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UNITED STATES PATENT OFFICE

2,246,032

PROCESS FOR THE PRODUCTION OF BETA GAMMA UNSATURATED KETONES

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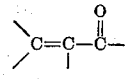
No Drawing. Original application December 27, 1937, Serial No. 182,005, now Patent No. 2,197,462, dated April 16, 1940. Divided and this application June 10, 1938, Serial No. 212,979

10 Claims. (Cl. 260—586)

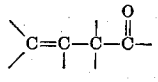
The present invention relates to a process for the production of beta gamma unsaturated ketones.

According to the present process, beta gamma unsaturated ketones are prepared from alpha beta unsaturated ketones by rearranging said alpha beta unsaturated ketones to the corresponding beta gamma unsaturated ketones and recovering the beta gamma unsaturated ketones substantially as fast as formed.

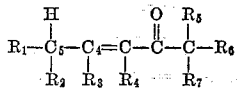
By an alpha beta unsaturated ketone is meant a ketone containing an ethylene linkage attached to the carbonyl group. These ketones contain a conjugated system of the structure



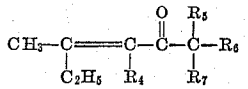
By a beta gamma unsaturated ketone is meant a ketone containing an ethylene linkage attached to the carbonyl group through a methylene group. These ketones contain the structural grouping

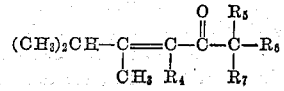


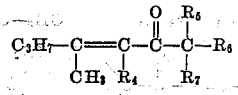
The alpha beta unsaturated ketones applicable in the present process may be designated by the general formula:

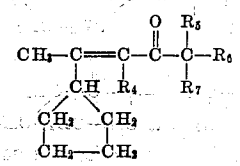


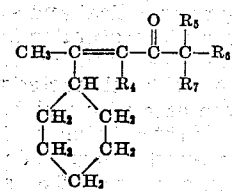
wherein R_1 through R_7 may be any member of the group consisting of hydrogen, aliphatic and cyclo-paraffinic groups, with the provisions that C^4 and/or C^5 be tertiary carbon atoms (s), and that the sum of the carbon atoms in $R_{1, 2, \text{and } 3}$ be not less than two. These applicable alpha beta unsaturated ketones, it is seen, contain at least seven carbon atoms. Examples of structures containing simple R_1, R_2, and R_3 radicals are:

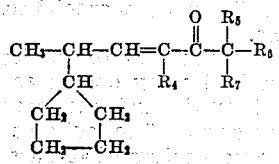


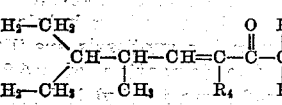


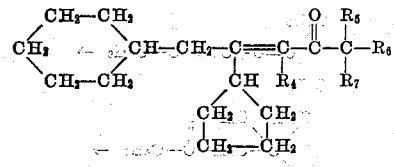


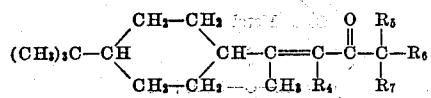


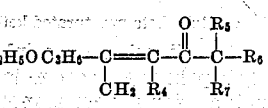


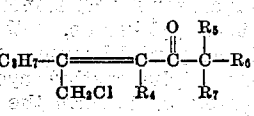


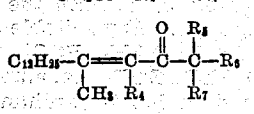






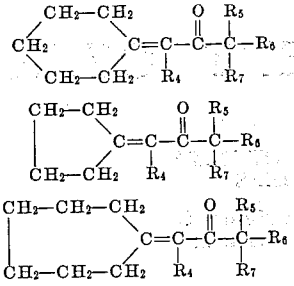




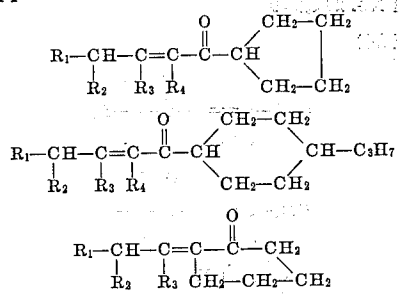


Moreover, R_2 may be connected with R_1 or R_3 by one or more methylene groups to form a poly-

methylene ring structure, for example, containing the groupings,

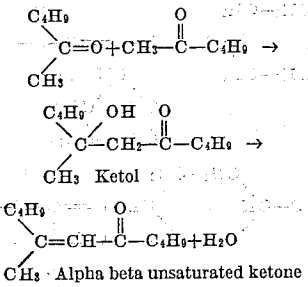


Likewise, compounds in which R_6 is connected to R_7 or R_4 by one or more methylene groups are also applicable. Examples of this structure are



