Ozonation of Compounds of the Type Ar-CH=CH-G;

Ozonation in Methanol

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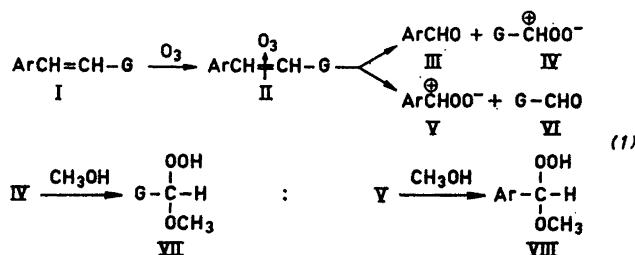
The ozonation of some substituted cinnamic esters and acids and of *p*-propenyl anisole was carried out in methanol at −78°C and the resulting solutions were subjected to decompositions under neutral, acid, and basic conditions. The yields of decomposition products indicate that a reaction between the initially formed methoxy hydroperoxides and aldehydes takes place to some extent prior to the decomposition. The yield of phenols follows the order of migratory aptitudes generally accepted. Acid decomposition gave the highest yield of phenols. Basic decomposition gave only the normal cleavage products, *viz.* acids and aldehydes. Decomposition paths are discussed.

The ozonation, mainly in inert solvents, of anethole (*p*-propenyl anisole, Ic) and cinnamic acid and its esters has received considerable attention by Briner and his school.[1] Their main contribution has been to follow the course of reaction by infrared and Raman spectroscopy. One observation relevant to the present paper was that aromatic aldehydes did not appear to be attacked by ozone as long as compounds with a reactive olefinic double bond were present in the ozonation solution. This is important because aromatic aldehydes alone are known to react with ozone.[2] Späth *et al.*[3] ozonized a series of substituted cinnamic esters and the corresponding benzaldehydes in chloroform and have found that the compounds which contained one or more methoxyl groups in the *ortho* and/or *para* position gave as products not only the expected benzoic acids and benzaldehydes, but also the corresponding phenols. Unfortunately, Späth always used a 50 % excess of ozone in his cinnamic esters ozonations and as the ozonation of benzaldehydes also gave phenols one cannot get a clear picture of true yields of the abnormal products. His work-up method included use of zinc and aqueous silver nitrate as decomposing

agents. Since this mixture should be reductive towards peroxidic functions, there might have existed a competition between reductions, giving aldehydes, and decompositions giving among others the abnormal products, phenols.

Abnormal ozonolyses giving products with fewer than the expected number of carbon atoms are well known and have been assumed to involve rearrangements. As to the stage at which such rearrangement occur, Leffler [4] and Young et al.[5] suggested that they occurred in an initial ozonide, while Criegee [6] proposed that the zwitterion was the immediate precursor to the rearrangement products. On the other hand, Milas [7] has shown that certain compounds which gave abnormal products on ozonation in inert solvents, gave the normal products, aldehydes or ketones, when ozonized in methanol and subsequently reduced.

The present work involves a study of abnormal product formation in the ozonation of compounds of the type Ar—CH=CH—G using methanol as solvents. According to the Criegee mechanism of ozonolysis [6,8] these reactions should occur as follows:

$$
\begin{array}{c}
\text{ArCH=CH-G} \xrightarrow{O_3} \text{ArCH} \overset{O_3}{+} \text{CH-G} \\
\text{I} \qquad\qquad \text{II}
\end{array}
\left<
\begin{array}{c}
\text{ArCHO + G}-\overset{\oplus}{\text{CHOO}}{}^{-} \\
\text{III} \qquad\qquad \text{IV} \\
\\
\text{Ar}\overset{\oplus}{\text{CHOO}}{}^{-} + \text{G}-\text{CHO} \\
\text{V} \qquad\qquad \text{VI}
\end{array}
\right.
\qquad (1)
$$

$$
\text{IV} \xrightarrow{CH_3OH} \underset{\underset{\text{OCH}_3}{|}}{\overset{\overset{\text{OOH}}{|}}{\text{G}-\text{C}-\text{H}}} \qquad : \qquad \text{V} \xrightarrow{CH_3OH} \underset{\underset{\text{OCH}_3}{|}}{\overset{\overset{\text{OOH}}{|}}{\text{Ar}-\text{C}-\text{H}}}
$$
$$
\qquad\qquad\qquad \text{VII} \qquad\qquad\qquad\qquad\qquad\qquad \text{VIII}
$$

