

UNITED STATES PATENT OFFICE

2,019,022

PREPARATION OF HIGH MOLECULAR
WEIGHT ALCOHOLS

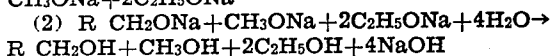
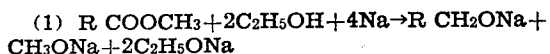
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No Drawing. Application June 9, 1934,
Serial No. 729,900

19 Claims. (Cl. 260—156)

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

The reduction of esters of high molecular weight acids to form the high molecular weight alcohol by reacting the esters with alkali metal and a lower aliphatic alcohol in a solution in the lower alcohol has long been known. The method originally proposed (U. S. Patent 868,252) consisted in placing pieces of alkali metal in a closed container and slowly adding thereto an ethyl alcohol solution of the ester to be reduced. A large excess of the solvent alcohol and the alkali metal were used. After the reaction was completed excess alkali metal and the alkali metal compounds were decomposed by treating with alcohol and water and the higher alcohol formed was recovered by distillation. The reactions involved may be represented as follows:



This method has not been adapted for economical commercial practice because of low yield of product and poor reduction efficiency, that is, a considerable portion of the alkali metal used is consumed with the evolution of hydrogen from the solvent alcohol rather than being used to reduce the ester. Another disadvantage of the process as originally proposed is that generally as the reaction proceeds the viscosity of the reaction mixture progressively increases until a highly viscous gel-like mass is produced and the surface of the alkali metal becomes coated over and is rendered unreactive.

In order to overcome the above disadvantages, various improvements have been proposed from time to time. One such improvement consists in the use of hydrocarbon solvents. In accordance with this improvement finely divided alkali metal is suspended in a hydrocarbon and the ester to be reduced, together with the hydrolytic alcohol, are added to the alkali metal suspension. In order to insure complete reduction of the ester an excess of both the alcohol and the alkali metal is used. While this improvement has resulted in an increase in yield and some increase in reduction efficiency, nevertheless it still permits considerable amounts of gaseous hydrogen to be evolved, which constitutes a waste of alkali metal. To decrease the amount of alkali metal lost by

hydrogen evolution it has been proposed to operate the reaction under hydrogen pressure. This method, however, has not resulted in high reduction efficiencies on a commercial scale.

An object of this invention is to provide an improved method for reducing esters to produce high molecular weight alcohols by reaction of alkali metal and aliphatic alcohol which will result in high sodium reduction efficiencies and high yields of the product. Other objects will be apparent from the following description of our invention.

We have discovered that the reaction of alkali metal and hydrolytic alcohol on high molecular weight esters may be carried out with substantially no side reaction between the hydrolytic alcohol and sodium to evolve gaseous hydrogen if the ratio between the alcohol and the ester added to the reaction mixture is at all times equal to not more than two moles of hydrolytic alcohol for each mole of ester group to be reduced. For example, if the ester to be reduced is a simple ester of a mono-basic, saturated fatty acid, e. g. methyl stearate, two moles of alcohol will be used to one mole of the ester. The corresponding glyceride, e. g. stearin or olein, will require six moles of alcohol per mole of glyceride, since the glyceride molecule contains three ester groups. Our improved process is distinguished from the prior methods in one respect by the fact that whereas prior methods used an excess of alcohol so that the alcohol functioned both as reactant and as solvent, in our process the alcohol functions only as reactant and does not exist in excess. In fact in our process, there is at all times substantially no free hydrolytic alcohol in the reaction mixture, since the alcohol reacts substantially as fast as it is added to the reaction mixture to form alkali metal alcoholate.

We have further discovered that improved results may be obtained by using secondary or tertiary alcohols as hydrolytic alcohols in the herein described reduction process. The use of these alcohols results in better yields of product and more satisfactory operation, as more fully explained hereinafter.

In reducing unsaturated fatty acid esters in accordance with our invention, we have found that the ethylenic linkages present in such esters are not reduced to any substantial extent, even when two or more double bonds are present, provided there is no conjugate unsaturation. In the case of esters containing conjugated double bonds, only one of the double bonds in the conjugate system will be reduced. Therefore, in accordance with our invention, in addition to two moles of

hydrolytic alcohol for each ester group to be reduced, we also add two moles of hydrolytic alcohol (together with at least an equivalent amount of alkali metal) for each conjugated double bond system ($-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$) in the ester molecule. If the ester contains only one double bond or a plurality of double bonds not conjugated, we add only two moles of the alcohol per ester group. In any case, the amount of alkali metal used will be sufficient to react with all of the alcohol added; an excess of alkali metal may be used if desired, without deleteriously affecting the result as long as the amount of hydrolytic alcohol does not exceed that theoretically required for the reduction of the ester.

