The Vespiary

Main Topics => Publications => Topic started by: xdragon on July 26, 2020, 07:18:46 PM

Title: **MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **xdragon** on **July 26, 2020, 07:18:46 PM**

I recently had some success with the formation of MDP2NP using the ionic liquid 2-hydroxyethylammonium acetate, inspired by this paper and carl:

Quote

J. Org. Chem. 2010, 75 (23), 8295-8298.
DOI: 10.1021/jo101696z

Instead of 2-HEAF as in the paper, the acetate instead of the formate was used as counter ion - acetic acid should also be easier to acquire for most of us.

While there are a lot of methods which promise high yields, I really like the reusability aspect of using this ionic liquid, as well as the fact that they use the nitroalkane reagent stochiometric. As nitromethane and nitroethane keep getting harder to acquire, using up as little as possible seems like a quite good goal to me.
As soon as time permits again, I plan to test a variety of substrates - as I am quite interested also in the butanamines, I really hope that decent yields could also be achieved with nitropropane.

For now, the writeup of my first test:

Quote

Preparation of 2-HEAA (2-hydroxyethylammonium acetate)
In an Erlenmeyer flask, to 10.67 g 2-aminoethanol (174.7 mmol) are added slowly 11.54 g acetic acid (192.2 mmol, 1.1 eq.). During the addition, the typical "amine salt mist" is noticed, the mixture gets rather hot and the solution takes on a slightly yellow colour. The flask was swirled and then let to cool down to room temperature in a water bath.

Notes:
- As the solvent is reusable, this scale should be enough if you just plan to do reactions on a research scale. On a larger scale, it would probably be wise to do this acid-base reaction with cooling and internal stirring.
- The viscosity of the ionic liquid is quite high, so **forget about pipetting** at room temperature. It might work at higher temperatures, but I just poured it.
- I do not think 1.1 equivalents are necessary, but I figured an excess of acetic acid wouldn't hurt, especially as mine is probably not exactly glacial.

Quote

Synthesis of MDP2NP (5-(2-nitroprop-1-en-1-yl)benzo[1,3]dioxole)
In a 50 mL Erlenmeyer flask equipped with a stirbar, 3.05 g piperonal of questionable quality (20.3 mmol, slightly brown-coloured) are dissolved in 9.94 g 2-HEAA (82.1 mmol, roughly 10 mL, slightly yellow-coloured, very viscous!) and 2.31 g nitroethane (30.8 mmol, 2.2 mL, 1.5 eq.). The mixture turned brown upon solution of the piperonal, and was now stirred at RT. After 20 min, the solution was already full of a yellow precipitate. Because of the high viscosity, the Erlenmeyer flask tipped over, without spilling the contents (yet again because of the high viscosity). In a rather desperate attempt it was tried to get stuff on the wall back into stirring by rinsing with another 0.28 g of nitroethane, bringing the total to 2.59 g (34.5 mmol, about 2.5 mL, 1.7 eq.).

After 2.3 h, 50 mL of water were added, the precipitate vacuum-filtered, rinsed with water and dried in an oven at 80 °C for 2 h. The crude MDP2NP amounted to 3.35 g, 16.2 mmol, 79% yield based on piperonal.

Recrystallisation in 27 mL MeOH yielded 2.91 g MDP2NP, dried on vacuum-pump. This material was again recrystallised from 28 mL MeOH to yield 2638 mg MDP2NP (12.73 mmol, 63%). Both times, the mixture was cooled from reflux to -18 °C, but the second time, it was left in the freezer overnight instead of just 2h.

Notes:
- The aqueous phase was extracted with 3x 15 mL EtOAc to get rid of organic impurities (nitroethane, benzaldehyde). While it was slightly yellow, no further MDP2NP could be crashed out of it with water. The mixture of ionic liquid/water is still to be boiled off from water to reuse the solvent.
- 2.3 h reaction time was an arbitrary number, I will try to follow the reaction with TLC next time - but I was too lazy because of the viscosity.
- The subsequent reaction has not been worked up yet.
- I think more ionic liquid might be needed, as I didn't scale up from the paper.
- I will try with less nitroethane, but I will probably keep a slight excess, like 1.1 eq.
- different substrates etc. are to be tested once I find the time. As said, I am quite interested in the BDB compounds, as well as other phenethylamines.
- Never again will I use MeOH for this recrystallisation, I was just being stupid. For MDP2NP, IPA will be used next time.

Pictures:
01:2 min after addition of the nitroethane
02: After the tipping over, around 20 - 30 min into the reaction
03: Crude MDP2NP
04: 2x recrystallised, probably need to work on my technique

Discussion:
Both monoethanolamine and acetic acid shouldn't be too hard to acquire, and once you have them, this ionic liquid should be quite reusable. The yield seems quite promising and can possibly be optimised after watching the reaction progress via TLC. There is no danger of polymerisation and crap, due to running the reaction at room temperature. I still have to learn some more practical work in the lab. That flask should have never tipped over, also, recrystallising MDP2NP with MeOH instead of IPA is just dumb. Nevertheless, I tried recovering some of the losses, but haven't weighed them yet.

I currently don't have much time for the lab, but I do have some interesting substrates to try on this one available to me.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **July 26, 2020, 08:02:25 PM**

Very nice and cool that you decided to post about it, even with pictures! :)
As a tip, keep in mind to remove the exif files for safety purposes.

