Tetrahedron Vol. 41, No. 11, pp. 2037 to 2043, 1985
Printed in Great Britain.

0040-4020/85 \$3.00 + .00

ELECTRONIC CONTROL OF STEREOSELECTIVITY—21

STEREOCHEMICAL PARALLELISM BETWEEN DIENOPHILIC CAPTURE AND SINGLET OXYGENATION OF ISODICYCLOPENTADIENE DERIVATIVES[1]

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(*Received in Japan* 17 *November* 1983)

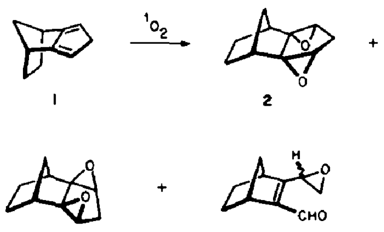
Abstract—The stereochemistry and product distribution resulting from reaction of 4′,5′,6′,7′-tetrahydrospirol[cyclopropane-1,2′]-[4,7]methano[2H]indene (**5**), *endo*-2-methyl (**6a**) and 2,2-dimethyl-4,7-dihydro-4,7-methano-2H-indene (**6b**), as well as 4′,5′,6′,7′-tetrahydrospiro[cyclopentane-1,2′]-[4,7]methano-[2H]indene (**7**) with singlet oxygen have been determined. Stereochemical assignments to the diepoxide products were readily deduced by ^{13}C-NMR comparison with the spectra of the parent isomers of established structure (X-ray). To unravel the stereochemistry of the epoxy aldehydes, recourse was made to 2D NOE experiments. The observed stereoselectivity and reaction profile of each substrate are analyzed and placed in proper mechanistic and energetic perspective.

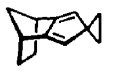
The manner in which singlet oxygen, $O_2(^1\Delta_g)$, reacts with cyclic conjugated dienes to form 1,4-endoperoxides continues to command attention and to be the subject of controversy.[2] The list of mechanistic possibilities includes the intervention of perepoxide intermediates,[3] rapid and reversible exciplex formation followed by collapse to product,[4] and a concerted Diels–Alder pathway.[5] One major impediment to our detailed understanding of these oxidative processes lies in their experimental enthalpies of reaction which happen to be zero.[5] Although this unusual $\Delta \underline{H}^{\ddagger} = 0$ phenomenon can be attributed to the electronically excited nature of singlet oxygen, kinetic treatments do not necessarily allow for clear-cut distinction between a single entropy-controlled step leading directly to endoperoxide and rate-determining entropy-controlled formation of a perepoxide intermediate that rapidly rearranges to product.

There is little question that endoperoxidation is an exothermic reaction which proceeds via an "early" transition state. As a consequence, singlet oxygen must be regarded as a highly electrophilic species that is particularly susceptible to subtle electron density changes in its reaction partners, barring of course its sensitivity to steric factors.[6] Recently, Clennan and Mehrsheikh-Mohammadi took clever advantage of these properties in their assessment of the kinetic behavior of 2-substituted and 2,5-disubstituted furans toward $^1O_2$.[7] They observed that the symmetric substrates reacted at approximately the same rate as their unsymmetrical analogues. On this basis, the proposal was advanced that the symmetrical furans react via a synchronous Diels–Alder transition state while the unsymmetrical furans proceed to product via a related, though asymmetric, transition state.

Isodicyclopentadiene (**1**) and derivatives of this ring system are recognized to exhibit significant π face stereoselectivity toward dienophile capture.[8] Knowledge of the sensitivity of $^1O_2$ to differing levels of π electron density above and below the cyclopentadiene ring in these substrates would clearly reveal more about its reputed "super" dienophile character. Since **1** and its homologues possess $\underline{C}_s$ symmetry, the prevailing electronic situation is simplified and important clues to interrelationships with more classical dienophiles could be provided.

