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tetrazole

5-DinitroMethylTetrazole

Although the synthesis of ethyl 5-tetrazolyldinitroacetate has not been reported, ethyl 5-tetrazolynitroacetate (**4a**) was prepared from ethyl 5-tetrazolylacetate (**6a**). Compound **4a** could be converted to dinitro **2a** by the oxidative nitration which was employed in the synthesis of 1,3,3-trinitroazetidine. By the known method of a dinitro group from an oxime group, ethyl 5-tetrazolyldinitroacetate could be prepared by the reaction of ethyl 5-tetrazolylacetate oxime with a mixture of nitric acid and sulfuric acid (mixed acids). Two nitro groups were directly introduced at the methylene position in the treatment of methyl cyanoacetate with mixed acids to give nitrile in 36% yield, the reaction being much lower yield with increasing size of the alkyl group. The reaction of commercially available ethyl 5-tetrazolylacetate (**6a**) with mixed acids and produces ethyl 5-tetrazolyldinitroacetate (**2a**) in high yield.

When ethyl 5-tetrazolyldinitroacetate (**2a**) was treated with water, 5-dinitromethyltetrazole (**1**) was readily given. Hydrolysis followed by decarboxylation was taken place completely within 2 hours at 50 degC. Only mono ammonium salt **9** was produced on reaction of ammonia. 5-Dinitromethyltetrazole is also produced by acidifying the Dinitromethyltetrazolate salt. (*Synthesis and Characterization of 5-Dinitromethyltetrazole*)

5-nitrotetrazole-2N-oxide

12.5g of the sodium salt of 5-nitrotetrazole is dissolved in 50mL water, then reacted with 45g of potassium peroxy-monosulfate ("Oxone") and 20g of potassium acetate, which acts as a buffer. The solution is stirred for 24 hours at 50 degC. A solution containing 0.09 moles of tertiary amine sulfate, such as Et3NH(+), Na(+), SO4(-2), dissolved in 200mL of water, is added. Then the 5-nitro tetrazole-2N-oxide is extracted using 300mL of ethyl acetate. The yellow product moves into the ethyl acetate layer. The 5-nitro tetrazole-2N-oxide product may be purified by crystallization from EtOAc or toluene, resulting in thin yellow crystals. The yield is 70%.

The calculated density for the hydroxylamine salt of 5-nitro tetrazole-2N-oxide is 1.87 g/cm3. The salt has a formula of CN6O4H4. Several salts of the nitrotetrazole oxide anion decomposed at between 153 and 211 degC.

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 guadininium 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 stirr 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 hte 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 ant 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.

Kommentare

Sie sind nicht berechtigt, Kommentare hinzuzufügen.