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PROCESS FOR THE PREPARATION OF THE ESTERS OF UNSATURATED ACIDS

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This invention relates to a process for the preparation of esters of the unsaturated monocarboxylic aliphatic organic acids and more particularly to the preparation of the acrylic acid esters from chlorformic acid esters and the olefinic hydrocarbons.

An object of the present invention is to provide a new and improved process for the preparation of the esters of the unsaturated aliphatic organic acids. Another object of the invention is to provide a process for the preparation of acrylic acid esters from chlorformic esters and ethylene. A further object of the invention is to provide a new and improved process for the preparation of the methyl ester of methacrylic acid. Another object of the invention is to provide a process for the preparation of the methyl ester of methacrylic acid including the preparation of the methyl ester of chlorisobutyric acid from methyl chlorformate and propylene. A still further object of the invention is to provide a process for the preparation of the methyl ester of methylacrylic acid by the series of steps which include the preparation of methyl chlorformate from phosgene and methanol, the addition reaction of methyl-chlorformate with propylene to form the methyl ester of betachlorisobutyric acid, and finally the dehydrohalogenation of the halogenated ester to give the methyl ester of methylacrylic acid. Other objects and advantages will hereinafter appear.

According to the present invention an ester of the unsaturated monocarboxylic aliphatic organic acids may be obtained in the following manner. Phosgene, or other carbonyl halide, is reacted with an aliphatic monohydroxy or polyhydroxy alcohol to form the alkyl ester of chlorformic acid; other suitable methods for making these esters may be employed. Thus, from methanol, methyl chlorformate is obtained; from ethanol, ethyl chlorformate; from glycerine, glycerol chlorformate, and like esters are obtained from the higher alcohols. The alkyl ester is then added to an olefinic hydrocarbon, such as ethylene, propylene, butylene, etc. to obtain the ester of a halogenated aliphatic carboxylic acid which is dehydrohalogenated to give an unsaturated aliphatic ester. The preparation of methyl methacrylate from phosgene, methanol, and propylene, when conducted in accord with my invention, will proceed substantially in accord with the equations:

(1) $COCl_2+CH_3OH \rightarrow ClCOOCH_3+HCl$
(methylchlorformate)

(2) $ClCOOCH_3+CH_3-CH=CH_2 \rightarrow$

$$CH_3-\underset{\underset{ClCH_2}{|}}{CH}COOCH_3$$

and/or

(3) $$CH_3-\underset{\underset{CH_2}{|}}{C}COOCH_3+HCl.$$

By the substitution of other mono- or polyhydroxy alcohols in the first equation and other olefinic hydrocarbons in the second, it will be realized by those skilled in the art that a plurality of unsaturated esters suitable as plasticizing agents, for use in the preparation of synthetic resins, as solvents, etc. may be obtained. From ethanol, methoxy ethanol, propanol, cyclohexanol, glycerol, etc. with phosgene and ethylene will be obtained, for example, respectively, ethyl, methoxy-ethyl, propyl, cyclohexyl and glyceryl acrylates, and with propylene, butylene, styrene, in lieu of ethylene, will be obtained the corresponding methacrylates, propacrylates, and phenacrylates.

Altho I usually prefer to obtain the alkyl chlorformate by the interaction of phosgene with alcohol, it may be prepared by the halogenation of an alkyl formate. The product designated under (3) above is, of course, not the sole product of the reaction; for example, under some conditions methyl crotonate is obtained as a result of the formation in reaction (2) of the methyl ester of betachlor-normal-butyric acid. It will be readily appreciated by those skilled in this art that by substituting an appropriate alpha beta unsaturated hydrocarbon for propylene acrylic acid derivatives can be obtained containing practically any desired group in the alpha position.

I shall now describe examples illustrating methods of conducting my process, but it will be understood that the details therein given will in no way limit the scope of my invention.

Example 1.—Methanol is mixed at room temperature and pressure with phosgene in an autoclave until approximately 30 kilograms of phosgene have been absorbed by approximately 10 liters of methanol; the temperature is then raised to approximately 50° C. and after substantially all of the hydrogen chloride has passed off aluminum chloride is added to give a solution containing 5–15% of aluminum chloride. Propylene is then introduced under a pressure of approximately 50 atmospheres, which pressure is maintained in the autoclave. Alcoholic caustic soda of approximately 10% strength is added after the reaction has proceeded to substantial completion and the methyl methacrylate obtained is separated and purified by known methods.

Example 2.—In lieu of introducing propylene as directed in Example 1, ethylene is introduced under a pressure of approximately 50 atmospheres. The methyl ester of acrylic acid is obtained and may be separated from the reaction products in the manner disclosed in the first example.

The condensation of the alkyl or aryl chlorformate with the olefinic hydrocarbon may be conducted at a temperature of from 35–150° C. or higher and at a pressure of from 1–100 atmospheres.

