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D E C I S I O N
of 10 February 2000

Case Number: T 0961/96 - 3.3.1

Application Number: 90101778.0

Publication Number: 0381130

IPC: C07D 213/36

Language of the proceedings: EN

Title of invention:

Production of alpha-unsaturated amines

Applicant:

Takeda Chemical Industries, Ltd.

Opponent:

-

Headword:

Alpha-unsaturated amines/TAKEDA CHEMICAL INDUSTRIES

Relevant legal provisions:

EPC Art. 56

Keyword:

"Inventive step (yes) - non-obvious solution"

Decisions cited:

T 0641/89, T 0713/97

Catchword:

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Boards of Appeal

Chambres de recours

Case Number: T 0961/96 - 3.3.1

D E C I S I O N
of the Technical Board of Appeal 3.3.1
of 10 February 2000

Appellant: Takeda Chemical Industries, Ltd.
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Decision under appeal: Decision of the Examining Division of the
European Patent Office posted 30 April 1996
refusing European patent application
No. 90 101 778.0 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: A. J. Nuss
Members: P. F. Ranguis
J. P. B. Seitz

Summary of Facts and Submissions

I. This appeal lies from the decision of the Examining Division refusing the European patent application No. 90 101 778.0 (publication No. 0 381 130) on the ground that the then pending:

Claims 1 to 9 filed with letter of 22 May 1995

did not involve an inventive step pursuant to Article 56 EPC in the light of the disclosure of the document:

(2) DE-A-3 305 202.

Furthermore, the Board will also refer in the present decision to the following documents cited in the search report, in the application as filed or by the Appellant:

(1) US-A-2 928 883

(3) DE-A-3 603 100

(4) Izvest.Akad.Nauk S.S.S.R., Otdel. Khim. Nauk, 1958, 841-845. (see. Chemical Abstracts, 53, 1111i (1959))

(5) J. Org. Chem., 25, 1312-1322 (1960)

(6) Izvest.Akad.Nauk S.S.S.R., Ser. Kim., 1963, (11), 1946-1947 (see. Chemical Abstracts, 60, 5325g (1964))

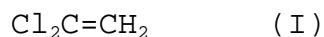
(7) Dokl. Akad. Nauk S.S.S.R., 149, 330-333 (1963),

(see. Chemical Abstracts, 59, 6215g)

- (8) US-A-2 209 000
- (9) J. Phys. Chem., 44, 275-296 (1940)
- (10) J. Am. Chem. Soc., 65, 1271-1272 (1943)
- (11) J. Am. Chem. Soc., 82, 3091-3099 (1960)
- (12) "Survey of Organic Synthesis", Calvin A. Buehler and Donald E. Pearson, Wiley - Intersciences, NY (1970), pp. 356-359
- (13) Partial translation in English of "Synthesis and Function of Fluorine Compounds", CMC Co., Ltd. Tokyo (1987), pp. 15, 34, 35, 155-157, 177

II. Claim 1, which was the sole independent claim of the said set of claims 1 to 9 read as follows:

"A process for the production of 1,1,1-trichloro-2-nitroethane which comprises reacting 1,1-dichloroethylene of the formula (I):



with nitric acid or its salt and hydrogen chloride or its salt to obtain a compound of the formula (II):



the reaction being carried out in an aqueous system to which an inert organic solvent may be added at 0-100°C

in a sealed vessel or at 0-40°C in an open system, and each of nitric acid and hydrogen halide being used in 0.5 to 5 equivalents."

III. The Examining Division held, considering document (2) as the closest prior art and the problem underlying the application as providing a process for the preparation of $\text{Cl}_3\text{C}-\text{CH}_2\text{NO}_2$, using dichloroethylene as starting material, that

the skilled person having regard to the teaching of (2), in particular Example 1, where $\text{CF}_2=\text{CH}_2$ is reacted with HF and HNO_3 to give $\text{CF}_3-\text{CH}_2-\text{NO}_2$, would have considered the use of HCl in the analogous reaction involving $\text{Cl}_2\text{C}=\text{CH}_2$ to form $\text{Cl}_3\text{C}-\text{CH}_2-\text{NO}_2$ and so arrive at the claimed process (point 1 of the Reasons).

IV. Together with the Statements of Grounds of appeal the Appellant (Applicant) filed six requests (a main request and five auxiliary requests), those requests therefore superseding the request on which the decision of the Examining Division was based.