In practicing our invention it is important that the hydrolytic alcohol and the esters to be reduced be added substantially simultaneously to the alkali metal and that there be no large excess of either alcohol or ester during the operation. If some of the alcohol should be added before adding the ester, or if the alcohol is added in excess of that required to reduce the ester present, the excess alcohol will react with the alkali metal to evolve hydrogen, even when the alkali metal is not present in excess, thus resulting in a waste of the alkali metal. On the other hand, we have found that if the ester is added to the sodium in the absence of the hydrolytic alcohol, the ester reacts with the alkali metal to form certain polymeric compounds (acyloins) which will not thereafter take part in the desired reaction.

In practicing our invention we prefer to use close to the theoretical amounts of alkali metal (that is, 4 gram atoms per mole of ester group to be reduced, plus 2 atoms for each conjugated double bond system), or at most only a slight excess, e. g. 1% excess to take care of traces of water or other reactive impurities which may be present. As mentioned above, a substantial excess of alkali metal may be used if desired without deleteriously affecting the reaction, provided that the hydrolytic alcohol is not used in excess. However the use of excess alkali metal ordinarily is of no advantage in practicing our invention and generally results in a loss of metal because of the difficulty of recovering unreacted metal after the reaction has been completed.

It will be apparent that various methods may be used to bring the ester, hydrolytic alcohol and alkali metal into reaction in accordance with our invention. We prefer first to form a suspension of finely divided alkali metal in a hydrocarbon solvent such as xylene and to add to this suspension with efficient agitation a hydrocarbon solvent solution of the ester to be reduced together with the hydrolytic alcohol in the ratio of 1 ester equivalent to 2 mols of the hydrolytic alcohol. The alcohol-ester solution is added slowly with rapid agitation, while the reaction mixture is heated or cooled as required to maintain the desired reaction temperature.

The temperature of the reaction mixture may vary between wide limits, for example from ordinary room temperatures of around 20–30° up to the boiling point of the solvent. In most cases we have found that the best yields are obtained by using a reaction temperature above the melting point of the alkali metal, e. g. between 100 and 110° C. when using sodium as the alkali metal.

After the reaction is complete, a small amount of a lower aliphatic alcohol, e. g. methanol, is added to decompose any traces of unreacted sodium which may be present. Water or acid then is added to decompose the alcoholates pres-

ent; we prefer to use a solution of about 9 normal sulfuric acid for this purpose. The acid solution should be added cautiously with rapid agitation and cooling as necessary. The reaction mixture then is washed with water to remove sulfates and distilled to separate the reaction product from the solvent. We prefer to distill off the hydrocarbon solvent at atmospheric pressure and then to distill off the product in a pure form by vacuum distillation.

The following examples illustrate specific methods of practicing our invention:

Example 1

Methyl laurate, 535 gms., together with 370 15 gms. of tertiary butyl alcohol were dissolved in 1500 cc. of xylene and slowly added during the course of one hour to a suspension of 230 gms. of finely divided sodium in another 1500 cc. of xylene, maintained at a temperature of 105° C. 20 After neutralizing the alkali with sulfuric acid and washing the xylene solution of the higher alcohol with water, the solvent was removed by distillation and the crude lauryl alcohol produced was vacuum distilled at 15 mm. pressure. The 25 yield of the crude lauryl alcohol, was 436 gms. or 92.9% of theory; the yield of pure lauryl alcohol was 88.0% of theory.

Example 2

Bayberry tallow (containing 6.5% free palmitic acid) 225 gms., together with 172 gms. of cyclohexanol were dissolved in 700 cc. of xylene and the mixture added in the course of one hour and forty minutes to a suspension of 79 gms. of finely 35 divided sodium in another 700 cc. of xylene maintained at a temperature of 100–105° C. The product, which consisted of cetyl alcohol, mixed with other higher alcohols, was separated and purified as in Example 1. The yield of the purified product was 81.2% of theory.

