

CHIRAL EPOXYALCOHOL RECOVERY IN ASYMMETRIC EPOXIDATION PROCESS ✓BACKGROUND OF THE INVENTION

The present invention is directed to an improvement in the process of asymmetric epoxidation of allylic alcohols. More specifically, the invention is directed to an improved method of recovery of the epoxidized product.

Epoxides are known to copolymerize with carbon dioxide in the presence of metal containing catalysts such as diethylzinc/additives, zinc carboxylates, and metal porphyrin complexes.

The resulting copolymers have alternating epoxide and carbon dioxide groups, and are polycarbonates. These copolymers have found uses in many areas, such as ceramic binders, evaporative pattern casting and adhesives. Epoxides shown to proceed readily in this reaction are ethylene oxide, propylene oxide, cyclohexene oxide, cis-2-butene oxide, and others.

U.S. Patent 3,374,153 teaches that the glycidol made from allyl alcohol epoxidation using organic hydroperoxide as oxidant and vanadium naphthenate as catalyst is recovered by azeotropic distillation employing a hydrocarbon capable of forming a low-boiling azeotrope with glycidol. The method requires that the excess hydroperoxide be destroyed by the addition of expensive trialkyl phosphites. Direct distillation of the product containing the phosphites involves certain hazards which are best avoided.

BRIEF SUMMARY OF THE INVENTION

It has now been found that the addition of phosphite and the distillation step can be eliminated by direct extraction of the water-soluble glycidol with water after the epoxidation reaction, thereby providing an economical means for separating the

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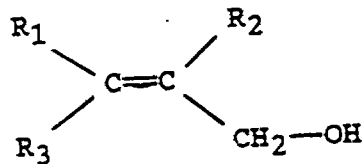


epoxyalcohol from the catalysts and the hydroperoxide oxidate which remain in the organic phase.

DETAILED DESCRIPTION OF THE INVENTION

The process of this invention comprises (a) reacting a mixture of an allylic alcohol, an organic hydroperoxide, and a metal catalyst in an organic solvent, (b) extracting the reaction mixture with water to separate the glycidol product from the reactants and catalyst which are insoluble in the water, (c) removing the water from the extractant, and (d) distilling off the glycidol.

The allylic alcohols suitable for use in the epoxidation reaction may have the following general formula:



where each of R_1 , R_2 , and R_3 , which may be the same or different, is selected from H, C_1-C_{10} linear or branched alkyl, phenyl, and substituted phenyl.

The organic hydroperoxides useful in the invention may be aliphatic hydroperoxides wherein the aliphatic groups have from one to 20 carbon atoms. Illustrative hydroperoxides are ethylbenzene hydroperoxide, cumene hydroperoxide, tert-butylhydroperoxide, and trityl hydroperoxide. The only criteria for the hydroperoxide is that it must be essentially insoluble in water.

The metal catalysts useful in the invention include various salts of vanadium, titanium, tantalum, zirconium, hafnium, niobium and molybdenum in conjunction with a chiral carbinol, such as diisopropyl tartrate. Particularly useful salts are the naphthenates, the isopropoxides, and other



alkoxides.

The useful organic solvents, whose only limitation is the need for water-insolubility, may include hexane, toluene, tetrahydrofuran, methylene chloride, methyl acetate, and mixtures of these. The solvent also should not react with the reactants in the medium to interfere with the transfer of the oxygen atom from the oxidant to the allylic unsaturation.

The epoxidation reaction temperature may vary from -100°C to 20°C and the times may vary from a few minutes to a few days.

The extraction of the glycidol product from the organic mixture is effected with water. Several consecutive extractions may be run to recover a maximum amount of the glycidol product.

After separating the aqueous extraction layers from the water-insoluble organic layers, the water extracts are combined and the water removed by flash distillation under suitable vacuum at about 50°C. The remaining glycidol product can then be fractionally distilled under vacuum to isolate the pure product.

The following examples are meant to further illustrate, but not to limit the invention.

