

(m, 3), 1.69 (s, 3), 1.59 (s, 3), 1.59-1.10 (m, 2), 0.87 (t, 3).

Peak C was assumed to have the structure corresponding to 15 with two more methyl groups because of its GLC retention time.

Alkylation of the Copper Dienolate of 2-Hexenoic Acid (4) with Dimethallyl Bromide (B). The copper dienolate formed from 200 mg (1.75 mmol) of 2-hexenoic acid and 720 mg CuBr·SMe₂ was treated with 1.40 g (7 mmol) of dimethallyl bromide. Product isolation gave the crude acid that was methylated with diazomethane. GLC analysis (column A, 2-min postinjection interval, 75-275 °C, 15 °C/min) revealed four peaks, A (157 °C), B (164 °C), C (175 °C) and D (250 °C) in a ratio of (A + B + C):D of 48:52. Further GLC analysis (column F, 130 °C) revealed that peak A consisted of two peaks (A₁ and A₂, retention times 8.6 and 9.2 min), that peak B had a retention time of 10.1 min, and that peak C had a retention time of 14.2 min; the ratio of A₁:A₂:B:C was 34:25:13:28. Peak A had the same retention time as that of material previously shown to be the *E* and *Z* α -alkylated products. Peak C had the same retention time as that of the material previously shown to be the 2*E* γ -alkylated product. Because of its retention time, peak B was presumed to be the γ S_N2' isomer, and peak D was assumed to be the dimethylated structure corresponding to 15.

Registry No. 1, 80-59-1; 2, 541-47-9; (E)-3, 107-93-7; *cis*-4, 1577-28-2; *trans*-4, 13419-69-7; *cis*-4 methyl ester, 13894-64-9; *trans*-4 methyl ester, 13894-63-8; (E)-6 methyl ester, 75716-89-1; (2*E*,6*E*)-7 methyl ester, 75716-90-4; (E)-8 methyl ester, 75716-91-5; (2*E*,6*Z*)-9 methyl ester trimethylsilyl ether, 75716-92-6; (2*E*,6*E*)-9 methyl ester trimethylsilyl ether, 75716-93-7; (2*Z*,6*Z*)-10 methyl ester, 75716-94-8; (2*Z*,6*E*)-10 methyl ester, 75716-95-9; 15, 75716-96-0; (E)-16 methyl ester, 75716-97-1; A, 106-95-6; B, 870-63-3; C, 6138-90-5; D, 25996-10-5; E, 75716-98-2; F, 75716-99-3; G, 26562-24-3; H, 930-22-3; I, 1838-94-4; J, 7437-61-8; K, 6790-37-0; trimethyl phosphonoacetate, 5927-18-4; butanal, 123-72-8; ethyl (Z)-3-methyl-2-hexenoate, 22210-22-6; (Z)-3-methyl-2-hexenol, 30804-76-3; (E)-3-methyl-2-hexenol, 30801-96-8; ethyl (2*E*)-3-methyl-2-hexenoate, 22210-21-5; methacrolein, 78-85-3; THF, 109-99-9; piperylene, 504-60-9; methyl (2*E*,6*E*)-farnesenate, 3675-00-1; methyl (4*E*)-5,9-dimethyl-2-(2-propenyl)-4,8-decadienoate, 61264-06-0; methyl (2*Z*,6*Z*)-farnesenate,

