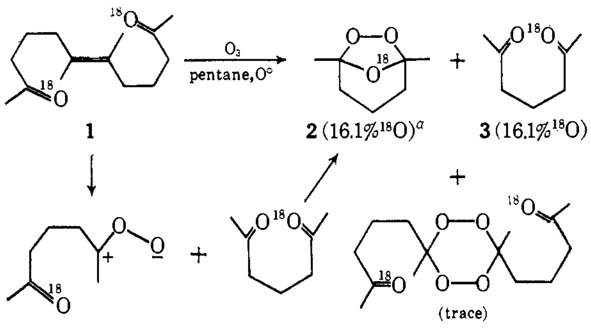
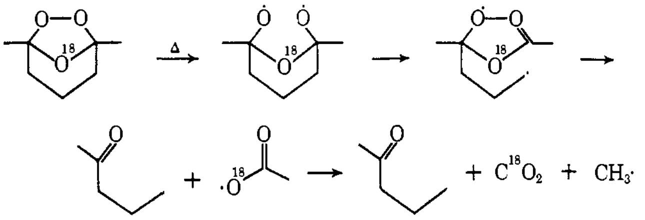
formation of zwitterion followed by condensation with a carbonyl group to give ozonide. Acyclic tetrasubstituted olefins do not yield ozonides; only cyclic olefins of the tetrasubstituted variety are known to give ozonides.[7,8] Acyclic tetrasubstituted olefins react predominantly to yield dimeric and 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

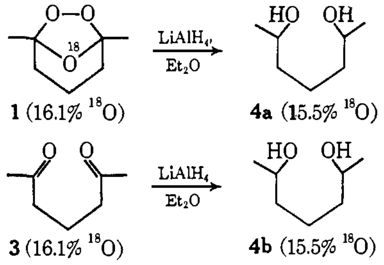


[a] Calculated by the difference of **1** and **3**.

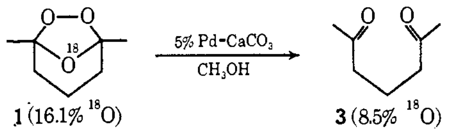
That the oxygen-18 label is, indeed, located at the ether oxygen is supported by the finding that 2-pentanone which constitutes a major product on thermolysis of **2** did not contain an isotopic label.[9] It will be observed that the thermal derivation of 2-pentanone from **2** most reasonably requires 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–$CaCO_3$ in methanol.



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

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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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(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.

(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.

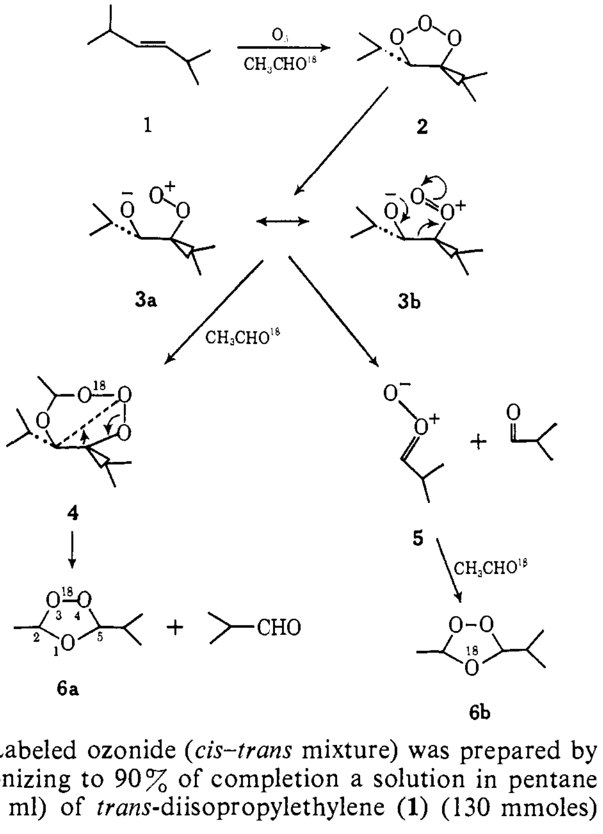
limited to those olefins and those conditions in which a molozonide intermediate[6] has sufficient lifetime to allow reaction (probably *trans*-disubstituted and relatively unhindered *cis*-disubstituted olefins).[2,4]

As demonstrated previously, the molozonide–aldehyde interchange mechanism,[2] from consideration of steric interactions, correctly predicts that *cis*-olefin will generate relatively more *cis*-ozonide than will the corresponding *trans*-olefin. It should be noted that this interpretation does not refer to the absolute values of the *cis*/*trans* ratios.

