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MANUFACTURE OF GLYCOLS FROM CONJUGATED ALIPHATIC DIOLEFINS

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This invention relates broadly to a novel method for the manufacture of glycols, and more particularly, to the production of aliphatic glycols from conjugated diolefins and selected alkali metals to yield the dimetallo diene derivatives which are converted to the glycols by suitable chemical reactions.

It is an object of this invention to provide a novel and effective method for the synthesis of aliphatic glycols utilizing relatively cheap and readily available raw materials.

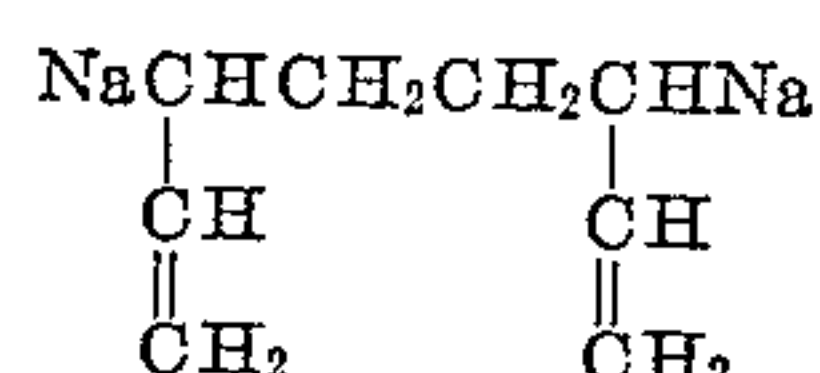
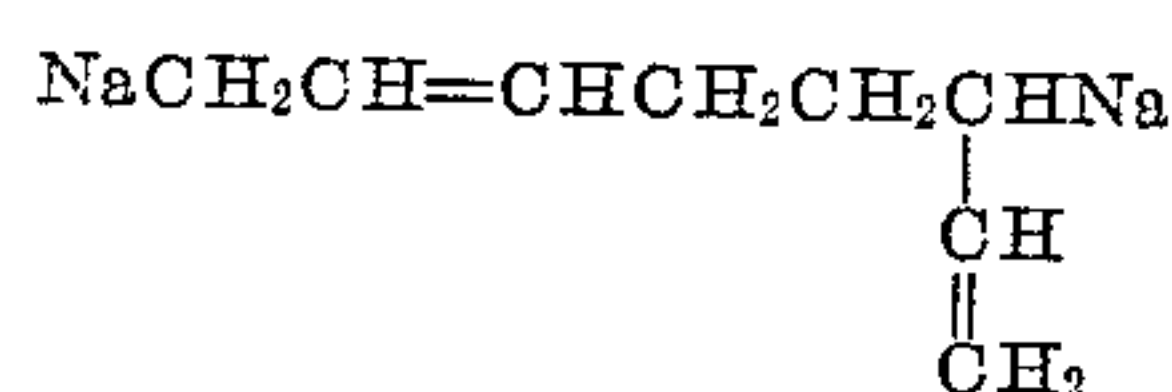
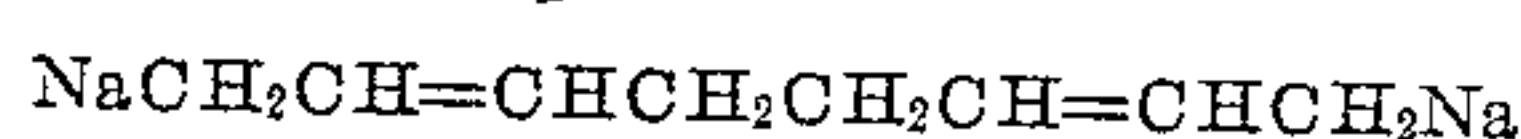
It is another object of this invention to react aliphatic conjugated diolefins selectively with an alkali metal such as sodium or potassium in dispersed form to obtain the dimetallo derivatives of dimerized dienes having twice the number of carbon atoms of the starting diolefins and react these dimetallo derivatives with oxidizing agents and isolate the corresponding glycols therefrom.

It is also a more particular object of this invention to selectively dimerize 1,3-butadiene using finely dispersed sodium to obtain disodiooctadienes and thereafter oxidize these products directly to obtain 8 carbon atom glycols and sodium salts thereof.

Other objectives of the invention will become apparent from the detailed description set forth below.

The present invention is carried out by initially treating an aliphatic conjugated diolefin with finely dispersed sodium or potassium in selected liquid ether medium and, if desired, in the presence of a relatively small amount of a polycyclic aromatic hydrocarbon and/or in the presence of a selected solid, friable attrition agent at controlled temperatures. The product obtained from this reaction is then treated with oxygen or oxygen-producing chemical compound or other oxidizing agent under selective reaction conditions to yield ultimately glycol products.

