

HOME

1,2,3-TRIAZOLES

1,2,4-TRIAZOLES

BASIC EXPLOSIVE

DADNE

DIAZO PRIMARIES

DPT

FURAZAN

NHN

NITROALKANES

NITROCUBANE

NITROGUANIDINE

NITROLIC ACIDS

PERCHLORATES

PYRAZOLE

TETRAZENE

TETRAZOLE

TRINITROMETHANE

SITEMAP

diazo primaries

DiazoDinitroPhenol

4,6-dinitrobenzene-2-diazo-1-oxide

120ml 5% HCl
10g Picramic Acid
3.6g Sodium Nitrite
Distilled Water to taste

- Place 120 mL of 5% hydrochloric acid in a 250-mL beaker, then immerse the beaker in a cooling bath
- Place the ice bath on top of a magnetic stirrer and drop a spin bar in the beaker. Slowly add 10 g of picramic acid to the acid solution while stirring rapidly, monitor the temperature with a thermometer. Be sure there is no sudden rise in temperature.
- Dissolve 3.6 g of sodium nitrite in 10 mL of water. After the picramic acid has dissolved, add the sodium nitrite solution all at once and continue stirring for 20 minutes.
- Filter the solution to collect the dark brown crystals that should have formed and wash them with cold water. The diazodinitrophenol thus formed can be used as is, or it can be purified by dissolving in hot acetone then precipitated by adding a water crashing the solution. This treatment will convert the diazodinitrophenol into bright yellow crystals.

The diazodinitrophenol must be dried before it will explode. A beaker is placed in a hot water bath with crystals in the beaker for 2 hours, then desiccated for 24.

The diazodinitrophenol must be stored in a sealed glass container. Storing the explosive moist, about 25% water, will increase safety. Dry immediately before use.

DDNP will detonate from shock, however will only deflagrate unconfined. Note that DDP does not have a hydroxyl group. There is an =O (double bonded!) in the 1-position, and a =N=N in the adjacent 2-position. An initial intermediate probably contained the more typical --OH and the --(+)N#N, which then converted through a resonance to form the final product.

Picric Acid can be reduced to Picramic Acid, where one of the nitro groups get converted into an amine. This can be done adding FeCl2, then a strong base. As far as I am aware, only one nitro gets reduced, picric acid being fairly susceptible due to 3 electron-withdrawing nitro groups, and Fe+2 ions not being a very strong reducing agent. (Iron metal and HCl react to form FeCl2 and H2) See the "Organic Precursor 1" section for a detailed synthesis of picramic acid.

Picramic Acid can then be treated with nitrosyl bisulfate to form a diazo compound, which can then react with mono nitrophenol (at room temp.) to form (HO)(NO2)2C6H2N=NC6H4(NO2).

The diazo could also be performed with plain HCl and NaNO2, but I think in this case, it will only work if there is only one (or none) nitro groups, for example mononitro aniline. However, starting with dinitro phenol, H2S would be required to reduce one of the nitro groups, Fe+2 would not be sufficient.

Nitrosyl compounds can be prepared by bubbling a mix of nitric oxide and nitrogen dioxide gases into concentrated sulfuric acid. The reaction is 3H2SO4 + NO +NO2 --> 2HSO4(NO) + HSO4(H3O).

The diazodinitrophenol must be dried before it will explode. Drying will take 24 hours if done at room temperature, or in 2 hours if the crystals are placed in a beaker suspended in hot water. The diazodinitrophenol must be stored in a sealed glass container. Storing the explosive moist, about 25% water, will increase safety. Dry immediately before use. DDNP will detonate if it is struck by a sharp blow, but it will only burn rapidly if ignited in the open, even several grams.

Diazo Perchlorate

diazoperchlorate-3-nitroaniline

This is a sensitive and moderately powerful primary, that can initiate other less sensitive compounds. PETN can be initiated with as little as 5mg of DPNA, even less if confined. DPNA is a white powder, but the final product in the procedure below may give a brown colored product. When dry it detonates very violently on contact with flame.

Even very minute quantities of the compound will easily detonate. The sample can be kept for 6 months in indirect sunlight without any significant loss in quantity or in power, although it does take on a slightly darker coloration.

One may likely be inclined to think that having more nitro groups on the molecule would make the diazo perchlorate compounds more sensitive, but actually the reverse of this seems to be the case. This seemingly paradoxical behavior can be explained by the additional intermolecular attraction between molecules from the presence of the nitro groups, the nitro groups can also be seen as further "diluting" the unstable diazonium group.

C6H5-N[+]≡N ClO4[-]

Benzenediazonium perchlorate spontaneously detonates when left to dry under sunlight. It detonates when lightly tapped with a metal spoon, showing very high sensitivity.

NO2C6H4-N[+]≡N

Minute quantities of 3-nitrobenzenediazoperchlorate easily detonate on exposure to flame, without need for any confinement. The white substance darkens in sunlight, first turning a medium brown, then dark brownish orange. There is no darkening if stored in the dark for several months. It does not appear to be hygroscopic, but the salt cakes up.

