Sciencemadness Discussion Board

Pepper.....OTC...Impossible?????

Froggy - 18-4-2007 at 17:53

Just a little bit of a compilation of sorts!!

INDEX
Step 1::Black Pepper to Piperine
file:///?Overall%20Tree|Pepper|798|0
Step 2::Piperine to Piperic Acid to Piperonal (3,4-methylenedioxybenzaldehyde)
file:///?Overall%20Tree|Pepper|1787|0
Step 3::Piperonal **condensation** with MEK to iso-Safrole
file:///?Overall%20Tree|Pepper|6109|0
Step 4::MPB oxidation via Baeyer/Villiger (Perboric Acid) and NaOH 'Sapon' to MDP-2-P
file:///?Overall%20Tree|Pepper|9958|0
Step 5::MDP-2-P reduction options... Sodium Borohydride/Methylamine
file:///?Overall%20Tree|Pepper|12065|0

Reagents and Equipment needed to start: file:///?Overall%20Tree|Need|97|0
Status: Able to make MDMA within 2 weeks of decision on $(x<150).
Need to organize methylamine synth! (10-15-05)
Confirm KMnO4 oxidation, order it! (10-19-05)
Reconfirm sources. Bootstrap FAN with lamp power. (02-17-06)

The route from pepper is tedious in the extreme. Perhaps the most tedious route imaginable. But, for those people who DON'T want to bother with chemical distributors, who can't get hold of sassy and who have more time than sense - it is a viable route.

Step 1::Black Pepper to Piperine
Return to Index: file:///?Overall%20Tree|Pepper|0|0

Title: Piperine
CAS: [94-62-2]
M(C17H19NO3) = 285.34 g/mol
mp 130°C, yellow crystals

Materials:

100g Black Pepper :
1L IPA (bp 82*C) : .
1L Acetone :
1 Microwave :

Procedure:

Microwave ~100g of crushed black pepper. Shake and extract with anhydrous IPA. Evaporate solvent to leave yellow crystals. Dissolve in Acetone, filter (If needed), then recrystallize the Piperine, mp 131øC <- Not bad!

Step 2::Piperine to Piperic Acid to Piperonal (3,4-methylenedioxybenzaldehyde)
Return to Index: file:///?Overall%20Tree|Pepper|0|0
Notes: file:///?Overall%20Tree|Piperic%20Acid%20Oxidation|344|0

Title: Piperic Acid. ----------
CAS Registry number: [5285-18-7]
CAS name(s): 5-(1,3-Benzodioxol-5-yl)-2,4-penta dienoic acid;
5-(3,4-methylenedioxyphenyl)-2,4-pentadienoic acid.
Molecular formula: C12H10O4;
Molecular weight: 218.21.
Percent Composition: C 66.05%, H 4.62%, O 29.33%.

Title: Piperonal
CAS Registry number: [120-57-0]
CAS name(s): 1,3-Benzodioxole-5-carboxaldehyde;
Additional name(s): 3,4-(methylenedioxy)**benzaldehyde**; heliotropin;
piperonyl aldehyde; dioxymethyleneprotocatechuic aldehyde.
Molecular formula: C8H6O3;
Molecular weight: 150.13.
Percent Composition: C 64.00%, H 4.03%, O 31.97%.
Properties: Colorless, lustrous crystals, mp 37° . Heliotrope odor. bp ~263° ;
bp(0.5) 88°. Sol in 500 parts water; freely sol in alcohol, ether. Keep in
cool place protected from light. LD50 orally in rats: 2700 mg/kg (Hagan).
Boiling point: bp ~263°; bp(0.5)88°
Melting Point: 37°

Store piperonal/**benzaldehyde** under a solution of hydrochinone in IPA/EtOH in the freezer so it doesn't decompose. 1g for every 25g of aldehyde is fine.

Overview:

Piperine to Piperonal Procedure, by The Cook
Hydrolize with NaOH in Alcohol. (MeOH/EtOH both verified)

Oxidize with Potassium Permanganate, to get a flask full of chopped-up molecules :-).

