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(54) **ISOMERISATION D'EPOXYALCENES EN 2,5-DIHYDROFURANES; COMPOSITIONS CATALYTIQUES UTILES A CETTE FIN**

(54) **ISOMERIZATION OF EPOXYALKENES TO 2,5-DIHYDROFURANS AND CATALYSTS COMPOSITIONS USEFUL THEREFOR**

(57) Disclosed are processes for the isomerization of epoxyalkenes to dihydrofurans by contacting an epoxyalkene with a catalyst comprising a quaternary organic onium iodide compounds, optionally deposited on a non-acidic support and/or in combination with a Lewis acid co-catalyst. The catalyst may comprise a supported catalyst, an unsupported catalyst or a solution of the catalytically-active components in an inert, organic solvent.

ISOMERIZATION OF EPOXYALKENES TO 2,5-DIHYDROFURANS AND CATALYST COMPOSITIONS USEFUL THEREFOR

Abstract of the Disclosure

Disclosed are processes for the isomerization of epoxyalkenes to dihydrofurans by contacting an epoxyalkene with a catalyst comprising a quaternary organic onium iodide compounds, optionally deposited on a non-acidic support and/or in combination with a Lewis acid co-catalyst. The catalyst may comprise a supported catalyst, an unsupported catalyst or a solution of the catalytically-active components in an inert, organic solvent.

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ISOMERIZATION OF EPOXYALKENES TO 2,5–DIHYDROFURANS AND CATALYSTS COMPOSITIONS USEFUL THEREFOR

This invention pertains to isomerization processes and, more particularly, to processes whereby γ,δ–epoxy–alkenes and γ,δ–epoxycycloalkenes are isomerized to obtain the corresponding 2,5–dihydrofuran compounds. This invention also pertains to novel catalyst systems useful in the described isomerization processes and to methods for the preparation of supported catalyst systems.

Dihydrofurans are reactive heterocyclic species which are useful in a variety of applications, e.g., as intermediates in the production of useful polymers and chemicals. However, the use of dihydrofurans for such purposes has heretofore been restricted due to the non–availability of cost–effective preparative procedures therefor.

In addition, dihydrofurans are readily reduced to produce the corresponding tetrahydrofuran species, which are also useful in a variety of applications, e.g., as polar aprotic reaction solvents, co–solvents, reactive intermediates in the production of useful polymers, copolymers, and the like.

U.S. Patents 3,932,468 and 3,996,248 disclose the production of 2,5–dihydrofurans by the rearrangement of substituted or unsubstituted epoxyalkenes with a homogeneous catalyst system comprising hydrogen iodide or hydrogen bromide and a transition metal Lewis acid in an organic solvent. This process suffers from a number of disadvantages including the use of corrosive hydrogen halides, the need for expensive, high–boiling tertiary amide solvents, e.g., N–methyl–2–pyrrolidinone, to

dissolve the transition metal Lewis acid. We have found that the process of U.S. Patents 3,932,468 and 3,996,248 also results in the unwanted production of up to 15% α,β-unsaturated aldehydes or ketones.

The thermal (i.e., non-catalytic) rearrangement of 3,4-epoxy-1-butene has been studied and shown by Crawford et al in the Canadian Journal of Chemistry, Vol. 54, pages 3364-3376 (1976) to produce a variety of products, including 2,3-dihydrofuran, cis and trans 2-butenal and 3-butenal.

Other reactions of epoxides have been reported. See, for example, U.S. Patent 4,600,800, where epoxides are converted to allylic alcohols by contacting an epoxide in the liquid phase with solid alumina catalysts.

Another example of the rearrangement of epoxides is described in the Journal of Organometallic Chemistry, Vol. 359, pages 255-266 (1989), wherein Sato et al report the formation of α,β-unsaturated aldehydes and ketones by the rhodium (I) catalyzed isomerization of 1,3-diene monoepoxides.

U.S. Patent 4,897,498 describes an efficient process for the preparation of γ,δ-epoxyalkenes by the selective monoepoxidation of dienes. Thus, a process is needed for the conversion of such epoxyalkenes to dihydrofurans in satisfactory selectivity and/or yields wherein the product may be readily recovered from the catalyst and the catalyst reused and used in continuous operation.

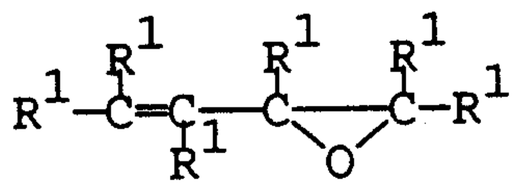
In accordance with the present invention, we have discovered a catalytic process for the isomerization of γ,δ-epoxyalkenes to produce dihydrofurans. The process provides high levels of epoxyalkene conversion with high selectivity to the desired dihydrofuran product. Long catalyst lifetimes are realized and the product may be

recovered by relatively simple means since the catalyst and reaction mixture are readily separated by such simple techniques as distillation, decantation, filtration, gas stripping methods, gas/liquid flow separation, and the like.

Our invention also provides novel catalyst systems, both supported and unsupported, which are useful, for example, to promote the isomerization of epoxyalkenes to dihydrofurans. Processes for preparing the supported catalyst systems are also provided herein.

In accordance with the present invention, there is provided a process for the isomerization of γ,δ-epoxy-alkenes to the corresponding 2,5-dihydrofuran compounds, which process comprises contacting a γ,δ-epoxyalkene or γ,δ-epoxycycloalkene with a catalytic amount of a quaternary organic onium iodide, e.g., a compound consisting of an ammonium, phosphonium or arsonium cation and an iodide anion, under isomerization conditions of temperature and pressure.

The γ,δ-epoxyalkene and γ,δ-epoxycycloalkene reactants may contain from 4 to 20 carbon atoms, preferably from 4 to 8 carbon atoms. Examples of the epoxyalkene and epoxycycloalkene reactants include compounds having the structural formula:

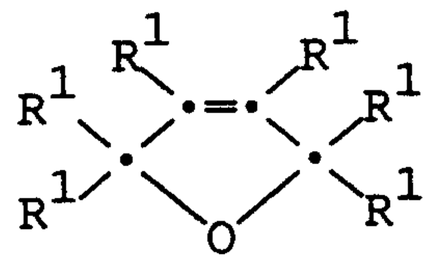


(I)

wherein each R^1 is independently selected from hydrogen, alkyl of up to 8 carbon atoms, a carbocyclic or heterocyclic aryl group of about 5 to 10 carbon atoms or halogen or any two R^1 substituents collectively may represent an alkylene group forming a ring, e.g., alkylene containing in the main chain up to 8 carbon atoms. The preferred epoxyalkene reactants comprise

compounds of formula (I) wherein only two of the R^1 substituents individually may represent lower alkyl, e.g., alkyl of up to 8 carbon atoms, or collectively represent straight or branched chain alkylene of up to 8 carbon atoms. Exemplary compounds contemplated for use in the practice of the present invention include 3,4-epoxy-3-methyl-1-butene, 2,3-dimethyl-3,4-epoxy-1-butene, 3,4-epoxycyclooctene, 3,4-epoxy-1-butene, 2,5-dimethyl-2,4-hexadiene monoepoxide, and the like. The epoxyalkene reactant of primary interest is 3,4-epoxy-1-butene.

The 2,5-dihydrofuran compounds obtained in accordance with our novel process have the structural formula:



(II)

wherein the R^1 substituents are defined above. Of the compounds which may be obtained in accordance with our invention, the most important is 2,5-dihydrofuran.

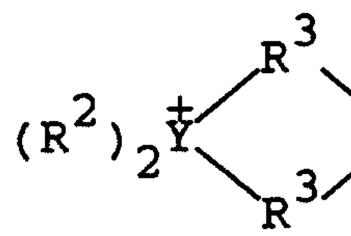
The quaternary onium iodide compounds which may be used as the catalyst in our novel process are known compounds and/or may be prepared according to published procedures. See, for example, U.S. Patent 3,992,432 and the references cited therein. Exemplary quaternary organic onium iodide compounds include mono-, di-, tri-, or tetra-substituted quaternary onium iodides, wherein said substituents are selected from hydrogen, alkyl or substituted alkyl groups, cycloalkyl or substituted cycloalkyl groups, carbocyclic aryl or substituted carbocyclic aryl groups, heteroaryl or substituted heteroaryl groups, ferrocenyl, wherein each of said substituents may be bonded to one another to form a cyclic, heterocyclic, polycyclic or poly-heterocyclic

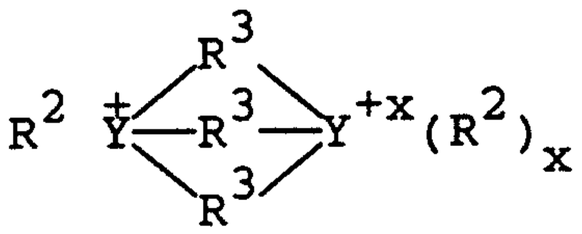
structure. When used on a support or as a melt, the onium compounds normally contain at least 6 carbon atoms, preferably at least 12 carbon atoms, and have melting points not greater than 225°C, preferably not greater than 200°C.

