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electrochem reduction of 1-nitroalkenes to amine Success! :)

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Name	electrochem reduction of 1-nitroalkenes to amine Success! :)
IndoleAmine	<p>: electrochem reduction of 1-nitroalkenes to amine Success!</p> <p>If you mean your strange precipitation/crystallization technique, you could take ideas for improvements from here</p>
Bumblebee	<p>electrochem reduction of 1-nitroalkenes to amine Success! :)</p> <p>EDIT: SWIM did it with success last night: read it at the new post now at the bottom</p> <p>Somebee remembered what it read on rhodium's a time ago. This bee read similar things in Fester's Purple Book...</p> <p>But this poor Bee, has no idea, what will it have to use, so that it does not lose??? :lol:</p>

Quote

Experimental

Electrolysis: Divided standard beaker-type cell (150 ml), cathode = Hg pool (19.5 cm²) or graphite P 127 (9 cm², Sigri), anode = Pt foil (2 cm², ref. electrode = SCE, Luggin capillary, diaphragm = glass frit (G4), current source = Wenking HP 88 (Bank Electronic). General procedure for the reduction of 1-nitroalkenes to oximes

The cathodic compartement of the cell was charged with 30 ml of 0.1M sulfuric acid in IPA/water (3:2, v/v), subsequently by 3 mmol of substrate. Then the anodic chamber was filled with 8 ml of supporting electrolyte and introduced into the catholyte properly in order to minimize the space between the electrodes. With stirring and cooling (10-15°C) controlled potential electrolysis was carried out at -0.25 to -0.55 V (SCE), depending on the substrate (for the graphite cathode the potentials were about 400 mA more cathodic). After 4.0-4.2 F*mol⁻¹ had been consumed (i < 10 mA) the catholyte was treated with 10 mmol of hydroxylammonium chloride in 25 ml of water and with sat'd NaHCO₃ until pH was approx. 5. After 1 h of stirring, 100 ml of water was added and the solution extracted with 3 portions of ether. The combined org. phases were washed with brine and water, dried (MgSO₄) and concentrated to afford essentially pure oximes. Final chromatographic purification (petr.ether/ether 4:1 to 2:1) afforded the oximes in the following

yields:

- * Phenylacetaldehyde oxime, 85%
- * (4-chlorophenyl)acetaldehyde oxime, 85% (graphite cathode 76%)
- * Phenylacetone oxime, 91% (graphite cathode 85%)
- * 1-Phenyl-2-butanone oxime, 92%
- * 4-Methoxyphenylacetone oxime, 91%

General procedure for the reduction of the 1-nitroalkenes to the amines

The cathodic compartement was charged with 70 ml of 0.3M sulfuric acid in IPA/water (2:1, v/v), subsequently by 6 mmol of the 1-nitro olefin. After introducing the anodic chamber filled with 20 ml of supporting electrolyte, controlled potential electrolysis (-1.1 to -1.3 V) was performed at 10-15°C with stirring. After 7 to 8 F*mol⁻¹ gas evolution increased, and the reduction was terminated. the acidic catholyte was partially evaporated at reduced pressure and the residue extracted twice with ether. To the remaining aqueous phase 2M NaOH was added (pH 13) and the resulting emulsion was extracted with five portions of ether; the combined extracts were dried (MgSO₄) and concentrated to afford the amines:

- * 2-Phenethylamine, 66%
- * Amphetamine, 60%
- * 4-Chloro- β -phenethylamine, 60-69%
- * 1-Amino-2-(3-cyclohexen-1-yl)ethane, 60-69%

Bumblebee

nobody who has experience with it? is it worthwhile... is it not?

what kind of power source?

I thought it is a good way around Hg-Salts and the contamination Problem.

I had one additional thought...

when i'm distilling off the ethanol along with the ethylacetate, would it not be possible to distill off the remaining acid (H₂SO₄, Acetic) as well?? so a smaller amount of NaOH would be needed to basify reaction mix, and the whole thing would become more easy to handle...

