



[5-ATZ\(5-Aminotetrazole\), the nitrotetrazolate ion and friends](#)

The_Davster - 15-11-2006 at 10:36 PM

There has been talk of tetrazoles and precursors in several threads, usually as off-topic discussion, I thought it would be an idea to do a bit of a collection of some of this into a single thread.

The 'My favorite Primary Explosive' thread on E&W, where the nitrotetrazoles are first mentioned.

<http://www.roguesci.org/forum/other-explosives/3158-my-favourite...>

Ironically, I found this thread after I had done all my research, which as Rosco posted all the patent refs in that thread, would have made my life much easier had I found that thread before I dug through the literature looking for refs to the patents.

5-ATZ

US patents 5424449 and 5594146 detail the synthesis of 5-ATZ from hydrazine, cyanamide, nitrite and ammonia, but as aminoguanidine is an intermediate in the synthesis, one can start with it. I have read that aminoguanidine hydrochloride is used in some pills that are supposed to make you live longer, and in my opinion is much preferable to the use of hydrazine 🙄. I have not looked further into the use of such antiaging pills as I have reagent aminoguanidine. I had worked out the amounts of aminoguanidine needed to pick up the procedure in the middle, but I lost my calculations, and then found what Microtek had already done it, so from there on I used his numbers. (Much thanks, I hope you do not mind me posting your procedure)

Quote:

- 6.45 g aminoguanidinium bicarbonate was suspended in 7 mL H₂O and neutralized with 5 mL 30 % HCl (dropwise addition although it cooled down rather a lot during addition).
- pH was checked with universal indicator strips and adjusted to ca pH 4.
- Another 5.3 mL 30 % HCl was added all at once.
- A soln of 3.5 g NaNO₂ in 7.5 mL H₂O was added from an addition funnel while stirring vigorously and keeping temp at 17-20 C with an ice bath (no salt). Addition proceeded smoothly with negligible evolution of NO_x (not visible and only just detectable by smell) until the very last drops which gave the evolution of NO_x which is typical of nitrite with acid. This likely signified that all the aminoguanidine had been diazotized.
- Stirring was continued for 20 minutes at 20 C after addition was completed.
- 4.9 mL 25 % ammonia soln was added all at once (pH was measured at this point and was found to be ca 6-7), the flask was equipped with a condenser and the mix was heated to beginning reflux. It was held there for 2 hours.
- While still hot, pH was adjusted to ca 4 with HCl and ammonia water; ca 1.8 mL 30 % HCl was required.[I found I actually had to basify instead at this step]
- Mix was allowed to cool very slowly by turning off the hotplate but letting the flask stay on it. Once it had cooled to room temp, it was placed in the refrigerator until a temp of 10 C had been reached. The product crystallized in very well defined plates beginning from ca 40 C.
- Almost all the mother liquor was easily decanted from the dense crystal mass, and 12 mL of H₂O was added to remove co-precipitated chloride.
- Mix was heated to 45 C with stirring and was then allowed to cool to 10 C.
- Not all of the product was dissolved in this operation.
- Product was removed by filtration and washed several times in the filter with cool water.

Works Great! Even did a melting point(or rather, decomposition point). The crystals are quite nice, but the solution tends to super-saturate(4/5 times), so introduction of a seed crystal at around 50C is a good idea. I added one at 60-70C once, and the resultant crystals looked different, but still had the same melting point. The crystals formed when a seed crystal is introduced at this temp do not look as pretty, and they hold more water taking longer to dry, so 40-50C seems ideal.

Nitrotetrazole(ate)

US patents 4093623 and 2066954 describe the prep of acid copper nitrotetrazolate from 5-ATZ, which can then be used to make other nitrotetrazolate compounds via metathesis. Example 6 of 4093623 was carried out on a scale just slightly greater than testtube scale, giving a precipitate of CuHNT(NT)_2 . I did not let this dry as it is said to be sensitive to shock and electrostatic discharge, and my winters are very dry. The acid copper salt was reacted with NaOH solution as per example 8 in the same patent, however I am simply using a slightly acidic solution of NaNT (pH=4, as per patent directions) instead of evaporating to get sodium nitrotetrazolate crystals. However the solution has turned a light yellow/green over a couple days, so it may be advantageous to keep it basic and then acidify before using the sodium salt to make other metal nitrotetrazolates.

Speaking of which, I prepared a very small amount of silver nitrotetrazolate, which simply leaves me in awe. It reminds me of silver fulminate in terms of how small an amount of it will go DDT, even when wet. (used flame to do this). Something silver azide does not do as well. I believe Rosco calls this an "unequivocal" primary. Sensitivity is said to be relatively low, but I have done no testing of this, and likely will not. This was more of a long wonderful chemical adventure than a search for an ideal primary. 🤩 I just decided to expend so much effort into getting to this point as I really adore the structure of tetrazoles. 🤖

Others which I have no experience with to date

Azidotetrazole:

<https://sciencemadness.org/talk/viewthread.php?tid=5129>

JoPEP, 30, 2005, page 17

Looks like crazy stuff, I should try it sometime

Nitraminotetrazole:

Can be done with either making the nitrate of ATZ, then dehydrating, or by using nitraminoguanidine in the tetrazole reaction. Unfortunately nitraminoguanidine requires hydrazine.

Thermochemica Acta 384 (2002) 113-120

ATZ-nitrate:

PEP, 30 (2005) No 3 191

5-halotetrazoles:

Been meaning to research these, I want to make iodo and bromo

I intended to write more under this section, but I am tired now, more later perhaps. There is also a complete route from cyanuric acid (pool chlorine stabilizer) to tetrazoles, I know Rosco is doing some work on this as well, but I intend to put a bunch more annoying steps in to avoid the use of hydrazine. But really I have only started this part, and that would be for another thread.

