chemical shifts of these signals indicate that all the sp-hybridized carbon atoms in XII have a hybrid character of an acetylene and a cumulene. Cf. S. Nakatsuji and M. Nakagawa, *Tetrahedron Lett.*, 3927 (1975).

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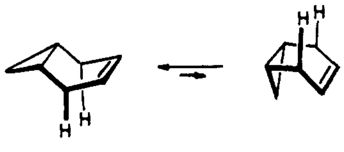
Reversal of Stereospecificity during Allylic Hydroperoxidation of 3-Norcarene and Bicyclo[4.2.0]oct-3-ene Derivatives Arising from Structurally Enforced Quenching of Singlet Oxygen by the Hydrazide Functionality

Sir:

The importance of the singlet ($^1\Delta_g$) state of oxygen to synthetic, mechanistic, and environmental chemistry is now well recognized. The wide ranging reactivity of $^1O_2$ is witnessed in its ability to effect allylic hydroperoxidation of simple olefins, 1,2-cycloaddition to alkenes of low ionization potential, and 1,4-endoperoxidation of conjugated dienes.[1] Without exception, the first of these reactions has been found to proceed with cis stereochemistry, being characterized by an exacting dependence on steric factors and the availability of an in-plane allylic hydrogen. The other pair of transformations proceed with equally impressive stereocontrol, full retention of stereochemistry occurring in every reported example.

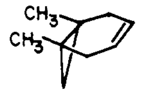
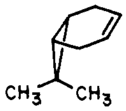
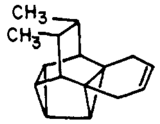
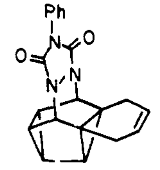
We have now investigated a heretofore unexplored parameter of singlet oxygen behavior, viz., rigid fixing of a functional group capable of quenching the $^1\Delta_g$ state within suitable proximity to the favored site of oxygenation. Since the observed end result is unprecedented redirection of $^1O_2$ attack to the more sterically congested surface of the molecule, the synthetic value of such a scheme is made evident, particularly if the functionality which causes singlet oxygen deactivation can later be extruded from the molecule. In this communication, attention is given to the allylic hydroperoxidation of 3-norcarene and bicyclo[4.2.0]oct-3-ene ring systems. The accompanying paper[2] describes a comparable assessment of the $^1O_2$ endoperoxidation of related norcaradienes and presents a unifying molecular orbital basis for the markedly contrasting observations made. The reader should recognize that our treatment is extra-mechanistic and therefore independent of the precise mechanistic details of the specific type of oxygenation, some of which remain highly controversial.

^{1}H NMR studies have indicated 3-norcarene to be capable of facile interconversion between boat conformations **1a** and **1b**.[3] These two forms are clearly not isoenergetic and stereochemical considerations suggest that **1a** with its quasi-equatorial cyclopropane ring should be somewhat favored over **1b**. However, models reveal the conformational equilibrium to be rather delicately balanced and to be expectedly sensitive to substitution on the cyclopropane ring and elsewhere. Of importance to the photooxygenation reaction, **1a** and **1b** share the common stereoelectronic feature of having two equivalent allylic C–H bonds properly aligned with the pπ orbitals of the double bond, as emphasized in the formulas. On a more general note, electrophilic attack on **1a** and **1b** from the less hindered direction leads unambiguously to different products, **1a** serving as progenitor to the syn isomer and **1b** to the anti counterpart. These expectations need not be borne out, however, in more highly substituted derivatives where additional steric factors may gain subtle importance.[4]



1a **1b**

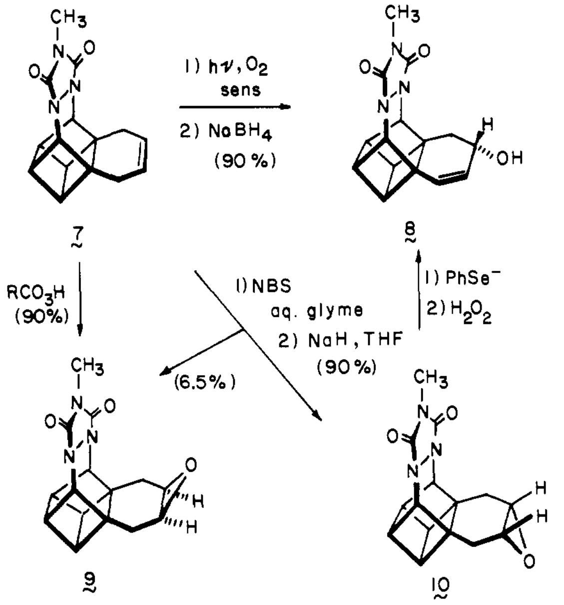
Table I. Product Distribution Data

Compd	Percentage composition (syn:anti)[a]		
	Epoxidation[b]	Bromohydrin formation[c]	Photo-oxygenation[d]
 **1**	61.6:38.4	87.4:12.6	100:0
 **2**	25.6:74.4	16.5:83.5	0:100
 **3**	0:100	0:100	0:100
 **4**	69:31	93:7	100:0
 **5**	35:65	—	0:100[f]
 **6**	7:84[e]	15:70[e]	91:0[e,g]

[a] The points of stereochemical reference are the cyclopropane ring and the attacking reagent. [b] *m*-Chloroperbenzoic acid in CH_2Cl_2 buffered with solid sodium bicarbonate, 25 °C; yields determined by VPC analysis except where noted. [c] *N*-Bromosuccinimide in aqueous glyme, 25 °C; yields determined by VPC analysis after conversion to epoxides with sodium hydride in refluxing tetrahydrofuran. [d] 10% Methanol in CH_2Cl_2 containing 10^{-3} M rose bengal; product analysis made subsequent to $NaBH_4$ reduction of the hydroperoxides. [e] Isolated yields determined after column chromatography on silica gel. [f] Lack of epimeric contamination determined by TLC analysis. [g] Independent synthesis achieved by phenylselenide anion promoted opening of the stereochemically related epoxide and H_2O_2 treatment.