I would really like to hear about how reusing that stuff goes, especially with different nitroalkanes.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **xdragon** on **July 26, 2020, 08:26:34 PM**

Originally my plan was to wait until I tried with other substrates, but as it is foreseeable that I do not have much time for the next few weeks/months I figured that the good thing about publishing on a clandestine chemistry forum is the possibility to rapidly exchange ideas and discuss chemistry, allowing for both positive and negative results.

The EXIF data has been taken care of, as I am aware of the possible risks.

I really, really hope it gives good results for the MDP2NB! I would be so happy about this, although I already started researching alternate pathways as a backup.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **July 26, 2020, 08:33:36 PM**

I have no doubt it will work just as well with 1-nitropropane.
I've been told(dude chime in if you read this!) that ethylamine acetate worked much better for 2,5-DMP2NB as Shulgins procedures for nitrobutenes did, for example a-ET or AEM in Tihkal/Pihkal, but he used ammonium acetate, so that could be expected.
This is one of the examples where Shulgins work really was far from optimised.

I hope I can get around making a nitrobutene at some point in the future myself too, would love to try a-ET.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **xdragon** on **July 26, 2020, 08:41:28 PM**

Indole-3-carboxaldehyde is among the group of interesting substrates. Let's see who can furfill his own wishes earlier.

Just so people aren't confused, carl is *not* referring to the ionic liquid for the 2,5-DMP2NB, as far as I am aware. Still, Shulgin was never the route to go for high yields ;)
It's solid chemistry though.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **July 26, 2020, 08:47:51 PM**

Yes, ethylamine acetate, not 2-HEAA from ethanolamine and not ethylamine :)

Well, I'm intending to go an unusual route for this aldehyde, chromate oxidation of indole-3-carbinol, which I don't even have yet so I guess its you :P

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **blade_runner** on **July 27, 2020, 02:12:11 AM**

Quote from: xdragon on July 26, 2020, 07:18:46 PM

> There is no danger of polymerisation and crap, due to running the reaction at room temperature.

Very interesting work. For what it's worth, there's a reference on Rhodium archives about running it at room temperature with methylamine HCl catalyst... for two weeks. Always interested me but I've never had a reason to try it.

Quote

> 250 g piperonal is dissolved in 900 ml 95% EtOH and there is added 150 mls nitroethane, 10g methylamine hydrochloride and 8g sodium carbonate. After a brief stirring the mixture is left in a dark place for 2 weeks. It is then poured into 7 L water, the precipitate filtered, washed with water and air-dried. Recrystallization from small qtties of EtOH. Yield 87%.

If you intend to reduce to the ketone, what are your plans? Standard Fe/HCl?

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **loft** on **July 27, 2020, 10:03:31 AM**

Quote from: carl on July 26, 2020, 08:33:36 PM

> I have no doubt it will work just as well with 1-nitropropane.
> I've been told(dude chime in if you read this!) that ethylamine acetate worked much better for 2,5-DMP2NB as Shulgins procedures for nitrobutenes did, for example a-ET or AEM in Tihkal/Pihkal, but he used ammonium acetate, so that could be expected.

User miamechin from hyperlab yielded 68% 2,5-DMP2NB with aq. 40% methylamine and GAA (https://www.hyperlab.info/inv/index.php?s=&act=ST&f=17&t=29158). I yielded (from what I found in my notes) 60% with ethylamine acetate. There were further repetitions but I seemingly didn't write them down.
I and others found nitrobutenes to be notoriously for oiling out, so keep that in mind.

Unfortunately I've had no success condensing 1-nitropropane and benzaldehyde (or at least getting a solid product out of it, I've never checked the reaction by TLC). IIRC this was also reported by Nichols (that nitroaldol doesn't work for P2NB).

I only tried 2-HEAF once on 2,5-DMBA w/ nitroethane, obtaining just a small yield of 29% and some goey oil. In retrospect with my current knowledge, this probably could have been worked up to increase the yield drastically.

@OP: First of all, congrats! I might even give this catalyst another try someday :)
Regarding your recrystallization: It's always wise to cool down the filtrate once more after filtering the re-xd product off. You can almost always obtain a second yield. I think it was from ORG's P2NP microwave technique, where it was stated to reheat the filtrate once more prior to refreezing.
Ever since, that's what I do as well :)
TLDR: When recrystallizing, heat the filtrate once more to a boil, then cool again to -18 °C to obtain a second, smaller yield of product.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **xdragon** on **July 27, 2020, 04:53:10 PM**

Quote from: blade_runner on July 27, 2020, 02:12:11 AM

> Very interesting work. For what it's worth, there's a reference on Rhodium archives about running it at room temperature with methylamine HCl catalyst... for two weeks. Always interested me but I've never had a reason to try it.

hxxps://chemistry.mdma.ch/hiveboard/methods/000516174.html

Was replicated in another forum (now taken down by law enforcement) with P2NP, and people quite liked it. I am fine with long reaction times, but not if shorter and similar high-yielding routes exist, of which there are a bunch.

Quote from: blade_runner on July 27, 2020, 02:12:11 AM

> If you intend to reduce to the ketone, what are your plans? Standard Fe/HCl?

Certainly not Fe/HCl. For now, I used the product of the condensation on a NaBH4/CuCl2 to get to plain MDA. I haven't worked up yet, but depending on the yield I might try getting to MDEA from there. But I also have plans for trying a Nef reaction on the nitropropane.

