PROPERTY OF

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Process for Making Alpha, Alpha-Dihalopropionic Acids.

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is for an improved process for making alpha,alpha-dihalopropionic acids. It relates more particularly to a procedure and catalysts for halogenating an alpha-halo-propionic acid to form a corresponding alpha,alpha-dihalopropionic acid.

Bass, in U.S. Patent No. 2,010,085 discloses a procedure for chlorinating organic acids, wherein anhydrous or substantially anhydrous propionic acid having dissolved therein at least a trace of an acyl halide, preferably a propionyl halide, is reacted with chlorine in the presence of a catalyst capable of forming an intermediate addition compound with the acyl halide to form alpha-chloropropionic acid in relatively high yield and as substantially the sole monochlorinated product, the relative high yield of more highly chlorinated by-products being, at the same time, reduced materially below the yields thereof ordinarily obtained through chlorinating said propionic acid, acid anhydride, or acyl halide, in the absence of such catalyst. The chlorination is carried out at temperatures between 50° and 140°, preferably from 90° to 100° C. in the presence of the halides, oxyhalides, oxygen acids, or oxides, of the elements phosphorus, arsenic, antimony, sulfur, selenium, or tellurium, as catalysts, and employing the chlorine in amount corresponding to approximately the quantity theoretically required to convert the propionic acid to its monochloro derivative. It is taught that both under-chlorination and over-chlorination should be avoided, since both the unreacted acid and the poly-chloro derivatives thereof can be separated from the alpha-chloro product only with difficulty.

The method heretofore proposed for chlorinating propionic acid to obtain alpha-chloropropionic acid cannot satisfactorily be applied by continuing the chlorination to produce alpha,alpha-dichloropropionic acid. The chlorination of alpha-chloropropionic acid is sluggish at temperatures of from 50° to 140° C., and usually results in the formation of a mixture of poly-chloro derivatives, including both alpha,alpha-dichloropropionic acid and alpha,beta-dichloropropionic acid, together with substantial amounts of higher poly-chloro derivatives such as alpha, alpha, beta-trichloropropionic acid, or in incomplete chlorination of the alpha-chloropropionic acid starting material. In either of such cases, the alpha,alpha-dichloropropionic acid product can be separated only with difficulty.

It is a primary object of the invention to provide an improved method for making an alpha,alpha-dihalopropionic acid. The invention provides a procedure and catalysts for carrying out the reaction of chlorine or bromine with an alpha-halopropionic acid to obtain a corresponding alpha,alpha-dihalopropionic acid in a form free, or nearly free, from other poly-halo derivatives. The invention also provides an improved method for making alpha,alpha-dichloropropionic acid by reaction of chlorine with alpha-chloropropionic acid.

According to the present invention there is provided in a process for halogenating propionic acid, the steps which consist in (1) reacting propionic acid with an approximately equimolecular proportion of chlorine or bromine at a temperature between 50° and 140° C. in the presence of a phosphorus-containing catalyst consisting of phosphorus, or a halide, oxyhalide, oxygen acid or oxide

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of phosphorus, whereby an alpha-halopropionic acid is obtained as substantially the sole halogenated derivative, and (2) reacting the alpha-halopropionic acid with an approximately equimolecular proportion of chlorine or bromine by heating said alpha-halopropionic acid at a reaction temperature between 150° and 225° C. in the presence of said catalyst while introducing the halogen into admixture with the liquid alpha-halopropionic acid.

The alpha-halopropionic acids to be employed are alpha-chloropropionic acid and alpha-bromopropionic acid. The alpha-halopropionic acids may be prepared in accordance with the procedure described in the aforementioned U.S. Patent No. 2,010,685.

