provided by aniline derivatives makes possible systematic observations which we find do bear on the mechanism of pepsin.

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Ozonolysis of *trans*-Di-*tert*-butylethylene. Mechanistic Considerations[1]

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Abstract: In general, ozonolysis of *trans*-di-*tert*-butylethylene (**1**) in nonpolar solvents leads to ozonide formation. Ozonolysis of **1** in polar solvents, however, does not give ozonide. Decomposition of the initial ozonide of **1** in a variety of solvents leads to similar results. Thus, the solvent effect is not due to a change in the structure of the first intermediate in the reaction. Decomposition of the initial ozonide of **1** in a variety of environments leads to no radical formation as indicated by ESR measurements. Treatment of the initial ozonide of **1** with increasing amounts of propionaldehyde leads to reduced and eventually no ozonide formation. The significance of these results to the ozonolysis mechanism problem is discussed, including a suggestion that ozonide formation may be nonconcerted under some circumstances.

Introduction

Studies on the ozonolysis of *trans*-di-*tert*-butylethylene (**1**) have proven particularly useful for gaining information on the mechanism of ozonolysis. In large part, this is due to the relatively high stability of the initial olefin–ozone adduct in this case. It is this stability, for example, which permitted Criegee and Schröder[3] to show that the initial adduct in this case is a crystalline compound which can be reduced to racemic di-*tert*-butylethylene glycol, thus demonstrating that the initial adduct is formed stereospecifically and that one carbon–carbon bond is still intact in this intermediate. The stability of the initial adduct also permitted Bailey et al.[4] to measure its NMR spectrum and to conclude that its structure is that of a 1,2,3-trioxolane.

While these studies on the ozonolysis of **1** have proven extremely useful regarding the general problem of the mechanism of ozonolysis, several reports using the same substrate have produced results which are somewhat perplexing. In the same report in which they observed formation of crystalline initial adduct upon ozonolysis of **1** in pentane at −75 °C Criegee and Schröder[3] also reported that similar ozonolyses carried out in ethyl ether, methylene chloride, and ethyl acetate gave *no ozonide*. Indeed in the cases of methylene chloride and ethyl acetate they also reported that no pivalaldehyde was formed. In the diethyl ether case, the aldehyde was found to be present, and an addition of methanol at the low temperature and subsequent warming led to formation of the methoxyhydroperoxide expected from addition of methanol to the carbonyl oxide produced from ozone cleavage of **1**.

Likewise, Bailey et al.[4] found that warming of the low-temperature solutions of the trioxolane of **1** in acetone-d_6 or Freon 11 led to pivalaldehyde, *but no ozonide formation*. In all of these cases, the carbonyl oxide is presumed to give polymeric product. Again in these studies[4] addition of methanol at the low temperature to a Freon 11 solution of the presumed trioxolane, formed from addition of ozone to **1**, followed by warming, led to methoxyhydroperoxide formation. Thus, in several of these studies the carbonyl oxide appears to be able to react with methanol or to polymerize, but to be unable to react with pivalaldehyde to produce the ozonide of **1**. Only in the nonpolar solvent pentane is ozonide formation consistently observed to follow decomposition of the trioxolane.

A related study is that of Story et al.[5] in which they report that addition of propionaldehyde to a low-temperature pentane solution of the trioxolane of **1**, followed by warming, gave no cross ozonide incorporating the propionaldehyde, and also led to a lower yield of the normal ozonide of **1** and propionic acid formation.

Most generally accepted schemes for the ozonolysis process call for initial adduct formation, usually a trioxolane, decomposition to give aldehyde and carbonyl oxide, and subsequent recombination of these latter fragments to give ozonide.[6] While stereochemical aspects of the process have led to further suggestions[7-11] for the mechanism, all have retained these basic elements.