I tried to attach a big review of tetrazole chemistry, but it is too big, and rapidshare is full currently. I'll post it when there is more room on rapidshare

[Edited on 16-11-2006 by The_Davster]

DeAdFX - 16-11-2006 at 12:55 AM

Phenyl cyanide + NaN_3 + $\text{NEt}_3\text{-HCl}$ is supposed to yield phenyl tetrazole. Since I do not know of good place to upload stuff I will send you the link discussing the synthesis.

Tetrazylazides

Rosco Bodine - 17-2-2007 at 09:51 PM

Liquid or plastic primaries are virtually unknown .

Ethyleneditetrazylazide is reportedly a way to do this .

I do not know of any information available concerning

synthesis of these tetrazylazides .

Attachment: [US2170943 Tetrazylazides.pdf](#) (80kB)

This file has been downloaded 580 times

The_Davster - 18-2-2007 at 03:19 AM

Is that archaic nomenclature? Could tetrazyl be the old name for tetrazoyl? Making the compound in question an 'ionic liquid' of whatever 2 molecules of 5-ATZ linked through nitrogens to the NH₂s on ethylene diamine is called, then protonated somewhere and the azide salt formed?

Or it could be a di substituted tetrazole ring...but I can't imagine a bridging ethylenediamine stabilizing any azotetrazole.

Really, I am very intrigued!

Rosco Bodine - 18-2-2007 at 03:50 AM

I don't understand the term tetrazyl either

wonder if it is equivalent to " tetrazolyl " ?

The germans used a different nomenclature and it is a bit confusing . The same thing occurs with regards to some of the other tetrazole patents . IIRC there are a few lines in COPAE about some of the different synonyms used for the same groups . Defintely encounterd this nomenclature confusion before , and it seems that it was Axt or Nick F who was good at sorting these out .

Anyway , those are reputable names on the patent , company and inventor alikeso there is likely something to this group of compounds , which they aren't saying too much about with regards to synthesis .

The attached file sheds some light on this whew what a synthesis , reserved for the skilled and not squeamish about toxic materials

[Edited on 18-2-2007 by Rosco Bodine]

Attachment: [US2179783 Tetrazylazide and Salts.pdf](#) (103kB)

This file has been downloaded 510 times

Rosco Bodine - 18-2-2007 at 04:13 AM

Here is more information expanding on that first patent

Attachment: [GB510992 Tetrazylazide Priming Explosives.pdf](#) (155kB)

This file has been downloaded 599 times

The_Davster - 18-2-2007 at 03:07 PM

From what I gather...The first German patent is only claiming an improved process for mass production of the azotetrazole...For which there are other known routes too, not involving cahones as big as would be necessary for that patent 😊

So now we are definatly getting somewhere...it is an azotetrazole. Excellent. Those are not impossible.

However the ethylene part of the molecule is still confusing.

Unfortunately, due to the standard synths of disubstituted tetrazoles, azotetrazole probably can't be used as the starting material. Unless it's an ethyl-azo disubstituted tetrazole, in which silver azotetrazole and ethyl iodide should give the product.

I wish the patent had a molecular structure for the compound...

Rosco Bodine - 18-2-2007 at 03:47 PM

Looks to me like all that is required for the ethylene derivative is to react ethylene dichloride with 2 equivalents of sodium tetrazylazide .

The basis for these salts is Tetrazylazoic Acid which seems to be hydrazoic acid which has been combined with a tetrazole ring now that should enhance the already incredible energy and also lend a greater stability if my guess is correct .

I have to wonder if the sodium tetrazylazide could be substituted for sodium azide in the azo-clathrate synthesis leading to a series of tetrazylazo-clathrates which would tame the overly sensitive straight lead tetrazylazide ...while manifesting extraordinary power .

My guess would be that the critical diameter on these tetrazylazides would be extremely smallcapillary sized det cord anybody ? Did somebody ask for explosive paint ?

This stuff should do the trick 🤖

[Edited on 18-2-2007 by Rosco Bodine]

The_Davster - 18-2-2007 at 04:11 PM

Oops, yeah, meant diiodoethane last post.

I don't know, I am a bit unsure whether what bridges the two tetrazoles is a -CH=CH- or a simple -CH2-CH2-. Archaic nomenclature can be a bit strange for such things. Either way, makes me very curious about what would happen with the -C(triplebond)C- variant, but dichloroacetylene as a starting point is...🤖. Diiodo would also probably work...

Hmm, I have some sodium nitrotetrazole crystals lying around, and diiodoacetylene is easyish to make (but rather toxic for my tastes)...I might just have a go on a variant like this... Should be safer than azotetrazole variants, as I have heard horror stories about azotetrazole. NaNT at least turns to a liquid before it dets with surprising violence.

(Rosco, thanks for bringing these up from obscurity, I had been in a chemistry slump and nothing was really catching my attention, these brought me out 🤖)

As for a substitute for NaN₃ in the azo-clathrates...Why not use both azotetrazole, and azide. 🤖 With some nitrotetrazole added to taste 🤖

[Edited on 18-2-2007 by The_Davster]

Rosco Bodine - 18-2-2007 at 04:24 PM

A cauldron full of complexes
is kind of like
a saucer full of secrets

What you get
might even trump
old Forrest Gump

with life that's like
a box of chocolates

You never really know
exactly what you are going to get ☹

I would add that a healthy dose of paranoia
would not be out of place concerning this class
of energetic materialsI'd definitely keep quantities
very small , recognizing that this sort of material is
right up there among the most energetic materials
known to science . It wouldn't take much of this stuff
doing the unexpected to do a lot of damage .

[Edited on 18-2-2007 by Rosco Bodine]

Rosco Bodine - 19-2-2007 at 01:57 AM

I was right in thinking this " tetrazyl " prefix is perhaps equivalent to " tetrazolyl " , and have been able to
further clarify exactly what it is , as well as a possibly easier method of synthesis .