- Claim 1 of the main request is the same as the request refused by the Examining Division, except that the expression "hydrogen halide" was replaced by "hydrogen chloride" and the expression "to the compound (I)" was added at the end of this claim.
- Claims 2 and 3 of the main request were amended with respect to the claims 2 and 3 of the request refused by the Examining Division insofar as the expression "or hydrogen bromide", after "hydrogen chloride", was deleted; the term "halide", after

"hydrogen" was replaced by the term "chloride" and the expression "to the compound (I)" was added after "0.5 to 5 equivalents".

Those amendments were made to overcome an objection raised by the Examining Division in the portion "Further Points" following the Reasons for the Decision.

- Claims 4 to 9 of the main request are the same as the claims 4 to 9 of the request refused by the Examining Division.

V. The Appellant, in his Statement of Grounds of Appeal submitted in essence that:

The Examining Division erred in considering that the substitution of "F" with "Cl" was obvious since the synthetic processes for organic fluorine compounds and organic chlorine compounds are greatly different. Furthermore, it was not obvious to use HCl instead of HF as a reaction reagent, since HF and HCl are greatly different in reactivity:

- The nucleophilic substitution of hydroxyl in alcohols by an halogen involves different reagents depending on whether F or Cl is involved.
- F₂ is not generally used in fluorination of aromatic systems, whereas Cl₂ is generally used.
- The most general method of synthesizing an organic fluorine compound is to utilize replacement of halogens by fluorine. It is known that such a

reaction does not easily proceed in the case of chlorine.

- The halogens compounds are divided into three portions: "fluorine compounds", "chlorine and bromine compounds" and "iodine compounds", and the person skilled in the art is not therefore directed to transfer reactions and results achieved with "fluorine compounds" to "chlorine and bromine compounds".

- It is well known that HF and HCl differ greatly in reactivity with olefins. HF is known to react with halogenated olefins extremely easily depending on the structure of the substrate (see the copy of the sworn declaration II submitted before the Patent and Trademark Office of the United States of America and submitted with the Statements of Grounds of appeal; documents (9), (10), (12) and (13)). For example, HF is known to react smoothly with 1,1-dichloro-ethylene at 65°C (see document (10)). On the other hand, in the reaction of 1,1-dichloro-ethylene with HCl, an anhydrous ferric chloride is requested (see document (8)).

- Also, it is assumed that hydrogen halide is an electrophilic reagent which reacts first with olefins by an initial attack of H⁺. In the reaction of HF with polyhalogenated olefins, however, there occurs a predominant nucleophilic attack by F⁻ (see document (11)).

The appellant concluded that the fact that HF is capable of undergoing an addition reaction on CF₂=CH₂ to

produce $\text{CF}_3\text{CH}_2\text{NO}_2$ as described in document (2) neither suggested the reaction of $\text{CF}_2=\text{CH}_2$ with HCl as claimed, nor enabled the person skilled in the art to infer the reaction result by analogy.

The appellant pointed out, furthermore, that Example 4 of document (2), and not Example 1 was the closest prior art, as Example 4 related to the same starting material ($\text{CCl}_2=\text{CH}_2$), the same procedure and the same product. Reference was made to the two sworn declarations, submitted with the Statements of Grounds of appeal, filed before the Patent and Trademark Office of the United States of America, wherein it was shown that the reaction of $\text{CCl}_2=\text{CH}_2$ with HF and HNO_3 yielded $\text{CCl}_3-\text{CH}_2-\text{NO}_2$ **and not** $\text{CFCl}_2-\text{CH}_2-\text{NO}_2$ as set out in the document (2), due to a side reaction.

- VI. The Appellant requested that the decision under appeal be set aside and that the case be remitted to the department of first instance with the order to grant a patent on the basis of the claims of either the main request or those of one of the auxiliary requests 1 to 5 submitted with the Statements of Grounds of appeal.

Reasons for the Decision

1. The appeal is admissible.

Main request

2. In the Board's judgment, the subject-matter of claims 1 to 9 does not contravene Article 123 (2) EPC as:

Claim 1 finds support in the description as originally filed (see page 14, two last lines; page 15, lines 6 to 12; page 16, lines 15 to 16; page 17, lines 5 to 7).

Claim 2 finds support in the description as originally filed (see page 14, two last lines; page 15, lines 6 to 12; page 16, lines 15 to 16; page 17, lines 5 to 7; page 7, line 6 to page 9, line 2).

Claim 3 finds support in the description as originally filed (see page 14, two last lines; page 15, lines 6 to 12; page 16, lines 15 to 16; page 17, lines 5 to 7; page 9, line 3 to the bottom of the page).

