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ACETALS AND PROCESS FOR MAKING THE SAME

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1

This invention concerns an improved process for making an acetal by reaction of a saturated aliphatic aldehyde and a primary or a secondary monohydric alkyl alcohol. It relates more particularly to procedure for carrying out the reaction in vapor phase in the absence of a catalyst.

It is known to prepare acetals by reacting an aldehyde with a monohydric alcohol in liquid phase in the presence of a catalytic amount of an acid such as hydrochloric acid or nitric acid, or in the presence of an inorganic salt, e. g. calcium chloride, calcium nitrate, aluminum chloride, or magnesium chloride, as a condensing agent, or in the presence of both an acid and a condensing agent.

The methods heretofore proposed for reacting an aldehyde with an alcohol in liquid phase in the presence of an acid catalyst, or a condensing agent, have not been entirely satisfactory for production of an acetal on a commercial scale, particularly with regard to the rate at which the reaction proceeds. The presence of traces of the catalyst material in the crude reaction product frequently catalyzes the reverse reaction so that much of the acetal product may be lost during recovery of the same from the reaction mixture, with resultant lower overall yields of acetal product.

It is an object of the invention to provide an improved process for reacting a saturated aliphatic aldehyde with a monohydric alkyl alcohol to form the corresponding acetal in the absence of a catalyst. Another object is to provide a process for carrying out the reaction in vapor phase. Still another object is to provide a process for making an acetal by reaction of a saturated aliphatic aldehyde and a monohydric primary or secondary alkyl alcohol in vapor phase in the absence of a catalyst. Other and related objects will become apparent from the following description of the invention.

The manner in which the reaction of a saturated aliphatic aldehyde and a monohydric alkyl alcohol proceeds in vapor phase in the absence of a catalyst varies widely, depending for the most part upon the aldehyde and the alcohol employed as reactants. In general, the lower aliphatic aldehydes and alkyl alcohols are most reactive to form the corresponding acetals, whereas many combinations of a saturated aliphatic aldehyde and a monohydric alkyl alcohol apparently undergo little, if any, reaction in vapor phase to form an acetal in the absence of a catalyst, particularly when both of the reactants contain more than three carbon atoms in the molecule.

2

We have now discovered that a saturated aliphatic aldehyde containing from 1 to 7 carbon atoms in the molecule and a primary or a secondary monohydric alkyl alcohol containing from 1 to 6 carbon atoms in the molecule can readily be reacted in vapor phase to form a corresponding acetal in good yield in the absence of a catalyst, when at least one of the reactants, i. e. the aldehyde or the alcohol, contains not more than one carbon atom in the molecule.

Accordingly, in a preferred embodiment, the invention concerns procedure for reacting in vapor phase, a saturated aliphatic aldehyde containing from 1 to 7 carbon atoms in the molecule and a primary or a secondary monohydric alkyl alcohol containing from 1 to 6 carbon atoms in the molecule, wherein at least one of the reactants, i. e. the aldehyde or the alcohol, contains a single carbon atom in the molecule. The reaction to form the acetal is carried out by passing the reactants through a heated zone wherein vapors of the aldehyde and the alcohol in admixture with each other are heated to a reaction temperature of not more than 600° C., preferably not more than 500° C., in the absence of a catalyst, cooling the effluent vapors to condense liquid product and separating the acetal from the condensed liquor.

A method of reacting in vapor phase, a saturated aliphatic aldehyde containing from two to three carbon atoms in the molecule and a monohydric lower alkyl alcohol, in the absence of a catalyst to form a corresponding acetal is claimed in our copending application Serial No. 147,135, filed concurrently herewith.

As the alcohol starting material, any of the primary or secondary monohydric alkyl alcohols containing from 1 to 6 carbon atoms in the molecule may be used. Examples of suitable alcohols are methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec.-butyl alcohol, isobutyl alcohol, n-amyl alcohol, isoamyl alcohol, 1-hexanol, 2-hexanol and 3-hexanol.