The same compound having the following *six* synonymous designations is described in PATR Vol.9 , T-124, 125

5 - Azido Tetrazole , Tetrazolyl Azide , 5 - Triazo - Tetrazole ,

Diazotetrazolimide , Tetrazylazoimide ,

[Tetrazolyl- (5)] - azoimide

It is also item #2 on page 2 of the attached patent .

In COPAE , page 447 , Davis describes in more detail the method mentioned in the patent , using tetracene as
the precursor , hydrolyzed using NaOH , to form an intermediate triazonitroso-aminoguanidine which is isolated
by addition

of copper acetate producing a precipitate of bright blue colored explosive copper salt . This salt after filtering
and washing and treatment with acid (probably HCl) gives
the Tetrazolyl Azide .

So essentially , Calcium Cyanamide , Hydrazine Sulfate ,
and sodium nitriteor Aminoguanidine Bicarbonate and
sodium nitrite are the precursors for tetracene , and this
eliminates the need for more extreme and toxic cyanogen and azide reagents proposed by the Friedrich patent .

Davis cites a reference providing more on this and I will be requesting it through channels here .

The Chemistry of Aminoguanidine and Related Substances ,
G.B.L. Smith , Chem. Rev. , 25 , 214 (1939)

Attachment: [GB185555 Tetrazole Initiator Compounds.pdf](#) (286kB)

This file has been downloaded 543 times

The_Davster - 19-2-2007 at 04:16 AM

There is also a route from 5-ATZ to azidotetrazole, I have it hardcopy and will dig it up hopefully. Just need to
find my folder on the tetrazoles...its around here somewhere.

Looks fun: <https://sciencemadness.org/talk/viewthread.php?tid=5129>

I also have JoPEP,30, 2005, page17 written down as a ref for them.

But for now, uploaded is the chemistry of aminoguanidine file you wanted:

I should move this out of the complex thread and into the tetrazoles thread I started a while back. Fine with you? These aren't really complexes....

EDIT: Crap, too big to attach here, I rapidshare.COM ed it
http://rapidshare.com/files/17182917/The_Chemistry_of_Aminoguanidin...

[Edited on 19-2-2007 by The_Davster]

The Chemistry of Aminoguanidine and Related Substances

Rosco Bodine - 19-2-2007 at 05:05 AM

Here's a smaller file

Thanks to kmno4

And yes any alternate routes are of interest .

Actually there are only a few of these tetrazoles of particular interest as most of them have been evaluated and ruled out for oversensitivity or other reasons .

Funny you should post that link for the thread about the acetic acidand yeah I was thinking about what was mentioned about the incompatibility , realizing that the copper precipitate of the nitroso derivative of tetracene must be formed in alkaline solution , and then separated from the sodium acetate in alkaline supernatant and filtrate , carefully rinsing out any acetate from the copper precipitate , *before* acidifying or else a nasty surprise awaits 😬

It would really be nice to have a more forgiving method , which doesn't involve copper saltsmaybe a calcium salt for example .

[Edited on 19-2-2007 by Rosco Bodine]

Attachment: [cr60081a003.pdf](#) (975kB)

This file has been downloaded 854 times

5-azidotetrazole via Ba(OH)₂ hydrolysis of tetracene

Rosco Bodine - 3-3-2007 at 11:04 PM

Thanks to Joeychemist and solo for this helpful reference .

See the last paragraph on page 5 ,
Alkaline degradation of IX (tetracene monohydrate) .

Evidently simply boiling tetracene with a base hydrolyzes it with the expulsion of one ammonia , and leads to ring closure and formation of 5-azidotetrazoleperhaps (hopefully) being present as the soluble 5-azidotetrazole salt of sodium , in the case where the base used for the hydrolysis is sodium hydroxide . This should simplify greatly the synthesis of 5-azidotetrazole where it is needed as an intermediate which will not be isolated , knowing

that it is produced *directly* by the alkaline hydrolysis of tetracene .

This finding is in contrast with what Davis reported on COPAE concerning the incorrectly alleged intermediate triazonitroso-aminoguanidine identified mistakenly by Hofmann via elementary analysis , whose composition was actually identical with the monohydrate copper salt of 5-azidotetrazole .

An interesting side note concerning the related derivative of tetracene , 5-aminotetrazole . I have read in PATR , tetracene quietly decomposes / converts completely to 5-aminotetrazole by nothing but gentle heat being applied to the sample of tetracene for several days , @90C less than 3 days .

[Edited on 4-3-2007 by Rosco Bodine]

Attachment: [The Structure of Tetracene.pdf](#) (778kB)

This file has been downloaded 591 times

The_Davster - 4-3-2007 at 03:04 AM

Excellent!

For the aminotetrazole though....90C for 3 days? Reflux diazotized aminoguanidine in ammonia for 3h...82% yields. Tried and true.

Rosco Bodine - 4-3-2007 at 04:11 AM

Yeah it is in PATR under " Tetrazene " , an Australian government study found that stab detonators containing tetracene would fail to function after storage at elevated temperatures because of the tetracene slowly changing to 5-aminotetrazole by thermal decomposition . They stated complete conversion at 90C in less than 3 days .

With regards to the reaction of the 5-azidotetrazole sodium salt with methyl or ethyl sulfate or chlorides , I wonder if other esters such as the nitrate or nitrite esters would work as well , or if the nitrite ester might lead to something different . I especially wondered about the reaction possibility for the nitrite esters since they are so easily made .

Rosco Bodine - 8-3-2007 at 09:47 PM

There is probably a workable general route to the useful energetic tetrazoles and related materials which uses OTC precursors .

