Ozonolysis. Steric and Stereochemical Effects in the Olefin

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Abstract: Ozonolysis of a series of *cis* and *trans* olefins indicates that the ozonide *cis*:*trans* ratio produced in both normal ozonides and cross-ozonides is a function of both olefin stereochemistry and steric effects in the olefin. Isolation of an epoxide in which the olefin stereochemistry has been preserved has been observed in the case of one *trans* olefin. The mechanistic consequences of these results are discussed.

It has now been amply demonstrated[2-9] that olefins can give both *cis* and *trans* ozonides. Of greater significance to the mechanism of ozonolysis are a few observations which indicate that the ozonide *cis*–*trans* ratio obtained can be a function of olefin stereochemistry. A different ozonide *cis*:*trans* ratio is obtained from the stereoisomers of di-*t*-butylethylene,[2] 1,4-dibromo-2,3-dimethylbutene-2,[3] methyl *p*-methoxycinnamate,[6] and a number of simple alkenes.[7-9]

Also of considerable importance to the study of the mechanism of ozonolysis are the reports by several groups[5,8-10] that unsymmetrical olefins give, in addition to the expected unsymmetrical ozonide *cis*–*trans* pair, two symmetrical ozonide *cis*–*trans* pairs derived from the cleavage of the olefin unsaturation. We have recently shown that a combination of these two important pieces of information, that is, the formation of cross-ozonides and the observation of ozonide *cis*–*trans* pairs, can be used to provide results which raise serious questions about the general validity of the Criegee mechanism of ozonolysis.[11] Specifically, it was shown that the ozonide *cis*:*trans* ratios observed in *cross-ozonides* are also dependent upon olefin geometry.[12] In these cases the intervention of an intramolecular stereoselective pathway, such as was considered to explain similar results in the normal ozonide cases,[8,9] is not possible. These results have led us to propose a new path to ozonide formation in which the molozonide assumes the role of a true intermediate in an exchange reaction with aldehydes, and, thus, exerts an influence on the ozonide *cis*:*trans* ratios produced.[13]

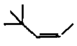
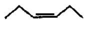
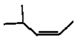
The observation that both ozonide and cross-ozonide *cis*:*trans* ratios can be dependent on olefin geometry provides a powerful new probe for studying the mechanism of ozonolysis. Effective use of this probe requires that the ozonide stereoisomer designations be made on an unequivocal basis, however. Such an assignment has recently become available[14] and is based on the fact that the *trans* isomer of a symmetrical ozonide must consist of a *dl* pair and, hence, be amenable to complete or partial resolution.

The establishment of a comprehensive mechanism of ozonolysis on a sound basis requires that a number of variables be studied in a systematic manner. We report here the results of such a study in which the major emphasis is on the effect of olefin steric factor and olefin stereochemistry.

Discussion of Results

We consider first the normal[15] ozonides produced upon ozonolysis of a series of olefins. In the *cis* series there is a clear dependence of the ozonide *cis*:*trans* ratios on the substituent size in the olefin as shown in Table I. A similar, although less-pronounced, effect

Table I. Normal Ozonide Stereoisomers from *cis* Olefins

Olefins	*cis*, %	*trans*, %	Total yield[a] of ozonides, %
	67	33	84
	66	34	85
	54	46	81
	53	47	81
	49	51	86
	42	58	91
	41	59	72
	39	61	48

[a] It should be noted that for unsymmetrical olefins this figure includes the yield of cross-ozonide.

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

(3) R. Criegee, S. S. Bath, and B. V. Bornhaupt, *ibid.*, **93**, 2891 (1960).

(4) O. S. Privett and E. C. Nickell, *J. Lipid Res.*, **4**, 208 (1963).

(5) G. Riezebos, J. C. Grimmelikhuysen, and D. A. Van Dorp, *Rec. Trav. Chim.*, **82**, 1234 (1963).

(6) P. Kolsaker, *Acta Chem. Scand.*, **19**, 223 (1965).

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

(8) O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965).