Quote from: loft on July 27, 2020, 10:03:31 AM

> User miamechin from hyperlab yielded 68% 2,5-DMP2NB with aq. 40% methylamine and GAA (https://www.hyperlab.info/inv/index.php?s=&act=ST&f=17&t=29158). I yielded (from what I found in my notes)

> 60% with ethylamine acetate. There were further repetitions but I seemingly didn't write them down.
> I and others found nitrobutenes to be notoriously for oiling out, so keep that in mind.

Thanks for bringing back miamechin's expertise with butanamines (and tryptamines and etc etc) to my mind, this is really interesting.

I would be comfortable with running a column, if need be. However, what would your advice be in such a case of oiling out?

Quote from: loft on July 27, 2020, 10:03:31 AM

> When recrystallizing, heat the filtrate once more to a boil, then cool again to -18 °C to obtain a second, smaller yield of product.

This is a really useful tip, although I assume that even just using IPA would have made things better for me.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **July 27, 2020, 05:15:42 PM**

I have to add, some of said nitrobutene lay around in a plastic bag for a few months here and it turned to oil somehow over time, I think when I received it, but when I was ready to work with it and took it out again, it had solidified by itself ???
And not just solidified to an amorphous mass but crystallised really.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **loft** on **July 27, 2020, 08:23:13 PM**

No need to run a column. Whenever a nitroalkene oils out, i.e. after cooling down in the freezer no crystallization occurs but a yellow/orange liquid separates, it can be separated (pipette or sep funnel), diluted with some alcohol (MeOH, EtOH, IPA work), shaken to homogenize and then put again in the freezer. This works in most cases!

Regarding this odd behaviour carl described: I can only assume that this is due to some kind of contamination, most likely remaining solvent. In case of 2,5-DMP2NB I had an extremely difficult time crystallizing it and then keeping it solid. If put in a vial for storage and it liquifies again, it again partially crystallized out when laying on the side. Really odd. And even though I've prepared this precursor numerous times I'm still hoping everytime that it will stay solid (you'll see that within a few hours).
It isn't hygroscopic though, as I've also had some laying around on a watch glass for weeks.
One thing I learned: Always place it on a watch glass or petri dish after thinking you isolated a solid. Don't place paper underneath, you might end up with yellow paper otherwise (this can still be extracted but it's messy).

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **July 27, 2020, 08:52:32 PM**

I have to say, that the precursor from loft was easily recrystallised, no issues, when I used it to reduce it.
This worked really well the way I was used to from other nitroalkenes.
Although I experienced a huge loss, I think it was due to solvent volume but he thinks it was due to impurities.
We will never know ???

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **xdragon** on **September 13, 2020, 03:13:07 PM**

Not much of an update regarding the reaction - although I will soon get some lab time in, as it seems - but instead a bit of a warning.

When I did the reaction, I didn't really research the melting point of 2-HEAA. I also wrote that the stuff can't be transferred by pipette. Turns out that it slowly crystallizes over the course of some months, at least in my case (with a bit of excess acetic acid). Seems like the mp is 65-66 °C[1], bp 210 °C[2].

Gonna update as soon as I start a new reaction with the same IL. Probably I will just heat it, add the reagents, and hope that it doesn't crystallize out. Which it didn't previously, so why worry...

1 DOI: 10.1021/jo01108a609
2 DOI: 10.1071/CH06363

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **September 13, 2020, 04:32:18 PM**

Quote from: xdragon link=topic=17911.msg54196629#msg54196629 date=1600009987bp 210 °C[sup

2[/sup].

Must be the bp under reduced pressure, because I've read that 2-HEAA decomposes at, I think it was around 165°C?
2-HEAF decomposes at aroound 150° already, I don't have the exact numbers in mind though.
But thats for atmospheric pressure, so careful while boiling these IL's dry after use.

Also, I think the nitroalkane will help to keep them liquid during the henry reaction.
Never seen them crystallise out though, but then again, I haven't kept it for long enough.

Also, why isn't this already in the publication section?
I thought I moved it there long ago? ???

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **xdragon** on **September 13, 2020, 06:46:43 PM**

No, that is under atmospheric pressure. I am not quite sure how they measured it in the paper (DSC curve doesn't show this temperature range), but I've found 103 - 104 °C at 0.7 mmHg in some other source, which could translate very well to the 210 °C at atmospheric pressure with the seemingly high heats of evaporation of ionic liquids.

I will remove the water under reduced pressure anyway. If you happen to find the source for the decomposition point again, please share! (Both for 2-HEAF and 2-HEAA)

Also, there seems to be no clear melting point, as other sources give like -6 °C. Judging by the DSC scan from the paper, that is because there is no clear melting point. So, heat it up and be fine, I guess.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **September 13, 2020, 07:29:54 PM**

Ok thats strange, and no I can't find it anymore.
Maybe I misinterpreted something and the acetate is more stable(which would make sense).
Mainly I was looking for the decomposition temperature of 2-HEAF, and when I did a surprised and quick search for 2-HEAA, maybe it was the boiling point under a certain amount of reduced pressure that I interpreted as decomposition?
I have to admit I haven't looked under that link, just at the short results I got googling it.. ::) sorry for the confusion!

The original paper about 2-HEAF confirms its low decomposition temperature, or rather, dehydration, as at 150.8°C it results in the formamide, I quote:
Quote

> Dehydration of the liquid salt commences around 150.8C, as it has been deduced from the TGA curve. Pure 2-hydroxyethyl formamide can be isolated by distillation at168–170.8°C (10 mm) as it has been evidenced by a separate experiment.

Guess we'll accept the fact that 2-HEAA is more stable and not the least bit less well working for our purposes.
About the melting point, understandable too.
Must be even more complicated due to any potential residues you introduced to it.
But there is no doubt it will work just as well as it did before.

