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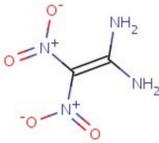
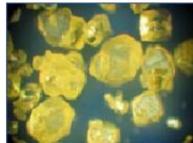
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DADNE



1,1-diamino-2,2-dinitro ethylene

DADNE, also called FOX-7, was first made by researchers in Sweden. It has a detonation velocity between 8335-8870 m/sec, between that of the RDX and HMX nitramines, with a pressure between 284-339 kbar. Its power is slightly below HMX, due to smaller molecular size, and thus lower density. The compound is, however, unusually dense for its small molecular weight. It is significantly more insensitive than the nitramine explosives, the amines being electron donating to the nitro groups, across the carbon-carbon double bond, there being some degree of aromaticity to the compound, which also lends a yellow tint to the crystals. The crystals have a melting point of 289 degC and a density of 1.63 g/cm3. DADNE is twice as resistant to impact as HMX. Despite very ideal properties, the main disadvantage is the complexity of the synthesis. Below, one detailed and tested synthesis, another route from the literature, and four more theoretic routes are listed.

Synthesis 1:

Acetamide Precursor

Boil a mixture of acetic acid (white vinegar) and ammonium hydroxide in a closed tube, this will first make acetamine. Dry, then heat under flame, again in sealed tube, with dry ammonium chloride, to make acetamide chloride. Ammonium acetate (solid, NH3 gas with glacial acetic acid, otherwise very difficult to dry) can also react with anhydrous ammonia (made by reacting solid ammonium chloride with calcium oxide, known as lime, and only a very small amount of water) to form acetamide. This route does not work very well, mostly plain acetamide is produced, so see the "organic precursors 1" section.

Sodium Ethoxide Precursor

One method that does not require elemental sodium to react with ethanol: Buy soda ash (Na2CO3) in buckets for pool alkalinity, and mix with a concrete ingredient, called "lime" (CaO). Small amounts of lime can be bought at a construction supply. These two react in water, forming solid CaCO3 (limestone) and leaving caustic soda (NaOH) dissolved in the water. The reaction is very slow. The CaCO3 must be removed as it is formed. Gloves and goggles should be worn, since the solution can give alkali chemical burns. The NaOH can burn aluminum foil, releasing small amounts of hydrogen gas.

Na2CO3 and CaO can also react with 90% alcohol being used, instead of water. In this case, CaCO3 and the monohydrate of NaOH precipitate at the bottom, pure alcohol at the top, and a small viscous middle layer forms. If isopropanol is the alcohol used, this liquid will be sodium isopropoxide, an ionic liquid (that is not very soluble in alcohol), and is a super base, more basic than NaOH. Ethoxide can be substituted for Methoxide, slightly more nitric acid is then required.

WARNING:

This liquid is very dangerous, much more so than concentrated sulfuric acid, for two reasons. Alkali burns are, in general, more serious than acid burns, because alkalies penetrate deeper and burn longer, according to emergency medical textbooks. Sodium Ethoxide is not your typical basic solution. While being a "super base" does not in itself make it any more dangerous, it is a completely concentrated base in liquid form, whereas sodium hydroxide can only exist in liquid form in moderately dilute solutions. Pure lye (NaOH) is solid, and so does not burn skin as fast as a liquid. Second, and more unusual, when sodium methoxide burns tissue, it deactivates pain receptors, so that a victim may not be aware that the compound is causing chemical burns. Thus, if working with one of the alkali alcohol-oxides, you may feel an insignificant cold point were a little droplet hit skin, then feel nothing, despite the droplet burning through flesh. Always wear long sleeves and long rubber gloves, preferably a rain poncho with the sleeves tucked into the gloves. Always wear protective eye goggles. Whereas eyes might survive a spill of diluted acid if immediately after they are rinsed with water, exposure to alkali solutions are a near guarantee of permanent damage.