a,	Ar = p-CH$_3$O-φ-,	G = COOCH$_3$	f,	Ar = p-CH$_3$-φ-	, G = COOCH$_3$
b,	„	G = p-CH$_3$O-φ-	g,	Ar = m-CH$_3$O-φ-	, „
c,	„	G = CH$_3$	h,	Ar = φ-	, „
d,	„	G = COOH	i,	Ar = p-NO$_2$-φ-	, „
e,	Ar = o-CH$_3$O-φ-,	G = COOCH$_3$	j,	Ar = 2,4-di-CH$_3$O-φ-	, „
			k,	Ar = 2,3-di-CH$_3$O-φ-	, „

The objectives of the present work were:
(1) to study the effects of different work-up conditions and variations of Ar and G on the extent of abnormality; (2) to determine the stage at which the abnormal reaction occurs; (3) to determine, if possible, the distribution of the zwitterions IV and V as Ar and G are varied; (4) to find out whether this distribution and the migratory aptitudes of the aryl groups are both important in determining the extent of abnormality.

The ozonations were carried out at a low temperature. Over-ozonation was carefully avoided and the resulting solutions were subjected to decomposition under neutral, acidic, or basic conditions in the absence of oxidizing or reducing agents. Although perchloric acid is normally considered an an oxidizing agent, it was shown unambiguously not to interfere with the final products in this work under the conditions applied. The results are shown in Table 1.

According to Criegee's mechanism the ozonation of one mole of a sym-. metrical molecule like 4,4'-dimethoxy stilbene (I b) in methanol should give

Table 1.[a]

Expt. No.	Ar	G	Method of decomp.	ArOH	ArCHO	ArCOOH	ArCOOCH$_3$	COOH|COOH	GLC[b] Column	Remarks
1	p-CH$_3$O-φ-	—COOCH$_3$	Bas.	0	86	9	1—2	54	Ap.L	Chemical analysis Total = 200 %
2	p-NO$_2$-φ-	»	»	0	49	40	0	54	–	
3	p-CH$_3$O-φ-	p-CH$_3$O-φ-	Neutr.	53	111	0	34	–	Ap.L	
4	»	—COOCH$_3$	»	40	25	14	15	51	»	Trace of dimethyl oxalate
5	2,4-di-CH$_3$O-φ-	—CH$_3$	»	70	15	1	5	–	»	
6		—COOCH$_3$	»	60	22	7	Trace	N.C.[c]	»	Acid-fraction impure
7	p-NO$_2$-φ-	—COOCH$_3$	Acid	0	31	0	61	42	–	Chemical analysis
8	m-CH$_3$O-φ-	»	»	0	31	2	55	N.C.[c]	PEG	
9	φ-	»	»	2	9	0	73	48	Ap.L	
10	p-CH$_3$-φ-	»	»	22	11	7	49	N.C.[c]	»	
11	o-CH$_3$O-φ-	»	»	67	16	14	Trace	42	»	Acid fraction impure
12	p-CH$_3$O-φ-	»	»	77	14	4	7	50	»	
13	»	—COOH	»	81	12	0	2	38	»	Acetyl dehyde detected
14	»	—CH$_3$	»	97	Trace	0	3	–	»	
15	2,3-di-CH$_3$O-φ-	—COOCH$_3$	»	31	9	12	35	N.C.[c]	»	Acid fraction impure

[a] Yields in per cent of theoretical. [b] See experimental section. [c] N.C. — not checked.