The production of Calcium Cyanamide or Zinc Cyanamide or Magnesium Cyanamideor perhaps some mixture of these cyanamides which might form more readily by pyrolytic decomposition of their cyanurate precursors , could then be reacted with Hydrazine Sulfate to form aminoguanidine as the intermediatewhich is then reacted with sodium nitrite or perhaps nitrosated , " diazotized " by other methods , and depending upon the pH at which this is done , the product is guanyl azide , or tetracene , or 5-aminotetrazoleby variations upon the process .

Guanyl Azide Picrate is itself another useful , stable and powerful energetic material which is satisfactory for use as a base charge in detonators .

To any of these products then can be applied subsequent treatments to obtain the desired tetrazole compound .

IIRC , the Zinc Cyanurate is the material which is converted at a somewhat lower temperature to the desired cyanamide . It still requires a low red heat , but this should be reachable without too much difficulty , in a rudimentary sort of furnace , or even in an open fire or over a burner .

A preliminary experiment I did seemed to produce the desired cyanurate precursor , but I haven't yet fired this material to see if the cyanamide is produced as expected , however it should work as this reaction is mentioned in several patents .

<https://sciencemadness.org/talk/viewthread.php?tid=2762&page=1#pid57...>

Tetracene can be produced from the reaction of the alkaline earth cyanamide and hydrazine sulfate , without isolation of the aminoguanidine intermediate , by treatment of the reaction mixture with NaNO_2 . I have a patent concerning this and I will find it and attach it later .

I expect there are perhaps a dozen different energetic materials which are of reported value , maybe half of those of special interest among this class of compounds .

[Edited on 8-3-2007 by Rosco Bodine]

The_Davster - 8-3-2007 at 10:26 PM

I actually made a dozen grams or so of the calcium cyanurate. In another post you say it decomps to HOCN. That should instantly combust at the required temps hopefully right? No toxic death cloud? 🤖

[Edited on 8-3-2007 by The_Davster]

Rosco Bodine - 8-3-2007 at 11:18 PM

Right ...cyanic acid should burn off , and then extinguish as the excess cyanic acid comes off at a lower temperature stage of the decomposition where the cyanurate is probably converted first to a straight cyanate .

The evolving cyanic acid vapor might not ignite within an electric furnace being gradually heatedbut it should ignite in a flame fired environment for sure . If you are using a metallic vent line , simply discharging it onto the flame of a small burner used as a pilot light should flare it off okay . If you wanted to bubble any offgassing into alkaline water you should use a trap or checkvalve to prevent any suckback of the liquid when the rate of gas evolution slows .

IIRC , The cyanuric acid is actually a trimer of cyanic acid , thermally decomposeda parallel sort of material as is trioxane and formaldehyde . Anyway , after the alkaline earth cyanurate is decomposed to its normal cyanatethe "extra" HOCN is goneand further decomposition as the material reaches red heat , evolves only CO_2 and when it finishes offgassing CO_2 all that should be left is pure white Calcium Cyanamide .

Of course this would not be a commercially viable process because it is counterintuitive to sort of reverse engineer the usual products of a process along a tangent to get back to an intermediate 🤖 in our case the alkaline earth cyanamide .

But for a lab scale approach to how easiest to take an

OTC material like chlorine stabilizer , cyanuric acid , and produce pure calcium cyanamide or other pure cyanamides from itthis would seem the most probable candidate as a method , doing a straightforward thermal decomposition of an intermediate which should produce nothing else but the desired product .

Attached is a patent describing the conditions for reaction of calcium cyanamide with hydrazine sulfate to form aminoguanidine in solution , and a filterable form of calcium sulfate residue by control of pH which influences the crystalline form of the of the calcium sulfate byproduct .

The aminoguanidine solution in this patent process is then neutralized with H₂SO₄ to form a solution of aminoguanidine sulfate , to which is added baking soda to precipitate insoluble aminoguanidine bicarbonate which is filtered out .

But you see at the point where the aminoguanidine freebase or sulfate is available in aqueous solution , other things can be done to obtain different products if aminoguanidine bicarbonate is not the desired end product .

Guanyl Azide or its salts , or tetracene , or 5-aminotetrazole , or other materials may be obtained by further reactions upon the aminoguanidine intermediate without any need for its isolation .

[Edited on 9-3-2007 by Rosco Bodine]

Attachment: [US3673253 Aminoguanidine Bicarbonate via Calcium Cyanamide and Hydrazine Sulfate.pdf](#) (385kB)

This file has been downloaded 512 times

5-Nitroaminotetrazole from 5-Aminotetrazole

Rosco Bodine - 10-3-2007 at 12:18 AM

The 5-aminotetrazole nitrate dehydration to form the 5-nitroaminotetrazole has been described as a somewhat analogous reaction to the dehydration of guanidine nitrate to form nitroguanidine . The conditions must be carefully controlled and the temperature kept low due to instability of the amino group of the amino tetrazole , which will be oxidized under too severe conditions . The free acidic 5-Nitroaminotetrazole should probably not be isolated as the dry material but left in solution , or converted to one of its more stable salts .

There are a few ways of doing the conversion directly from 5-Aminotetrazole , not requiring its nitrate as an intermediate . Attached is a patent which describes 5-Aminotetrazole being dissolved in concentrated H₂SO₄ and then nitrated with fuming (90%) HNO₃ added dropwise @20-25C , the mixture drowned over crushed ice and then neutralized with NH₄OH to precipitate the diammonium ? salt of 5-Nitroaminotetrazole . Other salts can be made from this . See page 4 , Column 5 , Example 1 .

Alternately to using the mixed acid , a Japanese patent JP11279164 describes that the nitration can be accomplished by addition of NH₄NO₃ to the solution of 5-Aminotetrazole in concentrated ? H₂SO₄ . Since I am unable to read Japanesethe details of the method are unclear . But it appears that the process is otherwise similar .

