Reactions of Methoxy Hydroperoxides Derived from Methyl Oleate. Catalytic Hydrogenation[1]

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Abstract

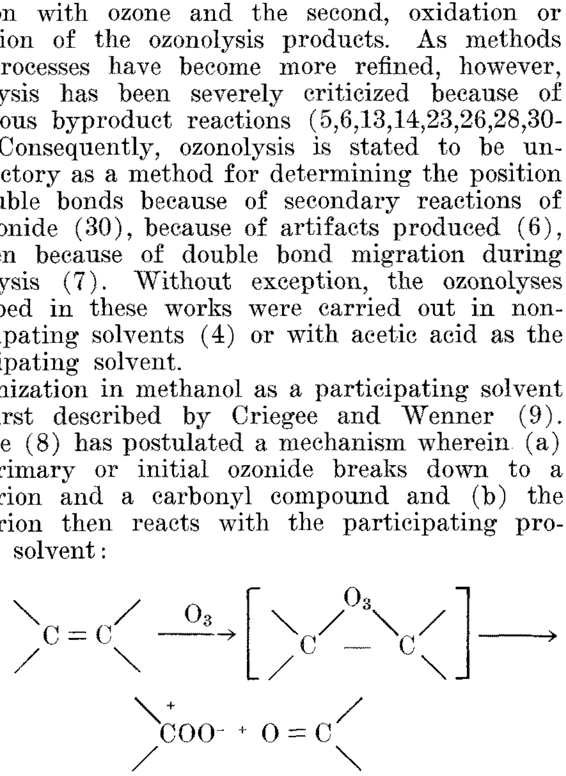
Yield improvements in carbonyl compounds obtained by catalytic hydrogenation of methyl oleate ozonolysis products have been achieved by use of catalyst poisons and by the proper choice of catalyst support. Byproduct dimethyl azelate formation with palladium on charcoal was about 20% in the absence of a poison; 10%, with sodium acetate present in the support; 8%, with triethyl amine in solution. Palladium on calcium carbonate-lead acetate gave about 7%, palladium on zinc oxide with pyridine or lead acetate present gave 9%. The literature is reviewed on the catalytic hydrogenation of methoxy hydroperoxides derived from ozonolyses in methanol.

Introduction

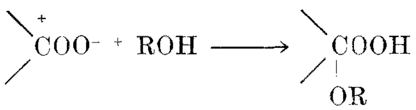
SINCE THE PIONEERING WORK of Molinari and Soncini (20) and Harries and Thieme (15), ozonolysis has been applied to unsaturated fatty acid derivatives as a means both for analysis and for synthesis (16). Acids, aldehydes, or alcohols may be produced in a two-stage process, the first of which involves reaction with ozone and the second, oxidation or reduction of the ozonolysis products. As methods and processes have become more refined, however, ozonolysis has been severely criticized because of numerous byproduct reactions (5,6,13,14,23,26,28,30-32). Consequently, ozonolysis is stated to be unsatisfactory as a method for determining the position of double bonds because of secondary reactions of the ozonide (30), because of artifacts produced (6), or even because of double bond migration during ozonolysis (7). Without exception, the ozonolyses described in these works were carried out in nonparticipating solvents (4) or with acetic acid as the participating solvent.

Ozonization in methanol as a participating solvent was first described by Criegee and Wenner (9). Criegee (8) has postulated a mechanism wherein (a) the primary or initial ozonide breaks down to a zwitterion and a carbonyl compound and (b) the zwitterion then reacts with the participating protolytic solvent:

(a)



(b)



In an alcohol, an alkoxyhydroperoxide is formed (R = alkyl). In an acid, an acyloxyhydroperoxide is formed (R = acyl). Thus, in methanol methoxyhydroperoxides are produced, and in acetic acid, acetoxyhydroperoxides.

