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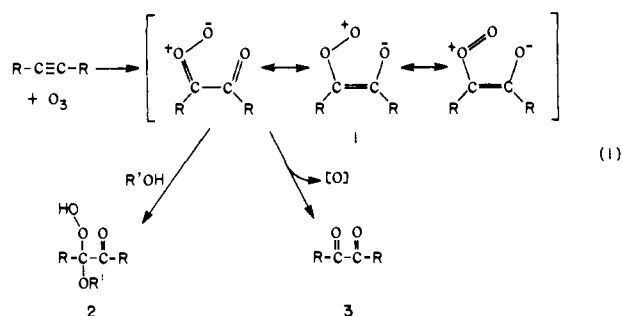
Alkene Epoxidation by Intermediates Formed during the Ozonation of Alkynes¹

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Abstract: The ozonation of various alkynes at -70°C produces low levels of at least one species capable of epoxidizing cyclohexene and other added alkenes. More detailed studies using 0.02 M 2-butyne in dichloromethane solution, ca. 0.8 equiv of ozone, and subsequent addition of excess alkene indicated the following: (1) up to a 30% yield (based on the amount of alkyne which reacts) of epoxide is formed; (2) three different epoxidizing species are involved, one (X) which is stable only at -70°C and which epoxidizes alkenes within 1 min at -70°C , the second (Y) which is stable to -15°C and epoxidizes alkenes within minutes at -25°C , and the third (Z) which was shown to be a peroxy acid; (3) the epoxidation of cis and trans alkenes by X is almost completely stereospecific, while that by Y is essentially nonstereospecific; (4) epoxidations by both X and Y show electrophilic character and a large steric effect (in competition experiments cis alkenes react more than an order of magnitude more rapidly than trans alkenes). The evidence is consistent with X being a five-membered ring trioxide (trioxolene). A definitive structure for Y could not be assigned, but it may be a three-membered ring peroxide. The relevance of this work to some enzymic oxygenations is considered.

Since many oxygenase-catalyzed reactions are believed to occur by an oxygen atom transfer or oxenoid mechanism,³⁻⁹ various studies in this laboratory have been aimed at investigating potential oxenoid agents and establishing the characteristics of each.^{6,7,10-12} For some of the enzyme-catalyzed reactions, one of us has suggested^{5,7} that the oxenoid reagent is an α -carbonyl carbonyl oxide, sometimes referred to as "vinylogous ozone" because it is a homologue of ozone having a carbon-carbon double bond between two of the oxygens. As shown in eq 1, vinylogous ozone (**1**) is believed to be an inter-



mediate in the ozonation of alkynes;¹³ if the reaction is carried out in the presence of protic solvents, compounds such as **2** are frequently isolated.¹⁴ In the absence of the protic solvent traps a major product of the alkyne ozonation reaction is the α -

diketone **3**. The formation of **3** indicates that **1**, or some species similar to it, can act as an oxygen atom transfer reagent, but the characteristics of such a transfer had not been investigated. The original goal of the present research was to determine these characteristics. During the study it was found that the alkyne ozonation reaction leads to a complex mixture of intermediates and products, at least three of which are capable of converting alkenes to epoxides. One of these intermediates appears to be the cyclized trioxide tautomer of **1**.² In this paper we report the experimental evidence for these oxidants and the characteristics of alkene epoxidation by each species.¹⁵

Experimental Section

Materials. All materials, including the alkynes, were of the highest purity possible and were shown by GC to be free of interfering impurities. Except for preliminary experiments, the dichloromethane used throughout this study was purified by extracting with concentrated sulfuric acid and 20% sodium hydroxide, washing with water, drying, and distilling from calcium hydride. Peroxyacetic acid and the epoxides of the various alkenes were prepared according to the procedures of Lewis.¹⁶ Ozone was prepared using a Welsbach Model T-408 laboratory ozonator with an oxygen feed.