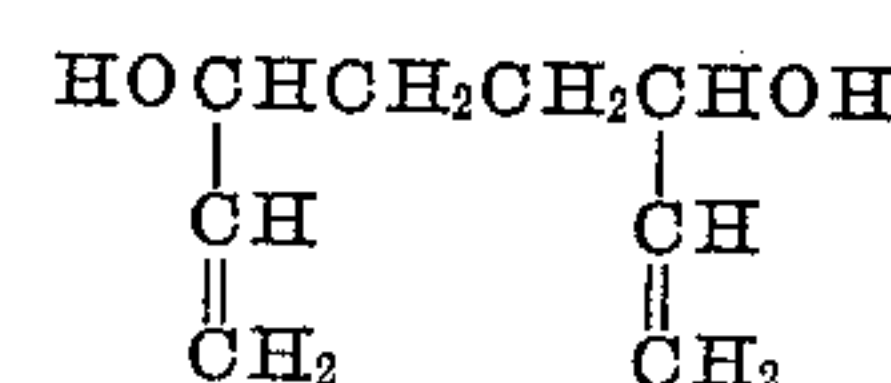
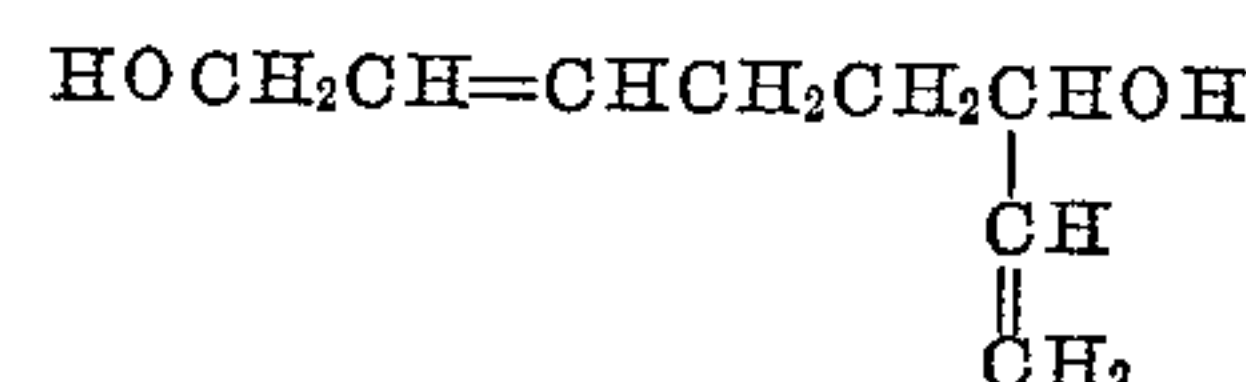
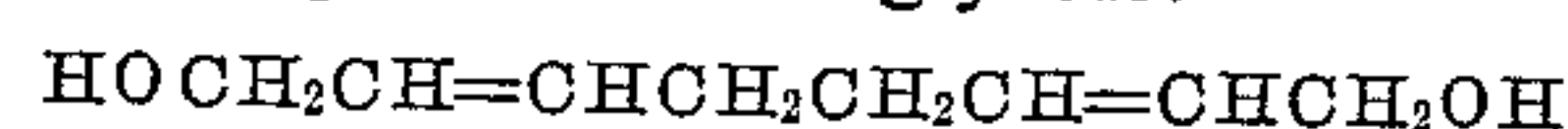
The initial step is a reaction which yields a dimerized product of the starting diolefin. For example, in the case where the initial reactants are sodium and butadiene, the dimeric product comprises the disodium derivatives of the aliphatic octadienes. A study of the structures indicates that this particular selective dimerization can yield the following isomeric products:



Accordingly, after the foregoing mixture of products

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has been oxidized, the major primary products obtained are the following unsaturated glycols:



If the reactants used are other diolefins, then the glycol products accordingly corresponding to such structures are likewise obtained.

The diolefins which are useful for this improved process include any aliphatic conjugated diolefin such as, for example, butadiene, isoprene, dimethylbutadiene, the pentadienes, such as the methyl-1,3-pentadienes, and the like. In general, it is desirable to use the conjugated aliphatic diolefins having from 4 to 8, inclusive, carbon atoms. Butadiene is particularly suited for use as the diolefin reactant.

Either sodium or potassium can be used as the alkali metal reactant. Sodium is preferred over potassium since it has been found that sodium gives excellent selectivity and yields of dimerized products, and it is cheaper and more readily available. Mixtures containing a major proportion of sodium are also useful.

