Patented June 19, 1951 2,557,159

UNITED STATES PATENT OFFICE

2,557,159

HALOGENATED UNSATURATED HIGHER FATTY ACIDS AND DERIVATIVES

Howard M. Teeter and John C. Cowan, Peoria, Ill., assignors to United States of America as represented by the Secretary of Agriculture

No Drawing. Application January 13, 1947, Serial No. 721,830

12 Claims. (Cl. 260—408)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

1

This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to us of any royalty thereon.

This invention relates to halogenated unsaturated higher fatty acids and derivatives thereof. More particularly, it relates to halogenated fatty acids and derivatives which contain substantially more substitutionally than additively introduced halogen. The invention further relates to the reaction of alkyl hypohalites with unsaturated higher fatty acids and their derivatives.

One object of this invention is the production of halogenated unsaturated higher fatty acids and their derivatives which contain conjugated systems.

A second object is the provision of unusually reactive intermediates for the preparation of derivatives of unsaturated and saturated higher fatty acids.

In the prior art, halogenation of unsaturated higher fatty acids and their derivatives has been accomplished by direct treatment with elementary halogen either with or without a solvent. This treatment results in addition to, and saturation of, the ethylenic double bonds in the fatty acid. Substitution of halogen for hydrogen also occurs as a secondary reaction. A second well known method of halogenation is the use of reagents such as iodine chloride or iodine bromide. These reagents add to the ethylenic double bonds and produce little substitution. Methods of direct halogenation, such as those ordinarily employed in organic chemistry, produce saturation of ethylenic double bonds as the primary reaction when applied to unsaturated higher fatty acids. Compounds such as ethylene or propylene may be halogenated directly at high temperatures to produce substitution rather than addition products; however, the use of high temperatures is not suitable in the case of unsaturated higher fatty acids because of polymerization and thermal decomposition. Indirect methods of halogenation such as replacement of an hydroxyl group or selective dehydrohalogenation are usually impractical with unsaturated higher fatty acids because the required intermediates are difficult to obtain.

We have discovered that unsaturated higher fatty acids and their derivatives, particularly, the lower alkyl and glyceride esters thereof, and mixtures of these acids and these derivatives,

2

may be substitutionally halogenated by reaction with alkyl hypohalites, and that the products resulting therefrom contain conjugated systems.

The unsaturated higher fatty acids employed in the invention include acids such as oleic acid, linoleic acid, ricinoleic acid, linolenic acid, and so forth, and also include mixtures of fatty acids obtained by saponification of vegetable drying oils such as linseed oil, and vegetable semidrying oils such as castor oil and soybean oil. The derivatives of unsaturated higher fatty acids employed in the invention include the esters of the above-mentioned unsaturated higher fatty acids, such as the alkyl esters like methyl oleate, methyl linoleate, and so forth; the unsaturated glycerides occurring in vegetable drying oils, such as the glycerides of linoleic and linolenic acids found in linseed oil, and the glycerides occurring in vegetable semidrying oils, such as the glycerol ester of ricinoleic acid found in castor oil. Also included are mixtures of the derivatives of unsaturated higher fatty acids which are obtained by saponification of vegetable drying and vegetable semidrying oils, since any saturated higher fatty acids that may be found in these mixtures do not effect the practice of the invention.

By "substitutional halogenation," as used herein, is meant the substitution of halogen for a hydrogen atom attached to a carbon atom. By "additive halogenation" is meant the addition of halogen to an ethylenic double bond with consequent loss of unsaturation of that bond.

The alkyl hypohalites suitable for use in our process are the tertiary alkyl hypohalites such as tert-butyl and tert-amyl hypochlorites.

In general, according to the invention, the unsaturated higher fatty acid or its derivative is reacted under substantially anhydrous conditions with the alkyl hypohalite at a suitable temperature of about from 30° to 100° C. A solvent, such as carbon tetrachloride, benzene, chloroform, or petroleum ether may be employed, if desired. Reaction occurs rapidly and is complete in about from one to sixty minutes depending upon the temperature and the reactivity of the particular alkyl hypohalite employed. The byproduct of reaction, which is the compound obtained from the alkyl hypohalite by replacing its reactive halogen by hydrogen, is removed by distillation, filtration, or washing.

The halogenated unsaturated higher fatty acid or its derivative thus obtained is a somewhat more viscous oil of a more pronounced yellow or orange color than the original. It gives an immediate precipitate with alcoholic silver nitrate, thus in-

dicating the presence of very reactive halogen.

