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PREPARATION OF 2-CHLOROBUTENE-2

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This invention relates to the preparation of 2-chlorobutene-2 and particularly to the preparation of this compound by the dehydrochlorination of 2,3-dichlorobutane.

2-Chlorobutene-2 has been prepared from 2,3-dichlorobutane by the method of British Patent 332,605 (1930) which involves treatment of the latter compound with alcoholic potassium hydroxide. That method requires the ues of relatively costly material, one of which is highly inflammable. Other disadvantages thereof which make the method unattractive for commercial application are that it is difficult to separate the reaction product from the alcohol and that the presence in the reaction mixture of alcohol results in the formation of by-product ether compounds.

It is an object of the present invention to provide an improved method of preparing 2-chlorobutene-2 from 2,3-dichlorobutane. A further object is the provision of a practical method for carrying out the dehydrochlorination of 2,3-dichlorobutane using an alkaline agent in an aqueous medium, whereby good yields of 2-chlorobutene-2 may be obtained. These and still further objects will be apparent from the ensuing description of the invention.

The above objects may be accomplished in accordance with my invention by subjecting 2,3-dichlorobutane to the action of an alkaline agent selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, and mixtures of alkali metal and alkaline earth metal hydroxides, in an aqueous medium at a temperature within the range of 118 to 250° C. By means of my improved method, yields of pure 2-chlorobutene-2 of the order of 90% may be readily obtained. The method is easily carried out and is practicable for commercial operations.

The use of aqueous solutions of strong alkali, such as sodium hydroxide, in preparing vinyl chloride and isopropenyl chloride from ethylene dichloride and propylene dichloride, respectively, is described by Young in U. S. Patent 1,752,049. That patent, which does not mention the treatment of four-carbon olefine dichlorides, states that the treatment of propylene dichloride with an alcoholic solution of potassium hydroxide yields propenyl chloride, whereas isopropenyl chloride is produced when the same material is treated with aqueous caustic at elevated temperature. From that disclosure it is apparent that the monochloro olefine product or products obtainable from a particular olefine dichloride by dehydrochlorination reactions with alkaline agents is or are not predictable. This is particularly true in the case of 2,3-dichlorobutane from which two monochlorobutenes, namely 2-chlorobutene-2 and 3-chlorobutene-1, are theoretically possible, and it could not have been predicted that the former compound could be obtained in substantially quantitative yields from 2,3-dichlorobutane by practicing the present method. Indeed, it is surprising and entirely unexpected that 2-chlorobutene-2 could be obtained in such good yields from 2,3-dichlorobutane by the present method in view of German Patent 246,572, which describes the preparation of 2,3-dihydroxybutane from the same dichlorobutane by treatment with aqueous calcium hydroxide at 75° C.

Particularly good results may be obtained by the present method when an alkali metal hydroxide, such as sodium hydroxide, is employed as the alkaline agent, by effecting the reaction at a temperature within the range 118 to 210° C. Operation within the range of 130 to 160° C. is particularly recommended. When using an alkaline earth metal hydroxide, such as lime, as the alkaline agent, operation at a temperature within the range of 150 to 250° C., and preferably 175 to 220° C., is effective. These temperature ranges may be varied somewhat depending upon the particular alkaline material used and also upon the concentration of the agent in the aqueous medium.

The concentration of the alkaline agent in the aqueous medium may be varied over a wide range. Concentrations within the range of 10 to 30% and preferably 15 to 25% give especially good results, although concentrations outside of these ranges may be employed. The amount of alkali used may also be varied considerably, but in order to effect as complete conversion as possible an excess of at least 5% over that amount theoretically required to convert the 2,3-dichlorobutane to 2-chlorobutene-2 should be used.

In order that the reaction may be carried out at the elevated temperatures indicated above, it will of course be necessary that the reaction mixture be maintained under suitable pressure during the course of the reaction. This may be conveniently done by effecting the reaction in a closed vessel, such as an autoclave or any of the usual bomb-type reactors.

I have discovered that best results are obtained when 2-chlorobutene-2 is removed from the reaction mixture as it is produced therein. This may be conveniently accomplished by equipping the reactor with a suitable stripping column

which functions to condense and return to the reaction mixture unconverted 2,3-dichlorobutane while permitting 2-chlorobutene-2 to escape in the vapor form. The vapors of 2-chlorobutene-2 are passed from the stripping column to a condenser where they are condensed in the form of crude product, which may be used as such or may be purified by usual distillation methods to separate unconverted 2,3-dichlorobutane not returned to the reactor by the stripping column.

The invention is further illustrated by the following examples.

Example 1

10 gram-moles of 2,3-dichlorobutene and 11.2 gram-moles of sodium hydroxide in the form of a 25% aqueous solution were charged into a pressure bomb which was provided with means for shaking and for heating the bomb to the desired temperature. The contents of the vessel were heated initially to a temperature of 130° C. During the 6½ hour reaction period the temperature was permitted to fall slowly to 115° C., after which the reaction mixture was treated to separate 2-chlorobutene-2. The desired compound was isolated from the mixture in an amount corresponding to a yield of 80% of the theoretical, calculated on the basis of the amount of 2,3-dichlorobutane not recovered as such. Of the original amount of 2,3-dichlorobutane charged into the bomb, 31% was converted to 2-chlorobutene-2.