one mole of hydroperoxide VIII a and one mole of p-methoxy benzaldehyde (III a). Decomposition of the ozonized solution of I b should give us an indication of the fate of such a methoxy hydroperoxide. Thus, by comparison of the yields of aromatic products from I b with those from anethole (I c) or methyl p-methoxy cinnamate (I a) one should be able to calculate the distribution of zwitterions IV and V produced during ozonolysis of I a and I c. The results, however, indicate that the reaction course is not that simple and that more than one reaction path is involved in these decompositions. Thus, while about 0.5 mole p-methoxy phenol was found from 4,4'-dimethoxy stilbene, 0.7 mole was obtained from anethole under identical conditions (Expts. 3 and 5, Table 1). Since about 0.5 mole of p-methoxy phenol is the maximum that could be produced from VIII a, even if VIII a were produced in 100 % yield from ozonolysis of I c, the fact that 0.7 mole of the phenol was found in experiment 5, Table 1, must mean that the phenol had some other precursor besides (or along with) VIII a. A likely explanation is that the decompositions wholly or partly occur via a hydroxy methoxy peroxide (IX or X), obtained by interaction of VIII and VI or III and VII (eqns. 2 and 3). Various ways by which VIII, IX and X could decompose are shown by eqns. 4, 5, 6, 7, 8, 9, 10 and 11. Eqns. 4—6 show the rearrangements to give the phenols. Eqns. 7—11 account for the aldehydes, esters and carboxylic acids produced.
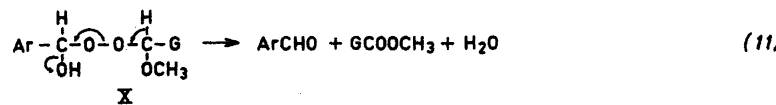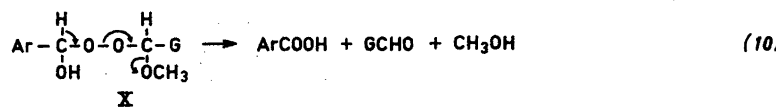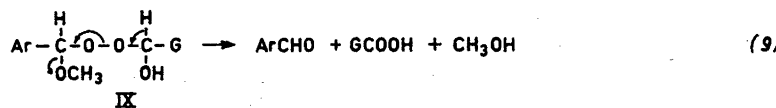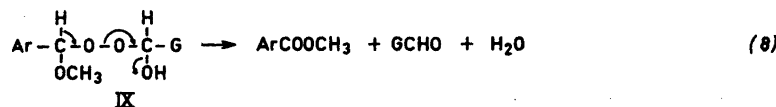
A check run to prove that such interactions occur between hydroperoxides and aldehydes of similar types and under similar conditions was done by ozonizing dimethyl fumarate in methanol and afterwards adding benzaldehyde. After decomposition the solution contained considerable amounts of methyl benzoate. Ruling out autoxidation and subsequent esterification by adding hydroquinone to the solution, this constitutes evidences that at least X and almost certainly IX are reasonable decomposition intermediates. That the reactions shown by eqns. 2—3 probably could take place at low temperature was established in another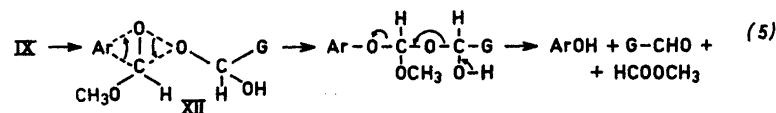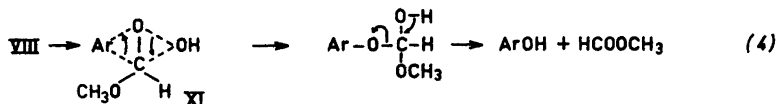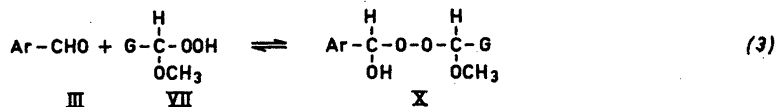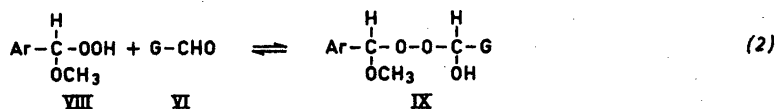 experiment by adding p-methoxy benzaldehyde to ozonized dimethyl fumarate and injecting the mixture on the gas chromatograph while the temperature was still well below 0°C. Methyl anisate showed up at once and the amount increased as the temperature was allowed to rise.

An explanation for the higher yield of phenol from I c than from I b by neutral decomposition (Table 1, expts. 3 and 5) might be that the equilibrium VIII b + VI b ⇌ IX (eqn. 2) is shifted to the left side, in comparison to the same equilibrium between VI c and VIII c, due to the low electrophilicity of the carbonyl carbon atom in VI b. The dehydration of VIII b to the anisate (eqn. 7) might introduce a strongly competitive alternative to the phenol decomposition and thereby also explain the higher yield of methyl anisate from I b. Methyl anisate can also be produced by eqn. 8, however.

The higher yield of anisic acid from I a than from the other compounds would be understood if eqn. 3 occurred to give more of peroxide X a (than of X b or X c) which could decompose as shown in eqn. 10.

