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(71) Applicants *(for all designated States except US)*: DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: SIELCKEN, Otto, Erik [NL/NL]; Vliekstraat 4, NL-6136 BG Sittard (NL). HAASEN, Nicolaas, Franciscus [NL/NL]; Lintjeshaag 20, NL-6141 MB Sittard (NL).

(74) Agent: CRAMWINCKEL, Michiel; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).

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(54) Title: PROCESS FOR THE PREPARATION OF PENTENOIC ACID OR PENTENOATE ESTER

(57) Abstract

Process for the preparation of pentenoic acid or a pentenoate ester starting from water or alcohol and a mixture of pentenoic acid chloride, chlorobutene and a palladium catalyst, wherein the mixture of pentenoic acid chloride, chlorobutene and the palladium catalyst is contacted with water or alcohol, the molar ratio of water or alcohol to pentenoic acid chloride is maintained lower than 1.2 and the molar ratio of chlorobutene to palladium is maintained higher than 10 during at least a substantial portion of the preparation.

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PROCESS FOR THE PREPARATION OF PENTENOIC ACID OR PENTENOATE ESTER

The invention relates to a process for the preparation of pentenoic acid or a pentenoate ester starting from water or alcohol and a mixture of pentenoic acid chloride, chlorobutene and a palladium catalyst.

Such a process is known from US-A-5288903. US-A-5288903 states that pentenoic acid is prepared by first preparing pentenoic acid chloride by carbonylation of chlorobutene with carbon monoxide in the presence of a palladium catalyst. After separation of carbon monoxide a mixture of pentenoic acid chloride, chlorobutene and the palladium catalyst is obtained. The palladium catalyst is first separated, before pentenoic acid chloride is converted with water to pentenoic acid (so-called hydrolysis) in a next step.

A disadvantage of this known process is that several separation steps between the two reaction steps are required. For instance, the palladium catalyst must be separated because it is unstable in the presence of water under the reaction conditions of the process as described in US-A-5288903. Decomposition of the catalyst results in a loss of catalyst activity and consequently in a lower yield of the pentenoic acid. It is therefore important that the catalyst activity remains high for a longer period. Another disadvantage of this known process is that the series of separation steps lengthens production time and compels the purchase of additional equipment for performing the separation steps. Consequently, manufacturing costs are significantly increased. A further drawback of this process is that during the required separation of the catalyst

pentenoic acid chloride is lost because of its chemically and thermally unstable character, which in turn lowers the pentenoic acid yield.

The aim of this invention is a process for the preparation of pentenoic acid or a pentenoate ester in which the decomposition of the palladium catalyst is at least substantially avoided and the need for additional separation steps during preparation of the pentenoic acid or pentenoate ester is obviated, so that a more simple process is provided.

This aim is achieved in that the mixture of pentenoic acid chloride, chlorobutene and the palladium catalyst is contacted with water or an alcohol, in which the molar ratio of water or an alcohol to pentenoic acid chloride is maintained lower than 1.2 and the molar ratio of chlorobutene to palladium is maintained higher than 10 during at least a substantial portion of the preparation.

It has been found that with the process according to the invention pentenoic acid or pentenoate ester can be prepared in the presence of the palladium catalyst without the latter being subject to degradation.

An advantage of the process according to the invention is that catalyst separation from the unstable pentenoic acid chloride is no longer necessary. Another advantage is that the relatively stable pentenoic acid or pentenoate ester end product can be separated from the reaction mixture by distillation easier in comparison to the distillation of the unstable pentenoic acid chloride as described above.