Several years ago, we reported that **1** reacts with singlet oxygen to produce ultimately **2** (44%), **3** (16%), and **4** (23%).[9] The stereochemical nature of **4** was left unspecified. The net stereoselectivity is less than that observed in other [4+2] cycloadditions (up to 100% below-plane). This lack of overwhelming face selectivity has been interpreted by others[10] to be the result of exciplex formation during which the fused bicyclic skeleton exerts no influence. However, theoretical calculations by Gleiter suggest that this should not be so.[8a,11] Accordingly, we have extended our investigation to include the spirocyclopropane **5** which because of spiroconjugation exhibits, like **1**, a strong predilection for below-plane dienophile capture[12] and the triad **6a**, **6b**, and **7** that undergoes Diels–Alder reaction preferentially from the exo direction.[12,13]





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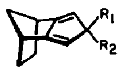
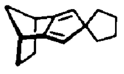


6a, $R_1 = H, R_2 = CH_3$
b, $R_1 = R_2 = CH_3$



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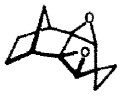
RESULTS

The spirocyclopropane example. When **5** was photooxygenated at room temp in 1,2-dichloroethane solution containing methylene blue as sensitizer, endoperoxidation proceeded rapidly. However, the endoperoxides did not persist during the conditions of reaction and workup. Careful ^{1}H-NMR analysis (300 MHz) of the unpurified reaction mixtures from several runs indicated that two major products had been formed in yields of 53 and 40%. The isolation of these substances was achieved by flash chromatography to remove the dye followed by medium pressure liquid chromatography on silica gel. The colorless crystalline substances so obtained proved to be the diepoxides **8** and **9** (major). No evidence was gained for formation of an epoxy aldehyde structurally related to **4**.



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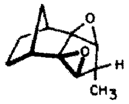
9

Stereochemical assignments to the individual diepoxide isomers follow predominantly from their ^{13}C-NMR spectra, both of which are simplified by virtue of C_s symmetry. The critical point is the excellent chemical shift correspondence with the data for **2** and **3** whose stereochemistries were earlier established unequivocally by X-ray analysis.[9] As seen in Table 1, the well-known anisotropy contributions of oxirane O atoms to C shifts[9,12–14] systematically affect the position of each framework carbon in a manner which is clearly diagnostic of their *exo* or *endo* orientation within the molecule.

Consequently, **5** exhibits a feeble preference for capture of singlet oxygen from its *endo* face.

The endo-*methyl derivative.* Although the sample of hydrocarbon **6a** employed in this study proved to be contaminated with **1**, analysis of its behavior toward singlet oxygen was not hampered. Purification of the oxidized material led to the isolation of **10** (13%), **11** (3%) and **12** (10%). The three-dimensional structures of **10** and **11** were likewise readily deduced on the basis of their ^{13}C-NMR spectra (Table 1). Particular attention is called to the systematic differences in the chemical shifts of the carbon atoms labelled 1–6 between the two isomers and their excellent correlativity with the values for **2**/**3** and **8**/**9**.



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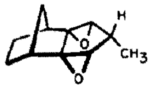

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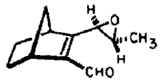


12

The ^{13}C and 300 MHz ^{1}H-NMR spectra of **12** revealed it to be an isomerically homogeneous substance. Although numerous proton signals were well separated, no definitive stereochemical assignments could be made, except for the trans disposition of the oxiranyl protons (J = 2.0 Hz).[15] Attempts to prepare a crystalline derivative of this epoxy aldehyde for eventual X-ray analysis failed due to the sensitivity of this molecule to varied chemical reagents. For these

