

References and Notes

- (1) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
- (2) An average geometry was derived from the coordinates of two independent molecules of THF in the structure of η -dliminobis(pentacarbonylchromium)-tetrahydrofuran solvate, as reported by G. Hutter, W. Gartzke, and K. Allinger, *J. Organomet. Chem.*, **91**, 47 (1975).
- (3) $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o^2)]^{1/2}$, where $w = 4F_o^2 / \sigma(F_o^2)$.
- (4) W. D. Hounshell, D. A. Dougherty, J. P. Hummel, and K. Mislow, *J. Am. Chem. Soc.*, **99**, 1916 (1977).
- (5) For a more favorable comparison with the X-ray results, the enantiomer of the structure calculated by the EFF method⁴ has been considered.

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Received April 5, 1978

Stereoselective Addition of Singlet Oxygen to 7-Isopropylidenenorbornene Derivatives. Possibility of π -Orbital Distortion in the Homoconjugated System¹

Sir:

Because of its relationship to 7-norbornenyl cation,² anion,³ radical,⁴ and 7-norbornenyldiene,⁵ 7-alkylidenenorbornene has received considerable attention. Heilbronner and Martin reported the photoelectron spectrum of 7-isopropylidenenorbornene and estimated the value of orbital splitting due to interaction between the exocyclic double bond and the C₂-C₃ double bond.⁶ Recently Hoffmann and Kurz observed polarization of the exocyclic double bond by measurement of ¹³C NMR spectrum of 7-methylenenorbornene⁷ and established that homoconjugation induces the polarization. It is also anticipated that homoconjugation will induce a distortion of the π orbital of the exocyclic double bond, so that the two sides of the exocyclic double bond will have unequal electron densities. We considered that this distortion could be revealed by chemical reactions, if the following conditions could be satisfied: (1) the chemical reaction should be sufficiently exothermic so that, according to the Hammond postulate,⁸ the transition-state structure would resemble that of the reactant; (2) the reagent should attack only the exocyclic double bond, but not the double bond in norbornene. For these reasons, singlet oxygen⁹ was chosen as a reagent, and the reactions with 7-isopropylidenenorbornene (**1**),¹⁰ the benzo derivative (**2**),¹¹ and the dimethoxycarbonyl derivative (**3**)¹² were investigated.

When a solution of **1**, **2**, or **3** in acetonitrile was photooxidized by irradiation with a 500-W tungsten-Brom lamp in the

Scheme I

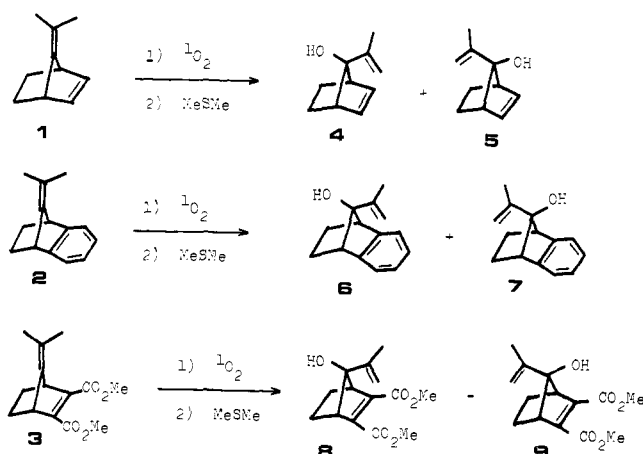
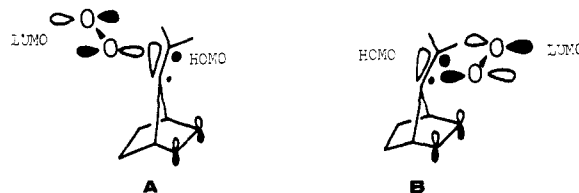


