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Stereoreversed Electrophilic Additions to 3-Norcarenes. Insight into the Relative Steric Demands of Singlet Oxygen in the Ene Reaction

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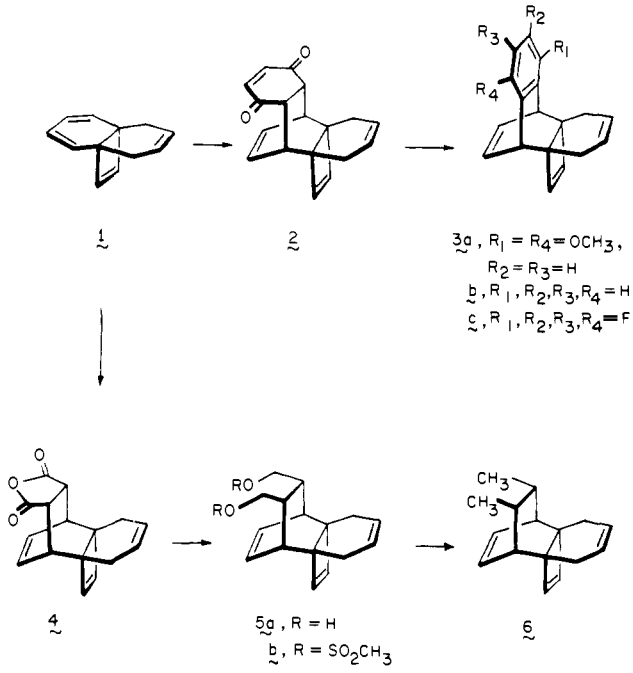
Abstract: Several snoutanes having a fused cyclohexene ring and therefore a 3-norcarene part structure entered into "ene" reaction with singlet oxygen and *N*-methyltriazolinedione with highly stereoselective or completely stereospecific approach to the anti surface (relative to the cyclopropane ring) of the double bond. When epoxidation and bromohydrin formation were examined, the preferred direction of electrophilic attack was shown to be syn. The several types of products were characterized spectroscopically and interrelated chemically. The absolute rates of reaction of the snoutanes and selected reference compounds toward $^1O_2$ were determined by pulse radiolysis techniques. These data revealed that urazoles are not effective quenchers of singlet oxygen as previously proposed. Lastly, the causative factors underlying the striking reversal in the stereochemistry of electrophilic additions to the snoutanes are discussed.

The preceding investigation has shown that electrophilic additions to a series of 3-norcarene derivatives proceed with a decided stereochemical preference for initial attack anti to the cyclopropane ring.[3] The allylic hydroperoxidations with singlet oxygen proved to be stereospecific, whereas epoxidation and bromohydrin formation were 62–93% stereoselective depending upon the substrate. The simple mechanistic picture to emerge is that the conformationally flexible hydrocarbons experience predominant or exclusive capture of the electrophilic reagent on that molecular surface opposite to the cyclopropane ring for the usual steric reasons. Since the stereoselectivity was uniformly in one direction, it was not possible to recognize any characteristics of those electrophilic reagents examined which may be regarded as distinctive. This paper describes a companion study to our earlier work in which 3-norcarene derivatives chosen with the intent of incorporating only a small additional structural perturbation are shown to undergo striking stereochemically reversed electrophilic behavior in a number of instances. Because the product-determining transition states are now imbalanced, certain interesting features which distinguish the steric demands of singlet oxygen and other "enophiles" from the more usual electrophilic species are made apparent.

Previously, the behavior of urazoles related to the molecules to be described toward $^1O_2$ was attributed to intramolecular quenching by the O=CN—NC=O functionality of the attacking reagent with resultant kinetic retardation and reversal of stereospecificity.[4] By means of suitable convincing ^1H NMR intercorrelations, certain of the original stereochemical assignments are now shown to be in error. Also, appropriate quenching studies have revealed urazoles not to be suitable quenchers of singlet oxygen as previous (nonrepeatable) experiments had indicated.[5] Finally, in light of the above, the measurement of certain absolute rate constants has been undertaken to resolve remaining kinetic questions. As will be shown, the stereochemical reversal previously attributed to frontier orbital controlled quenching can be traced instead to the steric demands of certain reagents.

Results

Synthesis. Preparation of the compounds selected for study was dependent in its initial stages on the ability of the known [4.4.2]propella-2,4,8,11-tetraene (**1**)[6] to enter into [4 + 2] cycloaddition with various dienophiles in highly stereoselective fashion from the direction anti to the cyclobutene ring. Exposure of **1** to *p*-benzoquinone and maleic anhydride at somewhat elevated temperatures produced **2** and **4** efficiently. O-Methylation of **2** afforded the dimethoxybenzene system **3a**. The parent hydrocarbon **3b** and tetrafluoro derivative **3c**



were made available by direct addition of the corresponding benzynes to **1**. Configurational assignments to **2** and **4**, made

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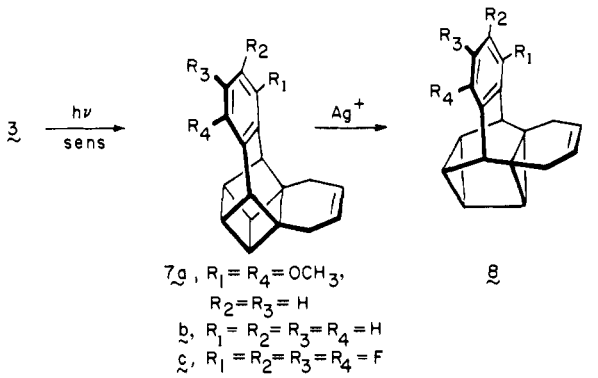
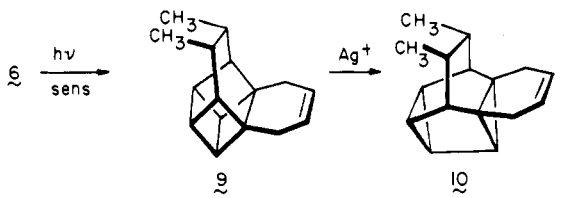
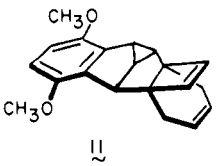
on the basis of the small vicinal coupling constants of the α-carbonyl protons ($J \approx 1.15$ Hz), agree fully with conventional Diels–Alder stereochemical findings. Since **4** was transformed to the dimethyl compound **6** by standard reductive steps which do not induce epimerization, the configurations of the methyl groups in this hydrocarbon must be directly related to the stereochemistry of the anhydride.

The remaining structural question concerns the direction of entry of the dienophile. Through sensitized irradiation of **3** and **6**, it was possible to gain access to the 1,8-bishomocubanes **7** and **9**. Such experiments demonstrate the proximate







nature of the cyclobutene and bicyclo[2.2.2]octene double bonds and accord uniquely with the illustrated formulas. Although the yields in these [2 + 2] photocycloadditions were not high, the caged molecules could easily be separated from dimeric and polymeric byproducts. Only in the case of **3a** was a secondary monomeric product isolated. This substance was identified by its ^{1}H NMR spectrum as **11**, the consequence of competing di-π-methane rearrangement. This is, of course, not an isolated occurrence. Previous work in this laboratory has shown that electron-rich aromatic rings exhibit a propensity for di-π-methane bond reorganization (with transient disruption of the benzenoid sextet) not shared by their more electron-deficient counterparts, including unsubstituted systems.[7]

When **7** and **9** were exposed to silver(I) ion, efficient rearrangement to the snoutanes **8** and **10**, respectively, was observed in agreement with precedent.[8] The resultant bond switching transforms the bicyclo[4.2.0]octane part structure heretofore present in all of the precursor molecules to a 3-norcarene unit. As with simpler norcarenes,[3] the double bond in **8** and **10** is amenable to syn and anti attack (the cyclopropane ring comprises the point of reference). The added structural perturbation is located on the anti surface of the π bond and is positioned somewhat remotely from the reaction center. The rigid geometry in the snoutane component of these molecules serves to predispose the ethano bridge in **10** and the aromatic ring in **8** to a relatively invariant position in space. The principal alteration is electronic. Thus, the benzo ring in **8a** is quite electron rich, while that in **8c** is electron deficient. The bridge in **10** has no pπ electrons. On this basis, the IPs of these molecules can be expected to vary widely.[9]

The conformational properties of **8** and **10** in the vicinity of the 3-norcarene part structure were not amenable to spectral analysis. Not only were the signals due to the allylic protons complex, but they overlapped uniformly with several cyclopropyl hydrogen absorptions at 60 and 100 MHz.