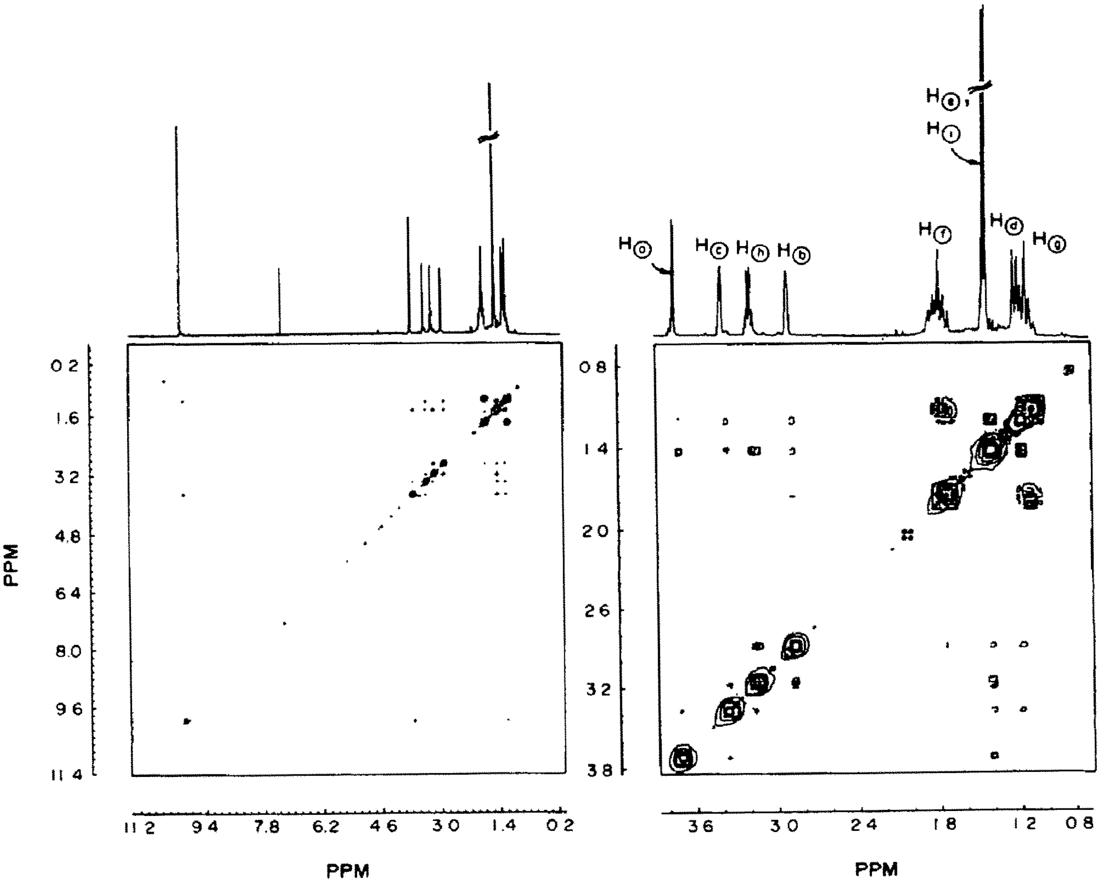
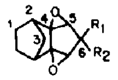


Fig. 1. Full scale (A, left) and expanded scale (B, right) NOESY spectrum of **12** taken at 300 MHz.

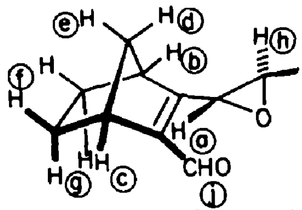
Table 1. Selected ^{13}C chemical shifts of the diepoxide isomers (ppm, $CDCl_3$ solution)



Compd.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
A. Exo series						
3	26.4	37.4	42.7	75.4	64.1	32.3
8	26.4	37.6	41.9	75.4	69.0	25.7
10	26.6	37.1	42.5	74.6	68.3	36.5
B. Endo series						
2	23.5	36.7	36.3	71.2	71.2	30.1
9	23.8	36.9	36.0	71.5	75.3	23.5
11	23.4	36.6	36.1	70.6	75.3	34.3

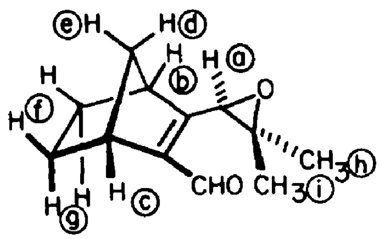
reasons, recourse was made to a NOESY experiment[16] which unequivocally showed the compound to possess the indicated structure (Fig. 1). Of particular relevence, intense nuclear Overhauser interactions were clearly observed between $H_{(b)}$ and $H_{(h)}$ as well as $H_{(a)}$ and $H_{(d)}/H_{(j)}$. These findings, together with the other NOE effects summarized in Table 2, substantiate the transoid configuration of the oxirane ring and denote its prevalent conformation to be as shown above the Table. In this particular arrangement, the existing spatial relationships as determined by Dreiding models fall into the range necessary to give rise to these phenomena. It follows that **12** results from above-plane singlet oxygen capture.