The oxalic acid produced in the experiment where G was —COOH or —COOCH$_3$ could have arisen via eqn. 9 or 11. Under the work-up conditions used most of the methyl or dimethyl oxalate goes into the aqueous layer where it will be rapidly hydrolyzed. Dimethyl oxalate could also be formed

directly by dehydration of VII (analogous to eqn. 7). One strange fact about Table 1 is that in experiments 4, 7, 9, 11—13 the yields of phenols, aromatic acids and esters and oxalic acid totaled more than 100 %, yet in no reaction (eqns. 4—11) are oxalic acid and the above aromatic products produced simultaneously. Oxalic acid has been shown, however, to be produced by a Cannizzaro reaction with glyoxylic acid or its methyl ester (*e.g.* from VI a or d). Since conditions for a Cannizzaro reaction are applied in the work-up, these strange results become understandable.

$$\underset{\substack{VIII \qquad\quad VI}}{Ar-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-OOH + G-CHO} \rightleftharpoons \underset{IX}{Ar-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-O-O-\underset{OH}{\overset{H}{\underset{|}{C}}}-G} \qquad (2)$$

$$\underset{\substack{III \qquad\quad VII}}{Ar-CHO + G-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-OOH} \rightleftharpoons \underset{X}{Ar-\underset{OH}{\overset{H}{\underset{|}{C}}}-O-O-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-G} \qquad (3)$$

$$VIII \rightarrow Ar\overset{O}{\underset{XI}{C}} OH \rightarrow Ar-O-\underset{OCH_3}{\overset{O-H}{\underset{|}{C}}}-H \rightarrow ArOH + HCOOCH_3 \qquad (4)$$

$$IX \rightarrow Ar\overset{O}{C}O\overset{G}{C}OH \rightarrow Ar-O-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}O\underset{O-H}{\overset{H}{\underset{|}{C}}}-G \rightarrow ArOH + G-CHO + HCOOCH_3 \qquad (5)$$

$$X \rightarrow Ar\overset{O}{C}O\overset{G}{C}OCH_3 \rightarrow Ar-O-\underset{O-H}{\overset{H}{\underset{|}{C}}}-O-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-G \rightarrow ArOH + H-\underset{OCH_3}{\overset{O}{\underset{|}{C}}}-O-\underset{|}{\overset{H}{C}}-G \qquad (6)$$

$$\underset{VIII}{Ar-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-O-O-H} \rightarrow ArCOOCH_3 + H_2O \qquad (7)$$

$$\underset{IX}{Ar-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-O-O-\underset{OH}{\overset{H}{\underset{|}{C}}}-G} \rightarrow ArCOOCH_3 + GCHO + H_2O \qquad (8)$$

$$\underset{IX}{Ar-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-O-O-\underset{OH}{\overset{H}{\underset{|}{C}}}-G} \rightarrow ArCHO + GCOOH + CH_3OH \qquad (9)$$

$$\underset{X}{Ar-\underset{OH}{\overset{H}{\underset{|}{C}}}-O-O-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-G} \rightarrow ArCOOH + GCHO + CH_3OH \qquad (10)$$

$$\underset{X}{Ar-\underset{OH}{\overset{H}{\underset{|}{C}}}-O-O-\underset{OCH_3}{\overset{H}{\underset{|}{C}}}-G} \rightarrow ArCHO + GCOOCH_3 + H_2O \qquad (11)$$
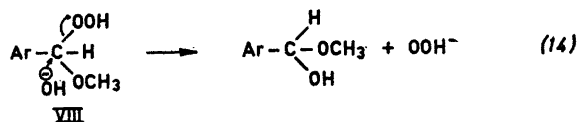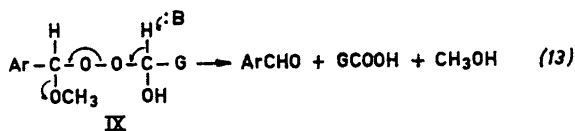
The main feature from the decomposition of the ozonized solutions with acid is the increased yields of phenols. Thus the yield of p-methoxy phenol increased from 40 % in neutral to 77 % in acid solution with methyl p-methoxy cinnamate, and from 70 % to more than 97 % with anethole. Since the conditions during ozonolyses have been kept constant, this increase must be due to different courses of decomposition. Reactions between hydroperoxides and carbonyl compounds to form hydroxy peroxides appear to be acid catalyzed,[9] and, thus, the equilibria 2 and 3 might be shifted more to the right in acid solutions. Rearrangements such as shown in eqns. 4—6 are also known to be acid catalyzed [9] and thus favored under acidic conditions.

