

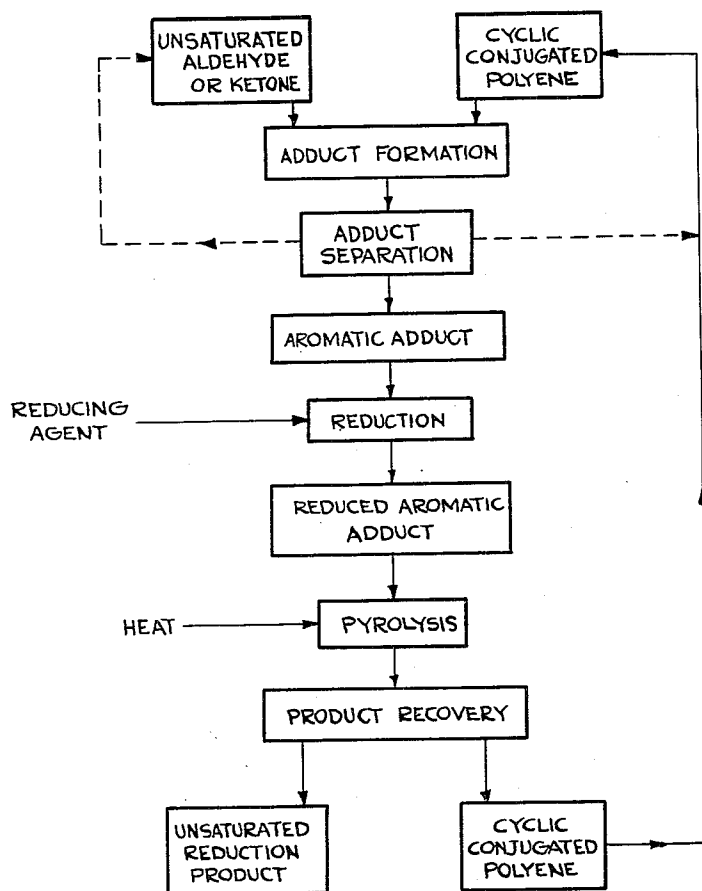
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REDUCTION OF 9,10 ANTHRACENE CARBOXYLIC ADDUCTS

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REDUCTION OF 9,10 ANTHRACENE CARBOXYLIC ADDUCTS

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This invention relates to the conversion of unsaturated aldehydes and/or ketones to olefinic reduction products by selective reduction of the carbonyl group or groups. It deals particularly with a new method of producing the corresponding primary or secondary alcohols or amines or other reduction products from olefinic aldehydes or ketones.

The reduction of saturated aldehydes or ketones is relatively easy to carry out well established methods. Application of these methods to olefinic aldehydes and ketones, however, results in simultaneous reduction of the olefinic bond to such an extent as to make them commercially impractical for the selective conversion of such aldehydes or ketones to the corresponding olefinic reduction product. Selective reduction of carbonyl groups in unsaturated aldehydes and ketones can be achieved by the use of reducing agents such as lithium aluminum hydride but such methods are far too expensive for practical large scale industrial use. Commercially feasible methods for the reduction of unsaturated aldehydes and ketones to the corresponding unsaturated alcohols are described in pending applications Serial Nos. 148,014, now abandoned, and 301,396, filed March 6, 1950, and July 28, 1952, respectively. While these methods are great improvements over prior procedures for producing olefinic alcohols from olefinic aldehydes and ketones, they still result in reduction of the olefinic double bond and/or other by-product formations to a greater extent than is desirable.