One factor in the successful production of the initial dimerized derivatives which are subjected to oxidation is the use of the alkali metal in dispersed form. If bulk sodium is used instead of dispersed sodium, it either yields no product or results largely in the formation of highly condensed polymers from the diolefin. These unwanted polymers can be substantially avoided by employing the alkali metal as a dispersion. Such dispersions are most conveniently made in an inert hydrocarbon or ether preliminary to reaction with the diene.

The reaction medium most suitable for reaction of the diolefin with the alkali metal has been found to consist essentially of certain types of ethers. The ether medium can be any aliphatic mono ether having a methoxy group, in which the ratio of the number of oxygen atoms to the number of carbon atoms is not less than 1:4. Examples include dimethyl ether, methyl ethyl ether, methyl n-propyl ether, methyl isopropyl ether, and mixtures of these methyl ethers. Certain aliphatic polyethers are also satisfactory. These include the acyclic and cyclic polyethers which are derived by replacing all of the hydroxyl hydrogen atoms of the appropriate polyhydric alcohol by alkyl groups. Examples are the ethylene glycol dialkyl ethers such as the dimethyl, methyl ethyl, diethyl, methyl butyl, ethyl butyl, and dibutyl glycol ethers, trimethylene glycol dimethyl ether, glycerol trimethyl ether, glycerol dimethyl ethyl ether and the like. Generally, the simple methyl monoethers such as dimethyl ether and the polyethers of ethylene glycols, such as ethylene glycol dimethyl ether are preferred. Hydrocarbon solvents such as isooctane, kerosene, toluene, and benzene cannot be used exclusively as the reaction media in the dimerization step, since they adversely affect the dimerization reaction of the diolefin and give little or no yield of dimer products.

The ethers used as reaction media should not contain any groups which are distinctly reactive towards sodium.

Further, the ether used must not be subject to extensive cleavage under the reaction conditions to yield irreversible reaction products during the dimerization process. Such cleavage action not only destroys the ether but also introduces into the reaction system metallic alkoxides which induce undesirable polymer forming reactions with the diolefins.

Although it is preferred that the reaction medium consist substantially of the ethers as specified, other inert liquid media can be present in limited amounts. The inert media are introduced with the alkali metal dispersion as the liquid in which the sodium is suspended, or they may be otherwise introduced into the reaction mixture. These inert materials have the principal effect of diluting the ethers. As such dilution increases, a minimum concentration of ether is reached below which the dimerization promoting effect is not evident. It is necessary to maintain the concentration of ether in the reaction mixture at a sufficient level such that it will have a substantial promoting effect upon the diolefin dimerization reaction.

It has also been found highly useful to employ in conjunction with the dimerization reaction one or more techniques of activation for the dimerization process. This can be done in a number of ways and has the effect of increasing the rate of reaction and making the reaction more selective. For instance, a relatively small amount of at least one compound of the polycyclic aromatic class can be included in the reaction mixture. By this term it is intended to include condensed ring hydrocarbons such as naphthalene and phenanthrene, as well as the uncondensed polycyclic compounds such as diphenyl, the terphenyls, dinaphthyl, tetraphenyl ethylene, and the like. The polyphenyl compounds such as diphenyl, the terphenyls, and their mixtures have been found to be particularly useful. Concentrations in the range of 0.1 to 10 weight per cent based on the amount of diolefins undergoing dimerization are ordinarily quite sufficient.

It has also been found advantageous to carry out the dimerization of the diolefin in the presence of at least one solid friable attrition agent. These activating materials have been found especially valuable for increasing the reaction rate where the dimerization is done in attrition type apparatus such as a ball mill or pebble mill. Friable materials are those which are relatively easily pulverized in this type of apparatus. These materials can further be used either alone or in conjunction with the polycyclic aromatic compounds. Materials which are suitable for use as the solid friable attrition agents include inorganic solids such as alkali metal salts, for example, sodium chloride, sodium sulfate and potassium sulfate. Also useful is the class of compounds which consists of metallic and non-metallic oxides which are not reactive with metallic sodium under the reaction conditions, for example, sand (silicon dioxide), diatomaceous earth (Celite), zircon, and rutile. Carbon, such as in the form of graphite, can also be used. The material can be utilized in a number of ways. For instance, it can be carried out by the addition to the reaction zone of a suitable attrition agent which has been preground or otherwise adjusted to a satisfactory, useful particle size. On the other hand, a relatively coarse size salt, oxide or other suitable material can be added to a pebble mill or ball mill and, in contact with the solid, alkali metal, the friable attrition agent is ground down to effective size.

