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PROCESS FOR PREPARING 1,3-ALKANEDIOLS
AND 3-HYDROXYALDEHYDES

This invention relates to a process for preparing 1,3-alkanediols and 3-hydroxyaldehydes by hydroformylating an oxirane (1,2-epoxide). In particular, the invention relates to a cobalt-catalysed process for preparing 1,3-propanediol by hydroformylating ethylene oxide and hydrogenating the hydroformylation product.

The hydroformylation of oxiranes to produce 3-hydroxyaldehydes has been discussed in "New Syntheses with Carbon Monoxide" edited by J. Falbe (1980), pp.131-132. The reaction is catalysed with a cobalt-based catalyst, or a phosphine-modified cobalt-based catalyst. The hydroformylation product, be it the 3-hydroxyaldehyde or the cyclic hemiacetal that is its dimer, may be converted into a 1,3-alkanediol by hydrogenation. This process is of particular importance to the preparation of 1,3-propanediol (PDO), an intermediate in the production of polyesters for fibres and films, that may be prepared by hydrogenating 3-hydroxypropanal (HPA). According to this textbook attempts have been made to improve the hydroformylation reaction by adding small amounts of alcohols, ethers, ketones and esters. According to US-A-3 687 981 also halogen containing inorganic compounds, e.g., inorganic salts and acids such as hydrochloric acid may be used as hydroformylation promoter.

It would be desirable to produce the hydroformylation product at improved rate. It is therefore an object of the invention to provide a process for preparing 1,3-alkanediols and 3-hydroxyaldehydes at improved rate. It is a further object of the invention to provide a process in which essentially all of the catalyst can be conveniently recycled.

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Accordingly, the invention provides a process for preparing 1,3-alkanediols and 3-hydroxyaldehydes by hydroformylating an oxirane with carbon monoxide and hydrogen in the presence of a cobalt-based catalyst and a promoter that is a lipophilic quarternary salt of a Group V element.

The oxirane comprises an organic compound, two carbon atoms of which are connected by an oxy linkage as well as by a carbon-carbon single bond. In general terms, the oxiranes comprise hydrocarbyl-epoxides, having at least 2, preferably up to 30, more preferably up to 20, most preferably up to 10 carbon atoms. The hydrocarbyl group may be aryl, alkyl, alkenyl, aralkyl, cycloalkyl, or even alkylene; straight chain or branched chain. Suitable examples of oxiranes include 1,2-epoxy(cyclo)alkanes, such as ethylene oxide, propylene oxide, 1,2-epoxyoctane, 1,2-epoxycyclohexane, 1,2-epoxy-2,4,4-trimethylhexane and the like, and 1,2-epoxyalkenes such as 1,2-epoxy-4-pentene and the like. Ethylene oxide and propylene oxide are preferred. In view of the demand for PDO, ethylene oxide (EO) is the oxirane most preferably used in the process of the invention.

The hydroformylation reaction is preferably carried out in a liquid solvent inert to the reactants and products, i.e., that is not consumed during the reaction. Upon completion of the reaction, the liquid solvent facilitates the separation of the hydroformylation product. The separation may be carried out by allowing the product to form a separate layer, as is disclosed in US-A-3 687 981. However, as discussed below, it is preferred to carry out the separation by extraction with an aqueous liquid. In general, ideal solvents for the hydroformylation process will (a) exhibit low to moderate polarity such that the 3-hydroxyaldehyde will be dissolved to a concentration of at least about 5 wt% under hydroformylation conditions, while significant

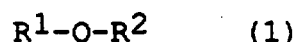
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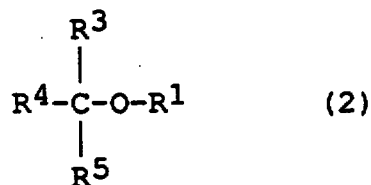
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solvent will remain as a separate phase upon extraction with the aqueous liquid, (b) dissolve carbon monoxide, and (c) be essentially non-water-miscible. By "essentially non-water-miscible" is meant that the solvent has a solubility in water at 25 °C of less than 25 wt% so as to form a separate hydrocarbon-rich phase upon extraction of the 3-hydroxyaldehyde from the hydroformylation reaction mixture. Preferably, this solubility is less than 10 wt%, most preferably less than 5 wt%. The solubility of carbon monoxide in the selected solvent will generally be greater than 0.15 v/v (1 atm, 25 °C), preferably greater than 0.25 v/v, expressed in terms of Ostwald coefficients.

The preferred class of solvents are alcohols and ethers which can be described according to the formula (1)



in which R^1 is hydrogen or a linear, branched, cyclic or aromatic C_{1-20} hydrocarbyl or mono- or polyalkylene oxide and R^2 is a linear, branched, cyclic or aromatic C_{1-20} hydrocarbyl, alkoxy or mono- or polyalkylene oxide, or R^1 , R^2 and O together form a cyclic ether. The most preferred hydroformylation solvents can be described by the formula (2)



in which R^1 is hydrogen or C_{1-8} hydrocarbyl and R^3 , R^4 and R^5 are independently selected from C_{1-8} hydrocarbyl, alkoxy and mono- or polyalkylene oxide. Such ethers include, for example, tetrahydrofuran, methyl-t-butyl ether, ethyl-t-butyl ether, phenylisobutyl ether, ethoxyethyl ether, diethyl ether, diphenyl ether, and diisopropyl ether. Blends of solvents such as t-

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butylalcohol/hexane, tetrahydrofuran/toluene and tetrahydrofuran/heptane can also be used to achieve the desired solvent properties. The currently preferred solvent, because of the high yields of HPA which can be achieved under moderate reaction conditions, is methyl-t-butyl ether.

The cobalt-based catalyst may be a modified cobalt carbonyl compound, for instance a phosphine-ligated compound or an unmodified cobalt carbonyl compound. Although phosphine-ligated catalysts are active for the described hydroformylation reaction, it is desirable to employ a process in which good yield and selectivity are achieved without a phosphine ligand because of the additional expense of the ligand. Therefore, the unmodified cobalt carbonyl compounds are preferred.