Synthesis for the Precursor

2-methoxy-2-methyl-4,5-imidazolidinedione

(used to prepare the explosive FOX-7)

Prepare compound shortly before its intended use, as it might not be thermally stable

Prepare a solution of 69.6 g of sodium methoxide in 1100 mL of methyl alcohol in a 2-L round bottomed flask. Add a magnetic stir bar to the flask and set it up for stirring. While stirring, add 36.48 g of acetamide hydrochloride to the flask and keep stirring until a well mixed suspension forms. Prepare a second solution of 55.88 g of diethyl oxalate in 400 mL of methyl alcohol. Attach an addition funnel to the flask and slowly add the diethyl oxalate solution drop by drop over a period of 3 hours. Maintain stirring throughout the addition. After the addition is complete remove the addition funnel and set up a cold water bath for the flask. Insert a thermometer in the flask and slowly add enough concentrated hydrochloric acid to lower the pH of the mixture to 9 while keeping the temperature below 30 °C. Use the cold water bath as necessary to lower the temperature.

At this point a precipitate of sodium chloride should have formed. Pour the contents of the flask over a filter to remove this solid. The salt collected on the filter paper can be discarded. Pour the liquid filtrate back into the flask and set the flask up for a distillation under reduced pressure. Very gently heat the flask to distill off the methyl alcohol. Heating more than very slightly will cause very low yields as the imidazolidinedione is not thermally stable. This alcohol should be fairly pure and can be recycled. In this situation the flask is distilled to dryness to remove all alcohol and leave a solid white powder. When very little alcohol remains reduce the heat to around 30 degrees until dry. At this point this is a mixture of waste sodium chloride, 2-methyl-4,5-imidazoleone and our final product. Add 320 mL of methyl alcohol to boiling and add it to the flask with the solid. Allow a few minutes for the soluble portions to dissolve and immediately filter the liquid while still hot to remove any insoluble impurities. This is just salt, which can be discarded and the liquid kept. Redistill this liquid until a volume of only 320 mL remains, and then place the liquid in a refrigerator to cool for 6 hours. This process will convert the 2-methyl-4,5-imidazoleone to the final product.

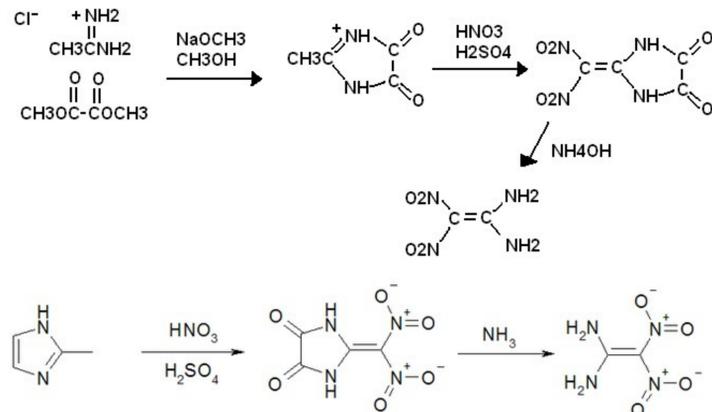
In the morning a white crystalline material should have precipitated in the bottom of the flask. Filter this liquid to collect the crystals and allow them to dry. The crystals should be 2-methoxy-2-methyl-4,5-imidazolidinedione with a yield around 64% or 35-36 g.

The synthesis of FOX-7 proceeds in 2 stages. The first stage nitrates an imidazole type ring, and the second stage breaks the ring forming the final product, 1,1-diamino-2,2-dinitroethylene.

Preparation of 2,2-dinitromethylene-4,5-imidazolidinedione. Place 198 mL of concentrated sulfuric acid (95% and up) in a 500-mL round bottomed flask and immerse the flask in a salt-ice bath to cool the acid. When the acid has cooled slowly add 35.4 g of 2-methoxy-2-methyl-4,5-imidazolidinedione, which should form a clear yellow solution. Set the flask up for magnetic stirring and attach an addition funnel. Slowly add 43 mL of 70% nitric acid to the flask over a period of 60 minutes while stirring. Keep the temperature of the mixture under 30 °C during the addition. After adding the acid, continue stirring for an additional 30 minutes without any cooling. The solution will change color from yellow, to deep red, and finally to a pale orange precipitate. Pour the contents of the flask over a filter to collect the precipitate and allow it to dry in the open air, or vacuum, at room temperature. Optionally the crystals can be washed with a few small portions of trifluoroacetic acid. This precipitate should be 2-(dinitromethylene)-4,5-imidazoleone in approximately 63% yield.

