

[Edited on 11-9-2007 by Engager]

On page 2 of this thread , in the second post there is a similar synthesis reported in US2064817 which uses a sodium acetate - acetic acid buffer for the diazotization .

I wonder if the buffer system has been tried and compared with your described method , to see if the use of the buffer can improve the yield above 50% . Also , even though it has been specified that a non-mineral acid buffer system be used , I wonder if boric acid - sodium borate has ever been tried and found to be unworkable .

Related to your interest in the metal ammonia complexes of these tetrazoles , which I have been following with interest here , also on page 2 of this thread was reported a Copper Ammonium Salt of Diazoaminotetrazole , described in US2004719 . On page three you show a sample of the non-complexed parent compound in matchbox #3 which you called CuDAT .

Quote:

Originally posted by Engager

I've attached photo of silver 5-nitrotetrazolate, among other tetrazole derivatives i've made so far. Upper-left to lower-right: 1. Copper-ammonium complex 5-nitrotetrazolate ($(\text{NH}_4)_2[\text{Cu}(\text{N}_4\text{C}-\text{NO}_2)_4(\text{H}_2\text{O})_2]$) - green primary (NH_4CuNT) ; 2. $(\text{N}_2\text{H}_4)_2(\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4)$ - dihydrazinium 5,5'-azotetrazolate (HZT) ; 3. $\text{Cu}_3(\text{N}_4\text{C}-\text{N}=\text{N}-\text{NH}-\text{CN}_4)_2$ - copper 5,5' diazoaminotetrazolate (CuDAT) ; 4. $\text{Cu}(\text{N}_4\text{C}-\text{NO}_2)_2 \cdot (\text{H}_2\text{O})$ - acid copper salt of 5-nitrotetrazole (CuNT) ; 5. $\text{Ag}(\text{N}_4\text{C}-\text{NO}_2)$ - silver 5-nitrotetrazolate (AgNT) ; 6. $\text{Na}_3(\text{N}_4\text{C}-\text{N}=\text{N}-\text{NH}-\text{CN}_4)$ - sodium 5,5'-diazoaminotetrazolate (NaDAT) ; 7. $\text{Na}_2(\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4)$ - sodium 5,5'-azotetrazolate (NaAT) ; 8. $\text{HN}_4\text{C}-\text{NH}_2 \cdot \text{H}_2\text{O}$ - 5-aminotetrazole monohydrate (ATZ).

[img]<http://www.scinemadness.org/talk/viewthread.php?action=attachment&tid=8144&pid=106891>[/img]

Your picture of CuDAT is not clear enough to be sure , but looks to be a crystalline lump material , whereas the patent US2004719 describes the CuDAT as being an amorphous powder .

I am curious about your method of synthesis for the CuDAT , and also am curious if you tried the complexing with ammonia as described in US2004719 . There is only mention of the usefulness of the ammonia complex as a sensitizer component in priming mixtures where it is used as a small percentage . Is there more information concerning the possible usefulness of the complex alone , or the parent compound CuDAT as an initiator , described in the Russian literature ? Have you done any experiments with either

the CuDAT or its diammine ammonia complex to see if these compounds have usefulness as "green primaries" ?

[Edited on 23-3-2008 by Rosco Bodine]

Engager - 23-3-2008 at 10:15 AM

Stickers on boxes may not be correct substance with sticker Cu(DATZ)2 on box is copper diazoaminotetrazole, that's why i listed correct names above picture. Actually Cu diazoaminotetrazole is amorphous, but when it dried it stucked to paper in some kind of lumps, in wet state it's olive green, but dry it is almost black. It's quite sensitive to friction, it exploded then i tried to grind it in mortar. Explosion was quite loud, but i don't find any usefull applications for it in literature, only mentions about it's existance. Surely it is highly sensitive and powerfull explosive, but i'm not sure about it's initiative power. I have not tried ammonium complex, because i think it's too sensitive.

I attached photo of wet product below:

[Edited on 23-3-2008 by Engager]



Rosco Bodine - 23-3-2008 at 10:44 AM

I was thinking that possibly the CuDAT or its diammine complex might substitute for lead azide in a binary composition with barium styphnate , as a lead free primary . This binary is supposed to have a greatly reduced mechanical sensitivity , excellent stability , good initiating power and is cheaply made .

See US3284255

<http://www.scinemadness.org/talk/viewthread.php?action=attachment...>

Another possible binary would be a mixture of the CuDAT or its diammine with guanylazide picrate . These same binary mixture schemes might also be useful with some of the other complexes which have been described , as a means of improving the economics and lowering the sensitivity for the combined mixture .

Another possibly useful guanylazide is the styphnate , but I have found no mention of this in the english language literature . Is there any mention of guanylazide styphnate

in the Russian literature ?

[Edited on 23-3-2008 by Rosco Bodine]

Engager - 28-3-2008 at 11:57 AM

I've tried synth of bis-tetrazole from previous post, with no success. I've used following procedure: 10.7g of sodium azide and 13g of ammonium chloride are dissolved in 150 ml of water, then 8.8g of glyoxime was added. Mixture is heated on water bath, until glyoxime fully dissolved and then refluxed for 6 hours. No color change occurred, no glyoxime precipitated after cooling, then 16.8g of soda is added to destroy ammonium salts, and solution is boiled on water bath for more 2 hours. Solution color changed from pale yellow to deep red, no product precipitated after cooling. Unreacted azide is destroyed by action of nitrous acid: 25 ml of sodium nitrite is dissolved in 100 ml of water, and is added to red reaction mixture, then solution of 20 ml conc. sulphuric acid in 140 ml of water is added by small portions. Destruction of azide is accompanied by vigorous evolution of nitrogen oxides, and foaming, addition of sulphuric acid was continued until mixture show acidic pH, iodine-starch paper test shown blue singnal (means excess of nitrite in reaction mixture).

Reaction mixture was allowed to sit for a night, and after very large prismatic crystals are precipitated - longest one 7 cm length with 0.5 cm width. Presence of bis-tetrazole was analyzed by addition of manganese (II) sulphate (Mn salt of bis-tetrazole reported to be insoluble in water), no precipitate was obtained from mother liquor and from solution of precipitated crystals. So structure of product obtained is unknown, but it is not bis-tetrazole, because no precipitate with MnSO₄. Structure of red intermediate in solution during synth pathway is also unknown.

Today i thought another way to make bis-tetrazole without use of dicyan. It's similar to synth of 5-aminotetrazole by Thiele method. Glyoxime must react with hydrazine forming corresponding hydrazone, which is "dimeric" analogue of aminoguanidine, diazotation with HNO₂ should result in "dimeric" guanylazide, which should form bis-tetrazole in way similar for guanylazide=>5-aminotetrazole. Proposed reaction scheme:



Any ideas about this possible path? Somebody have any information about intermediate products and their properties? Well be glad to hear any opinions about this synth path. The_Davster! What do you think about it?

[Edited on 28-3-2008 by Engager]

The_Davster - 28-3-2008 at 10:09 PM

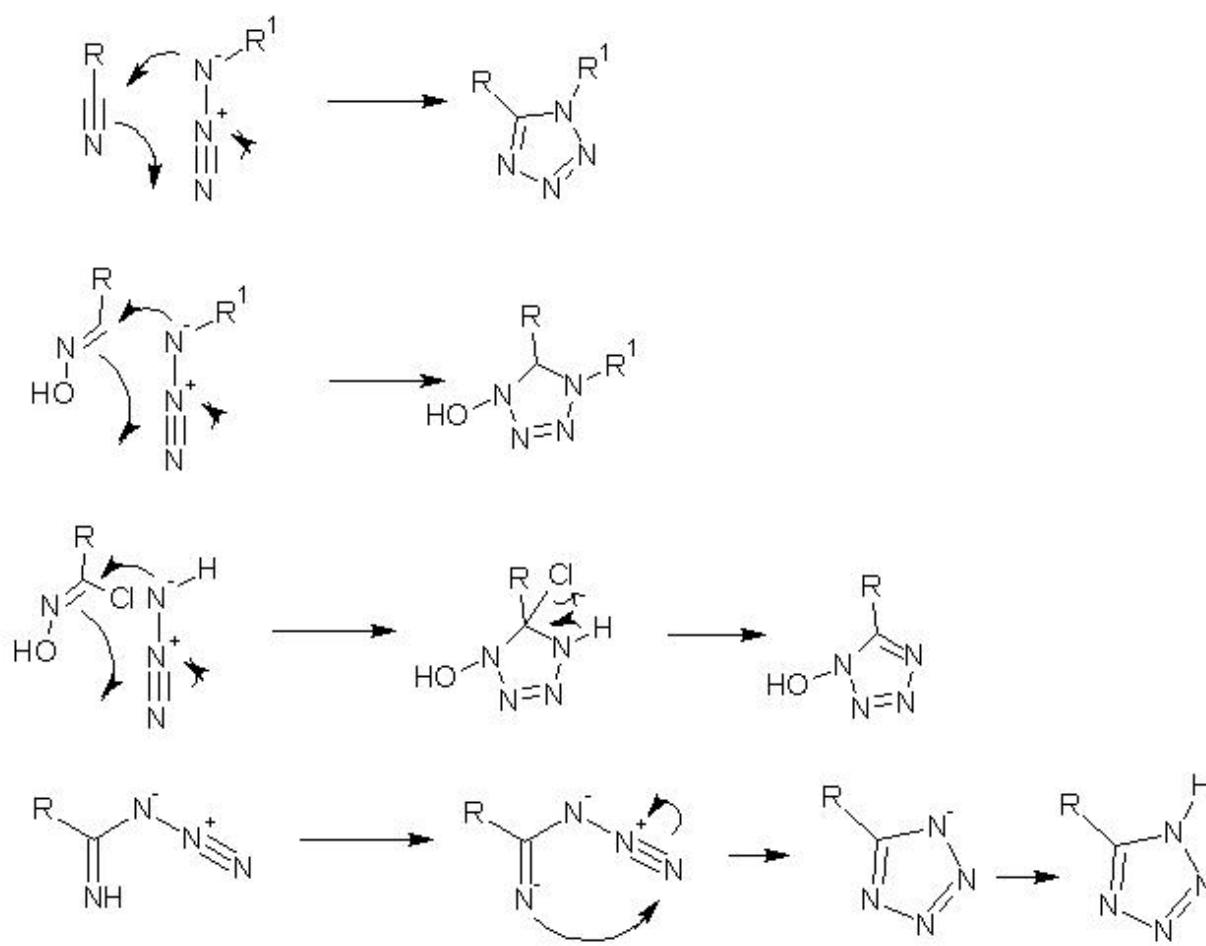
I do not know how much you have looked at the synthesis of furazans (<https://sciencemadness.org/talk/viewthread.php?tid=5813>), but the intermediate for the synthesis of diaminofurazan is diaminoglyoxime. Diaminoglyoxime is synthesized from glyoxime and hydroxylamine HCl. I believe the OH of hydroxylamine is necessary in the mechanism of hydroxylamine reacting with glyoxime. Without it there is no group to leave, and the mechanism will not work. If a HON₃ compound existed, it would be a good one to try in this reaction.