Example 2

20 gram-moles of 2,3-dichlorobutane and 22.4 gram-moles of sodium hydroxide in the form of a 25% aqueous solution were charged into a reaction bomb as described in Example 1. The contents of the bomb were heated to a temperature of 135 to 140° C. for a period of 2½ hours, after which 2-chlorobutene-2 was isolated from the reaction mixture in an amount corresponding to a yield of 82.6%, based upon the amount of dichlorobutane consumed. Of the dichlorobutane initially charged 52.2% was converted to the monochlorobutene.

Example 3

40 pounds of 2,3-dichlorobutane of 90% purity and 75 pounds of a 20% sodium hydroxide solution were charged into a horizontal 30-gallon autoclave, 15 inches I. D. by 3½ ft. long, provided with a paddle-type agitator operating at 80 R. P. M. The autoclave was also provided with a stripping column 15 feet long and 3 inches wide which was packed for 10 feet with ⅜ inch Raschig rings. This column was equipped with a bayonet-type reflux condenser in the top 5 feet of the column. Heat was applied to the autoclave so as to maintain a temperature in the reactor in the neighborhood of 150 to 160° C. During the reaction period cooling water was applied to the condenser in the stripping column so as to maintain a set reflux calculated to be about 20 pounds per hour. The vapor draw-off valve from the stripping column was adjusted so that product was removed from the reactor at the rate of about 4 pounds per hour. The reaction was stopped when the density of the distillate rose to 1.0, indicating that the material coming over then was substantially all water. By operation in this manner 26.2 pounds of crude product was obtained from which 22.1 pounds of pure product was recovered by usual distillation methods. The yield of purified product was 87.8% of the theoretical based upon the dichlorobutane employed.

Example 4

4 gram-moles of 2,3-dichlorobutane and 800 grams of a lime slurry containing 2.2 gram-moles of calcium hydroxide were charged into a shaker bomb as in the method of Example 1. The bomb and its contents were shaken for 6 hours, during which time the reaction mixture was maintained at a temperature of approximately 150° C. At the conclusion of the run it was found that 14% of the dichlorobutane charged into the bomb was converted to 2-chlorobutene-2, the yield of the latter compound being 89% of the theoretical based upon the amount of the dichloride not recovered as such.

Example 5

An experiment similar to that described in Example 4 was carried out at a temperature of 200° C. At the end of 6 hours 57% of the dichlorobutane charged had been converted to give a yield of 82.5% of 2-chlorobutene-2 based upon the amount of dichlorobutane not recovered as such.

It has been discovered that the rate of conversion when using lime as the alkaline material may be increased considerably by having present in the reaction medium a substantial amount of sodium hydroxide. Thus, in experiments carried out substantially as described in Examples 4 and 5 except that a temperature of 175° C. was employed, the rate of conversion was increased approximately 50% by substituting 0.4 mole of sodium hydroxide for 0.2 mole of calcium hydroxide. In general the use of 0.01 to 0.5 mole of sodium hydroxide per mole of calcium hydroxide is sufficient to increase substantially the reactivity of the latter. The proportions of the two agents may be varied so that sodium hydroxide predominates, but due to the relative cheapness of lime, the use of a mixture consisting chiefly of calcium hydroxide, but containing sufficient sodium hydroxide to increase substantially the reactivity of the former, is preferred.

One of the chief advantages of the present improved method is that cheap alkaline materials may be used. No costly inflammable solvent is required and an easy separation of the desired product is secured. The method may be practiced to give yields of 2-chlorobutene-2 approaching theoretical values and in general the compound may be obtained as substantially the sole organic reaction product.

Many widely different embodiments of the invention may be practiced without departing from the scope and spirit thereof. Accordingly, it is not intended that the invention be limited to the specific embodiments and descriptions thereof set forth above, except as indicated in the appended claims.

I claim:

1. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with an alkaline material selected from the group consisting of alkaline earth metal hydroxides, alkali metal hydroxides, and mixtures of alkali and alkaline earth metal hydroxides in an aqueous medium at a temperature of 118 to 250° C.

2. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with an alkaline material selected from the group consisting of alkaline earth metal hydroxides, alkali metal hydroxides, and mixtures of alkali and alkaline earth metal hydroxides in an aqueous medium at a temperature of 118 to 250° C. and with-

drawing 2-chlorobutene-2 from the reaction mixture as it is formed.

3. The method of claim 1 using an aqueous medium containing the alkaline material in a concentration of 10 to 30% by weight.

4. The method of claim 1 using an aqueous medium containing at least a 5% excess of the alkaline material in a concentration of 10 to 30% by weight.

5. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with sodium hydroxide in the form of an aqueous solution at a temperature of 118 to 210° C.

6. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with sodium hydroxide in the form of an aqueous solution at a temperature of 130 to 160° C.

7. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with a sodium hydroxide solution of 10 to 30% concentration by weight at 118 to 210° C.

8. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with a sodium hydroxide solution of 10 to 30% concentration by weight at 130 to 160° C.

9. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with calcium hydroxide in an aqueous medium at 150 to 250° C.

10. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with a 10 to 30% aqueous slurry of calcium hydroxide at 175 to 220° C.

11. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with an aqueous medium containing a mixture of alkaline materials including a substantial amount of sodium hydroxide and a preponderant amount of calcium hydroxide at a temperature of 118 to 250° C.

12. A method of preparing 2-chlorobutene-2 comprising reacting 2,3-dichlorobutane with an aqueous medium containing 0.01 to 0.5 mole of sodium hydroxide per mole of calcium hydroxide present therein at a temperature of 118 to 250° C.

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