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PREPARATION OF KETONES

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This invention relates to a process for producing ketones.

It is an object of this invention to provide a process to produce ketones from secondary alcohols in high yields and of exceptional purity.

Another object of this invention is to produce ketones from secondary alcohols by treating the latter in liquid phase with unsaturated cyclic hydrocarbons in the presence of a hydrogenation catalyst and under temperature and pressure conditions normally corresponding to the optimum conditions for hydrogenating said unsaturated cyclic hydrocarbons.

A specific object of this invention is to produce camphor from a borneol in the presence of a hydrogenation catalyst and an unsaturated cyclic hydrocarbon acting as a dehydrogenating or oxidizing agent.

Other and further important objects of this invention will become apparent from the disclosures in the following description and appended claims.

This invention more specifically deals with, for example, the following types of ketones: camphor, fenchone, cyclohexanone and acetone.

The corresponding alcohols serving as starting materials for the above named ketones are respectively borneol or iso-borneol, fenchyl alcohol, cyclohexanol and isopropyl alcohol.

I have found that secondary alcohols of the type mentioned above can be readily converted into the corresponding ketones by heating them in the liquid phase under pressure with an unsaturated cyclic hydrocarbon of the type that is readily hydrogenated such as, for example, benzene, naphthalene, abietene, or dipentene. The process is preferably carried out in the presence of a hydrogenation catalyst and under temperature and pressure conditions corresponding to the normal hydrogenation conditions for the respective hydrocarbon.

Thus, I have found that if a borneol (borneol or iso-borneol) is heated to about 200° C. in an autoclave with a quantity of benzene, toluene or other unsaturated cyclic hydrocarbon, at least equal to the amount theoretically necessary for absorbing all the hydrogen split off from the alcohol, and in the presence of a hydrogenation catalyst such as nickel a reaction results yielding camphor on the one hand in a high state of purity and yielding as a by-product hydrogenated benzene or toluene respectively. Although it has been known to use benzene or a similar hydrocarbon as a solvent or diluent in the oxidation of borneol to camphor, the benzene or similar hydrocarbon has been used only as a solvent for the alcohol. In other words, it was never appreciated in the art that the benzene hydrocarbons could be made to act as oxidizing or dehydrogenation agents by becoming hydrogenated themselves.

Thus in U. S. Patent 994,437 to Aschan dated June 6, 1911, hydrocarbons such as xylol, paraffin and petroleum are used as solvents in the preparation of camphor from a borneol. These hydrocarbons acted only as solvents in the process mentioned.

As a result, nowhere in the art has it been pointed out that the reaction could be facilitated by providing conditions generally favorable for hydrogenation such as theoretical quantities of reacting agents, the presence of a hydrogenation catalyst, and use of elevated temperatures and pressures.

I have found that when the aromatic hydrocarbon is present in quantities not less than that amount theoretically equivalent to the amount of hydrogen split off from the secondary alcohol, and the reaction carried out under pressure, the yields of ketone are considerably increased. This effect was not to be foreseen on the theory that the aromatic hydrocarbon acts merely as a diluent.

The following examples will serve to illustrate my invention in greater detail but it should be understood that my invention is not limited to the same and is susceptible to various modifications and variations as will be readily understood to those skilled in the art.

Example 1

1000 parts of borneol, 1000 parts of benzene and 40 parts of a hydrogenation catalyst, for instance nickel, are charged into an autoclave. The latter is closed, the air removed therefrom by evacuation or by blowing hydrogen through the autoclave, and the mass is heated to 200° C. and kept at this temperature and under its own pressure for 5 hours while stirring. The reaction mass is now cooled and filtered to remove the catalyst. The benzene and its hydrogenation products are now removed by distilling the reaction mass until the temperature rises to about 207° C., which corresponds to the boiling point of camphor. The residue in the still is substantially pure camphor and may be used as such. If desired, however, it may be subjected to sublimation for the sake of further purification. The fractions of benzene and hydrogenated benzene carry over with them some of the camphor, which may be recovered

from the fractions in any suitable manner, for instance, by redistillation. The total yield of camphor in this process after combining therewith the camphor recovered from the distillate, amounts to from 950 to about 958 parts by weight. If the initial borneol was pure, the product is of exceptionally high purity having a melting point of about 178° C.

