The Role of Pyridine in the Ozonolysis of Olefins: Evidence Against the Pyridine Oxide Route

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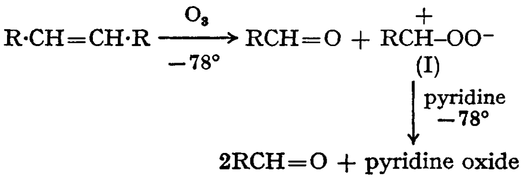
IT has been reported that pyridine, which itself is rather stable towards ozone,[1,2] can alter the course of the ozonlysis of olefins such that the corresponding carbonyl compounds (aldehydes[3] or ketones[4]) rather than ozonides or peroxides are the predominant reaction products. The specific action of pyridine in such reactions was ascribed to a spontaneous reduction of the intermediate zwitterion (I) by pyridine at the low temperatures of the ozonolysis reaction:[3]



$$\mathrm{R{\cdot}CH{=}CH{\cdot}R} \xrightarrow[-78^\circ]{O_3} \mathrm{RCH{=}O} + \overset{+}{\mathrm{RCH}}\mathrm{{-}OO^-}\ \text{(I)} \xrightarrow[-78^\circ]{\text{pyridine}} 2\mathrm{RCH{=}O} + \text{pyridine oxide}$$

However, on no occasion could pyridine oxide be isolated in the quantities required by this reaction scheme. This discrepancy was ascribed to a subsequent reaction between pyridine oxide and aldehyde to form acid and pyridine during the ensuing warm-up period.[5]

It is apparent that the ozonolysis of a tetrasubstituted olefin would not impart this problem and should, therefore, allow pyridine oxide to survive the experiment. In line with this reasoning we have ozonized tetramethylethylene in the presence of an equimolar amount of pyridine and monitored the reaction by n.m.r. spectroscopy.

The reactions were carried out at 0° in 1,2-dichloroethane and at -78° in methylene chloride as the respective solvents in the presence of equimolar amounts (based on the reactants) of 1,1,2,2-tetrachloroethane as an internal standard for the quantitative evaluation of the n.m.r. spectra. The n.m.r. spectra were recorded immediately after the samples were withdrawn and at approximately the same temperatures at which the reactions were carried out. The originally colourless reaction mixtures turned yellow seconds after the beginning of the ozone treatment and remained homogeneous until most of the olefin ($>80\%$) had disappeared.[6]

At no time during the reaction could we find positive evidence for the presence of pyridine oxide[7] which, according to the previously postulated mechanism, should have appeared roughly at the same rate at which the olefin disappeared. Instead, most of the pyridine (approx. 90%) remained unchanged during the double-bond cleavage reaction (Table). These data were corroborated by the observation that the total amount of acetone present at any given time corresponded only to approximately one, rather than both, moieties of the original olefin (Table) and that the solution was peroxidic.

TABLE

Ozonolysis of tetramethylethylene in the presence of pridine at 0°c

Olefin Conversion, %[a]	Mole % pyridine Expected[c]	Observed[a,b]	Mole % acetone Expected[c]	Observed
0	100	100	0	0
33	67	91	66	30·5
67	33	88	134	62·0

[a] Based on n.m.r. analysis; 1,1,2,2-tetrachloroethane as internal standard.
[b] Based on the intensity of the signals of the two α-protons.
[c] Expected if the following reaction sequence took place:

$$Me_2C{=}CMe_2 + O_3 + \text{pyridine} \rightarrow 2Me_2CO + \text{pyridine oxide.}$$

These observations demonstrate that the postulated role of pyridine as an oxygen acceptor or zwitterion-reducing agent does not represent a general type of reaction and certainly does not apply to the ozonolysis of a tetrasubstituted olefin such as tetramethylethylene. This result, coupled with the fact that reactions between pyridine oxide and simple aldehydes have been consistently negated,[8,9] made it questionable whether pyridine exerts the postulated role even in the ozonolysis of olefins that lead to aldehydic (*i.e.*, aldehyde and aldehyde-zwitterion) intermediates. For, as a consequence of the reported inertness of pyridine oxide towards aldehydes such reactions should again lead to a build-up of pyridine oxide as the reaction progresses. Preliminary experiments with a number of 1,2-disubstituted olefins did not, however, lead to the detection of pyridine oxide in any case. On the other hand it was shown that pyridine oxide which was deliberately added to the reaction mixtures survived the conditions of the ozonolysis.

These results call for a new explanation of the course of the pyridine-modified ozonolysis of olefins.

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[5] Seemingly in agreement with this explanation, good yields of aldehydes could only be obtained if the reaction mixture was reduced immediately after and at the low temperatures of the ozonolysis reaction.
[6] Considerable amounts of a dark coloured solid of a yet unknown structure precipitated during the later stages of the 0° reactions or on warm-up of the −78° reactions.
[7] Independent experiments with synthetic blends of pyridine and pyridine oxide in the same solvent system and at comparable concentrations showed that pyridine oxide can be unequivocally identified at concentrations as low as 10%. This identification is based on the different chemical shifts of the α-protons in pyridine oxide (centred at 8·18 p.p.m.) and pyridine (centred at 8·50 p.p.m.).
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