The observations[3-5] on the ozonolysis of **1** referred to above suggest that aspects of the mechanism other than stereochemical require further examination. In particular these

Table I. Results of Ozonolysis of *trans*-Di-*tert*-butylethylene in Various Solvents

Solvent	Temp, °C	Ozonide % yield[a]	Ref
Isopentane	−125	40	This work
	−90	55	This work
	−78	58	This work
Pentane	−90	53	This work
	−75	51	10
	−75	58	3
Diethyl ether	−90	25	This work
	−75	0	3
Ethyl acetate	−90	0	This work
	−75	0	3
Acetone	−90	0	This work
	−95	0	10
	−110	0	10
Methylene chloride	−90	0	This work
	−75	0	3
Trichlorofluoromethane	−95	0	10
	−110	0	10
Isopentane–cumene	−90	41[b]	This work
Isopentane–3-hexene	−90	45[b]	This work

[a] Yields based on reacted olefin. [b] Cumene or *trans*-3-hexene (2 mL) in isopentane (1 mL) were added to the cold (−90 °C) ozonolysis (isopentane) reaction mixtures.

Table II. Results of Decomposition of *trans*-Di-*tert*-butylethylene 1,2,3-Trioxolane in Various Solvents

Solvent	Temp, °C	Products[a]
CH_2Cl_2	−96	Aldehyde
CD_2Cl_2	−90	Aldehyde
CH_3COCH_3	−90	Aldehyde
$CH_3COOC_2H_5$	−95	Aldehyde
Cumene	−95	Aldehyde, ozonide
4-Octene	−95	Aldehyde, ozonide
Pentane	−127	Aldehyde, ozonide
Isopentane	−149	Aldehyde, ozonide
CH_3CH_2CHO	−80	Aldehyde

[a] Aldehyde is pivalaldehyde; ozonide is di-*tert*-butylethylene ozonide.

observations indicate a profound effect of the reaction medium on the course of the reaction. This fact plus the implications of recent theoretical calculations[12-15] have prompted us to examine further the ozonolysis of **1**.

Results

The results of ozonolyses of **1** in this work and those previously reported are shown in Table I. Unlike Criegee and Schröder we observe ozonide formation in diethyl ether. In methylene chloride we confirm their report of no ozonide formation, but unlike them we do find pivalaldehyde formation. We also have found that no ozonide is formed in acetone solvent. Ozonide is formed in all of the hydrocarbon solvents pentane, isopentane, isopentane–cumene, and isopentane–3-hexene. In a general sense ozonide is formed in relatively nonpolar solvents while no ozonide is formed in the relatively polar solvents.

In attempting to establish a reason for this general observation, it is convenient to view possible solvent effects as falling into two general categories. The first of these categories is termed a medium effect and includes effects due to (a) a change in rate of one or more steps involved in ozonide formation and (b) a change in the nature of one or more intermediates. The second general category includes effects due to solvent participation and includes, for example, (a) reaction of solvent with an ozonide precursor, e.g., methanol reacting

with a carbonyl oxide to produce a methoxyhydroperoxide; (b) solvent reaction with the trioxolane either in its closed form,
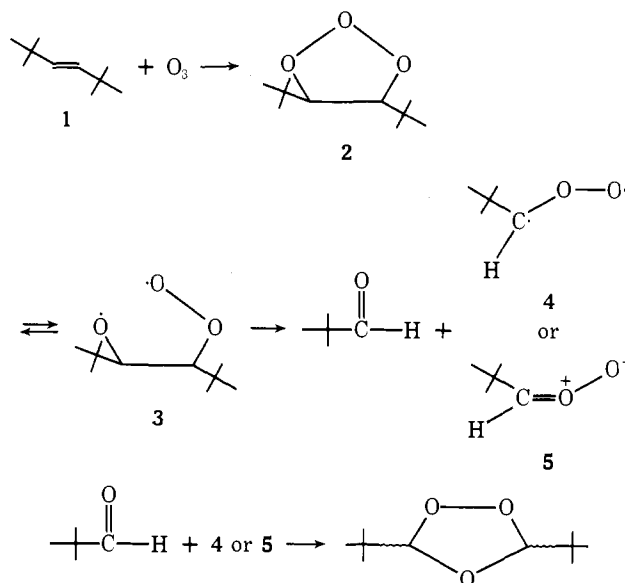
2, or in its open diradical form, **3**; (c) hydrogen atom or proton donation from the solvent to an ozonide precursor.

