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(54) Process for preparing aniline derivatives.

(57) A process for the preparation of an aniline, which aniline is substituted at a 2- or the 4-position by a chlorine or bromine atom, from the corresponding nitrobenzene which is unsubstituted at the said 2- or the 4-position, which comprises passing an electric current through a divided electrochemical cell having a graphite cathode, which cell contains, in the cathode compartment, a solution of the nitrobenzene in a medium comprising an aqueous hydrohalic acid selected from hydrochloric acid and hydrobromic acid.

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PROCESS FOR PREPARING ANILINE DERIVATIVES

The present invention relates to an electrochemical process for the preparation of certain 2- and 4-haloanilines.

W. Lob, Ber. Dtsch. Chem. Ges., 29, 1896 (1894) disclosed the preparation of 2- and 4-chloroaniline, by passing an electric current through a divided cell which contained, in the cathode compartment, a platinum cathode, nitrobenzene and concentrated hydrochloric acid. Elbs and Silbermann, Z. Elektrochem., 7, 590 (1902) also disclosed the preparation of certain 4-chloroanilines by electrochemical reduction using a divided cell which contained in the cathode compartment, a copper cathode, the corresponding nitrobenzene and a mixture of hydrochloric acid and an alcohol.

We have now found that when 2- and 4-haloanilines are prepared according to methods of the kind described in the above-mentioned references, the current yield is poor, particularly when the current density is high.

Current yield and current density are important factors to consider when scaling up electrochemical processes for industrial production. Thus the higher the current yield and the higher the current density at which the process can be performed, the smaller the cells required, and the lower the capital cost of the process.

Surprisingly we have now found that certain 2- and 4- haloanilines may advantageously be prepared at high current densities by the electrochemical reduction of the corresponding nitrobenzenes in hydrohalic acids by using a divided electrolysis cell with a graphite cathode.

Accordingly, the present invention provides a process for the preparation of an aniline, which aniline is substituted at a 2- or the 4-position by a chlorine or bromine atom, from the corresponding nitrobenzene which is unsubstituted at the said 2- or the 4-position, which comprises passing an electric current through a divided electrochemical cell having a graphite cathode, which cell contains, in the cathode compartment, a solution of the nitrobenzene in a medium comprising an aqueous hydrohalic acid selected from hydrochloric acid and hydrobromic acid.

Preferably the medium contained in the cathode compartment also comprises an organic solvent, otherwise a phase transfer catalyst or a non-ionic surfactant should preferably be included in the cathode medium. Suitable phase transfer catalysts include trialkylammonium halides, for example dodecyltrimethylammonium bromide. Suitable non-ionic surfactants include trialkylamine-N-oxides, for example dimethyldodecylamine-N-oxide.

When the selected hydrohalic acid is hydrochloric acid, the product of the process will be a chloroaniline, and when it is hydrobromic acid, the product of the process will be a bromoaniline.

The nitrobenzene may be unsubstituted or substituted. Generally it will contain only one nitro group. Preferably the nitrobenzene is unsubstituted or is substituted by at least one substituent selected from a halogen atom, an aryl group, an alkyl group, an alkylaryl group, an alkoxy group, a haloalkyl group, a haloalkoxy group, a cyano group, an alkanoyl group, a hydroxy group, an amino group, an alkylamino group, a dialkylamino group, a carboxy group, and an aminocarbonyl group. More preferably the nitrobenzene is substituted by one or two substituents selected from a fluorine atom, a methoxy group, a trifluoromethyl group, and a hydroxy group. For example, the nitrobenzene may be 2-fluoronitrobenzene, 4-fluoronitrobenzene, 2-nitroanisole, 2-nitrobenzotrifluoride, 3-nitrophenol or 4-fluoro-3-nitrophenol.

In this specification, unless stated otherwise, any alkyl group preferably contains from 1 to 6 carbon atoms, and any aryl group is preferably a phenyl group. A halogen atom may be, for example, a fluorine, chlorine or bromine atom.

