the peroxide bridge. Likewise, the finding of label in the peroxide bridge of ozonides formed by ozonolysis of olefins in the presence of labeled aldehydes suggests the operation of an additional path to ozonide as reported earlier.[10,16]

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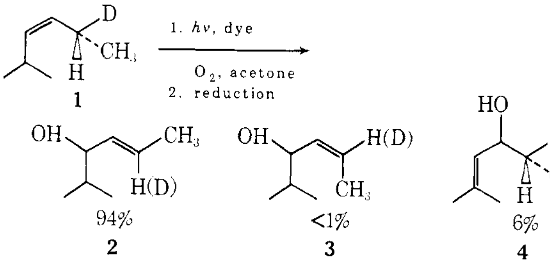
Stereochemistry of the Singlet Oxygen Ene Reaction with Olefins

Sir:

We wish to report the complete determination of the stereochemistry of the reaction of singlet molecular oxygen with a disubstituted olefin, (*R*)-(−)-*cis*-2-deuterio-5-methyl-3-hexene (**1**).[1,2] This optically, and geometrically, pure olefin is well suited to test the stereochemical requirements of this classical ene-like reaction. For example, in singlet oxygenations leading from olefin **1** to the predominant trans allylic alcohol **2**, a conventional ene mechanism would require that abstraction of the proton and concomitant carbon–oxygen bond formation give only (*S*)-**2**, while removal of deuterium and concomitant carbon–oxygen bond formation would lead to (*R*)-**2**. Our results offer clear support for a mechanism involving rate-determining attack on the double bond and are not consistent with our expectations for such an ene mechanism.



Rose Bengal sensitized oxygenation of **1** in oxygen-saturated acetone led to three products. For analytical purposes, the major product, trans allylic alcohol **2**, was converted to two sets of derivatives, the (−)-MTPA esters,[3] **5**, and the trimethylsilyl ethers, **6**.

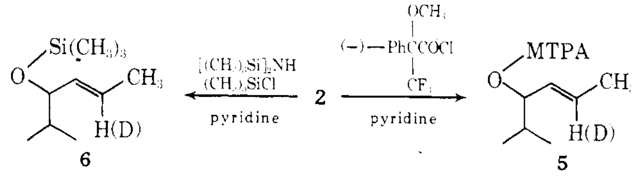


Table I. Analysis of Major Photooxygenation Product **2**

Solvent	D/H ratio[a]	D/H ratio[b]	*S*/*R* ratio[c]	*S*/*R* ratio[d]	Relative amounts[e] of R_H	R_D	S_D	S_H
Acetone	1.08	1.0	1.1	1.0	1	0	1	0
Methanol	2.3	2.0	1.1	1.0	2	1	3	0

[a] The ratio of monodeuterio **2** to perprotio **2** by mass spectral analysis of **6**. [b] The ratio of **2** containing deuterium at C_2 to **2** containing a proton at C_2 by average of nmr integration of **2**, **5**, and **6**. [c] By optical rotation of **2**; $[\alpha]^{20}D$ 1.1–1.5°. [d] By integration of fluorine signal in diastereomeric (−)-MTPA derivatives **5**. [e] By analysis of cmr spectrum of **5**.

Four products corresponding to **2** are conceivable,[4,5] with either *R* or *S* enantiomer containing either D or H at C_2. We designate these possibilities as R_H, R_D, S_D, or S_H. Treatment of the enantiomeric pair (*R*)-**2** and (*S*)-**2** with MTPA chloride converts them into a diastereomeric pair of MTPA esters. Since the C_2 carbon magnetic resonance lines appear at different positions in these two diastereomers, it is possible to assay the relative amounts of all four products, R_H, R_D, S_H, and S_D, in any reaction mixture.[6] The data of Table I indicate that only R_H and S_D are found in the singlet oxygenation of **1** in acetone and that they are formed in approximately equal amounts.

The mechanistic significance of this result may be grasped most easily by reference to the four transition-state representations shown below. Reactions a and a′ represent the concerted ene mechanism with attack from both the top (a) and the bottom (a′) of the incipient allyl unit shown. Note that a will lead to (*R*)-alcohol with a proton at C_2 while a′ leads to (*S*)-alcohol with a deuterium at C_2, in accord with the experimental findings. However, a complete rationalization of the experimental results would require that the concerted "ene" mechanism show very small (or zero) deuterium isotope effects.

