ketone mixture, it could be obtained in pure state in high yield by the acid-promoted isomerization of octalone **3a**. Hydrogenation of ketones **3a**[5b] and **6** produced decalones **7** (88% yield) and **8** (accompanied by **7** in 3% yield of the mixture; 85% overall yield).[9] The easy two-step preparation of ketone **8** now replaces an earlier synthesis of the compound by a circuitous route from ketone **7**[5b] and makes available the two C(3) epimers **7** and **8** in high yield.

The reaction of (–)-carvone (**1**) and isoprene (**2b**) led, by predominant anti addition,[3] to diastereomers **3b** and **5b**.[10] An even higher stereochemical preference is shown by the reactions of (–)-carvone (**1**) with (*E*)-piperylene (**2c**) and 1,3-dimethyl-1,3-butadiene (**2d**). In analogy with the behavior of 2-methyl-2-cyclohexenone[6] the last two cycloadditions produce both endo (**3c**, **3d**) and exo (**4c**, **4d**) products, the former predominating. The close similarity of the endo/exo product ratio of the two reactions and that of 2-methyl-2-cyclohexenone with (*E*)-piperylene (**2c**)[6] indicates the low influence of the isoprene methyl group on the diene–dienophile interaction complex even in cases of monosubstituted 2-cyclohexenones[1] and 2-methyl-2-cyclohexenones.

Experimental Section

The experimental conditions of the Diels–Alder reactions and the hydrogenations as well as the specifics on the spectral analyses of all ketones and on the instruments used are delineated in the Experimental Section of the adjoining publication.[3,6] The details of the reaction conditions are listed in Table I. The 2,4-dinitrophenylhydrazones were crystallized in 95% ethanol. The spectral data of octalones **3a** and **5a** and decalones **7** and **8** as well as the melting points of their 2,4-dinitrophenylhydrazones (**7**: mp 112–113 °C) were the same as those reported earlier.[5b]

Octalone 3b: IR 3095 (w, olefinic CH), 1710 (s, C=O), 1646 (w, C=C), 900 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 1.10 (s, 3, Me), 1.64 (s, 3, 6-Me), 1.75 (s, 3, Pr Me), 4.67, 4.78 (br s, 1 each, olefinic CH_2), 5.24 (br s, 1, H-7). 2,4-Dinitrophenylhydrazone: mp 109–110 °C. Anal. Calcd for $C_{21}H_{26}O_4N_4$: C, 63.30; H, 6.57; N, 14.06. Found: C, 63.41; H, 6.77; N, 13.90.

Octalone 3c: IR 3080, 3023 (w, olefinic CH), 1715 (s, C=O), 1646 (w, C=C), 890 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 1.20 (d, 3, *J* = 7 Hz, 8-Me), 1.37 (s, 3, Me), 1.78 (s, 3, Pr Me), 4.75 (br s, 2, olefinic CH_2), 5.45 (br s, 2, H-6, H-7). 2,4-Dinitrophenylhydrazone: mp 142–143 °C. Anal. Calcd for $C_{21}H_{26}O_4N_4$: C, 63.30; H, 6.57; N, 14.06. Found: C, 63.41; H, 6.77; N, 13.90.

Octalone 3d: IR 3080 (w, olefinic CH), 1715 (s, C=O), 1645 (w, C=C), 890 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 1.14 (d, 3, *J* = 7 Hz, 8-Me), 1.35 (s, 3, Me), 1.62 (s, 3, 6-Me), 1.77 (s, 3, Pr Me), 4.73 (s, 2, olefinic CH_2), 5.15 (br s, 1, H-7). 2,4-Dinitrophenylhydrazone: mp 170–171 °C. Anal. Calcd for $C_{22}H_{28}O_4N_4$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.12; H, 6.81; N, 13.78.

Octalone 4c: IR 3080, 3020 (w, olefinic CH), 1705 (s, C=O), 1646 (w, C=C), 900 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 0.80 (d, 3, *J* = 7 Hz, 8-Me), 0.91 (s, 3, Me), 1.74 (s, 3, Pr Me), 4.69, 4.74 (br s, 1 each, olefinic CH_2), 5.52 (m, 2, H-6, H-7). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.15. Found: C, 82.42; H, 10.16.

Octalone 4d: IR 3080 (w, olefinic CH), 1705 (s, C=O), 1647 (w, C=C), 905 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 0.76 (d, 3, *J* = 7 Hz, 8-Me), 0.86 (s, 3, Me), 1.66 (s, 3, 6-Me), 1.76 (s, 3, Pr Me), 4.68, 4.83 (s, 1 each, olefinic CH_2), 5.05 (br. s, 1, H-7). 2,4-Dinitrophenylhydrazone: mp 119–120 °C. Anal. Calcd for $C_{22}H_{28}O_4N_4$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.15; H, 6.78; N, 13.46.