It will be appreciated that the concentration of the nitrobenzene in the solution is not critical to the operation of the process, and will depend upon a number of factors such as the temperature and whether an organic solvent is used. Conveniently it will be in the range of from 5 to 250 gl^{-1}, preferably from 10 to 100 gl^{-1}. Since the anilines obtainable by the process according to the invention are generally more soluble in the cathode medium than the corresponding nitrobenzenes, the cathode compartment may conveniently contain some undissolved nitrobenzene.

We have found that in the process according to the invention, the halogen atom is generally inserted into the 4-position in preference to the 2-position. Thus, when the nitrobenzene is unsubstituted at the 2- and 4-positions then the main product will generally be a 4-haloaniline.

The divided electrochemical cell used in the process according to the invention may be any conventional divided electrochemical cell. It will be appreciated that the cell should be divided by a porous material which is selectively permeable to protons. Preferably the cell is divided by a cation exchange membrane.

Suitable membranes include perfluorinated cation exchange membranes such as those sold under the trade mark "NAFION", available from Du Pont de Nemours, and "FLEMION", available from the Ashahi Chemical Company.

The electrodes in the electrochemical cell may conveniently be configured as parallel planar or reticulated electrodes or as particulate beds. The anode is preferably an oxygen Dimensionally Stable Anode (DSA) or lead dioxide on lead or titanium. (Oxygen DSA electrodes consist of titanium coated with a mixture of transition metal oxides).

Particularily good results have been obtained using a filter-press cell.

A convenient electrolyte medium for use in the anode compartment is a mixture of sulphuric acid, for example from 1 to 5 molar sulphuric acid, and an organic solvent, for example that present in the cathode compartment.

The current yield obtainable by the process according to the invention has been found to be surprisingly high when compared with that obtainable by methods of the kind described by Lob, Elbs and Silbermann. Furthermore the current yield has not been found to be substantially affected by increasing the current density within normal practical working limits. Indeed in experiments using an electrochemical cell divided by a cation exchange membrane, the current yield was found to be high even at a current density of 10,000 A m^{-2}, approaching the practical working limit of the membrane. Generally, in the process according to the invention, a current density in the range of from 100 to 12,000 A m^{-2}, preferably from 500 to 6,000 Am^{-2} will be employed.

The voltage employed during the process according to the invention may vary during the course of the electrolysis. This variation would be expected by one skilled in the art. Conveniently the voltage will be in the range of from 3 to 20 volts, preferably not more than 10 volts.

When an organic solvent is used in the process according to the invention it should be one which is miscible with water. Preferred organic solvents are selected from C(2-4) alkanols, acetone, tetrahydrofuran, acetonitrile and acetic acid. More preferably, the organic solvent is selected from ethanol, propan-1-ol, propan-2-ol and acetic acid. The percentage by volume of the organic solvent in the solution will depend upon the particular solvent used and the desired concentration of nitrobenzene. Generally, it will be in the range of from 5 to 30.

The concentration of hydrohalic acid used in the medium in the cathode compartment is preferably in the range of from 3 to 12 molar, more preferably from 3 to 10 molar. When the hydrohalic acid is hydrobromic acid, the concentration of acid in the medium is preferably lower than that used when hydrochloric acid is selected, for example it may be in the range of from 2 to 5 molar.

The process may conveniently be effected at a temperature in the range of from 20 to 100 °C, preferably from 40 to 60 °C.

Haloanilines which may be prepared by the process according to the invention are useful as intermediates in the preparation of agrochemicals, pharmaceuticals, and dyes. For example, 4-chloro-2-fluoroaniline is useful in the preparation of a herbicidally active compound, as described in United State patent number 4,624,699

The invention will now be described in detail in the following Examples. Examples 1 to 23 illustrate the process according to the invention, while Examples 24 to 26 are comparative Examples.

