PRODUCTION OF ALIPHATIC ALCOHOLS
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The present invention relates to an improved process for the production of aliphatic alcohols, particularly primary aliphatic alcohols, said process involving conditions which cause a maximum yield of the product alcohol and a minimum formation of undesirable side reaction products.

In principle, aliphatic alcohols can be obtained from alkyl halides, e.g., 1-alkoxides from 1-alkyl bromides, by simple displacement with water in accordance with the following equation:

(1) \[ \text{RCH}_2\text{CH}_2\text{Br} + \text{H}_2\text{O} \rightarrow \text{RCH}_2\text{CH}_2\text{OH} + \text{HBr} \]

However, in the absence of special controls undesirable side reactions occur resulting in the production of by-products with consequent reduction in the yield of the primary product alcohol. Thus, by elimination of hydrogen bromide, olefins are produced in accordance with the following equation:

(2) \[ \text{RCH}_2\text{CH}_2\text{Br} \rightarrow \text{RCH} = \text{CH}_2 + \text{HBr} \]

Or by alcoholysis, ethers are produced in accordance with the following equation:

(3) \[ \text{RCH}_2\text{CH}_2\text{Br} \rightarrow \text{RCH}_2\text{CH}_2\text{OH} \rightarrow (\text{RCH}_2\text{CH}_2)_2\text{O} + \text{HBr} \]

It has been ascertained that the formation of olefin is favored by either too low or too high an OH—concentration in the hydrolyzing solution. Ether formation on the other hand is primarily a function of the solubility of both the alkyl halide and the corresponding alcohol in the hydrolysis mixture, the less the solubility the greater ether formation. It is also pointed out that the rate of the hydrolysis reaction is dependent on temperature, and particularly on the solubility of the alkyl halide in the hydrolyzing medium, i.e., higher temperatures and greater solubility increase rate of hydrolysis.

It has heretofore been proposed to suppress formation of dialkyl ether in the hydrolysis of a slightly water-soluble halide, e.g., octyl bromide, by diluting the organic phase with an inert solvent, e.g., n-octane. In accordance with this procedure the hydrolysis takes place in the aqueous phase in spite of the low solubility of the octyl bromide in water. Higher alkyl bromides, however, such as cetyl bromide hydrolyze at an uneconomically slow rate in aqueous alkaline media even when elevated temperatures are employed.

Broadly, the present invention contemplates a process which involves effecting the hydrolysis of the alkyl bromide or chloride at an elevated temperature and pressure in the presence of a base, water, and an organic liquid, e.g., acetone, soluble in the water and which is a cosolvent for the water, product alcohol and alkyl halide. Particularly amenable to such treatment are the 1-bromoalkanes obtained from olefins derived from cracked waxes and generally containing 5 to 20 carbon atoms in the molecule.

More particularly, it has been found that by the use of a mutual solvent for the water, alkyl bromide and alcohol, and by the careful control of hydroxyl ion concentration, alkyl bromide concentration and temperature, hydrolysis of primary alkyl halides of 5 to 20 carbon atoms can be effected in very high yields, that is, better than 90%. In accordance with the invention, ether and olefin formation are at a minimum, and the hydrolysis proceeds at a fast and economical rate.

As has been indicated, the crux of the invention resides in the use of a particular cosolvent, some of the requirements of which may be listed as follows:

1. Soluble with water, higher alkyl bromide and higher alcohol.
2. Does not react with alkyl bromide or alcohol.
4. Is easily separable from water solution of inorganic salts and from product alcohol.

In addition to acetone, solvents which meet these requirements are dioxane, methyl ethyl ketone and tetrahydrofuran.

Although alcohol is produced by direct reaction of water with the alkyl halide a base is required to react with the hydrogen bromide or hydrogen chloride released in the reaction because the aqueous halogen acid catalyzes the elimination of hydrogen bromide from the alkyl halide to form olefin and also reacts with the solvent and causes corrosion of the metal reaction vessel. On the other hand, OH—competes with water in the reaction with alkyl halide and in so doing also causes olefin formation. Therefore the stoichiometry of the system is such that all hydrogen halide liberated by the reaction of water with alkyl halide is neutralized but the concentration of OH—kept to a minimum at any time in the course of the reaction. Bases which fulfill these requirements are those which behave as buffers and maintain the pH above 7 and below about 12 at room temperatures, or those which by reason of their very low solubility maintain the OH—concentration in this range. Examples of such buffering bases are the monobasic alkali metal salts of carbonic acid, the alkali metal or alkaline earth metal salts of acetic acid, the alkaline earth metal oxides and hydroxides such as magnesium oxide and calcium hydroxide, etc. NaHCO₃ is a preferred base because its use results in optimum yields of alcohol and because it is soluble in the reaction system.

