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(54) IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF KETONES

(71) We, DIAMOND SHAMROCK CORPORATION, of 1100 Superior Avenue, Cleveland, Ohio 44114, United States of America, a Corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

Description

The present invention relates generally to the production of ketones from other ketones. More particularly, the invention relates to a method for the production of symmetrical or unsymmetrical ketones from other ketones, optionally in the presence of carboxylic acids or in general, from other ketones in admixture with a compound containing a -CO group and/or an -OH group and selected from carboxylic acids, carboxylic acid esters, additional ketones, aldehydes and alcohols.

An example of the method of the invention is the production of ketones from a starting mixture comprising other ketones and carboxylic acids, by passing such starting mixture over a ceria-alumina catalyst at a temperature in the range from 300° to 550°C, utilizing a very short contact time with the catalyst to achieve a conversion in the range of 85% or more while recovering most of the unconverted reactants for recycling.

An excellent example of such a preparation is the reaction of acetone with pivalic acid over a ceria-alumina catalyst to produce pinacolone. Pinacolone is an intermediate which is useful in the preparation of pharmaceutical products and pesticides, for which improved methods of manufacture have been sought for some time now. An electrolytic reductive coupling of acetone to form pinacol has been carried out on an experimental basis for a number of years, to produce small quantities of pinacol, which can then be converted to pinacolone but such processes have thus far failed to receive much commercial utilization because of the cost factors involved.

A thermo-chemical route as disclosed in the literature utilizes a pyrolysis of one or two carboxylic acids to yield symmetrical or unsymmetrical ketones, respectively. This type of reaction has been used commercially, despite the significant disadvantage that the raw materials used in the manufacture of the ketones are costly, because the selectivity of the reaction to unsymmetrical ketones is low.

Therefore, as with all chemical processes, it would be very desirable to be able to reduce the cost of a thermo-chemical route to pinacolone or other ketones for use in the chemical industry on a commercial basis.

According to this invention, a method is provided for preparing the desired ketone from one or more other ketones, which comprises subjecting one or more starting compounds consisting of (a) an unsymmetrical ketone or (b) two symmetrical ketones, optionally in admixture with at least one other compound containing a -CO- group and/or an -OH group and selected from carboxylic acids, carboxylic acid esters, additional ketones, aldehydes and alcohols, or (c) a symmetrical ketone in admixture with at least one such other compound, to a reaction, by passing such starting compound or mixture over or through a catalytically-active material at a reaction temperature in the range from above 300° to 550°C, preferably 400° to 500°C, and recovering the desired ketone from the resultant reaction products, the reaction being carried out in the absence of a diluent gas and the catalytically-active material being selected from iron filings, alumina, manganese oxides, thorium compounds and cerium compounds.

According to a preferred way of carrying out the method of the invention, a mixture of a ketone and a carboxylic acid is passed over the heated catalytically-active material and the desired ketone is recovered.

In accordance with one preferred embodiment of the method, for the production of an unsymmetrical ketone of the formula $RR'CO$, where R and R' are different hydrocarbon radicals, the starting compounds comprise a ketone of the formula R_2CO in admixture with a carboxylic acid of the formula $R'CO_2H$.

In accordance with another preferred embodiment of the method of the invention, a symmetrical ketone is produced by passing an unsymmetrical ketone through a heated bed of the catalytically-active material and recovering the desired symmetrical ketone.

In accordance with a further preferred embodiment of the method of the invention, an unsymmetrical ketone is produced from starting compounds which comprise a symmetrical ketone in admixture with a different symmetrical ketone.

