it is known that each additional alkyl substituent lowers the activation energy for rearrangement by *ca.* 2.5–3 kcal/mol.[21] Therefore, the **8** to **11** conversion need be exothermic by only *ca.* 8–9 kcal/mol.[22] The calculated exothermicity for the **8** to **11** reaction is, neglecting any strain on the bridgehead double bond, *ca.* −29 to −30 kcal/mol. Therefore, we estimate the strain of the bridgehead double bond in **11** to be 20–22 kcal/mol.[22,23] It now becomes clear why **5** is stable: comparable ring opening in that system would be endothermic by some 10–12 kcal/mol.[22,24] Similar considerations about the stability of **6** indicate that a bridgehead double bond in a six-membered ring has at least 30 kcal/mol strain energy.

We are continuing to investigate other facets of the chemistry of **8**, including what, if any, role is played by the 3,4 double bond.

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(21) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966). This effect is, of course, operative in the **1** to **2** conversion.

(22) This estimate of the bridgehead double bond strain in **11** would seem to be an upper limit, since the presumed intermediate **10** (and related transition states) must be relatively less stable than the corresponding one(s) for the **3** to **4** conversion. This serves to counteract the assumption of ref 20, and would require a greater exothermicity for the **8** to **11** conversion (which means a lower value for the bridgehead double bond strain energy).

(23) Compare this to the *ca.* 12 kcal/mol strain energy found for the bridgehead double bond of bicyclo[3.3.1]non-1-ene, which is a bridgehead double bond in an eight-membered ring [P. M. Lesko and R. B. Turner, *J. Amer. Chem. Soc.*, 90, 6888 (1968)].

(24) We note that 11,11-dibromotricyclo[4.4.1.$0^{1,6}$]undecane does not undergo ring opening even when ionized; rather a 1,2-alkyl shift is observed [D. B. Ledlie, *J. Org. Chem.*, 37, 1439 (1972)].

Philip Warner,* Richard LaRose
Chee-man Lee, Jon C. Clardy
Ames Laboratory—USAEC and Department of Chemistry
Iowa State University
Ames, Iowa 50010

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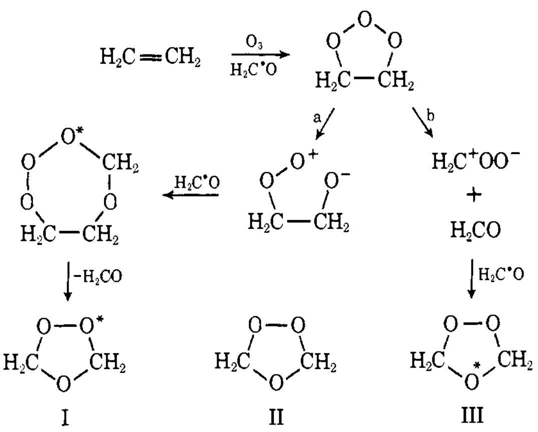
Oxygen-18 Formaldehyde Insertion in the Ozonolysis of Ethylene and the Microwave Spectrum of Oxygen-18 Ethylene Ozonide[1]

Sir:

We have recently determined the structure of ethylene ozonide (1,2,4-trioxacyclopentane) and shown that it has C_2 symmetry (half-chair conformation).[2] This result and the related finding that the ozonolysis of $HDC{=}CH_2$ produced the normal isotopic species, two singly deuterated species, and three doubly deuterated species were related to three mechanistic proposals. One proposal, the modified Criegee mechanism,[3] did not correlate with our results because it postulates a preferred conformation of the final ozonide which differs from that of ethylene ozonide. Two proposals, the Criegee[4] and the aldehyde interchange mechanisms,[5] were consistent with the results. This report discusses our initial experiments which distinguish between these two mechanisms in the ozonolysis of ethylene.

