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REDUCTION OF ESTERS

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This invention relates to the reduction of esters of fatty acids and more particularly to the production of high molecular weight alcohols by the reduction of the corresponding fatty acid esters by reaction with alkali metal and hydrolytic alcohol.

Heretofore various methods for producing high molecular weight alcohols by reacting high molecular weight fatty acid esters with alkali metal and a hydrolytic alcohol have been proposed. As these methods are ordinarily carried out, the fatty acid is dissolved in a suitable solvent and a hydrolytic alcohol and alkali metal are added thereto or alkali metal is suspended in the solvent and a mixture of the ester and the alcohol added thereto. The solvents ordinarily used are paraffinic hydrocarbons or aromatic hydrocarbons such as toluene and xylene and/or an excess of the hydrolytic alcohol. In these reactions there is a distinct tendency for the reaction products, which are alkali metal alcoholates, to form viscous or gelatinous colloidal solutions in the solvent media. The formation of such highly viscous solutions or gels often seriously interferes with the reaction by making efficient stirring difficult and by tending to coat the particles of alkali metal with the gelatinous or viscous material. This tendency is especially pronounced when the esters of aliphatic hydroxy acids or polybasic acids are reduced by these methods. In such cases the alcoholates formed by reduction of the hydroxy or polybasic acids are dialkali metal compounds, i. e., each molecule contains two metal alcoholate groups.

An object of the present invention is to provide an improved method for the production of high molecular weight alcohols by reduction of esters. A further object is to provide a method for reducing high molecular weight esters of aliphatic acids, wherein the formation of colloidal solutions of viscous or gelatinous nature is avoided, particularly in reducing the esters of high molecular weight hydroxy acids and polybasic acids of the aliphatic series. Other objects will be apparent from the following description of my invention.

I have discovered that by utilizing aliphatic ethers as solvent media in alkali metal-alcohol reduction of esters of high molecular weight acids, the formation of colloidal solutions or gels is entirely prevented. I have found that the alkali metal alcoholates produced by the above mentioned reduction of esters are more or less insoluble in the aliphatic ethers and hence are precipitated in crystalline form. The resulting slurry of crystalline alcoholates in the reaction mixture has no deleterious effect on the force of the reaction, does not materially increase the power required to stir or agitate the mixture, nor does it cause any appreciable decrease in the reactivity of the alkali metal. By this means I am able to reduce esters of high molecular weight hydroxy acids and polybasic acids with no difficulties, with good yields and with excellent utilization of alkali metal.

In one method of practicing my invention I dissolve an ester of a high molecular weight aliphatic acid in an aliphatic ether which has a boiling point above the melting point of the alkali metal to be used. I also dissolve in this solution a sufficient quantity of a suitable hydrolytic alcohol, for example, two mols of the alcohol per mol. of ester. In another portion of the aliphatic ether I suspend a finely divided alkali metal such as sodium. Then, while heating the ether containing the alkali metal to its boiling point, I slowly add thereto the ether solution of ester and hydrolytic alcohol. The mixture preferably is constantly stirred during the reaction. During the course of the reaction a fine precipitate of crystalline alcoholates is formed. After the reaction has reached completion, any unreacted sodium present is decomposed by adding a suitable low molecular weight alcohol, e. g., methanol or ethanol, or water. Additional water also is added to hydrolyze the alcoholates present. The non-aqueous solution then is separated and distilled or otherwise worked up in the usual manner to obtain the high molecular weight alcohol product. Obviously other methods of practicing my invention may be employed and will be apparent to those acquainted with the reduction of esters by the alkali metal-alcohol reaction.

My invention is applicable in general to the various methods heretofore proposed for carrying out this reaction, the only significant change required being the substitution of the usual alcohol and/or hydrocarbon solvent media by an aliphatic ether. The present invention is especially suitable for practicing the reduction method disclosed and claimed in the application, Serial Number 729,900 by N. D. Scott and myself which issued October 29, 1935, as U. S. Patent 2,019,022, which method comprises using the theoretical amount of hydrolytic alcohol and the use of certain types of hydrolytic alcohols.

