

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
7 February 2002 (07.02.2002)

PCT

(10) International Publication Number  
WO 02/10116 A3

(51) International Patent Classification<sup>7</sup>: C07C 69/74,  
69/63, 67/317, 67/307, 67/00, 209/56, 211/35

(US). NABIH, Thomas; P.O. Box 3904, Kingsport, TN 37664 (US). NOTTINGHAM, William, Dell; 4700 Lakepark Drive, Kingsport, TN 37664 (US). SPENCER, David, Chris; 1028 Allandale Circle, Kingsport, TN 37660 (US).

(21) International Application Number: PCT/US01/22704

(22) International Filing Date: 19 July 2001 (19.07.2001)

(74) Agent: BLAKE, Michael, J.; P.O. Box 511, Kingsport, TN 37662-5075 (US).

(25) Filing Language: English

(81) Designated State (national): JP.

(26) Publication Language: English

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(30) Priority Data:  
60/222,317 1 August 2000 (01.08.2000) US  
09/897,872 2 July 2001 (02.07.2001) US

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(71) Applicant: EASTMAN CHEMICAL COMPANY  
[US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).

(88) Date of publication of the international search report:  
10 May 2002

(72) Inventors: HUBBS, John, Clark; 507 Bell Hollow Road, Kingsport, TN 37664 (US). ATTRIDE, David, Carl; 2323 Wynwood Drive, Jonesborough, TN 37659 (US). BOAZ, Neil, Warren; 1342 Watauga Street, Kingsport, TN 37660 (US). CIULA, James, Charles; 902 Crooks Valley Road, Apartment 2, Kingsport, TN 37664 (US). MADDOX, John, Thorton; 111 Rose Lane, Jonesborough, TN 37659

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/10116 A3

(54) Title: PROCESS FOR THE PREPARATION OF ALKYL 1-METHYLCYCLOPROPANECARBOXYLATE

(57) Abstract: Disclosed is a 4-step process for the preparation of alkyl esters of 1-methylcyclopropanecarboxylic acid which comprises the steps of (1) converting  $\gamma$ -butyrolactone to  $\alpha$ -methyl- $\gamma$ -butyrolactone; (2) converting the  $\alpha$ -methyl- $\gamma$ -butyrolactone from step (1) to an alkyl 4-halo-2-methyl-butyrates; (3) producing a xylene solution of the alkyl 4-halo-2-methyl-butyrates; and (4) contacting the xylene solution of the alkyl 4-halo-2-methyl-butyrates from step (3) with an alkali metal alkoxide under conditions of temperature and pressure which causes vaporization of (i) an alkanol as it is formed and (ii) an alkyl 1-methylcyclopropanecarboxylate as it is formed from the alkyl 4-halo-2-methyl-butyrates. Also disclosed are processes whereby the alkyl 1-methylcyclopropanecarboxylate, prepared as described above, is converted to 1-methylcyclopropylamine.

INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/22704

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C07C69/74 C07C69/63 C07C67/317 C07C67/307 C07C67/00  
 C07C209/56 C07C211/35

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 7 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)  
 CHEM ABS Data, BEILSTEIN Data, EPO-Internal, PAJ, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 008 110 A (DEGUSSA) 31 May 1979 (1979-05-31) example 1 ---	1-10
Y	US 5 371 270 A (KAUFHOLD MANFRED ET AL) 6 December 1994 (1994-12-06) the whole document ---	1-10
A	SELVA, MAURIZIO ET AL: "Selective monomethylation of arylacetonitriles and methyl arylacetates by dimethyl carbonate" J. CHEM. SOC., PERKIN TRANS. 1 (1994), (10), 1323-8, XP002189419 cited in the application table 5 --- -/--	1

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
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*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  
  
6 February 2002

Date of mailing of the international search report  
  
15/03/2002

Name and mailing address of the ISA  
 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

Authorized officer  
  
Kardinal, S

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/22704

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>TSUTOMU ISHIKAWA ET AL.: "Studies on the Chemical Constituents of Xanthoxylum nitidum"                      CHEMICAL AND PHARMACEUTICAL BULLETIN.,                      vol. 43, no. 11, 1995, pages 2014-2018,                      XP002189420                      PHARMACEUTICAL SOCIETY OF JAPAN. TOKYO.,                      JP                      ISSN: 0009-2363                      cited in the application                      page 2215, paragraph 5</p>	1
A	<p>GB 2 008 111 A (DEGUSSA)                      31 May 1979 (1979-05-31)                      example 3</p>	1
A	<p>DE 30 26 094 A (DEGUSSA)                      28 January 1982 (1982-01-28)                      cited in the application                      example 3</p>	1
A	<p>US 3 503 971 A (NEIGHBORS RALPH P ET AL)                      31 March 1970 (1970-03-31)                      column 4</p>	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/22704

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2008110	A	31-05-1979	DE 2751133 A1 17-05-1979
			BE 872029 A1 14-05-1979
			FR 2409255 A1 15-06-1979
			IT 1109289 B 16-12-1985
			JP 54079254 A 25-06-1979
			NL 7808602 A 18-05-1979
-----			
US 5371270	A	06-12-1994	DE 4222497 A1 13-01-1994
			DE 59303417 D1 19-09-1996
			EP 0577949 A1 12-01-1994
			JP 7010808 A 13-01-1995
-----			
GB 2008111	A	31-05-1979	DE 2751134 A1 17-05-1979
			BE 872028 A1 14-05-1979
			CA 1136643 A1 30-11-1982
			CH 636593 A5 15-06-1983
			FR 2409254 A1 15-06-1979
			IL 55933 A 28-02-1982
			IT 1157707 B 18-02-1987
			JP 1414014 C 10-12-1987
			JP 54079224 A 25-06-1979
			JP 62023739 B 25-05-1987
			NL 7808304 A 18-05-1979
			-----
DE 3026094	A	28-01-1982	DE 3026094 A1 28-01-1982
			CA 1171098 A1 17-07-1984
			EP 0043949 A1 20-01-1982
			JP 57048952 A 20-03-1982
-----			
US 3503971	A	31-03-1970	CH 492724 A 30-06-1970
			CH 500662 A 31-12-1970
			DE 1695023 A1 23-03-1972
			FR 1560251 A 21-03-1969
			GB 1176884 A 07-01-1970
			US 3451802 A 24-06-1969
-----			