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Datasheet for the decision of 7 September 2006

Case Number: T 0457/04 - 3.3.10

Application Number: 00910854.9

Publication Number: 1163202

IPC: C07C 67/38

Language of the proceedings: EN

Title of invention:
Process for the carbonylation of conjugated dienes

Applicant:
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

Opponent:
-

Headword:
-

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step (no): - improvement (yes) - same technical problem in prior art - solution obvious"

Decisions cited:
-

Catchword:
-

Case Number: T 0457/04 - 3.3.10

DECISION
of the Technical Board of Appeal 3.3.10
of 7 September 2006

Appellant:

SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR Den Haag (NL)

Representative: -

Decision under appeal: **Decision of the Examining Division of the European Patent Office posted 24 November 2003 refusing European application No. 00910854.9 pursuant to Article 97(1) EPC.**

Composition of the Board:

Chairman: R. Freimuth
Members: P. Gryczka
P. Schmitz

Summary of Facts and Submissions

I. The present appeal lies from the decision of the Examining Division posted on 24 November 2003 refusing the European patent application No. 00 910 854.9 published under the International publication No. WO 00/56695.

II. The Examining Division held that the subject-matter of claim 1 of the then pending main request, first and second auxiliary request was novel but did not involve an inventive step when considering, *inter alia*, the teaching of document

(1) WO-A-97/38964.

Document (1) disclosed the carbonylation of ethylenically unsaturated compounds in the presence of catalysts corresponding to those required by the application in suit and addressed also the problem of obtaining higher conversion and selectivity to ester products. Although, the carbonylation of conjugated dienes was not specifically disclosed in document (1), that prior art document nevertheless taught that the ethylenically unsaturated compounds might have one or more double bonds and in this respect referred to dienes. Therefore, the skilled person knowing that a catalyst was effective for the carbonylation of olefins would apply the same catalyst to the carbonylation of conjugated dienes. The applicant's assertion that conjugated dienes were significantly less reactive than non-conjugated olefins was not supported by the teaching of general textbooks. The feature defining, that the mole ratio of conjugated diene to palladium cation was at least 300, was also derivable from the teaching of document (1). Therefore, the subject-matter of claim 1 of each of the then pending requests did not involve an inventive step (Article 56 EPC).

III. With letter dated 25 August 2006, the Appellant filed four amended sets of claims as main request and first to third auxiliary request.

Claim 1 of the main request read as follows:

"1. A process for the carbonylation of conjugated dienes, whereby a conjugated diene is reacted with carbon monoxide and a hydroxyl group containing compound in the presence of a catalyst system including:
(a) a source of palladium cations,
(b) a phosphorus-containing ligand,
(c) an acid,
wherein the phosphorus-containing ligand is a ligand having the general formula I

$$X^1\text{-}R\text{-}X^2 \qquad (I)$$

wherein X^1 and X^2 represent a substituted or non-substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R represents a bivalent organic bridging group, connecting both phosphorus atoms, containing from 1 to 4 atoms in the bridge; and wherein the molar ratio of conjugated diene to palladium cation is at least 300:1."

Claim 1 of the first auxiliary request differs from claim 1 of the main request by the addition of the feature that "the process is conducted in the absence of halides".

Claim 1 of the second auxiliary request differs in essence from claim 1 of the main request in that the acid component (c) is "the carboxylic acid which results from the carbonylation reaction of the conjugated diene with carbon monoxide and water".

Claim 1 of the third auxiliary request differs from claim 1 of the main request by the addition of both features added separately in the first and the second auxiliary request, namely that "the process is conducted in the absence of halides" and that the acid component (c) is "the carboxylic acid which results from the carbonylation reaction of the conjugated diene with carbon monoxide and water".

IV. Oral proceedings took place on 7 September 2006 before the Board in the absence of the duly summoned Appellant who had informed the Board with letter dated 4 September 2006 that he would not attend.

V. The Appellant argued in writing that document

(5) US-A-5 495 041

might be considered as closest prior art for the requests specifying that component (c) of the catalytic system was a carboxylic acid which resulted from the carbonylation reaction of the conjugated diene with carbon monoxide and water, since document (5) related to the carbonylation of butadiene in the presence of pentenoic acid. However, document (5) did not suggest the phosphorus-containing ligand specified in claim 1 of the application in suit and taught the use of a low molar ratio of butadiene to palladium cation. The examples of the application in suit showed that higher reaction rates were achieved in the presence of pentenoic acid when the phosphorus ligands and the high molar ratio of conjugated diene to palladium cation specified in claim 1 were used. This effect could not be expected from the teaching of document (5) alone or combined with other citations. Thus, the claimed subject-matter involved an inventive step.

