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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C07C 45/33, 29/50, 409/14, 27/12 | A1

(11) International Publication Number: WO 94/13613

(43) International Publication Date: 23 June 1994 (23.06.94)

(21) International Application Number: PCT/NL93/00259

(22) International Filing Date: 2 December 1993 (02.12.93)

(30) Priority Data:
9201101 16 December 1992 (16.12.92) BE

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(81) Designated States: BR, CA, JP, KR, PL, RU, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METHOD FOR THE CONTINUOUS PREPARATION OF A MIXTURE OF A CYCLOALKANONE, CYCLOALKANOL AND A CYCLOALKYLHYDROPEROXIDE

(57) Abstract

Method for the continuous preparation of a mixture of a cycloalkanone, a cycloalkanol and a cycloalkylhydroperoxide, according to which the corresponding cycloalkane is oxidized wherein the cyclic alkane has between 5 and 20 carbon atoms, in a continuous process, with the aid of an oxygen-containing gas, in the absence of a metal catalyst, at a temperature of between 130 and 200 °C, the oxidation being at least partly carried out in the presence of between 0.002 and 2 mmol of a phenolic compound per kg of reaction mixture (mmol/kg).

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METHOD FOR THE CONTINUOUS PREPARATION OF A MIXTURE OF A CYCLOALKANONE, CYCLOALKANOL AND A CYCLOALKYLHYDROPEROXIDE

The invention relates to a method for the continuous preparation of a mixture of a cycloalkanone, a cycloalkanol and a cycloalkylhydroperoxide, according to which a corresponding cycloalkane is oxidized wherein the cyclic alkane has between 5 and 20 carbon atoms, in a continuous process, with the aid of an oxygen-containing gas, in the absence of a metal catalyst, at a temperature of between 130 and 200°C.

Such a method for the preparation of a mixture of cyclohexanone, cyclohexanol and cyclohexylhydroperoxide in a continuous process is described in EP-A-0092867.

A drawback of this known method is that the selectivity of the oxidation reaction towards the desired products (cyclohexanone, cyclohexanol and cyclohexylhydroperoxide) is relatively low, as a result of which a significant amount of byproducts is formed.

The aim of this invention is to provide a method with which the selectivity of the cycloalkane oxidation reaction towards desired products is higher. In particular the aim of the invention is a method with which the selectivity towards cycloalkylhydroperoxide is higher.

This aim is achieved because the oxidation is at least partly carried out in the presence of between 0.002 and 2 mmole of a phenolic compound per kg of reaction mixture (mmol/kg).

It has been found that when the method according to the invention is used, the selectivity of the oxidation reaction towards a cycloalkanone, cycloalkanol and in particular towards cycloalkylhydroperoxide is higher,

without the rate being lower than when no phenolic compound is present.

In SU-A-686329 a method is disclosed for obtaining cyclododecylhydroperoxide by oxidation of cyclododecane in the presence of 0.01-30 wt.% of a phenolic compound. The experiments are conducted with 1 wt.% (1170 mmol/kg) phenol, 2.5 wt.% (230 mmol/kg) cresol and 0.2 wt.% (18 mmol/kg) resorcinol.
It is surprising that a significantly lower amount of phenolic compound than disclosed in these experiments has a favourably effect on the selectivity to cycloalkanone, cycloalkanol and cycloalkylhydroperoxide and more in particular to cyclohexanone, cyclohexanol and cyclohexylhydroperoxide.

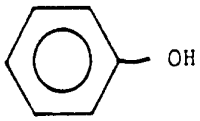
In an article in Kinetics and Catalysis USSR (1960, 1(1), 46-62) phenol and α-naphthol are mentioned and are used as inhibitors in the catalysed oxidation of n-decane. It is hence surprising that the oxidation reaction of a cycloalkane according to the invention is hardly slowed down by the addition of the phenolic compound.

The use of phenolic or dihydroxybenzene-like compounds during the oxidation of cyclohexane with the aim of increasing the selectivity is described in SU-A-197555. In contrast to the method according to the invention the oxidation reaction is catalysed with the aid of a metal catalyst at a temperature of between 200 and 250°C and results in a mixture of cyclohexanol and cyclohexanone. In addition, according to the examples of SU-A-197555 a large amount of phenolic compound is used per kg of reaction mixture (90 and 140 mmol/kg). It is hence surprising that the addition of small amounts of phenolic compound to an uncatalysed oxidation and at a lower temperature has a positive effect with respect to the selectivity at the same degree of conversion.