Fliszar, *et al.*,[6] and Story, *et al.*,[7] first utilized the fact that the two mechanisms predict a different site of incorporation of an aldehydic oxygen into the final ozonide. As shown below, the ozonolysis of ethylene in the presence of oxygen-18 formaldehyde should yield ozonides I, II, and III *via* the aldehyde interchange mechanism (paths a and b) but only II and III *via* the Criegee mechanism (path b). We have found only II and III when mixtures of ethylene and oxygen-18 formaldehyde were ozonized.



Mixtures of 0.19 *M* ethylene and 0.36 *M* formaldehyde (27 ± 1.4% oxygen-18 enriched) in methyl chloride were ozonized at −78°. The ozonide was separated from the solvent by low temperature vacuum distillation[2] employing fast warm-up procedures.[8]

The site and quantity of oxygen-18 enrichment in ethylene ozonide was determined by microwave spectroscopy. This technique could be used because the complete structure of ethylene ozonide was known;[2] hence the regions for the rotational transitions of the two different oxygen-18 species could be predicted. The spectrum of only one species enriched in oxygen-18 has been found as well as the spectrum of II. The transitions of the oxygen-18 enriched species were close to those predicted for III. Moreover, an intensity alternation arising from nuclear spin statistics was observed demonstrating that the C_2 symmetry axis was retained upon enrichment. This is only consistent with oxygen-18 enrichment at the ether position (ozonide III). Seven transitions arising from this species were assigned on the basis of their frequency fit and Stark effects. The rotational constants (megahertz) which fit the spectrum are $A = 8094.14 \pm 0.16$, $B = 7877.01 \pm 0.03$, and $C = 4469.11 \pm 0.02$. These can be compared with those calculated for III and I from the structure:[2] III, 8095, 7869, 4467; I, 8144, 7832, 4481.

A systematic search was conducted to identify spectra from I. Several frequency regions were investigated

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

(2) C. W. Gillies and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **94**, 6337 (1972).

(3) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *ibid.*, **90**, 1822 (1968).

(4) R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

(5) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **89**, 2429 (1967).

(6) S. Fliszar and J. Carles, *ibid.*, **91**, 2637 (1969); S. Fliszar, J. Carles, and J. Renard, *ibid.*, **90**, 1364 (1968).

(7) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968).

(8) R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1098 (1971).

where different transitions were predicted to occur. Because vibrational isotope effects are neglected in the structural work,[2] the frequency of these transitions cannot be exactly calculated; therefore, searches were carried out over several hundred megahertz on each side of the predicted frequencies. All low intensity transitions were examined for identifying Stark effects with a CAT but no transitions from I could be assigned. Since the spectrum of $H_2{}^{13}\overline{\text{COOCH}_2\text{O}}$ was seen in natural abundance during these experiments, the abundance of I must be quite low if present at all. We are conservative in setting a lower limit for the abundance of I because of the inability to precisely predict its spectrum and the possibility that its transitions may have been inadvertently overlooked. We estimate that the transitions of this species would have been readily observed if they were one-tenth as intense as those for species III. On this basis it is concluded that at least 90% of the oxygen-18 formaldehyde which incorporated into the ring went to the ether site. An independent synthesis of species I is planned in order to set a more precise lower limit for its concentration.

The amount of enrichment at the ether position was estimated from the relative intensity of transitions from species III and II.[9] A value of 0.28 ± 0.06 was obtained for the ratio of III/II. The Criegee mechanism for a statistical distribution of aldehyde and zwitterion predicts this ratio should vary from 0.21 for 100% completion to 0.27 for 50% completion of the ozonolysis. The exact amount of the ozone introduced was not determined; however, the yield was 53%. These results are not precise enough to set a definitive lower limit for incorporation at the peroxidic oxygen but they are consistent with the detection of only species II and III in the microwave spectrum.