The halogen may be chlorine or bromine. The halogen is usually employed in amount corresponding to approximately one molecular proportion of the chlorine or bromine per mole of the alpha-halopropionic acid starting material. The halogen is usually fed to a mixture of the liquid alpha-halopropionic acid and catalyst at a rate not substantially greater than the rate at which it is consumed in the reaction, and in amount corresponding to from 1 to 1.2 moles of the halogen per mole of the alpha-halopropionic acid employed. Optimum results are usually obtained when the chlorine, or bromine, is fed to the reaction mixture at a rate not exceeding that at which it is consumed in the reaction, and in amount corresponding to one molecular proportion of the halogen per molecular equivalent proportion of the alpha-halopropionic acid.

The phosphorus-containing catalyst may be phosphorus, or a halide, oxyhalide, oxygen acid, or oxide, of the element phosphorus. Examples of suitable phosphorus-containing catalysts are phosphorus, phosphorus trioxide, phosphorus pentoxide, phosphorus trichloride, phosphorus tribromide, phosphorus pentachloride, phosphorus pentabromide, phosphorus oxychloride, phosphorus oxybromide, phosphorus acid, phosphoric acid, or mixtures of any two or more of such compounds.

The phosphorus-containing compounds are herein referred to as catalysts since they are added for purpose of obtaining a catalytic effect and are necessary in the reaction. It is probable that the true catalyst for the reaction is a phosphorus-containing intermediate or complex of unknown composition, e.g. a complex of the phosphorus compound and an acyl halide of the alpha-halopropionic acid, formed *in situ*.

The phosphorus compound or catalyst is usually employed in amount corresponding to from 1 to 20, preferably from 3 to 7 per cent by weight of the alpha-halopropionic acid starting material.

The halogenating reaction can readily be carried out at temperatures between 150° and 225° C., preferably between 155° C. to 185° C., and at atmospheric pressure or approximately atmospheric pressure, or at superatmospheric pressures, e.g. at a gauge pressure of from 5 to 30 pounds per square inch such as to maintain the main body of the alpha-halopropionic acid in liquid condition.

In practice, an alpha-halopropinoic acid, e.g. alpha-chloropropionic acid, is placed in a reaction vessel, together with all, or a portion of, a desired amount of a phosphorus-containing catalyst. The mixture is stirred and heated to a reaction temperature within the above-stated range. The halogen, i.e. chlorine or bromine, is introduced into the liquid wherein it is dispersed. It reacts and forms a corresponding hydrohalic acid. The halogen is usually added at about the rate at which it is consumed in the reaction. The hydrohalic acid is vented from the reaction zone as it is formed. Feed of the halogen and reaction of the same is continued until an amount corresponding to approximately 1, and usually from 1 to 1.2, moles of the halogen per mole of the alpha-halopropionic acid starting material has been consumed in the reaction. A further amount of a phosphorus-containing catalyst may be added during the reaction if the latter tends to become sluggish. Satisfactory results have been obtained by adding a portion of the desired amount of catalyst prior to adding the halogen and adding further portions of the catalyst at intervals during the reaction.

Upon completion of the halogenation reaction the crude product is usually separated from the catalyst residue and is mixed with water in amount sufficient to react with the small proportions of acyl halides and anhydrides formed in the reaction and hydrolyze the same to the corresponding acids. Hydrolysis of the acyl halides and anhydrides can be effected by adding the required amount of water to the crude reaction mixture containing the catalyst, and thereafter separating the product from the catalyst residue.

The process can be carried out by halogenating propionic acid to form the corresponding alpha-halopropionic acid, e.g. by reacting chlorine with propionic acid at temperatures between 50° and 140° C. in the presence of a phosphorus-containing catalyst in accordance with the procedure described in the aforementioned U.S. Patent No. 2,010,685 to obtain a crude product consisting principally of alpha-chloropropionic acid, and employing the reaction mixture, i.e. the crude alpha-halopropionic acid, as the starting material which is reacted with a further amount of chlorine or bromine at temperatures between 150° and 225° C. to

form a corresponding alpha, alpha-dihalopropionic acid as herein described.

Following is a description by way of example of methods of carrying the invention into effect.

EXAMPLE 1.