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

(10) O. S. Privett and E. C. Nickell, *J. Am. Oil Chemists' Soc.*, **41**, 72 (1964).

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

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

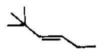
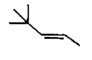
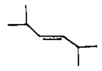
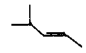
(13) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966).

(14) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **88**, 3655 (1966).

(15) The term normal ozonide is here used to describe the parent ozonide obtained upon ozonolysis of an olefin. For a symmetrical olefin this is a symmetrical ozonide. For an unsymmetrical olefin it is the unsymmetrical ozonide. The two symmetrical ozonides obtained in the latter case are here referred to as cross-ozonides.

is seen in the *trans* series for olefins below, and including, diisopropylethylene in steric requirements (Table II). In the *cis* series this effect is in the form of a higher per cent *cis* ozonide accompanying higher steric requirements in the olefin. The same effect is noticed in the *trans* series for olefins below diisopropylethylene. The remaining two members of the *trans* series, both of which contain a *t*-butyl group, do not follow this trend but instead give a much higher per cent *trans* ozonide. The results reported earlier by Schröder also fit well into these two series. For *cis*-di-*t*-butylethylene Schröder obtained a 70:30 *cis*:*trans* ratio, placing it at the top of the *cis* series, consistent with its higher steric requirements. Likewise, for *trans*-di-*t*-butylethylene he reported obtaining 100% *trans* ozonide, which places this result in the group at the top of the *trans* series. Apparently, the presence of the *t*-butyl group in the *trans* olefins introduces a new factor which disrupts the trend in the ozonide *cis*:*trans* ratios. Our observations with two members of this group indicate that these same olefins are also most prone to give olefin–ozone adducts which undergo rearrangements. One of these rearrangements, that which gives *t*-butyl formate, involves migration of the *t*-butyl group. These processes are undoubtedly competing with ozonide formation and are probably responsible for the change in trend in the ozonide *cis*:*trans* ratios as well as the lower yields obtained in these cases.

Table II. Normal Ozonide Stereoisomers from *trans* Olefins

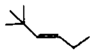
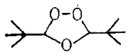
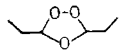
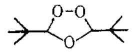
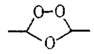
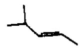
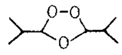
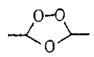
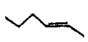
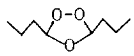
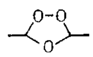
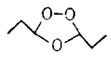
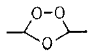
Olefins	*cis*, %	*trans*, %	Total yield[a] of ozonides, %
	29	71	16[b]
	30	70	32[b]
	53	47	47
	53	47	49
	48	52	66
	40	60	53[b]
	38	62	56
	38	62	36

[a] It should be noted that for unsymmetrical olefins this figure includes the yields of cross-ozonide. [b] Yield of one or both cross-ozonides could not be determined.

The difference in the steric effect between the *cis* and *trans* series is seen to diminish with size of substituent until the diethylethylene case (hexene-3) is reached where the ozonide isomer distribution is the same for both series at 53:47 (*c*:*t*). In fact with all of the olefins below hexene-3 in steric requirements both olefin series give approximately the same ozonide isomer distribution, and the steric effect on this ratio within either series is less pronounced than for those olefins having greater steric requirements than hexene-3.

