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ORGANIC MATERIALS AND METHOD OF
MAKING SAME

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This invention relates to a new and useful process for the manufacture of unsaturated fatty acids and their derivatives, and more particularly to a process of manufacturing unsaturated fatty acids from saturated and/or halogenated fatty acids.

Unsaturated fatty acids, particularly those of relative long-chain lengths, possess highly desirable properties not generally obtainable in fatty acids without unsaturated linkages. A soap prepared from unsaturated acids is many times as soluble in water (especially at room temperature) as the soap prepared from the corresponding saturated acids. Oleic acid, for example, produces a stable soap with alkali, which functions more effectively in cold water than the corresponding stearic acid soap. Furthermore, the presence of unsaturated groups in certain fatty acid molecules permits a more extensive use of the fatty acid since such groups under proper conditions are reactive with aromatic compounds; sulphonating, sulphating, phosphating and other acidifying agents; olefinic compounds; halogens and hydrohalides; sulphur and sulphur derivatives; oxygen and oxidizing agents. Consequently, these fatty acids find utility as intermediates in the preparation of high grade soaps and other washing and wetting agents, glycols, fat-splitting agents, synthetic resins, drying oils, and so forth.

Although many unsaturated fatty acids are highly desirable; there are others which do not have suitable properties because of the arrangement of the molecule, of the presence of other substituent groups in the molecule, or of the fact that for a specific purpose the proper number of unsaturated linkages do not exist. To illustrate, a hydroxy group or an unsaturated linkage too near the carboxyl group in a fatty acid will readily form a lactone or lactide structure. Obviously, the result is to produce a mixed product of variable properties of lower acid number, and, in the case of a lactide formation, of increased molecular weight. Certain of these fatty acids are unstable and may oxidize, polymerize, discolor and deteriorate generally.

Previous attempts to prepare stable unsaturated fatty acids from halogenated compounds have usually been unsatisfactory. If halogenated fatty acids are treated with caustic alkali, the initial reaction may be considered as replacement of the halogen atom by a hydroxyl group, and, by this procedure, under certain conditions, hydroxy fatty acid salts are obtained. However, in actual practice, because of several factors in-

cluding presence of liquid water, low temperature treatment and the like, certain secondary reactions also take place and complex mixtures of undesirable products are produced. The salts of such hydroxy fatty acids can be made to react further with the alkali at a slightly elevated temperature to eliminate water and to form salts of unsaturated acids. The fatty acids which are prepared by directly halogenating saturated fatty acids, in general, have the halogen substituents nearer to the carboxyl end of the fatty acid chain and hence the resulting unsaturated and/or hydroxy fatty acids have the unsaturated and/or hydroxy groups so positioned. These unsaturated acids and their salts are highly reactive and may be readily oxidized. Furthermore, when alpha, beta and gamma hydroxy fatty acid salts in such a complex mixture are treated with mineral acid, in order to liberate the free fatty acid, lactones and lactides are produced. The lactones are neutral compounds and can be regarded as internal esters which, upon saponification, give salts of hydroxy fatty acids. The corresponding salts of alpha, beta, and gamma unsaturated acids likewise can form corresponding lactones or lactides. Thus it is apparent that the alpha, beta and gamma unsaturated and/or hydroxy acids, which are the acids generally produced by the prior art methods from directly halogenated fatty acids, are highly reactive and would give rise to a mixture consisting of lactones, lactides and unchanged unsaturated or hydroxy acids.

It has now been found that valuable stable unsaturated fatty acids and their derivatives can be prepared conveniently and economically from saturated fatty acids, unstable unsaturated and/or hydroxylated fatty acids, and halogenated fatty acids. By the process of this invention it is possible to prepare products simulating those occurring naturally, such as highly desirable substitutes for olive oil fatty acids which find extensive use in the preparation of high grade soaps.