The cobalt-based catalyst can be supplied to the hydroformylation reactor as a cobalt carbonyl such as dicobaltoctacarbonyl or cobalt hydridocarbonyl. It may also be supplied in essentially any other form including metal, supported metal, Raney-cobalt, hydroxide, oxide, carbonate, sulfate, acetylacetonate, salt of a fatty acid, or aqueous cobalt salt solution. If not supplied as cobalt carbonyl, operating conditions should be adjusted such that cobalt carbonyls are formed, for instance via reaction with H_2 and CO as described in J. Falbe, "Carbon Monoxide in Organic Synthesis," Springer-Verlag, NY (1970). Typically, these conditions will include a temperature of at least 50 °C and a carbon monoxide partial pressure of at least 0.8 MPa (100 psig). For more rapid reaction, temperatures of 120 to 200 °C should be employed, at CO pressures of at least 3.5 MPa (500 psig). Addition of high surface area activated carbons or zeolites, especially those containing or supporting platinum or palladium metal, is known to accelerate the formation of cobalt carbonyls.

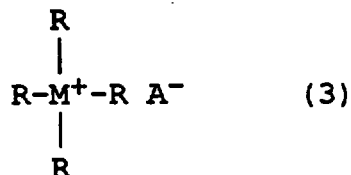
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The catalyst is preferably maintained under a stabilising atmosphere of carbon monoxide, which also provides protection against exposure to oxygen. The most economical and preferred catalyst activation and reactivation (of recycled catalyst) method involves converting the cobalt salt (or derivative) under H_2/CO in the presence of the catalyst promoter employed for hydroformylation. The conversion of Co^{2+} to the desired cobalt carbonyl is carried out at a temperature within the range of 75 to 200 °C, preferably 100 to 140 °C and a pressure within the range of 7.0 to 34.6 MPa (1000 to 5000 psig) for a time preferably less than about 3 hours. The preforming step can be carried out in a pressurised preforming reactor or in-situ in the hydroformylation reactor.

The amount of cobalt present in the reaction mixture will vary depending upon the other reaction conditions, but will generally fall within the range of 0.01 wt% to 1 wt%, preferably 0.05 to 0.3 wt%, based on the weight of the reaction mixture.

The hydroformylation reaction is carried out in the presence of a lipophilic quaternary salt of a Group V element to accelerate the reaction rate without imparting hydrophilicity (water solubility) to the active catalyst. By "lipophilic" is meant that the promoter tends to remain in the organic phase after extraction of the 3-hydroxyaldehyde with the aqueous liquid.

Lipophilic quaternary salts of Group V elements include those represented by formula (3)



in which each R group is selected independently from unsubstituted and inertly-substituted C_{1-25} linear, branched, cyclic or aromatic hydrocarbyl, alkoxy, or

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mono- or polyalkylene oxide, M is a Group V atom and is preferably a nitrogen, phosphorus or arsenic atom and A is a basic anion preferably having a conjugate acid of $pK_a > 2$ such as carboxylate, phenate and hydroxide, for example. Two or more of the R groups together may form a cyclic or aromatic structure. Such quaternary salts include benzyltri(n-butyl)ammonium acetate, benzyltrimethylammonium methoxide, benzyltrimethylammonium hydroxide and ethoxylated quaternary ammonium salts such as those available under the trademark "ETHOQUAD"; tetra(n-butyl)phosphonium acetate, tetraoctylphosphonium acetate, tetraphenylphosphonium hydroxide and benzyltrimethylphosphonium acetate; and tetraphenylarsonium acetate, tetra(n-butyl)arsonium acetate, and tetraoctylarsonium acetate.

The quaternary salt will be present in an amount effective to promote the hydroformylation reaction to the 3-hydroxyaldehyde, generally an amount within the range of 0.01 to 0.6 moles per mole of cobalt. An amount within the range of 0.05 to about 0.3 moles per mole of cobalt is preferred.

It is generally preferred to regulate the concentration of water in the hydroformylation reaction mixture, as excessive amounts of water reduce the selectivity towards the 1,3-alkanediols and 3-hydroxyaldehydes below acceptable levels and may induce formation of a second liquid phase. At low concentrations, water can assist in promoting the formation of the desired cobalt carbonyl catalyst species. Acceptable water levels will depend upon the solvent used, with more polar solvents generally more tolerant of higher water concentrations. For example, optimum water levels for hydroformylation in methyl-t-butyl ether solvent are believed to be within the range of 1 to 2.5 wt%.

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The hydrogen and carbon monoxide will generally be introduced into the reaction vessel in a molar ratio within the range of 1:2 to 8:1, preferably 1:1.5 to 5:1.

5 The reaction is carried out under conditions effective to produce a hydroformylation reaction mixture comprising a major portion of the 3-hydroxyaldehyde and a minor portion of by-product. Moreover, the level of 3-hydroxyaldehyde in the reaction mixture is preferably maintained at less than 15 wt%, preferably 5 to 10 wt%.

10 (To provide for solvents having different densities, the concentration of 3-hydroxyaldehyde in the reaction mixture can be expressed in molarity, i.e., less than 1.5M, preferably within the range of 0.5 to 1M.)

15 Generally, the hydroformylation reaction is carried out at elevated temperature less than 100 °C, preferably 60 to 90 °C, most preferably 75 to 85 °C, and at a pressure within the range of 3.5 to 34.6 MPa (500 to 5000 psig), preferably (for process economics) 7.0 to 24.2 MPa (1000 to 3500 psig), with higher pressures generally imparting

20 greater selectivity. The concentration of 3-hydroxyaldehyde in the intermediate product mixture can be controlled by regulation of process conditions such as oxirane concentration, catalyst concentration, reaction temperature and residence time. In general, relatively

25 low reaction temperatures (below 100 °C) and relatively short residence times within the range of 20 minutes to 1 hour are preferred.

In the practice of the invention method, it is possible to achieve 3-hydroxyaldehyde yields (based on the oxirane conversion) of greater than 80%. For instance,

30 with the hydroformylation of EO, formation of more than 7 wt% HPA in the dilute hydroformylation product mixture, at rates greater than 30 h⁻¹ are achievable. (Catalytic rates are referred to herein in terms of "turnover

35 frequency" or "TOF" and are expressed in units of moles per mole of cobalt per hour, or h⁻¹.) Reported rates are

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based on the observation that, before a majority of the oxirane, here EO, is converted, the reaction is essentially zero-order in EO concentration and proportional to cobalt concentration.

5 As mentioned above, separation of the hydroformylation product mixture is carried out economically most attractively by extraction with an aqueous liquid.