The mixture of pentenoic acid chloride, chlorobutene, water or alcohol and the palladium catalyst is preferably obtained by carbonylation of chlorobutene with carbon monoxide (CO) in the presence of a palladium catalyst as for instance described in

US-A-3338961. The carbonylation of chlorobutene is represented by equation (1):

$$\text{chlorobutene} + CO \xrightarrow{Pd\ (cat)} \text{pentenoic acid chloride} \quad (1)$$

When pentenoic acid chloride is reacted with water or alcohol to form pentenoic acid (hydrolysis) or pentenoate ester (so-called alcoholysis), respectively, hydrogen chloride is released. This reaction is represented by equation (2):

$$\text{Pentenoic acid chloride} + ROH \rightarrow \text{R-pentenoate} + HCl \quad (2)$$

(R = H or alkyl)

Chlorobutene is generally obtained by reaction of hydrogen chloride with butadiene as described for instance in US-A-3055954 and represented by equation (3):

$$HCl + \text{butadiene} \rightarrow \text{chlorobutene} \quad (3)$$

During at least a substantial portion of the preparation the molar ratio of water or alcohol to pentenoic acid chloride in the reaction mixture is preferably maintained in a range of not more than 1.2 and not less than 0.1, and more preferably in a range between 0.8 and 1.1. Most preferably, the molar ratio chosen will not be significantly lower or higher than 1. A larger excess of pentenoic acid chloride relative to water or alcohol is generally not advantageous, because the excess pentenoic acid chloride must be removed from the mixture of pentenoic acid or pentenoate ester, chlorobutene and pentenoic acid chloride. At a large excess of water or alcohol relative to pentenoic acid chloride, the palladium

catalyst becomes less stable.

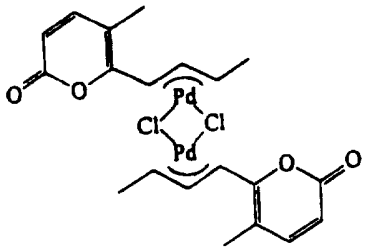
With "during at least a substatial portion of the preparation" is preferably meant more than 80% of the reaction time in case of a batch preparation process and more than 80% of the residence time in case of a continuous process.

The mixture of pentenoic acid chloride, chlorobutene and the palladium catalyst may still contain carbon monoxide that has been used in the preparation of this mixture for the carbonylation of chlorobutene according to equation (1). In the process according to the invention the reaction of pentenoic acid chloride with water or alcohol according to equation (2) can be carried out in the presence or absence of carbon monoxide. In the process as described in US-A-5288903 carbon monoxide has to be separated from the reaction mixture containing pentenoic acid chloride in order to prevent degradation of the product. The carbon monoxide can be separated from the mixture of pentenoic acid chloride, chlorobutene and the palladium catalyst by known processes. An obvious method is heating of the reaction mixture at low pressure. The carbon monoxide separation means an extra separation step. Surprisingly, it has been found that in the process according to the invention the hydrolysis or alcoholysis of pentenoic acid chloride can also be carried out in the presence of carbon monoxide, which is most advantageous if for example the starting mixture is obtained by carbonylation of chlorobutene according to equation (1).

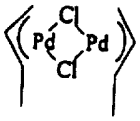
After performing the reaction set forth in equation (2), which yields a reaction mixture that is rich in pentenoic acid or pentenoate ester, the pentenoic acid or pentenoate ester can be recovered using any separation process known to one skilled in the art. Examples of suitable separation techniques are

extraction, crystallization and, preferably, distillation. The remaining mixture of chlorobutene, hydrogen chloride, optionally carbon monoxide, any non-converted pentenoic acid chloride and the palladium catalyst can advantageously be returned to the reaction and be reused in the process according to the invention.

The palladium catalyst is at least partly present in the form of π-allyl-palladium complexes. A very suitable palladium catalyst for the present process is the π-allyl-palladium complex as described in the above mentioned US-A-5288903, with the general formula:



This complex is an effective catalyst and is solid in the process according to the invention, and it can thus easily be separated from pentenoic acid or pentenoate and recycled to the reaction. Another example of these palladium complexes is a π-crotyl-palladium compound with the general formula:



These π-allyl-palladium complexes can be introduced as such into the reaction mixture or it can be formed in situ starting from zero-valent, divalent or tetravalent palladium components by reaction with chlorobutene, water or alcohol, and carbon monoxide.