The use of a phenolic compound during the uncatalysed oxidation of cyclododecane is described in an

article in Petroleum Chemistry USSR (1964, 3 (4), 295-301). This article describes an investigation into the reaction mechanism of the oxidation of cyclododecane. The phenolic compound is added to a batch process after a portion of the cyclododecane has already oxidized. The article contains no indication that the addition of such a phenolic compound in a continuous process could result in an increase in the selectivity.

The phenolic compound contains one or more groups according to Formula (1)

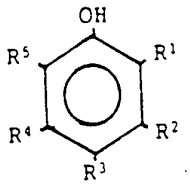


(1)

and is soluble in the cycloalkane under reaction conditions.

Such a phenolic compound is preferably an organic compound having a molecular weight of less than 1000 and having 1-5 aromatic rings.

A suitable group of phenolic compounds can be represented by Formula (2):



(2)

where R^1 through R^5 may, independently of one another, be an $-O-R^6$ group or an R^7 group, where R^6 and R^7 may, independently of one another, be H or organic groups having between 1 and 30 carbon atoms, whether or not substituted with ether, carbonyl, hydroxyl, amine, amide and ester groups,
and/or where R^1 and R^2 or R^2 and R^3 or R^3 and R^4 or R^4 and R^5 can together constitute an aliphatic or aromatic ring having 5, 6, 7, 8, 10 or 12 carbon atoms.

Examples of suitable phenolic compounds, whether or not substituted, are phenol, 2,6-ditertiary-butylphenol, 2,6-ditertiary-butyl-4-methylphenol,

m-cresol, bisphenol-A, biphenol, p-tertiary-butylphenol, 2-hydroxynaphthalene, 2,6-dimethylphenol, 2,4-ditertiary-butylphenol, 2,4,6-tritertiary-butylphenol, 2,4-dimethyl-6-tertiary-butylphenol, 1-hydroxynaphthalene, hydroquinone, pyrocatechol, resorcinol, p-phenoxyphenol and o-phenylphenol.

Preferably m-cresol, 2,4-ditertiary-butylphenol, 2,6-ditertiary-butylphenol and phenol are used.

Mixtures of the aforementioned phenolic compounds may also be used. Mixtures of phenolic compounds that are prepared during the preparation of a specific phenolic compound can for example be used advantageously because further purification is then not required.

The concentration of phenolic compound is generally smaller than 2 mmol/kg, preferably smaller than 1 mmol/kg and in particular smaller than 0.9 mmol/kg. The concentration of phenolic compound is generally greater than 0.002 mmol/kg, preferably greater than 0.01 mmol/kg and in particular greater than 0.05 mmol/kg. The invention also relates to a process wherein the concentration of phenolic compound is less than 0.01 wt.% relative to the reactionmixture. The above mentioned concentrations are the concentrations based on the amount of phenolic compound fed to the reaction mixture. The actual average concentration during the oxidation reaction shall be lower than the above mentioned concentration because part of the phenolic compound will disappear during the oxidation.

In general the invention relates to the oxidation of cyclic alkanes having between 5 and 20 carbon atoms. In particular the invention relates to the oxidation of cycloalkanes having between 6 and 12 carbon atoms. Examples of suitable cyclic alkanes are cyclohexane, cyclooctane and cyclododecane. In particular the invention relates to the oxidation of cyclohexane because the oxidation products cyclohexanol, cyclohexanone and cyclohexylhydroperoxide, separately or as a mixture, are used for many applications. More in particular the

invention relates to the oxidation of cyclohexane wherein phenol is used as phenolic compound because phenol is easily obtainable. Cyclohexylhydroperoxide can for example be used as an oxidizer in the preparation of alkane epoxide from a corresponding alkene. The cyclohexylhydroperoxide in the mixture can also be decomposed to obtain a mixture of cyclohexanone and cyclohexanol. This so-called K/A mixture is a product that is used as such for example in the preparation of adipic acid. The decomposition of the cyclohexylhydroperoxide generally takes place after cooling of the mixture, under the influence of a transition-metal catalyst such as cobalt or chromium. Preferably the decomposition of cyclohexylhydroperoxide is carried out with the aid of a method described in EP-A-004105 or EP-A-092867.

The temperature at which the oxidation is carried out is generally between 130 and 200°C. The temperature is preferably higher than 160°C. The temperature is preferably lower than 190°C.

