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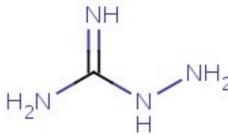
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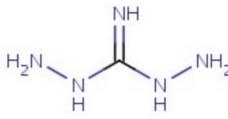
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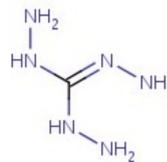
Amino Guanidine



aminoguanidine



diaminoguanidine



triaminoguanidine

Aminoguanidine (carbonate)

Synthesis: Two hundred and sixteen grams (2.07 moles) of nitroguanidine and 740 g. (11.3 moles) of purified zinc dust (Note 1) are thoroughly ground together in a mortar, and then enough water (about 400 mL.) is added with stirring with the pestle to form a thick paste. The paste is transferred to a 3-l. enameled can or beaker surrounded by an ice bath. A solution of 128 g. (2.14 moles) of glacial acetic acid in 130 ml. of water is cooled to 5° in another 3-l. beaker, which is fitted with a strong mechanical stirrer and surrounded by an ice bath. The paste of nitroguanidine and zinc dust, cooled to 5°, is added slowly with mechanical stirring, the temperature of the reaction mixture being kept between 5° and 15°. A total of about 1 kg. of cracked ice is added to the mixture from time to time as the mixture becomes too warm or too thick to stir. The addition of the paste is done over the time of about 6 hours, and the final volume of the mixture is about 1.5 L. (Note 2).

The mixture is then slowly warmed to 40degC on a water bath with continued stirring, and this temperature is maintained for 2–5 minutes, until reduction is complete (Note 3). The solution is immediately separated from the insoluble material by filtration on a large Büchner funnel, and the cake is sucked as dry as possible. The residue is transferred to the 3-L. beaker, washed well with 1 L of water, and then separated from the liquid by filtration. In the same manner, the residue is washed twice more with two 600-ml. portions of water. The filtrates are combined and placed in a 5-l. round-bottomed flask. Two hundred grams of ammonium chloride is added, and the solution stirred until they fully dissolve. The ammonium chloride prevents the coprecipitation of zinc salts when sodium bicarbonate is added to the solution to precipitate the aminoguanidine as the bicarbonate. If the solution is not clear at this step, it should be filtered.

The stirring is continued, and 220 g. (2.62 moles) of sodium bicarbonate is added during a period of about 10 minutes. The aminoguanidine bicarbonate begins to precipitate after a few minutes, and the solution is then placed in a refrigerator overnight. The precipitate is collected by filtration on a Büchner funnel. The cake is removed to a 1-l. beaker and mixed with a 400-ml. portion of a 5% solution of ammonium chloride and filtered. It is again washed with two 400-ml. portions of distilled water, the wash solution being removed each time by filtration. Finally the solid is pressed down on the Büchner funnel; the mat is broken up with a spatula and washed while on the funnel with two 400-mL portions of 95% ethanol and then with one 400-ml. portion of ether. After air drying, the aminoguanidine bicarbonate amounts to 180 g. (64% yield) of white solid, melting at 172° with decomposition. It should not be recrystallized from hot water, since decomposition will occur. The aminoguanidine bicarbonate thus prepared is pure enough for most purposes.

1. The zinc is purified by stirring 1.2 kg. of zinc powder with 3-L. of 2% hydrochloric acid for 1 minute.

The acid is removed by filtration, and the zinc is washed in a 4-L beaker with one 3-L. portion of 2% hydrochloric acid, three 3-L. portions of distilled water, two 2-L. portions of 95% ethanol, and finally with one 2-L. portion of absolute ether, the wash solutions being removed each time by filtration. Then the material is thoroughly dried and any lumps are broken up in a mortar.

2. The solution becomes basic to litmus after one-half to three-fourths of the paste has been added. Lower yields are obtained if a larger excess of acetic acid is employed.

3. The state of reduction can be determined by placing 3 drops of the reaction mixture in a test tube containing 5 ml. of a 10% solution of sodium hydroxide and then adding 5 ml. of a freshly prepared saturated solution of ferrous ammonium sulfate. A red coloration indicates incomplete reduction; when the reduction is complete, only a greenish precipitate is observed. The mixture should not be heated after this test shows that reduction is complete.

Methyl Trihydazinone

(Triamino Guanidine)

A solution of 74.5 parts by weight of guanidine nitrate in 400 parts by weight of 37.5% aqueous hydrazine, with 12 parts by weight of ammonium nitrate added, was heated for one hour at 82°C to 102°C to expel the ammonia formed by the reaction. The triaminoguanidine nitrate crystallized in 68% yield on cooling to 10°C. Repeating with 24 parts by weight of ammonium nitrate increased the yield of triaminoguanidine nitrate to 75%. Using 48 parts by weight of ammonium nitrate, increased the yield to 83%.

A solution of 73.5 parts by weight of guanidine nitrate in a mixture of 230 parts by weight of 65% hydrazine, 125 parts by weight of water, and 55 parts by weight of 70% nitric acid was heated for one hour at 80°C to 103°C. Triaminoguanidine nitrate crystallized in 80% yield on cooling to 10°C.