Octalone 5b: IR 3090 (w, olefinic CH), 1710 (s, C=O), 1648 (w, C=C), 890 (m, C=CH_2) cm^{-1}; ^{1}H NMR δ 1.03 (s, 3, Me), 1.65 (s, 3, 6-Me), 1.72 (s, 3, Pr Me), 4.67 (br s, 2, olefinic CH_2), 5.25 (m, 1, H-7). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.15. Found: C, 82.58; H, 10.15.

Hexalone 6. A solution of 800 mg of octalone **3a** and 160 mg of *p*-toluenesulfonic acid in 40 mL of toluene was heated at 80 °C for 24 h. Upon dilution with water the cooled mixture was extracted with ether. The extract was washed with 10% sodium bicarbonate solution, dried (Na_2SO_4), and evaporated under vacuum. Chromatography of the residue on silica gel and elution with 20:1 hexane-ether gave 700 mg (87%) of colorless, liquid ketone **6**: IR 3030 (w, olefinic CH), 1670 (s, C=O), 16.35 (w, C=C), 1386, 1372 (m, $CHMe_2$) cm^{-1}; ^{1}H NMR δ 1.12 (s, 3, Me), 1.12 (d, 6, *J* = 7 Hz, Pr Me_2), 5.60 (m, 3, H-2, H-6, H-7). 2,4-Dinitrophenylhydrazone: mp 135–136 °C. Anal. Calcd for $C_{20}H_{24}O_4N_4$: C, 62.48; H, 6.29; N, 14.57. Found: C, 62.59, H, 6.33; N, 14.50.

Acknowledgment. F.F., F.P., and A.T. thank the Consiglio Nazionale delle Ricerche and F.F. and A.T. the Ministero Pubblica Istruzione for financial support of the work in Perugia. A.T. and E.W. are indebted to NATO for grant (No. 257.81) support.

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(9) In view of the >90% anti addition[3] experienced in the **1**–**2a** cycloaddition (Table I) the claim of the exclusive formation of a syn adduct in the aluminum chloride catalyzed Diels–Alder reaction of 5-isopropyl-2-methyl-2-cyclohexenone with 1,3-butadiene (**2a**) [Yamamoto, K.; Kawasaki, I.; Kaneko, T. *Tetrahedron Lett.* **1970**, 4859] is suspect.

(10) In contrast to the report of the isolation of regioisomers (albeit with undefined stereochemistry) in 7% yield from an uncatalyzed reaction.[5a]

Ozonolysis of Some Tetrasubstituted Ethylenes

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The olefins 1,4-dibromo-2,3-dimethyl-2-butene, 1-bromo-2,3-dimethyl-2-butene, and 2,3-dimethyl-2-butene were ozonized under a variety of conditions. Ozonolysis of 1,4-dibromo-2,3-dimethyl-2-butene in acetone solvent leads to the unexpected products acetone diperoxide and triperoxide. The results are discussed with respect to questions of concertedness in ozonide formation, the need for activating groups in ozonide formation, and the possible intermediacy of dioxiranes.

As a result of extensive investigation the reaction between ozone and alkenes is now reasonably well understood.[1] It seems certain, for example, that the reaction is a complex one which occurs in three distinct steps (eq 1–3). Within the general framework of this three-step scheme lie a number of vexsome questions pertaining to the details of the mechanism. Much of the recent effort relative to this process has been aimed at understanding the apparent influence of olefin stereochemistry on ozonide stereochemistry. The work of Bailey and co-workers[1a] and Kuczkowski and co-workers,[1b] as well as some of our own

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(1) For an excellent survey of the current situation regarding the mechanism of ozonolysis, see: (a) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: new York; 1978; Vol. I. (b) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42.

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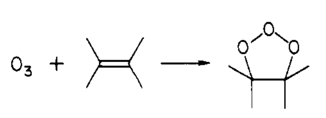
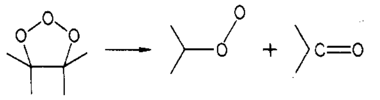
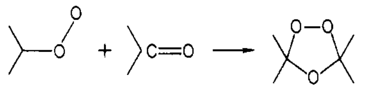

(1)


(2)


(3)

efforts,[2] have been helpful in this regard.

There are other aspects of the overall process concerning which our present level of understanding appears to be inadequate. There is, for example, the question of concertedness. The evidence to date is quite consistent with concertedness in steps 1 and 2. The situation with respect to step 3 is, in our judgement, not quite as clear. We have suggested[3-5] that this step may occur in a fashion that ranges from a concerted, or near-concerted, process to a distinct-two step process with the choice being determined by a number of factors including steric and stereochemical factors in the olefin as well as solvent and temperature influences. Some theoretical calculations[6] support the idea of a nonconcerted addition of carbonyl oxides to carbonyl compounds.

