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Reappraisal of the Stereochemistry of Electrophilic Additions to 3-Norcarenes. X-ray and ^{1}H NMR Analysis of Norcarene Epoxide Conformation. The Role of Magnetic Anisotropic Contributions of Epoxide Rings

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Abstract: The stereochemical outcome of the addition of singlet oxygen, Br^+, and peracid to four structurally varied 3-norcarenes has been investigated to obtain direct insight into prevailing product-determining steric effects in these systems. The various end products have been interconverted chemically to elucidate relative configuration. The stereochemical assignments have been established by reference to two 7,7-dibromo epoxides, the structures of which were elucidated by three-dimensional X-ray methods. Approach of an electrophile anti to the cyclopropane ring was seen to be preferred in each of the cases examined, although the product ratios did vary with the particular substitution plan. The preferred conformations of the 3-norcarene epoxides have been assessed by ^{1}H NMR spectroscopy through analysis of vicinal coupling constants. Finally, the question of epoxide ring anisotropy effects is addressed.

Recently, several papers from this laboratory described impressively stereocontrolled photooxygenation reactions of 3-norcarenes and norcaradienes which were interpreted in terms of effective quenching by proximate hydrazide functionality.[2-4] The electronic relaxation of $^1\Delta_g$ singlet oxygen was thought to arise when the ionization potentials of $^1O_2$, the hydrazide moiety, and the olefinic center, as well as the frontier orbital relationship between them, were properly ordered. Structural assignments to the individual products were made on the basis of their respective ^{1}H NMR spectra, supportive $Eu(fod)_3$ pseudocontact shifting in selected cases, and chemical interconversions where suitable.

In view of the important implications of these conclusions, we felt compelled to further substantiate these observations and test the scope of the phenomenon by more extensive experimentation. Unfortunately, we have not found it possible to duplicate certain fundamental experimental data reported earlier,[5] and have, in fact, shown that various hydrazides are not truly effective in their ability to quench the reactivity of singlet oxygen.[6] Subsequently, we concluded that some of the original stereochemical assignments were likely in error, despite the large number of experiments addressed previously to this question. Additional work of a totally unequivocal nature was obviously required and recourse has now been made to complementary three-dimensional X-ray crystallographic analysis.

The present paper addresses the general question of electrophilic additions (including $^1O_2$) to variously substituted 3-norcarene systems and analyzes those complications frequently associated with interpretation of the ^{1}H NMR spectra of epoxides. The ensuing paper[7] describes new results which show stereoelectronic control of singlet oxygen reactivity by hydrazides to be a myth.

Electrophilic Additions

3-Norcarene. Early ^{1}H NMR studies of the alicyclic methylene proton region of **1**, readily available from the Simmons–Smith cyclopropanation of 1,4-dihydrobenzene,[8]

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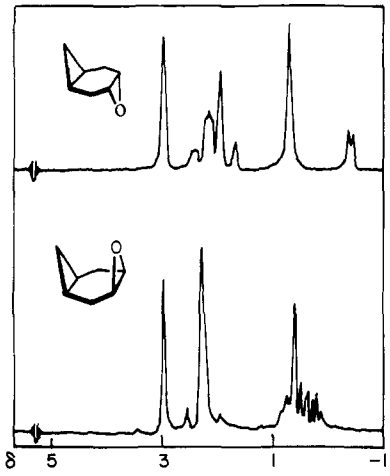
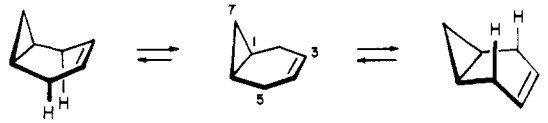


Figure 1. ^{1}H NMR spectra of 3-norcarene oxides **5** (top) and **5** (bottom) (60 MHz, $CDCl_3$, CH_2Cl_2 as internal standard).

were interpreted as consistent with either a cis boat (**1a**) or planar form (**1b**) for the parent system.[9] Notwithstanding, the trans boat form **1c** had been widely used to describe the



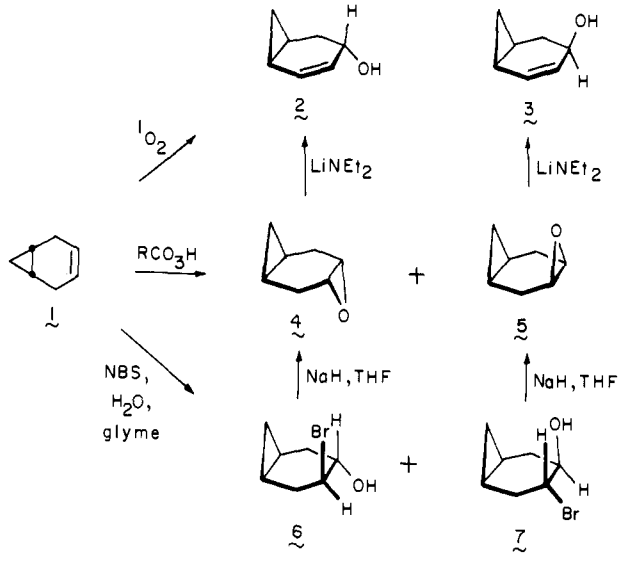
1a **1b** **1c**

three-dimensional character of 3-norcarene derivatives.[10] An inspection of molecular models reveals that certain (but not all) eclipsing interactions which prevail in **1a** and **1c** are avoided when the central ring is planar as in **1b**. In this context, Abraham's recent spectral examination of 3-carene (the 3,7,7-trimethyl derivative) is informative.[11] The data show H_{2anti} and H_{2syn} to have vicinal coupling constants of ca. 0 and 7.5 Hz, respectively, and a large J_{gem} value (20.0 Hz); these findings cannot be accounted for in terms of a rapidly interconverting mixture of 3,7,7-Me_3-**1a** and 3,7,7-Me_3-**1c**, but are compatible with the planar conformation 3,7,7-Me_3-**1b**. These deductions contradict those arrived at earlier by Acharya, who concluded that 3,7,7-Me_3-**1a** was favored.[12]

The actual conformational situation is almost certainly one in which the energy separating the three forms is low (barring excessive steric constraints), such that rapid mutual interconversion operates during any intended chemical transformation. Consequently, predictions concerning the stereoselectivity of attack at the double bond must necessarily be clouded with uncertainty in most instances. The large degree of confusion which has surrounded the simple epoxidation of (+)-3-carene speaks clearly to this point.[10a,b,13-15]

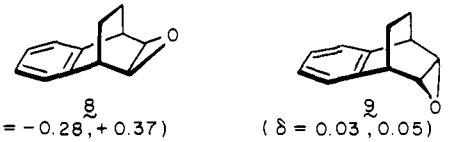
When a continuously oxygenated dilute solution of **1** and rose bengal in dichloromethane–methanol (9:1) was irradiated with a Sylvania DYV light source and the resulting allylic hydroperoxide was directly reduced with sodium borohydride, an isomerically pure alcohol was isolated whose spectral properties showed it to be either **2** or **3**. Since the stereochemical outcome of this highly stereoselective process could not be ascertained unequivocally from the ^{1}H NMR data, two additional sets of convergent experiments were initiated. In the first, **1** was oxidized with *m*-chloroperbenzoic acid in dichloromethane buffered with solid sodium bicarbonate at 25 °C and two epoxides, easily separated by vapor phase chromatography, were determined to be present in a 62:38 ratio. As can be seen in Figure 1, the cyclopropyl methylene protons of the major component (top) appear as two widely separated multiplets centered at δ −0.4 and +0.7 (the latter signal overlaps with those due to H_1 and H_6), while the same pair in the minor isomer (bottom) resonates closer together at δ 0.26 and 0.62 (with major H_1, H_6 overlap).

On the strength of earlier work by Tori and co-workers[16] who have shown that the bridge protons in *exo*-norbornene



2 **3** **1** **4** **5** **6** **7**

oxide, *exo*-norbornadiene oxide, *exo*-benzonorbornadiene oxide, and **8** are widely spaced while those in endo isomer **9** nearly overlap, we originally considered the major component to be the syn isomer **5**. To gain further evidence for these as-



8 (δ = −0.28, +0.37) **9** (δ = 0.03, 0.05)

signments, recourse was made to Eu(fod)$_3$ pseudocontact shifting. With the epoxide oxygen as the only Lewis basic functionality, the simplified version of the McConnell-Robertson equation[17,18]

$$\Delta\delta = \frac{K(3\cos^2\theta - 1)}{R^3}$$

was deemed applicable, given the anticipated presence of an axially symmetric dipolar magnetic field. For our models, the europium atom was placed 2 Å from the oxygen in the plane of the oxirane ring and bisecting the ∠COC.[19] Tables I and II summarize the shift sequences calculated for three conformations each of **4** and **5**. The relevant distances and angles were obtained with Dreiding models. Strikingly, we see that the extended boat conformations of **4** and **5** as well as the planar forms of both isomers lead to almost identical predictions, the exception being the relative ordering of H_1. In contrast, the two cis boat conformations differ appreciably, the predicted position of H_{7endo} being diametrically opposite in the two series.

