

ORIGINAL

<p style="text-align: center;">FORM 2 THE PATENTS ACT 1970 (39 of 1970) AND The Patents Rules, 2003 COMPLETE SPECIFICATION (See section 10 and rule13)</p>
<p>1. TITLE OF THE INVENTION: “INDUSTRIAL PROCESS FOR THE PREPARATION OF 3,3’ DICHLOROBENZIDINE DIHYDROCHLORIDE”</p>
<p>2. APPLICANT:</p> <p>(a) NAME: AGARWAL, SANDEEP</p> <p>(b) NATIONALITY: Indian</p> <p>(c) ADDRESS: Mohan Polyfab Pvt. Ltd., Plot No.6509 & 6510, GIDC, Near New Water Tank, Ankleshwar – 393 002, Gujarat, India.</p>
<p>3. PREAMBLE TO THE DESCRIPTION</p> <p>The following specification particularly describes the invention and the manner in which it has to be performed.</p>

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Technical field of the invention:

The present invention relates to a synthetic process for the preparation of 3,3'- dichloro benzidine dihydrochloride from 2,2'- dichlorohydrazobenzene by treating it with sulfuric acid and further precipitating 3,3'-dichlorobenzidine dihydrochloride using NaCl solution. The invention further relates to preparation of 2,2'-dichlorohydrazobenzene by reducing o-nitrochlorobenzene in presence of dianol-25 to obtain 2,2'-dichloroazoxybenzene, which on hydrogenation with activated Raney Nickel yields 2,2'-dichlorohydrazobenzene.

Background and prior art:

3,3'-dichlorobenzidine has the greatest economic importance of all known diphenyl bases. Both the free base and, in particular, the salts formed with mineral acids are valuable starting material for example for the production of azo dyes.

3,3'-dichlorobenzidine is generally prepared from o-nitrochlorobenzene by reduction followed by subsequent benzidine rearrangement of the resultant 2,2'-dichlorohydrazobenzene. There is ample literature available on preparation of 3,3'-dichlorobenzidine via 2,2'- dichlorohydrazobenzene.

US2794046 discloses a method for reduction of aromatic nitro compounds in presence of reducing agent, aldehyde and alkali metal hydroxide to obtain corresponding hydrazobenzenes. The invention further discloses the use of naphthoquinoid compound as reduction promoter.

In the process of US4550207, 4,4'-diaminodiphenyl compounds is prepared by reduction of azoxybenzenes, azobenzenes or mixtures of azobenzenes and azoxybenzenes with hydrogen or hydrazine in the presence of Raney nickel and subsequent rearrangement of the hydrazobenzenes in presence of a mineral acid. The reduction is carried out in aqueous or non-aqueous lower alcohols in the presence of alkali metal or alkaline earth metal hydroxides.

Reduction of aromatic nitro compounds to aromatic azoxy compounds using pure benzoquinone compound as reduction promoter is disclosed in US3821190.

IN206242 describes the preparation of 2,2'-dichlorohydrazobenzene by catalytic hydrogenation of o-nitrochlorobenzene in presence of Raney nickel and alkali hydroxide. In the process of the invention the preparation of 2,2'-dichloro-azoxybenzene is carried out by reaction of o-nitrochlorobenzene with formaldehyde in presence of aq. alkali metal hydroxide and employing dichlone as a catalyst.

JP63039848 relates to a method of synthesizing 2,2'-dichlorohydrazobenzene, 2,2'-dichloroazoxy benzene, 2,2'-dichloroazobenzene, or mixture of 2,2'-dichloroazoxy benzene. 2,2'-dichloroazobenzene are reduced with hydrazine hydrate in water under alkaline conditions and using Raney-Ni or alloy. The alkali concentration used is 3-25%, and more preferably 5-10%.

US5208376 describes process for the continuous preparation of 3,3'-dichlorobenzidine hydrochloride from 2,2'-dichlorohydrazobenzene by treatment with aqueous sulfuric acid, which comprises treating the 2,2'-dichlorohydrazobenzene in water immiscible aromatic solvent, in presence of alkali metal salt of an alkyl (C8-C23) polyglycol ether sulphate with sulfuric acid at a temperatures ranging 20 to 50°C.