Table I. Yields and Properties of the Products

starting compd	rxn time min	product (% yield; mp, °C)		product, chem shift (δ) of H _{5-exo}	
		anti	syn	anti	syn
1	15	4 (76; ^a oil)	5 (16; ^a 52-54)	4, 2.06 (m) ^c	5, 1.77 (m) ^c
2	20	6 (59; ^a 129-130)	7 (21; ^a 81-83)	6, 2.31 (m) ^d	7, 1.99 (m) ^d
3	120	8 (49; ^b 74-76)	9 (41; ^b oil)	8, 2.22 (m) ^c	9, 1.90 (m) ^c

^a Determined by NMR. ^b Isolated yield. ^c Measured in CCl₄. ^d Measured in CDCl₃.

presence of methylene blue as a sensitizer, followed by reduction with dimethyl sulfide¹³ in methanol, a pair of anti (**4**, **6**, and **8**) and syn (**5**, **7**, and **9**) alcohols was obtained (Scheme I). The yields and properties of the products are shown in Table I, along with the reaction conditions. The stereochemistries of **4**, **5**, **6**, and **7** were assigned by use of the NMR shift reagent, Eu(fod)₃. In addition, as shown in Table I, the chemical shift of the H_{5-exo} protons in all of the syn alcohols appear upfield with respect to the H_{5-exo} in the anti alcohols,¹⁴ because of anisotropic effect of the isopropenyl group. It is of interest to note that the product ratio of the anti to syn alcohols increases in the sequence of **3**, **2**, and **1**. Steric effects of the substituents attached to the C₂ and C₃ carbon, or of the H_{5-exo} protons, do not provide a rationalization for the observed stereoselectivity. A priori, this observation may be explicable by one or more of following factors. (1) The exocyclic double bond bends toward the C₂-C₃ double bond with variation of the angle $\angle C_7C_1C_2$, to increase through-space interaction. (2) The attacking molecular oxygen would experience antibonding interaction with the C₂-C₃ double bond on the syn side.¹⁵ (3) The π orbital of the exocyclic double bond distorts to the anti side by mixing in a σ orbital at the 7 position owing to the perturbation caused by the C₂-C₃ double bond. Concomitantly the geometry of the exocyclic double bond may change owing to hybrid deviation, sp² \rightarrow sp^{2+ α} .¹⁶ We could conclude that factor 1 is not important, because Heilbronner found a small value of IP_{v,2} - IP_{v,1} (0.5 eV) by measurement of the photoelectron spectrum for **1**.⁶ To differentiate between the other two factors, ¹³C NMR spectra of **1**, **2**, and **3** were measured (carbon chemical shifts, δ , at the C₇ and C₈: **1**, 148.6, 106.9; **2**, 148.6, 110.9; **3**, 143.9, 111.9).^{7,17-19} The larger the polarization (Δ , C₇ - C₈: **1**, 41.7; **2**, 37.7; **3**, 32.0), the more the product ratio, anti to syn, increases. The correlation with ¹³C NMR spectra would seem to indicate that factor 3 is more important than factor 2, although factor 2 is not excluded completely. It is possible that stereoselectivity arises from the orbital distortion resulting from the mixing of the π_7^* and σ_7 orbitals.²⁰ Thus, the HOMO represented by $\pi_7 - a\pi_2 - b\pi_7^* + c\sigma_7$ is distorted to the anti side, where mixing coefficients b and c will increase as the coefficient a increases (Figure 1). Orbital interactions in the perepoxide-like transition state are depicted in A and B.



Similar stereoselectivity was also observed in the case of crossed longicyclic compounds²¹ **10** and **11**. After the reduction of the oxidative products of **10**, alcohol **12**,^{22,23} in which the hydroxyl group is anti to the double bond, was produced in better yield (53%) than syn alcohol **13**^{22,23} (33%) (Scheme II).