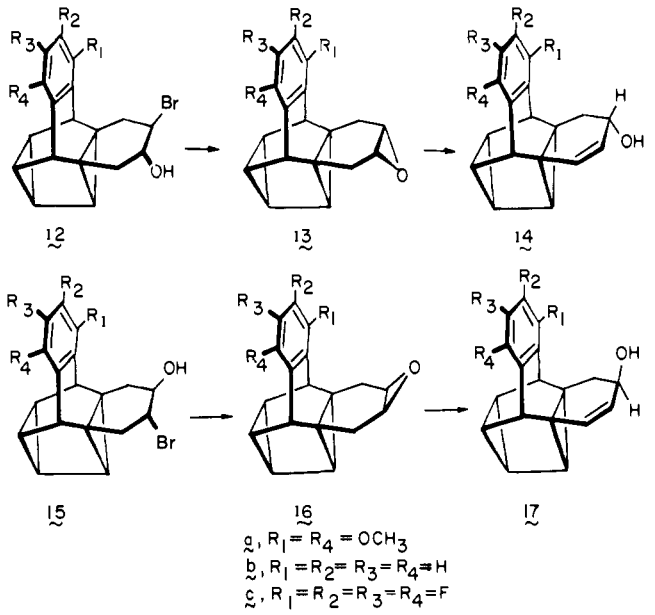
Electrophilic Additions to the Benzo Fused Derivatives. The direct epoxidation of dimethoxy derivative **8a** with *m*-chloroperbenzoic acid was conducted under both buffered and unbuffered conditions, but not cleanly as in the subsequent examples. At best, 22% of a single, isomerically pure epoxide could be obtained by preparative thin layer chromatography. The opposite isomer was not detected. However, since the pair of epoxides was later shown not to be stable to silica gel chromatography, reliable product ratios are not available (^{1}H NMR analysis was to no avail because of overlapping absorptions).

Through reaction of **8a** with *N*-bromosuccinimide in aqueous glyme, there was obtained a 62:38 ratio of bromohydrins which were amenable to separation by preparative layer chromatography. The pure isomers were converted directly to the corresponding epoxides in good yields by heating with sodium hydride in tetrahydrofuran. The epoxide formed from the minor bromohydrin was the same as that isolated from the direct epoxidation.

In an effort to assess the stereochemistry of these products, the epoxide formed from the major bromohydrin was treated with lithium diethylamide and converted to the related allylic alcohol. This product was formed as the major product in the "ene" reaction of **8a** with singlet oxygen. Previously,[3,10] we showed that the ^{1}H NMR spectra of 2-norcarenes, especially in the olefinic region, are very sensitive to substitution and stereochemistry. More specifically, earlier evidence had substantiated the fact that *anti*-2-norcaren-4-ols exhibit a low-field doublet having additional narrow coupling positioned slightly downfield of δ 5.5 and a second doublet in the δ 5.5–5.0 region. In contrast, the olefinic signals of the syn allylic alcohols are shifted to lower field and show greater multiplicity in the more shielded of these absorptions (which is generally seen as a nicely spaced doublet of doublets). Since the photooxygenation product exhibited a doublet of doublets (J = 11 and 1.5 Hz) at δ 5.75 and a doublet (J = 11 Hz) at δ 5.08, it was confidently assigned as **17a**.

The data therefore show singlet oxygen to attack **8a** with a 4:1 stereoselectivity from the anti direction. In contrast, bromonium ion attack on the syn surface of the π bond is favored by a factor of almost 2, a kinetic perference shared by peracid oxidation.

This striking stereoreversal is not restricted to **8a**, but is seen throughout the benzo fused series, irrespective of electronic character. Thus, the epoxidation of **8b** provided **13b** as the only isolable epoxide; small amounts of **16b** could have been formed concurrently and lost during workup of our small-scale reactions, but its percentage, if present at all, was very low. Bromohydrin formation provided **12b** and **15b** in a 1:2 ratio. Their independent cyclization led to both **13b** and **16b**, thereby making available a reference sample of the latter epoxide with which to check the earlier epoxidation. In the ^{1}H NMR spectrum of **13b**, the geminal methylene protons of the *syn*-norcarane oxide moiety appear as a well-defined AA′BB′ pattern (J = 15.5 Hz) having only very small additional coupling. As before,[3] such multiplicity is taken to mean that this epoxide preferably adopts a trans-boat conformation under the conditions of the spectral measurement. Another observation unique to **13b** is the appearance of the two basal cyclopropyl protons as a narrow multiplet at δ 2.3. As anticipated for **16b**,



12 13 14

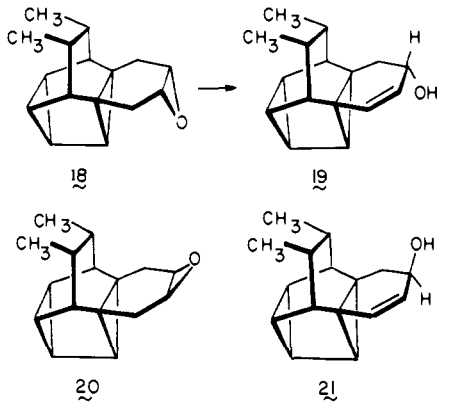
15 16 17

16 a, $R_1 = R_4 = OCH_3$
b, $R_1 = R_2 = R_3 = R_4 = H$
c, $R_1 = R_2 = R_3 = R_4 = F$

the cyclopropane proton anti to the epoxide ring experiences anisotropic shielding such that it now appears upfield at δ 1.63; the more distant basal cyclopropyl hydrogen remains at δ 2.25. Because the geminal methylene protons are seen as an AA'BB' system with doublet at δ 2.25 further coupled to the α-epoxy hydrogens and the doublet at δ 1.73 not noticeably split (compare 1,6-dimethylnorcar-3-ene oxide[3]), the cyclohexane ring in **16** is thought to be essentially planar.

The availability of **8c** in very limited quantities permitted only a small-scale photooxygenation to be conducted. Although the reaction proceeded slowly and secondary oxidation products therefore materialized, the olefinic region of the allylic alcohol isolated by preparative layer chromatography showed the molecule to be **17c**.

Stereochemical Behavior of 10. Since the question of the effect of a saturated ethano bridge on stereochemistry was of some interest, the reaction of **10** with peracid and singlet oxygen was examined. An entirely similar trend was observed. Whereas epoxidation led to a 65:35 mixture of **18** and **20**, photooxygenation proceeded with exclusive formation of **21** as revealed by TLC analysis. That the major epoxide was of opposite stereochemistry to **21** was again established by lithium diethylamide induced ring opening to give **19**. The low-field



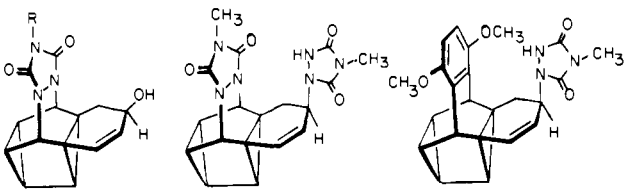
18 19

20 21

region of the ^{1}H NMR spectrum of **19** features a doublet (J = 10 Hz) at δ 6.10 and a doublet of doublets (J = 10 and 5 Hz) at δ 5.45, a pattern entirely comparable to those of the other syn allylic alcohols. The anti stereochemistry of **21** follows from identical considerations (see Experimental Section). In light of these findings, **10** is seen to follow the trend established in the benzo fused compounds.

Other Considerations. A major goal in developing the correlation of 2-norcaren-3-ol stereochemistry with olefinic ^{1}H NMR multiplicity[3] was to permit reassessment of the stereochemical response of the structurally related *N*-phenylurazole to these same reagents. Since the exclusive photooxygenation product is actually characterized by a doublet of doublets (J = 10.0 and 2.0 Hz) at δ 5.88 and a doublet (J = 10.0 Hz) at δ 5.46,[12] the molecule can now be confidently assigned the anti stereochemistry shown in **22.** This conclusion receives confirmatory support from the spectral properties of the allylic alcohol obtained via the major epoxide [δ 6.23 (d, J = 10 Hz) and 5.72 (dd, J = 10 and 6 Hz)] which conform to the pattern typical of the syn isomers. Consequently, contrary to our earlier claim,[4a,12] the stereoselectivity pattern of the urazole system parallels that of the other snoutanes examined herein (Table I). *Stereoreversed singlet oxygen attack occurs in each instance irrespective of the structural characteristics of the bridge.*

To expand our lines of mechanistic inquiry, attention was turned to the reaction of **8a** and the *N*-methylurazole with *N*-methyltriazolinedione (MTAD). As with $^1O_2$, this latter reagent enters readily into "ene" reactions and should therefore provide an additional point of reference for the steric demands of such processes. In both examples, reactions conducted in refluxing dichloromethane solution afforded a single adduct. The two substances were immediately recognized to be characterized by olefinic patterns uniquely typical of the anti allylic alcohols (see Experimental Section). Accordingly, they were formulated as **23** and **24,** respectively.



