suggests that the rate-determining step may be the formation of the olefin complex as suggested by Osborn.[2b] He proposed that the initial step is the formation of $RhCl(PPh_3)_2H_2$ (solvent), displacement of the solvent by the olefin, and stereospecific *cis* transfer of the bound hydrogen to the olefin in an actual intermediate or in an activated complex.[12] He postulated that the rate-determining step in the reaction is the displacement of the solvent from the complex and the complexing of the olefin. If the olefin in the complex occupies a position *cis* to both rhodium–hydrogen bonds as Osborn suggests we suggest that the *trans*-olefins probably do not form the complex as readily as the *cis* isomers. We suggest that the formation of the complex with the *trans* olefins is slower because of the orientation of the bulky groups of the *trans* isomers and possibly a suitable alignment of these groups with respect to the double bond may be necessary to form the complex.

The specific labeling of the double-bonded carbons of olefins is a potentially useful device in an analytical scheme for characterizing mixtures of olefins. Present indications are that mass spectra of the alkane-d_2 compounds reflect the location of the deuterium atoms so that characterization of single compounds or simple mixtures is possible. Work is proceeding on the development of a method for the analysis of olefins using homogeneous deuteration and mass spectrometry.

Experimental Section

The deuteration equipment was similar to the hydrogenation apparatus described by Joshel.[13] A Teflon-coated[14] magnet driven by an external motor was used as a stirrer. The reaction flask was equipped with a side arm that was fitted with a silicone-rubber plug which enabled the withdrawal of samples with a syringe during deuteration.

Gas chromatographic separations were performed on an Aerograph Autoprep Model A-700 instrument using a 0.25 in. × 30 ft column of 15% Tween 20 on Chromosorb P. All mass spectra of the deuterioalkanes were obtained on a Consolidated Electrodynamics Model 21-103 mass spectrometer at an ionization voltage of 70 eV. Nuclear magnetic resonance spectra on selected deuterioalkanes were obtained on a Varian HA-100.

The homogeneous catalyst tris(triphenylphosphine)rhodium(I) chloride was prepared from rhodium chloride trihydrate and triphenylphosphine as described by Young.[2a] The deuterium used at first was 98 mol %, but later deuterations were performed using 99.5 mol % deuterium. The olefins were of 98% or better purity as determined by gas–liquid partition chromatography.

The heterogeneous catalysts such as platinum black and palladium were prepared from chloroplatinic acid and palladium chloride, respectively, by reduction with sodium borohydride in the reaction flask just prior to use.

About 0.40 g of the olefin was weighed into the reaction flask and diluted with 20 ml of benzene. Catalyst A was added in the amount of 15 wt % of the olefin to be reduced. The deuteration apparatus was connected to a manifold and the system was alternately evacuated and filled four times with deuterium gas, at which time the magnetic stirrer was turned on. Pressure was maintained at slightly above atmospheric pressure (positive pressure of about 10 mm).[15] The deuteration was monitored periodically by withdrawing a small sample of the solution with a syringe and analyzing the solution by gas–liquid partition chromatography. The heterogeneous catalytic deuteration was performed using similar conditions as the homogeneous catalytic deuteration.

Registry No.—Decane-1,2-d_2, 19165-56-1; decane-3,4-d_2, 19165-57-2; decane-5,6-d_2, 19165-58-3; tris(triphenylphosphine)rhodium(I) chloride, 14694-95-2.

Acknowledgment.—The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U. S. Department of the Interior, and the University of Wyoming.

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[12] J. F. Bielmann and M. J. Jung, *J. Amer. Chem. Soc.*, **90**, 1673 (1968)

[13] L. M. Joshel, *Ind. Eng. Chem.*, **15**, 590 (1943).

[14] References to trade names are made for information only and do not imply endorsement by the Bureau of Mines.

[15] Atmospheric pressure at this altitude is approximately 585 mm.

Ozonolysis. Steric Effects in the Aldehyde

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The ozonolysis of 1-olefins results in little or no cross-ozonide formation. Ozonolysis of 3,3-dimethylbutene-1 in the presence of added aldehydes with varying substituent size indicates that both aldehyde substituent size and concentration have a pronounced effect on the ozonide *cis–trans* ratio in the new ozonide produced. Larger substituent size and lower aldehyde concentration lead to a higher percentage *cis*-ozonide. The effect of substituent size on the ozonide *cis–trans* ratio is essentially the same whether the substituent is located in the olefin or the aldehyde.