Analyses. Perkin-Elmer Series 881 gas chromatographs equipped with flame-ionization detectors were used for quantitative determinations. The following columns gave convenient separations of the reaction products as indicated: (1) 20% polypropylene glycol on Chromosorb W (12 ft \times $\frac{1}{8}$ in.); (2) 20% Carbowax 20 M on Chro-

mosorb W (12 ft × 1/8 in.); and (3) Chromosorb 101 (glass, 6 ft × 1/4 in.). An internal standard (anisole usually) was used in all cases and the amounts of products formed and reactants remaining were calculated by multiplying the observed peak areas by conversion factors determined using known amounts of the various compounds. Visible fixed wavelength measurements were made on a Gilford Model 260 spectrophotometer. Reaction mixtures were qualitatively analyzed via TLC (20:3 toluene-methanol) on silica gel containing fluorescent indicator. Peroxidic materials were detected on spraying the plates with a 1% solution of KI. Ozone was quantitated using standard iodometric techniques.¹⁷ Active oxygen determinations on peroxidic products stable at room temperature were performed according to the procedures of Mair and Hall.¹⁸ "Easily-reduced" peroxides were quantitated iodometrically after aliquots of the reaction mixtures were mixed with 5 ml of glacial acetic acid, 1 ml of saturated KI solution, and 2-3 ml of H₂O at room temperature. "Moderately-stable" peroxides were determined similarly, except that prior to titration with thiosulfate the mixture (which also contained 20 ml of isopropyl alcohol) was first treated on a steam bath for 15 min and then cooled. In cases where both peroxides were present a second aliquot of reaction mixture was first treated with an excess of diphenyl sulfide (10 min at room temperature) before being analyzed as for moderately stable peroxide.

Reaction Conditions. In the majority of experiments an interconnected two-chambered reaction vessel which maintained both reactants at the same temperature was used. In a typical experiment enough alkene in 10 ml of dichloromethane to give the desired molarity (0.2 M usually) in 60 ml was placed in the smaller chamber, and enough alkyne in 50 ml of dichloromethane to give the desired molarity (0.02 M usually) in 60 ml was placed in the larger chamber. The reaction vessel was cooled to the desired temperature (-70 °C; dry ice-acetone bath usually), and 0.7-0.9 equiv of ozone (in a 5% O₃/O₂ stream) were added over a period of about 12 min to the alkyne chamber through a sintered glass gas dispersion tube. Following ozonation, any unreacted O₃ (usually a very small amount, if any) was removed by a 2-3 min flush with N₂. Depending on the experiment being performed the alkyne-ozone mixture was then treated in various ways. To determine total epoxidizing activity, the alkene solution was added to the alkyne-ozone mixture at -70 °C by pressuring the alkene chamber with N₂. After about a minute, the reaction vessel was removed from the cooling bath, allowed to equilibrate to room temperature (over about 30 min), and analyzed by gas chromatography for the reaction products. In a few cases the solutions were allowed to stand at room temperature for several hours before GC analysis. To determine epoxidizing activity at various temperatures the alkene solution was frequently not added until the alkyne-ozone mixture had been warmed to some specified temperature, and sometimes the complete reaction mixture (containing alkyne, ozone, and alkene) was quenched at specified subambient temperatures by the addition of an excess of either diethyl sulfide or a saturated solution of sodium borohydride in absolute ethanol. Following the quench the solutions were warmed to room temperature and analyzed as before. To determine the products of the alkyne-ozone reaction alone the same procedures were followed except that no alkene was added.

Results and Discussion

Some General Characteristics of the Alkyne Ozonation-Cyclohexene Epoxidation. At -70 °C, ozone reacts rapidly (within seconds) with acetylene and alkyl-substituted acetylenes. This is evidenced by the fact that the deep blue coloration, which is characteristic of dissolved ozone, does not develop in solutions of these acetylenes in CH₂Cl₂. Phenyl-substituted acetylenes react more slowly, but after sitting for 10 min at -70 °C the blue color completely disappears. Perfluoro-2-butyne does not react appreciably with ozone at -70 °C¹⁹ (the blue color persists and all the dissolved ozone can be flushed out with N₂) and thus this alkyne could not be used for the alkene epoxidation experiments.