4176-78-7; methyl (2*Z*,6*E*)-farnesenate, 4176-77-6; methyl (2*E*-2,5,9-trimethyl-5-vinyl-2,8-decadienoate, 75717-00-9; methyl (2*E*,6*E*)-2,7,11-trimethyl-2,6,10-dodecatrienoate, 55786-72-6; methyl (2*E*,6*Z*)-2,7,11-trimethyl-2,6,10-dodecatrienoate, 55786-73-7; methyl (2*E*)-2,5-dimethyl-5-propyl-2,6-heptadienoate, 75717-01-0; methyl (2*E*,6*E*)-2,7-dimethyl-2,6-decadienoate, 75717-02-1; methyl (2*E*,6*Z*)-2,7-dimethyl-2,6-decadienoate, 75717-03-2; propyl iodide, 107-08-4; methyl 2-methyl-2-propyl-3-butenoate, 75717-04-3; ethyl iodide, 75-03-6; methyl 2-methyl-2-ethyl-3-butenoate, 75717-05-4; methyl iodide, 74-88-4; methyl 2,2-dimethyl-3-butenoate, 19757-86-9; methyl (2*E*)-2-methyl-2-pentenoate, 1567-14-2; acetaldehyde, 75-07-0; methyl 3-hydroxy-2-methyl-2-vinylbutanoate, 75717-06-5; methyl 2-bromoacetate, 96-32-2; dimethyl 2-methyl-2-vinylsuccinate, 70912-92-4; benzyl bromide, 100-39-0; methyl 2-benzyl-2-methyl-3-butenoate, 75717-07-6; methyl (2*E*)-2-methyl-5-phenyl-2-pentenoate, 75717-08-7; methyl (4*E*)-6-hydroxy-2-(isopropenyl)-4-hexenoate, 75717-09-8; methyl (2*Z*,6*E*)-8-hydroxy-3-methyl-2,6-octadienoate, 75750-97-9; methyl (2*Z*,6*Z*)-8-hydroxy-3-methyl-2,6-octadienoate, 75717-10-1; methyl (2*E*,6*Z*)-8-hydroxy-3-methyl-2,6-octadienoate, 75717-11-2; methyl (2*E*,6*E*)-8-hydroxy-3-methyl-2,6-octadienoate, 75717-12-3; methyl (4*E*)-6-hydroxy-2-vinyl-4-hexenoate, 75717-13-4; methyl (2*E*,6*E*)-octadienoate, 25172-05-8; methyl (2*E*,6*Z*)-2,7-dimethyl-8-hydroxy-2,6-octadienoate, 75717-14-5; methyl (2*E*,6*E*)-2,7-dimethyl-8-hydroxy-2,6-octadienoate, 75717-15-6; methyl 6-hydroxy-5-methyl-2-isopropenyl-4-hexenoate, 75717-16-7; methyl (2*Z*,6*E*)-8-methoxy-3,7-dimethyl-2,6-octadienoate, 75717-17-8; methyl (2*E*,6*E*)-8-methoxy-2,6-nonadienoate, 75717-18-9; methyl 6-hydroxy-2-vinyl-4-heptenoate, 75717-19-0; methyl (2*E*,6*E*)-8-hydroxy-2,6-nonadienoate, 75717-20-3; methyl (2*E*)-2-methyl-6-oxo-2-heptenoate, 75717-21-4; methyl (2*E*)-2-allyl-3-hexenoate, 62243-61-2; methyl (2*Z*)-2-allyl-3-hexenoate, 75717-22-5; methyl (E)-2-(1-buten-1-yl)-5-methyl-4-hexenoate, 75717-23-6; methyl (Z)-2-(1-buten-1-yl)-5-methyl-4-hexenoate, 75717-24-7; methyl (2*E*)-4-ethyl-7-methyl-2,6-octadienoate, 75717-25-8; methyl 2,5-dimethyl-6-hydroxy-2-vinyl-4-hexenoate, 75717-26-9; methyl 2,4-dimethyl-6-hydroxy-2-vinyl-4-hexenoate, 75717-27-0; methyl 2-methyl-2-vinyl-4-pentenoate, 66052-30-0; methyl (E)-2-methyl-2,6-heptadienoate, 66052-31-1; CuI, 7681-65-4; CoBr₂, 7789-43-7; MgCl₂, 7786-30-3; MnCl₂, 7773-01-5; AgBF₄, 14104-20-2; FeCl₂, 7758-94-3; ZnCl₂, 7646-85-7; NiBr₂, 13462-88-9; CdI₂, 7790-80-9; HgCl₂, 7487-94-7; Li, 7439-93-2.

Ozonation of Organic Compounds. 4. Ozonolysis of α,β -Unsaturated Carbonyl Compounds in Protic Solvents

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Ozonolysis of mesityl oxide, crotonic acid, and maleic acid was carried out in protic solvents such as methanol, *tert*-butyl alcohol, water, and acetic acid at 30 °C. Anomalous ozonolysis products were obtained in every solvent except in methanol and the ratio of anomalous ozonolysis to total ozonolysis was determined. It was suggested that these anomalous products were formed mostly by the rearrangement of carbonyl oxides of methylglyoxal and glyoxylic acid, 2c and 2d, because α -acetoxyalkyl and α -carboxylalkyl hydroperoxides were relatively stable at 30 °C.

It is well recognized that the ozonolysis of olefins in protic solvents proceeds as shown in Scheme I by a Criegee mechanism.^{1,2} It has been argued whether primary ozonide 1 decomposes to carbonyl oxide 2 or singlet biradical 3.^{2,3} However, 2 is considered to be more stable than 3

in protic solvents.⁴ In methanol, therefore, 2 reacts with alcohol to form methoxyalkyl hydroperoxides 4w.¹ Similarly hydroxyalkyl and acetoxyalkyl hydroperoxides (4x and 4y, respectively) are produced in the ozonolysis in water⁵ and acetic acid,⁶ respectively. Accordingly, *tert*-butylalkyl hydroperoxide 4z must be formed when ozo-

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(2) Criegee, R. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 745-52.