According to the reactions shown in the Japanese patent and also other English language references , the free acidic 5-Nitroaminotetrazole is obtained in solution by treatment of the ammonium or sodium salt with HCl .

The potassium salt is the salt specified for use in the reaction for producing " Stabanate " , the double lead salt of 5-Nitroaminotetrazole and Styphnic Acid , which is a patented US3310569 initiator having superior stability and 50% higher brisance in the sand test than lead styphnate . It is reportedly satisfactory for use as an initiator in detonators , although its performance in that regard is not disclosed .

[Edited on 15-3-2007 by Rosco Bodine]

Attachment: [US5516377 5-Nitroaminotetrazole by nitration of 5-Aminotetrazole.pdf](#) (521kB)

This file has been downloaded 510 times

Here's an older related journal reference

Rosco Bodine - 10-3-2007 at 01:01 AM

The Nitration of 5-Aminotetrazole

Attachment: [The nitration of 5-aminotetrazole.pdf](#) (398kB)

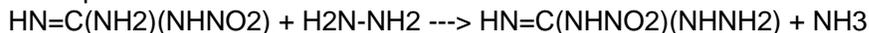
This file has been downloaded 537 times

Sobrero - 10-3-2007 at 11:43 AM

I have prepared 7.25g nitroaminoguanidine as follows: (Patent US2617826)

(hydrazine sulfate was made with Mr. Anonymous's recipe, nitroguanidine was made from homebrew guanidine nitrate)

200ml water was heated to 60°C and 11g NQ were added while stirring. 15.3g hydrazine sulfate, 100ml water and 6.90g NaOH were mixed and stirred until everything had gone into solution. This solution was slowly poured into the agitated and heated NQ-solution/suspension. Heating (60°C) and stirring was continued during half an hour. After 15 minutes all the NQ had dissolved. The liquid turned orange and during the experiment I smelled ammonia:



So after these thirty minutes, the solution was neutralised with concentrated hydrochloric acid (approx. 6ml HCl 29% was used). The liquid was allowed to cool to 5°C (fridge) and was left so for one hour for full precipitation of the NAQ (the colour... how should I say: slightly pale yellow - "blanc cassé" - light off-white colour?), . It was then filtered and washed with two portions of 15ml cold distilled water. Dried at 80°C. Yield: 7.25g or 57.6% yield.



BTW: I added two teaspoons of sodium nitrite and 10ml GAA to the filtrate. A very light foaming occurred (no smell or colour, I gess it's nitrogen) and after a few hours I noticed a white somewhat fluffy precipitate. I filtered it, washed it with some water and let it dry. Unfortunately it only burns (no deflagration or something energetic). Does anyone have an idea what this stuff is?

Now, can someone give some help for the synthesis of nitroaminotetrazole and nitroguanyl azide (starting from NAQ off course). The only documents I found was [Reaction of nitrous acid with nitroaminoguanidine](#) and [Ultraviolet absorption of 5-NATZ and it salts](#) but as can be seen no specific reaction conditions, weights, procedure, ... are given. PATR (page A259-260) is not very helpfull too

[Edite le 10-3-2007 par Sobrero]

Rosco Bodine - 10-3-2007 at 04:08 PM

Quote:

Originally posted by Sobrero

Now, can someone give some help for the synthesis of nitroaminotetrazole and nitroguanyl azide (starting from NAQ off course). The only documents I found was [Reaction of nitrous acid with nitroaminoguanidine](#) and [Ultraviolet absorption of 5-NATZ and its salts](#) but as can be seen no specific reaction conditions, weights, procedure, ... are given. PATR (page A259-260) is not very helpful too 😞.
[Edite le 10-3-2007 par Sobrero]

(Edit)

Nitroaminoguanidine is evidently an alternate precursor for nitroaminotetrazole .
The other path would be to reduce the nitroguanidine using zinc , to get aminoguanidine , and then nitrosation , followed by cyclization to 5-aminotetrazole and nitration as described earlier .

The entire article may provide some additional information concerning the alternate route described in the abstract which you just linked for nitroaminotetrazole from nitroguanylazide . I will request that article .
(Edit : See complete article attached in following post)

Nitroaminoguanidine can be nitrosated to form nitroguanylazideby a similar method as is used for conversion of aminoguanidine to guanyl azide .

The following excerpt US6350307 , page 9 , column 15 , line 30 , concerns guanyl azide

Preparation of Guanyl Azide

An initial charge of technical grade hydrochloric acid and distilled and demineralized water is indirectly cooled down to about 0.degree. C. Aminoguanidine bicarbonate is subsequently added at about 10.degree. C. in the course of about 30 minutes. Thereafter, the batch is indirectly cooled down to about 0.degree. C., and sodium nitrite solution is added up to max. 15.degree. C. in the course of about 3 hours. This is followed by stirring with nitrite excess for 15 minutes. Directly prior to transfer of the azo groups, the nitrite excess is removed with amidosulphonic acid.

A Ukranian patent (attached) describes this , including isolation of the product . There is an English summary on page 2 .

Abstract of UA16960U

A method for producing nitroguanilazide and derivatives thereof comprises nitrosation of N-nitro-N'-aminoguanidine (NAG) in the aqueous medium in the presence of sulphuric acid by potassium nitrite at a molar ratio of and providing water excess of 1.48 l H₂O/mole of NAG at the temperature of with subsequent keeping the reaction mixture at the room temperature during specified time, evaporation of reaction mass during a long time at the same temperature, three-stage extraction of solid remainder by anhydrous diethyl ether at the amount of 1.2 l (C₂H₅)₂O per 1 mole of output NAG, evaporation of ether remainder and obtaining nitroguanilazide (NGA) with an output of 77 %. At that for nitrosation nitrites of alkaline and alkaline-earth metals - MNO₂ (M=Na, Li, K, 1/2Ca, 1/2Mg, 1/2Ba, 1/2Sr) are used at a molar ratio of as acid H₂SO₄, HNO₃, H₃PO₄, HBr are also used, it is carried out at cooling, the reaction mass is filtered and cooled, keeping it in these conditions for 5-10 hours, the residue is filtered, dried and nitroguanylazide is obtained with an output of 40-55 %, and aqueous solution after filtration of NGA is extracted by diethylether at an amount of the extract is evaporated and additional amount of NGA is obtained (15-40%).

