a Dreyfus Teacher–Scholar Grant recipient, 1975–1980 and R.D.S. acknowledges support from the Massachusetts Institute of Technology Cabot Solar Energy Fund.

References and Notes

(1) Ru$_3$(CO)$_9$(PPh$_3$)$_3$ and Ru(CO)$_4$PPh$_3$ were prepared by the method of B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organomet. Chem.*, **67**, C75 (1974), and *J. Chem. Soc., Dalton Trans.*, 1876 (1976).
(2) M. Dartiguenave, Y. Dartiguenave, and H. B. Gray, *Bull. Chim. Soc. Fr.*, **12**, 4223 (1969).
(3) J. P. Candlin and A. C. Shortland, *J. Organomet. Chem.*, **16**, 289 (1969).
(4) R. A. Levenson, Ph.D. Thesis, Columbia University, 1970.
(5) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).
(6) R. G. Austin, R. S. Paonessa, P. J. Giordano, and M. S. Wrighton, *Adv. Chem. Ser.*, **No. 168**, 189 (1978).
(7) G. C. Bond and M. Hellier, *J. Catl.*, **4**, 1 (1965).

James L. Graff, Robert D. Sanner, Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Site Specificity in the Singlet Oxygen–Trisubstituted Olefin Reaction

Sir:

We report that the reaction of singlet oxygen with simple trisubstituted olefins shows a general preference for hydrogen abstraction on the more highly congested side of double bonds.

Many experimental aspects of the singlet oxygen reaction are well known.[1] Singlet oxygen is, for example, strongly electrophilic, showing a clear preference for highly substituted, electron-rich olefins;[2] the overall reaction occurs in the classical "ene" manner with invariable shift of the double bond;[3] and very low isotope effects are found variously reported from 1.05 to 1.96.[4] Despite this considerable body of data, no mechanistic rationalization is generally agreed upon. Concerted ene pathway[3,5] perepoxide intermediates,[2,6] diradicals,[7] and gradations in between all find experimental and theoretical support.

Studies of site specificity in the singlet oxygen ene reactions have received little attention. It is generally recognized that methyl and methylene hydrogens are reactive, and that isopropyl C–H and certain conformationally inaccessible hydrogen atoms are not.[3,8] Other more subtle features remain unexplored.

In this paper we report a general type of selectivity in the reactions of trisubstituted olefins. This selectivity does not appear to have been previously recognized and may hold important implications in the mechanism of the reaction.

In a series of trisubstituted olefins shown in Chart I, we find a strong preference for regiospecificity favoring hydrogen abstraction on that side of an olefin with two substituents. Olefins **1** and **2** clearly illustrate this point. The same trend is also noted in compounds **3**, **4**, and **5**, where reaction at the labeled site on the monosubstituted side is slight.[9] This heightened reactivity is demonstrated again in compound **6** and impressively so in **7**, even though one of the groups (cyclopropyl) is unreactive.

The presence of polar substituents does not alter this basic relationship (**8** and **9**, taken from Conia et al.[10] and **10** and **11** from this work). The fact that the cyclopropyl can be induced to react in **8** is probably a superposition of our effect and Goddard's anomeric effect explanation, recently published.[7]

This trend persists in reactions of styrene derivatives **12** and **13**, where reactivity of the methylene and methyl hydrogens is clearly dependent on their environment.