Instead of borneol in the above example, isoborneol may be used, with the same results.

Instead of nickel, nickel oxide or a nickel carbonate-copper carbonate mixture may be used. The catalytic mass may then be first reduced with hydrogen under pressure in the reaction mixture at the reaction temperature, whereupon the procedure is continued as before. This step, however, is not always essential, for the secondary alcohol itself will reduce part of the catalyst, which in turn will promote the dehydrogenation of the alcohol and the further reduction of the catalyst until all of the latter is in reduced state whereupon the hydrogenation of the hydrocarbon proceeds as before. The amounts of catalyst may be varied within wide limits.

In my preferred method, I use an amount of catalyst equal to from 2 to 6% by weight of the initial amount of alcohol. However, considerable variation in this proportion may be made. Thus, 1% and 10% are not extreme proportions.

It will be understood of course that the reaction mass must be free from catalyzer poisons such as sulfur compounds. For the same reason, it will be found advantageous to use an unsaturated hydrocarbon which has been pre-purified to rid it of catalyzer poisons in accordance with known methods.

The purity of the resultant camphor depends necessarily on the purity of the borneol compounds started with. If the initial material is pure, the product can be obtained substantially 100% pure.

Example 2

1300 parts of borneol, 650 parts of benzene and 78 parts of catalyst are treated in the same manner as in Example 1. The yield of camphor is substantially the same as in Example 1.

Example 3

An autoclave is charged with 650 parts of borneol, 1300 parts of benzene and 39 parts of nickel. The rest of the procedure is substantially the same as in Example 1 and the yield is substantially the same.

Example 4

1000 parts of fenchyl alcohol, 1000 parts of benzene and 40 parts of a mixed nickel catalyst comprising nickel and copper carbonates are charged into an autoclave. After reducing the catalyst with hydrogen as explained above, the reaction mass is heated at 225° C. for 5 hours under pressure. The reaction mass is fractionated to remove the benzene and its hydrogenation products and a high yield (about 97% of theory) of substantially pure fenchone is secured.

Example 5

An autoclave is charged with 400 parts of isopropyl alcohol, 1600 parts of naphthalene and 40 parts of a mixed nickel catalyst as used in Example 4. After reducing the catalyst, the reaction mass is heated at 225° C. under its own pressure for 5 hours. Upon fractionation as above, acetone is secured.

In a similar manner, cyclohexanol and benzene, cyclohexanol and naphthalene or cyclohexanol and dipentene may be heated together to give respectively cyclohexanone and hydrogenated benzene, cyclohexanone and tetrahydronaphthalene, or cyclohexanone and menthane, which may be separated from each other by fractionation as above.

Instead of benzene or naphthalene, toluene, abietene, or any other suitable unsaturated cyclic hydrocarbon may be used. The requisite of the hydrocarbon is that it shall not be in the hydrogenated state; in other words, it must contain double bonds capable of absorbing hydrogen.

Another requisite is that the unsaturated cyclic hydrocarbon be present in proportions at least theoretically equivalent to the quantity of hydrogen split off from the alcohol assuming that all of the alcohol will be converted into ketone. Large excesses of unsaturated substance may be used, and the yield is thereby generally increased.

For best purposes, an unsaturated hydrocarbon should be selected which after hydrogenation has a boiling point or boiling range considerably above or below the boiling point of the ketone formed, thereby facilitating the separation of the reaction products by fractionation. Furthermore, where the alcohol to be dehydrogenated has a high boiling point, the hydrocarbon selected should preferably be of a low boiling point to insure the formation of the requisite pressure without recourse to excessive temperatures. This pressure may vary considerably depending on the substance being hydrogenated. 100 and 300 pounds per square inch are convenient limits. However, this latter selection of boiling points is not absolutely essential, since the pressure in the vessel may be artificially built up by pumping in hydrogen or an inert gas such as CO_2.

The temperature in any specific case need not be maintained at a precise point, but may vary within substantial limits. Thus, while I have indicated 200° C. or 225° C. as the preferred temperature in the examples, the same may vary from 175 to 250° C. during the reaction without seriously affecting the results.

In the claims below, it should be understood that the term "a borneol" is meant to cover and include both borneol and isoborneol.

I am ware that numerous details of the process may be varied through a wide range without departing from the principles of this invention, and I, therefore, do not purpose limiting the patent granted hereon otherwise than necessitated by the prior art.