Materials:
Note: Must scale up.

2.18g(.01 M) Piperic Acid : "Step 1"
1gal MeOH/EtOH :
1gal HCl (35%) :
1gal Acetone :
3gal dH20 :
4.2g(.05 M) NaHCO3 :
3.16g(.02 M) KMnO4 :

Procedure:

2) Piperine added to NaOH in MeOH. refluxed till MeOH is gone, leaving Sodium Piperidiene and Piperic Acid as a Brown tar, crystallizing to yellow gunk upon cooling. -100ml dH20 added, solution was heated to boiling. Soln. acidified with HCl giving a yellow suspension, and brown oil floating ontop.

3) Solution was cooled, then ugly, chunky, yellow piperic acid was filtered. Filter cake was dissolved in acetone, and NaCl filtered out. Recrystallize, Note the change of odor.

4) A 1:2:5 oxidation was dreamed, similar to the asarone oxidation. 2.18g (.01 Mol) Piperic Acid was suspended (Suspended, it DON'T dissolve) in 150ml boiling dH20, containing 4.2g (.05 Mol) Sodium Bicarbonate. To this hot solution, 3.16g (.02 Mol) KMnO4 [Well, some didn't dissolve] in 75ml warm dH20 added with an eyedropper over about 40 min. (Notes ream an addition funnel, or lose your mind from boredom. Keep this slightly exothermic reaction CONSTANTLY stirred.)

5) During the additon of the permanganate, she dreamed that the pepperish smell subsided almost completely, with the formation of a NEW, milder, marshmallowy good smell. Mmmmm. /* The Cook thinks that the oxidation could be done 'on the fly', using the smell as an indicator. (If you're good) But last time she dreamed that, she oxidized it all into piperonylic acid. OOPS! */

6) The warm brown solution was filtered to leave a slightly yellow/tan solution. This was chilled overnight, as per the asarone oxidation, but the crystals were TINY! [Actually, this 'failure' has been a reoccurring dream, the main cause of the frustration in this rxn]

7) The Cook cursed the slightly cloudy solution, and in a fit of rage, added 25ml IPA. (To kill any remaining oxidizer) She dumped the solution into a pyrex dish, and set it on the heater for a few days.

8) The next time she slept (48h later), she dreamed the solution had evaporated into off-white, glassy chunks(YES!!). There was also some brown MnO2 at the bottom, and some tartaric acid, but that's not important. What is important is: that shit can be filtered/ recrystallized to give just over 1g of luscious translucent Piperonal rocks. MP was dreamed to be 41, so it ain't Lab Grade, but it ain't bad either, bees. She dreamed this substance had a wunnerful, indescribable odor that could be likened to marshmallow with a slight fruity, cherry overtone. It smelled so good, she ate it all, and died later that day, leaving no evidence or record other than this. So if any bees are feeling frisky, she'd like to know HOW BIG it can be scaled. If you dream the answer, point your flask towards hell, and yell real loud! ;-)

Step 3::Acid Catalyzed Aldol condensation of Piperonal with MEK to MPB deriv'

Return to Index: file:///?Overall%20Tree|Pepper|0|0

References:

1)"P2P [Phenylacetone] vial aldol and Baeyer/Villiger.pdf"
2)"Adol Condensation MEK, Baeyer_Villiger Peroxy acid, Saponification KOH, Hive Novel Discourse.pdf"
3)"mek-aldol-bcsj.pdf"

Overview:

An acid catalysed Aldol condensation of Benzaldehyde and Methyl Ethyl Ketone to give Methyl Phenyl Butenone:
C6H5CHO + CH3CH2COCH3 + HCl(g) ---> C6H5CH=C(COCH3)CH3

An acid (gas) catalysed Aldol condensation of Piperonal and Methyl Ethyl Ketone to
give Methyl Phenyl Butenone:
CH2O2C6H5CHO + CH3CH2COCH3 + HCl(g) ---> CO2C6H5CH=C(COCH3)CH3
CH2O2C6H3CH:CHCOC2H5

"Just remember that anything less than 2moles MEK to 1 PhCHO causes reduced yield and workup headaches due to polymerization. Ditto for the 24-28 hours at room temp procedures. I tried that with poor results." - bio

Materials:
Note: Must scale down.