It is further highly desirable in the process that the reaction temperature in the dimerization step be held below 0° C. The temperature range between -20° to -50° C. is the preferred one for diolefin dimerization. At higher temperatures, the ether diluents tend to yield cleavage products with the result that sufficient alkoxide by-products are formed to yield high molecular weight polymeric products.

In the second step of the reaction, the dimerized product from the diolefin is subjected to oxidation. This dimerized product is a mixture or organometallic dienes. From the dimerization of butadiene there is obtained, for in-

stance, a mixture of disodiooctadienes. The oxidation is best carried out in the simplest way and using the simplest reagents. It is essentially a liquid phase operation. This is necessary in order to avoid by-product formation and to obtain relatively clean reaction products. Thus, the preferred reactant is oxygen itself either as pure oxygen or admixed with inerts such as in dry air. Artificial mixtures can also be prepared in which oxygen concentration is adjusted and controlled. Ozone can also be employed. If desired, oxidation catalysts can also be used, but these are generally unnecessary for satisfactory results. Oxidizing materials which yield oxygen or its oxidizing equivalent can also be used. These include sodium peroxide, hydrogen peroxide, the persulfates, and other organic and inorganic peroxides. Other oxidizing agents which may be used include metal peroxides, nitrogen oxides, nitro-aromatic compounds such as nitrobenzene, and some metal salts. In general, the oxidation to form the glycols is carried out in neutral or alkaline reaction media. Acidic conditions are much less satisfactory.

The reaction of the dimetallic diene compounds with the appropriate oxidizing reagent is preferably carried out at a temperature below +50° C., preferably in the range of -50° to 0° C., although the precise temperature will, of course, depend on the oxidizing agent being used.

While proportions of various reactants are not critical, optimum yields of the dimetallic dimer intermediate can be obtained only if the alkali metal, for instance, sodium, is present in finely dispersed form and in amounts equivalent to or slightly in excess of the molecular equivalents of diolefin employed.

In the general practice of the invention, the dimerized derivatives are prepared by reaction of a conjugated diolefin with the alkali metal in a suitable ether medium, in the presence of a small amount of a polycyclic hydrocarbon and/or in the presence of a selected solid friable attrition agent. The resulting dimetallic diene then is allowed to react with the oxidizing agent, preferably an oxygen-containing gas, which is introduced into the mixture. The oxidation is carried out in the liquid phase with or without further dilution of reactants with an inert liquid or gaseous diluent. The resultant reaction product then is hydrolyzed by gradual contact with water or an alcohol to liberate the glycols from their sodium derivatives which are initially formed. The glycols are isolated from this final reaction mixture by extraction, distillation or other suitable means. If a water soluble attrition agent has been used, it can be dissolved away from the more insoluble organic products including the glycol products by water. If the material used is water insoluble, then the separation of the products can readily be accomplished by chemical or physical means.

This entire series of reactions may be carried out either in a batchwise or in a continuous manner and it is not intended to limit the process to any particular method of operation.

In the instance where butadiene is the aliphatic diolefin starting material, there results from this method a mixture of C₈ unsaturated glycols. After hydrogenation, the saturated glycols obtained include 1,8-octanediol, 1,6-octanediol, and 3,6-octanediol. The glycol products obtained by this particular synthesis constitute a series of compounds in which the two alcohol groups are separated by from 4 to 8 carbon atoms. If some other, higher molecular weight diolefin is employed in the initial reaction, then the structure of the final glycol products will vary accordingly.

The unsaturated glycols or their alkali metal alkoxides or other derivatives can be hydrogenated at the double bonds to yield the corresponding saturated compounds. This also affords a convenient and accurate way to identify the structures of the unsaturated intermediates as well as the final products.

These mixtures of unsaturated glycol products are useful in the synthesis of "drying oil" types of polyesters by

esterification with saturated and unsaturated di- and mono-basic acids, and in alkyd resins, and the like. They are also particularly useful for hydrogenation to the corresponding saturated glycols which are quite valuable in the synthesis of polyester plastics and rubbers, plasticizers, synthetic lubricants, polyurethanes, and other products.

The more detailed practice of the invention is illustrated by the following example, wherein parts are given by weight unless otherwise specified. The following is illustrative only, and the invention is not in any way intended to be limited thereto except as indicated by the appended claims.