It is an object of the present invention to overcome the foregoing and other disadvantages of previous methods of converting unsaturated aldehydes and ketones to olefinic reduction products. An important object is the provision of a new process comprising a combination of interrelated steps whereby such reductions can be carried out more efficiently and economically than heretofore. Another object is to provide novel reaction steps useful in said process. A special object is the conversion of olefinic aldehydes and ketones to adducts which protect the olefinic bond during reduction and from which the reduction product can be regenerated so as to obtain high conversions and yields of olefinic reduction product. Another special object is the provision of a method of producing unsaturated alcohols by pyrolysis of 9,10-dihydro-9,10-ethanoanthracene-11 alkanols or substitution products thereof wherein the substituents are attached to the anthracene ring or heterocyclic ring analogues thereof. Still other objects and advantages of the invention will be apparent from the following description of the new process and the reactions employed therein.

It has been found that unsaturated aldehydes and ketones can be successfully converted to olefinic reduction products in high yield by a series of reaction steps comprising first reaction of the unsaturated aldehyde or ketone with a cyclic unsaturated compound having a conjugated system of double bonds with which the unsaturated carbon atoms of said aldehyde or ketone under-

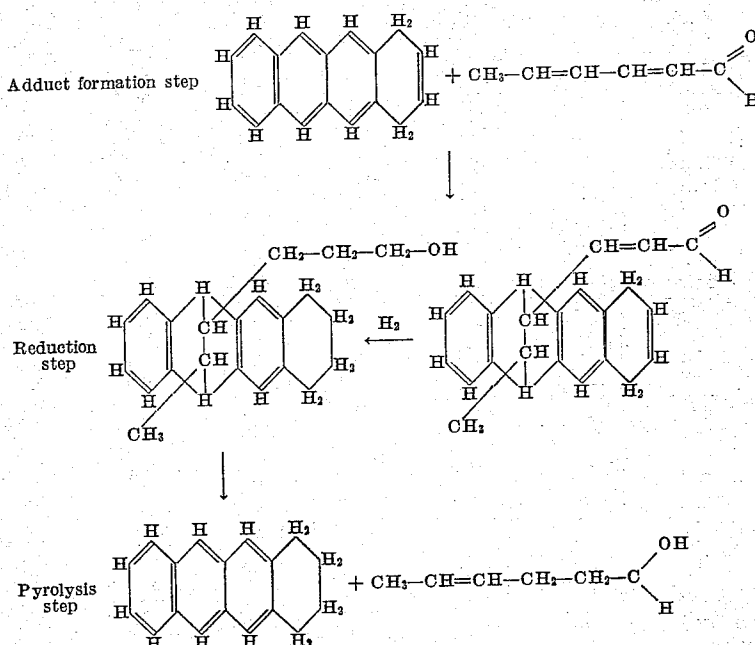
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go a 1,4-addition in which the double bond generated becomes an integral part of an aromatic system. The carbonyl group or groups of the resulting aromatic adduct are then reduced without altering the aromatic character of the adduct and the reduction product is decomposed to regenerate the starting cyclic polyene and produce the desired olefinic reduction product. The regenerated polyene can then be recycled to the first step of the process. The attached drawing is a flow diagram showing these steps of the new process as applied to one modification of the invention intended to be illustrative only. In this modification the decomposition of the reduced adduct as carried out by pyrolysis is exemplary of a type of reaction believed to be broadly new and valuable as a means of producing mono-olefinic alcohols, whether or not the other steps of the process are used for the preparation of the starting material for the pyrolysis.