For convenience, we represent mechanistic possibilities involving rate-determining attack on the double bond with the perepoxide[7] intermediates b and b′. Rationalization of the experimental results with this mechanism requires only[8] that little (or no) preference be shown in attacking the diastereotopic faces of the double bond in olefin **1**. We find the assumption that the chiral center in olefin **1** would induce little or no measurable asymmetry at C_4 in reactions on the double bond completely reasonable. For this reason and because "ene" reactions a and a′ would require a near zero primary deuterium isotope effect, we favor mechanisms involving rate-determining double bond attack, typified by b and b′.

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(1) (*R*)-(−)-*cis*-2-Deuterio-5-methyl-3-hexene (**1**) was prepared in several steps from (*S*)-(−)-ethyl lactate. Traces of *trans*-**1** were removed from the final reaction mixture by vpc ($AgNO_3$ in ethylene glycol, room temperature) to give *cis*-**1**, $\alpha^{20}D$ −0.225 (neat, 1dm). Mass spectral analysis showed approximately 90% monodeuteriation while repeated nmr integration showed 1.00 ± 0.05 protons at C_2. Ozonization of **1** gave 2-deuteriopropionic acid. The ORD of this acid was superimposable on points published[2] for enzymatically prepared material.

(2) J. Retey, A. Umani-Ronchi, and D. Arigoni, *Experientia*, **22**, 72 (1966).

(3) J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969). MTPA is α-methoxy-α-trifluoromethylphenyl acetate.

(4) We deduce from the experiments of Bartlett, Kuna, and Levene[5] that alcohol **2** is (*S*)-(+). Our resolution *via* the strychnine salt of the half acid phthalate gave **2** with $[\alpha]^{20}D$ 28.0 (*c* 5.37, ethanol) (lit.[5] gives $[\alpha]^{25}D$ 22.2 (*c* 14.66, ethanol)). We presume that the presence of the deuterium atom will influence these readings only slightly.

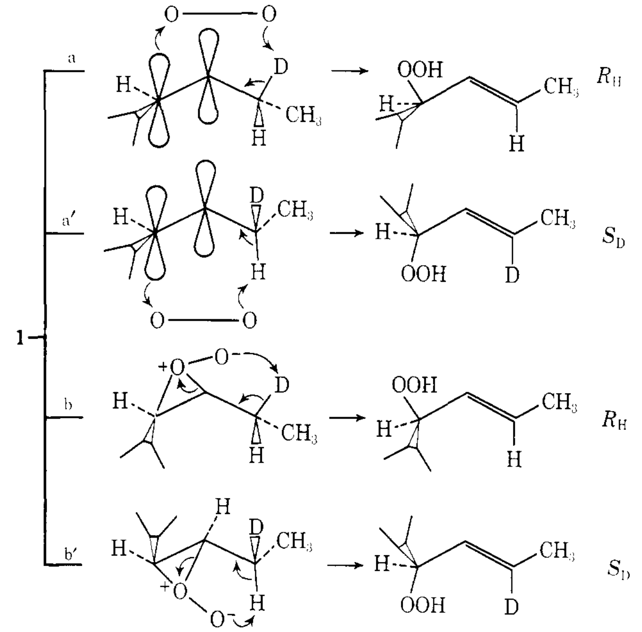
(5) P. D. Bartlett, M. Kuna, and P. A. Levene, *J. Biol. Chem.*, **118**, 503 (1937).

(6) One anticipates an intensity loss of ~10 in a proton decoupled ^{13}C resonance when deuterium replaces all the proton(s) on that ^{13}C, due to loss of nuclear Overhauser enhancement and introduction of splitting due to ^2H nuclear spin of 1.

(7) D. B. Sharp, Abstracts, 139th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 79P. K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965). W. Fenical, D. R. Kearns, and P. Radlik, *J. Amer. Chem. Soc.*, **91**, 7771 (1969).

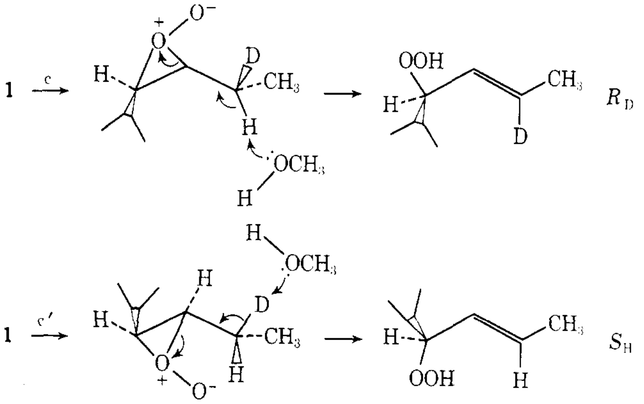
(8) In leading to trans product, perepoxide (b) is constrained to remove only D, and likewise b′ only H; thus, the D/H ratio must match the *S*/*R* ratio in this case as well as in the "ene" mechanism.