**Chart I.** Regioselectivity in the Reaction of Singlet Oxygen with Trisubstituted Olefins[a]
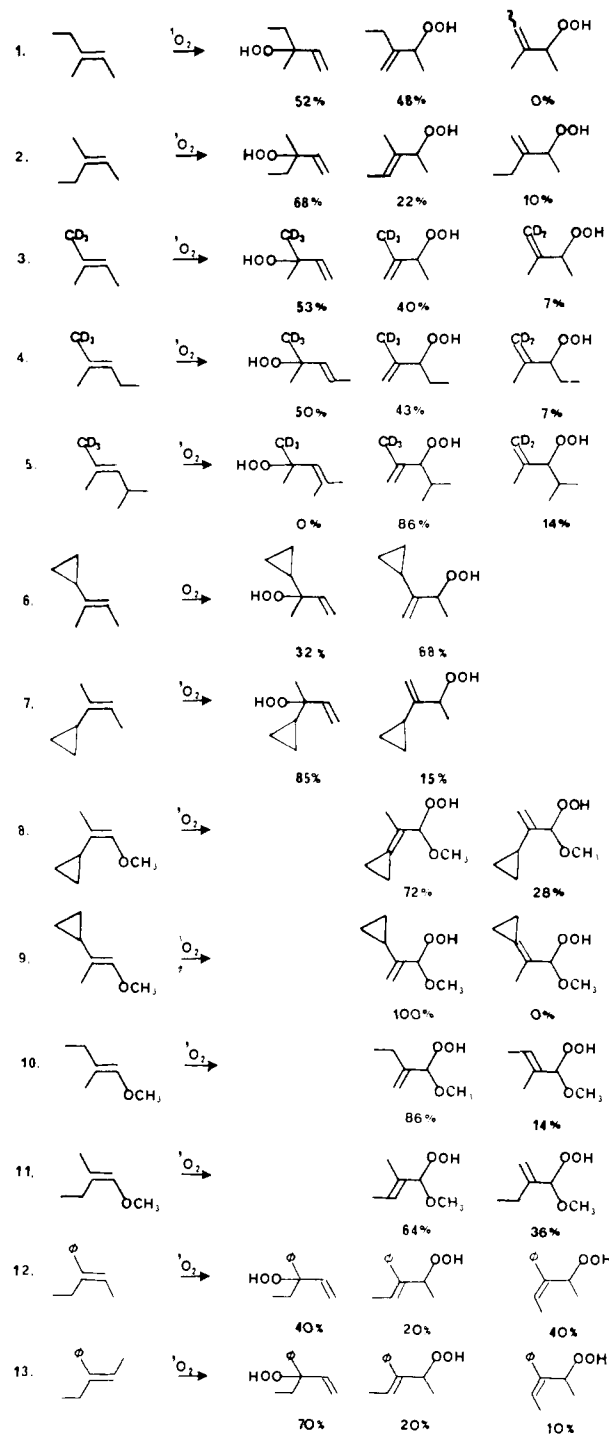
[a] The photooxidations were carried out at −10 °C, in acetone-d_6 with Rose Bengal as sensitizer. A Sylvania 275-W sun lamp was used for these experiments. Analyses were carried out by direct NMR examination of the hydroperoxide immediately after reaction. Reduction with dimethyl sulfide is then followed by NMR examination of the alcohol. Where appropriate the measurements were checked by gas chromatography. Entries 1 and 3 were also photooxidized in benzene-d_6 with tetraphenylporphyrin. Precisely identical results were obtained.

We cannot accommodate these results into a simple six-center concerted ene mechanism. Indeed, steric considerations in a concerted transition state would appear to favor results precisely opposite to ours. As shown below our results would require favoring the transition state (a) with pseudoaxial R

© 1979 American Chemical Society

groups in the reaction of $RCH{=}C(CH_3)_2$ derivatives (**3–5**, for example).

     a   b
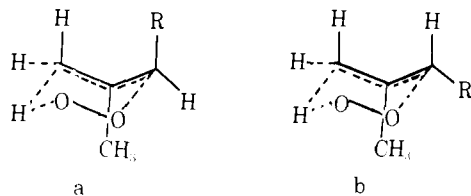
Likewise it is not clear why a peroxide intermediate should *favor* orientations which would lead to the observed products. Fukui[11] has argued that formulation c is favored over d where polar substituents (i.e., $R_3 = OCH_3$) are concerned, but this argument does not easily extend to the alkyl cases presented here. Similarly, Goddard's[7] explanation of Conia's results (**8**

     c   d
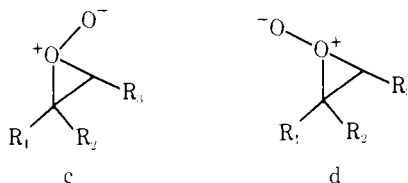
and **9**) based on conformational preferences in a diradical relies on the presence of the $-OCH_3$ grouping and again will not easily extend to the other examples presented here, but is probably important in the systems analyzed.

These results clearly demonstrate that the overall reactivity of a given C–H bond is greater on the more crowded side of the trisubstituted olefin. These results do not obviously support any of the current proposals for the singlet oxygen ene reaction. The observation is sufficiently general, however, that it must be incorporated into any ultimately successful rationalization of this reaction.