We (24) have reported on the use of methanol as a participating solvent (4,8,9) in the ozonation of methyl oleate to give high conversions (93%) to aldehydic compounds. Ackman et al. (1) also used methanol as an ozonation medium followed by oxidation with performic acid to produce high yields (> 95%) of acidic products. The dibasic acid fraction was of exceptional purity (ca. 98%), and the homologous acids formed were in an amt comparable to that formed by degradation of azelaic acid with performic acid. Acetic acid, methyl formate, or acetone gave significantly lower yields (ca. 75%). We have applied the technique of Ackman et al. for producing dodecanedioic and pentadecanedioic acids of high purity from the monoethenoid acids produced by hydrazine reduction of linolenic acid (12). Diaper and Mitchell (10) used methanol or ethanol with subsequent treatment by sodium borohydride to produce high yields of 9-hydroxynonanoic acid esters from oleate or ethyl undecylenate. Sodium borohydride reduction of ozonolysis products obtained in chloroform (27) or isopropyl alcohol (10) did not give as high yields. It may be concluded that use of methanol (or a similar alcohol) as a participating solvent is necessary to produce ozonolysis products which are most suitable for subsequent conversion to acids, aldehydes, or alcohols.

It is also apparent that certain specific reagents are needed for the second stage in the overall ozonization reaction. For example, performic acid is superior to peracetic in oxidative treatment of cyclohexene ozonolysis products (5). Reduction by zinc and acetic acid is superior to catalytic hydrogenation in the preparation of aldehydes from methyl oleate (24). Triphenyl phosphine is also a good reagent for aldehyde production (17). Sodium borohydride is superior to catalytic hydrogenation for the preparation of alcohols (10).

Because of its simplicity and economy of operation, catalytic hydrogenation would be the method of choice for aldehyde preparations if improved yields could be obtained. However, catalytic hydrogenation of ozonolysis products obtained by ozonation in methanol has invariably led to a major byproduct reaction, the formation of methyl ester. Thus, ozonation of methyl 5-hexenoate in methanol followed by hydrogenation with palladium gives dimethyl glutarate as well as the 5-carbon aldehyde ester (19). We have reported the formation of dimethyl azelate in the preparation of methyl azelaaldehydate (25). Diaper and Mitchell (11) have reported the formation of diethyl sebacate in the reductive amination of ethyl 10-undecenoate over Raney nickel. Thompson (29) has reported the formation of a methyl ester in the hydrogenation of dihydropyran ozonolysis products over platinum.

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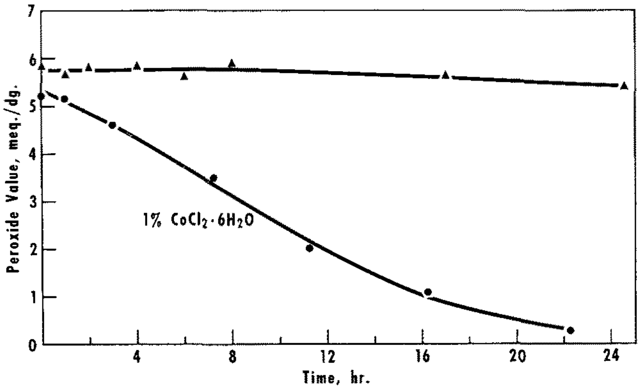

FIG. 1. Stability of methyl oleate methoxy hydroperoxides (–▲–) and their decomposition by cobaltous chloride (–●–) at methanol reflux temp.

We have discussed possible mechanisms for methyl ester formation and have demonstrated a means for reducing the amt of its formation by the use of pyridine during hydrogenation of methyl oleate ozonolysis products with palladium on charcoal (25). The use of a 10% pyridine in methanol solution resulted in a 93% conversion to aldehydes, as compared to the 75% conversion obtained in its absence. The use of pyridine has some disadvantage, largely manipulative, since elaborate washing is required to remove the pyridine before distillation. Accordingly, we have continued our search for a convenient catalyst system in the hydrogenation of ozonolysis products, and our results with palladium as a catalyst using a variety of poisons and supports are reported herein.

Experimental

Gas-Liquid Chromatography

A Pye-Argon chromatographic analyzer with a radium D ionization detector and an integrator was used. The column was a 4 ft × ¼ in. glass tube packed with 10% Craig polyester succinate on Chromosorb W (60/80 mesh). The volume of sample injected varied from 0.5 μl to 3 μl, depending upon the concn of the methanol solution. The temp was 155C, pressure drop ca. 440 mm, and the gas flow rate 50 cc/min. Relative retention volumes for the major compounds were reported earlier (25).