In what is apparently a general phenomenon, those alkynes which react with O₃ in CH₂Cl₂ at -70 °C product on ozonation at least one species which can rapidly epoxidize alkenes (added after ozonation). Thus, when a solution of alkyne (ca. 0.02 M) in dichloromethane is successively reacted at -70 °C

Table I. Cyclohexene Epoxidation by 2-Butyne-Ozone Adducts at Various Temperatures^a

Oxidant ^b	Temp alkene added, °C	Quench ^c temp, °C	Cyclohexene oxide yield, ^d %
X	-70	-70	10
X	-70	-50	11
X	-70	-30	11
X, Y	-70	-15	15
X, Y, Z	-70		30 ^e
Y	-25	-15	5
Z	20		15 ^e

^a For reaction conditions see Experimental Section; in all cases the ozone was added to the alkyne at -70 °C. ^b X, Y, and Z are defined in the text. ^c Quenched at this temperature with about a fourfold excess of diethyl sulfide. ^d Analyzed by GC column 2 isothermal at 100 °C (see Experimental Section). ^e GC analysis after 2 h at room temperature.

with 0.7-0.9 equiv of ozone, flushed with N₂, added to excess cyclohexene, and warmed to room temperature, a 5-30% yield (based on the amount of alkyne or O₃ which reacts) of cyclohexene oxide is formed. Some alkynes which give this reaction are: acetylene, 2-butyne, di-*tert*-butylacetylene, methylphenylacetylene, and diphenylacetylene. Using the 2-butyne-ozone-cyclohexene system the following general characteristics of the reaction were established: (1) cyclohexene oxide is the only major oxidation product of cyclohexene formed; no cyclohexanone was noted and only trace amounts (less than 1%) of cyclohex-2-enol and cyclohex-2-enone were observed;²⁰ (2) the alkene epoxidation is completely dependent on the *prior* reaction of alkyne with ozone; no epoxide is formed if the alkene itself is ozonized in the presence or absence of alkyne;²¹ (3) lower yields of epoxide are formed if the reaction conditions are altered in any one of the following ways: the ozone is reacted with the alkyne at -10 °C rather than -70 °C, more than 1 equiv of O₃ per equivalent of 2-butyne is used, tenfold higher concentrations of 2-butyne and ozone are employed. Control experiments established that the length of the N₂ flush (up to 30 min) has little effect on the epoxide yield.

The yield of epoxide calculated from the amount of O₃ consumed is 10-20% lower than when it is calculated on the basis of the amount of alkyne reacted. This is apparently due to reaction of O₃ with trace impurities in the solvent or to some decomposition to O₂; in the absence of alkyne and alkene about 15% of the added O₃ could not be accounted for after exhaustive flushing with N₂. For these reasons, the yields given in this paper are expressed as a percentage of the alkyne consumed.

2-Butyne Ozonation and Epoxidation Details. By quenching 2-butyne-ozone systems with ethyl sulfide at various temperatures, the 30% total yield of cyclohexene oxide was shown to result from the reaction of three apparently different epoxidizing species, as shown in Table I. Further information concerning the nature of these epoxidizing agents is obtained from the products observed on alkyne ozonation in the absence of alkene (Table II). The three reagents have been given the designations X, Y, and Z.

Species X, the "low-temperature" species, is responsible for about one-third of the epoxidation by the 2-butyne-ozone system. It is formed at -70 °C and reacts with alkenes within seconds at this temperature. This is evidenced by the fact that epoxidation of cyclohexene by X occurs even when the system is quenched at -70 °C with diethyl sulfide in less than a minute after adding the alkene. In the absence of alkene, X is stable

Table II. Products from the Reaction of 2-Butyne with Ozone in the Absence of Alkene^a

Quench ^b temp, °C	Yield of reaction products, %		
	Biacetyl ^c	Acetic acid/2 ^d	Stable peroxide
-70	69	14	
-15	62	30	
20	60	35	
	27	13	67 ^e

^a In all cases the alkyne and ozone were reacted at -70 °C and the products analyzed after warming to room temperature. ^b Quenched with about a fourfold excess of diethyl sulfide. ^c Determined spectrophotometrically at 418 nm. ^d Analyzed by GC column 3 isothermal at 137 °C (see Experimental Section). ^e About 70% of this is "moderately-stable" peroxide and about 30% "easily-reduced" peroxide (see text).

for at least minutes at -70 °C, but is completely decomposed (determined by loss of epoxidizing activity) when the temperature is raised to -30 °C. The results given in Table II indicate that reduction of X with diethyl sulfide yields biacetyl.