The yields of phenols from the different ringsubstituted cinnamic esters seem to follow, at least qualitatively, the expected migratory aptitudes of aryl groups. Thus the p-methoxy compounds gave high yields of phenols while p-nitro cinnamate gave no phenol at all. This constitutes a fair justification for proposing the transition states XI, XII, and XIII. The high yield of o-methoxy phenol from methyl o-methoxy cinnamate is rather unexpected based on migratory aptitudes alone. A possible route to the phenol is shown in eqn. 12.
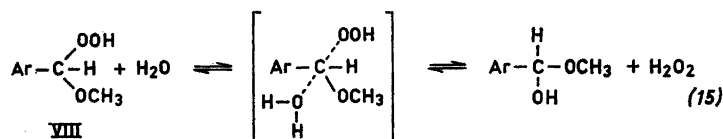

$$IX \bullet \qquad\qquad XIV \qquad\qquad (12)$$
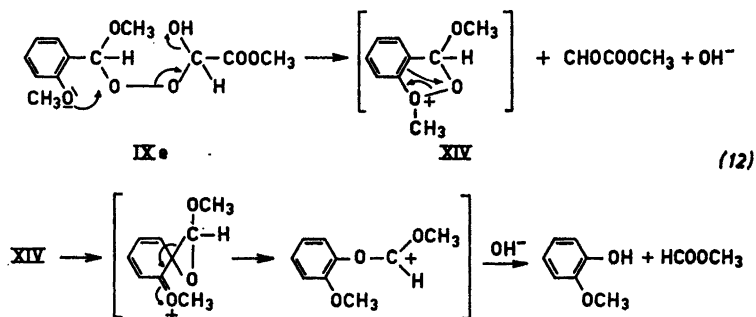
Such anchimeric assistance is known from Winstein's studies on the effect of o-methoxyphenyl substituents in β- or γ-positions in some brosylates.[10] The rate of solvolysis increased considerably compared to that of compounds with the methoxy group in *meta* or *para* positions. In those cases where migratory aptitudes of the Ar groups, and the resulting phenol yields, were low under acidic workup conditions, it was observed (Table 1) that the yield of "benzoate" ester was high. This is reasonable since reactions 7—11 could also be acid catalyzed, and three of these (7, 8, and 10) lead to aromatic esters or acids (which would be esterified under the acidic conditions).

The high yield of anisaldehyde from basic decomposition of ozonized methyl p-methoxy cinnamate could indicate that the zwitterion has been formed predominantly on the aliphatic side of the double bond (eqn. 1), since base-catalyzed decomposition of VIIIa should give methyl anisate. Other possibilities are base catalysis of reactions 9 and 11, as illustrated with eqn. 13. Yet another possibility might be that the hydroxide ions act as nucleophiles on the hydroperoxide VIIIa, giving anisaldehyde as ultimate product, as shown in eqn. 14.

$$Ar-\underset{\underset{OCH_3}{|}}{\overset{\overset{H}{|}}{C}} \cdot O-O \cdot \underset{\underset{OH}{|}}{\overset{\overset{H}{C}:B}{C}}-G \longrightarrow ArCHO + GCOOH + CH_3OH \quad (13)$$

$$IX$$

$$Ar-\underset{\underset{OH}{\overset{|}{O}}OCH_3}{\overset{\overset{COOH}{/}}{C}}-H \longrightarrow Ar-\underset{\underset{OH}{|}}{\overset{\overset{H}{/}}{C}}-OCH_3 + OOH^- \quad (14)$$

$$VIII$$

The hydrogen peroxide is then decomposed in the alkaline solution. The higher yield of p-nitrobenzoic acid (mostly formed by hydrolysis of the corresponding ester) from methyl p-nitro cinnamate could indicate that base catalyzed elimination with VIIIi (eqn. 7) competes more favourably with the above mentioned substitution (eqn. 14). This would be expected, since the acidity of the hydrogen to be removed in an elimination reaction must be higher in the p-nitro than in the p-methoxy compound. Hauser, Le Maistre and Rainsford [11] found that in the alkaline dehydrochlorination of some aldochloroimines of substituted benzaldehydes the p-nitro compound reacted 450 times faster than the p-methoxy compound. The fact that no p-MeO-phenol was produced from decomposition of the Ia reaction mixture under basic conditions must mean that reactions 7—11 (all of which can be base catalyzed as illustrated by (13) and/or (14)) occur more readily than do reactions 4—6 under alkaline conditions.