We have begun a series of experiments designed to identify more specifically the sizable solvent effect demonstrated by the work of ourselves and others (Table I) in the ozonolysis of **1**.

Trioxolane Decompositions. In order to examine the question of whether or not the observed effect is due to a change in the nature of the intermediate brought about by some solvent property, we have performed a series of experiments in which the same intermediate is decomposed in a variety of solvents. These experiments are made possible since, as shown by Criegee and Schröder,[3] ozonization of **2** in hydrocarbon solvents leads to precipitation of the intermediate. The reduction experiments of Criegee and Schröder[3] and the later NMR studies of Bailey et al.[4] strongly suggest that this intermediate is the trioxolane, **2**.

The solid intermediate was obtained by ozonizing **1** in pentane or isopentane at −110 to −130 °C and filtering off the solid at low temperature and pressure. The white solid was washed with cold isopentane and then placed in a variety of solvents and allowed to warm to room temperature. The solutions so obtained were analyzed by GLC with the results shown in Table II.

In each of these cases a common ozonization intermediate, probably **2**, is involved. Yet the decompositions indicate several different fates for the intermediate. As in the ozonolyses summarized in Table I, these decomposition experiments fall into two general categories. In the nonpolar solvents cumene, octene, pentane, and isopentane both ozonide and aldehyde are formed. In the polar solvents methylene chloride, dideuteriomethylene chloride, acetone, and ethyl acetate no ozonide is formed. In addition, decomposition of the solid intermediate in propionaldehyde solvent leads to no normal ozonide formation and no cross ozonide (incorporating propionaldehyde) formation.

Cumene and octene were used in order to test the possibility that the diradical **3** or the diradical form of the carbonyl oxide **4** might become involved in radical processes leading to a reduction in ozonide formation. Two recent theoretical studies[13,14] have concluded that the singlet diradical form of the carbonyl oxide is more stable than the zwitterionic form which is frequently invoked by workers in the field. As shown in Table II, however, these solvents give good yields of ozonide. While not completely excluding radical processes these results suggest

that any such processes do not interfere with the ozonide-forming reaction.

Ozonolyses in the Presence of Added Propionaldehyde. An additional set of experiments was carried out in which **1** was ozonized in isopentane at low temperature (-78 and -125 °C) and then the resulting ozonolysis mixture was treated with an added solution of isopentane containing varying amounts of propionaldehyde. The solutions were then allowed to warm up to room temperature, concentrated, and analyzed for ozonide by GLC. The results (Figure 1) indicate a progressive decrease in di-*tert*-butyl ozonide formation as the amount of added aldehyde is increased. At the highest propionaldehyde concentration used no ozonide is formed at -125 °C. In addition, no cross ozonide, incorporating the added propionaldehyde, was found under any of these conditions. These observations are thus similar to those made by Story et al.[6] except that we have studied conditions where normal ozonide formation is completely suppressed. The effect is nearly the same at -78 °C as at -125 °C. The slightly reduced effect of added aldehyde at the higher temperature could indicate that the ozonide-forming reaction competes more favorably at the higher temperature.

ESR Experiments. To further examine the possibility that radicals could be formed in the ozonolysis of **1** a number of experiments were carried out in which ESR scans were made during the decomposition of the trioxolane intermediate. Ozonolysis of **1** in hexane at -95 °C in an ESR sample tube led to the usual white precipitate of the trioxolane. The reaction mixture was degassed and the tube sealed. The sealed tube was then placed in the ESR probe which had been precooled to -100 °C. The reaction mixture was then allowed to warm up while scanning with the spectrometer. Scans conducted between -100 and -50 °C showed no evidence of radical production. In separate experiments the solid trioxolane was filtered off and then treated with hexane solutions of triphenylmethane and triphenylmethyl chloride. These solutions were handled in the same manner as the hexane solution, that is, ESR scans were made during trioxolane decomposition beginning at -100 °C. Finally an ozonolysis was carried out in methylene chloride at low temperature and the resulting solution checked for ESR signals during warmup in the spectrometer. In none of these cases was any evidence for radical production observed.

