

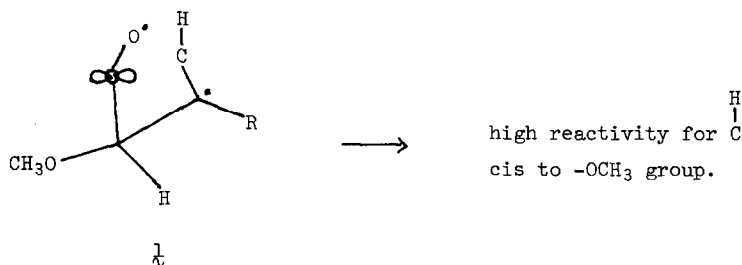
CONCERNING ZWITTERIONIC PEROXIDE OR DIRADICAL INTERMEDIATES
IN THE SINGLET OXYGEN-OLEFIN ENE REACTION

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Summary: Arguments are presented which show that zwitterionic or diradical intermediates in the singlet oxygen-olefin ene reaction would lead to a prediction that geminal groups would be competitive in the C-H abstraction reaction. Isotope effect data available from previous studies clearly show that such is not the case. Thus, these intermediates are inappropriate as a general description of this reaction.

The mechanism of the singlet oxygen-olefin ene reaction continues to be a controversial issue. Recent experimental observations and theoretical calculations have reintroduced biradicals or zwitterions as intermediates and we wish to comment on the appropriateness of these species in this reaction.

Conia's 1977 report¹ of regioselectivity in the photooxygenation of vinyl ethers prompted Goddard's proposal in 1978 of a biradical intermediate $\dot{1}$, with a conformational preference due to an anomeric effect. Conia's experiments can now be recognized as the first of a general set of

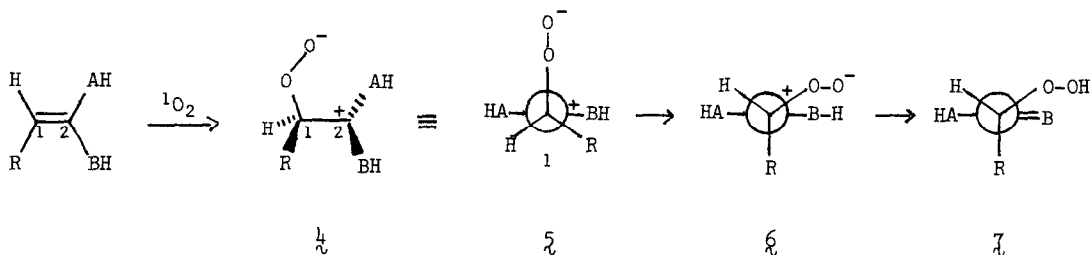


observations^{3a,b,c,d} in which singlet oxygen hydrogen abstracts preferentially from the more crowded side of trisubstituted olefins. Two representative examples, ^{3b,c} $\dot{2}$ and $\dot{3}$, are given



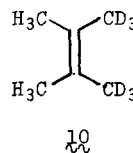
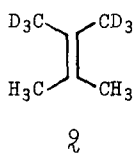
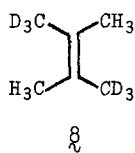
above, and it is clear that the pattern is general for phenyl, alkyl, cycloalkyl,^{3d} methoxy, and

silicon substituted olefins. Goddard's anomeric effect explanation is not obviously extendable to all of these systems. In an attempt to formulate a more general explanation, Jefford⁴ has recently invoked a zwitterionic species ζ . Newman projection ξ implies that BH abstraction



(through δ to yield γ) would involve the energetically lowest energy rotation, eclipsing H with AH only. This forms an interesting rationalization of the preferred abstraction on the crowded side.⁵

Unfortunately, a recent report from our laboratory^{3a,b} effectively eliminates any generally applicable biradical or zwitterionic rationalization. Our results clearly indicate that groups which are cis are competitive in CH abstraction and show isotope discrimination c.f. δ and ρ .

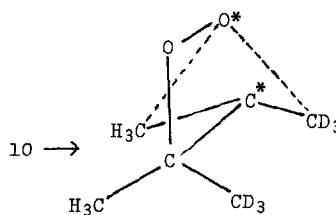
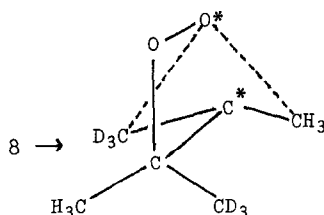


$$k_H/k_D = 1.41 \pm 0.03$$

$$k_H/k_D = 1.44 \pm 0.07$$

$$k_H/k_D = 1.07 \pm 0.04$$

Compound $\lambda\lambda$, in contrast, has both geminal and trans isotope competition available, but shows no discrimination. Formation of a Goddard- or Jefford-type intermediate carries with it the impli-



cation of geminal competition and suggests that δ and $\lambda\lambda$ should show identical, positive, isotope effects, clearly contrary to experiment. Interpretation of the results for olefin ρ are less obvious, but if one proposes that secondary isotope effects are negligible, biradical or zwitterionic formulations would predict no isotope competition, again in contrast to experiment.

We have reported⁶ that trisubstituted olefins show this same stereochemical dependence of the isotope effect; cis groups are competitive, groups with trans and geminal dispositions are not.

In addition to a considerable body of older data,⁷ three new pieces of information must be rationalized in any general description of the singlet oxygen-olefin ene reaction. (1) The process is clearly suprafacial with respect to the olefin component.^{8a,b,c} (2) Trisubstituted olefins show anomalous reactivity on the more crowded side. (3) Isotope effects show the unusual stereochemical dependence discussed here.

Zwitterionic or diradical species, while perhaps appropriate for a description of certain limited types of singlet oxygen reactions, fail to deal effectively with point 3 and perhaps⁹ point 1 above. Such species will continue to be inappropriate general descriptions of this reaction as suggested by Foote⁷ many years ago.

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- Significantly, no comment was made⁴ concerning the absence of Markovnikov directing effects which the ionic intermediate would predict. Compounds 2 and 3 obviously show no such effect, nor does any other data of which we are aware.
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9. Many singlet diradical reactions show some scrambling of stereochemistry in 2+2 reactions. While well established diradical and zwitterionic models in the ene reaction are not available, we point out that the Jefford model already requires some rotation in about C-C bonds. Additional rotation of projection 6 would lead to an apparent antarafacial reaction, again contrary to experiment.^{8b,c}
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