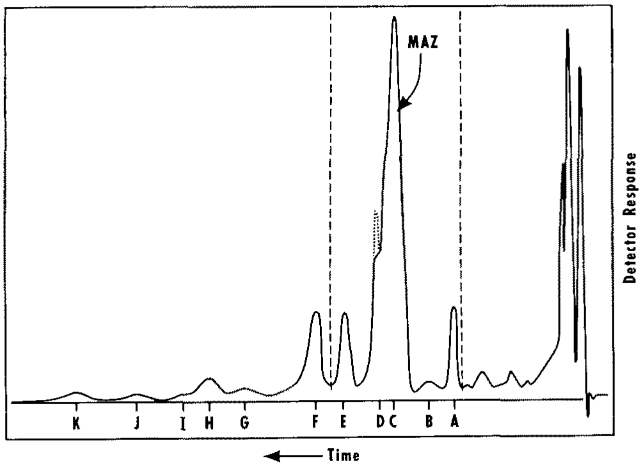

FIG. 2. Typical chromatogram of products obtained by reduction of soybean methyl ester ozonolysis products on a Pye chromatograph. Peaks within the vertical dotted lines include the major C-9 bifunctional compounds of interest. Methyl myristate (A) is also included since one of the geometrical isomers of the enol ether formed by cracking of the dimethyl acetal of methyl azelaaldehydate (MAZ) is masked by it. Peaks are identified in Table I. The method used for approximating the dimethyl acetal content is indicated by the dotted curve.

In some of the later experiments, an F & M Model 500 temp programmed chromatograph was used with a 4 ft × ¼ in. copper column packed with 20% silicone SF96 on 60–80 mesh Chromosorb. Operating conditions included: 220C injection port temp, 350C block temp, 7.9C/min heating rate, 100–290C programmed temp range, 150 ma bridge current, 50 ml/min helium flow, and 1–2 μl sample size.

Catalysts

The catalysts were obtained from commercial sources except for those described as follows:

Lindlar (18) catalyst (Pd/$CaCO_3$ poisoned with lead acetate), W-2 Raney nickel (22), and palladium on silica (3) were prepared according to the literature. To obtain 10% palladium on zinc oxide, 25 g of reagent-grade zinc oxide powder was suspended in 175 ml of distilled water, and a solution containing 4.25 g (2.5 g as palladium) of palladium chloride in 50 ml of water was added. The suspension was stirred for 5 min at room temp and 10 min at 80C. The hot suspension was transferred to a hydrogenation flask and shaken at 30 psig of hydrogen pressure until uptake of hydrogen ceased. The catalyst dispersion was filtered, and the catalyst was dried in vacuo at 40–50C. Supported catalyst recovered was 25.5 g. Some of this catalyst (7.89 g) was poisoned with lead acetate trihydrate (1.66 g) following the procedure for preparing Lindlar catalyst.

Alkali-washed palladium catalysts were prepared by stirring the catalyst for 1 hr in 10% sodium hydroxide solution, after which the catalyst was removed by filtration then dried in vacuo at 40–50C. The W-2 Raney nickel catalyst was suspended in 10 ml of methanol containing 0.05 g potassium hydroxide, then separated, and dried as before.

The pyridine-washed catalyst was prepared by allowing the catalyst to stand in pyridine at room temp for several days, filtering the pyridine dispersion, rinsing the catalyst with methanol, and allowing the catalyst to air dry.

Ozonization Procedure

The general procedure for ozonization in methanol has been previously reported (24). For example, pure methyl oleate (Applied Science Laboratories, 250 g) was ozonized in 800 ml of absolute methanol at 0C until a rapid increase of ozone concn in the exit gases occurrred as determined by the Welsbach Model C ozone meter. Other sources of ozonolysis product solutions included that obtained by pilot-plant ozonolysis of soybean methyl esters, but the source had no effect on the amt of dimethyl azelate produced in relation to methyl azelaaldehydate. Ozonolysis product solutions were stored under nitrogen at 0C, and aliquots were withdrawn periodically for the catalyst evaluation studies. These solutions were quite stable and could be stored indefinitely under such conditions. The only apparent change that occurred was a gradual transformation of aldehyde to acetal groups.

