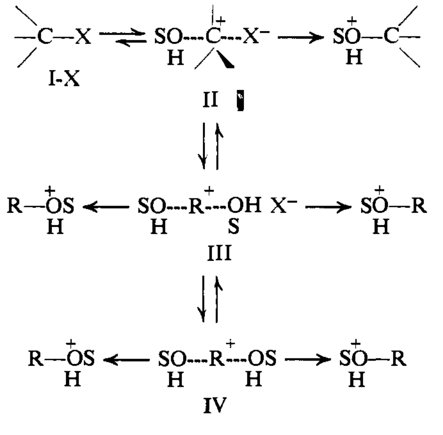
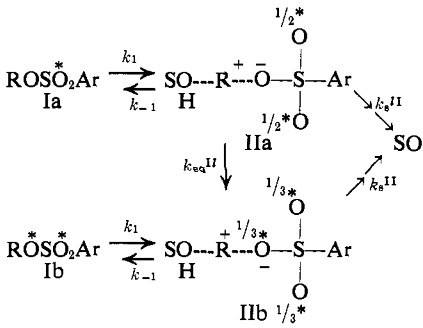
solvolysis of IA-OBs in the common solvolyzing solvents. Using $F_{eq} = [k_{eq}/(k_{eq} + k_t)]$ as a measure of the importance of such ^{18}O scrambling, we see that $100F_{eq}$ is 1.1, 6.5, 8.1, and 19.9 in MeOH, AcOH, HCOOH, and CF_3COOH, respectively. No very large changes in F_{eq} are introduced on addition of NaOAc, $LiClO_4$, or LiOTs in acetolysis. With *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate[7a] (IB-OTs) as substrate, ^{18}O scrambling is also observed to accompany solvolysis, the results being similar to those with IA-OBs. To check on the intramolecularity of the ^{18}O scrambling as opposed to a process involving exchange with an external arenesulfonate ion, solvolysis of IA-OBs and IB-OTs was followed under various conditions in the presence of ^{14}C-labeled HOTs, residual $ROSO_2Ar$ being counted for ^{14}C content. On the basis of the exchange rate constants observed, intermolecular exchange contributes only slightly to the k_{eq} values in the absence of arenesulfonate salt. For example, in acetolysis of IA-OBs without added salt, intermolecular exchange[8] accounts for perhaps 3% of k_{eq}. However, it may account for *ca.* 20% in the presence of added NaOAc. In solvolysis of IA-OBs in F_3CCOOH with added $NaOCOCF_3$, intermolecular exchange may account for *ca.* 6% of k_{eq}.

Solvolyses of the simple unactivated IA-OBs and IB-OTs systems are best discussed, as in eq 2, in terms of intermediates II ("intimate ion pair"), III ("solvent-separated ion pair"), and IV ("dissociated cation").[4b,9] Judging by the tremendous preference for inversion of configuration in solvolysis of such systems, *e.g.*, 2-octyl (IA),[5] *trans*-4-*t*-butylcyclohexyl (IB),[7a] and *exo*-3-bicyclo[3.2.1]octyl (IC)[7b] arenesulfonates, formation of solvolysis product occurs essentially exclusively from the "intimate ion pair" II, this species giving inverted product more rapidly than it progresses to III and IV. On this basis, the ^{18}O scrambling accompanying solvolysis of these systems is probably best represented as in eq 3 with ion-pair return (k_{-1}) and equilibration (k_{eq}^{II}) of sulfonate oxygen atoms in the intimate ion pair II (IIa → IIb) competitive with solvolysis (k_s^{II}).



(2)

The F_{eq} values in Table I would be an actual measure of ion-pair return $[(k_{-1}/(k_{-1} + k_s^{II})]$, provided $k_{eq}^{II} \gg k_{-1}$. However, since k_{-1} may be much larger than k_{eq}^{II}, F_{eq} provides only a lower limit to ion-pair return.[10] It is clear from Table I that these F_{eq} values are quite sensitive to the nature of the solvent. The much lower values for F_{eq} observed in MeOH, compared to AcOH, are in line with an expected decrease in the (k_{-1}/k_s^{II}) ratio on going from AcOH to the much more nucleophilic MeOH. It is interesting that the F_{eq} measure of ion-pair return in formolysis of IA-OBs and IB-OTs is comparable to F_{eq} in acetolysis.[11] While the (k_{eq}^{II}/k_s^{II}) and (k_{eq}^{II}/k_{-1}) ratios probably both increase on going from AcOH to HCOOH, total ion-pair return may well decrease, *i.e.*, k_{-1}/k_s^{II} decreases.