Table 2. Summary grid of 2D NOE experimental data involving **12**



	a	b	c	d	e	f	g	h	i	j
a	▨	–	–	X	–	–	–	–	X	X
b	–	▨	–	X	X	X	–	X	–	–
c	–	–	▨	X	X	–	–	–	–	–
d	X	X	X	▨	X	X	–	–	–	X
e	–	X	X	X	▨	–	–	–	–	–
f	–	X	–	X	–	▨	X	–	–	–
g	–	–	–	–	–	X	▨	–	–	–
h	–	X	–	–	–	–	–	▨	X	–
i	X	–	–	–	–	–	–	X	▨	–
j	X	–	–	X	–	–	–	–	–	▨

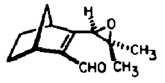
Table 3. Summary grid of 2D NOE experimental data involving **13**



	a	b	c	d	e	f	g	h	i
a	▨	–	–	X	*	–	–	X	–
b	–	▨	–	X	*	–	X	X	X
c	–	–	▨	–	*	–	–	–	–
d	X	X	–	▨	*	–	–	–	–
e	*	*	*	*	▨	*	*	*	*
f	–	–	–	–	*	▨	X	–	–
g	–	X	–	–	*	X	▨	–	X
h	X	X	–	–	*	–	–	▨	X
i	–	X	–	–	*	–	X	X	▨

* Indicates a complexity level too great to permit recognition of an effect.

The geminal dimethyl substitution plan. Sensitized photooxygenation of **6b** led uniquely to an isomerically pure epoxy aldehyde. Because of the extreme lability of this substance, it could be obtained in a pure state only with serious loss of material (18% isolated). Through application of NOESY techniques, it proved possible to identify this product as **13**. The observed nuclear Overhauser interactions are summarized in Table 3. The most relevant of these, *viz* those NOE effects which reveal a close spatial relationship between oxiranyl proton $H_{(a)}$ and $H_{(d)}$, between Me protons $H_{(h)}$ and $H_{(a)}/H_{(b)}$, and between Me protons $H_{(i)}$ and $H_{(b)}/H_{(g)}/H_{(h)}$, can arise only if oxygen has been introduced from the *exo* face. Should the converse be true, the common proximity of the protons in question does not materialize as seen clearly on examination of Dreiding models.



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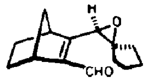


14

The consequences of spirocyclopentannulation. Interestingly, **7** also reacted with singlet oxygen to produce a single epoxy aldehyde. This substance was comparably identified as **14** by NOESY methods. In this instance, the full scale 2D spectrum (Fig. 2A) was again lacking in detail. However, scale expansion of the δ 4.0–0.8 region (Fig. 2B) as before proved highly informative. The data in Table 4 were compiled from this plot. Since pronounced NOE effects are observed