(3) Wadt, W. R.; Goddard, W. A., III *J. Am. Chem. Soc.* 1975, 97, 3004-21.

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(5) Criegee, R.; Lohaus, G. *Justus Liebigs Ann. Chem.* 1953, 583, 12-9.

(6) Criegee, R. *Justus Liebigs Ann. Chem.* 1949, 564, 9-15.

Table I. Ozonolysis of Mesityl Oxide in Protic Solvents at 30 °C for 20 min^a

run no.	1	2	3	4	5
solvent	H ₂ O	MeOH	t-BuOH	AcOH	<i>b</i>
initial olefin, mmol	5.92	5.56	7.12	7.55	5.16
$-\Delta$ olefin, mmol	2.5	2.9	3.4	4.6	
products, mmol					
peroxides	>1.5	2.83	1.44	3.21	2.06
HCOOH	0.70	<0.05	0.87	1.52	1.40
CH ₃ COOH	0.70	<0.05	0.86		1.40
CH ₃ COCOOH	<0.01	<0.01	1.17	0.10	0.0
after hydrolysis, mmol					
CH ₃ COCHO	1.8	2.8	1.4	<i>c</i>	<i>c</i>
CH ₃ COCH ₃	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
$-\Delta$ peroxides, ^d mmol	0.05	0.02	0.04	0.45	0.16
total ozonolysis, mmol	2.5	2.8	3.48	4.83	3.46
α^e	0.28	~0	0.25	0.31	0.46

^a 0.20 mmol/min of O₃ was introduced. ^b 0.01 N HCl (aqueous). ^c Found. ^d Amount of peroxides decomposed at 30 °C in the first 20 min after the ozonolysis (see text). ^e Ratio of anomalous ozonolysis to total ozonolysis.

Table II. Ozonolysis of Crotonic Acid (A) and Maleic Acid (B) in Protic Solvents at 30 °C^a

run no.	6	7	8	9	10	11	12	13
substrate	A	A	A	A	B	B	B	B
solvent	H ₂ O	MeOH	t-BuOH	AcOH	H ₂ O	MeOH	t-BuOH	AcOH
time, min	20	20	20	20	30	30	30	30
initial olefin, mmol	7.88	7.20	7.64	7.48	4.85	5.13	5.04	5.13
$-\Delta$ olefin, mmol	3.1	4.1	3.8	3.9	1.2	2.4	3.5	3.5
products, mmol								
peroxides	2.56	3.86	2.45	2.74	0.05	3.40 ^b	1.76	>2.43
HCOOH	0.70	<0.05	1.16	1.23	1.17	<i>c</i>	1.50	0.9
(COOH) ₂	0.00	0.00	0.19	0.00	0.00	<0.02	0.20	0.05
CH ₃ COOH	<0.05	0.0	<0.1					
after hydrolysis								
CHO(COOH)	2.62	4.07	2.41	2.57	1.34	4.8	5.0	6.5
$-\Delta$ peroxides, ^d mmol	0.20	<0.01	0.03	0.60			0.25	0.83
total ozonolysis, mmol	3.26	4.00	3.80	3.87	1.25	2.4	3.36	3.73
α^e	0.21	~0	0.31	0.32	0.94	~0	0.45	0.24

^a 0.20 mmol/min of O₃ was introduced. ^b Some were from methanol because of low reactivity of maleic acid toward ozone. ^c Found. ^d Amount of peroxides decomposed at 30 °C in the first 20 min (or 30 min in the case of B) after the ozonolysis (see text). ^e Ratio of anomalous ozonolysis to total ozonolysis.

olysis is carried out in *tert*-butyl alcohol.

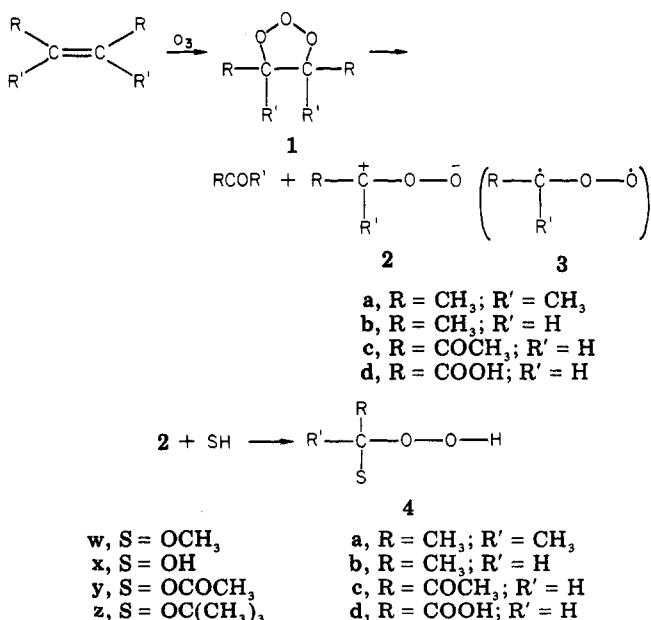
On the other hand, it is sometimes observed that not only the carbon–carbon double bond but also one of the adjacent carbon–carbon single bonds is cleaved by ozonolysis.^{1,7} This is called as anomalous ozonolysis and α,β -unsaturated carbonyl compounds are typical olefins which undergo anomalous ozonolysis.¹ However, only a few examples of anomalous ozonolysis of α,β -unsaturated carbonyl compounds in protic solvents have been reported and the mechanism of anomalous ozonolysis has not been conclusively established.

