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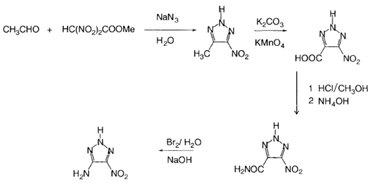
DNTZ

DinitroTriazole

This is a very energetic compound with a simple structure, a triazine ring with two nitro groups on it.

Note that LLM-116 (4-amino-3,5-dinitropyrazole) is stated to be calculated as having 90% the power of HMX. Comparing this with the molecular structure of DNTZ, LLM-116 has an additional carbon and one less nitrogen atom, while otherwise having a very similar structure. This indicates that DNTZ is likely as, or a little more powerful than HMX, and possibly more stable, since the nitrogens will serve as an electron donor through the aromatic ring.



Synthesis of ANTZ synthesized 4-amino-5-nitro-1,2,3-triazole (**ANTZ**) following a procedure described by Shevelev and coworkers. The synthesis involved the condensation of acetaldehyde with ethyl-2,2-dinitroacetate in the presence of NaN_3 to yield 3-methyl-5-nitro-1,2,3-triazole. This was oxidized to 3-carboxy-5-nitro-1,2,3-triazole which was converted by standard chemistry to ANTZ . ANTZ has a decomposition point of 297 °C, showing better thermal stability than 5-amino-3-nitro-1,2,4-triazole (**ANTA**).

First Part of the Synthesis

4-amino, 5-nitro, 1,2,3-triazole was synthesized by condensing acetaldehyse with ethyl 2,2-dinitro-acetate in the presence of sodium azide, to form 4-methyl, 5-nitro- 1,2,3-triazole. (the paper made a mistake and states it as "3-methyl-")

The cyclization reaction with the azide ion is very comlex. To get some idea of the intermediate steps, see the attachment at the bottom of the page. For step #3, a nitrous acid is pulled out under the alkaline conditions, leaving a double bond between carbons. (cyclize is the American spelling)

CH3CH=O (NO2)2CHC(=O)OCH2CH3. I think that (NO2)2CHC(=O)O(-) converts to (-)NO2=C(NO2)H and CO2. The (-)NO2=C(NO2)H would then condense with CH3CH=O, in a Michael-type addition, and the aldehyde would disproportionate, being reduced while oxidizing another free CH3CH=O under the alakine conditions. Then an azide ion would displace one of the nitro groups. So now the intermediate is CH3CH*C(=NO2)-)(-N=N=N). Where the * signifies a radical. This then spontaneously cyclizes, the electron moves toward a nitrogen in the ring, and then a hydrogen ion stick on. This is all just my own conjecture. So the methyl group on the resulting ring almost certainly comes from the methyl on the acetaldehyde. The carboxyl groups comes off as CO2. The original ester gets hydrolyzed by the NaN3, and in so doing acts as a dehydrating agent.

A simpler reaction might be able to utilize 1-nitro-acetone reacting with NaN3. This could potentially directly cyclize into 4- methyl, 5-nitro, 1,2,3-triazole. To help understand the cyclization, Nitroacetone can be thought of as having a CH3C(OH)=C=NO2H tautomer. See the section "nitroalkanes" for an easy synthesis for nitroacetone.

Now with the 3-methyl, 5-nitro, 1,2,3-triazole, the methyl group is oxidized to a carboxyl group (with permanganate, and using sodium carbonate). The triazol, because of the electron withdrawing nitro group) is actually fairly resistant to any oxidation, that NH group in the ring is not going to be oxidized by conc HNO3 during a short nitration. An ester of the carboxyl group is formed, addition of NH4OH gives a carboxy amide --C(=O)NH2 , and then bromine and NaOH oxidize this into an amine, which surprisingly does not get further oxidized, presumably because of the electron withdrawing nitro.

A carboxy-amine can get oxidized into an a plain amine, through a a Hofmann reaction with ordinary hypochlorite solution. It is known that acetamide CH3C(=O)NH2 reacts with hypochlorite to give off methylamine CH3NH2 gas. Obviously the methylamine escapes as soon as it is formed before it can be further oxidized (since it would be more vulnerable to oxidation than the initial acetamide. In the reaction the CH3C(=O)N** initially gets formed. This rearranges into an isocyanate CH3N=C=O, which hydrolyzes with H2O, giving off CO2, and leaving CH3NH2.
For more information about the Hoffman reaction,
http://users.ox.ac.uk/~mwalter/web_05/resources/name_reactions/hofmann.shtml

4-Amino,5-Nitro-1,2,3-Triazole (ANTZ) has a decomposition of 297degC, which is more thermally stable than 5-amino,3-nitro, 1,2,4-triazole.