A distinguishing feature of the products obtained is the presence of conjugated systems. In the products of the invention, the amount of conjugation present ranges from about 2 percent to over 25 percent, depending upon the reagents and conditions employed, and the conjugation is characterized by the frequent occurrence of triene, tetraene, and pentaene systems. By a conjugated system is meant a system of contiguous ethylenic double bonds arranged in accordance with the formula

$$(CH{=}CH)_n$$

When n equals 2, a diene system or diene conjugation is present; when n equals 3, a triene system, and so on.

The following examples are illustrative of the invention.

EXAMPLE

In a 500 ml., 3-necked flask equipped with thermometer, stirrer, and reflux condenser and kept in a constant-temperature bath at about 60° C., was placed 250 g. of alkali-refined soybean oil. By means of a dropping funnel having a long outlet tube extending through the reflux condenser to a point below the surface of the oil, 92 g. of tertiary butyl hypochlorite was added dropwise. An induction period of about 20 to 40 minutes, which terminated in a vigorous exothermic reaction, occurred upon initial addition of the hypochlorite. Following this period, the hypochlorite was added more rapidly. After all hypochlorite had been added, the reaction mixture was stirred at about 60° C. for about 60 minutes, in order to insure complete reaction. The reaction mixture was then stripped of volatile material by evacuating the flask at room temperature and passing an inert gas through the mixture for approximately two hours. The product contained 9.92 percent chlorine, and its viscosity and color, determined by Gardner standards, were H–I and 12–13, respectively. The product was further characterized by the presence of 14.6 percent diene, 5.1 percent triene, and 1.0 percent tetraene conjugation, determined spectrophotometrically. The total conjugation was 20.7 percent.

Additional examples and the results obtained are shown in the following table.

Table

Example No.	Fatty derivative	Positive halogen compound	Halogen in product	Color (Gardner)	Viscosity (Gardner)	Conjugation				
						Diene	Triene	Tetraene	Pentaene	Total
			Per cent (Cl)			*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
3	Soybean fatty acids, methyl ester.	t-Butyl hypochlorite	9.76	9	C	12.4	4.0	0.5		16.9
4	Linseed oil	do	9.10	14	I	13.1	5.0	5.1	2.0	25.2
5	Soybean fatty acids	do	8.14	11	E	2.3	3.9	1.0		7.2
6	Castor oil	do	10.65	9	J	4.4	0.9	0.2		5.5
7	Methyl oleate	do	3.51			2.4				2.4
8	Methyl linoleate	do	9.24			20.6	0.30			20.9

Having thus described our invention, we claim:

1. A process comprising reacting a member selected from the group consisting of an unsaturated higher fatty acid and the lower alkyl and glyceride esters thereof with a tertiary alkyl hypohalite under substantially anhydrous conditions at a temperature of about from 30° C. to 100° C. thereby to substitutionally halogenate said member without substantial loss of unsaturation thereof.

2. The process of claim 1 wherein the tertiary alkyl hypohalite is a tertiary alkyl hypochlorite.

3. The process of claim 1 wherein the tertiary alkyl hypohalite is tertiary butyl hypochlorite.

4. The process of claim 1 wherein the tertiary alkyl hypohalite is tertiary amyl hypochlorite.

5. A process comprising reacting an unsaturated higher fatty acid with a tertiary alkyl hypohalite under substantially anhydrous conditions at a temperature of about from 30° C. to 100° C. thereby to substitutionally halogenate said unsaturated acid without substantial loss of unsaturation thereof.

6. The process of claim 5 wherein the unsaturated higher fatty acid is oleic acid.

7. The process of claim 5 wherein the unsaturated higher fatty acid is linoleic acid.

8. A process comprising reacting a vegetable semidrying oil with a tertiary alkyl hypohalite under substantially anhydrous conditions at a temperature of about from 30° C. to 100° C. thereby to substitutionally halogenate the unsaturated components of the said oil without substantial loss of unsaturation thereof.

9. The process of claim 8 wherein the semidrying oil is soybean oil.

10. The process of claim 8 wherein the semidrying oil is soybean oil and the tertiary alkyl hypohalite is tertiary butyl hypochlorite.

11. A process comprising reacting a lower alkyl ester of an unsaturated higher fatty acid with a tertiary alkyl hypohalite under substantially anhydrous conditions at a temperature of about from 30° C. to 100° C. thereby to substitutionally halogenate said ester without substantial loss of unsaturation thereof.

12. The process of claim 11 wherein the ester of the unsaturated higher fatty acid is methyl linoleate.

HOWARD M. TEETER.
JOHN C. COWAN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,396,969	Price	Mar. 19, 1946

FOREIGN PATENTS

Number	Country	Date
402,880	Great Britain	Dec. 14, 1933

OTHER REFERENCES

Ziegler et al., Annalen der Chimie, Justus Liebigs, 1942, Band 551, pages 102 and 118.

Chemical Abstracts, vol. 32, 4524 (1938).