282.5g Piperonal (1.88 mols) : "Step 2" (file:///?Overall%20Tree|Piperonal|0|0)
300.0g MEK (4.16 mols) :
1L H2SO4 : Lunds
1L Muratic Acid :
1kg NaOH :
1L 95% EtOH : .
"Some" PH Paper : .

Procedure:

1) Methyl Phenyl Butanone (MePhBuO)..... 400g PhCHO and 600g MEK (both RA grade) were mixed in a 2L flask placed in an ice salt bath and cooled to -5 degrees. 80 grams of DRY HCL gas was passed over about 3 hours keeping the temp below 5-7 degrees. Stirring with the thermometer. (This is about a 1 to 2.2 mole ratio as given by twodogs. Rhodium has posted an apparent improvement of yield to 94% with 1 to 1 mole which has not been tried yet.) A saturated solution is what is strived for here. Previous results indicated about 85% of the calculated HCl was absorbed. An additional 15% was partly added to compensate and the solution was saturated before it was all added. Flask stoppered and left in bath to warm up overnight ca. 10 hours. The Vogel method of dripping 37% HCl into 98% H2SO4 was used with a H2SO4 dryer. Trap also used but not needed this time. Vogel says 31-33g HCl per 100ml.

/* MEK MolWeight(72.10g)
Piperonal MolWeight(150.14g)
PhCHO MolWeight(106.12g)
Hcl MolWeight(36.46g), 31-33g HCl per 100ml 37%
--0.42444 g HCl/ml 36% (it looks like Vogel is right)

Original Materials:
080.0g HCl (gas, dry)
400.0g PhCHO (3.77 mols)
600.0g MEK (8.32 mols)
MEK::PhCHO == 2.2

(1.415:1) Piperonal:Benzaldehyde, so, 565.93g Piperonal.

Reduced Materials:
040.0g HCl (gas, dry)
282.5g Piperonal (1.88 mols)
300.0g MEK (4.16 mols)
MEK::Piperonal == 2.21
*/

2) The resulting deep reddish brown reaction mix was washed with an equal volume of water separated then washed with a 20% excess of 10% NaOH separated then washed with 1/2 volume of brine separated and filtered to give 845ml Ph 7-8 solution. This was distilled at atmospheric collecting most of the first fraction 74-84 degrees PH1 and the second fraction at aspirator pressure most was collected 119-140 degrees. MePhBuO clear yellow fruity smelling oil 506.7 gram includes the forerun and after run. This was allowed to cool to ambient, then seeded causing immediate crystalization. Let set up in frig with stirring for a couple hours. Filter on buchner wash with 95% EtOH dried for 430 grams total very clean and dry light yellow (almost white) pleasant smelling crystals. These initially set up as long transparent light yellow needles. Happy now as had expected only 360 grams. Even returned to the vac dessicator to insure they were dry. Recrys of a little test resulted in very little improvement. This stuff is easy to crys in a relatively pure form. No GC/MS sorry.

Step 4::MPB oxidation via Baeyer/Villiger (Perboric Acid) and NaOH 'Sapon' to MDP-2-P
Return to Index: file:///?Overall%20Tree|Pepper|0|0

Title: MDP-2-P, 3,4-methylenedioxy phenyl-2-propanone

References:
bio, twodogs, from synthetikal forums (and Hive)
"Adol Condensation MEK, Baeyer_Villiger Peroxy acid, Saponification KOH, Hive Novel Discourse.pdf"
"P2P [Phenylacetone] via aldol and Baeyer_Villiger.pdf"

Overview:

The unsaturated ketone undergoes the Baeyer-Villiger oxidation with peroxy acids to give the enol ester of Phenyl propanone:
C6H5CH=C(COCH3)CH3 + RCO3H ----> C6H5CH=C(OCOCH3)CH3

Materials:
Note: Must scale down.

