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PROCESS FOR CATALYTIC ISOMERIZATION OF COMPOUNDS OF UNCONJUGATED POLYETHENOID ACIDS

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The invention relates to a process for a substantially complete catalytic conversion of compounds of unconjugated polyethenoid acids into compounds of conjugated ethenoid acids.

It is known that certain properties of unsaturated fatty acids and their derivatives can be altered by rearrangement of the structure of the double bond, either with respect to their steric position or their position in the carbon chain of the molecule of the fatty acid. This reaction is named "isomerisation." Unsaturated fatty acids having more than one —CH=CH— group in the chain are also known as "polyethenoid acids"; molecules with such contiguous groups having double bond between two carbon atoms such as —CH=CH—CH=CH— are known as conjugated ethenoid acids, while non-contiguous groups of this configuration will be considered as unconjugated ethenoid acids. The latter ones, namely the unconjugated polyethenoid acids occur in nature in large quantities, while conjugated polyethenoid acids are relatively seldom found in fats or oils of natural origin except for wood oils such as tung oil. The latter compound and also its derivatives are of great technical interest and, therefore, many attempts were made to isomerise unconjugated polyethenoid acids to conjugated ones. Theoretically, such a shifting of the double bond is possible because the conjugated form has a lower state of energy than the unconjugated form.

Because of the fact that conjugated unsaturated compounds are obtained by hydrogenation of fats, catalysts, similar to those used for hydrogenation, have been used for isomerisation, especially nickel catalysts. However, when using such catalysts, an incomplete isomerisation is achieved, and also unwanted side reactions occur; these side reactions, especially polymerisation and intramolecular cyclisation take place to a more or less large extent.

The known isomerisation with an excess of alkali metal hydroxide in an aqueous or alcoholic medium leads to a quantitative isomerisation. This reaction is also used for a quantitative determination of unconjugated polyethenoid acids, because the conjugated polyethenoid acids formed by the isomerisation of the unconjugated acids may be determined and measured by spectrophotometric methods. Not only on a technical scale but also in the analytical method a considerable excess of alkali metal hydroxide must be used, so that the conjugated fatty acids or fatty acid compounds are obtained in form of their alkali soaps and have to be recovered and isolated accordingly. These techniques differ in the use of a particular solvent, temperature and pressure.

Catalysts which may be used for this so-called alkali isomerisation at first react, under conditions applied so far, in stoichiometrical amounts or proportions with the

functional groups of the fatty acids or their compounds such as carboxyl groups, ester groups, amide groups, and similar groups before an isomerisation can be obtained. Thereby, a corresponding amount of the catalyst is inactivated and the isomerisation can be achieved only by addition of an excessive amount of catalyst.

The conditions of reaction in the analytical method involve several disadvantages, and in consequence potassium tertiary-butylate in tertiary-butanol is sometimes used as isomerisation agent. In that case the isomerisation can be carried out at a temperature of about 85° C. within a period of about 4 hours, although higher temperatures up to 140° C. are possible, a larger amount than the stoichiometric amount of potassium tertiary butylate always being used.

Surprisingly it has now been found that the quantitative alkali isomerisation of compounds of unconjugated polyethenoid acids, for example, esters of monohydric alcohols, amides and polyamides, and their mixtures can be achieved, if the compounds of unconjugated polyethenoid acids are treated with catalytic amounts of 0.05 to 5% by weight, preferably with 0.3 to 2% of alkali metal alcoholates, especially from monohydric alcohols, at a temperature between 60 and 180° C. preferably between 100 and 140° C. under conditions which avoid inactivation of the catalyst. The method may also be carried out in presence of monohydric alcohols or other polar or nonpolar solvents which are inert with respect to the catalyst. Dimethyl formamide and dimethyl sulphoxide are especially suitable.

The method according to the invention has the main advantage that isomerisation is possible without using more than stoichiometrical amounts of alkali metal alcoholates avoiding thereby the serious disadvantages connected therewith.