10 Preferably the aqueous liquid is water. The amount of water added to the hydroformylation reaction product mixture will generally be such as to provide a weight ratio of water:mixture within the range of 1:1 to 1:20, preferably 1:5 to 1:15. The addition of water at this stage of the reaction may have the additional advantage of suppressing formation of undesirable heavy ends.

15 Extraction with a relatively small amount of water provides an aqueous phase which is greater than 20 wt% 3-hydroxyaldehyde, preferably greater than 35 wt% 3-hydroxyaldehyde, permitting economical hydrogenation of the 3-hydroxyaldehyde to the 1,3-alkanediol. The water
20 extraction is preferably carried out at a temperature within the range of 25 to 55 °C, with higher temperatures avoided to minimise condensation products (heavy ends) and catalyst disproportionation to inactive, water-soluble cobalt compounds. In order to maximise catalyst
25 recovery discussed supra, it is preferred to perform the water extraction under 0.5 to 1.5 MPa (50 to 200 psig) of carbon monoxide at 25 to 55 °C.

30 After separation, the hydroformylation product is suitably hydrogenated to yield the 1,3-alkanediol by reaction with hydrogen in the presence of a hydrogenation catalyst. Hydrogenation can be carried out in aqueous solution at an elevated temperature during at least a portion of the hydrogenation step of at least 40 °C, generally within the range of 50 to 175 °C, under a
35 hydrogen pressure of at least 0.8 MPa (100 psig), generally within the range of 1.5 to 13.9 MPa (200 to

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2000 psig). The reaction is carried out in the presence of a hydrogenation catalyst such as any of those based upon Group VIII metals including nickel, cobalt, ruthenium, platinum and palladium, as well as copper, zinc and chromium and mixtures and alloys thereof. Nickel-based catalysts, including bulk, supported and fixed-bed forms, provide acceptable activities and selectivities at moderate costs. Highest yields are achieved under slightly acidic reaction conditions.

Commercial operation will preferably include efficient cobalt catalyst recovery with essentially complete recycle of cobalt to the hydroformylation reaction. The preferred catalyst recovery process involves two steps, beginning with the above-described extraction of the 3-hydroxyaldehyde from the hydroformylation product mixture. A majority of the cobalt catalyst will remain in the organic phase, with the remaining cobalt catalyst passing into the aqueous liquid phase. This organic phase can be recycled to the hydroformylation reactor, with optional purge of heavy ends. Optional further decobalting of catalyst in the aqueous liquid phase can be effected by suitable method such as complete or partial oxidation of cobalt followed by precipitation and filtration, distillation, deposition on a solid support, or extraction using a suitable extractant.

The process enables the production of PDO in high yield and selectivity without the use of a phosphine-ligated cobalt catalyst in the hydroformylation step. The process also enables the recovery and recycle of essentially all the cobalt catalyst.

The invention process can be conveniently described by reference to Figure 1. By way of example, the hydroformylation of EO as oxirane will be described. Separate or combined streams of EO (1), carbon monoxide and hydrogen (2) are charged to hydroformylation vessel (3), which can be a pressure reaction vessel such as a bubble column

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or agitated tank, operated batch-wise or in a continuous manner. The feed streams are contacted in the presence of an unmodified cobalt-based catalyst, i.e., a cobalt carbonyl compound which has not been prereacted with a phosphine ligand.

Following the hydroformylation reaction, the hydroformylation reaction product mixture (4) containing HPA, the reaction solvent, PDO, the cobalt catalyst and a minor amount of reaction by-products, is passed to extraction vessel (5), to which an aqueous liquid, generally water and optionally a miscible solvent, are added via (6) for extraction and concentration of the HPA for the subsequent hydrogenation step. Liquid extraction can be effected by any suitable means, such as mixer-setters, packed or trayed extraction columns or rotating disk contactors. Extraction can if desired be carried out in multiple stages. The water-containing hydroformylation reaction product mixture can be passed to a settling tank (not shown) for resolution into aqueous and organic phases.

The organic phase containing the reaction solvent and the major portion of the cobalt catalyst can be recycled from the extraction vessel to the hydroformylation reaction via (7). Aqueous extract (8) is optionally passed through one or more acid ion exchange resin beds (9) for removal of any cobalt catalyst present, and the decobalted aqueous product mixture (10) is passed to hydrogenation vessel (11) and reacted with hydrogen (12) in the presence of a hydrogenation catalyst to produce a hydrogenation product mixture (13) containing PDO. The hydrogenation step may also revert some heavy ends to PDO. The solvent and extractant water (15) can be recovered by distillation in column (14) and recycled to the water extraction process via a further distillation (not shown) for separation and purge of light ends. PDO-containing stream (16) can be passed to one or more

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distillation columns (17) for recovery of PDO (18) from heavy ends (19).

The invention process permits the selective and economical synthesis of PDO at moderate temperatures and pressures without the use of a phosphine ligand for the hydroformylation catalyst. The process involves preparation of a reaction product mixture dilute in HPA, then concentration of this HPA by water extraction for subsequent hydrogenation of HPA to PDO.

10 Comparative Example 1

0.87g of dicobaltoctacarbonyl, 1.5g toluene (internal marker), 2.0g deionised water and 146g methyl-t-butyl ether (MTBE) containing 0.2 wt% water were preheated for one hour in a 300 ml bolted-head stirred reactor at 80 °C under 4.2 MPa (600 psig) H₂ and 6.3 MPa (900 psig) 1:1 CO/H₂ synthesis gas. 10g EO were added to initiate the hydroformylation reaction. Samples were withdrawn for periodic analysis by capillary gas chromatography (with flame ionisation detector) to measure HPA hydroformylation reaction product. Sampling after about 40% conversion of EO indicated formation of 3.3 wt% HPA, at a rate (TOF) of 18 h⁻¹. This result is shown in Table 1 as run 1.

20 Example 1

25 This experiment illustrates the use of a quaternary phosphonium salt as a promoter of cobalt-catalysed hydroformylation of EO. The experiment was repeated with addition of various amounts (based on cobalt) of tetra(n-butyl)phosphonium acetate promoter. Results are shown in Table 1. For intermediate amounts of promoter, hydroformylation was accelerated, with highest rates for M+/Co molar ratios of 0.05 to about 0.3.