The process of this invention involves the introduction of at least one halogen into the alkyl chain of at least a portion of the fatty acids and/or their derivatives to be treated, followed by the treatment of the product with alkaline material at an elevated temperature above the melting point of the anhydrous soaps formed (usually above 200° C.) in an inert atmosphere, preferably steam, and in the substantial absence of air and liquid water. The products formed

are mainly soaps of stable unsaturated fatty acids.

The soaps of the stable unsaturated fatty acids can be treated with mineral acid to yield a stable unsaturated fatty acid with a minimum of lactone formation. The resulting acids can be used for the manufacture of soaps or can be converted into various other derivatives. These acids have unusually good stability, low acetyl number, low color and pleasant odor.

The saponification of the halogenated fatty acids, their glycerides or other derivatives subjected to the above process, may take place prior to this process or during it. In some cases when operating on very impure, low grade halogenated fatty material, it may be desirable to subject the material first to saponification and cleansing treatments by ordinary soap-making processes for the removal of certain impurities that may easily be removed in this way and which at the higher temperatures of the reaction may break down and cause a darkening of the reacting mass.

It has also been discovered that certain by-products resulting from the treatment, under the above named conditions of temperature and atmosphere, can be separated substantially completely as a vapor from the saponification mixture.

It has further been discovered, in cases where a sufficient amount of basic materials to convert all halogenated fatty matter into substantially halogen-free fatty acid salts has been employed, that undesirable impurities often found in such halogenated fats and/or fatty oils may be entirely removed from soaps made under the conditions of this invention.

It has also been found that these unsaturated fatty acids made from chlorinated fatty acids or their derivatives, when properly heated and kept from contact with oxidizing agents and liquid water, can be raised to temperatures as high as 350° C. without pyrolysis or decomposition taking place.

In carrying out the process, at least a portion of a fatty acid, fat, fatty oil, or related material is halogenated (preferably monohalogenated) by one of the known methods or by the method described in the copending application Ser. No. 267,626, filed April 13, 1939. The halogenated material is then introduced into a closed vessel constructed preferably in the shape of a still and provided with a means for heating. The halogenated material is heated to its melting point and is then subjected to a strong current of steam, which serves the purpose of effectively agitating the contents of the still, driving air from the still and guarding against the further entrance of any air. The temperature is usually permitted to rise well above the boiling point of water before introducing the alkaline material for dehydrohalogenation and saponification. A low temperature may be employed at the early stages of the process and it may subsequently be increased as the reaction progresses to temperatures as high as 350° C. In some cases the temperature of the halogenated material is first raised somewhat in excess of 200° C. at normal pressure before introducing the alkaline material, whereas in other cases it is found advantageous to pre-mix the halogenated fatty material and alkali. The method of adding the alkali depends largely on the properties of the material to be treated and the alkali used. At these elevated temperatures, about the melting point of the

substantially anhydrous soap, saponification and dehydrohalogenation take place rapidly. The deleterious action of air and local over-heating are both prevented by blowing a strong current of steam through the mass and carrying out the process in a closed system, and maintaining the temperature high enough to secure a proper degree of fluidity.

The process contemplates employing alkaline material either in solution in hydrated or in substantially anhydrous form. The alkaline material with or without water may be added separately or mixed with the halogenated fatty material. It has generally been considered essential that water or hydrated alkali be present, usually as a liquid, to effect saponification of any fatty oil for the formation of glycerine, fatty acids and soap thereof. Under the conditions that maintain in this process, a quantity of liquid water is not necessary, and in fact usually is not desired, since the dehydrohalogenation, de-esterification and saponification are brought about with ease by the alkali and steam, and at the temperatures of operation the relatively anhydrous soap is melted, hence no water or solvent is necessary to maintain fluidity. If alkaline solutions are employed, the water of solution evaporates with great rapidity leaving substantially no water (liquid) except that in the form of steam vapor. If carbonates are employed, carbon dioxide is evolved and the gas set free has an inert or protective action on the unsaturated fatty material, similar to the action of steam. The use of a strong current of steam or other inert gas vapor to maintain very thorough mixing and to effectively prevent local overheating of any portion of the mass, and the maintenance of the temperature mentioned, comprise conditions very favorable to rapid dehydrohalogenation, saponification and volatilization of glycerine, if formed in the saponification. Under these conditions, glycerine having a relatively high vapor pressure is swept from the still by the strong current of steam or other inert gas or vapor almost as fast as it is formed. The heating and agitation of the halogenated material and/or soap thereof is preferably held at the desired temperature, usually 250-300° C., until the reactions are substantially complete, at all times using a sufficiently strong current of steam to maintain thorough agitation and effectively exclude air. An alkaline or basic soap-making material sufficient to effect complete saponification and dehydrohalogenation, or a slight excess over that amount, is usually required.