The catalysts used in connection herewith belong to the group of interesterification or ester interchange catalysts, i.e. catalysts which can accelerate both the interesterification and isomerisation reactions. Their effectiveness decreases according to the following order: cesium, rubidium, potassium, sodium, lithium, magnesium, zinc. Potassium alcoholates are especially useful as isomerisation catalysts for technical purposes not only because of their adequate catalytic activity but also for their partially associated solubility.

Alkali metal compounds of any monohydric alcohol can be used as catalyst, for example, alkali metal compounds of methyl alcohol, ethyl alcohol, propyl alcohol, or butyl alcohol and also alkali metal amides. Potassium methylate is preferred. Alkali metals, alkali metal hydrides, organic alkali metal compounds, may be used so long as they react in the reaction mixture to form active catalysts such as alkali metal alcoholates or alkali metal amides. According to the invention the catalyst may be used in the amount of 0.05–5% by weight and preferably of 0.5–2%, based on the amount of the polyethenoid acid compound to be isomerised.

The activity of the mentioned catalysts can be increased remarkably by adding small amounts of all kinds of monohydric alcohols. A suitable procedure is to mix molar amount of alkali metal alcoholates with alcohols, whereafter this mixture is added to the polyethenoid acid derivative to be isomerised.

The temperature of treatment has an important influence on the rate of the reaction and also on the oc-

currence of undesired side reactions. A sufficient rate of isomerisation for practical purposes is only observed at temperatures above 60° C. while above a temperature of 140° C. side reactions will be observed to a noticeable extent. The best range of temperature is between 100 and 140° C.

To obtain the maximum activity of the mentioned catalysts certain conditions of reaction have to be fulfilled and maintained. The compounds of the polyethenoid acids to be isomerised have to be completely free from all compounds which will react with alcoholates, for example, water, free fatty acids, or hydroperoxides. If such compounds are present the catalyst will be partly or completely inactivated, so that the desired reactions occur only partly or do not take place. Therefore, such compounds should be removed or converted into inert compounds by conventional steps prior to isomerization.

For this isomerization reaction all esters of unconjugated polyethenoid acids with monohydric alcohols, especially those of the naturally occurring linoleic acid, linolenic acid and arachidonic acid and also of the higher polyethenoid acids of marine origin namely tri-, tetra-, penta- and hexethenoid acids may be used, furthermore any amides of the above mentioned fatty acids and all compounds and derivatives of these fatty acids, the functional groups of which are incapable of an inactivating reaction with the catalyst. According to the invention the isomerization reaction can be controlled in such a way that a partial conjugation of diene acids and more highly unsaturated fatty acids is favored.

The isomerization of the fatty acid esters and amides can be carried out so that interesterification or aminolysis takes place at the same time.

To control the progress of isomerization, a test is used as described by B. Sreenivasan and J. B. Brown in Journal of the American Oil Chemists Society, volume 33, page 521 (1956), and volume 35, page 89 (1958). According to this method the original substrate, the final product and also samples of the reaction mixture withdrawn at certain time intervals are analysed. The extent of the isomerization is given by the measured

$$E^{1\%}_{1\,cm.}$$

values in relation to the

$$E^{1\%}_{1\,cm.}$$

determined by the above method. The extent of isomerization of diethenoid acids is given by

$$\frac{E^{1\%}_{1\,cm.}\ @\ 234\ m\mu\ \text{determined} - \left(E^{1\%}_{1\,cm.}\ @\ 268\ m\mu\ \text{determined} \times \frac{631}{743}\right)}{E^{1\%}_{1\,cm.}\ @\ 234\ m\mu\ \text{analytical} - \left(E^{1\%}_{1\,cm.}\ @\ 268\ m\mu\ \text{analytical} \times \frac{631}{742}\right)} + 100$$

and the extent of isomerization of the triethenoid acids is given by

$$\frac{\text{determined } E^{1\%}_{1\,cm.}\ @\ 268\ m\mu}{\text{analytical } E^{1\%}_{1\,cm.}\ @\ 268\ m\mu} \times 100$$

In this it is assumed that the method of Sreenivasan and Brown results in complete isomerization.