VI. The Appellant requested in writing that the decision under appeal be set aside and that a patent be granted on the basis of the main request, alternatively on the basis of the first, second or third auxiliary request, all requests filed with the letter dated 25 August 2006.

VII. At the end of the oral proceedings the decision of the Board was announced.

Reasons for the Decision

1. The appeal is admissible.

2. The process in accordance with claim 1 of the third auxiliary request is included in the subject-matter of claim 1 of the main request, first and second auxiliary request. Therefore, a negative outcome with respect to inventive step for the process according to the third auxiliary would also apply to the process according to the main request, the first and second auxiliary request. In these circumstances, it is appropriate to

start with the examination of the third auxiliary request.

Third auxiliary request

3. *Amendments (Article 123(2) EPC)*

When compared to claim 1 as originally filed, claim 1 of the third auxiliary request includes as further features that "the process is conducted in the absence of halides", that the anion source (c) is "the carboxylic acid which results from the carbonylation reaction of the conjugated diene with carbon monoxide and water" and that "the molar ratio of conjugated diene to palladium cation is at least 300:1".

The first feature addressed above is based on page 10, lines 6 to 9 of the application as filed and the second one on page 3, lines 6 and 7 of said application.

According to the Appellant the third feature is based on page 3, line 3 of the application as filed. However, this passage indicates that the molar ratio is "well over 300:1" while the expression "at least 300:1" has been introduced into claim 1. It is thus questionable whether this modification is allowable with respect to the provisions of Article 123(2) EPC. However, a decision in this respect is not necessary, since the matter whether the molar ratio includes or not the limit value of 300:1 has no influence on the negative outcome with regard to inventive step (see point 5 below).

4. *Novelty*

It was not contested in the decision under appeal that the subject-matter of the then pending broader claims defined novel subject-matter. In view of the negative outcome with respect to the issue of inventive step, it is unnecessary to go into more detail with respect to novelty.

5. *Inventive step*

5.1 The patent application is directed to a process for the carbonylation of conjugated dienes. The carbonylation of conjugated dienes already belongs to the state of the art as illustrated by document (5) which is acknowledged in the application in suit on page 1, second paragraph. Since document (1), which was considered in the decision under appeal as representing the closest prior art, relates to the carbonylation of ethylenically unsaturated compounds in general but does not specifically describe the carbonylation of conjugated dienes, the Board considers in agreement with the Appellant (letter dated 25 August 2006, points 7 and 8) that document (5) represents the closest prior art and, hence, takes it as the starting point for assessing inventive step. To start from a carbonylation process which is specifically directed to conjugated dienes, reflects objectively the factual situation of the skilled person at the priority date of the present application.

5.2 Document (5) discloses a process for the preparation of a pentenoate ester by carbonylation of butadiene in the presence of carbon monoxide, alcohol and a catalyst system comprising palladium, a pentenoic acid and a phosphine ligand (claim 1). Water is added to the carbonylation reaction in a sufficient amount to result in a catalytically active level of pentenoic acid (column 3, line 64 to column 4, line 3; claim 6). Thus, document (5) also discloses a process carried out in the presence of a carboxylic acid, namely pentenoic acid, which results from the carbonylation reaction of the conjugated diene, namely butadiene, with carbon monoxide and water. Document (5) is silent about the absence or presence of halides in the reaction medium.

5.3 According to the application in suit the catalyst system used in the process disclosed in document (5) has only a moderate activity (page 1, lines 23 and 24). Having regard to this prior art, the technical problem to be solved by the subject-matter of the patent application was to provide an improved process for the carbonylation of dienes in terms of conversion rates (application in suit page 2, lines 12 to 18). This problem has also been indicated by the Appellant in the letter dated 25 August 2006, point 7.1. In these submissions the Appellant made reference to an amelioration of the "reaction rate" instead of using the term "conversion rate", both expressions defining in fact the rate of carbonylation.

5.4 As solution to this problem the patent application proposes the process according to claim 1, which is characterized in that the groups X^1 and X^2 of the phosphorus ligand of the catalyst system represent a substituted or non-substituted cyclic group with at least 5 ring atoms of which one is a phosphorus atom, in that the molar ratio of conjugated diene to palladium cation is at least 300:1 and, further, in that the process is explicitly carried out in the absence of halides.