EXAMPLE 1

Preparation of 4-chloro-2-fluoroaniline

A 120 ml jacketted glass beaker was provided with a planar graphite cathode (15.5 cm^2, placed vertically) and an anode compartment consisting of a glass hemisphere (volume ca. 10cm^3) fitted with a sintered glass disc (3cm diameter), a glass tube (for filling with electrolyte and venting the gas formed) and a platinum wire spiral anode (15 cm length of 1mm diameter wire wound into a spiral of ca. 3cm diameter). The cell was closed with an air-tight lid, fitted with a gas inlet tube (to introduce nitrogen below the surface of the catholyte) and a watercooled condenser. The catholyte was stirred vigorously by means of a magnetic stirrer bar. The cathode compartment was filled with 6M hydrochloric acid/15v% n-propanol (100 cm^3) and the anode compartment filled with 3M sulphuric acid/15v% n-propanol (10cm^3). After passing a current of 1.0 A through the cell at 70 °C for 5 minutes, 2-fluoronitrobenzene was added (1.5g) with further 0.5 g additions every 30 minutes until a total of 6.5 g had been added. The electrolysis was continued at 1.0 A and 70 °C for 5.5 hours. The catholyte was removed, diluted to 230 cm^3 with water and a sample (2.0

cm^3) neutralised, extracted with ether and analysed by gas chromatography. The results indicated that 2.9g of 4-chloro-2-fluoroaniline had been formed (current yield 39%).

EXAMPLE 2

Preparation of 4-chloro-2-fluoroaniline

A filter-press cell (* MICRO FLOW CELL available from Electrocell AB) was fitted with a graphite cathode, an oxygen DSA anode and a cation exchange membrane (* NAFION 423 available from Dupont de Nemours). A series of spacers (PolyTetraFluoroEthylene) and gaskets (* KALREZ, available from Dupont De Nemours) formed the cathode and anode compartments and left an area of 15 cm^2 of the cathode and the anode exposed. When the cell was assembled the distance between the cathode and anode was 6mm. A piece of gauze (PolyVinyliDeneFluoride available as " * SOLEF from Solvey, filament dia. ca 1 mm, mesh ca. 10 mm) was placed in each compartment to increase turbulence and mixing. The cathode and anode compartments were both connected to separate circulating electrolyte loops, each consisting of a peristaltic pump and a stirred reservoir with heating mantle (250 cm^3). The catholyte reservoir was filled with 6M hydrochloric acid/20v% n-propanol (200 cm^3) and the anolyte reservoir filled with 3M sulphuric acid/20v% n-propanol (250 cm^3). The contents of the reservoirs were circulated through the respective electrode compartments at 30 1. hr-1 while heating took place. When both catholyte and anolyte reached a temperature of 70 °C a current of 1.5 A was passed through the cell (1,000 $A.m^{-2}$). After 5 minutes 2-fluoronitrobenzene was added (20 g) and the electrolysis continued at 1.5A and 70 °C for 7.4 hours. The catholyte was removed, cooled, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that 7.2 g of 4-chloro-2-fluoroaniline had been produced (48% current yield).

EXAMPLE 3

Preparation of 4-chloro-2-fluoroaniline

An electrolysis was carried out with the same cell and procedure as described in Example 2, except that 40 g of 2-fluoronitrobenzene was added initially and a current of 6 A (4,000 Am^{-2}) was used. After 2.4 hours at 6 A and 70 °C, the catholyte was removed, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that 10.3 g of 4-chloro-2-fluoro-aniline had been produced (53% current yield).

EXAMPLE 4

Preparation of 4-chloro-2-fluoroaniline

An electrolysis was carried out with the same cell and procedure as described in Example 3, except that a current of 15 A (10,000 Am^{-2}) was used. The temperature in the cell rose rapidly from an initial value of 70 °C to 80 °C. After 1 hour at 15 A and 80 °C, the catholyte was removed, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that 10.1 g of 4-chloro-2-fluoroaniline had been produced (52% current yield).

EXAMPLE 5

Preparation of 4-chloro-2-fluoroaniline

* Trade marks

An electrolysis was carried out using the same cell and procedure as described in Example 3, but using 9M hydrochloric acid/20v% n-propanol as catholyte and operating at 52° C. After 3.6 hours at 6 A and 52° C, the catholyte was removed, cooled, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that 15.6 g of 4-chloro-2-fluoroaniline had been produced (53% current yield).