You are going to use the same aldehyde? And a different nitroalkane?
Then stripping the volatiles out of it under reduced pressure will surely work well enough to give you an equally good result the next time, as it will also remove any potential nitroalkane residues.
But in case of a different bbenzaldehyde, I would probably prefer to use a fresh batch of the IL instead.
Not that it would matter much in practice, more because it would give me a clean conscience about the purity of the final product, even if unwarranted.

Man, these ionic liquids really have a huge potential!
I wish that others would be as accessible and cheap as 2-HEAF/2-HEAA.... like, BMIM-PF6 as well as BMIM-BF4 look fascinating and seem to be really useful, but making or buying it is just out of question, sadly.
Well, buying the precursors and making it, that looks more affordable on the other hand...
But those substances really have a massive potential for the future!

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Corrosive Joeseph** on **September 13, 2020, 09:33:36 PM**

Quote from: xdragon on July 26, 2020, 07:18:46 PM

> using the ionic liquid 2-hydroxyethylammonium acetate, inspired by this paper and carl:

I presume you mean this - https://www.thevespiary.org/talk/index.php?topic=15609.0
I will link it here before it gets lost in the midsts of time.

/CJ

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **stoichiometric_steve** on **September 27, 2020, 08:32:08 AM**

I spent some time this week trying to get information on how NABH4 would react with the HEAF or HEAA, seems like it might actually be a suitable "solvent" for Nabh4, allowing for a one pot on the P2NP or nitrostyrene.

But then the Ionic liquid gets contaminated with water soluble borates, probably not a good idea if one wants to recycle it. Too bad!

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **November 22, 2020, 03:38:00 PM**

I've been experimenting with 1,2-aminoethanol/acetic acid, using "only" 1,5 eq. of the catalyst. Gives very high yield done neat with 4-f-benzaldehyde and nitroethane (mix the components, swirl and wait - within the hour you should have serious crystal formation), just tried same substrate with nitropropane and it seemed to have worked well too, although perhaps somewhat lower yield from the looks of it (not worked up yet). I did try 4-methyl-2,5-dimethoxybenzaldehyde and nitropropane, and got an intensely yellow product. Beaker was full of crystals, but I messed up the work up I believe (small scale, used IPA as solvent).

I've been quite ghettoish in procedure - mix aldehyde and nitroalkane, add GAA and last add 1,2-aminoethanol at a suitable rate to your scale and liking. No stirring, just swirling now and then. Really robust reaction is my initial impression from my few experiments.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **November 22, 2020, 03:47:52 PM**

I think you have to run the reaction longer for the production of nitrobutenes.
Look here: http://www.lambdasyn.org/synfiles/1-(4-fluorophenyl)-2-nitro-1-buten.htm

And by the way, its just 2-aminoethanol, 2-amino-1-ethanol, or simply ethanolamine :)

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **November 22, 2020, 04:17:02 PM**

Quote from: carl on November 22, 2020, 03:47:52 PM

> I think you have to run the reaction longer for the production of nitrobutenes.
> Look here: http://www.lambdasyn.org/synfiles/1-(4-fluorophenyl)-2-nitro-1-buten.htm
>
> And by the way, its just 2-aminoethanol, 2-amino-1-ethanol, or simply ethanolamine :)

Thanks! And you're right. I actually felt 1,2-aminoethanol were not...ehhh...right? It's just because it's what it says on the bottle. Ethanolamine feels more at home when vocalizing it.

UPDATE: The crude (not recrystallized) yield of 4-FP2NB was 85%. Stood in room temperatur without stirring overnight.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **November 25, 2020, 05:48:59 PM**

Made a small scale stab at 2,5-DMNS. Same ratios as earlier. Using nitromethane from a

race fuel claiming 25% nitromethane in it, straight. Within five minutes after adding the ethanolamine and when swirling the flask for the third time the whole contents turned into a solidified mass of crystals. :o ;D

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **November 25, 2020, 05:58:35 PM**

Wow! No heating needed?

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **StuffedBee** on **November 25, 2020, 06:16:42 PM**

So with the ethanolamine it is possible to just use the otc fuel directly without isolating the nitromethane first? Pretty cool! I wonder if this would work with 25% nitromethane in ethanol as well which is the commercial mixture around here

---

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **November 25, 2020, 06:39:20 PM**

Quote from: NeonCortex on November 25, 2020, 05:48:59 PM

> Made a small scale stab at 2,5-DMNS. Same ratios as earlier. Using nitromethane from a race fuel claiming 25% nitromethane in it, straight. Within five minutes after adding the ethanolamine and when swirling the flask for the third time the whole contents turned into a solidified mass of crystals. :o ;D

With the methanol contained in there still present?

Quote from: Sawdust and Honey on November 25, 2020, 05:58:35 PM

> Wow! No heating needed?

Still not, yes.
Just like the OP has also reported.
Just like in the original paper.

Quote from: StuffedBee on November 25, 2020, 06:16:42 PM

> So with the ethanolamine it is possible to just use the otc fuel directly without isolating the nitromethane first? Pretty cool! I wonder if this would work with 25% nitromethane in ethanol as well which is the commercial mixture around here

There is ricinus oil in there usually, to smear the engine parts which otherwise suffer damage from using nitromethane containing fuels.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **November 26, 2020, 04:34:58 PM**

Quote from: Sawdust and Honey on November 25, 2020, 05:58:35 PM

> Wow! No heating needed?