Discussion

The enormous effect of solvent on the course of ozonolysis of **1** is demonstrated by the data in Table I. Furthermore, a similar effect is noted when isolated intermediate (presumably trioxolane) decomposition is allowed to occur in most of these same solvents (Table II). Thus, the medium effect here does not appear to be due to the formation of different ozonolysis intermediates. The effect of solvent must be occurring after initial adduct formation.

While some of the solvents used might be expected to encourage radical formation from intermediates such as **3** or **4**, this does not seem to be a viable explanation for the observed results since ozonide formation does occur in cumene, for example, a solvent which might be expected to increase the likelihood of non-ozonide-producing radical reactions. Furthermore, the ESR experiments indicate that decomposition of the initial adduct fails to give detectable radical products even when the decomposition occurs in the presence of excellent radical sources such as triphenylmethane or triphenylmethyl chloride.

The earlier work of Criegee and Schröder[3] and Bailey et al.[4] confirmed that initial adduct decomposition gives carbonyl oxide in this case, since the expected methoxyhydroperoxide was formed when methanol was added to the low-temperature ozonolysis solutions.
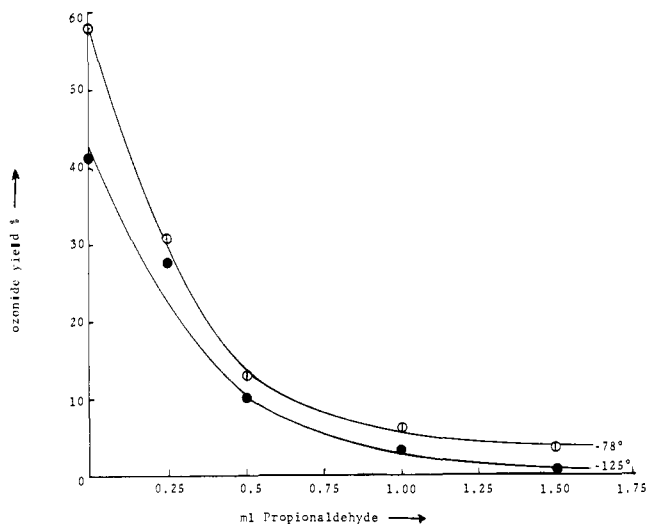

Figure 1. Effect of propionaldehyde added after ozonolysis on ozonide yield in the ozonolysis of *trans*-di-*tert*-butylethylene.

Several possible explanations for these intriguing results need to be considered further. One is that the trioxolane is decomposing in the usual manner to give aldehyde and carbonyl oxide, but that the solvent exerts a medium effect on the further reactions of these fragments. According to this explanation, the reaction medium in, for example, methylene chloride exerts a favorable influence on nonozonide-producing reactions such as carbonyl oxide dimerization or polymerization, while disfavoring the recombination of aldehyde and carbonyl oxide to give ozonide. This is essentially the explanation given by Bailey et al.[4,10] for the cases of trioxolane decomposition in Freon 11 or acetone-d_6 where aldehyde, but no ozonide, is formed.

The added aldehyde experiments reported here as well as those reported earlier by Story et al.[5] and Bailey et al.[16] raise additional questions concerning this explanation, however. Story et al. have shown[5] that ozonolysis of a number of other olefins in aldehyde solvent leads to complete or nearly complete suppression of ozonide formation. The observations were termed "reductive ozonolyses", and the explanation given[9] was that the aldehyde reacted with the initial adduct, formulated as the four-membered ring structure first suggested by Staudinger,[17] to oxidize the aldehyde to acid and produce a dioxetane which subsequently decomposed. Story et al. later reported[18] that the dioxetane intermediate could be isolated in several cases. Two other groups have since reported[16,19] that use of the Story et al. procedure does not lead to dioxethane formation, however.