Final Part of Synthesis

Preparation of 1,1-diamino-2,2-dinitroethylene. Dissolve the above produced 2-(dinitromethylene)-4,5-imidazoleone in 120 mL of distilled water, with stirring, in a 500-mL flask or beaker. Place the flask in a cold water bath and cool it to below 30 °C. Add 30% ammonium hydroxide to the flask at such a rate as to keep the temperature between 20-30 °C. Add enough ammonium hydroxide to reach a pH of approximately 9. One could also use the weaker 3-4% ammonium hydroxide as commonly available as cleaning solution. ("Pure ammonia") sold in containers is usually 70% NH4OH in water. Much larger quantities would be needed in that case, so use appropriately sized container. Stir the contents of the flask for 2 hours after adding all of the ammonia. Pour the material over a filter to collect the product. Thoroughly wash these crystals several times with water and allow them to dry under vacuum. What remains are bright yellow crystals of 1,1-diamino-2,2-dinitroethylene, aka FOX-7. Yield of the final product is around 54%.

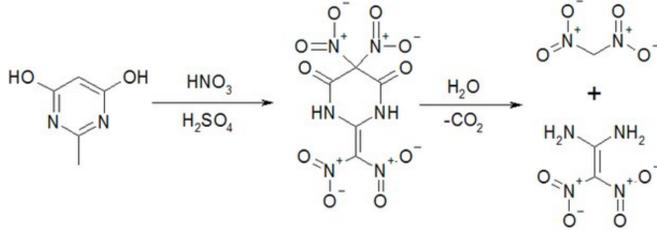


an alternate route directly uses 2-methyl imidazole, oxidizing it into the imidazolidinedione

Alternate Route 2

1,1-Diamino,2,2-DinitroEthylene can be synthesized by nitration, with concentrated nitric and sulfuric acids, of 4,6-dihydroxy, 2-methyl pyrimidine, where the methyl is on the carbon in the ring that is between the two Nitrogen atoms.

Low temperature nitrations of 2-methylimidazole gave, in addition known 2-methyl-5(4)-nitroimidazole, 2-(dinitromethylene)-5,5-dinitro-4-imidazolidinone, and parabanic acid. The tetranitro compound was also obtained by nitration of 2-methyl-4,5-dihydro-(1H)-5-imidazolone. Thermal decomposition of the tetranitro compound gave 2-(dinitromethylene)-4,5-imidazolidinedione, which also was the product from nitration of the new compound 2-methoxy-2-methyl-4,5-imidazolidinedione. Treatment of the new compound with aqueous ammonia gave 1,1-diamino-2,2-dinitroethylene.



Theoretical Route 3

Step 1, Preparation of 1,1-dichloro-2,2-dinitroethylene:

Into a 1000 mL round-bottomed flask prepare a mixture of 50 g of 1,1-dichloroethylene and 490 mL of concentrated (96-99%) sulfuric acid. Place the flask to a salt ice bath, dropwise add 85 mL (42,75 ml calculated) of concentrated (99-100%) nitric acid and maintain the temperature of the addition below 20 °C. After the addition is complete, remove the flask from the salt ice bath, stir the mixture for an hour and allow to heat to 30 °C during the period. The mixture is then stirred for additional 30 minutes and the temperature of the reaction is monitored at all times, a external cooling bad may help. After that, slowly stir the mixture into a large flask with 2000 mL of ice water, let stand the flask at 0 °C for an hour, pour the content of the beaker over a filter to collect the crude crystals of 1,1-dichloro-2,2-dinitroethylene. Wash them with with a portion of 10% sodium hydrogen carbonate solution, several small portions of cold water and let them dry on a warm place or under vacuum. Formation of nitrogen dioxide should be minimized, since this probably will react in an addition reaction to the double bond.