In the reaction numerous alkaline materials may be employed as saponifying and dehalogenating agents, including hydroxides or carbonates of the alkali metals, alkali earth metals or other metals and mixtures thereof. Sodium compounds are usually employed because of their low cost and the desirable properties of the resulting soaps. Potassium, magnesium and calcium oxides, hydroxides and carbonates or any given mixtures thereof produce low melting reaction mixtures and so facilitate low temperature treatment under the conditions hereinbefore described.

In order to illustrate the process of the present invention but not to limit the scope thereof, the following specific examples are set forth.

Example I

2000 grams of triple pressed stearic acid (containing approximately 50% palmitic acid), titre

55.7° C., were chlorinated until a chlorine content of 5.6% was reached. The chlorinated acid was fractionally crystallized and a portion of substantially pure monochloro-palmitic acid was separated. The chlorine content of this acid fraction was 13.8%.

100 grams of the monochloro-palmitic acid were heated to about 150° C. in a flask equipped with an efficient stirrer, while passing a current of steam through the flask to sweep out the air. 45 grams ϵ . soda ash were added to the chlorinated acid in small portions meanwhile gradually increasing the temperature to 250° C. The time of initial treatment was three hours. A sample was withdrawn and the treatment was renewed for another three hours at a temperature of 300° C. After completion of the reaction, the soaps from each step were dissolved in water and the fatty acids separated therefrom by treatment with dilute sulphuric acid. The fatty acid products were washed with aqueous sodium sulphate solution to remove sulphuric acid.

A comparison of the initial material and the acid products from both stages follows:

	Percent chlorine	Iodine value	Acid value
Fraction containing monochloropalmitic acid.....	13.8	Nil	187
After three hours treatment.....	2.9	40	122
After six hours treatment.....	Trace	60.5	200

Example II

A quantity of Chinese vegetable tallow fatty acids was submitted to direct chlorination at 90° C. until a chlorine content of 22% was attained.

205 grams of the resulting chlorinated Chinese vegetable tallow fatty acids were heated in a reaction vessel to a temperature of 150° C. 125 grams (25 grams excess) of sodium carbonate were then gradually charged into the reaction vessel and the temperature gradually increased to about 250° C. The total mixture was heated at about this temperature for four hours while continuously passing a current of steam there-through.

The soap product was treated with dilute mineral acid, as described in Example I, and the resulting fatty acids compared with the initial fatty acids employed.

	Percent chlorine	Iodine value
Chinese vegetable tallow fatty acids.....	Nil	45.1
Chinese vegetable tallow fatty acids, after chlorination.....	22.0	0.1
Fatty acids produced by dehydrochlorination.....	Trace	58.8

Example III

600 grams of chlorinated triple pressed stearic acid (13% chlorine) which contains some non-chlorinated stearic acid, were placed in a flask fitted with an efficient stirrer, heated in a metal bath, and 260 grams of solid anhydrous sodium carbonate added in small portions while passing an adequate current of steam there-through. The temperature of the reaction mixture was rapidly raised to 250° C. and maintained at a temperature between about 250–300° C. for a period of five hours. Samples were taken for analysis during this period to check the progress of the reaction. After completion of the reaction the soap was dissolved in water and the fatty acids split

by dilute sulphuric acid. Because of the tendency of the fatty acids to form emulsions, it was necessary to remove the excess mineral acid by washing with sodium sulphate.