As previously pointed out, it is essential in the first step of the process to choose for reaction with the starting olefinic aldehyde or ketone a cyclic unsaturated compound of a special type, namely, one which will form with said aldehyde or ketone an adduct having a cyclic ring structure of aromatic character. In other words, the cyclic unsaturated compound used must be one which will add to an olefinic double bond of the olefinic aldehyde or ketone used at carbon atoms each directly linked to at least one aromatic ring. Compounds having the anthracene structure are one suitable type which are effective as a class for this purpose. Suitable examples are anthracene, naphthanthracene, benzanthracene, alpha- or beta-anthrandan, cyclopenta-d,e-anthracene, naphtha-[2,3-f]quinoline, anthra[2,1-b]thiophene, anthra[2,1-b]thiophene, and the like. Substitution products of these compounds can be successfully used, examples of preferred compounds of this kind being the alkyl, phenyl, benzyl, hydroxy and alkoxy substitution products. As a general rule, hydrocarbons or hydroxy-substituted hydrocarbons are preferred when the reduction step of the process is to be carried out as a hydrogenation with metal catalysts, since longer catalyst life is usually obtained. By the use of other hydrogenation catalysts, particularly the so-called sulf-active catalysts in the second step, the process can be readily carried out with sulfur and/or nitrogen containing compounds such as the previously mentioned naphthaquinoline and anthrathiophene as well as analogues of anthracene type compounds such as alpha- and beta-anthrapyridines, for instance. There are special advantages in using for adduct formation alkyl anthracene, preferably those having 1 to 4 carbon atoms in the alkyl group or groups and not more than 4 carbon atoms in a single alkyl group. These compounds form, with the preferred unsaturated aldehydes and ketones of 3 to 8 carbon atoms, adducts which are believed to be new compositions. They are, unexpectedly, fluid at ordinary temperatures in contrast with the corresponding adducts of anthracene and other types of anthracene derivatives. Due to this fluidity they are easier to transport and handle in the process of the invention and have advantages and uses apart from that process such, for example, as high boiling solvents, as plasticizers, etc.

By the use of cyclic polyenes of the foregoing type one is able to form adducts with the olefinic aldehyde or ketone which have a difficultly reducible aromatic structure linked to the aldehyde or ketone group. As a result, it is feasible to reduce the carbonyl group or groups present selectively without altering the aromatic ring structure which, due to its stability, can also be split off from the reduced aldehyde or ketone with regeneration of the olefinic linkage through which the aldehyde or ketone becomes linked to unsaturated cyclic compound in forming the adduct. For these reasons the conjugated dienes usually used in forming ad-

ducts with unsaturated aldehydes and ketones by the Diels-Alder reaction cannot be used in the present process since they form alicyclic unsaturated rings which include two carbon atoms of the starting aldehyde or ketone. Hydrogenation of these unsaturated rings takes place as readily as, or more easily than, reduction of the carbonyl group or groups, and the hydrogenated products cannot be decomposed to regenerate the starting diene and form an olefinic reduction product corresponding to the starting aldehyde or ketone. It will be understood, however, that the presence of alicyclic unsaturated ring structures in the adducts, formed, according to the first step in the process of the invention, does not interfere with successful operation of the invention provided a double bond generated in the formation of the adduct becomes an integral part of an aromatic ring system. Thus, when acetylenic aldehydes or ketones are used in the process two double bonds will be formed, one of which becomes a part of an aromatic ring while the other will be a part of an alicyclic ring which will undergo hydrogenation along with the carbonyl group. The resulting reduced adduct will nevertheless be readily split according to the process of the invention to form an olefinic reduction product of the starting aldehyde or ketone since the carbon atoms of said aldehyde or ketone will be directly linked in the reduced adduct to an aromatic system. Likewise, there may be present in the adducts unsaturated alicyclic structures or other olefinic linkages at points removed from those at which the attachment of the unsaturated aldehyde or ketone takes place. These can undergo reduction along with the carbonyl group or groups with the result that the reduced adduct may give pyrolysis products which are more saturated than the starting cyclic compound and aldehyde or ketone from which adduct was initially prepared. However, these pyrolysis products will nevertheless be an olefinic reduction product of the starting aldehyde or ketone and an unsaturated cyclic compound which contains the essential structure for adduct formation, and the reduced adducts will be readily decomposed according to the invention because of the aromatic character of the ring structure to which the reduced aldehyde or ketone groups are attached. This can be seen from the following equations for one illustrative case in which both the starting compounds undergo hydrogenation in addition to reduction of the carbonyl group:



A disadvantage of using cyclic compounds of this type for adduct formation is, of course, that the consumption of reducing agent is greater when they are first introduced

but upon recycling after pyrolysis there is no further consumption of hydrogen by the adduct former.