At the experimental level, the intrinsic LIS parameters of the major epoxide ($H_3 > H_{2anti} > H_{2syn} > H_1 > H_{7endo} > H_{7exo}$) were seen to differ significantly from those of the minor isomer ($H_3 > H_{7endo} > H_{2syn} > H_{2anti} > H_1 > H_{7exo}$).[20] Although alterations in substrate conformation are known to occur upon coordination to lanthanide ions[19] and such effects must be given their due consideration, these data are best accommodated if the prior working assumption of epoxide stereochemistry is reversed.

As a means of resolving this dilemma, 7,7-dibromonorcarene (**10**) was subjected to epoxidation. The lone epoxide which was produced was established to be the anti isomer **11** by X-ray crystallographic analysis (see below). Tri-*n*-butyltin hydride

Table I. Calculated Paramagnetic Shifts for **4**

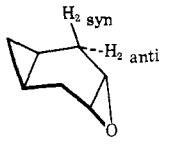
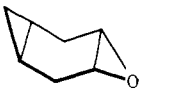
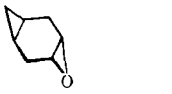
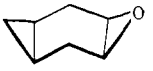
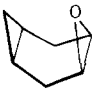
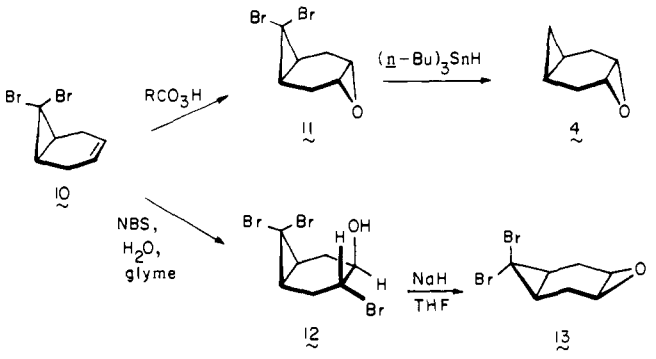
structure	proton	R, Å	R^3	θ, deg	$3\cos^2\theta - 1$	$(3\cos^2\theta - 1)/(R^3) \times 10^2$
	H_3	3.9	59.3	14	1.82	3.07
	H_{2syn}	5.2	141	18	1.71	1.22
	H_{2anti}	4.6	97.3	21	1.62	1.65
	H_1	3.7	50.6	62	−0.34	−0.67
	H_{7endo}	5.9	205	32	1.16	0.57
	H_{7exo}	5.7	185	54	0.04	0.02
predicted sequencing: H_3, H_{2anti}, H_{2syn}, H_{7endo}, H_{7exo}, H_1						
	H_3	3.9	59.3	14	1.82	3.07
	H_{2syn}	4.7	104	18	1.71	1.65
	H_{2anti}	3.7	50.6	35	1.01	2.00
	H_1	6.1	227	30	1.25	0.55
	H_{7endo}	5.6	176	0	−1.00	−0.57
	H_{7exo}	6.9	329	16	1.77	0.54
predicted sequencing: H_3, H_{2anti}, H_{2syn}, H_1, H_{7exo}, H_{7endo}						
	H_3	3.9	59.3	13	1.85	3.11
	H_{2syn}	5.2	141	9	1.93	1.37
	H_{2anti}	3.9	59.3	24	1.50	2.53
	H_1	6.3	250	43	0.60	0.24
	H_{7endo}	6.2	238	13	1.50	0.78
	H_{7exo}	7.1	358	29	1.29	0.36
predicted sequencing: H_3, H_{2anti}, H_{2syn}, H_{7endo}, H_{7exo}, H_1						

Table II. Calculated Paramagnetic Shifts for **5**

structure	proton	R, Å	R^3	θ, deg	$3\cos^2\theta - 1$	$(3\cos^2\theta - 1)/(R^3) \times 10^2$
	H_3	3.9	59.3	15	1.80	3.04
	H_{2syn}	3.5	42.9	33	1.11	2.59
	H_{2anti}	4.6	97.3	16	1.77	1.82
	H_1	6.0	216	22	1.58	0.73
	H_{7endo}	4.8	111	47	0.40	0.36
	H_{7exo}	6.5	275	40	0.76	0.28
predicted sequencing: H_3, H_{2syn}, H_{2anti}, H_1, H_{7endo}, H_{7exo}						
	H_3	3.9	59.3	15	1.80	3.04
	H_{2syn}	4.4	85.2	18	1.71	2.01
	H_{2anti}	5.2	140	17	1.74	1.24
	H_1	4.8	111	48	0.34	0.31
	H_{7endo}	1.9	6.86	31	1.20	17.5
	H_{7exo}	3.0	27	72	−0.71	−2.64
predicted sequencing: H_{7endo}, H_3, H_{2syn}, H_{2anti}, H_1, H_{7exo}						
	H_3	3.9	59.3	15	1.80	3.04
	H_{2syn}	3.9	59.3	31	1.20	2.02
	H_{2anti}	5.1	132	16	1.77	1.34
	H_1	5.9	205	38	0.86	0.42
	H_{7endo}	3.4	39.3	56	0.062	0.16
	H_{7exo}	5.2	141	58	−0.16	−0.11
predicted sequencing: H_3, H_{2syn}, H_{2anti}, H_1, H_{7endo}, H_{7exo}						

reduction of **11**, which could be cleanly accomplished under a variety of conditions, resulted in high-yield conversion to the major norcarene epoxide which, as a result, must necessarily be formulated as the anti isomer. *syn*-7,7-Dibromonorcarene oxide (**13**) was produced exclusively from **10** by the action of



N-bromosuccinimide in aqueous glyme, followed by cyclization of bromohydrin **12** with sodium hydride in refluxing tetrahydrofuran. Comparable treatment of **1** afforded **4** and **5** in a 13:87 ratio. It can therefore be concluded of the previous spectroscopic tests that lanthanide-induced shift techniques were reliable while those chemical shift criteria customarily applied to the ^{1}H NMR analysis of epoxides were not. The *apparent* lack of conventionality in the latter area will be discussed subsequently.

Ring opening of **4** with lithium diethylamide proceeded smoothly to give **2**, the product of 3-norcarene photooxygenation. Epoxide **5** was similarly converted to **3**, providing the opportunity to demonstrate that the syn allylic alcohol was not a contaminant in the photooxygenation product (the isomers are distinctive on VPC).

The pair of bromine atoms in **10** appears to generate sufficient steric hindrance on the syn face of the molecule to direct electrophilic attack exclusively anti. In the absence of the halogens, anti attack remains kinetically favored but at a re-

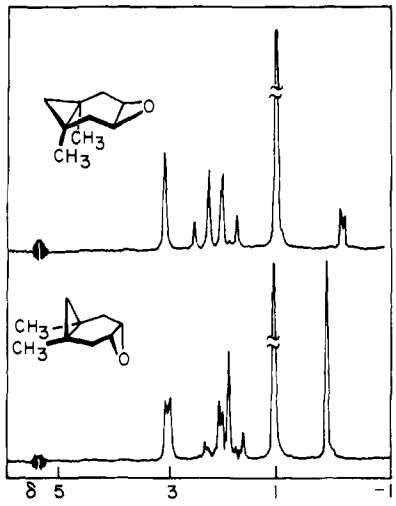
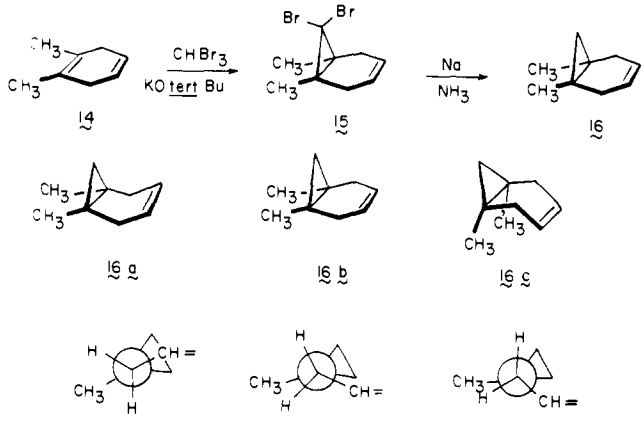


Figure 2. ^{1}H NMR spectra of 1,6-dimethylnorcarene oxides **19a** (bottom) and **20a** (top) (60 MHz, $CDCl_3$, CH_2Cl_2 as internal standard).

duced level. Epoxidation of **1** is the least stereoselective reaction (62% anti), followed by bromonium ion formation (87% anti). Allylic hydroperoxidation with $^1O_2$ is fully stereoselective.