I am an absolute newbie with not to many options to express what i mean with my traces of english :oops:

BB

nubee

can you remeber or find out the name of the book ?? as i feel it maybe available for download...

and yes, i too feel a certain "pull" towards the exploration of electrochemistry... :lol:

Bumblebee

Sorry, i talked about Uncle Festers purple book... :oops:

i meant SOMM (Secrets of methamphetamine manufacture, sixth edition) by Uncle Fester.

its available for download and to buy.

MargaretThatcher I'm a bit sceptical of these Fester electrochemical syntheses. Maybe they work. I don't know. There's that one with the palladium coin and a sheep gut condom. Sounds a bit dodgy to me.

You'll notice that the patent describes a controlled voltage reaction. Depending on the exact conditions, an incorrect voltage will either not work, encourage side reactions or over oxidise/reduce. When you have the thing working according to the patent, it is probably possible to simplify matters and create an exact recipe that works specifying current density applied for a certain time period.

There are lots of instructions for diy reference electrodes out there and it isn't too difficult to make your own voltage controlled source. You could even do it manually first time.

Bumblebee I were a bit sceptical too... thats whay i asked.
But i think it would be no problem to try and give the made experiences to you....

I also don't trust in everything what i read in "Secrets of Propane, 2-Amino N-Methyl 1-Phenyl manufacture" because some recipes were not tried by the author himself, and are theory or journal articles. But since i know that Fester is originally working as electroplater (respective in that industry), so i trust a bit more in his electrochemical recipes...

The calculation by Fester was made as follows:

Example:

1mol of P2nP

done in a 2500-3000ml Beaker

Quote

A reasonable size cathode in this case would measure at least 12cm by 6 cm for a face area of 72cm². 200 milliamps (0.2 amp) per square centimeter of face gives a required current flow of 14,4 amps, shown on the current meter.

the current meter is wired in on the line serving the anode...

Fairly heavy wiring would be needed to Carry that much current....

The reduction of 1-phenyl-2-nitropropene to 1-Phenyl 2-Aminopropane is an 8-electron reduction. So the theoretical amount of current needed to do the reduction is 8 faraday per mole of the nitroalkene in solution in the catholyte.

One faraday is 96500 coulombs, and a coulomb equals an amp-second. At 14.4 amps one farady passes into solution in 6700sec. this is 1,86 hours. Eight faradays flow in just under 15 hours. The process isn't 100% effecient so at least 12 to 16 faradays will be needed to do the reduction to completion. This will take 24 to 30 hours...

MargaretThatcher If you make or procure an SCE reference electrode, your chances of success will be higher. Thus you have 3 electrodes, the working electrode, the counter electrode and the reference electrode. The voltage is applied between the working and counter electrodes; the reference electrode is used only for measurement of potential difference with the working electrode.

<http://www.bioanalytical.com/products/ec/faqele.html>

In the patent, they will have used a potentiostat to control the potential difference, but you could do it manually.

Success, it works

Bumblebee

:D :lol: :) :o :D

Yeah! Right! Because SWIM has the right to do this legally we did it last night. So i got finally rid of that nasty P2NP i found a time ago.... :wink: :roll:

I am a simple mind, so i let that thing with the reference-electrode sit aside because it would get too much complicated for me and my abilities.

first i searched for a good cell divider... the glassing of a porcelain beaker was grinded off with a dremel and used in an attempt just with plain water and some H₂SO₄ to make it more conductive. there was only 100mA going through the solution... :cry: ...fucked it up...

Then i did think about the sheep's condom.... didn't find it anywhere... :(

then i found out that Cellophane is good for using it as the cell divider, but i lack of stability. The bags i formed got destroyed in the worm solution, but current passes by very good.

At least i found an little tiny terracotta flower pot without glaze or anything. This was just perfect it lets through 3-5A with my PC-Powersupply i used.