Taking advantage of the fact that the aldehyde oxygen is incorporated differently into the ozonide by the molozonide–aldehyde mechanism than by the Criegee mechanism, we have ozonized *trans*-diisopropylethylene (**1**) in the presence of acetaldehyde-O^{18}. As shown in Scheme I, ozonide **6a** produced according to the new mechanism will contain the oxygen-18 label at position 3. In ozonide **6b**, formed from the zwitterion **5**, however, the label will appear at position 1.[7]

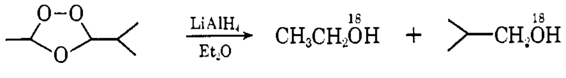
The structures in Scheme I are necessarily formalized; it is not crucial to the discussion for molozonide **2** cleavage to **3** to precede its reaction with aldehyde. By the same token, **4** need not exist as an actual intermediate but may only approximate a transition state in the aldehyde interchange.

Scheme I



Labeled ozonide (*cis–trans* mixture) was prepared by ozonizing to 90% of completion a solution in pentane (75 ml) of *trans*-diisopropylethylene (**1**) (130 mmoles) and acetaldehyde-O^{18} (88 mmoles) (47.8% by mass spectral analysis[8]) at Dry Ice–acetone temperature. The methyl isopropyl ozonide (**6**) was isolated as before,[2b,4] in 17% yield, based on acetaldehyde.

Location of the isotopic label was achieved by lithium aluminum hydride reduction of ozonide **6** followed by mass spectral analysis of the only products, ethanol (**7**) and isobutyl alcohol (**8**). The ethanol was found to contain 25.4% oxygen-18 and the isobutyl alcohol, 7.6% Since only oxygen from the peroxide bridge (O-3,4) is lost on reduction,[1] this result indicates that 15.2% oxygen-18 was incorporated at position 1 (**6b**) and the remainder, 32.6%, at position 3 (**6a**). It is noteworthy that ethanol should contain 47.8%/2 or

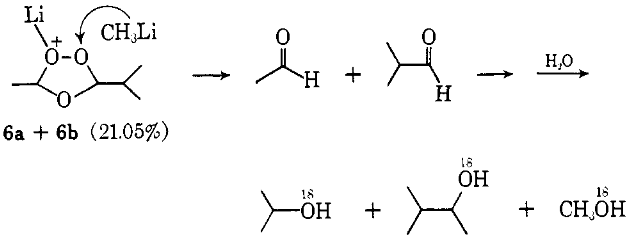


6a + **6b** (47.8% O^{18}) **7** (25.4%) **8** (7.6%)

about 24% oxygen-18 regardless of the isotopic distribution between positions 1 and 3 in **6**. The experimental value of 25.4% compares favorably and provides an internal check on the interpretation. Translation of the data to 100% oxygen-18 reveals that approximately 32% of ozonide **6** was formed *via* a pathway which placed the label at position 1 (**6b**), probably *via* the Criegee zwitterion mechanism, and that the remainder, 68%, was formed by a pathway which placed the isotopic label at position 3 (**6a**), probably *via* the monozonide–aldehyde mechanism.[2]

This interpretation requires that little, if any, steric effect is operative in the hydride reduction. If, in fact, a small steric effect is operative, it should function so as to cause excessive loss of O-3 rather than O-4. The necessity of prior coordination of a Lewis acid with the least hindered oxygen from the least hindered side of the molecule (both *cis* and *trans*) will probably force hydride displacement on the more hindered oxygen. Methyllithium reduction of **6** supports this interpretation.