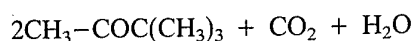
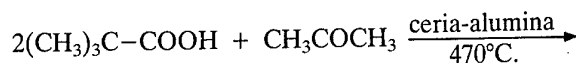
Unsymmetrical ketones may be produced according to the general reaction $R_2CO + 2R'CO_2H$ to yield $2RR'CO + CO_2 + H_2O$, wherein R is a hydrogen radical and R' is a hydrocarbon radical other than R. This reaction has been found to occur over catalytically-active materials with a relatively short contact time at a temperature in the range from above 300° to $550^\circ C$. Unsymmetrical ketones resulting from the above-cited reaction can be recovered in yields up to 80% or more. Groups representative of R and R' in the above-cited starting materials include aliphatic and araliphatic groups, such as methyl, ethyl, propyl, isopropyl, *t*-butyl, pentyl, hexyl and benzyl, as well as aromatic groups, such as phenyl, *p*-tolyl and naphthyl.

This reaction takes place when vapours of the reactants are passed over the heated catalytically-active material. The preferred catalyst system, from experience, is a cerium compound deposited on an alumina, silica or carbon support. The catalyst comprising a cerium compound on alumina forms the subject of our co-pending Application No. 7923366. (Serial No. 1591540)

In each specific case, conditions may need to be altered slightly to maximize yields. For example, acetone and pivalic acid react over a ceria-alumina catalyst at a temperature near $470^\circ C$. to produce pinacolone. When using a 2:1 molar ratio of acetone:pivalic acid with a 10 second contact time, the conversion of the pivalic acid to pinacolone is in the range of 80% of theoretical. Additionally, most of the unconverted reactants can be recovered and recycled into the reactor zone to accomplish higher yields. By recycling reactants, virtually 100% conversion rates are possible. This results in about 2 moles of pinacolone being produced for each mole of acetone consumed. In general, the reaction contact time of the reactants and the catalytically-active material is preferably up to 60 seconds.

The catalyst can be derived from cerium acetate converted to ceria on an alumina support, it having been found that a good activity will be produced if the ceria concentration is in the range of 1% to 10% calculated as CeO_2 to total weight. The amount used depends upon the specific surface area presented by the alumina support. Where the support is alumina of the kind available from Harshaw Chemical Company under the trademark Harshaw Al 1404 T-1/8, this equals approximately 190 square metres per gram, and the range of ceria concentration is preferably 5% to 10%. No treatment prior to use is necessary, but a slight ageing of the catalyst has been found to occur during initial use, as is usual with such catalyst systems. Thereafter this system provides good activity of a steady nature for periods in excess of 1,000 hours of use. The ceria-alumina catalyst provides a distinct advantage over thoria catalysts, because ceria is not radioactive, thus eliminating a hazard of thoria and the inconvenience of compliance with regulations covering its use.

It is believed that the above-described acetone and pivalic acid reaction to obtain pinacolone proceeds as follows.



It will be noticed that 2 moles of pivalic acid combine with 1 mole of acetone to provide 2 moles of pinacolone. It is believed that the pivalic acid forms a complex with the ceria-alumina catalyst system by losing its acidic hydrogen atom. Thereafter, the carbon to oxygen double bond is attacked by the methylene anion of the acetone to provide a shift of electrons to the oxygen atom and the loss of an oxygen atom with the coupling of the acetone by its methyl group thereto. This results in a probable intermediate of the formula $(CH_3)_3-CCOCH_2COCH_3$. It is believed that this intermediate is then hydrolyzed, causing

a cleavage which results in the formation of pinacolone and an acetic acid group, which thereafter reacts with a second complexed pivalic acid group to form more pinacolone. In this process, carbon dioxide and water are also formed.

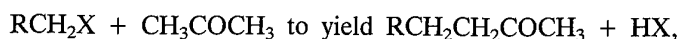
Further examples of the reaction of ketones and carboxylic acids or carboxylic acid esters to produce other ketones include: acetone and benzoic acid to obtain acetophenone; acetone and propionic acid to obtain methyl ethyl ketone and diethyl ketone; acetone and dimethyl succinate to obtain 2,5-hexanedione; acetone and phenylacetic acid to obtain phenylacetone; diethyl ketone and acetic acid to obtain acetone and methyl ethyl ketone; diethyl ketone and benzoic acid to obtain propiophenone; benzophenone and acetic acid to obtain acetophenone; benzoic acid and methyl ethyl ketone to obtain acetophenone and propiophenone; and acetone and dimethyl terephthalate to obtain *p*-diacetylbenzene.