Stability of Ozonolysis Product Solutions

To obtain some concept of the stability of ozonolysis product solutions, one such solution was sub-

TABLE I

GLC Analysis of Components Obtained by Reduction of Soybean Methyl Ester Ozonolysis Products

Component (peak)	Chemical reduction[a]	Hydrogenation at 1 atm					Hydrogenation at 20 atm	
		Lindlar[a]	Lindlar[b]	Pd/C,[a] Pyridine	Pd/CaCo$_3$	Raney Ni[b]	Lindlar[b]	Pd/CaCO$_3$[b]
Dimethyl azelate (E)	2.7	4.5	7.7	4.9	12.4	15.5	8.3	14.9
Aldehyde ester:								
Methyl azelaaldehydate (C)	71.9	59.7	37.1	62.0	29.6	23.9	30.0	23.7
Methyl 10-formyldecanoate (H)	6.3	7.2	3.6	6.2	3.5	2.2	2.4	2.2
Acetal ester:								
Methyl 9,9-dimethoxynonanoate (D)	....	6.6	28.6	6.6	30.1	27.9	36.4	36.5
Methyl 11,11-dimethoxyundecanoate (I)	....	....	2.5	....	2.8	3.2	3.0	1.9
Methyl esters:								
Methyl myristate (A)	5.7	5.9	5.3	6.5	5.8	5.1	5.3	4.3
Methyl palmitate (F)	9.2	7.7	8.2	9.1	9.4	12.3	8.6	10.6
Methyl stearate/oleate (K)	1.2	1.7	2.5	1.4	1.1	2.7	1.8	2.1
Unknowns:								
(B)[c]	1.4	1.6	1.8	1.5	2.0	1.8	1.9	1.5
(G)	1.7	5.1	1.0	1.8	2.2	3.6	1.0	1.3
(J)	....	....	1.7	....	1.1	1.8	1.3	1.0
Total	100.1	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total C-9 aldehydic products	71.9	66.3	65.7	68.6	59.7	51.8	66.4	60.2
Dimethyl azelate production,[d] wt%	3.6	6.4	10.5	6.7	17.2	23.1	11.3	19.8

[a] Laboratory ozonolysis solutions.

[b] Pilot-plant ozonolysis solutions.

[c] Contains at least some enol-ether resulting from the cracking of the dimethyl acetal in one of the geometric isomer forms. An equal amt of the opposite isomer appears under Peak A.

[d] Calculated as percent of methyl azelaaldehydate + methyl azelaaldehydate dimethyl acetal + dimethyl azelate.

mitted to methanol reflux temp intermittently over a period of several days for a total reflux time of 24 hr. The solution was kept under a nitrogen atmosphere during the entire period. Samples were withdrawn periodically and analyzed for peroxide content by the AOCS procedure, Cd 8–53 (2). The analyses were carried out by addition of the aliquot to a chloroform-glacial acetic acid solution containing ca. 1.6% potassium iodide and titration of the liberated iodine by standard thiosulfate solution. A second solution to which 1% of cobalt chloride had been added was treated similarly. The results are plotted in Figure 1.

Hydrogenation Procedures

Hydrogenations at atmospheric pressure were carried out in a reaction flask similiar to that used for ozonization (24). After the weighed catalyst was suspended in ca. 70 ml of methanol, the suspension was placed in the flask and flushed first with nitrogen then hydrogen for 15–20 min. Aliquots (30–50 ml) of the ozonolysis product solutions were added dropwise over a period of about 0.5 hr, and the hydrogenation was continued until a negative test for peroxide (potassium iodide in glacial acetic acid) was obtained. Hydrogenation was complete in 1.5–2.0 hr if the catalyst was fairly active, up to 6 hr if not. The exit gas from the hydrogenation flask was passed through a wet test meter to measure approximate rate of flow, which varied from 15 liter/hr to 150 liter/hr in early experiments, but was standardized at about 120 liter/hr for later experiments. No attempt was made to measure actual consumption of hydrogen. At completion of the reduction, the system was flushed with nitrogen, and the solution was filtered quickly, then stored at 0C until analysis could be carried out.

Hydrogenations at 300 psig of hydrogen pressure were done in an Aminco high-pressure hydrogenation apparatus, with a glass insert tube for the stainless steel bomb.