Ozonide **6** prepared as before from acetaldehyde containing 21.05% oxygen-18 was treated with an excess of methyllithium to give isopropyl alcohol (**9**), 3-methyl-2-butanol (**10**), and methanol in high yield. The reaction is interpretable in terms of the scheme shown below.



6a + **6b** (21.05%)

9 (11.88%) **10** (2.45%)

Mass spectral analysis of the products (glpc pure) revealed isopropyl alcohol (**9**) to contain 11.88% oxygen-18; 3-methyl-2-butanol (**10**) contained 2.45%. Interpreted in terms of methide displacement at oxygen (methide displacement at carbon will yield the same analysis), the ether-bridge oxygen (O-1) must have con-

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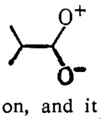
[6] P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Am. Chem. Soc.*, **88**, 4098 (1966); F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964); F. L. Greenwood, *ibid.*, **30**, 3108 (1965).

[7] This conclusion is drawn assuming that the zwitterion cannot add to the aldehyde carbonyl 1,3 through the oxygens as though it possessed the structure shown here. There is no evidence indicating that the zwitterion reacts in this fashion, and it would not account for the dependency of cross-ozonide stereoisomeric ratios on olefin geometry.



[8] Mass spectral analyses were performed by Gollub Analytical, Berkeley Heights, N. J., and by Morgan-Schaffer Laboratories, Montreal, Quebec. All analyses consist of at least two calculations, one using the parent ion where available and another using a suitable fragment. The acetaldehyde-O^{18} was prepared by exchange with water-O^{18} (Yeda); see M. Byrn and M. Calvin, *J. Am. Chem. Soc.*, **88**, 1916 (1966).

tained 4.90% oxygen-18. The remainder, 16.15%, must have been at O-3. On this basis isopropyl alcohol (**9**) should have contained 8.07 + 2.45 or 10.52% oxygen-18. The observed value of 11.88% constitutes a discrepancy of $\sim$10%, probably attributable to a small steric effect. Methide displacement on O-4 would be favored, thus producing isopropyl alcohol rich in O-3. From this experiment we conclude that about 77% of ozonide **6** was formed according to a reaction scheme which places the isotopic label at O-3, probably the molozonide–aldehyde interchange mechanism. We find, therefore, that hydride reduction of **6** places the amount of ozonide formed by the molozonide–aldehyde mechanism at about 68%, while methyllithium reduction provides an estimate of 77%. Since the steric effects are most likely opposite in direction, we consider it probable that the 9% spread in the two values provides a rough evaluation of the sum of the steric effects.

The labeling experiments, therefore, provide strong support for the mechanism written to account for the dependency of ozonide *cis/trans* ratios on olefin geometry.[2] In this particular case, under conditions of added aldehyde, approximately 75% of ozonide **6** was apparently formed through the molozonide–aldehyde reaction. It must be noted, however, that in a normal ozonolysis, aldehyde is not present initially and that, before the molozonide–aldehyde mechanism can become important, a sufficient quantity of aldehyde must be produced, presumably by fission of the molozonide to zwitterion and aldehyde. Under these conditions it would not be surprising to find the new mechanism somewhat less important than in the present study. Once sufficient aldehyde is obtained in the normal ozonolysis, however, production of zwitterion may well nearly cease since the molozonide–alehyde reaction does not deplete aldehyde concentration, and at sufficiently high aldehyde concentrations it is apparent that this reaction competes well with molozonide fission. The effect of reaction temperature must also be considered since at higher temperatures molozonide lifetime will be shortened.

The results obtained in this study are compatible with the Criegee mechanism[5] and, in fact, serve to further confirm it. It should also be understood that the conclusions drawn in this work are not necessarily inconsistent with the mechanistic proposal recently championed by Bailey in which it is suggested that the dependence of cross-ozonide *cis/trans* ratios of olefin geometry is a result of the formation of configurationally stable *syn* and *anti* zwitterions.[9]

Acknowledgment. We thank the Public Health Service, National Center for Air Pollution Control, for support of this work through Grant No. AP00505, and the General Research Office, University of Georgia, for purchase of the labeled water.

