that complex formation of the ion has occurred. The current investigation shows that a methanol, sodium perchlorate solution of cobalt drier plus methyl linoleate exhibits a very slight shift in the half-wave potential for the cobaltous ion from −1.12 v to −1.14 v. This shift was observed after the solution had been stored for 18 hours under a nitrogen atmosphere, and 2-1/2 hr of oxygen bubbling.

Alternatively, cobalt in the complex with methyl linoleate may be undergoing a rapid shift from the +2 to the +3 state and back again in a typical catalytic manner. That is, oxygen may oxidize cobalt to the +3 state which, in turn, is reduced to the +2 state by the closely associated ester. The half life of cobalt in the +3 state is comparatively short and can be detected only if the concentration of this oxidation state is increased abnormally by bubbling oxygen through the solution.

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Preparation of 2-Decyl-2-Hydroxymethyl-1, 3-Propanediol from Dodecanal and from Petroselinic Acid

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Abstract

Dodecanal was reacted with formaldehyde and potassium hydroxide in ethanol and with formaldehyde and calcium oxide in aqueous methanol to give about 30% of the theoretical yield of 2-decyl-2-hydroxymethyl-1,3-propanediol (DHP).

Petroselinic acid was ozonized in methylene chloride, and the ozonide reduced to aldehydes with formic acid and zinc. The methylene chloride solution was emulsified with water and reacted with formaldehyde and potassium hydroxide. A yield of 32% of DHP was isolated.

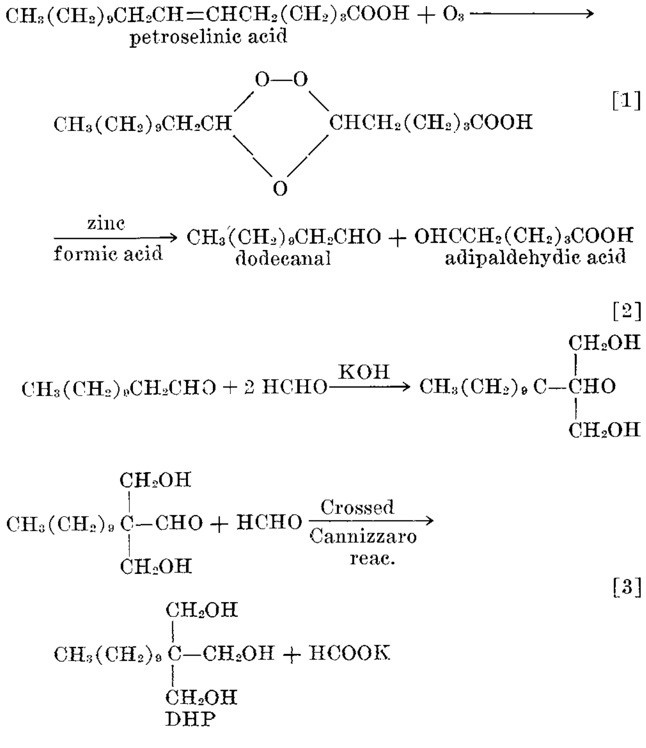
Pure 5,5,5-trimethylol valeric acid could not be isolated from the reaction mixture of formaldehyde and potassium hydroxide with the mixed aldehydes from petroselinic acid, but a small amount of material was isolated by ion exchange resins which had high infrared absorption for hydroxyl and carboxylic acid and which polymerized on standing.

Introduction

AMONG THE OILSEED PLANTS selected for further study in the new crops program of the U. S. department of Agriculture are several members of the Umbelliferae family including parsley (*Petroselinum sp.*),wild carrot (*Daucus carota*), and fennel (*Foeniculum vulgare*). The characteristic fatty acid of the seed oil from these plants is petroselinic (*cis*-6-octadecenoic) acid, and any industrial utilization of the oils would depend primarily on the petroselinic acid or its derivatives.