1,6-Dimethyl-3-norcarene. Our second line of inquiry dealt with **16,** prepared conveniently by regioselective dibromocarbene addition to the Birch reduction product (**14**) of *o*-

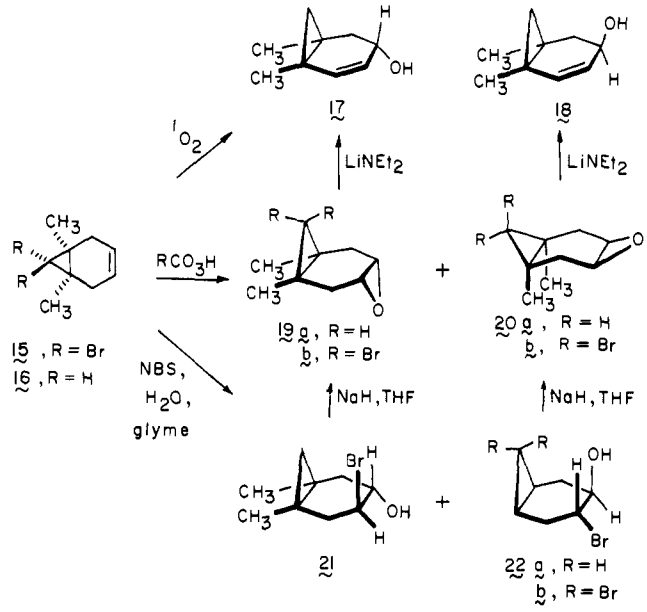


xylene and dehalogenation of **15** with sodium in liquid ammonia. The methyl groups in **16** introduce nonbonded steric interactions (see Newman projections) which could lower the energy of cis boat conformer **16a** relative to those of **16b** and **16c.** Were this factor uniquely influential, 1,6-dimethyl substitution might lessen the energy requirements for anti attack. However, the X-ray crystallographic findings described later point to the likelihood that the transition-state structures for the reactions being utilized might well be planar in the central ring, i.e., most closely related to **1b** and **16b.** If so, then the pendant methyl groups could have an untoward effect on the energetics of the anti pathway.

The singlet oxygenation of **16** produced the allylic alcohol **17** with 100% stereoselectivity. Proof of the indicated stereochemistry was achieved as before by epoxidation of the hydrocarbon, separation of the isomers, and base-promoted opening. Under our standardized conditions, the relative amounts of **19a** and **20a** proved to be 74:26. Individual treatment of the pure isomers gave **17** and **18,** respectively. Application of the NBS–aqueous glyme epoxide inversion scheme to **16** gave **19a** and **20a** in the ratio 17:83. Therefore, the presence of methyl groups at positions 1 and 6 does little to alter the stereochemical course of electrophilic additions to the π bond (relative to **1**).

As Figure 2 illustrates, anti epoxide **19a** shows a sharp singlet absorption of area 2 at δ 0.07 for its cyclopropyl methylene protons, whereas syn epoxide **20a** exhibits the same two protons at widely different chemical shifts (δ −0.20 and +0.97). Because these patterns are the *reverse* of those previously seen with the 3-norcarene oxides (Figure 1), concern was raised for the accuracy of our assignments and the behavior of dibromide **15** was investigated.

The epoxidation of **15** gave rise only to **19b,** the stereochemistry of which was again confirmed by X-ray analysis (see



below). The isomeric epoxide **20b** was obtained cleanly via bromohydrin **22b.** Tri-*n*-butyltin hydride reduction of **19b** furnished **19a.**

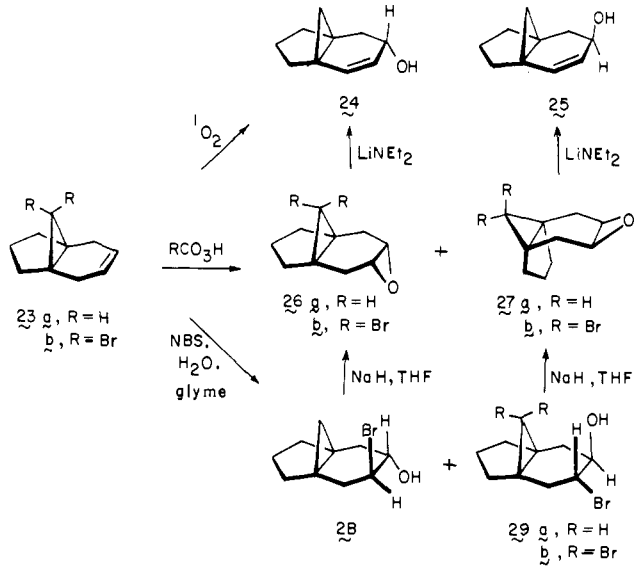
Again, we see that the ^{1}H NMR spectra of the epoxides demand further interpretation. No such difficulties appear to complicate the spectra of the epimeric 2-norcarene alcohols. This may be because a singlet pseudoboat conformation is adopted by these molecules in order to maximize overlap of the 1,7-σ bond with the p orbital at C_2.[21] Thus, the olefinic hydrogens of anti alcohols **2** and **17** are characterized by distinctive chemical shifts and multiplicities. For example, both components of the olefinic region are basically doublets; however, the one at lower field is more extensively spin coupled with neighboring protons than that found at ca. δ 5.3. The $\Delta\delta$ of the absorptions is 0.3–0.4 ppm. In contrast, the syn alcohols show greater multiplicity in their *more upfield* olefinic proton signal.[7]

[4.3.1]Propell-3-ene. To determine if annulation effects would be influential in modifying stereoselectivity, [4.3.1]-propell-3-ene (**23a**) was utilized as the basis of comparison. Whereas the direct epoxidation of **23a** produced **26a** and **27a** in a 69:31 ratio and the indirect pathway via **28** and **29a** generated a 7:93 mixture of the same tetracyclic epoxides, dibromide **23b** was converted exclusively to **26b** and to **27b** (via **29b**). With the assumption that the bromine atoms exert their usual overwhelming steric effect, the structural assignments to the dibromo epoxides were considered established. These were converted to **26a** and **27a** by tin hydride reduction and the latter were transformed into the isomerically pure allylic alcohols **24** and **25.** To complete the sequence, **23a** was photooxygenated; this reaction gave only **24.**

The stereochemical consequences of epoxidation, bromohydrin formation, and allylic hydroperoxidation reveal **1, 16,** and **23a** to be consistently more disposed to attack from the direction anti to the cyclopropane ring under conditions of kinetic control. There is seen throughout the series a gradual progression in the level of anti stereoselectivity which is lowest

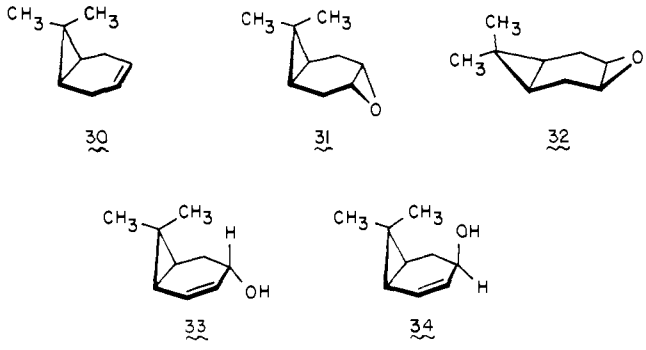
when epoxidation is involved and a maximum in the singlet oxygen examples. Such effects do not speak directly to the mechanism of the $^1O_2$ reactions, although they likely do have a direct bearing on the fact that singlet oxygen is the only reagent of the three which must abstract an allylic hydrogen to deliver product. The base of the cyclopropane ring must be approached more closely and the well-known sensitivity of singlet oxygen to prevailing steric factors is made apparent.

The ^1H NMR spectra of **26a** and **27a** (Figure 3) continue to exhibit highly pertinent features. Thus, the environment of H_{7exo} in the anti epoxide is such that increased shielding occurs



relative to the syn isomer. Contrariwise, H_{7endo} in **27a** is significantly downfield shifted. The spectra of allylic alcohols **24** and **25** follow the trend discussed earlier (see Experimental Section).

7,7-Dimethyl-3-norcarene. In an effort to link the above findings more closely to earlier work with (+)-3-carene, the 7,7-dimethyl derivative **30** was prepared through reaction of **10** with lithium dimethylcuprate.[22] When subjected to epoxidation, **30** was converted to anti epoxide **31,** the 100% ste-



reoselectivity paralleling that observed earlier with dibromide **10.** A sample of **32** was prepared via the bromohydrin. These configurational assignments are based upon ^1H NMR spectra (Figure 4) which conform to those obtained for the 3-carene oxides.[10b] In the case of **31,** two widely spaced methyl singlets are immediately apparent; the NMR results for **32** show two nearly overlapping methyl signals.