The high yield of aromatic aldehyde found by Subluskey, Harris, Maggiolo and Tumolo [12] from ozonolysis of anethole in methanol and subsequent steam distillation is interesting compared to that obtained by decomposing at room temperature without presence of water. It has been shown that 1-ethoxy-1-hydroperoxy ethane gives acetaldehyde, ethanol and hydrogen peroxide by treatment with water.[13] It is therefore possible that the hydrolysis of the ozonized solution of anethole takes place as shown in eqn. 15.

$$Ar-\underset{\underset{OCH_3}{\overset{|}{}}}{\overset{\overset{OOH}{/}}{C}}-H + H_2O \rightleftharpoons \left[Ar-\underset{\underset{\overset{|}{H}}{\overset{}{H-O}}}{\overset{\overset{OOH}{/}}{C}}-H \atop OCH_3 \right] \rightleftharpoons Ar-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-OCH_3 + H_2O_2 \quad (15)$$

$$VIII$$

At the elevated temperature the hemiacetal eliminates methanol and the resulting aldehyde is removed with steam. At lower temperatures the equilibrium is kept to the left and the decomposition of VIII gives phenols, acids, and/or esters.

It seems impossible to draw any conclusions as to whether moieties III and IV or moieties V and VI are produced predominantly during ozonolysis of the various unsymmetrical olefins (eqn. 1), because of participation of reactions 2, 3, 5, 6, 8, 9, 10, and 11. Even if V (and consequently VIII) were initially produced predominantly, rather than III, III might appear as a

major product in the final reaction mixture because of the occurrence of reactions 2, 9, and 15. Likewise, even though III might be dominant over V (and VIII) initially, high yields of phenol or aromatic carboxylic acids and esters might be in the final reaction mixture because of the occurrence of reactions 3, 6, and 10.

Thus, it appears that the following conclusions can be drawn from the work just described. Firstly, the work-up conditions employed effect greatly the extent to which the "abnormal" reaction to phenols occurs. These are produced under acidic conditions more than under neutral and not at all under basic conditions. This perhaps is true not only with the compounds studied here, but also with other types giving "abnormal"products. Secondly, the product analyses from the different work-up procedures indicate that rearrangements to the abnormal products take place at the methoxy hydroperoxide or the hydroxy peroxide (IX or X) stage rather than the initial ozonide or zwitterion stage. The stability of the latter two intermediates must be considered as infinitesimal compared to hydroperoxides or peroxides. Reduction experiments gave an active oxygen content of more than 90 % on the cold ozonation solutions and more than 70 % after the reaction mixture had come to room temperature. These results exclude rearrangement of any peroxidic precursors to the hydroperoxides or hydroxy peroxides. Thirdly, no conclusions can be drawn concerning the distribution of zwitterions IV or V (eqn. 1) and the effect of variation of the substituents upon the same.

In fact it appears that if one wants to study the distribution of zwitterions in participating solvents, the corresponding hydroperoxides have to be stable enough at room temperature to be isolated and thereby removed from the equilibra shown in eqn. (2) or (3).[14,15]

EXPERIMENTAL

General. The ozone source was a Welsbach T 23 Ozone Generator which gave a concentration of 4—6 % ozone in oxygen.

The gas liquid chromatography analyses were performed on Aerograph Autoprep A 700 equipped with a Disc Integrator on the Honeywell Recorder. The columns used were 30 % Apiezon L on HMDS-coated Chromosorb W, 8.5' × 1/4" (Ap.L.), 30 % Polyethylene glycol 20 M on HMDS-coated Chromosorb W, 8.5' × 1/4" (PEG). Standards used were the purest commercially available materials, purified by conventional methods if necessary.

The cinnamic acids were prepared from the corresponding benzaldehydes by the Knoevenagel reaction and were esterified with methanol and concentrated sulphuric acid. Yields were good. *p*-Methoxy propenyl benzene was commercially available. Ozonolyses solvents were pure and anhydrous.

