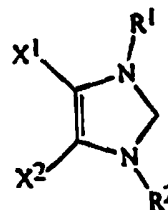




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <p>(51) International Patent Classification <sup>6</sup> :<br/>C07D 233/68, 233/28</p>  | <p>A1</p> | <p>(11) International Publication Number: <b>WO 98/27064</b><br/>(43) International Publication Date: 25 June 1998 (25.06.98)</p>   |
| <p>(21) International Application Number: PCT/US97/23443<br/>(22) International Filing Date: 16 December 1997 (16.12.97)<br/>(30) Priority Data:<br/>60/033,521 18 December 1996 (18.12.96) US<br/>(71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).<br/>(71) Applicant (for US only): KHASNIS, Dipti (executrix for the deceased inventor) [US/US]; 335 S. Waterford Lane, Wilmington, DE 19808 (US).<br/>(72) Inventor: KHASNIS, Dilip (deceased).<br/>(72) Inventors; and<br/>(75) Inventors/Applicants (for US only): ARDUENGO, Anthony, Joseph, III [US/US]; 5115 Washington Boulevard, Wilmington, DE 19809 (US). GOERLICH, Jens, Robert [DE/DE]; Eckermannstrasse 11, D-21335 Luneburg (DE).<br/>(74) Agent: SCHAEFFER, Andrew, L.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p> |           | <p>(81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, GW, HU, ID, IL, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TJ, TM, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b><br/><i>With international search report.<br/>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> |
| <p>(54) Title: RELATIVELY STABLE (1,3-DISUBSTITUTEDIMIDAZOL-2-YLIDENE)-TYPE CARBENES</p> <p>(57) Abstract</p> <p>This invention concerns a compound of formula (I) wherein: R<sup>1</sup> and R<sup>2</sup> are each independently hydrocarbyl or substituted hydrocarbyl; X<sup>1</sup> is an element or substituted element more electronegative than carbon; and X<sup>2</sup> is an element more electronegative than carbon, a substituted element more electronegative than carbon, hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group. A process for making these carbenes is also disclosed. The carbenes are useful in various catalysts and as ligands in transition metal compounds.</p>  |           |   |



(I)

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TITLERELATIVELY STABLE (1,3-DISUBSTITUTEDIMIDAZOL-  
2-YLIDENE)-TYPE CARBENESFIELD OF THE INVENTION

5 Relatively stable (1,3-disubstitutedimidazol-2-ylidene) carbenes are made by substituting relatively electronegative atoms such as halogen at the imidazole 4 and/or 5 positions.

BACKGROUND OF THE INVENTION

10 Carbenes have long been known as reactive intermediates in organic chemistry. Only recently have carbenes been known that are relatively stable, that is they may be isolated in macroscopic quantities and studied. These stable carbenes have the general structure (1,3-disubstitutedimidazol-2-ylidene) [see (I) below]. Even though they are much more stable than previously known carbenes, these types of carbenes are still highly reactive substances, for instance reacting  
15 quickly with air. Since these "stable" carbenes are useful in various ways, it would be desirable to be able to further stabilize such compounds to facilitate their ease of handling and for other reasons.

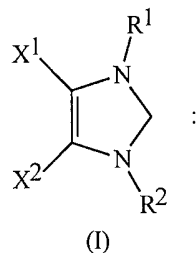
A. J. Arduengo, et al., J. Am. Chem. Soc., vol. 113, p. 361-363 (1991),  
A. J. Arduengo, et al., J. Am. Chem. Soc., vol. 114, p. 5530-5534 (1992) report  
20 the synthesis of (1,3-disubstitutedimidazol-2-ylidene) carbenes. Compounds such as are claimed herein are not disclosed.

A. E. Heinemann, et al., J. Am. Chem. Soc., vol. 118, p. 2023-2038 (1996)  
and C. Boehme, et al., J. Am. Chem. Soc., vol. 118, p. 2039-2046 (1996) report  
theoretical (calculational) studies of (1,3-disubstitutedimidazol-2-ylidene)-type  
25 carbenes.

Carbenes which have relatively electronegative atoms substituted at the imidazole 4 and/or 5 position(s) have been found to be more stable and are considered an object of the invention. Other objects and advantages of the present invention will become apparent to those skilled in the art upon reference to the  
30 attached drawing and to the detailed description of the invention which hereinafter follows.