A derivative that would probably be of much value in the preparation of alkyd resins and plasticizers (1,8,9) is 2-decyl-2-hydroxymethyl-1,3-propanediol (DHP) obtainable by reductive ozonization of petroselinic acid and reaction of the dodecanal with formaldehyde and an alkali.

The reaction of aldehydes with formaldehyde and alkalies is used on a commercial scale to manufacture trimethylol compounds from the shorter chain aldehydes and there is an extensive literature on the preparation and purification of these triols (2,3,4,6,7,10,11,14). The preparation of DHP from dodecanal or petroselinic acid does not seem to have been reported in the literature. In the reactions involved, formaldehyde condenses with the alpha hydrogens of the longer chain aldehyde to form methylol groups. Another molecule of formaldehyde reacts with the carbonyl group in a crossed Cannizzaro reaction to form a third methylol group. DHP can be formed from petroselinic acid according to the following equations if the ozonization is done in an inactive solvent:



$$\underset{\text{petroselinic acid}}{CH_3(CH_2)_9CH_2CH{=}CHCH_2(CH_2)_3COOH} + O_3 \longrightarrow$$

$$[1]$$

$$\xrightarrow[\text{formic acid}]{\text{zinc}} \underset{\text{dodecanal}}{CH_3(CH_2)_9CH_2CHO} + \underset{\text{adipaldehydic acid}}{OHCCH_2(CH_2)_3COOH}$$

$$[2]$$

$$CH_3(CH_2)_9CH_2CHO + 2\,HCHO \xrightarrow{KOH} CH_3(CH_2)_9\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}{-}CHO$$

$$CH_3(CH_2)_9\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}{-}CHO + HCHO \xrightarrow[\text{Cannizzaro reac.}]{\text{Crossed}}$$

$$[3]$$

$$CH_3(CH_2)_9\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}{-}CH_2OH + HCOOK$$

DHP

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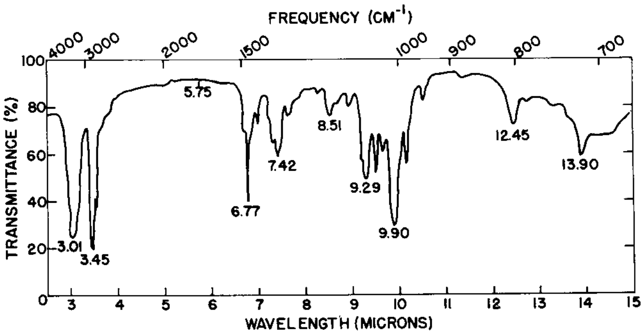

FIG. 1. Infrared spectrum of 2-decyl-2-hydroxymethyl-1,3-propanediol. The spectrum was obtained as a KBr disc at a concentration of 1 mg to 350 mg KBr with a Perkin-Elmer Infrared Spectrophotometer Model 21.

The authors prepared DHP from purchased dodecanal and from petroselinic acid, the highest yields obtained from either source being about 32% of the theoretical.

Experimental

Materials

The petroselinic acid used was prepared from parsley seed oil by the method of Fore, Holmes, and Bickford (5). The dodecanal used was purchased from K & K Laboratories, Jamaica, N. Y.

2-Decyl-2-hydroxymethyl-1,3-propanediol from Dodecanal. Twenty-five grams of dodecanal (0.11 mol based on 82.8% purity), 4.9 gm calcium oxide (0.09 mol), 40.1 ml aqueous formaldehyde (0.48 mol), 9.9 ml water and 50 ml methanol were mixed and vigorously stirred at room temperature for 67 hr. The aqueous methanol was evaporated. The residue was triturated with both ether and water, the solutions filtered and the filtrates combined. The ether-water mixture was acidified with sulfuric acid and the ether phase separated, dried with sodium sulfate, and evaporated to dryness. The residue from the ether phase was dissolved in 75 ml warm carbon tetrachloride and chystallized at room temperature overnight. The crystals were filtered out on a fritted glass filter and recrystallized to give 28% yield of DHP which had the following characteristics; found 68.3% C, 12.3% H, no alkoxy, mol wt 228.0 (calculated 68.2% C, 12.3% H, mol wt 246). The melting point was 80.4–81.2 C. The infrared spectrum is given in Fig. 1 which shows high absorption at 3.01 μ for the hydroxyl groups of the triol and the absence of aldehyde by the lack of absorption near 5.75 μ.