Ozonolyses. All ozonolysis solutions, except those of methyl *p*-nitro cinnamate and *p*-methoxy cinnamic acid, contained 10 mmoles of compound dissolved in 40 ml of methylene chloride and 35 ml of methanol. For solubility reasons 10 mmoles of methyl *p*-nitro cinnamate was dissolved in 150 ml of methylene chloride and 50 ml of methanol, while 10 mmoles of *p*-methoxy cinnamic acid was dissolved in 80 ml of methylene chloride and 70 ml of methanol. The temperature was maintained at −78°C (dry ice/acetone) during the ozonolyses. In all cases 10 mmoles of ozone was quantitatively absorbed. The solutions were swept with nitrogen for 10 min before work-up.

Acidic decomposition. After the ozonolysis solutions had been brought up to room temperature perchloric acid (3.5 ml, 70 %) was added and the solutions were evaporated to a volume of about 30 ml and left at room temperature until a test for active oxygen

(sodium iodide in acetonitrile) was negative. The time for this decomposition varied from 3—5 h for the *ortho*- and *para*-methoxylated compounds up to several days for the methyl *p*-nitro cinnamate. (Refluxing temperatures greatly speeded up the decompositions, but was not used in the runs of Table 1). Solid sodium bicarbonate was then added and the rest of the solvents evaporated. The residue was dissolved in water and carefully extracted with ether. From the aqueous layer any substituted benzoic acids were obtained by acidification. The filtrates from these precipitations were made alkaline and heated for 3—4 h and oxalic acid was determined as its calcium salt. The ethereal extracts were dried, evaporated, and examined in acetone solutions by gas liquid chromatography. Results are summarized in Table 1.

Neutral decomposition. The ozonolysis solutions were left at room temperature until tests for active oxygen (sodium iodide in acetonitrile containing a few drops of perchloric acid) were negative. This decomposition took several days. (Here, too, elevated temperatures allowed a shorter decomposition time, but was not used in the runs of Table 1). The solvents were evaporated and the residue dissolved in ether and extracted with saturated sodium bicarbonate solutions. The products were estimated as under acidic decomposition. For the results, see Table 1.

Alkaline decomposition. After the solution had come up to room temperature, potassium hydroxide (20 mmoles) in methanol was added (turbidity). After about 45 min the solution gave a negative active oxygen test. Concentrated hydrochloric acid was added, after which solid sodium bicarbonate was added and the solution evaporated almost to dryness. Water was added and the solution was extracted with ether. Estimation of products was as for acidic decomposition. Results are shown in Table 1.

Analyses of products from ozonolyses of methyl p-nitrocinnamate. The neutral products from ozonolyses of this ester could not be determined by GLC (low volatility), but it was found from infrared spectra that only methyl *p*-nitrobenzoate and *p*-nitrobenzaldehyde was present. The mixture was dissolved in methanol and an aqueous solution of potassium hydroxide was added. After one hour the solution was worked up as described under basic decomposition. A test run with pure samples of ester and aldehyde gave a recovery of 96.5 % *p*-nitrobenzoic acid (from the ester) and 94.2 % of *p*-nitrobenzaldehyde. No *p*-nitrobenzylalcohol was detected.

Reactions between ozonized dimethyl fumarate solutions and benzaldehydes. Dimethyl fumarate (10 mmoles) was dissolved in methanol (100 ml) and ozonized at —20°C. The ozone stream was cut off just short of one mole equivalent to avoid over-ozonation. Nitrogen was passed through the solution and, while the solution still was cold, freshly distilled benzaldehyde (10 mmoles) together with a few crystals of hydroquinone was added. When no more active oxygen was present, the solution was subjected to gas liquid chromatographic analysis, which showed that considerable amounts of methyl benzoate were formed. In another experiment anisaldehyde was added instead of benzaldehyde and the solution was analyzed on GLC before the solution had been warmed. A small peak for methyl anisate appeared; the amount increased as the solution warmed up.

Reductions. Methyl *p*-methoxy-cinnamate was ozonized at —78°C in a methanol/methylene chloride solution. After purging with nitrogen for 10 min, an aliquot was taken out while still cold and analyzed for active oxygen (with sodium iodide in acetonitrile/acetic acid). Found: 0.92 mole equivalent of active oxygen. The solution was then warmed to room temperature, and the active oxygen content was again determined. Found: 0.72 mole equivalent. An aliquot was then taken out and evaporated. Active oxygen analysis gave only 0.38 mole equivalent of theoretical amount.

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