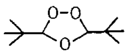
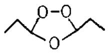
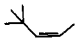
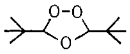
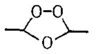
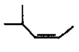
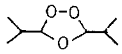
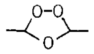
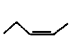
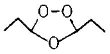
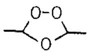
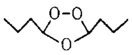
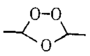
Examination of the ozonide *cis*:*trans* ratios obtained in the *cross*-ozonides reveals a similar trend to that observed in the *normal* ozonides, although fewer examples are available to support this general observation (Tables III and IV). The effect is quite clear in the *cis* series where the larger of the two cross-ozonides obtained for each olefin is quite sensitive to the steric factor in the olefin. Thus, in the series, *cis*-4,4-dimethylpentene-2, *cis*-4-methylpentene-2, and *cis*-pentene-2 the *cis*:*trans* ratios in the cross-ozonides di-*t*-butylozonide, diisopropylozonide, and diethylozonide were 74:26, 66:34, and 56:44 (*c*:*t*), respectively. A similar trend is perhaps discernible in the *trans* series, but this conclusion must be regarded as tentative. One point is clear, however. As reported earlier,[12] the *cis*:*trans* ratios for cross-ozonides are dependent on olefin geometry for a number of olefins. To us this observation is inconsistent with the Criegee zwitterion mechanism, in which the zwitterion precursor to ozonide should give the same ozonide *cis*:*trans* ratios for both olefin stereoisomers in both normal and cross-ozonides. In considering alternatives to this mechanism[13] we have considered several possible pathways as being in competition, with the Criegee zwitterion pathway retained as a possible contributing pathway.

Table III. Cross-Ozonide Stereoisomers from *trans* Olefins

Olefins	Cross-ozonide obtained	Ozonide stereoisomer distributions, % *cis*	*trans*	Yield of cross-ozonide, %
		*a*	*a*	*a*
		*a*	*a*	*a*
		*a*	*a*	*a*
		*a*	*a*	*a*
		50	50	11
		38	62	6
		*a*	*a*	*a*
		39	61	11
		41	59	8
		32	68	10

[a] Yield and isomer ratio could not be obtained but ozonides were produced.

Table IV. Cross-Ozonide Stereoisomers from *cis* Olefins

Olefins	Cross-ozonide obtained	Ozonide stereoisomer distributions, % *cis*	*trans*	Yield of cross-ozonide, %
		82	18	11
		62	38	12
		74	26	3
		46	54	9
		66	34	19
		49	51	12
		56	44	14
		44	56	18
		*a*	*a*	*a*
		43	57	16

[a] Yield and isomer ratio could not be obtained but ozonides were produced.

An additional observation can be made relative to the *cis*:*trans* cross-ozonide ratios obtained in the *cis* series. In many cases this ratio for the larger of the two cross-ozonides obtained is almost identical with the ratio obtained from the symmetrical *cis* olefin which would give the same ozonide. In the *cis*-4,4-dimethylpentene-2 case, for example, the di-*t*-butylozonide obtained has a 74:26 (*c*:*t*) ratio while Schröder[2] reported a 70:30 (*c*:*t*) ratio for the same ozonide from *cis*-di-*t*-butylethylene. Likewise, *cis*-4-methylpentene-2 gives a 66:34 (*c*:*t*) ratio for the diisopropylozonide, which is exactly the same ratio obtained from the symmetrical olefin, *cis*-2,5-dimethylhexene-3. A similar situation exists for the hexene-3 ozonides from *cis*-pentene-2 and *cis*-hexene-3 where the ratios are 56:44 and 53:47 (*c*:*t*), respectively. In the case of *cis*-*t*-butylethylethylene, on the other hand, the di-*t*-butylozonide produced has the remarkably high *cis*:*trans* ratio of 82:18. This result surely argues against a pure zwitterion mechanism for cross-ozonide formation. In fact, the cross-ozonides from the *cis* olefins taken as a whole suggest an intermediate for their production which is quite sensitive to steric factors in the olefin and, like the normal ozonides, the correlation is that higher steric requirements leads to a higher per cent *cis* ozonide being produced.