In another run, 25 gm of dodecanal (0.11 mol based on 79.7% purity) was dissolved in 100 ml absolute ethanol, 40.1 ml 36% aqueous formaldehyde (0.48 mol) and 0.5 gm Tween 85 emulsifier added. The solution was cooled below 20C in ice water and 9.1 gm solid 85% potassium hydroxide (0.14 mol) added pellet by pellet. When the temperature rose to 40C the container was set back into ice water while the rest of the potassium hydroxide was added. The solution was stirred at 30C for an hour after which it was stirred for 3 hr at 50–55C and allowed to stand overnight.

Fifteen milliliters of 30% hydrogen peroxide was added (14). After stirring for a few minutes, the ethanol was evaporated in a rotary vacuum evaporator at 85C. The residue was triturated several times with warm carbon tetrachloride and the solution poured through a filter, the final volume of the solution being about 200 ml. No crystallization took place at room temperature during five days. The solution was then set in the refrigerator at —5C overnight. Crystals formed and were filtered out on a fritted glass filter. These were redissolved in 75 ml warm carbon tetrachloride and recrystallized to yield 8.7 gm DHP or 32% of the theoretical yield. The infrared spectrum was almost identical with that of Fig. 1 and showed absence of any aldehydes. Analysis showed a small amount of ethoxy present, probably from the monoethyl ether of DHP (13).

2-Decyl-2-hydroxymethyl-1,3-propanediol from Petroselinic Acid. Twenty-five grams (0.088 mol) of petroselinic acid was dissolved in 200 ml methylene chloride and ozonized at —10 to 0C by a stream of oxygen from a Welsbach Laboratory Ozonator Model T-23 containing about 3% ozone. Completion of ozonization was determined by the darkening of an acidified solution of potassium iodide in a trap through which the exit gases were bubbled.

The solution was transferred to a beaker containing a magnetic stirrer and allowed to rise to room temperature (26C). Ten milliliters 90% formic acid and 10 gm zinc dust were gradually added over a period of 30 min. The solution was warmed to 33C, the source of heat removed and the solution stirred at room temperature for 23 hr, at which time it gave a very faintly positive test for peroxides. The sludge was then filtered out. One hundred fifty milliliters of water, 2 gm Span emulsifier, and several drops of phenolphthalein were added. Fifty per cent aqueous sodium hydroxide was added in small increments until the phenolphthalein end-point was reached. During the addition of the sodium hydroxide the solution heated to the boiling point (40C) of methylene chloride and had to be cooled in ice water. Ten milliliters of 50% sodium hydroxide (0.19 mol) and 48 ml 36% aqueous formaldehyde (0.58 mol) were added. Beaker was covered with aluminum foil and stirred for 5 hr at 30–35C and 63 hr at 25–30C.

The mixture was poured into a separatory funnel. The methylene chloride readily formed a lower layer which was drawn off. The water phase was rinsed twice with 50 ml ethyl ether which was added to the methylene chloride solution. When 50 ml water was shaken with the combined ether and methylene chloride solutions (250 ml) the mixture separated into two phases of approximately equal volume. These phases were separated and the solvent removed under reduced pressure in a rotary evaporator. In the case of the lower phase foaming was so excessive it was necessary to acidify it (hydrochloric acid was used) before drying could be completed. By crystallization from warm carbon tetrachloride 4.7 gm DHP was obtained from the upper phase and 2.3 gm from the lower phase, a total of 7.0 gm equal to 32% of the theoretical yield. These samples had infrared spectra almost identical with that shown in Fig. 1.

Discussion

Modifications of the procedure given for the preparation of DHP from petroselinic acid were tried, including catalytic reduction of the ozonides and variations in the time and temperature of reacting the aldehydes, alkali and formaldehyde. The yields by any one procedure were difficultly reproducible. The authors obtained the best yields by the procedure given.