22 23 24

With this evidence in hand, we see that $^1O_2$ and MTAD show a strong predilection to attack the 3-norcarene part structure of the snoutanes from the anti direction. The sole example where complete stereospecificity is not witnessed is the singlet oxygenation of **8a.** A probable cause for this bifurcate behavior is given in the Discussion. These stereochemical observations entirely parallel the characteristics previously determined for simpler 3-norcarenes.[3] The reversed stereoselectivity presently found for peracid oxidation and NBS bromination stands in contrast with the previous findings. This absence of stereochemical commonality in the product ratios is believed to have its origins in certain structural features unique to the snoutanes (see Discussion).

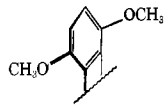
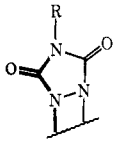
Determination of Rate Parameters and Quenching Studies. To gain added insight into our systems, a number of rates of singlet oxygenation were determined. For this purpose, use was made of the pulse radiolysis technique developed at The Center for Fast Kinetic Research, Austin, Texas.[13] With the use of their laser setup, a high-energy beam of photons was directed on dichloromethane solutions containing substrate, anthracene (A, 4.0×10^{-4} mol L^{-1}), and diphenylisobenzofuran (DPBF, 3.75×10^{-5} mol L^{-1}). Under these conditions, a large fraction of the initially absorbed energy is taken up by the anthracene in a form which can be used to sensitize the production of $^1\Delta_g$ singlet oxygen in aerated solutions according to the following scheme:

$$A \xrightarrow[\text{fast}]{e^-} {}^1A^*$$

$$^1A^* \rightarrow {}^3A^*$$

$$3A^* + O_2(^3\Sigma_g^-) \rightarrow O_2^*(^1\Delta_g) + A$$

Table I. Stereochemistry of Electrophilic Addition to the Various Snoutanes[a]

snoutane bridge substitution	singlet oxygen		NBS, H_2O glyme		MCPBA		MTAD	
	syn	anti	syn	anti	syn	anti	syn	anti
	21	79[b]	62	38	100[c]			100
		100	67	33	100			
		100			66	34		
		100	82	18	92	8		100

[a] Relative percentage values are given for all products *after physical separation of the isomers had been achieved.* [b] A small amount of an overoxygenation product was also isolated. [c] Both possible epoxides shown to be partially decomposed under the conditions of purification.

The role of the DPBF is that of a monitor, and therefore there exist three channels for singlet oxygen decay:

$$O_2^*(^1\Delta_g) \xrightarrow{k_d} O_2(^3\Sigma_g^-)$$

$$O_2^*(^1\Delta_g) + S \xrightarrow{k'} \text{loss of } O_2^*(^1\Delta_g)$$

$$O_2^*(^1\Delta_g) + \text{DPBF} \xrightarrow{k_m} \text{loss of DPBF}$$

When conditions are such that the initial concentration of $O_2^*(^1\Delta_g)$ is low compared to the initial concentrations of DPBF and substrate (S), the rate of loss of DPBF is given by

$$\frac{d(-[\text{DPBF}])}{dt} = k_m[\text{DPBF}][O_2^*]_0 \exp-\{k_d + k_m[\text{DPBF}] + k_s[S]\}t$$

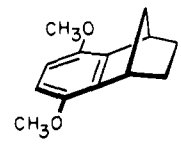
where S may act by chemical or physical (quenching) action and $[O_2^*]_0$ is the concentration of singlet oxygen at the end of the photon pulse. A plot of ln $(D_t - D_\infty)$ against time can be shown to be linear with a slope, k_{obsd}, given by the equation

$$k_{obsd} = k_d + k_m[\text{DPBF}] + k'[S]$$

where D_t and D_∞ are the DPBF optical densities at time t and at completion of the bleaching event. The rate parameters k_d, k_m, and k' can therefore be evaluated from plots of k_{obsd} against (a) DPBF concentration for k_d and k_m and (b) substrate concentration (at fixed DPBF) for k'. In this study, we have concerned ourselves only with the last option.

As noted above, k' can encompass both the rate constant for reaction of the substrate with singlet oxygen and the quenching rate constant, if such is operative. To assess the quenching potential, recourse was made to model systems **25** and **26** for comparison to **8a** and **8b**, respectively. Also, **28** and **29** were prepared to interlink with **27**.

As shown in Table II, rather high substrate concentrations were required in order to record measurable rate constants for **8a**, **8b**, and **27**. What is made abundantly clear is that urazoles such as **28** and **29** do have the capability to quench singlet oxygen at a rate which can be considered significant. The ordering of the rate constants for **8a**, **8b**, and **27** does not correlate



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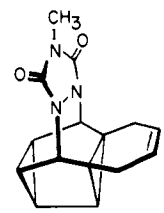

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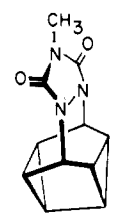

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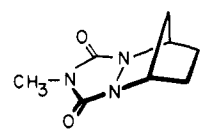

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with substrate ionization potentials (**8b** reacts too slowly). Additionally, the results realized with **25** and **26**, which suggest in particular that the 1,4-dimethoxybenzene ring is an effective inhibitor of $^1O_2$, also do not conform to any obvious trend. We attribute this apparent inconsistency to four factors: (a) k' is a composite rate constant; (b) the reaction rates are too slow for accurate measurement by this technique; (c) changes in the composition of the aromatic HOMO of **8a** and **8b** relative to the model systems which can be operative as a result of considerable mixing with the proximate Walsh cyclopropane orbital of appropriate symmetry in the snoutanes;[4] (d) alterations in solvent polarity which can arise from the need for relatively high substrate concentrations.

Further evidence for the latter hypothesis was obtained by assessing the effect of varying concentrations of **29** on the rate of reaction of cyclohexene with $^1O_2$ using the β approximation method.[14] Solutions in benzene–methanol (3:1) containing 5.28×10^{-4} M rose bengal were thermostated at 25 ± 1 °C and irradiated through Pyrex for 1-h intervals while constantly purged with oxygen. Subsequent to hydroperoxide reduction (trimethyl phosphite) and addition of a known quantity of internal standard (cyclohexanol), the extent of 2-cyclohexenol production was determined gas chromatographically (calibrated detector). Least-squares analysis of the data gave β =

Table II. Summary of Observed Rate Constants for Singlet Oxygen Consumption Determined by Pulse Radiolysis Methods

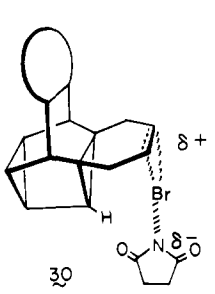
substrate	[S], mol L^{-1}	$k_d + k_m$[DPBF], s^{-1} [a]	k_{obsd}, s^{-1}	k', L mol^{-1} s^{-1}
8a	1.434×10^{-1}	$0.043\,54 \times 10^6$	$0.186\,76 \times 10^6$	9.99×10^5
8b	2.049×10^{-1}	$0.043\,54 \times 10^6$	$0.048\,75 \times 10^6$	2.54×10^4
27	8.03×10^{-2}	$0.043\,54 \times 10^6$	$0.051\,67 \times 10^6$	1.01×10^5
25	1.40×10^{-3}	$0.043\,54 \times 10^6$	$0.061\,78 \times 10^6$	1.3×10^7
26	1.20×10^{-1}	$0.043\,54 \times 10^6$	$0.048\,21 \times 10^6$	3.9×10^4
28	1.988×10^{-1}	$0.043\,54 \times 10^6$	$0.050\,31 \times 10^6$	3.41×10^4
29	1.10×10^{-1}	$0.043\,54 \times 10^6$	$0.047\,95 \times 10^6$	4×10^4

[a] Values obtained from blank runs on solutions lacking substrate (CH_2Cl_2, air saturated).

3.1 for cyclohexene. Since $\beta = k_d/k_r$ (k_r is the rate of allylic hydroperoxidation) and a reliable estimate of k_d in this solvent mixture is available (6.25×10^4 s^{-1}), k_r for cyclohexene is 2×10^4 L mol^{-1} s^{-1}. This value compares closely to the rate constant determined by the pulse radiolysis technique for 3-norcarene **8b** (Table II).