In some cases alcohols or aldehydes may be substituted for the carboxylic acid or ester to produce ketones by the method of the invention. It has been found that benzyl alcohol or benzaldehyde may be substituted for benzoic acid in the reaction with acetone to obtain acetophenone. It is believed that reactions using an aldehyde or alcohol as a starting material proceed by an oxidation-reduction disproportionation of the feedstocks. It is also possible that the ketonic products are formed through carboxylic acid intermediates.

It has also been found that the ceria-alumina catalyst provides good activity for rearrangements of ketones by themselves, such as methyl ethyl ketone alone to obtain acetone and diethyl ketone and acetone and diethyl ketone to obtain methyl ethyl ketone.

The ceria-alumina catalyst also provides good activity for numerous other chemical reactions besides the ketone reactions described above. This catalyst would be useful in reactions like: benzophenone and pivalic acid to obtain *t*-butyl phenyl ketone; 1,3-dichloroacetone and pivalic acid to obtain monochloropinacolone; and cyclopentanone and acetic acid to obtain 2,7-octanedione.

The ceria-alumina catalyst also provides good activity for many other reactions. For example, the following general reaction can be carried out:



where R is an activating substituent selected from a hydrogen atom or an alkyl or aryl group and X is a good leaving group such as a halogen.

The reaction of a symmetrical ketone of the formula $\text{RCH}_2\text{COCH}_2\text{R}$, where R is a hydrogen atom or an alkyl or aryl group, with formic acid to yield an aldehyde of the formula RCH_2CHO forms the subject of our co-pending Application No. 7923365. (Serial No. 1591539).

The method of the present invention provides a distinct economic advantage over prior methods, particularly for the production of pinacolone, over either the mixed acid pyrolysis route or the formation of the mixed anhydrides and subsequent pyrolysis to the ketones. Lower capital and operating costs are expected in the process of the present invention versus that of the mixed acid pyrolysis, because the heat of vaporization of acetone is less than that of acetic acid, thus requiring less energy. This advantage is increased by the fact that one mole of acetone is nearly equal to two moles of acetic acid used in the old methods. Further, about one-half as much carbon dioxide and water are produced, making it easier to condense and recover the product and unreacted materials. There is also less dilution of the reaction mixture with byproduct carbon dioxide and water, so that a reaction vessel only two-thirds to three-quarters as large as that used in the acid pyrolysis route may be used, resulting in savings in the cost of catalyst and reactor. In addition, smaller condensers with lower energy requirements will be adequate.

In order that those skilled in the art may more readily understand the present invention and certain preferred procedures by which it may be practised, the following specific examples are afforded to show the method of preparation of various ketones according to the general reaction cited above.

Example 1

An apparatus suitable for use in the above-described reactions was assembled having a vertical tube furnace constructed from "Pyrex" (Regd. Trademark) tubing for heating the reaction zone. The reaction tube contained a thermowell in the reaction zone to obtain accurate temperature readings. The upper section where the reactants enter contained a preheater segment to bring the reactants up to the reaction temperature, while the lower section contained a smaller heating segment to sustain this temperature. The preheater was thermostatically controlled to provide more heat when reactants were being fed into the upper section to maintain the temperature. The catalyst was positioned between glass beads so that it began just below the upper section and ran down approximately 75% of the length of the lower section and between the concentric thermowell and the glass containing the

reactor. The reactor was connected by means of a "Y" tube to a condensate receiver on the bottom and two water-cooled condensers in series on the vertically straight neck. For example, the lower condenser may be of the six bulb Allihn type and the upper one of the Friedrich's type. Also it might be desirable to use a feed reservoir on a triple beam balance connected to a metering pump to feed the reactants to the apparatus at a known rate. With a "Y" tube connected to the upper section of the tube furnace, the reactants may be fed into one branch and a thermocouple well placed in the other branch for measuring temperatures.

