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Glyoxylic Acid as Reductant in Ozonolysis. I

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The use of glyoxylic acid as a reducing agent in ozonolyses in protic solvents has been studied. When ketones are formed during the ozonolysis and subsequent reduction, the reaction is completed using equimolar amounts of glyoxylic acid. Whenever aldehydes are formed, excess of glyoxylic acid has to be used, probably due to autoxidation of the aldehydes. The presence of acid is a necessity and acetic acid is the solvent of choice.

Reduction of ozonolysis mixtures has been accomplished with a number of agents.[1] A common feature for most of them is that they leave their oxidation products as nonvolatile compounds in the mixture. The only exception to this is catalytic hydrogenation. However, if the ozonation is performed at low temperature, it is difficult to carry out the hydrogenation without increasing the temperature.

Glyoxylic acid is oxidized by hydrogen peroxide to formic acid and carbon dioxide.[2] It was therefore of interest whether the hydroperoxides formed by ozonolysis in protic solvents could oxidize glyoxylic acid to volatile products exclusively. A few disubstituted and one tetrasubstituted olefin were selected to test this reaction.

trans-Stilbene was ozonized in a mixture of acetic acid and methylene chloride. After addition of equimolar amounts of glyoxylic acid dissolved in glacial acetic acid, the decrease in active oxygen was followed iodometrically. (Fig. 1).

trans-4-Octene was ozonized in glacial acetic acid and subsequently one half, one, and two mol equivalents of glyoxylic acid, respectively, were added. (Fig. 2). Satisfactory reduction took place only when an excess of glyoxylic acid was used. The increase in the active oxygen content in the decomposition experiment, and when using semi- and equimolar proportions of glyoxylic

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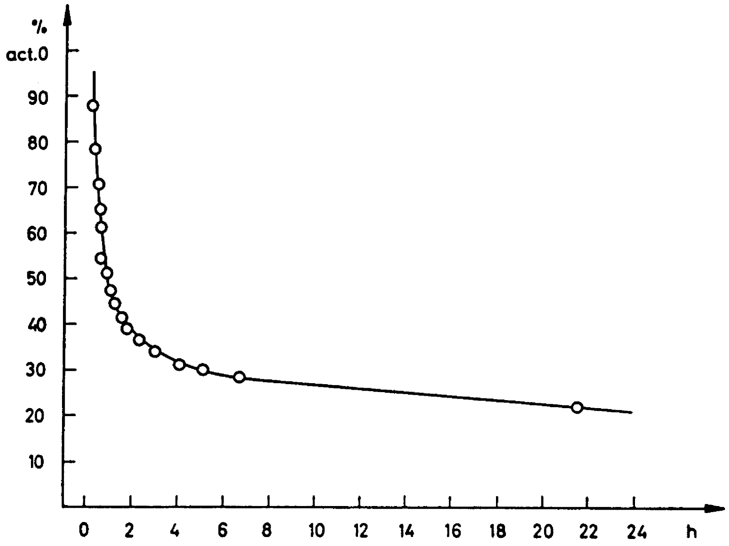

Fig. 1. Reduction of ozonized stilbene with one molar equivalent of glyoxylic acid monohydrate.