A charge of 22 pounds of a batch of alpha-chloropropionic acid, together with 0.66 pound of phosphorus trichloride as catalyst, was placed in a glass reaction vessel equipped with a reflux condenser and stirrer. The alpha-chloropropionic acid employed in the reaction was prepared by chlorinating propionic acid at a temperature of from 115° to 120° C. in the presence of 3 per cent by weight of phosphorus trichloride as catalyst until approximately one molecular proportion of chlorine per molecular equivalent proportion of the propionic acid initially used was consumed in the reaction. The alpha-chloropropionic acid starting material contained 92.5 per cent by weight of alpha-chloropropionic acid and 2.5 per cent of alpha,alpha-dichloropropionic acid. The mixture of alpha-chloropropionic acid and catalyst was stirred and heated to a temperature of 130° C. Chlorine was introduced into the liquid at a rate of approximately 0.12 pound of the chlorine per hour. After 2.5 pounds of chlorine was added, the temperature of the mixture was raised to 150° C. Chlorination was continued with stirring and heating of the mixture at a temperature between 150° and 160° C. for a period of 68.5 hours while adding 9.1 pounds of chlorine. Hydrogen chloride formed in the reaction, together with unreacted chlorine, was vented through the reflux condenser. A charge of 0.29 pound of phosphorus trichloride was added to the mixture and the chlorination continued for a period of 91 hours longer while adding 7.9 pounds of chlorine. Total chlorine fed to the reaction mixture was 19.5 pounds. Unreacted chlorine vented from the reaction was 2.14 pounds. The total reaction time was 176.5 hours. The mixture was cooled. The liquid product was separated from the catalyst residue. The crude product weighed 27.5 pounds. The catalyst residue weighed one pound. The liquid product had a density of 1.4380 at 25° C. The quantities of acyl chlorides present in the crude product were determined by hydrolyzing an aliquot portion of the same with water and titrating the hydrochloric acid with silver nitrate. The quantity of water theoretically required to hydrolyze the acyl chlorides present in the crude product was then added to the main body of said product and the latter was distilled. There were obtained 0.89 pound of a foretraction boiling at temperatures of from 45° at 168 millimetres absolute pressure to 111° C. at 42 millimetres pressure, 25.28 pounds of alpha,alpha-dichloropropionic acid product boiling at temperatures of from 93° C. at 12 millimetres absolute pressure to 126.5° C. at 8 millimetres pressure, and 1.2 pounds of tar-like residue. The distilled product was analyzed and found to consist of 2 per cent by weight of alpha-chloropropionic acid, 87 per cent alpha,alpha-dichloropropionic acid, 6 per cent alpha,alpha-dichloropropionic anhydride, 4 per cent alpha,alpha,beta-trichloropropionic acid and 1 per cent of unknown material. No alpha,beta- dichloropropionic acid was obtained.

EXAMPLE 2.

A charge of 542.5 grams of the batch of the alpha-chloropropionic acid described in Example 1, together with 16.5 grams of phosphorus trichloride was placed in a glass reaction flask equipped with a reflux condenser and stirrer. The mixture was stirred and heated to a temperature of 175° C. Chlorine was added at a rate of approximately 13 grams per hour while stirring and heating the mixture at a temperature between 175° and 180° C. Hydrogen chloride and unreacted chlorine were vented through the condenser. After 17 hours, 5.5 grams of phosphorus trichloride was added and the chlorination continued. Five hours later another 5.5 grams of phosphorus trichloride was added and the chlorination continued. Five hours later another 5.5 grams of phosphorus trichloride was added and the chlorination continued for 10 hours longer. The total chlorination time was 32 hours. A total of 420 grams of chlorine was fed to the reaction. The mixture was cooled to room temperature and the liquid separated from the catalyst residue by decanting. There was obtained 667 grams of crude product. Twelve cubic centimetres of water was added to hydrolyze acyl chlorides and anhydrides in crude product. Thereafter, the mixture was distilled. There was obtained 632 grams of distillate boiling at temperatures of from 37° C. at 23 millimetres absolute pressure to 77° C. at 0.7 millimetre pressure. It was analyzed and found to contain 97 per cent by weight of alpha,alpha-dichloropropionic acid, 2 per cent alpha,alpha,beta-trichloropropionic acid and 1 per cent alpha-chloropropionic acid. The yield of said product was 88.5 per cent. No alpha,beta-dichloropropionic acid was obtained.

