Ozonation of Allenic Hydrocarbons

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1,2-Butadiene, 3-methyl-1,2-butadiene, 4-methyl-2,3-pentadiene, 2,4-dimethyl-2,3-pentadiene, and 1,2-cyclononadiene were ozonized in methanol or methylene chloride at −78°C. The main products were carbonyl compounds (and in methanol their acetals or ketals) and carbon monoxide. Carbon dioxide was not detected at all. From the acyclic allenes acetic acid and traces of formic acid were found. It is suggested that the acids are formed from reaction of ozone with the corresponding conjugated dienes formed through rearrangement of allenes catalyzed by ozone. Some unidentified peroxidic compounds were also present.

The ozonation of allenes has not received the same attention as ozonation of olefines and to some degree acetylenes. One reason is probably the availability of allenes. However, the reaction of 1,1-dibromocyclopropanes with alkyllithium has provided an easy route to allenes.[1]

Reactions between ozone and allenes have mostly been carried out to establish the position of unsaturation in the molecules and therefore in most cases ozone has been used in large excess and thus obscured the study of the reaction proper.[1,2] Hartzler[3] ozonized 1-(2-methyl-propenylidene)-2-phenyl-cyclopropane (I) in ethanol and found that approximately one mole of ozone reacted per mole allene, giving beside acetone ethyl 1-hydroxy-2-phenyl-cyclopropanecarboxylate (IV). He suggested that IV was formed through rearrangement of the ethoxy hydroperoxide III from the reaction of ethanol with the Criegee zwitterion II.
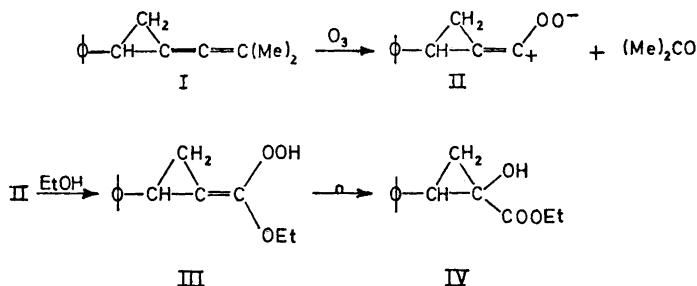
Table 1.[a]

	CO CH_3OH	CO CH_2Cl_2	$(CH_3)_2CO$ CH_3OH	$(CH_3)_2CO$ CH_2Cl_2	$(CH_3)_2C(OCH_3)_2$ CH_3OH	$(CH_3)_2C(OCH_3)_2$ CH_2Cl_2	Peroxidic functions CH_3OH	Peroxidic functions CH_2Cl_2	CH_3CHO CH_3OH	CH_3CHO CH_2Cl_2	$CH_3CH(OCH_3)_2$ CH_3OH	$CH_3CH(OCH_3)_2$ CH_2Cl_2	Acids[b] CH_3OH	Acids[b] CH_2Cl_2	Remarks
Me₂C=C=CMe₂	6.6	7.5	7.2	16.2	8.8	—	1.8	1.7	—	—	—	—	1.8[c]	0.8[d]	Formaldehyde present in both solvents
Me₂C=C=CHMe	4.6	5.0	2.6	7.3	4.7	—	2.5	2.9	0	5.8	5.3	0	1.1	1.2	*
MeHC=C=CHMe	5.3	5.7	3.7	8.0	5.7	—	1.2	1.6	—	—	—	—	0.4	0.3	*
MeHC=C=CH₂	6.2	N.c.[e]	—	—	—	—	1.8	N.c.[e]	8.5	N.c.[e]	0	N.c.[e]	0.2	N.c.[e]	*

[a] Figures given in mmoles (10 mmoles starting material ozonized).
[b] Acetic acid and traces of formic acid.
[c] After adding excess base and backtitrating, 2.5 mmole acid were found.
[d] After standing with water for six months, 2.8 mmole acid were found.
[e] Not checked.

In contrast to Hartzler, who only found traces of carbon dioxide, Smith et al.[4] ozonized three terminal allenes with some excess of ozone and found as much as 55 mole % of carbon dioxide. In addition they found acetaldehyde as one of the major products and described this as a result of the reaction of ozone with the 2-alkyne formed through isomerization of the terminal allenes. It might be noted that to the present authors' knowledge this is the first and only case where aldehydes have been found as products from ozonation of acetylenes. Bone[5] ozonized propadiene, 3-methyl-1,2-butadiene and 4-methyl-2,3-pentadiene (using large excess of ozone) and also found that carbon dioxide was formed together with the proper carbonyl compounds. These findings have led Taylor[6] to conclude ". . . the detection of carbon dioxide serves as a simple diagnostic test for the presence of an allene or similar cumulene compound".