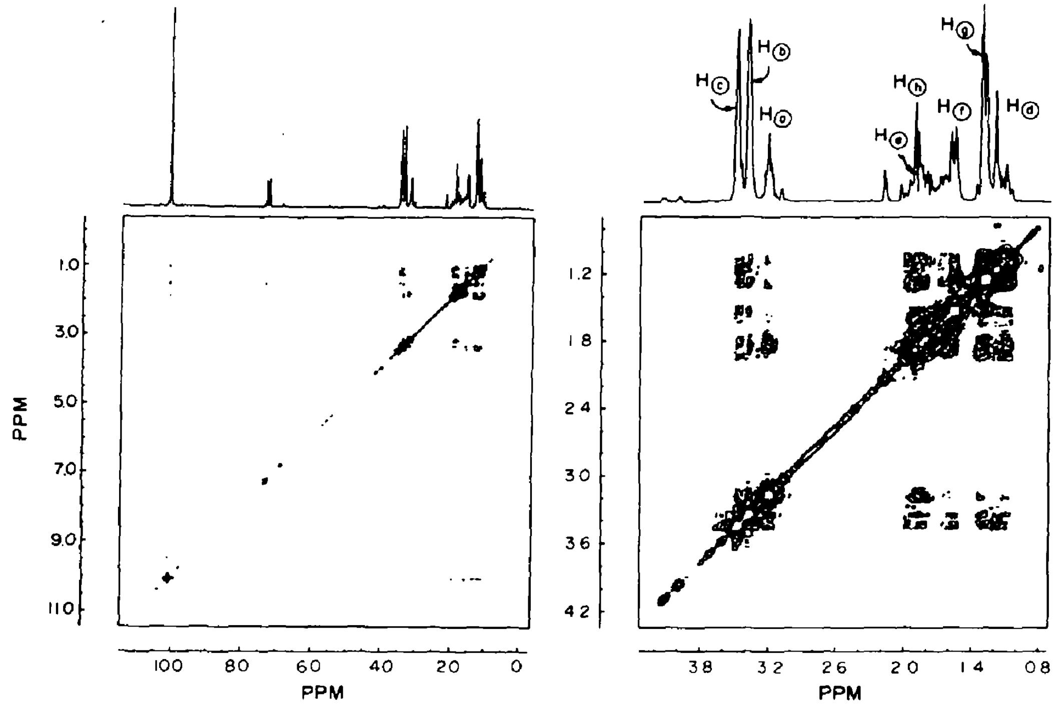
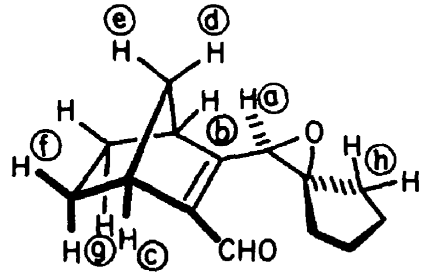


Fig. 2. Full scale (A, left) and expanded scale (B, right) NOESY spectrum of **14** taken at 300 MHz.

Table 4. Summary grid of 2D NOE experimental data involving **14**



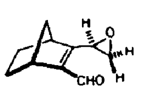
	a	b	c	d	e	f	g	h
a	▨	X	—	—	*	—	—	X
b	X	▨	—	—	*	X	X	X
c	—	—	▨	X	*	X	X	—
d	—	—	X	▨	*	—	—	—
e	*	*	*	*	▨	*	*	*
f	—	X	X	—	*	▨	X	X
g	—	X	X	—	*	X	▨	X
h	X	X	—	—	*	X	X	▨

* Indicates a complexity level too great to permit recognition of an effect.

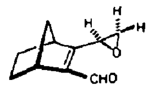
between $H_{(a)}$ and $H_{(b)}$, $H_{(b)}$ and $H_{(f)}/H_{(g)}/H_{(h)}$, $H_{(c)}$ and $H_{(f)}/H_{(g)}$, $H_{(f)}$ and $H_{(g)}/H_{(h)}$, as well as $H_{(g)}$ and $H_{(h)}$, the configuration of this epoxy aldehyde must be that resulting from *exo* attack by $^1O_2$.

Therefore, a strong preference for above-plane stereoselectivity is exhibited by singlet oxygen in its additions to **6a**, **6b**, and 7.

A reinvestigation of isodicyclopentadiene. Following recent acquisition of a 500 MHz NMR spectrometer, the oxygenation of **1** was repeated and the nature of epoxy aldehyde **4** was examined in more detail. Careful integration of various sets of signals which were now apparent at this field strength showed the substance to be comprised of a 75:25 mixture of isomers. All attempts to separate the two components proved unsuccessful and the application of NOESY techniques was therefore not possible. However, it is to be noted that this isomer distribution is essentially identical to that for **2** and **3** and remains invariant to reaction time and experimental conditions. Although a stereochemical parallelism is not demanded by these observations, mechanistic considerations to be discussed do not negate this notion. Consequently, we have tentatively formulated the major isomer as **4a** and the minor as **4b**.



