72940/87

600941

CONVENTION

AUSTRALIA

Patents Act

APPLICATION FOR A STANDARD PATENT

~~I~~/We The Dow Chemical Company

of 2030 Dow Center,
Abbott Road,
Midland,
Michigan 48640,
UNITED STATES OF AMERICA.

APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 29-6-90

hereby apply for the grant of a standard patent for an invention entitled:

PREPARATION OF DIAMINO-, DIBENZYLAMINO- AND DIALKYLAMINO- BENZENEDIOLS

which is described in the accompanying complete specification.

Details of basic application

Number of basic application: 864,063

Convention country in which basic application was filed: UNITED STATES OF AMERICA

Date of basic application : 16 May 1986

Address for Service:

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne 3000 AUSTRALIA

Dated: 14 May 1987

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
The Dow Chemical Company,

By: David B Fitzpatrick

FEE STAMP TO VALUE OF
$ 175 ATTACHED
MAIL OFFICER

Our Ref : 55466
POF Code: 1037/1037

AUSTRALIAN PATENT OFFICE
LS

6012q/1

LODGED AT SUB-OFFICE
14 MAY 1987
Melbourne

PATENT OFFICE 100
PATENT OFFICE 20 TWENTY DOLLARS
PATENT OFFICE 5 FIVE DOLLARS

14 MAY 1987
Melbourne

33588
AUSTRALIA
Patent Declaration

AUSTRALIA

Patents Act

DECLARATION FOR A PATENT APPLICATION

INSTRUCTIONS
(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

In support of the (a) convention application made by

(b) THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, UNITED STATES OF AMERICA

(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

(hereinafter called "applicant(~~s~~)" for a patent (c) for an invention entitled (d)
PREPARATION OF DIAMINO- AND DIALKYLAMINOBENZENDIOLS

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote*)

I/~~We~~ (e) Richard G. Waterman, General Patent Counsel
THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, United States of America

do solemnly and sincerely declare as follows:

1. ~~I am/We are the applicant(s).~~

(or, in the case of an application by a body corporate)

1. I am/~~We are~~ authorized to make this declaration on behalf of the applicant(~~s~~).

2. ~~I am/We are the actual inventor(s) of the invention.~~

(or, where the applicant(s) is/are not the actual inventor(s))

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f) Muthiah N. Inbasekaran, 5800 Lamplighter Lane, Midland, Michigan 48640, ; and Robert M. Strom, 789 W. Chippewa River Road, Midland, Michigan 48640, Both respectively in the UNITED STATES OF AMERICA

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote**)

~~is~~/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

(g) The applicant Company is the assignee of the said invention from the said actual inventor(s).

(Note: *Paragraphs 3 and 4 apply* **only** *to Convention applications)*

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application(~~s~~) for patent or similar protection on which the application is based is/~~are~~ identified by country, filing date, and basic applicant(s) as follows:

(h) US, May 16, 1986, Muthiah N. Inbasekaran and Robert M. Strom in the United States of America

4. The basic application(~~s~~) referred to in paragraph 3 hereof was/~~were~~ the first application(~~s~~) made in a Convention country in respect of the invention the subject of the application.

(k) Insert PLACE of signing
(l) Insert DATE of signing
(m) Signature(s) of declarant(s)
Note: No legalization or other witness required

Declared at (k) Midland, Michigan, 48640, U.S.A.
Dated (l) 5 May 1987

(m) THE DOW CHEMICAL COMPANY

SIGNATURE

CORP.
SEAL

To: The Commissioner of Patents

By: RG Waterman
RICHARD G. WATERMAN
General Patent Counsel

Agent: Phillips Ormonde & Fitzpatrick

No legalization or other witness required

(12) PATENT ABRIDGMENT (11) Document No. AU-B-72940/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 600941

(54) Title
PREPARATION OF DIAMINO- AND DIALKYLAMINO BENZENDIOLS

International Patent Classification(s)
(51)^4 C07C 089/00 C07C 091/44

(21) Application No. : 72940/87 (22) Application Date : 14.05.87

(30) Priority Data

(31) Number	(32) Date	(33) Country
864063	16.05.86	US UNITED STATES OF AMERICA

(43) Publication Date : 19.11.87

(44) Publication Date of Accepted Application : 30.08.90

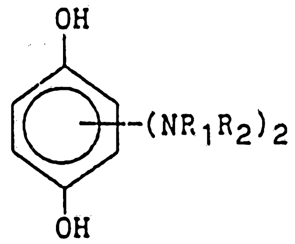
(71) Applicant(s)
THE DOW CHEMICAL COMPANY