Not unexpectedly, singlet oxygenation of **30** produced only **33.** The pair of allylic alcohols became independently available by treatment of **31** and **32** with phenylselenide anion and oxidative elimination of the β-seleno alcohols with hydrogen peroxide. 2-Norcarenes which carry a syn methyl group at C_7 are believed to relieve intramolecular crowding by adopting a pseudochair conformation rather than the customarily favored pseudoboat shape.[21a] This leads to marked alterations in the chemical shifts of the olefinic protons such that merging of the two signals into a multiplet of rather narrow width at an intermediate field position obtains. The spectra of **33** and **34** do not deviate from this norm.

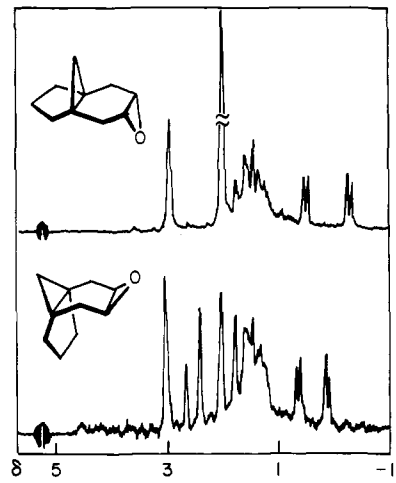


Figure 3. ^1H NMR spectra of [4.3.1]propell-3-ene oxides **26a** (top) and **27a** (bottom) (60 MHz, $CDCl_3$, CH_2Cl_2 as internal standard).

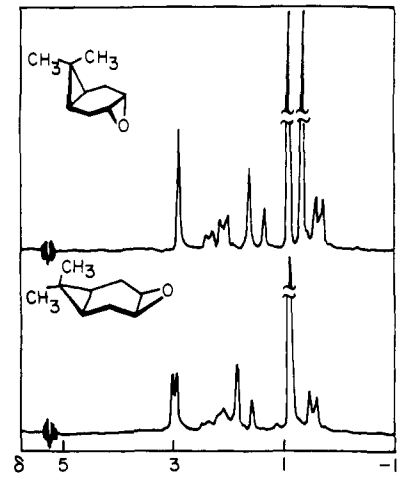


Figure 4. ^1H NMR spectra of 7,7-dimethylnorcarene oxides **31** (top) and **32** (bottom) (60 MHz, $CDCl_3$, CH_2Cl_2 as internal standard).

Three-Dimensional X-ray Crystal Structure Studies. The data crystal of **19b,** a colorless, rectangular prism of approximate dimensions 0.32 × 0.56 × 0.60 mm^3, was mounted on an automated four-circle diffractometer with an axis (later assigned as *c*) approximately collinear with the ϕ axis. Triclinic cell constants (a = 7.562 (3) Å, b = 10.438 (5) Å, c = 6.738 (2) Å, α = 86.15 (3)°, β = 76.76 (3)°, and γ = 75.10 (4)° at 21 °C) were determined by least-squares fit of the optimized setting angles of ten reflections in the range 13° < 2θ < 20° (Mo K$\bar{\alpha}$ = 0.710 69 Å). The crystal density was not measured owing to the reactivity or ready solubility in the available standards, but the calculated density of 1.96 g cm^{-3} is in good agreement with that found for brominated hydrocarbons. Using graphite monochromatized radiation, the data were collected at 21 °C by the ω–2θ scan technique, yielding, after correction for crystal decay, Lorentz and polarization effects, and absorption,[23] and averaging of multiply measured reflections, a final set of 1773 unique data, approximately one-third of which was less than 3σ above background. The space group was determined to be $P\bar{1}$ (C_2^1, no. 2) based upon the intensity statistics and this assignment was later confirmed by the successful refinement of the structure. The structure was

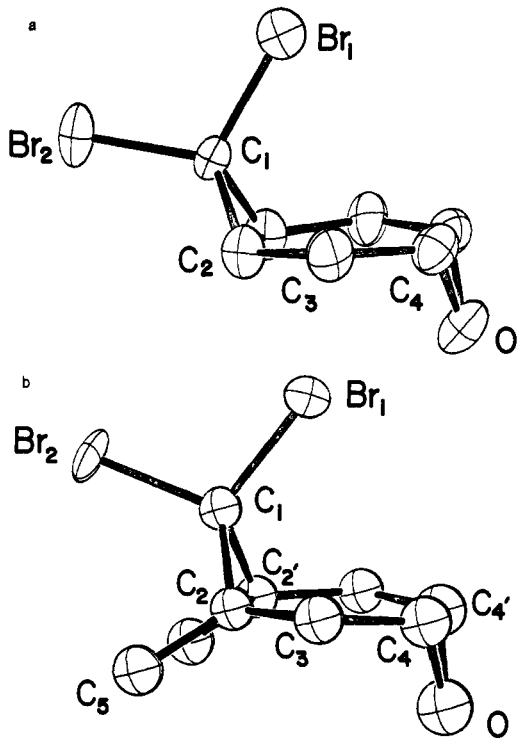


Figure 5. Final X-ray structures of **19b** (a) and **11** (b) showing the transoid configuration of the cyclopropane and epoxide rings across the approximately planar six-membered ring. The atomic numbering is that used in Table III; one-half of the molecule is related to the other by a mirror plane containing C(1) and O.

Table III. Bond Distances (Å) and Angles (deg) for **19a** and **11**[a]

	19a	**11**
C(1)-Br(1)	1.920 (9)	1.894 (9)
C(1)-Br(2)	1.913 (9)	1.927 (10)
C(1)-C(2)	1.519 (17)	1.493 (11)
C(2)-C(3)	1.517 (17)	1.505 (10)
C(3)-C(4)	1.492 (18)	1.502 (10)
C(2)-C(2)′	1.549 (17)	1.554 (14)
C(4)-C(4)′	1.450 (17)	1.458 (14)
C(4)-O	1.414 (16)	1.398 (10)
C(2)-C(5)	1.520 (17)	
Br(1)-C(1)-Br(2)	108.0 (6)	110.8 (5)
Br(1)-C(1)-C(2)	120.9 (9)	119.4 (7)
Br(2)-C(1)-C(2)	119.9 (9)	118.6 (6)
C(2)-C(1)-C(2)′	61.3 (10)	62.7 (6)
C(1)-C(2)-C(2)′	59.3 (10)	58.6 (3)
C(1)-C(2)-C(3)	116.4 (10)	121.9 (7)
C(2)′-C(2)-C(3)	119.8 (10)	120.8 (4)
C(2)-C(3)-C(4)	117.3 (10)	115.8 (6)
C(3)-C(4)-C(4)′	122.6 (16)	123.0 (4)
C(3)-C(4)-O	117.1 (13)	118.2 (7)
C(4)′-C(4)-O	59.2 (9)	58.6 (4)
C(4)-O-C(4)′	61.6 (11)	62.9 (8)
C(1)-C(2)-C(5)	120.0 (12)	
C(2)′-C(2)-C(5)	118.7 (16)	
C(3)-C(2)-C(5)	112.8 (12)	

[a] The reported values have been averaged for chemically equivalent bonds. The standard deviations in the parameters have been calculated using variances in the coordinates derived from the diagonal elements of the inverted matrix from the final least-squares cycle. The numbering scheme relates to that given in Figure 5 only.

solved by the heavy atom Patterson method and refined by conventional Fourier and full matrix least squares techniques. Hydrogen atom contributions were included in the calculations, their positions about the methyl groups being determined from difference Fourier maps, but their parameters were not refined. The conventional R factor at the current stage of refinement is 10.7% and the goodness of fit is 3.5. Substantial improvement is not expected because of the low quality of the data (the disagreement R index for the multiply measured reflections was 7.4% and the Bragg peaks were very broad); thus the values of the derived bond parameters given here (Table III) are essentially final. Tables of the values of the refined parameters are available as supplementary material.[24]

A colorless, crystalline fragment of **11** was mounted in a capillary tube and aligned on a four-circle automated diffractometer in a cold (−56 °C) N_2 gas stream to retard crystal decomposition. The orthorhombic cell constants (a = 10.918 (2) Å, b = 8.539 (2) Å, and c = 8.896 (2) Å) were obtained by least-squares refinement of the setting angles of 32 carefully centered reflections having $15° < 2\theta < 29°$. Using graphite monochromatized Mo $K\bar{\alpha}$ radiation and the ω-2θ scanning method, 1411 reflection intensities were measured, of which 666 were greater than 3θ above background. Correction for L_P, absorption, and crystal decay was performed in the same manner as for **19b.** Averaging of multiply measured reflections (chiefly check reflections) resulted in a final data set of 1285 unique reflections. Inspection of the intensities unambiguously determined the space group as *Pnma* (C_{2h}^{16}, no. 62; absences $hk0$, $h = 2n + 1$; $0kl$, $k + l = 2n + 1$) and the intensity statistics verified the centric nature of the distribution expected for *Pnma*. Assuming a comparable density to **19b** led to assignment of $Z = 4$, a calculated density of 2.146 g cm^{-3}, and the requirement that the molecule possesses a crystallographically imposed mirror plane.