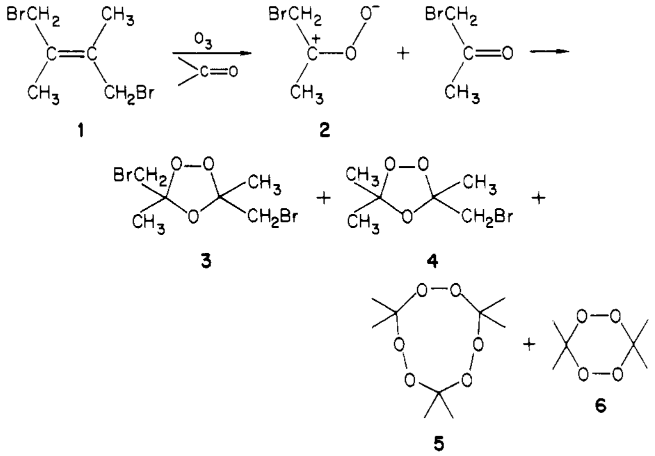
A second area where our understanding of the overall process is incomplete involves the subgroup of alkenes containing tetrasubstituted double bonds. The ozonolysis of tetrasubstituted ethylenes generally does not lead to ozonides but gives instead diperoxides and oligomers corresponding to the expected carbonyl oxides.[1a] There are two major exceptions to this general observation, however. When tetrasubstituted double bonds occur in four- or five-membered rings, then high yields of ozonides are obtained[7] even in very polar solvents such as acetic acid. The second exception occurs when the tetrasubstituted ethylene contains an electron-withdrawing group such as a bromine atom or an ester group. In these cases moderate yields of ozonide are obtained.

The work described here was carried out in order to shed additional light on these two less well understood areas, i.e., the question of concertedness in step 3 of the overall process and the question of what factors influence ozonide formation in the ozonolysis of tetrasubstituted ethylenes.

Results and Discussion

The failure of simple tetralkyl-substituted ethylenes, such as tetramethylethylene, to give ozonides has usually been attributed to the relative unreactivity of the expected carbonyl compound, i.e., acetone, in the case of tetramethylethylene. In contrast the ozonolysis of *trans*-1,4-dibromo-2,3-dimethyl-2-butene, **1**, does give ozonide in moderate yield.[8] In the latter case ozonide formation is presumable due to the increased reactivity of the ketone produced, i.e., bromoacetone. It does not seem likely that the failure of tetramethylethylene to give ozonide is related to steric factors in the expected ozonide since these factors must be at least as great in the ozonide of **1**. In order to test the idea of increased reactivity in the bromo ketone, we have carried out a number of related ozonolyses in which the allegedly activating bromine atom is in the ketone or carbonyl oxide or both.

The ozonolysis of **1** was carried out in acetone solvent at −78 °C. Under these conditions any monobromotetramethylethylene ozonide formed must arise from reaction of the ozonolysis-derived carbonyl oxide **2** with the "unactivated" ketone acetone. The reaction mixture was worked up by using a combination of preparative TLC and bulb-to-bulb distillation. The products were the ozonide **3** (trace) of the parent olefin, bromoacetone (80.9%), the monobromo ozonide **4**, (19.3%), acetone triperoxide, **5** (10.5%), and acetone diperoxide, **6** (2.6%).



The formation of the monobromo ozonide **4**, which must arise from reaction of carbonyl oxide **2** with acetone, demonstrates that the presence of an "activating" group in the ketone is not necessary in order to form a tetrasubstituted ozonide. The surprising result is that the reaction also produced peroxides **5** and **6**. These products have usually been considered as products of trimerization or dimerization of the carbonyl oxide, acetone oxide, **7**, produced, for example, via ozonolysis of tetramethylethylene. In the present case ozonolysis of **1** cannot give **7**. We have carried out a number of control reactions, e.g., separate treatment of acetone with O_3, exposure of ozonides **3** and **4** to the reaction conditions, or even prolonged standing. In none of these cases was the formation of either **5** or **6** observed. Likewise exposure of ozonide **4** to the GLPC conditions used indicates that it does not decompose to give **5** or **6**. Similarly acetone diperoxide itself is not converted to the triperoxide under the GLPC conditions.

We propose that products **5** and **6** arise from trimerization and dimerization, respectively, of dimethyldioxirane, **8**. We further propose that **8** arises from decomposition of an adduct, **9**, formed from addition of carbonyl oxide **2** to acetone. The adduct **9** may also serve as a precursor to the monobromo ozonide **4**.

This proposal incorporates several important features. First, it implies that ozonide formation, **4**, can occur via a nonconcerted addition of carbonyl oxide and carbonyl compound as suggested by ourselves[3-5] and others.[6] Second, decomposition of **9** to give **8** in the manner described represents a new synthesis of dioxiranes. Indeed, **9** resembles the intermediate **10**, which we have previously suggested[9] serves as a precursor to either **7** or **8** in those cases where reaction of simple ketones, such as acetone,

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[2] Higley, D. P.; Murray, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 4526.

[3] Murray, R. W.; Hagen, R. *J. Org. Chem.* **1971**, *36*, 1098.