Examples of such palladium components are metallic palladium; palladium halides; palladium nitrates; palladium carboxylates, for instance palladium acetate; palladium sulphonates; organo-palladium complexes, for instance palladium acetyl acetonate and palladium-bisbenzylideneacetone.

The palladium content in the reaction mixture may vary from 1 to 100,000 ppm Pd. Preferably, the palladium content is between 100 and 20,000 ppm.

Chlorobutene, used in the process according to the invention, is usually a mixture of the cis-1-chloro-2-butene, trans-1-chloro-2-butene and 3-chloro-1-butene isomers. In the above-mentioned process chlorobutene is used as solvent in the preparation of pentenoic acid and pentenoate ester.

The molar ratio of chlorobutene to palladium in the reaction mixture is higher than 10 during at least a substantial portion of the preparation. It has been found that the excess chlorobutene has a stabilizing effect on the π-allyl-palladium catalyst complex.

In the process according to the invention chlorobutene, pentenoic acid or pentenoate ester and high-boiling byproducts, which may be formed in the process according to the invention, can serve as solvent, so that as a rule the addition of an additional solvent is not necessary. If an additional solvent is added, an inert solvent is suitable as additional solvent. Examples of such solvents are sulphoxides and sulphones, for instance dimethyl sulphoxide and diisopropyl sulphone; aromatic solvents, for instance benzene, toluene and xylene; methyl esters, for instance methyl acetate and methyl valereate; ketones, for instance acetone and methyl isobutyl ketone; and mixtures of these solvents.

The alcohol is for instance an organic

alcohol with 1 to 20 carbon atoms and with one or more OH groups per molecule. The organic compound may be an aliphatic, cycloaliphatic or aromatic compound. Examples of suitable alcohols are phenol, cresol, tert-butyl catechol or cyclohexanol. The alcohol is preferably an aliphatic alcohol of which the aliphatic group is a linear or branched alkyl group. The alkyl group preferably has 1 to 6 carbon atoms. These aliphatic alcohols may be alkanols, represented by the formula ROH, examples being methanol, ethanol, propanol, isopropanol, butanol, tert-butanol, pentanol, hexanol and crotyl alcohol. Use can also be made of substituted alcohols, for instance ether-substituted alcohols such as the methyl ether of ethylene glycol. Most preferably use is made of methanol, ethanol or propanol, because the corresponding pentenoate esters can be readily isolated.

The temperature of the hydrolysis or alcoholysis is generally between 0°C and 200°C, for the hydrolysis preferably between 50°C and 180°C and for the alcoholysis preferably between 50°C and 130°C.

The pressure applied during the hydrolysis or alcoholysis may be between 0,1 MPa and 5 MPa.

The process according to this embodiment of the invention is preferably carried out continuously.

A preferred embodiment of the invention is a process in which pentenoic acid chloride is formed in situ by carbonylation of chlorobutene with carbon monoxide in the presence of the palladium catalyst according to reaction (1). In this embodiment pentenoic acid or pentenoate ester can be prepared in a single process step starting from chlorobutene. This means that the reactions (1) and (2) take place simultaneously in the reaction mixture.

In this embodiment of the invention chlorobutene serves both as solvent and as substrate.

The reaction temperature is generally between 25°C and 200°C and preferably between 80°C and 160°C.

The pressure applied during the reaction is preferably between 3 MPa and 40 MPa.