EXAMPLE 6

Preparation of 4-chloro-2-fluoroaniline

An electrolysis was carried out using the same cell as described in Example 3, but using gaskets which were thinner (reducing the cathode and anode compartment volumes by ca. 25%) and which left only 10 cm^2 of each electrode exposed. The catholyte reservoir was filled with 9M hydrochloric acid/20v% n-propanol (200 cm^3) and the anolyte reservoir filled with 3M sulphuric acid/20v% n-propanol. The contents of the reservoirs were circulated through the respective electrode compartments at 30 l. hr-1 while heating took place. When both catholyte and anolyte reached a temperature of 50° C a current of 4.0 A was passed through the cell (4000 $A.m^{-2}$). After 5 minutes 2-fluoronitrobenzene was added (40 g) and the electrolysis continued at 4.0 A and 50° C for 5.3 hours. The catholyte was removed, cooled, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that 16.4 g of 4-chloro-2-fluoroaniline had been produced (57% current yield).

EXAMPLE 7

Preparation of 4-chloro-2-fluoroaniline

An electrolysis was carried out using the same cell as described in Example 5 but using a 500 cm^3 catholyte reservoir containing 400 cm^3 of 9M hydrochloric acid/20v% n-propanol and 100 g of 2-fluoronitrobenzene. After 7.7 hours at 6 A and 52° C, the catholyte was removed and evaporated at 60° C and as an azeotrope with water. To effect complete removal of 2-fluoronitrobenzene an extra 750 cm^3 of water had to be added. Ether (100 cm^3) was added to the distillate and the separated ether layer washed with dilute sodium hydroxide (10 cm^3, 3M), followed by drying and flashing to give 2-fluoronitrobenzene (35 g, >95% pure) in n-propanol (55 cm^3). The remaining catholyte was neutralised with sodium bicarbonate and the anilines removed by evaporation at 60° C and 0.1 bar. An additional 500 cm^3 of water had to be added to effect complete removal of the anilines. Ether (100 cm^3) was added to the distillate and the separated ether layer washed with dilute sodium hydroxide (10 cm^3, 3M), followed by drying and flashing of the solvent to give 30 g of 4-chloro-2-fluoroaniline (48% current yield).

EXAMPLES 8-14

Preparation of 4-chloro-2-fluoroaniline

Electrolyses were carried out using the same cell and procedure as described in Example 6, but using 9M hydrochloric acid containing 20v% of one of the following organic solvents.

a. ethanol
b. methanol
c. acetone
d. isopropanol
e. tetrahydrofuran
f. acetic acid
g. acetonitrile

The catholyte reservoir was filled with 9M hydrochloric acid/20v% organic solvent (200 cm^3) and the

anolyte reservoir filled with 3M sulphuric acid/20v% organic solvent (250 cm^3). The contents of the reservoirs were circulated through the respective electrode compartments at 30 1. hr-1 while heating took place. When both catholyte and anolyte reached a temperature of 50°C a current of 4.0 A was passed through the cell (4000 A.m-2). After 5 minutes 2-fluoronitrobenzene was added (40 g) and the electrolysis continued at 4.0 A and 50 deg C until it was clear that cathode passivation was taking place (sharp increase in cell potential). The catholyte was removed, cooled, neutralised and extracted with ether. The current yields were determined by gas chromatographic analysis of the ether extract (see Table 1).

Table 1

Example	Organic solvent	Current Yield (%)
8	ethanol	54
9	methanol	51
10	acetone	33
11	2-propanol	58
12	THF	56
13	acetic acid	58
14	acetonitrile	49

EXAMPLE 15

Preparation of 2-amino-5-chloroanisole

The cathode compartment of the cell described in Example 1 was filled with 9M hydrochloric acid/20v% ethanol (100 cm^3) and the anode compartment filled with 3M sulphuric acid/20v% ethanol (10 cm^3). After passing a current of 1.0 A through the cell at 60°C for 15 minutes, 2-nitroanisole was added (2.0g) with further additions of 0.5 g every 30 minutes until a total of 5.0 g had been added. The electrolysis was continued for 5.6 hours at the same current and temperature. The catholyte was removed, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that 2-amino-5-chloroanilsole was present (2.2 g, 27% current yield).

EXAMPLE 16

Preparation of 2-amino-5-chlorobenzotrifluoride

The cathode compartment of the cell described in Example 1 was filled with 9M hydrochloric acid/20v% n-propanol (10 cm^3). After passing a current of 1.0 A through the cell at 50°C for 15 minutes, 2-nitrobenzotrifluoride was added (1.5 g) with further additions of 0.5 g every 30 minutes until a total of 5.0 g had been added. The electrolysis was continued for 5.0 hours at the same current and temperature. The catholyte was then removed, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that two major products had been formed. These were identified as 2-amino-5-chlorobenzotrifluoride and 2-aminobenzotrifluoride (ratio 2:1).

