An attempt to remove the acid adduct by dissolving the impure vinyl ester in absolute ethanol and eluting through a Dowex 1 column in the OH form resulted in alcoholysis of the vinyl ester to the ethyl ester, as shown by IR (Fig. 1 *E*). The vinyl peaks at 6.05, 10.55 and 11.50 μ and the carboxyl peak at 5.81 μ have been completely eliminated, and the ester peak has been shifted from 5.66 μ to 5.72 μ. These changes were interpreted as indicating that the acid had been removed, but that the vinyl ester had been completely converted to the ethyl ester.

The use of an activated alumina column for removing acid also presented a slight problem. Elution of the crude vinyl ester adduct through the alumina column with petroleum ether resulted in a substantial loss of product as well as the unsuccessful removal of acids. Washings with diethyl ether, acetone and ethanol did not remove the product from the column. However, when diethyl ether was used as the initial eluant, the alumina column proved to be the best means of purification.

ACKNOWLEDGMENTS

Infrared spectra by S. H. Miles; ultraviolet spectral data by R. A. Pittman; and microanalyses by L. E. Brown of the Southern Regional Laboratory.

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[Received August 10, 1965—Accepted October 14, 1965]

Reduction of Methyl Oleate Ozonolysis Products to Aldehydes with Activated Zinc

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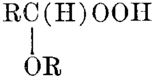
Abstract

Reduction of methyl oleate ozonolysis products with active zinc in the absence of acid or water gave an 88% yield of methyl azelaaldehydate. Under these neutral conditions, side reactions such as acetalization and aldehyde condensations could be more conveniently avoided than when zinc-acetic acid reduction is used. The activated zinc was prepared by treatment with acetic acid followed by washing to remove the acid.

Introduction

WE HAVE PREVIOUSLY described the ozonolysis of methyl oleate in participating, hydroxylic solvents to give mixtures of alkoxy hydroperoxides, $\mathrm{R}\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{C}}\mathrm{(H)OOH}$, and carbonyl compounds, RC(H)O (7). Reduction of the alkoxy hydroperoxides was accomplished by either zinc and acetic acid or catalytic hydrogenation. The latter procedure gave lower yields unless a poisoned palladium catalyst was used or a mixture of alcohol and carboxylic acid was present during reduction (6,8,9). Following either the chemical or catalytic methods of reduction, carboxylic acids that are present must be removed by elaborate washing with water or aqueous alkali lest the acid catalyze condensation or acetalization of the carbonyl compounds during distillation. We have found that an activated zinc can be used to reduce the ozonolysis products in good yield in an essentially neutral solution.



In examining the literature reporting the use of zinc dust and water for reductive ozonolysis (1,4,5), we found that usually some acid was present and ozonolysis had been performed in a nonparticipating solvent. We could find no comparative data for the reduction of methoxy hydroperoxides with zinc dust and water. We therefore undertook this reduction but in a participating solvent as well as a comparison of active zince reduction with that by zinc and acetic acid.

Experimental

Methods of Analysis

A Model 500 F & M temperature programmed chromatograph was used for analyses by gas-liquid chromatography (GLC). Details of both this method and the wet method of analysis have been previously described (9).

Ozonization

The general procedure for ozonization in methanol has been reported earlier (7,8). A standard ozonolysis solution was prepared and stored under nitrogen at 0C (9); aliquots were withdrawn and weighed as required.

Zinc Activation

Zinc powder or 30-mesh, granular zinc (42 g) was stirred vigorously with glacial acetic acid (100 ml) for 1 hr under a nitrogen atmosphere. Little, if any, hydrogen evolution could be detected. Filtration of the product was carried out so as to minimize air contact. The filter cake was washed quickly 3 or 4 times with 25–50 ml portions of methylene chloride but was left moist with solvent. The final wash indicated a pH of 6 or more with indicator paper. A rubber dam was then used to press the filter cake dry. If stored under nitrogen, the activated zinc could be kept for about 24–48 hr after which the activity became negligible.

Batch Reduction with Activated Zinc

An aliquot of standard ozonolysis solution (147.4 g, corresponding to 39.3 g of pure methyl oleate in

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[1] No. Utiliz. Res. and Dev. Div., ARS, USDA.

methanol) was added slowly via a dropping funnel to the active zinc in a filter tube with nitrogen bubbling slowly up through the medium-porosity fritted disk. The reaction was immediately exothermic and caused the mixture to reflux vigorously for about 1 hr. A milky-white, colloidal suspension that could not be filtered readily formed slowly. After the liquid portion was decanted from the residual zinc, the residue was stirred with ether and the ether was decanted. Extraction was repeated several times. The combined, milky-white ether dispersion was filtered by using Celite filter-aid. The still cloudy filtrate was diluted with 100 ml of ether in a separatory funnel and then washed with 200 ml of 5% ammonium chloride. An inorganic precipitate settled in the bottom aqueous layer. The aqueous mixture was filtered through a medium-porosity Buchner funnel, and the collected solid was washed with a little ether, which was then combined with the previous extract. The combined extracts were washed with 100 ml of saturated sodium chloride. The aqueous portions were combined and extracted twice with 50-ml portions of methylene chloride. The two organic extracts were dried, filtered and evaporated at room temperature and reduced pressure. No salts crystallized from either of the clear liquid residues, which were combined and analyzed (Table I).