No. Upon addition of ethanolamine the a considerable amount of heat is generated.

A recent decently sized experiment with normal benzaldehyde did not have any crystals upon standing overnight at RT. It was cooled in an ice bath initially, don't know how much that has affected this. I am actually thinking about doing a series of experiments measuring temperature in the mixture over time to understand the reaction better. Would be cool to have an UV/Vis to follow the reaction in an easy way also.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **November 26, 2020, 04:36:55 PM**

Quote from: StuffedBee on November 25, 2020, 06:16:42 PM

> So with the ethanolamine it is possible to just use the otc fuel directly without isolating the nitromethane first? Pretty cool! I wonder if this would work with 25% nitromethane in ethanol as well which is the commercial mixture around here

Yes, straight OTC fuel without any processing. My guess is it will work with ethanol based fuel too. I think you should try it out and report here. :)

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **November 26, 2020, 04:39:21 PM**

So you have not made the ionic liquid, and only added the reagents when it is cold? Because if you do it else, and with solvent present, you're just doing a normal henry.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **November 26, 2020, 04:44:03 PM**

Quote from: carl on November 25, 2020, 06:39:20 PM

> With the methanol contained in there still present?

Yes, no processing of the fuel at all.

Quote

> There is ricinus oil in there usually, to smear the engine parts which otherwise suffer damage from using nitromethane containing fuels.

The fuel I used contains 9% synthetic oil FYI.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **November 26, 2020, 04:46:38 PM**

Quote from: carl on November 26, 2020, 04:39:21 PM

> So you have not made the ionic liquid, and only added the reagents when it is cold?
> Because if you do it else, and with solvent present, you're just doing a normal henry.

Yes, exactly. I have thought about that. I have more trials in the pipeline to examine different factors, including making ionic liquid in advance and varying the amount of "catalyst" (I'm not sure the word "catalyst" is correct under the conditions used).

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **StuffedBee** on **November 26, 2020, 05:03:03 PM**

Nice! what yield did you get?

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **November 26, 2020, 11:35:30 PM**

Quote from: StuffedBee on November 26, 2020, 05:03:03 PM

> Nice! what yield did you get?

For what product are you asking? For 2,5-DMBA - it's still in the flask, didn't have time to work it up yet. I'll report as soon as it's worked up!

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **bsmathers** on **December 21, 2020, 07:31:15 PM**

I tried the ethanolamine acetate catalyst on 2,5-dimethoxybenzaldehyde. 5g of aldehyde and 1.3 equivalents of nitromethane were added to a beaker, 1.6 equivalents of acetic acid were then added, and finally 1.5 equivalents of ethanolamine were added with intermittent swirling and cooling on an ice bath. The reaction mixture immediately solidified upon complete addition of ethanolamine. The solid was broken up with a glass stirring rod and allowed to sit in the beaker at room temperature for 2.5 hours. 50ml of water was added, and the solid was rinsed with several portions of water. The crude nitrostyrene was dried and recrystallized from isopropanol. Final yield: 4.3g (68%).

This catalyst system looks quite promising-- I think the low yield is primarily due to solubility issues with 2,5-DMNS in particular. If I were to try this again I'd probably increase the amount of catalyst or add a cosolvent (isopropanol maybe?). Also running the reaction overnight is probably a good idea.

[EDIT: fixed a typo]

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **December 21, 2020, 07:32:51 PM**

> Quote
>
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So dimethoxy or dihydroxy in the end?

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **bsmathers** on **December 21, 2020, 08:07:41 PM**

> Quote from: Sawdust and Honey on December 21, 2020, 07:32:51 PM
>
> > Quote
> >
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>
> So dimethoxy or dihydroxy in the end?

Whoops, good catch. It was dimethoxybenzaldehyde.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **loft** on **December 22, 2020, 04:36:40 PM**

Quote from: bsmathers on December 21, 2020, 07:31:15 PM

> I tried the ethanolamine acetate catalyst on 2,5-dimethoxybenzaldehyde. 5g of aldehyde and 1.3 equivalents of nitromethane were added to a beaker, 1.6 equivalents of acetic acid were then added, and finally 1.5 equivalents of ethanolamine were added with intermittent swirling and cooling on an ice bath. The reaction mixture immediately solidified upon complete addition of ethanolamine. The solid was broken up with a glass stirring rod and allowed to sit in the beaker at room temperature for 2.5 hours. 50ml of water was added, and the solid was rinsed with several portions of water. The crude nitrostyrene was dried and recrystallized from isopropanol. Final yield: 4.3g (68%).
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>
> [EDIT: fixed a typo]

What I'd try:
- use a co-solvent: for nitrostyrenes GAA, for nitropropenes IPA or EtOH.
- I'd try smaller amounts of catalyst. Typically 0.1 - 0.15 eq amine is used.
- Decreasing the necessary amount of nitroalkane is of interest too. 1.1 eq are described to work just as well.
- Continue stirring the reaction for about 2 hours, don't let it just stand. Stirring-ability will be improved if a co-solvent is used. Maybe even at slightly elevated temperatures (< 50 °C).
- Make sure the water used for washing is cold. I'd use as little as possible. Ice-cold (dry) IPA would be good if available, also for dilution of the primary reaction mixture instead of water.
- Cool down the reaction mixture prior to filtration to reduce the solubility of the nitroalkene. This applies to both the crude product and the recrystallized one.
- Cool down the mother liquor / recrystallization solvent multiple times. There is a detailed synthesis of 2C-B described in publication, it was published by genesis. He described this multiple cooling process and achieved high yields.