In the examples the percentage isomerization is calculated on the basis of fatty acids.

The invention is illustrated by, but is not intended to be limited to, the following detailed examples showing various embodiments of the invention.

Example 1

5000 g. of the distilled methyl ester of soya bean fatty acids containing 6.3% linolenic acid and 46.0% linoleic acid, combined as esters, were heated to a temperature of 120° C. and mixed with 50 g. of dried potassium methylate. The mixture soon turned into a brownish color and was allowed to stand for a period of 5 hours being agitated from time to time. At certain time intervals several samples were taken and, after the catalyst had been removed by washing, they were used for spectrophotometrical determination of conjugated polyethenoid acids. The results are shown in the following table:

Reaction time in minutes	Percent isomerization of triethenoid esters	Percent isomerization of diethenoid esters
15	5	6
45	28	28
90	63	53
135	81	66
180	95	80
240	98	90
300	95	97

The results show that about 97% of the total ester of unconjugated polyethenoid acids is converted into the ester of the conjugated polyethenoid acids. Allowing for the margin of error of spectrophotometrical methods the isomerization may be considered as practically complete.

Within a range of temperature between 100 and 140° C. parallel experiments with the same material and the same catalyst gave corresponding results. At a temperature of 80° C. the reaction is considerably slower, and at a temperature of 60° C. only a very slow reaction rate was observed. The isomerization is also slowed down if the amount of catalyst decreases, and is hardly noticeable with an amount of 0.1% potassium methylate. An increase of the amount of the catalyst above 1% does not accelerate the reaction noticeably.

Analogous results were also obtained with ethyl, propyl and butyl esters of soya bean acids; in addition, potassium ethylate, propylate and butylate instead of potassium methylate gave the same results.

Example 2

A distilled methyl ester of soya bean oil acids having the same composition as described in Example 1 was used as substrate. The catalyst was prepared by grinding potassium methylate with different alcohols in a molar ratio of 1 mol of potassium methylate to 0.5–2 mols of methyl alcohol, ethyl alcohol, normal or isopropyl alcohol or normal or secondary butyl alcohol or lauryl alcohol or benzyl alcohol respectively. In this way solid or semi-solid compositions were formed which were added to the mixture heated up to the necessary reaction temperature and the catalyst was quickly and uniformly distributed by agitation.

The following run may be taken as an example. 5,000 g. of the methyl ester of soya bean fatty acids were reacted at a temperature of 140° C. The catalyst consisted of a mixture of 50 g. of potassium methylate and 53 g. of secondary butyl alcohol. The run was made as described in Example 1. The progress of the isomerization is shown by the results of the following table:

Reaction time in minutes	Percent isomerization of triethenoid esters	Percent isomerization of diethenoid esters
15	91	68
45	100	90
90	100	100
135	100	100
180	100	100

After a period of 45 minutes the isomerization of the ester of linolenic acid was already complete, while after a period of 90 minutes the ester of the linoleic acid was completely isomerized. Compared with the run described in Example 1 the reaction time had been decreased to less than one-third.

This run also shows that the range of temperature between 100 and 140° C. is most favorable for isomerization. The optimal composition of the catalyst is between a molar ratio of 1 mol of potassium methylate to 1–2 mols

of alcohol where ethyl alcohol, propyl alcohol or butyl alcohol is used, while for methyl alcohol the best ratio is 1:1.5–2. Here, the optimum concentration of the catalyst was also 0.5 to 1% of potassium methylate.

