The Vespiary

Main Topics => Drug Synthesis & Extraction => Topic started by: fuckyou on August 07, 2018, 02:13:17 PM

Title: **4-FA al/hg recipe**
Post by: **fuckyou** on **August 07, 2018, 02:13:17 PM**

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i want to share my experience in cookign 4-FA, a beautifull compound with stimulant and emphatogen properties.

So you need 4fluorobenzaldehyde and nitroethan, combine them in 1 : 1.1 equimolar ratio and make 4f-p2np my favourite method is with amonium acetate wich is most available for me.

Combine 10ml 4-fluorobenzaldehyde with 15ml nitroethan add 50ml GAA and 5g Amonium acetate and reflux for 1 hour on high heat. Let it cool and add to a ice afther a few seconds it will crystalize, filter and dissolve the crystals in minimum MeOH and let it crystlize for overnight, it produces very nice mini crystals wich can be filtered of a clothe to be collected.

Next active some aluminium foil with NaOH until aluminium oxide falls out and wash the aluminium with hot water, next add it to a solution of methanol and HgI2 (i dont have Hgcl2) and let it amalgamate in this time dissolve 5gr 4f-p2np in 35ml GAA and 30ml IPA and 10ml HCOOH and add it to the amalgamateed solution, exothermic reaction will start soon cool the flask in a cold water for 30m and then boil it slight for 1 hour. In this time you need to have prepared a cold NaOH solution 50% and add it slowly until ph14 reached, filter it to remove the mercury and extract with Xylene, decant Xylene and add it to a flask with stirrbar and 25g MgSo4 let it stir for a few hours ro remove all the water, wash the MgSo4 with Xylene in case it absorbed some freebase, and from there you can gass it with HCL acid for crystals or make sulfate salt and you will have a beautifull shiny powder. I preffer the hcl salt and this recipe gives me araud 60-70% yield. (2.8-3.5g yield).

Quality coments : I have tried it at a low doses under 100mg it works a lot like an amphetamine but with increased euphoria and energy and the drug make you want to socialize with others, at higher dosages such as 150mg + it work pretty like MDMA, with the difference it dont sedate you it work as a pure stimualnts but emphatogenic properties kich in :) Perfect for parties and dancing or having a good time with your girlfrend :)

Title: **Re: 4-FA al/hg recipe**
Post by: **carl** on **August 07, 2018, 05:03:29 PM**

Bee welcome :)

First, I would like you to add a reference to your post, as this section requires one added to it.

And then again, nice post, just made a little bit of that nitropropene too :D
But used ethanolamine acetate both as solvent as well as amine catalyst, and that works surprisingly very well, the yield was so far with both unsubstituted also with 4-F benzaldehyde both in the 90%, can really recommend that one.

Works at RT, few hours standing(or stirring), then precipitate the nitropropene completely afterwards, and can also be recycled easily, simply boiling it dry from water and any other remains like nitroalkane and benzaldehyde.

Your method works with far less GAA by the way ;)
Also the amount of ammonium acetate is a little bit too high, I would say?
Do you have problems with polymerisation?
If so, I would recommend the catalyst I mentioned, due to it working at RT, there is literally no polymerisation, and it is an ionic liquid.
The nitropropene precipitates during the synthesis already, that shifts the balance to the right side, i.e. the yield is very high since the already formed P2NP gets removed out of the reaction.

I have used for the reduction NaBH4 together with CuCl2, seems that it is also a high yielding reduction method.

Title: **Re: 4-FA al/hg recipe**
Post by: **fuckyou** on **August 07, 2018, 06:46:43 PM**

You mean i can use how much i want from that catalist and let it stay in a glass bottle closed for 3-4 hours and 90% of benzaldehyde will be converted to coresponding nitropropene ? Did this catalist work for all nitropropenes ? Does Ethanolamine work in the same way ? Can you compare methylamine or ethylamine catalyst to ethanolamine ? And what abaut Di-n-butilamine ?

I am doing it with more GAA because it heard amonium acetate form a lot byproducts and when using GAA acid it lower they production, its why i use more of it, i dont think it can make a problem and when my minimum flask is 1 liter i need to put somethink there to boil corectly :D, abaut the amonium acetate if i need to be corect i dont know exact how much i need, i just add enough to be shure it will do its work.