Reduction with Zinc and Acetic Acid

Since reduction of methyl oleate ozonolysis products by zinc and acetic acid is known to give good yields of aldehydes with little, if any, dimethyl azelate formation (24), results obtained by this method were compared with those by catalytic hydrogenation. To a weighed aliquot of the ozonolysis product solutions was added glacial acetic acid with magnetic stirring and cooling by means of an ice bath. Zinc powder was added gradually while the temp was maintained below 30C. The molar ratio of acid and zinc to methyl oleate used was about 6 and 2.2 to 1. The resulting mixture was filtered, and equal volumes of methylene chloride and water were added. The layers were separated. The methylene chloride extract was washed until free of acid, and the water washes were backwashed. The methylene chloride solution was dried over Drierite. The solvent was removed by evaporation at reduced pressure (water aspirator) and room temp (water bath).

Methods of Analysis

After reduction of the ozonolysis product solutions, analyses were made by GLC. In Figure 2 is given a representative chromatogram, that of a soybean methyl ester product solution and obtained with the Pye chromatograph. Each of the peaks is identified in Table I, which summarizes the relative amts of the various components in terms of peak area percent, corresponding to approximate weight percent, for selected catalysts. Only those components that boiled higher than methyl palmitate, including the bifunctional cleavage products, were considered in the calculations. The monofunctional cleavage products, caproaldehyde and pelargonaldehyde, were disregarded since their higher volatility made recovery difficult and analysis inexact. To obtain a measure of the relative efficiency of the various catalysts, the amt of the C-9 diester dimethyl azelate formed was related to the total amt of C-9 cleavage products and expressed as "dimethyl azelate production" in terms of weight percent. The results obtained with the various catalysts are summarized in Table II.

To obtain more quantitative, absolute values for the yields of aldehydic products and byproduct diester, dimethyl sebacate was introduced as an internal standard in selected GLC analyses. The following procedure was used. A weighed aliquot of the reduced ozonolysis product solution was placed in a rotary evaporator, and solvent was removed at water aspirator pressure and 25–30C. The residue was weighed, and percentage yield was calculated on the basis of the weight recovered. To the residue was added a weighed amt of dimethyl sebacate, which

TABLE II

Effect of Catalyst and Hydrogenation Conditions on Dimethyl Azelate Production

Catalyst amount, wt %	Hydrogen pressure, atm	Dimethyl azelate produced,[a] wt %		Remarks
		Solution A[b]	Solution B[c]	
0.5% Pd/Al_2O_3				
20	20	....	16.4	....
5% Pd/Al_2O_3				
1	1	14.3	....	....
5% Pd/$BaCO_3$				
1	1	....	13.5	....
1	20	....	16.3	....
5% Pd/$BaSO_4$				
1	1	9.9	....	....
5% Pd/$CaCO_3$				
1	1	12.6	....	....
1	20	....	18.9	....
2	1	....	15.1	Catalyst washed with alkali
5% Pd/$CaCO_3$-Pb. $(OAc)_2$ (Lindlar)				
1–2	1	....	12.8	....
5	20	....	13.8	....
10	1	5.6, 6.8	9.6	....
12	1	7.8	....	....
10	20	....	10.0	....
10	1	7.3	....	Recovered catalyst
10	1	....	10.7	Catalyst washed with pyridine
10	20	....	10.7	Catalyst washed with pyridine
10	1	6.2	....	Hydrogenation in 10% pyridine
5% Pd/ C				
1	1	....	18.7	....
1	20	....	17.7	....
2	1	....	18.2	Catalyst washed with pyridine
10%Pd/C				
1.6	1	19.7	....	....
1.8	1	22.1	....	....
4	1	14.0	....	....
0.2	1	8.7[d]	....	Hydrogenation in 1% pyridine
0.7	1	3.2[d]	....	Hydrogenation in 10% pyridine
1	1	13.4	....	Catalyst washed with alkali
1	20	....	15.2	Catalyst washed with alkali
1.5	1	7.3, 7.9, 8.1,	....	Hydrogenation in 10% triethyl amine
1.8	1	9.8	....	Hydrogenation with 10% (w/v) sodium acetate
Pd/SiO_2				
1	1	13.2	....	....
10% Pd/ZnO				
10	1	16.7, 16.9,	....	....
2	1	20.9	....	....
10% Pd/ZnO				
10	1	8.8	....	Hydrogenation in 10% pyridine
10% Pd/ZnO-$Pb(OAc)_2$				
15	1	9.5	....	....
Raney Nickel				
10	1	....	13.3, 16.5	....
10	20	....	20.5	....
10	20	....	17.1	Catalyst washed with alkali

[a] Calculated as percent of methyl azelaaldehydate + methyl azalaaldehydate dimethyl acetal + dimethyl azelate.