We have proposed a mechanism which we believe to be consistent with these observations[13] (Scheme I). According to this proposal an olefin can give either a molozonide **2** or a σ complex **3** with either of these adducts perhaps, but not necessarily, preceded by a π complex **1**. The percentage of each pathway taken will depend on the stereochemistry and steric factors present in the olefin. In general *cis* olefins are more likely than *trans* to take the σ-complex pathway, and those which are badly sterically hindered proceed almost exclusively *via* this pathway, at least in producing normal ozonides. The molozonide pathway has several alternatives available to it, one of which is to cleave to give the Criegee zwitterion **4** and a carbonyl compound **5**. The other alternative gives to the molozonide the role of a true intermediate which is visualized as cleaving to a zwitterionic form **6** either prior to or assisted by the approach of an aldehyde molecule, with which it will undergo an aldehyde exchange reaction. This latter reaction gives either normal ozonide or cross-ozonide, depending upon the nature of the aldehyde. The direction of cleavage of **2** shown here is contrary to that usually given[16] in which the single oxygen carries the positive charge. It is our contention that a structure in which the positive charge can be delocalized over two oxygen atoms will be more stable. The adduct between the opened molozonide and the aldehyde is a transitory intermediate **7** which can exist in four possible conformations **7a–d**. Two of these conformers are precursors to a *cis* ozonide and two to a *trans* ozonide.[13] This process for the case of *cis*-4-methylpentene-2 and isobutyraldehyde is depicted in Scheme I. Examination of scale molecular models for this case reveals that one of these conformations is preferred (**7c**), since it contains only H–H nonbonded repulsions. Since this conformation leads to *cis* ozonide, the ozonide formed in this aldehyde interchange is expected to have a higher per cent *cis* configuration as observed. A similar analysis starting with the *trans* isomer is depicted in Scheme II. Here a consideration of the possible conformations of the molozonide–aldehyde adduct shows no over-all preference for *cis* or *trans* ozonide precursor. Again, the experimental results are in keeping with this analysis; *e.g.*, see the cases of the diisopropyl ozonide formed from *trans*-4-methylpentene-2 and the hexene-3 ozonide formed from *trans*-pentene 2. It should be remembered that in all cases the observed *cis*:*trans* ratio is believed to be the net result of contributions from several pathways. In the cases just discussed, for example, these detailed pathways are seen as the dominant contributions to the observed ratio with other pathways making smaller contributions.

Another observation which seems to be generally true is that the *cis* olefins always give a higher yield of ozonide than the *trans*. This is true both for normal ozonides and cross-ozonides. Similar results with respect to normal ozonides have been reported by Schröder,[2] Greenwood and Haske,[7] and Lorenz and Parks.[8] We have also observed an increase in yields of free aldehyde in the *trans* series, as well as the production of acids which sometimes complicated isolation of the ozonides by glpc. Where the steric effect is especially pronounced as, for example, in *trans*-2,2-dimethylhexene-3, sufficient quantities of both ester and epoxide are produced to permit their isolation. The gas chromatograms also indicated that traces of these materials were formed in some of the other

