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PROCESS FOR THE PRODUCTION OF ALKYNES

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This invention relates to an improved process for producing alkynes by the dehydrohalogenation of halogen substituted alkanes and alkenes.

It is known to produce acetylene and the homologs thereof comprising the alkyne series of hydrocarbons by the elimination of hydrogen halide from halogenated hydrocarbons, as ethylene dibromide or mono-bromoethylene. However, the yield of alkyne obtained in this manner is small, frequently being but 20% to 30% of the maximum theoretical yield. This is particularly true when dealing with halogenated hydrocarbons containing four or more carbon atoms and is largely due to the uncontrolled nature of the reaction whereby other products than the desired alkyne or alkynes are also produced. For example, when dehydrohalogenating 1,2-dibromobutane with alcoholic potassium hydroxide, one obtains not only butyne-1 and -2, but also 1- and 2-bromobutene-1, 1- and 2-ethoxybutene-1, and butadiene-1,2.

It is therefore an object of the present invention to provide an improved process for obtaining alkynes from halogenated hydrocarbons. A more particular object is to provide a process of this nature whereby dehydrohalogenation of the starting materials proceeds in a controlled manner, with resultant high yield of alkyne and reduction in by-product formation.

The process of the invention whereby the foregoing and other objects are attained is based on the discovery that greatly improved yields of alkynes are obtained when the dehydrohalogenation of the halogenated hydrocarbon starting materials proceeds either in the absence of water, or with the prompt removal of any water which may be formed during the reaction.

When the reaction is to be conducted without water formation, an alkali metal alcoholate is employed as the dehydrohalogenating medium, particularly good results being obtained when the alcoholate comprises an anhydrous, alkali metal derivative of a high boiling hydroxylic material, as, for example, the ethyl or methyl ethers of ethylene glycol, diacetone glycol, and diacetone glycol monomethyl ether.

Alternatively, it has been discovered that good results can also be obtained when the dehydrohalogenation is accomplished through use of an alcoholic solution of alkali metal hydroxide provided that any water formed during the reaction is promptly and continuously removed. This removal may be effected in any one or more of several different ways. A preferred method is to add to the solution an organic liquid such as benzene or toluene which will form a low boiling azeotrope with the water without interfering in the dehydrohalogenation reaction, the azeotrope then being either distilled off with the alkyne or at some lower temperature. The water may be

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removed by bubbling a dry gas through the reacting solution. In some cases the alcohol solvent medium itself forms an azeotrope of satisfactory boiling point with the water formed. In still another method the halo-reactant itself, particularly the halo-alkene, may act to entrain the water through formation of an azeotropic mixture, this method being of the greatest practical value when the reaction is carried out in the presence of a high-boiling hydroxylic solvent.

Insofar as the mechanism of reaction is concerned whereby either dihalogenated alkanes or monohalogenated alkenes are dehydrohalogenated to produce the corresponding alkynes, the process of the present invention does not differ from those of the prior art. The dihalogenated alkanes are those wherein the halogen atoms, which are preferably chlorine or bromine, but may be fluorine or iodine, are attached to the same or adjacent carbon atoms, whereas in the halogenated alkenes the halogen atom is attached to one or the other of the carbon atoms linked by the double bond. For example, the alkynes appearing in the left hand column below may be obtained by dehydrohalogenating any of the halogenated hydrocarbons set against them in the right hand column, and in most cases other starting materials than those listed could have been used as well:

Alkyne	Boiling Point	Suitable Halogenated Starting Material
	°C.	
Butyne-1	8	1,1-dichlorobutane; 1,2-dibromobutane; 1-bromobutene-1.
Pentyne-2	55	2,3-dibromopentane; 3-chloropentene-2.
Hexyne-2	84	2,3-dichlorohexane; 3-bromohexene-2.
Heptyne-3	106	3,4-dibromoheptane; 4-bromoheptene-3.
Heptyne-1	100	1,2-dibromoheptane; 1,1-dichloroheptane; 1-bromoheptene-1; 2-chloroheptene-1.