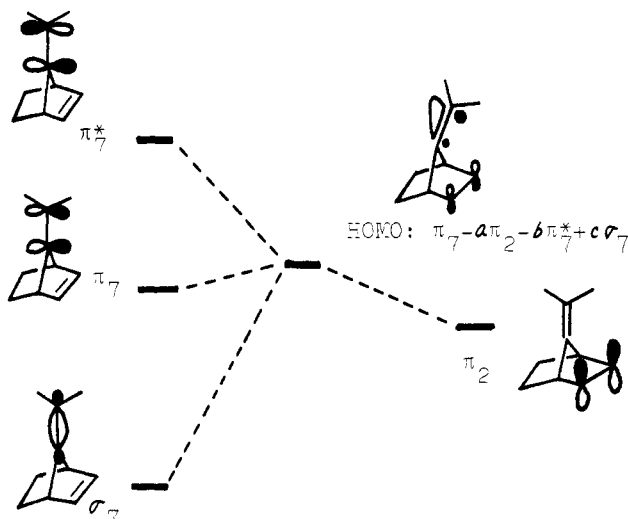
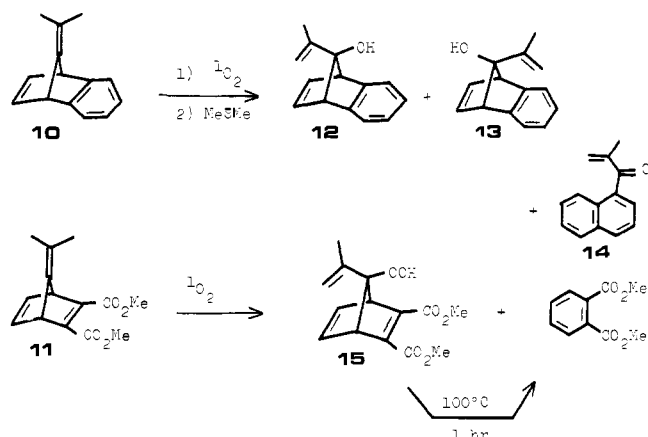


Figure 1. Mixing pattern of π_2 , π_7^* , and σ_7 orbitals with the π_7 orbital.

Scheme II



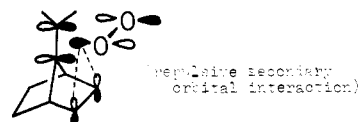
These products are accompanied by the fragmentation product, α -naphthylisopropenyl ketone (**14**)²² (4%). The photooxidation of **11** afforded only anti hydroperoxide **15**²⁴ (80%) and dimethyl phthalate, which was also produced in high yield from **15** by heating in CDCl_3 . No syn hydroperoxide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

References and Notes

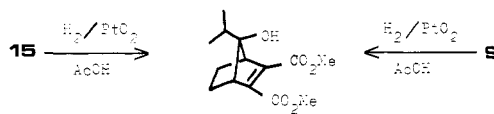
- (1) Organic Photochemistry, 43. Part 42: T. Mukai and Y. Yamashita, *Tetrahedron Lett.*, 357 (1978). After submitting this paper, we learned that L. A. Paquette et al. (*J. Am. Chem. Soc.*, following paper in this issue) had done an extensive study along the line similar to ours. We thank Professor Paquette for communicating their results to us in advance of the publication.
- (2) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955). S. Winstein and C. Ordonneau, *ibid.*, **82**, 2084 (1960).
- (3) J. K. Stille and K. N. Sannes, *J. Am. Chem. Soc.*, **94**, 8489 (1972).
- (4) J. K. Kochi, P. Bakuzis, and P. J. Krusic, *J. Am. Chem. Soc.*, **95**, 1516 (1973); T. Kawamura, Y. Sugiyama, M. Matsunaga, and T. Yonezawa, *ibid.*, **97**, 1629 (1975).
- (5) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968). R. A. Moss and C.-T. Ho, *Tetrahedron Lett.*, 3397 (1976), and references cited therein.
- (6) E. Heilbronner and H.-D. Martin, *Helv. Chim. Acta*, **55**, 1490 (1972). The small value of $\text{IP}_{v,2} - \text{IP}_{v,1}$ can be rationalized by the σ -orbital mixing (factor 3).
- (7) R. W. Hoffmann and H. Kurz, *Chem. Ber.*, **108**, 119 (1975), and references cited therein.
- (8) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