But I would not recommend isolation of the nitroguanyl azide , as much as I would personally have interest in the possible picrate , given that the analogous (non-nitro) guanyl azide picrate is already known and has been observed to be stable , and useful as a base charge for detonators . The possibility exists that the *Nitroguanyl azide picrate* , having its additional nitro group would also be interesting , and hopefully have adequate stability along with greater power than the already known " ordinary " guanyl azide picrate .

[Edited on 15-3-2007 by Rosco Bodine]

Attachment: [UA16960 Nitroguanylazide Ukranian patent.pdf](#) (279kB)

This file has been downloaded 425 times

Nitrosation products of Nitroaminoguanidine

Rosco Bodine - 10-3-2007 at 11:07 PM

The Reaction of Nitrous Acid with Nitroaminoguanidine

Here is the entire article associated with that single page linked above .

Attachment: [The Reaction of Nitrous Acid with Nitroaminoguanidine.pdf](#) (435kB)

This file has been downloaded 630 times

Rosco Bodine - 14-3-2007 at 01:21 AM

Here's an aminotetrazole related primary

Attachment: [US3663553 Di-Silver Aminotetrazole Perchlorate.pdf](#) (101kB)

This file has been downloaded 517 times

more metal complex salts

Rosco Bodine - 14-3-2007 at 05:26 PM

This patent has a few interesting complex salts , and also provides some citations of references which may be of more general interest .

Attachment: [US5962808 Metal Complex Oxidizer Salt Gas Generants.pdf](#) (538kB)

This file has been downloaded 598 times

5,5'-Diazoaminotetrazole

Rosco Bodine - 14-3-2007 at 09:14 PM

Also called

Bis(tetrazolyl)-5)-triazene ,

1,3-Bis(1H-tetrazolyl-5)-triazene ,

I,III,-Di-(tetrazolyl-5)-triazene ,

1,3-Di-[tetrazolyl-(5)]-triazene

The sodium salt is obtained by nitrosation of aminoguanidine dinitrate or aminoguanidine sulfate , by dropwise treatment with NaNO₂ solution added to a sodium acetate and acetic acid buffered solution of the aminoguanidine salt at 15C . 5-aminotetrazole by the same treatment gives the same product . The sodium salt is reportedly not explosive , but leads to other metallic salts by metathesis , which are explosive . The lead salt , and the lead double salt with lead styphnate are particularly interesting .

See PATR vol. 9 page T-121

Lead-5-5'-Diazoaminotetrazolate Styphnate is reportedly an " ideal replacement " for lead azide .

[Edited on 19-3-2007 by Rosco Bodine]

Attachment: [US2064817 Manufacture of Diazotized Tetrazole Derivatives.pdf](#) (98kB)

This file has been downloaded 479 times

Rosco Bodine - 14-3-2007 at 09:18 PM

US2090745 describes the single
Lead 5-5'-Diazoaminotetrazole salt

[Edited on 14-3-2007 by Rosco Bodine]

Attachment: [US2090745 Lead 5-5'-Diazoaminotetrazole.pdf](#) (93kB)

This file has been downloaded 452 times

The " Stabanate " patents

Rosco Bodine - 14-3-2007 at 09:30 PM

One of the useful things which can be done with
nitroaminotetrazole

US3310569

Crystalline Double Salt Pb Styphnate and Pb Nitroaminotetrazole

GB1069440 British patent same subject

Attachment: [US3310569 Stabanate.pdf](#) (506kB)

This file has been downloaded 432 times

Azotetrazole , 5,5'Azotetrazole

Rosco Bodine - 15-3-2007 at 03:05 AM

See PATR , Vol.1 , A-569

The sodium salt is produced in 76% yield from a solution of
5-aminotetrazole in 15% NaOH at 50C by oxidation with KMnO4 solution added dropwise . Unreacted KMnO4 is
decomposed with alcohol , and the solution is refluxed for 1 hour at 100C . On cooling the sodium salt is obtained as
crystals .

Attachment: [US5877300 5-5'azotetrazole and derivatives.pdf](#) (153kB)

This file has been downloaded 467 times

Lead Azotetrazole

Rosco Bodine - 15-3-2007 at 03:29 AM

Here is a British munitions patent for the
lead salt of 5,5'-Azotetrazole

Attachment: [GB986631 Lead Azotetrazole.pdf](#) (176kB)

This file has been downloaded 448 times

5-Nitrotetrazole

Rosco Bodine - 16-3-2007 at 04:42 PM

This is one of the energetic tetrazoles which is a bit trickier to make because of an unstable intermediate diazo compound involved in its formation . A special technique has been devised for avoiding explosion of the unstable intermediate which otherwise is problematic , and this special method has been further refined and described in a subsequent patent .

[Edited on 16-3-2007 by Rosco Bodine]

Attachment: [US2066954 C-Nitrotetrazole Initiator Compounds.pdf](#) (338kB)

This file has been downloaded 484 times

5-Nitrotetrazole improved method

Rosco Bodine - 16-3-2007 at 04:47 PM

This patent studies and refines the synthesis of 5-Nitrotetrazole , improving the safety and yields .