The formation of the adducts in the first step of the process can be readily carried out by simply heating the described adduct formers with the unsaturated aldehyde or ketone to be reduced. Temperatures of about 50° C. to about 400° C. can be used. However, a temperature between about 150° C. and 200° C. is preferred in order to secure high conversions in shorter reaction times. About ½ to 3 hours is usually sufficient to substantially complete the reaction which is preferably conducted under superatmospheric pressure; more preferably under at least 500 p. s. i. g. Pressures of the order of about 1000 to 3000 p. s. i. g. are advantageous. Solvents for the reactants and adduct are useful media for the reaction. Hydrocarbons such as benzene, toluene, paraffins, gasoline or kerosene fractions, the mixed hydrocarbons sold for use as heat transfer media under the trade name "Dowtherm" and the like are suitable solvents. Alcohols, ethers or the like can also be used as solvent—isopropyl alcohol, diethyl ether, etc., for example, being satisfactory. From about 1 part of organic solvent medium to 100 parts or more per part of unsaturated aldehyde or ketone can be employed. Stoichiometric proportions or an excess of either of the reactants can be used in forming the adducts. Advantageous ratios are about 1.0 to 2 moles of one of the reactants per mole of the other reactant. Where an excess of one of the reactants is employed, it is preferred to use the lower boiling reactant, usually the unsaturated aldehyde or ketone in excess since removal of the unreacted excess for recycling to the reaction is thereby facilitated.

It is usually unnecessary to separate the adduct from the reaction mixture in which it is prepared, although it is usually desirable, particularly where an excess of one of the reactants has been employed in forming the adduct, to remove any unreacted aldehyde or ketone and/or cyclic adduct formed therefrom before using the adduct in the reduction step of the process. The thus recovered reactant or reactants can then be recycled for further adduct formation.

The reduction of the carbonyl group or groups of the adduct formed in the first step of the process can be carried out in a number of different ways by reaction with hydrogen. One particularly convenient mode of reduc-

tion, where the production of olefinic primary or secondary alcohols is desired, is catalytic hydrogenation, most preferably in the liquid phase. The hydrogenation can

be carried out with the crude mixture from the adduct formation step preferably after removal of unconverted starting reactants but most preferably without removal of the solvent if solvent was used, by suspending a hydrogenation catalyst therein or otherwise contacting the mixture with the catalyst and subjecting the whole to the action of hydrogen.

Any of the hydrogenation catalysts known to the art may be used with varying degrees of effectiveness in the hydrogenation step of the present process. Of those which are especially adapted to use in accordance with the present invention, the catalysts known to the art as Raney's nickel and Adkins' copper-chromium oxide catalyst are very efficacious from the standpoints of both cost and efficiency. Other suitable hydrogenation catalysts are those consisting of or comprising one or more metals, or catalytically active compounds of metals, such as Fe, Co, Cu, Pd, Zr, Ti, Th, V, Pt, Ta, Ag, Mo, Al, and the like. The catalysts can be used with or without inert or catalytically active carriers or supports or activators.

In a preferred case e. g., when Raney nickel is employed as the hydrogenation catalyst in an amount from about 2 per cent to about 10 per cent of the product to be hydrogenated, the hydrogenation may be effected satisfactorily at temperatures of from about 30° C. to about 150° C. and under hydrogen pressures of from about 500 to about 5000 pounds or more per square inch. When other catalysts are employed, conditions leading to an equivalent degree of hydrogenation are preferably employed. Hydrogenation times of the order of about 0.5 to 8 hours are usually sufficient. At the conclusion of the hydrogenation, the catalyst can be separated from the mixture as by filtration, for example, and reused in the process. In some cases a reactivation treatment may be desirable before such reuse of the catalyst.