These applicable alpha beta unsaturated ketones, including their optical and stereo-isomers, constitute a class of unsaturated ketones differing in several respects from other unsaturated ketones. One notable characteristic of these compounds is the ease with which they may be alkylated. Unsaturated ketones of other structure, such as mesityl oxide, undecene-6-one-3, 3-methyl-cyclohexadienyl-2,6 acetone, etc., which are not alkylated under mild conditions are not applicable.

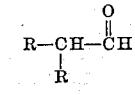
Unsaturated ketones of the desired structure may be prepared by any one of several known methods, the invention being independent of the mode of formation. One suitable method is through the condensation of ketones followed by dehydration of the resulting ketols. The reactions involved in the synthesis are illustrated by the case of the formation of 2,4,8-trimethyl-nonene-4-one-6 from methyl isobutyl ketone.



Alpha beta unsaturated ketone

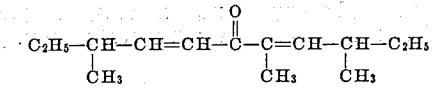
Any aliphatic, alicyclic, or aliphatic alicyclic ketone having a primary or secondary alpha carbon atom, such as, for example, methyl ethyl ketone, methyl isopropyl ketone, methyl cyclohexyl ketone, ethyl cyclopentyl ketone, cyclohexanone, cyclopentanone, alpha methyl cyclopentanone, etc., may be employed to form the starting material of my process. Any suitable catalyst such as CaC_2, Al_2O_3, $NaOC_2H_5$, $POCl_3$, H_2SO_4, HCl, HBr, HI, CaO, ThO_2, $ZnCl_2$, Na, aluminum halide, organo magnesium halide, sodium pyrosulfate, sodamide, triphenyl aluminum, etc., may be used to accelerate the reaction. In most cases the two reactions proceed under the same conditions to yield the desired alpha beta unsaturated ketone directly. If under mild (usually alkaline conditions) the ketol is obtained, this may be easily dehydrated by heating with a little acid. In this method of preparation all theoretically possible condensation products are formed to a certain extent, their relative quantity being determined by the ketone, catalyst, and conditions used. Thus, for example, when condensing methyl ethyl ketone with itself 3-methyl heptene-3-one-5, 3,4-dimethyl hexene-3-one-5, 3,6,7-trimethyl nonadiene-3,6-one-5, may be isolated. With Al_2O_3 as a catalyst, for example, 3-methyl heptene-3-one-5 is the predominant product, while with acid catalysts 3,4-dimethyl-hexene-3-one-5 predominates. The alpha beta, alpha' beta' doubly unsaturated trimer which is also applicable may be separated from the reaction product by fractionation, although this step is not necessary.

Another and convenient method for preparing the desired alpha beta unsaturated ketones is through the condensation of a ketone of the above-mentioned class with an alpha substituted aldehyde. Any aldehyde having the structure

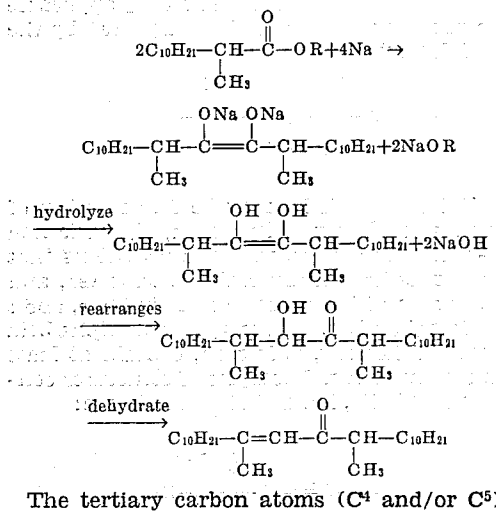


wherein R and R' represent aliphatic or cycloparaffinic groups may be employed. Thus, for example, methyl propaldehyde, ethyl propaldehyde, cyclopentyl propaldehyde are a few of the simpler aldehydes applicable.