In order to try to clear up the apparent controversy about the reaction between ozone and allenes, a series of allenes substituted with methyl groups and one cyclic allene, 1,2-cyclononadiene, were subjected to ozonolysis. Methanol or methylene chloride were used as solvents and the ozonolyses were carried out at low temperature to avoid possible side reactions.

The absorption of one mole equivalent of ozone was quantitative for all allenes; however, for 1,2-cyclononadiene a lower ozone concentration (25 mmole ozone per hour versus 45 mmole for the others) had to be used to ensure a quantitative absorption. After passing in more ozone the solution became bluish and iodine was formed in the potassium iodide trap. Gas chromatography showed that all starting material had reacted after absorption of one mole equivalent of ozone.

A survey of the analytical results from the ozonolyses is shown in Tables 1 and 2. Carbon dioxide was not detected at all. Carbon monoxide was found

Table 2.[a]

	CO		$(CH_3O)_2CH(CH_2)_6CH(OCH_3)_2$		Peroxidic functions	
	CH_3OH	CH_2Cl_2	CH_3OH	CH_2Cl_2	CH_3OH	CH_2Cl_2
1,2-Cyclo-nonadiene	6.8	5.9	7.1	7.2[b]	2.5	2.8

[a] Figures given in mmoles (10 mmoles starting material ozonized).
[b] Octandial-1,8 was present at the end of the ozonation, but conveniently estimated as its tetramethylacetal, to which it is readily transformed.

as a major component in the exit gases from all allenes. It was shown to be formed spontaneously after starting the ozone absorption. The yields did not increase after letting the ozonized solutions come to room temperature. Furthermore, the expected carbonyl compounds (or their ketals or acetals from ozonation in methanol) constituted the main products. Acetic acid and traces

of formic acid were found as products and the ketals and acetals are thought
to be secondary products whose formation is catalyzed by these acids.

The following discussion on mechanisms will be based mainly on the ozonol-
ysis of 2,4-dimethyl-2,3-pentadiene (tetramethylallene-TMA) since this
compound was most thoroughly studied.

Waters and Kiefer [7] have shown by methoxymercuration that the point
of electrophilic attack on allenes depends very much upon the degree of alkyla-
tion. For instance, in allene the central atom is mercurated less than 5 %,
while in tetramethylallene 90 % of the molecules are mercurated at the central
atom. It is therefore safe to conclude that the central sp-hybridized carbon-
atom in TMA is the most nucleophilic one. Furthermore, addition is also
considered to take place at the more substituted double bond. If we omit
any possible intermediate step for ozonation of tetramethylallene, a primary
ozonide (V) is thought to be formed:
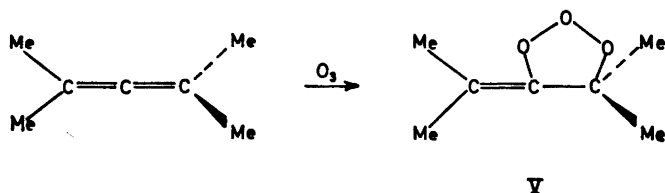
If the primary ozonide is considered to decompose in a conventional
Criegee manner, two pathways (a and b) are possible, leading to zwitterions
VI and VII
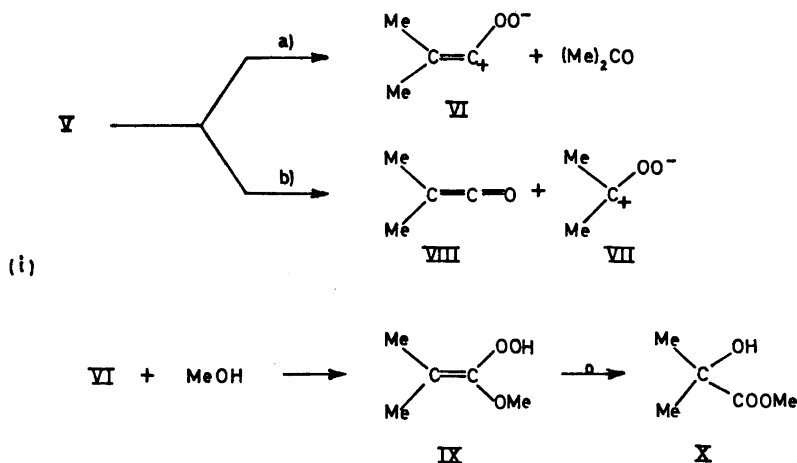
According to Hartzler methyl α-hydroxyisobutyrate (X) should be formed
from IX, provided his mechanism is correct. Only traces of X were detected