SUMMARY OF THE INVENTION

This invention concerns a compound of the formula



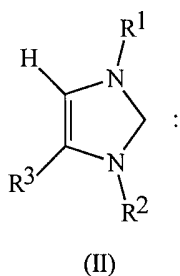
5 wherein:

$R^1$  and  $R^2$  are each independently hydrocarbyl or substituted hydrocarbyl;

$X^1$  is an element or substituted element more electronegative than carbon; and

10  $X^2$  is an element more electronegative than carbon, a substituted element more electronegative than carbon, hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group.

This invention also concerns a process for the production of a carbene, comprising, contacting, in a liquid medium at a temperature of about  $-40^{\circ}\text{C}$  to  
 15 about  $+100^{\circ}\text{C}$ , a first compound of the formula



with a second compound  $\text{E-X}^3$  which is a source of electrophilic halogen,  
 20 wherein:

$R^1$  and  $R^2$  are each independently hydrocarbyl or substituted hydrocarbyl;

$R^3$  is an element more electronegative than carbon, a substituted element more electronegative than carbon, hydrogen, hydrocarbyl, substituted  
 25 hydrocarbyl or an inert functional group; and

$X^3$  is halogen;

and provided that a  $\text{pK}_a$  of  $\text{H-E}$  is about 6 to about 30.

### BRIEF DESCRIPTION OF THE DRAWING

Figure 1 shows the structure of the carbene made in Example 1, as determined by X-ray crystallography.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 Herein certain terms are used and they are defined below:

“Hydrocarbyl” is a monovalent group containing only carbon and hydrogen, and may be chiral or achiral. Unless otherwise stated it is preferred that hydrocarbyl (and substituted hydrocarbyl) groups contain 1 to 30 carbon atoms.

10 “Substituted” means a group that is substituted and contains one or more substituent groups that do not cause the compound to be unstable or unsuitable for the use or reaction intended. Substituent groups which are generally useful include nitrile, ether, ester, halo, amino (including primary, secondary and tertiary amino), hydroxy, oxo, vinylidene or substituted vinylidene, silyl or substituted silyl, nitro, nitroso, sulfinyl, sulfonyl, sulfonic acid alkali metal  
15 salt, boranyl or substituted boranyl, and thioether.

By a “functional group” is meant a group such as acyl [-C(O)-alkyl] which does not cause the appropriate compound to be unstable or unsuitable for its use. A typical definition of a functional group may be found in R. T. Morrison, et al., Organic Chemistry, 6th Ed., Prentice Hall, Englewood Cliffs, NJ, 1992,  
20 p. 167-168.

The phrase “more electronegative than carbon” as measured by the familiar Pauling Electronegativity Scale, see for instance J. E. Huheey, Inorganic Chemistry, 2nd Ed., Harper and Row, New York, 1978, p. 162. Also included within the definition of “more electronegative than carbon” are groups that are  
25 effectively more electronegative than carbon even though the atom bound directly to the imidazole ring may by itself not be more electronegative than carbon. See for instance J. E. Huheey, Inorganic Chemistry, 2nd Ed., Harper and Row, New York, 1978, p. 164. An atom that is more electronegative than carbon is bound to the carbon atom at the 4 or 5 position of the imidazole ring.

30 In (I) and other carbenes herein, the “colon” at the two position of the ring represents the two non-bonding electrons of the carbene group.

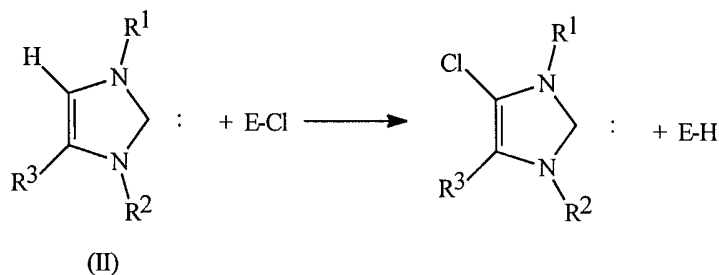
In (I) it is preferred that R<sup>1</sup> and R<sup>2</sup> are independently hydrocarbyl. Preferred groups for R<sup>1</sup> and R<sup>2</sup> are mesityl, tolyl and adamantyl, and mesityl is more preferred.