Of course all of these experiments should be conducted on a smaller scale <= 1 g to minimize losses of valuable reagents :)

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **December 28, 2020, 09:37:14 PM**

A trial with 0.1 eq. ethanolamine and acetic acid, on 3,4,5-TMBA and nitromethane straight from the jug of fuel (25% nitro, 9% synthetic oil, methanol). A small dash of IPA was added and the mixture (*sans* ethanolamine) was heated gently to dissolve the benzaldehyde. Upon addition of ethanolamine, while warm, the mixture coloured yellow more or less instantly, as expected. Benzaldehyde did not precipitate when heat was

ceased. It did not solidify after a few minutes like with the high amount ethanolamine. When 20 hrs had passed with stirring at RT the contents in the beaker was an opaque yellow slurry, not the strong orange that might be expected. It is left to stir.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **loft** on **December 29, 2020, 02:11:30 PM**

I'd cool it down in the fridge. Scratch the inside wall if nothing precipitated after reaching fridge temperature.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **December 29, 2020, 04:47:39 PM**

Properly purified TMNS is yellow and not orange.
This only demonstrates how clean that catalyst is.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **January 01, 2021, 05:55:27 PM**

Quote from: carl on December 29, 2020, 04:47:39 PM

> Properly purified TMNS is yellow and not orange.
> This only demonstrates how clean that catalyst is.

I realized that later. Had images of 2,5-DMBA in my head. Any idea what solubility of 3,4,5-DMBA in IPA? Tried recrystallizing , not too successful, probably used to little IPA. Think the oil from the fuel is messing with proper crystallisation. Will distill fuel to try it without oil.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **blade_runner** on **January 01, 2021, 07:42:34 PM**

Quote from: NeonCortex on January 01, 2021, 05:55:27 PM

> Quote from: carl on December 29, 2020, 04:47:39 PM
>
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20-30 ml 91% IPA per 1 g nitrostyrene. It sounds like a lot but you should get >90% recovery if you freeze precipitate it. You want to dissolve all the nitrostyrene and, once dissolved, add enough IPA such that the solution goes from opaque yellow to clear yellow. If you stop at opaque yellow the crystals will be mushy, similar to what it looks like post-acidification in the nitrostyrene reaction, and not shard-like.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **loft** on **January 02, 2021, 03:24:57 PM**

Quote from: blade_runner on January 01, 2021, 07:42:34 PM

> 20-30 ml 91% IPA per 1 g nitrostyrene.

That equals about 30 mg/mL 91% IPA. Sounds all right! (The solubility of 2,5-DMNS is about 60 mg/mL dry IPA at boiling.)

Solubility of 3,4,5-TMNS in boiling MeOH is about 0.2 g/mL.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **February 24, 2021, 02:42:21 PM**

Honorable Dudes and Dudesses!

1. *I do not want to encourage sloppy chemistry of any kind.* **BUT**...

2. ...if you ever find yourself with a kind of botched nitroaldol catalyzed as per standardized alkylamine means, don't curse just quite yet. Perhaps you tried splashing in some extra GAA and amine, doing a heat cycle, cooling; with an actual resulting product crashing out but the yield makes you want to curse again - especially when thinking about all the precursor material that is lost even if you take the time to purify the leftover mess. If you get to this point - not really knowing if you should simply give up on it. **FEAR NOT!** Because...

3. **Ethanolamine might very well be your knight in shining armor!**

For starters - just toss in a suitable amount, perhaps 0.3 eq. GAA and 0.3 eq ethanolamine - in that order. GAA and ethanolamine has very close molecular weights, so it's pretty much equal masses needed - 2% less GAA mass-wise or so if you're picky. No premixing or dripping in slowly with noble addition funnels needed. Simply place your vessel with the mess of a supposedly botched nitroaldol mix on your trusty scale, put a funnel in it for easy pouring, tare. Add GAA, then add ethanolamine, then stir. It will heat up, but not dangerously so IMHE. Let it stir for an arbitrary amount of time. Until it has come close to RT again perhaps? Then let it stand over night, or chuck it in the fridge if you fancy that. Return next day - there is a high likelihood you will be greeted by a beaker with barely any liquid left in it. If this is not the case - repeat the procedure, perhaps up the amounts a little. At no point should you need more than 2 eq. initially used amine + ethanolamine added together.

Beware of the ketchup effect when emptying! 8)

I know, this is not exactly elegant, but can resuscitate an elegantly planned experiment that went sideways.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **April 05, 2021, 02:15:44 PM**

Attempt number nth:
4.14g 2,5-dimethoxybenzaldehyde (1 mol eq., 25mmol)
2g nitromethane (1.3 mol eq.)
2.3g GAA (1.5 mol eq.)
2g ethanolamine (around 1.3 mol eq.)

Aldehyde was weighed out and directly into the beaker nitromethane was added. Some dissolved. Then the GAA was added and with very slight warming all of the aldehyde

dissolved. When adding the ethanolamine dropwise, the mixture got very hot and started almost boiling. Initially entire 2.3g of ethanolamine was destined to be added, but due to the exotherm the plan was obviously thrown out the window ::)

So some of ethanolamine was left in the pippete. Then I watched in awe how the whole, now deep black red mixture solidified and dense, long needle crystals formed in the beaker. The mixture was then flooded with around 15ml of GAA and it was stirred for the next 30 minutes or so. The smell of the aldehyde was apparent, so that's why I decided to let it react for half an hour.

