Figure 1. Mixing pattern of π_2, π_7^*, and σ_7 orbitals with the π_7 orbital.

Scheme II
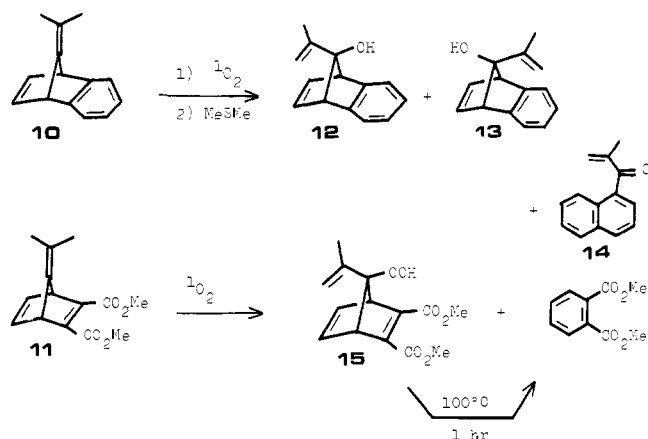
These products are accompanied by the fragmentation product, α-naphthylisopropenyl ketone (14)[22] (4%). The photooxidation of 11 afforded only anti hydroperoxide 15[24] (80%) and dimethyl phthalate, which was also produced in high yield from 15 by heating in $CDCl_3$. No syn hydroperoxide was detected in the NMR spectrum of the reaction mixture.

Thus, in both cases, 10 and 11, the main product is characterized by attack of molecular oxygen from the anti side to the unsubstituted double bond. Since this bond can more strongly interact with the exocyclic double bond, these findings are in accord with the results which are observed for the homoconjugated compounds, 1, 2, and 3.

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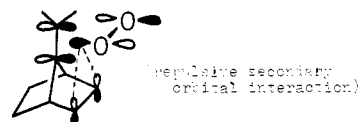
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(23) Configuration of the hydroxyl group of 12 or 13 was determined by use of Eu(fod)₃.

(24) Under the reduction condition, hydroperoxide 15 gave an unidentified product $C_{14}H_{18}O_5$ instead of the expected alcohol. Stereochemistry of 15 was determined as shown.
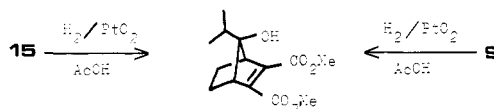
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Electronic Control of Stereoselectivity. 1. Singlet Oxygen and Related Electrophilic Additions to Aryl-Substituted 7-Isopropylidenebenzonorbornenes[‡]

Sir:

In recent years, much theoretical and experimental attention has been directed to defining more precisely the mechanism by which singlet ($^1\Delta g$) oxygen effects the allylic hydroperoxidation of olefins. At the center of the controversy lies the question whether these oxygenations proceed by a concerted ene pathway or involve transient perepoxide intermediates. Although computational methods have demonstrated the workability of frontier electron theory and the preferred energetics of perepoxide intervention,[1] clear-cut experimental substantiation of mechanism is still lacking and, in fact, the

Table I. Measured Vertical Ionization Potentials and Calculated Orbital Energies of the 7-Isopropylidenebenzonorbornenes[a]

compd	band	$I_{V,J}$	assignment	ZDO	MINDO/3
2	①	8.20	a'(π)	8.18 (a')	8.58 (a')
	②	8.70	a''(π)	8.85 (a')	8.95 (a'')
	③	8.85	a'(π)	8.94 (a'')	8.98 (a')
1	①	7.70	a''(π)		7.69 (a'')
	②	8.20	a'(π)		8.66 (a')
	③	8.70	a'(π)		8.93 (a')
3a	①	8.75	a''(π)		9.14 (a'')
	②⎫	9.03	a'(π)		9.23 (a')
	③⎭		a'(π)		9.54 (a')

[a] All values are in electronvolts.

general applicability of HOMO–LUMO control to $^1O_2$ reactivity[2] remains unclear.[3]

