

PREPARATION OF OXIRANE COMPOUNDS

The present invention relates to a process for the preparation of oxirane compounds.

Processes for preparing oxirane compounds such as propylene oxide, have been known for a long time.

5 US-A-3,350,422 describes a method comprising reacting olefinically unsaturated compounds, preferably propylene, with an organic hydroperoxide in the presence of an effective dissolved catalytic amount of a soluble vanadium compound. It is described that during the
10 epoxidation reaction the organic hydroperoxide is converted almost quantitatively to the corresponding alcohol. The alcohol can be recovered as co-product, or reconverted to the hydroperoxide by dehydration to olefin, hydrogenation of the olefin, and oxidation to
15 hydroperoxide, or by hydrogenolysis to hydrocarbon followed by oxidation to hydroperoxide.

NL-C-1010372 describes a process comprising reacting propene with ethylbenzene hydroperoxide to obtain propylene oxide and 1-phenyl ethanol. The 1-phenyl
20 ethanol is subsequently dehydrated to obtain styrene, which is a useful starting material for other chemical reactions. NL-C-1012749 describes a similar process in which propene is reacted with cumenehydroperoxide to obtain propene oxide and 2-phenyl-2-propanol. The latter
25 is described to be subsequently dehydrated into alpha-methylstyrene which is described to be an industrially applicable compound.

A further process in which hydroperoxides are used, is a process in which phenol and acetone are prepared
30 with the help of cumene. Such process generally comprises oxidizing cumene into cumene hydroperoxide, and

converting cumene hydroperoxide into phenol and acetone, preferably with the help of an acidic catalyst. Such process has been described in EP-A-361755.

5 It has now been found that it is advantageous to integrate the process for preparing oxirane compounds and the process for preparing ketone and/or aldehyde and phenol. In such integrated process, there is not only an advantage in the economy of scale in the hydroperoxide manufacture, but it has further surprisingly been found
10 that undesirable by-products of one process can be converted into desired products in the other process.

Another advantage of the integration of the processes compared with a process solely preparing oxirane compounds is that only part of the alkylaryl hydro-
15 peroxide is converted back into the alkylaryl starting compound in the integrated process which causes that less by-products are built up compared with a process in which alkylaryl is recycled in full. In the latter kind of processes, a bleed stream is generally necessary to
20 prevent excessive build up of by-products. A bleed stream has the disadvantage that useful compounds are removed from the process as well.

Although parts of the process according to the present invention are known per se, there is no teaching
25 or hint in the prior art to combine the processes according to the present invention.

The present invention relates to a process for the preparation of oxirane compounds, phenol and ketones and/or aldehydes, which process comprises:

- 30 (i) oxidation of an alkylaryl to obtain an alkylaryl hydroperoxide,
(ii) contacting at least part of the alkylaryl hydro-
peroxide obtained in step (i) with olefin in the presence of a catalyst to obtain an oxirane compound and alkylaryl
35 hydroxyl,

(iii) reacting at least part of the alkylaryl hydroperoxide obtained in step (i) to obtain phenol and a ketone and/or aldehyde,

(iv) separating oxirane compound from reaction product of step (ii),

(v) contacting at least part of the reaction product from which the oxirane compound has been separated, with hydrogen to obtain alkylaryl at least part of which is recycled to step (i).

Although ethylbenzene is the alkylaryl compound most widely used in the preparation of an oxirane compound at present, it has been found that process step (i) can be carried out at higher conversion and higher selectivity if the alkylaryl compound employed is an alkylbenzene in which the alkyl substituent is a branched alkyl substituent comprising from 3 to 10 carbon atoms. A more preferred alkylaryl compound contains 1 or 2 alkyl substituents. An alkylaryl compound containing several substituents has the advantage that it can contain several hydroperoxide groups. However, in view of potential side-reactions, it is preferred that there are no more than 3 substituents, more preferably no more than 2 substituents. More preferably, the alkylaryl compound is cumene and/or di(iso-propyl)benzene. Although mixtures of different alkylaryl compounds can be employed, a single type of compound is preferred in order to be able to optimise the process conditions for this specific compound. Most preferably, the alkylaryl compound is cumene or di(iso-propyl)benzene.

The alkylaryl for use in the present invention, can be prepared in any way known to be suitable by someone skilled in the art. For cumene, a suitable preparation process has been described in EP-A-361755 and in EP-A-371738.

The oxidation of the alkylaryl can be carried out by any suitable process known in the art. The oxidation can be carried out in the liquid phase in the presence of a diluent. This diluent is preferably a compound which is liquid under the reaction conditions and does not react with the starting materials and product obtained. However, the diluent can also be a compound necessarily present during the reaction. For example, if the alkylaryl is cumene the diluent can be cumene as well.

The product obtained in step (i) can be used as such in step (ii) and step (iii), or it can be preferred to separate off some compounds, or it can be preferred to use only part of the product obtained in the process according to the present invention and to use another part in another process.