Example 3

Cottonseed oil, 450 gms., and 244 gms. of tertiary butyl alcohol were dissolved in 1500 cc. of 45 xylene and slowly added in the course of two and one-half hours to a stirred suspension of 152 gms. of finely divided sodium in another 1500 cc. of xylene at 100–110° C. Yield of higher alcohols, 90.4%. Iodine number of higher alcohol mixture, 123 (gms. I_2 per 100 gms. alcohol). Iodine number of original cottonseed oil 110. Calculated iodine value for mixture of alcohols; 122.

Example 4

Beef tallow, 666 gms., along with 346 gms. of secondary butyl alcohol were dissolved in 700 cc. of xylene and added in the course of 3 hours and 40 minutes to a stirred suspension of 217 gms. 60 of finely divided sodium in 1000 cc. of xylene at 105–110° C. The yield of higher alcohols was 90.6% of theory.

Example 5

China-wood oil, 407 gms., and 412 gms. of 65 tertiary butyl alcohol were dissolved in 1500 cc. of xylene and the mixture added in about three hours to a stirred suspension of 256 gms. of finely divided sodium at 100–110° C. The ratio of ester to sodium to hydrolyzing alcohol was made 70 1:6:4 instead of 1:4:2, since one of the conjugated double bonds is reduced along with the eleostearic acid ester group giving an alcohol isomeric with linoleyl alcohol. The yield of this alcohol was 91.8% of theory. The iodine num- 75

ber (Method of Ber. 59B, 1390-7 (1926)) of the China-wood oil was 230-235. The higher alcohol produced had an iodine number of 166. The calculated value, assuming the unsaturation to be $\frac{1}{3}$ reduced, would be 165.

Example 6

Spermacetti, 200 gms., together with 65.0 gms. of tertiary butyl alcohol was dissolved in 700 cc. of toluene and this solution was added slowly to a stirred suspension of 40.5 gms. of finely divided sodium in 700 cc. of toluene at 105° C. The yield of higher alcohols was 96.2% of theory.

Example 7

Cocoa butter, 132 gms., together with 43.2 gms. of absolute ethanol was dissolved in 700 cc. of xylene and the mixture added in 45 minutes into a suspension of 43.2 gms. of finely divided sodium in 1000 cc. of xylene. The yield of purified higher alcohols was 84.9% of theory.

In a similar manner abietic acid esters, wool grease, menhaden oil, cod liver oil, linseed oil and phenyl acetate esters can be reduced to higher alcohols corresponding to the acids present in the ester or glyceride reduced.

In practicing our invention it is important that sufficient of the hydrocarbon solvent is used in proportion to the amount of ester to be reduced, in order to prevent the excessive increase in the viscosity of the reaction mixture. The increase in viscosity of the reaction mixture as the reaction proceeds appears to be due to the various alkali metal alcoholates which are formed by the reaction. As shown by the equation given above, three alkali metal alcoholates may be formed, namely (a) from the hydrolytic alcohol used (b) from the alcohol component of the ester and (c) the alcoholate of the higher molecular weight alcohol produced by reduction of the ester. We have found that alkali metal alcoholates are insoluble or only slightly soluble in hydrocarbon solvents. In general, the alkali metal alcoholates of the lower alcohols, e. g. ethyl or methyl alcohol, are substantially insoluble in most hydrocarbon solvents, while those formed from higher alcohols and especially branched chain higher alcohols have a slight degree of solubility which tends to increase in proportion to their molecular weights. In most cases it would be practically impossible to use sufficient hydrocarbon solvent to dissolve more than a small portion of the alcoholates formed by the reaction. If the alcoholate is formed by a reaction of alkali metal with the alcohol in the presence of the hydrocarbon solvent, an insoluble precipitate forms which is more or less gelatinous in nature and greatly increases the viscosity of the mixture. On the other hand, we have found that when the alcoholates are formed by reacting sodium with the alcohol and the ester in substantially the theoretical proportions, the alcoholates produced are formed chiefly in the form of colloidal suspensions, that is, in the form of sols rather than gels and hence increase the viscosity to only a relatively small extent. The amount of solvent required in the reduction of a given amount of ester depends therefore on the alcohol component of the ester and on the alcohol used as hydrolytic alcohol. For example, we have found that the formation of sodium methylate in the reaction mixture tends to increase the viscosity of the mixture to a greater extent than the alcoholates of higher alcohols; hence in general, smaller amounts of solvent are

required in the reduction of the glycerides than in the reduction of methyl esters of the high molecular weight acids. As regards the hydrolytic alcohols to be used, as stated above, those of higher molecular weight form alkali metal alcoholates which are somewhat more soluble in hydrocarbon solvents than those formed from a lower molecular weight alcohol. The alkali metal compounds of methanol, for example, are highly insoluble in hydrocarbon solvents and for this reason methanol is not recommended as hydrolytic alcohol. Other alcohols such as ethanol and normal butanol may be used with good results, however, providing that the concentration of the ester to be reduced is kept sufficiently low and an excess of hydrolytic alcohol is avoided.