Example 3

3,000 g. of distilled propyl ester of cotton seed fatty acids containing 45.5% linoleic acid combined as ester, were heated to a temperature of 140° C. and mixed with a catalyst composition with stirring; the catalyst was obtained from 15 g. potassium methylate and 22 g. of isopropyl alcohol. When the reaction temperature was maintained at such a level with occasional stirring, the isomerization was 85% complete after a period of 15 minutes; after a period of 45 minutes an isomerization of 98% had taken place; after a period of 90 minutes an isomerization of 100% was obtained.

After cooling of the reaction mixture and removal of the catalyst by washing with hot water an extremely light colored product was obtained, as it was in the Examples 1 and 2.

Example 4

With mixtures of esters containing large amounts of linolenic acid and small amounts of linoleic acids a superimposition of isomerization reactions of the esters of linolenic and linoleic acid was observed. The rate of isomerization of the triply unsaturated acid is substantially larger than the corresponding rate of the doubly unsaturated acid. However, during the further reaction the content of the conjugated tri-ethenoid acid is reduced, while the content of conjugated di-ethenoid acid exceeds the value calculated from the content of linoleic acid. The reason for this is, on the one hand, that the isomerization of linolenic acid occurs in two steps whereby a conjugated di-ethenoid acid is formed during the first step, while the conjugated tri-ethenoid acid is formed only during the second step. On the other hand, the ester of the conjugated tri-ethenoid acid undergoes a further change during treatment whereby a cyclic di-ethenoid acid ester is formed. This will be illustrated by the following typical example.

5,000 g. of distilled methyl ester of linseed oil acids containing 43.8% of linolenic acid and 14.3% of linoleic acid, combined as esters were heated to a temperature of 120° C. and mixed with stirring with a catalyst prepared from 50 g. of potassium methylate and 43 g. of isopropyl alcohol. The mixture immediately turned a dark brown color and was maintained at a temperature of 120° C. with occasional stirring. Samples were taken periodically and the content of the several conjugated acids was determined spectrophotometrically. The results are given in the following table.

Reaction time in minutes	Percent isomerization of triethenoid esters	Percent isomerization of diethenoid esters
15	88	70
30	97	75
45	93	80
90	90	90
135	88	100

After a reaction period of 30 minutes the linolenic acid is completely isomerized while isomerization of linoleic acid requires more time. If it is desired to obtain products containing a large amount of conjugated tri-ethenoid acids, the treatment is discontinued after a suitable period, in the above example, after 30 minutes. The run was repeated under the same conditions for a period of only 30 minutes and an extremely light colored product was obtained containing 53.0% of conjugated fatty acids, which corresponds to a total isomerization of about 92%.

By changing the temperatures and concentration of the catalyst it is easy to obtain a total isomerization of almost 100%. For this purpose a temperature of 120° C. is best, and the amount of catalyst may be twice as much as in the run described above. Under these conditions a product was obtained after a period of 1½ hours in which the unconjugated poly-ethenoid fatty acids were converted into conjugated acids up to an extent of 98%.

Example 5

3,000 g. of the methyl ester of linseed oil fatty acids were heated in a three necked reaction flask having a capacity of 5,000 ml. and equipped with a stirrer, condenser, thermometer, gas inlet tube and gas outlet tube. The ester was heated up to a temperature of 120° C. under a nitrogen blanket. Whilst continuously stirring and introducing nitrogen at a low rate 200 ml. of a 14% solution of potassium tertiary butylate in tertiary butanol were added within a period of 10 minutes during which tertiary butanol and some methyl alcohol was distilled off. The mixture was maintained under these conditions at a temperature of 120° C. for 3 hours after which the mixture was cooled and washed several times with water and dried under vacuum.