- (9) R. W. Denny and A. Nickon, "Organic Reaction", Wiley, New York, N.Y., 1973, p 133; D. R. Kearns, *J. Am. Chem. Soc.*, **98**, 6554 (1969); S. Inagaki and K. Fukui, *ibid.*, **97**, 7480 (1975); M. J. S. Dewar and W. Thiel, *ibid.*, **97**, 3978 (1975); A. A. Frimer, P. D. Bartlett, A. F. Boschung, and J. G. Jewett, *ibid.*, **99**, 7977 (1977).
- (10) H.-D. Martin and D. Forster, *Angew. Chem., Int. Ed. Engl.*, **11**, 54 (1972).
- (11) R. Muneyuki and H. Tanida, *J. Am. Chem. Soc.*, **31**, 1988 (1966). P. L. Watson and R. N. Warrener, *Aust. J. Chem.*, **26**, 1725 (1973).
- (12) V. Kurz and R. Ruhmann, *Justus Liebigs Ann. Chem.*, **566**, 1 (1950).
- (13) M. A. P. Dankleff, R. Curci, J. O. Edwards, and H. Y. Pyun, *J. Am. Chem. Soc.*, **90**, 3209 (1968).
- (14) Similar upfield shift was observed: J. A. Berson, T. T. Miyashi, and G. Jones, II, *J. Am. Chem. Soc.*, **96**, 3468 (1974).
- (15) (a) The idea of this secondary orbital interaction described below was suggested by Professor K. N. Houk, to whom the authors express their gratitude. (b) P. Caramella, G. Cellarino, A. C. Coda, A. G. Invernizzi, P.



Grunanger, K. N. Houk, and F. M. Albini, *J. Org. Chem.*, **41**, 3349 (1976), and references cited therein. See also H. R. Pfandler, H. Tanida, and E. Haselbach, *Helv. Chim. Acta*, **42**, 383 (1974); E. Haselbach and M. Rossi, *ibid.*, **59**, 278 (1976).

- (16) This does not necessarily mean that the real geometry of **1**, which would be anticipated by taking into account of all occupied orbitals of **1**, may change owing to the hybrid deviation. However, during approach of singlet oxygen, the particularly important orbital (i.e. HOMO) should be stabilized by the geometrical change. This is compatible with INDO calculation for 7-methylenenorbornene which was done by Professor K. Fukui (unpublished result). The authors express their gratitude to him for his helpful suggestion.
- (17) Chemical shifts in parts per million to lower field from Me_4Si in CDCl_3 .
- (18) D. E. Dorman, M. Jautelat, and J. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).
- (19) K. Tori, M. Ueyama, T. Tsuji, H. Matsumura, H. Tanida, and H. Iwamura, *Tetrahedron Lett.*, 327 (1974).
- (20) S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, **98**, 4054 (1976).
- (21) M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 6193 (1971). See also S. Inagaki, H. Fujimoto, and K. Fukui, *ibid.*, **98**, 4693 (1976).
- (22) The yields of **12**, **13**, and **14** were sensitive to moisture or temperature of treatment (yields described in the sentence are at 20 °C). However, the product ratio of **12** to **13** was always nearly constant.
- (23) Configuration of the hydroxyl group of **12** or **13** was determined by use of $\text{Eu}(\text{fod})_3$.
- (24) Under the reduction condition, hydroperoxide **15** gave an unidentified product $\text{C}_{14}\text{H}_{16}\text{O}_5$ instead of the expected alcohol. Stereochemistry of **15** was determined as shown.



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Received March 1, 1978

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 peroxide intermediates. Although computational methods have demonstrated the workability of frontier electron theory and the preferred energetics of peroxide intervention,¹ clear-cut experimental substantiation of mechanism is still lacking and, in fact, the

[†] Dedicated to Professor M. S. Newman on the occasion of his 70th birthday.