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 Under Construction-1  
 Under Construction-2  
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 Compositions  
 Less Energetic Basic Compounds  
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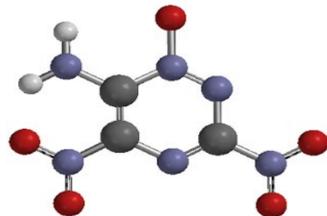
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## Triazines

### 6-amino-3,5-dinitro-1,2,4-triazine-1-oxide



This synthesis was designed by this site, and the resulting compound is designated (by this site) "**EC-401**"

see the attachment below, fairly self-explanatory the heating should probably be done in a pressure cooker or distillation apparatus, boiling off the more volatile triazine, which could be collected. The hydrazine could be condensed (using anhydrous KOH) with the formamide before the reaction, forming an "amidrazone" with a structure HC(=NH)NHNH2. This would be more trouble, but might possibly improve yields.

The reduction (with Fe+2) is analogous to synthesis of picramic acid, the nitro site is specific, because this is the only site where the amine can be directly electron donating to the other two nitro groups. This would produce 6-amino-3,5-dinitro-1,2,4-triazine, which could then be oxidized, analogous to oxidation of 2,6-diamino-3,5-dinitro-1,4-pyrazine in the last step of the LLM-105 synthesis (not on this site). The resulting compound would be more powerful than LLM-116 or LLM-105 (2,6-diamino-3,5-dinitro-1,4-pyrazine-1-oxide).

There are two other routes that could substitute for the final oxidation, so trifluoroacetic acid is NOT necessarily required. A catalyst can be used to allow the H2O2 to oxidize the heterocyclic nitrogen. Selective mono *N*-oxidation of substituted pyrazines in good yields using 30% dilute H<sub>2</sub>O<sub>2</sub> as an oxidant with a specially prepared titanium silicate catalyst is possible. Or methyl cyanide can activate the H2O2 so that it can oxidize the cyclic nitrogen atom.

#### Preparation of the Catalyst

Add a solution of titanium peroxide to ethyl silicate (with or without an organic solvent) to obtain a gel. Hydrolyze the homogeneous gel previously obtained, by adding an organic base to the gel. The amount of organic base should be only 6-15% of the amount of silica gel. Next, add deionised water after the yellowish-white color of the gel begins to turn into a greenish-white color. Stir the greenish-white gel for about 1 hour, then heat the gel in a pressure cooker at 100 -110 C. The gel must be constantly heated in this way for at least 20 hours. Further heating, up to 2 days, is preferable. This will result in a solid composite product. Separate out the resultant solid composite material, dry, and bake at a 350-500C temperature to obtain the final product. This is a catalyst and so only a small quantity need be prepared. The organic base should be an organic amine with lots of bulky organic groups on it, either a tri- or tetra-alkyl amine, such as tetrapropyl ammonium hydroxide. Alternatively positively charged coated silica particles can be used instead of the ethyl silicate. These can be prepared by mixing an aqueous colloidal silica with stabilized basic aluminum acetate. The aluminum composition is stabilized with a small quantity of boric acid, which controls the hydrolysis of the aqueous solution of basic aluminum acetate.

The catalyst produced above is known as TS-1 and is basically a porous titanium silicate crystal with a structure analogous to *zeolite*. TS-1 is not yet commercially available. It can also catalyze the oxidation by H2O2 of imines R2C=NH into oximes R2C=NOH.

#### Methyl Cyanide Activation

At a pH of 8 , H2O2 reacts with CH3CN to form a peroxy-carboximidic acid intermediate CH3C(=NH)O--OH. This is unstable and immediately oxidizes whatever reducing agent is in solution. If no reducing agent is present, acetamide will result and oxygen gas will escape from solution. Other nitriles beside methylcyanide also will work, possibly even addition of threads of acrylic fabric (synthetic wool) will work. An alkaline solution of a nitrile and H2O2 can also oxidize an alkene to an epoxide. I am not entirely sure that the amine will not be vulnerable however. The trifluoroacetic acid and H2O2 route are known to create an N-oxide while leaving the amine on the electron deficient (because of two nitro groups) ring unoxidized, but the strong acidity might be important in protecting the amine group. The fact that the ring is electron deficient makes the amine less vulnerable to oxidation, but I am unsure if this is enough without strongly acidic conditions. The methyl cyanide activation necessitates alkaline conditions.