OK we set it up as follows:

A beaker 1000ml was filled with 300ml catholyte made out of 2 parts EtOH, 1 part H₂SO₄, and one part Acetic Acid (we did use GAA because we had nothing else) it has got the smell of ethylacetate instantly after mixing...

in the catholyte the flower pot (diam:4cm) was placed, and filled with dil. 5% H₂SO₄.

The P2NP (15g) was stirred into the catholyte which got yellowish coloured.

in the Catholyte was placed the Cathode made out of copper (50mm x 60mm t=3mm) and in the anolyte a piece of graphite (ca 2x2cm and 10cm long).

the Beaker was placed in a water bath on the magstirrer, and equipped with a stirbar.

the electrodes were connected to the 12V output of a PC-powersupply with an amperemeter in line.

the power was switched on and a lot of Hydrogen formed in the catholyte at the cathode. He let it run for 12 Hours @3-4,5A. Anolyte was filled up 2 times with H₂O because of the evaporation.

A lot of heat was produced but external cooling with a water bath did it hold in a 40°C area...

after the 12 hours the yellow P2NP colour and the smell was gone, and the catholyte seemed white to light yellow.

the cathode was in good condition but the anode was now just 5mm in diameter where it came in touch with the anolyte,:shock: .

the formed ethylacetate was distilled out of the solution and we stopped at a temperature of 110°C in the distilling flask (we are both no distilling experts and i hate distillations because make everytime something false and i am not patient enough...) but i think we didn't become all the ethylacetate out of solution.

the residue (about 200ml) was chilled, and made basic with NaOH, and Voila: strong smell of 1-phenyl-2-aminopropane :D :shock: :D.

a brown oil floats to the top (seemed to be ca 6ml),

the water layer was still yellowish and Ph around 4 so we added some more

NaOH-solution and suddenly there were clouds in the water layer and the colour turned to blue-grey (???), the water was strongly basic to ph-paper, so i stopped adding more NaOH.

200ml toluene was added, and the freebase extracted (there was a lot of brown/greyish mess in the water layer that formed an emulsion as we tried to separate.

the first pure light yellowish toluene layer was collected and a second extraction with toluene was done again... we tried to destroy the foamy emulsion between the layers with some IPA but then a big crystalline mass appeared at the bottom:oops: (what is this???)

toluene was poured off and put to the first extraction we done.

the toluene was washed 3 times with H₂O and set aside. It appears as a yellow liquid and holds still a lot of freebase i think, a piece of paper soaked in the toluene and dried at the air smelled like good product :wink: :lol:

i don't know if he should try to crystallize it now or after a distillation (you know: no experts... blah) since the half of the product will stick to the walls of the distilling setup...

i think we try to dry the Toluene and crystallize once and then recrystallize from ___?? ...

so long

BB

thenewrunne

bumblebee! That's just awesome. I was looking for "real" experimental information on the electro-method.

Will you be doing more trials of this? Would you mind putting together a more formal report about it so we have less of a problem following the path you took?

Bumblebee

i will first have to figure out what the extraction problems are, otherwise i can't tell for sure what is better or not in the reaction when the product gets lost while extracting... :)

for sure we try again maybe scaled up a bit.

@thenewrunne: what do you mean with a more formal report? If you mean my english... it's not really easy for me to express what i mean and have seen because i have another native language. which part couldn't you follow. :)

this was meant as a raw writeup of the experiment. To show that and how it works. If i forgot anything... ask :wink:

we will try to do this at a lower voltage next time using the 5V 15A Output from the Computer-Power Supply...

the fine thing is that there is nothing in this reaction that can be put on a "watched list". neither the acetic acid nor the sulfuric.... and ethanol and power from your power supply cannot be forbidden.... :D

MargaretThatcher

Superb results. Let us know if this gets right through to the finished product and an idea of yield.