While the process of the invention is broadly applicable to the preparation of all members of the alkyne series, it is preferably used only in the preparation of those alkynes having at least four carbon atoms. The dehydrohalogenation process here described is practiced in the solution phase, and those alkynes and halogenated alkanes and alkenes having less than four carbon atoms have such a low boiling point that it is difficult to retain them in the liquid phase except at low temperatures. However, the reaction by which halogenated alkanes and alkenes are converted into alkynes through removal of one or two molecules of hydrogen halide, respectively, is an endothermic one. It is normally conducted at temperatures above 75° C., and for periods which may range from several minutes to two or three hours.

However the dehydrohalogenation of the pres-

ent invention be carried out, a hydroxylic compound is used, in the one case to dissolve the alcoholate and the halogenated alkane or alkene starting material, and in the other case to dissolve the alkali metal hydroxide and the said starting materials. By "hydroxylic" compounds it is meant to include alcohols and other organic compounds related thereto which contain the (OH) group, and of the compounds coming within this class it is preferred to use those having a boiling point in excess of 100° C. While a wide variety of hydroxylic compounds, including amyl, isoamyl, hexyl and isohexyl alcohols, as well as such polyhydric alcohols as ethylene glycol and propylene glycol, for example, are satisfactory for use in the process of the present invention, it is preferred to employ an ether derivative of a polyhydric alcohol as, for example, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, glyceryl monomethyl ether, glyceryl monoethyl ether, glyceryl dimethyl ether, glyceryl diethyl ether, diacetone glycol monomethyl ether and beta-methyl, glyceryl monomethyl ether. All the compounds mentioned in the paragraph fall within the term "hydroxylic compounds" and have boiling points in excess of 100° C.; most of them boil above 150° C.

The anhydrous alkali metal alcoholates employed to dehydrohalogenate the halogen substituted alkane or alkene starting materials may be prepared by dissolving the desired quantity of alkali metal hydroxide in an excess of the hydroxylic compound with heating. It is preferred that the hydroxylic compound employed be a high-boiling ether derivative of a polyhydroxylic material, as the monoalkyl ether derivatives of ethylene glycol, for example, and of the various alkali metal hydroxides, those of sodium or potassium are preferred, though the more expensive cesium, lithium, and rubidium hydroxides can be used. The solution is then cooled and any water present is removed. This can be most conveniently and thoroughly accomplished by adding a liquid organic compound such as benzene, toluene or xylol, for example, which is capable of forming a low boiling azeotrope with water and then subjecting the mixture to slow distillation until all water present has been azeotropically distilled off leaving the alkali metal alcoholate dissolved in the excess of hydroxylic compound. Any residue of benzene or other organic liquid added may be removed by distillation or left in the solution.

In dehydrohalogenating partially halogenated hydrocarbons to produce alkynes through use of anhydrous alcoholate solutions of the type described above, suitable alkane or alkene starting materials are first dissolved in the alcoholate solution, care being taken to make sure that the said starting materials themselves contain no water. If there is doubt on this score, the materials may be dried by subjecting them to a preliminary distillation step, or by other known means. With either type of starting material i. e., dihalogenated alkane or monohalogenated alkene, it is essential for the highest yields of alkyne product that the reactants be combined in such proportions that the amount of alkali metal present as a component of the alcoholate be at least equivalent to the amount of halogen present as a component of the starting materials, and preferably there should be present an excess of the alkali metal, i. e., an excess of the alcoholate. This excess may range anywhere from

about 5 to as much as 100%, or even more. For example, when dehydrohalogenating 1,2-dibromohexane to a hexyne through use of the potassium alcoholate of ethylene glycol monoethyl ether, there should be used at least two moles of the alcoholate for each mole of the alkane, and were 1-bromohexene-1 to be the starting material, there should be used at least one mole of the alcoholate for each mole of the alkene. It is also possible to employ the anhydrous alcoholate solution to effect partial dehydrohalogenation of the dihalogen alkanes and thereby form the monohalogen substituted alkene; when the latter product is that desired, the quantity of alkali metal present should be equivalent to but one-half of the halogen present in the dihalogen alkane, and no excess of alkali metal should be used. 1-bromohexene-1, for example, may be formed in this manner from dibromohexane through the use of one mole of the dibromohexane and one mole of the alcoholate. However, it is not necessary to the formation of the monohalogen substituted alkene that the reaction be carried on in the absence of water, a fact which will also be discussed in a succeeding portion of this description.