In some situations amine groups must be protected. One such method, designed by this site, is addition of pure acetone, followed by addition of acetic anhydride. This will put both an acetyl and an isopropylene (-C(CH3)=CH2) group on the amine, and the isopropylene will inevitably be oxidized to an epoxide, wasting nitrile and H2O2. These groups will hydrolyze off after the oxidation by addition of concentrated NH4OH solution, leaving the plain amine intact. This would only be relevant if using the H2O2 and titanium silicate catalyst route, since alkaline conditions would prematurely hydrolyze off the protecting groups.

A better route might just be to only partially nitrate the triazine, with only two nitro groups, since addition of the last nitro group will take a longer time period than addition of the first two. Then oxidize with activated H2O2 (this will not attack the hydrogen atom). After this, FeSO4 with NaOH would probably reduce a nitro to an amine, and then the compound could be nitrated again, to result in about an equal mix of 6-amino-3,5-dinitro-1,2,4-triazine-1-oxide and 5-amino-3,6-dinitro-1,2,4-triazine-1-oxide. The last of which would not be as stable as the first. The amine groups on each compound could be oxidized to nitro groups with concentrated H2SO4 and H2O2, then the resulting trinitro-triazine-N-oxide could be reduced into the homogenous isomer 6-amino-3,5-dinitro-1,2,4-triazine with the FeSO4/NaOH.

#### Using H2O2 and Acetic Acid

"Oxidation of 2,6-diamino-3,5-dinitropyridine by refluxing with a 30% solution of H2O2 in acetic acid produced 2,6-diamino,3,5-dinitropyridine-N-oxide in 80% yield."

*R. Hollins, L. Merwin, R Nissan, Journal of Heterocyclic Chemistry 33, p895 (1996)*

*H. Ritter, H. Licht. Journal of Heterocyclic Chemistry, 32, p585 (1995)*

First, add Acetic anhydride to form a protective acetyl on the amine, then add dilute acetic acid. Here is the synthesis for *Pyridine-N-oxide hydrochloride* the amounts will have to be adjusted if using the protected-amino,nitrotriazine derivative instead. Amino,Dinitro-triazine weighs 186 grams per mole, so to substitute it in the synthesis below, about 260g should be used. The protective acetyl is not really necessary, but probably will improve yields. The peroxyacetic acid can also be prepared by gradually adding Ac2O into a solution of H2O2 and the triazine to be oxidized. There must be enough Ac2O added to absorb the water, but too much will cause exothermic decomposition.

#### Step1

In a 1 L flask with a thermometer, 110 g. (1.4 moles) of pyridine is added . The solution is stirred, and 1L of 10% peracetic acid (used to clean oranges before they are juiced at juicing stores) is gradually added to raise the temperature to 85C. If the temperature varies more than 5 degrees below or above this, more acid is added or further addition of acid is postponed accordingly. The addition will take about 1 hour. Then the mixture is stirred until the temperature cools to 40C. Note that

Alcohol may be used as a solvent for this without this solvent being oxidized.

#### Step2

*Pyridine-N-oxide hydrochloride*. The acetate is converted to the hydrochloride by bubbling hydrogen chloride gas into the reaction mixture. The acetic acid and excess peracetic acid are removed by warming over the steam bath under vacuum, preferably while being stirred by a magnetic setup, or by having the flask swirled around. The pyridine-N-oxide hydrochloride that is left is purified by heating for 30 minutes with 300 mL of isopropanol. This is cooled to room temperature and filtered. The colorless crystals are washed with 50mL more of the alcohol, followed by 50mL of ethyl ether, giving 140-150g of crystals with a melting point of 180C.

#### Formamide

Strongly heat formic acid with ammonium hydroxide in a sealed tubed, reflux for 30 minutes.