We have discovered that the use of alkali metal alcoholates of secondary and tertiary alcohols, i. e. alcohols having two or more carbon atoms attached to the carbon atom to which the hydroxyl group is attached, permits a much greater amount of a given ester to be reduced in a given amount of a hydrocarbon solvent than the alcoholates of normal alcohols of the same molecular weights. For example, when using either tertiary or secondary butyl alcohol as the hydrolytic alcohol in the reduction of the higher fatty acid esters in accordance with our invention and using xylene as a solvent, good results may be obtained with a concentration of 38 grams of a glyceride per 100 cc. of solvent. On the other hand, if ethanol or normal butyl alcohol is used as the hydrolytic alcohol, the concentration of the glyceride cannot be more than 10 to 15 grams per 100 cc. of solvent; if the concentration is higher than this, the reaction mixture becomes too viscous to permit efficient stirring before the reaction is completed.

The employment of the aforementioned secondary and tertiary alcohols in accordance with our invention is not restricted to the alkali metal reduction processes where the ratio of hydrolytic alcohol to ester is limited as described above. The above enumerated advantages accruing from the use of the secondary or tertiary alcohols may be obtained over a wide range of ratio of hydrolytic alcohol to ester. Furthermore, the addition of secondary or tertiary alcohol to a reaction mixture employing a primary alcohol will give improved results, the degree of improvement depending chiefly upon the proportion of secondary or tertiary alcohol present.

Various organic liquids, inert to alkali metals and having boiling points sufficiently high to allow of their use at the desired reaction temperatures, may be used as solvents in accordance with our invention. Examples of suitable solvents are aromatic hydrocarbons such as xylene or toluene and aliphatic hydrocarbons, e. g. petroleum fractions, preferably those high in paraffin hydrocarbons, ethers, e. g. dibutyl ether, tertiary amines, etc. If the solvent selected contains substances reactive with alkali metal, an excess of the metal should be used to allow for the consequent side-reactions, or, preferably, the solvent should be purified before use, e. g. by treatment with sodium to remove the reactive constituents.

An important advantage of our novel method resides in the discovery that it permits reduction of unsaturated esters with little or no reduction of the ethylenic linkages, thereby resulting in the production of unsaturated higher alcohols, which have useful properties. This is illustrated by Example 3. Heretofore it has not been possible to reduce the unsaturated esters with alcohol and

alkali metal without materially reducing the double bonds. A further important advantage is that substantially no free hydrogen is evolved, waste of alkali metal and hydrolytic alcohol is avoided, the material cost is decreased and the process is consequently more efficient than prior methods. A further advantage resides in the employment of secondary and tertiary alcohols, e. g. secondary or tertiary butyl alcohol, as hydrolytic alcohols, which results in a more fluid reaction mixture.

Although our method does not require the employment of high pressures or the addition of extra reactants such as hydrogen or carbon dioxide during the reduction reaction, these may be used in practicing our invention if desirable. However, such additional measures ordinarily are of no advantage in our process.

We claim:

1. A process for the reduction of a higher organic acid comprising reacting an ester of said acid simultaneously with alkali metal and the approximately theoretical quantity of a hydrolytic alcohol in a solvent medium substantially inert to alkali metals.

2. A process for the reduction of a higher fatty acid comprising reacting an ester of said acid simultaneously with alkali metal and the approximately theoretical quantity of a hydrolytic alcohol in a hydrocarbon solvent medium.

3. A process for the reduction of a higher organic acid comprising reacting an ester of said acid simultaneously with the approximately theoretical quantities of both alkali metal and a hydrolytic alcohol in sufficient hydrocarbon solvent to maintain the reaction in a state of fluidity.

4. A process for the reduction of a higher fatty acid comprising reacting an ester of said acid simultaneously with sodium and the approximately theoretical quantity of a butyl alcohol in a solvent medium substantially inert to alkali metals.

5. A process for the reduction of a higher fatty acid comprising reacting a glyceride of said acid simultaneously with the approximately theoretical quantities of both sodium and tertiary butyl alcohol in sufficient xylene to maintain the reaction in a state of fluidity.