Oxidation of ANTZ to DNTZ

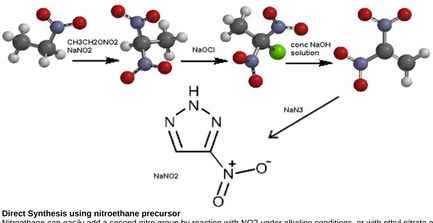
ANTZ was then oxidized by 30% H2O2 and concentrated H2SO4 to yield 2,5-dinitro-1,2,3 triazole (DNTZ), which was isolated as the potassium salt by treatment with KOH in Ethanol.

Direct Nitration of Triazole
Nitation of 2-methyl-1,2,3-triazole with concentrated H2SO4 and nitric acids at 20 degC, first added one nitro group. Further nitration at 100 degC added the second nitro group (2N-methyl-4,5-dinitro-1,2,3-triazole).
Another souce mentions that, with the methyl group replaced by a phenyl group, an initial nitration was performed at 5deg, adding one nitro group to the triazole ring, then further nitration at 40 degC not only added a second nitro group, but also formed the 1-N-oxide on the ring.

It may be expected that NO2 could react with methyl triazole to put a nitro on the methyl group, in a similar reaction to that on toluene, since the aromatic ring should activate the methyl group to nitration. (normally it is the other way around, with the methyl group on toluene activating the benzene ring to easy nitration). See the "polytetranitrostyrene" section for more information.

"The inertness of the carbon atoms in a 1,2,3-triazole ring toward nitration is due to distribution of the electron density away from the carbon atoms, which carry a partial positive charge, preventing addition of a nitronium cation. Direct nitration of the unsubstituted 1,2,3-triazole ring, has not ever been observed, at least with nitronium ions (one such alternate method is described on this page). However, as described on this page, a nitration is possible if there is a methyl or phenyl group on a nitrogen atom in the 2-position, or if there is a previous nitro group on a carbon atom. A phenyl group on a nitrogen atom bonded to a carbon (in the 1- or 3- positions), however, will not activiate the 1,2,3-triazine ring for nitration..

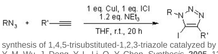
Attempts at nitration of 4-phenyl-1,2,3-triazole only added nitro groups to the phenyl ring, even under rigorous nitration conditions. Nitration of 2-phenyl-1,2,3-triazole first introduces a nitro group onto the para- position on the phenyl ring, then adds a nitro group onto the 4- position of the triazole ring. It is likely that the aromatic phenyl ring facilitates removal of an electron from the triazole ring, leaving a radical that the resultant nitrogen dioxide can then bond to.



Direct Synthesis using nitroethane precursor
Nitroethane can easily add a second nitro group by reaction with NO2 under alkaline conditions, or with ethyl nitrate ester in the presence of nitrite ions. 1,1-dinitroethane can then either react with chlorine or bromine, again under alkaline conditions, to add the halogen onto the 1-position. A strong solution of base can then pull out the hydrogen bromide, leaving 1,1-dinitroethane. This would then likely condense with sodium azide in a Michael-type addition (using NaOH catalyst), resulting in sodium nitrite and 4-nitro-1,2,3-triazole. This could then be nitrated to 4,5-dinitro-1,2,3-triazole. The NH group in the triazole ring is not vulnerable.

Unusual Isomer of DNTZ
Reaction of 4-Nitrotriazole with NO2BF4 and AcONO2, using acetonitrile (0degC) or methylene chloride (20degC) solvents,
produced 1N,4-dinitrotriazole, where one of the nitro groups is on a nitrogen atom. This also formed another byproduct, with the second nitro group in the 2-position, which could not be isolated (thermally unstable).

Alternate Preparation of Triazole
Reaction of 1-Nitro propylene CH3CH=CHNO2 with NaN3 led to 4-methyl-triazole. The 1-Nitro propylene could be prepared from 1-nitropropane reacting with NO2 under alkaline conditions, forming 1,1-dinitropropane, then reaction with a highly concentrated NaOH to form 1-nitropropylene and NaNO2.



synthesis of 1,4,5-trisubstituted-1,2,3-triazole catalyzed by copper(I) iodide
Y.-M. Wu, J. Deng, Y. L. Li, Q.-Y. Chen, *Synthesis*, **2005**, 1314-1318.

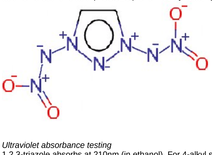
CuI results from simple mixture of Cu(+2) and iodide ions, which forms a CuI insoluble precipitate and elemental iodine. The iodo-triazole can then be condensed with NH3 to substitute the iodine group with an amine (--NH2) group.

Alternatively CaC2 and an organic azide can be used, in which case a CuI catalyst and sodium ascorbate (vitamin C) is used, a solvent consisting of two molar equivalents of CH3CN, and one equivalent of water was used. This then forms a plain triazole, with only one sidegroup on the nitrogen atom in the 1-position.