A number of experimental facts which suggest that some modification to the Criegee[2] mechanism of ozonolysis should be considered have now been reported. Perhaps the most striking of these observations is the dependence of cross-ozonide *cis–trans* ratios on olefin stereochemistry.[3-6] These observations have stimulated several new suggestions regarding the mechanism. One, in the form of a working hypothesis, has as its

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[1] (a) To whom all correspondence should be addressed at the Chemistry Department, The University of Missouri at St. Louis, St. Louis, Mo. 63121. (b) Chemistry Department, The University of Adelaide, Adelaide, Australia.

[2] R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

[3] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3143 (1966).

[4] F. L. Greenwood, *ibid.*, **88**, 3146 (1966).

[5] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

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

TABLE I

SUMMARY OF OZONIDE EXPERIMENTAL DATA

Ozonide	Yield, %	Calcd, % C	Calcd, % H	Calcd, % O	Found, % C	Found, % H	Found, % O	Solvent	Nmr, τ (multiplicity)[a]	Wt ratio
4-Methylpentene	80	54.53	9.15	36.32	54.26	9.00	36.69	CCl_4	4.87 (s), 4.91 (t), 5.05 (s), 7.90–8.60 (m), 9.04 (d)	1:1:1:3:6
Hexene-1	78	54.53	9.15	36.32	54.67	9.02	36.16	C_6H_6	4.97 (t), 5.15 (s), 5.25 (s), 8.32–8.9 (m), 9.2 (t)	1:1:1:6:3
3-Methylbutene-1	92							CCl_4	4.88 (s), 5.04 (s), 5.19 (s), 7.9–8.6 (m), 9.03 (d)	1:1:1:1:6
Butene-1	85							CCl_4	4.90 (s), 4.97 (t), 5.04 (s), 8.0–8.6 (m), 9.07 (t)	1:1:1:2:3
3,3-Dimethylbutene-1	88	*b*						CCl_4	4.85 (s), 5.09 (s), 5.30 (s), 9.07 (s)	1:1:1:9

[a] τ values are relative to external tetramethylsilane. Abbreviations used are s, singlet; d, doublet; t, triplet, m, multiplet. [b] R. Criegee, A. Kerckow, and H. Zinke, *Chem. Ber.*, **88,** 1878 (1955).

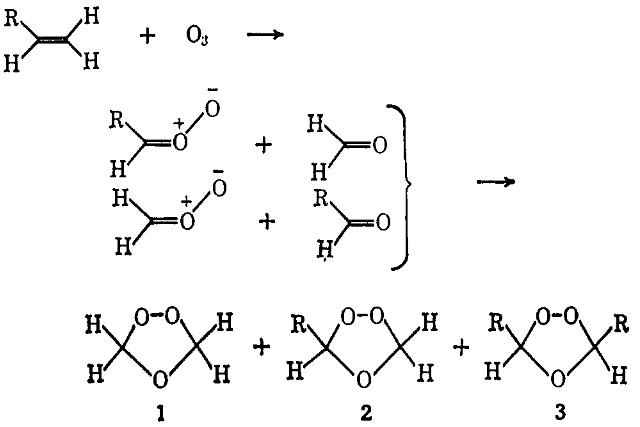
basis the proposal that there may be a competing path to ozonide formation which involves direct interaction of aldehyde and molozonide.[5,7] Some support for this proposal has been obtained in one case by means of an ^{18}O tracer technique.[8] Application of a similar technique in another case was interpreted to indicate predominance of the Criegee mechanism or perhaps a modified version of the molozonide–aldehyde mechanism.[9] Finally, a modified version of the Criegee mechanism has been suggested[6] the essence of which is that initial ozonides may stereoselectively decompose to give mixtures of *syn* and *anti* zwitterions which then stereoselectively recombine with aldehydes to give the final ozonides.

All of the various mechanistic pathways which have been proposed have in common the reaction of an aldehyde with some other species whether it be the molozonide, zwitterion, or a mixture of *syn* and *anti* zwitterions. Because of this essential nature of the aldehyde to all of the mechanistic proposals we decided to study the effect of aldehyde substituent size on ozonide *cis–trans* ratio. That is, we would hopefully determine what specific demands, if any, the aldehyde brings to the ozonide-forming reaction. The observation of ozonide *cis–trans* ratios and the dependence of these ratios on various reaction conditions has been amply demonstrated as an important probe with which to study the mechanism.

