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DECISION
of 19 August 2004

Case Number: T 0173/01 - 3.3.1

Application Number: 97918568.3

Publication Number: 0892781

IPC: C07C 319/06

Language of the proceedings: EN

Title of invention:

Catalytic hydrogenolysis of organic thiocyanates and disulfides to thiols

Applicant:

E.I. DU PONT DE NEMOURS AND COMPANY

Opponent:

-

Headword:

Thiols/DU PONT DE NEMOURS

Relevant legal provisions:

EPC Art. 54, 56, 123(2)

Keyword:

"Main and sole request: amendments - supported by the application as filed (yes); novelty (yes); inventive step (yes) - non obvious solution"

Decisions cited:

-

Catchword:

-



Case Number: T 0173/01 - 3.3.1

D E C I S I O N
of the Technical Board of Appeal 3.3.1
of 19 August 2004

Appellant:

E.I. DU PONT DE NEMOURS AND COMPANY
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Delaware 19898 (US)

Representative:

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Decision under appeal:

Decision of the Examining Division of the
European Patent Office posted 31 July 2000
refusing European application No. 97918568.3
pursuant to Article 97(1) EPC.

Composition of the Board:

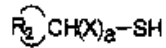
Chairman: P. P. Bracke
Members: P. F. Ranguis
C. Rennie-Smith

Summary of Facts and Submissions

I. The present appeal lies from the decision of the Examining Division to refuse the European patent application No. 97 918 568 (European patent publication No. 892 781 and international publication No. 97/37971) on the ground that the process according to the then pending request did not involve an inventive step pursuant to Article 56 EPC.

II. Claim 1 of that request, the sole independent claim, read as follows:

"1. A process for the preparation of a thiol of Formula I or II



II

wherein

X is $(CH_2)_m$ wherein m is 1 or 2;

a is zero or 1;

R₁ is:

C₁-C₃₀ linear, branched, or cyclic alkyl optionally substituted with a C₁-C₃₀ perfluoroalkyl;

C₁-C₃₀ perfluoroalkyl;

H-D-G or F-E-G wherein

D is $-(CH_2)_b-$;

E is $-(CF_2)_b-$;

G is $-[A-(CH_2)_c]_d-(CH_2)_e-$, $-[A-(CF_2)_c]_d-(CF_2)_e-$, $-[A-(CF_2)_c]_d-(CH_2)_e-$, or $-[A-(CH_2)_c]_d-(CF_2)_e-$;

wherein each A is independently selected from the group consisting of $-N(R_3)-$, $-C(O)N(R_3)-$, $-CO_2-$, $-SO_2N(R_3)$, $-O-$, and $-S-$; wherein R₃ is H, C₁-C₃₀ alkyl, or C₁-C₃₀

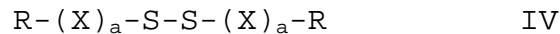
perfluoroalkyl; each b and e is independently zero or a positive integer of 1 to 29, and each c and d is independently a positive integer of 1 to 30, provided that $b+e+(cxd)$ is less than or equal to 30; and C_6-C_{30} aryl optionally substituted with C_1-C_{24} alkyl, C_1-C_{24} perfluoroalkyl, F, Br, Cl, $N(R_3)_2$, $CON(R_3)_2$, $CO_2(R_3)$, $CO(R_3)$, $SO_2N(R_3)_2$, $O(R_3)$, or $S(R_3)$ wherein R_3 is H, C_1-C_{30} alkyl, or C_1-C_{30} perfluoroalkyl; and R_2 is -D-G- or -E-G- wherein D, E and G are as defined above provided that $b+e+(cxd)$ is less than or equal to 8;

said process comprising reacting hydrogen with

A. a thiocyanate of Formula III



B. a disulfide of Formula IV



wherein R is R_1 , $H-R_2$ or $F-R_2$ as defined above and X and a are as defined above, wherein the reaction with thiocyanate is conducted in the presence of a catalyst comprising a Group VIII metal or mixture thereof; and the reaction with thiocyanate or with disulfide is conducted in the presence of a catalyst comprising a Group VIII metal or mixture thereof in the presence of a modifier metal selected from a group consisting of Group IB, Group IIB, Group IIIA, Group IVA and Group VA metal or mixture thereof, said catalyst being on a porous insoluble support."

III. The Examining Division only objected to the subject-matter of Claim 1 insofar as it related to the hydrogenolysis of compounds of Formulas III and IV in the presence of a catalyst comprising a Group VIII metal or mixture thereof, namely without modifier, on a

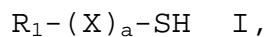
porous insoluble support. The Examining Division held in that respect that in view of document

(1) US-A-5 202 443,

the closest state of the art, which disclosed the hydrogenolysis of 1-[(2S)-2-methyl-1-oxo-3-rhodanidopropyl]-L-proline in the presence of palladium on charcoal, it would have been obvious for the person skilled in the art, in the absence of any unexpected effect, to use a compound of formula III as defined in Claim 1 in the conditions of the process of document (1) in order to produce the corresponding thiols.

