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CONDENSATION OF KETONES

Charles A. Cohen, Elizabeth, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

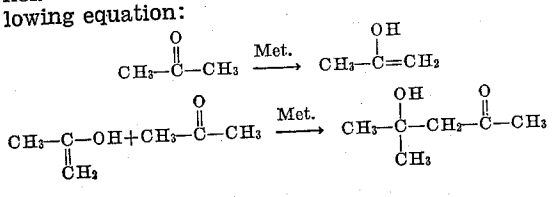
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10 Claims. (Cl. 260—594)

The present invention relates to an improved ketol condensation. More particularly, it relates to an improved method for the catalytic condensation of acetone (dimethyl ketone) to form diacetone alcohol.

The condensation of acetone to diacetone alcohol is an old and well known reaction. In a study of the mechanism of this reaction, Koelichen (Zeitschrift für Physicalische Chemie, vol. 33, page 129) determined that it was the hydroxyl ion concentration which controlled the speed and completeness of this reaction. A number of patents covering this reaction and means for controlling the hydroxyl ion concentration have issued as, for example, U. S. Patent 1,066,474 to Doerflinger, 1,075,284 to Crockett, 1,082,424 to Hoffmann, 1,550,792 to Edmonds, 1,654,103 to Thomson, 1,701,473 to Ellis, and 1,937,272 to Guinot, etc. Previous workers (Freer: Liebigs Annalen, vol. 278, p. 116) have studied the action of alkali metals on acetone, but worked under conditions such that no ketol condensation products were formed.

It has now been found that it is not necessary to have any free hydroxyl ions present to effect the ketol condensation, but, in fact, it has been found to be exceedingly advantageous to eliminate the hydroxyl ion completely from the reaction zone. The present invention is based upon the discovery that the elements of the first and second group of the periodic table, as a solution of the reaction product of these metals with organic materials, other than acids, having labile hydrogen atoms in a solvent such as an anhydrous aliphatic alcohol which is miscible with ketones, readily catalyze the ketol condensation. Also, the metal itself may be brought into solution in a solvent in which case the metal may enter into chemical combination with the solvent. This does not, however, lessen the activity of the metal as a ketol condensation catalyst. It is believed that the true mechanism of the condensation of ketones, as for example, acetone to diacetone alcohol, involves the initial enolization of part of the ketones to the corresponding unsaturated alcohol which condenses with another part of ketone to form the keto-alcohol. This may be graphically shown by the following equation:



Alkali metals or alkali metal alcoholates are known to be enolizing agents but in the past have always been employed in substantially molar proportions. It has now been found that catalytic quantities of the alkali or alkaline earth metals or their alcoholates should be employed and that quantities in the range of one one-hundredth to one ten-thousandth of a mol of the catalyst per liter of the ketone is sufficient to cause ketol condensation. It has also been found that in working with these catalytic materials, moderately low temperatures are advantageously employed to give increased yields, a shorter time of reaction and an absence of higher condensation products. The range of acceptable temperatures is between 0° C. and 20° C. Temperatures much in excess of 20° C. bring about side reactions the products of which discolor the desired product and lower the yield somewhat. The amount of catalyst to be used is to be determined by the quality of ketone used. If the ketone is substantially neutral and free from esters and acids, the quantity of catalyst is as previously stated. However, with some commercial ketones which have a high acidity, sufficient of the catalyst to neutralize the acidity and yield catalytic proportions in excess will be required. Another way of stating the amount of catalyst used is to say that the amount of catalyst to add to the ketones should be the same as the amount of metal which, when added to a volume of water equal to the volume of ketone, would give the water a pH equivalent of from 8 to 10. Sodium and calcium are metals in the first and second group, the isopropylates of which for example catalyze this reaction. Various anhydrous alcohols, such as ethyl, isopropyl, methyl and amyl alcohols, may be used as solvents for the metallic catalyst if desired, although their presence is not always required. The catalyst may be present in the solvent in any proportion up to the limit of its solubility. Since the amount of solvent, if employed, is in most cases less than 1%, it is not necessary to employ elaborate methods for its separation and may, in most cases, be disregarded entirely because it will be substantially completely removed from the condensation product along with the unreacted ketone, by distillation. Although the reaction proceeds readily under the conditions employed, the reaction time differs depending on the purity of the acetone and the temperature employed. With pure acetone, for instance, the reaction is complete in from .5 to 4 hours at a temperature of 15° C. In any event, the com-

plete time of reaction can be ascertained by measuring the refractive index of the reacting mixture. When there is no longer a perceptible change in the refractive index, the reaction is complete. When the reaction is complete, the catalyst is removed by reacting it with an acid. Any acid, such as sulphuric acid may be used for this purpose. The salt formed by the reaction between the acid and the catalyst is insoluble and may be removed by filtration. Since theoretically the ketone will not all condense, in one reaction, the unreacted ketone may be recycled, thus making the process a continuous one. The condensed ketone produced according to this invention, is substantially pure but may be further purified by distillation under vacuum if desired. The products of this reaction are useful as intermediates, as, for example, those of acetone in the production of mesityl oxide or hexylene glycol, or methyl isobutyl ketone or diolefines.