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Table 1

Run	M+/Co	H ₂ O (wt%)	HPA (wt%)	TOF (h ⁻¹)
1	0.00	1.5	3.3	18
2	0.01	1.5	3.3	25
3	0.03	1.5	2.6	20
4	0.07	1.5	5.7	40
5	0.21	0.2	4.3	44
6	0.24	2.0	5.0	34
7	0.37	1.5	4.3	33
8	0.59	1.5	4.2	16

Example 2

This example illustrates water extraction of cobalt catalyst under a carbon monoxide atmosphere in the presence of a lipophilic phosphonium acetate promoter. The reaction mixture from Run 6 of Example 1 was extracted with 30g of deionised water under 1.5 MPa (200 psig) carbon monoxide at 25 °C. 94.83g of upper organic layer containing 2184 ppmw cobalt were isolated. 24.90g of lower aqueous extract (containing most of the HPA product) were recovered and were found to contain 88 ppmw cobalt. These results correspond to 98.5% of total cobalt separated from aqueous product and remaining with the organic layer after extraction.

Example 3

This experiment illustrates recycle of cobalt catalyst in lipophilic phosphonium acetate-promoted hydroformylation. 10.875g of dicobaltoctacarbonyl, 7g of 70% tetra(n-butyl)phosphonium acetate by weight in methanol, 18.75g toluene (marker), 25g deionised water and 1838.0g MTBE were charged to a 3.8 l (1-gallon) bolted-head stirred reactor and heated under 13.9 MPa (2000 psig) H₂ and 5.6 MPa (800 psig) CO. After 1 hour, 123g of EO were added to initiate reaction. 1:1 CO/H₂ synthesis gas was added to replenish that depleted as

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hydroformylation progressed. The reaction was terminated after 50 minutes, with formation of HPA product at a rate of 39 h^{-1} . 375g of deionised water were added to extract HPA at 38°C under 1.5 MPa (200 psig) 1:1 synthesis gas. 495g of aqueous extract were recovered, yielding HPA product corresponding to 66% of EO consumed during reaction. Less than 7% of the cobalt catalyst was extracted into the aqueous phase.

The aqueous extract was removed from the reaction, and for subsequent cycles the remaining organic phase was reheated under synthesis gas ($2.6 \text{ H}_2/\text{CO}$) for one hour, and 120-130g of EO were added to perform recycle reactions, through 12 reaction cycles. Results are shown in Table 2.

HPA product in water extracts, as shown by gas chromatographic analysis, corresponded to yields (based upon EO consumed) of 70-89% at zero-order hydroformylation rates of $30\text{-}45 \text{ h}^{-1}$. Hydroformylation rates remained essentially constant for subsequent recycles, relative to the observed variability in rate measurements. Cobalt recycle (% total cobalt retained in organic phase after water extraction) in the organic phase ranged from 93 to 99%. Less than 17 ppmw phosphorus as the tetra(n-butyl)-phosphonium promoter partitioned into the aqueous phase.

These experiments demonstrate the convenience of recycle of the cobalt catalyst with the organic layer following water extraction for separation from HPA product, in the presence of the lipophilic phosphonium acetate promoter. The recycle catalyst largely retains its catalytic activity and selectivity. Only minor amounts of promoter are lost to the aqueous phase upon extraction.

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Table 2

Cycle #	TOF (h ⁻¹)	Min. HPA % Yield	Co Recycle (%)	P Loss (ppm)
1	38.78	66.15	93.2	13
2	32.90	77.86	97.9	NA
3	31.80	74.43	98.7	<15
4	35.70	80.01	99.5	<15
5	32.94	78.76	99.5	16
6	32.21	76.16	98.0	<15
7	31.93	71.14	98.7	<15
8	38.33	78.57	96.6	<15
9	36.48	76.50	96.9	<15
10	36.49	72.03	94.6	<15
11	37.44	74.98	97.3	14
12	42.66	89.02	96.3	10

Comparative Example 2

A hydroformylation reaction was carried out with 0.87 g dicobaltoctacarbonyl, 1.5g toluene (internal marker) and 147g MTBE. After pre-equilibration of the reaction mixture for 1 hour under 1:1 CO/H₂ at 80 °C, 20g EO were added. After three hours, 3.7 wt% HPA was formed, for a rate (TOF) of 4.6 h⁻¹.

Comparative Example 3

Comparative Example 2 was repeated with 0.077g of potassium chloride. Only 3.7 wt% HPA was formed in 3.5 hours at 80 °C for a rate (TOF) of 4.0 h⁻¹. A second run was conducted under otherwise identical conditions, with 0.06g sodium chloride instead of potassium chloride. At approximately 25% conversion of EO, a zero-order rate of only 4.3 h⁻¹ was achieved. These experiments demonstrate the limited effectiveness of neutral salts of strong acids and bases in promoting the hydroformylation reaction despite claims to the contrary in US-A-3 687 981.

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Example 4

Comparative Example 2 was repeated with the addition of 0.46g of a 40% solution of benzyltrimethylammonium methoxide in methanol. 4.73 wt% HPA was formed in less than 2 hours, for a rate (TOF) of 11.8 h^{-1} , i.e., a 2.6-fold rate increase over unpromoted Comparative Example 2.

Example 5

Comparative Example 2 was repeated using ammonium hydroxide (Run 2, comparative), "ETHOQUAD" 2C/11 (trade-mark, a bis(C₁₂₋₁₃ alkyl)(hydroxyethyl)methylammonium acetate used in Runs 3 and 5), benzyltrimethylammonium methoxide (Run 4) and benzyltrimethylammonium hydroxide (Run 6* at H₂:CO = 2.3:1). Results are shown and compared with previous examples in Table 3. The quaternary ammonium acetate promoted the reaction similarly to the methoxide. While quaternary ammonium hydroxide promoted the reaction, ammonium hydroxide did not.

Table 3

Run	M+	A-	M+/Co	TOF (h^{-1})	HPA (wt%)
1	-	-	0	4.6	3.7
2	NH ₄	OH	0.2	3.6	3.1
3	NR ₄	OAc	0.1	12.5	5.4
4	NR ₄	OMe	0.2	11.9	4.7
5	NR ₄	OAc	0.5	12.2	5.6
6*	NR ₄	OH	0.3	34.5	7.5

Example 6

A series of experiments was done to determine the effect of extraction under carbon monoxide on the recovery of cobalt following hydroformylation.