If the molar ratio of water or alcohol to pentenoic acid chloride is lower than 1 in this embodiment, the remaining mixture may still contain pentenoic acid chloride. This amount of pentenoic acid chloride can be separated from the reaction mixture and be reused in the process according to the invention. However, if the amount of remaining pentenoic acid chloride is small, the pentenoic acid chloride is preferably converted to pentenoic acid or pentenoate ester in a separate hydrolysis or alcoholysis step, respectively, without requiring separation of the pentenoic acid chloride from the reaction mixture. Generally such a separate step takes place at a lower temperature and pressure. Such an additional hydrolysis or alcoholysis is advantageous because it is difficult to separate the unstable pentenoic acid chloride from the reaction mixture, for instance by distillation. The temperature of this additional hydrolysis or alcoholysis may be between 0° and 200°C and is dependent of the boiling point of water or the alcohol at the pressure used. The temperature for the hydrolysis is preferably between 50°C and 180°C, and for the alcoholysis preferably between 50 and 130°C. At a higher temperature the palladium catalyst is increasingly subject to degradation. The pressure of this additional hydrolysis or alcoholysis may be between 0.1 MPa and 5 MPa.

The process according to this embodiment of the invention is preferably carried out continuously.

The process according to the invention can be applied most advantageously, and most preferably, if chlorobutene is formed in situ by chlorination of

butadiene with hydrogen chloride according to reaction (3). In this embodiment pentenoic acid or a pentenoate ester can be prepared from butadiene in one single process step without the need for product separation after every reaction step, so that a higher yield of pentenoic acid or pentenoate ester can be obtained using a simple process. This means that the reactions (1), (2) and (3) take place simultaneously in the reactor.

The invention therefore also relates to a process for the preparation of pentenoic acid or pentenoate ester starting from butadiene in which butadiene is contacted with carbon monoxide, an alcohol or water in the presence of the palladium catalyst and chlorobutene, the molar ratio of water or alcohol to pentenoic acid chloride is maintained lower than 1.2 and the molar ratio of chlorobutene to palladium is maintained higher than 10 during at least a substantial portion of the preparation.

Another advantage of the above embodiment is that, from an investment point of view, the preparation of pentenoic acid or pentenoate ester is more attractive economically than a process comprising several reaction steps. In addition, it has surprisingly been found that almost no reaction of chlorobutene with water or alcohol to undesired byproduct takes place.

The butadiene of the present process can be used in pure form, or in admixture with other aliphatic compounds. An example of such mixture is technical grade butadiene which can comprise butadiene plus 1-butene, 2-butene and/or isobutene and inhibitors such as tert-butyl catechol.

In this embodiment of the invention chlorobutene serves as solvent, as substrate and as reaction product. Pentenoic acid chloride serves as a

source of hydrogen chloride. The hydrogen chloride is generated in situ. In principle, no hydrogen chloride is added. In a commercial process there will always be small hydrogen chloride losses, which can be compensated by hydrogen chloride addition.

If pentenoic acid chloride is still present in the reaction mixture obtained with this embodiment, the measures as described above can be applied.

Unless indicated otherwise, the reaction conditions for this embodiment are the same as the reaction conditions as indicated above for the hydrolysis or alcoholysis.

The carbon monoxide can be used in its pure form or diluted with an inert gas, for instance nitrogen, rare gases or carbon dioxide. As a rule, more than 5% H_2 is undesirable, as this may cause hydrogenation of butadiene under the carbonylation conditions. The CO content is not critical as long as at least a stoichiometric amount of CO relative to butadiene is added to the carbonylation reaction.

From EP-A-648731 it is known to prepare pentenoic acid starting from butadiene by carbonylation with carbon monoxide and water in the presence of chlorobutene and a π-crotyl-palladium complex. Pentenoic acid chloride is not formed in this known process. Applicant has further found that the palladium catalyst is unstable and precipitates if one wants to prepare the pentenoate ester under the conditions as described in EP-A-648731.