The following example is given for the purpose of illustrating the invention.

Example

1000 parts by volume of acetone were cooled to between 0° C.–10° C. 5 parts by volume of a 1 gm. per 100 cc. solution of metallic sodium in anhydrous isopropyl alcohol were then stirred into the cool acetone. The mixture was occasionally agitated for one hour after which the sodium was removed by the addition of stoichiometrical proportions of sulphuric acid dissolved in anhydrous alcohol. The sodium salt of the acid precipitated and was removed by filtration. The clear filtrate was fractionated, taking overhead the excess acetone which was recycled. 140 parts by volume of pure diacetone alcohol remained in the still bottoms. When distilled at reduced pressure the diacetone alcohol boiled at 79° C. at a pressure of 35 mms. of mercury.

The foregoing disclosure and example is given for the purposes of illustration only and is not to be construed as in any way limiting the invention.

What is claimed is:

1. The process of producing keto-alcohols which comprises condensing ketones in a medium free of hydroxyl ions and in the presence of an anhydrous metal alcoholate, the metal element of which is selected from the first and second groups of the periodic table.

2. The process of producing diacetone alcohol which comprises condensing acetone at 0°–20° C. in a medium free of hydroxyl ions and in the presence of an anhydrous metal alcoholate the metal element of which is selected from the first and second groups of the periodic table.

3. A process of producing diacetone alcohol which comprises condensing acetone at 0–20° C. in a medium free of hydroxyl ions and in the presence of one one-hundredth to one ten-thousandth mol per liter of acetone of an anhydrous metal alcoholate, the metal element of which is selected from the first and second groups of the periodic table.

4. The method of producing diacetone alcohol which comprises condensing acetone at 0–20° C. in a medium free of hydroxyl ions and in the presence of an anhydrous sodium ethylate in the proportion of one one-hundredth to one ten-thousandth mol of sodium ethylate per liter of acetone and recovering the diacetone alcohol.

5. The process of producing diacetone alcohol which comprises condensing acetone at 0–20° C. in a medium free of hydroxyl ions and in the presence of one one-hundredth to one ten-thousandth of a mol of metallic sodium per liter of acetone dissolved in anhydrous ethyl alcohol and recovering the diacetone alcohol.

6. The method of producing diacetone alcohol which comprises condensing acetone at 0–20° C. in a medium free of hydroxyl ions and in the presence of one one-hundredth to one ten-thousandth of a mol of metallic sodium per liter of acetone dissolved in an anhydrous aliphatic saturated alcohol containing from 1 to 6 carbon atoms, distilling off the unreacted acetone and recovering the diacetone alcohol.

7. The method of producing diacetone alcohol which comprises condensing acetone at 0–20° C. in a medium free of hydroxyl ions and in the presence of one one-hundredth to one ten-thousandth of a mol of metallic sodium per liter of acetone dissolved in an anhydrous aliphatic saturated alcohol containing from 1 to 4 carbon atoms, precipitating the catalyst with an acid, distilling off the unreacted acetone and recovering the diacetone alcohol.

8. The method of producing diacetone alcohol which comprises condensing acetone at 0–20° C. in a medium free of hydroxyl ions and in the presence of one one-hundredth to one ten-thousandth of a mol of anhydrous sodium methylate per liter of acetone dissolved in an anhydrous aliphatic saturated alcohol containing from 1 to 6 carbon atoms, distilling off the unreacted acetone and recovering the diacetone alcohol.

9. The method of producing diacetone alcohol which comprises condensing acetone at 0–20° C. in a medium free of hydroxyl ions and in the presence of one one-hundredth to one ten-thousandth of a mol of anhydrous sodium isopropylate per liter of acetone dissolved in an anhydrous aliphatic saturated alcohol containing from 1 to 6 carbon atoms, distilling off the unreacted acetone and recovering the diacetone alcohol.

10. A method of producing diacetone alcohol which comprises condensing acetone at 0–20° C. in a medium free of hydroxyl ions and in the presence of one one-hundredth to one ten-thousandth of a mol of metallic sodium per liter of acetone dissolved in an anhydrous aliphatic saturated alcohol containing from 1 to 6 carbon atoms, removing the catalyst by precipitation with sulfuric acid, filtering, distilling off the unreacted acetone from the filtrate and recovering the diacetone alcohol.

CHARLES A. COHEN.