As described later in detail, there are four intermediates which may possibly give anomalous products: primary ozonide, carbonyl oxide, ozonide, and hydroperoxide. We have ozonized several α,β -unsaturated carbonyl compounds at 30 °C in protic solvents such as water, methanol, *tert*-butyl alcohol, and acetic acid, aiming specifically at measuring the formation of anomalous products and elucidating the mechanism of anomalous ozonolysis to find out which of the four intermediates is the most important precursor.

Results

In Tables I and II are summarized the results of mesityl oxide, crotonic acid, and maleic acid in protic solvents at 30 °C. Since many of the products are unstable, the analyses of the products were carried out as described in the experimental section as early as possible after the

Scheme I. Ozonolysis of Olefins in Protic Solvents



ozonolysis. Peroxides were measured by iodometry and the other products were determined by high-pressure liquid chromatography (LC), using an aqueous solution of 0.01% phosphoric acid as an eluent. Isotachophoretic analysis was also applied for quantitative and qualitative analysis of acids. The amounts of acids determined by these two different methods agreed well.

(7) Young, W. G.; Mckinnis, A. C.; Webb, I. D.; Roberta, J. D. *J. Am. Chem. Soc.* 1946, 68, 293–6.

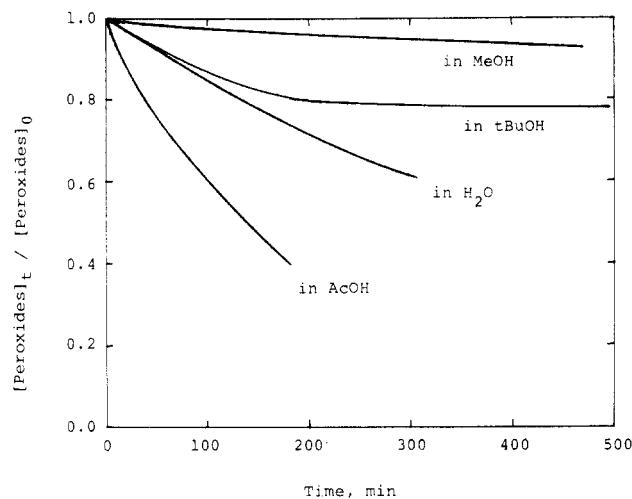
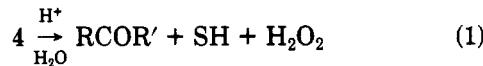


Figure 1. Decomposition of peroxides produced in the ozonolysis of mesityl oxide in protic solvents under air at 30 °C.

Peroxides measured by iodometry must be mostly hydroperoxides **4**.¹ However, **4** was readily hydrolyzed under acidic conditions as shown in eq 1.¹ Table I shows that



the amounts of methylglyoxal found by LC and peroxides measured by iodometry are in satisfactory agreement. Similarly, Table II shows about equal amounts of glyoxylic acid and peroxides in the ozonolysis of crotonic acid. Moreover, little change was observed in the product distribution measured by LC with and without adding reducing agent such as dimethyl sulfide or acidic iodide. These results indicate that the hydrolysis of **4** proceeded rapidly and completely in an aqueous solution of 0.01% phosphoric acid and that little decomposition of **4** to anomalous products occurred during analysis.

The formation of ozonide should be small in the ozonolysis of mesityl oxide and crotonic acid in protic solvents. This is supported by the fact that the ozonide prepared by the ozonolysis of methyl vinyl ketone in carbon tetrachloride gave formic and acetic acids by hydrolysis in LC rather than the corresponding carbonyl compounds, whereas, as described above, the peroxides formed in protic solvents gave the corresponding carbonyl compounds almost quantitatively.

The disappearance of olefins was followed by LC and/or GLC. Total ozonolysis calculated from the amounts of products was in good agreement with the olefins reacted.