Discussion

The mechanistic significance of the present results may best be grasped by reference to the four transition-state representations **30–33** shown below. For illustrative convenience,



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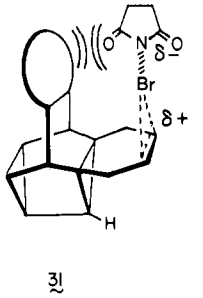

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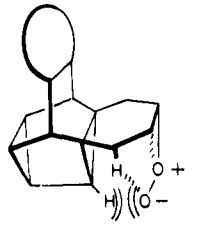

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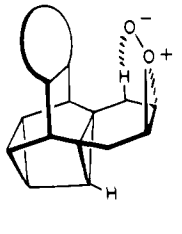

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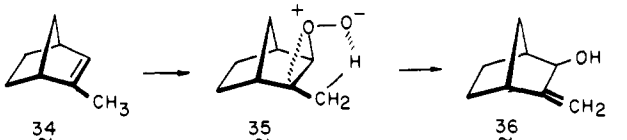
(unsymmetrical) perepoxide structures[15] have been employed in the singlet oxygen formulations. Rationalization of the experimental results requires that different kinetic preferences be shown in attacking the syn and anti faces of the 3-norcarene double bond in the snoutanes, which phenomenon does not prevail in simpler analogues where anti bonding proceeds exclusively.[3] Access of $^1O_2$ and MTAD to that surface of the π bond shared by the cyclopropane ring has remained hindered, whereas NBS and *m*-chloroperbenzoic actually prefer syn attack by a significant margin. An attractive working hypothesis views the "tying back" of the norcaranyl cyclopropane through bonding to the second three-membered ring as a nonperturbing factor in the maintenance of the planar cyclohexene conformation generally preferred by 3-norcarenes.[3,16] With the added assumption that the transition states in question are reactant-like, one would expect from consideration of molecular models that the steric environment for syn attack by NBS and *m*-chloroperbenzoic acid is less congested than that associated with anti attack. Given the transition-state descriptions generally accepted for this pair of reactions,[17,18] the bulk of the reagent is seen not to manifest itself in the close proximity of the double bond, but at a somewhat more remote distance. Consequently, in the syn transition state exemplified by **30**, the proximal cyclopropyl hydrogen offers appreciably less steric impedence to attack than the substituted ethano bridge in the anti transition state (**31**). In the latter instance, geometric and proximity factors combine to cause the buildup of serious steric interference as illustrated. Such considerations conform to our knowledge of typical one-step cyclic additions where steric factors present in the reactant are frequently determinative of stereochemistry.[19] The exo/endo ratio of 200:1 observed for the epoxidation of norbornene is exemplary.[20]

The "ene" reagents typified by $^1O_2$ and MTAD depend upon the availability of at least one allylic C–H bond which is properly aligned stereoelectronically with the pπ orbitals of the double bond. Such a necessary condition requires that the atom comprising the negative terminus of the "ene" dipole approach the allylic hydrogen to effect its ultimate migration. This precondition for effective reaction necessitates a particular orientation of the "enophile" as shown for singlet oxygen in **32** and **33**. In the syn bonding process, the reagent must enter into the immediate vicinity of the cyclopropane ring (see **32**). This event presents steric constraints of much greater magnitude than those prevailing during anti attack as a direct result of the greater remoteness of the ethano bridge in **33**.

At this point, it becomes important to recognize not only the high sensitivity of singlet oxygen to steric factors,[20] but also the various ways in which such effects can develop within differently constructed cyclic olefins. In cases where the allylic hydrogen is positioned on a pendant methyl group as in **34**, the trailing perepoxide oxygen must actually be oriented *away from* the region of major steric interference (cf. **35**). Nonetheless, the composition of the allylic alcohol product mixture **36** is 98.5% exo and only 1.5% endo.[21] Since this ratio is less than that observed upon epoxidation of norbornene, the cyclic "ene" transition state has been characterized as "loose".[21] The entire range of available data including the present results are not consistent with such a mechanistic picture. Care must be taken to draw comparisons between like processes. Not surprisingly then, the snoutanes undergo "ene" reactions only from the far less congested anti direction, since the allyl hydrogen abstraction process must proceed *internally* within the existing six-membered ring (see **32** and **33**).



34 35 36

Syn approach to **8**, **10**, and **27** is apt to be minimally perturbed by the extensively varied electronic features which have been purposefully positioned on the snoutane bridge. Any stereoelectronic control of syn transition states of the type observed recently by Mukai[22] and Paquette[23] and their coworkers should therefore be negligible. Of the examples where anti attack is favored, the reaction of 1,4-dimethoxybenzene derivative **8a** with singlet oxygen is the only one which is not

fully stereoselective. This result may be a consequence of the fact that the trailing negatively charged oxygen is required to be projected into the vicinity of the electron-rich aromatic ring. Under these circumstances, untoward electronic forces may arise to a degree sufficient to cause syn attack to become competitive.

Finally, the present observations attest to the fact that the urazole ring is *not* capable of quenching $^1O_2$, despite its often favorable ionization potential (8.0 and 8.6 eV, respectively, for **27** and **29**) relative to cyclohexene (>9 eV) and other olefinic π bonds, and the appropriate antisymmetric nature of its highest occupied orbital (n_-).[4] This factor distinguishes urazoles from amines which are known to quench $^1O_2$ physically[24] at rate constants which increase as the individual ionization potentials decrease,[25] as well as other good electron donors such as sulfides,[28] phenols,[27] and azides.[28] The carbonyl groups adjacent to the urazole nitrogens have been shown to exert a powerful electron-withdrawing effect.[5,29] Presumably as a consequence of such deactivation, the ability to quench singlet oxygen is lost.

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with Varian T-60, Varian A-60A, and Bruker HX-90 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on a Perkin-Elmer Model 467 instrument and mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Preparative VPC work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

1,4,8a,9,10,10a-Hexahydro-4a,9a:9,10-diethenoanthracene-5,8-dione (2). A mixture of [4.4.2]propella-2,4,8-11-tetraene (**1**,[6] 780 mg, 5.0 mmol), freshly sublimed *p*-benzoquinone (540 mg, 5.0 mmol), and anhydrous methanol (2 mL) was heated at the reflux temperature for 3 h, cooled, and filtered to isolate the precipitated product. The yellow solid was washed well with cold ethanol and dried to give 880 mg (67%) of **2**: mp 189–192 °C (long yellow rods from ethanol); ν_{max}^{Nujol} 1676, 1272, 1159,1083, 858, 788, and 743 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.66 (s, 2 H), 6.05 (m, 2 H), 5.83 (m, 2 H), 5.63 (s, 2 H), 3.08 (m, 4 H), and 2.23 (m, 4 H); *m/e* calcd 264, obsd 264.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.74; H, 6.14.

1,4,9,10-Tetrahydro-5,8-dimethoxy-4a,9a:9,10-diethenoanthracene (3a). A 50% dispersion of sodium hydride in oil (1.00 g) was washed twice with petroleum ether and dried under a stream of nitrogen. Dry dimethyl sulfoxide (3 mL) was added, followed by dropwise addition to a magnetically stirred solution of **2** (1.10 g, 8.3 mmol) in the same solvent (20 mL). The resulting orange-colored reaction mixture was stirred at room temperature for 30 min prior to the addition of methyl iodide (3.4 g, 24 mmol). Stirring was maintained for an additional 90 min, at which point 20% aqueous ammonium chloride was introduced to precipitate the product. The solid was separated by filtration, washed well with water, and dried to furnish 1.21 g (100%) of **3a** as a tan powder. An analytical sample was prepared by preparative TLC on silica gel and recrystallization from methanol: white rods, mp 165–166 °C; ν_{max}^{Nujol} 1493, 1255, 1248, 1221, 1089, 1065, 1040, 789, 753, and 712 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.58 (s, 2 H), 6.39 (dd, J = 4.5 and 3.7 Hz, 2 H), 5.80 (s, 2 H), 5.55 (br m, 2 H), 4.02 (dd, J = 4.5 and 3.7 Hz, 2 H), 3.77 (s, 6 H), and 1.88 (br, m, 4 H); *m/e* calcd 292, obsd 292.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.80. Found: C, 82.08; H, 6.94.