35 In (I) it is preferred that both X<sup>1</sup> and X<sup>2</sup> are an element more electronegative than carbon or a substituted element more electronegative than carbon. Useful electronegative elements include the halogens, oxygen, nitrogen, and sulfur, chlorine and bromine are preferred, and chlorine is especially preferred. A “substituted electronegative element” simply means that this element

is bound to at least one atom other than a carbon atom at the 4 or 5 position of the imidazole ring. For instance, the other group(s) bound to the electronegative atom may be hydrocarbyl, substituted hydrocarbyl or a functional group.

Specific useful groups which may be bound to the electronegative atom include, but are not limited to, nitrile, ether, ester, halo, amino (including primary, secondary and tertiary amino), hydroxy, oxo, vinylidene or substituted vinylidene, silyl or substituted silyl, nitro, nitroso, sulfinyl, sulfonyl, sulfonic acid alkali metal salt, boranyl or substituted boranyl, and thioether. Of course any substituent group anywhere in the carbene should not cause the carbene to be unstable, for instance as by reacting with the carbene group itself.

In one process for making (I), a compound of formula (II) is contacted with a source of electrophilic halogen, the compound E-X<sup>3</sup>. X<sup>3</sup> is a halogen atom which will be substituted for a hydrogen in the 4 and optionally 5 position of (II). It is preferred that X<sup>3</sup> is chlorine or bromine and more preferred that it is chlorine. "E" represents the remainder of the molecule which is the source of the electrophilic halogen (SEH). For instance, the reaction could be considered to be represented by the equation:



20

wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and E are as described above. Formally, one may think of the second compound as acting during the reaction as E<sup>-</sup> and Cl<sup>+</sup>.

E-X<sup>3</sup> should not contain strongly acidic protons, such as in carboxylic acid or certain hydroxyl groups such as those in primary or secondary alcohols. It should also not contain any other electrophilic sites that would interfere with the desired reaction. Finally, the product of the process containing the "E" group, H-E, should have a pK<sub>a</sub> as measured in water (or extrapolated from water by known methods) of 6 to about 30, preferably about 9 to about 22, more preferably about 12 to about 18.

Useful SEH's include perhalocarbons containing at least one of the types of halogen atoms desired in the carbene. Such compounds include carbon tetrachloride, chlorotrifluoromethane, bromotrifluoromethane, bromotrichloromethane, 1,1,1-trichloro-2,2,2-trifluoroethane, chloropentafluorobenzene, and bromopenta-

fluorobenzene. Carbon tetrachloride is preferred. When  $X^3$  is F,  $E-X^3$  may be the cation  $FNR^5_3^+$  wherein  $R^5$  is alkyl or taken together form one or more rings which may contain a nitrogen atom. It is preferred that  $NR^5_3$  be part of (an alkyl substituted) 1,4-diaza-2.2.2-bicyclooctane ring system. N-Chlorosuccinimide and N-bromosuccinimide may also be used as sources of electrophilic halogen.

The process may conveniently be carried out at a temperature of  $-40^\circ\text{C}$  to about  $+100^\circ\text{C}$ , preferably about  $-20^\circ\text{C}$  to about  $+40^\circ\text{C}$ , and more preferably about ambient (room) temperature (typically about  $20-30^\circ\text{C}$ ). A liquid may be used in the process, and may dissolve one or more of the starting materials and/or products. Useful inert liquids include ammonia, ethers, saturated hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons and tertiary alcohols. Halogenated solvents, which may also act as SEH's may also be used as the liquid. In order to prevent side reactions, the process is preferably carried out in an inert atmosphere, under substantially anhydrous conditions.

If there are hydrogen atoms in both the 4 and 5 positions of the imidazole ring, it is generally desirable to replace both hydrogens with halogen by using a molar ratio of SEH to (II) of 2:1. When a 4,5-dihalo-1,3-disubstitutedimidazol-2-ylidene is desired, a higher proportion of the SEH may be used, especially if the product halogenated carbene does not react significantly with the SEH.

Another general procedure for the preparation of these exceptionally stable carbenes involves a variation on procedure of A. J. Arduengo et al., J. Am. Chem. Soc. Vol. 114, pp. 5530-5534 (1992). In this variation a 1,4,5-tri(substituted)-imidazole is alkylated on the 3-nitrogen with an alkyl halide to produce a 1,4,5-tri(substituted)-3-alkylimidazolium halide. This imidazolium halide can be deprotonated by strong bases such as NaH as described by Arduengo et al. to produce a 1,4,5-tri(substituted)-3-alkylimidazol-2-ylidene. When the substituents in the 4 and/or 5 positions of the starting 1,4,5-tri(substituted)imidazole are elements more electronegative than carbon as described above in this invention then the resulting carbene will have the enhanced stability of the carbenes of this invention. Such 1,4,5-tri(substituted)imidazoles are commercially available (for example 1-methyl-5-chloroimidazole) or can be made by standard synthetic procedures known to those skilled in the art.

