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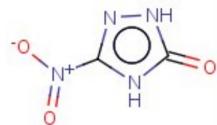
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## NitroTriazoles 1

(this covers the 1,2,4-triazol compounds. information on 1,2,3-triazol is in the "DNTZ" section)

### 3-nitro-1,2,4-triazol-5-oxide



*detonation velocity:* 8510-8590 m/sec    *density:* 1.93 g / cubic cm  
 has a minimum diameter requirement for detonation, somewhat analogous to ammonium nitrate must be kept away from moisture, hydrolyzes with water, analogous to nitrourea unlike HMX, this compound has hydrogen bonds that allow the small molecules to pack closely together This compound is thermally stable. When heated to 120degC for 24 hours, this compound gives off 0.3 cubic cm of decomposition gasses per gram, which is only a third as much as HMX gives off under similar conditions. Rapid decomposition begins at 240 degC. This compound can form salts with ammonia. It is already being used by the USA Airforce as an insensitive explosive.

#### *synthesis:*

Condensation of semicarbazide hydrochloride with a concentrated solution of formic acid (if exactly equal molar ratios were not used, then the excess formic acid can later be distilled off): A mixture of 47 g of semicarbazide and 115 g of 98% formic acid and 200 mL of ethanol is refluxed (heated to 100 degC and stirred) for 1 hour and then the excess of formic acid and the ethanol are distilled off. 58 g of white solid formilsemicarbazide crystallized, with a melting point of 129 degC. This is then dissolved in 150 mL of formic acid and refluxed for 1 hour. The excess of formic acid is distilled off. 25 g of a white solid are obtained which is mostly 1,2,4 triazol-3-oxide. The white solid can then be directly nitrated. 70% nitric acid is gradually added, the mixture is then heated to near boiling, 55-60 degC. The reaction generates even more heat, so the heat source is removed. Brown nitrogen dioxide gas is evolved from the solution. Alternatively, if a regular nitration with concentrated acids is done, it will give the final product in 70% yield. After nitration, the mixture is cooled to 0-10 degC and filtered with water. The product, 3-nitro-1,2,4-triazol-5-oxide, is crystallized, then dried at 70 degC.

#### *Preparation of Semicarbazide*

A mixture of 30 g of 100% Hydrazine Hydrate with 30,1 g of urea is heated at 110 degC for 4 hours. After cooling,100 mL of pure ethanol are added with stirring. After standing for 8 hours, a white solid is filtered off and washed with pure ethanol. This product initially melts at 94 degC; after recrystallization with methanol or ethanol the melting point reaches 96.5C.

#### Theoretical:

5-amino,1,2,4 triazole can be reacted with Ac2O, then anhydrous Cu(NO3)2 added. Then concentrated HNO3 is slowly added to the mixture with rapid stirring. The solution is then diluted with water. The solution is then boiled down, cooled, and crystals precipitated out. These crystals are then treated with just enough hydrazine hydrate to hydrolyze off the three acetyl groups on the molecule, any more could hydrolyze open the ring. This may produce 3-nitro-1,2,4-triazol-5-nitramine, which would be more powerful and possibly stable with respect to hydrolysis.

### 3-amino,5-nitro-1,2,4-triazole

*detonation velocity:* 8450-8460 m/sec  
*detonation pressure:* 314 kbar  
 low sensitivity  
*density:* 1.82 g/cm3.  
*melting point:* between 238.2 - 244 degC

**3-amino,5-nitro-1,2,4-triazole (ANTA)** is lemon-yellow in color. ANTA can form salts if very strong bases are used (sodium ethoxide). A solution of these salts in pure EtOH (the salt would hydrolyze with water) can react with dinitro-paradichlorobenzene in 60% yield to give a compound with an 8.5 km/sec deonation velocity. Aminotriazole (3-AT) is used as a herbicide, and can be nitrated into ANTA. Alternatively dinitrotriazole can be reduced in the procedure below, but this seems like somewhat of a waste of precious hydrazine.

#### *Synthesis:*

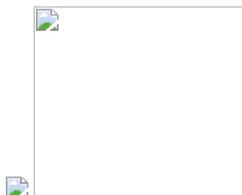
The salt of 3,5-dinitro-1,2,4-triazole can be reduced with hydrazine hydrate into ANTA. Hydroxylamine is also a reactive reducing agent, like hydrazine, and it is likely that the hydrazine and hydroxylamine salts of 3,5-dinitro-1,2,4-triazole do not exist.