Attachment: [US4093623 Copper Salt intermediate for 5-Nitrotetrazole.pdf](#) (469kB)

This file has been downloaded 473 times

Copper Ammonium Salt of Diazoaminotetrazole

Rosco Bodine - 16-3-2007 at 05:44 PM

While on the subject of copper salts of tetrazoles

Here's an interesting one which I haven't run across before

It seems possible that similar ammonium salt could be possible for silver , zinc , iron , cobalt , chromium and nickel .

[Edited on 16-3-2007 by Rosco Bodine]

Attachment: [US2004719 Copper Ammonium Salt of Diazoaminotetrazole.pdf](#) (190kB)

This file has been downloaded 491 times

The_Davster - 16-3-2007 at 06:18 PM

Ok threads merged.

Rosco, thanks for posting all the patents and articles, I know I made mention of a few in the first post, but having them all in one spot online is really convenient.

" Green Primaries "

Rosco Bodine - 16-3-2007 at 06:33 PM

There is a double salt formed from either sodium or ammonium nitrotetrazole , combined with either copper or iron nitrotetrazole as a stable dihydrate .

These compounds are presently being investigated as relatively non-toxic replacements for lead azide and lead styphnate containing compositions which have been the established standard primaries in use for many decades .

Attachment: [Green Primaries 1.pdf](#) (662kB)

This file has been downloaded 502 times

Present State of the Art

Rosco Bodine - 16-3-2007 at 06:42 PM

More of the same from Los Alamos

concerning the so called
" Green Primaries "

<http://www.sciencemadness.org/scipics/Green Primaries 2.pdf> (2.96 MiB)

[Edited on 25-3-2007 by Rosco Bodine]

Tetrazole Double Salts

Rosco Bodine - 16-3-2007 at 07:12 PM

Quote:

*Originally posted by
The_Davster*

Ok threads merged.

Rosco, thanks for posting all the patents and articles, I know I made mention of a few in the first post, but having them all in one spot online is really convenient.

Thanks for merging these threads .

You are welcome concerning the file collection . I was making a dedicated folder of tetrazole related files and decided to share the folder with summary notes and commentary to save others covering the same ground .

It's long overdue to collect most of the pertinent tetrazole related references in one place . I tried not to hop around too much , but to keep the related files together in some intelligent sequence , or as close as I could keep 'em somewhat topically collated .

I still think tetrazoles deserves a sticky thread status , to keep from digging it up when it gets pages behind , and avoid a lot of new lookups or newcomers or the lost posting new topics that are already right there on top in an existing thread .

They are sort of the " top dawg " energetic materials so as suchon top is not out of place as a place for the topic for them to be 🍷

Anyway , back on topic ...

As a general rule it has been the case that many of the energetic tetrazoles are not satisfactory alone as initiators , for being too sensitive , or not having the desired crystalline form and densityhowever the same tetrazole salts also

as a general rule form double salts , either combining with other tetrazole salts as in the above described " green primaries " , or in forming basic salts , or some combined basic salts where a basic metal tetrazole is coprecipitated with a basic picrate or a basic styphnate . Some of these combined salts may have desirable properties which is more than just the simple sum of the precursors properties observed separately . There are only a few of these combined salts reported , which I have been able to find anyway , so there could be many different possible mixed salts , or even possibly "tetrazo-clathrates" 🍷 , which have not been reported , and some of these materials could have excellent properties as initiators . The idea is not new , and the attached patent gives some insight into one method of coprecipitation , where the combined solution of the sodium salts of the acidic energetic tetrazoles and/or other acidic energetic materials is run into a solution of the lead salt or other metallic salt , resulting in a coprecipitation of the mixed salt . There are other strategies for the formation of mixed salts , but this is a good one as a starting point for such experiments .

[Edited on 16-3-2007 by Rosco Bodine]

Attachment: [US1580572 Tetrazole Double Salts.pdf](#) (143kB)

This file has been downloaded 443 times

The_Davster - 16-3-2007 at 09:35 PM

US patent 4093623 in regards to the synth of nitrotetrazoles is the one which I found to work well, albeit a large volume and a volumous sludge of a precipitate of the Cu-nitrotetrazole. Gravity filtration should not even be considered, and a small ammount of final yield comes from a large volume of sludge necessitating a disporportionately large buchner funnel for filtration. This is what severly limits all nitrotetrazole synthesis that I have read.

It appears the green types or primarys are starting to come on the market, in the form of nontoxic primers.

<http://www.sellier-bellot.cz/nontox-cartridges.php?product=10>

No idea the composition though...

Rosco Bodine - 17-3-2007 at 01:01 AM

I don't know if this has already been tried or not .

Something from the " Green Primaries 1 " development may be applicable here , so that instead of the acid copper salt of nitrotetrazole being the intermediate , which has filtration problemspossibly the crystalline " green primary " double salt , $\text{Na}_2[\text{Cu}(\text{NT})_4] \cdot 2\text{H}_2\text{O}$ could be produced directly . If workable this would avoid having to digest the acid copper nitrotetrazole with caustic soda to produce the sodium salt and then subsequently reacting that with copper nitrate to form the double salt " green primary " .

Possibly using Copper Nitrate , easily made from copper carbonate and HNO_3 if necessary , and using HNO_3 for the mineral acid would be better than using the copper sulfate and sulfuric acid . These would simply be substituted in the method of US4093623 , in proportions which would favor the formation of the double salt " green primary " .

Running the two solutions of equal volume simultaneously and slowly in separate equal streams into the mixing and reaction vessel might give a denser precipitate .

The completed addition mixture is held at reflux for five hours and cooled for crystallization in the synthesis reported for the green primary $\text{Na}_2[\text{Cu}(\text{NT})_4] \cdot 2\text{H}_2\text{O}$, and that extended heating is possibly for crystal growth , as I would expect the actual chemical reaction is not sluggish , but rapid .