The aldehyde reactant is selected from the saturated aliphatic aldehydes such as formaldehyde or its homologues containing from 1 to 7 carbon atoms in the molecule. Examples of aliphatic aldehydes which are suitable are, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, 2-methylbutyraldehyde, isovaleraldehyde, n-capronaldehyde, 2-methylvaleraldhyde, 4-methylvaleraldehyde, heptyl aldehyde, and 2-ethylvaleraldehyde.

The reactants, i. e. the aldehyde and the alcohol, are preferably employed in anhydrous, or

substantially anhydrous condition, although the reaction may be carried out in the presence of appreciable amounts of water vapor, or steam. For convenience in handling, formaldehyde is usually employed in admixture with water as an aqueous solution containing 30 per cent by weight or more of formaldehyde.

The aldehyde and the alcohol may be used in any desired proportions, but for reasons of economy, it is preferred to employ the reactants in approximately stoichiometric proportions, i. e. in amounts corresponding to about two molecular proportions of the monohydric alkyl alcohol per molecular equivalent proportion of the saturated aliphatic aldehyde.

The reaction may be carried out at atmospheric, subatmospheric, or superatmospheric pressure, but is preferably carried out at atmospheric pressure, or slightly above, e. g. at pressures of from 2 to 50 pounds per square inch gauge, and in the substantial absence of air, or oxygen. The reaction is usually carried out by passing a mixture of the vapors of the alcohol and the aldehyde through a heated tube, or other suitable reaction vessel, preferably constructed of non-metallic material such as glass, quartz, graphite, ceramic, or glass enameled steel, in the presence or absence, of steam, or an inert gas such as nitrogen, or helium, as a diluent or sweep gas, to provide a positive flow of vapor through the reaction zone. Such diluent gases usually provide more uniform distribution of heat throughout the reaction and reduce the tendency toward decomposition of the reactants, or the products.

The reaction time, i. e. the time of heating the vapors at a reaction temperature, to obtain the maximum yield of acetal will vary depending upon the aliphatic aldehyde and the alcohol employed in the reaction. The vapors should not be heated at a reaction temperature for a time such as to cause excessive decomposition of the reactants, or products. The reaction time can readily be controlled by regulating the flow of the reactant vapors to the reaction zone. In general, satisfactory results are obtained by heating the mixture of vapors to a reaction temperature for a contact time of from 0.1 to 10 seconds.

The saturated aliphatic aldehyde and the monohydric alkyl alcohol, i. e. the reactants, may be fed separately into admixture with each other in a preheater, or vaporizer, maintained at a temperature above the boiling point of the reactants to rapidly vaporize the same, or the reactants may be mixed together in the desired proportions and the mixture rapidly vaporized by feeding the same into a vaporizing chamber. Such vaporizing chamber may conveniently be an adjacent portion of the reaction vessel, e. g. one end of a heated tube, so that the vapors are quickly heated to a reaction temperature. In practice, the aliphatic aldehyde and the alcohol are preferably mixed together in the desired proportions and the mixture is vaporized by feeding the same into a preheater, or vaporizer, maintained at a temperature sufficiently above the boiling point of the reactants to rapidly vaporize the same. The mixture of vapors is immediately passed through a heated zone wherein the vapors are heated to a reaction temperature of not more than 600° C. for a contact time of from 0.1 to 10 seconds to cause a reaction between the saturated aliphatic aldehyde and the monohydric alcohol and form the corresponding acetal. The effluent reaction vapors are cooled to condense the liquid product, i. e. the acetal together with water formed in the reaction and any unreacted aldehyde and alcohol, and separate it from the permanently gaseous components such as hydrogen, or carbon monoxide, which may also be formed in the reaction, or from inert gas, e. g. nitrogen, which may be used as a sweep gas in the process. The condensed liquor is fractionally distilled to recover the acetal product and separate it from the lower boiling ingredients, e. g. the unreacted aldehyde and alcohol, and the higher boiling residue. The aldehyde and the alcohol thus recovered may be reused in the process.

The following examples illustrate practice of the invention, but are not to be construed as limiting the scope thereof.