A thoria catalyst was prepared from 40 grams of thorium nitrate tetrahydrate $[\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}]$ in water, impregnated on 200 ml. or 172 grams of Harshaw Alumina catalyst A11404 T 1/8. The wetted alumina was stripped of water in a rotary evaporator under aspirator vacuum. The alumina was transferred to a large porcelain dish where it was heated strongly while aspirating the NO_x from it through a water trap. The resulting loose material was then placed in the reactor tube with glass beads ahead of and behind the catalyst zone.

The apparatus was then flushed out with acetone vapour to clear it of any residues and the catalyst temperature gradually rose to 440° to 485°C . The feed reservoir was changed from acetone to a 2:1 molar ratio of acetone:pivalic acid. The condensate samples removed were composed of 4 to 5 parts red organic layer over a colourless aqueous layer. Product purification and gas chromatographic studies of the organic layer showed the presence of pinacolone in a yield ranging as high as 90% of theoretical on a single pass. Recovery of reactants and recycling can achieve even higher yields.

Example 2

A ceria catalyst was prepared from 100 grams of cerium acetate hydrate $[\text{Ce}(\text{OAc})_3 \cdot \text{XH}_2\text{O}]$ and 400 ml. of water at room temperature, agitation being employed to dissolve nearly all of the cerium acetate material. The solution was filtered and the filter was rinsed with several portions of water to result in approximately 460 ml. of filtrate. The solution was then combined with 1050 and tumbled in a gallon jug. The solution was absorbed, leaving no freely-pourable liquid and thus wetting the alumina. The mixture was dried in a porcelain dish at approximately 200°C . for 15 hours and then installed in the apparatus according to Example 1.

The system was flushed out according to Example 1 and the feed reservoir charged with a 2:1 molar ratio of acetone:pivalic acid. Pinacolone product was recovered from the condensate in yields up to 90% of theoretical as evidenced by gas chromatographic studies.

Examples 3-12

Using the apparatus of Example 1 and the catalyst of Example 2, other reactions were performed in a fashion similar to Examples 1 and 2. In each case, the reaction products were confirmed by mass spectra and quantitatively measured by gas chromatographic studies. These reactions are summarized in the following Table. "Molar Ratio" refers to the ratio of the reactants in the order stated in the feed reservoir. With the exception of the pinacolone, no effort was made to maximize the yields.

TABLE

EX.	Reactants	Reaction Temp. °C.	Molar Ratio	% Yield	Product(s)
3	benzoic acid: acetone	420-440	1:33	25	acetophenone
4	acetone: propionic acid	430	1:1	38 52	methyl ethyl ketone diethyl ketone
5	acetone:dimethyl succinate	470	3:1	2	2,5-hexandione
6	acetone:phenyl- acetic acid	430-455	4:1	60	phenylacetone
7	diethyl ketone: acetic acid	420-440	1:1	40 55	acetone methyl ethyl ketone
8	diethyl ketone: benzoic acid	430-480	4:1	8	propiophenone
9	benzophenone: acetic acid	430-480	1:5	7	acetophenone
10	benzoic acid: methyl ethyl ketone	450	1:4	21 17	acetophenone propiophenone
11	methyl ethyl ketone	400	-	6 12	acetone diethyl ketone
12	acetone:diethyl ketone	440-500	1:1	14	methyl ethyl ketone
13	acetone:dimethyl terephthalate	440-460	40:1	2	<i>p</i> -diacetylbenzene
14	acetone: benzaldehyde	480-490	2:1	25	acetophenone
15	acetone:benzyl alcohol:water	480-485	2:1:2	5	acetophenone