EXAMPLE 3.

A charge of 542.5 grams of the batch of the alpha-chloropropionic acid described in Example 1, together with 27 grams of phosphorous acid (H_3PO_3) as catalyst was placed in a glass reaction vessel and chlorinated by procedure similar to that described in Example 2. A total of 500 grams of

chlorine was fed to the reaction mixture at a temperature of 175° to 180° C. over a period of 53 hours. Unreacted chlorine and HCl were vented through the reflux condenser. The mixture was cooled to room temperature and the liquid product separated from the catalyst residue. Twelve grams of water was added to the liquid product, after which it was distilled. There were obtained 571 grams of liquid product as distillate boiling at temperatures of from 56° C. at 2 millimetres absolute pressure to 110° C. at 3 millimetres and 32 grams of residue. The product was analyzed and found to contain 95 per cent by weight of alpha,alpha-dichloropropionic acid, 2 per cent unknown product and 3 per cent alpha-chloropropionic acid. No alpha,beta-dichloropropionic acid was obtained.

EXAMPLE 4.

A charge of 542.5 grams of the batch of the alpha-chloropropionic acid described in Example 1, together with 16 grams of phosphorus pentoxide as catalyst was placed in a glass reaction flask equipped with a reflux condenser and stirrer. The mixture was stirred and heated at a temperature of from 175° to 180° C. Chlorine was introduced at a rate of approximately 7 grams per hour over a period of 58.5 hours. HCl and unreacted chlorine were vented through the reflux condenser. A total of 426 grams of chlorine was fed to the reaction. The mixture was cooled, and the liquid product separated from the catalyst residue. 3.5 cc. of water was added to the product, after which it was distilled. There were obtained 594 grams of liquid product as distillate boiling at temperatures of from 72° C. at 7 millimetres absolute pressure to 83.5° C. at 1 millimetre pressure and 30 grams of residue. The product was analyzed and found to contain 6 per cent by weight of alpha-chloropropionic acid, 83 per cent of alpha,alpha-dichloropropionic acid, 4 per cent of alpha,alpha-dichloropropionic anhydride, 2 per cent of alpha,alpha-beta-trichloropropionic acid and 5 per cent unknown. No alpha,beta-dichloropropionic acid was obtained.

EXAMPLE 5.

A charge of 542.5 grams of the batch of the alpha-chloropropionic acid described in Example 1, together with 27 grams of phosphorus pentachloride as catalyst, was placed in a glass reaction flask equipped with a reflux condenser and stirrer and chlorinated by introducing chlorine into the stirred and heated mixture at a temperature of from 175° to 180° C. over a period of 50 hours. HCl and unreacted chlorine were vented through the reflux condenser. A total of 440 grams of chlorine was fed to the reaction. The mixture was cooled and the liquid product decanted from the catalyst residue. 4.5 cc. of water was added to the liquid product after which it was distilled. There were obtained 617 grams of liquid product as distillate boiling at temperatures of from 70° C. at 10 millimetres absolute pressure to 89° C. at 0.5 millimetre pressure and 25 grams of residue. The product was analyzed and found to contain 1 per cent by weight of alpha-chloropropionic acid, 90 per cent alpha,alpha-dichloropropionic acid, 3 per cent alpha,alpha-dichloropropionic anhydride, 5 per cent alpha,alpha-beta-trichloropropionic acid and 1 per cent unknown product. No alpha,beta-dichloropropionic acid was obtained.

EXAMPLE 6.