The aliphatic ethers suitable for carrying out my invention, of course, should be substantially inert to the alkali metals in order to prevent loss

of the alkali metal by side reactions. In practicing my invention I prefer to select a solvent ether which has a boiling point not lower than the melting point of the alkali metal to be used, since these ester reduction reactions ordinarily are best carried out at a temperature above the melting point of the metal. However, it is not essential that the ether have such a high boiling point, since some reaction will occur below the melting point of the alkali metal, although the yield obtained at such low temperatures ordinarily is small. It should also be noted that the limitation that the ether preferably should have a melting point above the boiling point of the alkali metal does not restrict the invention to the employment of what are ordinarily considered high boiling ethers, since certain low melting alkali metal alloys may be used, e. g., sodium-potassium alloys, which have melting points as low as around 20° C. When using such low melting alloys as reducing agents, a low boiling ether such as diethyl ether may be advantageously employed in practicing my invention. I have obtained the best results in general by using dialkyl glycol ethers, e. g., dimethyl and diethyl glycol ethers and ethyl butyl glycol ether. Examples of other aliphatic ethers which are suitable for practicing my invention are trialkyl glycerol ethers, e. g., trimethyl glycerol ether, glycol formal, glycerol formal, the tetra-alkyl pentaerythrites, and dinormal-butyl ether.

My invention is further illustrated by the following examples:—

Example 1

Methyl ricinoleate (b. p. 2 mm. 180–200), 301 gms., was reduced with 130 gms. of sodium in 1400 cc. of diethyl glycol ether, at 119° C. (the boiling point of the ether), using tertiary amyl alcohol 176 gms., as the hydrolytic agent. The sodium was suspended in 900 cc. of the ether and when the refluxing temperature was reached, the ester and tertiary amyl alcohol, dissolved in the other 500 cc. of solvent, were added to the stirred suspension of sodium. Twenty minutes were required for this addition, following which the reaction mixture was stirred an additional twenty minutes. The unchanged sodium was decomposed by cautiously adding water to the slowly refluxing ether solution. The sodium hydroxide formed separated as an aqueous layer below the ether and was withdrawn. After one or two additional washings with water, the remaining alkali was neutralized and the soaps decomposed with a little mineral acid. The ether was then recovered by distillation and the ricinoleyl alcohol vacuum-distilled at 180–205° C.$_{2\ mm.}$ The yield was 246 grams or 90.1%.

Example 2

Castor oil, one mol. (313 gms.) sodium, 5 atoms (115 gms.—one atom excess) and 2 mols (228 gms.) of methyl hexalin as hydrolytic alcohol were reacted with sodium in diethyl glycol ether in a manner exactly similar to that used in Example 1, except that the temperature was held at 100° C. instead of 119° C. The yield of ricinoleyl alcohol isolated was 178 gms. or 62.5%.

Example 3

Dimethyl sebacate (m. p. 38° C.), 115 gms., was reduced in 1000 cc. of diethyl glycol ether with 92 gms. of sodium and 148 gms. of tertiary butyl alcohol at 100–105° C., by the method of Example 1. Practically no sodium remained unchanged and hydrogen equivalent to only 0.18 atom of sodium was wasted during the reduction. This is equivalent to a sodium reduction efficiency of 95.5%. The decamethylene glycol isolated melted at 72–73° C.

Example 4

Dimethyl sebacate, 0.10 mol., was reduced in 150 cc. trimethyl glycerol ether at 125° C. using 0.8 atom of sodium and 0.4 mol. of tertiary amyl alcohol. The yield of decamethylene glycol, m. p. 73–75° C., isolated was 62.5%.

Example 5

Dimethyl sebacate, 0.10 mol., was reduced in 130 cc. of ethyl butyl glycol ether at 120° C. using 0.8 atom of sodium and 0.4 mol. of tertiary amyl alcohol. The yield of decamethylene glycol isolated by distillation at 2 mm. (b. p. 180–190° C.) was 17 gms. or 97%. Practically no sodium remained unchanged in this reduction and the hydrogen wastage was practically nil, as evidenced by no perceptible gas evolution.