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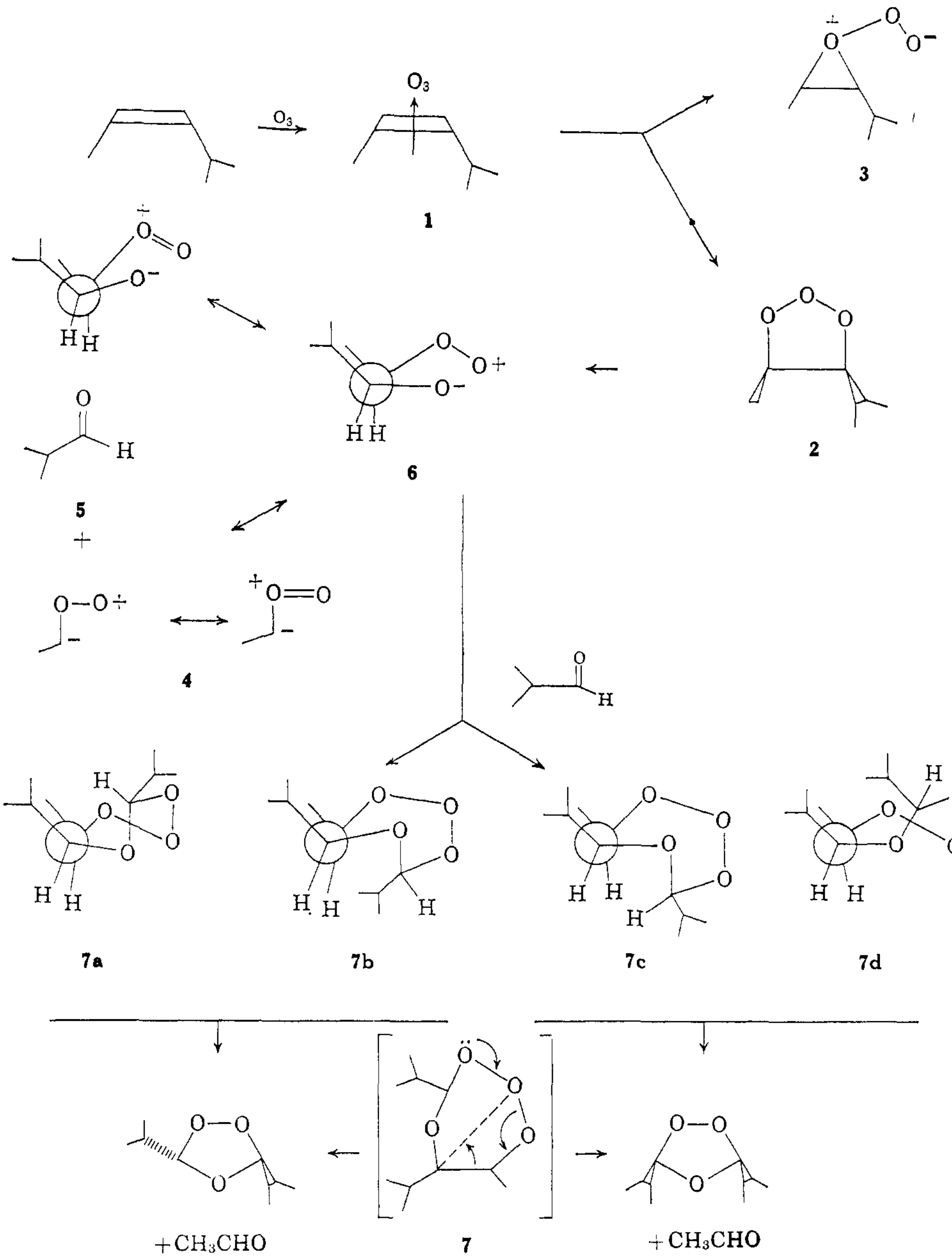
(16) R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 32.

Scheme I



trans olefins. All of these observations seem to be consistent with the mechanistic scheme described above. That is, ozonolysis of a *trans* olefin is expected to involve a greater percentage of the pathways originating with molozonide. These pathways involve the polar intermediates **4** and **6**, either of which can undergo rearrangements to give the acids and esters. These pathways might also be expected to give lower yields of ozonides since they involve a greater degree of separation of olefin fragments. The *cis* isomers, on the other hand, are more likely than the *trans* to proceed *via* the pathway involving the σ complex **3**, which can proceed directly to normal ozonide without involving the molozonide or separation of olefin fragments. Important to this view is the reported[17] absence of a molozonide upon ozonolysis of *cis*-di-*t*-butylethylene, whereas the *trans* isomer gives a molozonide which is stable at $-75°$. Greenwood[7] has suggested that *cis* olefins in general may also give molozonides which are much less stable than those from the *trans* isomers. The conclusion was based in part upon the production of a white solid upon ozonolysis of *cis*-hexene-3, and the subsequent explosive decomposition of this material upon warm-up. While Greenwood's interpretation seems reasonable, it may be that the unstable species which is found in the *cis* case is not a molozonide at all, but a different species, perhaps the σ complex or something related to it. Besides explaining the higher yields the σ complex pathway may be the reason for the observed greater retention of configuration for hindered *cis* olefins.