Also, depending on the electrode geometry, you have a cathode area of around 30 cm², giving a current density of around 100 mA/cm² (half the patent). Be interesting to see how low a current you can go and still get a product. If you draw a voltage/current graph, you might be able to see where reduction kicks in. If you have a cathode with a

high enough hydrogen over-potential, you can reduce without getting any hydrogen evolution. Copper may be high enough, I don't know.

Nice one. :-)

Bumblebee should we make the sulphate ore the HCl salt out of it? I think we try making the sulfate with dil. H₂SO₄ in IPA... dripping it in a nd look what comes out, right?

tom-a-rom-rinbow very exciting! as fun as the amalgam reactions are i too think the electroreductions deserve more attention. i wonder if these can be scaled more effectively, given that you can directly control the reaction rate and that there are no stirring problems due to sludge... :twisted:

i have no experience with amph, but think it can be crystallized directly from toluene by titration with dilute h₂so₄. i would dry the toluene over MgSO₄ or similar first. sometimes adding a 5-10% portion of diethyl ether before cooling will help crystallization.

otherwise hcl gas is easy to generate by addition of hcl to conc h₂so₄ (be sure to stir or shake after every 1-2ml or these two will form separate layers). but Propane, 2-Amino 1-Phenyl .hcl is reported to be very hygroscopic and hard to crystallize.

thenewrunne @thenewrune: what do you mean with a mor formal report? If you mean my english... its not really easy for me to express what i mean and have seen because i have anothe native language. wich part couldn't you follow. Smile
this was meant as a raw writeup of the experiment. To s how that and how it works.
If i forgot anything... ask Wink
[/quote:bdfdc4354c]

No, the english if fine. More of just setting it up in a standard "Materials"
"Procedures" "Results" sections like on Rhodium. I followed everything you read.

Your experiments, if properly documented, could be the first of the "new"
Electroreductive reactions. From what I've read on here the electroreductions are not done before they are hard to duplicate. You have figured it out, we need you to share the knowledge and have others duplicate it so we can depend on the reaction.

As raw chemicals get harder and harder to find, doesn't it make sense to start using reactions that use fewer chemicals? If we put the same about of effort into perfecting this reaction as we did on Al/Hg reactions (as an example), we could enable other SyntheitkalBees (known as SBees :)) to increase their chances of success.

Bumblebee ok. :D
i will first determine how much yield we got from the first. monday i can buy some drying agents, to get everything waterfree, and i report back how many sulfate it yielded. if I find a way to make it free of H₂O with the equipment we already have i do it earlier.

i'm too lazy to distill it first because of the small scale, and since no Hg or other Poisons were used i skip it.
i hope all the pollution will stay in the toluene... i try to vacuumfilter it wash with icecold ipa in the buchner funnel and we will see if it looks white enough. when not, i will recrystallize....

-wich solvent to rextallize Amph-sulfate??

-any suggestions to determine purity? i fear that it is possible that the H₂SO₄ will form some other salts with reaction byproducts or acetic acid comounds?!? :?

re: electrochem reduction of 1-nitroalkenes to amine Success

bio

.....-any suggestions to determine purity?.....

Propane, 2-Amino 1-Phenyl dl (means racemic) Sulfate

Melting Point 280-281 (FYI Dextro isomer >300)

Will be depressed if impure somewhat proportionally

Density 1.15 (25/4)

BTW great work and a few more experiments should give you a current yield and density which is optimum and this will simplify the procedure. Perhaps do some patents searching for similar type reactions for clues of the optimum current density which will allow a more painless scale up.

If you need any help or with the write up just holler!

re: electrochem reduction of 1-nitroalkenes to amine Success

QuickFitAbuser

Hhmm, very interesting, being an old sheep Gut condom abuser from way back, and with an interest in coulombs, this is Very good reading.

Would like some more exact info on your electrode size vs current, but I get the general idea, and it would appear to work with a high efficiency.

Good Work, bumbleBee.