Example 1

A solution consisting of 198 grams (6.2 moles) of methanol and 271 grams of an aqueous solution containing 36 per cent by weight of formaldehyde was fed at an average rate of about 2.5 cc. of the solution per minute, together with a stream of nitrogen flowing at a rate of about 25 cc. per minute at 25° C. and 1 atmosphere, into one end of a heated quartz tube 60 centimeters long having an internal diameter of 4 centimeters, packed with ¼ inch ceramic saddles to form a bed 48 centimeters deep. The solution was immediately vaporized and the mixture of vapors was heated to a temperature of approximately 350° C. for a contact time of about 6 seconds during passage through the bed. By contact time is meant the time for flow through the bed of an infinitesimal portion of the vapor mixture. The effluent vapors were cooled to condense the liquid product and separate it from the nitrogen employed as a sweep gas. There was obtained 436 grams of condensed liquor. The condensed liquor was fractionally distilled and found to consist of 3.0 per cent by weight of unreacted formaldehyde, 5.9 per cent of methyl formate, 34.3 per cent of methylal, 16.6 per cent of unreacted methanol and 40.2 per cent of water. The methylal product corresponds to a yield of 50.5 per cent based on the combined weight of the formaldehyde and methyl alcohol starting materials.

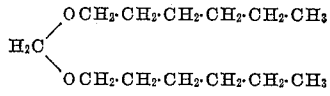
Example 2

A solution consisting of 198 grams (6.2 moles) of methyl alcohol and 196 grams (4.5 moles) of acetaldehyde was fed at a rate of about 3.9 cc. of the solution per minute into the heated quartz tube described in Example 1. The solution was immediately vaporized and the mixture of vapors heated to a reaction temperature of 350° C. for a contact time of about 4 seconds during passage through the tube. The effluent vapor was cooled to condense liquid product. There was obtained 385 grams of liquid condensate. It was fractionally distilled. There were obtained 140 grams of unreacted acetaldehyde, 121 grams of methyl alcohol, 103 grams of dimethylacetal and 21 grams of water. The yield of dimethylacetal was 26.2 per cent, based on the combined weight of the acetaldehyde and the methyl alcohol starting materials. The yield of dimethylacetal was 94.5 per cent of theoretical, based on the methanol consumed in the reaction.

Example 3

A solution consisting of 183 grams (1.8 moles) of normal hexyl alcohol and 19 grams (0.63 mole) of formaldehyde dissolved in 30 grams of water was fed at a rate of 3.9 cc. of the solution per minute into one end of a heated glass tube 94 centimeters long having an internal diameter of

2.54 centimeters. The tube was packed with ¼ inch ceramic saddles to form a bed 60 centimeters deep, consisting of an upper preheating zone 28 centimeters long and a lower reaction zone 32 centimeters long. The solution was rapidly vaporized in the preheating zone and the mixture of vapors was immediately heated to a reaction temperature of 460° C. for a contact time of about 1.4 seconds during passage through the reaction zone. By contact time is meant the time required for flow through the reaction zone of an infinitesimal portion of the vapor mixture. The effluent vapor was cooled to condense liquid products. There was obtained 230 grams of liquid condensate. The condensate was fractionally distilled. There were obtained 4 grams of formaldehyde, 33 grams of water, 102 grams (1 mole) of unreacted normal hexyl alcohol and 91 grams (0.42 mole) of 1,1-dihexoxy methane boiling at 150°–155° C., at an absolute pressure of 30 millimeters of Hg. The 1,1-dihexoxy methane was redistilled. A fraction boiling at 147.5° C. at 25 millimeters pressure had a specific gravity of 0.8360 at 25° C. compared to water at the same temperature, a refractive index $n_D^{25°}=1.4215$ and a freezing point of minus 24.7° C. The 1,1-dihexoxy methane is a new compound having the formula:



The new compound is useful as a solvent and also in the manufacture of perfumes.