Whatever method of reduction is employed, the resulting product can be decomposed as previously indicated to liberate the desired olefinic reduction product of the starting unsaturated aldehyde or ketone and regenerate the cyclic polyene for reuse in the first step of the process. It has been found that pyrolysis of the reduced adduct is one of the most advantageous methods of carrying out such decomposition. Heating of the reduced adduct at about 250° C. to 400° C. is usually effective. The pyrolysis is preferably carried out at ordinary pressures, although higher pressures can be used and subatmospheric pressures are sometimes advantageous in promoting prompt removal of the olefinic reduction product. Such removal is advantageous in any case as a means of preventing undesirable further reaction of the product. As a rule, heating for a period of about 2 to about 60 minutes is sufficient for substantially complete pyrolysis to the desired products.

The process is applicable to the reduction of a wide variety of unsaturated, preferably olefinic, aldehydes and ketones which may be aliphatic, alicyclic or aromatic-substituted aldehydes. The aldehydes and ketones may be substituted by hydroxy, ether, mercapto, sulfide, keto, amino, and the like groups or halogen atoms. However, when mercapto-, sulfide-, amino- and halogen-substituted aldehydes and ketones are used, it is desirable to employ chemical reduction or catalytic hydrogenation with a so-called "sulf-active" or other poison-resistant catalyst since these substituents tend to shorten the life of most hydrogenation catalysts. Acrolein, crotonaldehyde, methacrolein, tiglic aldehyde, alpha-ethyl acrolein, beta-methyl crotonaldehyde, alpha,beta-dimethyl crotonaldehyde, alpha,gamma-dimethyl crotonaldehyde, beta-ethyl crotonaldehyde, 2-hexenal, alpha-isobutyl acrolein, alpha-amyl acrolein, citral, cinamaldehyde and the like, are representative of the alpha,beta-olefinic aldehydes to which the new process can be applied with special advantage because this type of unsaturated aldehyde gives particularly great difficulty in reduction to unsaturated alcohols by prior methods. The new process is equally successful,

however, in the reduction of aldehydes having an olefinic double bond or an acetylenic linkage further removed from the aldehyde group. Typical examples of such aldehydes which have been so used are vinyl acetaldehyde, 3-pentenal, 4-pentenal, methyl vinyl acetaldehyde, isopropenyl acetaldehyde, citronellal, rhodinal, and 2-phenyl-4-hexenal. Cyclo-olefinic aldehydes such, for example, as can be produced as Diels-Alder adducts of dienes with olefinic aldehydes are a particularly useful sub-group of starting materials for use in the new process. These include, for instance tetrahydrobenzaldehyde produced as an adduct of butadiene and acrolein, the methyl tetrahydrobenzaldehydes produced as adducts of acrolein with pentadiene, isoprene, or dimethyl pentadiene; 1-methyl-3-cyclohexenecarboxaldehyde and 6-methyl-3-cyclohexenecarboxyaldehyde from butadiene with methacrolein and crotonaldehyde, respectively, and 2,5-endomethylene-tetrahydrobenzaldehyde from acrolein and cyclopentadiene, for instance. Among the unsaturated ketones which can be similarly reduced are olefinic ketones such, for instance, as methyl vinyl ketone, methyl allyl ketone, ethyl isopropenyl ketone, mesityl oxide, phorone, isophorone, methyl cyclohexenyl ketone, vinyl phenyl ketone, benzyl acetone and the like, and acetylenic ketones of which butyn-2-one, ethynyl acetone, 2-pentanone-3-yne and the like are typical. Cyclic unsaturated ketones which can be reduced in the same way include, for example, the tetrahydroacetophenones, the tetrahydrobenzophenones, irone, ionone, etc., those obtainable by addition of dienes with olefinic ketones, for instance, adducts of butadiene, pentadiene, isoprene, cyclopentadiene, the hexadienes and the like with vinyl, allyl and other olefinic ketones being particularly useful sources of the corresponding olefinic alcohols when used as starting materials in the new process. Instead of individual unsaturated aldehydes or ketones, mixtures of two or more such aldehydes or of two or more unsaturated ketones can be reduced in the same way. The unsaturated aldehyde or unsaturated ketone or mixtures thereof need not be pure, but can contain other compounds including saturated aldehydes or other compounds which may undergo simultaneous reduction, or inert compounds which will not interfere with the reaction.