Upon analysis the initial acid and products were found to have the following values:

	Percent chlorine	Iodine value	Acid value
Triple pressed stearic acid.....	Nil	3.0	212.5
Chlorinated triple pressed stearic acid.....	13.0	Nil	-----
After 1/4 hour treatment.....	2.7	17.5	134
After 2 hours treatment.....	1.2	30.1	166
After 5 hours treatment.....	0.6	40.2	196

Example IV

Coconut oil fatty acids were chlorinated until a chlorine content of 16.9% was obtained. 300 grams of the chlorinated coconut oil fatty acid were treated for one and one-half hours at about 270–290° C. with 156 grams of soda ash added in small quantities. The mixture was continuously subjected to a current of steam during the treatment.

The products were cooled, dissolved in water, and acidified with dilute sulphuric acid to split out the fatty acid. The resulting unsaturated fatty acids were washed free of mineral acid with aqueous sodium sulphate solution.

Example V

The procedure of Example IV was followed with the modification that the chlorinated coconut oil fatty acids were reacted with the soda ash for a period of two and one-half hours rather than one and one-half hours.

Example VI

The procedure of Example IV was followed with the modification that the chlorinated coconut oil fatty acids were reacted with the soda ash for a period of five hours rather than one and one-half hours.

A comparison of the fatty acid products and reactants follows:

	Percent chlorine	Iodine value	Acetyl value	Acid value
Coconut oil fatty acids.....	Nil	9.5	5	263
Coconut oil fatty acids after chlorination.....	16.9	Nil	-----	-----
Fatty acids from Ex. IV.....	4.2	40.6	56.5	167
Fatty acids from Ex. V.....	1.2	43.5	63.8	201
Fatty acids from Ex. VI.....	Nil	48.8	13.8	254

Example VII

738 grams of triple pressed stearic acid were treated with chlorine at 90° C. until a chlorine content of 12.4% was reached. Fractional crystallization from acetone yielded a fraction consisting essentially of dichlorostearic acid.

200 grams of this fraction were agitated and heated with steam to about 150° C. in a flask to displace the air therein. 120 grams of soda ash were added to the chlorinated acid fraction in small amounts meanwhile gradually raising the temperature to about 300° C. This temperature was maintained for a total period of five hours. The soap product was dissolved in water and the fatty acids separated therefrom by treatment with dilute sulphuric acid. The fatty acid products were washed with aqueous sodium sulphate solution to remove the sulphuric acid.

Upon analysis the initial reactants and the

products were found to have the following values:

	Percent chlorine	Iodine value	Acid value
T. P. stearic acid.....	Nil	3.0	212.5
Dichlorostearic acid.....	19.2	Nil	163.6
Fatty acids produced by dehydrochlorination.....	1.4	*75.1	186.3

* NOTE.—After ten days exposure of the acids with the iodine solution, instead of the usual one-half hour, the iodine value of these fatty acid products was found to be 90.7%.

Although the above examples are directed to the treatments of chlorinated acids, the treatment of brominated and other halogenated acids is similarly conducted. For economical reasons and convenience, chlorinated fatty materials are preferably used, but brominated or other halogenated acids can be employed.

The following table indicates the unusually high solubilities of the unsaturated soaps prepared by the present method.

Solidifies at 25° C. at the following concentrations:

	Percent
Sodium soap of T. P. stearic acid, titer 55.2° C.....	0.25
Sodium soap of commercial red oil, (distilled, titer 17° C.).....	9
Sodium soap of unsaturated acids obtained by treatment of chlorinated T. P. stearic acid.....	13
Sodium soap of acids obtained by treatment of monochloro-palmitic acid containing 13.8% chlorine.....	8
Sodium soap of acids obtained by treatment of chloro-stearic acid possessing a chlorine content of 19.2%.....	12

The solubility of other salts is likewise improved, not only in water but also in other liquids.