Example 4

A solution consisting of 78 grams (1.34 moles) of propionaldehyde and 101 grams (3.15 moles) of methyl alcohol was fed at a rate of 4 cc. of the solution per minute into the heated tube described in Example 3. The solution was immediately vaporized in the preheating zone and the mixture of vapors was heated to a reaction temperature of 350° C. for a contact time of about 1.3 seconds during passage through the reaction zone. The effluent vapor was cooled to condense liquid product. There was obtained 177 grams of liquid condensate. It was analyzed and found to consist of 4.5 per cent by weight of propionaldehyde, 13 per cent of methyl alcohol, 70 per cent of dimethylacetal of propionaldehyde and 12.5 per cent of water. The acetal product corresponds to a yield of 69.4 per cent, based on the combined weight of the propionaldehyde and the methyl alcohol starting materials.

Example 5

A solution consisting of 339 grams (2.97 moles) of heptaldehyde and 191 grams (5.95 moles) of methyl alcohol was fed at a rate of about 2.5 cc. of the solution per minute into the reactor described in Example 3. The solution was immediately vaporized and the mixture of vapors heated to a temperature of 460° C., for a contact time of about 2.5 seconds during passage through the reaction zone. The effluent vapor was cooled to condense liquid product. There was obtained 525 grams of liquid condensate. An amount of the condensate weighing 366 grams was dried over calcium chloride and the organic layer separated. There was obtained 242 grams of liquid. It was fractionally distilled. There were obtained 153 grams of methanol, water and unreacted heptaldehyde, 54 grams of 1,1-dimethoxy heptane boiling at 83°–83.5° C. at 25 millimeters absolute pressure and having a specific gravity of 0.844 at 25° C. compared to water at the same temperature, and 35 grams of higher boiling liquid residue. The yield of 1,1-dimethoxy heptane was 14.6 per cent, based on the combined weight of the heptaldehyde and the methyl alcohol starting materials.

Other modes of applying the principle of the invention may be employed instead of those explained, change being made as regards the method or products herein disclosed, provided the steps or products stated by any of the following claims or the equivalent of such stated steps or products be employed.

We claim:

1. A process for making an acetal which comprises passing a vapor mixture containing as the essential reactants a saturated aliphatic aldehyde having from 1 to 7 carbon atoms in the molecule and a monohydric alkyl alcohol having from 1 to 6 carbon atoms in the molecule, in which vapor mixture at least one of the reactants contains not more than one carbon atom in the molecule, through a heated zone wherein the mixture of vapors is heated to a reaction temperature of from 350° to 600° C. in the absence of a catalyst for a contact time of from 0.1 to 10 seconds, cooling the effluent vapors to condense liquid product and separating the acetal from the condensed liquid.

2. A process for making an acetal which comprises passing a vapor mixture containing as the essential reactants formaldehyde and a monohydric alkyl alcohol having from 1 to 6 carbon atoms in the molecule through a heated zone wherein the mixture of vapors is heated to a reaction temperature of from 350° to 600° C. in the absence of a catalyst for a contact time of from 0.1 to 10 seconds, cooling the effluent vapor to condense liquid product and separating the acetal from the condensed liquid.

3. A process for making an acetal as claimed in claim 2 wherein the alcohol is ethyl alcohol.

4. A process for making an acetal as claimed in claim 2 wherein the alcohol is normal propyl alcohol.

5. A process for making an acetal as claimed in claim 2 wherein the alcohol is normal butyl alcohol.

6. A process for making 1,1-dihexoxy methane which comprises passing a vapor mixture containing as the essential reactants formaldehyde and normal hexyl alcohol through a heated zone wherein the mixture of vapors is heated to a reaction temperature of from 350° to 600° C. in the absence of a catalyst for a contact time of from 0.1 to 10 seconds, cooling the effluent vapor to condense liquid product and separating the 1,1-dihexoxy methane from the condensed liquid.

7. A process for making an acetal which comprises passing a vapor mixture containing as the essential reactants methyl alcohol and a saturated aliphatic aldehyde having from 1 to 7 carbon atoms in the molecule through a heated zone wherein the mixture of vapors is heated to a reaction temperature of from 350° to 600° C. in the absence of a catalyst for a contact time of from 0.1 to 10 seconds, cooling the effluent vapor to condense liquid product and separating the acetal from the condensed liquid.

8. A process for making an acetal as claimed in claim 7 wherein the aldehyde is formaldehyde.

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