The stereochemical consequences of direct epoxidation and bromohydrin formation of several 3-norcarenes (Table I) reveal **1** and **4** to be more disposed to attack from the direction syn to the cyclopropane ring. In contrast, the structural features in **2**, **3**, **5**, and **6** are such that approach of the electrophile from the anti direction is kinetically preferred. That epoxidation and bromohydrin formation proceed with like stereoselectivity (although generally more accentuated when Br$^+$ is the electrophile) was established by base-promoted cyclization of the bromohydrins. The major epoxide isolated from each of these experiments was invariably the epimer of that obtained by the more direct procedure. Structural assignments to the individual epoxides follow from their respective ^{1}H NMR spectra and supportive Eu(fod)$_3$ pseudocontact shifting in selected cases.

The photooxidations of **1-6** were conducted in a dichloromethane-methanol (9:1) solvent system with rose bengal or methylene blue as sensitizer (comparable stereochemical results). For characterization the hydroperoxides were reduced ($NaBH_4$) without purification to the respective allylic alcohols. Lithium diethylamide promoted ring opening[5] of the epimeric epoxides provided the authentic samples necessary for establishment of stereochemical configuration. With reference to Table I, the data for hydrocarbons **1-5** are seen to parallel precisely the previously established stereoselectivities and reflect the anticipated enhancement of attack from the less congested face of the olefinic plane.[1]



Like photooxygenation of **6** proceeds at a much slower rate than **5** and gives rise only to the product of *opposite* configuration. This most unusual stereochemical reversal involving $^1O_2$ attack from the more sterically encumbered direction appears to be a general reactivity pattern of hydrazides of this type. Thus, the *N*-methyl congener of **6** and the bishomocubane derivative **7** behave comparably!

Pertinent to an understanding of these results are the report by Ouannis and Wilson that $^1O_2$ is efficiently quenched by amines[6] and the finding by Ogryzlo and Tang that there exists a good correlation between the quenching efficiency of the amine and its ionization potential.[7] Briefly summarized, an increase in electron availability is conducive to an increase in k_q. Since the pK_a of a nitrogen base parallels in magnitude its IP and hydrazines are characterized by low pK_a's,[8] such molecules can be expected to be efficient quenchers. Indeed, their effectiveness toward photoexcited ketones has recently been established by Cohen.[9] Because the capability of hydrazides to cause electronic relaxation of $^1\Delta_g$ singlet oxygen was less obvious,[10] the ionization potentials of several representative molecules were measured by photoelectron spectroscopy. The observed IP values (8-8.6 eV)[2,11] are remarkably low and therefore such functional groups are thought to be capable of entering into efficient charge-transfer interaction under the conditions of our experiments.

Based upon such considerations, the "anomalous" behavior of **6, 7,** and related olefins is viewed as the result of efficient deactivation by the hydrazide moiety of $^1O_2$ approach from the more open anti direction. Syn attack can operate without incurring such interactions, although the greater level of steric hindrance leads to an obvious decrease in reactivity.[12]

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References and Notes

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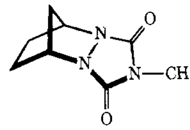
(10) In related work, the capability of hydrazides (e.g., i) to appreciably reduce $^1O_2$ reactivity in binary mixed solutions (CH_1Cl_2-CH_3OH, CH_2Cl_2-CH_3CN, CH_2Cl_2) with ii has been demonstrated.



i

ii

(11) R. Gleiter, private communication.
(12) For example, **5** undergoes complete allylic hydroperoxidation in 2 h while **6** reacts only to 67% completion after 22 h.

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Endoperoxidation of Conformationally Fixed Norcaradienes by Singlet Oxygen. Frontier Molecular Orbital Basis for the Operability of $^1O_2$ Quenching by Hydrazides

Sir:

Just as study of the allylic hydroperoxidation of various 3-norcarenes has revealed the capability of hydrazides to quench $^1\Delta_g$ oxygen as it functions in this reaction,[1] so the endoperoxidation of structurally related norcaradienes should similarly lend itself to an evaluation of a possible hydrazide directive effect on such (4 + 2) cycloadditions. Significantly, the stereochemical outcome of the two oxygenation modes should *not* be identical if the conditions of HMO perturbation theory are rigorously adhered to.

The stereospecificity of norcaradiene endoperoxidation has been experimentally assessed in five different systems (Table I), two of the illustrated examples (**1b, 2**) having been independently studied by others.[2,3] To facilitate product identification, the first-formed endoperoxides were thermally rearranged to their trishomobenzenoid diepoxide isomers without loss of configuration.[4] Because ^1H NMR data revealed the cyclopropyl protons in the diepoxides to be only marginally shielded, the oxygen atoms are assumed to be anti to the three-membered ring. This important stereochemical point was established conclusively by x-ray crystal structure analysis of **8** (Figure 1), the crystals of which form in the orthobombic system with $a = 13.404$, $b = 15.147$ (3), and $c = 16.020$ (4) Å. Systematic extinctions in $0kl$ (absent if $k = Zn + l$), $h0l$ (absent if $l = Zn + l$), and $hk0$ (absent if $h = Zn + l$) sug-