The phase problem was solved by the heavy-atom Patterson method and refined by Fourier and least-squares analysis. All the nonhydrogen atoms were given anisotropic thermal parameters and all but the coordinates and isotropic temperature factors of the hydrogen atoms were refined in the least squares. The final R factor and goodness of fit for all 1285 reflections were 10.0% and 1.90. The final difference Fourier map possessed several peaks of ca. 1.3 e Å^{-3} in the vicinity of the bromine atoms. We ascribe the high R factor and residual difference Fourier features to the inadequacies of the absorption corrections and to the large number of very weak reflections (the R factor for the most significant $I > 3\sigma(I)$ data is about 7.2%). The bond distances and angles calculated from the refined parameters[24] are given in Table III. The structures of the two compounds are illustrated in Figure 5. The conformation of the multiply fused ring system is surprisingly unperturbed by the presence of the methyl groups in **19b.** The six-membered rings in the two compounds are essentially planar, although each possesses a very small boat-form pucker. The C(3) and C(3)′ methylene carbon atoms in **19b** are about 0.07 Å above the plane of the remaining four carbon atoms. In **11,** the corresponding value is 0.08 Å. This translates into dihedral angles of 6.4° for **19a** and 7.6° for **11** for the two four-atom planes C(3)-C(1)-C(1)′-C(3)′ and C(3)-C(4)-C(4)′-C(3)′. Both the cyclopropane and epoxide three-membered rings in the pair of compounds are much closer to orthogonality to the mean plane of the six-membered ring than the 120° that would be expected from consideration of the geometries of cyclopropane rings fused to medium-sized carbocycles.[25]

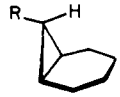
Despite the relatively low accuracy (by current standards) of the results in Table III, the consistency of the result for **19b** and **11** recommends a greater reliability than the esd's suggest. We consequently view the much longer than normal C(2)-C(2)′ distances as real, and quite in keeping with available predictions[26] of π-acceptor and π-donor substituent effects on the opposite cyclopropane C-C bond. Similar effects were noted by Lauher and Ibers[27] in the case of 1,1-dibromo-2,2-diphenylcyclopropane, but the interpretation was made more

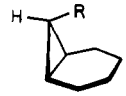
difficult by the presence of the phenyl substituents. The remaining bonds in the structure are all normal in comparison with standard values.[28]

Long-Range Anisotropy Effects of Epoxide Rings. The magnetic anisotropy effects of cyclopropane rings has been a subject of immediate concern to a number of investigators for almost 2 decades. Initially, the high shifts of protons directly bonded to three-membered carbon rings were attributed to a ring current effect,[29] a concept also utilized at that time to rationalize long-range shielding phenomena. This theory was never firmly established and more recent work has resulted in development of more semiquantitative treatments.[31] The two hypotheses which have emerged are referred to as the group anisotropy and bond anisotropy models (Figure 6). In the latter instance, the contour of the magnetic field arises from the combined fields of the three cyclopropane C–C bonds, and a proton which finds itself on a line which makes an angle greater than 55° 44′ with the center of the nearest cyclopropane bond should experience anisotropic shielding. According to the group anisotropy model, a proton positioned at an angle less than 55° 44′ with the plane of the cyclopropane ring at its center should be deshielded. Therefore, the models can be distinguished only when a proton falls into that rather limited region of space where the screening predictions differ in sign. Hahn and Howard have acquired experimental data which agree completely with group anisotropy theory and have concluded that this concept is the superior one in its present application.[32]

NMR studies on epoxides have been more limited and have not lent themselves as conveniently to a model. At first, it was believed that epoxide rings exerted magnetic anisotropic effects comparable to those of their cyclopropane congeners. However, later work[16] showed this assumption to be incorrect. Tori and his co-workers concluded that a proton situated above the plane of the ring is more shielded, whereas a proton located near the plane or in the neighborhood of the heteroatom is less shielded. However, their data base was quite limited. More recent investigations now suggest that shielding above and below the plane of an epoxide ring can be expected except when the proton is close to the oxygen atom, in which case deshielding results.[33,34] At least two supportive ^{13}C NMR studies have become available.[35]

For the present purposes, it is also important to recognize that H_{7endo} protons in simple 7-substituted norcaranes such as **35a**[21] and **35b**[36] resonate at *higher* field than their H_{7exo} counterparts in **36a** and **36b**, respectively. For example, H_7





35 a, R = CH_3
b, R = Cl

36 a, R = CH_3
b, R = Cl

appears as a multiplet at δ 0.6–0.3 in **35a** and at δ 0.7–0.9 in **36a.** The methyl groups, on the other hand, are nearly indistinguishable (δ 0.96 and 0.94, respectively). Apparently, H_{7endo} is subjected to various local diamagnetic anisotropy effects generated by the C–C bonds of the cyclohexane ring.

On this basis, the NMR results for **4** which reveal H_{7endo} to resonante above Me_4Si can be considered consistent only with an enhanced diamagnetic contribution from the carbon atoms of the epoxide ring.[10b] The protons bonded to the identical C_2, C_5 methylene groups of this molecule should in principle permit, by analysis of their vicinal spin–spin interactions, a direct assessment of the dominant conformation. To this end, use has been made of the Karplus equation[37] as modified by Abraham and Gatti for vicinal couplings to cyclopropane rings (J_{vic} = 10 $\cos^2 \Phi$)[38] and by Tori et al. for similar interactions to epoxide rings (J_{vic} = 5.1 $\cos^2 \Phi$).[39] The experimentally determined signal widths for H_{2exo} (8–8.5 Hz) and H_{2endo} (3.5 Hz) do not agree with those calculated for the cis boat conformation (2.0 and 2.0 Hz) or the trans boat form (7.5 and 0 Hz), but approximate most closely the values computed for the planar ring structure (9.5 and 3.5 Hz). A similar analysis applied to **5** (again using Dreiding models) indicates the preponderant geometry also to be planar, since either boat alternative would generate coupling constants larger than those observed (see below). The spectra illustrated in Figure 1 serve clearly to accentuate the very visible effects of syn–anti stereochemical modification on otherwise planar cyclohexane rings.

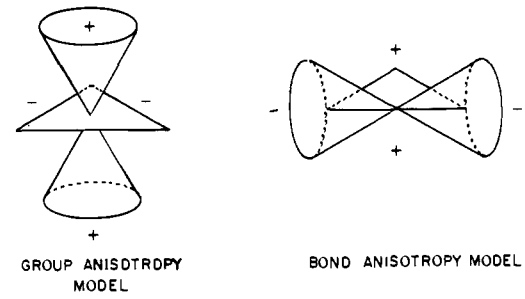


Figure 6.

As concerns epoxide **19a,** we see that the $J_{2exo,3}$ and $J_{2endo,3}$ values of 0 and 3.8 Hz, respectively, estimated for the planar conformation agree uniquely with the observed multiplicity (Figure 2). For comparison purposes, its cis boat geometry is projected to generate related spin interactions of 1.3 and 1.3 Hz, and its trans boat shape 2.1 and 4.9 Hz. Analogous reasoning has led us to the conclusion that the nicely symmetric AA′BB′ pattern exhibited by syn epoxide **20a** arises from preferential adoption of the trans boat conformation ($J_{2endo,3}$ = $J_{2exo,3}$ = 1.3 Hz) and not the cis boat (4.9, 2.1 Hz) or planar geometries (3.8 and 0 Hz).

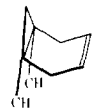
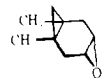
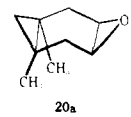
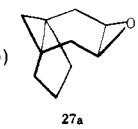
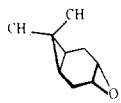
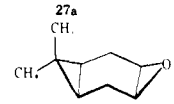
The close similarity of the methylene multiplicities of **20a** and **27a** (Figure 3) provides convincing evidence that these epoxides share a common trans boat preference. The fact that the chemical shifts of H_{2exo} and H_{2endo} in **26a** have merged to a single line of relatively narrow width is taken to indicate that neither the cis boat nor planar forms constitute the predominant ground-state conformation. In this instance, the anti epoxide appears to prefer adoption of a planar geometry where H_{2endo} and H_{2exo} have become accidentally equivalent, perhaps because of the pendant trimethylene bridge.