[4] Su, J. S.; Murray, R. W. *J. Org. Chem.* **1980**, *45*, 678.

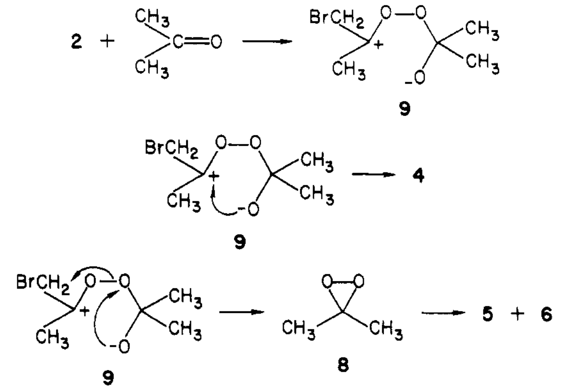
[5] Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2197.

[6] Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180.

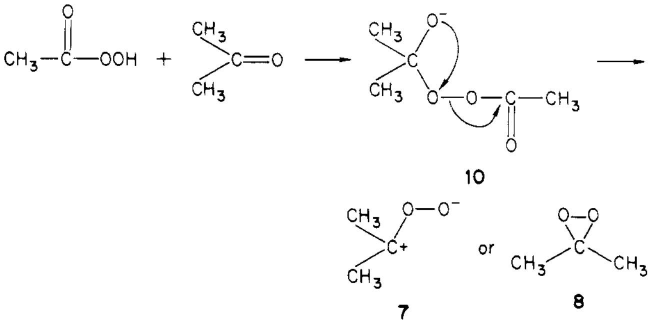
[7] Bailey, P. S. *Chem. Rev.* **1958**, *58*, 925.

[8] Criegee, R., Bath, S. S.; von Bornhaupt, B. *Chem. Ber.* **1960**, *93*, 2891.

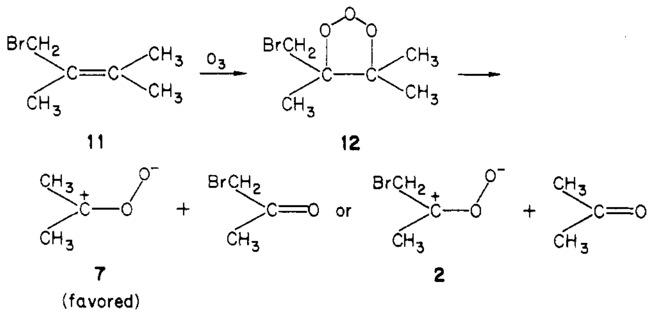
[9] Murray, R. W.; Ramachandran, V. *Photochem. Photobiol.* **1979**, *30*, 187.



do not display Baeyer–Villiger[10] behavior but instead give ketone di- and triperoxides. Edwards et al. have suggested[11] that 8 may be formed in similar fashion from the reaction of acetone with persulfate.



Next the ozonolysis of the monobromo olefin, 1-bromo-2,3-dimethyl-2-butene, 11, was carried out in a variety of solvents (Table I). When the ozonolysis is carried out in pentane or ether, then the products are the parent ozonide 4, the dibromo ozonide 3, bromoacetone, and the peroxides 5 and 6. A similar ozonolysis in tetrahydrofuran or acetone leads to the same products, but now the dibromo ozonide is present in trace amounts only. Finally, ozonolysis in methylene chloride gives all of the same products except that the monobromo ozonide 4 is absent. The yield of the dibromo ozonide 3 in methylene chloride is also lower than that obtained in pentane and ether. There does not appear to be any simple rationalization of the solvent dependence of the yields of the products obtained (Table I). One observation can be made. In general, ozonolysis of 11 leads to a decomposition of the initially formed trioxolane, 12, which favors formation of carbonyl oxide 7 rather than 2. This is evidenced by the



high yields of bromoacetone obtained (Table I). This conclusion was given additional support when olefin 11 was separately ozonized in methanol in order to trap carbonyl oxides 2 and 7 as their corresponding methoxy hydroperoxides. In this case the products, 2-methoxy-2-hydroperoxypropane, 13, and 1-bromo-2-methoxy-2-hydroperoxypropane, 14, were obtained in yields of 40.8% and 5.3%, respectively, thus confirming the approximate carbonyl oxide distribution predicted by the bromoacetone yields observed in Table I. It is interesting that Fliszar had earlier[12] both predicted and observed a carbonyl oxide distribution favoring the methyl-bearing carbonyl oxide over the one containing the bromomethyl substituent when 1,2-disubstituted olefins are ozonized. Thus he predicted a distribution favoring methyl (86.5%) over bromomethyl and observed (via methanol trapping) a distribution in which the methyl-containing carbonyl oxide was favored by 86.6%. In our case the respective yields of methoxy hydroperoxides indicates that the dimethyl-substituted carbonyl oxide is favored (88.5%). Compound 14 had not been described previously and in this instance an authentic sample was prepared by ozonizing the dibromo olefin 1 in methanol.