The basic reason for *cis* olefins being more likely to involve the σ complex than the *trans* is perhaps seen from a critical examination of the steric requirements for its formation with the aid of scale models. The formation of the complex is depicted as involving approach of the ozone molecule so that the plane of the three oxygen atoms is perpendicular to the plane containing the olefinic carbon atoms. The complex itself is seen as having one end oxygen of the ozone

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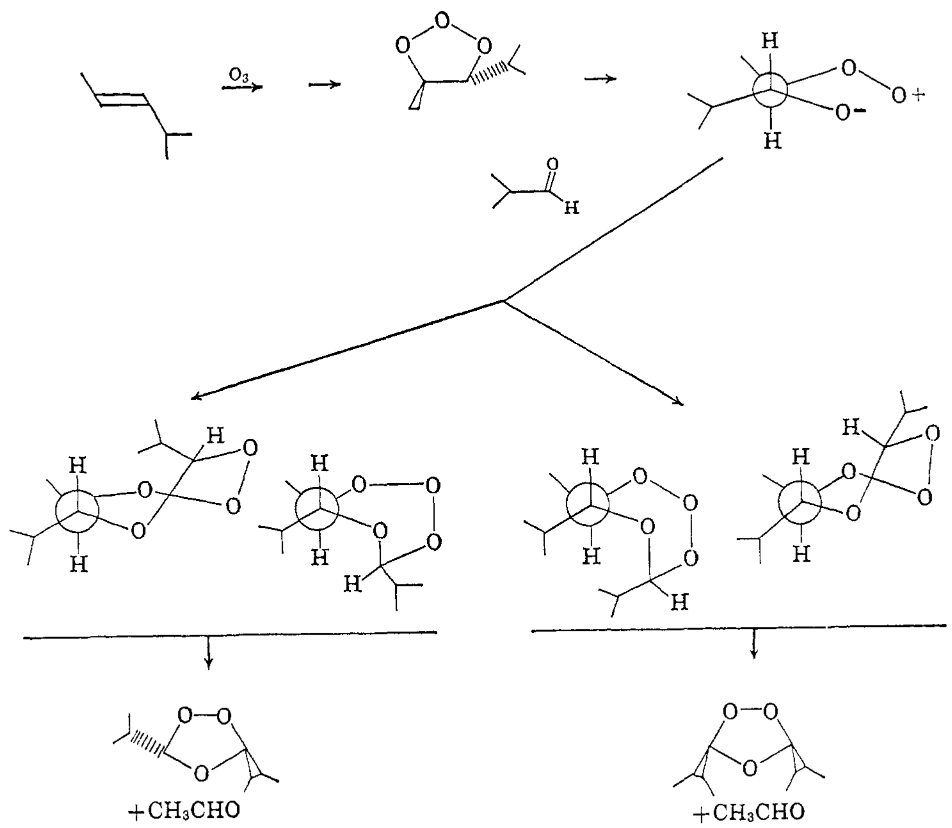
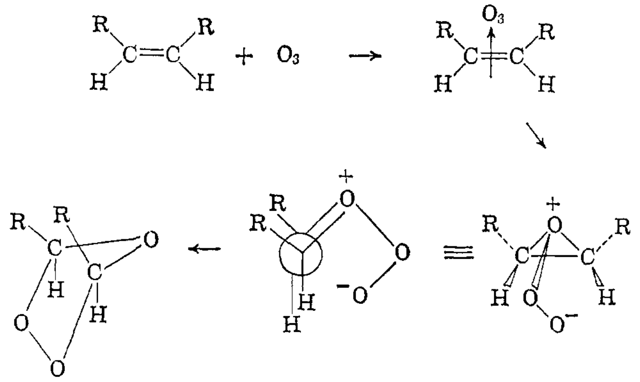
(17) R. Criegee and G. Schröder, *Chem. Ber.*, 93, 689 (1960).

Scheme II



molecule above the olefinic carbon plane and the other end oxygen below this plane. It is this assembly which it is proposed can proceed stereospecifically and intramolecularly to ozonide. Formation of such an assembly and its subsequent internal rearrangement are both more difficult in a *trans* olefin than in the *cis* isomer.