If I am wrong here, and the azide did add somehow to the glyoxime, I cannot see it easily cyclizing, unlike the reaction of a nitrile with an azide, the tetrazole ring is not formed immediately, a nonaromatic system is formed, and an OH is left on the nitrogen, and there are no simple methods for elimination forming the ring. See the attachment for what I mean.

However if R1 on the azide is a hydrogen or just a negative charge, this could be used to make the tetrazole ring, but only if dichloroglyoxime was used instead of glyoxime, as it would provide a nice leaving group for elimination making the tetrazole ring. But the OH group may be left intact....

In the most recent scheme you posted, I think it could work, or at least I could draw a mechanism by which it could easily work in the presence of a strong base.

[Edited on 28-3-2008 by The_Davster]



Axt - 23-5-2008 at 07:16 PM

Quote:

Originally posted by

The_Davster

dichloroglyoxime was used instead of glyoxime, as it would provide a nice leaving group for elimination making the tetrazole ring. But the OH group may be left intact....

Arr confirmed, I posted it in the "Glyoxime, Diaminofurazan and Some Energetic Derivatives" before realising the discussion here. <http://www.scinemadness.org/talk/viewthread.php?tid=5813>

I'll attach a previous article regarding the diazidoglyoxime intermediate here, although these authors failed to cyclise the azide to tetrazole. See the link above for the cyclisation via HCl in ether.

[Edited on 24-5-2008 by Axt]

Attachment: [Evidence on the Existence of Azidoximes - Journal of Organic Chemistry \(1961\), 26 952-4.pdf](#) (348kB)

This file has been downloaded 175 times

The_Davster - 23-5-2008 at 08:02 PM

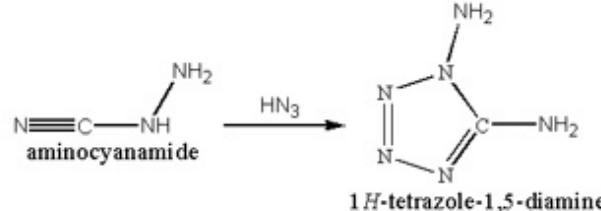
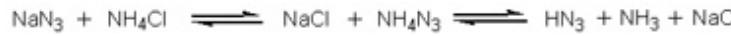
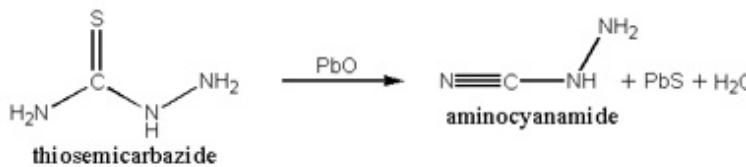
I like! 😊

I wonder if 5-ATZ would react with dichloro glyoxime, which could then be formed into a tetrazole substituted furazan?

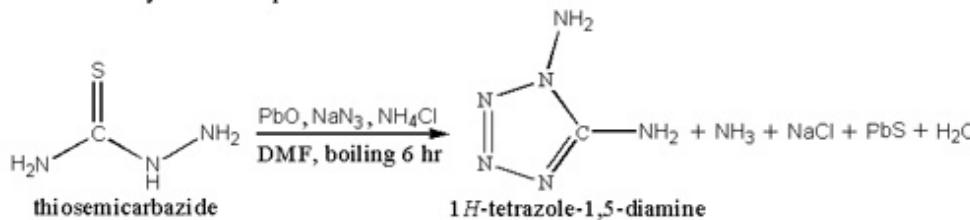
I think the tetrazole ring would be stable under the ring closing conditions required for making a furazan.

Engager - 12-6-2008 at 12:22 PM

Finally I got all chemicals I need for synth of DAT (1,5-diaminotetrazole), I found reference on path from thiosemicarbazide via desulfurization and reaction of intermediate with ammonium azide in dimethylformamide solution:



Summary reaction equation:



Synth from reference, attached to this message (translated from Russian): 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 186-187°C with decomposition (from water). Good soluble in hot water, and water-ethanol mixtures, acids, dimethylformamide, moderately soluble in cold water, ethanol, insoluble in tetrahydrofuran, ethylacetate, methylene chloride, either.

However, side reaction of HN3 and PbO surely exists and some lead azide will also form.

Question is how safe is to boil this mixture on water bath? Do anyone have references on energetic materials which can be made from DAT? (I heard that some complexes such as with Fe(ClO4)2 are proposed as lead azide replacement primaries). Any known properties of DAT salts with strong acids?

[Edited on 12-6-2008 by Engager]

Attachment: [diaminotetrazole.djvu](#) (61kB)

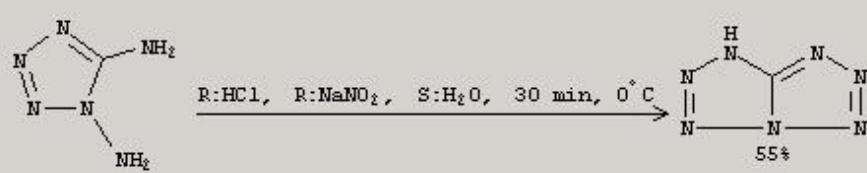
This file has been downloaded 161 times

Axt - 12-6-2008 at 03:29 PM

Nitrosation of diaminotetrazole. There was only five (prepared and isolated) structures in the scifinder database that had a string of 7 nitrogens, at least that I could see. Of which only two looked notably energetic, this being one and [this](#) the other.

Personally I wouldn't have a problem heating a small amount of Pb azide dispersed in a solvent to 100°C, unless it wanted to bump and splutter but that shouldn't be a problem with DMF. Patent SE154979 precipitates Pb(N3)2 from Pb(NO3)2 + NaN3 at 90°C, a more extreme example is US3345130 which precipitates it from molten KNO3/NaNO3 at 225°C!! (Pb(N3)2's decomposition temp is >300°C).

[Edited on 13-6-2008 by Axt]



NOTE: Reactants: 1, Reagents: 2, Solvents: 1,
Steps: 1, Stages: 1

[Journal of the Indian Chemical Society, 82\(2\), 172-174; 2005](#)

Axt - 12-6-2008 at 03:42 PM

And an article on diaminotetrazole perchlorate.

The_Davster - 12-6-2008 at 09:57 PM

I imagine it would have a plethora of interesting condensation products with formaldehyde or glyoxal. Unfortunately I do not know what work has been done on this, I will research it at work.

As for the lead azide, I have heard (High Energy Density Materials, Klapoetke) that this synthesis will produce "large amounts" of lead azide, and that is why the method from diaminoguanidine is preferred. But this may only be important on industrial scale.

DMF boils at a higher temperature than a boiling water bath, and should be safe from thermal issues. I would advise swirling to mix the reaction as opposed to magnetic or hand stirring to keep friction to a minimum.

Also, the Indian paper Axt posted...an isomer of azidotetrazole/tetrazyl azide! I could have sworn I have seen a paper on interconverting the two, or was it a theoretical discussion paper?

Anyway, in terms of derivitaves, the nitrate and perchlorate are in the attached paper, as are the methylation products with azide, nitrate, and dinitramide counterions

Attachment: [DAT derivs.pdf](#) (493kB)