Claim 4 is supported by the originally filed claim 6.

Claim 5 is supported by the originally filed claim 8.

Claim 6 is supported by the originally filed claim 9.

Claim 7 is supported by the originally filed claim 10.

Claim 8 is supported by the originally filed claim 11.

Claim 9 is supported by the originally filed claim 12.

3. The claims are also clear. Thus, no objection arises under Article 84 EPC.
4. After examination of the cited prior art documents, the Board has reached the conclusion that the subject-matter as defined in the claims as granted is novel. Since novelty had never been contested by the Examining Division, it is not necessary to give reasons for this

finding.

Inventive step

5. It remains to be decided whether or not the present request involves an inventive step as required by Article 56 EPC. In accordance with the "problem-solution approach" consistently applied by the Boards of Appeal to assess inventive step on an objective basis, it is necessary to establish the closest prior art being the starting point, to determine in the light thereof the technical problem which the invention addresses, to verify that the technical problem is solved by all the embodiments encompassed within the claimed solution and to examine whether the claimed solution is obvious or not in view of the state of the art.

5.1 The Examining Division and also the Appellant started from document (2), the Examining Division referring in particular to Example 1, while the Appellant adhered to Example 4. In fact, the Examining Division started from document (2) owing to the fact that both document (2) and the claimed invention appear to relate to the same kind of reaction of an halogenated olefin with an halogen halide (HF and HCl respectively) and nitric acid.

The Board disagrees with this approach for the following reasons:

First, electing document (2) as the closest prior art would mean that an equivalence in reaction between HF and HCl in the kind of addition reaction cited above

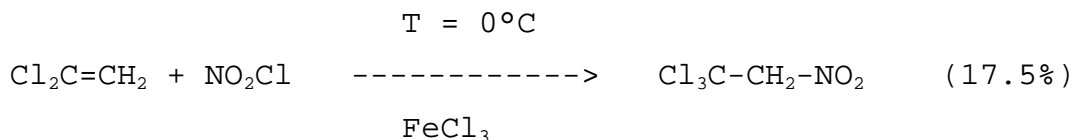
was generally known in the art, which is however not the case as the Board will show below (see point 5.4). Such a finding could not have been reached without the knowledge of the invention and is therefore the result of an inadmissible ex post facto analysis.

Moreover, in the present situation, where the claimed invention relates to the preparation of a known compound (1,1,1-trichloro-2-nitroethane) at a high yield (see page 4, lines 4 to 8 of the application in suit), the documents to be considered for determining the closest prior art should be those which describe these compounds and their manufacture. The reason is that only such documents allow the technical results and effects of the respective processes to be compared validly (see T 641/89 , point 3.1 of the reasons for the decision, not published in OJ EPO and T 713/97, point 4.2 of the reasons for the decision, not published in the OJ EPO, both decisions being cited in Case Law of the Boards of Appeal of the EPO, 1998, I.D.3.1). For this reason also, the process for the preparation of fluorinated nitroalkanes described in document (2) and which cannot yield 1,1,1-trichloro-2-nitroethane does not qualify as the closest prior art nor do documents (3), (6) and (7) which relate to the preparation of fluorinated nitro alkanes.

Only documents (1), (4) and (5) actually disclose addition products such as those resulting from the process of present claim 1. Moreover, documents (4) and (5) are acknowledged as background art in the description of the application in suit and presented as being the closest prior art over which the claimed process has advantages. The disclosure of document (1)

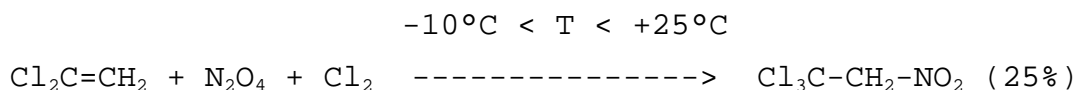
is similar to that of document (5).

Document (4) teaches the following:

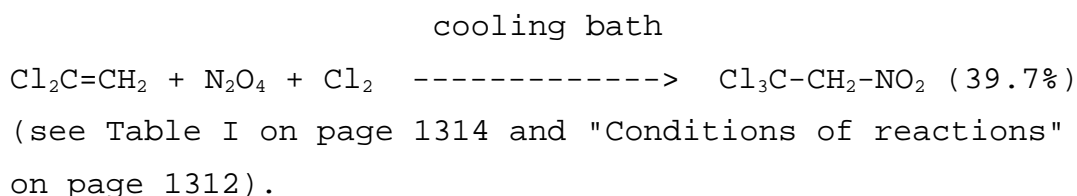


This method shows the disadvantage that nitryl chloride is explosive (page 2, lines 15 to 50 of the application in suit).