The pressure at which the oxidation is carried out generally lies between 0.1 and 5 MPa. The pressure is preferably higher than 0.4 MPa. The pressure is preferably lower than 2.5 MPa. In the case that cyclohexane is oxidized the pressure will generally be higher than 0.6 MPa and lower than 2.0 MPa.

The oxidation is carried out in continuous mode and preferably takes place in a system of reactors connected in series or in a compartmentalized tube reactor. The reaction is generally carried out autothermally or by controlling the temperature. The temperature is generally controlled by discharging heat of reaction via a stream of gas, via intermediate cooling or via other methods known to a person skilled in the art. In order to ensure that transition metals (which promote the decomposition of cycloalkylhydroperoxide) do not make their way into the mixture to be oxidized, reactors with an inert inside wall are preferably chosen. To this end

use can for example be made of reactors having an inside wall of passivated steel, aluminium, tantalum, glass or enamel. This is particularly important in the case of small production capacities, in which case the wall surface versus the liquid volume is disadvantageous. In the case of large capacities separate inertisation of the wall is not absolutely necessary. It will be clear that if a negligible amount of metal ions make their way into the oxidation mixture, which have no essential influence on the reaction, then, within the framework of the present invention, one can speak of an uncatalysed cycloalkane oxidation. In contrast with the uncatalysed cycloalkane oxidation, the catalysed oxidation - which generally involves the addition of a metal such as cobalt and chromium - yields a reaction mixture with relatively little cycloalkylhydroperoxide relative to cycloalkanone + cycloalkanol.

Generally the product of the uncatalysed oxidation of cyclohexane comprises at least an amount of cyclohexylhydroperoxide in wt.% that is comparable with the amount of cyclohexanol + cyclohexanone in wt.%. Often the mixture contains more than 2x as much cyclohexylhydroperoxide as cyclohexanol + cyclohexanone after the reaction. In contrast with this, the catalysed oxidation yields a mixture that contains less than 50% cyclohexylhydroperoxide relative to the amount of cyclohexanol + cyclohexanone in wt.%. Often this is even less than 40% peroxide relative to the amount of cyclohexanol + cyclohexanone in wt.%.

The concentration of cycloalkylhydroperoxide in the reaction mixture as it leaves the (last) oxidation reactor is generally between 0.1 and 8.0 wt.%. The cycloalkanone concentration of this mixture is generally between 0.1 and 10 wt.%. The cycloalkanol concentration of this mixture is generally between 0.1 and 15 wt.%. The degree of conversion of cycloalkane relative to this reaction mixture is generally between 0.5 and 25 %. The

degree of conversion of cyclohexane is generally between 2 and 6%.

In the case of a series of connected reactors or a compartmentalized tube reactor the phenolic compound can be supplied separately to each reactor (or compartment). It has been found that it is preferable if the concentration of phenolic compound in the first reactors is relatively lower than the concentration in the last reactor or reactors. It may also be advantageous to supply a phenolic compound to one or more reactors only and not to all of the reactors.

Oxygen as such, air, with increased or reduced oxygen content, or oxygen mixed with nitrogen or another inert gas can be chosen as the oxygen-containing gas. Air is preferable, but the air can be mixed with extra inert gas to prevent the risk of explosions. In general, in order to prevent the risk of explosion, so much oxygen-containing gas is fed to the reactors, in such a manner, that the concentration of oxygen in the offgas remains below the explosion limit. The supplied amount of oxygen (calculated as pure oxygen) is generally between 0.1 and 50 Nl per l of cycloalkane. This amount is dependent on the reaction rate and oxygen is preferably present in a small excess but this is not critical because the amount of oxygen is generally not limiting.

The invention will be further elucidated with reference to the following non-limiting examples.

Example I

Into a double-walled glass reactor (volume equal to a liquid contents consisting of 270 g of cyclododecane (of 170°C)) equipped with 4 baffles, a turbine mixer, coolers, a thermometer and two feed pipes melted cyclododecane was fed through one feed pipe, with the aid of a pump, at a rate of 732 g/h and through the other pipe a solution of the additive in melted cyclododecane, with the aid of a second pump, at a rate of 90 g/h. The

residence time was hence 20 minutes. 2,6-ditertiary-butylphenol was used as the additive. The feed rate of the additive was controlled so that the concentration in the reactor was 0.96 mmol/kg.

The product was drained from the reactor via an overflow pipe with the aid of a control valve. The reaction temperature was 170°C. The speed of the stirrer was 2000 min^{-1}. Air was supplied at the bottom of the reactor via a gas distribution system at a rate of 30 Nl/h. Analyses of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 73.4, 4.4 and 15.2 mol%, respectively, (total 93 mol%) at a degree of conversion of cyclododecane of 4.4 mol%.