This file has been downloaded 203 times

The_Davster - 21-6-2008 at 02:14 PM

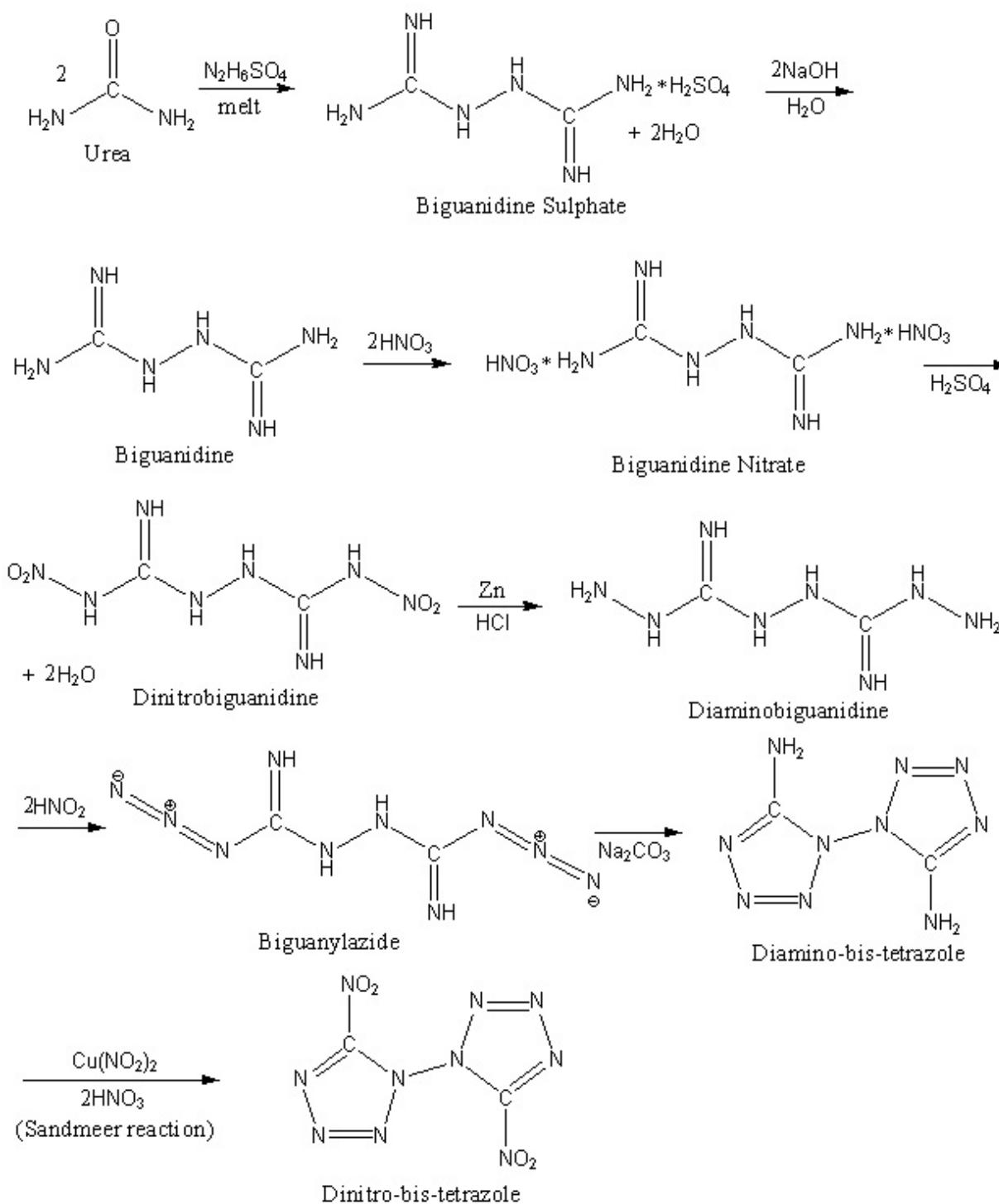
A paper on DAT condensation with glyoxal... reactions with formaldehyde appear nonexistent.

Attachment: [DAT condensations.pdf](#) (572kB)

This file has been downloaded 168 times

Engager - 14-7-2008 at 09:06 PM

Recently I made some biguanide sulphate, and got an interesting idea, about how another interesting tetrazole can be made. How does it look? Someone have synth procedure for biguanidine or its salts (first made by Thiele in last century)?



The_Davster - 15-7-2008 at 11:34 AM

I can find no problems with the synth, and I REALLY like the idea.

The molecule has to be some sort of a record...8 nitrogens connected in a row 😱. I think the diamino version may be explosive by itself, let along the dinitro one 😱😱

Sobrero - 16-7-2008 at 03:58 AM

Perhaps dinitrobiguanidine can be made by reaction of fuming nitric acid (or mixed acids) with biguanidine sulphate, just like nitroguanidine can be made from guanidine sulphate + HNO₃. This would shorten the synthesis somewhat 😊.

497 - 16-7-2008 at 04:22 AM

God that is a lot of nitrogens. I like it. Any practical information on the synth or explosive properties?

Nick F - 16-7-2008 at 08:08 AM

Even looking at it scares me a little bit, but yeah, I like it 😊.

The only potential problem that I can see could be acid hydrolysis of some of the intermediates, eg dinitroguanidine into N-amino-N'-nitroguanidine and nitrourea.

It's definitely worth trying though!

Rosco Bodine - 16-7-2008 at 01:15 PM

A couple of thoughts on first look...
will have to dig through some references later....

There may be a possible shortcut from the biguanidine sulfate to the diaminobiguanidine via reaction with hydrazine, ammonia being byproduct.

Possibly a variation on the reaction for producing guanidine salts via calcium cyanamide and ammonium nitrate might preferentially produce the biguanidine salt.

Polymerization to undesired materials could be a real complication, too. Beware the red goo 😱

[Edited on 16-7-2008 by Rosco Bodine]

Engager - 17-7-2008 at 05:34 AM

Some references on biguanidine:

1. Justus Liebig's Annalen der Chemie, Volume 273, Issue 2-3 (p 133-144). J.Thiele "Uber Nitrosoguanidin" ; <http://www.scinemadness.org/talk/viewthread.php?action=attachment...>
2. Justus Liebig's Annalen der Chemie, Volume 270, Issue 1-2 (p 1-63) J.Thiele "Uber Nitro And Amidoguanidine" ; <http://www.scinemadness.org/talk/viewthread.php?action=attachment...>

Corresponding English translations:

3. http://www.rsc.org/delivery/_ArticleLinking/DisplayArticleForFree.c...
page 389 J. Thiele Nitrosoguanidine
4. http://www.rsc.org/delivery/_ArticleLinking/DisplayArticleForFree.c...
page 1295 J.Thiele Nitro and Amidoguanidin

guanyl azide (diazoguanidine) revisited

Rosco Bodine - 17-7-2008 at 01:13 PM

In the second article above is mentioned again a material of interest, diazoguanidine, as the nitrate m.p. 129C which was also identified near the end of page 2 as the picrate in the early part of this thread. A parallel British patent GB470418 by the same inventor gives a little more detail about the preparation of the picrate. Analogously, by using half the molar proportion of magnesium stypnate, a guanylazide stypnate would be expected. And likewise using the sodium or ammonium salt of some of the acidic tetrazoles, the guanyl azide salt of those would be expected. Some of these may form mixed metal salts of possible interest also.

And there may be a shortcut to the aminoguanidine precursor from reaction of the ordinary guanidine nitrate salt with hydrazine. And likewise the di and triaminoguanidine bases via this and other routes should be kept in mind as possibly useful in forming salts with the acidic tetrazoles.

Anyway, aside from the new compounds proposed by Engager, there is a reminder there in the readings which also points back to the beginning of the thread and these other possibilities. It seems like deja vu all over again 😱

@Engager , in that next to the last reaction above, instead of Na₂CO₃ for the base, you should use NH₄OH. Right?

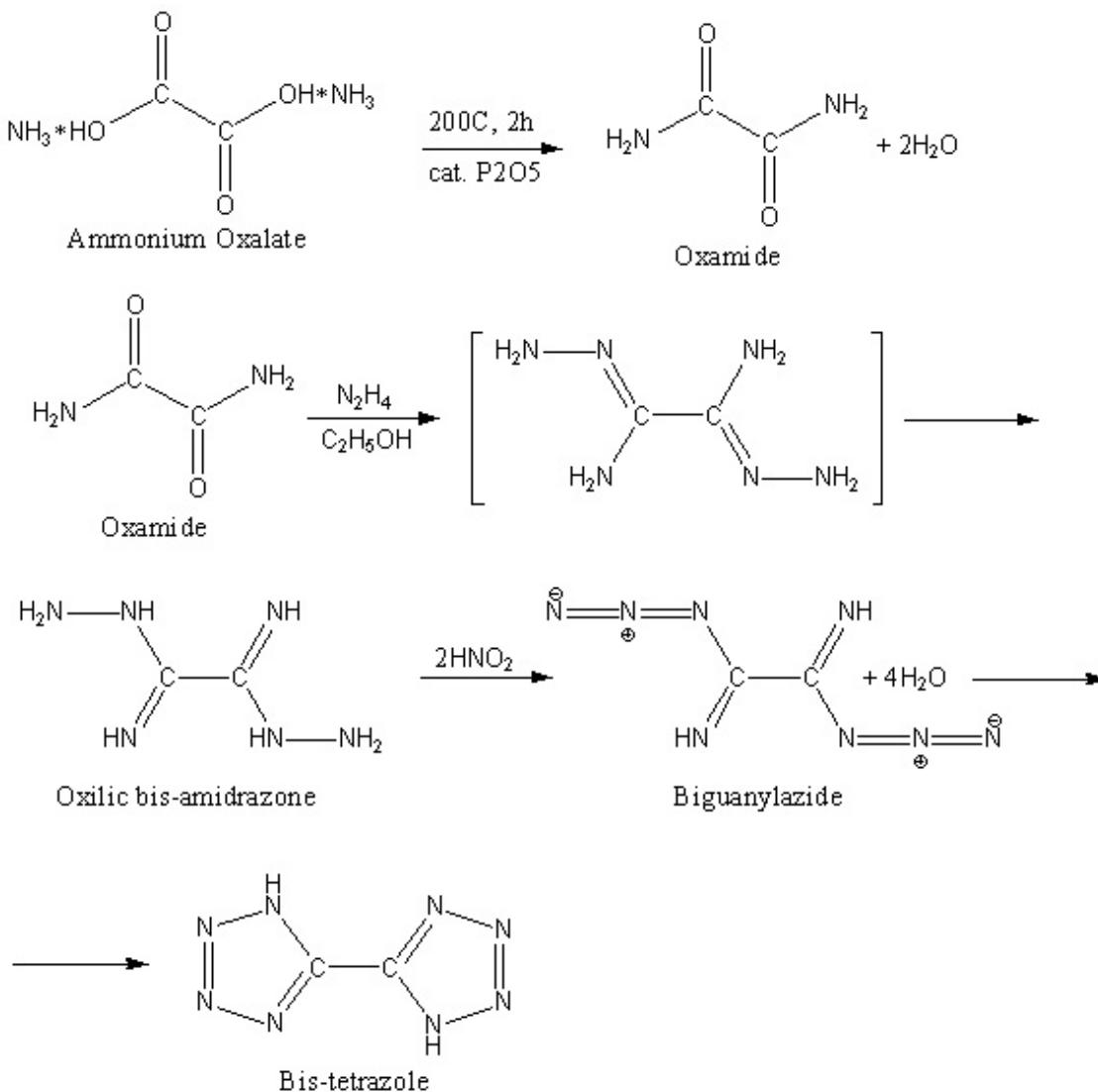
[Edited on 17-7-2008 by Rosco Bodine]

Attachment: [GB470418 Guanyl Azide Picrate base charge.pdf](#) (265kB)

This file has been downloaded 160 times

Engager - 18-7-2008 at 06:15 AM

Yesterday i decided to try another alternative route to bis-tetrazole. It is well known that it simply forms on action of nitrous acid on oxalic bis amidrazone (see attached patent for example). Main problem with less complicated synths is that they require to work with highly toxic dangerous gas cyanogen. As i wrote in posts before, attempts to react glyoxime with hydrogen azide, and additon of HNO₂ to mix of glyoxime and hydrazine vere unsuccessful, however i decided to try another route:



First i made ammonium oxalate from ammonia and oxalic acid:

39g of oxalic acid dihydrate was dissolved in 60 ml of water at 60C, solution is quickly filtered to the flask containing 54 ml of 25% ammonia solution. White precipitate forms imidately, solution is cooled to 25C to further reduce product solubility, and then filtered. Resulting white glistening crystals of pure ammonium oxalate monohydrate were filtered and air dried. Yield is 34.1g (77.5%).