I dont have problem with polymerization because i know what color shoud it look and how it need to smell and never leting it too much on the heat, i have 2-3 fails when it became more reddish then orange and maybe its some sort of polymerization and in that cases i wash it with cold water and let it overnight in the fridge to crystalize.

Hm you gona reduce the nitropropEne to nitropropAne with Nabh4 but what you gona do with CuCl2, i know for Nabh4 and Zn/GAA two step reduction but i dont have Nabh4, its too expensive chemical and since i work on very low scale al/hg work good for me.

Title: **Re: 4-FA al/hg recipe**
Post by: **carl** on **August 07, 2018, 10:12:58 PM**

Oh I can compare EtNH2 to MeNH2!
But both only as aqueous solution, and I have to say, besides this ionic liquid ethanolamine acetate(or formate), ethylamine 70% was among the best and cleanest catalysts too!
Also high yielding, which was definitely not the same as I experienced with aq. methylamine...
Even better with a tiny quantity GAA, to have ethylamine acetate as the active catalyst instead.
For a nitroethene, trimethoxy was it, I have likewise achieved yields well in the 90 percents, but one has to consider that nitroethenes form easier as nitropropenes.

Actually I like both the same, the ethanolamine and ethylamine acetates, but since I am not that used to the former, the ionic liquid(yet).
Never used solely ethanolamine, but whatever9999 did and he is convinced of its use too as it seems.
But the really large excess is not needed at all, also not the less large excess I have used in the linked thread.
Latest approach was with only 4ml of "HOEtAc", on 50mmol of benzaldehyde, and just 55mmol nitroalkane(and that was the one for the 4F-derivative..)
So there is a large potential yet open to get explored, I would say.
I hope other will follow on that path that whatever9999 has seemingly walked on as one of the first clandestine chemists, and I am lucky I followed simply out of curiosity.

Dibutylamine? Never used that, would that even work?
I am not sure, since it is a dialkylamine and not mono-...
Other members have seemingly used it, but no consistens yields if any.
I already wondered when the use of this amine was brought up not long ago(with problems achieving the nitropropene), if it would even work at all?

But look here, another member, who brought that idea up, has it already used on trimethoxybenzaldehyde :)
Here: ionic liquid P2NP (https://www.thevespiary.org/talk/index.php/topic,15609.msg54173502.html#msg54173502)
A look in the corresponding paper doesn't seem to indicate any difference to other amine catalysts, it still is, besides being a liquid, an amine acetate which are known to work very good in this synthesis.
But that this salt is liquid instead.

As for the quantity, I tried it using only a few ml, more than the quantity one would use for another amine acetate though, but I could use equimolar nitroethane to benzaldehyde and still got this astonishing high yields out of the synthesis.
Definitely superior to the usual method, also because one can reuse the liquid after just a little purification work, and given that ethanolamine is a cheap amine... then the little bit more wouldn't even matter if it would be discarded after every use, in my opinion.

Ok well, no wonder that you have no problems with polymerisation, when you are experienced with the production of nitrostyrenes, experience is most valuable with their preparation.
Not with the use of this ethanolamine acetate, though... ;)
Never before had such an unproblematic catalyst/route, not even comparable to the 3 weeks left at RT or the quick microwave method, this beats both of them, massively even!

As for the reduction method with NaBH4 and CuCl2, gives directly the amine and so I wondered initially too, and now that I finally tried it, I am convinced that it is a superior method to the NaBH4/Zn reduction, also Al/Hg, it really is much more than the sum of both other methods... :)
I guess, and it also has looked like this, that it modifies the borohydride similar as to what other metal salts can achieve on it, it change its reduction power considerably to a much different or wider skills to reduce more or even other functional groups due to this.
The black particles precipitating after the green CuCl2 is added(possibly CuO?) would fit into that explanaition very likely too ;)

Here are references and personal experiences, also you can read me there doubting that it really is that good ;)
NaBH4 copper chloride (https://www.thevespiary.org/talk/index.php/topic,15090.0.html)

Then I forgot about this method, and never got to attempt it... which was, to be honest, a huge loss , this neat and very fast route directly to the amine.
And no messing(as promised in the title) with the masses of metal salts after basification as seen with the borohydride/zinc reduction, it is rather easy and straightforward, no massive volume after the reduction, etc, simply advantageous, I was very surprised about all of these advantages afterwards.
Could simply steamdistill the amine off, and got a yield of over 70% so far!
And there is still some amine in the mother liquor...
Also one can do an A/B using solvent, and it would be very straight forward due to the tiny final volume, not like moving an half liter of fluid...(or even more!)...