Example II

Example I was repeated. The feed rate of the additive was controlled so that the concentration in the reactor was 0.094 mmol/kg. Analyses of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 61.6, 12.1 and 18.4 mol%, respectively, (total 92.1 mol%) at a degree of conversion of cyclododecane of 4.4 mol%.

Example III

Example I was repeated. The feed rate of the additive was controlled so that the concentration in the reactor was 0.48 mmol/kg. Analyses of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 68.0, 4.3 and 18.1 mol%, respectively, (total 90.4 mol%) at a degree of conversion of cyclododecane of 5.0 mol%.

Comparative experiments A + B

Example I was repeated but no additive was added. Analyses of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 54.6, 13.3 and 18.8 mol%, respectively, at a degree of conversion of cyclododecane of 4.67 mol%. This experiment was repeated. Analyses of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 51.7, 15.3 and 19.5 mol%, respectively, (total 86.5 mol%) at a degree of conversion of cyclododecane of 4.7 mol%.

Example IV

Example I was repeated only now phenol was used as the additive. The feed rate of the additive was controlled so that the concentration in the reactor was 1.0 mmol/kg. Analyses of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 59.6, 14.8 and 18.7 mol%, respectively, (total 93.1 mol%) at a degree of conversion of cyclododecane of 4.4 mol%.

Example V

Example IV was repeated only now the feed rate of the additive was controlled so that the concentration in the reactor was 0.8 mmol/kg and the cyclododecane feed was lowered in such an amount that the degree of conversion of cyclododecane was 4.7 mol%. Analyses of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 58.0, 12.5 and 17.8 mol%, respectively, (total 92.0 mol%).

Example VI

Example V was repeated only now the feed rate of the additive was controlled so that the concentration in the reactor was 0.48 mmol/kg. and the cyclododecane conversion was 5.1 mol%. Analysis of the effluent of the reactor showed that the selectivity towards cyclododecyl-hydroperoxide, cyclododecanol and cyclododecanone was 61.4, 6.3 and 15.3 mol%, respectively, (total 91.1 mol%).

Comparative experiment C

Example VI was repeated but no additive was added. The degree of conversion of cyclododecane was 5.1 mol% as in Example VI. Analysis of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanone and cyclododecanol was 48.6, 11.7 and 17.4 mol%, respectively (total 77.6 mol%).

Example VII

Example I was repeated only now 2,6-ditertiary-butyl-4-methylphenol was used as the additive. The feed rate of the additive was controlled so that the concentration in the reactor was 0.94 mmol/kg. Analysis of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 59.2, 13.2 and 18.5 mol%, respectively, (total 91.9 mol%) at a degree of conversion of cyclododecane of 4.5 mol%.

Example VIII

Example VII was repeated. The feed rate of the additive was controlled so that the concentration in the reactor was 1.9 mmol/kg. Analysis of the effluent of the reactor showed that the selectivity towards cyclododecyl-hydroperoxide, cyclododecanol and cyclododecanone was 63.1, 8.6 and 17.0 mol%, respectively, (total 88.7 mol%) at a degree of conversion of cyclododecane of 4.6 mol%.

Example IX

Example I was repeated only now m-cresol was used as the additive. The feed rate of the additive was controlled so that the concentration in the reactor was 1.1 mmol/kg. Analyses of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 65.0, 8.1 and 18.5, respectively, (total 91.6 mol%) at a degree of conversion of cyclododecane of 4.3 mol%.

Example X

Example I was repeated only now 4-methoxyphenol was used as the additive. The feed rate of the additive was controlled so that the concentration in the reactor was 1.0 mmol/kg. Analysis of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 60.7, 13.2 and 17.8 mol%, respectively, (total 91.7 mol%) at a degree of conversion of cyclododecane of 4.4 mol%.

Example XI

Example I was repeated only now 2,4,6-tritertiary-butylphenol was used as the additive. The feed rate of the additive was controlled so that the concentration in the reactor was 1.0 mmol/kg. Analyses of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 65.7, 9.9 and 16.4 mol%, respectively, (total 92.0 mol%) at a degree of conversion of cyclododecane of 4.5 mol%.

Example XII

Example I was repeated only now 2,4-ditertiary-butylphenol was used as the additive. The feed rate of the additive was controlled so that the concentration in the

reactor was 1.1 mmol/kg. Analysis of the effluent of the reactor showed that the selectivity towards cyclododecylhydroperoxide, cyclododecanol and cyclododecanone was 67.4, 5.4 and 18.3 mol%, respectively, (total 91.1 mol%) at a degree of conversion of cyclododecane of 4.5 mol%.