A number of catalysts may be employed in these reactions, such, for example, as the chlorides of aluminum, iron, bismuth, boron, or corresponding bromides and equivalent condensation catalysts, promoted or unpromoted activated charcoal are also suitable. In many instances also these same catalysts may be used in the dehydrohalogenation of the halogenated esters of the saturated acids to the alkyl ester of the unsaturated acid, altho the caustic method is preferable. The catalyst, therefore, need not, in certain instances, be removed from the products resulting from the interaction of the chlorformates with the olefinic hydrocarbon, but may be left in the product to be used in effecting the removal of hydrogen chloride during the last reaction.

From a consideration of the above specification it will be realized that any modifications or improvements in the process hereinbefore described will come within the scope of the invention without sacrificing any of its advantages.

I claim:

1. A process for the preparation of an ester of an unsaturated aliphatic carboxylic acid which comprises reacting the ester of a halogenated formic acid with an olefinic hydrocarbon, and dehydrohalogenating the resulting ester of a halogenated saturated aliphatic monocarboxylic acid to an unsaturated ester.

2. A process for the preparation of an ester of an unsaturated aliphatic carboxylic acid which comprises reacting the ester of a halogenated formic acid with ethylene, and dehydrohalogenating the resulting ester of a halogenated propionic acid to an unsaturated ester.

3. A process for the preparation of an ester of an unsaturated aliphatic carboxylic acid which comprises reacting the ester of a halogenated formic acid with propylene, and dehydrohalogenating the resulting ester of a halogenated isobutyric acid to an unsaturated ester.

4. A process for the preparation of an ester of methylacrylic acid which comprises preparing an ester of chlorformic acid by reacting phosgene with an alcohol, effecting an addition reaction between this ester and propylene, thereby obtaining the ester of betachlorisobutyric acid, and finally dehydrohalogenating this ester to obtain an ester of methylacrylic acid.

5. A process for the preparation of an ester of methylacrylic acid which comprises preparing an alkyl chlorformate by reacting phosgene with an aliphatic alcohol, effecting an addition reaction between this ester and propylene, thereby obtaining the alkyl ester of betachlorisobutyric acid, and finally dehydrohalogenating this ester to obtain an alkyl ester of methylacrylic acid.

6. A process for the preparation of an ester of methylacrylic acid which comprises preparing a hydroaryl chlorformate by reacting phosgene with a cyclohexanol, effecting an addition reaction between this ester and propylene, thereby obtaining the hydroaryl ester of betachlorisobutyric acid, and finally dehydrohalogenating this ester to obtain an aryl ester of methylacrylic acid.

7. A process for the preparation of the methyl ester of methylacrylic acid which comprises preparing methylchlorfomate by reacting phosgene with methanol, effecting an addition reaction between methyl chlorformate and propylene, thereby obtaining the methyl ester of betachlorisobutyric acid, and finally dehydrohalogenating the methyl ester of betachlorisobutyric acid to obtain methyl methacrylate.

8. In a process for the preparation of an ester of an unsaturated aliphatic monocarboxylic acid, the step which comprises reacting a halogenated formic ester with an olefinic hydrocarbon.

9. In a process for the preparation of an alkyl ester of acrylic acid, the step which comprises reacting an alkyl halogenated formate with ethylene.

10. In a process for the preparation of an alkyl ester of methacrylic acid, the step which comprises reacting an alkyl halogenated formate with propylene.

11. In a process for the preparation of the methyl ester of methacrylic acid, the step which comprises reacting methyl chlorformate with propylene.

12. In the process for the preparation of the methyl ester of methacrylic acid, the step which comprises reacting methyl chlorformate with propylene in the presence of a catalyst selected from the group consisting of a chloride of iron, bismuth, aluminum, and boron.

13. A process for the preparation of an ester of an unsaturated aliphatic carboxylic acid which comprises reacting the ester of a halogenated formic acid with an olefinic hydrocarbon in the presence of a metal halide catalyst, and dehydrohalogenating the resulting ester of the halogenated saturated aliphatic monocarboxylic acid to an unsaturated ester.

14. A process for the preparation of the methyl ester of methacrylic acid which comprises preparing methyl chlorformate by reacting phosgene with methanol, condensing the methyl chlorformate with propylene in the presence of a metal halide catalyst, thereby obtaining the methyl ester of betachlorisobutyric acid, and finally dehydrohalogenating the methyl ester of betachlorisobutyric acid to obtain methyl methacrylate.

15. A process for the preparation of an ester of an unsaturated aliphatic carboxylic acid which comprises reacting the ester of a halogenated formic acid with an olefinic hydrocarbon in the presence of a condensation catalyst and dehydrohalogenating the resulting ester of the halogenated saturated aliphatic monocarboxylic acid to an unsaturated ester.

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