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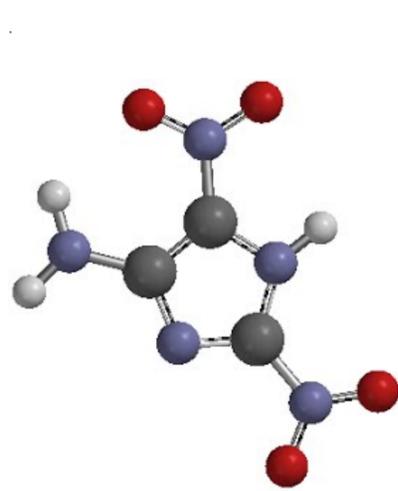
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Imidizoles and Pyrazoles

5-Amino-2,4-Dinitro-1,3-Imidazole, energetic salts of 2,4,5-trinitro-imidizolate



<https://sites.google.com/site/energeticscribble/pyrazoles>

Preparation of 1,4-dinitroimidazole from nitroimidazole:

4-nitroimidazole (8.9 g) is dissolved in 18 mL of glacial acetic acid and the mixture was cooled to 0 deg C. To this mixture, 5 mL nitric acid (98%), which has a density of 1.52 gm/cm³, was added dropwise over a period of 30 minutes, while stirring continuously and keeping the temperature below 5 degC. To this mixture, acetic anhydride (15 mL) was added dropwise while stirring at 0 deg C for 2 hours. The mixture is then stirred at room temperature for another 8 hours. The mixture turns golden-yellow color, then was poured onto crushed ice, stirred and filtered, and finally dried to get 8.5 grams of 1,4-dinitroimidazole, which has a melting point of 92 deg C.

ANTA is lemon-yellow in color and melts at 244 degC. It has a detonation velocity of 8460 m/sec, detonation pressure of 314 kbar, and a density of 1.82 g/cm³.

synthesis for ANTA:

ADNT 29 grams 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.

4-amino-3,5-dinitropyrazole

4-amino-3,5-dinitropyrazole) is calculated as having 90% the power of HMX. 4-Amino-3,5-Dinitro pyrazole has a density of 1.9 g/mL and decomposes at 178degC. The compound is 7.7 times less sensitive to impact than HMX.

Synthesis of 4-Nitropyrazole

Pyrazole 40.0g (587.5mmol) was added gradually into stirred conc. sulfuric acid (96%) 270mL in a 1L flask (with a wide opening) with a cooling bath. 70% nitric acid 40mL was then added dropwise over 10 minutes, generating heat. The bath temperature was raised to 55C. The reaction mixture was stirred at 55C for 7 hours, then cooled to room temperature and poured onto ice (1kg) in a large beaker. The mixture was made basic (pH=8) by addition of concentrated ammonia (more heat generated) and the pH of the obtained hot mixture was adjusted by addition of a solution of HCl (6 Molar concentration) to about pH=3. The mixture was allowed to crystallize at room temperature for 10 hours, the precipitated crude product was collected by filtration and washed with ice-cold water. Cooling to 5 degC overnight produced additional crude product. The combined two fractions of crude nitropyrazole (containing some inorganic byproducts) were recrystallized from water (250mL, left to warm to room temperature for 8 hours, the pure product (46.4g) was collected by filtration, washed with ice water, and dried, leaving white large crystals. Evaporating the liquid left from the filterings, then recrystallizing the residue from 50mL of water, provided additional 4.1g of pure product. The total yield is 75%.

Derivatives of 4-Nitropyrazole

The nitro pyrazole can then be reduced with HCl/Zn, then renitrated to 4-Amino, 3,5-Dinitro pyrazole.

If desired, another group may be stuck on to the 1-position before the HCl/Zn reduction. For example, Bromo-Furazan will react and stick on to the N-atom in the ring, a molecule of HBr being eliminated. For these types of reactions, the Bromo-compound is slowly added in gradual additions, with small additions of CaCO₃ in between that are just enough to neutralize the HBr formed. Iodofurazan could be used instead, in which case the resulting CaI₂ byproduct may be a convenient source of reduced iodine (hydrogen iodide) for other reactions. (1-Bromo-furazan is simply made by reacting a small quantity of Br₂ to excess ethylene-furazan dissolved in a hydrocarbon solvent/kerosene, it is suggested to do the reaction away from sunlight, using incandescent lights (regular filament lightbulb) to avoid a radical initiated reaction).

4-Amino, 3,5-Dinitro pyrazole may also be prepared by aminating 3,5-Dinitro pyrazole with 1,1,1-Trimethylhydrazinium iodide, (which is known for substituting amines in place of a hydrogen on an aromatic ring) and sodium tert-butoxide (NaOC(CH₃)₃). This gave a 70% yield.

Another compound, the nitration product of 1-Guanyl,4-Amino-1,2-diazole can be seen in the second attachment below. This compound is estimated to be between 95-100% as powerful as HMX, as well as being very insensitive. This could enable compositions of HMX that would both be safe for field use, as well as more powerful than conventional compositions. A general ratio would be 60%HMX, and 40% of the compound. Unfortunately, a convenient synthesis for 1-Guanyl,4-Amino-1,2-diazole has not been developed.

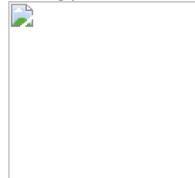
If you would like to pursue this idea, 4-nitropyrazole (diazole) can be prepared by simple nitration of pyrazole, the main reaction will put a nitro on the 4-position (on the central carbon atom not bonded to either of the nitrogen atoms in the ring). (view the third attachment below)

Alternatively, a variation of this would be the nitration product of 3-Guanylamino,1,2-diazole.

For the guanylamino pyrazole, consider sodium cyanamide reacting with the hydrochloride of 3-amino pyrazole. Production of 3-aminopyrazoles by the reaction of a hydrazine with a 2,3-halosubstituted propionitrile or a 2-halosubstituted acrylonitrile.

Synthesis of 3-aminopyrazole

55 g (1.1 moles) of hydrazine hydrate is added to a solution of 285 g (2.06 moles) of K₂CO₃ in 400 ml of water and then 123 g (1 mole) of 2,3-dichloropropionitrile is dripped in at from 10 to 20C while stirring vigorously. The solution becomes yellow and cloudy during the dripping and after a short time crystals of KCl are deposited. The solution is stirred for 5 hours at room temperature, then stirred for 24 hours at 50-60C, then is allowed to cool. The crystals are filtered and washed with ether or ethyl acetate and the filtrate is extracted for 48 hours with ether or for 24 hours with ethyl acetate. The solvent is then distilled off. The crude oil which remains (62 g) is distilled in a high vacuum. 56 g (68% yield) of the pyrazole is obtained, which has a boiling point of 105-108C under reduced pressure (0.025 mmHg). When the distillate is seeded it becomes solid and has a melting point of 36 to 40C.



molecular structure  vial of 3-aminopyrazole

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|  EC230.bmp (845k) | Anders Hoveland, Nov 1, 2010, 10:18 AM | v.1 |  |
|  ImidazoleReaction.bmp (2070k) | Anders Hoveland, Nov 1, 2010, 10:18 AM | v.1 |  |

Comments