The "intermediate-temperature" species Y, which is responsible for about one-sixth of the alkene epoxidation, is apparently formed at -70 °C, but reacts with alkenes only at temperatures in the range of -25 to -15 °C. In this temperature range it epoxidizes cyclohexene in minutes and is decomposed (shows no epoxidation activity) above -15 °C.

The remaining one-half of the epoxidation by the 2-butyne-ozone system is due to a "room-temperature" species Z, which appears in all respects to be peroxyacetic acid. It is apparently formed at some temperature above -70 °C, yields acetic acid on reduction, is stable for hours at room temperature, and requires ca. 2 h at room temperature to epoxidize added cyclohexene. The stable peroxide titrated at room temperature (Table II) in unquenched 2-butyne-ozone systems is about 25-30% "easily-reduced" peroxide (see Experimental Section). This easy reduction is characteristic of peroxy acids.¹⁸ Thus, peroxyacetic acid is present in sufficient quantities to account for species Z epoxidations.

In addition to the three epoxidizing agents, the results given in Table II indicate that an additional peroxide species is formed from the ozone-alkyne reaction at -70 °C. It represents about 50% of the alkyne consumed, does not epoxidize cyclohexene even at room temperature, and titrates with KI as a "moderately-stable" peroxide (see Experimental Section). It decomposes slowly on standing for days at room temperature and can apparently initiate the autoxidation of cyclohexene.²⁰ Upon reduction with diethyl sulfide it yields an equimolar amount of biacetyl. This material is most likely a mixture of polymeric peroxides and ozonides observed in comparable systems by other workers.^{13,14}

The above species (X, Y, Z, and the polymeric peroxide) account for about 80% of the reacted alkyne under the usual conditions employed. In addition, low levels of biacetyl and acetic acid are always observed in these systems. α -Diketones as well as anhydrides are normally observed products from the ozonation of alkynes.^{13,14,22} The yield of acetic anhydride under our usual conditions is probably too low to detect (limit of detection, 10%).

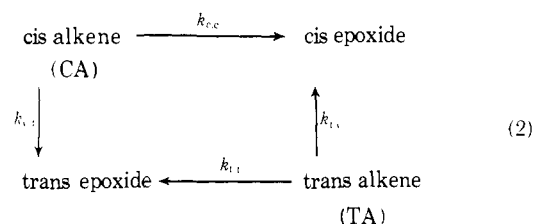
Under more concentrated conditions (2-butyne and ozone increased tenfold), the products change considerably, and the total alkene epoxidizing activity drops to about one-fourth that in the dilute system. Furthermore most of the epoxidizing activity is due to species Z (peroxyacetic acid); very little X and Y appear to be formed. Due to this result, a detailed product analysis of the concentrated system was not pursued. However,

qualitatively, under these conditions, acetic anhydride now accounts for about 40-50% of the alkyne consumed and the peroxide species stable at room temperature drops to less than 20% of the alkyne consumed.

A small effect of O₂ on the amount of cyclohexene epoxidation is observed. When the O₂ carrier gas for the O₃ is replaced by N₂,²³ reductions of up to 30% in the yield of cyclohexene oxide are observed. Such reductions are primarily due to the formation of lower levels of Y and Z.