Ammonium oxalate was converted to oxamide by following method:

28.4g of ammonium oxalate monohydrate is ground to fine state and mixed with 0.66 of P2O5 (catalyst) and wetted with 20 ml water. Mixture is placed to round bottom flask with attached air condenser, joined with distillate flask (to keep condensed water escaping from reaction mixture) and gas outlet (to vent toxic side products such as CO or (CN)2 outside of building). All connections must be tight to ensure no toxic reaction gasses can enter room atmosphere. Flask with reaction mixture is heated on wax bath to 200C for 2 hours. Solid residue was washed with 2 portions 250 ml of hot water to remove soluble impurities and then filtered to obtain insoluble product - oxamide with 63% yield.

Next I tried to condense resulted oxamide with hydrazine salts in water and alcohol. Because oxalic bis amidrazone is unstable at temps more than 50C heating can not be applied to help this reaction attempts. Hydrazine salt was used because according to information from the books amidrazone are stable in acidic conditions and unstable in alkaline, however no reaction occurred at all - oxamide does not dissolve. Then another method is tried, some N2H5Cl is dissolved in ethanol and freebased by sodium hydroxide. Oxamide was fast dissolved and solution was filled with white flakes of product, which is insoluble in alcohol, probably oxalic bis amidrazone =)

[Edited on 18-7-2008 by Engager]

Attachment: [EP1136476B1.pdf](#) (207kB)

This file has been downloaded 141 times

Rosco Bodine - 18-7-2008 at 11:09 PM

You might try Copper Acetate in mild acetic acid at pH 4 and add Sodium Nitrite for the diazotization of the oxalic bis-amidrazone (oxamide dihydrazone) and simultaneous conversion to the energetic copper salt of the BHT as the end product precipitate.

Also the use of Copper Nitrate in dilute HNO₃ with NaNO₂ would probably work parallel to the prior art example 1, analogous to the silver salt. Other metal salts should form similarly, shortening the synthesis if the metal salt is what is wished to be the end product.

You might want to have a robot do the work while you remain safely behind a barricade 

Attached is the US7122676 filing for the same patent which is easier to navigate.

[Edited on 19-7-2008 by Rosco Bodine]

Attachment: [US7122676 preparation of 5,5'-bi-1H-tetrazole.pdf](#) (115kB)

This file has been downloaded 157 times

Axt - 21-7-2008 at 02:31 AM

"1 H-Tetrazolo[1,5-d]tetrazole: A solution of sodium nitrite (0.01 mol) in water (5 ml) was added dropwise to a stirred solution of compound diaminotetrazole (0.01 mol) in conc. HCl (5 ml). The reaction mixture was kept at 0° C for 30 min and the precipitated solid was filtered, washed with water, dried and crystallized from ethanol. Yield 0.6 g (55%), m.p. 210°C." J. Ind. Chem. Soc. 82, 172-174, (2005) [attached].

Attachment: [Use of 1,5-diaminotetrazole in the synthesis of some fused heterocyclic compounds.pdf](#) (263kB)

This file has been downloaded 165 times

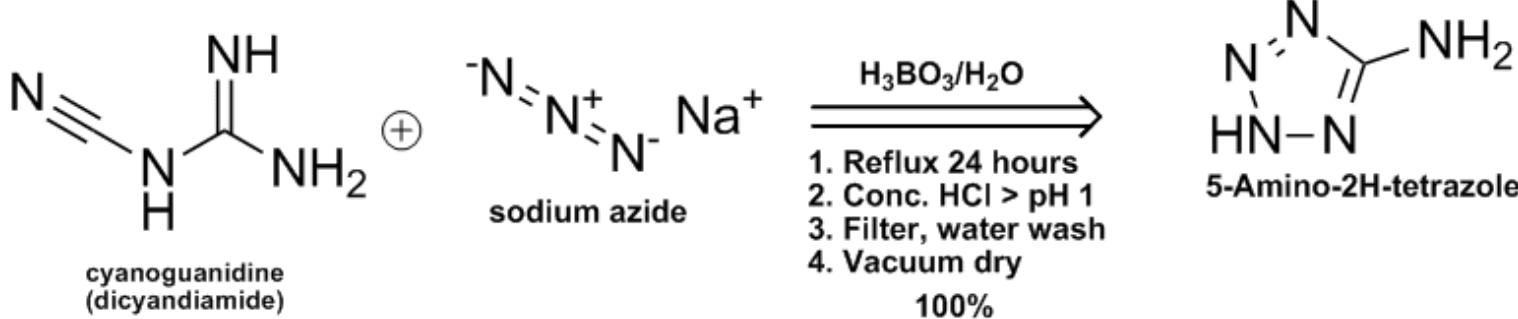
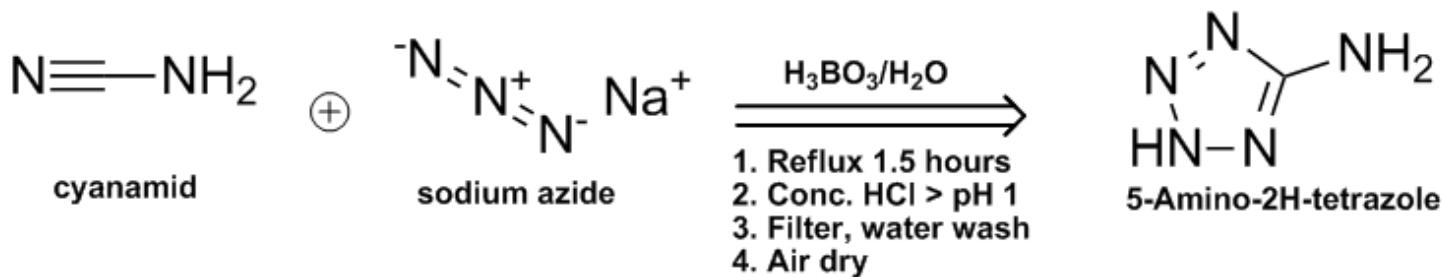
Ritter - 30-7-2008 at 11:22 AM

5-Aminotetrazole on eBay: item 300165803620. \$70.50 for 500 gm of 97.0% min. material.

Ref US 5451682 <http://tinyurl.com/6hoacl> & ChemDraw abstract of 2 azide routes to 5-AT from either cyanamid

or dicyandiamide.

[Edited on 30-7-2008 by Ritter]



Engager - 30-7-2008 at 11:55 AM

Synth of DAT has been attempted using procedure i've mentioned somewhere above, however some serious difficulties has been encountered. Insoluble product after boiling tends to be rock hard, and if it contains significant amount of lead azide this could result in hazard situation then attempted to separate this black sludge from glass vessel. Liquid was decanted and insoluble black residue on walls of flask was successfully destroyed without problems by long standing with weak nitric acid. Particles of PbS are very small and it is very hard to filter them completely, to get transparent solution whitch has dark orange color.