1-Monosubstituted 1,2,3-triazoles have been prepared by a reaction of azides with vinyl acetate under microwave irradiation.
S. G. Hansen, H. H. Jensen, *Synlett*, **2009**, 3275-3278.

Since plain 1,2,3-tetrazole cannot be directly nitrated, there must be a phenyl group on one of the nitrogen atoms. Bromobenzene can condense with the triazole, or dinitrochlorobenzene can be used. If plain bromobenzene was used, the nitration will first add a nitro group in the para position (at the opposite end) of the benzene ring, with the sunsequent nitro group being added to the triazole ring (on one of the two carbon atoms). Further nitration will add more nitro groups to the benzene ring. The resultant trinitrophenyl group (the benzene ring with three nitro groups) can be hydrolyzed off the triazole using with water (without heating), resulting in a picric acid byproduct and the desied nitrotriazole.

Nitroimino (=N--NO2) groups added to the nitrogen atoms in the ring
Treatment of 1,2,3-Triazole with BaO, Ba(NO3)2, and hydroxylamine-O-sulfonic acid HOSO2--ONH2, makes an 1N,3N-di-nitroimino triazole anion, (C2H2N7O4)(-), where a continuous chain of seven nitrogen atoms exist, both hydrogens being bonded to the carbon atoms. NH_2OH reacts with chlorosulfuric acid to give hydroxylamine-O-sulfonic acid. Chlorosulfuric acid (HOSO2Cl) is formed by reacting anhydrous HCl with SO3.



Ultraviolet absorbance testing
1,2,3-triazole absorbs at 210nm (in ethanol). For 4-alkyl substituted derivitives of triazole, this is shifted to 216nm. 4-amino-1,2,3-triazole (with the amino group on a carbon atom in the ring) absorbs at 239nm. 2-phenyl triazole absorbs at 262nm.

1,2,3-Triazole ideas

Apparently nitroacetone can be used to make nitrogenous rings, supporting my idea that nitroacetone should be able to condense with sodium azide to form
4-methyl,5-nitro-1,2,3-triazole.

"One-pot synthesis of 5-nitropyridines by the cyclocondensation of nitroacetone, triethyl orthoformate and enamine"
Galina P. Sagitullina, Anna K. Garkushenko, Evgeny G. Atavin, and Reva S. Sagitullin
Department of Organic Chemistry, F. M. Dostoevsky Omsk State University, 644077 Omsk, Russian Federation

Could one perhaps condense CH2O and excess nitromethane (using the nitroaldol condensation reaction, simply heat with NaOH) to make nitroethanol (which is poisonous and easily absorbs through skin)? Then oxidize nitroethanol with a selective oxidizer such as 2-Iodoxybenzoic acid (no water can be present or the nitro group will disproportionate off from the acidity in a Meyer reaction) or pyridinium chlorochromate. This would then form 2-nitroacetaldehyde O2NCH2CH=O. This could then potentially cyclize with sodium azide to form plain 4-nitro-1,2,3-triazole, without the methyl group that would have resulted if nitroacetone had been used. Possibly heating in concentrated nitric acid (100degC) could simultaneously oxidize the methyl group to a carboxyl, then *decarboxylate* the molecule, and finally add a nitro group in. While plain 1,2,3-triazole cannot be directly nitrated, 4-nitro-1,2,3-triazole is more susceptible.

At least for benzoic acid, decarboxylation proceeds readily by heating (only 100degC) if there is another electron withdrawing group (such as a chlorine atom) on the ring. (this would result in chlorobenzene and carbon dioxide).

Some information about 2-Iodoxybenzoic acid: it can oxidize methanol to formaldehyde in 94% yield, and can similarly oxidize ethylene glycol (vehicle anti-freeze) to glyoxal. However, dimethyl sulfoxide (DMSO) can not be used as a solvent for the latter, as its presscence will cause the ethylene glycol to be oxidized to formaldehyde instead. The 2-Iodoxybenzoic acid can then be re-oxidized and recycled after completion of the reaction.
2-Iodoxybenzoic acid can be prepared by the slow addition, over a half hour, of potassium bromate (76.0 g, 0.45 mol) to a vigorously stirred sulfuric acid mixture (0.73 M, 730 mL) containing 2-iodobenzoic acid (85.2 g, 0.34 mol).

Here is the nitroaldol condensation procedure between nitroethane and CH2O. A lesser ammount of nitromethane could very easily substitute for the nitroethane:
75.1g Nitroethane, 0.3g calcium hydroxide and 80g 40% formaldehyde solution was dissolved in 75ml ethanol with stirring and was allowed to stand for 48h at room temperature. Distillation at 100-105°C/13 mmHg (85-86°C/6 mmHg, 99°C/10 mmHg) gave 48g 2-nitropropanol (46%) and 14.3g of 2-nitro-2-methyl- 1,3-propanediol, the latter remained as a crystalline residue in the distillation flask after distillation of the 2-nitropropanol.