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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.

Suitable outlets can often be found for many of the products co-produced in the prior art processes for
30 manufacturing oxirane compounds. However, it can be

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beneficial to be able to produce solely the oxirane compound such as propylene oxide.

5 A process has now been found which makes it possible to prepare oxirane compounds without the need to prepare further compounds at the same time.

The present invention relates to a process for the preparation of oxirane compounds, which process comprises:

- 10 (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,
15 (iii) separating oxirane compound from reaction product of step (ii),
(iv) 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
20 recycled to step (i),
in which process the alkylaryl is an alkylaryl compound comprising more than 1 alkyl substituent.

It has been found that the use of an alkylaryl compound comprising more than 1 alkyl substituent in a
25 process as described above makes that the amount of alkylaryl can be smaller than in a similar process in which ethylbenzene or cumene are used. Without wishing to be bound to any theory, it is thought that an alkylaryl substituent containing more than 1 alkyl substituent does
30 not only have the option to carry more than 1 hydroperoxide group, but that furthermore the alkyl substituents which are present are converted faster into a hydroperoxide group, measured as number of hydroperoxide groups per litre of alkylaryl per hour
35 oxidation time.

The alkylaryl compound employed in the process according to the present invention is an alkylaryl compound comprising more than 1 alkyl substituent. If a mixture of alkylaryl compounds is present in the process according to the present invention, the mixture of alkylaryl compounds is to have on weight average more than 1 alkyl substituent. Preferably, the alkylaryl compound for use in the present invention comprises more than 1 alkyl substituent, at least one of which is a branched alkyl substituent comprising from 3 to 10 carbon atoms. 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. The alkylaryl compound or mixture of alkylaryl compounds preferably has, on weight average, of from 1.5 to 2.5 substituents. Most preferably, the alkylaryl compound contains about 2 alkyl substituents. Most preferably, the alkylaryl compound is 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.

Preferably, the alkylaryl for use in the present invention is prepared in a process for preparing cumene in which process propene is reacted with benzene in the presence of a suitable catalyst. Such processes have been described in EP-A-361755 and in EP-A-371738. These processes generally have di-isopropylbenzene as a by-product. Conventionally, the crude reaction product is sent to a first distillation column where benzene is separated off. Subsequently, the bottom product of the first column is sent to a second column where cumene is separated off, and finally, the bottom product of the

second column is sent to a third distillation column where di-isopropylbenzene is separated off.

Conventionally, di-isopropylbenzene is sent to a transalkylation unit where di-isopropylbenzene is reacted with benzene in the presence of a transalkylation catalyst to obtain cumene. The process according to the present invention, preferably uses part of the di-isopropylbenzene prepared in the process of reacting propene and benzene.

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 di(iso-propyl)benzene, the diluent can be di(iso-propyl)benzene as well. As will be known to someone skilled in the art, water can be present during oxidation. If water is present, the water preferably is slightly basic. The water preferably has a pH of between more than 7 to 8.

The product obtained in step (i) can be used as such in step (ii), or it can be preferred to separate off some compounds, or it can be preferred to only use part of the product obtained and to use another part in another process. Someone skilled in the art will appreciate that a wide range of compounds can be present in the product of step (i), as each alkyl group can be converted into a hydroperoxide group, into a hydroxyl group or can remain unconverted. Surprisingly, it was found that it is not required to purify the product of step (i) before use in step (ii).

It has been found that compounds containing ortho-substituted alkylaryls are less preferred for use in the process according to the present invention. It was found that ortho-substituted alkylaryls generally are less
5 reactive. Preferably, at least 80 %wt of the alkylaryls for use in step (i) of the process of the present invention are meta-substituted or para-substituted alkylaryls. More preferably, at least 90 %wt, more specifically at least 95 %wt, of the alkylaryls for use
10 in the process of the present invention are meta-substituted or para-substituted alkylaryls.

In order to prevent build-up of less reactive alkylaryls in the process according to the present invention, it is especially preferred that the process
15 according to the present invention comprises a further step by which at least part of less reactive alkylaryl compounds are removed. Preferably, such process step is subjecting at least part of the product of step (i) to distillation. The bottom product can be used in step
20 (ii). The product distilled off will contain a relatively large amount of less reactive alkylaryls. This product can be sent to a transalkylation unit as described above. In the transalkylation unit the product can be converted into a product containing more reactive compounds or can
25 be converted into compounds containing a single alkyl substituent on the aromatic group.

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
30 hydroxyalkylaryl. 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
35 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 100×10^5 N/m².

The olefin to be used in the process in 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
5 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,
10 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 ratio (mol/mol) of hydrogen to alkylaryl hydroxide contacted with the catalyst is preferably at
15 least 0.5, more preferably at least 1.0, most preferably at least 1.4. The hydrogenation treatment is 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.
20 Preferred catalysts are catalysts containing from 0.5 to 5 %wt of metal or a metal compound on a carrier. 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
25 Elements described in the Handbook of Chemistry and Physics, 63rd Edition. Most preferably, the metal present as metal or metal compound is palladium. It was found that such catalysts can give a high conversion.

Catalysts suitable for use in hydrogenating at least
30 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 (iv) 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

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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 hydrogenation, the hydrogenated product can be recycled in total or in part. If only part of the hydrogenated product is recycled, the desired fraction can be separated off in any way known to be suitable to someone skilled in the art.

C L A I M S

1. Process for the preparation of oxirane compounds,
which process comprises:

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

5 (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,

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

(iv) 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),

15 in which process the alkylaryl is an alkylaryl compound
comprising more than 1 alkyl substituent.

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
20 from 3 to 10 carbon atoms.

3. Process according to claim 1 or 2, in which process
the alkylaryl compound is an alkyl aryl compound
containing about 2 alkyl substituents.

25 4. Process according to claim 3, in which process the
alkylaryl compound is di(iso-propyl)benzene.

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 x 10⁵ 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 of process step (iv) is carried out at a temperature of from 180 to 330 °C, and a pressure of from 0.1 to 50 x 10⁵ N/m².