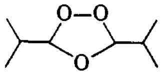
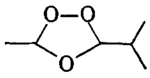
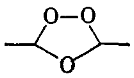
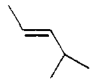
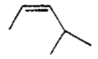
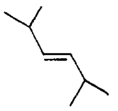
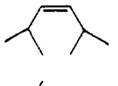
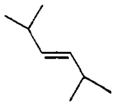
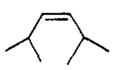
Table I. Summary of Ozonide *cis–trans* Ratios Observed

Olefins	 **1,2**	 **6**	 **5**
 4	50:50	48:52	38:62
 3	66:34	49:51	49:51
	53:47	. . .	. . .
	66:34	. . .	. . .
	$\xrightarrow{CH_3CHO}$ 56:44	47:53	. . .
	$\xrightarrow{CH_3CHO}$ 56:44	40:60	. . .

methylpentene-2 (**4**) was 50:50 (*c*:*t*) while that obtained from the *cis* olefin (**3**) was 66:34 (*c*:*t*). Likewise, the ratios in butene-2 ozonide (**5**), the other cross-ozonide, were 38:62 (*c*:*t*) from **4** and 49/51 from **3**[15] (Table I). These surprising results clearly indicate that *cross-ozonides are not produced exclusively by a Criegee zwitterion–carbonyl combination pathway* if, indeed, the Criegee zwitterion is involved at all.[16,17]

We have observed that the *cis*:*trans* ratio of methyl isopropyl ozonide (**6**) produced by ozonolysis of *cis*- and *trans*-diisopropylethylene in the presence of added acetaldehyde is also dependent upon olefin geometry, but that, in this case, the *cis*-olefin gives a *cis*:*trans* ozonide ratio less than 1, in sharp contrast to the previous example; the *trans*-olefin, on the other hand gives approximately the same *cis*:*trans* ratio.

To eliminate the possibility that ozonide formation may be reversible under any of the reaction conditions a control reaction was run whereby an ozonide of known *cis*:*trans* ratio was present during ozonolysis of another olefin and also in the presence of an added aldehyde. The *cis*:*trans* ratio of the recovered ozonide was unchanged.

The assignment of *cis* and *trans* structures to the ozonide geometric isomers was made on the basis of gpc, infrared, and nmr data as before.[5,18]

theoretical ozone required. In the aldehyde experiments, the same amount of olefin was used, but the solvent consisted of 23 ml of pentane and 2 ml of aldehyde. The ozonide analyses were made by gpc at 70° or lower using a 10-ft 10% cyanosilicone column. These conditions gave sufficient separation of the *cis–trans* isomers to permit separate integration. All ozonides gave correct C, H, and O analyses and had infrared and nmr spectra completely consistent with the assigned structures.

(15) Ozonide *cis*:*trans* ratios reported are the result of several integrations of the gpc peak area and have a maximum variation of ±0.5%. Control experiments demonstrated that the gpc conditions used do not affect the ozonide *cis*:*trans* ratios.

(16) We have observed the dependence of cross-ozonide *cis*:*trans* ratios on olefin geometry in several other cases as well.

(17) In the accompanying communication we consider some new proposals for the mechanism of ozonolysis.

(18) R. W. Murray, P. R. Story, and L. D. Loan, *J. Am. Chem. Soc.*, **87**, 3025 (1965).

R. W. Murray, R. D. Youssefyeh
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

Paul R. Story
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

Received April 9, 1966

The Ozonolysis Reaction. A Working Hypothesis

Sir:

Evidence has been presented in the preceding communication clearly demonstrating that the Criegee zwitterion cannot constitute the sole pathway to ozonide formation upon ozonolysis of the carbon–carbon double bond.[1] The factors influencing the ozonolysis reaction have not been at all well understood, and it now appears that the one unifying concept available, the Criegee zwitterion mechanism,[2] is, at best, somewhat limited and bears reexamination.

In the course of our investigations of the mechanism of this reaction, we have developed a working hypothesis, based on work in our own and in other laboratories, which we believe provides a cohesive framework for understanding the reaction of ozone and olefins.

In brief, it is our thesis that ozone and the double bond (**1**) first form a π complex, **2**, as previously suggested by Bailey,[3,4] regardless of the olefin structure. The fate of the π complex **2** is then determined principally by the steric requirements of the double bond substituents.[5]

***trans* and Sterically Unhindered *cis* Olefins.** There is good evidence[6,7] for the intermediacy of a molozonide in the ozonolysis of most *trans* olefins; reasonably unhindered *cis* olefins probably also lead to a molozonide (**3**). Consequently, we propose that the initial π complex, in these cases, collapses to the molozonide **3**.