Part of the product of step (i) is used in step (iii), namely reaction of the alkylaryl hydroperoxide to obtain phenol and ketone and/or aldehyde. The phenol obtained can contain substituents. The reaction of the alkylaryl hydroperoxide can be attained by contacting the alkylaryl hydroperoxide with an acidic catalyst such as acidic catalysts containing sulphur. As the acidic catalyst can be used sulphuric acid, hydrochloric acid, perchloric acid, sulphur dioxide and sulphur trioxide; organic acids such as benzene-sulphonic acid, p-toluenesulphonic acid, cresolsulphonic acid and chloroacetic acid; solid acids such as silica-alumina, alumina and acidic ion exchange resins; heteropolyacids such as tungstosilicic acid, tungstophosphoric acid and molybdophosphoric acid. Preferably, sulphuric acid and/or cresolsulphonic acid are used. The amount of catalyst to be used is usually in the range of from 0.0001 to 1 %wt, based on the reaction mixture to be treated. The reaction temperature is usually in the range of from 30 to 150 °C.

The alkylaryl hydroperoxide can be subjected to the reaction of step (iii) after other compounds have been separated off from the reaction product of step (i). However, it is preferred to subject part of the reaction product of step (i) directly to the decomposition reaction step (iii).

The reaction in step (iii) usually produces by-products. By-products which are frequently found, are ethylbenzene and 1-methyl styrene. In order to further increase the yield of the present process, the desired products phenol and ketone and/or aldehyde can be separated from the reaction product of step (iii), after which either all or part of the remaining reaction product is subjected to the hydrogenation of step (v). Therefore, the process according to the present invention preferably comprises separating at least part of the phenol and ketone and/or aldehyde from the reaction product of step (iii), and contacting either all or part of the remaining reaction product with hydrogen in step (v). Compounds which are obtained in step (iii) and which are preferably sent to step (v), are ethylbenzene and 1-methyl styrene. Therefore, any fraction of the reaction product of step (iii) which is sent to step (v) preferably contains ethylbenzene and/or 1-methyl styrene. Reaction product of step (iii) can be sent to step (v) as such, or the reaction product of step (iii) is combined with reaction product of step (iv) from which oxirane compound has been separated off, before being sent to step (v).

The desired phenol and ketone and/or aldehyde can be separated from the reaction product of step (iii) in any way known to someone skilled in the art. Preferably, the phenol and ketone and/or aldehyde are substantially removed from the reaction product of step (iii), while at least part of the reaction products other than phenol and

ketone and/or aldehyde is sent back to the integrated process.

Usually, no heavy by-products need to be removed from the integrated process according to the present invention as sufficient heavy by-products are removed by process step (iii). However, if it is preferred to remove additional heavy by-products, this is preferably done by removing heavy by-products from the reaction product of step (iii) after the phenol and ketone and/or aldehyde have been substantially removed and before at least part of the remainder of the reaction product is sent back to the process.

If light by-products are to be removed from the integrated process according to the present invention, this is preferably done before recycling reaction products of the present process to step (i) of the present process. The light by-products are preferably removed from reaction product of step (v) and/or reaction product of step (iii) from which at least part of the phenol and ketone and/or aldehyde has been removed.

Preferably, the alkylaryl used in the process according to the present invention is cumene as this gives the commercially attractive compounds phenol and acetone in step (iii).

In step (ii), alkylaryl hydroperoxide obtained in step (i) is contacted with olefin in the presence of a catalyst to obtain an oxirane compound and hydroxy-alkylaryl. A catalyst which can suitably be used in such process comprises titanium on silica and/or silicate. A preferred catalyst is described in EP-B-345856. Such catalyst comprises titanium in chemical combination with a solid silica and/or inorganic silicalite which catalyst is obtainable by a) impregnating the silicium compound with a stream of gaseous titanium tetrachloride, b) calcining the obtained reaction product of step a) and

c) hydrolysis of the product of step b). The reaction generally proceeds at moderate temperatures and pressures, in particular at temperatures in the range of from 0 to 200 °C, preferably in the range from 25 to 200 °C. The precise pressure is not critical as long as it suffices to maintain the reaction mixture in a liquid condition. Atmospheric pressure may be satisfactory. In general, pressures can be in the range of from 1 to $100 \times 10^5 \text{ N/m}^2$.

The olefin to be used in step (ii) of the process of the present invention depends on the oxirane compound to be prepared. Preferably, the olefin contains from 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms. Most preferably, the olefin is propene.

At the conclusion of the epoxidation reaction, the liquid mixture comprising the desired products is separated from the catalyst. The oxirane compound can then be separated from the reaction product in any way known to be suitable to someone skilled in the art. The liquid reaction product may be worked up by fractional distillation, selective extraction and/or filtration. The catalyst, any solvent which might be present and any unreacted olefin or alkylaryl hydroperoxide may be recycled for further utilization.