#### If acetamide is used instead

If acetamide is used instead then 3-methyl pyrazine will result. In this case, the cold nitration will only put two nitro groups on, then the methyl can be oxidized to a carboxyl with hot moderately acidified permanganate, heated to 80 degC with concentrated H2SO4 which will decarboxylate it, giving off CO2, and finally nitrated again with mixed acids. Actually, because a of the nitrogens in the ring, it might be possible to just oxidize the methyl group (to a carboxyl) with a moderately acidic aqueous solution of chlorine. (It is also worth noting that plenty of acetamide byproduct is produced from methyl cyanide reacting with H2O2, the reaction also giving off O2)

Alternatively, a single step oxidative nitration is likely possible with hot mixed acids.

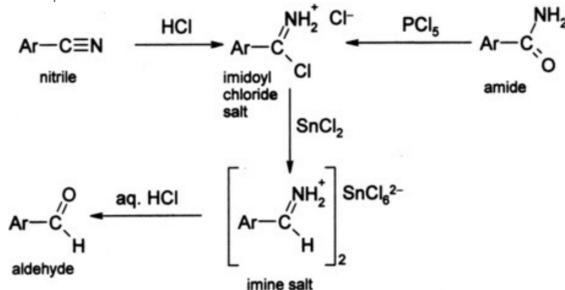
There is a possibility that the oxidation of the methyl group, decarboxylation, and subsequent nitration, can be performed in a single step. Hot (75degC) 75% concentrated sulfuric acid with nitric acid being gradually added in small additions over a period of 5 minutes. Nitrogen dioxide should be constantly bubbled into the nitration bath, beginning prior to and during the nitration. There should be at least three times more sulfuric acid than nitric acid used. This procedure and ratio will minimize carboxyl groups being replaced by hydroxyl groups. Some of the triazine will just end up decarboxylated, and not nitrated, so the product should be nitrated again with concentrated mixed acids. This modified procedure will inevitably produce hydroxy-substituted triazine byproducts, which should be much more soluble in water than the desired product of trinitrotriazine.

LLM-105 is overrated. The synthesis is complex, and the result is not particularly powerful. It would be much easier just to mix some HMX into TATB, this would probably give a composition with similar performance and insensitivity, at a much lower price. And what ever happened to DADNE? That compound never gets any attention. To make a cheaper substitute for LM-105, one could probably just mix a small proportion of TATB into DADNE. These are just some of the reasons that this site ignores that new compound

The scientists that come up with target molecules do not seem to have any sense. This is even the opinion of many of the synthesis chemists. Sometimes some of the proposed target molecules even have an amino group and nitro on the same carbon! I would certainly not like to be the designer of such a "theoretic" molecule when the synthesis chemists begin their ridicule of the proposal. Most chemists are not very creative, beyond trying to stick different combinations of simple groups onto nitrogenous rings, so it is not surprising that virtually no practical new compounds have been found since HMX in 1930.

### 5-amino,4,6-dinitro-1,2,3-triazine

Monochloroethylene reacts with NaCN to form CH2=CHCN. This "cyanoethylene" can then undergo the procedure shown in the picture below.



The reaction with SnCl2 should be conducted with a solvent other than water, since H2O reacts with SnCl4. (I have actually made the tetrachloride and reacted it with water, SnCl4 is a liquid at room temperature)

This will produce "allyl-aldehyde" CH2=CHCH=O. This compound could condense with hydrazoic acid HN3 to form 1,2,3-triazine. Limited nitration of this triazine will give a 70% yield of 5-nitro-1,2,3-triazine. The nitro can then be reduced to an amine with Zn/HCl (aluminum foil could be used instead, with either HCl or NaOH). The 5-amino-triazine can then be nitrated again to 5-amino,4,6-dinitro-1,2,3-triazine. There will also be a small amount of the other isomer, 4-amino,5,6-nitro, but this is difficult to separate out. Reaction of an appropriate amount of NaN3 and heating with this mix, might turn the

5,6-nitro byproduct into 4-amino,5,6-furoxan-1,2,3-triazine, while leaving the primary compound alone. While less energetic, the presence of 30% furoxan-triazine would give the combined composition more resistance to being initiated (making it more insensitive).

This compound is similar to LLM-116, except with one less hydrogen and one more nitrogen, which means more powerful, but also a little more sensitive.

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Č [1,2,4-triazine-oxide.bmp](#) (1041k)

Anders Hoveland, Nov 5, 2010, 12:46 PM

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## Comments