Following the dissolution of the halogen substituted hydrocarbon starting materials the solution is heated to bring about the dehydrohalogenation desired. This may be accomplished by maintaining the solution at or above the temperature at which the alkyne boils and recovering the latter as it is distilled off; alternatively, the alkyne may be separated by solvent extraction or other physical means, though the distillation method of separation is preferred.

For best results, the heating step by which the alkyne is formed should be carried on at temperatures above 75° C., and preferably above 100° C. The solution should be maintained at such elevated temperatures until dehydrohalogenation is complete, the alkyne product being distilled off substantially as fast as it is formed.

The dehydrohalogenation reaction for the production of alkynes which is described in the preceding paragraphs proceeds without the formation of water and therefore no provision need be made to eliminate this component, a sample reaction being.

$$\underset{\text{1, 2-dichloropentane}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2Cl} + \underset{\substack{\text{potassium alcoholate}\\ \text{of ethylene glycol}\\ \text{monoethyl ether}}}{2C_2H_5OCH_2{\cdot}CH_2OK} \longrightarrow$$

$$\underset{\text{pentyne-1}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}C{\equiv}CH} + 2KCl + \underset{\substack{\text{ethylene glycol mono-}\\ \text{ethyl ether}}}{2C_2H_5{\cdot}OCH_2{\cdot}CH_2OH}$$

This reaction is a very efficient one, and total alkyne yields as high as 90% to 95% of the maximum theoretical yield have been obtained, the yield of the alkyne-1 product being as high as 75 to 80%.

When formation of the alkyne is not effected through use of an anhydrous alcoholate solution, the alkyne may be produced by dissolving the halogenated alkane or alkene starting material in a solution of alkali metal hydroxide in a hydroxylic solvent, and thereafter heating the solution with simultaneous elimination of water. Representative solutions of the type here under consideration are those formed by dissolving either 1,2-dibromohexane or 2-monobromohexene-1 and potassium hydroxide or sodium hydroxide in a solvent such as ethylene glycol monomethyl ethyl or ethylene glycol monoethyl ether. In preparing these solutions, care should be taken to make

sure that the alkali metal hydroxide is added first, and the solution cooled before the halogen substituted starting material is introduced. A sample reaction of the type here encountered is,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CHCl \cdot CH_2Cl + 2KOH \xrightarrow{\text{in presence of ethylene glycol monomethyl ether solvent}} CH_3 \cdot CH_2 \cdot CH_2 \cdot C \equiv CH + 2KCl + 2H_2O$$

1,2-dichloropentane → pentyne-1

With either type of starting material, i. e., dihalogenated alkane or mono-halogenated alkene, the reactants should be combined in such proportions that the amount of alkali metal hydroxide present is at least equivalent to the amount of halogen present in the hydrocarbon starting material, and it is preferred that there be an excess of alkali metal hydroxide present over this equivalent amount required to form alkali metal halide salts with the halogen constituent of the said starting material. In using this method of dehydrohalogenation, the same conditions of reaction should prevail as were noted above for use with the anhydrous alcoholate solutions, i. e. a reaction temperature above 75° C., and preferably above 100° C., with the elevated temperatures being maintained until the reaction is substantially complete. Once the reaction is begun, it is important to an efficient production of the alkyne that any water present be removed and kept removed as fast as it is formed. In some cases this may be accomplished by bubbling a dry inert gas through the liquid, particularly when the solution is heated at temperatures in excess of 100° C. Another method of removing the water which may be practiced in an efficient manner when the reaction is carried out at temperatures above 100° C. is to utilize a portion of the halogen substituted reactant present, and particularly the monohalogen alkene, which is either added as a starting material or formed as an intermediate product from the dihalogen alkane, to form a water azeotrope. Still another method of removing the water is to add to the solution an organic liquid such as, for example, benzene, toluene or amyl alcohol, the added liquid being one which is capable of forming an azeotrope boiling below 100° C. with any water present. For example, toluene, which boils at 110.8 C. forms a water azeotrope boiling at 84.1° C. The various amyl alcohols have even higher boiling points, while still forming water azeotropes of a relatively low boiling point. In many cases it proves convenient to add a succession of amounts of the non-aqueous azeotrope forming liquid. When the water present is eliminated in the manner described above, it does not remain in the solution long enough to interfere with the reaction, and as a result, greatly improved yields of the desired alkyne produce are obtained. While the process of this reaction is not so efficient as that wherein anhydrous alcoholate solutions are employed as the dehydrohalogenation medium, nevertheless total alkyne yields in excess of 75% of the maximum theoretical yield have been obtained.