Further, by using two mols of aldehyde to one mol of ketone having a hydrogen atom attached to each of the alpha carbon atoms, an alpha beta, alpha' beta' doubly unsaturated ketone, which is likewise applicable, may be made. For example, by reacting two mols of methyl butaldehyde with methyl ethyl ketone and dehydrating, one obtains



Another method of producing the desired alpha beta unsaturated ketones is through the dehydration of the corresponding acyloins. This may be accomplished according to the scheme



The tertiary carbon atoms (C^4 and/or C^5) in the above-mentioned alpha beta unsaturated ketone structure counteract to a certain extent the tendency of the unsaturated bonds to conjugate, i. e., to form static alpha beta unsaturated ketones. This counteracting tendency manifests

itself in the formation of an equilibrium mixture of alpha beta and beta gamma unsaturated ketone in which the beta gamma ketone content may range from traces to an appreciable amount, depending upon the size and character of the radicals, $R_{1, 2, 3, \text{and } 4}$. Although it usually requires a considerable time for equilibrium to become established under normal conditions, a few unsaturated ketones of the above structure equilibrate quite rapidly and, therefore, make the preparation of the pure alpha beta ketone difficult. It is to be understood, however, that the formation of an equilibrium mixture containing some beta gamma ketone instead of the pure alpha beta ketone does not detrimentally affect the applicability of these compounds in the present invention.

By subjecting the alpha beta unsaturated ketone (or an equilibrium mixture of alpha beta and beta gamma unsaturated ketone) to a fractional distillation at a rate not exceeding the rate of rearrangement, the lower boiling beta gamma unsaturated ketone may be continually removed causing the rearrangement to proceed to completion. This method of producing the desired beta gamma unsaturated ketone is quite simple and generally applicable to the ketones of the above-mentioned structure.

By simply fractionating in most cases the rearrangement takes place at too slow a rate, even at elevated temperatures, to be economically practical. This may be remedied, however, by the use of a small amount of a substance which catalyzes the rearrangement, i. e., increases the mobility of the system. It is found that alkali metal alkoxides in particular, such as the various alcoholates of sodium, lithium, potassium, aluminum, magnesium, etc., are suited. Other catalysts, such as alcoholic alkali and even mineral acid may sometimes be used.

Although the catalysts are usually effective in very small amounts, it is found that the rate of rearrangement is somewhat dependent upon the amount of catalyst present, being somewhat higher at catalyst concentration of about 3 to 5%.

While the lower boiling alpha beta unsaturated ketones are conveniently rearranged at their normal boiling points, such high molecular weight unsaturated ketones as are unstable at their normal boiling points may be rearranged at a somewhat lower temperature by carrying out the rearrangement under a suitably diminished pressure.

The beta gamma unsaturated ketones, which, according to the present invention, are fractionated from the rearranging mixture substantially as fast as formed, differ from the alpha beta unsaturated ketones in several respects. They show essentially no exaltation of the molecular refraction and have lower boiling points, melting points, refractive indices, and densities. Furthermore, these compounds behave differently on being hydrogenated. In the hydrogenation of the alpha beta unsaturated ketones severe conditions are usually required and the yields are generally poor due to the simultaneous formation of considerable amounts of hydrocarbons and saturated ketones. On the other hand, the corresponding beta gamma unsaturated ketones undergo hydrogenation under more favorable conditions and in a clean-cut manner to yield the corresponding alcohols in excellent yields.

The freshly distilled beta gamma unsaturated ketones tend to revert to the equilibrium mixture upon being allowed to stand. Therefore, when operating with a system having a high mobility it is preferable to utilize the freshly prepared material as promptly as possible. Since, however, in the majority of cases, the rate of rearrangement at normal temperatures and in the absence of a rearrangement catalyst is exceedingly slow, ample time for convenient execution is allowed.

The following example illustrates the preparation of a beta gamma unsaturated ketone by rearrangement of an alpha beta unsaturated ketone according to the process of the present invention.