in our experiments. If the cleavage of the primary ozonide V follows pathway b), the subsequent reactions with methanol would lead to methyl isobutyrate and 2-methoxy-2-hydroperoxy-propane, respectively. Methyl isobutyrate was shown not to be present at all. An authentic sample of 2-methoxy-2-hydro-peroxy-propane (made by ozonation of tetramethylethylene in methanol) [8] was shown to decompose in the gas chromatograph to acetone and methyl acetate, and as methyl acetate was shown not to be a product from the ozonation solution under similar decomposing conditions, pathway b) must be excluded.

A third reaction path must be considered especially since it has some similarity to the proposed mechanism for the reaction between ozone and acetylenes [9].
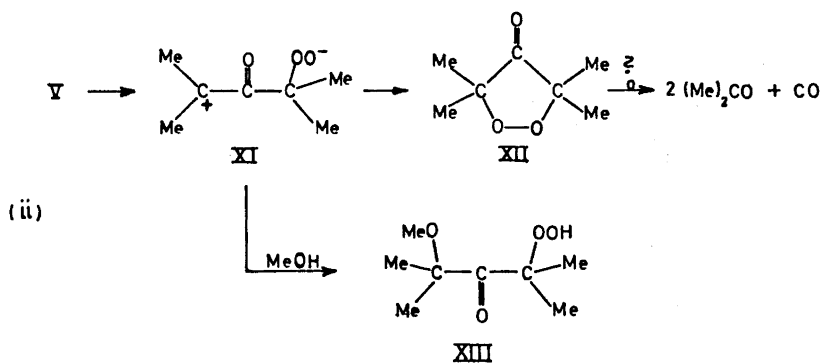

However, it is difficult to understand that a peroxide like XII should decompose spontaneously to acetone and carbon monoxide at $-80°C$ in solution. Furthermore, from the experiences with ozonation of acetylenes in inert and protic solvents, one would normally expect a zwitterion like XI to react with methanol to form XIII, thus giving different results from methylene chloride and methanol.

Since the product analyses gave only a little more than 2 mole equiv. acetone (in methanol the sum of acetone and its methyl ketal) per mole equivalent carbon monoxide in both methylene chloride and methanol it is proposed that the main reaction is common in both solvents:
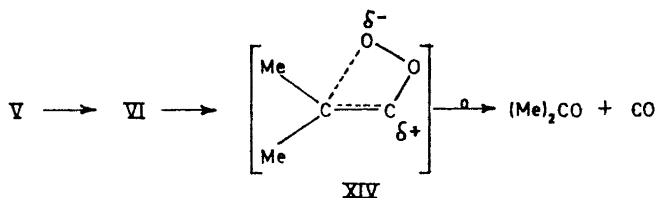
The excess acetone may be explained by accepting that part of the starting material reacts according to (ii) forming peroxide XII or hydroperoxide XIII (in methylene chloride or methanol, respectively) which under the pyrolytic conditions used in the gas chromatographic analyses would give acetone. This assumption is strengthened by the fact that if the ozonized solution is reduced with triphenylphosphine prior to analysis, the yield of acetone is decreased. This decrease is comparable to the content of active oxygen after ozonolysis.