In a modification of the foregoing feature of the invention, dihalogen alkanes such as are obtainable by halogenating alkene-1 products containing at least 4 carbon atoms in the molecule, are first treated with an alkali metal hydroxide on a mole-for-mole basis in the presence of a suitable hydroxylic solvent medium, and preferably, one of the higher-boiling type as glycol monoethyl ether or glycol monomethyl ether, in order to effect dehydrohalogenation to the mono-

halogen-alkenes which are removed from the reaction mixture, for example, by solvent extraction or by the conventional distillation procedure or by distillation with steam. We have found that this reaction is one which may be carried out without elimination of water, but it has also been found that this reaction proceeds in the most efficient manner when the higher-boiling hydroxylic materials such as the glycol monoalkyl ethers are utilized as the solvent medium. The monohalogen alkenes thus obtained, if desired after separation by fractional distillation, are then treated with an alkali metal hydroxide in the presence of a glycol monoalkyl ether or other high-boiling hydroxylic compound in which the monohalogen alkenes are sufficiently soluble, and the resulting mixture is then distilled under conditions whereby alkyne-1 products are distilled off substantially as formed, while any water present or produced is continuously removed by entrainment or azeotropic distillation with higher-boiling components of the mixture. In many cases, the monohalogen alkene component itself serves to form an azeotropic mixture, and the reaction may be carried out without the addition of other materials, a portion of the said monohalogen alkene leaving the solution in the form of an azeotrope while the balance is converted into the desired alkyne product.

The following examples illustrate the manner in which the present invention finds application:

Example I

It was desired to prepare hexyne-1 from a mixture of 1-chlorohexene-1 and 2-chlorohexene-1. An anhydrous alcoholate solution was prepared by dissolving 21 grams of potassium hydroxide in 108 cc. of ethylene glycol monoethyl ether, the solution being maintained at a temperature of about 100° C. during the course of this addition. The mixture was then cooled to about 50° C., and 60 cc. of benzene were then added. The resulting mixture was then subjected to slow distillation whereby all water present was azeotropically distilled off leaving the anhydrous potassium derivative of ethylene glycol monoethyl ether dissolved in the excess of ethylene glycol monoethyl ether.

To the alcoholate solution obtained in the manner described above were added 28 grams of a water-free mixture of 1- and 2-chlorohexene-1, obtained by heating a mixture of 80 parts of 1,2-dichlorohexene (obtainable by chlorinating hexene-1) and 25 parts of potassium hydroxide dissolved in 150 parts of glycol monoethyl ether on a water bath for 2 hours and then steam-distilling the resulting mixture to recover the 1-chlorohexene-1 and 2-chlorohexene-1 products. The alcoholate chlorohexene solution obtained in this manner was then gradually heated until it reached a temperature of 130° C., and it was maintained at this temperature for a period of 1.5 hours. During this time the hexynes formed were distilled off and recovered by condensation. A quantity of approximately 15 grams of hexyne-1 boiling at 71° C. was obtained in this manner, representing a yield of about 78% of the maximum theoretical yield. However, other hexynes than hexyne-1 were also recovered in the amount of approximately 3 grams so that the total hexyne yield was 94% of the maximum theoretical yield.

Example II

A mixture of heptynes consisting predom-

inantly of heptyne-1 may be prepared from 1,2-dibromoheptane by heating the solution formed by dissolving 30 grams of potassium hydroxide in 250 cc. of ethylene glycol monoethyl ether, cooling the solution, and then adding to it 50 grams of 1,2-dibromoheptane and 100 cc. of toluene. On being heated this solution will lose substantially all of its water in the form of a water-toluene azeotrope as the temperature reaches approximately 84 to 85° C., and with continued heating above this temperature small amounts of the azeotrope will be continuously recovered as the 1,2-dibromoheptane is converted into the form of the various heptynes. By the time the solution has been heated for one or more hours at a temperature between 130 and 140° C., the desired reaction will be substantially complete and approximately 15 grams of mixed heptynes will have been recovered as a distillate, of which approximately 12 grams will be heptyne-1. This represents a heptyne-1 yield of 65%.