One starting material for the process, (II), can be made by methods known in the art, see for instance A. J. Arduengo, et al., J. Am. Chem. Soc., vol. 113, p. 361-363 (1991), A. J. Arduengo, et al., J. Am. Chem. Soc., vol. 114, p. 5530-5534 (1992) and T. Kratz, Synthesis, p. 561 (1993). The precursor carbenes (II) are usually quite reactive, so should be handled with care in an inert atmosphere.

Stable 1,3-disubstitutedimidazol-2-ylidene-type carbenes are useful for the condensation of formaldehyde to commercially useful organic compounds [J. H. Teles, et al., *Helv. Chem. acta*, vol. 79, p. 61-83 (1996)], for the preparation of certain carbene containing transition metal complexes (Canadian Patent Application 2,165,925) which in turn are useful for making aldehydes (Canadian Patent Application 2,165,891) and aromatic olefins (Canadian Patent Application 2,165,888).

In the following non-limiting Examples, the following abbreviations are used:

10                   rt - room temperature  
                      THF - tetrahydrofuran

#### EXAMPLE 1

##### Preparation of 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene

To a solution of 0.400 g (1.32 mmol) of 1,3-dimesitylimidazol-2-ylidene in 10 ml of THF was added a solution of 0.405 g (2.63 mmol) of  $\text{CCl}_4$  in 4 ml of THF and the solution was stirred at rt for 20 min. Subsequent removal of volatiles under reduced pressure gave 0.410 g (83.3%) of a yellowish brown solid. Quality crystals were obtained from cooling a solution of the carbene in a mixture of THF and hexane (2:1). Mp. 180-182°C (dec.).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 2.09$  [s, 6 H, para- $\text{CH}_3$ ], 2.12 [s, 12 H, ortho- $\text{CH}_3$ ], 6.75 [s, 4 H, meta-CH].  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 17.86$  [s, ortho- $\text{CH}_3$ ], 20.99 [para- $\text{CH}_3$ ], 116.16 [s, C-4,5], 129.30 [s, meta-C], 136.05 [s, ortho-C], 138.53 [s, para-C], 138.90 [s, ipso-C], 219.89 [s, C-2]. Analysis calculated for  $\text{C}_{21}\text{H}_{22}\text{Cl}_2\text{N}_2$  (373.3): C, 67.56; H, 5.94; N, 7.50. Found: C, 66.94; H, 5.74; N, 7.32.

25                   Crystal data: at -65°C with Mo  $\text{K}\alpha$  radiation: a = 2235.0 (6), b = 1051.2 (1), c = 829.0 (2) pm,  $\beta = 93.57$  (3)°, monoclinic, C2/c, Z = 4,  $\mu(\text{Mo}) = 3.38 \text{ cm}^{-1}$ , 1176 unique reflections with  $I > 3\sigma(I)$ . The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on F. Chlorine, carbon and nitrogen were refined with anisotropic thermal parameters. Hydrogens were modeled in fixed positions. The largest residual electron density in the final difference Fourier map was 0.17  $\text{e}/\text{\AA}^3$  near C16. The data/parameter ratio was 7.42. The final R factors were  $R = 0.038$  and  $R_w = 0.037$ . The structure of this compound is shown in Figure 1.

#### COMPARATIVE EXPERIMENT 1

35                   To a solution of 0.40 g (0.10 mmol) of 1,3-di-1-adamantylimidazol-2-ylidene in 5 ml of ethyl ether was added 5 ml of chloroform. The color of the mixture immediately became dark violet and a solid precipitated, which was filtered off and dried in vacuo.  $^1\text{H NMR}$  proved it to be 1,3-di-1-adamantyl-2-dichloromethylimidazolium chloride. This reaction illustrates the high reactivity of



(1,3-disubstitutedimidazol-2-ylidene)-type carbenes that do not contain electronegative atoms bound to the 4 and/or 5 position(s) to chloroform.