Hydroformylations were conducted on 300 ml or 3.79 l (1 gallon) scales in the presence "ETHOQUAD" 2 C/11, (a trademark) as lipophilic promoter (0.1 moles, relative to cobalt) at 80 °C in MTBE, and 2.3:1 to 3.0:1 H₂/CO (with total pressures given in Table 4).

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Reactions were restricted to formation of less than 10 wt% HPA prior to water extraction. Water extractions were carried out at 25 to 40 °C and 0.5 to 2.2 MPa (50 to 300 psig) CO, with varying amounts of water added to give organic/aqueous phase ratios of 1.5:1 to 4:1. As can be seen from Table 2, the use of a lipophilic ammonium salt promoter and extraction under CO enabled the recycle of 90% or more of the cobalt catalyst with the hydroformylation reaction solvent, while HPA was preferentially concentrated and extracted into the aqueous phase at a greater than 10:1 ratio. Thus, cobalt catalyst and HPA were efficiently separated. Moreover, Run 7 represented a recycle of catalyst from Run 6 (3.79 l scale). For Run 7, a hydroformylation rate of 33 h⁻¹ was obtained, compared with a rate of 35 h⁻¹ in Run 6. This illustrates that the invention enables the majority of the catalyst to be recycled in essentially active form.

Table 4

Run	Hydrof. MPa (psig)	% Co*	HPA wt%	
			AL	OL
1	10.4 (1500)	91.4	12.1	1.1
2	10.4 (1500)	91.5	20.3	0.9
3	10.4 (1500)	90.4	21.7	1.2
4	10.4 (1500)	94.4	23.2	0.8
5#	10.4 (1500)	81.5	17.7	1.4
6	19.1 (2750)	99.2	22.7	0.7
7#	19.1 (2750)	92.1	24.8	1.6

* Percent total cobalt retained in organic layer.

Recycled catalyst.

Comparative Example 4

Comparative Example 1 was repeated in the absence of added water and with addition of 0.14g of sodium acetate trihydrate as promoter, added at a ratio Na/Co of 0.2.

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HPA was formed at a rate of 41 h^{-1} . After cooling and addition of 30g deionised water for extraction, only 77% of the cobalt catalyst remained with the upper solvent layer. 23% of the cobalt was extracted with the aqueous product. This fraction corresponds approximately to the amount of sodium acetate added to promote the reaction.

Example 7

Comparative Example 1 was repeated with addition of 0.8g of tetraoctylphosphonium acetate promoter, for a ratio of 0.29 moles promoter per mole of cobalt. At approximately 40% conversion, 3.19 wt% HPA had been formed at a rate of 27.9 h^{-1} , or a 50% rate increase over that observed in the absence of promoter in Comparative Example 1, Run 1. Ultimately, 8.1 wt% HPA was formed at 90% conversion.

Following the reaction, the reaction product mixture was cooled to room temperature. 30.5g of deionised water were added for extraction of HPA under 4.2 MPa (600 psig) synthesis gas. After 30 minutes, mixing was terminated and 33.3g of an aqueous product layer containing 27 wt% HPA were isolated. The aqueous layer contained 57 ppm cobalt, or only 1% of the total cobalt charged. The upper organic layer (110.5g) was analysed to contain 0.19 wt% cobalt, or negligible loss relative to the initial cobalt charge. Recycle of 99% of the cobalt catalyst with the organic layer represents reduction in cobalt loss by a factor of 23, relative to that observed with sodium acetate promotion in Comparative Example 4.

Example 8

Comparative Example 1 was repeated with addition of 0.4g of tetraphenylarsonium acetate promoter, for a ratio of 0.18 moles of promoter per mole of cobalt. At about 40% conversion, 3.9 wt% HPA had been formed at a rate of 43.5 h^{-1} , or more than 2.3 times the rate observed in the absence of promoter in Comparative Example 1. The reac-

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tion was terminated following formation of 7.3 wt% HPA, at an EO conversion of approximately 80%.

5 Following the reaction, the mixture was cooled to room temperature. 30.2g of deionised water were added for
10 extraction of product under 1.5 MPa (200 psig) synthesis gas. After 30 minutes, mixing was terminated and 33.0g of an aqueous product layer containing 20.5 wt% HPA were isolated. The aqueous layer contained only 39 ppm cobalt, or less than 1% of the total cobalt charged. The upper
10 solvent layer (108.4g) was analysed to contain 0.2 wt% cobalt. Recycle of more than 99% of the cobalt catalyst with the upper solvent layer represents reduction in cobalt loss by a factor of 23, relative to that observed with sodium acetate promotion in Comparative Example 4.



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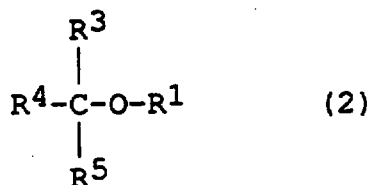
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1. A process for preparing 1,3-alkanediols and 3-hydroxyaldehydes by hydroformylating an oxirane with carbon monoxide and hydrogen in the presence of a cobalt-based catalyst and a promoter that is a lipophilic quarternary salt of a Group V element.
2. A process as claimed in claim 1, wherein the oxirane is a hydrocarbyl-epoxide having of 2 up to 30 carbon atoms.
3. A process as claimed in claim 1, wherein the oxirane is ethylene oxide.
4. A process as claimed in any one of claims 1 to 3, carried out in the presence of an inert, essentially non-water-miscible solvent.
5. A process as claimed in claim 4, wherein the solvent is an alcohol or ether according to formula (1)



in which R^1 is hydrogen or a linear, branched, cyclic or aromatic C_{1-20} hydrocarbyl or mono- or polyalkylene oxide and R^2 is a linear, branched, cyclic or aromatic C_{1-20} hydrocarbyl, alkoxy or mono- or polyalkylene oxide, or R^1 , R^2 and O together form a cyclic ether.

6. A process as claimed in claim 4, wherein the solvent is an alcohol or ether according to formula (2)



in which R^1 is hydrogen or C_{1-8} hydrocarbyl and R^3 , R^4 and R^5 are independently selected from C_{1-8} hydrocarbyl, alkoxy and mono- or polyalkylene oxide.