Examples of the onium iodide catalysts are compounds conforming to the formulas

(III) $(R^2)_4Y^+ \quad I^-$,

(IV) $I^- \quad (R^2)_3Y^+-R^3-Y^{+x}(R^2)_{2+x} \quad I_x^-$,

(V) $I^- \quad$  $\quad I_x^-$, or

(VI) $I^- \quad$  $\quad I_x^-$,

wherein

each R^2 independently is selected from hydrogen, alkyl or substituted alkyl moieties having up to 20 carbon atoms, cycloalkyl or substituted cycloalkyl having 5 to 20 carbon atoms, or aryl or substituted aryl having 6 to 20 carbon atoms; or when Y is P, each R^2 also may be selected from alkoxy of up to 20 carbon atoms, cycloalkoxy of 5 to 20 carbon atoms, aryloxy of 6 to 10 carbon atoms or halogen;

two or three R^2 substituents collectively may represent joined hydrocarbylene groups, e.g. alkylene having 4 to 6 main chain carbon atoms or unsaturated groups such as —CH=CHCH=CHCH= and lower alkyl substituted alkylene and unsaturated groups, which form a mono- or poly-cyclic ring with the Y atom to which they are bonded;

each R^3 is independently selected from hydrocarbylene moieties or substituted hydrocarbylene moieties;

x is 0 or 1, and

Y is N, P or As; provided that the quaternary onium iodide compound contains at least 6 carbon atoms. The substituted groups and moieties referred to above bear one or more substituents such as groups having the formulas

$$-OR^4, \quad -O-\overset{O}{\overset{\|}{C}}-R^4, \quad -\overset{O}{\overset{\|}{C}}-O-R^4, \quad -Si(R^4)_3 \text{ and } X$$

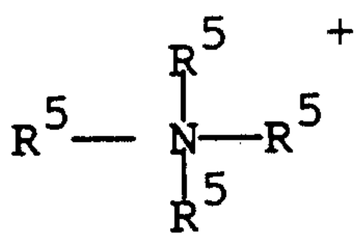
wherein each R^4 is independently selected from hydrogen or alkyl of up to 20 carbon atoms and X is halogen. As used herein, the terms "hydrocarbylene moieties" refers to alkylene moieties having up to 6 carbon atoms, arylene or polyarylene moieties having 6 to 20 carbon atoms.

The preferred onium iodide catalysts are the quaternary ammonium and quaternary phosphonium iodide compounds. Exemplary ammonium compounds include tetrapentylammonium iodide, tetrahexylammonium iodide, tetraoctylammonium iodide, tetradecylammonium iodide, tetradodecylammonium iodide, tetrapropylammonium iodide, tetrabutylammonium iodide, monooctylammonium iodide, dioctylammonium iodide, trioctylammonium iodide, N-octylquinuclidinium iodide, N,N′-dimethyl-N,N′-dihexadecylpiperazinium diiodide, dimethyl-hexadecyl-[3-pyrrolidinylpropyl]ammonium iodide, N,N,N,N′,N′,N′-hexa(dodecyl)octane-1,8-diammonium diiodide, N,N,N,N′,N′,N′-hexa(dodecyl)butane-1,4-diammonium diiodide, N-octylpyridinium iodide, and the like.

Exemplary phosphonium compounds include tetraoctylphosphonium iodide, tetrabutylphosphonium iodide, triphenyl(hexyl)phosphonium iodide, triphenyl(octyl)-

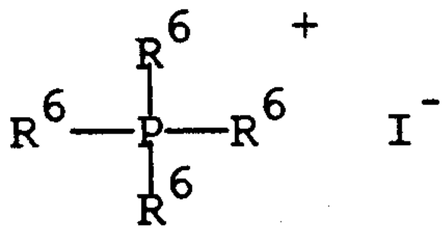
phosphonium iodide, tribenzyl(octyl)phosphonium iodide, tribenzyl(dodecyl)phosphonium iodide, triphenyl(decyl)-phosphonium iodide, triphenyl(dodecyl)phosphonium iodide, tetrakis(2-methylpropyl)phosphonium iodide, tris(2-methylpropyl)(butyl)phosphonium iodide, triphenyl(3,3-dimethylbutyl)phosphonium iodide, triphenyl(3-methylbutyl)phosphonium iodide, tris(2-methylbutyl)(3-methylbutyl)phosphonium iodide, triphenyl[2-trimethylsilylethyl]phosphonium iodide, tris(p-chlorophenyl)(dodecyl)phosphonium iodide, hexyl-tris(2,4,6-trimethylphenyl)phosphonium iodide, tetradecyltris(2,4,6-trimethylphenyl)phosphonium iodide, dodecyltris(2,4,6-trimethylphenyl)phosphonium iodide, and the like.

Tetra-substituted ammonium and phosphonium iodide compounds containing a total of 16 to 60 carbon atoms are especially preferred. Such compounds have the formulas



(VII)

and



(VIII)

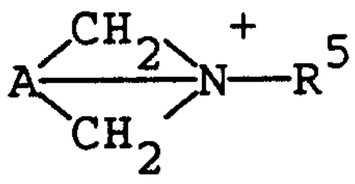
wherein

each R^5 substituent independently is selected from alkyl of up to 20 carbon atoms and each R^6 substituent is independently selected from R^5, benzyl, phenyl or phenyl substituted with up to 3 substituents selected from lower alkyl (alkyl of up to 4 carbon atoms) lower alkoxy or halogen; or

two R^5 substituents collectively may represent alkylene of 4 to 6 carbon atoms including alkylene of 4 to 6 carbon atoms substituted with lower alkyl;

provided, as specified above, that the quaternary iodide compounds contain 16 to 60 carbon atoms.

Another group of preferred ammonium iodide compounds are comprised of N-alkyl-azabicycloalkane and N-alkyl- and N,N'-dialkyl-diazabicycloalkane iodide compounds containing 6 to 12 ring carbon atoms, e.g., bicyclic compounds having the general formula

(IX) 

wherein R^5 is defined above and A is the residue of an azabicycloalkane or diazabicycloalkane having 6 to 12 ring carbon atoms (including the 2 carbon atoms in the above general formula), e.g., azabicyclooctane, azabicyclononane, diazabicyclooctane and the like.

The onium iodide compounds described hereinabove may be employed in combination with a Lewis acid to catalyze the isomerization process of our invention. Examples of such optional Lewis acid co-catalysts include the alkali metal halides, zinc halides, magnesium halides, tin (II) halides, tin (IV) halides, titanium (IV) halides, titanium (IV) tetra-lower-alkoxides, zirconium (IV) halides, manganese (II) halides, iron (III) halides, or iron (III) acetylacetonate. Preferably, the Lewis acid co-catalyst is an alkali metal iodide, zinc iodide, zinc chloride, magnesium iodide, tin (II) iodide, tin (IV) iodide, titanium (IV) iodide, titanium (IV) tetramethoxide, titanium (IV) tetraethoxide, titanium (IV) tetraisopropoxide, zirconium (IV) iodide, manganese (II) iodide, manganese (II) chloride, iron (III) iodide, iron (III) acetylacetonate or a combination thereof. The Lewis acid co-catalysts which are particularly preferred are polarizable iodides, such as, for example, titanium (IV) iodide, zirconium (IV) iodide, and, especially, zinc iodide and tin (II) iodide.

The Lewis acid co-catalyst alternatively may be selected from organotin (IV) and organoantimony (V) compounds such as hydrocarbyltin trihalides, dihydrocarbyltin dihalides, trihydrocarbyltin halides, tetrahydrocarbyltin compounds and tetrahydrocarbylantimony halides. Examples of such organometallic compounds include compounds having the formula

$(R^7)_n—Sn—Hal_{(4-n)}$ and $(R^7)_4—Sb—Hal$

wherein

each R^7 independently is selected from alkyl or substituted alkyl moieties having up to 20 carbon atoms, cycloalkyl or substituted cycloalkyl having 5 to 20 carbon atoms, carbocyclic aryl or substituted carbocyclic aryl having 6 to 20 carbon atoms, or heteroaryl or substituted heteroaryl moieties having 4 up to 20 carbon atoms;

Hal is a halogen atom such as bromo or, preferably, iodo; and

n is 1, 2, 3 or 4.

Examples of organometallic compounds include dibutyltin diiodide, tributyltin iodide, trioctyltin iodide, triphenyltin iodide, tributyltin bromide, trimethyltin iodide, butyltin triiodide, tetrabutyltin, tetraoctyltin, triphenyltin iodide, tribenzyltin iodide, dimethyltin diiodide, diphenyltin diiodide, triphenyltin bromide and tetraphenylantimony iodide.

The preferred organometallic compounds comprise tin (IV) iodides having the above general formula and a total carbon content of 3 to 24 carbon atoms wherein

each R^7 substituent independently is selected from alkyl of up to 12 carbon atoms, benzyl, phenyl or phenyl substituted with up to 3 substituents selected from lower alkyl, lower alkoxy or halogen;

Hal is iodo; and

n is 2 or 3.

The quaternary organic onium iodide catalyst, or the quaternary organic onium iodide-Lewis acid catalyst system, may be employed in the process provided by this invention in either a supported or unsupported form. The supported catalysts of this invention comprise an essentially non-acidic catalyst support material having one or more quaternary organic onium iodide compounds distributed on the surface thereof as a substantially continuous and uniform film and, optionally, one or more of the Lewis acids described above, e.g., an alkali metal halide, zinc halide, magnesium halide, tin (II) halide, tin (IV) halide, titanium (IV) halide, titanium (IV) lower alkyl alkoxide, organotitanium (IV) halide, zirconium (IV) halide, manganese (II) halide, iron (III) halide, iron (III) acetylacetonate or one of the organotin compounds or organoantimony halides described hereinabove.

The essentially non-acidic support may be in the form of a powder or shaped material having sufficient structural integrity to allow passage of gaseous reactant through a packed or fluidized bed of the supported catalyst under reaction conditions. Preferred support materials employed in the practice of the present invention are materials having a particle size in the range of 20 up to 200 microns and having a crush strength of at least 4.4 Kg. Support materials having crush strengths of at least 22 Kg. are especially preferred.

A variety of shapes are suitable for use as the support material employed in the practice of the present invention. For example, pellets, spheres, rings, saddles, extruded cylinders, and the like can be employed, so long as such materials have dimensions and

packing characteristics so as to allow for the ready passage of gaseous reactant and product through a packed or fluidized bed of the catalyst under reaction conditions.