Methyl propyl ketone is condensed with itself by refluxing over calcium carbide. The product consists of unreacted methyl propyl ketone and 4-methyl-nonene-4-one-6, with a small amount of isomeric alpha beta dimers and trimers. After distilling off the unreacted methyl propyl ketone, the condensation products are charged, along with about 1% of sodium ethoxide, into a suitable fractionating apparatus. The mixture is brought to boiling, held under total reflux for a few minutes, and then fractionated while maintaining the stillhead tempertaure below the boiling point of the 4-methyl-nonene-4-one-6 (195.5° C. at 760 mm.). In the absence of a rearrangement catalyst, the fractionation will be very slow. The distillate consists essentially of 4-methyl-nonene-3-one-6.

Upon the completion of the rearrangement and removal of the ten carbon unsaturated ketones, the stillhead temperature may be allowed to rise to the boiling point of the doubly unsaturated beta gamma, beta' gamma' trimer which may be collected separately. During this latter operation it is preferable to conduct the rearrangement and fractionation under a diminished pressure.

The present application is a division of my application Serial No. 182,005, filed December 27, 1937 which issued as U. S. Patent 2,197,462 on April 16, 1940.

I claim as my invention:

1. A process for the production of a beta gamma unsaturated ketone which comprises the steps of heating an alpha beta unsaturated ketone and separating the isomeric beta gamma unsaturated ketone from the reaction mixture at substantially the rate of formation from the alpha beta unsaturated ketone.

2. A process for the production of a beta gamma unsaturated ketone which comprises the steps of heating an alpha beta unsaturated ketone and fractionally distilling the isomeric beta gamma unsaturated ketone from the reaction mixture at a rate not exceeding the rate of formation from the alpha beta unsaturated ketone.

3. A process for the production of a beta gamma unsaturated ketone which comprises the steps of heating an alpha beta unsaturated ketone in the presence of an alcoholate of an alkali-forming metal and separating the isomeric beta gamma unsaturated ketone from the reaction mixture at substantially its rate of formation from the alpha beta unsaturated ketone.

4. A process for the production of a beta gamma unsaturated ketone which comprises the steps of heating an alpha beta unsaturated ketone in the presence of from about 1% to 5% of an alcoholate of an alkali-forming metal and separating the isomeric beta gamma unsaturated ketone from the rection mixture at sub-

stantially its rate of formation from the alpha beta unsaturated ketone.

5. A process for the production of a beta gamma unsaturated ketone which comprises the steps of heating an alpha beta unsaturated ketone in the presence of an alcoholate of an alkali-forming metal and removing the lower-boiling isomeric beta gamma unsaturated ketone by fractional distillation at substantially its rate of formation by a rearrangement reaction tending to establish an equilibrium mixture of alpha beta and beta gamma unsaturated ketones.

6. A process for the production of a beta gamma unsaturated ketone which comprises the steps of heating an alpha beta unsaturated ketone at a temperature not substantially greater than the normal boiling temperature and separating the isomeric beta gamma unsaturated ketone from the reaction mixture at substantially the rate of formation from the alpha beta unsaturated ketone.

7. A process for the production of a beta gamma unsaturated ketone which comprises the steps of heating an alpha beta unsaturated ketone at a temperature not substantially greater than the normal boiling temperature in the presence of an alcoholate of an alkali-forming metal and fractionally distilling the isomeric beta gamma unsaturated ketone from the reaction mixture at substantially the rate of formation from the alpha beta unsaturated ketone.

8. A process for the production of a beta gamma unsaturated ketone which comprises the steps of heating an alpha beta unsaturated ketone at substantially the boiling temperature under diminished pressure in the presence of an alcoholate of an alkali-forming metal and fractionally distilling the isomeric beta gamma unsaturated ketone from the reaction mixture at substantially the rate of formation from the alpha beta unsaturated ketone.

9. A process for the production of a beta gamma unsaturated ketone which comprises heating an alpha beta unsaturated ketone in the presence of a rearrangement catalyst, and separating the isomeric beta gamma unsaturated ketone from the reaction mixture at substantially its rate of formation therein.

10. A process for the production of a beta gamma unsaturated ketone which comprises heating an alpha beta unsaturated ketone in the presence of a rearrangement catalyst of the group consisting of the alcoholates of the alkali-forming metals and the alcoholic alkali solutions, and separating the isomeric beta gamma unsaturated ketone from the reaction mixture at substantially its rate of formation therein.

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