Then the mixture was flooded with portions of water and transferred into a beaker. In total around 200ml of water was used in washes. The clay-like nitrostyrene lumps were flooded with water and very strong stirring started. In the end, after a filtration and couple washes, drying on the pump and in air around 90% yield of crude, still a bit moist lumps was obtained. Photo in attachments.

Now - what to recrystallize it from? Some use isopropanol, some use ethyl acetate. Last time I used IPA it was very difficult the recrystallize it properly as the product just crashed out after putting it in the freezer and formed a slush instead of nice, clean needles.

Oh! I should probably add that the mp was tested and came out as a very clean 118-120C, which corresponds to the literature value. I'm sure it's slightly impure though, as there's a faint smell of the aldehyde and I'd like to recryst. it.

UPDATE

After recryst. the yield is 84% - 4.4g out of 4.14g of aldehyde. Nice sparkling crystals. Probably not as nice as xdragon's, but the purity is absolutely proper.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **xdragon** on **April 05, 2021, 04:28:29 PM**

Instant nitrostyrene formation with 2-HEAA mirrors my experience[1] ::)

2-HEAA seems promising first, but equimolar + cosolvent (essentially like you did to fix your reaction) is probably the better way to go (for letting the reaction succeed at RT, at small scales). Not sure how 2-HEAF fares, perhaps it is less like honey.[2] However, why didn't you let the 2-HEAA preform and cool down?

Did you recrystallize slowly? Did you have enough iPrOH? Even though it can get quite crowded in the flask when putting it into a freezer, mine still came out as fine needles.[3]

Edit:
[1] with a comparable amount of preformed 2-HEAA (~5 g) but just 1 g of 2,5-DMBA, after adding the nitromethane dropwise, it didn't take long until the (at that point) suspension couldn't be stirred anymore, so that GAA had to be used as solvent as well

[2] then again, the reason why they use as much in the original paper is because of viscosity issues...

^{3} from iPrOH (to answer Johnathan)

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Johnathan Ferrous** on **April 05, 2021, 05:16:05 PM**

Just to clarify, what did you end up using for the crystallization this time?

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **loft** on **April 05, 2021, 05:20:36 PM**

Sometimes those nitroalkenes oil out instead of crystallizing. In those cases you can redissolve the frozen oil/crashed out product by heating and add little more IPA, cool again in the freezer and check if it crystallized properly. Otherwise repeat.
About 17 mL/g anhydrous IPA is needed for 2,5-DMNS.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Johnathan Ferrous** on **April 05, 2021, 05:47:44 PM**

I see. I am still trying to work on my 2C-B synth from homemade (there is a word for that but I can't remember it right now) nitromethane. This could be useful to me.

/JF

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **April 05, 2021, 05:51:25 PM**

Quote from: xdragon on April 05, 2021, 04:28:29 PM

> However, why didn't you let the 2-HEAA preform and cool down?

Good question. I underestimated the exotherm on larger scales. I did this reaction twice before, but with 0.5g of $OHEtNH_2$ and the exotherm was very mild. This time I made exactly this mistake of not adding the preformed salt but making it in situ.

Quote from: xdragon on April 05, 2021, 04:28:29 PM

> Did you recrystallize slowly? Did you have enough iPrOH? Even though it can get quite crowded in the flask when putting it into a freezer, mine still came out as fine needles.

I was probably too impatient and added an initiation crystal and tossed it into the refrigerator. This caused it to crash out too quickly, even after adding more than enough to dissolve everything of IPA.
I'll attempt the recryst once again.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **xdragon** on **April 05, 2021, 06:07:40 PM**

Quote from: Sawdust and Honey on April 05, 2021, 05:51:25 PM

> I did this reaction twice before, but with 0.5g of $OHEtNH_2$ and the exotherm was very mild. This time I made exactly this mistake of not adding the preformed salt but making it in situ.

Which scale (based on benzaldehyde), which outcome (approximate yield), if I may ask?

Quote from: Sawdust and Honey on April 05, 2021, 05:51:25 PM

> I'll attempt the recryst once again.

If you don't watch your nitrostyrene recrystallisation until the free-floating flask reaches RT air-cooled, you are missing out on one of the greatest spectacles of chemistry!

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **April 05, 2021, 06:12:32 PM**

Quote from: xdragon on April 05, 2021, 06:07:40 PM

> Which scale (based on benzaldehyde), which outcome (approximate yield), if I may ask?

Always 25mmol, crude yields from 50-80%, but the product was a little lighter in color. The product would precipitate out after the reaction only if I used small amounts of GAA as the cosolvent and cooled the mixture down in the fridge. Otherwise the mixture was a liquid even after 8h of reaction.

Quote

> If you don't watch your nitrostyrene recrystallisation until the free-floating flask reaches RT air-cooled, you are missing out on one of the greatest spectacles of chemistry!

I surely will! If anything happens, that is. ::)

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **April 06, 2021, 02:24:27 PM**

Wow, I mistakenly edited the post and removed the bulk of it instead of adding an edit. Can any of the admins see the edit history and reverse the edit so that all the reaction info is there?

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Johnathan Ferrous** on **April 06, 2021, 03:48:02 PM**

If anyone quoted you we can use that.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **RhinoJackson** on **April 06, 2021, 10:51:24 PM**

Quote from: Sawdust and Honey on April 06, 2021, 02:24:27 PM

> Wow, I mistakenly edited the post and removed the bulk of it instead of adding an edit.
> Can any of the admins see the edit history and reverse the edit so that all the reaction info is there?