(72) Inventor(s)
MUTHIAH N. INBASEKARAN; ROBERT M. STROM

(74) Attorney or Agent
PHILLIPS,ORMONDE & FITZPATRICK

(56) Prior Art Documents
AU 35851/50 155341 C07C 089/00
AU 35722/50 155699 C07C 089/00
US 3557159

(57) The benzenediol compounds prepared by the process of the present invention correspond to the following general formula:



(II)

wherein: R_1 and R_2 are as defined in formula (I).

.../2

CLAIM

1. A process for preparing diamino-, dibenzylamino- and dialkylamino- benzenediols which comprises reacting a diaminodihalo-, dibenzylaminodihalo- or dialkylaminodihalo- benzoquinone with a hydrogenating agent in the presence of a solvent and a noble metal-containing catalyst under suitable reaction conditions such that the corresponding benzenediol is produced.

2. A process as claimed in Claim 1 wherein the benzoquinone starting material corresponds to the following general formula:

$$(X)_2\text{-B-}(NR_1R_2)_2 \qquad (I)$$

wherein: B is 1,4-benzoquinone; each X is independently a chlorine, bromine, fluorine or iodine atom; and R_1 and R_2 independently are a hydrogen, C_1-10 alkyl or benzyl group.

AUSTRALIA

Patents Act

600941

COMPLETE SPECIFICATION

(ORIGINAL)

Class
Int. Class

Application Number: 72940/87
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority

Related Art:

This document contains the amendments made under Section 49 and is correct for printing

---

APPLICANT'S REF.: Dow Case 33,588-F

Name(s) of Applicant(s):
THE DOW CHEMICAL COMPANY

Address(es) of Applicant(s):
2030 Dow Center,
Abbott Road,
Midland,
Michigan 48640, UNITED STATES OF AMERICA

Actual Inventor(s):
Muthiah N. Inbasekaran and Robert M. Strom

Address for Service is:
PHILLIPS, ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia, 3000

Complete Specification for the invention entitled:

PREPARATION OF DIAMINO-, DIBENZYLAMINO- AND DIALKYLAMINO- BENZENEDIOLS

AUSTRALIAN PATENT OFFICE
LS

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

PREPARATION OF DIAMINO- AND DIALKYLAMINOBENZENEDIOLS

This invention concerns the hydrogenation of benzoquinone compounds. More specifically, it pertains to a process for the hydrogenation of diaminodihalo-, dibenzylaminodihalo and dialkylaminodihalobenzoquinones to produce diamino-, dibenzylamino- and dialkylaminobenzenediols.

Diamino-, dibenzylamino and dialkylaminobenzenediols are useful as monomers in the preparation of polybenzoxazoles (PBO). Polybenzoxazoles can be prepared by reacting certain benzenediols with bisacids, bisacid halides, bisesters or bisnitriles. Polybenzoxazole fibers have high tensile strength and thermal stability and are desirable for aerospace and other applications requiring rigid materials.

The known methods for preparing the benzenediol monomers typically involve a multi-step synthesis wherein expensive reagents are required and overall yield is poor. For example, one method involves oxidative bishydroxylation of hydroquinone with hydrogen peroxide and an alkali to produce 2,5-dihydroxy-p-benzoquinone. The reaction of hydrogen chloride and methanol with the dihydroxybenzoquinone yields 2,5-dimethoxy-p-benzoquinone which is aminated with ammonia and then reduced with stannous chloride in concentrated hydrochloric acid to give 2,5-diamino-1,4-benzenediol with an overall yield of only about 20 percent. See R. Wolf, M. Okada and C. S. Marvel, J. Polymer Science, Part A, 6, 1503 (1968).

A direct reduction of 2,5-diamino-1,4-benzoquinone with stannous chloride and HCl to produce 2,5-diamino-1,4-benzenediol is described in Beilstein's Handbuch der Organischen Chemie, 4th ed., Main Work, V. 13, p. 791. This process suffers from the fact that the diaminobenzoquinone starting material is not readily commercially available but must be prepared from the cheaper hydroquinone by the multi-step process mentioned above. Other methods involve the reduction of a dihalodiaminobenzoquinone to the corresponding dihalodiaminohydroquinone without the elimination of the halogen substituents. See, for example, U.S. Patent 4,337,196; British Patent 1,130,275 and French Patent 1,544,504.