It is possible to treat saturated or unsaturated aliphatic mono- and poly-carboxylic acids and their derivatives having an alkyl acid radical of at least eight carbon atoms with or without hydroxy, sulphate, hydrocarbon and/or other substituent radicals to obtain stable unsaturated acid derivatives by this process. Oils, ordinarily considered of a grade unsuitable for use in the preparation of soaps and the like because of their disagreeable odor and color and their tendency to become rancid, can be halogenated and treated by this process to produce highly desirable soap-making products of good color, odor, and resistance to rancidity.

Among the suitable fatty materials which can be halogenated and treated according to the present invention are hardened fish oils, coconut oil, tallow, palm oil, certain grades of garbage grease and Chinese vegetable tallow, castor oil, montan wax, spermaceti, and the various individual fatty acids thereof alone or in admixture; acids produced by the oxidation of petroleum; naphthenic acids; monocarboxylic acids such as behenic acid, caprylic acid, lauric acid; and polycarboxylic acids such as sebacic acid. In the case of halogenated oils, fats, waxes, or other esters, the glycerine or other alcohols are removed as a vapor with the steam, recovered separately, and used for other purposes. Of course, other derivatives than the acids and their esters, such as the acid halides or the amides, may be similarly used.

The degree of unsaturation attained in the fatty acid is substantially dependent on the de-

gree of halogenation. For the preparation of cold water soaps and similar materials a fatty acid with a single olefinic linkage is desirable. However, in preparing drying oils and the like, the higher degrees of unsaturation are necessary and the degree of halogenation must be correspondingly increased in order to produce a polyolefinic structure by the present process. Polyolefinic fatty acids would likewise be produced from halogen-containing hydroxy and/or unsaturated fatty acids by this process. Although direct halogenation is normally preferred, the method of introducing the halogen into the acid radical is not so limited since any halogenated acid can be submitted to the subsequent treatment. Under suitable conditions hydrohalides, such as HBr and HI, will react with certain fatty acids, usually unsaturated, to form the corresponding halogen derivatives and these can be treated by the above described process. Other methods of halogenation include the treatment with phosphorous halides, hypochlorite, chloriodine, and/or with halogens, such as iodine, in the presence of solvents such as acetic acid, alcohol, carbon tetrachloride, or other halogenated hydrocarbons.

The process may be conducted at atmospheric pressure, but certain advantages are obtained by operating at diminished pressures, particularly for the removal of the last traces of volatile matter from the liquid mass of melted soap. Although increased pressures may be employed, they are not desirable because higher temperatures are usually required, especially with polyhalogenated acids, in order to hold the quantity of liquid water or other solvent to a minimum and thus reduce the quantity of hydroxy acid soaps formed. The volatile products may be condensed together or separately by fractional condensations. In the case of halogenated oils and fats, glycerine may be condensed in concentrations exceeding 99%, while permitting water vapor to remain in the vapor phase. Unsaponifiable matter carried over by the steam may be condensed and separated from the glycerine in which it is substantially insoluble.

The process may be carried out as a batch process, treating a given amount of halogenated fatty material with approximately the definite amount of alkaline material necessary to dehalogenate and convert it into soap, or it may be carried out as a semi-continuous process by treating a certain amount of said halogenated material with the corresponding amount of alkali, removing a portion of the unsaturated soap thus formed, preferably while still in a hot, liquid condition, and adding further quantities of halogenated material and alkali in such a way as to maintain the mass at the preferable reacting temperature at all times. The preferred temperature for products of best quality in good yields is one sufficiently above the melting point of the substantially anhydrous soap so that it is in thin, liquid condition, and the water and glycerine are readily volatile but preferably not higher than 350° C. However, the reaction described may in certain cases be carried out at temperatures as low as 200° C., so long as the relatively anhydrous soap remains thinly melted. It is desirable at times to mix high-melting fatty acids or salts with low-melting fatty acids or salts in order to obtain a thin mix of desired melting point.