EXAMPLE 2

To a solution of 0.374 g (1 mmol) of 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene in 20 ml of hexane was added 1 ml of a 1M solution of methyl chloride in diethyl ether. No apparent reaction took place. After stirring for 2 days, the solvent was evaporated. <sup>1</sup>H NMR analysis of the residue showed it to be unchanged starting material. Similar(1,3-disubstitutedimidazol-2-ylidene)-type carbenes but with hydrogen atoms in the 4 and 5 positions readily react with methyl chloride.

EXAMPLE 3

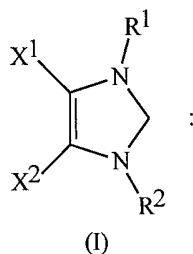
Separate solutions of 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene and 1,3-dimesitylimidazol-2-ylidene in C<sub>6</sub>D<sub>6</sub> were prepared and exposed to air. After 12 h, analysis by <sup>1</sup>H NMR showed the 1,3-dimesitylimidazol-2-ylidene had reacted to give a mixture of products. <sup>1</sup>H NMR analysis of the 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene solution after 2 days showed the starting material was essentially unchanged.

Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous modifications, substitutions and rearrangements without departing from the spirit or essential attributes of the invention. Reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

CLAIMS

What is claimed is:

1. A compound of the formula



5

wherein:

R<sup>1</sup> and R<sup>2</sup> are each independently hydrocarbyl or substituted hydrocarbyl;

- 10 X<sup>1</sup> is an element or substituted element more electronegative than carbon; and

X<sup>2</sup> is an element more electronegative than carbon, a substituted element more electronegative than carbon, hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group.

- 15 2. The compound as recited in Claim 1 wherein X<sup>1</sup> is said electronegative element.

3. The compound as recited in Claim 1 wherein X<sup>1</sup> and X<sup>2</sup> are both said electronegative element.

- 20 4. The compound as recited in Claim 2 wherein X<sup>1</sup> is chlorine or bromine.

5. The compound as recited in Claim 3 wherein X<sup>1</sup> and X<sup>2</sup> are chlorine or bromine.

6. The compound as recited in Claim 4 wherein X<sup>1</sup> is chlorine.

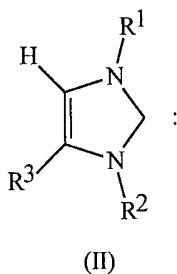
- 25 7. The compound as recited in Claim 1 wherein said electronegative element or said substituted electronegative element is oxygen, nitrogen, phosphorous or sulfur.

8. The compound as recited in Claim 1 wherein said electronegative elements or said substituted electronegative elements of X<sup>1</sup> and X<sup>2</sup> are oxygen, nitrogen, phosphorous or sulfur.

- 30 9. The compound as recited in Claim 1 wherein R<sup>1</sup> and R<sup>2</sup> are mesityl.

10. The compound as recited in Claim 5 wherein R<sup>1</sup> and R<sup>2</sup> are mesityl.

11. A process for the production of a carbene, comprising, contacting, in a liquid medium at a temperature of about -40°C to about +100°C, a first compound of the formula



with a second compound E-X<sup>3</sup> which is a source of electrophilic halogen,  
5 wherein:

R<sup>1</sup> and R<sup>2</sup> are each independently hydrocarbyl or substituted hydrocarbyl;

R<sup>3</sup> is an element more electronegative than carbon, a substituted element more electronegative than carbon, hydrogen, hydrocarbyl, substituted  
10 hydrocarbyl or an inert functional group; and

X<sup>3</sup> is halogen;

and provided that a pK<sub>a</sub> of H-E is about 6 to about 30.

12. The process as recited in Claim 12 wherein R<sup>3</sup> is hydrogen.

13. The process as recited in Claim 12 wherein said second compound is a  
15 perhalocarbon.

14. The process as recited in Claim 13 wherein said perhalocarbon is carbon tetrachloride.

15. The process as recited in Claim 11 wherein said temperature is about -20°C to about +40°C.

20 16. The process as recited in Claim 11 wherein R<sup>1</sup> and R<sup>2</sup> are mesityl.