IV. At the oral proceedings which took place on 19 August 2004, the Appellant submitted as sole request a set of nine claims. Claim 1, the sole independent claim read as follows:

"1. A process for the preparation of a thiol of Formula I



wherein

X is $(CH_2)_m$ wherein m is 1 or 2;

a is zero or 1;

R₁ is:

C₁-C₃₀ linear, branched, or cyclic alkyl optionally substituted with a C₁-C₃₀ perfluoroalkyl;

C₁-C₃₀ perfluoroalkyl;

H-D-G or F-E-G wherein

D is $-(CH_2)_b-$;

E is $-(CF_2)_b-$;

G is $-[A-(CH_2)_c]_d-(CH_2)_e-$, $-[A-(CF_2)_c]_d-(CF_2)_e-$, $-[A-(CF_2)_c]_d-(CH_2)_e-$, or $-[A-(CH_2)_c]_d-(CF_2)_e-$;

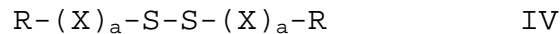
wherein each A is independently selected from the group consisting of $-N(R_3)-$, $-C(O)N(R_3)-$, $-CO_2-$, $-SO_2N(R_3)$, $-O-$, and $-S-$; wherein R_3 is H, C_1-C_{30} alkyl, or C_1-C_{30} perfluoroalkyl; each b and e is independently zero or a positive integer of 1 to 29, and each c and d is independently a positive integer of 1 to 30, provided that $b+e+(cxd)$ is less than or equal to 30; and C_6-C_{30} aryl optionally substituted with C_1-C_{24} alkyl, C_1-C_{24} perfluoroalkyl, F, Br, Cl, $N(R_3)_2$, $CON(R_3)_2$, $CO_2(R_3)$, $CO(R_3)$, $SO_2N(R_3)_2$, $O(R_3)$, or $S(R_3)$ wherein R_3 is H, C_1-C_{30} alkyl, or C_1-C_{30} perfluoroalkyl;

said process comprising reacting hydrogen with

A. a thiocyanate of Formula III



B. a disulfide of Formula IV



wherein R is R_1 , as defined above and X and a are as defined above, wherein the reaction with thiocyanate or with disulfide is conducted in the presence of a catalyst comprising a Group VIII metal or mixture thereof in the presence of a modifier metal selected from a group consisting of Group IB, Group IIB, Group IIIA, Group IVA and Group VA metal or mixture thereof, said catalyst being on a porous insoluble support."

V. The Appellant requested that the decision under appeal be set aside and that a patent be granted on the basis of the request and amended description filed during the oral proceedings.

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

Reasons for the Decision

1. The appeal is admissible.

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

2.1 The subject-matter of Claim 1 before the Board results from the limitation of the subject-matter of Claim 1 as originally filed through the deletion of the final compounds of formula II and the cancellation of the embodiment relating to the hydrogenolysis reaction in the presence of a catalyst comprising a Group VIII metal or mixture thereof, without modifier, thereby restricting the process to an hydrogenolysis reaction in the presence of a catalyst plus a modifier metal as defined in Claim 1. Such amendments merely limit the subject-matter originally claimed to a subject-matter already explicitly disclosed in the application as originally filed and are, therefore, admissible.

The subject-matter of Claims 2, 3, 7 to 9 corresponds to that of Claims 2, 3, 7 to 9 as originally filed. The subject-matter of Claims 4 to 6 corresponds to that of Claims 4 to 6 as originally filed, except that every use of the word "about" has been deleted.

The amendments in the description result from bringing the description into conformity with the wording of the claim.

2.2 In view of the above, it is concluded that the amendments meet the requirements of Article 123(2) EPC.

3. *Article 54 EPC - Novelty*

3.1 The subject-matter of Claim 1 is novel over the disclosure of document (1) since that document relates to a process involving the hydrogenolysis of a starting product (1-[(2S)-2-methyl-1-oxo-3-rhodanidopropyl]-L-proline) not within the scope of said Claim 1.

3.2 The Board also finds that the subject-matter of Claim 1 is novel over documents

(2) EP-A- 134 200 and

(3) US-A- 5 493 058,

cited in the international search report since neither of those two documents discloses a process for manufacturing mercaptans by hydrogenolysis of disulfides in the presence of a catalyst comprising a Group VIII metal or mixture thereof **in the presence of** a modifier metal selected from a group consisting of Group IB, Group IIB, Group IIIA, Group IVA and Group VA metal or mixture thereof, said catalyst being on a porous insoluble support.

4. *Article 56 EPC - Inventive step*

4.1 In accordance with the "problem-solution" approach consistently applied by the Boards of Appeal, it is necessary, as a first step, to establish the closest state of the art, then to determine in the light thereof the technical problem which the invention addresses and solves and, as a final step, to examine whether or not the claimed solution to this problem is

obvious in view of the state of the art. The closest state of the art is normally a prior art document disclosing subject-matter aiming at the same objective as the claimed invention.