After completion of the reaction and removal of glycerine and unsaponifiable matter, it is pre-

ferred to draw off the soap in a liquid state while taking suitable precautions to exclude contact of air with the hot soap. One way of doing this is to draw the liquid soap off through a valve and pipe, and steam may be used to keep this pipe free from air. The soap may be discharged into and beneath the surface of a mass of water or hydrated melted soap, and the quantity of water employed need not be greater than that necessary to leave an amount of water in the finished soap substantially equivalent to that obtained in other soap-making processes. Other means may be used for drawing off the hot soap in such a manner as to exclude air oxidation while it is at a temperature that this would readily occur.

In the halogenation of unsaturated acid compounds, alone or in mixtures, the compounds may be treated with hydrohalides and/or with halogens under conditions that hydrohalide addition and/or halogen substitution rather than simple di-halogen addition occur.

A particularly desirable process of halogenation involves the treatment of a relatively saturated fatty acid compound such as Chinese vegetable tallow or the acids thereof with halogens such as chlorine, preferably by the procedure of the copending application Serial No. 267,626 so that halogen substitution takes place and hydrohalide gas is evolved. The hydrohalide gas—admixed with halogen if desired—is then passed into an unsaturated fatty acid compound or mixtures containing such compounds, e. g., tallow, palm oil, tall oil, or the like, under conditions whereby the hydrohalide adds at the double bond and substantially all direct halogenation, conducted simultaneously or subsequently, is by substitution preferably of saturated acid compounds present. For example, tallow or the acids thereof may be treated with hydrogen chloride gas so that the hydrohalide adds to the double bonds of the unsaturated acid compounds present in the tallow. The saturated acid compounds present may then be chlorinated by the direct action of chlorine so that relatively uniform mixtures or fractions of monohalogenated fatty acid compounds are obtained. The individual halogen containing fractions preferably are separated during these treatments by the method described more fully in the copending application Serial No. 267,626. If the hydrohalide treatment were omitted, the chlorine would probably first add to the unsaturated acid compounds present to form dihalogenated derivatives which would not be reconverted to the mono-olefinic acid compound in the subsequent treatment.

The halogenated fractions from both raw materials are relatively uniformly monohalogenated, and hence they are particularly suitable for preparing oleic acid soap substitutes by the alkali treatment of either or both the materials or fractions or admixtures thereof at an elevated temperature in an inert atmosphere and in a substantially anhydrous condition.

From monohalogenated acids, the yield is usually about 90–95% and hence it is apparent that only a small loss is brought about in subjecting the fatty materials to this treatment. Decomposition and/or polymerization is likewise very small as shown by the above yields.

However, there is apparently a definite molecular rearrangement of some of the initially formed unsaturated linkages in the fatty acids. The products are stable and in general have lower melting points than unsaturated fatty acids hav-

ing the unsaturated linkages in the relatively unstable positions near the carboxyl group. This highly desirable result is one of the features of this invention. Water-soluble soaps comprising alkali metal, ammonium, alkyl amine, alkylol amine and like salts of these unsaturated fatty acids are suitable for use by themselves or may be made into toilet or laundry soap, or soap powders with or without soaps of saturated fatty acids and other agents by any of the well-known methods of utilizing soap. They are especially adapted for use in cold water because of their high solubility, and the sodium soap obtained by the method of Example I is particularly suitable for use in washing silk in which olive oil soaps are now commonly employed.