IN213318 describes the preparation of 3,3'-dichlorobenzidine hydrochloride by catalytic hydrogenation of 2,2'-dichloroazoxybenzene using Raney nickel, in presence of acetone as a solvent. Subsequent rearrangement of 2,2'-dichlorohydrazobenzene to 3,3'-dichlorobenzidine hydrochloride is done using anhydrous HCl gas/liquid at 1-55°C.

CN 101225054 describes a preparation method of 2, 2'-dichlorohydrazobenzene, wherein 2-chloronitrobenzene and the sodium hydroxide are heated to react in water solution when the supermolecular compound Beta-cyclodextrin exists and the 2,2'-dichlorohydrazobenzene is obtained.

The processes disclosed in prior arts results in huge amount of amine byproducts, thus decreases overall yield of the final product. Excessive use of mineral acids for the final

rearrangement of 2,2'-dichlorohydrazobenzene to 3,3'-dichlorobenzidine hydrochloride poses purification problems.

In order to eliminate the difficulties and disadvantages of the above mentioned prior art processes and to improve the yield and purity of the desired product, 3,3'-dichlorobenzidine dihydrochloride, present inventor has come up with a new improved process for preparing 3,3'-dichlorobenzidine dihydrochloride.

Object of the invention:

The object of the present invention is to provide an improved synthetic method for 3,3'-dichlorobenzidine dihydrochloride by ameliorating one or more disadvantages of existing methods to enhance the yields and purity.

Summary of the invention:

The present invention discloses an improved process for the preparation of 2,2'-dichloroazoxybenzene, which comprises conversion of o-nitrochlorobenzene to 2,2'-dichloroazoxybenzene in presence of formaldehyde, caustic lye solution, a reduction promoter and foaming agent/dispersing agent. Further hydrogenating 2,2'-dichloroazoxybenzene in presence of caustic lye solution and activated Raney Nickel catalyst in DMF, under vacuum conditions to get 2,2'-dichlorohydrazobenzene; followed by rearrangement reaction in presence of sulfuric acid to yield 3,3'-dichlorobenzidine sulfate, which upon treatment with salt solution yields 3,3'-dichlorobenzidine dihydrochloride.

Detailed description of the invention:

The invention will now be described in detail in connection with certain preferred and optional embodiments, so that various aspects thereof may be more fully understood and appreciated.

Accordingly, in one embodiment, the invention provides an improved process for preparation of 2,2'-dichloroazoxybenzene which comprises the reduction of o-nitrochlorobenzene in presence of formaldehyde and caustic lye solution, wherein the said reaction is characterized by the addition of foaming agent/dispersing agent, dianol 25

and reduction promoter, diclone 25; followed by stirring the reaction mass at a temperature range of 50-55⁰C to obtain 2,2'- dichloroazoxy benzene in crude form, which upon washing with water yields pure 2,2'- dichloroazoxy benzene.

The sequence of the above process steps as follows:

- i) charging 48% caustic lye in water in MS Jacket reactor;
- ii) cooling the above said alkali solution to 40⁰C;
- iii) adding o-nitrochlorobenzene in caustic lye solution;
- iv) charging Dianol 25 and Diclone to the above reaction mass;
- v) starting continuous addition of HCHO(37%) at a temperature range of 50-55⁰C;
- vi) obtaining 2,2'-dichloroazoxybenzene in crude form; and
- vii) washing crude 2,2'-dichloroazoxybenzene by water and isolated pure 2,2'-dichloroazoxybenzene at 70⁰C.

Addition of Dianol 25 (2,4-diaminophenol dihydrochloride) as a dispersing and foaming agent, forms additional feature of the invention. The use of Dianol 25 reduces the reaction time and also helps in the easy separation of crude 2,2'-dichloroazoxybenzene from the mother liquor.

In another aspect, the invention discloses a process for preparing 2,2'-dichlorohydrazobenzene from 2,2'-dichloroazoxybenzene which comprises hydrogenating the 2,2'-dichloroazoxybenzene in presence of activated Raney Nickel in DMF under inert atmospheric conditions (in presence of N₂ atmosphere) at temperature ranging at about 65-85⁰C to obtain 2,2'-dichlorohydrazobenzene. After completion of the hydrogenation reaction, the temperature is increased to 90⁰ C to separate the 2,2'-dichlorohydrazobenzene from the mother liquor.