When Bailey et al.[16] found a similar effect of added aldehyde on ozonide yield, with accompanying oxidation of the aldehyde, they argued that it was not necessary to invoke a Staudinger molozonide reduction mechanism, but that the aldehyde oxidation could have been brought about by the trioxolane, the Criegee carbonyl oxide zwitterion, or some species in between. When they confirmed Story's observation[18] that ozonolysis of ethylidenecyclohexane in pinacolone does not give ozonide, Kopecky et al.[19] suggested that pinacolone exerts a general (e.g., polar) effect on the reaction. On the other hand, Story et al.[5] have reported that ozonolysis of ethylidenecyclohexane or *trans*-diisopropylethylene in acetone solvent leads to good yields of normal ozonides whereas ozonolysis of either of these olefins in propionaldehyde, or of ethylidenecyclohexane in cyclohexanone, leads to no ozonide formation. Thus, the simple explanation of a general medium effect does not seem satisfactory for all of the carbonyl-containing solvents.

Scheme I

1

2 **3**

nonozonide products

3 —?→

5

6

nonozonide products

6 —→
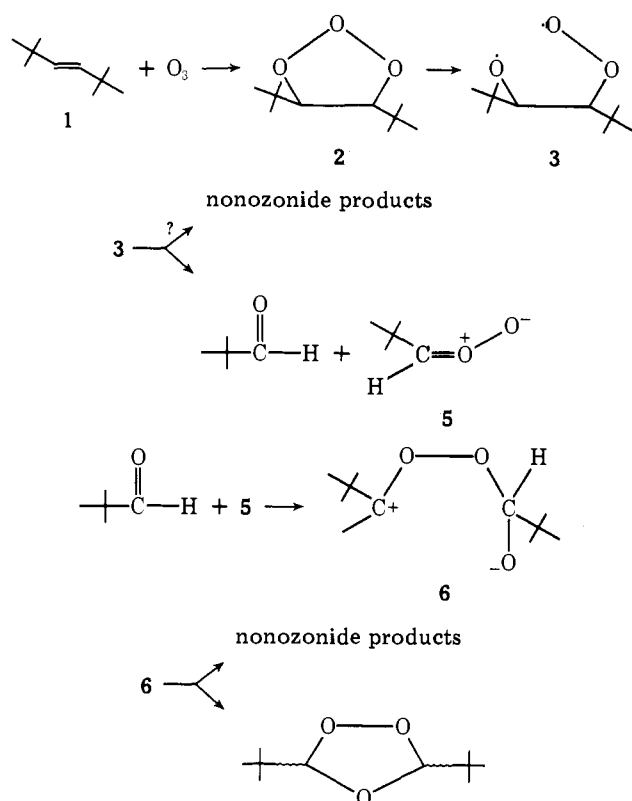
If some solvents are exerting a general medium effect then this interpretation requires further elaboration, i.e., at what stage or stages in the total process is this effect exerted?

Another explanation which ought to be considered is the possibility that one or more of the steps involved in ozonide production is nonconcerted. Hiberty[20] has calculated that the concerted and nonconcerted decompositions of the trioxolane have approximately the same energy requirements. In addition, Wadt and Goddard[13] have proposed, for the case of ethylene, that the trioxolane intermediate is likely to decompose in a stepwise manner giving first the diradical produced by breaking one O–O bond. This raises the question as to whether the corresponding diradical, **3**, in the case of ozonolysis of **1** might get involved in non-ozonide-producing reactions. If such a process were to play a role, then it might be expected to be more important in the presence of added aldehyde where the aldehyde could become involved in reactions with **3**. At the moment there is no evidence which would require such a process, however.

Despite the fact that the recombination reaction of carbonyl oxide and aldehyde has been considered[10,11] to be concerted, it is possible that it also occurs in a stepwise fashion and that the solvent plays a role in determining the fate of the intermediates, **6**, produced in this stepwise addition.[21] If such a process were involved, closure of intermediate **6** to give ozonide might be expected to be favored and to approach a concerted process in the nonpolar solvents consistent with the experimental observations. On the other hand, polar solvents would tend to lend stability and a longer lifetime to **6**, thus increasing the opportunities for non-ozonide-producing processes to occur. Such processes could include reaction with carbonyl oxide, reaction with aldehyde, reaction with trioxolane, or polymerization.