Isolation of the epoxide in the case of *trans*-*t*-butylethylethylene provides further valuable information which may be highly pertinent to the mechanistic scheme described above. While the production of epoxides upon ozonolysis has been reported previously,[18] this appears to be the first case of isolation of an epoxide where the olefin is capable of giving both *cis* and *trans* epoxides. The epoxide obtained from this *trans* olefin has the *trans* structure as evidenced by the fact that it is identical with that obtained by peracid epoxidation of the same olefin. This could be a very significant result in that it may provide evidence for an initial olefin–ozone adduct in which the olefin stereochemistry is preserved, and which is capable of proceeding to products, in this case the epoxide. Such an initial adduct could be the π complex proposed earlier by Bailey[18] or the σ complex proposed by us.[13] This is the type of complex which we have proposed may proceed stereospecifically to ozonide particularly in the case of hindered *cis* olefins. Further work on the mechanism of production of epoxides and their stereochemistry is in progress.

The results described here indicate a definite influence of olefin stereochemistry and steric factors on the ozonide *cis*:*trans* ratios produced. Olefin stereochemistry also exerts a strong influence on the total yield of ozonide as well as on the possibility of producing such minor products as acids, esters, and epoxides. We have attempted to describe a mechanistic scheme to account for all of these observations and, while we feel that the scheme proposed does provide a cohesive framework for the ozonolysis reaction, it has some obvious shortcomings. Further refinement of the scheme must await the results of studies in progress on the effects of solvent, concentration, and temperature.

Experimental Section

The nmr spectra were determined on a Varian A-60 high-resolution nmr spectrometer. Elemental analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. 11377. The glpc analyses were carried out on an Aerograph Model A-700 gas chromatograph using a 10 ft, 10% cyanosilicone column.

Ozonolyses. A Welsbach Model T-23 ozonator was used as a source of ozone. The ozonolyses were carried out at *ca.* −70° using a 1 *M* solution of the olefin in pentane. Ozonolysis was continued to 75% of the theoretical ozone required. The reaction mixtures were analyzed by glpc using an Aerograph Model 471 digital integrator to obtain quantitative data. The assignment of *cis* and *trans* structures to the ozonide geometric isomers was made on the basis of glpc, infrared, and nmr data and the correlation of these data with the unequivocal assignment based on partial resolution

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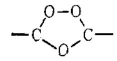
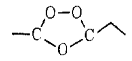
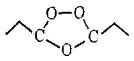
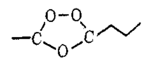
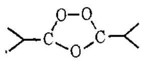
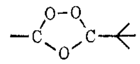
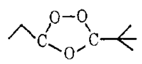
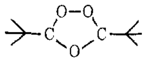
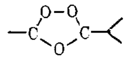
(18) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