Example

A laboratory size dispersion device was charged with 1200 parts of flint pebbles, 50 parts of anhydrous sodium chloride, and approximately 750 parts of purified dimethyl ether. The mixture was agitated at 300 R. P. M. for fifteen minutes, then treated with 46 parts of a 50% sodium dispersion in isooctane (containing about 0.5% dimer of linoleic acid) and 2.0 parts of p-terphenyl. The blue color of the sodium terphenyl complex developed within two minutes. Fifty-four parts of 1,3-butadiene was then passed into the agitated reactor at the rate of 2.0 parts per minute. The mixture was agitated for fifteen minutes after the butadiene addition was complete. Pure oxygen was then bubbled through the mixture, the temperature being held at -23°C . The initial rate of oxygen flow was 0.5 part per minute. Over a two hour addition period this rate was gradually increased to 2.0 parts per minute. After a total addition time of six hours, the flow of oxygen was terminated and the system was purged with nitrogen. The unreacted sodium was destroyed by the addition of about 160 parts of methanol. The resulting reaction slurry was then decanted from the reaction vessel and poured onto crushed ice.

After standing overnight, the material was acidified with concentrated hydrochloric acid and extracted continuously with diethyl ether for fifteen hours. The ether extract was hydrogenated over 5% palladium on carbon at 50 p. s. i. until the hydrogen uptake had ceased. The solution was then filtered free of catalyst and stripped of solvent. The residual oil was dissolved in a small volume of diethyl ether and cooled for several hours at -40°C ., yielding a crystalline precipitate of 1,8-octanediol, M. P. $59-60^{\circ}\text{C}$., M. P. (lit.) 63°C ., bisphenylurethane, M. P. $169-170^{\circ}\text{C}$., M. P. (lit.) $172-172.5^{\circ}\text{C}$.. The mother liquors from the precipitation were found to contain 1,6-octanediol (B. P. $235-240^{\circ}/760\text{ mm.}$) and 3,6-octanediol (B. P. $230-235^{\circ}/760\text{ mm.}$).

What is claimed is:

1. The method of preparing a mixture of unsaturated glycols in which the hydroxyl groups are separated by at least four carbon atoms, which comprises dimerizing a conjugated aliphatic diolefin in the presence of a finely divided alkali metal selected from the group consisting of sodium and potassium at a temperature below about 0°C . and in the presence of an active ether diluent and a polycyclic aromatic hydrocarbon dimerization activator, thereafter subjecting the resulting organometallic diene to oxidation by an oxidizing substance, and hydrolyzing the salts of the glycols thus obtained.

2. The method of claim 1 wherein the conjugated aliphatic diolefin is 1,3-butadiene.

3. The method of claim 1 wherein the alkali metal is sodium.

4. The method of claim 1 wherein the oxidation is carried out with an oxygen-containing gas.

5. The method of claim 1 wherein the unsaturated glycols are subjected to reduction by hydrogenation, and recovering corresponding saturated glycols.

6. The method of preparing a mixture of unsaturated glycols in which the hydroxyl groups are separated by at least four carbon atoms, which comprises dimerizing a conjugated aliphatic diolefin in the presence of a finely divided alkali metal selected from the group consisting of sodium and potassium at a temperature below about 0°C . and in the presence of an active ether diluent and a solid friable attrition agent dimerization activator, thereafter subjecting the resulting organometallic diene to oxidation by an oxidizing substance, and hydrolyzing the salts of the glycols thus obtained.

7. The method of claim 6 wherein the conjugated aliphatic diolefin is 1,3-butadiene.

8. The method of claim 6 wherein the alkali metal is sodium.

9. The method of claim 6 wherein the oxidation is carried out with an oxygen-containing gas.

10. The method of preparing a mixture of unsaturated glycols in which the hydroxyl groups are separated by at least eight carbon atoms and containing substantial amounts of branch chain glycols having at least one C_2 branch per molecule, which comprises dimerizing a conjugated aliphatic diolefin with a finely divided alkali metal selected from the group consisting of sodium and potassium at a temperature below about 0°C ., in the presence of an active ether diluent and a polycyclic aromatic hydrocarbon dimerization activator, thereafter subjecting the resulting organometallic diene to oxidation by an oxidizing substance, and hydrolyzing the salts of the glycols thus obtained.

11. The method of preparing a mixture of unsaturated glycols in which the hydroxyl groups are separated by at least eight carbon atoms and containing substantial amounts of branch chain glycols having at least one C_2 branch per molecule which comprises dimerizing a conjugated aliphatic diolefin with a finely divided alkali metal selected from the group consisting of sodium and potassium at a temperature below about 0°C ., in the presence of an active ether diluent and a solid friable attrition agent dimerization activator, thereafter subjecting the resulting organometallic diene to oxidation by an oxidizing substance, and hydrolyzing the salts of the glycols thus obtained.

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