iodide and *tert*-butyl iodide are consistent with a simple model composed of two spheres representing I and the R group. Other investigations[6] with random orientations show these reactions are direct and do not form a long-lived complex, so the reactivity is assumed to be proportional to the fraction of the I end visible. The relative sizes of such spheres are in rough accord with intuitive estimates based on van der Waals radii and, as expected, *tert*-butyl is found to be larger than methyl.

Chloroform shows no dependence on orientation, even though the molecule can be better oriented than CH_3I.[3,7] Because the analogous reaction of chloroform with cesium is observed not to form a long-lived complex,[8] we assume a complex is not formed for the potassium reaction. The lack of orientation dependence is not surprising since there are three potentially reactive sites and one would expect the small lone hydrogen atom to be rather inefficient in shielding the large chlorine atoms. Effects of substituents other than H have not yet been investigated.

The behavior of CF_3I is not in accord with "chemical intuition" and is consequently the most fascinating of the cases studied. Reaction occurs with roughly equal probabilities at either end, and again a long-lived complex is not formed. However, as shown in Figure 1, the scattered product is observed at significantly different scattering angles depending on orientation. For "heads" orientation the product scatters backwards in the center of mass system (CM) whereas the product is scattered forwards in the CM for "tails" configuration. Data given elsewhere strongly suggest that the product is KI in both cases.[4b,9] These features seem to be accounted for by a charge transfer model in which an electron is transferred (at ~5 Å) to the electrophilic CF_3I from the easily ionized K atom. This transfer is followed by an immediate dissociation of the CF_3I^- ion to give CF_3 and I^-. The I^- ion is ejected in the CM direction in which the molecular axis is oriented. This nicely predicts two different laboratory peaks as observed for the heads and tails configurations.[9]

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

(6) G. H. Kwei, J. A. Norris, and D. R. Herschbach, *J. Chem. Phys.*, **52**, 1317 (1970).
(7) G. Marcelin, Ph.D. thesis, Rice University, 1973 (unpublished).
(8) K. R. Wilson and D. R. Herschbach, *J. Chem. Phys.*, **49**, 2676 (1968).
(9) P. R. Brooks, *Discuss. Faraday Soc.*, in press.
(10) Alfred P. Sloan Fellow.

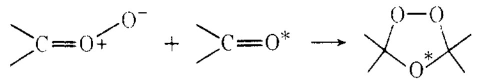
George Marcelin, Philip R. Brooks* [10]
Department of Chemistry, Rice University
Houston, Texas 77001
Received September 20, 1973

Ozonides from the Photooxidation of Diazo Compounds in the Presence of ^{18}O Labeled Aldehydes and $^{18}O_2$

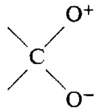
Sir:

One of the most puzzling aspects of the ozonolysis reaction is the apparent ability of olefin stereochemistry to affect the amounts and stereochemistry of the ozonide products.[1–8] Such observations have led to several additional suggestions[1,9–14] for the mechanism of ozonolysis all of which retain the proposal made by Criegee[15] that ozonide can be formed by addition of a zwitterion or carbonyl oxide to a carbonyl group. One of these additional suggestions[1,9–12] includes the possibility that ozonide may also be formed by a route which is more complex than a simple zwitterion–carbonyl recombination reaction.

We have earlier[10,16] attempted to obtain evidence for a nonzwitterion path to ozonide through the use of an ^{18}O tracer procedure. This procedure assumes that operation of the zwitterion–carbonyl recombination mechanism will place the ^{18}O label entirely in the ether bridge when ozonolysis is carried out in the presence of ^{18}O-labeled aldehyde.



Finding of ^{18}O in the peroxide bridge is then interpreted as evidence for a nonzwitterion path to ozonide. In our earlier work[10,16] considerable evidence was found for peroxide bridge labeling in the cases of dialkyl-substituted ozonides. Using a similar technique, Fliszár and coworkers[17–19] have found that in the ozonolysis of phenylethylenes in the presence of ^{18}O-labeled benzaldehyde the label is incorporated exclusively in the ether bridge in the diaryl-substituted ozonides obtained. In all of this earlier work, the assumption was made that the structure of the zwitterion has no contribution from forms such as



1

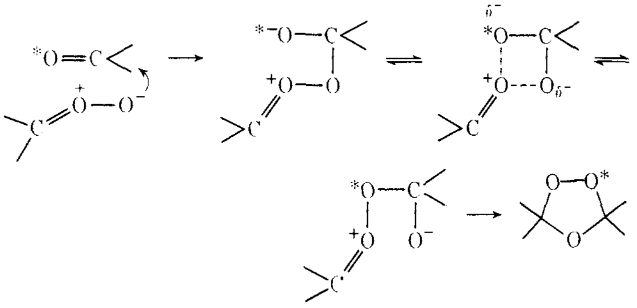
Fliszár and coworkers have now been able to rule out any contribution from structure **1** to ozonide formation based on a very elegant experiment involving the ozonolysis of an unsymmetrical olefin in alcohol solvent and analysis of the alkoxy hydroperoxides produced.[20]