Table V. Summary of Ozonide Experimental Data

Ozonide		Elemental anal. Calcd, % C	H	O	Found, % C	H	O	Nmr data τ (multiplicity)[a]	Wt ratio
	*trans*	46.15	7.75	46.10	46.36	7.80	46.00	4.75 (q), 8.72 (d)	1:3
	cis	46.15	7.75	46.10	46.01	7.66	. . .	4.70 (q), 8.63 (d)	1:3
	*trans*	50.83	8.53	40.63	50.82	8.49	40.56	4.7–5.15 (m), 8.2–8.7 (m), 8.67 (d), 9.05 (t)	2:2:3:3
	cis	50.83	8.53	40.63	50.77	8.46	. . .	4.79 (q), 4.95 (t), 8.0–8.5 (m), 8.68 (d), 9.07 (t)	1:1:2:3:3
	*trans*	54.53	9.15	36.32	54.39	9.21	34.17	5.04 (t), 8.05–8.6 (m), 9.03 (t)	1:2:3
	cis	54.53	9.15	36.32	54.62	8.65	. . .	5.02 (t), 8.1–8.9 (m), 9.09 (t)	1:2:3
	*trans*	54.53	9.15	36.32	54.38	9.00	36.67	4.68–5.05 (m) [8.4–9.3 (m), 8.68 (d), 9.07 (t)]	1:5[b]
	cis	54.53	9.15	36.32	54.71	9.24	36.21	4.68–5.16 (m) [8.25–9.3 (m), 8.71 (d), 9.1 (t)]	1:5[b]
	*trans*	59.98	10.07	29.96	60.10	10.23	29.84	5.25 (d), 7.86–8.47 (m), 9.09 (d)	1:1:6
	cis	59.98	10.07	29.96	59.96	10.18	30.02	5.23 (d), 7.86–8.62 (m), 9.11 (d)	1:1:6
	*trans*	57.51	9.65	32.84	57.26	9.61	. . .	4.9 (q), 5.3 (s), 8.67 (d), 9.08 (s)	1:1:3:9
	cis	57.51	9.65	32.84	57.63	9.52	33.01	4.79 (q), 5.32 (s), 8.68 (d), 9.11 (s)	1:1:3:9
	*trans*	59.98	10.07	29.96	59.92	9.85	29.83	5.08 (t), 5.35 (s), 8.15–8.65 (m) [8.96 (t), 9.10 (s)]	1:1:2:12[b]
	cis	59.98	10.07	29.96	60.18	9.89	30.12	5.01 (t), 5.35 (s), 8.15–8.70 (m) [9.12 (t), 9.13 (s)]	1:1:2:12[b]
	*trans*	63.79	10.71	25.50	63.33	10.53	. . .	5.37 (s), 9.08 (s)	1:9
	cis	63.79	10.71	25.50	63.55	10.68	25.61	5.3 (s), 9.10 (s)	1:9
	*trans*	54.53	9.15	36.32	54.76	9.27	36.58	4.87 (q), 5.19 (d), 7.94–8.45 (m), 8.67 (d), 9.06 (d)	1:1:1:3:6
	cis	54.53	9.15	36.32	54.74	9.02	. . .	4.78 (q), 5.20 (d), 7.94–8.5 (m), 8.69 (d), 9.09 (d)	1:1:1:3:6

[a] Abbreviations used are: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] Corresponds to the weight ratio for the total peaks indicated in the bracket.

of the *trans-dl* pair for diisopropylozonide.[14] The *cis* isomer has the longest glpc retention time. In the infrared spectra the *trans* isomer is characterized by a band at *ca.* 1320 cm^{-1} which is absent in the *cis* isomer. Likewise the *cis* isomers have a band at *ca.* 830 cm^{-1} which is missing in the *trans* spectra. Examination of the data in Table III will reveal a consistent correlation in the nmr spectra as well. For a symmetrical ozonide the methine hydrogens are always at lower field in the *cis* isomer. In the case of an unsymmetrical ozonide at least one of these protons will be at lower field in the *cis* isomer.

The *cis*:*trans* ratios reported are the result of several integrations of the glpc peak areas and have a maximum variation of ±0.5%. Control experiments demonstrated that the glpc conditions used do not affect the ozonide *cis*:*trans* ratios. A summary of yields, analytical data, and nmr data is given in Table V.

In the case of *trans*-2,2-dimethylhexene-3 sufficient quantities of two additional materials were produced to permit their isolation. The first of these has a relatively low glpc retention time (6.2 min at 70°). Its nmr spectrum consists of just two singlets at 2.21 and 8.58 with an integrated area ratio of 1:9. Of the two most likely structures for this material, the aldehyde, pivalaldehyde, is eliminated on the basis of nmr spectra since the aldehyde has two sharp singlets at 0.52 and 8.87. This material is therefore assigned the other possible structure containing highly deshielded protons, namely *t*-butyl formate. The second new material, isolated in 4% yield, has nmr and infrared spectra identical with those for authentic *trans*-2,2-dimethylhexene-3 epoxide obtained by the epoxidation of *trans*-2,2-dimethylhexene-3 using *m*-chloroperbenzoic acid.

Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.94; H, 12.60.

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