Among the products from the ozonolysis of mesityl oxide, formic and acetic acids are formed from anomalous ozonolysis, which leads to cleavage not only of the olefinic bond but also of the adjacent carbon–carbon single bond to give products with fewer than the expected number of carbon atoms. It should be noted that formic and acetic acids were formed in equal amounts as shown in Table I. Similarly, formic acid and carbon dioxide are the anomalous products from the ozonolyses of crotonic acid and maleic acid. The ratio of anomalous ozonolysis to total ozonolysis, α , is calculated, for example, as $0.70/2.5 = 0.28$ in run 1 in Table I.

After the ozonolysis, an aliquot of the reaction mixture was allowed to stand at 30 °C under air and the thermal stability of the peroxides was examined. Figures 1 and 2 show the rate of decomposition of peroxides produced in the ozonolysis of mesityl oxide and crotonic acid, respectively. The rate increases in the order of methanol > *tert*-butyl alcohol > water > acetic acid. The amount of

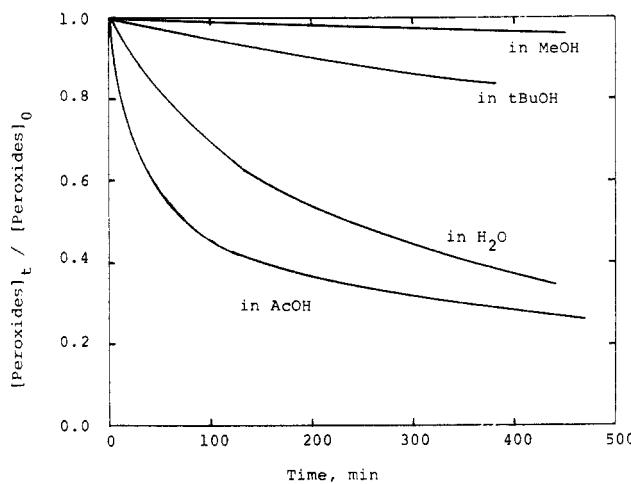


Figure 2. Decomposition of peroxides produced in the ozonolysis of crotonic acid in protic solvents under air at 30 °C.

peroxides decomposed in the first 20 or 30 min after the ozonolysis is also shown in Tables I and II. With the decay of the peroxides the amounts of anomalous products increased and those of methylglyoxal (in Table I) and glyoxylic acid (in Table II) decreased.

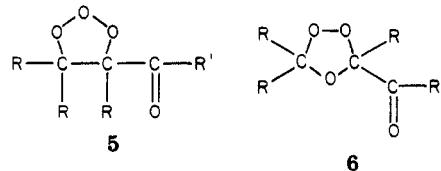
In the ozonolysis of mesityl oxide in methanol, **4wa**, **4wc**, acetone, and methylglyoxal were the major products and the anomalous ozonolysis products, i.e., formic acid and acetic acid, were not found.

The structure of **4wa** and **4wc** was confirmed by their NMR spectra. The ratio of **4wa** to **4wc** was estimated as 3 to 7 from NMR. **4wa** and **4wc** were very stable at 30 °C as shown in Figure 1. Hence, the Baeyer–Villiger oxidation of methylglyoxal by **4wa** and **4wc** should not be important under these conditions.

In *tert*-butyl alcohol, formic and acetic acids were formed in equal amounts besides **4za** and **4zc** in the ozonolysis of mesityl oxide. Pyruvic acid was also observed. It was found that **4za** prepared by the ozonolysis of tetramethylethylene in *tert*-butyl alcohol was very stable at 30 °C. Moreover, when methylglyoxal was treated with **4za** for 180 min at 30 °C, no formic, acetic, and pyruvic acids were formed. These results suggest that the decomposition of peroxides in Figure 1 should be due to the decomposition of **4zc**.

Discussion

Precursors of Anomalous Products. There are four intermediates which might possibly give anomalous products; they are primary ozonide **5**, carbonyl oxides **2c** and **2d**, ozonide **6**, and hydroperoxides **4c** and **4d**.



$R' = \text{CH}_3, \text{OH}$

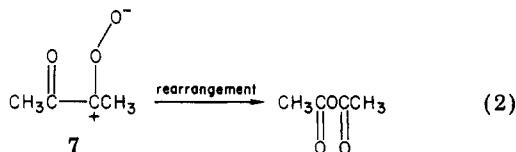
Firstly, the possibility that primary ozonide **5** rearranges to anomalous products must be excluded by the following results. Pappas et al.⁸ ozonized maleic acid in methanol at -60 °C, added dimethyl sulfide to the cold reaction mixture, and warmed it gradually to room temperature. They obtained glyoxylic acid as a normal ozonolysis

(8) Pappas, J. J.; Keaveney, W. P.; Grancher, E.; Berger, M. *Tetrahedron Lett.* 1966, 36, 4273–8.