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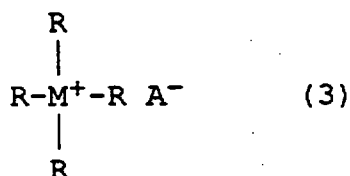


- 20 -

7. A process as claimed in any one of claims 1 to 6, wherein the cobalt-based catalyst is an unmodified (i.e., non-phosphine-ligated) cobalt carbonyl compound.

8. A process as claimed in any one of claims 1 to 7, wherein the amount of cobalt-based catalyst is in the range of 0.01 wt% to 1.0 wt% based on the weight of the reaction mixture.

9. A process as claimed in any one of claims 1 to 8, wherein the lipophilic quarternary salt of the Group V cation is represented by formula (3)



in which each R group is selected independently from unsubstituted and inertly-substituted C₁-25 linear, branched, cyclic or aromatic hydrocarbyl, alkoxy, or mono- or polyalkylene oxide, M is a Group V atom and is preferably a nitrogen, phosphorus or arsenic atom and A is a basic anion having a conjugate acid of pK_a >2.

10. A process as claimed in claim 9, wherein the lipophilic quarternary salt is selected from benzyltri(n-butyl)ammonium acetate, benzyltrimethylammonium methoxide, benzyltrimethylammonium hydroxide and ethoxylated quarternary ammonium salts; tetra(n-butyl)-phosphonium acetate, tetraoctylphosphonium acetate, tetraphenylphosphonium hydroxide and benzyltrimethylphosphonium acetate; and tetraphenylarsonium acetate, tetra(n-butyl)arsonium acetate, and tetraoctylarsonium acetate.

11. A process as claimed in any one of claims 1 to 10, wherein the lipophilic quarternary salt of the Group V element is present in an amount in the range of 0.01 to 0.6 moles per mole of cobalt.

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12. A process as claimed in any one of claims 4 to 11, wherein the solvent contains water levels in the range of 1.0 to 2.5 wt%.

5 13. A process as claimed in any one of claims 1 to 12, wherein the oxirane is hydroformylated with hydrogen and carbon monoxide in a molar ratio within the range of 1:2 to 8:1.

10 14. A process as claimed in any one of claims 1 to 13, wherein the level of 3-hydroxyaldehyde in the reaction mixture is maintained at less than 15 wt%.

15 15. A process as claimed in any one of claims 1 to 14, wherein the hydroformylation reaction is carried out at elevated temperature less than 100 °C and at a pressure within the range of 3.5 to 34.6 MPa.

16. A process as claimed in any one of claims 1 to 15, wherein the hydroformylation product is separated by extraction with an aqueous liquid.

20 17. A process as claimed in claim 16, wherein water is added to the hydroformylation reaction product mixture to provide a water:mixture weight ratio within the range of 1:1 to 1:20.

18. A process as claimed in claim 16, wherein the cobalt-based catalyst is recycled.

25 19. A process as claimed in any one of claims 1 to 18, wherein the 3-hydroxyaldehyde is hydrogenated to yield the 1,3-alkanediol.

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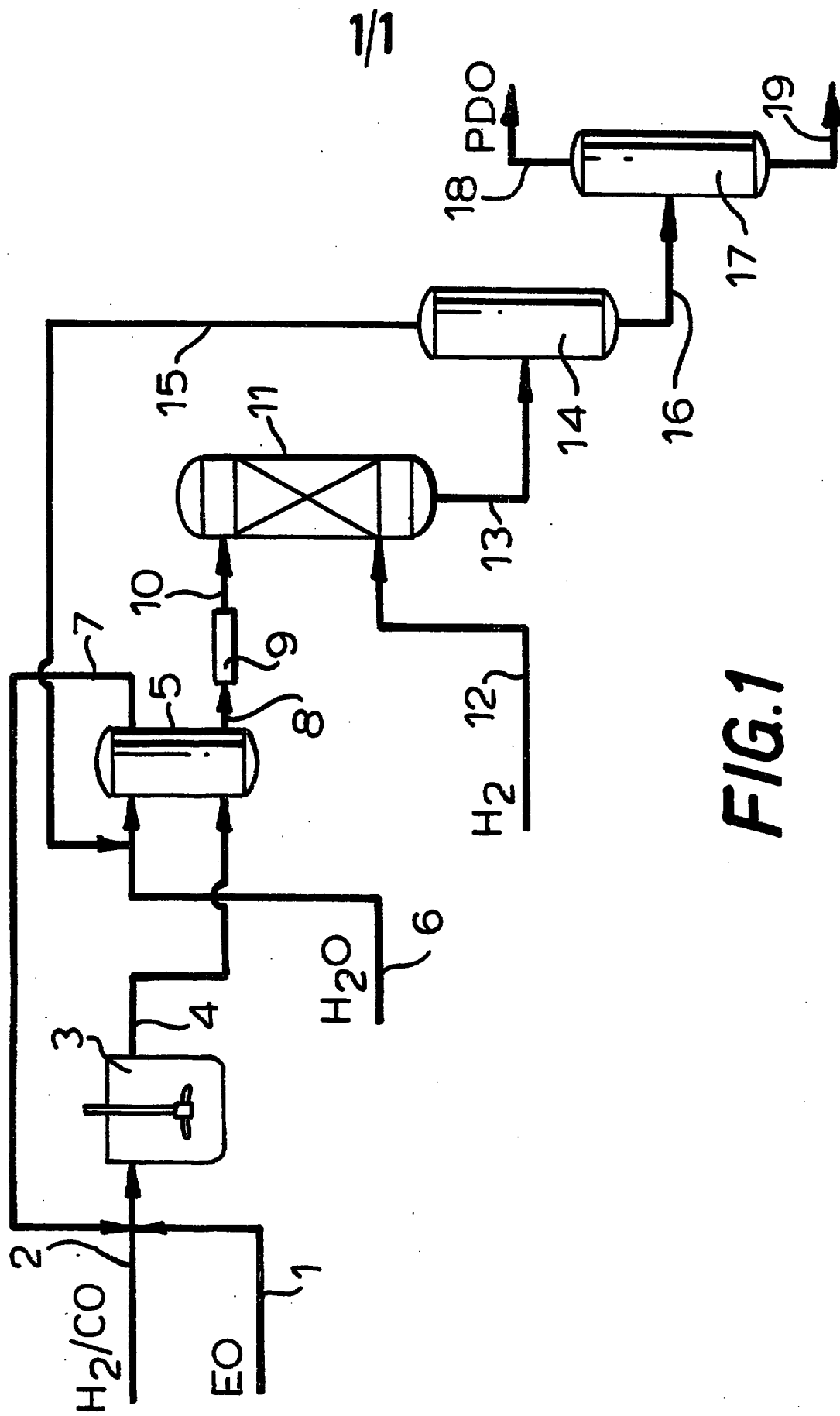