A charge of 612 grams of alpha-bromopropionic acid, together with 36.6 grams of phosphorus tribromide as catalyst was placed in a glass reaction flask equipped with a reflux condenser and stirrer. The mixture was stirred and heated at a temperature between 175° and 180° C. Bromine was added at a rate of approximately 40 grams of bromine per hour over a period of 15.5 hours. A total of 640 grams of bromine was fed to the reaction. Hydrogen bromide formed in the reaction was vented through the reflux condenser. The mixture was cooled and the liquid poured from the reaction vessel. There were obtained 683 grams of liquid product and 15 grams of solid catalyst residue. Seven cubic centimetres of water was added to the crude liquid product with stirring, after which it was distilled. There were obtained 216 grams of a fore-fraction boiling at a temperature of from 39° C. at 10 millimetres absolute pressure to 106° C. at 7 millimetres pressure, 549 grams of alpha,alpha-dibromopropionic acid boiling at 106° to 107° C. at 7 millimetres pressure and 105 grams of residue. The alpha,alpha-dibromopropionic acid product was analyzed and found to contain 68.6 per cent by weight of bromine.

EXAMPLE 7.

A charge of 4500 pounds of propionic acid, together with 190 pounds of phosphorus trichloride as catalyst, was stirred and heated at a temperature between 120° and 125° C. while feeding 4800 pounds of chlorine into the liquid over a period of 32.5 hours. Hydrogen chloride formed in the reaction and unreacted chlorine were vented from the reaction. An aliquot portion of the reaction product was withdrawn and analyzed. It was found to contain 98 per cent by weight of alpha-chloro-propionic acid and 2 per cent of alpha,alpha-dichloropropionic acid. Another portion of 75 pounds of phosphorus trichloride as catalyst

was added to the main body of the reaction mixture. The chlorination was continued by feeding chlorine to the mixture while raising the temperature from 125° C. to 176° C. over a period of 7 hours. Thereafter, chlorine was fed to the mixture at a temperature between 176° and 180° C. over a period of 20 hours. Another portion of 25 pounds of the phosphorus trichloride catalyst was added and the chlorination continued for 25 hours longer. The total reaction time was 84.5 hours. The reacted mixture was cooled to 90° C. and 65 pounds of water added with stirring. The mixture was cooled to room temperature. The liquid product was separated from the catalyst residue. An aliquot portion of the liquid product was withdrawn and analyzed. It was found to contain 10 per cent by weight of alpha-chloropropionic acid, 88 per cent of alpha, alpha-dichloropropionic acid, 1 per cent of alpha,alpha-dichloropropionic acid anhydride and 1 per cent alpha,alpha,beta-trichloropropionic acid.

In place of the alpha-bromopropionic acid employed in Example 6, alpha-chloropropionic acid can be used and brominated to form the corresponding alpha-chloro-alpha-bromopropionic acid. In place of the chlorine employed in the Examples 1 to 5, bromine can be employed in molecular equivalent proportions to form the corresponding alpha-chloro-alpha-bromopropionic acid.

What we claim is:—

1. In a process for halogenating propionic acid, the steps which consist in (1) reacting propionic acid with an approximately equimolecular proportion of chlorine or bromine at a temperature between 50° and 140° C. in the presence of a phosphorus-containing catalyst consisting of phosphorus, or a halide, oxyhalide, oxygen acid or oxide of phosphorus, whereby an alpha-halopropionic acid is obtained as substantially the sole halogenated derivative, and (2) reacting the alpha-halopropionic acid with an approximately equimolecular proportion of chlorine or bromine by heating said alpha-halopropionic acid at a reaction temperature between 150° and 225° C. in the presence of said catalyst while introducing the halogen into admixture with the liquid alpha-halopropionic acid.