29 grams of ammonium dinitrotriazolate (ADNT) is added to 38.5 g hydrazine hydrate. The reaction mixture was stirred for 10 minutes while being warmed to 78-80 °C and left at this temperature about 1.5 hours to fully react. Then the mixture was cooled by adding water to the mixture, and adding 10% solution of HCl (reducing the pH to about 4.0). ANTA, which is precipitated from the mixture separates from the liquid and is dried under vacuum. The amount of ANTA obtained is 19.8 grams, giving 94% yield. Normally, the yield reaches to 96%.

Heating the mixture to 80°C is recommended, because it will greatly accelerate the reaction, which otherwise might be a few days. On the other hand, the temperature must not exceed 80 °C, otherwise there will be decomposition and the yield decreases rapidly. The mixture was cooled by adding water to the mixture, the preferred pH after addition of HCl to the mixture is 4.0.

ANTA separation from solution is possible by filtration or centrifugation. Dilute HCl is recommended for safety, but more concentrated HCl may also be used. After the reaction mixture was cooled to room temperature and acidified by adding enough hydrochloric acid to lower the pH to between 2 and 4. The ANTA then precipitates and is filtered off.

If the product is isolated from the mixture before acidification by HCl, the addition of the acid will cause the ANTA to decompose, and only hydrazine hydrochloride will be obtained. The hydrochloride of ANTA starts to decompose at 100 °C to give off poisonous hydrazine vapor.



3-amino,5-nitro-1,2,4-triazole

4-amino-1,2,4-triazole

### 4-amino-1,2,4-triazole

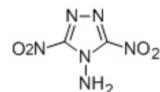
1345g of formic acid, in at least 95% concentration, is added over a half hour into 150g of pure liquid hydrazine hydrate. A distillation is performed on the mixture, which is slowly heated to 165degC, and the distillation continued for three hours. The water is gets distilled out. The reaction mixture is cooled to 80degC and then 1740 g of isopropanol are added.

The heat is kept at 75degC until the solid is completely dissolved, then allowed to slowly cool. The mixture is then cooled to 5degC and the product is filtered out. The crystals are washed with 150 g of cold isopropanol and dried.

This is my idea, the product is probably EXTREMELY powerful (more than HMX), and decently insensitive:

The 4-amino-1,2,4-triazole can be reacted with Ac2O and nitrated. 70-95% nitric acid could then be slowly added to perform a nitration at 0degC, but not too much should be added, and the reaction time should be kept under 3 minutes. Alternatively the solution can be diluted with water, the diacetyl amino triazol filtered out, then redissolved in water and nitrated by bubbling nitrogen dioxide into the solution. (note that NO2 can only be used to effect nitrations on a limited assortment of compounds). The nitrated compound is then crystallized out. Hydrazine hydrate is then added, hydrolyzing off the two acetyl groups on the molecule, but any more could hydrolyze open the ring. The dinitro,diacetyl amino triazole should weigh 258g/mol. Hydrazine hydrate weighs 50g/mol. Exactly two moles of hydrazine should react with one mole of the triazol, therefore exactly 0.3875 grams of pure concentrated liquid hydrazine hydrate should be added for every gram of the solid diacetyl dinitro amino triazol. The solution should now contain hydrazine acetate, water, and the final product, 3,5-dinitro, 5-amino, 1,2,4-triazole. The amine will serve to stabilize the molecule by being electron donating to the nitro groups.

The Ac2O may not be sufficiently protective of the amine group, because the amine is part of a hydrazone group, and as such likely has reactivity analogous with hydrazine. In this case, acetone can be used in conjunction with Ac2O to put both an acetyl, and an isopropylene group (-C(CH3)=CH2) onto the amine. A short cold nitration will not degrade these to groups to a great extent. Afterwards, treatment with ammonium hydroxide will hydrolyze off both groups and leave the amine. There would also be an interesting byproduct of nitroacetones. Normally the initial formation of nitro groups is immediately followed by disproportionation, but in this case, the acetone group would become stuck in the unsaturated tautomer, thus protecting the nitro from disproportionation and resultant oxidization to a carboxyl group. **See the attachment below** for the theoretical reaction diagram. This is an interesting way to protect an amine group, that is on a nitrogen atom, from oxidation, while still being able to easily recover the amine.



CH2O reacts with ammonia salts, the reaction can be written as:  
 (2)CH2O + NH4ClO4 ==> CH3NH2\*HClO4 + HCO2H    the products are methylamine perchlorate and formic acid.

In the attachment below, Diisopropyl ketone would work better than actone (combined with Ac2O), because the resulting group would not be vulnerable to oxidation by NO2.

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Č amino-dinitro-triazinol.bmp (689k)

Anders Hoveland, Oct 24, 2010, 3:44 PM

v.1

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## Comments