The possibility that incorporation of ^{18}O in the peroxide bridge need not indicate a nonzwitterion path to

---

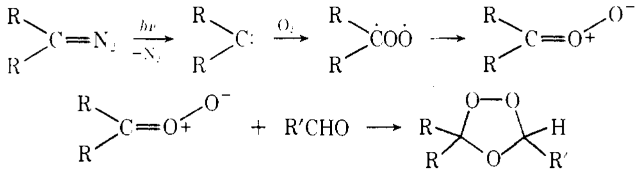
(1) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **89**, 2429 (1967).
(2) O. Loren and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965).
(3) R. Criegee, S. S. Bath, and B. von Bornhaupt, *Chem. Ber.*, **93**, 2891 (1960).
(4) G. Schröder, *ibid.*, **95**, 733 (1962).
(5) P. Kolsaker, *Acta Chem. Scand.*, **19**, 223 (1965).
(6) F. L. Greenwood and B. J. Haske, *Tetrahedron Lett.*, 631 (1965).
(7) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3143 (1966).
(8) F. L. Greenwood, *ibid.*, **88**, 3146 (1966).
(9) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966).
(10) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968).
(11) R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968).
(12) P. R. Story, J. A. Alford, W. C. Ray, and J. R. Burgess, *J. Amer. Chem. Soc.*, **93**, 3044 (1971).
(13) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *ibid.*, **90**, 1822 (1968).
(14) S. Fliszár and J. Carles, *Can. J. Chem.*, **47**, 3921 (1969).
(15) R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).
(16) R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1103 (1971).
(17) S. Fliszár, J. Carles, and J. Renard, *J. Amer. Chem. Soc.*, **90**, 1364 (1968).
(18) S. Fliszár and J. Carles, *ibid.*, **91**, 2637 (1969).
(19) J. Castonguay, M. Bertrand, J. Carles, S. Fliszár, and Y. Rousseau, *Can. J. Chem.*, **47**, 919 (1969).
(20) G. Klutsch, J. Grignon, J. Renard, and S. Fliszár, *ibid.*, **48**, 1598 (1970).

ozonide, as we had earlier concluded,[10–16] has been raised by Fliszár and coworkers.[14] According to this view, finding of ^{18}O in the peroxide bridge is consistent with an exclusive zwitterion mechanism if the following additional path to ozonide is available.



We now wish to present evidence which suggests that operation of this latter scheme is highly unlikely for phenylethylenes and which indicates that operation of an exclusive zwitterion–carbonyl recombination pathway leads to specific labeling of ozonides in the manner assumed earlier.

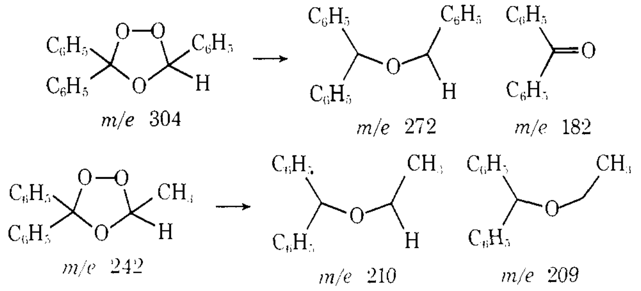
We recently described[21,22] a method of producing ozonides which does not involve ozonolysis. The method involves the photooxidation of diazo compounds in the presence of aldehydes and is interpreted as proceeding as follows



The obtaining of ozonides in this manner provides independent evidence for the involvement of the Criegee zwitterion in ozonide formation and provides a way of forming ozonides exclusively *via* this route without need for consideration of some of the more complex pathways which have been suggested as occurring in some ozonolysis reactions. We have now used this method to determine the fate of an ^{18}O tracer (a) when it is present in the aldehyde and (b) when it is contained in the oxygen molecule.

A solution of diphenyldiazomethane (0.97 g, 5.0 mmol) in acetonitrile was photooxidized[23] in the presence of 0.5 ml of ^{18}O-labeled benzaldehyde[25] (44.7 atom % by mass spectrometry). The reaction mixture was worked up by dry column chromatography (silica gel) and the crude triphenyl ozonide was recrystallized from warm anhydrous methanol to give 0.15 g (10%) of white glittering plates, mp 93–94° (lit.[19] mp 95°). A similar photooxidation was carried out using 0.97 g (5.0 mmol) of diphenyldiazomethane in acetonitrile solution, 1.0 ml (10.0 mmol) of benzaldehyde, and 250 ml of ^{18}O-labeled oxygen (Miles Laboratories, 63.3 atom % enrichment claimed). This process gave 0.10 g (7%) of triphenyl ozonide *via* the same work-up as described above. Finally a solution of 0.97 g (5.0 mmol) of diphenyldiazomethane in acetonitrile was photooxidized in the presence of 3.0 ml (53 mmol) of acetaldehyde and using the same ^{18}O-labeled oxygen described above. Work-up of this reaction mixture gave *ca.* 5% of 1,1-diphenyl-1-propene ozonide.