Examples of the materials which may be employed as the support include zinc oxide, zinc carbonate, magnesium oxide, silica, alumina, titanium oxide, lanthanum oxide, boron nitride, boron carbide, silicon nitride, silicon carbide, tin oxide, calcium oxide, barium oxide, strontium oxide, zirconium oxide, carbon, boron phosphate, or zirconium phosphate, as well as mixtures of any two or more thereof. The preferred support materials contemplated for use in the practice of the present invention include zinc oxide, zinc carbonate, magnesium oxide, silica, alumina, titanium oxide, boron nitride, silicon nitride, silicon carbide, calcium oxide, barium oxide and carbon as well as mixtures of any two or more thereof. Silica, alumina, titanium oxide and zinc oxide are particularly preferred support materials.

The amount of the quaternary organic onium iodide component of the novel catalyst compositions of this invention can vary substantially depending, for example, on the particular support material and the form, e.g., surface area, thereof, the mode in which the isomerization process is operated, the particular quaternary onium iodide present, the presence or absence of a Lewis acid co-catalyst, etc. The amount of the onium iodide, calculated as weight iodide, typically will be in the range of 0.1 to 30 weight percent based on the total weight of the catalyst. Preferred loading levels fall in the range of 0.5 up to 20 weight percent (same basis).

When present, the quantity of Lewis acid component of the catalyst compositions generally is in the range

of 0.01 to 30 weight percent, based on the total weight of the catalyst. The preferred quantity of the inorganic Lewis acid co-catalysts, e.g., titanium (IV) iodide, zirconium (IV) iodide, zinc iodide and tin (II) iodide, is in the range of 0.02 up to 5.0 weight percent based on the total weight of the catalyst.

Another embodiment of the catalyst compositions provided by our invention comprise a support material having deposited thereon (i) 0.1 to 30 weight percent of an organic onium iodide and (ii) about 0.01 to 30 weight percent of an organotin (IV) compound or organoantimony (V) halide, based on the total weight of the catalyst composition. These catalyst compositions preferably comprise:

(i) 0.5 to 20 weight percent of a tetra-substituted ammonium and/or phosphonium iodide compound of formula (VII) and/or (VIII); and

(ii) 0.02 to 20 weight percent of an organotin iodide containing a total of 3 to 24 carbon atoms and having the formula

$$(R^7)_n—Sn—I_{(4-n)}$$

wherein

each R^7 substituent independently is selected from alkyl of up to 12 carbon atoms, benzyl, phenyl or phenyl substituted with up to 3 substituents selected from lower alkyl, lower alkoxy or halogen; and

n is 2 or 3; on

(iii) a support material selected from silica, alumina, zinc oxide, titanium oxide, boron nitride and silicon carbide.

The supported catalysts described herein may be prepared by a variety of procedures as will be readily apparent to those skilled in the art. For example, the

supported catalysts may be prepared by the steps comprising:

(a) impregnating a suitable support with a solution of one or more quaternary organic onium iodide compound and, optionally, one or more Lewis acids, and thereafter

(b) removing the solvent from the impregnated support.

Solvents contemplated for use in the impregnation step include polar solvents capable of substantially dissolving the quaternary organic onium iodide and the optionally employed Lewis acid. Such solvents include water, lower alcohols such as methanol, ethanol, isopropyl alcohol, and the like. Preferred solvents are those which can be easily removed by standard evaporative techniques once the desired impregnation has been carried out.

The volume of solvent required is 0.5 to 20.0 ml of solvent (plus quaternary organic onium iodide and, optional Lewis acid) per gram of support, the minimum volume of solvent being defined as that volume required to cover the catalyst support. The support and impregnation solution are agitated (typically by rotary tumbling) for 0.2 to 2.0 hrs at slightly elevated temperatures, e.g., 20 to 60°C, to maximize interaction of support and catalytic components. The solvent is preferentially removed by rotary evaporation at reduced pressure at temperatures ranging from 40 to 100°C, or alternatively by drying in a heated forced air oven, or further alternatively by spray-drying the catalyst solution on the support. After drying, the catalyst is ready to be loaded into a reactor.

Prior to contacting the catalyst with an epoxyalkene under isomerization conditions, the catalyst optionally may be subjected to pre-treatment conditions

of time and temperature sufficient to activate said catalyst relative to non-pretreated catalyst. Typical pre-treatment conditions of time and temperature comprise a temperature at least as high as the melting point of said quaternary organic onium iodide, but no greater than 225°C, for a time in the range of 0.1 up to 10 hours.

The conditions of temperature and pressure and the space velocity employed in our novel isomerization process can vary considerably depending on various factors such as the activity of the catalyst used, the degree of conversion and/or selectivity desired, the gas hour space velocity employed, the mode of operation and the like. For example, the process may be carried out at a temperature in the range of 60 to 225°C although temperatures of 100 to 200°C are more typical. The total reaction pressure may be in the range of 1.02 to 70 bar (absolute) with the preferred range being 1.1 to 20 bar total pressure.

The gas hourly space velocity may be varied substantially, e.g., from 1 to 10,000, although our process normally is performed using gas hourly space velocities in the range of 10 up to 5,000 (hr^{-1}). The epoxyalkene reactant may constitute up to 100% of the feed composition or may be fed along with an inert diluent wherein volume ratio of the epoxyalkene:inert diluent can vary over a wide range of values, typically within 1:100 to 4:1. Exemplary inert gas diluents include helium, argon, nitrogen, carbon dioxide, or hydrocarbons which are gaseous under reaction conditions. Preferably, the epoxyalkene concentration is in the range of 5 up to 80 volume percent of the feed composition.

The isomerization process may be carried out using the catalysts described herein either in a supported or

unsupported form. Thus, the supported catalysts may be utilized in fixed or fluidized beds using reactor configurations well-known to those skilled in the art.

When the catalyst is unsupported, it can be used at temperatures either below, at or above the melting point of the quaternary organic onium iodide salt. When the catalyst is at or above its melting point and exists as a substantially liquid phase, it is necessary to maintain the catalyst in a reactor volume such that the passage of the gaseous feed and product molecules is not restricted, yet contains the catalyst in the reactor volume. An up-flow reactor is suitable for this purpose since the gaseous feed maintains the catalyst in the appropriate position in the reactor, yet permits the passage of unreacted feed and reaction products through the liquid, or substantially liquid, phase catalyst and into the downstream refining/recycle apparatus. In an especially preferred mode of operation, the catalyst is in a vessel with a closed bottom and the feed is added through a gas dispersion apparatus below the level of the catalyst. The unreacted feed and reaction products can exit from the top of the reactor.

The unsupported catalyst system preferably is used in our process as a melt of an intimate mixture of one or more of the quaternary onium iodide compounds and, optionally, one or more of the Lewis acid co-catalysts described hereinabove. The onium iodide:co-catalyst weight ratio of the unsupported catalyst system can vary substantially, e.g. from 500:1 to 1:100, depending on the particular co-catalyst selected. The preferred onium iodide:co-catalyst weight ratios depend on whether the co-catalyst is (1) an organotin (IV) compound or an organoantimony (V) halide or (2) one of the other Lewis acids described herein above. Thus, for the unsupported catalyst systems containing an inorganic

Lewis acid, such as titanium (IV) iodide, zirconium (IV) iodide, zinc iodide and tin (II) iodide, the preferred onium iodide:co-catalyst weight ratio is 200:1 to 5:1 and for the organotin (IV) compounds and organoantimony (V) halides the preferred onium iodide:co-catalyst weight ratio is 1:100 to 50:1. Particularly preferred unsupported catalyst systems comprise a mixture of one or more of the tetra-substituted ammonium or phosphonium iodide compounds described hereinabove and tin (II) iodide, zinc iodide or an organotin iodide.

The unsupported quaternary organic onium iodide and/or Lewis acid catalyst may be used with an inert organic solvent if desired to alter the reaction conditions and/or reactor configuration. The optional, inert organic solvent may be used, for example, to change the concentration of the quaternary organic onium iodide and/or the Lewis acid or to assist in heat and/or mass transfer characteristics of the catalytic process.

Thus, another embodiment of our invention comprises the isomerization of an epoxyalkene to the corresponding 2,5-dihydrofuran in the presence of a homogeneous catalyst solution. This embodiment may be carried out in the presence of one or more of the above-described organometallic compounds although reaction rates are relatively slow if an organic onium iodide is not included. Accordingly, the homogeneous catalyst solution preferably comprises a catalytic amount of

(i) one or more of the above-described organometallic compounds and (ii) one or more of the above-described organic onium iodides in (iii) an inert organic solvent, i.e., a solvent which does not react with the γ,δ-epoxyalkene or γ,δ-epoxycycloalkene reactants or the 2,5-dihydrofuran products. Examples of the solvents which may be used include aliphatic and aromatic hydrocarbons such as heptane, toluene, specific or mixed xylenes, pseudocumene, and mesitylene; halogenated hydrocarbons such as chlorobenzene, 1,2-dichlorobenzene, and 1,1,2,2-tetrachloroethane; ketones such as cyclohexanone, 5-methyl-2-hexanone, and 2-heptanone; ethers such as 2,5-dihydrofuran, tetrahydrofuran, and bis(2-methoxyethyl)ether; esters such as isobutyl acetate; and tertiary amides such as N-methyl-2-pyrrolidinone, N-cyclohexyl-2-pyrrolidinone, N-ethyl-2-pyrrolidinone, and N,N-dimethylacetamide. Normally, for ease of separation, the solvent or mixture of solvents employed have boiling points at least 20°C above the boiling point of the 2,5-dihydrofuran product and the unsaturated aldehyde or ketone by-products.

The concentrations of the organometallic compound and the optional onium iodide in the inert, organic solvent can be varied substantially depending, for example, on the particular catalytically-effective components present, the design of the reactor system, etc. Typically, the concentration of the organometallic compound will be 1 to 50 weight percent and the concentration of the onium iodide compound, when present, will be 1 to 70 weight percent, both concentrations being based on the total weight of the catalyst solution. Normally, the mole ratio of onium iodide to organometallic compound is at least 1:1.