In this embodiment of the process according to the invention, the molar ratio of the water or the alcohol to butadiene in the reaction mixture is preferably lower than 1 or equal to 1. More preferably, water or alcohol and butadiene are added to the reaction mixture in such amounts that a stoechiometric amount is achieved. As is evident from the above

reaction scheme, hydrogen chloride is released in the reaction between pentenoic acid chloride and water or alcohol. In the state-of-the-art process this hydrogen chloride may cause the formation of many byproducts, such as alkyl chlorides, as a consequence of chlorination of olefinically unsaturated compounds, other than butadiene, present. These side reactions also result in chlorine losses. By adding such an amount of water or alcohol and butadiene to the reactor that the molar ratio is lower than 1 or equal to 1, it proves to be possible to restrict these side reactions.

The process according to this preferred embodiment is preferably carried out semi-continuously or continuously. By introducing, for instance, chlorobutene, carbon monoxide and the palladium catalyst into the reactor once only, at the start-up of the reaction, and supplying water or alcohol and butadiene after a temperature and pressure increase, the reaction can be carried out entirely continuously. Butadiene and water or alcohol can be added to the reaction mixture continuously or intermittently. The flow leaving the reactor contains pentenoic acid or pentenoate ester, chlorobutene, butadiene, palladium catalyst, hydrogen chloride, carbon monoxide and optionally pentenoic acid chloride. Pentenoic acid or pentenoate ester are separated from this mixture and chlorobutene, butadiene, hydrogen chloride, carbon monoxide and the palladium catalyst are recycled to the reactor.

In a commercial process the reaction is preferably carried out continuously. If pentenoic acid or pentenoate ester is prepared starting from butadiene, a continuous process, as explained above, is particularly advantageous. In a continuous process butadiene and water or alcohol will be added to the reaction mixture in such an amount that at least an

equimolar amount of butadiene, relative to water or alcohol, is present as described above. An example of such an embodiment is to add fresh water or alcohol and butadiene in an equimolar ratio and carbon monoxide according to the process of the invention to a continuously stirred tank reactor (CSTR) or in a series of two or more of these reactors or in a plug flow reactor (PFR) and to recycle the palladium-catalyst, hydrogen chloride and chlorobutene.

The various embodiments of the process according to the method according to the invention are represented in Figures 1 through 5. Figures 1 through 5 will be explained for the preparation of pentenoic acid or pentenoate ester. The separation step in the figures 1 through 5 may contain several separation steps but is represented as one single step for ease of survey. Some recycling streams are not represented for the same reason.

In Figure 1, chlorobutene is added via flow 1 to reactor A, in which the catalyst and carbon monoxide are present. (In reactor A chlorobutene is carbonylated with carbon monoxide to form pentenoic acid chloride according to reaction (1)). Via flow 2 the mixture of pentenoic acid chloride, chlorobutene, the palladium catalyst and carbon monoxide is passed to reactor B. Via flow 3 water or alcohol is introduced into reactor B, where the hydrolysis or alcoholysis of pentenoic acid chloride to pentenoic acid or pentenoate ester takes place. Via flow 4 the mixture of chlorobutene, the palladium catalyst, hydrogen chloride, carbon monoxide, (any non-converted pentenoic acid chloride) and pentenoic acid or pentenoate ester is passed to separation step C. In separation step C the pentenoic acid or pentenoate ester is separated from the mixture. The mixture of chlorobutene, the palladium catalyst, hydrogen chloride, any non-converted pentenoic acid

chloride, and carbon monoxide is discharged via flow 5. The pentenoic acid or pentenoate ester is discharged via flow 6.

In Figures 2 and 3 chlorobutene is added via flow 7 to reactor D, in which the catalyst and carbon monoxide are present, via flow 7 and water or alcohol via flow 8. (In reactor D pentenoic acid or pentenoate ester is prepared from chlorobutene in one reaction step). If the mixture leaving reactor D (flow 12) contains non-converted pentenoic acid chloride, this pentenoic acid chloride can be converted with water or alcohol (via flow 13) to pentenoic acid or pentenoate ester in the hydrolysis or alcoholysis step E. Via flow 9 or flow 14 the mixture of chlorobutene, palladium catalyst, hydrogen chloride, carbon monoxide and pentenoic acid or pentenoate ester is passed to separation step F. The mixture of chlorobutene, palladium catalyst, hydrogen chloride and carbon monoxide is discharged via flow 11 or flow 16. The pentenoic acid or pentenoate ester is discharged via flow 10 or flow 15.