(3)

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(7) (a) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955); M. Whiting, private communication; (b) C. W. Jefford, J. Gunsher, and B. Waegell, *Tetrahedron Letters*, 3405 (1965); C. W. Jefford, D. T. Hill, and J. Gunsher, *J. Am. Chem. Soc.*, **89**, 6881 (1967).

(8) In the case of IA-OBs, exchange with HOBs or NaOBs was assumed comparable to that with HOTs or NaOTs, respectively.

(9) A. Streitwieser, Jr., *Chem. Rev.*, 56, 571 (1956); S. Winstein, *et al.*, *J. Am. Chem. Soc.*, 78, 328 (1956); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951).

(10) Even with bridged ion pairs, as in acetolyses of 3-phenyl-2-butyl toluenesulfonate, ion-pair return occurs with incomplete ^{18}O equilibration, k_{eq} being *ca.* half as large as k_{rac} (R. Thies and H. L. Goering, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S38; R. Thies, Ph.D. Thesis, University of Wisconsin, 1967).

(11) Superficially, this appears to contrast with the situation in solvolysis of RX systems leading to bridged ions, where the measured total ion-pair return in HCOOH is very much less important than in AcOH.[3c-e,4b]

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Mechanisms of Ozonolysis. Reductive Cleavage of Ozonides

Sir:

In order to test our recent mechanistic proposal[1] for the ozonolysis reaction we have utilized oxygen-labeling techniques in which labeled aldehyde is introduced into the ozonolysis mixture. In the absence of adequate mass spectral fragmentation patterns or infrared spectral assignments for ozonides, we have determined isotopic distribution through ozonide reduction followed by mass spectral analysis of the resulting products. Unequivocal location of the isotopic label in the product ozonide is, of course, critical for a proper interpretation of the mechanisms of ozonide formation.[2]

We now wish to report the synthesis of a specifically labeled ozonide which, in turn, has permitted an assessment of the mechanisms of reductive cleavage of ozonides. Application of the present findings to the mecha-

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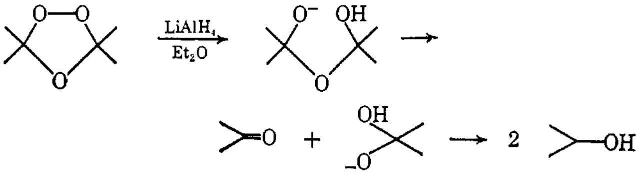
(1) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *J. Am. Chem. Soc.*, **88**, 3144 (1966).

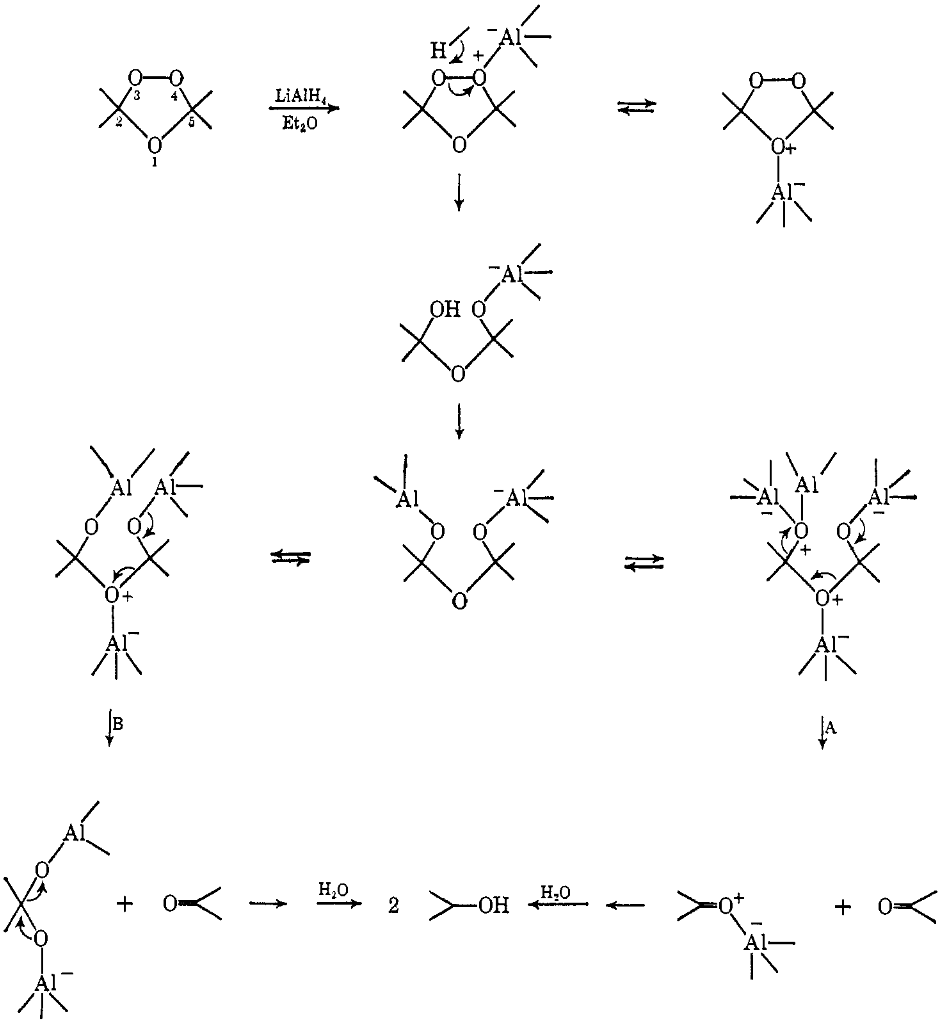
(2) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, Abstracts of Papers, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 12–16, 1966, Paper S5; P. R. Story, C. E. Bishop, J. R. Burgess, J. B. Olson, R. W. Murray, and R. D. Youssefyeh, Preprints of Papers, Vol. II, International Oxidation Symposium, San Francisco, Calif., Aug 27–Sept 1, 1967, p 327.