(NO2)2C6H3-N[+]≡N

The diazotization step for preparing 3,5-dinitrobenzenediazoperchlorate requires 60% concentrated sulfuric acid, as dilute nitrous acid by itself is not sufficient to diazotize the amino group when there are two nitro groups on the benzene ring. Small quantities of 3,5-dinitrobenzenediazoperchlorate deflagrate when burned, whereas similar such quantities of 3-nitrobenzenediazoperchlorate would detonate.

(procedure by "Microtek")

Benzamide from Benzyl Chloride Route

If 3-nitroaniline is unable to be obtained, the following route may be of use, if benzyl chloride is available. Note that the main product of the nitration of aniline is 2-nitro aniline, which is unsuitable as a precursor for this specific compound. It is however useful for the synthesis of another primary compound. You might also see <http://www.sciencemadness.org/talk/viewthread.php?tid=14063&page=2#pid185674> for an unual, and low-yeild alternate route to make benzyl chloride.

- 4 mL benzoyl chloride was added dropwise with stirring to 20 mL of the strongest possible aqueous ammonia. Temp was maintained at 5-8 C throughout, and conversion of the acid chloride to the amide (pure white flakes) was instantaneous.

The product was recrystallized from hot water (though not above 80 C as the amide may hydrolyse to benzoic acid at ca. 100 C) to obtain slightly more than 4 g pure benzamide. When drying benzamide, the temp was kept below ca 50 C to minimize conversion to benzoic acid.

Benzamide can also be formed by anhyrous ammonia reacting with benzoic acid, or sulfur can be burnt with chlorine, and the poisonous gases cooled to collect red liquid sulfur dichloride. This reacts with benzoic acid to form benzyl chloride, elemental sulfur, and sulfur dioxide gas. Benzyl chloride can then react with anhydrous ammonia to form benzamide. Heating ammonium benzoate in a closed tube over a flame would also work.

3-nitrobenzamide from Benzamide

nitration of benzoic acid puts the nitro in the 3-position, while nitration of phenol puts the initial nitro groups in the 2 and 4 positions.

- 4 g benzamide was dissolved in 24 mL 96 % H2SO4 and cooled to 5 C

- 9 mL 62 % HNO3, cooled to -10 C was added dropwise with magnetic stirring while keeping temp below 8 C.

- After addition, mix was stirred another 10 min, and then soln was poured onto 80 g ice and stirred vigorously to precipitate a voluminous off-white solid.

- This was filtered off and washed several times with cold water and then added to about 25 mL alcohol and stirred for about an hour.

- 70 mL water was added slowly to the stirred alcohol solution (which did not dissolve all) to precipitate the product which had by then attained a much more dense structure.

2.15 g 3-nitrobenzamide was recovered after drying.

3-nitroaniline from 3-nitrobenzamide (by Hofmann rearrangement)

- 6 mL 15 % NaOCl was diluted to 41.5 mL with water, and 1.0 g NaOH was dissolved in it.

- The solution was stirred and 2.0 g 3-nitrobenzamide was added in one portion.

- The temp was immediately increased to 80 C, and held there for 30 min by use of a paint stripper gun. During this stage, the solid nitrobenzamide was dissolved and the soln changed colour from pale yellow to deep orange.

- After the 30 min, temp was lowered to 50 C (the product began to settle out) and 1.05 g Na2S2O5 in 13 mL water was added to reduce remaining hypochlorite and stop further reaction (to 3-nitrobenzoic acid).

- Mix was cooled to 0 degC and filtered.

- Product was recrystallized from 93% ethanol to recover 0.4 g 3-nitroaniline (this was extremely wasteful; lots of the product crystallized slowly in the filtrate, but the goal was the highest degree of purity rather than yield)

DPNA from 3-nitroaniline, Synthesis #1

Begin with 3-nitroaniline, HClO4, HCl & NaNO2: 1ml HClO4 (70%) + 1ml HCl (30%) in 50ml water (you can thus use much less concentrated acids). Add 1g of 3-nitroaniline, which will readily dissolve. Prepare a solution of 1g NaNO2 in 20ml water. Both solutions are placed in an ice bath until they reach 0°C, then mix them together at once, and you will get a pale-brown precipitate in the minute (do not let it unattended for hours, as bigger crystals then grow and these have often unintentionally detonated using this synthesis. Filter, wash and dry.

DPNA from 3-nitroaniline, Synthesis #2

- 0.6 mL 60 % HClO4 and 0.5 mL 30 % HCl was added to 25 mL water along with a stir bar.

- In another beaker, 0.5 g NaNO2 was dissolved in 10 mL water.

- These two solutions were placed in the freezer until temp had reached 0 degC.

- 0.4 g 3-nitroaniline was dissolved in the dilute acid.

- With rapid stirring, the sodium nitrite solution was added in one portion to the acidic soln, and within about 10 seconds, a white precipitate formed.

- Stirring was continued for 5 minutes and the product was collected by filtration. It was then washed in the filter with water until nearly 7 pH.

Kommentare