Example 6

Dimethyl sebacate, 23 gms., was reduced at 65° C. in dimethyl glycol ether, using a slight excess of potassium, with tertiary amyl alcohol as the hydrolytic agent. A 42% yield of decamethylene glycol was isolated from the reduction product.

Example 7

Dimethyl sebacate, 23 gms., was reduced at 60° C. in glycol formal, (b. p. 77° C.), using a 10% excess of sodium potassium alloy (60% potassium) and tertiary amyl alcohol as the hydrolytic agent. Fifteen gms. (85% yield) of crude decamethylene glycol resulted.

Example 8

Methyl abietate, 553 gms. (1.75 mols) was reduced by reaction with 174.8 gms. (7.6 mols) of sodium and 281.2 gms. (3.8 mols) of tertiary butyl alcohol in 1500 cc. of diethyl glycol ether. The reaction temperature was maintained at about the boiling point of the ether solvent and the mixture was stirred constantly until the reaction was complete. By this means, 275 gms. of abietyl alcohol was obtained, corresponding to a yield of 54.6%.

In practicing my invention I prefer to use the method disclosed and claimed in co-pending application Serial No. 729,900 by N. D. Scott and myself which issued October 29, 1935, as U. S. Patent 2,019,022. This method comprises in part avoiding the use of an excess of hydrolytic alcohol, i. e., in using no more than the theoretical amount of alcohol to effect the desired reduction. By this means efficient reduction is obtained without undue wastage of alkali metal. It should be noted that when employing this method, if the ester to be reduced is an ester of a hydroxy acid or of a polybasic acid, less than 2 mols of hydrolytic alcohol are required per mol. of ester group to be reduced as compared with the reduction of the ester of a monobasic acid which does not contain hydroxy groups and which requires two mols of alcohol per ester group. For example, in the reduction of methyl ricinoleate by this method the following reaction occurs:—

$$\underset{\text{Methyl ricinoleate}}{C_{17}H_{32}(OH)COOCH_3} + 4Na + \underset{\text{Tertiary amyl alcohol}}{C_5H_{11}OH} \longrightarrow \underset{\text{Disodium derivative of ricinoleyl alcohol}}{C_{17}H_{32}(ONa)CH_2ONa}$$

In this reaction the hydroxyl group in the methyl ricinoleate takes part in the reduction and thus the ester itself functions partially as hydrolytic alcohol.

Various modifications of my herein described process may be made without departing from the spirit and scope of my invention. For example, my invention is not restricted to the employment of a pure aliphatic ether as a reaction solvent but various mixtures containing aliphatic ethers may be employed. For example, the addition of material quantities of an aliphatic ether to a reaction mixture employing hydrocarbon and/or alcohol as solvent will aid materially in decreasing the viscosity of the solution and in inhibiting the formation of gelatinous masses which interfere with the proper operation of the reaction. Although my invention is especially useful in the reduction of esters of hydroxy acids and polybasic acids of high molecular weight, it is equally applicable to the reduction of various other high molecular weight acids to produce corresponding high molecular weight alcohols, e. g., various esters and glycerides of lauric, palmitic, oleic, and stearic acids and the like and various naturally occurring glycerides or glyceride mixtures such as cocoanut oil, fish oils, linseed oil, and other saponifiable fats and oils, and the resin acids, e. g. abietic acid, pimaric acid and various acidic resinous products obtained from natural sources, e. g., wood products such as rosin, pin oil and the like.

I claim:

1. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid with an alkali metal and a hydrolytic alcohol in the presence of an aliphatic ether which is substantially inert to said metal and the boiling point of which is not lower than the melting point of said metal.

2. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid with an alkali metal and a hydrolytic alcohol in a solvent medium comprising an aliphatic ether substantially inert to said metal selected from the group consisting of dialkyl ethers, dialkyl glycol ethers, trialkyl glycerol ethers, glycol formal, glycerol formal and tetra-alkyl pentaerythrites, the boiling point of which ether is not lower than the melting point of said alkali metal.

3. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid with sodium and a hydrolytic alcohol in a solvent medium consisting of a dialkyl glycol ether which is substantially inert to sodium and the boiling point of which is not lower than the melting point of sodium.

4. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid with a sodium-potassium alloy and a hydrolytic alcohol in a solvent medium comprising an aliphatic ether which is substantially inert to said alloy and the boiling point of which is not lower than the melting point of said sodium-potassium alloy.

5. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid selected from the group consisting of hydroxy acids and polybasic acids with an alkali metal and a hydrolytic alcohol in the presence of an aliphatic ether which is substantially inert to said metal and the boiling point of which is not lower than the melting point of said metal.

6. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid selected from the group consisting of hydroxy acids and polybasic acids with an alkali metal and a hydrolytic alcohol in a solvent medium comprising an aliphatic ether substantially inert to said metal, the boiling point of which is not lower than the melting point of said alkali metal.

7. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid selected from the group consisting of hydroxy acids and polybasic acids with an alkali metal and a hydrolytic alcohol in a solvent medium comprising an aliphatic ether substantially inert to said metal selected from the group consisting of dialkyl ethers, dialkyl glycol ethers, trialkyl glycerol ethers, glycol formal, glycerol formal and tetra-alkyl pentaerythrites, the boiling point of which ether is not lower than the melting point of said metal.

8. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid selected from the group consisting of hydroxy acids and polybasic acids with a sodium-potassium alloy and a hydrolytic alcohol in a solvent medium comprising an aliphatic ether which is substantially inert to said alloy and the boiling point of which is not lower than the melting point of said sodium-potassium alloy.

9. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight aliphatic acid selected from the group consisting of hydroxy acids and polybasic acids with sodium and a hydrolytic alcohol in a solvent medium consisting of a dialkyl glycol ether which is substantially inert to sodium and the boiling point of which is not lower than the melting point of sodium.

10. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid selected from the group consisting of hydroxy acids and polybasic acids with sodium and a hydrolytic alcohol in a solvent medium consisting of a trialkyl glycerol ether which is substantially inert to sodium and the boiling point of which is not lower than the melting point of sodium.

11. A process for the production of high molecular weight alcohols comprising reacting an ester of a high molecular weight acid selected from the group consisting of hydroxy acids and polybasic acids with sodium and a hydrolytic alcohol in a solvent medium consisting of dimethyl glycol ether.

12. A process for the production of high molecular weight alcohols comprising reacting an ester of ricinoleic acid with an alkali metal and a hydrolytic alcohol in a solvent medium consisting of an aliphatic ether substantially inert to said metal selected from the group consisting of dialkyl ethers, dialkyl glycol ethers, trialkyl glycerol ethers, glycol formal, glycerol formal and tetra-alkyl pentaerythrites, the boiling point of which ether is not lower than the melting point of said alkali metal.

13. A process for the production of high molecular weight alcohols comprising reacting an ester of ricinoleic acid with sodium and a hydrolytic alcohol in a solvent medium consisting of a dialkyl glycol ether which is substantially

inert to sodium and the boiling point of which is not lower than the melting point of sodium.

14. A process for the production of high molecular weight alcohols comprising reacting an ester of sebacic acid with an alkali metal in a hydrolytic alcohol in a solvent medium consisting of an aliphatic ether substantially inert to said metal selected from the group consisting of dialkyl ethers, dialkyl glycol ethers, trialkyl glycerol ethers, glycol formal, glycerol formal and tetraalkyl pentaerythrites, the boiling point of which ether is not lower than the melting point of said alkali metal.

15. A process for the production of high molecular weight alcohols comprising reacting an ester of sebacic acid with sodium and a hydrolytic alcohol in a solvent medium consisting of a dialkyl glycol ether which is substantially inert to sodium and the boiling point of which is not lower than the melting point of sodium.

VIRGIL L. HANSLEY.

CERTIFICATE OF CORRECTION.

Patent No. 2,096,036. October 19, 1937.

VIRGIL L. HANSLEY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 14, for the words "melting point above the boiling" read boiling point above the melting; page 3, first column, line 31, for "pin" read pine; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of January, A. D. 1938.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

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