At this point, the planar character of **31** and the trans boat nature of **32** are self-evident.

To summarize, the above analysis provides supportive evidence for the conclusion that the four anti epoxides (**4, 19a, 26a,** and **31**) and syn epoxide **5** exist predominantly in conformations which have a relatively flat central ring, while **20a, 27a,** and **32** favor trans boat geometries.

There now remains the key question of why the chemical shifts of the syn and anti substituents positioned at C_7 vary to the extent that they do within each of the three structural subgroups. To provide additional comparison and because electron diffraction measurements suggest that a fused three-membered ring frequently has the same effect on the conformation of a six-membered ring as an internal double bond,[40] the data for the 3-norcarene precursors are utilized as points of reference. In the parent hydrocarbon system **1**, the combined anisotropic effects of the C—C and C=C bonds cause H_{7endo} and H_{7exo} to overlap with H_1 and H_6 as a broad multiplet of area 4 at δ 0.8–0.2. From a knowledge of the properties of **35** and **36,** the endo proton can be safely assumed to resonate on the high-field side of the multiplet and the exo proton on the low. In [4.3.1]propell-3-ene (**23a**), the $\Delta\delta_{gem}$ of the C_7 hydrogens is reduced to zero, undoubtedly because of the enhanced shielding of H_{7exo} by the trimethylene bridge.

Table IV. Summary of $\Delta\delta$ Values for the 3-Norcarene Oxides

compd	proton chemical shifts 7endo	7exo	compd	proton chemical shifts 7endo	$\Delta\delta^a$	7exo	$\Delta\delta^a$	compd	proton chemical shifts 7endo	$\Delta\delta^a$	7exo	$\Delta\delta^a$
 1	0.2-0.8[b] (multiplet)		 4	−0.4	+0.6	0.55	−0.25	 5	0.62	−0.4	0.26	+0.5
 16	−0.07	0.69	 19a	0.07	−0.14	0.07	+0.6	 20a	0.97[e]	−0.9	−0.20[e]	+0.9
	(0.25)[c]	(0.35)[c]		(+0.2)[d]		(−0.3)[d]			(−0.7)[d]		(+0.6)[d]	
 23a	0.35 (singlet)		 26a	−0.17	(+0.5)	0.06	(−0.25)	 27a	0.71	(−0.4)	0.18	(+0.2)
 30	0.80	1.04	 31	0.76	(+0.04)	1.04	(−0)	 32	0.95	(−0.15)	0.90	(+0.14)

[a] The $\Delta\delta$ values are given relative to the chemical shifts observed for the 3-norcarene. [b] These protons overlap with H_1 and H_6 in this region. [c] Chemical shifts calculated for the planar six-membered ring conformation of **16** based chiefly upon data for 1 and **23a**. [d] These values relate to planar **16**. [e] Assignments substantiated by nuclear Overhauser experiments.

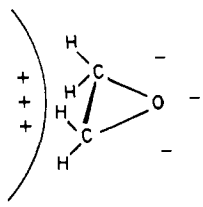


Figure 7.

On the other hand, the $\Delta\delta_{gem}$ value for **16** is large (0.76 ppm), chiefly because of the marked upfield shift of H_{7endo} (Table IV). This phenomenon denotes adoption by **16** of enhanced levels of the cis boat conformation, as anticipated earlier on conformational grounds.

The long-range shieldings caused by the anti epoxide rings in **4**, **19a**, and **26a** do not parallel those in the 3-norcarenes *in an immediately obvious way* and point out the extreme level of caution which must be exercised in extrapolating such data, even when very closely related molecules are involved. Thus, the $\Delta\delta_{gem}$ for **19a** is now zero, while those for **4** and **26a** are quite large. Additionally, the methyl groups in **31** appear little affected (relative to **30**) by introduction of the anti epoxide ring. In contrast, the syn epoxides are more systematically related (Table IV).

Nonetheless, reliable correlation of this seemingly diverse collection of shift data is possible provided that proper attention is given to conformational similarities and differences. For example, our experimental results show epoxides **4** and **5** to exist in planar conformations comparable to that presumably adopted by **1**.[11] Given these three-dimensional similarities, the anti epoxide ring in **4** is seen to generate *relative to* **1** an upfield shift for H_{7endo} of 0.6 ppm and a downfield shift for H_{7exo} of 0.25 ppm (Table IV). The situation is reversed in **5**, H_{7endo} being deshielded (0.4 ppm) and H_{7exo} shielded (0.5 ppm) *as compared to* **1**. Such an analysis clearly demonstrates that progression from **4** to **5**, or vice versa, results in a *crossing* of the two sets of resonance lines. The data for **23a**, **26a**, and **27a** show a remarkably similar trend, despite adoption by the syn epoxide of a trans boat geometry. The properties of the **30–32** triad are again in the same direction, although the magnitudes of the shift changes are lessened in this series because of increased distances.

At first glance, the group **16**, **19a**, and **20a** is seen to generate anomalous correlations. This is because a correction must be applied to the data for **16**, since this 3-norcarene uniquely adopts a cis boat conformation which leads to more intense anisotropic perturbations in the region around C_7. However, with values of H_{7endo} and H_{7exo} shifts adapted to the hypothetical planar form, the $\Delta\delta$'s are seen to correlate closely with those in the other examples (Table IV).

At this point, it should be mentioned that the simple anisotropy model illustrated in Figure 7[10b] is not sufficiently detailed to account entirely for our observations. Moreover, it is likely that the screening effects emanating from the rearside of an epoxide ring are dependent not only on distance (the result of shielding contours[31d]) but also on group anisotropy contributions (a $\cos^2$ angular dependence) as summarized in the previously cited McConnell equation. Such added considerations concisely explain, for example, the significantly enhanced shielding of H_{7exo} in **5**, **20a**, and **27a** relative to their 3-norcarene counterparts as well as that encountered in the *exo*-7-methyl group of **32** (as compared to **30**).

The epoxides prepared in this study serve to illustrate some of the problems which can arise even for closely related structures. Although the bond anisotropy treatment can sometimes be helpful in predicting $\Delta\delta$, it takes account neither of the electron cloud volume around the three-membered ring nor of the effect of the oxygen p orbitals. On occasion, slight changes in 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. The development of an accurate and convenient method by which shielding effects of an epoxide ring might be estimated must therefore take these many factors into account. In the interim, the working concepts detailed herein should find application, but only with utmost reasonable precaution.

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with Varian T-60, Varian EM-360, and Bruker HX-90 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on a Perkin-Elmer Model 467 instrument. Mass spectra were recorded on an AEI-MS9 spectrometer at ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Generalized Epoxidation Procedure. *syn*- and *anti*-Bicyclo[4.1.0]-hept-3-ene Oxides (4 and 5). To an ice-cooled, stirred slurry of sodium bicarbonate (1.6 g, 0.020 mol) and 3-norcarene (**1**,[8] 1.0 g, 0.010 mol) in dichloromethane (50 mL) was added dropwise a solution of 85% *m*-chloroperbenzoic acid (3.02 g, 0.015 mol) in the same solvent (50 mL). The reaction mixture was stirred for 12 h at room temperature and washed with water (50 mL), saturated sodium sulfite solution (2 × 50 mL), saturated sodium bicarbonate solution (2 × 50 mL), and brine (50 mL) prior to drying. The solvent was evaporated and the residue (100% yield) was separated into its two components by preparative VPC (12 ft × 0.25 in. 30% di-*n*-butyl tetrachlorophthalate, 110 °C).

For **4** (62%): *m/e* calcd 110.0732, obsd 110.0734. Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.02; H, 9.17.

For **5** (38%): *m/e* calcd 110.0732, obsd 110.0734. Found: C, 76.37; H, 9.25.

7,7-Dibromo-1,6-dimethylbicyclo[4.1.0]hept-3-ene (15). To a mechanically stirred slurry of potassium *tert*-butoxide (44.2 g, 0.394 mol), 3,5-dihydro-*o*-xylene (21.50 g, 0.197 mol), and distilled pentane (250 mL) cooled to −30 °C under a nitrogen atmosphere was slowly added during 2.25 h a solution of bromoform (50.0 g, 0.197 mol) in pentane (225 mL). The reaction mixture was warmed to room temperature during 4 h and poured into water, whereupon the layers were separated. The organic phase was washed with water (200 mL), dried, and evaporated. Most of the solid product was taken up in petroleum ether (bp 30–60 °C) and filtered to remove the insoluble bis adduct, mp 147.2–147.8 °C (from ethyl acetate). The petroleum ether solution was evaporated and the residue sublimed (80 °C and 45 mm) to give 23 g (41.5%) of **15** as white crystals: mp 105–106 °C; $\nu_{max}^{CHCl_3}$ 2820, 1660, 1450, 1420, 1140, 1030, 1010, and 920 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 4.58 (t, J = 0.5 Hz, 2 H), 1.91 (s, 4 H), and 1.10 (s, 6 H).