In Figures 4 and 5 butadiene is fed via flow 17 to reactor G, in which the palladium catalyst, carbon monoxide and chlorobutene are present, and water or alcohol is fed via flow 18. Any non-converted pentenoic acid chloride is converted via flow 22 to pentenoic acid or pentenoate ester via flow 22 in the hydrolysis or alcoholysis step I with water or alcohol via flow 23. Via flow 19 or flow 24 the mixture of chlorobutene, butadiene, palladium catalyst, hydrogen chloride, carbon monoxide and pentenoic acid or pentenoate ester is sent to separation step H. The pentenoic acid or pentenoate ester is discharged via 20 or 25. The mixture of chlorobutene, butadiene, palladium catalyst, hydrogen chloride and carbon monoxide is recycled to reactor G via flow 21 or flow

26.

Pentenoic acid or pentenoate ester can be, for example, advantageously used as an intermediate compound in the preparation of ε-caprolactam and adipic acid, raw materials for the preparation of nylon-6 and nylon-6,6, respectively.

The invention will be further elucidated by means of the following, non-restrictive examples.

Example I

A 150 ml Parr autoclave was charged with 1.27 mmoles of π-crotyl-palladium complex and 648 mmoles of chlorobutene. The reactor was closed and purged three times with CO, after which the pressure was raised to 2 MPa. Subsequently, 97 mmoles of butadiene were pumped into the reactor in 3 minutes. Then the temperature was raised to 120°C and the CO pressure to 7.5 MPa, after which 417 mmoles of butadiene and 380 mmoles of methanol were introduced in four hours into the reactor by means of a continuous feed using two pumps (104 mmol butadiene/hour and 95 mmol methanol/hour). After 4.5 hours the reactor was cooled to room temperature, following which 400 mmoles of methanol were added. The reaction mixture was analyzed by means of gas chromatographic analysis. It was found to contain: 145 mmoles of butadiene, 304 mmoles of chlorobutene and 639 mmoles of methyl-3-pentenoate.

The reaction mixture was then brought under a nitrogen atmosphere in a vacuum distillation set-up, where all volatile components were removed at 100°C and 1 mm Hg. The homogeneous residue (5.5 g) was then returned to the autoclave under nitrogen. Then 665 mmoles of chlorobutene were introduced into the autoclave under nitrogen, after which a CO purge was applied and the pressure was brought at 2 MPa. Subsequently, in 3 minutes 97 mmoles of butadiene were

pumped into the autoclave and the temperature was raised to 120°C and the pressure was brought at 7.5 MPa CO. The above procedure was repeated, with 460 mmoles of butadiene and 400 mmoles of methanol being metered in 4 hours. The reaction was ended after 4.5 hours as described above. The reaction mixture contained: 12 mole % butadiene, 26 mole % chlorobutene and 57 mole % methyl-3-pentenoate.

Example II

Example I was repeated with 1.73 mmoles of π-crotyl-palladium complex and 446 mmoles of chlorobutene. Initially, 66 mmoles of butadiene were pumped into the reactor, following which 588 mmoles of butadiene and 581 moles of methanol were fed in 4 hours at 120°C and 7.5 MPa CO. After 4.5 hours' reaction the reaction mixture contained:
111 mmoles of butadiene, 580 mmoles of methyl-3-pentenoate, 191 mmoles of chlorobutene and 95 mmoles of 3-pentenoic acid chloride.

