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PURIFICATION OF CYCLIC OLEFINIC KETONES

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This application is a continuation-in-part of our co-pending application Serial No. 570,466, filed December 29, 1944, now abandoned.

This invention relates to an improved process for purifying cyclic olefinic ketones, particularly when the latter are present in admixture with products formed incidental to the preparation of said cyclic ketone.

An object of this invention is an improved process for separating a cyclic olefinic ketone from a mixture consisting of an aliphatic olefinic ketone and a cyclic olefinic ketone.

Another object of this invention is an improved process for removing aliphatic olefinic ketones from a mixture of alkyl ketone condensation products including aliphatic olefinic ketones and cyclic ketones.

A further object of this invention is to provide an improved process for separating mesityl oxide and phorone from isophorone present in a mixture of condensation products of acetone.

One specific embodiment of the present invention relates to a process for separating cyclic olefinic ketones from aliphatic olefinic ketones which comprises treating a mixture of said cyclic and aliphatic olefinic ketones with an aqueous solution of an acid-acting salt at a temperature of from about 100° to about 350° C. to convert aliphatic olefinic ketones into alkyl ketone, and separating said alkyl ketone from unconverted cyclic olefinic ketone.

Another embodiment of this invention relates to a process which comprises condensing an alkyl ketone to form a reaction mixture comprising essentially a cyclic olefinic ketone and an aliphatic olefinic ketone, treating said reaction mixture with an aqueous solution of an acid-acting salt at a temperature of from about 100° to about 350° C. to convert said aliphatic olefinic ketone into alkyl ketone, separating said alkyl ketone from unconverted cyclic olefinic ketone, and recycling said alkyl ketone to further condensation treatment.

A further embodiment of this invention relates to a process for treating a mixture of condensation products of an alkyl ketone with an aqueous solution of an acid-acting salt at a temperature of from about 100° to about 350° C. to convert aliphatic olefinic condensation products of alkyl ketones into alkyl ketone, and separating said alkyl ketone from unconverted cyclic, mono-olefinic ketone condensation products of said alkyl ketone.

A still further embodiment of the present invention relates to a process which comprises

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treating a mixture of acetone condensation products including mesityl oxide, phorone, and isophorone at a temperature of from about 150° to about 350° C. with a dilute aqueous solution of an acid-acting salt whereby said mesityl oxide and phorone are converted into acetone, and separating said acetone from unconverted isophorone.

Acetone may be condensed and cyclized to isophorone by several known methods, but in most of the cases a number of by-products are also formed including unsaturated aliphatic ketones such as mesityl oxide and phorone. Accordingly, when isophorone is the desired reaction product, the yield of this desired material is decreased by the appearance of the mentioned by-products. These different by-products not only cause a loss in yield of desired cyclic, mono-olefinic ketone, but they are also sometimes troublesome to dispose of in large scale commercial operations.

We have observed that mesityl oxide and phorone are converted into acetone by treatment at an elevated temperature in the presence of a relatively large volume of a dilute aqueous solution of an acid-acting salt, while isophorone remains substantially unchanged during this treatment and is recoverable from the reaction mixture in relatively high purity.

While the process of our invention is particularly applicable to the purification of isophorone derived from acetone, this process is also utilizable in purifying homologues of isophorone such as are obtainable by condensation of certain other ketones. An alkyl ketone which is convertible into a homologue of isophorone has at least one hydrogen atom combined chemically with the carbon atom adjacent to the carbonyl carbon atom, while the other carbon atom adjacent to the carbonyl carbon atom is combined chemically to at least two hydrogen atoms. Thus, homologues of isophorone are formed by the condensation of such ketonic compounds including methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, diethyl ketone, ethyl propyl ketone, ethyl isopropyl ketone, etc.

The process of this invention is effected in the presence of a catalyst comprising essentially an aqueous solution of an acid-acting salt. Suitable catalytic materials include particularly aqueous solutions of magnesium chloride, aluminum chloride, iron chloride, nickel chloride, ammonium chloride, and the corresponding bromides and sulfates. The concentration of the acid-acting salt is generally from about 0.05 to about 10% by weight of the total aqueous solution. The cata-

lysts preferred for our process comprise aqueous solutions of acid-acting salts of such concentrations that the solutions have a pH value of less than about 6. The volume of solution used relative to the ketone condensation product undergoing treatment should be such that water is present in more than 200% of the theoretical quantity necessary for conversion of the unsaturated dimers of the alkyl ketones into said alkyl ketones. The temperature of the reaction mixture should be from about 100° to about 350° C. but is preferably from about 150° to about 250° C. It is also desirable to carry out the process at a superatmospheric pressure to maintain in liquid phase a substantial proportion of the reactants and solution of hydrolyzable salt.

The process is carried out by commingling a mixture of the alkyl ketone condensation products with one or more volumes of an aqueous solution of an aicd-acting salt at a temperature and for a time sufficient to convert aliphatic unsaturated ketonic condensation products of alkyl ketones into said alkyl ketones with substantially no influence upon the cyclic, mono-olefinic ketones present in said alkyl ketone condensation product. Thus, when acetone condensation products comprising mesityl oxide, phorone, and isophorone are so treated, the mesityl oxide and phorone are converted into acetone which is dissolved in the aqueous solution and is readily separable from unconverted isophorone. The acetone present in said aqueous solution may then be recovered by suitable means and/or subjected to condensation reaction to produce additional quantities of isophorone. The organic material from which mesityl oxide and phorone were so separated and comprising essentially isophorone is then washed, dried, and distilled to give a fraction comprising substantially pure isophorone.