To measure the extent of the isomerization obtained, samples of the material were tested spectrophotometrically before and after isomerization with respect to the content of unconjugated and conjugated fatty acids, giving the following results:

	Isomerization		After further analytical isomerization
	Before	After	
Percent linoleic acid	16.4	---	---
Percent linolenic acid	43.9	---	---
Percent total unconjugated poly-ethenoid acids	60.3	---	---
Percent isomerized di-ethenoid acids	---	15.2	15.0
Percent isomerized tri-ethenoid acids	---	42.6	42.3
Percent total isomerized poly-ethenoid acids	---	57.8	57.3

Allowing for the fact that up to 10% tertiary butyl ester is obtained by this method, a practically complete isomerization of the untreated material is achieved, which is confirmed by the further analytical isomerization and measurements of the treated product.

Example 6

1,000 g. of the methyl ester of soya bean fatty acids, 350 ml. of n-heptane and 310 ml. of tertiary butyl alcohol were heated to boiling in a glass flask of 2,000 ml. capacity being equipped with an inserted thermometer a rectification column having 12 theoretical plates and a condenser. Then 50 ml. of a 5% solution of potassium tertiary butylate in tertiary butanol were added and heated under complete reflux conditions for a period of 2 hours. The content of the flask was at a temperature between 105 and 110° C. As soon as the distillate began to separate into two phases the alcoholic phase was continuously removed and the heptane phase was returned to the rectification column. During this treatment several samples of the content of the still were taken at certain time intervals in order to analyse their content of conjugated and unconjugated fatty acids and also the amount of tertiary butyl ester. The time of the treatment and the analytical results are shown in the following table:

Time of treatment (hours)	0	6	12	20	30
Tertiary butyl ester (percent by by weight)	---	42	58	79	99.5
Isomerized diethenoid acid, percent	0.1	37.2	41.5	49.5	48.7
Isomerized triethenoid acid, percent	0	8.0	7.6	7.2	7.0

While the starting material contained 55.7% of linoleic acid and 8% of linolenic acid, combined as ester, the further analytical isomerization and the corresponding

spectrophotometrical test of the completely esterified product gave a content of 48.3% of isomerized di-ethenoid fatty acids and 6.8% of isomerized tri-ethenoid fatty acids. Taking into account the difference between the molecular weight of the methyl ester used and the butyl ester obtained, a practically complete isomerization of the unconjugated polyethenoid acid is obtained. This was achieved after a treatment of about 20 hours, namely before the methyl ester used had been quantitatively converted into the corresponding tertiary butyl ester.

Example 7

By using the apparatus as described in Example 5, 2,800 g. of distilled methyl ester of fish oil fatty acids were heated to a temperature of 140° C. to which 300 ml. of a hot 5% solution of caesium tertiary butylate in tertiary butanol were added. After having distilled the bulk of the tertiary butanol in a stream of nitrogen, the mixture was stirred under vacuum at the temperature of 140° C. for two further hours, so that the complete time of treatment was two and a half hours.

Samples were taken from the mixture at intervals of 30 minutes and were measured spectrophotometrically. The results are shown in the following table:

	After 30 minutes	After 60 minutes	After 90 minutes	After 120 minutes	Further analytical isomerization
$E^{1\%}_{1\ cm.}$ at 375 mμ (Conjugated hexa ethenoid acid.)	1.06	1.14	1.27	1.33	7.97
$E^{1\%}_{1\ cm.}$ at 346 mμ (Conjugated penta ethenoid acid.)	5.11	4.95	6.49	6.18	37.17
$E^{1\%}_{1\ cm.}$ at 315 mμ (Conjugated tetra ethenoid acid.)	34.80	35.50	39.56	35.98	80.53
$E^{1\%}_{1\ cm.}$ at 268 mμ (Conjugated triethenoid acid.)	165.96	166.03	163.89	143.49	112.83
$E^{1\%}_{1\ cm.}$ at 233 mμ (Conjugated diethenoid acid.)	163.83	163.36	165.49	150.11	113.0

It is evident that the isomerization leads to a substantially complete conversion of the unconjugated polyethenoid acids to acids containing conjugated systems. After 30 minutes the isomerization is practically completed. This example shows furthermore, that the isomerization could also be carried out partially, i.e. unconjugated polyethenoid acids having 3 or more double bonds may be converted into the corresponding conjugated di-ethenoid acids of tri-ethenoid acids.