Methanol (as 50% of the solvent) when present during the ozonation of 2-butyne reduces subsequent cyclohexene epoxidation by at least 75%. The amounts of X, Y, and Z are apparently reduced uniformly, since trapping experiments¹⁵ similar to those of Table I indicate lower yields irrespective of the quench temperature. If the methanol is added after the alkyne-ozone reaction, but prior to cyclohexene addition only a slight reduction (ca. 30%) in the amount of epoxidation is observed. The above results indicate that all of X, Y, and Z are relatively stable to methanol, but that some intermediate involved in their formation is trapped by methanol. Further information concerning this intermediate comes from results obtained in the absence of alkene. Under conditions similar to those of Table II, but with 50% methanol as solvent, only a 9% yield of biacetyl is observed in the absence of a sulfide quench, but a 90% yield is found when the system is quenched at -15 °C. The increased yield of biacetyl is presumably due to the reduction of 2 (eq 1) formed by trapping the vinylogous ozone intermediate (1) with methanol. The above results thus imply that vinylogous ozone is an intermediate in the formation of X, Y, and Z.

Stereospecificity of 2-Butyne-Ozone Epoxidations. By using several different concentration ratios of *cis*- and *trans*-3-hexene in internal competition experiments, and by quenching the reaction systems at the appropriate temperatures, the stereochemical aspects of epoxidations by X, Y, and Z were investigated. The raw data¹⁵ were analyzed in terms of the relative rate constants for the processes shown in eq 2 by using



the relation shown in eq 3. Table III summarizes some of the

$$\frac{[\text{cis epoxide}]}{[\text{trans epoxide}]} = \frac{[\text{CA}]k_{c,c} + [\text{TA}]k_{t,c}}{[\text{TA}]k_{t,t} + [\text{CA}]k_{c,t}} \quad (3)$$

data; for each oxidant $k_{c,c}$ was arbitrarily set equal to 100.

In contrast to epoxidations by peroxyacetic acid, where only a slight (1.3) preference for the *cis* alkene over that for the *trans* is observed, both X and Y show a high (20- to 30-fold) preference for reaction with the *cis*-hexene. This must presumably be due to some steric effect for these epoxidations. Whereas epoxidations by X are almost, but not quite, completely stereospecific, epoxidations by Y are almost totally nonstereospecific. In both cases some intermediate which allows partial equilibration must be involved. Epoxidations by oxidant Z (not shown in Table III) are completely stereospecific, as expected for peroxyacetic acid. In control experiments it was found that the results shown in Table III are not due to isomerization of either the reactant alkenes or product epoxides under the reaction conditions. Both retain their stereochemical identities throughout the reaction.

Relative Reactivity of Various Alkenes to the 2-Butyne-Ozone Oxidants. Table IV summarizes some data obtained from competition experiments. The comparable reactivity of

Table III. Relative Rates for the Epoxidation of *cis*- and *trans*-3-Hexenes by 2-Butyne-Ozone Oxidants^a

Oxidant	Epoxidation temp, °C	Relative rate constants			
		$k_{c,c}$	$k_{c,t}$	$k_{t,c}$	$k_{t,t}$
X	-70	(100)	7	0.1	6
X + Y	-70 to -15	(100)	50	0.1	5
Y	ca. -25	(100)	640 ^b	2 ^b	25 ^b
Peroxyacetic acid	20	(100)	0	0.1	80

^a For reaction and quenching conditions see footnotes to Table I. The products were analyzed using GC column 1 isothermal at 100 °C (see Experimental Section). ^b Calculated from the data obtained for oxidants X and X + Y; thus, these values are probably less accurate than the others.

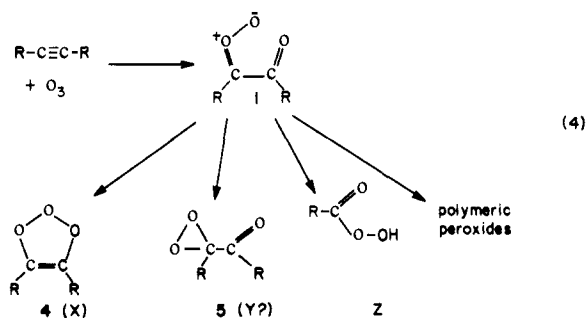
Table IV. Relative Rates of Epoxidation of Various Alkenes by 2-Butyne-Ozone Adducts^a