Other agents which may be advantageously added to the unsaturated soap products, (preferably mono-olefinic fatty acid soaps) include alkaline soap builders such as sodium carbonate, sodium silicate, sodium orthophosphate, borax, and the corresponding potassium and ammonium salts thereof; water-soluble, water-softening salts of hexametaphosphoric, tetraphosphoric and pyrophosphoric acids; soaps of chlorinated acids, long chain alkyl sulphates and sulphonates, aromatic sulphonates, and other wetting and detergent agents; perfumes; germicides and medicaments; anti-oxidants; solvents and various other materials.

As indicated above, the unsaturated fatty acid soaps can be treated with mineral acid to form stable unsaturated fatty acids. These acids in turn may be converted into chemical derivatives such as esters, mono-, di-, and tri-glycerides, salts, amides, acid halides, anhydrides, nitriles, or even be transformed into the corresponding ketones or alcohols by suitable treatment.

The unsaturated acids can be condensed with one or more aromatic nuclei in forming sulphonated fat-splitting or wetting agents. The acids or esters thereof may be copolymerized with unsaturated compounds such as vinyl acetate, and/or methyl methacrylate or formed into esters of vinyl alcohol and then polymerized. They may be reacted with polyhydric alcohols and poly-basic acids such as glycerol, phthalic anhydride, and maleic anhydride to form drying or non-drying resins depending on the degree of unsaturation attained. The more highly unsaturated acids can be formed into glycerides and used as drying oils or sulphurized either as acids or glycerides to form a rubber modifying agent. They may be reduced to unsaturated alcohols, e. g., by hydrogenation under pressure, which alcohols may be converted into alkyl sulphates. Long-chain alcohol esters of the unsaturated fatty acids are suitable as wax substitutes. They may be sulphonated directly or in the form of esters to form monopole soap substitutes. They may be treated to form phosphoric acid esters thereof, such as the pyrophosphates or orthophosphates. Numerous other desirable agents may be similarly prepared from these stable unsaturated fatty acids.

As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that we do not intend to limit ourselves to the specific embodiments thereof except as indicated in the appended claims.

We claim:

1. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises heating an organic compound having a halogen-

substituted aliphatic carboxylic radical containing at least eight carbon atoms with an alkaline material, to a temperature not lower than the melting point but not above the decomposition temperature of the substantially anhydrous soap products in an inert atmosphere and in the substantial absence of air and liquid water.

2. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises heating an organic compound having a halogen-substituted aliphatic carboxylic radical containing at least eight carbon atoms with an alkaline material, to a temperature below 350° C. but not lower than the melting point of the corresponding substantially anhydrous soap in an inert atmosphere and in the substantial absence of air and liquid water.

3. The process of preparing unsaturated aliphatic acids and derivatives which comprises heating a halogen-substituted fatty acid containing at least eight carbon atoms with an alkaline material, to a temperature not lower than the melting point but not above the decomposition temperature of the substantially anhydrous soap products in an inert atmosphere and in the substantial absence of air and liquid water.

4. The process of preparing unsaturated aliphatic acids and derivatives which comprises heating a glyceride of a halogen-substituted fatty acid containing at least eight carbon atoms with an alkaline material, to a temperature not lower than the melting point but not above the decomposition temperature of the substantially anhydrous soap products in an inert atmosphere and in the substantial absence of air and liquid water.

5. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises heating an organic compound having a chlorine-substituted aliphatic carboxylic radical containing at least eight carbon atoms with an alkaline material, to a temperature not lower than the melting point but not above the decomposition temperature of the substantially anhydrous soap products in an inert atmosphere and in the substantial absence of air and liquid water.

6. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises heating an organic compound having a chlorine-substituted aliphatic carboxylic radical containing at least eight carbon atoms with an alkaline material, to a temperature below 350° C. but not lower than the melting point of the corresponding substantially anhydrous soap in an inert atmosphere and in the substantial absence of air and liquid water.

7. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises heating a chlorine-substituted fatty acid containing at least eight carbon atoms with an alkaline material, to a temperature below 350° C. but not lower than the melting point of the corresponding substantially anhydrous soap in an inert atmosphere and in the substantial absence of air and liquid water.

8. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises heating an organic compound having a halogen-substituted aliphatic carboxylic radical containing at least eight carbon atoms with an alkaline material, to a temperature not lower than the melting point but not above the decomposition temperature of the substantially anhydrous soap products and thoroughly agitating the mixture in the substantial absence of liquid water and in an atmosphere free of oxygen while intimately con-

tacting the mixture with a stream of water vapor.

9. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises heating an organic compound having a halogen-substituted aliphatic carboxylic radical containing at least eight carbon atoms with an alkaline material, to a temperature below 350° C. but not lower than the melting point of the corresponding substantially anhydrous soap and thoroughly agitating the mixture in the substantial absence of liquid water and in an atmosphere free of oxygen while intimately contacting the mixture with a stream of water vapor.

10. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises heating a halogen-substituted fatty acid containing at least three carbon atoms with an alkaline material, to a temperature not lower than the melting point but not above the decomposition temperature of the substantially anhydrous salt products and thoroughly agitating the mixture in the substantial absence of liquid water and in an atmosphere free of oxygen while intimately contacting the mixture with a stream of water vapor.

11. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises heating a chlorine-substituted fatty acid with an alkaline material, to a temperature not lower than the melting point but not above the decomposition temperature of the substantially anhydrous soap products and thoroughly agitating the mixture in the substantial absence of liquid water and in an atmosphere free of oxygen while intimately contacting the mixture with a stream of water vapor.

12. The process of preparing stable unsaturated fatty acids and derivatives which comprises heating a soap of a halogen-containing fatty acid with sufficient free alkali to combine with the halogen, to a temperature in excess of the melting point of the soap when anhydrous but not above the decomposition temperature of the unsaturated fatty acid soap product, excluding substantially all air from the melted mixture, and intimately contacting the melted mixture with a current of steam at a pressure less than atmospheric.

13. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises halogenating the carbon chain of an aliphatic carboxylic radical of a compound containing such a group and then heating the resulting halogen-substituted derivative with sufficient alkali to saponify the carboxylic radical and to combine with the halogen substituents, to a temperature not lower than the melting point but not above the decomposition temperature of the resulting substantially anhydrous salt in the absence of air and liquid water.

14. The process of preparing stable unsaturated fatty acid soaps which comprises heating a mixture of unsubstituted aliphatic and halogen-substituted fatty acid derivatives with alkali, to a temperature not lower than the melting point but not above the decomposition temperature of the resulting substantially anhydrous soaps in an inert atmosphere and in the substantial absence of liquid water.

15. The process of preparing stable unsaturated fatty acid derivatives which comprises heating a mixture of halogen-substituted palmitic acid, halogen-substituted stearic acid and stearic acid with an alkali, to a temperature not lower than the melting point but not above the decom-

position temperature of the resulting substantially anhydrous soap products in the absence of air and liquid water.

16. The process of preparing stable unsaturated aliphatic acids and derivatives which comprises halogenating the carbon chain of an aliphatic carboxylic radical of a compound containing such a group and then heating the resulting halogen-substituted derivative with sufficient alkali to saponify the carboxylic radical and to combine with the halogen substituents, to a temperature not lower than the melting point but not above the decomposition temperature of the resulting substantially anhydrous salt in the absence of air and liquid water and intimately contacting the melted mixture with a current of steam.

17. The process of preparing stable unsaturated fatty acids and derivatives which comprises heating an equivalent weight of monochlorosubstituted fatty acid containing sixteen to eighteen carbon atoms inclusive with two equivalent weights of alkali, to a temperature of about 250°-300° C. in the substantial absence of air and liquid water and intimately contacting the melted mixture with a current of steam.

18. A product of the process of claim 1.

19. A product of the process of claim 17.

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