EXAMPLE 17

Preparation of 2-chloro-5-aminophenol

The cathode compartment of the cell described in Example 1 was filled with 9M hydrochloric acid/20v% ethanol (100 cm^3) and the anode compartment filled with 3M sulphuric acid/20v% ethanol (10 cm^3). After

passing a current of 1.0 A through the cell at 60 °C for 15 minutes, 3-nitrophenol was added (1.5 g) with further additions of 0.5 g every 30 minutes until a total of 5.0 g had been added. The electrolysis was continued for 5 hours at the same current and temperature. The catholyte was diluted with water (100 cm^3) and extracted with ether (2 X 50 cm^3). The aqueous phase was neutralised with sodium bicarbonate and the light brown solid precipitated was collected and dried (2.5 g, identified by n.m.r. and mass spectrometry as 2-chloro-5-aminophenol, 37% current yield).

EXAMPLE 18

Preparation of 2-chloro-4-fluoroaniline

The cathode compartment of the cell described in Example 1 was filled with 9M hydrochloric acid/20v% ethanol (100 cm^3) and the anode compartment filled with 3M sulphuric acid/20v% ethanol (10 cm^3). After passing a current of 0.5 A throught the cell at 60 °C for 15 minutes, 4-fluoronitrobenzene was added (1.5 g) with further additions of 0.5 g every 30 minutes until a total of 5.0 g had been added. The electrolysis was continued for 6.5 hours at the same current and temperature. The catholyte was removed, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that 2-chloro-4-fluoroaniline was present (1.48 g, 34% current yield).

EXAMPLE 19

Preparation of 4-bromc-2-fluoroaniline

The cathode compartment of the cell described in Example 1 was filled with 4.5 M hydrobromic acid/20%v n-propanol (100 cm^3) and the anode compartment filled with 3M sulphuric acid/20v% n-propanol (10 cm^3). After passing a current of 1.0 A through the cell at 50 °C for 15 minutes, 2-fluoronitrobenzene was added (1.5 g) with further additions of 0.5 g every 30 minutes until a total of 5.0 g had been added. The electrolysis was continued for 4.5 hours at the same current and temperature. The catholyte was removed, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that 4-bromo-2-fluoroaniline was present (3.85 g, current yield 48%).

EXAMPLE 20

Preparation of 5-amino-2-chloro-4-fluorophenol

The cathode compartment of the cell described in Example 1 was filled with 9M hydrochloric acid/5v% ethanol (95 cm^3) and the anode compartment with 3M sulphuric acid/10% ethanol (10 cm^3). After passing a current of 1 A through the cell at 60 °C for 5 minutes, 4-fluoro-3-nitrophenol (4.0g) was added in ethanol (5 cm^3). The electrolysis was continued at the same current and temperature for 3 hours. The catholyte was removed, diluted with water (50 cm^3) and extracted with ether (100 cm^3). The aqueous phase was neutralised and extracted with ether (3 x 50 cm^3) and ethyl acetate (75 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated under vacuum to give a black solid (2.0g), identified by n.m.r. spectroscopy as 5-amino-2-chloro-4-fluorophenol.

EXAMPLE 21

Preparation of 4-chloro-2-fluoroaniline

A filter press cell (ELECTROCELL MP CELL available from Electrocell AB) was fitted with a graphite cathode (surface area 100 cm^2), an oxygen DSA anode and a cation exchange membrane (NAFION 423,