Example 8

3600 g. of the methyl ester of soya bean fatty acids were heated together with 180 g. of ethylene diamine to a temperature of 140–160° C. for a period of four hours, after which the methyl alcohol liberated was removed under vacuum. The mixture partially converted into the diamides contained 6.3% linolenic acid and 49.4% linoleic acid in the combined form. After heating to a temperature of 120° C. 10 g. of potassium methylate were added with stirring and the mixture was left at this temperature for one hour. The catalyst was removed by adding 50 g. of fuller's earth followed by filtration. The light colored product thus obtained contained 6.3% isomerized tri-ethenoid acid and 49.1% isomerized di-ethenoid acid, corresponding to a total isomerization of nearly 100%.

In this run the amount of ethylene diamine used was equivalent to the content of polyethenoid fatty acid.

This shows that the amides of unconjugated polyethenoid acids are completely isomerized with small amounts of catalysts within a relatively short time.

Example 9

Example 2 was repeated with 50 g. of sodium amide as catalyst instead of the 50 g. potassium methylate. The obtained degree of isomerisation was the same as in Example 2.

Example 10

Example 2 was repeated with 30 g. potassium metal as catalyst instead of the 50 g. potassium methylate. The obtained degree of isomerisation was the same as in Example 2.

Example 11

Example 2 was repeated with 80 g. of triphenyl sodium as catalyst instead of the 50 g. potassium methylate. The obtained degree of isomerisation was the same as in Example 2.

It will be appreciated from the above that this invention is not limited to the materials, steps, conditions and other details specifically described above and can be carried out with various modifications. Thus, it will be understood that the process of this invention is broadly applicable to any unconjugated polyethenoid acid compounds and products containing them. The unconjugated polyethenoid acid compounds used as starting materials are monohydric alcohol esters, or amides or polyamides of the unconjugated polyethenoid acids which can be used in mixture with each other or with other materials. As examples of such monohydric alcohol esters, amides and polyamides the following are mentioned: the esters of primary, secondary and tertiary aliphatic alcohols with 1–18 carbon atoms, of primary, secondary and tertiary aromatic alcohols, the amides of ammonia aliphatic and aromatic monoamines and polyamides of aliphatic and aromatic diamines and triamines. It will be observed that the aforementioned alcohols can be called hydrocarbyl alcohols, and the amines can be called hydrocarbyl mono and polyamines. The esters of the aliphatic alcohols disclosed in the examples can also be termed esters of alkanols. In all cases, these starting materials are treated substantially in a manner analogous to that described in the above Examples 1–8.

The catalysts used in carrying out the present invention are alcoholates, especially of monohydric alcohols with 1–18 carbon atoms, of the alkali metals potassium, sodium, lithium, rubidium, cesium, such as alkali metal alcoholates of methyl, ethyl, propyl, butyl, tertiary butyl, lauryl, stearyl, oleyl, benzyl alcohols, alkali metal amides, and substances, such as alkali metals, alkali metal hy-

drides, and organic alkali metal compounds, e.g. triphenyl sodium, which form in the reaction mixture the mentioned active isomerisation catalysts. The alkali metal alcoholates can be called alkali metal hydrocarbyl alcoholates. The specific alcoholates set forth in this paragraph except that from benzyl alcohol can be termed alkali metal alkanolates.

The unconjugated polyethenoid acid compounds are treated with the catalysts of the invention in amounts of 0.05–5.0%, preferably with 0.3–2.0% based on the weight of said compounds, at a temperature between 60° and 180° C., and preferably between 100° and 140° C. under conditions which do not cause inactivation of the catalyst. The alkali metal alcoholates described above can be used as catalyst in mixture with a monohydric aliphatic or aromatic alcohol, e.g. methyl, ethyl, n- or isopropyl, n- or secondary butyl alcohol, or lauryl, palmityl, oleyl alcohols, benzyl alcohol, in a proportion of one mol of alkali metal alcoholate per 0.1–5.0 mols and preferably per 0.5–2.0 mols of said monohydric alcohols. Furthermore, said alkali metal alcoholate catalysts can be also added to the starting materials to be isomerized in the form of solutions of the alkali metal alcoholates in said monohydric alcohols.