The following examples illustrate in more detail suitable methods of carrying out the various steps of the new process and show some of its advantages:

Example 1

Acrolein was reacted with anthracene using 89 grams of anthracene (0.5 mole) and 28 grams of acrolein (0.5 mole). After heating for two hours at 170° C., 33 grams of anthracene (37% of the charge) was recovered. The remainder, weight 84 grams, was a light colored viscous syrup which contained the desired anthracene-acrolein adduct as shown by the following analysis on the highly insoluble 2,4-dinitrophenylhydrazone derivative (M. P. 206-207° C.) which it formed:

	Found	Calculated for C ₂₃ H ₁₅ N ₄ O ₄
C	67.0	66.7
H	4.8	4.4
N	13.4	13.5

This residue was hydrogenated in ethanol solution using 10% by weight of Raney nickel catalyst and 1000 p. s. i. g. pressure of hydrogen. At 100° C. approximately the theoretical amount of hydrogen for selective reduction of the carbonyl group to carbinol was absorbed in about three hours after which no further absorption could be detected. The product (M. P. 106-107° C.) crystallized readily from toluene-petroleum ether or etha-

nol-water mixtures in excellent yield and analyzed as follows:

	Found	Calculated for $C_{17}H_{16}O$
C.....	86.1	86.4
H.....	6.8	6.8

Pyrolysis of the hydrogenated anthracene-acrolein adduct at 300° C. proceeded smoothly to give better than a 95% yield of allyl alcohol as confirmed by mixed melting point (68–69° C.) of the phenyl urethane, analyzing as follows:

	Found	Calculated for $C_{16}H_{14}O_2N$
C.....	67.6	67.8
H.....	6.5	6.3
N.....	7.8	7.4

Using methyl vinyl ketone instead of acrolein under the same conditions gives an equally good yield of methyl vinyl carbinol.

Example II

Equimolar amounts of acrolein and anthracene were heated at 160° C. for 2 hours in an amount of "Dowtherm A" equal to the weight of anthracene and the resulting mixture was hydrogenated at 75° C. with Raney nickel catalyst under 1000 p. s. i. g. pressure of hydrogen. After pyrolysis of the product at 300° C. a 75.5% conversion of acrolein to allyl alcohol in a yield of 79.8% was obtained.

In the same way, using methacrolein and anthracene as the starting materials, a good yield of methallyl alcohol is obtained while, with mesityl oxide in place of the methacrolein, 4-methyl-3-pentene-2-ol is recovered in excellent yield.

Example III

The effect of pressure in the adduct formation step was shown by tests in which the adduct was formed by reacting equimolar amounts of acrolein and anthracene in benzene (the weight of benzene being equal to that of the anthracene) at 160° C. for 2 hours, followed by hydrogenation of the adduct in the presence of Raney nickel catalyst after removal of the unreacted acrolein and anthracene and pyrolysis at 300° C. of the resulting 9,10-dihydro-9,10-ethano-anthracene-11-methanol. Using atmospheric pressure in the adduct formation step, an overall conversion of acrolein to allyl alcohol of about 75% was obtained. When the adduct formation was carried out under 1000 p. s. i. g. of nitrogen pressure, the conversion increased to 80%.

Example IV

The advantage of using an excess of one of the reactants in forming the adducts for hydrogenation and pyrolysis is shown by the following tests made in the reaction of acrolein with anthracene in benzene solution at 160° C. using 2 hours' reaction time and 1000 p. s. i. g. of nitrogen pressure followed by hydrogenation of the resulting 9,10-dihydro-9,10-ethano-anthracene-11-carboxaldehyde and pyrolysis of the hydrogenation product as described in Example II.