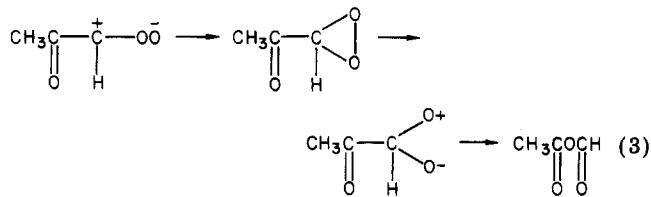
product in 91% yield by this procedure, in contrast to our previous result⁹ that formic acid was obtained as an anomalous product in greater than 70% yield in the ozonolysis of maleic acid in water at 30 °C. It has been observed^{8,10,11} for several olefins which give anomalous products under usual workup conditions that the amounts of anomalous products were decreased to none or little when the ozonolysis was carried out at low temperatures of -10 to -70 °C and reductive workup procedures were employed. It is noteworthy that primary ozonides of some aliphatic cis and trans olefins were stable only below -130 and -110 °C, respectively.¹²

For all olefins studied, none or only a trace amount of anomalous products was formed in the ozonolysis in methanol (runs 2, 7, and 11). This also suggests that the rearrangement of primary ozonide, the first possible precursor, to anomalous products should not be important in any solvents.

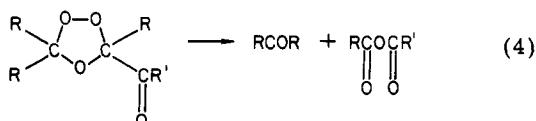
The second possible precursor is the carbonyl oxide. The formation of formic acetic anhydride¹³ in the ozonolysis of mesityl oxide in pentane at 0 °C indicates the contribution of the rearrangement of carbonyl oxide 2c. Furthermore, DeMore and Lin¹⁴ observed an unstable precursor to acetic acid anhydride in the ozonolysis of 2-butyne at -45 °C by in situ infrared spectroscopy. The precursor showed a strong carbonyl absorption at 1740 cm⁻¹ and it gave acetic acid anhydride (eq 2) and other



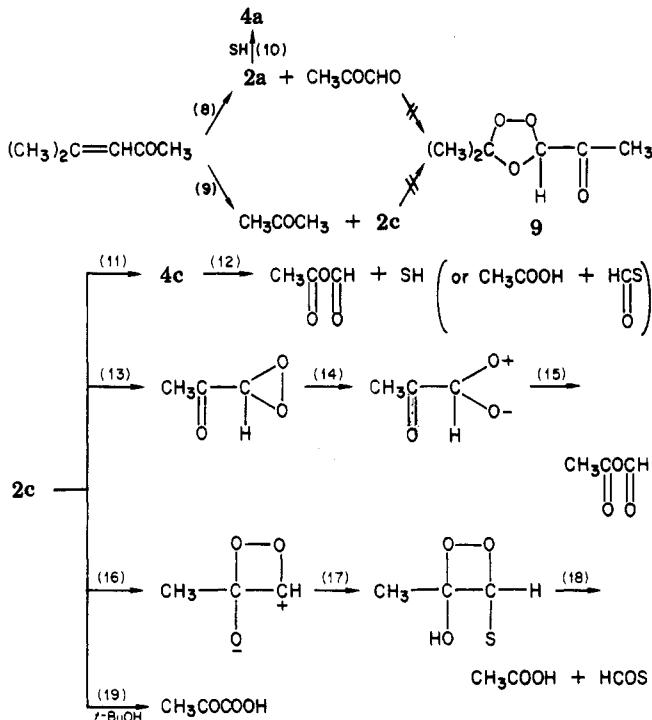
products upon warming to room temperature from -45 °C. These results indicate that the structure of the precursor should be carbonyl oxide 7. Similar results were obtained in the case of propyne and 1-butyne.¹⁴ Criegee² suggests that the rearrangement of 2c proceeds as shown in eq 3.



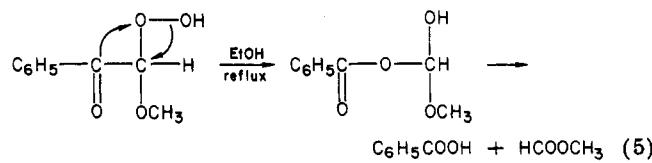
Thirdly, the ozonide 6 has been suggested¹ to rearrange as shown in eq 4.