The desired results were obtained by ozonizing a 1-olefin in the presence of a series of aldehydes in which the substitutent size was varied. The ozonide *cis–trans* ratios in the new ozonides produced were then examined. The ozonide *cis–trans* ratios produced in this manner are the result of various aldehydes reacting with the same precursor to ozonide formation, whatever that precursor or precursors may be.

In addition to examining steric effects in the aldehyde we have, as an outgrowth of this work, also begun a corollary study of the ozonolysis of 1-olefins with emphasis on the mechanistic consequences of the results. As shown in Table I these 1-olefins give high yields of ozonides. In this respect they are like *cis*-olefins and unlike *trans*-olefins.[5,6] Also, the ozonolysis of 1-olefins leads to little or no cross-ozonide formation. Formally, at least, these ozonolyses ought to give two zwitterions and two aldehydes which upon random combination ought to give three ozonides, namely, ethylene ozonide, **1**, the parent olefin ozonide, **2**, and a third symmetrical ozonide, **3** (Scheme I).

SCHEME I



Obviously other factors must be superimposed on this simple scheme. Thus it may be that the 1-olefin does not cleave in a statistical manner, but that formation of formaldehyde, for example, is highly favored. While, in the case of styrene, the reported[10–13a] data indicate about a 50/50 split between the possible modes of decomposition of the molozonide, little quantitative data is available for other 1-olefins. In addition the methods used to assay the direction of split are complicated by the possibility of bimolecular reaction between reactive solvent and molozonide as opposed to the generally assumed reaction between reactive solvent and zwitterion, with the latter formed as a result of prior decomposition of the molozonide.

Vrbaski and Cvetanovic[13b] have reported the formation of small amounts (10% of the main ozonide) of ethylene ozonide in the ozonolysis of isobutene and 1-butene at −78° in ethyl chloride. It may be that in this more polar solvent the direction of initial adduct cleavage is altered somewhat.

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

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

(9) S. Fliszar, J. Carles, and J. Renard, *ibid.*, **90,** 1364 (1968).

(10) S. Fliszar, *Can. J. Chem.*, **44,** 2351 (1966).

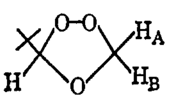
(11) W. P. Keaveney, M. G. Berger, and J. J. Pappas, *J. Org. Chem.*, **32,** 1537 (1967).

(12) E. Briner, S. Fliszar, and M. Ricca, *Helv. Chim. Acta*, **42,** 749 (1959).

(13) (a) E. Briner, C. Christol, S. Fliszar, and G. Rossetti, *ibid.*, **46,** 2249 (1963); (b) T. Vrbaski and R. J. Cvetanovic, *Can. J. Chem.*, **38,** 1063 (1960).

Nevertheless, our results in the case of 3,3-dimethyl-1-butene for example, indicate that even when ozonolysis is carried out at fairly high olefin concentration (2.0 *M*), the ratio of parent ozonide to the cross-ozonide, di-*t*-butylozonide, is at least 20/1. The other expected cross-ozonide, ethylene ozonide, would probably not survive even the mild glpc conditions used.

Two other aspects of the 1-olefin ozonolysis work are worth mentioning before going on to consider the results obtained with added aldehyde. The nmr spectra of the resultant ozonides (Table I) indicate that the ring methylene protons, H_A and H_B, as in 3,3-dimethyl-1-butene ozonide (**4**), for example, appear as separate singlets. That is, these geminal protons have a coupling constant, $J \cong 0$ Hz. This is consistent with similar observations in 1,3-dioxolans where it has been found that introduction of the oxygen atoms increased the value of J from a large negative value in cyclopentane to values close to 0 for 1,3-dioxolan itself.[14]

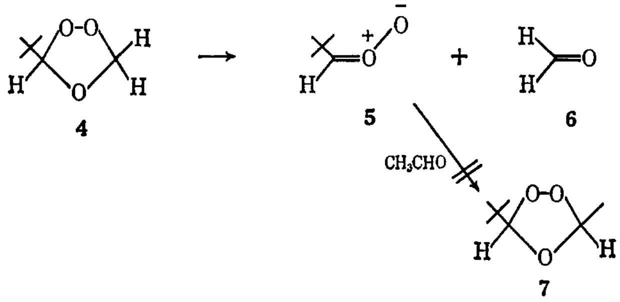


4

This same ozonide, **4**, was found to be relatively unstable. It slowly decomposed upon standing overnight at room temperature whereas all of the other ozonides involved in this work were completely stable under these conditions. In fact there are not many cases known where an ozonide has been isolated and subsequently found to decompose at room temperature. One other such case is that of 2,3,3-trimethylbutene-1 ozonide reported by Criegee, Kerckow, and Zinke.[15] These two examples suggest that, at least in the case of 1-olefins, the instability may be due to steric crowding on one side of the ozonide ring.