The intervention of an intermediate such as **6** might also provide an explanation for the added aldehyde results (Figure 1). In the experiments reported here, ozonolysis of **1** in isopentane led to ozonide formation presumably via trioxolane

formation and decomposition, followed by recombination of the carbonyl oxide and aldehyde fragments. Yet when increasing amount of propionaldehyde are added to the ozonolysis solution decreasing amounts of normal ozonide are produced with no cross ozonide formation. These results are difficult to explain using a medium effect alone. On the other hand, it is possible that the added propionaldehyde intervenes at the stage where suggested intermediate **6** is produced. Reaction of **6** with propionaldehyde would lead to higher molecular weight products. In this connection it is important to reiterate that while increasing amounts of propionaldehyde lead to decreasing amounts of the normal ozonide of di-*tert*-butylethylene, the fact that this occurs without producing cross ozonide incorporating propionaldehyde indicates that the added aldehyde is apparently not decreasing ozonide yield by consuming carbonyl oxide fragments. On the other hand, the observation that normal ozonide is formed in the presence of propionaldehyde under some conditions indicates, according to current mechanistic proposals, that carbonyl oxides are present. It may be that pivalaldehyde can compete successfully with propionaldehyde because it is formed proximal to the carbonyl oxide.

It is also likely that intermediate **6** with *tert*-butyl groups has a slower rate of closure to ozonide, because of steric interference, than similar intermediates with less bulky groups. The observation that the solid initial adduct from diisopropylethylene does lead to ozonide formation, when allowed to warm up in methylene chloride, tends to support this possibility. These possibilities are summarized in Scheme I.

It is also possible that the polar solvents decrease the reactivity of the zwitterion **5**. If this is responsible for the experimental observations then it would have to be argued that syn zwitterions are more susceptible to this effect than anti zwitterions since *cis*-di-*tert*-butylethylene does give some ozonide in polar solvents.[4] This question may be answered by a more thorough study of the ozonolysis of the cis isomer including a study of both yield and stereochemical effects. Such a study has been initiated in this laboratory.

At the moment these possibilities must be regarded as speculative. It is clear from the results reported here that the solvent effect and the added aldehyde effect cannot be due to a change in the structure of the initial adduct. Explanations based on a general solvent medium effect do not seem to be satisfying, particularly for the added aldehyde experiments. Initial adduct decomposition does not lead to detectable radical formation even in environments which should encourage radical formation so that radical processes which detract from ozonide yield do not seem likely.

It is interesting to note that several formulations for the structure of the viscous higher molecular material ("oligomer") which is always obtained in some quantity in ozonolysis reactions are actually polyozonides[22-24] or other materials incorporating both carbonyl oxide and aldehyde fragments. Such formulations would seem to admit of a nonconcerted addition of carbonyl oxide and aldehyde. It is possible that further investigations of these higher and molecular weight materials will prove useful with respect to the mechanism problem. We have begun such investigations and will report the results separately.

Current mechanistic schemes for the ozonolysis reaction[10,11] rely heavily on a concerted formation of ozonide to explain ozonide stereochemistry. To the extent that the reaction could be nonconcerted under some experimental conditions these schemes would have to be modified. These schemes generally do reasonably well in predicting the observed ozonide stereochemistry. The difference between the present level of success and nearly complete correlation with experimental data could be related to such subtleties as the degree of concertedness of ozonide formation.

At the same time the introduction of the possibility of non-concerted ozonide formation could aid in providing a rationale for the previously reported[25] effects of olefin concentration on ozonide yield and stereochemistry.

In many ways, however, the ozonolysis of *trans*-di-*tert*-butylethylene is somewhat anomalous. What we have presented are new data on this particular olefin along with some interpretative speculation. The possible further extension of such speculation to the general ozonolysis mechanism problem must await further experimentation.

Experimental Section

A. General. NMR spectra were recorded with a Varian T-60 spectrometer. Analytical and preparative VPC work was done on a Varian Aerograph Model A-705 gas chromatograph equipped with a thermal conductivity detector or on an Aerograph Model 600-D flame ionization gas chromatograph. The chromatographs were connected to a Vidar Model 6300 digital integrator. Infrared spectra were recorded on a Perkin-Elmer Model 137 or 337 infrared spectrophotometer. ESR experiments were run on a Varian E-12 ESR spectrometer.