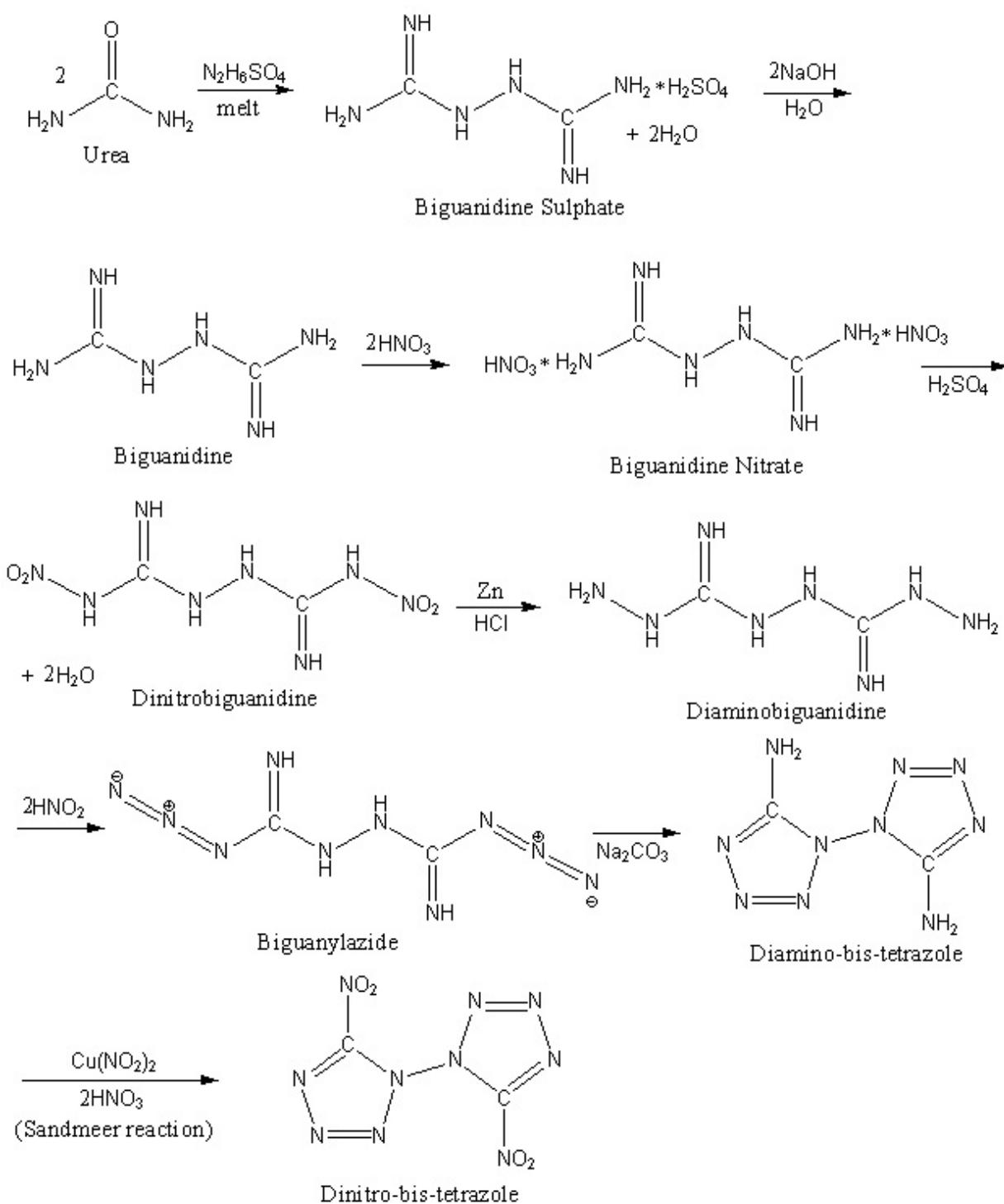
Another more serious problem has arisen on evaporation of DMF. At boiling water bath in vacuum made by water-stream vacuum pump, DMF is not distilled with any visible speed. Removal of DMF at ordinary pressure is impossible in this case because DMF boiling point is to close to DAT decomposition temperature. It is quite interesting to know that is b.p of DMF in vacuum about ~50 mm. Hg. How to solve solvent removal problem?

Ritter - 30-7-2008 at 03:19 PM

Quote:

Originally posted by Engager

Recently i made some biguanide sulphate, and got an interesting idea, about how another interesting tetrazole can be made. How does it look?

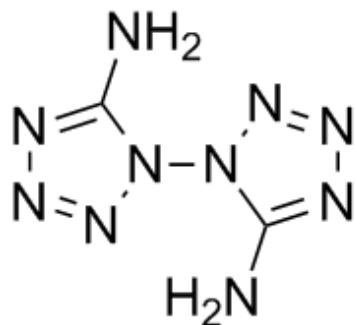


I'm curious to find out if this diamine can be oxidized to create multiple intermolecular azo linkages, basically polymerizing it into a polymer that would be about 86% nitrogen.

The synthesis of 1,1'-dinitro-3,3'-azo-1,2,4-triazole uses alkaline permanganate to oxidize the amino function to the azo group.

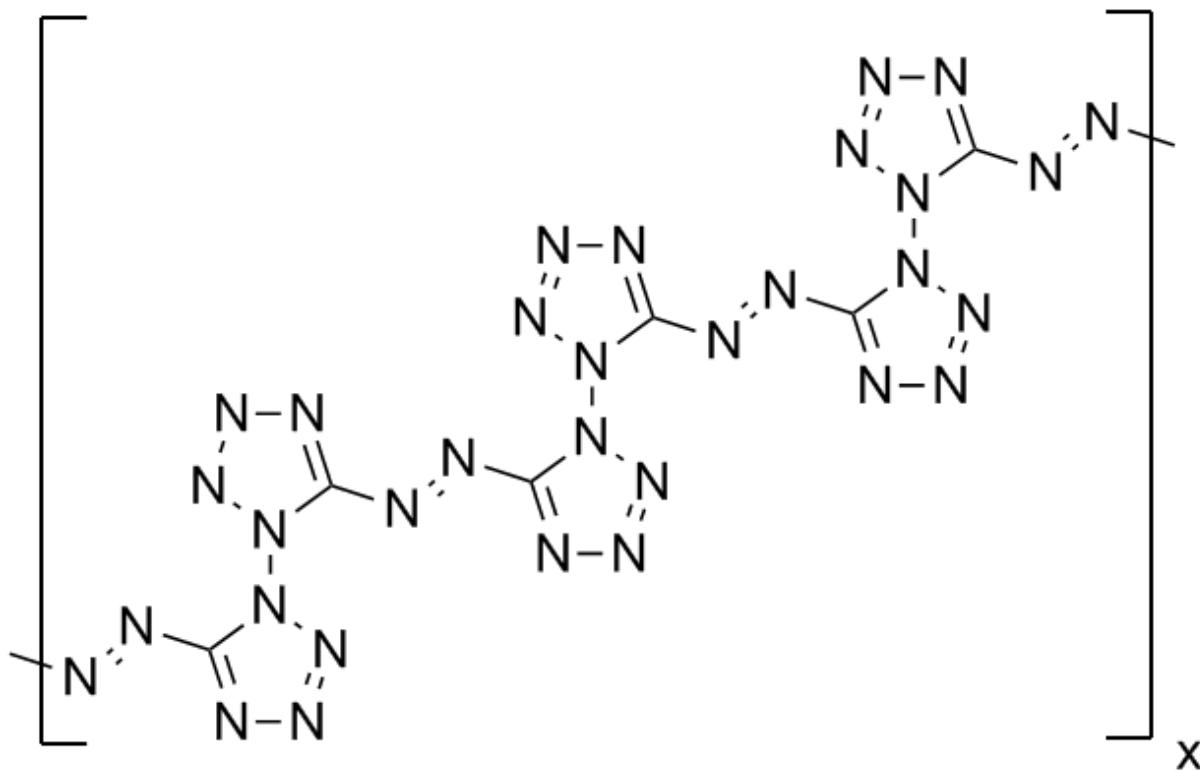
It would be poly(5,5'-azo-1,1'-bitetrazole) or thereabouts. Are high nitrogen polymers of this type known or even possible?

[Edited on 30-7-2008 by Ritter]



1,1'-bitetrazole-5,5'-diamine

Elemental Analysis: C, 14.29; H, 2.40; N, 83.31



Elemental Analysis: C, 13.85; N, 86.15

Engager - 30-7-2008 at 06:06 PM

Strange effects observed during attempt to separate DAT from reaction mixture. First of all I tried to precipitate DAT with tetrahydrofuran (DAT is insoluble or weakly soluble in it), this resulted in no precipitate; same thing happens when ethylacetate is added.

Next thing that was tried is benzene, if it is added in large excess to DMF in reaction mixture (3-4 times vol) mixture orange color diminishes and some cream colored product is precipitated, it is glueish like and can not float free in solution. This product is isolated with filtration (product №1), when filtrate is allowed to stand for some time formation of strange brown oily layer is observed, most of liquid is decanted and oily layer is collected by means of separating funnel (product №2). Then brown oil with strange angry smell is diluted with water (1:1 vol) large quantity of white product is separated momentarily and color disappears to very slightly yellowish transparent, product is separated by filtering (product №3).

Some observations on products: product №1 is good soluble in hot water, however small quantity of insoluble material remained. Then a drop of this solution is added to drop of CuSO₄ solution, this results in immediate formation of brown precipitate. It is most likely that №1 product is traces of unreacted material -

inorganic salts, which are weakly soluble in benzene, may be containing some azide. Product №2 is very strange, benzene and DMF are miscible with each other in all possible volume rates, so formation of this layer remains mysterious. This brown oil is heavier than mixture of benzene with DMF so it flows on the bottom.

My first idea about that layer was that it is layer with tetrazylazide which can form as byproduct in synth of DAT as mentioned in (5-Azido-1H-tetrazole - Improved Synthesis, Crystal Structure and Sensitivity Data article)

<http://www.scinemadness.org/talk/viewthread.php?action=attachment...>

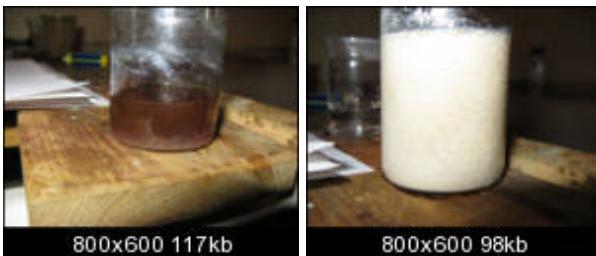
Synthesis of tetrazylazide mentions about its extraction from some brown oily layer, as described in this reference:

<http://www.scinemadness.org/talk/viewthread.php?action=attachment...>

But I have to revise it because 5-azidotetrazole and its alkali metall salts are perfectly soluble in water, so this product is likely to be DAT because it is weakly soluble in cold water. However I'm not completely sure in it.

Any ideas what all these products could be? How to explain this observations? May be someone know qualitative tests for DAT?

I've attached some pictures of this mysterious brown oil, and precipitate it forms on dilution by water:



[Edited on 31-7-2008 by Engager]

Rosco Bodine - 30-7-2008 at 08:30 PM

Maybe filter and dry the precipitate gotten from dilution with water.
Redissolve in alcohol and precipitate with methylene chloride to see if crystallization occurs.

I think you probably have DAT there as the white precipitate from dilution with water, pure enough for use as is, for further reactions like nitrosation as Axt described, or for permanganate oxidation and possible polymer formation as Ritter speculated above.

@Ritter

Please edit your attached images width to ~600 pixels so the images don't foul up the text formatting on the page. The width will be the first pixel dimension stated in the image properties, to resolve any confusion about which number there specifies the width.