Process step (ii) can be carried out with the catalyst in the form of a slurry, of a moving bed or a fluidized bed. However, a fixed bed is preferred for large-scale industrial application. The process may be carried out in a batch-wise manner, semi-continuously or continuously. The liquid containing the reactants may then be passed through the catalyst bed, so that the effluent from the reaction zone is substantially free from catalyst.

Subsequently, at least part of the reaction product containing hydroxyalkylaryl from which an oxirane compound has been separated off, is subjected to hydrogenation. A hydrogenation treatment which can be used comprises contacting reaction product with hydrogen at a temperature of from 100 to 330 °C, preferably of from 140 to 330 °C, preferably of from 180 to 330 °C, preferably of from 180 to 320 °C, and a pressure of from 0.1 to 100×10^5 N/m², more preferably of from 0.1 to 50×10^5 N/m², most preferably of from 0.1 to 30×10^5 N/m². The hydrogenation treatment is preferably carried out in the presence of a hydrogenation catalyst. Generally, the hydrogenation catalyst will contain a metal on a solid carrier which metal catalyses hydrogenation. Preferred catalysts are catalysts containing from 0.5 to 8 %wt of metal or a metal compound on a carrier, more preferably of from 0.5 to 5 %wt. Preferably, the metal present as metal or metal compound is one or more metal chosen from Group 1b, 2b, 3a, 4a, 4b, 5b, 6b, 7b and 8 of the Periodic Table of the Elements described in the Handbook of Chemistry and Physics, 63rd Edition. Most preferably, the metal present as metal or metal compound is palladium. The solid carrier preferably is charcoal.

Catalysts further preferably used in hydrogenating at least part of the reaction product containing hydroxyalkylaryl from which an oxirane compound has been separated off, are the catalysts described in US 5,475,159. These catalysts are catalysts comprising a copper compound, a zinc compound and at least one compound selected from the group consisting of aluminium, zirconium, magnesium, a rare earth and mixtures thereof. Such catalysts were found to give good results at relatively low temperature. In step (v) of the present

process, these catalysts are preferably used at a temperature of from 100 to 250 °C. Preferably, such catalysts comprise from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper. Further, such catalysts preferably contain from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc. A preferred catalyst contains from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, and from about 0.1 percent by weight to about 20 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of rare earth. A further preferred catalyst contains from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, and from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of aluminium. A further preferred catalyst contains from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, and from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of zirconium. Another preferred catalyst contains from about 10 percent by weight to about

80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of zirconium, and from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of aluminium. And a further preferred catalyst contains from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of magnesium, and from about 0.1 percent by weight to about 20 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of rare earth.

After the reaction with hydrogen in step (v), the product obtained can be recycled in toto or in part. If only part of the hydrogenated product is recycled, the desired fraction can be separated off in any way suitable known to someone skilled in the art.

C L A I M S

1. Process for the preparation of oxirane compounds, phenol and ketones and/or aldehydes, which process comprises:

(i) oxidation of an alkylaryl to obtain an alkylaryl hydroperoxide,

(ii) contacting at least part of the alkylaryl hydroperoxide obtained in step (i) with olefin in the presence of a catalyst to obtain an oxirane compound and alkylaryl hydroxyl,

(iii) reacting at least part of the alkylaryl hydroperoxide obtained in step (i) to obtain phenol and a ketone and/or aldehyde,

(iv) separating oxirane compound from reaction product of step (ii), and

(v) contacting at least part of the reaction product from which an oxirane compound has been separated, with hydrogen to obtain alkylaryl at least part of which is recycled to step (i).

2. Process according to claim 1, in which process the alkylaryl compound is an alkylbenzene in which the alkyl substituent is a branched alkyl substituent comprising from 3 to 10 carbon atoms.

3. Process according to claim 1 or 2, in which process the alkylaryl compound is cumene and/or di(iso-propyl)benzene.

4. Process according to any one of claims 1 to 3, in which decomposition by-products obtained in step (iii) are sent to step (v).

5. Process according to any one of claims 1 to 4, in which in step (ii) alkylaryl hydroperoxide is contacted with propene at a temperature in the range of from 0 to

200 °C, and a pressure in the range of from 1 to 100×10^5 N/m² in the presence of a catalyst comprising titanium on silica and/or silicate.

5 6. Process according to any one of claims 1 to 5, in which the hydrogenation in process step (v) is carried out at a temperature of from 140 to 330 °C, and a pressure of from 0.1 to 50×10^5 N/m² in the presence of a hydrogenation catalyst.

10 7. Process according to any one of claims 1 to 6, in which at least part of the phenol and ketone and/or aldehyde are separated from the reaction product of step (iii), and either all or part of the remaining reaction product is contacted with hydrogen in step (v).

15 8. Process according to any one of claims 1 to 7, in which process step (v) at least part of the reaction product from which an oxirane compound has been separated obtained in step (iv), is contacted with hydrogen and a catalyst comprising a copper compound, a zinc compound and at least one compound selected from the group
20 consisting of aluminium, zirconium, magnesium, a rare earth and mixtures thereof.