Critical reexamination of the cleavage path usually depicted for molozonides[8,9] leads us to suggest an alternative pathway which can accommodate the finding that olefin geometry influences the structure of cross-ozonides.[1]

Using *trans*-4-methylpentene-2 (**1**) to illustrate, we contend that the most reasonable intermediate on heterolysis of the molozonide **3** is structure **4**.[10] This zwitterion (**4**) may, of course, cleave further to produce the Criegee zwitterion (**5**) and a carbonyl fragment. Recombination of these fragments may produce cross-ozonides, but ozonides whose geometry should be

(1) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Am. Chem. Soc.*, **88**, 3143 (1966).

(2) R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957).

(3) P. S. Bailey, *Chem. Ind.* (London), 1148 (1957).

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

(5) We shall consider at this time only simple olefins containing no heteroatoms or other substituents which may introduce special electronic effects.

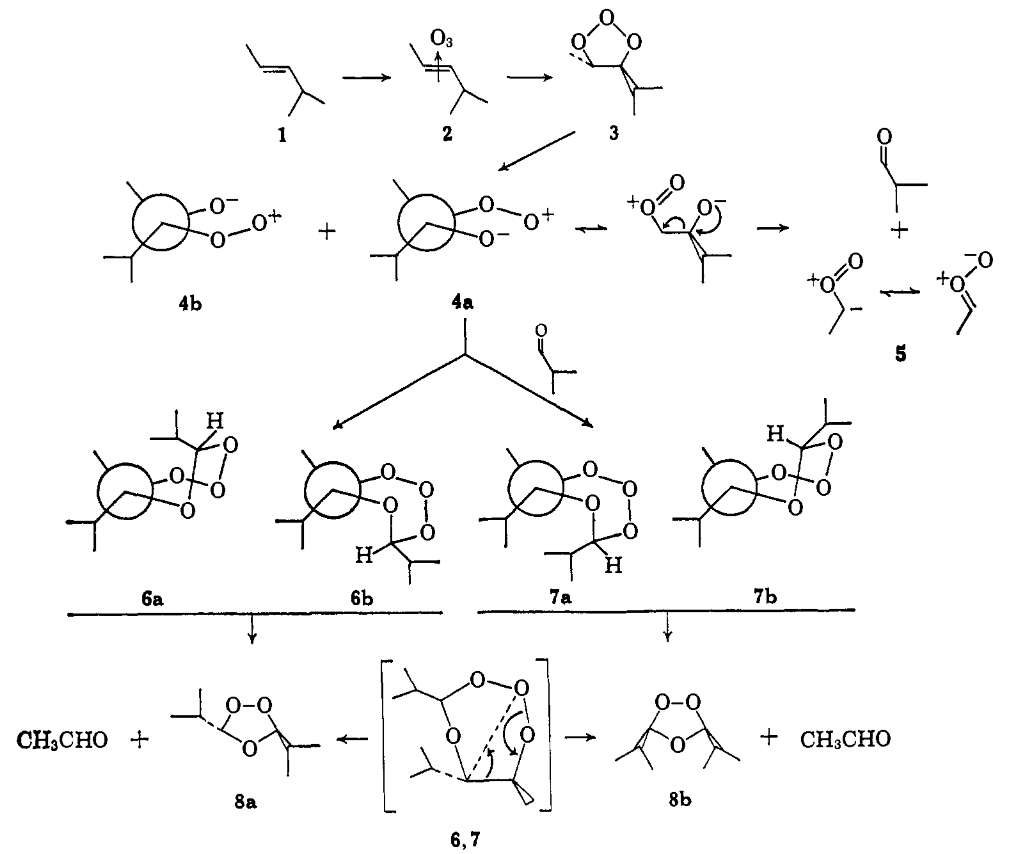
(6) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).

(7) F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964).

(8) R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 32.

(9) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963).

(10) This proposal is made on the grounds that a structure in which the positive charge can be delocalized over two oxygen atoms will be more stable than one involving a single positive oxygen.[8]