Finally, tetramethylethylene, 15, was ozonized by using bromoacetone as solvent. The products obtained were acetone diperoxide (31.1%), acetone triperoxide (14.5%), and the monobromo ozonide 4 (12.4%). While the ozonolyses are not strictly comparable because of a difference in olefin concentration used, it is interesting to note that the yield (12.4%) of 4 obtained in this case is very similar and in fact slightly less than that obtained (19.3%) when the dibromo olefin 1 is ozonized in acetone solvent. Thus it appears that in the reaction between a ketonic carbonyl oxide and a ketone the presence of an "activating" group in the ketone is not required. To us this means that the failure, to date,[13] of tetramethylethylene to give its parent ozonide must not be associated with the inherent reactivity of the ozonolysis fragments and that an alternative explanation should be sought.

Experimental Section[14]

Instrumentation. NMR spectra were recorded on a Varian T-60 or JEOL FX-100-FT NMR spectrometer with deuteriochloroform as the solvent and tetramethylsilane as internal standard. Infrared spectra were recorded with Perkin-Elmer Models 137 or 337 infrared spectrophotometers using neat samples. The spectra were calibrated with the 1601.4-cm^{-1} band of polystyrene film. Analytical and preparative GLPC work was carried out an a Varian-Aerograph Model A-705 gas chromatograph. Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Chromatography. The gas chromatography column used 7% β,β'-dioxypropionitrile on Chromosorb G (60–80 mesh) dimethyldichlorosilane (DMCS) treated $^1/_4$ in. × 6 ft, was purchased from Varian Aerograph, Palo Alto, CA. Analytical thin layer chromatography plastic plates, precoated with a 0.1-mm thickness of silica gel with fluorescent indicator UV-254, were obtained from Eastman Kodak Co., Rochester, NY. Preparative thin layer chromatography plates (20 × 20 cm) precoated with a 0.25-mm thickness of silica gel with fluorescent indicator UV-254 were purchased from Analtech., Inc., Newark, DE.

Materials. *n*-Pentane, anhydrous diethyl ether, tetrahydrofuran, chloroform, methanol, methylene chloride, and bromine (all Reagent grade) were obtained from Fisher Scientific Co., Fairlawn, NJ. Ether, pentane, and THF were redistilled twice, first from sodium benzophenone and then under argon from

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[10] For a review of the Baeyer–Villiger reaction, see: Smith, P. A. S. "Molecular Rearrangements"; Interscience: New York, 1963; p 568.

[11] Edwards, J. O.; Pater, R. H.; Curci, R.; DiFuria, F. *Photochem. Photobiol.* **1979**, *30*, 63.

[12] Fliszár S.; Granger, M. *J. Am. Chem. Soc.* **1970**, *92*, 3361.

[13] K. Griesbaum, W. Volpp, and R. Greinert reported at the 189th ACS meeting in Miami Beach, FL, on April 30, 1985, that they had obtained the ozonide of tetramethylethylene by ozonizing the olefin on polyethylene.

[14] The ozonides and other peroxides described herein while generally safe to handle should be accorded the usual precautions associated with organic peroxides. In particular acetone triperoxide should be handled with great care.

Table I. Results of Ozonolysis of 1-Bromo-2,3-dimethyl-2-butene in Various Solvents

	products[a]				
solvent	acetone triperoxide	acetone diperoxide	bromoacetone	monobromo TME ozonide	dibromo TME ozonide
pentane	0.29 (20.3)	0.53 (27.9)	2.69 (70.79)	0.6 (15.8)	0.11 (2.9)
ether	0.29 (20.3)	0.49 (25.8)	2.67 (70.26)	0.35 (9.2)	0.09 (2.4)
THF	0.15 (11.8)	0.43 (22.6)	3.43 (90.26)	0.09 (2.4)	trace
acetone	0.31 (24.4)	0.48 (25.2)	3.70 (97.36)	0.06 (1.6)	trace
methylene chloride	0.16 (12.6)	0.55 (28.9)	2.78 (73.16)	nil	0.04 (1.1)

[a] Numbers in parentheses represent the percentage conversion from the maximum possible amount of carbonyl oxide produced, based on the amount of O_3 passed through the solution which was 3.8 mmol in each case. In all cases 5 mmol of olefin was used.

calcium hydride. Methylene chloride was redistilled under argon from calcium hydride. Acetone (reagent grade) was purchased from Mallinckrodt, Inc. and was redistilled from anhydrous potassium carbonate. 2,3-Dimethyl-2-butene (99%, Gold Label) and 2,3-dimethyl-1,3-butadiene were obtained from Aldrich Chemical Co., Milwaukee, WI. Bromoacetone, purchased from Fluka Chemical Co., was dried with anhydrous magnesium sulfate and was redistilled under vacuum. Authentic acetone diperoxide and acetone triperoxide were prepared by ozonolysis of tetramethylethylene in pentane following Criegee's procedure.[15] Authentic *trans*-3,5-dimethyl-3,5-bis(bromomethyl)-1,2,4-trioxolane (trans-dibromo TME ozonide) was synthesized following Criegee's procedure.[16]