The preferred catalyst solutions comprise

(i) 1 to 25 weight percent of an organotin iodide containing about a total of 3 to 24 carbon atoms and having the formula

$$(R^7)_n—Sn—I_{(4-n)}$$

wherein

each R^7 substituent independently is selected from alkyl of up to 8 carbon atoms, benzyl, phenyl or phenyl substituted with up to 3 substituents selected from lower alkyl, lower alkoxy or halogen; and

n is 1, 2, 3 or 4; and

(ii) 1 to 25 weight percent of a tetra-substituted ammonium or phosphonium iodide of formula (VII) and/or (VIII); and

(iii) an inert organic solvent selected from hydrocarbons and chlorinated hydrocarbons having up to 10 carbon atoms.

Toluene, mixed or specific xylene isomers, chlorobenzene, mixed or specific dichlorobenzene isomers, pseudocumene, and mesitylene are particularly preferred solvents.

The isomerization process may be carried out in the liquid phase using the catalyst solutions described hereinabove by contacting a γ,δ-epoxyalkene or γ,δ-epoxycycloalkene at a temperature of 50 to 200°C, preferably 100 to 150°C, depending on the solvent or mixture of solvents employed. The process may be carried out at atmospheric or super-atmospheric pressures, e.g., up to 22 bar (absolute).

The process employing the catalyst solution may be carried out in a batch, semi-continuous or continuous mode of operation. For example, batch operation may comprise refluxing a mixture of the γ,δ-epoxyalkene and catalysts, e.g. tributyltin iodide and tetraheptyl-

ammonium iodide, in a solvent such as p-xylene for a time sufficient to convert essentially all the epoxide to the 2,5-dihydrofuran. The products are then separated by distillation from the mixture. The undistilled catalyst solution may be reused in a subsequent reaction.

The catalyst solution preferably is employed in a continuous mode of operation wherein a γ,δ-epoxyalkene or γ,δ-epoxycycloalkene is added to a recirculated catalyst solution which is then introduced into a continuous reactor. After isomerization, the reaction stream is fed to a distillation system for removal of product or products and recycle of the catalyst solution. Examples of continuous reactor designs in which the process can be performed are continuous stirred tank reactors and plug flow reactors.

Our novel isomerization process and the catalyst systems, compositions and solutions useful in practicing the process are further illustrated by the following examples.

PREPARATION OF CATALYSTS

EXAMPLE 1

Tetrabutylammonium iodide (1.786 g) was dissolved at 25°C in ethyl alcohol (80 mL) in a 250 mL, round-bottom flask. Zinc oxide (5.0 g, ultrapure) powder was added and the mixture was agitated for twenty minutes at 40°C on a rotary evaporator. The zinc oxide used had a surface area of 3.8 square meters per g (m^2/g) and a particle diameter in the range of 75 to 150 microns. The alcohol was then removed on the rotary evaporator at 40°C under vacuum. The supported catalyst obtained contained 18.2 weight percent tetrabutylammonium iodide.

EXAMPLE 2

Tetradodecylammonium iodide (51.24 g), zinc iodide (1.06 g) and ethyl alcohol (200 mL) were placed in a one-liter, fluted flask and placed on a rotary evaporator and agitated for five minutes in a 60°C bath. Silica extrusions (400 g, Calsicat SiO_2 pellets, 6.64 mm diameter having a surface area of approximately 0.5 m^2/g and a general composition of 100% SiO_2) were then added and agitation continued for twenty minutes in the bath at 60°C. The alcohol was then removed on the rotary evaporator at 60°C under vacuum. The supported catalyst obtained contained 11 weight percent tetradodecylammonium iodide and 0.23 weight percent zinc iodide.

EXAMPLE 3

Triphenyl(hexyl)phosphonium iodide (0.250 g) and zinc iodide (0.0050 g) were placed in a 50-mL flask and then silica (2.0 g) was added. The silica support material was prepared by grinding the silica extrudate described in Example 2 and classifying the ground material and using the portion which passed a 10 mesh sieve and was retained on a 20 mesh. The flask was placed on a rotary evaporator and agitated for 20 minutes with the flask in the bath at 60°C. Methanol was removed while the flask was in the 60°C bath using vacuum. The supported catalyst obtained (2.25 g) contained 11 weight percent triphenyl(hexyl)phosphonium iodide and 0.11 weight percent zinc iodide.

The catalyst compositions set forth in the examples of Table I were prepared using the procedures described in the preceding examples. The Weight Percent given in Table I refers to the weight percent of the quaternary onium iodide present based on the total weight of the catalyst. The zinc oxide and silica used as the support

materials were the same as the support materials described in Examples 1 and 3.

TABLE I

Example	Quaternary Onium Iodide	Support	Weight Percent
4	Tetrapropylammonium iodide	ZnO	15.8
5	Tetrabutylammonium iodide	ZnO	22
6	Tetrapentylammonium iodide	ZnO	20.4
7	Tetrahexylammonium iodide	ZnO	22.5
8	Tetraoctylammonium iodide	ZnO	26.0
9	Tetradecylammonium iodide	ZnO	18.0
10	Tetradodecylammonium iodide	ZnO	21.0
11	Trioctylammonium iodide	ZnO	21.0
12	Dioctylammonium iodide	ZnO	18.0
13	Octylammonium iodide	ZnO	13.0
14	N,N'-Dimethyl-N,N'-hexa-decylpiperizinium diiodide	ZnO	20.0
15	N,N-Dimethyl-N-hexadecyl-N-[3-pyrrolidinonopropyl]-ammonium iodide	ZnO	19.0
16	N,N,N,N',N',N'-hexa-(dodecyl)-octane-1,4-diammonium diiodide	ZnO	30.0
17	N,N,N,N',N',N'-hexa-(dodecyl)-butane-1,4-diammonium diiodide	ZnO	29.0
18	N-Octylpyridinium iodide	ZnO	16.0
19	Tetraoctylphosphonium iodide	SiO_2	11.0
20	Tetrabutylphosphonium iodide	SiO_2	11.0
21	Tetradodecylammonium iodide	SiO_2	11.0

The catalysts set forth in Table II were prepared from a quaternary onium iodide compound, a Lewis acid

co-catalyst and a support material according to the procedures described in Examples 1-3. The Weight Percent given for each example refers to the weight of the co-catalyst present on the supported catalyst based on the total weight of the catalyst. The materials described in Examples 1 and 3 were used as the catalyst supports. The onium iodide compound and the weight percent thereof present on each catalyst and the support material of each of the Table II examples were:

Examples 22-32: 11% Tetradodecylammonium iodide on SiO_2
Examples 33-42: 26% Tetraoctylammonium iodide on ZnO
Examples 43-48: 11% Tetraoctylphosphonium iodide on SiO_2
Examples 49-51: 11% Tetrabutylphosphonium iodide on SiO_2

TABLE II

Example	Co-catalyst	Weight Percent
22	ZnI_2	0.22
23	$ZnCl_2$	0.22
24	SnI_2	0.27
25	SnI_2	0.54
26	SnI_2	1.10
27	MgI_2	0.22
28	MnI_2	0.22
29	ZrI_4	0.27
30	TiI_4	0.22
31	Titanium tetra-isopropoxide	0.22
32	Iron (III) acetyl-acetonate	0.11

TABLE II (cont.)

Example	Co-catalyst	Weight Percent
33	ZnI_2	1.7
34	SnI_2	2.2
35	SnI_4	1.8
36	LiI	1.5
37	ZnI_2	0.9
38	ZnI_2	3.4
39	ZnI_2	8.5
40	SnI_2	0.27
41	SnI_2	0.54
42	SnI_2	1.1
43	ZnI_2	0.055
44	ZnI_2	0.11
45	ZnI_2	0.15
46	ZnI_2	0.23
47	ZnI_2	0.55
48	SnI_2	0.11
49	ZnI_2	0.11
50	ZnI_2	0.55
51	ZnI_2	2.3

The supported catalysts described in Example 52-57 were prepared by procedures analogous to Example 3 using the silica support material described in Example 3, zinc iodide and the quaternary ammonium iodide compound given in each example. Each catalyst contained 11 weight percent of the quaternary ammonium iodide compound and

0.11 weight percent zinc iodide, based on the total weight of the catalyst.

EXAMPLE 52

N-Hexyl-1,4-diazabicyclo[2.2.2]octane iodide

EXAMPLE 53

N-Tetradecyl-1,4-diazabicyclo[2.2.2]octane iodide

EXAMPLE 54

N-Hexyl-1,4-diazabicyclo[2.2.2]octane iodide hydroiodide

EXAMPLE 55

N-Octylazabicyclo[2.2.2]octane iodide

EXAMPLE 56

N-Methyl-N-dodecylpyrrolidinium iodide

EXAMPLE 57

Tetrakis-(3-methylbutyl)ammonium iodide

The supported catalysts described in Example 58-71 were prepared by procedures analogous to and using the silica support material described in Example 3, zinc iodide and the quaternary phosphonium iodide compound given in each example. Each catalyst contained 11 weight percent of the quaternary phosphonium iodide compound and 0.11 (Examples 58 and 60) or 0.055 (Examples 59 and 61-72) weight percent zinc iodide, based on the total weight of the catalyst.

EXAMPLE 58

Tribenzyl(octyl)phosphonium iodide

EXAMPLE 59

Triphenyl(hexyl)phosphonium iodide

EXAMPLE 60

Tribenzyl(dodecyl)phosphonium iodide

EXAMPLE 61

Triphenyl(octyl)phosphonium iodide

EXAMPLE 62

Triphenyl(decyl)phosphonium iodide

EXAMPLE 63

Triphenyl(dodecyl)phosphonium iodide

EXAMPLE 64

Tris(2-methylpropyl)(butyl)phosphonium iodide -

EXAMPLE 65

Tris(2-methylpropyl)(3-methylbutyl)phosphonium iodide -

EXAMPLE 66

Tris(3-chlorophenyl)(dodecyl)phosphonium iodide -

EXAMPLE 67

Triphenyl(3-methylbutyl)phosphonium iodide

EXAMPLE 68

Triphenyl(trimethylsilylmethyl)phosphonium iodide

EXAMPLE 69

Tris(2,4,6-trimethylphenyl)(hexyl)phosphonium iodide

EXAMPLE 70

Tris(2,4,6-trimethylphenyl)(dodecyl)phosphonium iodide

EXAMPLE 71

Tris(2,4,6-trimethylphenyl)(tetradecyl)phosphonium iodide

EXAMPLE 72

Tetrakis(2-methylpropyl)phosphonium iodide

EXAMPLE 73

Silica support material described in Example 3 was contacted with tetraoctylphosphonium iodide, tetradodecylammonium iodide and zinc iodide to obtain a supported catalyst bearing 5.5 weight percent tetraoctylphosphonium iodide, 5.5 weight percent tetradodecylammonium iodide and 0.22 weight percent zinc iodide.