609g MD-MPB : "Step 3"
2.3L Glacial Acetic Acid :
2L Toulene :
1kg NaOH :
615g Sodium perborate : non-chlorine bleach. (*4H2O)

Procedure:

3) Baeyer-Villiger Oxidation..... To a 6 liter FB flask on the mag stirrer hotplate in a water bath was added 2.3L Glacial Acetic Acid (RA) 615g NaPerborate 4H2O and 430g MePhBuO with stirring. This starts endothermic and mag stirring is inadequate until heat is added and the stuff dissolves. Added the crystals over ca. 1/2 hour while heating to about 45 deg. After the induction period added ice and or heating periodically to keep the solution temp 55-65 deg. Can get into this more later if anyone actually is ready to do it. Stir vigorously keeping the temp as above for 6 hours. If it gets hotter as long as controllable it's OK. Be very carefull here I already had a near runaway..... Proceed slowly and carefully..... Cool to ambient then either dilute with water or recover the NaBO2 and acid first. Now extract with toluene or DCM. I used DCM this time and wish I didn't. Anyway extracted with 1.2L DCM washed with water and brine then removed solvent to leave the enol ester.

4) Hydrolysis and P2P..... enol ester added to 2.25L 10% NaOH in 50/50 w/w EtOH/H2O and stirred 2 hours. Extracted with DCM 300/200/200ml (again wish I had used PhMe) washed with water and brine removed solvent and collected 162g P2P at aspirator pressure (almost all between 119-140 deg). OVER.

Step 5::MDP-2-P reduction to MDMA options... Sodium Borohydride/Methylamine
Return to Index: file:///?Overall%20Tree|Pepper|0|0

Title: MDMA, 3,4-methylenedioxy-N-methylamphetamine
file:///?Overall%20Tree|Example|8766|0

Optional MDP-2-P Purification with Bisulfite:
http://www.erowid.org/archive/rhodium/chemistry/eleusis/bisulfite.h...

Use water-based Borohydride with solid methylamine (and NaOH) Gyrogearloose
file:///?Overall%20Tree|Example|8766|0

LabTop
file:///?Overall%20Tree|Example|13580|0

Materials:

Methylamine : file:///?Overall%20Tree|Methylamine|1|0
MDP2P : "Step 4"
HCl :
MeOH :
NaBH4 :

Procedure:

Dissolve 1,25 kg Methylamine in 12.5 L MeOh (-20*C). Do this slowly.

Cool reaction vessel to +5 C and start mag mixer anti-clockwise. Add at +5 C 25 L of MDP2P.

Add NaBH4 ~3 soupspoons per time. Use a funnel and wash every time with methanol. It'll stick, keep things shut.

The temperature shouldn't rise much, only to 15*C or so (from the additions).

Keep this slow addition up for ~7 hours. The final temp will be 25C.

Let the mix (no longer cooled) react for 36 hours.

After this time, you prepare 200 L clean water, which you mix with 2 liter 33% HCl solution.

...

This mix you add to the cooling tank (fast), then you messure the pH, should be between 11,5 and 12. (If you add coincidently too much acid,you will see greenish fat form in and on the fluid.) Stop after 10 min. the mixer and let the raw brown base precipitate 30 min to the bottom and tap off the base through the valve at the bottom. Stop tapping when you see lighter color (water) coming.

Add now 3 liter methylenechloride (dichloromethane=CH2Cl2) to the tank, mix 10 min., stop the mixer, wait again 30 min. and tap off the rest of the base, now diluted in the CH2Cl2.This gives totally ca. 43 L raw base.