Example XIII

An experiment with cyclohexane was carried out in a setup equipped for tests under pressure similar to the setup described in Example I. 2,6-dibutyl-tertiary-4-methylphenol was used as the additive. The feed rate of the additive was chosen so that the concentration in the reactor was 1.25 mmol/kg. Analyses of the effluent of the reactor showed that the selectivity towards cyclohexylhydroperoxide, cyclohexanol and cyclohexanone was 92.3 mol% at a degree of conversion of cyclohexane of 3.5 mol%.

Example XIV

Example XII was repeated only now phenol was used as the additive. The feed rate of the additive was chosen so that the concentration in the reactor was 0.6 mmol/kg. Analyses of the effluent of the reactor showed that the selectivity towards cyclohexylhydroperoxide, cyclohexanol and cyclohexanone was 91.5 mol% at a degree of conversion of cyclohexane of 3.4 mol%.

Example XV

Example XIV was repeated. The phenol concentration was 0.3 mmol/kg and the total selectivity was 91.9 mol% at a degree of conversion of cyclohexane of 3.5 mol%.

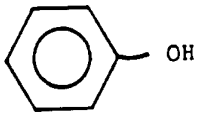
Comparative experiment D

Example XII was repeated only now without the addition of an additive. Analyses of the effluent of the reactor showed that the selectivity towards cyclohexylhydroperoxide, cyclohexanol and cyclohexanone was 89.4 mol% at a degree of conversion of cyclohexane of 3.4 mol%.

C L A I M S

1. Method for the continuous preparation of a mixture of a cycloalkanone, a cycloalkanol and a cycloalkylhydroperoxide, according to which the corresponding cycloalkane is oxidized wherein the cyclic alkane has between 5 and 20 carbon atoms, in a continuous process, with the aid of an oxygen-containing gas, in the absence of a metal catalyst, at a temperature of between 130 and 200°C, characterised in that the oxidation is at least partly carried out in the presence of between 0.002 and 2 mmol of a phenolic compound per kg of reaction mixture (mmol/kg).

2. Method according to claim 1, characterised in that the phenolic compound contains one or more groups according to Formula (1)

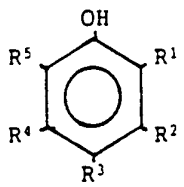


(1)

and is soluble in the cycloalkane under reaction conditions.

3. Method according to claim 2, characterised in that the phenolic compound has a molecular weight of less than 1000 and has 1-5 aromatic rings.

4. Method according to claim 3, characterised in that the phenolic compound is represented by Formula (2):



(2)

where R^1 through R^5 may, independently of one another, be an $-O-R^6$ group or an R^7 group, where R^6 and R^7 may, independently of one another, be H or organic groups having between 1 and 30 carbon atoms, whether or not substituted with ether, carbonyl, hydroxyl, amine,

amide and ester groups, and/or where R^1 and R^2 or R^2 and R^3 or R^3 and R^4 or R^4 and R^5 may together constitute an aliphatic or aromatic ring having 5, 6, 7, 8, 10 or 12 carbon atoms.

5. Method according to any one of claims 1-4, characterised in that the concentration of phenolic compound in the reaction mixture lies between 0.01 and 1 mmol/kg.

6. Method according to any one of claims 1-5, characterised in that the concentration of phenolic compound is smaller than 0.9 mmol/kg.

7. Method according to any one of claims 1-6, characterised in that the concentration of phenolic compound is smaller than 0.01 wt.%.

8. Method according to any one of claims 1-7, characterised in that the cyclic alkane has between 5 and 20 carbon atoms.

9. Method according to claim 8, characterised in that the cyclic alkane is cyclohexane.

10. Method according to claim 9, characterised in that the phenolic compound is phenol.

11. Method according to any one of claims 1-10, characterised in that the temperature during the oxidation lies between 160 and 190°C.

12. Method according to any one of claims 1-11, characterised in that the pressure during the oxidation lies between 0.1 and 5 MPa.

13. Method as substantially described in the introduction and the examples.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/NL 93/00259

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07C45/33 C07C29/50 C07C409/14 C07C27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 8307, Derwent Publications Ltd., London, GB; AN 16790K & SU,A,686 329 (LADYGIN B YA) 7 May 1982 cited in the application see abstract ---	1-12
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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