***trans*-1,4-Dibromo-2,3-dimethyl-2-butene.** A cooled solution of bromine (40.0 g, 0.25 mol) in 75 mL of chloroform was added, dropwise, to a solution of 2,3-dimethylbutadiene (20.5 g, 0.25 mol) in 100 mL of chloroform at −17 °C. The mixture was continuously stirred mechanically during the addition (2 h). The stirring was continued for an additional hour at −17 °C and 0.5 h at 0 °C after Br_2 addition was complete. Chloroform and excess bromine were removed in vacuo and the residue was recrystallized twice from pentane: mp 47–48 °C (lit.[17] mp 47.5 °C); yield 47 g (77%); ^1H NMR δ 1.89 (s, 6 H), 4.00 (s, 4 H).

1-Bromo-2,3-dimethyl-2-butene. A solution of 2,3-dimethylbutadiene in chloroform was allowed to react (−17 °C, 3.5 h) with a slight molar excess of HBr, dissolved in chloroform. The mixture was stirred continuously during reaction and the stirring was continued for an additional 24 h at 0 °C. At the end of the reaction period excess HBr was removed by washing the solution with aqueous sodium bicarbonate solution. The chloroform layer was dried with anhydrous sodium sulfate and chloroform was removed in vacuo by using a rotary evaporator. The residue was distilled under argon using a 30 cm × 8 mm Vigreux column filled with glass helices. The fraction collected at 60–65 °C (30 mm) was redistilled to give 1-bromo-2,3-dimethyl-2-butene (98.5% pure): bp 64 °C (30 mm) (lit.[18] bp 61–65 °C (30 mm)); ^1H NMR δ 1.73 (s, 3 H), 1.80 (s, 6 H), 3.98 (s, 2 H).

General Ozonolysis Procedure. Ozone was produced in a Welsbach Model T-408 ozone generator and was delivered as an ozone/oxygen stream at a rate of 0.18–0.19 mmol of O_3 min^{-1}. The ozonolysis solutions were purged with argon for 10 min before and after passing the O_3/O_2 stream. The ozone flow rate was determined iodometrically immediately prior to each ozonolysis. In most cases ozonolysis were carried out to less than 100% of the theoretical requirement of the olefin.

Ozonolysis of 1-Bromo-2,3-dimethyl-2-butene. 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 pentane case is given here.

The olefin (815 mg, 5 mmol) was dissolved in pentane (18 mL) and the solution cooled to −78 °C in a dry ice/acetone bath. The solution was purged with argon for 10 min and then O_3 (0.19 mmol min^{-1}) was passed through the solution for 20 min. The reaction mixture was again purged with argon for 10 min and then allowed to warm up to room temperature. The reaction mixture was made up to 20 mL volumetrically with pentane and this solution was divided into two equal portions, A and B. Portion A was directly analyzed by GLC. The column temperature was 60 °C and the helium flow rate was 100 mL/min. GLC analysis of this mixture revealed it to be a mixture of several products with GLC retention times 8, 12, 22, and 35 min. These products were separated by preparative GLC. The compounds with GLC retention times 8, 12, and 22 min were identified as acetone diperoxide, acetone triperoxide, and bromoacetone, respectively. Acetone diperoxide and acetone triperoxide were identified by comparison of their GLC retention times, NMR, and melting point data with those of authentic materials. Acetone diperoxide had mp 131–132 °C (lit.[15] mp 131–132 °C) and acetone triperoxide had mp 91–93 °C (lit.[15] mp 90–93 °C). Bromoacetone was identified by comparing its GLC retention time, TLC R_f value, NMR, and IR spectra with those of the authentic.

The compound having a retention time of 35 min was identified as 3,3,5-trimethyl-5-(bromomethyl)-1,2,4-trioxolane (monobromo TME ozonide). The ozonide was a colorless, lachrymatic liquid: ^1H NMR δ 1.487 (s, 3 H), 1.509 (s, 3 H), 1.644 (s, 3 H), 3.437 (AB q, J = 11 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.323 (q), 23.491 (q), 25.441 (q) 34.705 (t), 107.612 (s), 109.952 (s); IR (cm^{-1}, neat) 2924 (s), 1377 (s), 1276; 1267 (s), 1214 (s), 1172 (s), 1095, 986 (s), 899 (m), 894 (m), 824 (m). Anal. Calcd for $C_6H_{11}BrO_3$: C, 34.15; H, 5.25; Br, 37.86; O, 22.74. Found: C, 34.02; H, 5.40; Br, 37.59; O, 22.84.