Now we remove the CH2Cl2, Methanol and the water in a simple distillation setup, without vacuum, with magnetic mixer/ heater, mixerpin teflon, glassware with NS29 connections (20 L 2-neck flatbottom flask PYREX!, thermometer, cooler 60 cm, glas-alonge and 10 L collecting flat-bottom erlenmeyer flask).

Start at 35->55 C for CH2Cl2, then 55->85 C for methanol and 130 C for all the water. Re-use the CH2Cl2 and the methanol! Now you are left with ca 28 L half-clean base.(light brown).

Now we will clean the raw base by 2 times recrystallisation with acetone 98%, (m)ethanol 98%, and after that washing min. 3 times with acetone 98%. Use 20 L P.P. plastic buckets to do this.

Mix 5 L base (cold) and 10 L icecold acetone. Leaf inductionmotor-mixer on. Bubble HCl-gas 99% through with 1 meter StainlessSteel pipe, (inner diameter min 5mm) until white crystals form. Stop when pH= 7,3 and start with the next 5 L base. The first one will rise again to ca. pH=8,0. Later you can bubble again a littlebit HCl-gas through until again pH=7.0 . Let the crystals precipitate and pour the upper acetone off.

Re-dissolve the wet crystals now in the minimum quantity of HOT(nearly boiling) (m)ethanol in a metal bucket (because its hot !) until you see no more crystals, so you have a saturated solution in (m)ethanol!

Pour 5 L of this solution back in the plastic bucket, and add 5 L -15 C Acetone. When cooling down, you will see crystals form again,in a dirty solution. Wait until no more crystals come, pour off again and dissolve again in hot (m)ethanol. Do this as many times until you have snowwhite crystals. Dry on glasplates on the floor with blower.

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4) Borohydride reductions (notes: file:///?Overall%20Tree|Borohydride%20Notes|0|0)

http://www.erowid.org/archive/rhodium/chemistry/redamin.aqueous.nab...
http://designer-drugs.com/pte/12.162.180.114/dcd/chemistry/redamin....

http://www.erowid.org/archive/rhodium/chemistry/redamin.nabh4.html
http://www.erowid.org/archive/rhodium/chemistry/redamin.ti-nabh4-me...

Materials:

1-(2,4-dimethoxyphenyl)-2-propanone (250 mmol, 1 molar equiv.)
Methylamine HCl (375 mmol, 1.5 m.eq.) [file:///?Overall%20Tree|Methylamine|0|0]

NaOH (375 mmol, 1.5 m.eq.)
Sodium Borohydride (145 mmol, 0.58 m.eq.) [
Isopropanol (IPA)
Water

Procedure:

To a solution of 1-(2,4-dimethoxyphenyl)-2-propanone (48.56g, 250 mmol) in 300 ml IPA was added a solution of methylamine hydrochloride (25.3g, 375 mmol) in 30 ml water followed by dropwise addition of a solution of NaOH (15g, 375 mmol) in 40 ml water during 10 minutes while stirring the mixture violently. When the addition was complete the mixture was stirred for another hour at room temperature.

A solution of sodium borohydride (5.5g, 145 mmol) in 20 ml water containing 25 mg NaOH (to prevent decomposition) was then added dropwise over 30 minutes while the mixture was stirred violently. When addition was complete the stirring was continued for two hours. The residual borohydride was destroyed by addition of 2M hydrochloric acid (1:5 37% HCl:H2O) until gas evolution ceased and pH 3 was reached. The alcohol was removed by distillation in a rotovap and the aqueous solution diluted with 100 ml water, extracted once with 50 ml toluene, made strongly alkaline with 25% aq. NaOH and then extracted with 2x50 ml toluene. The combined alkaline extracts was dried over MgSO4 and the solvent removed by distillation. The residual oil was dissolved in 200 ml EtOAc and 5N HCl/IPA was added in portions until pH 5 was reached. Several times the acid addition had to be stopped and the formed crystals removed by filtration. The salt was then recrystallised in IPA.

Yield: 48.5g 2,4-Dimethoxymethamphetamine HCl (79%).

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guy - 18-4-2007 at 18:04

begone