A simple economical process is needed that would provide a high yield and allow both the reduction of the benzoquinone and the elimination of the halogen substituents. Such a process would allow the effective production of diamino-, dibenzylamino- and dialkylaminobenzenediol monomers for use in preparing the highly desirable polybenzoxazoles.

The present invention provides such a straightforward and inexpensive one-step process that provides a high yield of diamino-, dibenzylamino- and dialkylaminobenzenediols. This process comprises reacting, under suitable reaction conditions, a readily available diaminodihalo,-dibenzylaminodihalo- or dialkylaminodihalobenzoquinone with a hydrogenating agent in the presence of a solvent and a noble metal-containing catalyst. It has surprisingly, been found that the use of a noble metal-containing catalyst in the present process results in a high yield and provides for reduction of the benzoquinone and elimination of the halogen substituents.

The diamino-, dibenzylamino- and dialkylaminobenzenediols so produced can be condensed with bisacids, bisacid halides, bisesters or bisnitriles to produce polybenzoxazoles. Polybenzoxazole fibers have high tensile strength and thermal stability and hence have great potential for various industrial applications.

~~The present invention provides such a straightforward and inexpensive one-step process that provides a high yield of diamino- and dialkylaminobenzenediols. This process comprises reacting, under suitable reaction conditions, a readily available diaminodihalo- or dialkylaminodihalobenzoquinone with a hydrogenating agent in the presence of a solvent and a noble metal-containing catalyst. It has surprisingly been found that the use of a noble metal-containing catalyst in the present process results in a high yield and provides for reduction of the benzoquinone and elimination of the halogen substituents.~~

~~The diamino- and dialkylaminobenzenediols so produced can be condensed with bisacids, bisacid halides, bisesters or bisnitriles to produce polybenzoxazoles. Polybenzoxazole fibers have high tensile strength and thermal stability and hence have great potential for various industrial applications.~~

According to the process of the present invention, the benzoquinone starting material is contacted with a hydrogenating agent in the presence of a solvent and a catalyst. The preferred benzoquinone compounds used as the starting material in the present invention correspond to the following general formula:

$$(X)_2\text{-B-}(NR_1R_2)_2 \qquad \text{(I)}$$

wherein: B is 1,4-benzoquinone; each X is independently a chlorine, bromine, fluorine or iodine atom, most preferably chlorine; and R_1 and R_2 independently are a hydrogen, C_{1-10} alkyl or benzyl group, most preferably hydrogen.

Typical benzoquinone compounds of formula (I) include, for example, 2,5-dichloro-3,6-diamino-1,4-benzoquinone, 2,5-dibromo-3,6-diamino-1,4-benzoquinone, 2,5-dichloro-3,6-dibenzylamino-1,4-benzoquinone, 2,5-dichloro-3,6-dimethylamino-1,4-benzoquinone, 2,5-dichloro-3,6-diethylamino-1,4-benzoquinone; preferably 2,5-dichloro-3,6-diamino-1,4-benzoquinone, 2,5-dichloro-3,6-dimethylamino-1,4-benzoquinone and 2,5-dichloro-3,6-dibenzylamino-1,4-benzoquinone. The most preferred benzoquinone starting material is 2,5-dichloro-3,6-diamino-1,4-benzoquinone.

The benzoquinone starting materials of formula (I) can be prepared by methods well-known in the art. The typical preparation usually involves the reaction of excess ammonia or ammonium hydroxide with tetrahaloquinone. See, for example, U.S. Patent 4,337,196.

A hydrogenation catalyst is advantageously employed in the practice of the present process. The catalyst can be any material which contains a noble metal and will catalyze the conversion of the benzoquinone starting material of formula (I) in the presence of a hydrogenating agent to the desired benzenediol. Examples of typical catalysts include, for example, noble metals on carbon, noble metal oxides, and noble metals supported on alkaline earth carbonates. Noble metals herein refer to gold, silver, platinum, palladium, iridium, rhodium, mercury, ruthenium and osmium. Preferred catalysts include palladium on carbon, platinum on carbon, and platinum oxide. The most preferred hydrogenation catalyst is palladium on carbon. The catalyst is employed in an amount which is sufficient to catalyze the conversion of starting material in the presence of a hydrogenating agent to the corresponding benzenediol. Typically, from 0.0005 to 0.1 molar equivalents of catalyst are present per equivalent of benzoquinone starting material. Preferably, from 0.02 to 0.05 equivalents of catalyst are present throughout the reaction.