Hydrolysis is effected by heating and agitating the mixture of halide, water, acetone and the base, e.g., NaHCO₃, in suitable apparatus, e.g., an autoclave provided with means for heating and agitation, and for controlling temperatures and pressures. It has been found that the reaction may be carried out satisfactorily at elevated temperatures ranging from about 190°C, preferably 200°C to 250°C, preferably 230°C, with autogeneous pressures ranging from about 400 p.s.i.g. to 1000 p.s.i.g. At these temperatures a substantially homogeneous liquid phase is provided during reaction.

The reaction proceeds satisfactorily when about 1 equivalent of the base per equivalent of the alkyl halide is employed. It is advantageous, however, to employ an excess of the base, and 2 equivalents of the base per equivalent of the alkyl halide can be cited as an upper practical limit.

For good results the proportions of acetone and water in the reaction mixture will range, by volume, from about 40% acetone to 80% acetone; the water, 20 to 60%. Desirably, the proportions of acetone and water range from about 50—75% acetone, and 50—25% water. In carrying out the reaction, the acetone and water combined can be present in a weight ratio to the bromoalkane ranging from about 3 to 15, a ratio of 5—10 being preferred.

The reaction is continued until hydrolysis is effected, generally within a period of time varying from about 1 hour to about 4 hours, the reaction proceeding faster at the higher temperatures.

The following examples are given further to illustrate the practice of the invention.
Example 1
A slurry of sodium bicarbonate comprising 39.8 g. sodium bicarbonate and 254 ml. water was placed in an autoclave. 96.3 g. hexadecyl bromide and 635 ml. acetone were then added. The autoclave was sealed and while stirring (590 r.p.m.) it was heated to a temperature of 218° C. over a period of 1 hour 15 minutes. The temperature was maintained at 218°-220° C. for an additional hour. At the end of the reaction the autoclave was cooled to about 50° C., that is, to a temperature at which the alcohol remains molten. The autoclave was then rinsed with acetone and 1-N hydrochloric acid to neutralize the sodium bicarbonate. The reaction mixture was diluted with an equivalent volume of water and then extracted with n-pentane. (Other suitable water-insoluble solvents such as benzene, carbon tetrachloride, chloroform, petroleum ether and the like can be used for extraction.) The pentane extract was washed with water and then dried over magnesium sulfate. The dried solution was filtered and evaporated. The residue was melted and a vacuum applied to remove the last traces of pentane. On distillation a yield of 94.8% of the theoretical yield of hexadecanol was recovered.

Example 2
5.80 g. of hexadecyl bromide, 36 ml. of 60% aqueous dioxane and 0.73 g. of calcium oxide were placed in an ampoule. The ampoule was then heated, while shaking, to a temperature of 220° C. over a period of 1 hour, and maintained at this temperature for 1 hour. After the reaction the ampoule was cooled and the products worked up as in Example 1. Analysis for alcohol content by Zerewitinoff active hydrogen determination showed the yield to be 92.5%.

Example 3
Example 2 was repeated except that 36 ml. of pure water was substituted for the 60% dioxane solvent. The yield of alcohol was 52.7%. This example shows that in the absence of a co-solvent the yields of desired alcohol are very inferior.

Example 4
Example 2 was repeated except that 36 ml. of 60% n-butanol in water was substituted for the 60% dioxane solvent. The yield of alcohol was 44%. This example shows that n-butanol is a much inferior co-solvent to acetone or dioxane.

Example 5
Example 2 was repeated except that 36 ml. of 20% acetone in water was substituted for the 60% dioxane solvent and the time at temperature was increased to 6 hours. The yield of alcohol was 71%. This example illustrates that the yield of alcohol is adversely affected by a low acetone content in the solvent.

Example 6
Example 2 was repeated except that magnesium oxide was substituted for the calcium oxide employed in Example 2, the magnesium oxide being employed in chemically equivalent amounts to the calcium oxide. Analysis of the product gave a percent yield of hexadecanol of 95.6.

Example 7
Example 2 was repeated except that calcium carbonate was employed in place of the calcium oxide in equivalent amounts. Analysis showed the yield to be 96.8%.