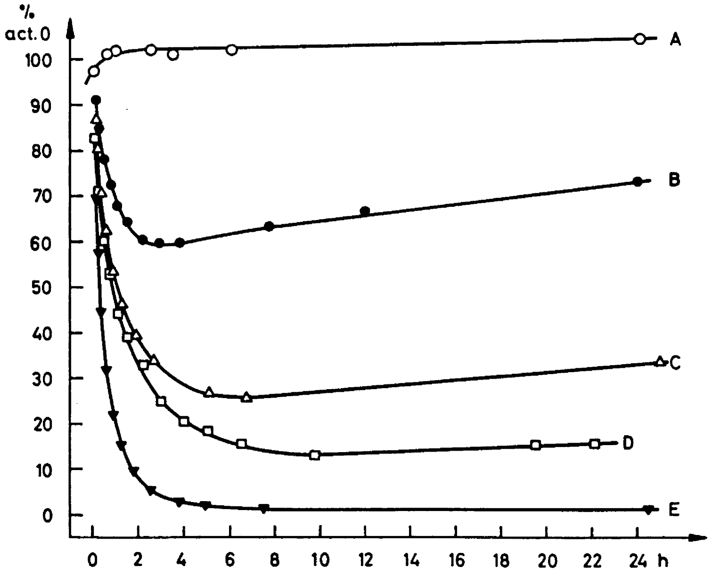

Fig. 2. Decomposition and reduction of ozonized *trans*-4-octene. A. decomposition in glacial acetic acid. B. Reduction with semimolar equivalent of glyoxylic acid monohydrate. C. Reduction with molar equivalent of glyoxylic acid monohydrate. D. As in C, but in a nitrogen atmosphere. E. Reduction with 2 mol equivalents of glyoxylic acid monohydrate.

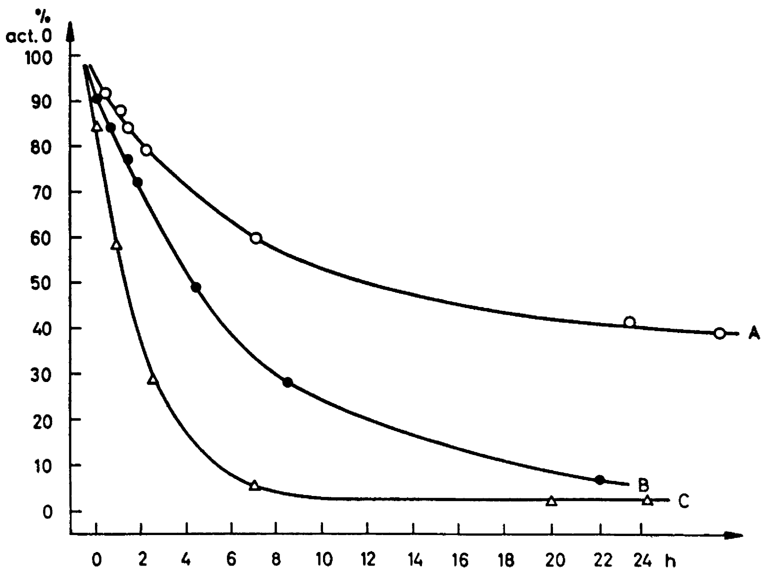

Fig. 3. Reduction of ozonized 2,3-dimethyl-2-butene with glyoxylic acid monohydrate. A. Semimolar equivalent. B. Molar equivalent. C. 2 mol equivalents.

acid, is probably due to autoxidation of the butyraldehyde formed in the ozonolysis. In fact, benzaldehyde and butyraldehyde were both shown to undergo autoxidation (probably to peracids)[3] under the prevailing conditions. Carrying out the reduction in a nitrogen atmosphere a more "normal" reduction took place. When ozonizing 2,3-dimethyl-2-butene where the reduction product is acetone, autoxidation is avoided. Reduction with semimolar proportions of glyoxylic acid goes halfway and with equimolar proportions goes approximately to completion. (Fig. 3).

The reduction of the ozonized solution of anethole (1-(4-methoxyphenyl)-1-propene) in glacial acetic acid followed the same general pattern (Fig. 4). More than one mol equivalent glyoxylic acid had to be used to ensure an approximately complete reduction in a reasonable time. Since it was shown that autoxidation of benzaldehyde or acetaldehyde did not take place in methanol, ozonolysis was carried out in this solvent. However, no reduction with glyoxylic acid was achieved, even in the presence of small amounts of trifluoroacetic acid. If, after ozonolysis in methanol, acetic acid was added in excess, reduction took place, but at a much lower rate. According to the proposed mechanism[4] protonation of glyoxylic acid (or its monohydrate) is involved. The presence of the much stronger base methanol will therefore slow down the reaction drastically.