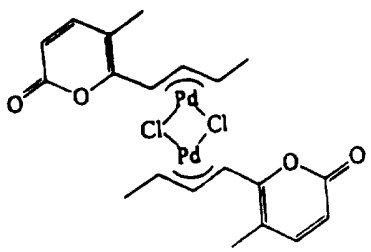
Comparative Experiment A

A 50 ml Parr autoclave was charged with 0.75 mmoles of π-crotyl-palladium complex, 9.1 mmoles of chlorobutene, 96.7 mmoles of methanol and 200.3 mmoles of methyl-3-pentenoate.

The reactor was closed and purged with 2 MPa CO, after which 101.1 mmoles of butadiene were introduced into the reactor from a side ampoule. The temperature was raised to 140°C and the pressure to 15 MPa CO, while the reaction mixture was being stirred at a speed of 1200 rpm. After reaction the catalyst was found to have fully precipitated.

C L A I M S

1. Process for the preparation of pentenoic acid or a pentenoate ester starting from water or alcohol and a mixture of pentenoic acid chloride, chlorobutene and a palladium catalyst, characterized in that the mixture of pentenoic acid chloride, chlorobutene and the palladium catalyst is contacted with water or alcohol, the molar ratio of water or alcohol to pentenoic acid chloride is maintaining lower than 1.2 and the molar ratio of chlorobutene to palladium is maintained higher than 10 during at least a substantial portion of the preparation.
2. Process according to claim 1, characterized in that the molar ratio of water or alcohol to pentenoic acid chloride is between 0.8 and 1.1.
3. Process according to any one of claims 1-2, characterized in that pentenoic acid chloride is formed in situ by carbonylation of chlorobutene with carbon monoxide.
4. Process according to any one of claims 1-3, characterized in that chlorobutene is formed in situ by chlorination of butadiene with hydrogen chloride.
5. Process according to claim 4, characterized in that water or alcohol and butadiene are supplied in a molar ratio lower than 1.
6. Process according to any one of claims 1-5, characterized in that a π-allyl-palladium complex with the formula



is used as catalyst.

7. Process according to any one of claims 1-6, characterized in that a pentenoate ester is prepared.

8. Process according to any one of claims 1-7, characterized in that the preparation is carried out continuously.

9. Process according to claim 8, characterized in that the preparation is carried out in one or more continuously stirred reactors.

10. Process according to any one of claims 4-9, characterized in that the pentenoate ester is prepared in a continuous process in which butadiene and alcohol are supplied in at least an equimolar ratio to a reactor containing chlorobutene, carbon monoxide and the palladium catalyst.

11. Process according to claim 10, characterized in that the pentenoate ester is isolated from a continuous flow leaving the reactor and that remaining chlorobutene, butadiene, hydrogen chloride, carbon monoxide and the palladium catalyst are recycled to the reactor.