None of the reaction paths proposed so far, do explain the presence of acetic acid from tetra- and dimethylallene, traces of formic acid and formaldehyde from tri- and tetramethylallene. These products must involve a rupture of a carbon-carbon single bond or a rearrangement of the allene prior to the reaction with ozone. The first possibility does not seem very likely since the starting materials are hydrocarbons; such abnormal ozonolyses normally require a heteroatom in β-position to the double bond.[10] Rearrangement of 2,3-dienes to the more thermodynamic stable 2-alkynes or 2,4-dienes seems more feasible here. However, in the case of tetramethylallene rearrangement to the 2-alkyne would imply a migration of a methyl group, while formation of the conjugated diene involves only a proton shift. Such a shift is normally base-catalyzed, but a recent paper by Taylor and Wright[11] describes the isomerisation of tetramethylallene to 2,4-dimethyl-1,3-pentadiene in the presence of olefins with strongly electronegative substituents. The weakening of a C−H bond was suggested to take place through a π-complex like XV, the olefinic double bond being electrophilic due to the electronegative substituents.
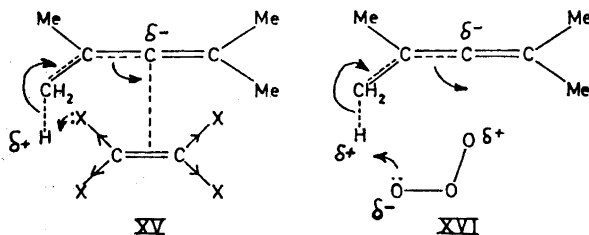
The ozone molecule may here play the same role as the olefin, causing isomerisation through intermediate XVI. The tetramethylallene was shown by gas chromatography to be free from isomers. Ozonation of pure 2,4-dimethyl-1,3-pentadiene with one mole equivalent ozone gave about 5 % acetic acid presumably through anomalous reactions. This is less than found from the tetramethylallene experiments, but it must be remembered that the most likely point of attack of ozone on the conjugated diene will be at the most alkylated double bond while acetic acid probably is formed through attack on the terminal double bond:
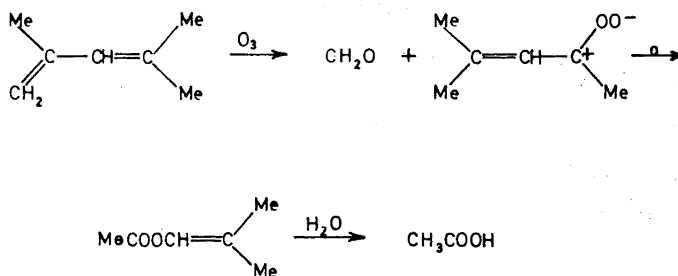
The observed decrease in acid yields with decreasing substitution of the allenes strengthens the above assumption, and the presence of formaldehyde is also explained by this scheme.

Carbon monoxide was not a product from ozonation of 2,4-dimethyl-1,3-pentadiene. It must therefore be concluded that carbon monoxide is a product of ozonation of allenes.

EXPERIMENTAL

General. The ozone source was a Welsbach T 23 Ozone Generator.

1,2-Butadiene and 3-methyl-1,2-butadiene were obtained from Chemical Samples Co., Columbus, Ohio, and 2,4-dimethyl-2,3-pentadiene from Aldrich Chem. Co. 4-Methyl-2,3-pentadiene and 1,2-cyclonoadiene were prepared through reaction of methyllithium with the 1,1-dibromocyclopropanes derived from 2-methyl-2-butene and cyclooctene, respectively.[1]

The solvents used were pure and anhydrous.

Gaschromatographic analyses. The apparatus used was a Varian Aerograph model 202 with thermal conductivity detector and with a Disc integrator on the recorder system. These columns were used: Porapak T-50/80 mesh (A), Porapak Q-50/80 mesh (B), 20 % SE-30 on Chromosorb HMDS-60/80 mesh (C), and 10 % polyethylene glycol 1000 on Chromosorb HMDS-60/80 mesh (D).

Ozonolysis. 10 millimoles of the allenes were normally dissolved in 50 ml of methanol or methylene chloride and ozonized at $-78°C$ (acetone/dry ice). The absorption of 10 mmoles of ozone was quantitative, and gaschromatographic analyses showed that essentially all the starting materials had reacted.

Analyses. (Results see Tables 1 and 2).

Carbon monoxide was estimated through its ability to reduce iodine pentoxide to iodine and carbon dioxide. The apparatus was set up in a conventional manner, and both iodine and carbon dioxide was determined.

Acetone was estimated directly on the ozonation mixture and after adding triphenylphosphine. When ozonizing in methanol column B was used at 150°C, and when using methylene chloride column D at 50°C was used.

Acetone dimethyl ketal was estimated using column B a 150°C.

Acetaldehyde and *acetaldehyde dimethyl acetal* was estimated using column D at 50°C.

Acids were estimated by titration of the cold ozonation solutions. Positive identifications were done by evaporating the titrated solutions, washing the residue with ether and running the PMR spectra of the salts. The salts were also dissolved in N/10 hydrochloric acid and the acids gaschromatographically identified on column A at 185°C. Only acetic acid and traces of formic acid were found by this procedure.

Octandial-1,8 and *octandial-1,8-tetramethylacetal* was estimated gaschromatographically with column D at 150°C.

Peroxide contents were determined in a conventional way with sodium iodide in glacial acetic acid.

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