Document (1) describes in Example V the following reaction:



Document (5) discloses the following reaction:



The processes described in both document (1) and (5) require the use of toxic dinitrogen tetroxide and chlorine gas (see page 2, lines 52 to 54 of the application in suit).

In the Board's judgment, document (5) is the appropriate starting point for investigating inventive step as it leads to the better yield and, therefore, presents the maximum similarity with the claimed

invention.

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

In view of the closest prior art, i.e. document (5), the technical problem underlying the application in suit consists of providing a **further** process for the production of 1,1,1-trichloro-2-nitro-ethane from 1,1-dichloroethylene at a high yield avoiding the use of the toxic dinitrogen tetroxide and chlorine gas.

A yield higher than that known from documents (5) has not been shown for everything claimed, as the Board notes that, when using HCl and NO₃Na (Example 16), the yield is of 35.9%, i.e. slightly below that achieved by the closest state of the art. Therefore, if the technical problem had been defined in terms of providing a higher yield on the basis of the best yields reported in the examples of the application in suit, the Board would have to conclude that this technical problem is not solved for all embodiments encompassed within claim 1.

- 5.3 The claim 1 of the application proposes, as the solution to this problem, a process which comprises reacting 1,1-dichloroethylene with nitric acid or its salt and hydrogen chloride or its salt to obtain 1,1,1-trichloro-2-nitro-ethane, the reaction being carried out in an aqueous system to which an inert organic may be added, at 0-100°C in a sealed vessel or at 0-40°C in an open system, and each of nitric acid and hydrogen chloride being used in 0.5 to 5 equivalents to 1,1-

dichloroethylene.

The description of the application, in particular the Examples 1-8, 13-18 and 23, demonstrates that the claimed subject-matter represents a solution to the technical problem defined above (see point 5.2). When HCl and HNO₃ are used, the yields are at least 52.2%. When NaCl and HNO₃ are used the yield is of 48.2% (ex. 7) and when HCl and NO₃Na are used the yield is of 35.9% (ex. 16).

- 5.4 It remains to be decided whether or not the proposed solution to the problem underlying the patent in suit is obvious in view of the cited prior art.

As document (5) teaches the reaction of 1,1-dichloroethylene with N₂O₄ and Cl₂ to obtain 1,1,1-trichloro-2-nitroethane (see point 5.1 above), the question to be answered is whether or not the person skilled in the art would have been led to replace in the said reaction the reactants N₂O₄ and Cl₂ by HCl and HNO₃, or a salt thereof (in the specific conditions as claimed) in view of the prior art teaching the reaction of a dihalo-1,1-ethylene with HF and HNO₃ as disclosed, in documents (2), (3), (6) and (7).

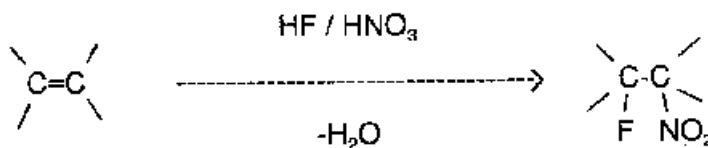
The Examining Division held that:

The skilled person having regard to the teaching of document (2), in particular Example 1, where CF₂=CH₂ is reacted with HF and HNO₃ to give CF₃CH₂NO₂, would consider the use of HCl in the analogous reaction involving CCl₂=CH₂ to form CCl₃CH₂NO₂ and so arrive at the claimed process.

In the Board's opinion, the Examining Division erred in assessing *a priori* that the person skilled in the art would have been directed to replace HF by HCl in view of the prior art cited.

Indeed, the Board notes that none of the documents referred to by the Examining Division teaches a clear equivalence in reaction between HF and HCl for addition reactions of the type to be considered here, i.e. involving haloolefins.

The teaching of document (2), is limited to the reaction of a double bond with HF and HNO₃:

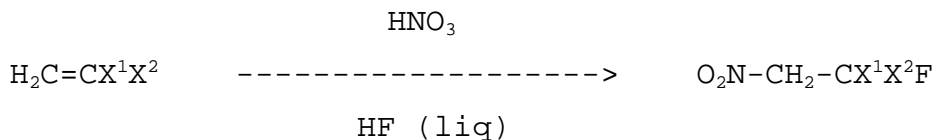


and, in particular, to the reaction of an halogenated double bond with HF and HNO₃.