FIG. 1

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference TH 0535 PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP 95/ 03868	International filing date (day/month/year) 28/09/1995	Priority date (day/month/year) 30/09/1994
International Patent Classification (IPC) or national classification and IPC C07C45/58		
Applicant SHELL INTERNATIONALE RESEARCH MIJ. B.V. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

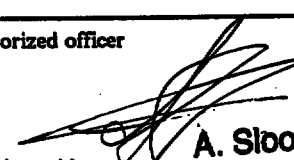
2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consists of a total of 6 sheets.

3. This report contains indications and corresponding pages relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 25/04/1996	Date of completion of this report 23. 01. 97
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer  A. Sloopweg Telephone No.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Intern. application No.

PCT/EP95/03868

I. Basis of the report

1. This report has been drawn up on the basis of (Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.):

☐ the international application as originally filed.

☒ the description, pages 3-18 _____, as originally filed,
pages _____, filed with the demand,
pages 1, 2, 2a _____, filed with the letter of 07.11.96,
pages _____, filed with the letter of _____,

☒ the claims, Nos. _____, as originally filed,
Nos. _____, as amended under Article 19,
Nos. _____, filed with the demand,
Nos. 1-18 _____, filed with the letter of 07.11.96,
Nos. _____, filed with the letter of _____,

☐ the drawings, sheets/fig _____, as originally filed,
sheets/fig _____, filed with the demand,
sheets/fig _____, filed with the letter of _____,
sheets/fig _____, filed with the letter of _____.

2. The amendments have resulted in the cancellation of:

☐ the description, pages _____.

☐ the claims, Nos. _____.

☐ the drawings, sheets/fig _____.

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

1. STATEMENT

Novelty (N)	Claims 1-18 _____	YES
	Claims _____	NO
Inventive Step (IS)	Claims 1-18 _____	YES
	Claims _____	NO
Industrial Applicability (IA)	Claims 1-18 _____	YES
	Claims _____	NO

2. CITATIONS AND EXPLANATIONS

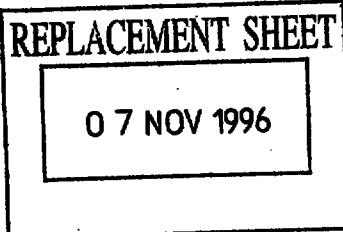
- 1). The closest prior art is considered to be WO94/18149 (D1). This document describes the catalytic hydroformylation of epoxides to 3-hydroxyaldehydes and 1,3-diols. The process of D1 uses a cobalt catalyst. Example comp.11 (table 7 of D1, p.23) discloses a process wherein the epoxide is hydroformylated using a phosphineligated-cobalt catalyst in the presence of R_4NBr (wherein R is t-butyl). In the description the application also mentions the presence of pyridinium-, pyrazinium, and pyrimidinium salts. Example 16 in table 5 uses pyridinium paratoluenesulfonate as a promotor. These are all quaternary salts of a group V element as defined in claim 1 of the application.
- 2). The present application specifically states in claim 1 that the cobalt catalyst used does not have a phosphine ligand. As such claim 1 is considered as satisfying Art. 33(2) PCT.

- 3). It cannot be considered obvious to leave out the phosphine ligand in the process of D1 to arrive at the present claim 1. It has furthermore been shown with the aid of comparative examples that the presently claimed process has unexpected advantages when compared to the prior art process. The process of claim¹ can therefore also be considered as satisfying Art. 33(3) PCT.
- 4). Claims 2-18 are dependent on claim 1 and can therefore also be considered to satisfy Art. 33(2) and (3) PCT.

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

- 1). The document D1 has not been identified in the description nor as the relevant background art disclosed therein been discussed. The requirements of Rule 5.1(a)(ii) PCT are, thus, not fulfilled.



- 1 -

TH 0535 PCT

PROCESS FOR PREPARING 1,3-ALKANEDIOLS
AND 3-HYDROXYALDEHYDES

This invention relates to a process for preparing 1,3-alkanediols and 3-hydroxyaldehydes by hydroformylating an oxirane (1,2-epoxide). In particular, the invention relates to a cobalt-catalysed process for preparing 1,3-propanediol by hydroformylating ethylene oxide and hydrogenating the hydroformylation product.

The hydroformylation of oxiranes to produce 3-hydroxyaldehydes has been discussed in "New Syntheses with Carbon Monoxide" edited by J. Falbe (1980), pp. 131-132. The reaction is catalysed with a cobalt-based catalyst, or a phosphine-modified cobalt-based catalyst. The hydroformylation product, be it the 3-hydroxyaldehyde or the cyclic hemiacetal that is its dimer, may be converted into a 1,3-alkanediol by hydrogenation. This process is of particular importance to the preparation of 1,3-propanediol (PDO), an intermediate in the production of polyesters for fibres and films, that may be prepared by hydrogenating 3-hydroxypropanal (HPA). According to this textbook attempts have been made to improve the hydroformylation reaction by adding small amounts of alcohols, ethers, ketones and esters. According to US-A-3 687 981 also halogen containing inorganic compounds, e.g., inorganic salts and acids such as hydrochloric acid may be used as hydroformylation promoter.

Finally, from WO94/18149 a process for preparing 1,3-alkanediols and 3-hydroxyaldehydes is known, which process is carried out in the presence of a phosphine-ligated cobalt catalyst. This process leaves room for improvement in respect of the reaction rate and

AMENDED SHEET

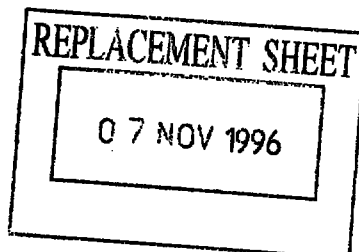
selectivity towards HPA. Besides, the process is not really attractive in respect of catalyst recycle.