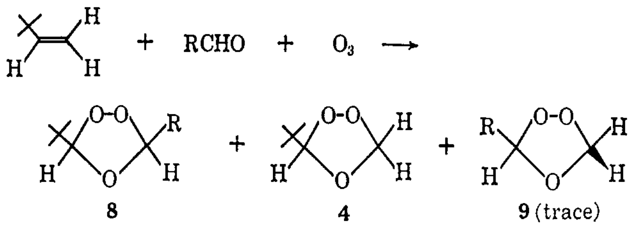
We have attempted to take advantage of this decomposition behavior to test for the possibility of reversible ozonide formation. Thus if **4** were to decompose into fragments **5** and **6** which presumably represent one of the two possible combinations leading to its formation, then it ought to be possible to intercept zwitterion **5** by adding an excess of a different aldehyde (Scheme II).

SCHEME II



We have tested this possibility by storing pure ozonide **4** in the presence of a threefold excess of acetaldehyde. While considerable decomposition of **4** occurred over a 24-hr period, no evidence for 4,4-dimethylpentene-2 ozonide (**7**) or any other new ozonide, could be found using glpc analysis. There are numerous instances now reported where an added aldehyde is allegedly reacting with a zwitterion intermediate to give a new ozonide incorporating the aldehyde. The results found here would seem to indicate, therefore, that the decomposition of **4** does not involve production of zwitterion **5** or of the other possible zwitterion, namely, formaldehyde carbonyl oxide.

Added Aldehyde Experiments.—The results of adding various aldehydes to the ozonolysis of 3,3-dimethylbutene-1 are shown in Figure 1. The aldehydes were also added in different concentrations which provided a separate aldehyde concentration effect result. In each case the ozonide of 3,3-dimethylbutene-1 is formed along with a new ozonide, **8**, which incorporates the added aldehyde. While, theoretically, there are two such new ozonides possible, only one is formed in appreciable yield. This one is that which formally is the adduct between the added aldehyde and pivalaldehyde carbonyl oxide. The other predicted ozonide, **9**, which represents the adduct between the added aldehyde and formaldehyde carbonyl oxide is present in a glpc detectable amount, but is estimated to be formed in less than one-tenth of the amount of **8**. As with the earlier observation that 1-olefins give little or no cross-ozonides, this result again suggests that the direction of cleavage of the initial olefin–ozone adduct is heavily in favor of the path which leads to formaldehyde and pivalaldehyde carbonyl oxide. This point will be examined further in a separate study.



Ozonides **8** can exist as *cis–trans* pairs and should reflect the sensitivity of ozonide precursor to steric effects in the added aldehyde. As shown in Figure 1 there is indeed a pronounced and regular sensitivity to steric bulk in the aldehyde. As the size of the aldehyde substituent is increased from ethyl to isopropyl to *t*-butyl, the percentage of *cis*-ozonide in ozonide **8** increases sharply. Since the nonaldehyde reacting partner in all of these cases is the same, the stereochemical effects transmitted to ozonide **8** must be due to the aldehyde. These results indicate that proposals for the mechanism must give adequate weight to requirements in the aldehyde.

The ozonide-producing reaction is also sensitive to the concentration of the added aldehyde. Above an aldehyde concentration of approximately 1.0 *M* the *cis–trans* ratio produced in ozonide **8** is constant. Below this aldehyde concentration the *cis–trans* ratio is very sensitive to aldehyde concentration and is altered drastically in favor of more *cis*-ozonide at low added aldehyde concentrations. The effect is so pronounced that in the case of added pivalaldehyde ozonide **8** produced is almost completely the *cis* isomer at 0.125 *M* added aldehyde concentration (Figure 1).

In order to study further the effect of steric bulk on

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[14] R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, No. 7, 355 (1966).