Examples 74-83 describe supported catalysts prepared from a quaternary ammonium compound and a variety of support materials. The percent given in each of the examples refers to the weight percent of the quaternary ammonium compound specified on the support based on the total weight of the catalyst. The catalysts of Examples 78-83 also contained 0.23 weight percent zinc iodide.

EXAMPLE 74

26% Tetraoctylammonium iodide on silicon nitride powder having a surface area of 11.9 m^2/g and a mean particle size of 60 microns.

EXAMPLE 75

26% Tetraoctylammonium iodide on boron nitride powder having a surface area of 2.9 m^2/g, a bulk density of 2.1 g/cm^3 and a particle diameter in the range of 50-100 microns.

EXAMPLE 76

22% Tetrabutylammonium iodide on zinc carbonate powder having a particle diameter in the range of 75-150 microns.

EXAMPLE 77

22% Tetrabutylammonium iodide on magnesium oxide powder having a surface area of 1.0 m^2/g and a particle diameter in the range of 75-150 microns.

EXAMPLE 78

11% Tetradodecylammonium iodide on alumina (Calsicat SE) spheres: 3.2 mm diameter spheres with a surface area of 10 m^2/g, a total pore volume = 0.44 cc (Hg)/g, packing density of 0.81 g/cm^3, crush strength = 8.2 Kg, and a general composition by weight percent of: Al_2O_3 = 99.7, SiO_2 = 0.1, Na_2O = 0.1 and Fe_2O_3 = 0.08.

EXAMPLE 79

11% Tetradodecylammonium iodide on alumina (Norton 5552) rings: 6.35 mm rings having a surface area of 0.43 m^2/g, a total pore volume of 0.37 cc (Hg)/gm, a median pore diameter of 7μ, a packing density of 0.80 g/cm^3, and a chemical composition by weight percent of: Al_2O_3 = 93.1, SiO_2 = 5.6, Fe_2O_3 = 0.3, TiO_2 = 0.1, CaO = 0.1, MgO = 0.3, Na_2O = 0.1, K_2O = 0.1.

EXAMPLE 80

11% Tetradodecylammonium iodide on alumina (Norton 08228) pellets: 4.76 mm diameter pellets with a surface

area of 0.25 m^2/g, a total pore volume of 0.23 cc (Hg)/gm, a median pore diameter of 19µ, a packing density of 0.90 g/cm^3, and a chemical composition by weight percent of: Al_2O_3 = 84.7, SiO_2 = 13.4, Fe_2O_3 = 0.21, TiO_2 = 0.47, CaO = 0.21, MgO = 0.12, Na_2O = 0.15, K_2O = 0.26.

EXAMPLE 81

11% Tetradodecylammonium iodide on zinc oxide (Calsicat ZnO) extrudate: 3.2 mm diameter extrudate with a surface area of 3.0 m^2/g, a packing density of 1.5 g/cm^3, a crush strength of 11 pounds, and a nominal chemical composition of 100% ZnO.

EXAMPLE 82

18% Tetradecylammonium iodide on alumina (Norton 82326) spheres: 4.76 mm iameter spheres having a surface area of 0.39 m^2/g, a total pore volume of 0.36 cc(Hg)/g, a median pore diameter of 5.4 microns, a packing density of 0.94 g/cm^3, and a chemical composition by weight percent of: Al_2O_3 = 93.1, SiO_2 = 5.6, Fe_2O_3 = 0.3, MgO = 0.3, TiO_2 = 0.1 and Na_2O = 0.1.

EXAMPLE 83

18% Tetradecylammonium iodide on titanium dioxide (Degussa) extrudate: 3.2 mm diameter extrudate having a surface area of 50 m^2/g and a chemical composition by weight percent of: TiO_2 = 99.5, Al_2O_3 = 0.3, and SiO_2 = 0.2.

The following examples illustrate the preparation of the catalyst compositions comprising an organic onium iodide and an organotin halide on a catalyst support material.

EXAMPLE 84

Triphenyl(hexyl)phosphonium iodide (0.75 g) and triphenyltin iodide (0.0151 g) were placed in a 50 mL flask and dissolved in 30 mL of anhydrous methanol at

30°C. To this solution was added 6.0 g of silica support. The silica support material was prepared by grinding silica pellets 4.76 mm (0.1875 inch) in diameter and classifying the ground material and using the portion which passed a 10 mesh sieve and was retained on a 20 mesh. The flask was placed on a rotary evaporator and agitated for 20 minutes with the flask in the bath at 50°C. Methanol was removed while the flask was in the 60°C bath using vacuum. The supported catalyst obtained (6.75 g) contained 11 weight percent triphenyl(hexyl)phosphonium iodide and 0.22 weight percent triphenyltin iodide.

EXAMPLE 85

A supported catalyst consisting of 11 weight percent tetradodecylammonium iodide and 0.22 weight percent tributyltin iodide on silica was prepared according to the general procedure described in Example 84.

EXAMPLE 86

A supported catalyst consisting of 11 weight percent tetradodecylammonium iodide and 1.1 weight percent triphenyltin iodide on silica was prepared according to the general procedure described in Example 84.

ISOMERIZATION OF EPOXYBUTENES

The supported catalysts described hereinabove were used to isomerize 3,4-epoxy-1-butene under steady state conditions in a 1 atmosphere, single-pass flow reactor system. The reactor tube was constructed of Pyrex glass and the catalyst charge (between 0.1 and 20.0 g) was held in place by means of a Pyrex glass frit. The geometries of the reactor and catalyst particles as well as bed depth were chosen to maintain and measure the

true kinetic and catalytic aspects of the reaction. Gas hourly space velocities (GHSV, mL gas fed per hour per mL catalyst) for all experiments fell within the range of about 30 up to 3000. A chromel/alumel thermocouple sheathed in stainless steel was embedded within the catalyst bed to measure the true reaction temperature.

The 3,4-epoxy-1-butene reactant was added by flowing helium through a liquid-vapor saturator containing the liquid reactant. The reactant was maintained at constant temperature by coupling the saturator to a refrigerated constant temperature circulator bath which was capable of maintaining the temperature of the liquid-vapor saturator at $\pm$1°C accuracy from -10°C to +120°C. The helium flow used to sweep the 3,4-epoxy-1-butene vapor from the saturator to the reactor inlet was maintained using a mass flow controller over the range 2-100 mL (standard temperature and pressure) per minute. The feed compositions fed to the reactor consisted of from 0.01 to 0.33 bar 3,4-epoxy-1-butene pressure (absolute) with the balance He to give a total pressure of approximately 1 to 1.5 bar at GHSV ranging from 30 to 3000. Reaction product analyses (as well as feed composition analyses) were made using an in-line gas sampling loop connected directly to the inlet of a Varian 3760 gas chromatograph. The reaction products were analyzed using a packed Chromosorb 101 column (2.44 meters by 2 mm interior diameter Pyrex glass capillary column) connected to a flame ionization detector.

Further, by means of a switching valve, it was possible to divert the feed stream through the in-line sample loop prior to passage over the catalyst. In this way, quantitative analysis of the feed stream and comparison to the corresponding data from the reactor effluent were possible, thereby providing very accurate

measurements of both conversion levels and product selectivities. Output from the flame ionization (FI) detector was integrated using a computing integrator which was programmed to give both absolute quantities and rates of formation. All reactor exit lines were heated and maintained at 125-140°C to prevent product condensation.

The GC analysis was performed using the following temperature programming schedule: an initial temperature of 100°C was held for 2 minutes, followed by a temperature program rate of +10°C per minute up to a final temperature of 200°C which was held for 7 minutes. The helium GC carrier rate was 20 mL per minute.

The catalyst and conditions employed and the results obtained in each of the isomerization experiments are set forth in Tables III and IV wherein Temp is the temperature in °C at which the reaction occurred, Press is the 3,4-epoxy-1-butene partial pressure in bars absolute of the gas fed, GHSV is defined above, Conv is the mole percent of moles 3,4-epoxy-1-butene converted to other compounds per moles of 3,4-epoxy-1-butene fed and Select is the mole percent of 3,4-epoxy-1-butene converted to 2,5-dihydrofuran based on the moles of 3,4-epoxy-1-butene converted.

EXAMPLE 87-114

These examples demonstrate the use of supported catalysts bearing only a quaternary onium iodide as the catalytic component. In Examples 87-96 and Examples 99-101 the catalysts were subjected to a pretreatment at elevated temperatures in an inert atmosphere for 30-60 minutes prior to starting the reactant feed. The pretreatments were performed at 140°C except in Examples 87 and 88 wherein temperatures of 160°C and 150°C, respectively, were used.

TABLE III

Example	Catalyst of Example	Temp	Press	GHSV	Conv	Select
87	4	130	0.03	240	6	21
88	1	140	0.03	240	48	68
89	5	140	0.03	240	49	68
90	5	160	0.03	240	52	63
91	6	140	0.03	240	28	78
92	7	140	0.03	240	17	83
93	8	130	0.03	240	41	94
94	8	125	0.03	540	9	91
95	8	130	0.03	540	13	94
96	8	140	0.03	540	26	95
97	9	130	0.03	240	58	90
98	10	130	0.03	240	78	94
99	11	130	0.03	240	79	69
100	12	130	0.03	300	73	40
101	13	130	0.03	300	67	61
102	14	130	0.03	300	5	31
103	14	170	0.03	300	82	58
104	15	130	0.03	300	2	3
105	15	167	0.03	300	55	65
106	16	130	0.03	300	49	94
107	16	130	0.09	300	32	91
108	17	130	0.03	300	97	90
109	17	130	0.03	600	93	90

TABLE III (cont.)

