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Reduction of Nitroalkenes with Aluminium Amalgam

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I. Introduction

This procedure describes an efficient, high-yielding and completely OTC way of reducing virtually any nitrostyrene **OR** phenyl-2-nitropropene using aluminium amalgam.

Initially this approach to reducing nitroalkenes was pursued by **SunLight**[1] based on an old German reference[2]. However, due to the suboptimal work-up strategy, his results were far from ideal, which lead to this direction of research being almost completely buried in vain.

Luckily, some four years later an adventurous HyperLab Bee (who modestly wished to remain anonymous) decided to once again take a look at this procedure. His experiments ended in a complete and unquestionable success!

This news was privately communicated to certain reputable Hive and HyperLab members (who also wished to keep their names private) in order to verify the author's results. Very soon they also reported a pronounced success with this reaction.

II. Experimental

#1: The original procedure by *Hyperlab Bee #1*.

Into a 3 liter kitchen jar.....yes, exactly :-).

So... into a 3 liter kitchen jar there�s placed:

- 75 mmoles of any nitrostyrene or phenylnitropropene (that should bee ~20 g) *[Note 1]*
- 200 mls GAA
- 300 mls IPA
- 100 mls water
- 0.75-1.3 g $Hg(NO_3)_2$ *[Note 2]*

Lastly, 40 g of kitchen Al foil is dumped into the soup.

The suspension is incubated for 30-40 mins after which it assumes black color and starts heating up.

At this moment SWIM simply takes the whole shebang and shakes it violently until the full dissolution of the nitro. At this point the mixture is usually vigorously boiling and is so hot that it can't bee held with bare hands.

From that moment the reaction proceeds for 5-10 mins, leaving a grey aluminous sludge as the result. The sludge is immediately dissolved in 300 g KOH in 800 mls water (which makes the mixture again boil so violently that the jar's bottom once fell off - after that we switched to using plastic canisters). Surprisingly, this treatment seems to not harm the product at all

The result is a two-phase mixture, the upper layer being the desired amine in IPA.

The procedure has been tested multiple times on the nitroalkenes corresponding to TMA-2, TMA-6 and 2C-H. It always gave yields not less than 70%. *[Note 3]*

[Note 1]: the nitroalkene must bee purified (rextallization from IPA) as much as possible. Using dirty nitroalkenes results in a sharp drop in yield.

[Note 2]: the actual quantity of mercuric salt was never accurately measured - SWIM just added it at the tip of the knife.

[Note 3]: The lowest yield thus far was 12 mls of 2C-H freebase from 20 g of 2,5-diMeO-nitrostyrene.

Credits:

The author wants to thank:

Jess The Rabbit - the Muse, without whom nothing of the above would ever happen!

SunLight � for his original work that has been the source for everything that happened.

Bees of HyperLab:
- **Earendel** for being of an invaluable help
- **Mescalito** for pointing the author's attention into this direction.
- **Antoncho** for his assistance in translation and being a friend :-)

Experimental

#2: The experimental trials by *Hive Bee #1*.

A 3-necked 2L RB was equiped with a reflux condenser and a magnetic stirbar. The setup was charged with 100 mL GAA, 50 mL H2O and 150 mL IPA. The mixture was stirred and 1.0 g Hg(II) chloride was added. When all salt was dissolved, 10.0 g 4-methoxyphenyl-2-nitropropene was added.

21 g Al foil was ripped in small pieces (ca 1 x 3 cm) which were pressed (not firmly) into bals. When the nitropropene went into solution, the Al foil was added one ball after the other. The initially yellow solution colours greenish with a hint of black, and as the reaction proceeds, changes to a unattractive grey. All Al is added over a 30 min period. This prevents the reaction mixture from overheating. Alot of heat is produced during the reaction... When I noticed that gas evolution and bubbling of the slurry had stopped, I decided to add another 100 mL GAA (2 x 50 mL). This restarted the reaction.