2. A process according to Claim 1, wherein the phosphorus-containing catalyst is phosphorus trichloride.

3. A process according to Claim 1 or Claim 2, wherein the halogen is chlorine.

4. A process for making an alpha,alpha-dihalopropionic acid which comprises reacting an alpha-halopropionic acid, consisting of alpha-chloropropionic acid or alpha-bromopropionic acid, with an approximately equimolecular proportion of chlorine or bromine at a temperature between 150° and 225° C. in the presence of a phosphorus-containing catalyst consisting of phosphorus or a halide, oxyhalide, oxygen acid or oxide of phosphorus.

5. A process according to Claim 4, wherein the phosphorus-containing catalyst is phosphorus trichloride.

6. A process according to Claim 4 or Claim 5 wherein the halogen is chlorine.

7. A process according to Claim 4 or Claim 5 or Claim 6, wherein the alpha-halopropionic acid is alpha-chloropropionic acid.

8. A process for halogenating propionic acid substantially as described in any of the specific examples hereinbefore described.

9. Halogenated propionic acid when prepared by the process claimed in any one of the preceding claims.

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was added to the main body of the reaction mixture. The chlorination was continued by feeding chlorine to the mixture while raising the temperature from 125° C. to 176° C. over a period of 7 hours. Thereafter, chlorine was fed to the mixture at a temperature between 176° and 180° C. over a period of 20 hours. Another portion of 25 pounds of the phosphorus trichloride catalyst was added and the chlorination continued for 25 hours longer. The total reaction time was 84.5 hours. The reacted mixture was cooled to 90° C. and 65 pounds of water added with stirring. The mixture was cooled to room temperature. The liquid product was separated from the catalyst residue. An aliquot portion of the liquid product was withdrawn and analyzed. It was found to contain 10 per cent by weight of alpha-chloropropionic acid, 88 per cent of alpha, alpha-dichloroproprionic acid, 1 per cent of alpha,alpha-dichloropropionic acid anhydride and 1 per cent alpha,alpha,beta-trichloropropionic acid.

In place of the alpha-bromopropionic acid employed in Example 6, alpha-chloropropionic acid can be used and brominated to form the corresponding alpha-chloro-alpha-bromopropionic acid. In place of the chlorine employed in the Examples 1 to 5, bromine can be employed in molecular equivalent proportions to form the corresponding alpha-chloro-alpha-bromopropionic acid.

What we claim is:—

1. In a process for halogenating propionic acid, the steps which consist in (1) reacting propionic acid with an approximately equimolecular proportion of chlorine or bromine at a temperature between 50° and 140° C. in the presence of a phosphorus-containing catalyst consisting of phosphorus, or a halide, oxyhalide, oxygen acid or oxide of phosphorus, whereby an alpha-halopropionic acid is obtained as substantially the sole halogenated derivative, and (2) reacting the alpha-halopropionic acid with an approximately equimolecular proportion of chlorine or bromine by heating said alpha-halopropionic acid at a reaction temperature between 150° and 225° C. in the presence of said catalyst while introducing the halogen into admixture with the liquid alpha-halopropionic acid.

2. A process according to Claim 1, wherein the phosphorus-containing catalyst is phosphorus trichloride.

3. A process according to Claim 1 or Claim 2, wherein the halogen is chlorine.

4. A process for making an alpha,alpha-dihalopropionic acid which comprises reacting an alpha-halopropionic acid, consisting of alpha-chloropropionic acid or alpha-bromopropionic acid, with an approximately equimolecular proportion of chlorine or bromine at a temperature between 150° and 225° C. in the presence of a phosphorus-containing catalyst consisting of phosphorus or a halide, oxyhalide, oxygen acid or oxide of phosphorus.

5. A process according to Claim 4, wherein the phosphorus-containing catalyst is phosphorus trichloride.

6. A process according to Claim 4 or Claim 5 wherein the halogen is chlorine.

7. A process according to Claim 4 or Claim 5 or Claim 6, wherein the alpha-halopropionic acid is alpha-chloropropionic acid.

8. A process for halogenating propionic acid substantially as described in any of the specific examples hereinbefore described.

9. Halogenated propionic acid when prepared by the process claimed in any one of the preceding claims.

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