17. The process as recited in Claim 11 wherein said second compound is a perhalocarbon.

18. The process as recited in Claim 11 wherein said second compound is N-chlorosuccinimide or N-bromosuccinimide.

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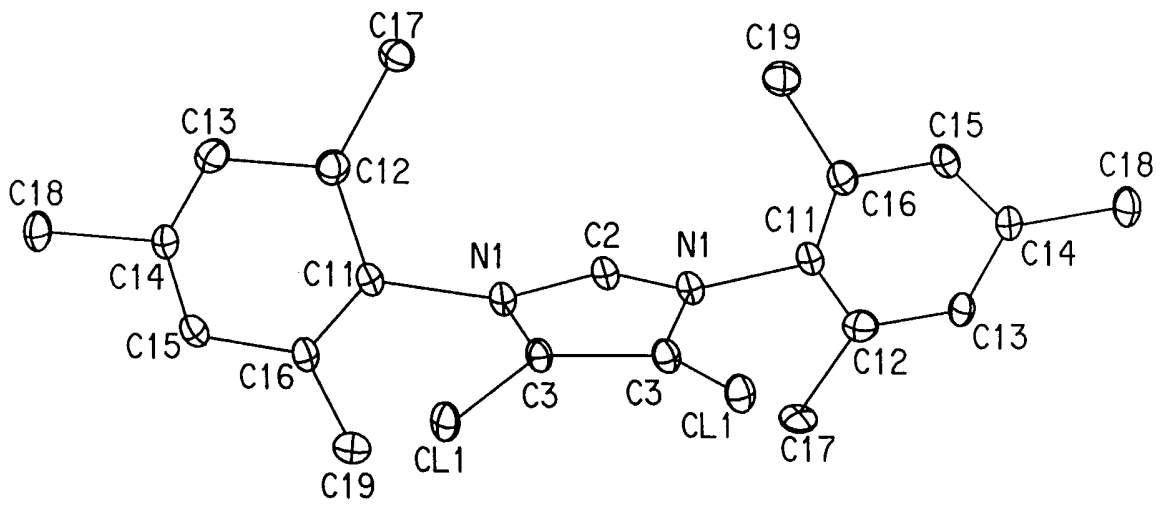


FIG. 1

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/23443

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 6 C07D233/68 C07D233/28

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 C07D

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        | ARDUENGO A J ET AL: "ELECTRONIC STABILIZATION OF NUCLEOPHILIC CARBENES" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 114, no. 4, 1 July 1992, pages 5530-5534, XP002032799 cited in the application see the whole document<br>--- | 1-18                  |
| A        | KUHN N ET AL: "Synthesis of Imidazol-2-ylidenes by Reduction of Imidazole-2(3H)-thiones" SYNTHESIS, no. 6, June 1993, STUTTGART DE, pages 561-562, XP002060701 cited in the application see the whole document<br>---<br>-/--       | 1-18                  |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- "&" document member of the same patent family

Date of the actual completion of the international search

30 March 1998

Date of mailing of the international search report

17/04/1998

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| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT |  |                       |
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| Category °   | Citation of document, with indication, where appropriate, of the relevant passages                     | Relevant to claim No. |
| A  | EP 0 719 753 A (HOECHST AG) 3 July 1996<br>cited in the application<br>see the whole document<br>---   | 1-10                  |
| A  | EP 0 719 758 A (HOECHST AG) 3 July 1996<br>cited in the application<br>see the whole document<br>----- | 1-10                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

In. ational Application No

PCT/US 97/23443

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|------------------|-------------------------|------------------|
| EP 0719753 A                           | 03-07-96         | DE 4447067 A            | 04-07-96         |
|  |                  | AU 4070595 A            | 04-07-96         |
|  |                  | CA 2165891 A            | 30-06-96         |
|  |                  | CN 1132734 A            | 09-10-96         |
|  |                  | FI 956233 A             | 30-06-96         |
|  |                  | JP 8231459 A            | 10-09-96         |
|  |                  | PL 312033 A             | 08-07-96         |
|  |                  | US 5663451 A            | 02-09-97         |
|  |                  | ZA 9510938 A            | 16-07-96         |
|  |                  |                         |                  |
| EP 0719758 A                           | 03-07-96         | DE 4447068 A            | 04-07-96         |
|  |                  | AU 4070495 A            | 04-07-96         |
|  |                  | CA 2165888 A            | 30-06-96         |
|  |                  | CN 1132738 A            | 09-10-96         |
|  |                  | FI 956237 A             | 30-06-96         |
|  |                  | JP 8231438 A            | 10-09-96         |
|  |                  | PL 312032 A             | 08-07-96         |
|  |                  | US 5703269 A            | 30-12-97         |
|  |                  | ZA 9510927 A            | 04-07-96         |
|  |                  |                         |                  |