4a

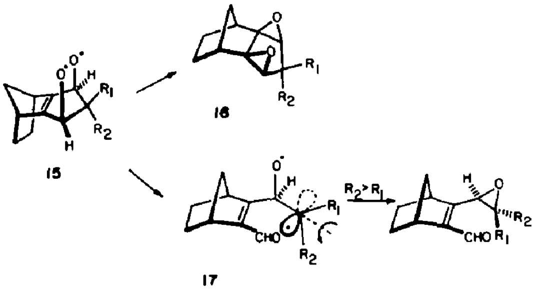


4b

DISCUSSION

Mechanistic details of endoperoxide decomposition. Singlet oxygenation of conjugated cyclic dienes results in endoperoxide formation.[17] Thermal or photochemical rearrangement of these labile products normally leads to stereospecific formation of *syn*-diepoxides.[18] When a cyclopentadiene ring is involved, ring cleavage with formation of a *cis*-4,5-epoxy-2-pentenal may be competitive.[19,20] To our knowledge, the factors which control the eventual outcome of the two reaction channels for cyclopentadiene endoperoxide decomposition have never been commented upon, despite extensive discussion of peripheral questions.[17,18]

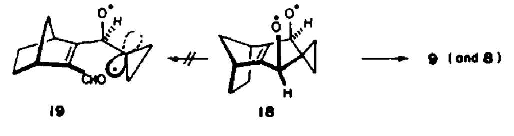
The observation that **6b** and **7** give rise only to epoxy aldehydes is taken as an indication that cleavage of a ring C—C bond in oxygen-centered biradical **15** is kinetically preferred to intramolecular double bond capture (the pathway to **16**) when R_1 and R_2 are simple alkyl residues. The tertiary nature of the carbon-centered radical in **17** is undoubtedly responsible for the exclusivity. However, because $R_1 = R_2$ in these examples, one is not able to determine if clockwise or counterclockwise rotation (or both) occurs in progressing to oxirane ring formation.



These conclusions are nicely reinforced by the reactivity profile exhibited by monomethyl derivative **6a**. In this instance, C—C bond cleavage is slowed sufficiently because of the incipient secondary nature of the carbon radical to allow diepoxide production to dominate by a factor of 1.6:1. Significantly, the stereochemistry of epoxy aldehyde **12** reveals that rebonding in **17** proceeds with *net inversion of configuration*. Consequently, this intermediate appears to be capable of rotation about the free radical interconnective bond, ring closure occurring ultimately to deliver the less sterically encumbered *trans* isomer.

In this connection, the response of **1** to singlet oxygenation is also mechanistically informative. The diepoxide–epoxy aldehyde ratio in this instance (2.6:1) signals that intervention of primary free radical **17** ($R_1 = R_2 = H$) is reasonably competitive with the generation of **16** ($R_1 = R_2 = H$), although less so than in the monomethyl example. These results are fully consistent with recent studies by Beckwith and others dealing with the regioselectivity of free radical–olefin cyclization reactions.[21]

The behavior of **5** toward $^1O_2$ is interesting. Because C—C bond homolysis within **18** (and its isomer) would lead in this instance to energetically disfavored[22]



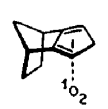
cyclopropyl radicals such as **19**, this pathway is rendered non-competitive relative to that which delivers diepoxides **9** (and **8**).

The electronic origins of stereoselectivity. It now becomes useful to call attention to stereochemical parallelisms with more classical Diels–Alder behavior. When parent hydrocarbon **1** is involved, high levels (often > 97%) of below-plane dienophile capture are routinely encountered.[23–25] An identical π-face selectivity is exhibited by **5**.[12] Nonetheless, where singlet oxygen is concerned, a marked drop off in stereoselection is seen, although vestiges of a preference for bonding to the *endo* surface persist (3:1 for **1**; 1.3:1 for **5**). A substantially better correlation obtains for the three systems which exhibit a marked preference for Diels–Alder cycloaddition from the above-plane direction (**6a**, **6b** and **7**).[12,13] With the exception of **6a** which is subject to approximately 12% *endo* attack by $^1O_2$, a strong bias for *exo* bonding continues to operate.

As elaborated upon in detail elsewhere,[8] the control of stereoselection in these systems cannot be attributed to differing steric factors in the norbornane ring because these are too remote from the seat of reaction. Rather, this remarkable behavior is believed to owe its origins to "orbital tilting" within ψ_1 of the diene as a result of strong σ/π mixing involving the high-lying sigma levels of the bicycloheptane ring. While this electronic perturbation causes disrotatory tilting of the terminal diene orbitals in the direction of the apical methylene group, the effect can be overridden and rotation fostered in the opposite direction by alkyl substitution as in **6a**, **6b**, and **7** (but not **5** due to spiroconjugative effects).