We claim as our invention:

1. The method of forming an alkyne from a halogenated hydrocarbon, said method comprising forming an anhydrous alcoholate of sodium hydroxide and ethylene glycol monoethyl ether, dissolving said alcoholate in an excess of said ethylene glycol monoethyl ether, dissolving in the resulting solution a halogenated hydrocarbon selected from the group consisting of alkanes having two halogen atoms attached to a single carbon atom, alkanes having a halogen atom attached to each of two adjacent carbon atoms, and alkenes having a halogen atom attached to an unsaturated carbon atom, the content of sodium in said alcoholate being at least equivalent to the content of halogen in said hydrocarbon, the solution so formed being anhydrous in nature, and heating said anhydrous solution at a temperature above 75° C. to effect dehydrohalogenation of said halogenated hydrocarbons to form said alkyne.

2. The method of forming an alkyne from a halogenated hydrocarbon said method comprising forming an anhydrous alcoholate of potassium hydroxide and ethylene glycol monoethyl ether, dissolving said alcoholate in an excess of said ethylene glycol monoethyl ether, dissolving in the resulting solution a halogenated hydrocarbon selected from the group consisting of alkanes having two halogen atoms attached to a single carbon atom, alkanes having a halogen atom attached to each of two adjacent carbon atoms, and alkenes having a halogen atom attached to an unsaturated carbon atom, the content of potassium in said alcoholate being at least equivalent to the content of halogen in said hydrocarbon, the solution so formed being anhydrous in nature, and heating said anhydrous solution at a temperature above 75° C. to effect dehydrohalogenation of said halogenated hydrocarbons to form said alkyne.

3. The method of forming an alkyne from a halogenated hydrocarbon, said method comprising forming an anhydrous alcoholate of alkali metal and ethylene glycol monoethyl ether, dissolving said alcoholate in an excess of said ethylene glycol monoethyl ether, dissolving in the resulting solution a halogenated hydrocarbon selected from the group consisting of alkanes having two halogen atoms attached to a single carbon atom, alkanes having a halogen atom attached to each of two adjacent carbon atoms, and alkenes having a halogen atom attached to an unsaturated carbon atom, the content of alkali metal in said alcoholate being at least equivalent to the content of halogen in said hydrocarbon, the solution so formed being anhydrous in nature, and heating said anhydrous solution at a temperature above 75° C. to effect dehydrohalogenation of said halogenated hydrocarbons to form said alkyne.

4. The method of forming an alkyne from a halogenated hydrocarbon, said method comprising forming an anhydrous alcoholate of an alkali metal and an ether derivative of a polyhydric alcohol having a boiling point in excess of 100° C., dissolving said alcoholate in an excess of said alcohol, dissolving in the resulting solution a halogenated hydrocarbon selected from the group consisting of alkanes having two halogen atoms attached to a single carbon atom, alkanes having a halogen atom attached to each of two adjacent carbon atoms, and alkenes having a halogen atom attached to an unsaturated carbon atom, the solution so formed being anhydrous in nature, and heating said anhydrous solution at a temperature above 75° C. to effect dehydrohalogenation of said halogenated hydrocarbons to form said alkyne.

5. The method of forming an alkyne from a halogenated hydrocarbon said method comprising forming an anhydrous alcoholate of an alkali metal and a hydroxylic liquid having a boiling point in excess of 100° C., dissolving said alcoholate in an excess of said liquid, dissolving in the resulting solution a halogenated hydrocarbon selected from the group consisting of alkanes having two halogen atoms attached to a single carbon atom, alkanes having a halogen atom attached to each of two adjacent carbon atoms, and alkenes having a halogen atom attached to an unsaturated carbon atom, the content of alkali metal in said solution being at least equivalent to the content of halogen attached to said hydrocarbon, the solution so formed being anhydrous in nature, and heating said anhydrous solution at a temperature above 75° C. to effect dehydrohalogenation of said halogenated hydrocarbons to form the alkyne.

6. The method of forming alkynes comprising forming an anhydrous solution of a monohaloalkene having a halogen atom attached to an unsaturated carbon atom thereof in an anhydrous solution of an alkali metal alcoholate and heating the resulting monohalo-alkene-containing solution.

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