Anal. Calcd for $C_9H_{12}Br_2$: C, 38.60; H, 4.32. Found: C, 38.60; H, 4.24.

1,6-Dimethylbicyclo[4.1.0]hept-3-ene (16). To 200 mL of cold (−78 °C) anhydrous liquid ammonia was added 12.0 g (0.52 g-atom) of sodium metal in portions with stirring. During 2.5 h, a solution of **15** (22.36 g, 0.079 mol) in dry ether (110 mL) was added dropwise and the ammonia was then allowed to evaporate. The residue was blanketed under nitrogen and treated slowly with methanol followed by water. The organic phase was separated and the aqueous layer was extracted with pentane (150 mL). The combined organic layers were washed with dilute hydrochloric acid and dried prior to solvent removal and product distillation. There was obtained 4.35 g (45.4%) of **16**: bp 58–61 °C (50 mm); ν_{max}^{film} 2860, 1660, 1450, 1380, 1025, and 870 cm^{-1}; ^1H NMR (δ, CCl_4) 5.44 (t, J = 2 Hz, 2 H), 2.11 (s, 4 H), 1.10 (s, 6 H), 0.66 (d, J = 4 Hz, 1 H), and −0.08 (d, J = 4 Hz, 1 H).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.53; H, 11.80.

***anti*-7,7-Dibromonorcar-3-ene Oxide (11).** Epoxidation of a 2.40-g (0.953 mmol) sample of **10**[9] according to the general procedure gave **11** in 97% yield as colorless crystals: mp 50–51 °C (from hexane followed by sublimation); ^1H NMR (δ, $CDCl_3$) 3.0 (d, J = 1 Hz, 2 H), 2.44 (*AA'*BB', J = 16, 8, and 1 Hz, 2 H), 1.87 (AA'*BB'*, J = 16 and 1 Hz, 2 H), and 1.20 (m, 2 H).

Anal. Calcd for $C_7H_8Br_2O$: C, 31.38; H, 3.00. Found: C, 31.57; H, 3.08.

***anti*-1,6-Dimethyl-7,7-dibromonorcar-3-ene Oxide (19b).** From 1.00 g (3.57 mmol) of **15**, there was isolated 1.02 g (96%) of **19b** as white crystals: mp 90–94 °C after sublimation at 50 °C and 0.05 mm; ^1H NMR (δ, $CDCl_3$) 3.4–3.0 (m, 2 H), 2.6–1.6 (m, 4 H), and 1.23 (s, 6 H).

Anal. Calcd for $C_9H_{11}Br_2O$: C, 36.51; 4.09. Found: C, 36.72; H, 4.20.

***syn*- and *anti*-1,6-Dimethylnorcar-3-ene Oxides (19a and 20a).** Epoxidation of **16** (1.22 g, 0.01 mol) according to the previous guidelines afforded in near-quantitative yield a 74:26 mixture of **19a** and **20a** which was separated by preparative VPC (5 ft × 0.25 in. 30% di-*n*-butyl tetrachlorophthalate, 130 °C). Combustion analysis was conducted on the mixture obtained by distillation at 61 °C and 7 mm: *m/e* calcd 138.1045, obsd 138.1047.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.99; H, 10.32.

***anti*-10,10-Dibromo[4.3.1]propell-3-ene Oxide (26b).** From 2.00 g (6.71 mmol) of **23b**, there was obtained 1.98 g (94%) of **26b** as white crystals, mp 105–106 °C (sublimation at 60 °C and 0.07 mm).

Anal. Calcd for $C_{10}H_{12}Br_2O$: C, 38.99; H, 3.93. Found: C, 39.21; H, 4.04.

***syn*- and *anti*-[4.3.1]Propell-3-ene Oxides (26a and 27a).** From 67 mg (0.5 mmol) of **23a**, there was produced in near-quantitative yield a 69:31 mixture of **26a** and **27a** which was separated by VPC (6 ft × 0.25 in. 12% OV-11, 150 °C): *m/e* calcd 150.1045, obsd 150.1047.

For **26a**: Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H , 9.39. Found: C, 79.73; H, 9.64.

For **27a**: Found: C, 80.20; H, 9.50.

7,7-Dimethylbicyclo[4.1.0]hept-3-ene (30). To ice-cold ethereal methyllithium (612 mL of 1.8 M, 1.0 mol) was slowly added under nitrogen with stirring 95.2 g (0.50 mol) of dry cuprous iodide. After 2 h at room temperature, the reaction mixture was cooled to −20 °C, 12.6 g (0.05 mol) of **10** was introduced, and the flask was maintained at −12 °C for 104 h with occasional shaking. The mixture was then poured onto cold saturated ammonium chloride solution made alkaline with ammonium hydroxide and ether was added. The organic layer was washed twice with saturated ammonium chloride–ammonium hydroxide solution, water, and brine before drying and evaporation of solvent. Distillation of the residue gave 1.4 g (23%) of **30**: mp 75–80 °C; ν_{max}^{film} 3000, 2930, 1455, 1260, 1090, and 800 cm^{-1}; ^1H NMR (δ $CDCl_3$) 5.53 (m, 2 H), 2.6–1.9 (m, 4 H), 1.01 (s, 3 H), 0.79 (s, 3 H), and 0.75–0.55 (m, 2 H).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.32; H, 11.39.

***anti*-7,7-Dimethylnorcar-3-ene Oxide (31).** From 134 mg (1.1 mmol) of **30**, there was obtained 138 mg (90%) of **31** as the exclusive product: *m/e* calcd 138.1045, obsd 138.1047.

Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 77.89; H, 10.42.

Generalized Bromohydrin Formation Procedure. To a magnetically stirred solution of **1** (0.94 g, 0.01 mol) in dimethoxyethane–water (9:1, 75 mL) was added dropwise a solution of *N*-bromosuccinimide (1.96 g, 0.011 mol) in dimethoxyethane (50 mL) during 1 h. After 2 h at room temperature, the excess NBS was destroyed by addition of saturated sodium bisulfite solution (10 mL). The solvent was removed in vacuo and the residue was leached with chloroform (3 × 40 mL). The combined chloroform extracts were washed with saturated sodium bicarbonate solution (40 mL) and brine (40 mL) before drying. Removal of solvent left a quantitative crude yield of **6** and **7** which was directly cyclized without characterization.

Generalized Bromohydrin Cyclization Procedure. The mixture of **6** and **7** produced above and sodium hydride (4.21 g of 57% in oil, 0.1 mol) washed with pentane (three times) in dry tetrahydrofuran (20 mL) was stirred at room temperature under nitrogen for 24 h. The progress of the reaction was arrested by pouring into saturated ammonium chloride solution (20 mL). The tetrahydrofuran and water were removed under reduced pressure and the residue was leached with chloroform (3 × 30 mL). The combined chloroform extracts were washed with brine, dried, and evaporated. There was obtained 0.98 g (89%) of a 13:87 mixture of **4** and **5**.

***syn*-7,7-Dimethylnorcar-3-ene Oxide (32).** Treatment of **30** with NBS in aqueous tetrahydrofuran and subsequent NaH-promoted cyclization provided **32** as a colorless liquid: *m/e* calcd 138.1045, obsd 138.1047.

Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.36; H, 10.28.

Generalized Tri-*n*-butyltin Hydride Reduction Procedure. Conversion of 11 to 4. To a nitrogen-blanketed solution of **11** (1.00 g, 0.373 mmol) in hexane (5 mL) was added tri-*n*-butyltin hydride (232 mg, 0.80 mmol) and the mixture was stirred at the reflux temperature for 28 h. The solvent was evaporated and the product was separated from higher boiling byproducts by distillation at 90–100 °C and 25–35 mm. Pure **4** was isolated by preparative VPC (12 ft × 0.25 in. 20% Carbowax 20M, 140 °C).

***syn*-7,7-Dibromonorcar-3-ene Oxide (13).** A 300-mg (1.19 mmol) sample of **10** was converted to bromohydrin **12** in the predescribed manner. The unpurified product was treated with excess sodium hydride in dry tetrahydrofuran as before to give **13** which was sublimed at 40–50 °C and 0.1 mm and further purified by VPC (1 ft × 0.25 in. 10% SE-30): ^1H NMR (δ, $CDCl_3$) 3.09 (d with additional splitting, J = 4 Hz, 2 H), 2.8–2.1 (br m, 2 H), 1.9–1.7 (m, 2 H), and 1.9–1.5 (d, J = 16 Hz, 2 H).