Nor can the disparity in π-facial stereoselectivity noted particularly for **1** and **5** toward singlet oxygen be plausibly attributed to product development control, since MINDO/3 calculations on various *exo*/*endo* endoperoxide pairs show them to differ by negligibly small heats of formation.[9] Product ratios closely approaching 1:1 would consequently be expected in all examples (not observed). Rather, the stereochemical outcome of these reactions appears to be influenced by a subsidiary factor of a different sort.

The case for reversible exciplex formation. It is our belief that $^1O_2$ is indeed responsive to the energetic consequences resulting from bonding to electronically different diene π faces. Where this reactive species is concerned, however, serious consideration must be accorded to reversible exciplex formation. In a recent elegant study, Gollnick and Griesbeck demonstrated not only that the interaction of $^1O_2$ with acyclic dienes proceeds via initial exciplex formation, but that *the principal fate of these exciplexes is decomposition into oxygen and diene.*[26] Although the question of whether the expelled oxygen molecule continues to reside in the electronically excited singlet state or becomes deactivated (in whole or in part) to the triplet ground state requires resolution, a reactivity inherently different from that of ordinary dienophiles is already apparent. The real possibility exists, therefore, that **1** (and **5**) initially captures $^1O_2$ to generate exciplex **20** far more rapidly than **21**. However, those electronic factors



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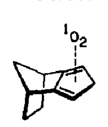

21

which favor preliminary interaction as in **20** might well also contribute to its more rapid disintegration to starting materials. Since **21** would be less prone to reversibility, the final observable outcome would be isolation of quantities of products resulting from above-plane capture. Additional work is obviously needed to resolve this interesting issue. Whatever the case, simple alkyl substitution as in **6** and **7** dramatically lessens the importance of this phenomenon. It may well be that the added steric encumbrance to diene capture offered by these groups discourages exciplex intervention to the point where it may be bypassed in favor of direct endoperoxide formation. Under these circumstances, the normal impact of "orbital tilting" would again be made fully evident.

In conclusion, the apparent lack of stereoelectronic control witnessed in the reaction of certain isodicyclopentadienes with singlet oxygen may not reside in a lack of recognition of "orbital tilting", but to an electronically facilitated reversal of exciplex formation on that π face which is most conducive to bonding in the first instance.

EXPERIMENTAL

General photooxygenation procedure. The diene (2.0 mmol) and methylene blue (5 mg) were dissolved in 1,2-dichloroethane (100 ml, distilled from calcium hydride and stored over molecular sieves) and the soln was irradiated at 18° with a Sylvania 500-W tungsten halogen lamp while a stream of O_2 was vigorously bubbled through the system. At 15 and 30 min intervals, additional 5 mg portions of the dye were introduced. At the end of this time, the solvent was removed *in vacuo* to yield a thick blue oil or solid. Analysis by ^{1}H-NMR indicated the absence of starting material in all cases except **6a**. Methylene blue was removed from the sample by Kugelrohr distillation. Non-distillable samples were passed through a silica gel column (elution with 30% EtOAc in petroleum ether) in order to remove most of the dye. The resultant product mixture was reanalyzed by ^{1}H-NMR. In those instances where a discrepancy in product ratios between unpurified and purified mixtures was noted, the first data set is reported. The cited values were reproduced in duplicate experiments. Product separation was subsequently achieved by MPLC on silica gel (same solvent system) and the individual components were characterized as detailed below.

Photooxygenation of **5**. The product mixture in this instance consisted of **8** (40%), **9** (53%), and various minor contaminants (7%), but no epoxy aldehyde. Following MPLC, there was isolated 20 mg (18%) of **8** and 28 mg (24%) of **9**.