The isolated ozonide from preparative GLC was used to make up a standard solution for GLC analysis to obtain ozonide yield. The yields of the products were determined by GLC analysis and peak integration (cut and weigh method) with peak callibration based on authentic materials. The yields of acetone triperoxide, acetone diperoxide, bromoacetone, and monobromo TME ozonide were 0.29, 0.53, 2.69, and 0.6 mmol, respectively. Portion B of the original reaction mixture was concentrated under vacuum (0.1 mm, 45 °C) and the residue was subjected to TLC analysis on 20 × 20 cm, 0.25-mm thick, silica gel glass plates with use of a mixture of hexane and ether (95:5) as developing solvent. The TLC fraction with the same R_f value (0.55) as authentic *trans*-3,5-dimethyl-3,5-bis(bromomethyl)-1,2,4-trioxolane was removed from the plate with ether. The ether was removed and the residue was recrystallized with pentane. The produce was identified as *trans*-3,5-dimethyl-3,5-bis(bromomethyl)-1,2,4-trioxolane by comparison of melting point, NMR, and TLC R_f values with those of an authentic sample. The yield of dibromo TMD ozonide, mp 41 °C (lit.[16] mp 42 °C), was 0.11 mmol.

The yields of various products obtained by using other solvents are given in Table I.

Ozonolysis of *trans*-1,4-Dibromo-2,3-dimethyl-2-butene in Acetone. A solution of olefin (605 mg, 2.5 mmol) in 18 mL of acetone was cooled to −78 °C, flushed with argon for 10 min, and then ozonized for 12 min (0.19 mmol O_3/min). The reaction mixture was again purged with argon for 10 min and then was allowed to warm up to room temperature. The solvent was removed on the rotary evaporator. The residue was chromatographed on four 20 × 20 cm, 0.25 thick, silica gel plates with use of a mixture of hexane and ether (95:5) as developing solvent. The portions with R_f values 0.65, 0.60, 0.55, and 0.42 were removed from the plates with ether. The TLC fraction with R_f 0.42 was further purified by distillation (bulb to bulb). This product was identified as bromoacetone by comparison of its IR, NMR GLC retention time, and TLC R_f values with those of an authentic sample. The compound had bp 45–46 °C at 30 mm (lit.[8] bp 48 °C at 30 mm). The TLC fraction with R_f 0.55 was purified further by recrystallization with pentane. This material was identified as *trans*-dibromo-TME ozonide by comparison of its NMR, melting point, and TLC R_f values with those of an authentic

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sample prepared following the procedure of Criegee et al.[8] The melting point of the product was 40 °C (lit.[8] mp 42 °C). The mother liquor from the recrystallization also contains a small amount of material whose NMR spectrum indicates that it is probably the cis isomer of the ozonide. The TLC fractions with R_f values 0.65 and 0.60, consisting mainly of various peroxides, were further purified by preparative GLC. GLC analysis of both the fractions revealed them to be mixtures of three components with GLC retention times of 8, 12, and 35 min. The components with GLC retention times of 8 and 12 min were identified as acetone diperoxide and acetone triperoxide, respectively, by comparison of their GLC retention times, TLC R_f values, and NMR spectra with those of the authentic compounds. The TLC R_f values for the authentic di- and triperoxide also were the same as those assigned to the product materials prior to GLC analysis. Acetone triperoxide had mp 91 °C (lit.[15] mp 90–93 °C) and acetone diperoxide had mp 131–132 °C (lit.[15] mp 131–132 °C). The component with a GLC retention time of 35 min was identified as 3,3,5-trimethyl-5-(bromomethyl)-1,2,4-trioxolane by comparison of its NMR and GLC retention time with those of an authentic sample prepared as reported in the previous experiment. The yields of all the products, except for dibromo TME ozonide, where the isolated yield was determined, were determined by GLC peak area (cut and weigh method) with authentic compounds used for calibration. The yields were found to be 6.69 mmol (81%) for bromoacetone, 0.13 mmol (5.7%) for dibromo TME ozonide, 0.44 mmol (19.3%) for monobromo TME ozonide, 0.08 mmol (10.5%) for acetone triperoxide, and 0.03 mmol (2.6%) for acetone diperoxide.

A number of control reactions were run as follows. When acetone is ozonized at −78 °C as described above, then no acetone triperoxide or acetone diperoxide is formed. Similarly, passing O_3 into solutions of monobromo TME ozonide or dibromo TME ozonide in acetone led to no acetone diperoxide or acetone triperoxide production. In a separate experiment it was shown that a solution of monobromo TME ozonide in $CDCl_3$ did not lead to the formation of acetone triperoxide or acetone diperoxide after storage at room temperature for a week. In separate experiments it was also shown that monobromo TME ozonide and dibromo TME ozonide are stable in acetone solution and do not lead to production of either acetone triperoxide or acetone diperoxide. When ozonation of acetone diperoxide was carried out in acetone, then no acetone triperoxide is formed. When attempted interconversion of acetone diperoxide was carried out either under GLC conditions or under ozonation conditions, then no acetone triperoxide is formed. In a separate experiment it was also shown that monobromo TME ozonide does not decompose under the GC conditions used to give acetone triperoxide or acetone diperoxide.