A solvent is advantageously employed in the present process. Such solvents preferably are compounds having at least one oxygen atom therein, such as, for example, water, ethers, esters, ketones, alcohols, or carboxylic acids. Specific examples of preferred solvents include water, methanol, ethanol, propanol, dimethylformamide or dioxane. Water is the most preferred solvent. Preferably, from 1 to 50 volumes of solvent are employed per volume of benzoquinone starting material of formula (I). More preferably, from 5 to 10 volumes of solvent are employed.

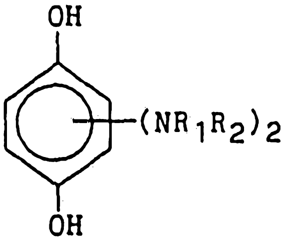
Hydrogenating agents are well-known. The hydrogenating agent employed in the process of the present invention can be any material which will supply hydrogen to the reaction. In the present process hydrogen gas or hydrazine is preferred. The hydrogenating agent is used in an amount sufficient to hydrogenate the benzoquinone starting material of formula (I). When hydrogen is employed, the molar ratio of hydrogen gas to benzoquinone starting material is between 3:1 and 30:1; preferably, about 5:1. Typically, from 4 to 8 molar equivalents of hydrazine are employed per equivalent of benzoquinone starting material. Preferably, from 3 to 6 molar equivalents of hydrazine are employed.

The present process is conducted under suitable reaction conditions such that the corresponding benzenediol is produced. Such suitable conditions are given below.

The process of the present invention can be carried out at any temperature and pressure at which the reaction will proceed. Preferably, the process is carried out between 20 and 100°C, most preferably between 20 and 50°C. The process can be carried out at sub- or superatmospheric pressures with atmospheric pressure being preferred for convenience. A total reaction time of from 4 to 72 hours is generally adequate to convert the starting material of formula (I) to the corresponding benzenediol.

Surprisingly, in the process of the present invention, the halogen atoms are removed from the benzoquinone ring system and the benzoquinone is converted to the corresponding benzenediol. As the halogen atoms are removed, a hydrogen halide is believed to be produced. While not wanting to be bound by any theory, it is believed that a unique feature of the present invention is the ability of the amino groups to capture the hydrogen halide as it is produced and thereby avoid acid poisoning of the catalyst. The presence of the amino groups apparently eliminates the need for the addition of external base as the reaction proceeds and thereby offers an added economic advantage. Furthermore, the hydrogen halide thus trapped by the amino groups apparently helps to stabilize the benzenediol and thereby avoids oxidative decomposition of the product. Both by avoiding catalyst poisoning and effectively stabilizing the final product, the amino groups appear to aid in generating surprisingly high yields.

The benzenediol compounds prepared by the process of the present invention correspond to the following general formula:



(II)

wherein: R_1 and R_2 are as defined in formula (I).

Typical benzenediols include, for example, 2,5-diamino-1,4-benzenediol, 2,5-dibenzylamino-1,4-benzenediol, 2,5-dimethylamino-1,4-benzenediol, 2,5-diethylamino-1,4-benzenediol; preferably 2,5-diamino-1,4-benzenediol, 2,5-dimethylamino-1,4-benzenediol or 2,5-dibenzylamino-1,4-benzenediol. The most preferred benzenediol is 2,5-diamino-1,4-benzenediol.

The product of formula (II) can be recovered using known recovery methods such as, for example, filtration or washing. The product is generally isolated and stored as a hydrohalide salt in order to prevent oxidative decomposition. It is also suitable common practice to isolate the product as a salt of any mineral acid such as sulfuric, nitric or phosphoric acid. Typical yields of the benzenediol of formula (II) are at least 50 to 90 percent based on the benzoquinone starting material of formula (I). Preferably, the yield will be at least about 70 percent. The maximum yields generally are obtained when hydrogen gas is directly applied.

The following examples are given to illustrate the invention and should not be construed as limiting its scope.

Example 1

To a reaction vessel was added 24.6 g of 2,5-dichloro-3,6-diamino-1,4-benzoquinone, 1.6 g of 10 weight percent palladium on carbon and 300 ml of water. The mixture was vigorously stirred and hydrogen gas simultaneously passed through the mixture for 48 hours at ambient temperature. The mixture was then filtered and washed with 50 ml of water. Then, 150 ml of concentrated hydrochloric acid was added, with cooling, to the filtrate. After 30 minutes, the white crystals were filtered, washed with small amounts of ethanol and ether, and suction dried. The yield of 2,5-diamino-1,4-benzenediol bishydrochloride was 87.3 mole percent (22.10 g) based on the benzoquinone starting material.