Example 8
Example 2 was repeated except that 36 ml. of 80% acetone in water was substituted for the 60% dioxane. The yield of hexadecanol was 86%. This example demonstrates that the specified upper limit of co-solvent concentration should not be exceeded.

Example 9
Example 2 was repeated except that an equivalent amount of sodium hydroxide was substituted for the calcium oxide. The yield in this case was 75.4%. This shows that a weak base is necessary in order to obtain high yields.

Example 10
Tetradecyl chloride was hydrolyzed in 60% aqueous dioxane at 275° C. for 6 hours in the presence of excess magnesium oxide. The yield of tetradecanol was 94.1%.

Example 11
194.3 g. (0.538 mole) of 1-bromoeicosane was mixed with 1035 ml. of acetone and water, the acetone being present in an amount by volume of 70% and the water in an amount of 30% by volume, the mixture containing in addition 38.7 g. (0.387 mole) of calcium carbonate. The mixture was heated, with shaking, in a 2.5 liter stainless steel autoclave for one hour at 250° C. When cool, the reaction mixture was diluted with water and extracted with pentane which, in turn, was washed with fresh water. The pentane solution was dried and evaporated. Analysis of the residual product showed that the yield was 131.3 g. or 81.8% of theory of n-eicosanol.

Example 12
110.6 g. (0.500 mole) of 1-bromodecane was mixed with 100 ml. of an acetone-water mixture, the acetone being present in an amount by volume of 60%, and the water 40% by volume, the acetone-water mixture containing in addition 53.9 g. (0.641 mole) of sodium bicarbonate. The mixture was heated, with stirring, in a 2 liter stainless steel autoclave for one hour at 216° C. When the reaction mixture was cool, the acetone was removed by distillation and the residue extracted thoroughly with pentane. The pentane solution was washed with water, dried and evaporated. On distillation of the product, 73.5 g. of 1-decanol was recovered, i.e., a yield of 93.6% of theory.

Example 13
55.9 g. (0.353 mole) of 1-bromohexane was mixed with 945 ml. of an acetone-water mixture, 70% by volume, acetone and 30% by volume water, containing 55.9 g. (0.667 mole) of sodium bicarbonate. The mixture was heated, with stirring, in a 2 liter stainless steel autoclave for one hour at 210° C. When the reaction mixture was cool, the acetone was removed by distillation and the residue extracted with pentane. The pentane solution was not washed with water, but was dried with a desiccant and the solvent evaporated. Analysis of the mixture by Zerewitinoff active hydrogen analysis indicated a yield of 29.4 g. or 86.5% of theory of n-hexanol. The actual yield of alcohol in this case is probably greater than 90%. Due to the increased water solubility of the low molecular weight alcohol, it is very likely that some product was lost to a water phase in the workup procedure.

Example 14
Hexadecyl bromide (5.8 g.), methyl ethyl ketone (21.6 ml), water (14.4 ml) and calcium carbonate (1.50 g) were sealed in a glass tube and heated for 1 hour at 210° C. When cool, the tube was opened and the product extracted into pentane which was then washed, dried and evaporated. Analysis of the residue showed that the yield of hexadecanol was 94.7% of theory.

We claim:
1. A process for hydrolyzing a primary alkyl halide containing from 5 to 20 carbon atoms in the molecule selected from the group consisting of alkyl bromides and chlorides to produce the corresponding primary alcohols with a minimum of undesirable side reaction products, which comprises hydrolyzing in a confined zone at autogenous pressure and at a temperature within about the
range 190° C. to 250° C. the alkyl halide in the presence of acetone, water and a base capable of maintaining the pH above 7 and below about 12, the proportions, by volume, of acetone and water ranging from about 40% to 80% acetone and 20% to 60% water, the acetone and water combined being present in an amount sufficient to keep the alkyl halide in solution during the reaction.

2. Process according to claim 1, wherein the base is sodium bicarbonate.

3. Process according to claim 1, wherein the alkyl halide is a 1-bromoalkane containing 5 to 20 carbon atoms in the molecule.

4. Process according to claim 1, wherein the acetone and water combined are present in a weight ratio to the alkyl halide ranging from about 3 to 15.

5. Process according to claim 4, wherein the acetone and water combined are present in a weight ratio of 5 to 10.

6. Process according to claim 5, wherein the mixture is heated to a temperature of about 210° C. to 230° C.

7. Process according to claim 5, wherein the proportions, by volume, of acetone and water range from about 50–75% acetone, and 50–25% water.

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