available from Dupont de Nemours). The cathode and anode compartments were both connected to separate circulating electrolyte loops, each consisting of a centrifugal pump and a stirred reservoir with heating mantle (6 dm^3). To the catholyte reservoir was added 9M hydrochloric acid (4.5 dm^3) and 2-fluoronitrobenzene (700 g) and to the anolyte reservoir 4.5 M sulphuric acid (4.5 dm^3). The contents of the reservoirs were heated to 55 °C, under nitrogen and circulated through the respective electrode compartments at 4.5 $dm^3 . min^{-1}$. A current of 40 A (4 $kA.m^{-2}$) was passed through the cell for 6.3 hours. The catholyte was removed from the reservoir and the cathode compartment of the cell and the catholyte reservoir washed with water (1 dm^3) and the washings combined with the catholyte. After standing overnight at room temperature the 2-fluoronitrobenzene (lower layer) was removed and the catholyte extracted with ether (3 x 0.5 dm^3). The combined extracts were added to the 2-fluoronitrobenzene phase and the resulting ether solution dried ($MgSO_4$) and evaporated to give 2-fluoronitrobenzene (336 g). The catholyte was neutralised to pH 4 with concentrated ammonia (2.6 dm^3) and extracted with dichloromethane (3 x 0.5 dm^3). The combined ether extracts were dried ($MgSO_4$) and evaporated to give 4-chloro-2-fluoroaniline (178 g, 49% selectivity). The current yield was 52%.

EXAMPLE 22

Preparation of 4-chloro-2-fluoroaniline

An electrolysis was carried out with the same cell and procedure as described in Example 21, except that dodecyltrimethylammonium bromide (10 g) was also added to the catholyte reservoir prior to beginning the electrolysis. After 6.3 hours at a current of 40 A, the electrolysis was stopped and the catholyte removed from the reservoir. The cathode compartment of the cell and catholyte reservoir were washed with water (1 dm^3) and the washings combined with the catholyte. After standing overnight at room temperature the 2-fluoronitrobenzene (lower layer) was removed and the catholyte extracted with dichloromethane (3 x 0.25 dm^3). The combined extracts were added to the 2-fluoronitrobenzene phase and the resulting dichloromethane solution dried ($MgSO_4$) and evaporated to give 2-fluoronitrobenzene (336 g). The catholyte was neutralised to pH 4 with concentrated ammonia (2.6 dm^3) and extracted with dichloromethane (3 x 0.25 dm^3). The combined ether extracts were dried ($MgSO_4$) and evaporated to give 4-choro-2-fluoroaniline (185 g, 51% selectivity). The current yield was 54%.

EXAMPLE 23

Preparation of 4-chloro-2-fluoroaniline

An electrolysis was carried out with the same cell and procedure as described in Example 21, except that dimethyldodecylamine-N-oxide (6 g) was also added to the catholyte reservoir prior to beginning the electrolysis. After 6.3 hours at a current of 40 A, the electrolysis was stopped and the catholyte removed from the reservoir. The cathode compartment of the cell and the catholyte reservoir were washed with water (1 dm^3) and the washings combined with the catholyte. After standing overnight at room temperature the 2-fluoronitrobenzene (lower layer) was removed and the catholyte extracted with dichloromethane (3 x 0.25 dm^3). The combined extracts were added to the 2-fluoronitrobenzene phase and the resulting dichloromethane solution dried ($MgSO_4$) and evaporated to give 2-fluoronitrobenzene (350 g). The catholyte was neutralised to pH 4 with concentrated ammonia (2.6 dm^3) and extracted with dichloromethane (3 x 0.25 dm^3). The combined ether extracts were dried ($MgSO_4$) and evaporated to give 4-choro-2-fluoroaniline (182 g, 52% selectivity). The current yield was 53%.

EXAMPLE 24 - COMPARATIVE EXAMPLE

Preparation of 4-chloro-2-fluoroaniline

A 120 ml jacketted glass beaker was provided with planar platinum plate cathode (12.5 cm^2, placed

vertically) and an anode compartment consisting of glass hemisphere (volume ca. 10 cm^3) fitted with a sintered glass disc (3 cm dia.), a glass tube (for filling with electrolyte and venting the gas formed) and a platinum wire spiral anode (15 cm length of 1 mm dia. wire wound into a spiral of ca. 3 cm dia.). The cell was closed with an air-tight lid, fitted with a gas inlet tube (to introduce nitrogen below the surface of the catholyte) and a watercooled condenser. The catholyte was stirred vigorously by means of a magnetic stirrer bar.