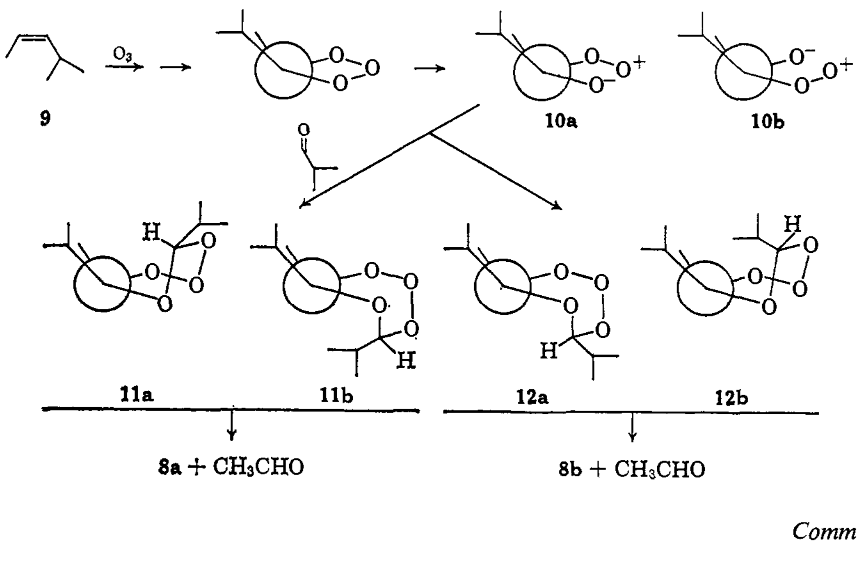


affected little by the geometry of the source olefin. If, however, we assign to **4** the role of an actual intermediate, we are provided with an alternative route to ozonide formation. As shown in the equation, interception of **4a** by reaction with isobutyraldehyde, in what is essentially an aldehyde interchange reaction, yields the transitory intermediates, **6** and **7**, which may rapidly collapse to the cross-ozonides **8** and acetaldehyde. There exist four possible conformations of the reactants, **4a** and isobutyraldehyde; two of these, **6a** and **6b**, generate *trans*-ozonide **8a** and the other two, **7a** and **7b**, yield the *cis*-ozonide **8b**. Examination of scale molecular models of **6** and **7** and the probable transition states for steric effects reveals that, on balance, there should be little preference for *cis*- or *trans*-ozonide **8b** or **8a** from the *trans*-olefin **1**. The observed *cis*:*trans* ratio is, in fact, 50:50.[1]

Ozonolysis of the *cis*-olefin **9**, however, leads to a significantly different conclusion. In this case, condensation of **10a** with isobutyraldehyde may, as with the *trans*-olefin, lead to two possible intermediates, **11** and **12**, but with a clear preference, on steric grounds, for **12a**, which suffers only H–H nonbonded repulsions and leads to *cis*-ozonide **8b**. The observed *cis*:*trans* ratio is 66:34.[1]

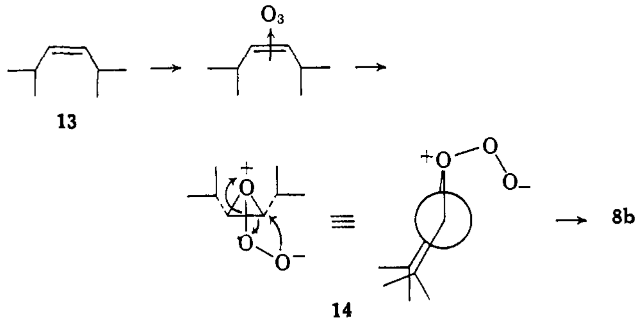
The scheme outlined here is helpful in understanding the rather surprising finding[1] that cross-ozonide geometry is dependent, to at least some extent, on olefin geometry and, further, that *cis*-olefins generate a significantly higher *cis*:*trans* ratio than *trans*-olefins.

Sterically Hindered Disubstituted *cis*-Olefins. Rather hindered *cis*-olefins behave differently than *trans*-olefins or unhindered *cis*-olefins and do not appear to follow the mechanistic scheme just outlined. For example, *cis*-di-*t*-butylethylene gave 70% *cis*-ozonide while the *trans*-olefin gave 100% *trans*-ozonide[11] and, further,



the existence of a *trans*-molozonide was established by its reduction to the corresponding glycol.[6] No such conclusive evidence has been found for the existence of a *cis*-molozonide, although Greenwood[12] has found some indication of their formation from simple *cis*-olefins.

It is our contention that the ozone–olefin π complex involving hindered *cis*-olefins, instead of always forming a molozonide which would force the bulky substituent groups even closer, has an additional, more attractive path open to it, that is, it may collapse to a σ complex (**14**), as illustrated for *cis*-diisopropylethylene (**13**), which we find gives a *cis*:*trans* ozonide ratio of 66:34.[13] We propose that this σ complex, or some variation of it, rearranges in a concerted stereospecific manner to *cis*-ozonide **8b**, thus accounting for the high *cis*:*trans* ozonide ratio[1] and for the high yields of total ozonide from *cis*-olefins.[11,13] The observations that highly hindered olefins yield epoxides[4] and that ozonolysis of araucarolone diacetate[14] and Feist's acid[15] results in cleavage of the bond adjacent to the olefinic bond also support the σ-complex interpretation.



---

[11] G. Schröder, *Chem. Ber.*, 95, 733 (1962).