Step 2, Preparation of condensation product

Dissolve the obtained 1,1-dichloro-2,2-dinitroethylene (around 96 g) from the previous step in 800 mL of toluene in a large round-bottomed flask. Place the flask to a weighing machine and bubble dry ammonia gas through the solution until the FOX-7 precipitates and no weight is increased. Pour the content of the flask over a filter to collect the crystals, wash them several times with small portions of water and dry them under vacuum. Yield is 73 g or 97% of ammonium dinitromethylcyanide. 1,1-diamino-2,2-dinitroethylene can not be made by direct condensation of ammonia with dichloroethylene.

1,1-dinitroethylene can be prepared by reacting refluxing NaOH with 1,1,2-trichloroethane.

Theoretical Route 4:

Acetaldehyde and oxalic chloride both dissolved in an organic solvent, can be combined anhydrous ammonia to form CH3CH(NH)2C2O2 in moderate yield. This is then reacted with red fuming 98% Nitric Acid, saturated with NO2. It is important that a lesser concentration not be used, since this would allow the initial nitro to hydrolyse/ disproportionante. (NO2)3CCH(NH)2C2O2 should be the main product. This will react with a concentrated NaOH solution to form (NO2)2C=C(NH2)2, also leaving NaNO2 and Na2C2O4 solution. The concentration of NaOH should not be too strong, or further undesired products may form.

Theoretical Synthesis from Trinitroethane :5:

1,1,1-trinitro ethane reacts with KOH to form 1,1-dinitroethylene and KNO2.
Journal Russian Chemical Bulletin
S. S. Novikov1, I. S. Korsakova1 and K. K. Babievskii
N. D. Zelinskii Institute of Organic Chemistry Academy of Sciences USSR, USSR
(they authored several articles about similar compounds)

Dinitroethylene can be expected to react with chlorine gas, to generate 1,1-dinitro,2,2-dichloro ethylene, A condensation with anhydrous ammonia will only give NH4(+) NCC(NO2)=(NO2)(-) not DADNE. Instead, organic amines or even anhydrous hydrazine must be condensed on. For instance, formamide NH2CH(=O) may be condensed on, then oxidized off with bromine, leaving DADNE. First bromine oxidizes off the hydrogen on the formamide condensates, forming (NO2)2C=C(NHC(=O)Cl)2. This then hydrolyzes (with water) to DADNE with CO2 and HCl byproducts. Bromine will not oxidize the amines because they are on an electron withdrawing molecule, the acidity of the solution will also protect them. If hydrazine is condensed on, 1,1-dinitro,2,2-hydrazino ethylene will form. There might also be formation of polymerization products (if not enough hydrazine is present) or even a di-hydrazine salt of 3,6-bis-[dinitromethyl]-1,2,4,5-tetrazine.

It is probably easier to make 1,1,1-trinitroethane than the normal imidazolidinedione precursor. For example, from ethyl nitrolic acid CH3C(=NOH)NO2 reacting with more NO2. A google books "organic chemistry of explosives" claims that the double nitrolate of ethane can be nitrated to hexanitroethane by being treated with concentrated H2SO4 and HNO3 dissolved in CH2Cl2 (92% yield). Obviously this would be unsuitable for ethyl nitrolic acid, since the methyl group would get oxidized, but perhaps using NO2, which is known to form psuedonitrosoles from oximes. There are references on my site about NO2 oxidizing nitroso groups or nitrites. For specifics about ethyl nitrolic acid there is information already posted on this site for ethyl nitrolic acid, or see A. Hantzsch and O. Graul (Ber. 1898, 31, p. 2854), Ethyl nitrolic acid results from nitric acid nitration of acetone.

When heated in the presence of a base, DADNE can hydrolyze to urea and dinitromethane.

Ethers can be prepared by distilling the alcohol and carboxyl- containing acid with fairly concentrated sulfuric acid, although too strong a concentration may further dehydrate the ether.

☺

acetamidine.pdf (112k)

Anders Hoveland, Nov 18, 2010, 6:59 PM

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Comments