Alkene	Relative rate constants for epoxidation by				
	X	X + Y	Y ^b	Z	Peroxyacetic acid ^c
Cyclohexene	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
1-Methylcyclohexene	3.8	4.5	7.4	11	11
Methylenecyclohexene	0.40	0.54	0.97	1.3	1.4
1-Octene	0.026	0.035	0.056	0.050	0.033
<i>cis</i> -3-Hexene	0.51	0.60	0.83		
<i>trans</i> -3-Hexene	0.05				

^a Determined from competition experiments; each reaction mixture contained cyclohexene and another alkene in equimolar amounts in large excess. The relative reactivities were calculated from the relative molar yields of epoxides (determined using GC column 1 isothermal at 100 and 125 °C) obtained using appropriate quenching conditions (see footnotes to Table I). ^b Calculated from the data obtained for oxidants X and X + Y; thus, these values are probably less accurate than the others. ^c In dichloromethane at room temperature.

Z to the peroxyacetic acid reference is further evidence that Z is in fact this oxidant. The raw data suggest that epoxidations by X and Y possess less electrophilic character than peroxyacetic acid, but the inhibition of epoxidation due to steric effects (see previous section) significantly bias these results. Thus on the basis of electronic effects alone, the relative reactivities of 1-methylcyclohexene and methylenecyclohexane should be about tenfold higher. Consequently, epoxidations by X and Y apparently have considerably more electrophilic character than those by peroxy acids. The large difference in the reactivities of methylenecyclohexane and *trans*-3-hexene indicates that epoxidation by X proceeds through an unsymmetrical transition state.

Possible Structures and Pathway for Formation of X, Y, and Z. Indicated in eq 4 are possible structures for X, Y, and Z and



a general pathway for their formation, which is consistent with the results reported here and in other more general studies.^{13,14,22,24} The present and earlier results obtained with alcoholic solvents indicate that essentially all the alkyne ozonation products are formed with the vinyllogous ozone (1) as an intermediate. However, the observation that some epoxidizing activity by all of X, Y, and Z is found even in 50% methanol indicates that none of X, Y, and Z is vinyllogous ozone (1) itself. Very probably a vibrationally excited form of 4 is on the pathway to the formation of 1 from the alkyne and O₃. However, due to the amount of energy released in this step,

its lifetime should be very short; DeMore²² has calculated it to be 10⁻¹² s or less. The ring-opened form 1 is presumably relaxed by the solvent and then gives rise to the observed products.

It is certainly reasonable that polymeric peroxides would be formed from 1. Carbonyl oxides react with themselves to give cyclic diperoxides or with carbonyls to give ozonides. Thus, with both functional groups in the same intermediate (1) it is not surprising that these represent over 50% of the alkyne ozonation products under our usual reaction conditions (dichloromethane as solvent). It is known that diperoxides and ozonides are relatively stable^{13,14,25} and are not capable of epoxidizing alkenes at room temperature or below, so none of X, Y, and Z can be such species.

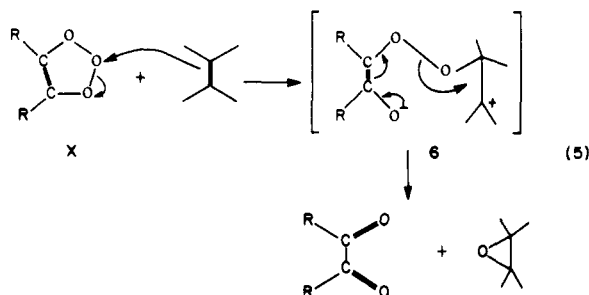
As indicated previously, all the evidence concerning Z suggests that it is peroxyacetic acid (in the 2-butyne-ozone system). The mechanism by which it is formed is unclear, but under all conditions tried some of the product had the characteristics of a peroxy acid.