WHAT WE CLAIM IS:-

1. A method for the production of a ketone from one or more other ketones, which comprises subjecting one or more starting compounds consisting of (a) an unsymmetrical ketone or (b) two symmetrical ketones, optionally in admixture with at least one other compound selected from carboxylic acids, carboxylic acid esters, additional ketones, aldehydes and alcohols, or (c) a symmetrical ketone in admixture with at least one such other compound, to a reaction, by passing such starting compound or mixture over or through a catalytically-active material at a reaction temperature in the range from above 300° to 550°C and recovering the desired ketone from the resultant reaction products, the reaction being carried out in the absence of a diluent gas and the catalytically-active material being selected from iron filings, alumina, manganese oxides, thorium compounds and cerium compounds.
2. A method according to claim 1, which comprises passing a mixture of a ketone and a carboxylic acid over the heated catalytically-active material and recovering the desired ketone.
3. A method according to claim 1 or 2, for the production of an unsymmetrical ketone of the formula $RR'CO$, where R and R' are different hydrocarbon radicals, wherein the starting compounds comprise a ketone of the formula R_2CO in admixture with a carboxylic acid of the formula $R'CO_2H$.
4. A method according to claim 1, for the production of a symmetrical ketone, which comprises passing an unsymmetrical ketone through a heated bed of the catalytically-active material and recovering the desired symmetrical ketone.
5. A method according to claim 1 or 2, for the production of an unsymmetrical ketone, wherein the starting compounds comprise a symmetrical ketone in admixture with a different symmetrical ketone.
6. A method according to claim 5, wherein the symmetrical ketones are acetone and diethyl ketone and the unsymmetrical ketone is methyl ethyl ketone.
7. A method according to claim 1, for the production of a ketone of the formula $RCH_2CH_2COCH_3$, wherein R is an activating substituent selected from a hydrogen atom or an alkyl or aryl group, wherein acetone in admixture with a compound of the formula RCH_2X , wherein X is a good leaving group, is passed through a heated bed of ceria-alumina catalytically-active material and the desired ketone of the formula $RCH_2CH_2COCH_3$ is recovered.
8. A method according to any preceding claim, wherein the catalytically-active material is ceria on a support.
9. A method according to claim 8, wherein the support is alumina.
10. A method according to claim 9, wherein the alumina support has a specific surface area of 190 sq. m/g.
11. A method according to any of claims 8 to 10, wherein the ceria has a concentration in the range from 1% to 10%.
12. A method according to claim 11, wherein the ceria concentration is in the range from 5% to 10%.
13. A method according to any of claims 8 to 12, wherein the ceria is derived from cerium acetate.
14. A method according to any preceding claim, wherein the reaction temperature is in the range from 400° to 500°C.
15. A method according to any preceding claim, wherein the reaction contact time of the reactants and the catalytically-active material is up to 60 seconds.
16. A method according to claim 2, wherein the ketone is acetone and the carboxylic acid is pivalic acid to yield pinacolone.
17. A method according to claim 2, wherein the ketone is acetone and the carboxylic acid is benzoic acid to yield acetophenone.
18. A method according to claim 2, wherein the ketone is acetone and the carboxylic acid is propionic acid to yield methyl ethyl ketone and diethyl ketone.
19. A method according to claim 2, wherein the ketone is acetone and the carboxylic acid is phenylacetic acid to yield phenylacetone.
20. A method according to claim 2, wherein the ketone is diethyl ketone and the carboxylic acid is acetic acid to yield methyl ethyl ketone.
21. A method according to claim 2, wherein the ketone is diethyl ketone and the carboxylic acid is benzoic acid to yield propiophenone.
22. A method according to claim 2, wherein the ketone is benzophenone and the carboxylic acid is acetic acid to yield acetophenone.
23. A method for the production of a ketone from one or more other ketones according to claim 1, substantially as herein described.

24. A ketone, when produced by a method according to any preceding claim.

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