***syn*-7,7-Dibromo-1,6-dimethylnorcar-3-ene oxide (20b)** was isolated as colorless crystals: mp 89.5–90.5 °C, after sublimation at 40–50 °C and 0.07 mm; ^1H NMR (δ, $CDCl_3$) 3.1–3.0 (m, 2 H), 2.2–2.05 (m, 4 H), and 1.20 (s, 6 H).

syn-10,10-Dibromo[4.3.1]propell-3-ene oxide (**27b**) when sublimed at 60 °C and 0.07 mm was isolated as colorless crystals, mp 104–106 °C. Recrystallization from ether raised the melting point to 120–122 °C; ^{1}H NMR (δ, $CDCl_3$) 3.25 (m, 2 H) and 2.7–1.4 (br m, 10 H).

Generalized Photooxygenation Procedure. A norcarene (100 mg) and rose bengal (40 mg) were dissolved in dichloromethane–methanol (9:1, 150 mL). A gentle stream of oxygen was bubbled through this solution with concomitant irradiation from a Sylvania DYV projector bulb housed in a water- and air-cooled jacket. When reaction was complete, sodium borohydride (100 mg) was added and stirring was maintained for 30 min. This solution was washed with water (3 × 25 mL), dried, and decolorized with activated charcoal. The solvent was evaporated and the residual allylic alcohols were analyzed as to their relative proportion and purified by preparative VPC.

For **2** (5 ft × 0.25 in. 5% XF-1150, 110 °C): 40% isolated yield; ^{1}H NMR (δ, $CDCl_3$) 5.97 (d of m, J = 11 Hz, 1 H), 5.30 (d with fine splitting, J = 11 Hz, 1 H), 3.88 (m, 1 H), 3.22 (s, 1 H), 2.5–2.0 (br m, 4 H), ca. 0.85 (m, 1 H), and 0.25 (m, 1 H); *m/e* calcd 110.0732, obsd 110.0734.

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.94; H, 9.21.

For **17** (5 ft × 0.25 in. 5% SF-96, 118 °C): 40% isolated yield; ^{1}H NMR (δ, $CDCl_3$) 5.70 (dd, J = 11 and 2 Hz, 1 H), 5.27 (d with fine splitting, J = 11 Hz, 1 H), 4.18–3.73 (br m, 1 H), 2.57 (s, 1 H), 2.42–2.00 (m, 2 H), 1.17 (s, J = 6 Hz), 0.68 (d, J = 4 Hz, 1 H), and 0.22 (d, J = 4 Hz, 1 H); *m/e* calcd 138.1047, obsd 138.1045.

Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.15; H, 10.19.

For **24** (6 ft × 0.25 in. 12% OV-11, 150 °C): ^{1}H NMR (δ, $CDCl_3$) 6.03 (dd, J = 11 and 2 Hz, 1 H), 5.36 (d with fine splitting, J = 11 Hz, 1 H), 4.38–3.9 (br m, 1 H), 2.72–2.3 (m, 1 H), 2.44 (s, 1 H), 2.10–1.10 (br m, 7 H), 0.72 (d, J = 5 Hz, 1 H), and 0.47 (d, J = 5 Hz, 1 H); *m/e* calcd 150.1045, found 150.1048.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.69; H, 9.36.

For **33** (5 ft × 0.25 in. 5% SF-96, 98 °C): ^{1}H NMR (δ, $CDCl_3$) 5.82–5.58 (m, 2 H), 3.9–3.5 (m, 1 H), 2.3–0.9 (m, 5 H), 1.12 (s, 3 H), and 0.80 (s, 3 H); *m/e* calcd 138.1045, obsd 138.1048.

Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.28; H, 10.27.

General Procedure for Lithium Diethylamide Promoted Epoxide Ring Openings. *syn*-Bicyclo[4.1.0]hept-2-en-4-ol (3). To 1.66 mL of 2.2 M *n*-butyllithium in hexane (2.56 mmol) cooled to 0 °C under nitrogen was slowly added 510 mg (7 mmol) of diethylamine dissolved in dry ether (5 mL). After 30 min, the solution was allowed to warm to room temperature, 60 mg (0.545 mmol) of **5** in 2 mL of ether was introduced, and stirring was maintained for 48 h. The ethereal solution was washed with saturated ammonium chloride solution (2 × 25 mL) and water (20 mL) prior to drying. Alcohol **3** was isolated by preparative VPC on a 12 ft × 0.25 in. 8% Carbowax column (110 °C) as a colorless liquid (24 mg, 40%): ^{1}H NMR (δ, $CDCl_3$) 6.25 (d of m, J = 11 Hz, 1 H), 5.58 (dd, J = 11 and 5 Hz, 1 H), 4.5–4.0 (br m, 1 H), 1.9 (br s, 3 H), 1.55–0.7 (br m, 3 H), and ca. 0.52 (m, 1 H); *m/e* calcd 110.0732, obsd 110.0734.

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.86; H, 9.18.

For **18**: ^{1}H NMR (δ, $CDCl_3$) 6.1 (d, J = 10 Hz, 1 H), 5.62 (dd, J = 10 and 5 Hz, 1 H), 3.4 (br m, 1 H), 2.0–0.8 (br m, 5 H), 1.24 (s, 3 H), and 1.20 (s, 3 H); *m/e* calcd 138.1047, obsd 138.1045.

For **25** (decomposed under VPC conditions; purified by distillation, bp 60 °C at 0.5 mm): ^{1}H NMR (δ, $CDCl_3$) 6.32 (d, J = 10 Hz, 1 H), 5.62 (dd, J = 10 and 5 Hz, 1 H), 4.42–4.15 (br m, 1 H), 3.6–3.0 (br m, 1 H), and 2.6–0.6 (m, 10 H); *m/e* calcd 150.1045, obsd 150.1047.

***syn*-7,7-Dimethylbicyclo[4.1.0]hept-2-en-4-ol (34).** A solution of diphenyl diselenide (136 mg, 0.438 mmol) in absolute ethanol (5 mL) was treated with sodium borohydride (36 mg, 0.957 mmol) in several portions and stirred until the yellow color had faded. A 109-mg (0.438 mmol) sample of **32** dissolved in tetrahydrofuran (15 mL) was added and heating at the reflux temperature was continued for 5 h. To the cooled solution was added 30% hydrogen peroxide (2 mL) and the resulting mixture was stirred overnight at 25 °C. The precipitate was removed by filtration and the solvent was evaporated. The residue was leached with chloroform (3 × 30 mL) and the combined organic extracts were washed with brine, dried, and evaporated. The residual oil was purified by VPC (7 ft × 0.25 in. 10% QF-1, 115 °C) to give 30 mg (28%) of **34**: ^{1}H NMR (δ, $CDCl_3$) 5.60 (narrow m, 2 H), 4.5–4.1 (br m, 1 H), 2.67–1.88 (br m, 2 H), 1.67–0.70 (br m, 3 H), 1.10 (s, 3 H), and 1.00 (s, 3 H); *m/e* calcd 138.1047, obsd, 138.1044.

Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.32; H, 10.24.

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Supplementary Material Available: The refined crystallographic parameters for **11** and **19a** (2 pages). Ordering information is given on any current masthead page.

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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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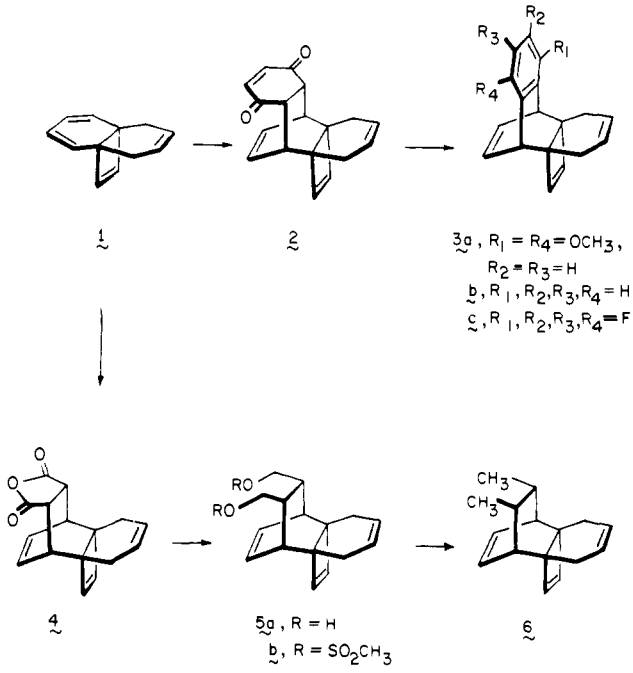
Abstract: Several snoutanes having a fused cyclohexene ring and therefore a 3-norcarene part structure entered into "ene" reaction with singlet oxygen and *N*-methyltriazolinedione with highly stereoselective or completely stereospecific approach to the anti surface (relative to the cyclopropane ring) 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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