Nickon, *et al.*,[9] and Kopecky, *et al.*,[10] have also found small isotope effects in singlet oxygen reactions. Such results have been interpreted, particularly by Nickon, to support the concerted ene mechanism with hydrogen (deuterium) abstraction occurring late on the reaction coordinate.



The results obtained by treating olefin **1** with singlet oxygen in methanol make the concerted ene mechanism more difficult to accept[11] (see Table I). The D/H ratios now no longer match the S/R ratios, primarily due to the appearance of product R_D at the expense of R_H.

This uncoupling of the enantiomeric and isotopic ratios alone is difficult to understand within the framework of the concerted ene mechanism. The results can, however, be accommodated to the perepoxide mechanism by employing the more basic protic solvent methanol in an assisted β elimination as shown below.



The mechanisms displayed, c and c′, competing with unimolecular reorganizations (b and b′) could clearly generate the larger isotope effects found. Note that when solvent removal of a proton in a trans β elimination (c) competes with deuterium removal by path b, sizable quantities of solvent-derived product, R_D, are found. On the other hand, when the competition is reversed and solvent removal of deuterium competes with intramolecular proton abstraction, little or no solvent-derived product, S_H, can be found. This would appear to be a sensible expectation.

In summary, we believe that the results presented are not consistent with a conventional picture[14] of a concerted ene mechanism. These experiments likewise provide no *direct* evidence in support of the perepoxide intermediate. We feel that our results most reasonably require irreversible attack on the double bond as the rate-determining step in this reaction. The perepoxide formulation is used here for illustrative purposes only, but we believe that it provides a satisfactory picture of this reaction. Charge transfer or π complexes between olefin and singlet oxygen might also be proposed to explain these results.

Finally, it should be noted that these results may be peculiar to relatively unreactive disubstituted olefins. The methods outlined here are obviously applicable to more highly substituted systems and to other ene-type reactions; such approaches are currently under investigation.

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[9] A. Nickon, *et al.*, *J. Amer. Chem. Soc.*, **94**, 5517 (1972).

[10] K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968).

[11] The ratio of products **2**, **3**, and **4** observed in acetone is very close to those reported earlier for similar olefins.[12] This product ratio and the absence of the isomers of compound **2**, R_D and S_H in the acetone solvent experiments, serve to establish the intermediacy of singlet oxygen and the absence of radical-chain oxidations. In methanol, the absence of isomer S_H and the ratio of products **2**, **3**, and **4** again argues against radical-chain reactions. This contention was checked by examining the rate change exhibited when CH$_3$OH was replaced by CD$_3$OD. Results similar to those reported by Kearns[13] were found, again implicating singlet oxygen as the reactive intermediate.

[12] C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

[13] P. B. Merkel, R. Nilsson, and D. B. Kearns, *J. Amer. Chem. Soc.*, **94**, 1030 (1972).

[14] We note that the result in acetone can be explained by a concerted ene transformation with a small isotope effect and that the result in methanol can be accommodated to a *mixture* of concerted mechanisms. We shall discuss this possibility along with a full description of these experiments.

Molecular Beam Chemistry. Unimolecular Decomposition of Chemically Activated Chlorobromoalkyl Radicals

Sir:

In crossed-beam reactive scattering experiments, the time resolution is reduced to the duration of a single collision. When this is long compared to vibrational periods of the transient collision complex, the distributions in energy and angle of the reaction products provide information about the unimolecular decomposition of the complex.[1–4] The beam technique thus

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[1] W. B. Miller, S. A. Safron, and D. R. Herschbach, *Discuss. Faraday Soc.*, **44**, 108 (1967); *J. Chem. Phys.*, **56**, 3581 (1972).

[2] D. O. Ham and J. L. Kinsey, *J. Chem. Phys.*, **48**, 939 (1968); **53**, 285 (1970).

[3] J. M. Parson and Y. T. Lee, *J. Chem. Phys.*, **56**, 4658 (1972); J. M. Parson, K. Shobatake, Y. T. Lee, and S. A. Rice, *ibid.*, **59**, 1402 (1973).

[4] D. D. Parrish and D. R. Herschbach, *J. Amer. Chem. Soc.*, **95**, 6133 (1973), and references cited therein.