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DEHYDRATION OF ALKYL KETONES

Vladimir N. Ipatieff, Chicago, and Carl B. Linn, Riverside, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention relates to a process for dehydrating an alkyl ketone in the presence of a particular catalyst. More specifically the invention is concerned with a process for manufacturing mesitylene from acetone.

An object of this invention is to provide an improved process for dehydrating an alkyl ketone to produce unsaturated compounds.

Another object of this invention is the production of cyclic unsaturated compounds.

A further object of this invention is the production of trialkyl benzene hydrocarbons.

A still further object of this invention is the production of unsaturated compounds including higher molecular weight unsaturated ketones and trialkyl benzene hydrocarbons by treating an alkyl ketone at an elevated temperature in the presence of a salt, and particularly a halide, of a metal of the iron group consisting of iron, cobalt, and nickel.

One specific embodiment of this invention relates to a process which comprises reacting an alkyl ketone at a temperature of from about 150° to about 450° C. in the presence of a halide of a metal of the iron group.

A further embodiment of this invention relates to a process for producing mesitylene which comprises reacting acetone at a temperature of from about 250° to about 450° C. in the presence of a halide of a metal of the iron group consisting of iron, cobalt, and nickel.

Alkyl ketones utilizable as starting materials for our process comprise dialkyl ketones and alkyl aryl ketones. We prefer to charge to our process methyl ketones including acetone, methyl ethyl ketone, methyl propyl and methyl isopropyl ketones, other methyl alkyl ketones, acetophenone, etc. These compounds yield mesitylene type hydrocarbons; that is, acetone yields mesitylene whereas the other methyl ketones yield symmetrical trialkyl and triaryl benzene hydrocarbons. However, aliphatic ketones other than the methyl ketones are converted by our process into unsaturated organic compounds including unsaturated ketones such as mesityl oxide and isophorone and also into olefins and into hexa-alkyl benzene hydrocarbons. The benzene hydrocarbons formed in this process are true unsaturated organic compounds because they will combine with hydrogen in the presence of a hydrogenation catalyst to produce cyclohexane hydrocarbons which are saturated hydrocarbons.

The catalysts utilizable in our process comprise salts of a mineral acid and of a metal of the iron group. The preferred catalysts comprise the middle halides (that is, the chlorides and bromides) of iron, cobalt, and nickel. These different catalytic materials may be used individually or in combination with one another.

After this treatment, the reaction product is

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separated into unconverted ketone, small amounts of unsaturated ketones, the poly-alkyl benzene hydrocarbon, and higher boiling condensation products. The unconverted ketone and unsaturated ketones formed in the process are then subjected to further conversion treatment in the presence of the catalyst to produce an additional quantity of polyalkyl benzene hydrocarbon.

In order to obtain a relatively high yield of mesitylene from acetone, or of other poly-alkyl benzene hydrocarbons from other methyl ketones, we prefer to operate our process in a continuous manner. This is accomplished by commingling the alkyl ketone and an aqueous solution of a metal salt and passing the commingled mixture through a reactor maintained at a temperature of from about 150° C. to the critical temperature of the reaction mixture. When employing high proportions of catalyst solution relative to the amount of ketone charged, the preferred maximum operating temperature will thus approach the critical temperature of water, namely, about 374° C. with an operating pressure of 225 or more atmospheres. In general, the operating pressure employed is at least that needed to keep the reaction mixture in substantially liquid phase and thus prevent the deposition and accumulation of the catalyst in the heated reaction zone as would occur at lower pressures. In order to produce relatively high yields of mesitylene and its homologs, it is preferred to treat the alkyl ketone at a temperature of at least 250° C. as at lower temperatures production of mesityl oxide is the principal reaction of the process.

The catalyst solution so employed in the continuous treatment of an alkyl ketone is recovered from the reaction products and recycled for treating an additonal quantity of the alkyl ketone. Not only the catalyst solution, but also the unsaturated carbonyl compounds including mesityl oxide and isophorone, which are by-products of the dehydration of acetone, are recycled and commingled with the fresh alkyl ketone being charged to the process.