Example	Catalyst of Example	Temp	Press	GHSV	Conv	Select
110	18	130	0.03	240	72	80
111	19	120	0.03	300	1	19
112	19	130	0.03	300	2	31
113	19	140	0.03	300	2	41
114	20	160	0.03	300	0.4	54

EXAMPLES 115-250

These examples demonstrate the favorable effect of using a Lewis acid co-catalyst in conjunction with a quaternary onium iodide compound as evidenced by an increase in the conversion of the 3,4-epoxy-1-butene reactant and/or increasing the selectivity to the desired 2,5-dihydrofuran. In Examples 137-140 the catalysts were subjected to a pretreatment in flowing helium at 140°C for 30-60 minutes prior to starting the reactant feed.

TABLE IV

Example	Catalyst of Example	Temp	Press	GHSV	Conv	Select
115	2	125	0.17	75	64	91
116	2	125	0.17	190	38	94
117	2	130	0.17	75	83	93
118	2	130	0.17	190	50	93
119	2	130	0.17	750	14	92
120	21	120	0.09	300	0.2	36
121	21	130	0.09	300	0.3	45
122	21	140	0.09	300	0.6	67

TABLE IV (cont.)

Example	Catalyst of Example	Temp	Press	GHSV	Conv	Select
123	22	130	0.09	300	28	93
124	23	130	0.09	300	15	87
125	24	120	0.09	300	5	99
126	24	130	0.09	300	7	99
127	24	140	0.09	300	8	98
128	25	120	0.09	300	7	94
129	25	130	0.09	300	12	93
130	26	120	0.09	300	10	96
131	27	130	0.09	300	6	75
132	28	130	0.09	300	8	93
133	29	130	0.09	300	15	98
134	30	130	0.09	300	2	95
135	31	130	0.09	300	6	71
136	32	130	0.09	300	8	95
137	33	130	0.03	300	86	90
138	34	130	0.03	300	84	85
139	35	130	0.03	300	56	72
140	36	130	0.03	300	73	85
141	37	130	0.03	300	62	89
142	38	130	0.03	300	90	82
143	39	130	0.03	300	92	62
144	40	120	0.09	300	7	99
145	40	140	0.09	300	8	98
146	41	120	0.09	300	13	94

TABLE IV (cont.)

Example	Catalyst of Example	Temp	Press	GHSV	Conv	Select
147	42	120	0.09	300	10	96
148	42	130	0.09	300	15	65
149	43	130	0.09	300	12	97
150	44	130	0.09	300	16	95
151	44	130	0.13	300	15	95
152	45	120	0.09	60	79	98
153	45	120	0.09	240	35	95
154	46	120	0.09	300	30	97
155	46	130	0.09	300	32	96
156	46	140	0.09	300	37	94
157	47	120	0.09	300	55	85
158	48	120	0.09	300	7	93
159	48	130	0.09	300	11	94
160	49	120	0.09	300	18	97
161	49	130	0.09	300	23	96
162	50	120	0.09	300	54	85
163	51	125	0.03	300	92	80
164	51	135	0.03	300	93	75
165	51	150	0.03	300	96	68
166	52	140	0.09	300	10	85
167	52	150	0.09	300	16	85
168	52	160	0.09	300	23	83
169	53	140	0.09	300	6	91
170	53	150	0.09	300	12	88

TABLE IV (cont.)

Example	Catalyst of Example	Temp	Press	GHSV	Conv	Select
171	53	160	0.09	300	26	86
172	53	170	0.09	300	44	80
173	53	180	0.09	300	56	75
174	54	131	0.09	300	18	80
175	54	141	0.09	300	27	82
176	55	130	0.09	300	9	88
177	55	140	0.09	300	11	90
178	55	160	0.09	300	13	82
179	56	120	0.09	300	10	75
180	57	120	0.09	300	10	88
181	57	130	0.09	300	13	87
182	57	140	0.09	300	18	87
183	57	160	0.09	300	34	88
184	3	130	0.09	300	17	85
185	3	140	0.09	300	27	86
186	3	150	0.09	300	42	88
187	3	160	0.09	300	50	86
188	3	170	0.09	300	57	85
189	58	120	0.09	300	18	93
190	58	130	0.09	300	26	94
191	58	140	0.09	300	30	94
192	58	150	0.09	300	43	93
193	59	130	0.09	60	38	89
194	59	140	0.09	60	84	89

TABLE IV (cont.)

Example	Catalyst of Example	Temp	Press	GHSV	Conv	Select
195	59	140	0.09	120	60	91
196	60	130	0.09	300	35	95
197	60	160	0.09	300	55	92
198	61	140	0.09	300	26	90
199	61	160	0.09	300	41	90
200	62	140	0.09	300	30	92
201	62	160	0.09	300	45	90
202	63	130	0.09	300	37	94
203	64	130	0.09	300	27	90
204	65	140	0.09	300	24	92
205	66	140	0.09	300	26	79
206	67	130	0.09	300	9	61
207	67	170	0.09	300	15	75
208	68	140	0.09	300	11	62
209	69	160	0.09	300	12	71
210	69	180	0.09	300	68	95
211	70	160	0.09	300	64	93
212	71	140	0.09	300	34	95
213	71	160	0.09	300	50	94
214	72	140	0.09	300	12	80
215	72	160	0.09	300	28	85
216	73	125	0.09	300	21	95
217	73	130	0.09	300	37	94
218	74	130	0.03	540	5	81

TABLE IV (cont.)

Example	Catalyst of Example	Temp	Press	GHSV	Conv	Select
219	74	150	0.03	540	20	80
220	75	130	0.09	540	3	80
221	75	130	0.03	540	7	80
222	75	160	0.03	540	29	73
223	76	140	0.03	240	15	50
224	76	160	0.03	240	50	49
225	77	140	0.03	540	10	35
226	77	160	0.03	540	15	41
227	77	170	0.03	240	59	61
228	78	125	0.17	150	65	51
229	79	125	0.09	75	55	86
230	79	125	0.09	190	29	84
231	80	125	0.17	90	68	93
232	80	125	0.17	250	34	92
233	80	125	0.17	500	16	93
234	80	125	0.17	1000	8	93
235	80	130	0.17	1000	18	93
236	81	125	0.17	250	8	78
237	81	130	0.17	250	13	85
238	82	130	0.03	60	11	64
239	82	135	0.03	60	25	77
240	82	140	0.03	60	48	83
241	83	130	0.03	160	32	63
242	83	135	0.03	160	36	64

TABLE IV (cont.)

Example	Catalyst of Example	Temp	Press	GHSV	Conv	Select
243	83	140	0.03	160	53	67
244	84	150	0.09	600	8	81
245	84	160	0.09	600	10	78
246	85	130	0.09	300	14	98
247	85	130	0.09	600	8	98
248	85	140	0.09	300	22	98
249	86	130	0.09	300	13	99
250	86	140	0.09	300	26	98

EXAMPLE 251-255

Using the catalyst of Example 2 and the isomerization procedure described hereinabove, two other γ,δ-epoxyalkenes and a γ,δ-epoxycycloalkene were isomerized to 2,5-dihydrofuran compounds. The reactants used and the desired dihydrofuran product obtained were:

Example	Reactant	Dihydrofuran Product
251,252	2-Methyl-3,4-epoxy-1-butene	3-methyl-2,5-dihydrofuran
253,254	2,3-Dimethyl-3,4-epoxy-1-butene	3,4-Dimethyl-2,5-didihydrofuran
255	3,4-epoxycyclooctene	9-oxa-bicyclo[4.2.1]-non-7-ene

The results obtained are set forth in Table V wherein Conv is the mole percent of moles of reactant converted to other products per moles of reactant fed and Select is the percent moles of reactant converted to the desired 2,5-dihydrofuran product based on the moles of reactant converted.

TABLE V

Example	Temp	Press	GHSV	Conv	Select
251	126	0.04	60	65	66
252	126	0.04	120	46	67
253	127	0.03	60	51	81
254	127	0.05	60	46	81
255	130	0.01	60	61	90

EXAMPLE 256-300

These examples demonstrate the use of the unsupported catalyst systems of this invention in the isomerization of 3,4-epoxy-1-butene to 2,5-dihydrofuran according to the general procedure described relative to the preceding isomerization examples. Because the catalyst can exist in a substantially molten state if the process is operated above the melting point of the quaternary onium iodide salt, the reactor was operated in an upward flow mode whereby the gaseous feed entered below the catalyst bed and passed through a gas dispersion frit upon which the unsupported catalyst system was supported to maintain the catalyst in the proper position in the reactor. Alternatively, the catalyst was maintained in a vessel with a closed bottom into which the feed gas was added below the level of the substantially molten catyalyst by means of a gas dispersion apparatus. In both reactor configurations,. the gaseous reactor effluent comprising unreacted feed and product exited the top of the reactor into the downstream assembly described hereinabove.

In the examples utilizing an unsupported catalyst system, the catalyst components were heated in an inert gas flow, typically 100 mL (STP) per minute of helium, until both catalyst components existed in a molten state. At this point, a partial pressure of 3,4-epoxy-1-butene was introduced into the carrier gas stream and

the catalytic reaction was initiated. Typical molar concentrations of 3,4-epoxy-1-butene in the carrier gas varied from 3 to 25%, with 9 to 10 % being the most commonly used feed concentration.

The unsupported catalyst systems listed below were prepared by physically and intimately mixing the components while in the solid state and were used in Examples 256-326. For catalyst components which were potentially air sensitive, care was taken to prevent contact with air while loading into the catalytic reactor.