Concentrated hydrochloric acid (100 cm^3) was introduced into the cathode compartment and dilute sulphuric acid (10 v%, 10 cm^3) was introduced into the anode compartment. After passing a current of 0.2 A through the cell for 5 minutes, 2-fluoronitrobenzene was added (30 g) and the electrolysis continued at 0.2 A and room temperature for 11 hours. The catholyte was removed, neutralised and extracted with ether. Analysis of the ether extract by gas chromatographed indicated that traces of 4-chloro-2-fluoroaniline were present (0.08 g, 3% current yield).

EXAMPLE 25 - COMPARATIVE EXAMPLE

Preparation of 4-chloro-2-fluoroaniline

The cathode compartment of the cell described in Example 24 was filled with 6M hydrochloric acid/15v% n-propanol (10 cm^3). After passing a current of 0.4 A through the cell at 70 °C for 15 minutes, 2-fluoronitrobenzene was added (5.0 g) and the electrolysis continued for 11.5 hours at the same current. The catholyte was removed, neutralised and extracted with ether. Analysis of the ether extract by gas chromatography indicated that 4-chloro-2-fluoroaniline was present (0.58 g, 9% current yield).

EXAMPLE 26 - COMPARATIVE EXAMPLE

Preparation of 4-chloro-2-methylaniline

The reduction of 2-nitrotoluene was carried out under conditions described by Elbs and Silbermann ,Z. Elektrochem., 1902, 7, 590, (4M hydrochloric acid/50% ethanol, 50 °C, copper cathode, 1 kA. m^{-2}). The selectivity to 4-chloro-2-methylaniline was found to be 32% (90% conversion). Using a graphite cathode under the same conditions the selectivity to 4-chloro-2-methylaniline was 46% (100% conversion).

Claims

1. A process for the preparation of an aniline, which aniline is substituted at a 2- or the 4-position by a chlorine or bromine atom, from the corresponding nitrobenzene which is unsubstituted at the said 2- or the 4-position, which comprises passing an electric current through a divided electrochemical cell having a graphite cathode, which cell contains, in the cathode compartment, a solution of the nitrobenzene in a medium comprising an aqueous hydrohalic acid selected from hydrochloric acid and hydrobromic acid.

2. A process as claimed in claim 1, in which the medium in the cathode compartment comprises an organic solvent.

3. A process as claimed in claim 1 or claim 2 in which the nitrobenzene is unsubstituted or is substituted by at least one substituent selected from a halogen atom, a phenyl group, a C(1-6) alkyl group, a C(1-6) alkylphenyl group, a C(1-6) alkoxy group, a C(1-6) haloalkyl group, a C(1-6) haloalkoxy group, a cyano group, a C(1-6) alkanoyl group, a hydroxy group, an amino group, a C(1-6) alkylamino group, a C(1-6) dialkylamino group, a carboxy group, and an aminocarbonyl group.

4. A process as claimed in claim 3, in which the nitrobenzene is 2-fluoronitrobenzene, 4-fluoronitrobenzene, 2-nitroanisole, 2-nitrobenzotrifluoride, 3-nitrophenol, or 4-fluoro-3-nitrophenol.

5. A process as claimed in any one of claims 1 to 4, in which the cell is divided by a cation exchange membrane.

6. A process as claimed in any one of claims 2 to 5, in which the organic solvent is selected from a C-(2-4) alkanol, acetone, tetrahydrofuran, acetonitrile and acetic acid.

7. A process as claimed in claim 6, in which the organic solvent is selected from ethanol, propan-1-ol, propan-2-ol and acetic acid.

8. A process as claimed in any one of claims 2 to 7, in which the percentage by volume of the organic solvent in the medium is in the range of from 5 to 30.

9. A process as claimed in any one of claims 1 to 8, in which the concentration of hydrohalic acid in the medium is in the range of from 3 to 10 molar.

10. A process as claimed in any one of claims 1 to 9, in which the temperature is in the range of from 40 to 60 °C.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 20 2315

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE-A-2 617 808 (BASF AG) * Page 1, claims; page 4, lines 20-29 * ---	1	C 25 B 3/04 C 07 C 87/60
A	DE-C- 235 955 (C.N. OTIN et al.) * Example 1 * -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 25 B 3

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30-01-1989	GROSEILLER PH.A.

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