Ozonolysis of 2,3-Dimethyl-2-butene in Bromoacetone. The olefin (2.1 g, 25 mmol) was dissolved in 10 mL of bromoacetone. The solution was cooled to 0 °C with an ice–water bath and was purged with argon for 10 min. In order to prevent the evaporation of TME, the ozonation vessel was fitted with a dry ice/acetone reflux condenser. The ozone/oxygen stream (O_3, 0.19 mmol/min) was passed through the solution for 95 min and the reaction solution was flushed again with argon for 10 min. The solution was allowed to warm up to room temperature and was made up to 25 mL volumetrically with ether. The solution was analyzed by GLC and found to contain acetone diperoxide, acetone triperoxide, and monobromo TME ozonide. The products were identified by comparison of their GLC retention times, NMR spectra, and melting point data with those of authentic compounds. The yields of acetone diperoxide, acetone triperoxide, and monobromo TME ozonide as determined by GLC were 2.80 mmol (31.1%), 0.87 mmol (14.5%), and 2.23 mmol (12.4%), respectively. The crude reaction mixture was examined for the presence of the di- and triperoxides of bromoacetone. Only traces of materials corresponding to these products could be detected.

Ozonolysis of *trans*-1,4-Dibromo-2,3-dimethyl-2-butene in Methanol. A solution of the olefin (1.21 g, 15 mmol) in 20 mL of methanol was cooled to 0 °C in an ice–water bath, flushed with argon for 10 min, and then ozonized for 25 min (0.19 mmol O_3/min). The reaction mixture was again flushed with argon for 10 min and was allowed to warm up to room temperature. Methanol and bromoacetone were removed under vacuum at 40 °C and at 10 mm. The residue was subjected to bulb-to-bulb distillation under high vacuum. The product was redistilled again to give 1-bromo-2-hydroperoxy-2-methoxypropane, bp 60 °C (bath temperature) at 0.1 mm); yield 0.825 g (89%); ^1H NMR δ 1.495 (s, 3 H), 3.41 (s, 3 H), 3.505 (AB q, J = 11 Hz, 2 H), 8.375 (br s, 1 H); IR (cm^{-1}, neat) 3322 (br s), 2924 (s), 1427 (m), 1347 (s), 1272 (m), 1255 (s), 1222 (s), 1183 (s), 1117 (m), 1087 (m), 1042 (s), 901 (m), 833 (s), 769 (m). Anal. Calcd for $C_4H_9BrO_3$: C, 25.97; H, 4.90; Br, 43.19; O, 25.94. Found: C, 26.00; H, 5.13; Br, 42.96; O, 26.36.

Ozonolysis of 1-Bromo-2,3-dimethyl-2-butene in Methanol. The olefin (1.63 g, 10 mmol) was dissolved in methanol (25 mL) and the solution cooled to 0 °C in an ice–water bath. The solution was purged with argon for 10 min and then ozone (0.19 mmol O_3/min) was passed through the solution for 50 min. The reaction solution was again purged with argon for 10 min and then allowed to warm up to room temperature. The room-temperature solution was fractionated under vacuum. The first fraction (24 mL), which distilled at 20 °C (30 mm), was found to contain acetone and methanol. Acetone was identified by comparing its NMR and GLC retention time with those of the authentic. The second fraction which distilled at 40–48 °C (30 mm), was further purified by redistillation. The product was identified as bromoacetone by comparison of its GLC retention time, NMR spectrum, and TLC R_f values with those of an authentic sample. The yield of bromoacetone was 1.23 g (90%). The third fraction which distilled at 58–65 °C (18 mm) was purified further by bulb-to-bulb distillation. The product had bp 64–65 °C at 18 mm and was identified as 2-methoxy-2-hydroxperoxypropane by comparison of its NMR spectrum with that of an authentic sample prepared by using Criegee's procedure.[19] The yield of the product was 432 mg (40.75%). The residue (100 mg) obtained after the fractionation of the original reaction solution was found to contain mainly 1-bromo-2-hydroperoxy-2-methoxypropane (53% yield). The product was identified by comparison of its TLC R_f value and NMR spectrum with those of an authentic sample of 1-bromo-2-hydroxyperoxy-2-methoxypropane prepared as described above.

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Registry No. **1**, 6044-73-1; (*cis*)-**3**, 98821-13-7; (*trans*)-**3**, 98821-12-6; **4**, 98838-20-1; **5**, 17088-37-8; **6**, 1073-91-2; **11**, 5072-70-8; $BrCH_2COCH_3$, 598-31-2; $Me_2C{=}CMe_2$, 563-79-1; $Me_2C(OOH)(OMe)$, 10027-74-4; $CH_2{=}C(Me)(Me)C{=}CH_2$, 513-81-5; $BrCH_2(OMe)C(OOH)CH_3$, 98821-14-8.

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