References and Notes

(1) (a) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (b) A. M. Trozzolo, Ed., *Ann. N.Y. Acad. Sci.*, **171**, 50 (1970).
(2) K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965).
(3) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
(4) (a) K. R. Kopecky and J. H. van de Sande, *Can. J. Chem.*, **50**, 4034 (1972); (b) A. Nickon et al., *J. Am. Chem. Soc.*, **94**, 5517 (1972); (c) L. M. Stephenson, D. E. McClure, and P. K. Sysak, *ibid.*, **95**, 7888 (1973).
(5) (a) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **83**, 1498 (1961); (b) A. Nickon, N. Schwartz, J. B. Di Giorgio, and D. A. Widdowson, *J. Org. Chem.*, **30**, 1711 (1965); (c) A. Nickon and W. L. Mendelson, *Can. J. Chem.*, **43**, 1419 (1965); (d) C. S. Foote, *Pure Appl. Chem.*, **27**, 635 (1971).
(6) (a) D. B. Shart, Abstracts, 139th National Meeting of the American Chemical Society, New York, Sept 1960, p 79P; (b) W. Fenical, D. R. Kearns, and P. Radlick, *J. Am. Chem. Soc.*, **91**, 7771 (1969); (c) F. McCapra and I. Beheshti, *J. Chem. Soc., Chem. Commun.*, 517 (1977); (d) M. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **97**, 3978 (1975).
(7) L. B. Harding and W. A. Goddard, *Tetrahedron Lett.*, **No. 8**, 747 (1978).
(8) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **81**, 6330 (1959).
(9) One might argue that **3–5** are simply consistent with a large isotope effect. An effect on the order of $K_H/K_D = 5{-}7$ would be required, however, substantially larger than any previously observed. Demonstrations which show the isotope effect to be small in compound **3** come from the recognition that the ratio of tertiary to secondary hydroperoxide from trimethylethylene, 50:50, is almost exactly the same as in our trideuteriomethyl derivative, 53:(40 + 7) = 53:47.
(10) G. Rousseau, G. LePerche, and P. M. Conia, *Tetrahedron Lett.*, **No. 29**, 2517 (1977).
(11) S. Inagaki, H. Fujimoto, and K. Fukui, *Chem. Lett.*, 749 (1976).

Michael Orfanopoulos, Sr. M. Bellarmine Grdina
L. M. Stephenson*
Department of Chemistry, Case Western University
Cleveland, Ohio 44106
Received June 26, 1978

Book Reviews

Structure Determination by X-Ray Crystallography. By M. F. C. LADD (University of Surrey) and R. A. PALMER (University of London). Plenum Press, New York. 1977. xvi + 393 pp. $29.50.

This book is a welcome addition to the field of single crystal X-ray diffraction. It provides basic introductory material in an area which has few texts for the novice. Main topics discussed include crystal geometry, space groups, diffraction theory, Fourier theory, film techniques, and approaches to the phase problem. Many examples and drawings are included to clarify the more difficult material. The inclusion of many crystallographic problems and solutions using real chemical compounds has helped greatly to bridge the gap between theory and practice for the nonprofessional crystallographer.

     William M. Butler, *University of Michigan*

Minicomputers and Large Scale Computations. Edited by PETER LYKOS (Illinois Institute of Technology). American Chemical Society, Washington, D.C. 1977. xi + 239 pp. $21.50.

This collection of papers presented at the June 1, 1977 Symposium in Montreal describes a number of scientific problems which have been approached using minicomputers. Several papers deal with complex mathematical problems including: simultaneous partial differential equations, algebraic eigenproblems, and general numbercrunching with a minicomputer. Other topics include large scale simulation, theoretical chemistry calculation, molecular dynamics, APL and analysis, vector processors, fluid mechanics, process design, and molecular orbital calculation. Computer-aided data acquisition and analysis for both X-ray structure and cloud chamber studies are included.

     William M. Butler, *University of Michigan*

Carboniogenic Activity of Zeolites. By PETER A. JACOBS (Katholieke Universiteit Leuven, Belgium). Elsevier, Amsterdam and New York. 1977. xvi + 253 pp. $29.50.

Zeolites are crystalline aluminosilicates with a three-dimensional framework. They are among the most important industrial catalysts. Because of their unique porous crystalline properties, they also have considerable scientific interest. This volume covers a great deal of ground, ranging from crystal structure to the use of zeolites in industrial processes. The principal aim is to review developments between 1970 and 1975. (The earlier literature is well covered by other books and reviews, and there is no need for repetition.) Nevertheless, this book is well balanced, giving a complete picture even to a reader unacquainted with earlier literature. The volume should prove to be an excellent reference for students and researchers interested in catalysis over zeolites. The author is well known for his work in the field of zeolites.

The first of five chapters briefly describes the crystal chemistry of zeolites of catalytic importance. This chapter is more superficial then the others; however, an adequate bibliography is attached so the reader can find more details, if needed.

The second chapter presents an overview of industrial catalytic processes using zeolites. Catalytic cracking, hydroisomerization, hydrocracking, selective forming, (sic!, instead of "Selectoforming"), and low temperature isomerization and disproportionation of aromatics are discussed briefly, perhaps too briefly.

The third chapter, characterization of the acid sites in zeolites, contains an excellent table summarizing the various hydroxyl groups present in zeolites. Acid activity is associated with the $3650\text{-}cm^{-1}$ OH infrared band.