In conclusion, the results reported here and in ref 2 imply that the Criegee mechanism satisfactorily accounts for the major products obtained in ozonizing ethylene. The lower limit set for the concentration of ozonide I in this study indicates that the aldehyde interchange mechanism as well as the proposal of Fliszar and Carles[10] to account for peroxidic ^{18}O incorporation are not very important at $-78°$ for ethylene. While the site of oxygen-18 enrichment found for ethylene is consistent with a report on arylalkenes,[6] it differs from alkylalkenes where enrichment occurs at both positions.[7,11,12] We intend to further investigate the ozonolysis of ethylene at lower temperatures in different solvents to determine if even small amounts of oxygen-18 can be found at the peroxide site. Conformational studies of alkyl-substituted ozonides as well as studies of aldehyde insertion reactions of alkyl-substituted alkenes are also planned. These studies should establish whether the ozonolysis mechanism for ethylene is different from other alkyl-substituted alkenes.

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(9) A. S. Esbitt and E. B. Wilson, Jr., *Rev. Sci. Instrum.*, **34**, 701 (1963).

(10) S. Fliszar and J. Carles, *Can. J. Chem.*, **47**, 3921 (1969).

(11) R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1103 (1971).

(12) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Amer. Chem. Soc.*, **93**, 3042 (1971).

Charles W. Gillies, Robert L. Kuczkowski*
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

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Book Reviews*

Chemistry for Changing Times. By John W. Hill (University of Wisconsin, River Falls). Burgess Publishing Co., Minneapolis, Minn. 1972. xiii + 272 pp. $5.50.

This is a book for a college course about chemistry for the student not majoring in any science. Its primary aim is to interest such students, in the belief they will then inevitably learn something of the subject, and, if the interest kindled is sufficiently high, that they will continue to learn after the course is over. To achieve this goal, the traditional approach of teaching a curtailed version of classical chemistry is abandoned.

The subject starts with a brief consideration of the philosophy of science, moves rapidly through general and physical chemistry, and reaches organic chemistry, "where the action is," at the end of the first quarter of the book. The viewpoint throughout is unabashedly sociological and environmental, so that there is hardly a page on which chemistry is not related to the world at large. The treatment is largely descriptive, and there is no attempt to teach the student how to *do* chemistry: how to name, how to make, how to calculate. Drawings and photographs are used abundantly. Portraits of a few prominent chemists, seemingly randomly selected, are shown where a particular accomplishment is discussed; the choice of the accomplishment is not in all instances a felicitous one, and, for example, Professor Louis Fieser might not be entirely pleased to see his chemical fame based entirely upon the invention of napalm.

The approach of this book has a definite appeal to today's youth, and it will probably be quite successful in its aim. The highly topical approach which is responsible for this, however, will probably hasten the obsolescence of the material. The problems at the end of each chapter are as much a departure from tradition as the text, and generally have no fixed answer. Examples are: "Examine the label of a can of fruit, etc.; make a list of the food additives in each; try to determine the function of each additive;" "discuss the pros and cons of a persistent pesticide." Each chapter ends with a long list of suggested readings, taken extensively from the popular paper-back literature, but also including articles from "Scientific American," "Ramparts," "Chemistry," "New Republic," and even "Boys' Life." A most useful feature is a list of visual aids for each chapter, with specific information on source and cost.

Professor Hill's treatment of his subject is bound to evoke a very mixed reaction in the profession, owing to its "revolutionary" approach, but it is an experiment well worked out, notwithstanding a number of technical faults. From those for whom it is written, it is likely to receive high acclaim.

Comprehensive Chemical Kinetics. Volume 13. Reactions of Aromatic Compounds. Edited by C. H. Bamford and C. F. H. Tipper (University of Liverpool). American Elsevier, New York, N. Y. 1972. xi + 508 pp. $53.50.

Like the previous volumes in this series, this one is a valuable reference work. It consists of an enormous chapter on "Kinetics of Electrophilic Aromatic Substitution," by R. Taylor, and two small chapters (Nucleophilic Aromatic Substitution, by S. D. Ross, and Aromatic Rearrangements, by D. L. H. Williams). Some

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* Unsigned book reviews are by the Book Review Editor.