BioAssay pending?

re: electrochem reduction of 1-nitroalkenes to amine Success

MargaretThatcher

What is needed is to determine the actual working electrode voltage wrt a standard reference electrode. However, if the reaction works with the described conditions, it probably isn't too sensitive to voltage: as long as the PD is high enough, it will work.

If you have a high hydrogen overvoltage electrode, you might just be able to turn up the voltage until hydrogen starts to be evolved and then reduce the voltage a little. The reaction proceeds without hydrogen coming off. This would be a good way to set the voltage.

re: electrochem reduction of 1-nitroalkenes to amine Success

MargaretThatcher

I think one thing you might try is to keep the hydrogen overpotential of the cathode as high as possible, otherwise the hydrogen production which you describe competes with the reaction.

You could try a different cathode. Also, keep the electrode as smooth as possible (highly polished) and the temperature as low as possible.

Metal Overpotential

Mg 0.7

Zn 0.7

Al 0.5

Cd 0.5

Sn 0.45

Pb 0.45**Au 0.35****Cu 0.25****Ag 0.1****re: electrochem reduction of 1-nitroalkenes to amine Success****Bumblebee**

I crystallized the freebase today...

The freebase stands now for 3 or 4 days around in some toluene and i bought some MgSO₄ and dried for 1 hour, and filtered.i dripped in dil. H₂SO₄ in IPA but no crystals appeared. i checked PH with some wet Ph paper and it was still basic. I continued dripping in the diluted acid solution until the ph was around 8. Then i tried to use a electronic PH-Meter to determine the correct PH. I didn't know if it works in nonpolar, but i tried anyway, and it showed a stably PH of 8,7 and wasn't tilling around.

I added dil. sulfuric until Ph was 6,4.

I concentrated the solvent in an aspirator vacuum, until some yellow oil climbed up on the side of the flask, the rest got evaporated and i was left with ca 3-4 (estimated) ml oily crystalline mass at the bottom of the flask. i treated with some cool diethylether and nearly the complete oil seemed to crystallize...

the big lumps were broken up with a glass rod, swirled and the ether sucked off in a buchner funnel.

after drying there were 4,6g of almost white chrystals with a strong benzedrine smell. Bioassay confirmed success... :D

it is not that much of Product i thought i would get out of the pooled extracts, but it is alright for the first attempt.

what has done to improve this?

next time i will think about using less Voltage (use just the 5V out from PC Supply).

while the 12V out from those Pwrsupplies will give you up to 5 A the 5volt output serves you with up to 15 A.

and i think a better cooling is needed in the process due to the heat that the current produces.

re: electrochem reduction of 1-nitroalkenes to amine Success**icecool**Shouldn't chemicals that are being dried with MgSO₄ be dried for at least 12 hours?**re: electrochem reduction of 1-nitroalkenes to amine Success****Bumblebee**Shouldn't chemicals that are being dried with MgSO₄ be dried for at least 12 hours? [/quote:f3018ffd19]

That would explain why i got such a low yield! :)

I have so much to do with my job at the moment, if i find some minutes to do some research i will do so!

re: electrochem reduction of 1-nitroalkenes to amine Success**synthetika**

bumblebee,

Very encouraging results, and well done,

This is certainly of great interest to alot of members here,

Yes, I remember in 1999 or thereabouts when the hunt was on for Natural Sheep Condoms, for the fester Palladium Special

It is fascinating to see actual real world results on the electrochemical reactions such as this,

Getting the nitro compound to the amine, has always been close to the hearts of many bees, and well done, for showing another alternative,

Great Post, and I am sure that some basic tweaking will lead to better yields, and success for all those that want to use this method,

Keep up the good work, and if you like, you can send any of our mods, a copy of a complete write-up, and we can start to get these perfected methods well documented,

Synthetika

re: electrochem reduction of 1-nitroalkenes to amine Success

MargaretThatcher This is a real breakthrough. I wonder what the yield would be with MDP2NP. Also, lead might be a better working electrode (mercury would be the best from hydrogen overpotential considerations).

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