It would be desirable to produce the hydroformylation product at improved rate. It is therefore an object of the invention to provide a process for preparing 1,3-alkanediols and 3-hydroxyaldehydes at improved rate. It is a further object of the invention to provide a process in which essentially all of the catalyst can be conveniently recycled.

Accordingly, the invention provides a process for preparing 1,3-alkanediols and 3-hydroxyaldehydes by hydroformylating an oxirane with carbon monoxide and hydrogen in the presence of a cobalt-based catalyst and a promoter, characterized in that the cobalt-based catalyst is a non-phosphine ligated catalyst and the promoter is a lipophilic quaternary salt of a Group V element.

The oxirane comprises an organic compound, two carbon atoms of which are connected by an oxy linkage as well as by a carbon-carbon single bond. In general terms, the oxiranes comprise hydrocarbyl-epoxides, having at least 2, preferably up to 30, more preferably up to 20, most preferably up to 10 carbon atoms. The hydrocarbyl group may be aryl, alkyl, alkenyl, aralkyl, cycloalkyl, or even alkylene; straight chain or branched chain. Suitable examples of oxiranes include 1,2-epoxy(cyclo)alkanes, such as ethylene oxide, propylene oxide, 1,2-epoxyoctane, 1,2-epoxycyclohexane, 1,2-epoxy-2,4,4-trimethylhexane, and 1,2-epoxyalkenes such as 1,2-epoxy-4-pentene. Ethylene oxide and propylene oxide are preferred. In view of the demand for PDO, ethylene oxide (EO) is the oxirane most preferably used in the process of the invention.

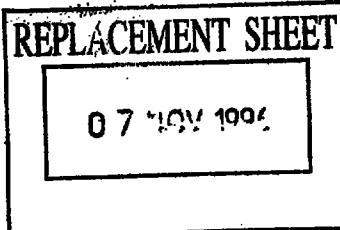
The hydroformylation reaction is preferably carried out in a liquid solvent inert to the reactants and products, i.e., that is not consumed during the reaction. Upon completion of the reaction, the liquid solvent facilitates the separation of the hydroformylation



- 2a -

5 product. The separation may be carried out by allowing the product to form a separate layer, as is disclosed in US-A-3 687 981. However, as discussed below, it is preferred to carried out the separation by extraction with an aqueous liquid. In general, ideal solvents for the hydroformylation process will (a) exhibit low to moderate polarity such that the 3-hydroxyaldehyde will be dissolved to a concentration of at least about 5 wt% under hydroformylation conditions, while significant

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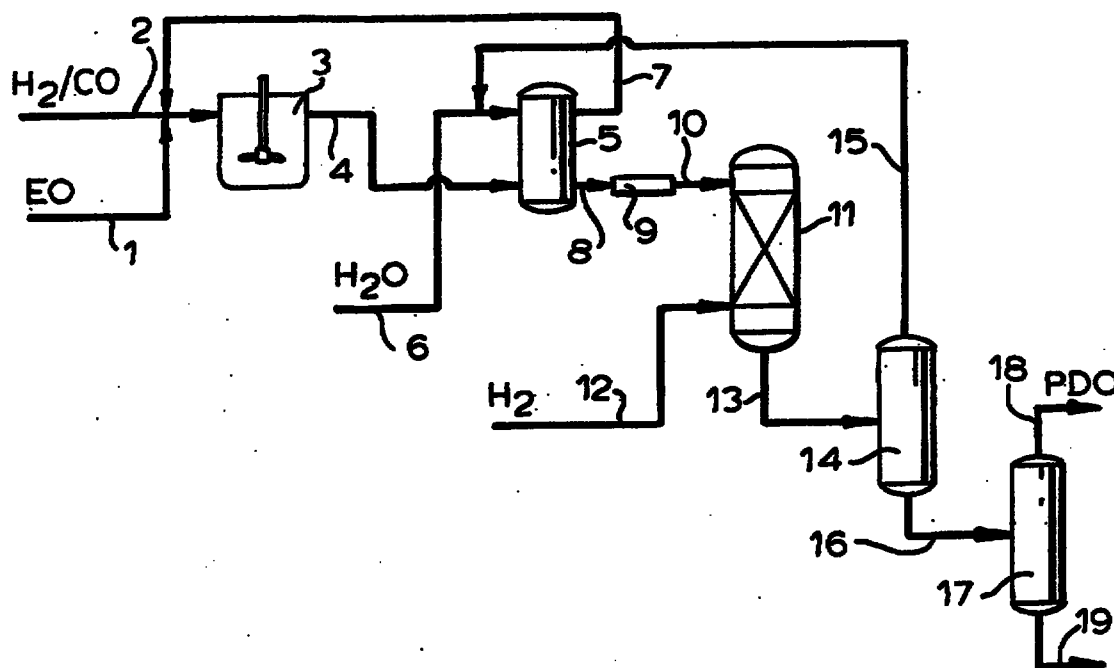




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/EP95/03868		(72) Inventors: ARHANCET, Juan, Pedro; 20667 Castle Bend Drive, Katy, TX 77450 (US). FORSCHNER, Thomas, Clayton; 2211 Woodland Drive, Richmond, TX 77469 (US). POWELL, Joseph, Brown; 10506 Normont Drive, Houston, TX 77070 (US). SEMPLE, Thomas, Carl; 401 Falingleaf Drive, Friendswood, TX 77546 (US). SLAUGH, Lynn, Henry; 11911 Cypresswood Drive, Houston, TX 77070 (US). THOMASON, Terry, Blane; 14203 Highcroft Drive, Houston, TX 77077 (US). WEIDER, Paul, Richard; 15014 Tramore, Houston, TX 77083 (US).	
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(71) Applicant (for all designated States except CA): SHELL INTERNATIONALE RESEARCH MAATSCHAPPI B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).	
(71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400-4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: PROCESS FOR PREPARING 1,3-ALKANEDIOLS AND 3-HYDROXYALDEHYDES



(57) Abstract

A process for preparing 1,3-alkanediols and 3-hydroxyaldehydes by hydroformylating an oxirane with carbon monoxide and hydrogen in the presence of a cobalt-based catalyst and a promoter that is a lipophilic quaternary salt of a Group V element. The process enables the production of 1,3-propanediol in high yields and selectivity.

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