(i) Tetradodecylammonium iodide (1.20 g) and zinc iodide (24.0 mg)

(ii) Triphenyl(hexyl)phosphonium iodide (1.00 g) and zinc iodide (5.0 mg)

(iii) Triphenyl(hexyl)phosphonium iodide (0.50 g), tris-(2,4,6-trimethylphenyl)(hexyl)phosphonium iodide (0.50 g) and zinc iodide (5.0 mg)

(iv) Tetradodecylammonium iodide (20.0 g) and tributyltin iodide (0.52 g)

(v) Tetradodecylammonium iodide (10.0 g) and dibutyltin diiodide (0.30 g)

(vi) Tetradodecylammonium iodide (10.0 g) and triphenyltin iodide (0.29 g)

(vii) Triphenyl(hexyl)phosphonium iodide (10.0 g) and tributyltin iodide (0.07 g)

(viii) Triphenyl(hexyl)phosphonium iodide (10.0 g) and dibutyltin diiodide (0.21 g)

(ix) Tetradodecylammonium iodide (10.0 g) and trioctyltin iodide (0.36 g)

(x) Triphenyl(hexyl)phosphonium iodide (10.0 g) and trioctyltin iodide (0.25 g)

(xi) Tetrabutylarsonium iodide (8.00 g) and trioctyltin iodide (0.54 g)

(xii) Tetraoctylarsonium iodide (8.00 g) and trioctyltin iodide (0.38 g)

(xiii) Triphenyl(hexyl)phosphonium iodide (11.6 g) and triphenyltin iodide (0.24 g)

(xiv) Triphenyl(hexyl)phosphonium iodide (11.6 g) and triphenyltin iodide (0.59 g)

(xv) Triphenyl(hexyl)phosphonium iodide (11.6 g) and triphenyltin iodide (2.33 g)

(xvi) Triphenyl(hexyl)phosphonium iodide (6.0 g) and triphenyltin iodide (6.0 g)

(xvii) Triphenyl(hexyl)phosphonium iodide (2.0 g) and triphenyltin iodide (10.0 g)

(xviii) Triphenyl(hexyl)phosphonium iodide (0.60 g) and triphenyltin iodide (11.4 g)

(xix) Triphenyl(hexyl)phosphonium iodide (0.10 g) and triphenyltin iodide (10.0 g)

(xx) Triphenyl(hexyl)phosphonium iodide (2.0 g) and tricyclohexyltin iodide (10.4 g)

(xxi) Triphenyl(hexyl)phosphonium iodide (2.0 g) and tribenzyltin iodide (10.9 g)

The ratio of zinc iodide to quaternary onium iodide compound(s) in each of catalyst systems (i) and (ii) is the same as the analogous ratio for the supported catalysts of Examples 22 and 59, respectively.

TABLE VI

Example	Catalyst System	Temp	Press	GHSV	Conv	Select
256	(i)	110	0.09	500	17	77
257	(i)	120	0.09	500	44	90
258	(i)	130	0.09	500	60	93
259	(i)	140	0.09	500	88	94
260	(ii)	140	0.09	1200	25	91

TABLE VI (cont.)

Example	Catalyst System	Temp	Press	GHSV	Conv	Select
261	(ii)	150	0.09	1200	30	90
262	(ii)	160	0.09	1200	36	87
263	(ii)	160	0.09	2400	18	91
264	(iii)	130	0.09	600	17	82
265	(iii)	140	0.09	600	43	92
266	(iii)	160	0.09	600	59	86
267	(iii)	180	0.09	600	72	80
268	(iv)	130	0.09	120	95	95
269	(iv)	130	0.09	300	75	98
270	(iv)	130	0.09	600	60	99
271	(v)	130	0.09	240	96	96
272	(v)	130	0.09	600	83	97
273	(v)	130	0.09	1200	34	96
274	(vi)	130	0.09	240	98	98
275	(vi)	130	0.09	600	78	99
276	(vi)	130	0.09	1200	55	99
277	(vi)	140	0.09	240	98	95
278	(vi)	140	0.09	600	89	98
279	(vi)	140	0.09	1200	75	98
280	(vii)	140	0.09	120	68	81
281	(vii)	140	0.09	600	24	88
282	(viii)	130	0.09	240	71	93
283	(viii)	130	0.09	600	37	94

TABLE VI (cont.)

Example	Catalyst System	Temp	Press	GHSV	Conv	Select
284	(viii)	130	0.09	1200	21	94
285	(viii)	140	0.09	240	80	90
286	(viii)	140	0.09	1200	22	92
287	(ix)	130	0.09	600	40	99
288	(ix)	130	0.09	1200	20	98
289	(ix)	140	0.09	600	68	98
290	(ix)	140	0.09	1200	46	99
291	(ix)	140	0.09	240	89	96
292	(x)	130	0.09	300	53	90
293	(x)	130	0.09	600	30	92
294	(x)	130	0.09	1200	14	94
295	(x)	140	0.09	600	43	91
296	(x)	140	0.09	1200	20	93
297	(xi)	130	0.09	300	80	97
298	(xi)	130	0.09	600	65	98
299	(xii)	130	0.09	300	28	98
300	(xii)	130	0.09	600	18	98
301	(xiii)	130	0.10	300	38	93
302	(xiii)	130	0.10	600	22	94
303	(xiv)	130	0.10	300	80	93
304	(xiv)	130	0.10	600	67	93
305	(xiv)	140	0.10	300	88	92
306	(xiv)	140	0.10	600	74	92
307	(xv)	130	0.10	300	87	95

TABLE VI (cont.)

Example	Catalyst System	Temp	Press	GHSV	Conv	Select
308	(xv)	130	0.10	600	69	95
309	(xv)	140	0.10	300	91	95
310	(xv)	140	0.10	600	71	94
311	(xv)	140	0.25	600	64	95
312	(xvi)	130	0.10	300	100	97
313	(xvi)	130	0.10	600	99	97
314	(xvii)	130	0.10	300	100	98
315	(xvii)	130	0.10	600	100	98
316	(xvii)	130	0.25	300	99	97
317	(xvii)	130	0.25	1000	91	97
318	(xviii)	130	0.10	300	80	97
319	(xviii)	130	0.10	600	67	97
320	(xviii)	130	0.25	600	62	97
321	(xix)	130	0.10	300	68	96
322	(xix)	130	0.10	600	56	96
323	(xx)	130	0.10	300	14	96
324	(xx)	130	0.10	600	9	96
325	(xxi)	130	0.10	300	70	85
326	(xxi)	130	0.10	600	54	81

EXAMPLES 327-331

The following examples illustrate the isomerization of 3,4-epoxy-1-butene to 2,5-dihydrofuran using the catalyst solutions described hereinabove. The gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890A gas chromatograph with a DB5-30W

capillary column; temperature program 35°C (4.5 minutes), 20°C/minute to 260°C (hold 6 minutes). 1H NMR analyses were performed on a Varian Gemini 300 spectrometer (300 MHz) using CDCl3 as solvent and tetramethylsilane as internal standard.

EXAMPLE 327

To a nitrogen-purged, 500-mL, four-neck flask equipped with a thermometer, addition funnel, condenser, magnetic stirrer, and heating mantle was charged 170.57 g of p-xylene, 21.62 g (0.05185 moles) of tributyltin iodide, and 39.76 g (0.07394 moles) of tetraheptyl-ammonium iodide. The mixture was heated to 109°C and 34.04 g (0.4857 moles) of 3,4-epoxy-1-butene was added dropwise over 15 minutes at 109-117°C. Thirty minutes after the addition the reaction was complete as shown by GC. After cooling, the condenser was replaced with a fractional distillation apparatus and the mixture distilled. A 36.81 g fraction boiling at 62-134°C was collected which had the following GC assay: 0.11% furan, 0.32% 3,4-epoxy-1-butene, 1.32% crotonaldehyde, 88.86% 2.5-dihydrofuran, and 9.39% p-xylene. The yield of 2,5-dihydrofuran was 96.1%.

EXAMPLE 328

To a nitrogen-purged, 500-mL, four-neck flask equipped with a thermometer, addition funnel, condenser, magnetic stirrer, and heating mantle was charged 213.58 g of p-xylene, 28.81 g (0.06910 moles) of tributyltin iodide, and 32.27 g (0.05785 moles) of dodecyltri-phenylphosphonium iodide. The mixture was heated to 110°C and 34.66 g (0.4945 moles) of 3,4-epoxy-1-butene was added dropwise over 18 minutes at 110-119°C. Thirty-five minutes after the addition the reaction was complete as shown by GC. After cooling, the condenser was replaced with a fractional distillation apparatus and the mixture distilled. A 35.22 g fraction boiling

at 59-105°C was collected which had the following GC assay: 0.2% 3,4-epoxy-1-butene, 0.4% crotonaldehyde, 87.2% 2.5-dihydrofuran, and 8.6% p-xylene. The yield of 2,5-dihydrofuran was 87.2%.

EXAMPLE 329

The process of this invention may be operated continuously as shown by this example. The continuous reaction system consists of a heated, plug-flow reactor (465 mL, U-tube of Pyrex glass) into which the 3,4-epoxy-1-butene and recirculated catalyst solution is pumped. After a residence time in the reactor at the rearrangement temperature the homogeneous reaction stream feeds into the center of a fractional distillation column. The volatile materials are condensed with a water-cooled condenser and collected in the receiver. The stripped catalyst solution from the distillation pot is returned to the reactor along with fresh 3,4-epoxy-1-butene. This system was charged with a solution of 41.7 g (0.100 mole) of tributyltin iodide, 47.4 g (0.123 mole) of tetrabutylphosphonium iodide, and 525 mL of o-dichlorobenzene. The reactor tube was heated to 130°C and the distillation pot was heated to reflux (pot temperature 205-213°C). The catalyst solution was recycled at a rate of 30.2 mL/minute and 3,4-epoxy-1-butene was fed at a rate of 1.2 g/minute giving a total flow rate through the reactor of 32 mL/minute for a reactor residence time of 15 minutes. A total of 400.2 g (5.710 mole) of 3,4-epoxy-1-butene was fed to the system and 371.5 g of distillate (bp 66°C) was obtained. The distillate had a GC analysis of 92.7% 2,5-dihydrofuran, 2.95% of 3,4-epoxy-1-butene, and 0.48% of crotonaldehyde. The assay yield of 2,5-dihydrofuran was 86.1%.