5.5 Comparative example F of the patent application describes the carbonylation of butadiene in the presence of palladium cations, pentenoic acid and 1,2-P,P' bis (ditert-butylphosphine)ethane (Table I, page 20). In this example the phosphorous ligand is a ligand falling under the formula of the preferred ligands envisaged by the closest prior art document (5) (formula (4), column 4). An initial carbonylation rate of 30 mole CO/grams atom Pd/hour was observed (Table II, page 21).

In example 4, the reaction was carried out under the same conditions as comparative example F with the exception that the phosphorous ligand was a ligand as required by claim 1 of the application in suit, namely 1,2-P,P' bis (1,5-dimethyl, 9-phosphabicyclononyl) ethane (Table I, page 20). An initial carbonylation rate of 300 mole CO/grams atom Pd/hour was observed (Table II, page 21).

The comparison of these two examples shows the impact of the process modification which distinguishes the claimed process from the closest prior art, namely the nature of the phosphorus ligand. Thus, it can be concluded from these experimental data that the claimed process effectively provides an improvement of the reaction rate (300 compared to 30 mole CO/grams atom Pd/hour) and that, consequently, the problem underlying the application has been successfully solved.

5.6 Finally, it remains to be decided whether or not the proposed solution to the problem underlying the patent application is obvious in view of the cited state of the art.

5.6.1 The skilled person seeking to improve the carbonylation reaction rate would turn its attention to document (1) which belongs to the same technical field since it relates to the carbonylation of ethylenically unsaturated compounds and addresses the same technical problem as the patent application in suit (page 1, lines 22 to 24).

According to document (1) the carbonylation of ethylenically unsaturated compounds in general, including compounds which have more than one double bond, such as dienes (page 8, lines 32 to 33, page 9, lines 19 to 20, 22 and 23) is conducted in the presence of a catalytic system comprising palladium and as particularly preferred bidentate phosphorous ligands, [3,3,1] and [4,2,1] isomers of 1,2-P,P'-bis(9-phosphabicyclononyl)ethane, 1,2-P,P'-bis(dimethyl-9-phosphabicyclononyl)ethane, 1,3-P,P'-bis(9-phosphabicyclononyl)propane, 1,3-P,P'-bis(dimethyl-9-phosphabicyclononyl)propane (claims 1 and 9; page 6, lines 11 to 16). These ligands fall under the formula (I) defining the ligands in claim 1 of the application in suit. Furthermore, document (1) teaches to conduct the reaction with amounts preferably in the range of 10^{-7} to 10^{-2} mole atom of palladium per mole of ethylenically unsaturated compound (page 7, line 25 to 28, in connection with page 4, lines 15 and 16). This ratio corresponds to a molar ratio of ethylenically unsaturated compound to palladium cation of 10^2 to 10^7 and covers, thus, the molar ratio of conjugated diene to palladium cation of at least 300:1 defined in claim 1 of the application in suit. In addition, the process of document (1) does not require the presence of halides in case of a coreactant other than an aromatic alcohol (claim 1). In fact, as illustrated by its example 3, document (1) also teaches that the carbonylation reaction can be carried out in the absence of halides.

The Board concludes from the above that document (1) gives a clear incentive on how to solve the technical problem underlying the patent in suit of improving the carbonylation reaction rate, namely by using as phosphorous ligand a ligand as defined in present claim 1 and by carrying out the reaction in the absence of halides with a molar ratio of conjugated diene to palladium of least 300:1.

For these reasons, the subject-matter of claim 1 lacks the required inventive step.

5.6.2 The Appellant argued on the basis of the comparative experiments described in the application in suit that it was unexpected that the use of pentenoic acid as component of the catalytic system resulted in a higher reaction rate than the use of substituted benzoic acid. However, since the closest prior art document (5) already teaches the use of pentenoic acid, the Appellant's argument is devoid of merit.

5.7 Consequently, the third auxiliary request has to be refused since the subject-matter of claim 1 thereof lacks the required inventive step (Article 56 EPC).

Main request, first and second auxiliary request

6. The process according to claim 1 of the third auxiliary request is comprised within the subject-matter of claim 1 of the main request, first and second auxiliary request (see point 2 above). Therefore, the subject-matter of claim 1 of these requests lack, at least to that extend, inventive step for the same reasons as the third auxiliary request (point 5 above). Thus, the main request, first and second auxiliary request must also be refused.

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar:	The Chairman:
C. Moser	R. Freimuth