The Raney Nickel is activated by dispersing in DMF, which forms another aspect of the invention.

The sequence of the above process comprises the following steps:

- i) charging 2,2'-dichloroazoxybenzene in Hydrogenator (S.S. Autoclave 316);

- ii) adding caustic lye and water to the above mass (of step 1) to maintain 3% alkalinity of the total mass;
- iii) purging of nitrogen and charging activated Raney Ni catalyst in Dimethylformamide (DMF) under vacuum conditions to the reaction mass of step 2;
- iv) hydrogenating 2,2'-dichloroazoxy benzene with Raney Nickel catalyst in DMF at temp range of 65-85⁰C to get 2,2'-dichlorohydrazobenzene;
- v) purging of nitrogen to remove the hydrogen from the reactor; and
- vi) increasing the temperature up to 90⁰C to separate 2,2'-dichlorohydrazobenzene from its alkaline mother liquor.

Purging with nitrogen (step 3) is done to remove the oxygen from Hydrogenator, so that the Raney nickel does not deactivate at the time of charging.

In another embodiment, the invention provides advancement/improvement over the existing technologies of preparing 3,3'-dichlorobenzidine dihydrochloride, which comprises mixing 2,2'-dichlorohydrazobenzene with toluene to obtain HBT, followed by filtering and washing the HBT with water to remove the traces of o-chloroaniline along with Raney Nickel, formed during the hydrogenation reaction. The HBT mixture (2,2'-dichlorohydrazobenzene with toluene) is further treated with sulfuric acid, to achieve the rearranged product 3,3'-dichlorobenzidine sulfate, which is separated from toluene on hot water treatment at 90⁰C.

The rearranged product, sulphate salt of 3,3'-dichlorobenzidine is further treated with NaCl solution to precipitate out the desired product, 3,3'-dichlorobenzidine dihydrochloride, directly from the reaction mass, which forms another key aspect of the present invention.

The above process is carried out as mentioned below:

- i) charging 2,2'-dichlorohydrazobenzene and toluene in S.S Reactor to get HBT (2,2'-dichlorohydrazobenzene in toluene);

- ii) filtering the HBT of the step 1 to Brick line reactor to remove byproduct o-chloroaniline and Raney Nickel by washing with 3% HCl to get pure HBT;
- iii) treating 56%-58% H₂SO₄ with pure HBT (2,2'-dichlorohydrazobenzene in toluene) at a temperature of 20-25°C in Jacketed lead line reactor under chilling to get rearranged product 3,3'-dichlorobenzidine sulfate;
- iv) adding hot water to the above sulphate salt of step 3, followed by heating at temperature 90°C;
- v) separating the sulphate salt from toluene and transferring the sulphate salt to another brick line reactor in the last stage of isolation;
- vi) adding 30% NaCl solution to the sulphate salt of the step 5, to precipitate out 3,3'-dichlorobenzidine dihydrochloride of the present invention; and
- vii) filtering, centrifuging and drying 3,3'-dichlorobenzidine dihydrochloride to get it in powder form.

The following examples, which include preferred embodiments, will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purpose of illustrative discussion of preferred embodiments of the invention.

Examples:

Example 1

Preparation of 2,2'-dichloroazoxybenzene:

240 gm of 48% caustic lye is charged in 100ml water in MS Jacket reactor. Alkali solution is cooled to 40°C and 450gm o-nitrochlorobenzene is added in caustic lye solution. 0.5 gm Dianol 25 and 4.5gm Diclone is charged to the above reaction mass. 350 gm HCHO (37%) is continuously added at a temperature range of 50-55°C to obtain 2,2'-dichloroazoxybenzene in crude form. Washing crude 2,2'-dichloroazoxybenzene with 20 lit water to obtain pure 2,2'-dichloroazoxybenzene.

Yield- 300 gm.

Example 2

Preparation of 2,2'-dichlorohydrazobenzene:

290 gm 2,2'-dichloroazoxybenzene is charged in Hydrogenator (SS316 Autoclave). 30 gm caustic lye and 20 ml water is added to the above mass to maintain 3% alkalinity of the total mass. Nitrogen is purged and 1 gm Activated Raney Ni catalyst is charged in 0.5 lit Dimethylformamide (DMF) under vacuum conditions. 700 Grams hydrogen gas is introduced at temperature range of 65-85⁰C to get 2,2'-dichlorohydrazobenzene; Nitrogen is again purged to remove the hydrogen from the reactor. Temperature is increased up to 90⁰C to separate 2,2'-dichlorohydrazobenzene from its alkaline mother liquor.