Moles of Acrolein Used per Mole of Anthracene	Conversion to Allyl Alcohol (Percent of theoretical)
1.5.....	92.6 based on anthracene.
1.0.....	81.0 based on anthracene or acrolein.
0.5.....	86.7 based on acrolein.

By ultraviolet analysis the losses of anthracene were found to be not more than 2% in the process.

Example V

An adduct of beta-methyl anthracene with acrolein was produced using equimolar proportions of the reactants, a reaction temperature of 160° C. and a pressure of 1000 p. s. i. g. The adduct was hydrogenated under 1000 p. s. i. g. pressure of hydrogen at 75° C. with Raney nickel catalyst and the hydrogenated adduct pyrolyzed at 300° C. A 77.4% conversion of acrolein to allyl alcohol in 90.6% yield was obtained.

Under the same conditions using crotonaldehyde in place of acrolein an equally good yield of crotyl alcohol is obtained.

Example VI

When 9,10-dimethyl anthracene was used in the process of Example V instead of beta-methyl anthracene, the final conversion of acrolein to allyl alcohol with four hours' reaction at 130° C. in the adduct formation step was 85% of the theoretical.

With methyl cyclohexenyl ketone in place of acrolein under the same conditions, a high yield of methyl cyclohexenyl carbinol was obtained.

It will thus be seen that the new process is capable of considerable variation not only with respect to the types of unsaturated aldehydes and ketones which can be successfully reduced but also in regard to the kinds of olefinic reduction products which can be obtained. It will also be apparent that the operating conditions can be varied widely in each of the steps of the process. The invention will therefore be recognized as not limited to the procedures disclosed by way of example nor by any theory proposed in explanation of the improved results which are obtained.

We claim as our invention:

1. A process for selectively reducing the carbonyl group of a carbonyl compound of the group consisting of mono-olefinic aldehydes and olefinic ketones having not more than 14 carbon atoms per molecule which comprises reacting said carbonyl compound with an anthracene compound of the group consisting of anthracene and the alkyl and aryl anthracenes in solution in a liquid hydrocarbon at about 50° C. to about 400° C. under a pressure of 500 to about 3000 p. s. i. g., hydrogenating the carbonyl group of the resulting 9,10-dihydro-9,10-ethano-anthracene carbonyl compound by reacting said compound with gaseous hydrogen at about 30° C. to about 150° C. in the presence of a hydrogenation catalyst of the group consisting of Raney nickel and copper-chromium oxide catalysts under a hydrogen pressure of from about 500 to about 5000 pounds per square inch, and pyrolyzing the hydrogenation product by heating it at about 250° to 400° C. to produce an olefinic alcohol corresponding to the starting carbonyl compound and regenerate said anthracene compound.

2. A process in accordance with claim 1 wherein the carbonyl compound is an alpha,beta-monoolefinic aldehyde of 3 to 8 carbon atoms per molecule and the anthracene compound is an alkyl anthracene having 1 to 4 carbon atoms in the alkyl groups.

3. A process for producing allyl alcohol which comprises reacting acrolein with an anthracene compound of the group consisting of anthracene and the alkyl anthracenes in solution in a liquid hydrocarbon at about 150° to about 200° C. under a pressure of 500 to about 3000 p. s. i. g., hydrogenating the carbonyl group of the resulting 9,10-dihydro-9,10-ethano-anthracene-11-carboxaldehyde by reaction with gaseous hydrogen at about 30° C. to about 150° C. in the presence of a hydrogenation catalyst of the group consisting of Raney nickel and copper-chromium oxide catalysts under a hydrogen pressure of about 500 to about 5000 pounds per square inch, and pyrolyzing the hydrogenation product to produce allyl alcohol and regenerate said anthracene compound.

4. A process in accordance with claim 3 wherein the

acrolein is reacted with an excess of alkyl anthracene having 1 to 4 carbon atoms in the alkyl groups and the hydrogenation is carried out with about 2 to about 10% of Raney nickel based on the 9,10-dihydro-9,10-ethano-anthracene-11-carboxaldehyde present.

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