As already mentioned above, the process of the invention can be carried out in the presence in the reaction mixture of solvents which do not interfere with the activity of the catalyst employed. As further examples of such solvents—which are used preferably in an amount of 10 to 50%, based on the weight of the starting material to be treated—the following are mentioned: methyl, ethyl, isopropyl, butyl, amyl alcohol, pentane, hexane, heptane, heptylene-(1), octylene-1, benzene, toluene.

As likewise already mentioned above, according to a modification of the invention alkali metals or alkali metal compounds which reacts in the reaction mixture with components thereof with the formation of active isomerization catalysts, can be added to the starting material to be isomerized in carrying out the process of the invention.

The term "inert solvent" is used herein to denote volatile solvents which do not interfere with the activity of the catalyst employed, such as aliphatic or aromatic hydrocarbons e.g. dimethyl formamide or dimethyl sulfoxide.

The percent and parts mentioned herein are by weight if not otherwise stated.

The compounds of conjugated fatty acids obtained by the method of this invention, or mixtures containing these compounds, are valuable industrial products which can be used in many ways. For instance their polymerisation by heating takes place at a very fast rate and, therefore, the products can be converted into light colored polymer compounds by moderate heating, e.g. at 260–280° C. The polymers thus formed can be used as ingredients of lacquers or coating compositions in conventional manner. Furthermore the conjugated fatty acid compounds of this invention can be used as ingredients of plasticizers for organic plastic materials, and as reaction components in the preparation of resins, such as alkyd resins or maleinate resins, in conventional manner.

What is claimed is:

1. A process for the catalytic isomerization of unconjugated polyethenoid fatty acid compounds to conjugated isomers thereof, by treatment of the starting material selected from the group consisting of unconjugated polyethenoid fatty acid esters of monohydric alcohols, said alcohols being hydrocarbyl alcohols having 1 to 18 carbon atoms; and unconjugated polyethenoid fatty acid amides from hydrocarbyl mono and polyamines, consisting essentially of treatment of the starting material consisting essentially of one of these compounds with 0.05–5.0% by weight of a catalyst selected from the group consisting of alkali metal hydrocarbyl alcoholates and alkali metal amides at a temperature between 60° C. and 180° C.

2. A process according to claim 1 in which said compound is an ester of a hydrocarbyl alcohol which is an alkanol.

3. A process according to claim 2 in which said catalyst is an alkali metal alkanolate.

4. A process according to claim 1 wherein said compound is a methyl ester of an unconjugated polyethenoid fatty acid.

5. A process according to claim 4 wherein said alkanolate is a methylate.

6. A process according to claim 2 wherein said catalyst is formed in situ from an alkali metal and an alkanol.

7. A process according to claim 1 in which the catalyst is used in an amount of 0.3 to 2% by weight of the polyethenoid fatty acid compound.

8. A process according to claim 1 carried out at a temperature between 100° C. and 140° C.

9. A process according to claim 1 in which the catalyst is a mixture of 1 mole of the alkali metal alcoholate with 0.5 to 2.0 moles of a monohydric hydrocarbyl alcohol containing 1–18 carbon atoms.

10. A process according to claim 9 in which the alcoholate is an alkanolate and the alcohol is an alkanol.

11. A process according to claim 1 in which the catalyst is a potassium alkanolate.

12. A process according to claim 1 in which the isomerization is carried out in an inert solvent.

13. A process according to claim 12 in which the solvent is dimethyl formamide.

14. A process according to claim 12 in which the solvent is dimethyl sulfoxide.

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