The following examples are given to indicate the type of results obtained in our process although not with the intention of limiting unduly the broad scope of the invention.

Example I

A rotatable steel autoclave of 850 cc. capacity was charged with 157 grams of acetone, 20 grams of water, and 10 grams of nickel chloride, $NiCl_2 \cdot 6H_2O$. Hydrogen was then introduced to the charged autoclave to 100 atmospheres pressure after which it was heated at 250° C. for 12 hours. The reaction product consisted of 155 grams of an upper layer and 20 grams of a lower layer, the latter containing the catalyst. Distillation of the upper layer gave 115 grams of un-

converted acetone, 14 grams of water, 4.5 grams of liquid boiling from 60° to 160° C. consisting mostly of mesityl oxide, 3.5 grams of a mesitylene fraction, and 1.6 grams of higher boiling material.

Example II

The autoclave employed in Example I was charged with 157 grams of acetone, 20 grams of water, 10 grams of ferric chloride, hydrogen was introduced to the autoclave to a pressure of 100 atmospheres; and the charged autoclave was then heated at 150° C. for 12 hours. The recovered reaction products consisted of 154 grams of upper layer and 14 grams of lower layer. Distillation of the upper layer yielded 131 grams of acetone, 8.5 grams of water, 5 grams of a mesityl oxide fraction, and 1.6 grams of higher boiling liquid organic compounds.

Example III

In this run 394 grams of acetone and 50 grams of ferric chloride were heated at 200° C. for three hours in a rotatable steel autoclave at an operating pressure of 10 atmospheres. In addition to the used catalyst, the reaction products recovered contained 11 grams of condensible gas (mostly isobutylene), 230 grams of unconverted acetone, 8 grams of mesityl oxide, 10 grams of mesitylene, 9 grams of isophorone, 54 grams of liquid organic material boiling above 220° C., and a total of 72 grams of water, acetic acid, and other products.

Example IV

This run was similar to that of Example III except that the mixture of acetone and ferric chloride was heated at 300° C. for three hours at an operating pressure of 42 atmospheres. The resultant reaction products contained 23 grams of condensible gas (mostly isobutylene), 180 grams of unconverted acetone, 10 grams of mesityl oxide, 8 grams of mesitylene, 3 grams of isophorone, 35 grams of organic liquids boiling above 220° C., and a total of 135 grams of water, acetic acid and sludge-like material.

The character of the process of the present invention and its commercial value are evident from the preceding specification and examples although neither section is intended to limit unduly the broad scope of the invention.

We claim as our invention:

1. A process for dehydrating an alkyl ketone which comprises contacting said ketone at a temperature of from about 150° to about 450° C. in the presence of a catalyst comprising as its essential catalytically active ingredient a salt of a metal of the iron group and of a middle halogen.

2. A process for dehydrating an alkyl ketone which comprises contacting said ketone at a temperature of from about 150° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of a salt of a metal of the iron group and of a middle halogen.

3. A process for dehydrating an alkyl ketone which comprises contacting said ketone at a temperature of from about 150° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of a salt of iron and of a middle halogen.

4. A process for dehydrating an alkyl ketone which comprises contacting said ketone at a temperature of from about 150° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of a salt of cobalt and of a middle halogen.

5. A process for dehydrating an alkyl ketone which comprises contacting said ketone at a temperature of from about 150° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of a salt of nickel and of a middle halogen.

6. A process for dehydrating acetone to produce mesitylene which comprises contacting said acetone at a temperature of from about 150° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of a salt of a metal of the iron group and of a middle halogen.

7. A process for dehydrating acetone to produce mesitylene which comprises contacting said acetone at a temperature of from about 150° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of iron chloride.

8. A process for dehydrating acetone to produce mesitylene which comprises contacting said acetone at a temperature of from about 150° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of cobalt chloride.

9. A process for dehydrating acetone to produce mesitylene which comprises contacting said acetone at a temperature of from about 150° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of nickel chloride.

VLADIMIR N. IPATIEFF.
CARL B. LINN.

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