Furthermore, as far as 1,1-dichloroethylene is concerned the Applicant has provided a copy of two declarations filed before the Patent and Trademark Office of the United States of America showing that the reaction of 1,1-dichloroethylene with HF / HNO₃ did not occur as set out in the Table of document (2) but yielded in fact a side product, which is 2,2,2-trichloronitroethane (26.8%). In reproducing the example, the person skilled in the art would thus have noted that the reaction with 1,1-dichlorovinylidene did not yield the expected product and for this reason

would have disregarded this document.

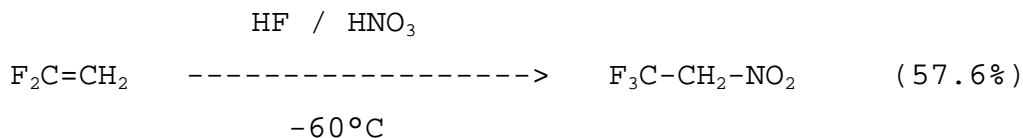
Document (3) does not give any further information, either, as it simply mentions the reaction:



wherein X₁, X₂ are Cl or F

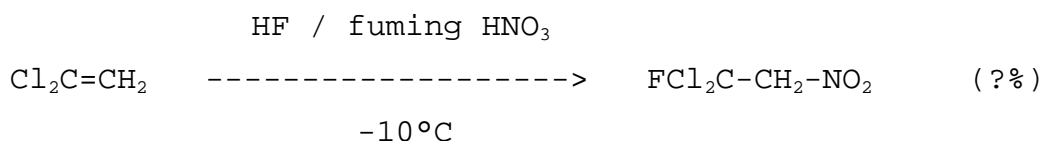
The Board further notes that the references "EP-OS- 1 101 133" and "EP-OS- 1 101 134" on page 5, line 11 of this document are erroneous, so that they do not provide any further information.

Document (6) describes the following reaction under anhydrous conditions:



This document thus gives no incentive to the person skilled in the art to apply the disclosed information to HCl and even less under reaction conditions such as those used in the claimed invention.

Document (7) describes the following reaction:



Again no incentive is provided to apply the disclosed information to HCl under the claimed reaction conditions.

To summarize, the disclosure of documents (2), (3), (6) and (7) do not provide to the person skilled in the art the teaching which would have directed him to replace HF by HCl. The other documents cited do not fill the gap and rather show that there exists a difference between the reactions involving the halogens such as Cl, Br and I on one hand and on the other hand the reaction involving F.

For instance, document (5) which is a quite exhaustive study of the reaction of nitrohalogenation of olefins involving mixtures of dinitrogen tetroxide and halogens never mentions F_2 , not even as a possibility, although numerous examples are given with Br_2 , Cl_2 or I_2 . This finding corroborates the submissions of the Appellant that among the halogens, fluor occupies a special position in that its chemistry differs significantly from that of Cl, Br and I (see point V above). By contrast, the documents (2), (3), (6) and (7) are in an unequivocal manner directed to the addition of HF in combination with HNO_3 on haloolefins.

Moreover, the Appellant has cited the documents (8) to (13) in order to underline the specific character of HF with respect to other hydrogen halides.

The Board notes that none of these documents teaches an equivalence in the hydrohalogenation of a double bond, as far haloolefins are concerned, between, on the one hand HF and on the other hand HCl.

Documents (9), (10) and (11) only deal with the addition of HF on olefins,

Document (8) only deals with the addition of HCl on 1,1-dichloroethylene,

Document (12) separates the case of HI, HBr and HCl from HF.

Document (13) mentions that the addition of HF on olefin is either a nucleophilic addition of Markovnikov type (as it is well known in the case of HI, HBr and HCl) or an electrophilic addition which is different from other halogenations. It seems that the latter is actually the fact in the addition on fluoroolefin (see document (11) cited in point V above).

- 5.5 The Board concludes that it was not obvious to propose a process for the production of 1,1,1-trichloro-2-nitro-ethane such as defined in claim 1 of the main request and, therefore, its subject-matter involves an inventive step within the meaning of Articles 52(1) and 56 EPC.

For the same reasons, the Board concludes that the subject-matter of dependent claims 2 to 9 involves an inventive step.

6. In view of the above, there is no reason to deal with the Appellant's auxiliary requests.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the Examining Division with the order to grant a patent with the set of claims of the main request submitted with the Statements of Grounds of Appeal received 21 August 1996 and the description to be adapted thereto.

The Registrar:

The Chairman:

E. Görgmaier

A. Nuss