[15] See Table I, footnote *b*.

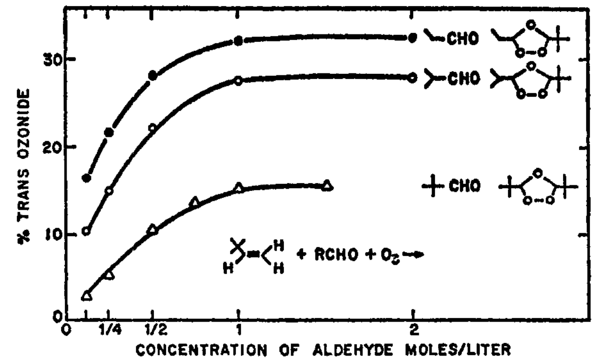

Figure 1.—The percentage of *trans*-ozonide obtained as a function of added aldehyde concentration in the ozonolysis of 3,3-dimethylbutene-1.

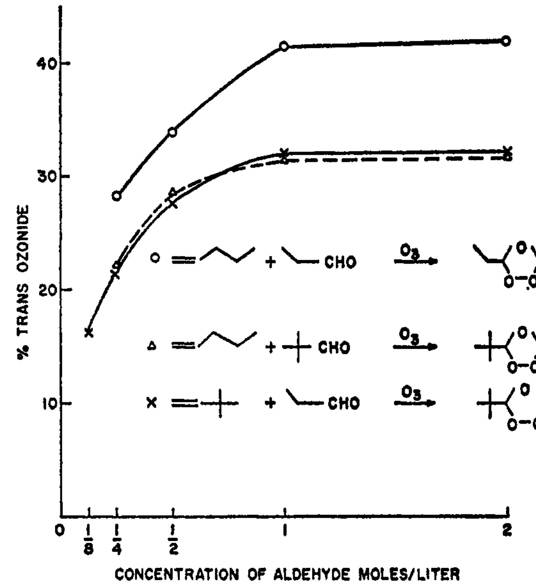

Figure 2.—The percentage of *trans*-ozonide obtained as a function of added aldehyde concentration in the ozonolysis of 3,3-dimethylbutene-1 and pentene-1.

the *cis–trans* ratio in ozonide **8** we have attempted to determine whether the steric effect is felt the same way depending upon whether the same steric requirement is present in either the olefin or the aldehyde. Thus pentene-1 was ozonized in the presence of added pivalaldehyde so that the *cis–trans* ratio in the new ozonide produced, **10**, could be compared with that in ozonide **8** in the case of the ozonolysis of 3,3-dimethylbutene-1 in the presence of propionaldehyde. In addition pentene-1 was also ozonized in the presence of propionaldehyde to determine whether this olefin reffected a sensitivity to aldehyde steric requirements comparable to that already seen in 3,3-dimethylbutene-1. The results of these experiments are shown in Figure 2. As seen in the uppermost curve pentene-1 does respond to aldehyde steric effects as reflected in the *cis–trans* ratio in the ozonide formed by diversion of intermediate by propionaldehyde. In this case the constant ozonide *cis–trans* ratio achieved has the expected higher percentage *trans*-ozonide presumably because of an over-all reduced steric requirement.

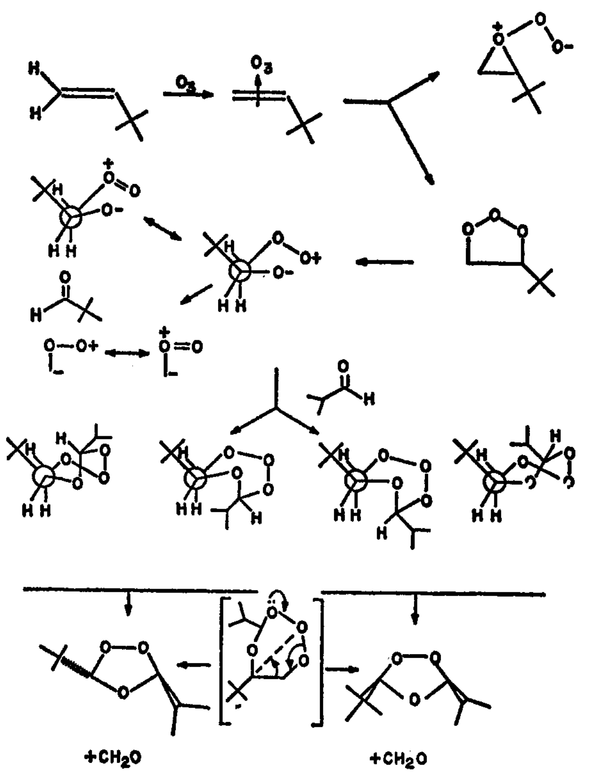

Figure 3.—Schematic of possible mechanism of ozonide formation for 3,3-dimethylbutene-1 with added aldehydes.