The last possible precursors to anomalous products are hydroperoxides **4c** and **4d**. Bailey et al.¹⁵ studied the rearrangement of methoxyalkyl hydroperoxide **8**, which

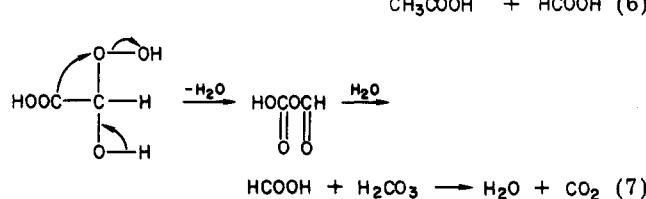
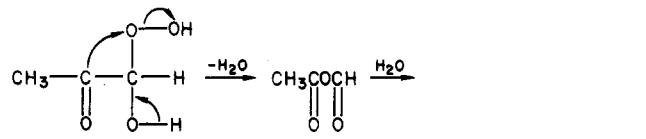


has a structure similar to 4wc in hot alcohol and concluded that reaction 5 is the major pathway. Acetoxyalkyl¹⁸ and



tert-butoxyalkyl hydroperoxides **4yc**, **4yd**, **4zc**, and **4zd** may decompose similarly.

Hydroxyalkyl hydroperoxides **4xc** and **4xd** are the intermediates of the Baeyer–Villiger oxidation of methylglyoxal and glyoxylic acid by hydrogen peroxide, respectively. These reactions should proceed as follows^{1,17} to give the same products as anomalous ozonolysis (eq 6 and 7).



Ozonolysis of Mesityl Oxide. Scheme II shows the proposed major reaction pathways in the ozonolysis of α,β -unsaturated carbonyl compounds in protic solvents, mesityl oxide being taken as an example. The primary ozonide of mesityl oxide decomposes either to 2a and

(9) Yamamoto, Y.; Niki, E.; Shiokawa, H.; Kamiya, Y. *J. Org. Chem.* 1979, 44, 2137-42.

(10) Raulins, N. R.; Sibert, L. A. *J. Org. Chem.* 1961, 26, 1382-6.

(11) Kolsaker, P.; Bailey, P. S. *Acta Chem. Scand.* 1967, 21, 537-46.

(12) Greenwood, F. L. *J. Org. Chem.* 1965, 30, 3108-11. Durham, L.

J.; Greenwood, F. L. *Ibid.* 1968, 33, 1629-32. Greenwood, F. L.; Durham, L. J. *J. Org. Chem.* 1969, 34, 3363-6.

(13) Criegee, R.; Bath, S. S.; Bornhaupt, B. *Chem. Ber.* 1960, 83, 7.

(14) DeMoss, W. B.; Lin, C. I. *J. Org. Chem.* 1973, 38, 285.

(16) Criegee, R.; Lederer, M. *Justus Liebigs Ann. Chem.* 1953, 583, 29-36.

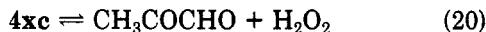
29-36.
(17) Bunton, C. A. "Peroxides Reaction Mechanism"; Edwards, J. O., Ed.: Wiley-Interscience: New York, 1962; pp 11-27.

methylglyoxal (eq 8) or to **2c** and acetone (eq 9). **2a** and **2c** react with protic solvents to form **4a** and **4c**, respectively (eq 10 and 11). As mentioned before, the formation of ozonide **9** should be small. Accordingly, anomalous products from mesityl oxide, formic and acetic acids, should be formed by the rearrangement of carbonyl oxide **2c** or hydroperoxide **4c** or the Baeyer–Villiger oxidation of methylglyoxal by hydroperoxide **4**.

Ozonolysis of mesityl oxide in methanol gave no anomalous products (run 2) and this suggests that **2a** and **2c** are highly reactive toward methanol and hydroperoxides **4wa** and **4wc** are very stable at 30 °C.

On the other hand, anomalous products were formed in the ozonolysis in *tert*-butyl alcohol (run 3). Their amount (0.86 mmol) was more than 20 times larger than that of **4zc** decomposed (1.44 → 1.40 mmol) at 30 °C in the first 20 min after the ozonolysis. Therefore, anomalous products must have arisen neither from the rearrangement of **4zc** nor from the Baeyer–Villiger oxidation of methylglyoxal but from the rearrangement of carbonyl oxide **2c**. Reactions 13–15 were proposed by Criegee,² but reactions 16–18 are also possible.

Anomalous products were also observed in the ozonolysis in water (run 1). They have been assumed to be formed by the rearrangement of **4xc** as shown in eq 6. However, the decomposition of **4xc** was too slow to account for all the anomalous products observed, even taking into consideration that **4xc** was in equilibrium with methylglyoxal and hydrogen peroxide (eq 20), the equilibrium constant



for methylglyoxal being assumed to be larger than that of acetaldehyde, 48.08 M⁻¹.¹⁸

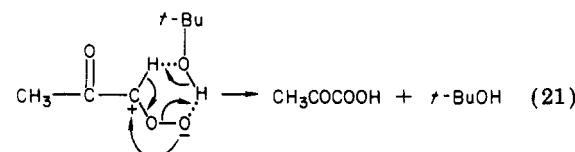
The ozonolysis in acetic acid also gave anomalous products (run 4). The decomposition of **4yc** was relatively fast as shown in Figure 1 because hydrogen ion accelerates this reaction.^{9,17} The acceleration by hydrogen ion is supported by the results of the ozonolyses of mesityl oxide in water and in an aqueous solution of 0.01 N hydrochloric acid, the ratio of anomalous ozonolysis to total ozonolysis, α , being 0.28 and 0.46, respectively (runs 1 and 6). But the decomposition of **4yc** was not so fast as to explain the formation of all the anomalous products observed.