I claim as my invention:

1. The process of converting a secondary alcohol into the corresponding ketone which comprises heating the secondary alcohol under pressure in the liquid phase with an unsaturated cyclic hydrocarbon in the presence of a hydrogenation catalyst.

2. The process of converting a secondary alcohol into the corresponding ketone, which comprises heating the secondary alcohol under pressure in the liquid phase with an unsaturated cyclic hydrocarbon and a hydrogenation catalyst, the unsaturated cyclic hydrocarbon being present in a proportion not less than that theoretically required for complete reaction with all of the hydrogen eliminated from the alcohol.

3. The process of converting a terpene secondary alcohol into the corresponding ketone, which

comprises heating the alcohol under pressure in the liquid phase with an aromatic hydrocarbon capable of being hydrogenated, in the presence of a hydrogenation catalyst.

4. The process of converting a terpene secondary alcohol into the corresponding ketone, which comprises heating the alcohol under pressure in the liquid phase with an aromatic hydrocarbon in the presence of a hydrogenation catalyst, the quantity of aromatic hydrocarbon being not less than that theoretically required for complete reaction with all of the hydrogen liberated during the reaction.

5. The process of converting a terpene secondary alcohol into the corresponding ketone, which comprises heating the alcohol under pressure in the liquid phase with an aromatic hydrocarbon which is a member of the group consisting of benzene and homologues of benzene, and in the presence of a hydrogenation catalyst, the amount of aromatic hydrocarbon being equal to at least one-third the molecular quantity of the secondary alcohol.

6. A process of making camphor, which comprises heating a borneol in the liquid phase in a closed vessel in the presence of an aromatic hydrocarbon which is a member of the group consisting of benzene and homologues of benzene and in the presence of a hydrogenation catalyst, the amount of aromatic hydrocarbon being equal to at least one-third the molecular quantity of borneol compound started with.

7. The process of producing camphor in high yields, which comprises heating in the liquid phase one mole of a borneol with at least one-third of a mole of benzene in the presence of a nickel catalyst in a closed vessel at about 200° C.

8. The process of producing camphor, which comprises heating in the liquid phase and under pressure one mole of a borneol with at least one-third of a mole of benzene in the presence of a hydrogenating catalyst.

9. The process of converting a secondary alcohol into the corresponding ketone which comprises heating the secondary alcohol under pressure in the liquid phase in the presence of a hydrogenation catalyst with an unsaturated cyclic hydrocarbon which after hydrogenation has a boiling point remote from that of the ketone formed.

10. The process of producing camphor in high yields, which comprises heating with a hydrogenation catalyst, a borneol in the liquid phase in a closed vessel in the presence of an unsaturated cyclic hydrocarbon which after hydrogenation has a boiling point considerably remote from that of the camphor formed.

11. The process of converting a secondary alcohol into the corresponding ketone which comprises heating the secondary alcohol in the liquid phase with an unsaturated cyclic hydrocarbon and a hydrogenation catalyst at a pressure sufficient for hydrogenation of the unsaturated cyclic hydrocarbon under the conditions of reaction, the unsaturated cyclic hydrocarbon being present in a proportion in substantial excess of that theoretically required for complete reaction with all of the hydrogen eliminated from the secondary alcohol.

12. The process of producing camphor which comprises heating a borneol, in the liquid phase, with benzene and a hydrogenation catalyst at a pressure sufficient for hydrogenation of the benzene under the conditions of reaction, the benzene being present in a proportion in substantial excess of that theoretically required for complete reaction with all of the hydrogen eliminated from the borneol.

13. The process of producing camphor which comprises heating a borneol, in the liquid phase, with benzene and a hydrogenation catalyst at a pressure sufficient for hydrogenation of the benzene under the conditions of reaction, the amount of benzene being equal to about three to about six times the molecular quantity theoretically required for complete reaction with all of the hydrogen eliminated from the borneol.

14. The process of producing camphor which comprises heating isoborneol, in the liquid phase, with benzene and a hydrogenation catalyst containing nickel at a temperature of about 200° C., under a pressure of about 100 to 300 pounds per square inch, the amount of benzene being equal to about three to about six times the molecular quantity theoretically required for complete reaction with all of the hydrogen eliminated from the isoborneol.

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