The following examples are given to illustrate the character of results obtained by the process of our invention, although these data are not introduced with the intention of unduly restricting the broad scope of the invention.

Example I

49 grams of mesityl oxide and 150 grams of an aqueous solution containing 2 to 3% by weight of ferric chloride were heated at 210° C. for 2.5 hours in a rotatable steel autoclave of 450 cc. capacity. The reaction product contained acetone but no mesityl oxide, showing that the mesityl oxide underwent conversion into acetone.

Example II

In another run at the same temperature and operating conditions, 30 grams of phorone when treated with an aqueous solution containing 3% by weight of ferric chloride yielded 73% of acetone and 27% of unconverted phorone.

Example III

49 grams of isophorone and 150 grams of an aqueous solution containing 3% by weight of ferric chloride were contacted in a rotatable steel autoclave at 211° C. for 2 hours. At the end of the run and after the autoclave and reaction mixture had cooled to room temperature, all of the isophorone was recovered unchanged from the reaction mixture.

Example IV

A mixture of acetone condensation products consisting of 10% of isophorone, 25% of phorone, and 65% of mesityl oxide upon treatment with 4 volumes of an aqueous solution containing 3% by weight of ferric chloride at 225° C. for 1 hour yields an organic liquid product comprising essentially isophorone. The aqueous solution of ferric chloride contains acetone in an amount equivalent to the mesityl oxide and phorone present in the acetone condensation product undergoing treatment.

Example V

A mixture consisting of 40 grams of mesityl oxide, 15 grams of phorone and 25 grams of isophorone and 125 grams of an aqueous solution containing 3% by weight of ammonium chloride was heated at 260° C. for 2 hours in a rotatable steel autoclave of 450° cc. capacity. During this treatment about 80% of the mesityl oxide and 90% of the phorone were converted into acetone.

The novelty and utility of the process of the present invention are evident from the preceding specification and examples, although neither section is introduced to limit unduly the generally broad scope of the invention.

We claim as our invention:

1. A process for separating a cyclic olefinic ketone from a mixture containing said cyclic olefinic ketone and an aliphatic olefinic ketone which comprises treating said mixture with an aqueous solution of an acid-acting salt at a temperature of from about 100° to about 350° C. to convert the aliphatic olefinic ketone into alkyl ketone, and separating said alkyl ketone from unconverted cyclic olefinic ketone.

2. A process which comprises treating a mixture of alkyl ketone condensation products comprising cyclic mono-olefinic ketones and aliphatic olefinic ketones with an aqueous solution of an acid-acting salt at a temperature of from about 100° to about 350° C. to convert the aliphatic olefinic ketones into an alkyl ketone, and separating said alkyl ketone and the unconverted cyclic, mono-olefinic ketone.

3. A process which comprises treating a mixture of alkyl ketone condensation products comprising cyclic and aliphatic olefinic ketones with an aqueous solution of an acid-acting salt at a temperature of from about 100° to about 350° C. and at a superatmospheric pressure to convert the aliphatic olefinic ketones into an alkyl ketone, and separating said alkyl ketone and the unconverted cyclic, mono-olefinic ketone.

4. A process which comprises treating a mixture of acetone condensation products including mesityl oxide, phorone, and isophorone at a temperature of from about 100° to about 350° C. with a dilute aqueous solution of an acid-acting salt to convert said mesityl oxide and phorone into acetone, and separating said acetone and unconverted isophorone.

5. A process for preparing substantially pure isophorone which comprises treating a mixture of acetone condensation products including mesityl oxide, phorone, and isophorone with a dilute aqueous solution of an acid-acting salt at a temperature of from about 100° to about 350° C. and at a pressure sufficient to maintain the reaction mixture in liquid phase to convert said mesityl oxide and phorone into acetone, and separating said acetone and unconverted isophorone.

6. A process for preparing substantially pure isophorone which comprises treating a mixture of acetone condensation products including mesityl oxide, phorone, and isophorone with a dilute aqueous solution of an acid-acting chloride salt at a temperature of from about 100° to

about 350° C. and at a pressure sufficient to maintain the reaction mixture in liquid phase to convert said mesityl oxide and phorone into acetone, and separating said acetone and unconverted isophorone.

7. A process for preparing substantially pure isophorone which comprises treating a mixture of acetone condensation products including mesityl oxide, phorone, and isophorone with an aqueous solution containing from about 0.05 to about 10% by weight of an acid-acting chloride salt at a temperature of from about 100° to about 350° C. and at a pressure sufficient to maintain the reaction mixture in liquid phase to convert said mesityl oxide and phorone into acetone, and separating said acetone and unconverted isophorone.

8. A process for preparing substantially pure isophorone which comprises treating a mixture of acetone condensation products including mesityl oxide, phorone, and isophorone with an aqueous solution containing from about 0.05 to about 10% by weight of ferric chloride at a temperature of from about 100° to about 350° C. and at a pressure sufficient to maintain the reaction mixture in liquid phase to convert said mesityl oxide and phorone into acetone, and separating said acetone and unconverted isophorone.

9. A process for preparing substantially pure isophorone which comprises treating a mixture of acetone condensation products including mesityl oxide, phorone, and isophorone with an aqueous solution containing from about 0.05 to about 10% by weight of ammonium chloride at a temperature of from about 100° to about 350° C. and at a pressure sufficient to maintain the reaction mixture in liquid phase to convert said mesityl oxide and phorone into acetone, and separating said acetone and unconverted isophone.

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