Yield- 232 gm.

Example 3

Preparation of 3,3'-dichlorobenzidine dihydrochloride:

360 gm 2,2'-dichlorohydrazobenzene and 33 gm of fresh toluene is charged in S.S Reactor. HBT (2,2'-dichlorohydrazobenzene in toluene) is filtered to Brick line reactor to remove byproduct o-chloroaniline and Raney Nickel by washing with 3% HCl to get pure HBT. Pure HBT is charged in 400 gms of 56%-58% solution of H₂SO₄ at a temperature of 20-25⁰C in Jacketed lead line reactor under chilling to get 3,3'-dichlorobenzidine sulfate, followed by addition of hot water and further heating at temperature 90⁰C. Sulphate salt is separated from toluene and transferred to another brick line reactor. 1.3 lit of 30% NaCl solution is added to the sulphate salt to precipitate out 3,3'-dichlorobenzidine dihydrochloride. Finally 3,3'-dichlorobenzidine dihydrochloride is filtered, centrifuged and dried to get 3,3'-dichlorobenzidine dihydrochloride in powder form.

Yield- 358 gm


Purity- 74%.

We claim,

1. A process for industrial preparation of 3,3'-dichlorobenzidine dihydrochloride comprising the steps of:
 - i. reducing o-nitrochlorobenzene using formaldehyde in aqueous caustic lye solution in presence of a reduction promoter and dispersing/foaming agent, followed by water treatment to obtain 2,2'-dichloroazoxybenzene in pure form;
 - ii. hydrogenating 2,2'-dichloroazoxybenzene using activated Raney Nickel in DMF under inert atmosphere in presence of caustic lye to obtain 2,2'-dichlorohydrazobenzene;
 - iii. mixing 2,2'-dichlorohydrazobenzene with toluene to get HBT (2,2'-dichlorohydrazobenzene in toluene);
 - iv. filtering the HBT to remove byproduct o-chloroaniline along with Raney Nickel, followed by washing with HCl solution to get pure HBT;
 - v. treating pure HBT with H₂SO₄ solution at a temperature of 20⁰C - 25⁰C under chilling to get 3,3'-dichlorobenzidine sulfate;
 - vi. isolating 3,3'-dichlorobenzidine sulfate on hot water treatment at 90⁰C;
 - vii. precipitating 3,3'-dichlorobenzidine dihydrochloride directly from 3,3'-dichlorobenzidine sulfate by the addition of NaCl solution and
 - viii. filtering, centrifuging and drying of 3,3'-dichlorobenzidine dihydrochloride to get it in powder form.
2. The process as claimed in claim 1, wherein Diclone is used as a reduction promoter.
3. The process as claimed in claim 1, wherein Dinol 25 is used as dispersing/foaming agent.

4. The process as claimed in claim 1, wherein caustic lye in step (i) is used in 48% concentration.
5. The process as claimed in claim 4, wherein the said aqueous caustic lye solution is cooled to 40⁰C, before reacting with o-nitrochlorobenzene.
6. The process as claimed in claim 1, wherein pure 2,2'-dichloroazoxybenzene is isolated at temperature of 70⁰C.
7. The process as claimed in claim 1, wherein 2,2'-dichlorohydrazobenzene is isolated from its alkaline mother liquor under inert conditions at 90⁰C.
8. The process as claimed in claim 1, wherein the formaldehyde used is in 37% concentration and is continuously added at a temperature range of 50-55⁰C.
9. The process as claimed in claim 1, wherein the hydrogenation of 2,2'-dichloroazoxybenzene is conducted at a temperature range of 65-85⁰C.
10. The process as claimed in claim 1, wherein, the alkalinity is maintained at 3% during the hydrogenation reaction.
11. The process as claimed in claim 1, wherein 3% HCl is used for washing to remove byproduct o-chloroaniline and Raney Nickel.
12. The process as claimed in claim 1, wherein 56%-58% H₂SO₄ is used for the rearrangement of pure HBT.
13. The process as claimed in claim 1, wherein the NaCl solution used is in 30% concentration.

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