Column Reduction with Activated Zinc

Reduction was achieved on a smaller scale with a column of active zinc. Granular zinc mixed with strands of glass wool was placed in a 7 in. x ¾ in. glass column and activated with glacial acetic acid for several hours. The active zinc was then rinsed with a minimum volume of dry methanol sufficient to remove the acid. An ozonolysis product solution (21.25 g of a 25.30% solution of methyl oleate ozonized in methanol) was then added dropwise under nitrogen over a period of 1 hr or more. The column was washed three times with 10-ml portions of methanol. The last wash contained no carbonyl compounds as indicated by a test with 2,4-dinitrophenylhydrazine reagent.

The eluate gave a weakly positive test for peroxide and therefore was recycled through the column to get a negative test. Usually at least one recycle was necessary. The reduced solution was diluted with methylene chloride and then washed with water to remove the soluble zinc salts. After separation of the clear layers, an emulsified layer still remained, and this was filtered through a Buchner funnel. A small amount of a white, inorganic solid was collected on the filter paper, and this solid was washed with methylene chloride. Then the nonaqueous layers were combined, dried and carefully evaporated by means of a rotary evaporator at room temperature or below. A clear liquid residue (6.07 g, 101.8%) was obtained and was analyzed by GLC (9). This analysis for carbonyl indicated a conversion of 91 mole per cent; dimethyl azelate production was 4.6% by weight (Table 1).

Repeated use of the active zinc column led to rapid loss of activity and an impermeable mass of oxidized zinc, which required days of soaking in mineral acid before it could be removed. A hot band can be felt in the region of the column where the reduction occurs. It is desirable to keep this activity near the top of the column by regulating the flow rate.

TABLE I

A Comparison of Reduction Systems

Reduction system	DMA production,[a] weight %	Carbonyl yield,[b] mole %
Zn, HOAc	3.6	92
Active Zn	4.9	88.1
Zn, H_2O [c]	9.9	62.5

[a] By GLC (9): calculated as per cent of the total C_9 fractions methyl azelaaldehydate + methyl azelaaldehydate dimethyl acetal + dimethyl azelate.

[b] By wet analysis (hydroxylamine hydrochloride method) (9).

[c] This system requires external heating for completion of reduction.

Reduction with Zinc and Water

To 50 ml of methanol containing 3.0 g of zinc powder was added dropwise within 10 min 21.28 g (25 ml) of a standard ozonolysis solution which corresponded to 5.675 g of methyl oleate. No temperature change was observed. Then 10 ml of water was added. A temperature rise of 5C was noted. The mixture was heated and refluxed at 70C for several hours. A peroxide test at that time was weakly positive. Five milliliters of water was added and refluxing was continued another hour after which no peroxide was detected. The white, colloidal mixture was filtered with only methanol for washing and transfer. To the still cloudy filtrate were added 50 ml of ether, 35 ml of water and 30 ml of saturated sodium chloride in a separatory funnel. The ether extract was separated, and the aqueous layer was washed three times with 20 ml portions of ether. Ether extracts were combined, dried, filtered and evaporated under reduced pressure at room temperature or below. A clear, pale-yellow liquid residue weighing 5.82 g (92.6%) was obtained. Wet analysis gave 62.5 mole per cent and GLC, 61.9 mole per cent of carbonyl (Table I). Two new minor peaks following the C_{11} fractions on the chromatogram were not identified.

Discussion

Zinc was activated by pretreatment with glacial acetic acid followed by filtration and washing to remove the acid. Sometimes we have added the activated zinc to the ozonolysis product solution in a reaction flask, and other times we have poured the solution through a column of the activated zinc, but either method is satisfactory. The only difficulty encountered has been the production of a colloidal inorganic product, presumably zinc oxide, that causes emulsions during aqueous washes for removal of the soluble salts. However, these difficulties have been largely overcome, and we have found this method to be rapid and convenient. On a preparative scale it is still necessary to utilize a simple wash with dilute ammonium chloride to remove cholloidal zinc salts completely before distillation (2) and as an aid to filtration. On a smaller scale where only semiquantitative or qualitative analysis by GLC was desired, we found that the zinc salts could be removed adequately by filtration with a little filter-aid.

Others may find this procedure useful for reducing ozonolysis products that are sensitive to acid. Ozonides obtained in nonparticipating solvents also appear to be susceptible to this reducing agent, but peroxides of ether do not. The Jones reductor, a reducing column of amalgamated zinc, was ineffective for us when used in the absence of acid, as was catalytic hydrogenation with Raney zinc (3) under ambient conditions.