Sodium borohydride is among the, given the very valuable and diverse usage, among the cheaper chemicals in my opinion?
A supplier that is not really cheap but what is available for me, lists 100g of it for just 22€, that is far from being expensive, in my opinion at least.
It suffices for an half mole of nitropropene, and it is so high yielding, that this corresponds to at least a third mole of final amine... at least! :o
I would if I was in your position, keep my eyes open and get a stock of it when you have it in reach, it simply pays of ;)
The scale in which I tried the NaBH4/CuCl2 was even smaller than your scale, I used only 1,81g 4F-P2NP, or 10mmol...
Well, together with 2,4g borohydride, but that are also just 63mmol.
You have to use such a large excess as it seems, only disadvantage if one wants to call this tiny flaw a disadvantage at all.
For me, this is now surely after only one trial together with a few mistakes made, enough to convince me about the success that others had, and became the method of choice for nitroalkene -> amine.

I can not do more than try to convince other people that this is really a true winner, as good as it does sound ;)

Title: **Re: 4-FA al/hg recipe**
Post by: **Tsathoggua** on **August 26, 2018, 10:31:06 AM**

You are only getting 1/3 mol in the microwave carl?

Try using a mixture of triethylenetetramine acetate, look for a certain epoxy glue hardener that contains this, by RS, if you want the specific item name, PM Tsath'. It is a mixture of triethylenetetramine and a cyclic diamine, and its absolute fucking magic in the MW, even years old, crude and unpurified, best Knoevanagel cat Tsath' has ever used. Near or quantitative yields in the MW. 20 minutes and stoichiometric yields, what isn't to like?

Title: **Re: 4-FA al/hg recipe**
Post by: **carl** on **August 26, 2018, 01:24:45 PM**

Don't know where you read that statement, but I haven't said anything like this?

I got the MW method to work, but you haven't got what I was saying: that the other method using an amine based ionic liquid is in my opinion a much better choice as this, because it involves not nearly as much work, polymer, smell ;)

Title: **Re: 4-FA al/hg recipe**

Post by: **Tsathoggua** on **August 26, 2018, 07:23:20 PM**

Bugger, Tsath' can only see your saying you were getting something like 1/3 return, although he cannot remember the post content prior to your edit.

Still, damn, will have to try this compared to the MW route, because microwave Knoevanagel condensations are the bee's balls already, tough bar to beat. Still, for P2NP and with the right catalyst, yields can be almost stoichiometric. And no GAA either, just straight nitro and benz, add amine nuke cycles, shock freeze to crash out the nitroalkene, and you are golden. Literally. Triethylenetetramine neutralized with a little GAA, 20% of a cyclic diamine, can't find out now, because the bloody bastards that made the stuff no longer use the same recipe. Its now only 10% triethylenetetramine and the rest some polyamide of tetraethylenepentamine. FUCKFUCKFUCKFUCK! this is a recent change, could have sworn the mixture as it used to be was in Tsath's notes somewhere, but will have to do some digging, it seems to be buried further than expected in his notebooks. Damn, not pleased about that. The stuff they used to make, this epoxy potting compound hardener mixture, it serves as a really, really damn good Knoevanagel cat as the acetate salt.

Title: **Re: 4-FA al/hg recipe**
Post by: **fuckyou** on **August 27, 2018, 04:43:57 PM**

xm i buyed the ethylamine 70% and i proud can say its the best catalist. it gives me 99% yield based on benzaldehyde afther 2 recrystalizitions of the product.

Title: **Re: 4-FA al/hg recipe**
Post by: **regri** on **July 13, 2020, 05:12:36 AM**

Quote from: carl on August 07, 2018, 10:12:58 PM

> .....I was very surprised about all of these advantages afterwards.
> Could simply steamdistill the amine off, and got a yield of over 70% so far!

are you talking about 4-fa here? can 4-fa obtained by steam distillation?

Title: **Re: 4-FA al/hg recipe**
Post by: **carl** on **July 13, 2020, 01:49:38 PM**

Yes it is volatile with steam just like amphetamine.

Title: **Re: 4-FA al/hg recipe**
Post by: **TryItYoullLikeIt** on **July 13, 2020, 03:07:08 PM**

damn, i just found a supplier for that aldehyde...but where they hell is everyone getting the nitroethane? or did we finally find a decent synthesis?