nisms of ozonolysis is contained in the following communication.[3]

Lithium aluminum hydride reduction of ozonides might, at first glance, appear to be rather random at best. The reaction is known to produce alcohols quantitatively for a net loss of one oxygen atom and, probably, best estimates would call for a statistical loss from all three oxygens. Gaylord has investigated this reaction[4] and formulates it as



Closer examination of the probable reaction sequence, however, would lead one to seriously consider the possibility of selective loss of oxygen from the peroxide bridge. Accordingly, we formulate the hydride reduction in the following semischematic fashion.



Essentially, the set of reactions above argues that the ether-bridge oxygen (O-1) does not at any time become equivalent in leaving ability to oxygens 3 and 4 in the peroxide bridge. This proposition is made on the grounds that Lewis acid coordination, probably by aluminum (as aluminum oxide or alkoxide; lithium ion would also be suitable) is necessary for loss of an oxygen. Moreover the aluminum species in coordinating with the ether oxygen (O-1) will no doubt retain a full negative charge, at least on the time scale of the reaction. Consequently, even if the fragmentation to carbonyl intermediates is not concerted as shown in sequence A but, instead, proceeds by sequence B to produce the hydrate salt, it is still unlikely that the oxygens become equivalent. The better leaving group at every turn is, therefore, the coordinated peroxide-bridge oxygen. In order to test this mechanistic premise we have synthesized a specifically labeled ozonide and carried out its reduction.

Following the method of Lohaus,[5] we have synthesized dimethyldodecenedione (**1**) and labeled it using 40.61% oxygen-18 water (Yeda) according to the general procedure of Byrn and Calvin.[6] Lohaus has shown that ozonolysis of **1** gives the ozonide of 1,2-dimethylcyclopentene (**2**) and 2,6-heptanedione in good yield. This type of ozonolysis is one most likely to proceed according to the Criegee mechanism,[7] *i.e.*,

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[3] P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *J. Am. Chem. Soc.*, **90**, 1907 (1968).

[4] N. G. Gaylord, "Reduction With Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp 687, 708; N. G. Gaylord, *Experientia*, **8**, 351 (1954).

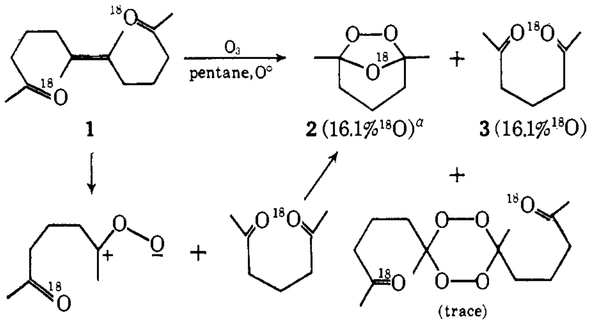
[5] G. Lohaus, *Ber.*, **87**, 1708 (1954).

[6] M. Byrn and M. Calvin, *J. Am. Chem. Soc.*, **88**, 1916 (1966).

[7] R. Criegee, *Record Chem. Progr.*, **18**, 111 (1957); R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 29.