1,4,9,10-Tetrahydro-4a,9a:9,10-diethenoanthracene (3b). A solution of anthranilic acid (880 mg, 6.4 mmol) in acetone (10 mL) was added dropwise to a mechanically stirred refluxing solution of **1** (0.50 g, 3.2 mmol) and isoamyl nitrite (660 mg, 6.4 mmol) in dichloromethane (10 mL) under a nitrogen atmosphere. Upon completion of the addition (ca. 15 min), the dark solution was heated at reflux for 3 h, cooled, and freed of solvent in vacuo. The dark oil was taken up in hexane (50 mL) and washed with 5% sodium hydroxide solution (3 × 20 mL) and water (3 × 20 mL) prior to drying. Evaporation left 950 mg of crude product which crystallized on standing. Purification by alumina chromatography (pentane elution) gave 430 mg (58%) of **3b** as a colorless, crystalline solid: mp 73–74 °C (from hexane); ^{1}H NMR (δ, $CDCl_3$) 7.25–6.80 (m, 4 H), 6.44–6.23 (pseudo-t, 2 H), 5.70 (s, 2 H), 5.6–5.4 (m, 2 H), 3.54–3.33 (pseudo-t, 2 H), and 2.00–1.83 (m, 4 H); *m/e* calcd 232.1252, obsd 232.1256.

Anal. Calcd for $C_{18}H_{16}$: C, 93.10; H, 6.90. Found: C, 92.87; H, 7.09.

5,6,7,8-Tetrafluoro-1,4,9,10-tetrahydro-4a,9a:9,10-diethenoanthracene (3c). A pentane solution of *n*-butyllithium (18.75 mL of 1.6 M, ca. 30 mmol) was added by syringe to a magnetically stirred solution of **1** (1.56 g, 10 mmol) and pentafluorobenzene (5.04 g, 30 mmol) in 30 mL of ether cooled to −70 °C under nitrogen. Stirring at −70 °C was maintained for 2 h and the solution was allowed to warm slowly to room temperature during 4 h. After 3 h, the mixture was heated at reflux for 30 min, cooled to 0 °C, and treated dropwise with 2 M hydrochloric acid (20 mL). Ether was added to increase the total volume to 200 mL and the organic phase was separated and washed with water (3 × 50 mL) prior to drying and solvent evaporation. The crude oil (5.9 g) thus obtained was rapidly filtered through a silica gel (40 g) column (pentane elution) and the leading fraction was further purified by medium-pressure liquid chromatography (silica gel, hexane elution). There was obtained 530 mg (17%) of pure **3c** in addition to 110 mg of slightly impure adduct. Recrystallization from ethanol provided colorless prisms: mp 100–101 °C; ν_{max}^{Nujol} 1493, 1303, 1213, 1012, 919, 770, 741, and 674 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.41 (dd, J = 4.7 and 3.3 Hz, 2 H), 5.77 (s, 2 H), 5.62 (m, 2 H), 3.97 (m, 2 H), and 2.32–1.58 (m, 4 H); *m/e* calcd 304.0875, obsd 304.0881.

Anal. Calcd for $C_{18}H_{12}F_4$: C, 71.05; H, 3.98. Found: C, 70.93; H, 3.96.

1,2,3,4,5,8-Hexahydro-1,4:4a,8a-diethenonaphthalene-2,3-dicarboxylic Anhydride (4). A solution of **1** (5.0 g, 0.032 mmol) in benzene (150 mL) was heated at reflux for 24 h, cooled, and freed of solvent in vacuo. Excess maleic anhydride was removed by sublimation (heating up to 100 °C at 0.1 mm) and the residue was purified by recrystallization from chloroform–pentane. Pure **4** was obtained as colorless crystals: mp 161.0–162.5 °C (7.0 g, 86%); ν_{max}^{KBr} 1860, 1780, 1220, 1085, 930, and 795 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.25–6.05 (m, 2 H), 5.90–5.78 (m, 2 H), 5.65 (s, 2 H), 3.27 (t, J = 1.5 Hz, 2 H), 3.05–2.82 (m, 2 H), and 2.25–2.09 (br s, 4 H); *m/e* calcd 254.0947, obsd 254.0942.

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.59; H, 5.51. Found: C, 75.19; H, 5.40.

1,2,3,4,5,8-Hexahydro-1,4:4a,8a-diethenonaphthalene-2,3-dimethanol (5a). Adduct **4** (1.00 g, 3.94 mmol) was added to a stirred slurry of lithium aluminum hydride (224 mg, 5.91 mmol) in anhydrous tetrahydrofuran (60 mL) and the mixture was heated at reflux under nitrogen for 5 h. After cooling, the minimum amount of freshly prepared saturated sodium sulfate solution to destroy the excess hydride was added and the insoluble aluminate salts were filtered and washed thoroughly with tetrahydrofuran (3 × 50 mL). The combined organic layers were dried and evaporated to furnish 920 mg (96%) of diol **5a**: mp 150.5–152.0 °C; ν_{max}^{KBr} 3400, 1025, and 755 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.17–5.85 (m, 2 H), 5.85–5.68 (m, 2 H), 5.55 (s, 2 H), 4.30–3.33 (br m, 6 H), and 2.67–2.0 (m, 8 H); *m/e* calcd 244.1466, obsd 244.1463.

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.69; H, 8.20. Found: C, 78.29; H, 8.11.

1,2,3,4,5,8-Hexahydro-1,4:4a,8a-diethenonaphthalene-2,3-dimethanol Dimethanesulfonate (5b). To a cold (0 °C) solution of **5a** (4.7 g, 0.019 mol) and triethylamine (5.05 g, 0.050 mol) in dichloromethane (250 mL) was added dropwise a solution of methanesulfonyl chloride (4.81 g, 0.042 mol) in dichloromethane (20 mL). After 30 min at 0 °C, water (20 mL) was added and the separated organic phase was washed with 10% hydrochloric acid (2 × 50 mL), saturated sodium bicarbonate solution (2 × 50 mL), and brine (100 mL) prior to drying. Evaporation left 6.80 g (89%) of **5b** as an oil which crystallized on scratching. Recrystallization from chloroform–pentane gave colorless crystals: mp 108.0–108.5 °C; $\nu_{max}^{CHCl_3}$ 1460, 1430, and 1180 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.22–6.01 (m, 2 H), 5.87–5.72 (m, 2 H), 5.60 (s, 2 H), 4.3–4.0 (m, 4 H), 3.0 (s, 6 H), 2.55–2.25 (m, 4 H), and 2.20–2.05 (m, 4 H).

Anal. Calcd for $C_{18}H_{24}O_6S_2$: C, 54.00; H, 6.00. Found: C, 53.84; H, 6.00.

1,2,3,4,5,8-Hexahydro-2,3-dimethyl-1,4:4a,8a-diethenonaphthalene (6). Dimesylate **5b** (900 mg, 2.25 mmol) was added to a

slurry of lithium aluminum hydride (855 mg, 22.5 mmol) in dry tetrahydrofuran (125 mL) and the mixture was heated at reflux for 16 h. The cooled reaction mixture was treated with 5 mL of freshly prepared sodium sulfate solution. The precipitated aluminate salts were filtered off and washed thoroughly with tetrahydrofuran (3 × 50 mL). The combined filtrates were dried and evaporated. Chromatography of the residue on basic alumina afforded 355 mg (70%) of **6** on pentane elution and 75 mg (12%) of the cyclic ether when the polarity was increased to chloroform–pentane (1:1). The latter compound was not characterized. Analytically pure **6** was obtained by VPC methods (6 ft × 0.25 in. 5% SE-30, 132 °C): mp 70.5–71.0 °C; $\nu_{max}^{CCl_4}$ 3030, 2960, 2900, 2840, 1470, 1380, and 660 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.12–5.90 (m, 2 H), 5.80–4.68 (m, 2 H), 5.57 (s, 2 H), 2.30–1.85 (br m, 8 H), and 0.84 (d, J = 7 Hz, 6 H); *m/e* calcd 212.1568, obsd 212.1565.

Anal. Calcd for $C_{16}H_{20}$: C, 90.57; H, 9.43. Found: C, 90.31; H, 9.34.