About 90 minutes after addition of the Al, the reaction mixture was treated with aqueous NaOH: first with 150 g NaOH in 400 mL water, followed by 75 g NaOH in 200 mL water and by 50 g NaOH in 150 mL water. This reaction is very exothermic, so beware... When all aqueous NaOH was added, there were two phases, viz a clear orange upper layer with IPA smell and the Al sludge. The orange layer was isolated and diluted with aqueous HCl (20 mL conc HCl + 80 mL H2O). The mixture was extracted with DCE (2 x 40 mL). The organic layer had a red colour, while the aqueous phase had a yellow appearance. The latter was made alkaline with 5 M NaOH solution and extracted with 100 mL chloroform. The organic phase was dried over anhydrous sodium sulfate and the solvent removed under reduced pressure and recuperated. This yielded 5.9 g of an amber oil.

Yield: 69.9%

Notes

I have had the impression that impure nitropropene does have a negative influence on the yields, as was stated by *HyperLab Bee #1* as well. I have tried TMA yesterday, and yields were awful. The starting nitropropene, however, was far from pure. Today, I tried a new 4-MA batch with impure starting product; 20.0 g 4-methoxyphenyl-2-nitropropene yielded 5.0 g freebase after the workup I previously described. However, my end products have always been very pure.

I made a small modification, however. Of the 40 g Al that I added, there was only 5 g made available for the reaction start. Once the reaction started (in a violent way), the reaction was maintained by gradually adding all Al, each additiopn being accompanied by another small portion of Hg salt. This way, there was no solvent loss via the reflux condenser. Also, when no more fumes escaped from the top of the condenser, additional GAA was added. This did not restart the reaction, even though some Al was clearly left unreacted.

#3. Reduction of 3,4-methylenedioxy-P2NP by *Hive Bee #2*.

55 g recrystallized 3,4 methylenedioxyphenyl-2-nitropropene was dissolved in a warm solution of 600 mls HOAc and 1000 mls IPA in a 5Liter flask with magnetic stirring and heating mantle. 1 g HgCl2 dissolved in 300 mls H2O was added and mixture was brought up to 60 �C. A total of 90 grams of regular thickness kitchen aluminum foil was shredded by folding a sheet in half(doubling it over) and running it through a cross-cut paper shredder. This was added in 20 gram portions at a rate which kept the temperature at approx 70 �C for the entire rxn. Mag stirring was not impeded by using foil of this type and the rxn was over in about 4 hours. 1000 mls 50% NaOH soln was added at a rate which prevented boiling over, phases separated and the liquified Al/NaOAc phase was tapped off leaving a light orange IPA soln organic layer in the funnel. IPA was stripped off at the rotovap leaving behind a thick deep red oil which smelled of amine. Acid/base cleanup resulted in a dark red oil which was not suitable for crystallization. Oil was distilled (105-108�C, 1.5 mmHg) to **yield 32 grams (approx. 65% yield)** of water-white MDA base.

Notes:

Experiments were performed on 50 g substrate
1) HOAc reduced to 500 ml, Al was reduced to 60 g. Yield = 24 g MDA base

2) HOAc reduced to 500 ml and 100 g aluminum was divided into three portions of 33 g which were added as the previous increment was consumed.
Yield = 35 g MDA base.

#4. Reduction of unsubstituted P2NP by *HyperLab Bee #2*.

Into a 3-L FBF there was placed 100 mls water, 250mls GAA and a solution of 1g mercury in 2-3 mls conc. HNO3.
52 g (2 packs 10 meters each) of Al foil were folded into 7-8 layers, cut in pieces 3x3 cm and loaded into the flask.
The flask was heated to 40 �C. When the start of amalgamation was clearly visible in several minutes, heating was discontinued and into the reaction there was added a suspension of 30 g ***non-recrystallized*** phenyl-2-nitropropene in a mixture of 50 mls GAA and 100mls IPA (nitropropene was obtained ***a la***

Barium�s MeAm condensation - an important notion since this method gives the product of superior purity).