6. A process for the reduction of a higher fatty acid comprising reacting a glyceride of said acid simultaneously with the approximately theoretical quantities of both sodium and secondary butyl alcohol in sufficient xylene to maintain the reaction in a state of fluidity.

7. A process for the reduction of a higher fatty acid comprising reacting an ester of said acid simultaneously with alkali metal and a hydrolytic alcohol in a solvent medium substantially inert to alkali metals, the amount of hydrolytic alcohol added per mol of ester being approximately equal to 2 mols of alcohol for each ester group plus 2 mols of alcohol for each conjugated pair of ethylenic linkages in the ester molecule and the amount of alkali metal present being sufficient to react with the alcohol added.

8. A process for the reduction of a higher fatty acid comprising reacting an ester of said acid simultaneously with sodium and a hydrolytic alcohol in a hydrocarbon solvent, the amount of hydrolytic alcohol added per mol of ester being approximately equal to 2 mols of alcohol for each ester group plus 2 mols of alcohol for each conjugated pair of ethylenic linkages in the ester molecule and the amount of alkali metal present being sufficient to react with the alcohol added.

9. A process for the reduction of an unsaturated fatty acid comprising reacting an ester of said acid simultaneously with sodium and a hydrolytic alcohol in a hydrocarbon solvent, the amount of hydrolytic alcohol added per mol of ester being approximately equal to 2 mols of alcohol for each ester group plus 2 mols of alcohol for each conjugated pair of ethylenic linkages in the ester molecule and the amount of alkali metal present being sufficient to react with the alcohol added.

10. A process for the reduction of higher fatty acids comprising dissolving an ester of a higher fatty acid and a hydrolytic alcohol in the ratio of approximately 2 mols of alcohol to one mol of the ester in a hydrocarbon solvent and reacting the solution with a suspension of alkali metal in a solvent inert to alkali metals.

11. A process for the reduction of higher fatty acids comprising dissolving a glyceride of a higher fatty acid and a hydrolytic alcohol in the ratio of approximately 6 mols of alcohol to one mol of the glyceride in a hydrocarbon solvent, the atmospheric boiling point of which is not lower than about 100° C. and reacting the solution with a suspension of sodium in an organic liquid containing approximately 12 atoms of alkali metal per mol of said glyceride at a temperature above the melting point of the alkali metal.

12. A process for the reduction of higher fatty acids comprising dissolving an ester of a higher fatty acid and a butyl alcohol in the ratio of approximately two mols of the alcohol to one mol of the ester in xylene and reacting the solution with approximately four gram-atoms of sodium per gram-mol of said ester suspended in a liquid hydrocarbon having a boiling point above 100° C., at a temperature above the melting point of sodium.

13. A process for the reduction of higher fatty acids comprising dissolving a glyceride of a higher fatty acid and tertiary butyl alcohol in the ratio of approximately 6 mols of the alcohol to one mol of the glyceride in xylene and reacting the solution with a hydrocarbon suspension of sodium containing approximately 12 gram-atoms of sodium per gram-mol of said glyceride at a temperature of 100° to 110° C.

14. A process for the reduction of higher fatty acids comprising dissolving a glyceride of a higher fatty acid and secondary butyl alcohol in the ratio of approximately 6 mols of the alcohol to one mol of the glyceride in xylene and reacting the solution with a hydrocarbon suspension of sodium containing approximately 12 gram-atoms of sodium per gram-mol of said glyceride at a temperature of 100° to 110° C.

15. A process for the reduction of a higher fatty acid comprising reacting an ester of said acid simultaneously with alkali metal and an alcohol having at least two carbon atoms attached to the carbinol group.

16. A process for the reduction of a higher fatty acid comprising reacting an ester of said acid simultaneously with alkali metal and the approximately theoretical amount of an alcohol having at least two carbon atoms attached to the carbinol group in a solvent medium substantially inert to alkali metals.

17. A process for the reduction of a higher fatty acid comprising reacting an ester of said acid simultaneously with alkali metal and tertiary butyl alcohol.

18. A process for the reduction of a higher

fatty acid comprising reacting an ester of said acid simultaneously with alkali metal and an alcohol having at least two carbon atoms attached to the carbinol group in a hydrocarbon solvent medium.

fatty acid comprising reacting an ester of said acid simultaneously with alkali metal and tertiary butyl alcohol in a hydrocarbon solvent medium.

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19. A process for the reduction of a higher