What post exactly? I'll see if it's in my archive.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Corrosive Joeseph** on **April 06, 2021, 10:54:51 PM**

Quote from: Sawdust and Honey on April 06, 2021, 02:24:27 PM

> Can any of the admins see the edit history and reverse the edit so that all the reaction info is there?

Vesp is the only admin, all the rest of the staff are moderators. There is no edit history that I know of and the only thing that would show up in the "Moderation Log" is if you actually deleted the thread. Sorry ???

/CJ

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **April 06, 2021, 11:17:23 PM**

Quote from: Sawdust and Honey on April 05, 2021, 02:15:44 PM

> After recryst. the yield is 84% - 4.4g out of 4.14g of aldehyde. Nice sparkling crystals. Probably not as nice as xdragon's, but the purity is absolutely proper.

This one, I clicked modify instead of quote and mistakenly deleted the contents. It contained the reaciton. Anyways, it was 1.3mol eq catalyst and the baseline is that you should pre-prepare the catalyst and then add add it to the mixture. It worked out well, good yield and pure crystals, mixture solidified after a couple seconds.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **RhinoJackson** on **April 07, 2021, 03:59:23 PM**

Quote from: Sawdust and Honey on April 05, 2021, 02:15:44 PM

> Attempt number nth:
> 4.14g 2,5-dimethoxybenzaldehyde (1 mol eq., 25mmol)
> 2g nitromethane (1.3 mol eq.)
> 2.3g GAA (1.5 mol eq.)
> 2g ethanolamine (around 1.3 mol eq.)
>
> Aldehyde was weighed out and directly into the beaker nitromethane was added. Some dissolved. Then the GAA was added and with very slight warming all of the aldehyde dissolved. When adding the ethanolamine dropwise, the mixture got very hot and started almost boiling. Initially entire 2.3g of ethanolamine was destined to be added, but due to the exotherm the plan was obviously thrown out the window ::)
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> Then the mixture was flooded with portions of water and transferred into a beaker. In total around 200ml of water was used in washes. The clay-like nitrostyrene lumps were flooded with water and very strong stirring started. In the end, after a filtration and couple washes, drying on the pump and in air around 90% yield of crude, still a bit moist lumps was obtained. Photo in attachments.
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> Now - what to recrystallize it from? Some use isopropanol, some use ethyl acetate. Last time I used IPA it was very difficult the recrystallize it properly as the product just crashed out after putting it in the freezer and formed a slush instead of nice, clean needles.
>
> Oh! I should probably add that the mp was tested and came out as a very clean 118-120C, which corresponds to the literature value. I'm sure it's slightly impure though, as there's a faint smell of the aldehyde and I'd like to recryst. it.

:)

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **April 07, 2021, 04:26:39 PM**

Thanks, updated the original post to show just that :)

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **April 07, 2021, 11:36:45 PM**

Actually preforming the ionic liquid that is the topic was finally tried. 2 eq. with respect to

aldehyde. Just slightly above 1 eq. nitromethane. Product looked very similar to what is in Sawdust honey's photos after one recrystallization. Melting point checked out, similarly. IIRC yeild came to 93%.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **April 07, 2021, 11:43:34 PM**

That's cool. I'd consider that relatively pure.
I think that less catalyst can be safely used, even 1 mol eq. should be sufficient. I like this method a lot since there's no worrying about the reaction going to completion. After adding the catalyst it all crystallizes, then you add a bit of GAA to slurry it up and let it stir for as long as you deem necessary. After a recrystallization not even a hint of the aldehyde smell remains. And (at least mine) smells quite potently, although I have to say I like the smell a lot.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **NeonCortex** on **April 07, 2021, 11:57:37 PM**

I'm going to try adding GAA when the RM has solidified next time around, and let it stir a while more.

It's a bit perplexing that you had such a strong exothermic reaction as you describe. I've done this reaction in pretty much the sloppiest manner you can, on significantly larger scales and never had a runaway. It has sure become warm, even hot, after dumping the ethanolamine in in one go on as few dozen grams of aldehyde. One time I had a slight fear it might run away, so I cooled it a short while in some water.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **April 08, 2021, 10:38:19 PM**

Quote from: Sawdust and Honey on April 07, 2021, 11:43:34 PM

> And (at least mine) smells quite potently, although I have to say I like the smell a lot.

What does it smell like?
I am sure you have a smell-less sample, you already thought of comparing those two? ;)

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **Sawdust and Honey** on **April 08, 2021, 10:42:18 PM**

Quote from: carl on April 08, 2021, 10:38:19 PM

> Quote from: Sawdust and Honey on April 07, 2021, 11:43:34 PM
>
> > And (at least mine) smells quite potently, although I have to say I like the smell a lot.
>
> What does it smell like?
> I am sure you have a smell-less sample, you already thought of comparing those two? ;)

It's very difficult to describe a smell like that. I'd call it musty, but I call every smell musty.
I don't doubt the purity of my aldehyde, it's been GC-MS'd and came out to be at least 99% pure.

Title: **Re: MDP2NP - 2-HEAA catalysed Henry condensation**
Post by: **carl** on **April 08, 2021, 10:55:41 PM**

I don't doubt the purity, a 0,01% impurity can be sufficient for a certain arome to be present.
Just for me, its odorless(check the respective sample! :P).
But 3,4,5-TMBA smelled to me very, very faintly of vanilla, not vanillin itself(or maybe sufficiently diluted).

We know that the smells of most aromatic aldehydes are very intense and can be measured in ppm.