[Edited on 30-7-2008 by Rosco Bodine]

Ritter - 30-7-2008 at 08:46 PM

Quote:

*Originally posted by
Rosco Bodine*

@Please edit your attached images width to ~600 pixels so the images don't foul up the text formatting on the page.

[Edited on 30-7-2008 by Rosco Bodine]

??? 810x685 pixels for that image. Looks fine to me. Do you prefer 600x600 or ?x??

The_Davster - 30-7-2008 at 11:40 PM

I have never seen white DAT, only a light brown powder. I think removal of residual lead sulfide particles must be very difficult.

Engager - 2-8-2008 at 06:42 PM

Finally I got my hands on this crazy molecule from 2 nitrotetrazoles. Molecular structure was computed with 6-31G** DFT B3LYP functional, mesh in the plot is crystalline cell 0.001 e/bohr³ electron density isosurface. After heat of formation, heat of explosion and density were computed from quantum chemistry, velocity of detonation was calculated in usual manner by empirical equations. Correction coefficient was obtained by division of 5-NTZ measured/calculated VOD's. Calculated values listed below.



Molecular Mass: 228.0866 g/mol

Heat of formation: +219.90203 kcal/mol

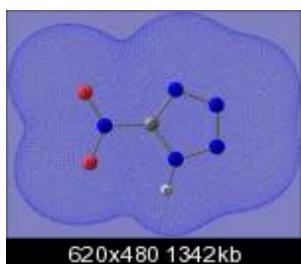
Calculated Crystal Density: 1.996817 g/cm³

VOD: 9916 m/sec (1.99) calculated and justified by divergence coefficient from 5NTZ REAL/CALC.

Explosion gas volume: 687,45818 l/kg

Heat of explosion: 5,5461 Megajoules/kg

For comparison corresponding 5-NTZ properties are listed below:



Molecular Mass: 115.05124 g/mol

Heat of formation: + 83,59606 kcal/mol

Calculated Crystal Density: 1.771954 g/cm³

VOD: 8900 m/sec (1.73)(experimental) ; 9059 m/sec (1.77)

Explosion gas volume: 778.8 l/kg

Heat of explosion: 4,3227 Megajoules/kg

General note to all people who think that positive heat of formation is wrong - no, you are! This compounds are endothermic as are HN₃, azotetrazole, diaminotetrazine and other high nitrogen explosives! The positive heats of formation are exactly the reason of high energy in this explosive compounds. So all this positive heats of formation are correct - learn basic thermochemistry!

[Edited on 3-8-2008 by Engager]

The_Davster - 6-8-2008 at 10:56 AM

Attached is a simple synthesis of Nitraminotetrazole in a one step reaction from aminotetrazole.

100% nitric acid is used, but it is one step from 5-ATZ which IMO is an improvement over

- a) synthesis of nitraminoguanidine then diazotization
- b) preparation of ATZ-nitrate, then dehydration.

Attachment: [natz1.pdf](#) (650kB)

This file has been downloaded 339 times

Swany - 16-9-2008 at 09:27 PM

So, is there a quintessential tetrazole-based complex that puts all other primaries (or tetrazoles) to shame? Personal favorites? I have some aminotetrazole, sodium azide, sodium nitrite and a urge to explore. Any requests or ideas on where to start?

[Edited on 16-9-2008 by Swany]

The_Davster - 16-9-2008 at 10:19 PM

Silver nitrotetrazole

The nitrotetrazolato-ferrate complexes are cool as well, but no experience to date with them.

[Edited on 16-9-08 by The_Davster]

Swany - 17-9-2008 at 07:54 PM

I think I will prepare some CuNT and maybe some tetrazole azides, perhaps even a crack at some energetic bidentate ligands. The sodium iron salts look interesting and no one has had luck yet.

EDIT: Bidentate energetic ligands look interesting as well for that matter, though I am not sure if I will get to any of them.

[Edited on 17-9-2008 by Swany]

Swany - 18-9-2008 at 11:44 PM

Preparation of CuNT:

20.8g NaNO₂ and 11.0g CuSO₄.5H₂O were dissolved in 75mL dist. H₂O and placed in a large beaker upon a cold water bath with magnetic stirring and a slow stream of air above the solution. A solution of 10.8g 5-ATZ in 180mL H₂O with 12.8mL 70% HNO₃ and 0.4g CuSO₄ was added dropwise over the course of 3 hours. Gas was evolved and the very dark green solution slowly turned light green with a similarly colored precipitate over the course of the addition. It was then stirred for 30 more minutes and 20mL of 50% HNO₃ was added dropwise, and stirring was continued for 30 more minutes. The product was collected on a buchner funnel and washed with dilute HNO₃, then with portions of water.

This is how far I am-- and I seriously doubt I will dry large portions of the product. Most will probably be converted into the sodium salt then other anionic complexes.

Engager - 19-9-2008 at 05:30 PM

Acid copper salt is not so sensitive to fear it so much, i used large quantities of dry products up to 20g without any hazard situations. As for aims of synth AgNT is definitely worth trying, but is quite sensitive and extremely powerfull primary explosive. Some complexes have good initiating power as well and far less sensitive, but are bit harder to produce. In my oppinion best aim is BNCP, powerful modernistic primary explosive, i tried this complex and it was very good in many ways.

Rosco Bodine - 20-9-2008 at 02:05 AM

@Swany

You asked for ideas, so I'm offering one for consideration. Back on page 2 of this thread, fifth post down from the top, was posted a bit of information regarding Azotetrazole , 5,5'Azotetrazole, and a related patent US5877300 containing a synthesis which Engager confirmed and described on page 3 of the thread.

Engager made a (di)hydrazine derivative salt of 5,5'Azotetrazole.

The patent described a (di)guanidine salt , and it seemed that as a natural followup, the next interest would be the possibility of a (di)guanylazide salt of 5,5'Azotetrazole.

This perhaps would be covering new ground. It has continued to intrigue me what might be the energetic properties of the guanyl azide salts which may form with the acid tetrazoles, which themselves can be formed as the later derivatives of the same guanyl azide which is their precursor. It is something of an incestuous marriage of the parent and daughter compounds which could result in interesting energetic offspring, or morons  perhaps , but it would seem to be a logical experiment to find exactly what does result from that deliberate "inbreeding" marriage of energetic structures. There are other possible guanyl azide salt combinations where a different acid tetrazole could substitute for the 5,5'Azotetrazole.

Swany - 22-9-2008 at 12:12 AM

Thats an intriguing idea Rosco. I might look into that this next weekend.

In other news, I tried to make some Sodium ferro-nitrotetrazolates by dissolving some CuNT in NaOH soln, filtering the precipitated CuOH, adjusting the solution to acidic with HCl, estimating an amount of FeCl₂.6H₂O to add, doing so, boiling off a large amount of liquid, and throwing it in the freezer, vacuum filtering and washing with cold water. I received a crop of pale orange stuff, not unlike what the CuNT I made looked like. It is powderable, not unlike an amorphous nitric acid ester, like a fresh ppt. of MHN or ETN dried. On contact with flame it burns very rapidly, and heating it will result in DDT, as will heating it and then initiating with flame contact. The CuNT I had was still more likely to DDT, but my ratios in preparing the iron salt were determined in a most qualitative manner. I will weigh some out and try it next time.

User - 24-1-2009 at 07:22 AM

Ive been reading about tetrazoles alot.

Now I am wondering what is found to be the substance with the highest primairy potential?

Now and then i can't see the trees through the forest 

Engager - 22-2-2009 at 09:09 PM

I'm finaly completed a big compilation work on derivatives of tetrazole. Everyone who is interested in this topic is welcome to review it [Here](#).

[Edited on 23-2-2009 by Engager]

Rosco Bodine - 22-2-2009 at 10:41 PM

Here's the link for the locally stored file

http://sciencemadness.org/scipics/Energetic_Derivatives_Of_Tetrazol...

The file size appears to exceed the limit allowed for attachments so you won't see the download count, but you should still be able to get the file by the link.

PHILOU Zrealone - 24-2-2009 at 06:57 AM

Quote:

Originally posted by Ritter

I'm curious to find out if this diamine can be oxidized to create multiple intermolecular azo linkages, basically polymerizing it into a polymer that would be about 86% nitrogen.

It would be poly(5,5'-azo-1,1'-bitetrazole) or thereabouts. Are high nitrogen polymers of this type known or even possible?

A tricyclic molecule might also be formed if the two amino groups being on the same side... when bridging You then get a symetric molecule based on cyclohexaring -C(N-N)2C- core with two cyclopentating ears then looking a bit like Mickey Mouse 

[Edited on 25-2-2009 by PHILOU Zrealone]

Attachment: [noname01.pdf](#) (11kB)

This file has been downloaded 133 times

hokk - 9-3-2009 at 11:53 AM

Quote:

Originally posted by Engager

I'm finally completed a big compilation work on derivatives of tetrazole. Everyone who is interested in this topic is welcome to review it [Here](#).

[Edited on 23-2-2009 by Engager]

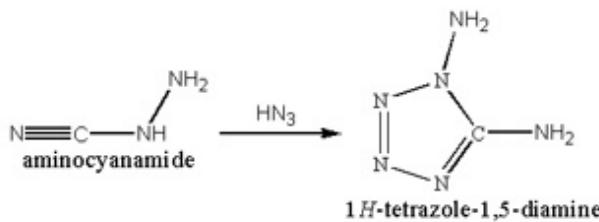
Great work! Interesting reading indeed.

A thought: Since you have so much experience with the tetrazole derivates, a chapter with your own opinions where you compare the different tetrazoles regarding different factors (ease of synthesis, cost, dangers, performance, stability etc.) would be very valuable.

