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13 August 1998 (13.08.98)

(54) Title: PREPARATION OF CARBOXYLIC COMPOUNDS AND THEIR DERIVATIVES

(57) Abstract

A palladium–catalyzed arylation of an olefin with aryl halide and/or substituted aryl halide is conducted in a liquid polar organic solvent, and (ii) secondary or tertiary amine that boils (1) below the boiling temperature of the solvent if only one solvent is used or (2) below the boiling temperature of at least one, but not necessarily all, of the solvents if more than one is used. With the reaction mixture so formed (which comprises olefinically–substituted aromatic compound, amine–hydrohalide and solvent) is mixed a concentrated aqueous solution of inorganic base having a base strength greater than the base strength of the amine. This converts amine–hydrohalide to free amine and alkali metal halide, and forms (i) an aqueous phase containing dissolved alkali metal halide, and (ii) an organic phase comprising olefinically–substituted aromatic compound, amine and solvent. After separating these phases, amine is distilled off from the organic phase under low temperature and pressure conditions that suppress thermal oligomerization of the olefinically–substituted aromatic compound contained in the organic phase. The organic phase, when substantially freed of amine, is subjected to a palladium–catalyzed carboxylation with carbon monoxide and water and/or alcohol. The relatively high specific gravity of the aqueous phase greatly facilitates the phase separation, and enables efficient recovery of amine and recycle of solvent.

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INTERNATIONAL SEARCH REPORT

Intern. nal Application No
PCT/US 98/00298

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C2/86 C07C41/30 C07C51/14 C07C67/38 C07C51/487

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.
A	US 5 536 870 A (WU TSE-CHONG) 16 July 1996 cited in the application	1-66
A	US 3 922 299 A (HECK RICHARD F) 25 November 1975	1-66
X	FR 1 545 270 A (BOOTS PURE DRUGS CY LTD) 8 November 1968 see example 1	67-81
X	DE 19 34 460 A (SYNTEX CORP) 5 February 1970 see example 10	67-81
X	WO 91 16286 A (HOECHST AG) 31 October 1991 see page 8, line 21 - page 9	82-95

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 June 1998	03. 07. 98

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	Janus, S

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 98/00298

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-55

   Process for the preparation of carboxylic acids or derivatives thereof by a two step process including a Heck vinylation of an aromatic halide in the presence of an amine having a boiling point lower than that of at least one constituent of the solvent mixture, in order to allow, after neutralisation by an inorganic base of the ammonium halide formed during said reaction, distillation of said amine prior to the second step, which is a carboxylation of the olefinic group.

2. Claims: 56-66

   Process for the vinylation of aromatic halides through a Heck reaction in the presence of an amine characterised by the fact that, after the neutralisation of the ammonium halide formed during the reaction by an aqueous inorganic base, the resulting aqueous phase must have a minimum density of 1.08.

3. Claims: 67-810

   Process for the purification of an arylcarboxylic acid contaminated by an ether compound, essentially by a neutralisation, extraction, acidification and back-extraction process.

4. Claims: 82-95

   Process for the vinylation of aromatic halides through a Heck reaction in the presence of an amine characterised by the fact that the ammonium halide formed during the reaction is extracted in an acidic aqueous phase.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/US 98/00298

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