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Received December 11, 1967

(9) P. S. Bailey, International Symposium on the Chemistry of Organic Peroxides, Deutsche Akademie Der Wissenschaften, Berlin-Adlershof, Sept 13–15, 1967.

Circular Dichroism in Copper(II) Complexes of Some Bisglycylethylenediamine Analogs

Sir:

Some principles underlying the stereoselectivity of polydentate ligands have been delineated by Corey and Bailar,[1] imposition of a particular chiral hand depending in part upon nonplanarity of a five-membered chelate ring which in this respect is similar to a six-membered carbocyclic ring. Support for these principles has, for example, been obtained[2] where a nonplanar propane-1,2-diamine ring may be presumed present.[3] An apparent absence of stereoselectivity in some bis(α-amino acid)copper(II) complexes has been interpreted in favor of chelate ring planarity.[4] The data of Wellman, *et al.*, concerning helicity of bis(α-amino acid)copper(II) complexes and the nonplanarity of the bidentate amino acid ligands is of some interest, then, and we report here some observations concerning the three ligands (see Figure 1): I, N,N′-bisglycyl-(−)-propane-1,2-diamine; II, N,N′-bisglycyl-(−)-cyclohexane-1,2-*trans*-diamine; and III, N,N′-bis(+)-alanylethane-1,2-diamine, which support their empirical octant rule.[5] I and II have been prepared by modification of Asperger and Liu's method for III[6] using respectively (+)-propane-1,2-diamine (dihydrochloride, $[\alpha]_D$ −3.7°) and (−)-cyclohexane-1,2-*trans*-diamine, (dihydrochloride, $[\alpha]_D$ −16°), resolved *via* their *d*-tartrates. For III, L-alanine ($[\alpha]_D$ +14.25°), purchased from Nutritional Biochemicals Corp., was used. I, then, possesses absolute configuration *S*[7] and III configuration *S*,[8] and II may by inference[9] be assigned configuration *R*.

In basic solution (pH >10), formation of a biuret complex with Cu(II) is signalled by development of a red color, maximum absorbance at 520–550 mμ. Under these circumstances, when 2 equiv of hydrogen ion is liberated per mole of complex,[10] the four ligand atoms are constrained approximately in a plane. The bisamide complexes may be viewed operationally as bisaminoacidates, the amino acid ligands making the same octant contribution[5] whether they be *cis* or *trans*. III, then, is virtually identical with bis-(+)-alaninatocopper(II) with α-CH and CO in negative octants and a presumed minor contribution from the bridging CH_2's in positive octants, that is, a negative Cotton effect over-all. In I the situation is reversed, any preference being wholly with the bridging ring which lying in positive octants produces a minor positive Cotton effect. In I there is little induced asymmetry required of the terminal rings, but in II, although the bridging CH_2's are evidently in negative octants, the terminal CO's are very strongly directed into positive octants. In

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(1) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(2) F. P. Dwyer, F. L. Garvan, and A. Shulman, *ibid.*, **81**, 290 (1959).

(3) Y. Saito, H. Iwasaki, and H. Ota, *Bull. Chem. Soc. Japan*, **36**, 1543 (1963).

(4) R. D. Gillard, H. M. Irving, R. M. Parkins, N. C. Payne, and L. D. Pettit, *J. Chem. Soc., A*, 1159 (1966).

(5) (a) K. M. Wellman, W. Mungall, T. G. Mecca, and C. R. Hare, *J. Am. Chem. Soc.*, **89**, 3647 (1967); (b) *Chem. Eng. News*, 48 (Oct. 2, 1967).

(6) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, 4, 1395 (1965).

(7) Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

(8) P. Brewster, E. D. Hughes, C. K. Ingold, and P. A. D. S. Rao, *Nature*, **166**, 178 (1950).

(9) R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966); R. D. Gillard, *Tetrahedron*, **21**, 503 (1965).

(10) A. Zuberbuhler and S. Fallab, *Helv. Chim. Acta*, **50**, 889 (1967).