We have now examined the stereochemistry of singlet oxygen addition to the four 7-isopropylidenebenzonorbornenes **1–3** and made direct comparison with other prototypical electrophilic reactions. Recourse to such a series of closely related molecules obviates the often encountered complications of steric and conformational variability, while allowing extensive electronic alteration to be implemented. The photoelectron spectra of **1–3a** below 10 eV consist of three peaks
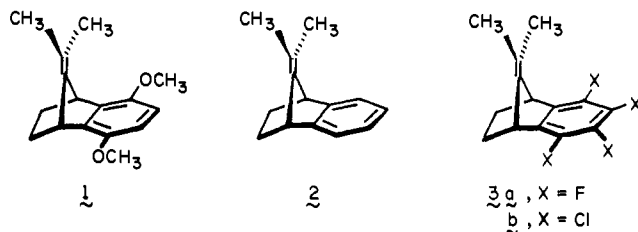
which, on the basis of previous findings,[4] clearly result from two π MO's localized predominantly on the benzene ring and a third on the exocyclic double bond. Full analysis of orbital sequencing was achieved through application of Koopmans' theorem ($-\epsilon_J = I_{V,J}$) and utilization of both a ZDO model and MINDO/3 procedures.[5] The quite good agreement between calculation and experiment (Table I) make evident substantial mixing of π and σ orbitals. In **2** and **3a**, the HOMO is seen to be that MO (a',π) having large coefficients at the benzene ring. In **1**, the other benzene π orbital (a'') is the HOMO due to strong interaction with the methoxyl groups. The fluorine substituents in **3a** shift all bands toward higher energies. The resultant homoconjugation (for **2**, $\beta = -0.318$ eV) leads to spectroscopically (^{13}C NMR)[6] recognizable polarization of the exocyclic double bond.[7]

At the experimental level, we have observed that **1** and **2** are attacked by $^1O_2$ predominantly from the anti direction (leading to **5-OH**), but that this stereoselectivity is appreciably reversed in the case of **3a** and **3b** (Table II). The stereochemistries of

the products were assigned on the basis of (a) the higher field position of the methyl signals in **5**, a circumstance attributable to shielding by the underlying aromatic ring;[8a] (b) upfield shifting of the exo protons on the ethano bridge in **4** relative to **5** as a result of the anisotropy of the isopropenyl group;[8b] and (c) lanthanide shifting with Eu(fod)$_3$ in selected examples.
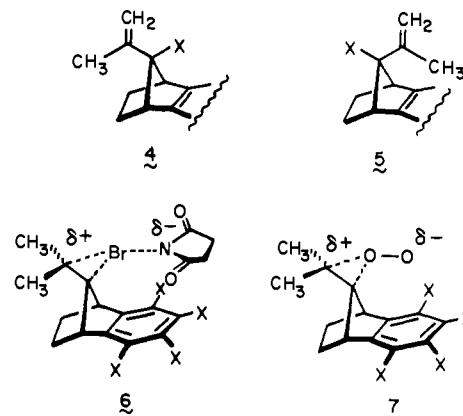
Clearly, the observed *variable* stereoselectivity cannot be dictated by steric effects, but must have an electronic origin. To permit more precise definition of the parameter(s) responsible, recourse was made to model electrophilic reactions proceeding through more well-understood transition states. In the first example, **1–3** were treated with N-bromosuccinimide in a glyme–water (9:1) solvent system at 25 °C. The relative proportions of **4-Br** and **5-Br** (Table II) proved identical within experimental error with those realized for $^1O_2$. On exposure of **1–3** to N-methyltriazolinedione (CH_2Cl_2, 25 °C), an ene reaction believed to proceed through a highly dipolar transition state[9] ensues. Again, no derivation from the previously established distribution of **4** and **5** (now X = N-methylurazole) was seen (Table II).

The peracid oxidation of olefins is an electrophilic process which has less propensity than any of the above for charge buildup in the activated complex.[10] With m-chloroperbenzoic acid (CH_2Cl_2, 25 °C), **1–3** were smoothly oxidized to mixtures of epoxides enriched in the anti isomer in every instance (Table II).[11]

The observed switch in the syn/anti ratios suggests the possible operation of several mechanisms. The predominant anti addition in the case of **1** and **2** is explainable in terms of the shape of ψ_2, the wave function having a large coefficient at the *exo*-methylene group. The considerable mixing of this bond with a high lying σ orbital causes a distortion of the π orbital in such a way that overlap with an orbital approaching from the anti side is favored (Figure 1).

However, when electron-withdrawing substituents are positioned on the benzene ring, a second stereoselectivity determining factor can gain importance. Thus, such groups as fluoro and chloro effectively reduce the electron density above and below the aromatic ring as dramatically illustrated by contour

Table II. Electrophilic Additions to the 7-Isopropylidenebenzonorbornenes **1–3**

	singlet oxygen[a]				NBS, H_2O–glyme[a]		N-methyltri-N-azolinedione[a]		m-chloroperbenzoic acid[a]	
	CH_3OH[b]		CH_2Cl_2[c]							
compd	syn	anti[d]	syn	anti[d]	syn	anti[d]	syn	anti[d]	syn	acid[a]
1	17	83	21	79	14	86	16	84	11	89
2	24	76	20	80	19	81	19	81	17	83
3a	56	44	54	46	55	45	57	43	37	63
3b	59	41	52	48	58	42	59	41	31	69