Example 2

To a reaction vessel was added 23.5 g of 2,5-dichloro-3,6-dimethylamino-1,4-benzoquinone, 2.0 g of 10 weight percent palladium on carbon and 400 ml of water. The mixture was vigorously stirred and hydrogen gas simultaneously passed through the mixture for 72 hours at ambient temperature. The mixture was then filtered and washed with 50 ml of water. Then, 200 ml of concentrated hydrochloric acid was added, with cooling, to the filtrate. After 30 minutes, the white crystals were filtered, washed with small amounts of ethanol and ether, and suction dried. The yield of 2,5-dimethylamino-1,4-benzenediol bishydrochloride is 85.0 mole percent (20.31 g) based on the benzoquinone starting material.

The examples demonstrate that the process of the present invention is a simple and efficient method capable of producing surprisingly high yields of diamino-, dibenzylamino and dialkylaminobenzenediols.

LS

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for preparing diamino-, dibenzylamino- and dialkylamino- benzenediols which comprises reacting a diaminodihalo-, dibenzylaminodihalo- or dialkylaminodihalo-benzoquinone with a hydrogenating agent in the presence of a solvent and a noble metal-containing catalyst under suitable reaction conditions such that the corresponding benzenediol is produced.

2. A process as claimed in Claim 1 wherein the benzoquinone starting material corresponds to the following general formula:

$$(X)_2\text{-}B\text{-}(NR_1R_2)_2 \qquad \text{(I)}$$

wherein: B is 1,4-benzoquinone; each X is independently a chlorine, bromine, fluorine or iodine atom; and R_1 and R_2 independently are a hydrogen, C_1-10 alkyl or benzyl group.

3. A process as claimed in Claim 2 wherein the benzoquinone starting material is 2,5-dichloro-3,6-diamino-1,4-benzoquinone, 2,5-dibromo-3,6-diamino-1,4-benzoquinone, or 2,5-dichloro-3,6-dibenzyalmino-1,4-benzoquinone.

4. A process as claimed in any one of Claims 1 to 3 wherein the hydrogenating agent is hydrogen gas, the molar ratio of hydrogen gas to benzoquinone starting material being in the range 3:1 to 30:1.

5. A process as claimed in any one of Claims 1 to 3, wherein the hydrogenating agent is hydrazine.

6. A process as claimed in any one of Claims 1 to 5, wherein the solvent is an oxygen-containing compound.

7. A process as claimed in any one of Claims 1 to 5, wherein the solvent is water.

8. A process as claimed in any one of Claims 1 to 7, wherein the catalyst is a noble metal supported on an alkaline earth carbonate.

9. A process as claimed in any one of Claims 1 to 7, wherein the catalyst is a noble metal supported on carbon.

10. A process as claimed in any one of Claims 1 to 7, wherein the catalyst is palladium on carbon.

11. A process as claimed in any one of Claims 1 to 10, wherein from 0.02 to 0.05 equivalents of catalyst are present per mole of benzoquinone.

12. A process as claimed in Claim 1 for the preparation of 2,5-diamino-1,4-benzenediol which comprises reacting hydrogen gas with a 2,5-dihalo-3,6-diamino-1,4-benzoquinone, a noble metal-containing a catalyst and a solvent, under suitable conditions such that a 2,5-diamino-1,4-benzenediol is produced in a yield of greater than 70 percent based on the benzoquinone.

13. A process as claimed in Claim 12, wherein the 2,5-dihalo-3,6-diamino-1,4-benzoquinone is 2,5-dichloro-3,6-diamino-1,4-benzoquinone.

14. A process as claimed in Claim 12 or Claim 13, wherein the solvent is water.

15. A process as claimed in any one of Claims 12 to 14, wherein the catalyst is palladium on carbon.

16. A process as claimed in any one of Claims 1 to 15, wherein the benzenediol is produced in a yield of from 50 to 90 percent based on the benzoquinone.

17. A process as claimed in Claim 1, substantially as hereinbefore described with reference to any one of the examples.

DATED: 5 June 1990

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
THE DOW CHEMICAL COMPANY