[12] F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965).

[13] O. Lorenz and C. R. Parks, *J. Org. Chem.*, 30, 1976 (1965), report a *cis*/*trans* ratio of 1.

[14] C. R. Enzell and B. R. Thomas, *Tetrahedron Letters*, 225 (1965).

[15] A. T. Bottini and J. D. Roberts, *J. Org. Chem.*, 21, 1169 (1956).

Paul R. Story
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

R. W. Murray, R. D. Youssefyeh
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey 07971

Received April 9, 1966

Ozonolysis. VIII. Alkene and Ozonide Geometry in the Alkene–Ozone Reaction

Sir:

It has become clear that alkene geometry plays an important role in determining the course of the alkene–ozone reaction. Alkene geometry is important in determining the stability of the molozonide,[1] and with symmetrically disubstituted alkenes it appears to control the amount of reactants that are converted to ozonide. Schröder[2] first noted this with *cis*- and *trans*-di-*t*-butylethylene. In the current studies with the *cis* and *trans* isomers of 2-butene, 2-pentene, and 3-hexene it was uniformly true that, under the same experimental conditions, the *cis* isomer gave superior yields of ozonide. Specifically, *cis*-3-hexene was converted to ozonide in 85% yield, whereas from the *trans* isomer 45% was the best yield obtainable. Comparable conversions to ozonide were realized with the other alkenes, with the best yields of ozonide from *cis* alkenes being obtained from a hydrocarbon solvent and from an ether solvent in the case of the *trans* alkenes.

With the development of a column for vapor phase chromatography which effected the complete separation of the stereoisomeric ozonides, it became possible to examine the relationship between alkene geometry and ozonide geometry. Typical data for 3-hexene and 2-butene are given in Table I. An interesting solvent effect which would appear to be dependent on nucleophilicity and not polarity is apparent in the data of Table I (n-C_5H_{12}, $\mu < 0.05$ D.; CH_2Cl_2, $\mu = 1.47$ D.; Et_2O, $\mu = 1.18$ D.; Me_2O, $\mu = 1.31$ D.).

Table I. Stereoisomeric Ozonides from *cis*- and *trans*-Alkenes[a]

Alkene	Reaction temp, °C	Solvent	Ozonide isolated, mmoles	% stereoisomeric ozonides[b] α form	β form
cis-3-Hexene	−30	n-C_5H_{12}	44	52	48
	−30	Et_2O	40	62	38
trans-3-Hexene	−30	n-C_5H_{12}	11	59	41
	−30	CH_2Cl_2	12	54	46
	−30	Et_2O	22	66	34
	−70	Et_2O	21	67	33
	−110	Et_2O	18	66	34
cis-2-Butene	−30	n-C_4H_{10}	36	65	35
	−70	Me_2O	31	71	29
trans-2-Butene	−30	n-C_4H_{10}	18	66	34
	−70	Me_2O	17	70	30

[a] All data are calculated on the basis of 50 mmoles of ozone reacting with excess alkene. [b] Present information does not permit unambiguous assignment of configuration. The α form is the stereoisomer of shorter retention time.

The ozonation of 2-pentene, as reported earlier[3] for a *cis*–*trans* mixture of the alkene, becomes complicated by the fact that now three ozonides, *i.e.*, 2-butene ozonide, 2-pentene ozonide, and 3-hexene ozonide, are formed. The solvent has a much more striking effect on the relative amounts of these three ozonides than does alkene geometry, as is illustrated in Table II. It is clear that the formation of "crossed-ozonides" is much more pronounced in the ether solvent.

2-Pentene geometry does appear to influence the relative proportions of stereoisomeric ozonides more in the hydrocarbon solvent than in the ether solvent. This is evident from the data of Table III.

The above-described results were obtained by treating *ca.* 40 mmoles of alkene in 200–250 ml of solvent with 90–95% of the theoretical amount of ozone which was introduced at the rate of *ca.* 600 mg/hr. The solvent was removed *in vacuo* on a rotary evaporator with the reaction flask in a bath which was maintained at −50 to −70°, depending on the solvent. The ozonide was collected in a liquid nitrogen cooled trap *in vacuo* on the rotary evaporator by permitting the reaction flask to warm to 25°, and the ozonide subsequently was distilled *in vacuo*. All analyses were performed on the sample of distilled ozonide. The residue remaining in

---

[1] R. Criegee and G. Schröder, *Chem. Ber.*, 93, 689 (1960); F. L. Greenwood, *J. Org. Chem.*, 29, 1321 (1964); F. L. Greenwood, *ibid.*, 30, 3108 (1965).

[2] G. Schröder, *Chem. Ber.*, 95, 733 (1962).

[3] L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, 87, 737 (1965).