The remaining two curves in Figure 2 demonstrate a rather remarkable result. As reflected in the ozonide *cis–trans* ratios produced, the ozonide-forming process demonstrates exactly the same sensitivity to steric bulk *whether that bulk is present in the olefin or the aldehyde*, and this observation is true over a wide range of aldehyde concentrations.

The results in Figures 1 and 2 indicate a regular and significant effect of aldehyde substituent size on ozonide *cis–trans* ratio. The meaning of these results in terms of the mechanism problem is still not completely clear. In a general way the results appear to be somewhat consistent with the mechanistic proposals made earlier[5,7] in which it is suggested that aldehyde may react with molozonide to provide another path to ozonide formation. An application of this approach to the reaction of added aldehydes with 3,3-dimethylbutene-1 is shown schematically in Figure 3 with isobutyraldehyde used for illustration. A detailed analysis of the operation of this scheme will not be given here since it has been discussed earlier.[5,7,16] The scheme does predict that *cis*-ozonide would be formed preferentially in this pathway since only a precursor to *cis*-ozonide suffers only H–H nonbonded repulsions. Other precursors have somewhat less desirable steric interactions. Likewise this preference for *cis*-ozonide should be enhanced as the substituent size in the aldehyde is increased.

Results of a similar application of the molozonide–aldehyde pathway scheme to the case where the probing substituent can be either in the olefin or the aldehyde are shown in Figure 4. Here again the scheme predicts

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[16] R. W. Murray, *Trans. N. Y. Acad. Sci.*, **29**, 854 (1967).

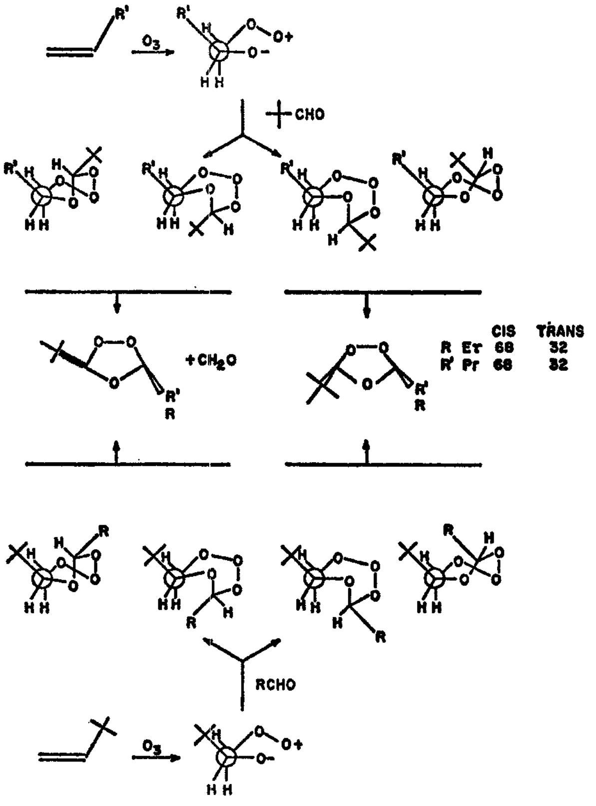

Figure 4.—Schematic showing influence of substituent size in olefin and aldehyde on ozonide formation.

a predominance of *cis*-ozonide. More importantly such a mechanistic path would seem to permit substituent bulk to have a similar influence on ozonide *cis–trans* ratio whether it is located in the olefin or the aldehyde, in keeping with the experimental results.

Interpretation of the aldehyde concentration dependence results is even more difficult—the shapes of the curves in Figures 1 and 2 suggest that what may be happening is that at higher aldehyde concentrations a shorter lived ozonide precursor may be intercepted to give a particular ozonide *cis–trans* ratio. When the aldehyde concentration is sufficiently high this path might be expected to dominate so a constant ozonide *cis–trans* ratio would be produced. The lower aldehyde concentrations would then represent a transition period in which another path which gives a different ozonide *cis–trans* ratio is still influencing the final ozonide *cis–trans* ratio. This other path could be the zwitterion–aldehyde path or some other path.