It has been reported[5] that pyruvic acid is oxidized twelve times faster by hydrogen peroxide than glyoxylic acid. However, reduction of an ozonized acetic acid solution of anethole using two mol equivalents of pyruvic acid was

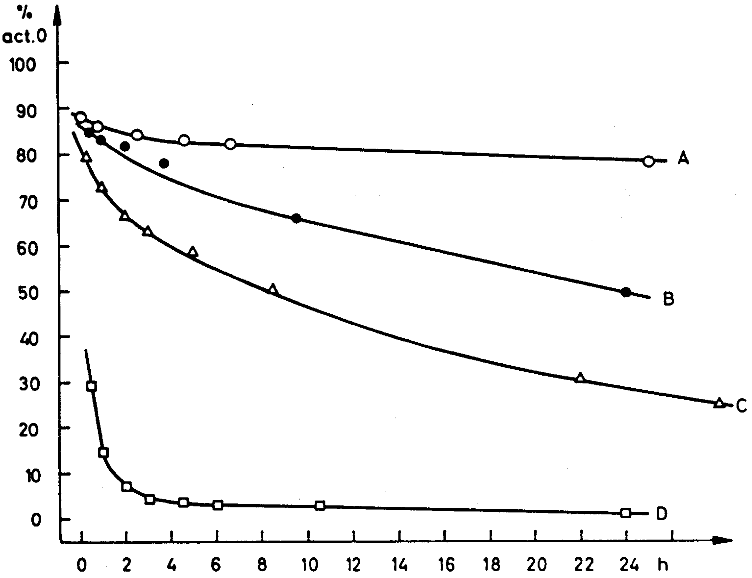

Fig. 4. Decomposition and reduction of ozonized anethole. A. Decomposition in glacial acetic acid. B. Reduction with 2 mol equivalents of glyoxylic acid monohydrate in methanol/acetic acid (3:7). C. Reduction with 2 mol equivalents of pyruvic acid. D. Reduction with 2 mol equivalents of glyoxylic acid monohydrate in acetic acid.

much slower than with glyoxylic acid (Fig. 4). This may be due to steric effects in the supposed rate-determining step, *viz.* the reaction between the protonated α-keto acid and the hydroperoxide formed during the ozonolysis.[4]

The yields of reduction products by using glyoxylic acid (or its monohydrate) are shown in Table 1.

Table 1.

Compound ozonized	Reduction product	Yields, %
2,3-Dimethyl-2-butene	Acetone	98 [a]
Anethole	Anisaldehyde	84 [a]
4,4′-Dimethoxystilbene	Anisaldehyde	90 [b]

[a] Estimation by GLC. [b] Estimation by weighing the residue after washing with aqueous sodium bicarbonate. Purity 97–98 % (GLC).

Reduction of peroxidic products normally formed in ozonation in nonprotic solvents (ozonides, dimeric peroxides) with glyoxylic acid was not feasible.

EXPERIMENTAL PART

General. The ozone source was a Welsbach T 23 ozone generator which gave a concentration of 4 – 6 % ozone in oxygen.

Reduction procedure. After the ozonolysis solution was purged for 3 min with nitrogen at 25°C, it was transferred to a volumetric flask, the reducing agent was added, the solution diluted to correct volume and the flask kept at 25 ± 0.1°C. Aliquots (5 ml) were taken out and deoxygenated by adding small pieces of solid carbon dioxide. Sodium iodide in acetonitrile (5 ml of a 10 % solution) was added and the reduction vessel stoppered tightly and left in the dark for 1 h before being titrated with 0.01 N sodium thiosulphate (after dilution with large volumes of ice-water). Blanks were determined.

Gas liquid chromatography. Acetone was estimated using a Varian Aerograph Model 200 (Thermal Conductivity Detector) with a Polyethylene glycol 1000 on Chromosorb WHMDS (60/80 mesh) column. Anisaldehyde was estimated using a Varian Aerograph Model 1520 (Flame Ionisation Detector) with an Apiezon L (20 %) on Chromosorb WHMDS (60/80 mesh) column.

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