B. General Ozonolysis Procedure. A Welsbach Model T-408 ozonator was used as a source of ozone. The sample stream output of the ozonator was used with ozone delivery varying from 0.11 to 0.18 mmol O_3/min. In most cases, ozonolyses were carried out to less than 100% of theory. Yields were calculated on the basis of the amount of olefin reacted. Reaction mixtures were analyzed by GLC using, in most cases, a 20 ft by 0.125 in. aluminum column packed with 7% β,β'-oxydipropionitrile on DMCS-treated Chromosorb G. Quantitative data were obtained using the Vidar digital integrator. Yields were obtained by calibrating GLC peak areas using pure samples and under conditions where no ozonide decomposition was detectable.

C. Materials. The *trans*-di-*tert*-butylethylene in 99% purity was obtained from Chemical Samples Co. and used as received. Propionaldehyde was distilled under nitrogen and stored under argon prior to use. The solvents used were all reagent grade.

Ozonolysis of *trans*-Di-*tert*-butylethylene. The ozonolysis was carried out in a variety of solvents (shown in Table I). The procedure was approximately the same in all cases. A detailed procedure for the isopentane case is given here.

The olefin (141.3 mg, 1.01 mmol) was dissolved in isopentane (5 mL) and the solution cooled to −92 °C in an acetone–solid acetone bath. The solution was purged with argon for 5 min and then ozone (0.19 mmol/min) was passed through the solution for 9 min. A trap containing aqueous KI was placed in series with the reaction vessel so that total reacted ozone could be measured. The reaction solution was again purged with argon for 5 min and then allowed to slowly warm to room temperature. The reaction solution was brought to a volume of 5 mL in a volumetric flask and analyzed by GLC. Yield was 55%. The ozonide was identified by comparing its properties with those previously reported.[26] Yields obtained using other solvents are given in Table I. In separate experiments it was shown that the ozonide is stable in CH_2Cl_2 and acetone solutions. Reliable yield data for pivalaldehyde were not available since it was found that this yield changed as the reaction mixture stood.

The 1,2,3-Trioxolane of *trans*-Di-*tert*-butylethylene. A solution of 0.2 mL of *trans*-di-*tert*-butylethylene in 5 mL of isopentane was cooled to −125 °C in a pentane-solid pentane bath. The solution was purged with argon for 5 min and an ozone stream (0.18 mmol O_3/min) was passed through the solution for 5 min. The white precipitate (trioxolane) which formed was filtered off at −110 °C at reduced pressure (10^{-2} mmHg). The precipitate was then washed with cold (−110 °) isopentane. Cold (−90 °C) CH_2Cl_2 (5 mL) was added to the precipitate and the mixture was then allowed to warm slowly (7–10 h) to room temperature. The resulting solution was then analyzed by

GLC. This procedure was repeated using a variety of solvents with the results shown in Table II. The solid precipitate was observed to dissolve in the polar solvents used.

The 1,2,3-Trioxolane of *trans*-Diisopropylethylene. Using a procedure similar to that for the case of *trans*-di-*tert*-butylethylene the solid troxolane of *trans*-diisopropylethylene was prepared, filtered, and washed. This material was allowed to warm up in methylene chloride. The room temperature solution was analyzed and found to contain diisopropylethylene ozonide.

Effect of Added Propionaldehyde. A solution of *trans*-di-*tert*-butylethylene (151.1 mg, 1.08 mmol) in 5 mL of isopentane was cooled to −125 °C, flushed with argon for 5 min, and then ozonized for 5 min (0.11 mmol O_3/min). The reaction solution was again flushed with argon (5 min) and then precooled (−90 °C) solutions containing varying amounts (0.25–1.75 mL) of propionaldehyde in isopentane (total volume 3 mL) were added. The resulting solutions were agitated by bubbling argon through them. They were then allowed to warm slowly (20 h) to room temperature. The volumes were reduced to ca. 3 mL by careful evaporation of isopentane and then brought to 5 mL by adding hexane. The solutions were then analyzed by GLC. The entire process was repeated except that the ozonolysis was carried out at −78 °C. The resulting ozonide yields are shown in Figure 1.

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