The results may also be consistent with the modified Criegee mechanism recently suggested by Bailey, *et al.*[16] Thus larger substituents might be expected to lead to more *anti* zwitterion and therefore, according to this scheme, more *cis*-ozonide.

At this point these attempts to provide a mechanistic explanation of the results are meant to be purely speculative. The results themselves are striking and in our opinion are important to those interested in stereochemical control in the ozonolysis reaction. Final resolution of the mechanism problem involved will probably require use of one of the labeling techniques recently described.[8,9]

Experimental Section

Procedures and Equipment.—A Welsbach Model T-23 ozonator was used as a source of ozone. The sample stream output of the ozonator was used with ozone delivery of 0.4 mmol of O_3/min. All ozonolyses were carried out to 75% of theory, in pentane solvent (total volume 25 ml), and at −70°. The reaction mixtures were analyzed by glpc on a Varian-Aerograph Model 700 gas chromatograph. In most cases a 10 ft 10% XE-60 cyanosilicone column was used. Maximum column temperature was 50° and maximum detector temperature was 88°. Direct on column injection was used. Quantitative data were obtained with an Aerograph Model 471 digital integrator. The ozonide *cis–trans* ratios reported are the result of an least five separate integrations of the glpc peak areas. The integrations were done on samples which were determined to be pure by nmr. Yields were obtained by calibrating glpc peak areas using pure samples and under conditions where no ozonide decomposition was detectable. A summary of yield, analytical data, and nmr data is given in Table I. Nmr spectra were run on a Varian A-60 high resolution nmr spectrometer.

In the added aldehyde experiments the olefin was present in 0.5 *M* concentration. The aldehyde concentration varied as shown in Figure 1. In the pure olefin runs the olefin concentration was 1.0 *M*, except as otherwise noted.

The assignment of ozonide *cis* and *trans* configurations was based on glpc, infrared, and nmr data and the correlation of these data with the unequivocal assignment made in the case of diisopropylozonide.[17] Elemental analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. 11377.

Materials.—All olefins (Chemical Samples Co.) were at least 99% pure. All aldehydes were distilled immediately before use.

Ozonolysis of 3,3-Dimethylbutene-1.—Solutions of the olefin up to 2.0 *M* were ozonized according to the general procedure given above. Even at the highest concentration used there was insufficient cross-ozonide produced to permit their glpc peak areas to be integrated. It is estimated that a ratio of cross-ozonide to normal ozonide of 1/20 would have permitted this integration.

The normal ozonide was somewhat unstable. In order to collect a pure sample, glpc column and detector temperatures of 40 and 60°, respectively, had to be used. Pure ozonide deposited a white solid upon standing overnight. This material was not further identified.

When a solution of this ozonide in pentane was stored with a threefold excess of acetaldehyde at room temperature for 24 hr, no 2,2-dimethylpentene-3 ozonide was formed as determined by glpc. Thus the decomposition of 1-olefin ozonide was probably not occurring through the free pivalaldehyde carbonyl oxide.

Ozonolysis of 1-Olefins with Added Aldehyde.—The general procedure given above was followed using varying concentrations of propionaldehyde, isobutyraldehyde, and pivalaldehyde with 3,3-dimethylbutene-1, and varying concentrations of propionaldehyde and pivalaldehyde with pentene-1. The results are shown in Figures 1 and 2. Yields of the new ozonide incorporating the added aldehyde and pivalaldehyde carbonyl oxide were generally about one-third those of the 1-olefin ozonide. Only trace quantities of the other possible ozonide expected in the presence of added aldehyde, that is, the ozonide incorporating the added aldehyde and formaldehyde carbonyl oxide, could be detected.

Registry No.—4-Methylpentene-1, 691-37-2; ozonide of 4-methylpentene-1, 18963-59-2; 1-hexene, 592-41-6; ozonide of 1-hexene, 767-09-9; 3-methylbutene-1, 563-45-1; ozonide of 3-methylbutene-1, 18963-61-6; 1-butene, 106-98-9; ozonide of 1-butene, 18963-62-7; 3,3-dimethylbutene-1, 558-37-2; **4,** 18963-63-8.

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(17) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3655 (1966).