A solution of 73.5 parts by weight of guanidine nitrate in 215 parts by weight of 70% aqueous hydrazine in 180 parts by weight of water with 48 parts by weight of hydrazine nitrate added, was heated for one hour at 80°C to 104°C. Thereafter, upon cooling to 10°C, TAGN crystallized in 80% yield. Inventor: Haury, Vernon E. (Simi Valley, CA)

1. reacting guanidine nitrate with from 1 to 2 moles of hydrazine per mole of guanidine nitrate in alcohol to produce a solution of monoaminoguanidine nitrate, diaminoguanidine nitrate, or mixtures there of in alcohol;

2. filtering the alcohol solution to remove alcohol insoluble solid impurities;

3. adding additional hydrazine to bring the total amount of hydrazine added to 3 or slightly more moles per mole of guanidine nitrate used;

4. adjusting the pH of the alcohol solution to from 4.5 to 5.5 by adding nitric acid; and

5. isolating the product triaminoguanidine nitrate.

Guanidine nitrate is only slightly soluble and the final product, triaminoguanidine (TAGN) nitrate, is insoluble in alcohol. However, the intermediates monoaminoguanidine nitrate (MAGN) and diaminoguanidine nitrate (DAGN) are soluble in alcohols.

Use only enough hydrazine to convert the guanidine nitrate to monoaminoguanidine nitrate or diaminoguanidine nitrate. Between 1 to 2 moles of hydrazine are added for each mole of guanidine nitrate.

Next, the solid impurities are filtered out from the solution.

Finally, more hydrazine is added to convert the monoaminoguanidine and diaminoguanidine nitrates to the final product, triaminoguanidine nitrate. Enough hydrazine is added to bring the total molar ratio of hydrazine to guanidine nitrate to 3:1 or slightly more. 40-70% Nitric acid is added to adjust the pH of the reaction mixture to 4.5 - 5.5, or preferably about 5.

Purer TAGN was achieved by crystallizing the triaminoeuanidine nitrate, first at room temperature (20degC) then with cooling (5degC). Ethanol, or Isopropyl Alcohol may be used, although 1-Propanol is preferable.

122 grams (1 mole) of guanidine nitrate and 200 grams of solvent were initially added to the flask, the mixture was agitated and then 150 grams of 64% hydrazine in water was added. The addition of the nitric acid improved the reaction yield from 63 to 69%. Unlike water as a solvent, alcohol gave a higher product yield of 95%, as compared to 57 to 69 with water.

One of the reasons for the crystallization is that the nitrate of triaminoguanidine is much less soluble in ethanol than guanidine nitrate. This may be because there are three nitrate anions associated with each TAG cation, and thus the compound has stronger intermolecular ionic forces.

Triaminoguanidine Dinitramide

Triaminoguanidine dinitramide was prepared from triaminoguanidine perchlorate and potassium dinitramide, with an 82% recovery of the product. It is very sensitive, with an impact sensitivity of 2J, and a friction sensitivity of 24N.

DiaminoGuanidine

Nitroguanidine reacts with one equivalent of hydrazine hydrate to form nitaminoguanidine.

R. Henry, R. Makosky, G. Smith, Journal American Chem. Society, 1951, Issue #73, p474.

Nitraminoguanidine (NH2NHC(=NH)NHNO2) reacts with HCl and NaNO2 to make Nitro guanylazide in 75% yield, while reduction of nitraminoguanidine with Zn powder affords diaminoguanidine.

"Nitroaminoguanidine, NH2NHC(=NH)NHNO2, on diazotization yields nitroguanidine and nitroguanyl-azide which may be isomerized to 5-nitramine-tetrazole. Nitroguanyl azide acts as a dibasic acid when titrated with alkalis, as it is quantitatively isomerized to the dibasic nitramine-tetrazole."

Nitroguanyl-azide has the structure [-]N=N[+]=NC(=NH)NHNO2. "Nitramine-tetrazole" refers to a compound with the structure (N4H2C)=NNO2. Note that "nitramines" of tetrazoles actually exist as a more stable tautomer which incorporates nitrimino groups instead of real nitramine groups, with two hydrogens attached to nitrogen atoms in the ring.

The amino guanidines can be used as precursors for many other cyclic tetrazoles.

Tetrazole-Triazole Salts

"The nitrogen-rich energetic material 3,4,5-triamino-1-tetrazolyl-1,2,4-triazole (TATT) was synthesized from diaminoguanidine using a straightforward method. The assumption that a 1,2,4-triazole ring is an intermediate in the one-pot reaction is supported by the synthesis of TATT from an analogous reaction of 3,4,5-triamino-1,2,4-triazole with cyanogen azide. TATT·HNO₃ crystallizes in the monoclinic system. TATT has excellent thermal stability which resembles triaminotritrobenzene (TATB), but with a higher positive heat of formation and greater impact insensitivity.

"A thermally stable nitrogen-rich energetic material—3,4,5-triamino-1-tetrazolyl-1,2,4-triazole (TATT)"

Guo-Hong Tao, Brendan Twamley and Jean'ne M. Shreeve; J. Mater. Chem., 2009, 19,



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