[a] Reagent. [b] Rose bengal was used as sensitizer. [c] The sensitizer in these experiments was polymer-bound rose bengal (Photox). [d] The percentage values given were obtained from carefully integrated ^1H NMR spectra of reaction mixtures prior to isolation and characterization of the individual components and are normalized to 100%. In the case of the singlet oxygen reactions, analysis was made only after NaBH$_4$ reduction of the allylic hydroperoxide mixtures.
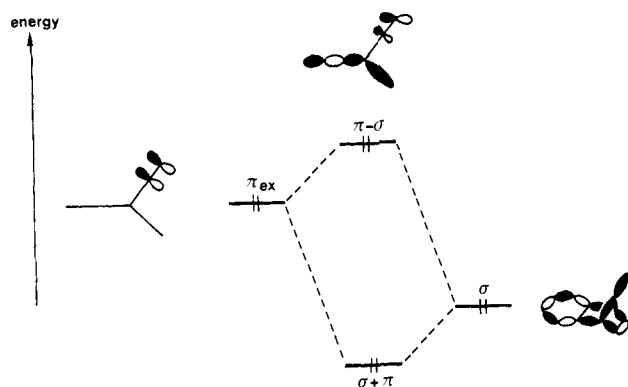
Figure 1. Interaction diagram between the exocyclic π orbital and a high lying σ orbital to visualize the distortion of the resulting linear combination.

diagram plots of the calculated electrostatic potential fields (EPF).[12] The plot for **3a** is seen to display an intensely positive region above and below the benzene ring, while those for **1** and **2** reflect the absence of meaningful long-range electrostatic interaction. Accordingly, the transition states for uniparticulate electrophilic additions[13] and for those biparticulate electrophilic processes where closely trailing δ^- fragments are involved can be expected to receive added stabilization when the attacking reagent is positioned above the electron-deficient benzenoid portions of **3a** and **3b**. The transition states which develop during syn attack by *N*-methyltriazolinedione[9] and *N*-bromosuccinimide (**6**)[14] are representative of our thinking. Since peracid oxidations do not proceed by way of similar charge-separated activated complexes,[10] they are not similarly affected. The stereoselectivity of $^1O_2$ attack is essentially identical with that of the first two of these model reactions and, therefore, the intervention of transition states such as **7** is inferred.

A third factor may come into play if the π electrons of the exocyclic double bond experience partial rehybridization as they come under the influence of the electrostatic field provided by the approaching electrophile. Stabilizing bishomoconjugative interaction can develop when the benzene ring is unsubstituted or endowed with electron-donating groups, and favor anti attack. This effect would be negated by the presence of electron-withdrawing aryl substituents, as solvolytic studies on *anti*-7-benzonorbornenyl sulfonates have so convincingly demonstrated.[15]

Whatever the situation, the singlet oxygenations of the 7-isopropylidenenorbornenes are not proceeding under frontier orbital control, the customarily low activation energy of $^1O_2$ ene reactions[16] notwithstanding, nor is the HOMO (π_s–π_{ex}) responsible for the NBS and urazole reactions. This conclusion is supported by the finding that **1** and **2** give nearly identical syn/anti ratios despite the existing differences in the nature of their HOMO's.

To the extent that the electrophile–stereoselectivity profiles employed herein provide valid model comparisons, the intervention of perepoxide-like transition states are directly implicated.

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Hydridocyclophosphazenes. Synthesis via Organocopper Reagents

Sir:

The reactions of organometallic reagents with cyclic phosphazenes, $(NPX_2)_{3 or 4}$ (X = Cl or F) normally yield partially alkylated or arylated cyclic phosphazenes and ring-opened species.[1-3] We report here the unusual reaction of methylmagnesium chloride with hexachlorocyclotriphosphazene, $(NPCl_2)_3$, in tetrahydrofuran in the presence of $(n\text{-}Bu_3PCuI)_4$, which gave, after treatment with 2-propanol, high yields (76%) of an air- and moisture-sensitive crystalline product identified as I.

A typical experimental procedure was as follows. Hexachlorocyclotriphosphazene (5.0 g, 0.014 mol) and $(n\text{-}Bu_3\text{-}CuI)_4$ (3.0 g, 0.0019 mol) were stirred together in tetrahydrofuran (150 mL) at 0 °C, and MeMgCl (25 mL of a 3.0-mol solution in THF) was added dropwise over 30 min. After this