The above results and discussion suggest that most of anomalous products are formed by the rearrangement of carbonyl oxide **2c**.

The formation of pyruvic acid from mesityl oxide in *tert*-butyl alcohol (run 3) is very interesting. None or only a trace amount of pyruvic acid was observed in other solvents (runs 1, 2, 4, and 6). Therefore, the ozonolysis of methylglyoxal to pyruvic acid can be ruled out. Furthermore, the amount of pyruvic acid observed was many times as much that of **4zc** that would decompose during ozonolysis as estimated from Figure 1. Accordingly, pyruvic acid must have arisen from **2c** (eq 19).

It was expected that the ozonolysis of mesityl oxide in aprotic solvents gave formic, acetic, and pyruvic acids by the rearrangement of **2c** and **9**.¹⁹ Actually, about 0.50

mmol of formic and acetic acids was formed in the ozonolysis in carbon tetrachloride or nitromethane at 30 °C in 20 min. However, only 0.01 mmol of pyruvic acid was observed. Hence, *tert*-butyl alcohol must participate in reaction 19 presumably as shown in eq 21.



Similar results were obtained in the ozonolysis of crotonic acid and maleic acid as shown in Table II. Formic acid was observed as an anomalous product in every solvent except methanol. This must be formed similarly by the rearrangement of carbonyl oxide **2d**. Oxalic acid was observed only when *tert*-butyl alcohol was used as solvent and this suggests that the reaction of **2d** with *tert*-butyl alcohol like eq 21 is plausible.

Experimental Section

Materials. α,β -Unsaturated carbonyl compounds and organic solvents were those of the highest grade available commercially. Little impurities, such as acid, that interrupt product analysis were observed. Water was purified by passage through an ion-exchange resin followed by distillation. Ozone was produced in a standard ozone generator, Nippon Ozone Co., Ltd., Model O-3-2, by charging pure oxygen dried beforehand by silica gel.

Ozonolysis Procedures. Ozonolysis was carried out as described in a previous paper.⁹ Ozone was introduced at a speed of 0.20 mmol/min.

Analytical Methods. A high-pressure liquid chromatograph (LC) equipped with UV detector, Japan Spectroscopic Co., Ltd., Model Tri Rotor and Uvidec 100-II, was mostly used for the analysis of products. An aqueous solution of 0.01% phosphoric acid was used as eluent and an ion-exchange-type column, Showa Denko Co., Ltd., Model Shodex C-811, was used. Formic acid, acetic acid, oxalic acid, glyoxylic acid, pyruvic acid, and methylglyoxal were identified from the LC elution time by comparison with authentic samples. Quantitative analyses were performed also with LC by monitoring the absorption at 200 nm. Acetone and hydrogen peroxide were also determined qualitatively. Carboxylic acids were also identified similarly by isotachophoretic analysis and measured quantitatively by using a Shimadzu isotachophoretic analyzer, Model IP-1B. An aqueous solution of 0.01 M glutamic acid was used as a terminal electrolyte, and an aqueous solution containing 0.01 M L-histidine and 0.01 M L-histidine hydrochloride was used as a leading electrolyte. Peroxides were determined by iodometric titration. The hydroperoxides **4** were so easily hydrolyzed under acidic conditions, as shown in eq 1, that the corresponding carbonyl compounds and hydrogen peroxide were detected by LC. However, some of the ozonide of methyl vinyl ketone decomposed to formic and acetic acids in the acidic aqueous carrier solution during LC.

¹H NMR spectra were determined on Varian 360A spectrometer: **4wa** (CCl₄) δ 1.43 (s, 6, CH₃), 3.26 (s, 3, OCH₃); **4wc** (CDCl₃) δ 2.05 (s, 3, CH₃), 3.43 (s, 3, OCH₃); ozonide of methyl vinyl ketone (CCl₄) δ 2.13 (s, 3, CH₃), 5.07 (s, 1, H), 5.30 (s, 1, H), 5.80 (s, 1, H).

Registry No. Mesityl oxide, 141-79-7; crotonic acid, 3724-65-0; maleic acid, 110-16-7.

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(19) Criegee, R. *Adv. Chem. Ser.* 1972, 112, 22–34.