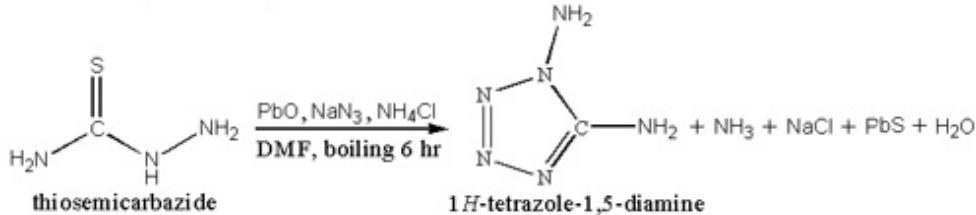
Engager - 13-3-2009 at 06:17 AM

Quote:

Originally posted by Engager



Summary reaction equation:



Synth from reference: 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). Good soluble in hot water, and water-ethanol mixtures, acids, dimethylformamide, moderately soluble in cold water, ethanol, insoluble in tetrahydrofuran, ethylacetate, methylene chloride, either.

Yesterday i've finaly made successful 1,5-diaminotetrazole synthesis, using one step method from thiosemicarbazide. Thiosemicarbazide & sodium azide & ammonium chloride & lead (II) oxide are refluxed in excess of dimethylformamide. Regretably synth is a real hell, due to many practical difficulties. First of all desulfurization of thiosemicarbazide by lead oxide leads to formation of lead sulphide, witch solidifies to hard solid layer on bottom of reaction vesel, this leads to difficulty with stirring, forcing you to spend a lot of time

to crush this layer at any stirring step. Layer is quite dense and hard, so caution is needed to avoid breaking a glass of reaction vesel. Filtration of risidual lead sulphide particles also makes trouble - this stuff passes through filtering paper! Second big difficulty is vacuum removal of dimethylformamide (it can't be distilled without decomposition at atmospheric pressure). DMF is readily distilled by heating filtered reaction mixture on water bath at 5-10 kPa. Pressure must be controled to not exceed this boundaries, if pressure is too high DMF will not destill while heated on water bath, but if pressure is too low, mixture will boil up imidately, with such intensity, that foaming liquid throws over to condenser. Low pressure also greatly lowers boiling point, so fumes became difficult to condense and can pass through to the oil in vacuum pump, penetrating long condenser without visible difficulty. Vacuum caused dissolved gasses to leave a boiling liquid and it imidately comes to overheated state, so boiling capillary is absolutely essential (it is also used to control pressure in reaction vesel). To make matters worse, residual lead sulphide particles block boiling capillary, forcing you to stop distilation, repressurize vessel and clean up capillary. Anyway vacuum evaporation to dryness and recrystallization from water gave wanted 1,5-diaminotetrazole crystalls with 55% yield, crystalls are probably contaminated by lead sulphide and have light brown coloration mentioned by Davster.

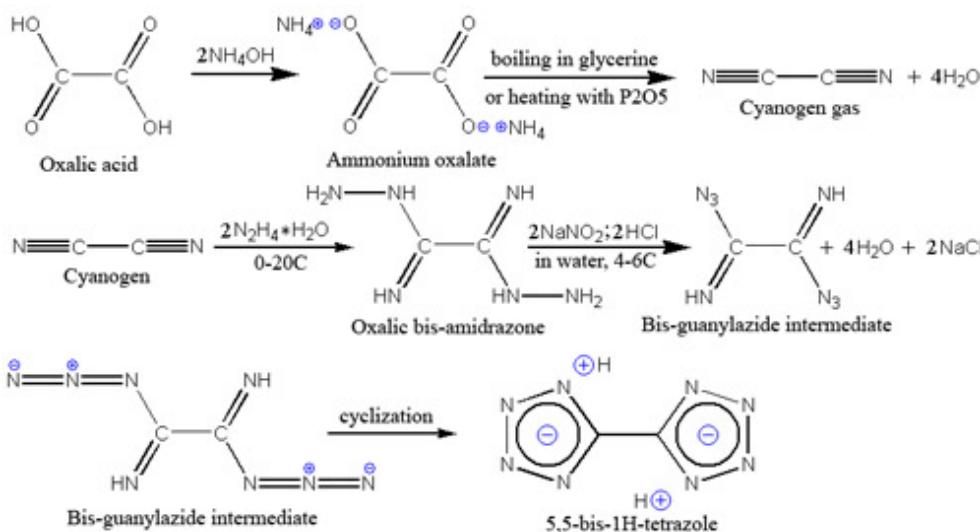


[Edited on 13-3-2009 by Engager]

Engager - 20-3-2009 at 09:11 AM

Recently i got an idea how bis-tetrazole can be made from oxalic acid, hydrazine hydrate and sodium nitrite. All this chemicals are readily accessibe everywhere so this can be usefull. All reactions give almost quantative yield, however they involve some nasty toxic products and must be carried out on open air with gas mask or under efficent hood. This way of synthesis is patented both in US and in EU (patents EU1136476B1 and US7122676).

Oxalic acid is reacted with ammonia to give ammonium oxalate, witch is subsequently dehydrated on heating in glycerine first to oxamide intermediate with evolution of 2 molecules of water, and finaly to cyanogen with evolution of 2 more molecules of water. Evolved cyanogen is reacted with hydrazine hydrate at temperature slightly lower then room temperature, to form oxalic bis-amidrazone (oxalic acid dihydrazide). Oxalic bis-amidrazone is isolated by filtering and is reacted with nitrous acid to form bis-guanylazide intermediate witch is isomerized to form 5,5'-bis-1H-tetrazole nucleus. Resulted solution can be treated to precipitate some insoluble bis-tetrazole salt (such as Mn), and precipitate can be boiled with NaOH to get pure sodium bis-tetrazolate solution. Reaction scheme is shown below:



All chemicals here are readily accessible, may be some one will give it a try?

PHILOU Zrealone - 31-3-2009 at 07:45 AM

Engager,
 Could it be possible that the cyclisation happens on the =NH hold on the other C than the one holding the N3 making thus a bicyclic compound with two hexarings based on a naphtalene skeleton (1.2.3.4.5.6.7.8-octaazanaphthalene).

It could be denser than the bis tetrazole.

Attachment: [1.2.3.4.5.6.7.8-octaazanaphthalene.pdf](#) (11kB)

This file has been downloaded 104 times

[Edited on 31-3-2009 by PHILOU Zrealone]

Engager - 31-3-2009 at 10:26 AM

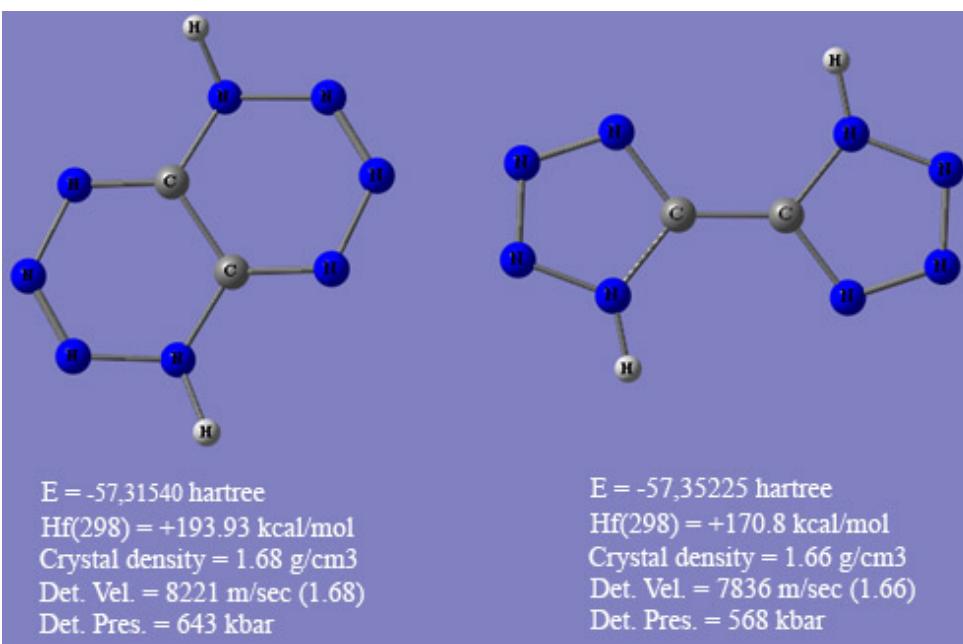
Quote: [Originally posted by PHILOU Zrealone](#)

Engager,
 Could it be possible that the cyclisation happens on the =NH hold on the other C than the one holding the N3 making thus a bicyclic compound with two hexarings based on a naphtalene skeleton (1.2.3.4.5.6.7.8-octaazanaphthalene).

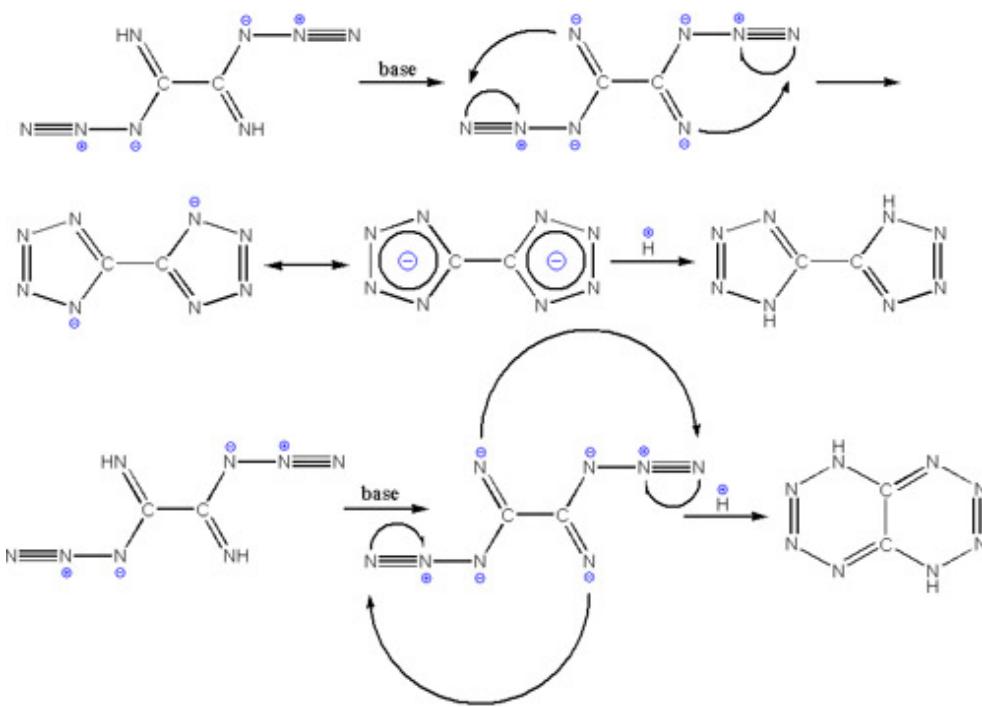
It could be denser than the bis tetrazole.