After no more DHP would crystallize from the carbon tetrachloride solution of the crude product, distillation of the residue in a Todd Fractionator yielded a fraction distilling at 195–205C at less than 1 mm pressure from which a small amount of DHP was crystallized by dissolving the fraction in warm carbon tetrachloride.

It should be possible to form 5,5,5-trimethylol valeric acid from adipaldehydic acid, the other fragment resulting from the reductive ozonization of petroselinic acid, when the mixed aldehydes are reacted with formaldehyde and alkali. The authors were not successful in isolating from the complex reaction mixture a fraction which could be proven to be pure trimethylol valeric acid. After acidifying the alkaline water solution from the reaction mixture it was evaporated to dryness. The residue was then extracted with hot absolute ethanol. From the ethanol solution, the acids were absorbed on a Dowex 1 ion exchange resin column in the hydroxl form, the column rinsed to neutrality, and the acids eluted with normal hydrochloric acid. Evaporation of the eluate gave a very viscous almost colorless liquid. This had an infrared spectra similar to that expected of trimethylol valeric acid with high absorption for hydroxyl and carboxyl groups and which readily polymerized on standing.

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Instrumental Study of Aldehyde Oils and Their Reaction with Selected Amines[1]

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Abstract

Unsaturated aldehyde oils prepared by partial ozonization of soybean oil gave infrared and nuclear magnetic resonance spectra in qualitative accord with the structures expected. Infrared spectra indicated that the unsaturation present was in the *trans* form. Reactions of dialdehyde oil with various amines proceeded with surprising ease at room temperatures to give facticelike, crosslinked products.

Introduction

THE PREPARATION of aldehyde oils by ozonization of soybean oil has been reported previously (2–4). Complete ozonization of soybean oil gave a product that contains up to an average of 2.5 aldehyde groups per molecule after removal of nonester fragments. This product is highly reactive and can undergo a number of resin-forming reactions. Partial ozonization of soybean oil may be controlled to give products having an average of one or two aldehyde groups per molecule (2,4). These "monoaldehyde" and "dialdehyde" oils have varying degrees of residual unsaturation depending upon the method used for reducing the ozonolysis products. Reduction by zinc and acetic acid has no effect on residual unsaturation. Neither does catalytic hydrogenation in the presence of pyridine, but without pyridine the residual double bonds are at least partially saturated to give a heterogeneous mixture of solid and oil. Also in the absence of pyridine, the use of a catalyst causes relatively large amounts of carboxylic ester to be formed and results in lower yields of aldehydic products.

Partial ozonization of soybean oil to give mono- or dialdehyde oils has the advantages of giving a product of lesser and more controllable reactivity, of economic use of ozone, and of producing lesser amounts of byproduct caproaldehyde, pelargonaldehyde, and malonaldehyde than does complete ozonization. Residual unsaturation, particularly in monoaldehyde oil, furthermore offers the possibility of acting as an additional reaction site.

Infrared (IR) and nuclear magnetic resonance (NMR) spectra of some aldehyde oils as well as reactions of dialdehyde oil with selected diamines are discussed in this paper.

Experimental

Instrumental Analyses

IR spectra were obtained with a Perkin-Elmer 221-G spectrophotometer (5). The spectra of liquid oil samples were obtained from thin films on sodium chloride plates. The solid derivatives were incorporated in potassium bromide pellets for IR absorption analysis.

NMR spectra were obtained with a Varian HR-60 spectrometer equipped with an electronic integrator. NMR samples were dissolved in a deuterated chloroform solution.

Preparation of Aldehyde Oils

Various aldehyde oils were prepared in the pilot-plant facilities of the Northern Laboratory by methods described previously (2–4): monoaldehyde oil, by hydrogenation over Pd/$CaCO_3$ of soybean oil ozonolysis products (25 parts) in ethyl acetate (60 parts)

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[2] A laboratory of the No. Utiliz. Res. & Dev. Div.