Of all the epoxidants (X, Y, and Z), X is perhaps the most interesting because of its high reactivity even at low temperatures. All of the evidence is consistent with X being the cyclic trioxolene 4. Of particular note are the observations that X on reduction with diethyl sulfide gives biacetyl, it is unstable at temperatures above -50 °C, and the epoxidation results in 50% methanol indicate it is not 1 itself. One can estimate²⁶ that ring closure of 1 to 4 is exothermic by a small amount, so it is reasonable that 4 would be in an energy well and relatively stable at -70 °C, but it would decompose (presumably through 1) at higher temperatures. Trioxolane species, which are similarly stable only at comparable subambient temperatures, are detectable intermediates in the normal course of ozonolysis of alkenes.²⁷⁻²⁹

Not much information is available concerning the structure of Y; that illustrated (5) in eq 2 is quite speculative and is based on some recent calculations of Wadt and Goddard,²⁹ which suggest that such three-membered ring peroxides may be stable forms of carbonyl oxides. Y is only formed in small amounts

and its most striking reactivity characteristic is that it epoxidizes alkenes with almost a complete lack of stereospecificity (Table III). A structure such as **5** might be expected to react in that fashion because initial attack on the alkene with oxygen-oxygen bond fission would probably be followed by a slow oxygen-carbon fission. During this time the intermediate (radical or ionic) could lose stereochemical identity by rotation about the single bond. Another possibility for the structure of **Y** is a dimeric trioxide of some kind. Its stability characteristics (unstable above -15°C) are about what would be expected for such a species.²⁶ A cyclic diperoxide has been proposed by DeMore and Lin²² as a possible structure for a thermally unstable species they observed during the -45°C ozonation of various alkynes. However, this is an unlikely structure for **Y** because diperoxides do not show the observed instability at subambient temperatures.

Suggested Mechanisms for Epoxidation by X. Shown in eq 5 is a mechanism for the epoxidations by **X**, which is consistent



with all the present results. The lack of complete stereochemical retention indicates that the epoxidation is not concerted. With **6** as an intermediate some equilibration could result. The observed electrophilic character of the epoxidation (Table IV) is also consistent with an intermediate such as **6**. The difference in the reactivities of the cis and trans alkenes (Table III) is presumably because **X** must approach in a plane approximately parallel to the alkene plane, but above or below it. With cis alkenes the transition state can thus be reached with no steric interaction between the alkene substituents and **X**, whereas this is not possible with the trans alkenes.

Possible Relation to Some Enzymic Reactions. This has been discussed in the previous communication.² In this regard the most significant result of the present work is that it indicates that either the cyclized trioxide **4** or its open form **1** is a potent oxygen atom transfer or oxenoid reagent.³⁻⁹ One can estimate that such a species is at least 10^3 times more reactive than peroxy acids because the reagent formed from 2-butyne epoxidizes alkenes at -70°C , whereas peroxyacetic acid will only give a similar reaction at room temperature or above. Thus, the suggestion⁵⁻⁷ that a vinylogous ozone (**1**) is the oxidant in various enzymic reactions seems reasonable. The present work indicates **1** may exist in the cyclized form **4** and this may be true for some of the enzymic cases too. However the difference in energy between **1** and **4** is expected to be small,²⁶ so de-

pending on the effects of the rest of the structure (the **R** groups in **1** and **4**), either may be the more stable form.

References and Notes

- (1) (a) This research was supported by research grants (AM 13448 and CA 17717) from the National Institutes of Health. (b) Taken from the Ph.D. thesis of R.E.K., The Pennsylvania State University, 1975. (c) A preliminary communication on part of this work has appeared.²
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- (29) Two other possible routes to **1** (or its tautomers) were briefly explored.¹⁵ One approach involved the ozonation of a keto phosphonium ylide. Ramirez and co-workers³⁰ reported that such a reaction gives α -dicarbonyl compounds and a phosphine oxide. It seemed that **1** might be an intermediate in the reaction, but no epoxidation of cyclohexene was observed by this system. The other approach is based on the recent work of Higley and Murray,³¹ who showed that carbonyl oxides can be prepared by reacting singlet oxygen with diazo compounds. A similar reaction of α -diazo ketones would thus be expected to give **1**. Treatment of α -diazoacetophenone³² with singlet oxygen (generated photochemically or from the triphenylphosphite-ozone adduct³³) in the presence of cyclohexene at -40 – 0°C yielded a small amount of epoxide with the latter system, but this system also gave some epoxide in the absence of the diazo ketone. Further work will be needed to clarify whether **1** (or a tautomer of **1**) is responsible for any of the epoxidation in these reactions.
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