For **8**: colorless crystals, m.p. 138.5–142°; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.15 (s, 2H), 2.35 (br s, 2H), 1.89–1.63 (m, 6H), 1.00–0.94 (m, 2H), 0.70–0.65 (m, 2H); ^{13}C-NMR ($CDCl_3$, ppm): 75.35, 68.99, 41.90, 37.58, 26.41, 25.68, 9.90, 6.17; mass spectrum *m/e* calc 190.0994, obs. 190.0955.

For **9**: colorless crystals, m.p. 174–175.5° (from hexane–EtOAc); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.39 (s, 2H), 2.43 (br s, 2H), 1.72–1.59 (m, 6H), 1.03 (t, J = 8 Hz, 2H), 0.72 (t, J = 8 Hz, 2H); ^{13}C-NMR ($CDCl_3$, ppm): 75.30, 71.46, 36.85, 36.02, 23.84, 23.45, 10.44, 5.29. (Found: C, 75.67; H, 7.51. Calc for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.)

Photooxygenation of **6a**. The crude mixture was subjected to sequential Kugelrohr distillation and chromatography on silica. Diepoxides **10** and **11** and epoxy aldehyde **12** were seen to be produced at levels of 13, 3 and 10%, respectively.

For **10**: colorless solid, m.p. 54–55° (from ether–hexane); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.36 (s, 2H), 2.41–2.32 (m, 4H), 1.91–1.88 (m, 2H), 1.73 (d, J = 9 Hz, 1H), 1.59–1.56 (m, 2H), 0.95 (d, J = 8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, ppm): 74.57, 68.21, 42.54, 37.07, 36.47, 26.57, 13.18. (Found: C, 74.08; H, 7.94. Calc for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.)

For **11**: colorless solid, m.p. 80–89°; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.60 (s, 2H), 2.39 (s, 2H), 2.17 (q, J = 8 Hz, 1H), 1.87–1.65 (m, 6H), 0.94 (d, J = 8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, ppm): 75.23, 70.58, 36.58, 36.14, 34.33, 23.40, 13.01; mass spectrum *m/e* calc 178.0994, obs. 179.1101.

For **12**: pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.97 (s, 1H), 3.73 (d, J = 2 Hz, 1H), 3.38 (br s, 1H), 3.20–3.14 (m, 1H), 2.89 (br s, 1H), 1.85–1.61 (m, 2H), 1.42 (d, J = 5 Hz, 4H), 1.23–1.11 (m, 3H); ^{13}C-NMR ($CDCl_3$, ppm): 186.34 (d), 163.09 (s), 146.86 (s), 56.21 (d), 53.66 (d), 46.70 (t), 44.33 (d), 40.88 (d), 25.55 (d), 25.30 (d), 17.63 (q); mass spectrum *m/e* calc 178.0994, obs. 178.0998.

Photooxygenation of **6b**. The epoxy aldehyde **13**, which was the only characterizable product isolated in this experiment, was obtained in 18% yield after distillation and chromatography. The colorless oil exhibited the following spectral properties: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.04 (s, 1H), 3.48 (br s, 1H), 3.36 (br s, 1H), 2.97 (heptet, J = 6.7 Hz, 1H), 1.99–1.86 (m, 2H), 1.32–1.28 (m, 1H), 1.20–1.05 (m, 9H); ^{13}C-NMR ($CDCl_3$, ppm): 188.65, 157.54, 151.85, 75.45, 47.22, 45.87, 41.08, 39.42, 25.50, 24.54, 18.21, 18.02; mass spectrum *m/e* calc 192.1151, obs. 192.1171.

Photooxygenation of **7**. Distillation of the crude reaction mixture yielded 46% of a bright yellow oil identified principally as **14**. Following MPLC, this sensitive compound was obtained as a pure colorless oil in 9% yield; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.09 (s, 1H), 3.49 (br s, 1H), 3.39 (br s, 1H), 3.23–3.21 (m, 1H), 1.99–1.55 (m, 11H), 1.30 (d, J = 7.8 Hz, 2H), 1.15 (m, 1H); ^{13}C-NMR ($CDCl_3$, ppm): 189.15, 157.85, 151,78, 77.10, 50.21, 47.21, 45.87, 41.27, 29.51, 29.32, 26.32 (2C), 25.68 (2C); mass spectrum *m/e* calc 218.1307, obs. 218.1342.

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