1,2,3,6,7,11b-Hexahydro-8,11-dimethoxy-1,7,2,6a-ethanediylidene-6a*H*-cyclobut[*e*]anthracene (7a). A nitrogen-purged solution of **3a** (1.21 g) in acetone (500 mL) was irradiated for 2 h with a 450-W Hanovia lamp (Vycor filter). The solvent was removed in vacuo and the residue was chromatographed on neutral alumina (elution with 5% ether in petroleum ether). Early fractions afforded 75 mg (6%) of **11**, two recrystallizations of which from hexane gave fine, colorless prisms: mp 100.5–101 °C; ν_{max}^{Nujol} 1493, 1278, 1254, 1096, 1082, 784, 747, and 675 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.60 (d, J = 8 Hz, 1 H), 6.42 (d, J = 8 Hz, 1 H), 6.12 (d, J = 4 Hz, 1 H), 5.82 (d, J = 4 Hz, 1 H), 5.45 (m, 2 H), 3.80 (s, 3 H), 3.74 (s, 3 H), and 3.0–1.4 (series of m, 8 H); *m/e* calcd 292.1463, obsd 292.1469.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 82.09; H, 6.98.

Continued elution furnished 0.40 g (33%) of **7a:** mp 118–119 °C (from methanol); ν_{max}^{Nujol} 1493, 1254, 1189, 1089, 962, and 802 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.73 (s, 2 H), 5.68 (m, 2 H), 4. 6 (m, 2 H), 3.80 (s, 6 H), 2.90 (m, 4 H), and 2.43–1.62 (AB with additional coupling; J_{AB} = 16 Hz, 4 H); *m/e* calcd 292.1463, obsd 292.1469.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 81.98; H, 6.94.

1,2,3,6,7,11b-Hexahydro-1,7,2,6a-ethanediylidene-6a*H*-cyclobut[*e*]anthracene (7b). A solution of **3b** (1.5 g) and acetophenone (2.0 g) in 400 mL of benzene was purged with nitrogen for 15 min, then irradiated (450-W Hanovia, Pyrex) under continual nitrogen purging for 11 h. Workup as described above furnished 525 mg (35%) of **7b** which was purified for analysis by VPC methods (2 ft × 0.25 in. QF-1, 140 °C). The solid melted at 122.5–124 °C; ^{1}H NMR (δ, $CDCl_3$) 7.20 (s, 4 H), 6.75–6.55 (m, 2 H), 3.82–3.62 (m, 2 H), 3.08–2.73 (m, 4 H), 2.21 (m, 2 H), and 1.74 (d with additional splitting, J = 16 Hz, 2 H); *m/e* calcd 232.1252, obsd 232.1256.

Anal. Calcd for $C_{18}H_{16}$: C, 93.10; H, 6.90. Found: C, 92.68; H, 7.00.

1,2,3,6,7,11b-Hexahydro-8,9,10,11-tetrafluoro-1,7,2,6a-ethanediylidene-6a*H*-cyclobut[*e*]anthracene (7c). A solution of **3c** (2.63 g) in 400 mL of benzene containing acetophenone was purged with nitrogen, then irradiated for 7 h with a Pyrex filtered 450-W Hanovia lamp. The solvent was evaporated and the residual oil was eluted (pentane) down a short column of alumina (basic, activity I). There was obtained a white, crystalline mixture (0.69 g) of **7c** with lesser amounts of unreacted **3c.** Recrystallization from ethanol furnished pure bishomocubane as colorless prisms: mp 149.5–151 °C; ^{1}H NMR (δ, $CDCl_3$) 5.63 (m, 2 H), 4.10 (m, 2 H), 3.01 (m, 4 H), 2.25 (d with additional coupling, J = 16 Hz, 2 H), and 1.70 (d, J = 16 Hz, 2 H); *m/e* calcd 304.0875, obsd 304.0881.

Anal. Calcd for $C_{18}H_{12}F_4$: C, 71.05; H, 3.98. Found: C, 70.97; H, 4.10.

1,2,5,6,6a,6b,6c,6d-Octahydro-9,12-dimethoxy-1,6-*o*-benzenobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene (8a). A magnetically stirred solution of **7a** (97 mg) and silver nitrate (270 mg) in 6 mL of dioxane–water (4:1) was heated at 75 °C under a nitrogen atmosphere for 19 h. The cooled mixture was diluted with water (25 mL) and extracted with chloroform (1 × 20 mL, 2 × 10 mL). The combined organic extracts were washed with water, dried, and evaporated to give 250 mg of **8a** as long, white needles: mp 169–170 °C (from methanol); ν_{max}^{Nujol} 1496, 1260, 1247, 1092, 1084, 961, 799, and 718 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.66 (s, 2 H), 5.32 (m, 2 H), 3.92 (m, 2 H), 3.82 (s, 6 H), and 2.80–1.47 (series of m, 8 H); *m/e* calcd 292.1463, obsd 292.1469.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 81.82; H, 6.83.

1,2,5,6,6a,6b,6c,6d-Octahydro-1,6-*o*-benzenobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene (8b). Bishomocubane **7b** (80 mg) was heated at 60 °C in a 20% benzene solution of silver perchlorate (15 mL) for 8 h. Upon cooling, the silver ion was precipitated by washing with saturated brine (3 × 25 mL) and the organic phase was dried and evaporated. There remained 71 mg of pure **8b,** mp 153–155 °C, an analytical sample of which was obtained by preparative VPC (2 ft × 0.25 in. 10% QF-1, 140 °C): ^{1}H NMR (δ, $CDCl_3$) 7.28–7.00 (m, 4 H), 5.38–5.23 (m, 2 H), 3.60–3.25 (m, 2 H), and 2.33–1.50 (series of m, 8 H).

Anal. Calcd for $C_{18}H_{16}$: C, 93.10; H, 6.90. Found: C, 92.84; H, 6.94.

1,2,5,6,6a,6b,6c,6d-Octahydro-9,10,11,12-tetrafluoro-1,6-*o*-benzenobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene (8c). A solution of **7c** (0.50 g) and silver nitrate (2.3 g, 7 molar equiv) in 20 mL of dioxane–water (4:1) was heated at reflux for 3 days while under nitrogen and stirred magnetically. The solvent was evaporated and the residue was taken up in ether (100 mL) and water. The organic layer was separated, washed with brine and water, then evaporated. The resulting yellowish, viscous oil was chromatographed on neutral alumina (pentane elution) to give 0.15 g of **8c** as colorless crystals: mp 103–105 °C (from ethanol); ^{1}H NMR (δ, $CDCl_3$) 5.30 (m, 2 H), 3.80 (m, 2 H), and 2.58–1.53 (series of m, 8 H); *m/e* calcd 304.0875, obsd 304.0881.

1,2,5,6,6a,6b,6c,6d-Octahydro-7,8-dimethyl-1,6-ethanobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene (10). A solution of **6** (0.50 g) dissolved in 400 mL of acetone–benzene (5:95) was placed in a quartz tube and irradiated with a Hanovia 450-W lamp through a Corex filter for 3 h. The solvent was removed on a rotary evaporator and the crude photolysate was purified by preparative TLC (silica gel, hexane elution) yielding 0.15 g (30%) of almost pure **9** as an oily, colorless solid.

A magnetically stirred solution of **9** (0.20 g, slightly impure) and silver nitrate (0.25 g, 1.5 equiv) in 10 mL of dioxane–water (4:1) was heated at 60 °C for 3 h, cooled, poured into water (50 mL), and extracted with pentane (3 × 25 mL). The combined pentane extracts were washed with water (20 mL) and brine (2 × 15 mL) prior to drying and solvent evaporation. There was obtained 170 mg (34% overall) of **10:** mp 74–76 °C; $\nu_{max}^{CCl_4}$ 3030, 2960, 2900, 2830, 1470, 1380, 1070, 1025, and 665 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 6.56–6.40 (m, 2 H), 2.32–2.18 (m, 4 H), 2.10–1.13 (series of m, 8 H), and 0.98 (d, J = 7 Hz, 6 H); *m/e* calcd 212.1565, obsd 212.1568.

Anal. Calcd for $C_{16}H_{20}$: C, 90.57; H, 9.43. Found: C, 90.25; H, 9.72.

Epoxidation of 8a. *syn*-3,4-Epoxy-1,2,3,4,5,6,6a,6b,6c,6d-decahydro-9,12-dimethoxy-1,6-*o*-benzeno[1,3]cyclopropa[1,2,3-*cd*][cyclopropa[*gh*]pentalene (13a). *m*-Chloroperbenzoic acid (116 mg of 85% purity, 0.57 mmol) was added in small portions to a stirred solution of **8a** (150 mg, 0.51 mmol) in dichloromethane (5 mL). After being stirred overnight, the reaction mixture was washed with 0.5 M sodium bicarbonate solution and water, dried, and evaporated. The residue was chromatographed twice on 20 × 20 cm silica gel plates (benzene elution), giving several bands. The band at R_f 0.83 afforded 31 mg of unreacted **8a.** The major band (R_f 0.47) yielded 35 mg (22%) of the isomerically pure epoxide **13a,** while a band at R_f 0.33 gave 19 mg of a mixture of unidentified compounds. No trace of epoxide **16a** was detected. Recrystallization of **13a** from ethyl acetate gave long, colorless needles: mp 212 °C; ^{1}H NMR (δ, $CDCl_3$) 6.54 (s, 2 H), 3.95–3.7 (m, 2 H), 3.79 (s, 6 H), 2.78 (m, 2 H), 2.27 (dd with additional fine splitting, J = 15.5 and 4 Hz, 2 H), 1.75 (d, J = 15.5 Hz, 2 H), and 1.6 (m, 4 H); *m/e* calcd 308.1412, obsd 308.1418.

Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.70; H, 6.60.

3-Bromo-1,2,3,4,5,6,6a,6b,6c,6d-decahydro-9,12-dimethoxy-1,6-*o*-benzeno[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalen-4-ol (12a and 15a). A solution of *N*-bromosuccinimide (233 mg, 1.31 mmol) in 10 mL of glyme was added dropwise to an ice-cooled, magnetically stirred solution of **8a** (310 mg, 1.06 mmol) in 90% aqueous glyme (10 mL). The reaction mixture was stirred for 1 h at room temperature, then treated dropwise with 10% sodium bisulfite solution (2 mL). The mixture was evaporated to near dryness and the residue was taken up in ether and water. The aqueous phase was separated and further extracted with ether (total of 50 mL). The combined ether layers were washed with water, dried, and evaporated. The residue was chroma-

tographed on a 20 × 20 cm silica gel plate (elution with 50% ether in hexane). The R_f 0.53 band furnished 138 mg of **15a** and the R_f 0.45 band afforded 86 mg of **12a** (total yield 54%, ratio 62:38 isolated). These products were not characterized, but cyclized directly.

Cyclization of 12a. Sodium hydride (32 mg of 50% in oil) was washed well with hexane and dried under a nitrogen atmosphere. A solution of **12a** (86 mg) in 5 mL of tetrahydrofuran was added and the mixture was heated at reflux under nitrogen for 9 h, cooled in an ice bath, and treated with 5 drops of 10% ammonium chloride solution. The solvent was evaporated and the residue was taken up in ether (50 mL), washed with water (2 × 20 mL), dried, and evaporated to yield 50 mg (73%) of **13a**, the ^{1}H NMR spectrum of which was indistinguishable from that of the direct epoxidation.

Cyclization of 15a. By the same procedure, 138 mg (0.35 mmol) of **15a** was treated with 58 mg of 50% sodium hydride in oil (1.2 mmol) in tetrahydrofuran. Workup as before afforded 103 mg (96%) of **16a** as white needles: mp 210 °C dec (from ethyl acetate); ^{1}H NMR (δ, $CDCl_3$) 6.60 (s, 2 H), 3.85–3.6 (m, 2 H), 3.80 (s, 6 H), 2.75 (narrow m, 2 H), 2.48 (d, J = 15 Hz, 2 H), 2.4–2 (m, 2 H), 1.74 (d, J = 15 Hz, 2 H), and 1.65–1.3 (m, 2 H); *m/e* calcd 308.1412, obsd 308.1418.

Photooxygenation of 8a. 1,2,3,6,6a,6b,6c,6d-Octahydro-9,12-dimethoxy-1,6-*o*-benzenobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalen-3-ol (14a and 17a). A solution of **8a** (105 mg) and rose bengal (500 mg) in 130 mL of 50:50 methanol–dichloromethane was irradiated with a Sylvania DYV lamp while being continuously purged with oxygen for 26 h. After 10 h, a further 250 mg of rose bengal dissolved in methanol (20 mL) was added. The reaction mixture, which had been cooled throughout the photooxygenation with an external ice bath, was stirred at room temperature with sodium borohydride (0.5 g) for 2 h. The volatiles were removed in vacuo, dichloromethane (75 mL) was added, and the solution was washed well with water prior to drying and evaporation. The crystalline residue was subjected to preparative layer chromatography (silica gel, ether elution). There were recovered 25 mg of starting material (**8a**), 13 mg of syn alcohol **14a**, 49 mg of anti alcohol **17a**, and 18 mg of an unidentified product. Pure **17a** was obtained as fine, white crystals from methanol: mp 176–178 °C; ^{1}H NMR (δ, $CDCl_3$) 6.58 (s, 2 H), 5.75 (dd, J = 10 and 3 Hz, 1 H), 5.22 (d with additional fine coupling, J = 10 Hz, 1 H), 3.97 (m, 2 H), 3.72 (s, 6 H), 3.8–3.6 (m, 1 H), 2.22 (m, 3 H), and 1.8–0.8 (br m, 4 H); *m/e* calcd 308.1412, obsd 308.1418.

Ring Opening of Epoxide 13a. *n*-Butyllithium (2.0 mL of 1.25 M in hexane, 2.5 mmol) was added via syringe to an ice-cooled, magnetically stirred solution of diethylamine (183 mg, 2.5 mmol) in 6 mL of anhydrous ether. After 15 min, a solution of **13a** (95 mg, 0.3 mmol) in 10 mL of the same solvent was added dropwise. The mixture was allowed to come to room temperature where it was stirred for 60 h before being poured into ice and water. The ether phase was washed well with 10% aqueous ammonium chloride solution and water before drying. Evaporation left an oil which was purified by preparative layer chromatography on silica gel (ether elution). There was isolated 45 mg (44%) of **13a:** ^{1}H NMR (δ, $CDCl_3$) 6.63 (s, 2 H), 6.12 (d, J = 11 Hz, 1 H), 5.39 (dd, J = 11 and 6 Hz, 1 H), 4.07 (t, J = 7 Hz, 2 H), 3.9 (m, 1 H), 3.79 (s, 6 H), and 2.4–1.05 (series of m, 7 H); *m/e* calcd 308.1412, obsd 308.1418.

***syn*-3,4-Epoxy-1,2,3,4,5,6,6a,6b,6c,6d-decahydro-1,6-*o*-benzeno[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene (13b).** From 122 mg of *m*-chloroperbenzoic acid (85% purity, 0.60 mmol) and 116 mg (0.50 mmol) of **8b** in dichloromethane (20 mL) which had been allowed to stir overnight, there was isolated 71 mg (57%) of pure **13b** after recrystallization from methanol. A further recrystallization gave colorless prisms: mp 219–222 °C; ν_{max}^{Nujol} 1000, 806, 794, 747, and 729 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.12 (m, 4 H), 3.32 (t, J = 3 Hz, 2 H), 2.77 (narrow m, 2 H), 2.26 (d with additional fine coupling, J = 15 Hz, 2 H), 1.73 (d, J = 15 Hz, 2 H), and 1.65 (m, 4 H).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.55; H, 6.62.

3-Bromo-1,2,3,4,5,6,6a,6b,6c,6d-decahydro-1,6-*o*-benzeno-[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalen-4-ol (12b and 15b). Treatment of 380 mg (1.64 mmol) of **8b** with 320 mg (1.8 mmol) of *N*-bromosuccinimide in 90% aqueous glyme as described above gave 0.57 g of crude, crystalline bromohydrin mixture. Preparative layer chromatography (silica gel, 50% ether in hexane as eluent) gave 213 mg (40%) of **15b** and 108 mg (20%) of **12b.** These compounds were individually converted to the corresponding epoxides: *m/e* calcd 328.0463, obsd for **15b** 328.0470, obsd for **12b** 328.0470.

***anti*-3,4-Epoxy-1,2,3,4,5,6,6a,6b,6c,6d-decahydro-1,6-*o*-benzeno[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene (16b).** A mixture of **15b** (211 mg, 0.64 mmol), sodium hydride (100 mg of 50% in oil, 2.1 mmol), and tetrahydrofuran (6 mL) was heated at reflux for 9 h and worked up as above to give 151 mg (96%) of **16b** as long, white needles: mp 189 °C (from benzene–hexane); ν_{max}^{Nujol} 1008, 910, 853, 807, 788, and 761 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.12 (m, 4 H), 3.25 (m, 2 H), 2.75 (m, 2 H), 2.48 (d with additional fine coupling, J = 15 Hz, 2 H), 2.28 (m, 1 H), 2. 233 (m, 1 H), 1.73 (d with additional fine coupling, J = 15 Hz, 2 H), and 1.58 (m, 2 H); *m/e* calcd 248.1201, obsd 248.1206.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.98; H, 6.52.

