J = 3.0 Hz, 2 H), 3.57 (s, 2 H), 2.65 (m, 2 H), 2.07 (d, J = 15.5 Hz, 1 H), 2.03–1.37 (series of m, 3 H); ^{13}C NMR ($CDCl_3$) 66.4, 49.7, 37.4, 30.0, 23.5 ppm; mass spectrum, m/e calcd 178.0630, obsd 178.0634.

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.34; H, 5.71.

Epoxidation of 12. Epoxidation of **12** (279 mg, 1.72 mmol) with 483 mg (2.3 mmol) of 85% *m*-chloroperbenzoic acid in the predescribed manner afforded 247 mg (81%) of **21** as colorless oil which solidified on standing. Recrystallization from ether–hexane (1:4) gave pure **21** as white prisms: mp 116–117 °C; ν_{max} (CCl_4) 3020, 2955, 2920, 920, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.72 (d, J = 3.2 Hz, 2 H), 3.38 (s, 2 H), 2.62 (m, 2 H), 2.25 (d, J = 15.5 Hz, 1 H), 1.98 (m, 3 H); ^{13}C NMR ($CDCl_3$) 72.4, 63.2, 49.1, 38.5, 33.8, 31.2; mass spectrum, m/e 178.0630, obsd 178.0633.

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Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.27; H, 5.73.

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Registry No. 5, 6675-72-5; 6, 6675-71-4; 10, 75101-90-5; 11, 75101-91-6; 12, 75171-61-8; 13, 75101-92-7; 14, 75101-93-8; 15, 75171-62-9; 20, 75101-94-9; 21, 75171-63-0.

Supplementary Material Available: Fractional coordinates and thermal parameters (Table I), bond distances (Table II), and bond angles (Table III) for 11 (3 pages). Ordering information is given on any current masthead page.

Electronic Control of Stereoselectivity. 6. Directionality of Singlet Oxygen Addition to 1,4-Dimethoxynaphthalenes Laterally Fused to Bridged Bicyclic Systems[1]

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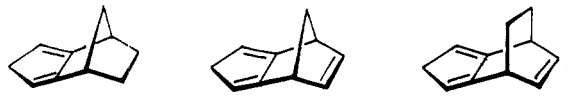
The photooxygenation in methanol solution of 1,4-dimethoxynaphthalene derivatives having bridged bicyclic systems fused at C_2,C_3 with rose bengal as sensitizer leads to formation of stereoisomeric epoxynaphthoquinone monoketals. These products, which are readily hydrolyzed in acid solution to the epoxynaphthoquinones, possess an epoxide oxygen which serves as a stereochemical marker for the directionality of singlet oxygen addition. For the norbornyl and norbornenyl cases, endo bonding by $^1O_2$ is preferred; the reverse is true for the pair of bicyclo[2.2.2]octenyl derivatives studied. This contrasting stereoselection was compared to the stereochemical consequences of alkaline hydroperoxidation of the corresponding naphthoquinones. In each instance, the reaction course was opposite to that observed with singlet oxygenation. Both processes are analyzed from the theoretical viewpoint, use being made of the photoelectron spectra of the substrate molecules, detailed evaluation of frontier orbital effects, and prevailing σ/π interactions. While the alkaline hydroperoxidation results can be interpreted in terms of standard kinetic and steric control, an understanding of the directionality of $^1O_2$ capture appears dependent on our appreciation of the contributions made by the σ electrons of the bicyclic moieties upon the aromatic π orbitals. The tilting caused by such interactions is thought to be the source of the experimentally observed exo/endo ratios.

The intrinsic ability of norbornenes to direct electrophilic additions to their exo surface and of 2-norbornyl cations to capture nucleophiles stereospecifically from the same direction has been a topical issue in physical organic chemistry for a long time. Steric effects have been shown to be of such considerable importance that the possibility of implicating the operation of complementary electronic effects has continued to be elusive.[4,5] We have considered that experimental evidence for significant interaction between norbornyl and norbornenyl σ electrons and proximal π electrons in neutral molecules might be observed at somewhat longer range where steric factors are inconsequential. Indeed, stereochemical identification of the Diels–Alder adducts to **1** (90–100% endo), **2** (100% endo), and **3** (variable) has caused us to develop an appreciation for the existence of directed electronic effects in bridged bicyclic systems.[1,6–8] Theoretical calculations indicate that σ–π mixing in **1** and **2** causes tilting of the diene p orbitals in a manner which is highly conducive to kinetically favored endo dienophile capture; in the case of **3**, this unusual feature is not seen to the same extent.[6]



1 **2** **3**

Where photooxygenation is concerned, the conversion of **1** and **2** to the respective endo peroxides is now recognized not to occur stereospecifically.[1] Evidently, the latter cycloaddition proceeds by a modestly interactive concerted $(4 + 2)\pi$-bonding scheme. To explain the nonconformance of singlet oxygen to the general pattern of endo dienophile capture, we have suggested that the crux of the matter lies in the excited-state nature of $^1O_2$ which reveals itself (a) in virtually complete control of the endoperoxidation process by entropic factors, with atypical disregard for enthalpy changes ($\Delta H^{\ddagger} \approx 0$ kcal/mol),[9,10] and (b) in a loss of that discriminatory ability for exo/endo stereoselection which is characteristic of Diels–Alder reactions because of the quite diverse energies in the π_1(S) levels of the cyclo-

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