EXAMPLE I

Epoxidation of allyl alcohol using titanium isopropoxide/L(+)-diisopropyl tartrate catalyst and cumene hydroperoxide oxidate was carried out in methylene chloride in the presence of molecular sieves at -15°C for 16 hours to give 65% yield of glycidol. The molecular sieves were filtered off and 400g of this solution containing 22g of glycidol was extracted with 100g of water after stirring at 190 rpm for 5 minutes at 0°C. There was obtained 10.8g of glycidol in this first extraction. Extraction of the organic layer with an



additional 100g of water yielded 5.8g more of glycidol. Glycidol recovery in two extractions was 75% of the total present in the organic mixture. The two aqueous fractions were combined and the active oxygen analyzed to be 320 ppm, indicating low cumene hydroperoxide extraction. Subsequent water removal and fractional distillation gave 99% pure glycidol. The enantiomeric excess of the (S)-glycidol made was determined to be 88% by the Mosher ester/ ^{13}C NMR method.

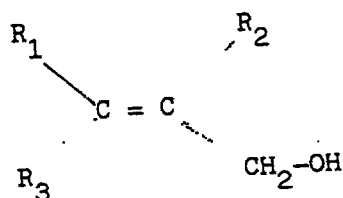
EXAMPLE II

10 To show that the extraction can be applied to other water-soluble epoxyalcohols, the following experiment was tried. Epoxidation of methallyl alcohol using titanium isopropoxide/L(+)-diisopropyl tartrate catalyst and cumene hydroperoxide oxidate was carried out in methylene chloride in the presence of molecular sieves at -15°C for 16 hours to give 87% yield of methyl glycidol. The molecular sieves were filtered off and 200g of this solution containing 19.1g of methyl glycidol was diluted with 204g of methylene chloride and extracted with 100g of water. There was obtained 6.2g of methyl glycidol in 20 this first extraction. Extraction of the organic layer with an additional 100g of water yielded 4.1g more of methyl glycidol. Methyl glycidol recovery in two extractions was 54% of the total present in the organic mixture. The two aqueous fractions were combined and the active oxygen analyzed to be 247 ppm, indicating low cumene hydroperoxide extraction. Subsequent water removal and fractional distillation gave 99% pure methyl glycidol. The enantiomeric excess of the (S)-methyl glycidol made was determined to be 89% by the Mosher ester/ ^{13}C NMR method.

CLAIMS

1. The process comprising (a) reacting a mixture of an allylic alcohol, an organic hydroperoxide, and a metal catalyst in an organic solvent, (b) extracting the reaction mixture with water to separate the glycidol product from the reactants and catalyst which are insoluble in the water, (c) removing the water from the extractant, and (d) distilling off the glycidol.

2. The process of claim 1 wherein the allylic alcohol has the following general formula:



where each of R_1 , R_2 , and R_3 , which may be the same or different, is selected from H, C_1-C_{10} linear or branched alkyl, phenyl, and substituted phenyl.

3. The process of claim 2 wherein the allylic alcohol is selected from allyl alcohol, cinnamyl alcohol, and methallyl alcohol.

4. The process of claim 1, claim 2 or claim 3 wherein the organic hydroperoxide is selected from aliphatic hydroperoxides wherein the aliphatic group has from one to 20 carbon atoms and the hydroperoxide is essentially insoluble in water.

5. The process of claim 4 wherein the hydroperoxide is selected from ethylbenzene hydroperoxide, cumene hydroperoxide, tert-butylhydroperoxide, and trityl hydroperoxide.

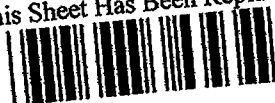


6. The process of any one of claims 1 to 5 wherein the metal catalyst comprises a naphthenate or alkoxide of a metal selected from the group consisting of vanadium, titanium, tantalum, zirconium, hafnium, niobium, and molybdenum used in conjunction with a chiral carbinol.

7. The process of claim 6 wherein the chiral carbinol is a dialkyl tartrate.

8. The process of any one of claims 1 to 7 wherein the organic solvent is selected from the group consisting of hexane, toluene, tetrahydrofuran, methylene chloride, methyl acetate, and mixtures of these.

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