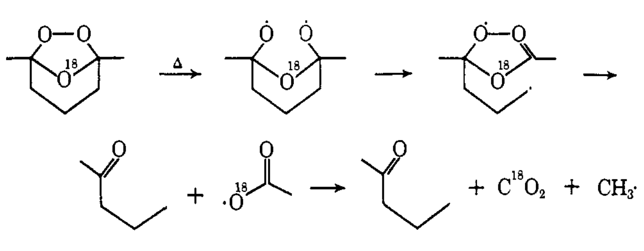
formation of zwitterion followed by condensation with a carbonyl group to give ozonide. Acyclic tetrasubstituted olefins do not yield ozonides; only cyclic olefins of the tetrasubstituted variety are known to give ozonides.[7,8] Acyclic tetrasubstituted olefins react predominantly to yield dimeric and polymeric peroxides. The possibility of zwitterion polymerization is reduced in this system (**1**) by the presence of the intramolecular carbonyl. Of equal importance is the observation from examination of molecular models that the internal carbonyl is sterically restrained from reacting with a molozonide intermediate, even if present, thus further ensuring that ozonide is formed *via* the Criegee mechanism shown in Scheme I.

Scheme I

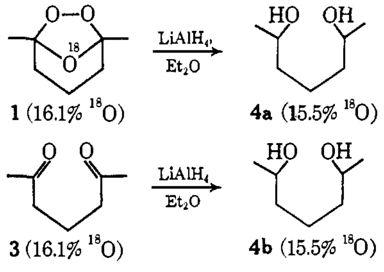


^{a} Calculated by the difference of **1** and **3**.

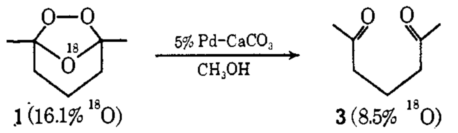
That the oxygen-18 label is, indeed, located at the ether oxygen is supported by the finding that 2-pentanone which constitutes a major product on thermolysis of **2** did not contain an isotopic label.[9] It will be observed that the thermal derivation of 2-pentanone from **2** most reasonably requires extraction of the carbonyl oxygen from the peroxide bridge (O-2,3).



Lithium aluminum hydride reduction of the ozonide **1** has been found to produce 2,6-heptanediol (**4a**) containing 15.5% isotopic label, *i.e.*, essentially no isotopic label was lost during reduction. The diol **4** was analyzed by mass spectrometry. Since **4** does not give a parent ion in its mass spectrum, reliability of the analysis was checked by analyzing diol **4b** obtained by reduction of **3** and, thus, containing a known amount of label. The two diols (**4a** and **b**) gave identical mass spectral analyses. We conclude, therefore, that hydride reduction of the ozonide **1** and, by extension, other saturated, alkyl-substituted ozonides, occurs with loss of oxygen only from the peroxide bridge.



We have also reduced the ozonide **1** by catalytic hydrogenation to the dione **3** using $Pd\text{-}CaCO_3$ in methanol.



Under these conditions we find, as expected, that approximately one-half of the label is lost.

Acknowledgment. We thank the U. S. Public Health Service, National Center for Air Pollution Control, for support of this work through Grant No. AP00505.

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Received December 11, 1967

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(8) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(9) The absence of label in the 2-pentanone was determined from infrared and mass spectra. We have examined the thermolysis and photolysis of several ozonides in detail: P. R. Story, W. H. Morrison, III, T. K. Hall, J-C. Farine, and C. E. Bishop, to be published.

Evidence for a New Mechanism of Ozonolysis

Sir:

In the preceding communication[1] we have established that lithium aluminum hydride reduction of an alkyl ozonide and, by extension, other saturated alkyl ozonides, to give alcohols proceeds with loss of oxygen only from the peroxide bridge; *i.e.*, all of the ether-bridge oxygen is retained in the alcohol products. Knowledge of the fate of the ozonide oxygens on hydride reduction is critical to our scheme for testing a new mechanism of ozonolysis recently proposed for certain types of olefins.[2] We wish to report here the results of oxygen-18 labeling experiments which support the new mechanism.

It has become clear from results reported by several investigators that more than one mechanism is operative in ozonolysis. The need for a new mechanism was emphasized by our earlier finding that *cis/trans* ratios of cross ozonides[3] formed from unsymmetrical olefins were dependent on olefin geometry,[2b,4] a result contrary to the Criegee zwitterion mechanism.[5]

According to the earlier proposal,[2] ozonides may be formed not only through the intermediacy of the Criegee zwitterion and aldehyde but also by reaction of aldehyde with the molozonide intermediate. In effect, we proposed that the reaction of aldehyde with molozonide competes with cleavage of the molozonide to Criegee zwitterion and aldehyde (and with subsequent recombination of aldehyde and zwitterion). It is clear that the new mechanism, for which supporting evidence is offered here, is not generally applicable and must be

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(1) C. E. Bishop and P. R. Story, *J. Am. Chem. Soc.*, **90**, 1905 (1968).

(2) (a) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966); (b) R. W. Muray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

(3) L. D. Loan, R. W. Murray, and P. R. Story, *ibid.*, **87**, 737 (1965).

(4) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **88**, 3143 (1966).

(5) R. Criegee, *Record Chem. Progr.*, **18**, 111 (1957); R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 29.