[b] Obtained by laboratory ozonolysis of pure methyl oleate.

[c] Obtained by pilot-plant ozonolysis of soybean methyl esters.

[d] Reference 25.

TABLE III

Comparison of Analytical Methods for Product Aldehydes[a]

Replicate analysis number	Methyl azelaaldehydate[a] yield, % by GLC analysis[b]		Total carbonyl yield, %, by wet analysis
	Without internal standard[c]	With internal standard	
1	78.0	70.4	72.4
2	78.2	75.4	72.0
3	78.7	...	72.8
4	78.3	69.8	72.4
5	78.8	73.2	72.6
Average	78.4 ± 0.3	72.2 ± 2.1	72.4 ± 0.2

[a] Analyses carried out on product aldehydes formed in a single, representative run by catalytic hydrogenation of pure methyl oleate ozonolysis products with 10% palladium on charcoal.

[b] GLC analyses F & M Model 500 chromatograph.

[c] Calculated from the equation $\frac{100}{1 + N'}$, where N = (mole fraction dimethyl azelate)/(Σ mole fractions of methyl azelaaldehydate and its acetal).

was selected as a standard least likely to interfere with other peaks. The mixture was thoroughly mixed and samples were then taken for GLC analysis. The ratio of peak area for the various components to that for dimethyl sebacate was then calculated, and and this figure was used to calculate the actual weight of the component in the original solution. A correction was applied to the peak area for each component to account for losses on the GLC column from the use of dimethyl sebacate. This correction factor was determined just before analysis of the product solutions by the use of a standard made up of pure components. These correction factors varied from day to day, depending upon operating conditions and the condition of the column. Representative values obtained on a Silicone SF-96 column for each of the components were: methyl azelaaldehydate, 1.04; methyl azelaaldehydate dimethyl acetal, 1.12; dimethyl azelate, 1.03. Values obtained by this method, given in Table III, are compared with those from GLC analysis according to the method described and with those obtained by wet analysis as follows:

Wet analyses for carbonyl compounds were made by conventional oximation methods. The hydroxylamine hydrochloride was 1 *N* in 75% ethyl alcohol, and the solution had a pH of 3.2. The hydroxylamine hydrochloride solutions containing the aldehyde samples were refluxed for 2 hr, cooled, and titrated with 0.1 *N* NaOH to the pH of a blank. This method cannot be used on products containing acids, ethyl acetate, bases (e.g., pyridine), or buffers (e.g., zinc acetate).

Discussion

Ozonolysis of methyl oleate in methanol produces a mixture in equimolar quantities of aldehydes (pelargonaldehyde and methyl azelaaldehydate) and methoxy hydroperoxides $RC(H)(OCH_3)OOH$, where $R = CH_3(CH_2)_7$– and $CH_3OOC(CH_2)_7$– (24). The methoxy hydroperoxides are relatively stable, and a concd solution of hydroperoxides in the aldehyde has been made by removal of methanol solvent (24). They may be kept for prolonged periods in methanolic solution, as shown by the little change in peroxide content that occurred at methanol reflux temp (Fig. 1). This stability made possible withdrawal of aliquots over a period of several weeks from a single ozonolysis solution, thereby obviating an ozonolysis run for each catalyst test. However, in the presence of cobaltous chloride, decomposition did occur (Fig. 1). Decomposition in the presence of other similar metallic salts would probably occur as readily. Accordingly, contamination by such materials should be avoided.

The catalyst tests were carried out chiefly on palladium, with supports and poisons as the variables studied. The hydrogenations were performed at ambient conditions by bubbling hydrogen rapidly through the ozonolysis product solution.

Dimethyl azelate production varied, depending upon the support used (Table II). The supports may be listed according to increasing dimethyl azelate production in the laboratory ozonolysis solutions as follows: $BaSO_4$, $CaCO_3$, SiO_2, Al_2O_3, ZnO, and charcoal. With pilot-plant solutions, which contained some dimethyl azelate resulting from methoxy hydroperoxide decomposition prior to the introduction of of the catalyst, the order was: $BaCO_3$, Al_2O_3, $CaCO_3$ and charcoal. Obviously, $BaSO_4$ is the most desirable support; charcoal, the least.