EXAMPLE 330

To a nitrogen-purged, 100-mL, three-neck flask equipped with a thermometer, condenser, magnetic stirrer, and heating mantle was charged 50 mL of p-xylene, 4.35 g (0.0104 moles) of tributyltin iodide, 6.49 g (0.0121 moles) of tetraheptylammonium iodide and 10.28 g (0.1222 moles) of 3,4-epoxy-3-methyl-1-butene. The mixture was heated to reflux (119°C). After two hours the reaction was complete as judged by GC. After cooling, the condenser was replaced with a distillation head and the mixture distilled. A 17.26 g fraction boiling at 82-120°C was collected which had the following NMR weight-percent assay: 70.3% p-xylene, 24.3% 3-methyl-2,5-dihydrofuran, and 5.5% 2-methyl-2-butenal. The yield of 3-methyl-2,5-dihydrofuran was 40.8% and the yield of 2-methyl-2-butenal was 9.2%.

EXAMPLE 331

To a nitrogen-purged, 25-mL, three-neck flask equipped with a thermometer, condenser, magnetic stirrer, and heating mantle was charged 12.5 mL of p-xylene, 0.94 g (0.023 moles) of tributyltin iodide, 1.69 g (0.00314 moles) of tetraheptylammonium iodide and 3.10 g (0.0235 moles) of 3,4-epoxycyclooctene (94.1%). The mixture was heated to reflux (125°C). After five hours the reaction was complete as shown by GC. After cooling, the tetraheptylammonium iodide solids were filtered then the filtrate was filtered through a small pad of silica gel and rinsed with p-xylene. The solvent was distilled off at atmospheric pressure leaving 2.43 g of an oil which had the following NMR weight-percent assay: 42.8% 9-oxabicyclo[4.2.1]non-7-ene and 57.2% p-xylene. The yield of 9-oxabicyclo[4.2.1]non-7-ene was 35.7%.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Process for the isomerization of a γ,δ-epoxyalkene or a γ,δ-epoxycycloalkene to the corresponding 2,5-dihydrofuran which comprises contacting a γ,δ-epoxyalkene or a γ,δ-epoxycycloalkene in the liquid phase with a solution of a catalytic amount of an organotin (IV) compound or organoantimony compound in an inert, organic solvent.

2. Process according to Claim 1 wherein the solution comprises 1 to 50 weight percent of an organometallic compound having the formula

$(R^7)_n$–Sn–$Hal_{(4-n)}$ and $(R^7)_4$–Sb–Hal

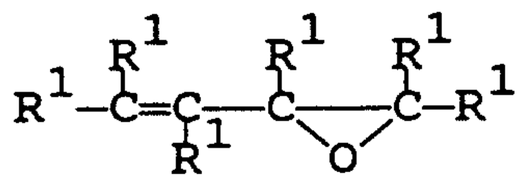
wherein

each R^7 independently is selected from alkyl or substituted alkyl moieties having up to 20 carbon atoms, cycloalkyl or substituted cycloalkyl having 5 to 20 carbon atoms, aryl or substituted aryl having 6 to 20 carbon atoms;

Hal is bromo or iodo; and

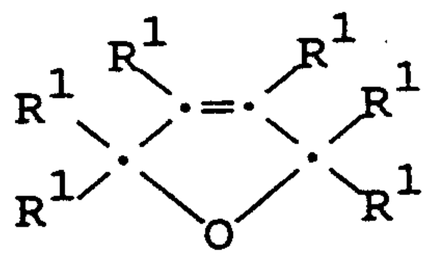
n is 1, 2, 3 or 4; in an inert organic solvent.

3. Process according to Claim 1 for the isomerization of a γ,δ-epoxyalkene or a γ,δ-epoxycycloalkene having the formula



(I)

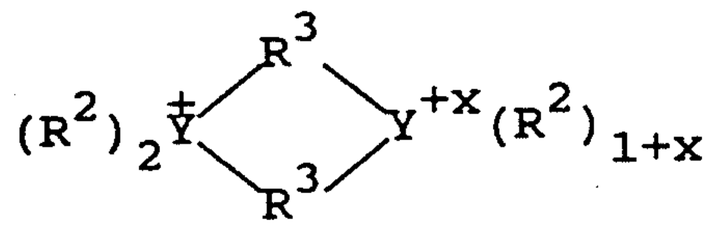
to the corresponding 2,5-dihydrofuran having the formula



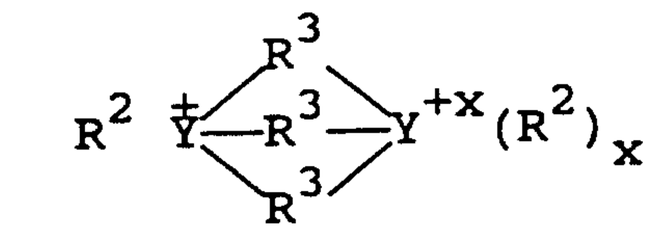
wherein each R^1 is hydrogen or up to 2 R^1 substituents each may be alkyl of up to 8 carbon or collectively straight or branched chain alkylene of up to 8 carbon atoms, which comprises contacting the γ,δ-epoxyalkene or a γ,δ-epoxycycloalkene in the liquid phase at a temperature of 50 to 200°C with a solution of a catalytic amount of a catalyst comprising (1) at least one quaternary organic onium iodide compound containing at least 6 carbon atoms and the formula

$$(R^2)_4Y^+ \quad I^-,$$

$$I^- \quad (R^2)_3Y^+-R^3-Y^{+x}(R^2)_{2+x} \quad I_x^-,$$



$$I^- \quad (R^2)_2 \overset{+}{Y} \quad Y^{+x}(R^2)_{1+x} \quad I_x^-, \text{ or}$$



$$I^- \quad R^2 \overset{+}{Y}-R^3-Y^{+x}(R^2)_x \quad I_x^-,$$

wherein

each R^2 is independently selected from hydrogen, alkyl or substituted alkyl moieties having up to 20 carbon atoms, cycloalkyl or substituted cycloalkyl having 5 to 20 carbon atoms, aryl or substituted aryl having 6 to 20 carbon atoms, ferrocenyl; or when Y is P, each R^2 also may be selected from alkoxy of up to 20 carbon atoms, cycloalkoxy of 5 to 20 carbon atoms, aryloxy of 6 to 10 carbon atoms or halogen;

two or three R^2 substituents collectively may represent joined hydrocarbylene groups which form a mono- or poly-cyclic ring with the Y atom to which they are bonded;

each R^3 is independently selected from hydro-carbylene moieties or substituted hydrocarbylene moieties;

x is 0 or 1, and

Y is N, P or As;

(2) an organometallic compound having the formula

$(R^7)_n$—Sn—$Hal_{(4-n)}$ and $(R^7)_4$—Sb—Hal

wherein

each R^7 independently is selected from alkyl or substituted alkyl moieties having up to 20 carbon atoms, cycloalkyl or substituted cycloalkyl having 5 to 20 carbon atoms, aryl or substituted aryl having 6 to 20 carbon atoms;

Hal is bromo or iodo; and

n is 1, 2, 3 or 4; in an inert organic solvent.

4. Process according to Claim 3 wherein the process is carried out at a temperature of 50 to 200°C in a catalyst solution comprising (1) 1 to 70 weight percent, calculated as weight iodide, of at least one quaternary ammonium or phosphonium iodide: (2) 1 to 50 weight percent of an organometallic compound containing 3 to 24 carbon atoms and having the formula

$(R^7)_n$—Sn—$I_{(4-n)}$ and $(R^7)_4$—Sb—I

wherein

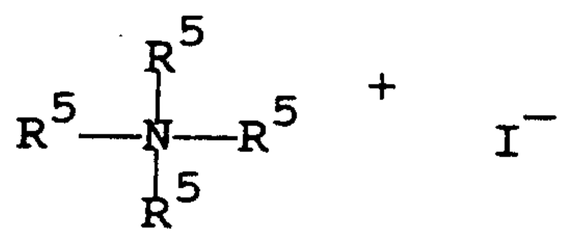
each R^7 substituent independently is selected from alkyl of up to 8 carbon atoms, benzyl, phenyl or phenyl substituted with up to 3 substituents selected from lower alkyl, lower alkoxy or halogen; and

n is 2 or 3; and

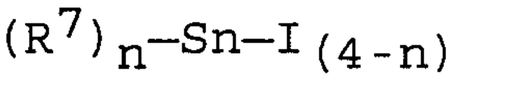
(3) an inert organic solvent, wherein the concentrations of components (1) and (2) are based on the total weight of (1), (2) and (3).

5. Process according to Claim 4 for the isomerization of 3,4-epoxy-1-butene to 2,5-dihydrofuran which comprises contacting 3,4-epoxy-1-butene in the liquid phase at a temperature of 100 to 150°C with a catalyst solution

comprising (1) 1 to 25 weight percent, calculated as weight iodide, of one or more quaternary ammonium iodides having the formula



wherein each R^5 substituent is independently selected from alkyl of up to 20 carbon atoms and the quaternary ammonium iodide contains 16 to 60 carbon atoms, (2) 1 to 25 weight percent of an organotin (IV) iodide containing 3 to 24 carbon atoms and having the formula



wherein

each R^7 substituent independently is selected from alkyl of up to 8 carbon atoms, benzyl, phenyl or phenyl substituted with up to 3 substituents selected from lower alkyl, lower alkoxy or halogen; and

n is 2 or 3; and

(3) an inert organic solvent.

6. Process according to Claim 5 wherein the inert organic solvent is selected from toluene, xylene, chlorobenzene, dichlorobenzene, pseudocumene or mesitylene.