***syn*-3,3-Epoxy-1,2,3,4,5,6,6a,6b,6c,6d-decahydro-1,6-*o*-benzeno[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene (13b).** Submission of **12b** to the standard procedure gave **13b** as colorless prisms, mp 221–222 °C (from benzene–hexane). The spectra of this substance were identical with those of the epoxide obtained from the direct epoxidation reaction.

***syn*-1,2,3,6,6a,6b,6c,6d-Octahydro-1,6-*o*-benzenobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalen-3-ol (14b).** *n*-Butyllithium (1.0 mL of 1.5 M solution in hexane, 1.5 mmol) was added via syringe to an ice-cooled, magnetically stirred solution of diethylamine (109 mg, 1.5 mmol) in 5 mL of anhydrous ether under a nitrogen atmosphere. After 15 min, a solution of **13b** (50 mg, 0.20 mmol) in the same solvent (10 mL) containing a small amount of tetrahydrofuran to aid dissolution was added dropwise. The mixture was stirred at room temperature for 72 h and subsequently quenched by pouring into ice water. Additional ether was added; the organic layer was separated, washed with 10% aqueous ammonium chloride and water, dried, and evaporated. There was obtained 49 mg (98%) of **14b:** ^{1}H NMR (δ, $CDCl_3$) 7.15 (m, 4 H), 6.08 (d, J = 9.5 Hz, 1 H), 5.38 (dd, J = 9.5 and 5 Hz, 1 H), 3.92 (br t, 1 H), 3.55 (m, 2 H), and 2.43–0.87 (complex series of m, 7 H); *m/e* calcd 248.1201, obsd 248.1206.

***anti*-1,2,3,6,6a,6b,6c,6d-Octahydro-1,6-*o*-benzenobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalen-3-ol (17b).** Sodium borohydride (19 mg, 0.5 mmol) was added to a solution of diphenyl diselenide (65 mg, 0.21 mmol) in 3 mL of ethanol at room temperature. When the solution had turned colorless, 90 mg (0.363 mmol) of **16b** in tetrahydrofuran was introduced and the mixture was heated at reflux for 4 h. With ice cooling, 1.5 mL of 30% aqueous hydrogen peroxide was added and oxidation was allowed to proceed overnight at room temperature. A solid byproduct was filtered off and the filtrate partially evaporated before being partitioned between ether (50 mL) and water. The ether phase was washed with 10% sodium carbonate solution and water, dried, and evaporated to leave an oily residue. Preparative layer chromatography (silica gel, ether elution) gave pure **17b** (38 mg, 42%) as the only isolable product. Recrystallization from benzene–hexane afforded tiny, colorless rosettes: mp 134–135 °C; ν_{max}^{Nujol} 3340, 3230, 1278, 1110, 1035, and 759 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.12 (m, 4 H), 5.78 (dd, J = 10 and 3.5 Hz, 1 H), 5.15 (d, J = 10 Hz, 1 H), 3.53 (m, 2 H), 2.27 (m, 3 H), and 1.77–0.73 (series of m, 4 H); *m/e* calcd 248.1201, obsd 248.1206.

Photooxygenation of 8b. An 87-mg sample of **8b** dissolved in 100 mL of 90:10 dichloromethane–methanol containing 50 mg of rose bengal was irradiated as above for 6 h. The solution was then stirred with sodium borohydride (0.5 g) for 2 h and processed as previously described to give after TLC on silica gel (ether–hexane, 1:1, elution) 60 mg of recovered **8b** and 20 mg (80%) of isomerically pure **17b** whose spectra were indistinguishable from those of the earlier sample.

Epoxidation of 10. From 106 mg (0.5 mmol) of **10,** there was isolated 105 mg of **18** and **20** (ratio 65:35). Isomer separation was achieved by preparative VPC (6 ft × 0.25 in. 12% OV-11, 205 °C) with partial decomposition of the epoxides.

For **18:** ^{1}H NMR (δ, $CDCl_3$) 2.98 (narrow m, 2 H), 2. 1 (d, J = 18 Hz, 2 H), 1.85 (d, J = 18 Hz, 2 H), 1.70 (m, 2 H), 1.65–1.40 (m, 4 H), 1.42–1.25 (m, 2 H), and 1.00 (d, J = 7 Hz, 6 H); *m/e* calcd 228.1514, obsd 228.1517.

For **20:** ^{1}H NMR (δ, $CDCl_3$) 2.94 (narrow m, 2 H), 2.08 (narrow m, 4 H), 2.1–1.8 (m, 2 H), 1.8–1.2 (series of m, 6 H), and 0.96 (d, J = 8 Hz, 6 H); *m/e* calcd 228.1514, obsd 228.1517.

Ring Opening of 18. A 125-mg sample (0.55 mmol) of crude **18** was treated with 4.0 mL of 1.5 M *n*-butyllithium in hexane (6.0 mmol) and 438 mg (6.0 mmol) of diethylamine according to the general procedure. There was obtained 52 mg (42%) of **18:** ^{1}H NMR (δ,

$CDCl_3$) 6.02 (d, J = 9 Hz, 1 H), 5.53 (dd, J = 9 and 4 Hz, 1 H), 4.1 (br m, 1 H), 2.4–0.6 (series of m, 11 H), and 0.98 (d, J = 7 Hz, 6 H); *m/e* calcd 228.1515, obsd 228.1521.

Photooxygenation of 10. A 150-mg sample of somewhat impure **10** was subjected to sensitized photooxygenation (50 mL of methanol, 200 mL of dichloromethane) as before (2 h). Sodium borohydride (0.5 g) was added and the solution stirred for 2 h. Workup led to the isolation of a crystalline residue (150 mg, 93%), the ^{1}H NMR spectrum of which showed it to be **21.** By preparative layer chromatography and recrystallization from pentane, pure **21,** mp 107 °C, was obtained: ^{1}H NMR (δ, $CDCl_3$) 5.85 (dd, J = 10 and 2 Hz, 1 H), 5.32 (dd, J = 10 and 0.5 Hz, 1 H), 4.01 (m, 1 H), 2.5–1.2 (series of m, 11 H), and 1.02 (d, J = 6 Hz, 6 H); *m/e* calcd 228.1514, obsd 228.1521.

***anti*-1,2,3,6,6a,6b,6c,6d-Octahydro-10-methyl-3-(4-methyl-3,5-dioxo-1,2,4-triazolidin-1-yl)-9*H*-1,6[1′,2′]-*endo*-*s*-triazolobenzo-[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalene-9,11(10*H*)-dione (23).** A solution of the diazasnoutane (38 mg, 0.142 mmol) and *N*-methyltriazolinedione (16 mg, 0.142 mmol) in 3 mL of dichloromethane was heated at reflux for 48 h. The solvent was evaporated to leave an adduct, the ^{1}H NMR spectrum of which showed it to be **23:** ^{1}H NMR (δ, $CDCl_3$) 7.25 (s, 1 H), 6.15 (dd, J = 10 and 3 Hz, 1 H), 5.37 (d, J = 10 Hz, 1 H), 4.96 (m, 2 H), 4.25 (m, 1 H), 3.05 (s, 6 H), and 2.5–0.75 (m, 6 H).

4-Methyl-1-(1,2,3,6,6a,6b,6c,6d-octahydro-9,12-dimethoxy-1,6-*o*-benzenobenzo[1,3]cyclopropa[1,2,3-*cd*]cyclopropa[*gh*]pentalen-3-yl)-1,2,4-triazolidine-3,5-dione (24). A solution of **8a** (73 mg, 0.25 mmol) and *N*-methyltriazolinedione (28 mg, 0.25 mmol) in 10 mL of dichloromethane was heated at reflux overnight. The resulting product was recrystallized from ethyl acetate to afford colorless crystals: mp 190 °C; ν_{max}^{Nujol} 3170, 1680, 1477, 1237, 1060, and 709 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.28 (m, 1 H), 6.60 (s, 2 H), 6.05 (dd, J = 10 and 3 Hz, 1 H), 5.00 (d with fine coupling, J = 10 Hz, 1 H), 4.27 (m, 1 H), 4.07 (m, 2 H), 3.78 (s, 3 H), 3.75 (s, 3 H), 2.93 (s, 3 H), and 2.57–0.96 (series of complex m, 6 H); *m/e* calcd 405.1688, obsd 405.1695.

Pulse Radiolysis Studies. These experiments were performed at the center for Fast Kinetics Research, Patterson Building, University of Texas, Austin, Texas 78712, by Mr. Larry Hertel under the guidance of Dr. M. A. J. Rodgers of the CRKF staff.

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