The next 5-7 minutes the reaction proceeded rather smoothly... I only turned away from it for some half a minute... and when I turned around once again I saw that the mixture inside the flask tries to surpass the last inches of the flask�s neck! Grabbing the flask I rushed to the sink..... and then..... it was like as if I was standing on Baikonur�s starting table trying to hold back the rocket-launcher �Soyuz� during its blastoff.... The reactive stream of "exhaust gasses" � hydrogen and IPA vapours - was quite something.

Thanks goodness, cooling helped and the foam only slightly escaped the flask. The fireworks lasted for a minute or two, after which the flask was placed into a cold water bath for 15 mins and its contents were periodically shaken by hand. Cooling was removed and the reaction was allowed to stand for another 40-50 minutes. At first the temperature held itself at 85 � spontaneously, then a little heating had to bee applied.

The obtained grey porridge in which there still was some unreacted aluminium was cooled and cautiously basified with 500 g KOH in 500mls water. Two layers formed: the lower, aqueous, with some unreacted hydroxides and the upper, consisting of IPA and the product. The mixture was extracted with 2x150 mls ether, the pooled extracts dryed and the solvent stripped off at rotovap. 25 g of crude amphetamine base was obtained as a muddy (inorganics) liquid of skin color.

It was vacuum distilled with a short column. 1st fraction � 0.8g, b.p. 67-72 C/6 mmHg, 2nd fraction � the product, 20.8 g, b.p.72 C. And this is despite heating with a gas flame, instead of a bath!

So, the **yield was 20.8g (83.5%)** of a crystally clean product. And if we are to count the 1st fraction, from which a goodly amount of a colorless sulfate was later made, we get a yet higher figure. Moreover, a certain quantity of amphetamine was lost in rotovap � the bath�s temperature was 80 �� and vacuum � around 20 �C. In the morning it formed white granules of carbonate on the rotor�s walls.

In addition I want to note that the quantity of foil used can bee evidently less as it doesn�t react fully anyway. I think 30-35 g should bee enough.

Another note � I researched a little the reaction of Al foil with various proportions of water:IPA:GAA and it appears that the originally used mixture gives the fastest reaction rate.

Well, that's it. I'm throwing all my LAH into the trashcan tomorrow morning :-)

References

1. Sunlight, **Reduction of 2,5-Dimethoxynitrostyrene** (1999)
2. **Monatsh. Chem. 79, 72-77 (1948)**

   Direkte Reduktion des Nitrokorpers zum Amin:
   1g 2,3-Dimethoxy-ω-nitrostyrol wurde in einer Mischung von je 1ccm. Essigsaure, Alkohol und Wasser in der Warme gelost und 2g feine Al-Spane eingetragen. Die Reduktion kam nach Zusatz von wenig $HgCl_2$ in Gang und wurde nach etwa 2-stundigem Stehen bei 20�C auf dem warmen Wasserbade vervollstandigt. Die Aufarbeitung erfolgte in analoger Weise wie bei der Reduktion des Oxims. Bei der Destialltion erhielten wir im ganzen 0.58g Destillat (bei 1 Torr und 80 bis 110�C Luftbadtemperatur), das 0.67 g Pikrat lieferte.

Translation by Osmium (1998):

Direct reduction of the nitro compound to the amine:
1g 2,3-dimethoxy-ω-nitrostyrene was dissolved by warming in a mixture of 1ml AcOH, 1ml EtOH and 1ml H_2O and 2g fine Al turnings were added. The reduction started after the addition of some $HgCl_2$ and was completed by heating on a warm water bath after standing for two hours at RT. Workup was done in an analogous manner to the oxime (apparently filtration, solvent remolval, acid-base extraction). 0.58g was obtained after distillation at 1mmHg, 80-110�C, air bath temperature. From that 0.67g of the picrate salt was obtained.