4.2 The Examining Division took document (1) as the closest state of the art. However, document (1) relates to a process for preparing 1-[(2S)-3-mercapto-2-methyl-1-oxopropyl]-L-proline and does not concern, therefore, a process for preparing a compound within the definition of the compounds of formula (I) of Claim 1 (cf. point IV above). It aims, thus, at a different objective than the claimed invention and cannot for that reason qualify as the closest state of the art.

4.3 Documents (2) and (3) were cited in the international search report and are, therefore, part of the examination-appeal proceedings.

4.3.1 Document (2) discloses a process for manufacturing aliphatic mercaptans through hydrogenolysis of solid aliphatic disulfides in the presence of 0.01 to 5 wt.% with respect to the disulfide of a metal catalyst from the platinum metal group (cf. page 2, 2nd paragraph) which leads to a yield higher than 95% (cf. page 5, lines 1 to 6). As metal catalyst from the platinum metal group, Ru, Rh, Pd, Os, Ir and Pt, all catalysts of Group VIII, are cited and, in particular, Pd is preferred (cf. page 4, lines 1 to 2). Aliphatic disulfides of formula $F(CF_2)_a-R^1-S-S-R^2-(CF_2)_bF$ are preferred (cf. page 2, 4th paragraph). Since the aliphatic mercaptans obtained by the said process fall within the definition of the compounds of formula (I)

of Claim 1 (cf. point IV above), this document aims at the same objective as the claimed invention.

4.3.2 Document (3) discloses a process for manufacturing methyl mercaptan by catalytic hydrogenolysis of dimethyl disulphide in the presence of a catalyst consisting of a sulphide or a mixture of sulphides of at least one transition metal. Preferred transition metals are nickel, cobalt, molybdenum and/or tungsten (cf. column 2, lines 47 to 60). This document also aims at the same objective as the claimed invention.

4.3.3 Although each of documents (2) or (3) could qualify as the closest state of the art, document (2), in the Board's judgment, is the more relevant since it encompasses a substantial part of the compounds obtained by performing the process of Claim 1, whereas document (3) only relates to the preparation of methyl mercaptan. The outcome of the present decision would be the same starting from document (3).

4.4 In the next step, the technical problem which the invention addresses in the light of the closest state of the art is to be determined.

It is explained in the European application that the conversion of a thiocyanate derivative to the corresponding thiol by hydrogenolysis using a palladium on charcoal catalyst leads to low yields (cf. page 1, lines 15 to 19). That finding is confirmed by comparative example No. 2.

However, since the process according to document (2) involving the hydrogenolysis of aliphatic disulfides in

the presence of palladium on charcoal leads to aliphatic mercaptans with a high yield (cf. point 4.3.1 above), the technical problem to be solved in view of document (2) can only be seen as the provision of an alternative process for the production of organic thiols in a high yield.

- 4.5 As the solution to this problem, the claimed invention proposes to conduct the reaction in the presence of a catalyst comprising a Group VIII metal or mixture thereof in the presence of a modifier metal selected from a group consisting of Group IB, Group IIB, Group IIIA, Group IVA and Group VA metal or mixture thereof, said catalyst being on a porous insoluble support (cf. point IV above), the difference compared with the disclosure of document (2) consisting in the combination of the Group VIII metal or mixture thereof with a modifier as above defined.

In view of the description of the application, in particular the examples Nos. 1, 3, 5, 7, 8, 9 and 11 to 18, the Board is convinced that the technical problem defined above (cf. point 4.4) is solved within the whole scope of Claim 1.

- 4.6 It remains to be decided whether or not the claimed solution is obvious in view of the cited prior art.
- 4.6.1 Starting from document (2), the person skilled in the art would have noted that document (3) proposed to use a sulphide of a transition metal of Group VIII like Ni or Co or of Group VIb like Mo or W or a mixture of NiMo, NiW or CoMo (cf. column 4, Table 2) for the hydrogenolysis of dimethyl disulphide in methyl

mercaptan. Such a teaching does not give any suggestion to perform the reaction in accordance with the claimed invention since the metals of Group VIb used in combination with Ni or Co are different to the modifier metal defined in Claim 1.

Likewise, document (1) which discloses a reaction involving Pd on charcoal would have not directed the person skilled in the art towards the invention since no modifier is present.

- 4.7 In the absence of any document teaching or even hinting at the preparation of a thiol of formula I by reacting hydrogen with a thiocyanate of formula III or a disulfide of formula IV in the presence of a catalyst and a modifier as defined in Claim 1, it is concluded that Claim 1 meets the requirement of Article 56 EPC. The same applies to dependent Claims 2 to 9 which represent particular embodiments of the subject-matter of Claim 1.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the first instance with the order to grant a patent on the basis of the claims 1 to 9 and pages 1 to 12 of the amended description filed during the oral proceedings.

The Registrar:

The Chairman:

N. Maslin

P. P. Bracke