[Edited on 31-3-2009 by PHILOU Zrealone]

Yes it is probably little denser, comparsion of computed properties shown on picture below:



Mechanism of cyclization shows that cyclization to 1.2.3.4.5.6.7.8-octaazanaphthalene in presence of base may also be possible.



However 1.2.3.4.5.6.7.8-octaazanaphthalene has higher energy and heat of formation (higher thermodynamic instability), so cyclization to bis-tetrazole must be favoured. I'm not sure molecule your propose exists, but if so it must exist as small impurity in bis-tetrazole, made by cyclization of amidrazone.

[Edited on 31-3-2009 by Engager]

Microtek - 2-4-2009 at 04:31 PM

That octaazanaphthalene looks quite a lot like a reduced form of DTTO. If it happened to be even a minor product of this reaction, I think a study into possible oxidative procedures might be justified.....

User - 6-4-2009 at 01:16 PM

Well it could just be that I missed this, anyways.

Is there a significant difference in yield between using the original thiele's method, or the alternate with HCl

when forming 5-atz from AGBC.

Is there anyone who can support this with data or experimental results?

Engager - 7-4-2009 at 05:20 AM

As far as i know there are two methods leading to 5-ATZ, both described with yields in "explosive derivatives of tetrazole" article.

1. Thiele method uses aminoguanidine bicarbonate + sodium nitrite, yields are good - about 65-70%. It doesn't matter which acid you use, just need to know that corresponding salt of aminoguanidine will be in solution.

2. Schtolle method uses dicyandiamide + hydrogen azide, this method can give up to ~99% yield, but requires a lot of time, and forces to work with solution of highly toxic and volatile hydrogen azide. HN₃ was generated from NaN₃ + HCl, however other acid can also be used.

PHILOU Zrealone - 7-4-2009 at 09:18 AM



Based on the calculation of Engager:

5-NTZ: (5-nitrotetrazole)

Hf°= 83.6 kcal/mol

Density = 1.77 g/ccm

VOD max = 9059 m/s

bis-5,5'-NTZ (bis-5,5'-nitrotetrazole):

Hf°= 219 kcal/mol

Density = 1.99 g/ccm

VOD max = 9916 m/s

bis 5,5' HTZ (bis-5,5'-H-tetrazole):

Hf°= 171 kcal/mol

Density = 1.66 g/ccm

VOD max = 7836 m/s

OAN (1.2.3.4.5.6.7.8-octaazanaphthalene):

Hf°= 194 kcal/mol

Density = 1.68 g/ccm

VOD max = 8221 m/s

One can estimate the properties of dinitrooctaazanaphthalene 😊

DNOAN (dinitrooctaazanaphthalene):

Hf°= +/- 240 kcal/mol

Density = +/- 2.01 g/ccm

VOD max = +/- 10300 m/s

I'm happy to see the calculation of Engager goes in the same way as my theory of the power, density, VOD sequence ...

that follows the rule polymer > tetramers > trimers > dimers > monomer.

The sensitivity should follow the rule polymer >or= tetramers >or= trimers >or= dimers >or= monomer.

In this case the "bis-" molecules are kind of dimers of monomers 😊

[Edited on 7-4-2009 by PHILOU Zrealone]

[Edited on 7-4-2009 by PHILOU Zrealone]

[Edited on 7-4-2009 by PHILOU Zrealone]

Attachment: [DNOAN.pdf](#) (12kB)

This file has been downloaded 99 times

[Edited on 7-4-2009 by PHILOU Zrealone]

User - 7-4-2009 at 02:55 PM

Thanx engager, that's what i meant.

I was just wondering if the type of acid used would make difference in yield.

It is well known that nitric is much more expensive and only if it would result in higher yields it could be worth the extra money.]

Thou considering what you said, that it wont make a difference using HCl would be the most logical option (also because its more widely available).

Btw, would addition of "too much" carbonate be of any influence.

Might sound like a stupid question, I ask this because the acid i used is rather old and the concentration might no longer be accurate.

Is it wise to add just a little extra carbonate or leave it acidic and stick to original amounts.

Engager - 7-4-2009 at 09:53 PM

You better to determine exact concentration of your acid and recalculate requested volume, because change in amount of acid will distract whole following synth procedure. You can determine concentration of your acid by weighting empty measuring cylinder, then filling it with exactly 100 ml of acid and weighting cylinder again. This will give you a density value calculated as $(M(\text{with 100ml}) - M(\text{empty}))/100$, after determination of acid density you can use concentration/density table data to determine concentration. Then concentration of your acid is known, just recalculate volume of your acid required to get same number of moles as moles of nitric acid in original procedure.

Engager's Tetrazole Paper as pdf

Rosco Bodine - 20-9-2009 at 08:17 AM

The paper which Engager has shared with us has been converted to a pdf which is more efficient for reading and printing. Sorry for my being delayed in getting to this file conversion.
Here is the download link.

[http://sciencemadness.org/scipics/tetrazoles\(english\).pdf](http://sciencemadness.org/scipics/tetrazoles(english).pdf)

file is 8.89 MB and 31 pages Thanks to Engager for your excellent work

<http://www.youtube.com/watch?v=kLuzaKVjVxA&fmt=18> Jade Forest

[Edited on 20-9-2009 by Rosco Bodine]

Engager - 14-10-2009 at 11:00 AM

Synthetic route to tetrazoles from urea and ammonium nitrate: [In prepublication](#)

5 phenyl Tetrazole

franklyn - 15-10-2009 at 03:17 AM

The salient problem as I see it with high energy density nitrogen heterocyclic compounds is the number of steps to synthesis. The following citation outlines a synthesis of the Tetrazole moiety as depicted in the attachment below.
Apparently DMSO solvent facilitates higher yield.

[5 phenyl Tetrazole](#)

<http://www.che.gatech.edu/ssc/images/pdf%20research/synthesis.pdf>

Yields often are much higher under solvent free conditions. An advantage of using no solvent (or less solvent), is that reaction times can also be shorter. This baits the question whether acetonitrile can be substituted and provide a facile pathway to the group described in this other paper here.

1 & 2 Methyl-5-Nitrotetrazoles

<http://handle.dtic.mil/100.2/ADA099627> , refers to this next url

<http://www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA099627&Location=U2&doc=G...>

Disney, M.E. Crown Zellerbach, unpublished results, Jan. 12, 1967
The reaction of sodium azide with nitriles, such as benzonitrile,
occurs readily in DMSO to give 5-phenyl tetrazole



Rosco Bodine - 15-10-2009 at 09:51 AM

So....what are the prospects for an attempted synthesis of guanylazide fulminate 😐

other of the guanylazide salts may be interesting also

guanylazide tetrazylazide would be another possibility,

and of course guanylazide styphnate

[Edited on 16-10-2009 by Rosco Bodine]

franklyn - 16-10-2009 at 12:02 PM

On it's own the aryl compound is of no interest , unless one were to nitrate it.

I was just noting the potential of procuring tetrazole in good yield as a leaving group.

Of course if you regard this impertinent I'll refrain from doing so again.

Rosco Bodine - 16-10-2009 at 04:49 PM

franklyn, the production issue for the mad science community does not involve the number of steps being so much of an issue, but rather the issue of more concern is the facile synthesis routes, which parallels fecal synthesis routes, that is to say being able to most easily make your desired shit from mundane feedstock materials, even if the production requires that each bite be chewed twenty-three times in advance of the ultimate production of your desired shit. It really chaps my ass also that nitriles and azides are not abundantly on the shelves at the local grocer, but heyyou gotta play with the hand you are dealt. Instead of zinc dust for example, I would wonder how the reduction of nitroguanidine may alternately proceed using amalgamated sheet zinc, or amalgamated aluminum wire from electrical cable, or the electrolytical reduction possibility using a mundane material for a cathode. But probably even more pertinent I would wonder about the possibly even more facile route presented by possibly reacting any guanidine salt with hydrazine sulfate to produce aminoguanidine, or diaminoguanidine, or triaminoguanidine, dependant upon the ratio of hydrazine sulfate utilized for the reaction.

franklyn - 16-10-2009 at 11:00 PM

I'm all for obtaining novel end products from mundane feedstock.
I'm much less enthusiastic about taking the long way around to get there. We are not reduced to procuring precursors for CHNO HEDM by resorting to lumps of coal , water , and air , as often

depicted in the distopian wasteland of popular fiction.
I do know that technically it is now feasible to build a machine perhaps the size of a refrigerator the only input to which would be air, water condensed from air, and electricity, the continuous product of which would be a brisant high value explosive. Surely a novel energy storage scheme for photovoltaics. Doubtlessly there would be export restrictions on such technology.

Rosco Bodine - 8-11-2009 at 10:11 PM

Quote: [Originally posted by Engager](#) 

Synthetic route to tetrazoles from urea and ammonium nitrate: [In prepublication](#)

There's another thread we shall properly call a keeper 
I have converted that thread to a pdf for convenience in saving, portability, and/or printing that file.

Attachment: [Tetrazoles via Urea - NH₄NO₃ - precipitated silica.pdf](#) (1.8MB)

This file has been downloaded 58 times
