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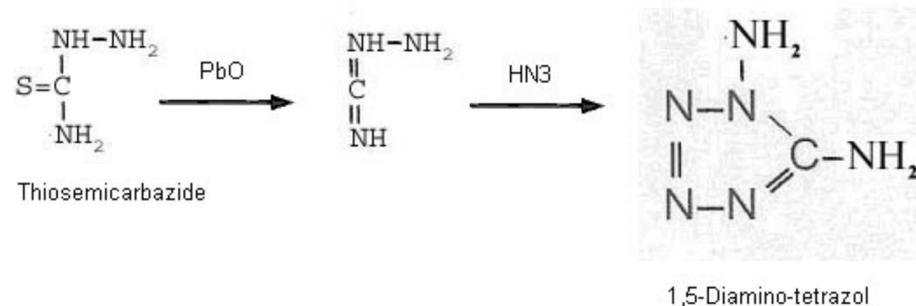
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Diamino Tetrazole



The reaction is conducted in pure ethanol, in a CO₂ atmosphere. 45% yield.

Synthesis #1

18g (0.2 mol) thiosemicarbazide, 16.3g (0.25 mol) sodium azide, 13.4g (0.25 mol) NH₄Cl and 89.2g (0.4) PbO are mixed in 350 ml of dimethylformamide on boiling water bath for 6 hours. Mixture is filtered hot, and filtrate is evaporated to dryness in vacuum. Residue is dissolved in 50 ml of hot water, filtered hot and slowly cooled. Precipitate is filtered, washed with cold water and dried. Yield is 11.8g (59%), white crystals, melting point 186-187C with decomposition (from water). Lead Azide is also a byproduct in the above.

Synthesis #2:

Preparation of 1,5-diamino tetrazole:

55 ml of an aqueous solution containing 4.5 g of diamino guanidinium chloride and 1.5 mL of concentrated HCl are prepared. This should be done under a fume hood and the reaction should be done behind a protective iron plate. Diazotisation with sodium nitrite is carried out at 2 to 4°C using an inert gas. 20 ml of nitrite solution containing 2.5 g of NaNO₃ are added dropwise with strict observation of the required temperature. After 45 minutes, the pH value of the reaction mixture is adjusted to 8.0 to 8.2 with Na₂CO₃ and stirred slowly at 45°C for 25 minutes, still under nitrogen. After that, nitrogen is passed over and a vacuum is used to pull concentrate the solution until dry (keep a safe distance!). After cooling, repeated extraction with a little ethyl alcohol at 60°C and recrystallization from water as before is carried out. mp 185°C (low yield). The pH must be within a narrow range to avoid formation of even more sensitive azide-compounds.

There are some interesting energetic salt possibilities with this compound, since it can serve as a base. Nitroformate and dinitramide salts are possible, as well as formation of an adduct with NitroTetrazole.

Hydrazine is reacted with the hydrogen cyanide and sulfur, preferably (but not necessarily) in an organic solvent, forming hydrazine thiocyanate. Conversion of hydrazine thiocyanate to thiosemicarbazide takes place at a temperature of about 90°, not exceeding 130° C. **The reactants and product give off extremely poisonous vapor.** Carbon disulfide reacts with ammonium hydroxide to form ammonium thiocyanate, without heating.

From Ammonium Thiocyanate and Hydrazine Sulfate:

This reaction must be conducted under a fume hood because hydrogen sulfide is produced during the refluxing. 36.7 g of hydrazine sulfate was added to 30 ml of water in a 250ml flask. The pH of the solution was brought to 4 with sodium hydroxide solution. The hydrazine sulfate soon dissolves, with the intermediate formation of hydrazinium hydrogen sulfate. 30g of ammonium thiocyanate was added and the mixture was gently agitated in a warm water bath until the thiocyanate dissolved. 60 ml of methanol was added and the mixture was stirred for a half hour to finish the precipitation of ammonium sulfate. The solution was filtered and the ammonium sulfate was washed with 92% ethanol. The combined liquid was then transferred to a 500 ml round bottomed flask. A stir bar was added and 1 ml of acetone was added. A reflux condenser was attached and the mixture was refluxed for 18 hours. The solution turns to a yellow color during refluxing and produces hydrogen sulfide; after 9 hours another 1 mL of acetone was added. After 16 hours the mixture was filtered to remove a small quantity of crystals. After 24 hours of settling, a large crop of crystals formed which was then filtered off and washed with methanol. The white crystals melted at 181 degC. 75% Yield.

Diamino Tetrazole is soluble in hot water, water-ethanol mixtures, acids, and dimethylformamide. Moderately soluble in cold water and ethanol. Insoluble in tetrahydrofuran, ethylacetate, methylene chloride.

Both the perchlorate and dinitramide salts of DiaminoTetrazole have melting points "well below 100degC, yet have high decomposition onsets".

As a sidenote, 1,5-diamino tetrazole will react with a solution of HCl and NaNO₂ (30minutes at 0degC) to form another double-ringed compound (formula CN₇H) in a 55% yield.

From Diaminoguanidine

The reaction of nitrous acid with diaminoguanidine can either lead to diaminotetrazole as the product in 58% yield by a 1:1 molar ratio in a mineral acid (HCl) as reported by the attached article. Alternately when the reaction uses a molar ratio of 2:1 and a buffered pH as described in the Lieber and Levering article attached previously, a 77% yield of Tetrazolyl Azide is reported.

A solution of diaminoguanidinium chloride (1.5g in 20mL water and 0.5mL hydrochloric acid (37%) was cooled to 0degC (some of the solid precipitated out). Keeping the temperature between 0-2degC, a solution of sodium nitrite (0.83g in 5mL water) was slowly added. The reaction was allowed to stand in ice water for 30 minutes. The pH was then raised to a value of 8, using sodium carbonate. The reaction was stirred for 20 minutes at 40degC, then evaporated to dryness under reduced pressure, with nitrogen gas used to displace air. The remaining crude product was extracted with three separate portions of hot pure ethanol (15mL portion each). This left the final product, 1,5-diamino-tetrazole after evaporation.

Comments