The most pronounced improvement in aldehyde yield was obtained through the use of catalyst poisons. As reported earlier (25), pyridine was most effective (Table II). In order of decreasing effectiveness, other poisons were: lead acetate, triethyl amine, sodium acetate, and sodium hydroxide. The lead acetate, sodium acetate, and sodium hydroxide were deposited on the catalyst support, in contrast to pyridine and triethyl amine which were used in the solvent medium.

The study on catalytic hydrogenation of ozonolysis products is continuing in this Laboratory, and the effect of using various participating solvents during ozonolysis and hydrogenation will be reported shortly (21).

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Urethane Foams from Animal Fats I. Oxyethylated 9, 10-Dihydroxystearic Acid[1]

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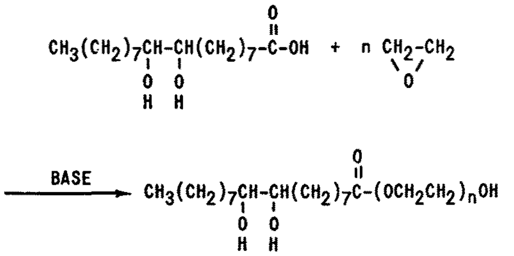
Abstract

Threo- and *erythro-*9,10-dihydroxystearic acids were reacted with 2, 4, 6 and 8 moles of ethylene oxide. The oxyethylated polyols from the *threo* acid, adjusted to equivalent weight 100 with triisopropanolamine, were converted to satisfactory rigid foams by mixing with corresponding amts of isocyanate-terminated oxypropylated sorbitol prepolymers of three viscosities. Typical foam properties had maxima for the tetra- or hexaoxyethylene polyol, and most properties paralleled prepolymer viscosity.

THE STRAIGHTFORWARD preparation of the 9,10-dihydroxystearic acids from oleic acid (1,2), their trifunctionality and hydrocarbon chains suggested study of their value as components of urethane foams. The present report describes the 2-stage preparation of foams based on oxyethylated dihydroxystearic acid as the major "polyol" and the reaction product of oxypropylated sorbitol and excess tolylene diisocyanate as the "prepolymer."

Oxyethylation of Dihydroxystearic Acids

Threo- and *erythro-*9,10-dihydroxystearic acid were converted to triols by base-catalyzed reaction with ethylene oxide at 7 psi and 180C, in an apparatus previously described (3). The reaction is summarized by equation 1, in which *n* has the average values 2, 4, 6 and 8:



$$CH_3(CH_2)_7\underset{\underset{H}{O}}{CH}-\underset{\underset{H}{O}}{CH}(CH_2)_7-\overset{\overset{O}{\|}}{C}-OH + n\ \underbrace{CH_2-CH_2}_{O}$$

$$\xrightarrow{BASE} CH_3(CH_2)_7\underset{\underset{H}{O}}{CH}-\underset{\underset{H}{O}}{CH}(CH_2)_7\overset{\overset{O}{\|}}{C}-(OCH_2CH_2)_nOH \qquad (1)$$

As with simple carboxylic acids (4,5), it is considered that the acid group is consumed in the first stages of reaction with ethylene oxide, to form ethylene glycol monoesters. With additional ethylene oxide, reaction presumably continues to a larger extent at the β-oxyethanol and to a smaller extent at the vicinal secondary glycol functions, still disfavored by comparatively low acidities (3). Owing to self-alcoholysis during oxyethylation, the products are more complex than diagrammed and comprise a mixture of monoesters, diesters, and free polyethylene glycol (6,7).

In most of the oxyethylations, 4 mole % KOH based on the dihydroxystearic acid was used as catalyst. Residual catalyst then had to be neutralized (as by concentrated hydrochloric acid) before use of the products in the foaming stage, to avoid overcatalysis of urethane formation. In several preparations, neutralization was avoided by using 2 mole

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[1] Presented at the AOCS meeting in Chicago, 1964.

[2] E. Utiliz. Res. Devel. Div., ARS, USDA.