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[Received September 7, 1965—Accepted November 3, 1965]

The Reaction of Picric Acid with Epoxides

I. A Colorimetric Method[1]

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Abstract

A colorimetric method has been developed for the analysis of epoxides by reaction with picric acid. Picric acid was found to be the best of several acidic chromophores in its reaction with epoxides. Despite a nonquantitative reaction, the product concentration is proportional to the original concentration, i.e., it follows Beer's Law.

The reaction variables were studied with methyl mono- and diepoxystearates, epoxidized cottonseed oil and *Vernonia anthelmintica* oil. The general applicability of the method was demonstrated by reaction with butyl epoxystearate, styrene oxide, a number of 3-substituted propylene oxides and two commercial epoxy resins.

Introduction

EPOXIDES HAVE SHOWN a growing industrial importance, particularly in the polymer field. The metabolic fate of the oxirane moiety is of more than academic interest since some PVC food packaging film is plasticized with epoxidized glycerides and since traces of epoxides are generated in heated fats via the hydroperoxides (1–6).

Most of the recent work on fatty epoxides is reassuring; no toxic or carcinogenic activity can be attributed to the oxirane function. Some researchers, however, have reported deleterious effects on growth rates of rats fed epoxidized soybean oil (10). Others have found that the feeding of *Vernonia* oil (rich in epoxyoleic acid) results in a build-up of epoxides in the tissue of rats (11). It is clear that the metabolic fate and function of epoxides is not yet fully understood.

Unquestionably this lack of knowledge is largely due to the overall complexity of the problem but what has made its solution even more difficult is the lack of a specific, sensitive method of assay for the oxirane moiety. Maerker has recently summarized the various analytical difficulties encountered in this area (12). The purpose of this paper is to show that picric acid reacts with the oxirane moiety to give an hydroxy picryl ether to an extent which is proportional to the concentration of epoxide present. Application of this picric acid reaction to the determination of epoxides in heated oils will be discussed in a later paper.

Perhaps the most specific method for oxirane determination to date is that of Morris and Holman (17) in which the epoxides are converted to the chlorohydrins. The increase in -OH concentration is measured by near infrared spectrophotometry. Unfortunately, this method is time consuming and its lower limit of sensitivity is 0.3% oxirane. It was reasoned that, if an acidic reagent having chromophoric properties could be made to add exclusively to the oxirane moiety, a simple and sensitive method might result. Davies and Savige used 2,4-dinitrothiophenol to obtain crystalline derivatives of 1,2-epoxides (18). More recently Kaufmann and Schickel have treated terminal epoxides with mercaptans (19).

We used a number of such acidic reagents, including: 2,4-dinitrophenol, 2,4-dinitrobenzenesulfonic acid, 2,4,6-trinitrobenzoic acid and picric acid. Only trinitrobenzoic acid and picric acid showed indications of reaction with epoxidized oils. Picric acid was chosen for further studies since it was found to form a colored derivative which in base gave an absorption maximum at a wavelength where picric acid did not. This permits analysis of the derivative in the presence of excess reagent. This is illustrated by Figure 1.

The probable derivative formed is that shown in Figure 2. The product is an hydroxy-picryl ether (see Results).

Experimental Procedures

Preparation of Epoxides

Epoxidation of the various products was carried out at 60C in benzene using standard procedures (13). The performic acid was generated in situ by reacting formic acid with 70% aqueous H_2O_2 containing a catalytic amount of H_2SO_4. The progress of epoxidation was followed by removing aliquots at regular intervals, washing to neutrality and analyz-

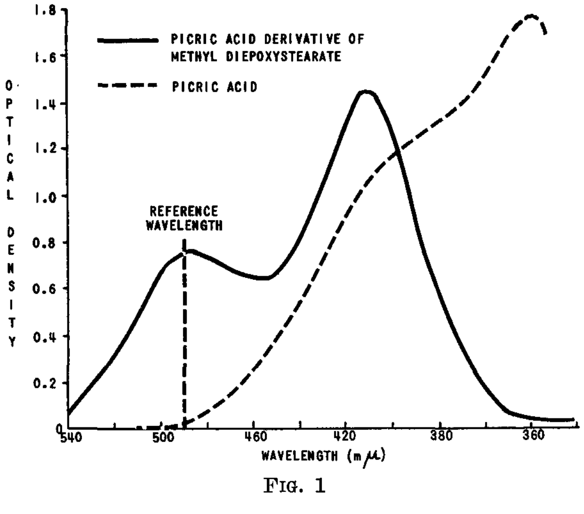

FIG. 1

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[1] Presented in part at the First World Fat Congress, Hamburg, Germany, in October, 1964, and at the AOCS Meeting in Houston, Texas, April 1965.