The ozonides obtained were then analyzed by mass spectrometry.[27] The fragmentation patterns observed were similar to those reported by Fliszár and coworkers.[17–19] The important fragments are those given here.



In the case of the triphenylethylene ozonide no parent ion could be observed. When this ozonide was obtained from labeled benzaldehyde, the fragment with *m/e* 272 contained 41.3 ± 0.2% ^{18}O indicating that essentially all of the label is incorporated at the ether bridge.[28] When the triphenylethylene ozonide was obtained by the use of labeled O_2 the fragment with *m/e* 272 which arises from loss of oxygen contained 0.2 ± 0.5% label while that with *m/e* 182 contained 51.1 ± 0.5% label. In both of these cases then operation of the zwitterion–aldehyde path to ozonide does not involve any significant exchange between oxygen atoms of the combining species.

In the case of the 1,1-diphenyl-1-propene ozonide obtained by using labeled O_2, the parent ion with *m/e* 242 can be observed and was found to contain 46.2 ± 0.2% ions bearing one ^{18}O atom and 33.8 ± 0.2% ions bearing two ^{18}O atoms. The ion with *m/e* 210, arising from loss of oxygen, contained 0.0 ± 0.9% label. Likewise the ion with *m/e* 209 arising from a further loss of hydrogen contained 0.0 ± 0.3% label. Thus the peroxide bridge is composed exclusively of oxygen atoms arising from the zwitterion and none of the zwitterion oxygen is incorporated in the ether bridge as would be allowed by the Fliszár, *et al.*,[14] scheme referred to above. We conclude that operation of the pure zwitterion path to ozonide in the presence of labeled aldehyde does not lead to significant labeling in

---

[21] R. W. Murray and S. Suzui, *J. Amer. Chem. Soc.*, **93**, 4963 (1971).

[22] R. W. Murray and A. Suzui, *ibid.*, **95**, 3343 (1973).

[23] The photooxidation apparatus used was similar to that described in the literature.[24] A General Electric DWY 650-W lamp was used at 90 V and without filter.

[24] C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Amer. Chem. Soc.*, **90**, 975 (1968).

[25] The labeled benzaldehyde was prepared by hydrolyzing benzaldehyde diethyl acetal[26] with H_2O (60 atom % ^{18}O enriched) and a trace of *p*-toluenesulfonic acid.

[26] T. H. Fife and L. K. Jao, *J. Org. Chem.*, **30**, 1492 (1965).

[27] The mass spectra of the ozonides were obtained using an AEI Model MS 12 mass spectrometer, operated with an ionizing potential of 70 eV and an ion source temperature of 110–130°. At least two spectra were recorded for each sample. The measured peak heights were corrected for natural isotope abundances. Additional corrections for variations from natural abundances and/or contributions to peak height by extraneous ions were made on the basis of spectra of unlabeled compounds. The specified error limits are equal to one standard deviation.

[28] The difference between the observed labeling at this fragment and that expected (44.7%) for 100% ether bridge incorporation could be due to loss of label in the aldehyde due to the presence of small amounts of water. In the case of unsymmetrical ozonides it is not possible to accurately determine the per cent label in the unobserved parent ion by analyzing the labeling in other significant ions as was done by Fliszár, *et al.*,[17] in the case of stilbene ozonide.

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]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation through Grant No. GP 29373X.

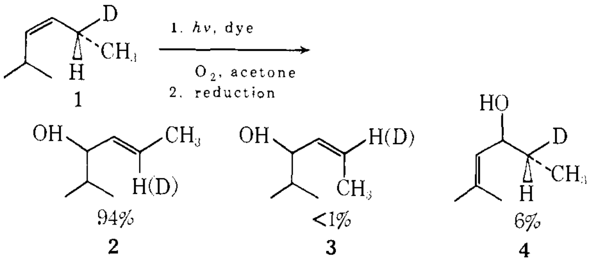
R. W. Murray,* D. P. Higley
Department of Chemistry, University of Missouri—St. Louis
St. Louis, Missouri 63121

Received June 27, 1973

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**.

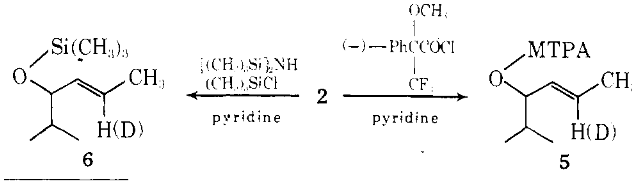


Table I. Analysis of Major Photooxygenation Product **2**

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′.

---

(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.