Fig. 1

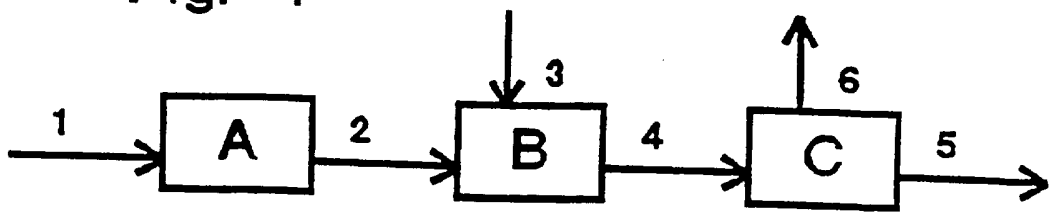


Fig. 2

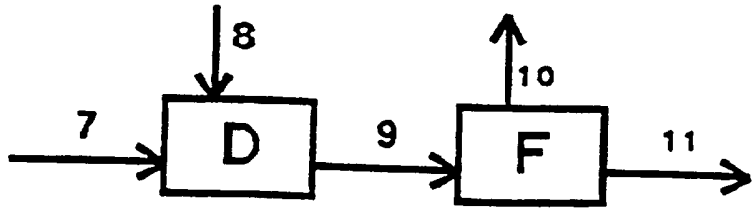


Fig. 3

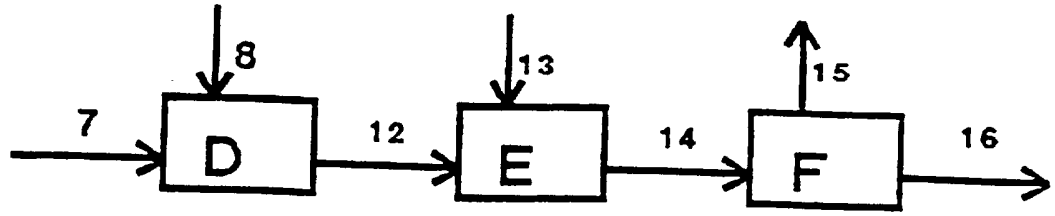


Fig. 4

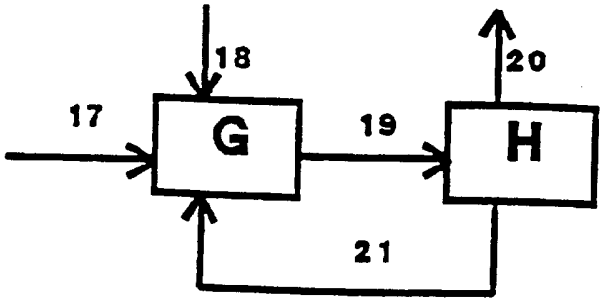
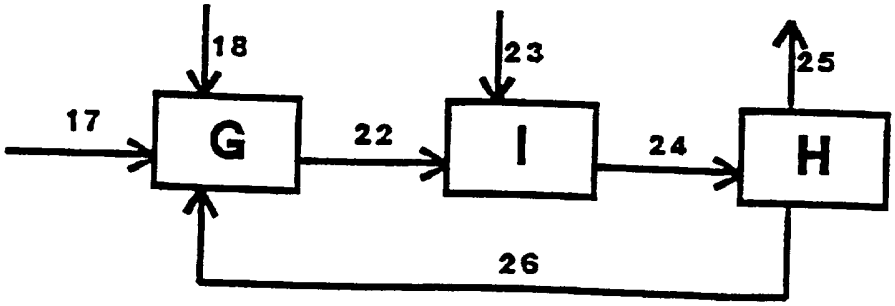


Fig. 5



INTERNATIONAL SEARCH REPORT

Inv onal Application No
PCT/NL 97/00050

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C57/03 C07C57/66 C07C51/04 C07C51/58 C07C69/533 C07C67/14

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 6 C07C

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 640 580 A (E.I.DU PONT DE NEMOURS & CO.) 1 March 1995 cited in the application see page 3, line 12 - line 18 see page 3, line 24 - line 32 see page 4, line 5 - line 29 see page 4-5; example 1 see claims 1,3-7 ---	1-6
Y	EP 0 648 731 A (RHONE-POULENC CHIMIE) 19 April 1995 cited in the application see column 3, line 6 - line 14 see claims 1-14 --- -/--	1-6

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
7 May 1997	20 May 1997 (20.05.97)

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Klag, M

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 97/00050

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 987 274 A (I.C.I.) 24 March 1965 see page 1, line 25 - line 66 see page 2; examples 2,6,7 see claims 1,3,5,7-12 ---	1-6
Y	GB 1 080 867 A (SHELL) 23 August 1967 see page 2, line 7 - line 21 see page 2, line 55 - line 117 see page 3, line 8 - line 14 see page 3, line 37 - line 50 see page 5; example 11 see claims 1,4,5,8,10,12-14 -----	1-6

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/NL 97/00050

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