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pyrazole

Imidizoles and Pyrazoles

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

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.

Oxidizing ANTA

ANTA can be oxidized using 30% concentrated H₂O₂ with sodium tungstate.

Using this method under alkaline conditions, 3,5-diamino-1,2,4-triazole can be oxidized to 3-amino,5-nitro-1,2,4-triazole, which can be obtained in 60% yield because the reaction rate for further oxidation is slower. The products of further oxidation are 3,5-dinitro-1,2,4-triazole and a lesser quantity of N,N'-azoxy-3,3'-bis[5-amino-1,2,4-triazole]. "*Oxidation of Amino Derivatives of 1,2,4-Triazole*" T.P. Kofman, E.A. Paketina. *St. Petersburg State Technological Institute, Russia* (1997)

Alternatively, sodium perborate can be used as the oxidizer.

"*Oxidation of 3-Amino-1,2,4-triazoles to 3-Nitro-1,2,4-triazoles with Sodium Perborate*"

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Oxidation of ANTA with "Oxone" might form N,N'-azoxy-3,3'-bis[5-nitro-1,2,4-triazole], with the structure (O₂N)(C₂N₃H)N=N(-->O)(C₂N₃H)(NO₂), or even possibly oxidize one of the triazole rings further to add one more oxygen atom to the molecule.

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

bulk density: 1.11g/cm³

solubility in water at 20degC: 0.52% by weight

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%.

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

Kommentare