I have not performed this reaction so I have no direct knowledge of this or what may happen . It very well could be that simply holding the acid copper nitrotetrazole precipitate of the US4093623 patent at a high temperature of say 95C or so for several hours might cause sufficient crystal growth to produce a readily filterable product . It is understandable how there may be some reluctance to subject these materials to digestions at elevated temperatures ☹ , for fear of that proverb involving curiosity and cats being realized , as much as any expectation of improvement on a process .

However , von Herz did report conversion of the acid copper salt to the sodium salt and copper oxide , under the condition of elevated temperature , provided by " boiling aqueous suspension with soda lye (NaOH) " . See US2066954 , page 2 , line 3 .

Of course the acid copper salt had been filtered and rinsed free of excess acid prior to this treatment , but even so this would indicate that possibly the pH could be adjusted for a

" one pot synthesis " of the copper based
" green primary "and also that the temperature
could possibly be raised somewhat in hopes of obtaining a more easily filterable acid copper salt by the
method reported in the patent .

Another thought I had is that possibly ammonium nitrate , could be used for decomposition of the excess NaNO_2
for either reaction strategy . This could possibly not work however because of the possibility of complexation of
the ammonia with the copper .

Quite a few things to ponder about this one , and only some experiments would tell the tale on these things .

Update: attached is the " patent pending " application from
the same inventors concerning several of the green primaries

[Edited on 19-3-2007 by Rosco Bodine]

Attachment: [US2006030715 Complex Nitrotetrazole Primary Explosives.pdf](#) (316kB)

This file has been downloaded 500 times

A possible simplified method for aminoguanidine

Rosco Bodine - 23-3-2007 at 01:27 PM

While studying these tetrazole patents ,
I found a related matter mentioned in a patent
US5041661 (attached) ,
concerning the production of aminoguanidines ,
where the use of guanidine nitrate is described
as the precursor reacted with 1, 2, or 3 moles
of hydrazine to form mono , di , or triaminoguanidine nitrate .

The reaction follows the same course essentially as when
nitroguanidine is reacted with hydrazine to form nitroaminoguanidinebut using guanidine nitrate
leads to a non-nitro , plain aminoguanidine product .

It seems likely that aminoguanidine bicarbonate could be made and isolated from the reaction mixture of
any soluble guanidine salt with hydrazine sulfate having been digested for a time at the appropriate pH ,
then treated with CO_2 or sodium bicarbonate .

If possible , this would eliminate having to convert guanidine nitrate to nitroguanidine and reduce to obtain
the aminoguanidine . Reacting the guanidine nitrate or any other soluble guanidine salt with hydrazine should
give the aminoguanidine directly 

The patent only describes the reaction as being applicable
for the nitrate salt of guanidine , but it would seem to me
likely that any guanidine salt should work as well .

Evolution of ammonia would be a sure sign the reaction is proceeding , if it goes as expected .

If workable this would provide a convenient alternative precursor for those who have a guanidine salt available ,
but do not have cyanamide .

Attachment: [US5041661 Aminoguanidine , Diaminoguanidine or Triaminoguanidine via Guanidine Nitrate
and Hydrazine.pdf](#) (285kB)

This file has been downloaded 528 times

More of interest concerning triaminoguanidine

Rosco Bodine - 23-3-2007 at 02:34 PM

It is known that aminoguanidine forms from the reaction of calcium cyanamide and hydrazine sulfate .

The inference I get from reading descriptions of these reactions , is that the mono-aminoguanidine being formed will subsequently add further amino groups to form diaminoguanidine and triaminoguanidine , in the same reaction system , depending upon the availability of additional hydrazine for formation of the higher , poly-aminoguanidines .

Dicyandiamide will reportedly depolymerize in such a reaction system , to provide the mono-cyanamide component , reacting with three hydrazines to form triaminoguanidine . See US3285958 attached . Possibly also the level of amination of the aminoguanidine produced is also dependant upon the quantity of hydrazine available for reaction by this method , and it may be possible to secure the mono-aminoguanidine nitrate , (or other acid salt) simply by adjusting the quantity of hydrazine available in the reaction system to be only sufficient for the desired product .

While the monoaminoguanidine salts are of special interest as tetrazole precursors , the Triaminoguanidine salts are stable , powerful , useful high explosives also , the nitrate and the picrate are initiator sensitive secondary high explosives , and the perchlorate is a fuse sensitive HE primary which is probably useful as either an initiator or as a single component charge in detonators . A chlorate salt and other energetic salts have also been mentioned , but their properties have not been described in any of the references I have seen .

Attachment: [US3285958 Triaminoguanidine Nitrate from Dicyandiamide and Hydrazine.pdf](#) (298kB)

This file has been downloaded 436 times

chemoleo - 23-3-2007 at 09:51 PM

I just love these nitrogen-rich compound reactions!

The patent mentions the condensation of phenylhydrazine and dicyandiamide. Interestingly, dinitrophenylhydrazine is a common reagent for ketone detection, and thus should be possible to obtain relatively easily. A condensation with dicyandiamide should give (dinitrophenyl-NHNH)2C=N-NH-(dinitrophenyl), or possibly a nitrate salt thereof. Thus a potentially very interesting combo-energetic compound, being a nitrate salt, containing N-N bonds, and nitrophenyl moieties! Not many EM's could claim that!

Diazoguanidine (guanylazide)

Rosco Bodine - 25-3-2007 at 03:10 AM

Guanylazide is also called Diazoguanidine or Azidoformamidine .

As an intermediate for 5-aminotetrazole the guanyl azide is not isolated but is cyclized with ammonia .

Freeform Guanylazide is unstable and is only isolated as its stable salts .

The guanylazide picrate has been mentioned earlier on the first page of this thread . It has been patented US2125462 (attached) for use as a base charge in detonators .

Possibly the styphnate could also be interesting , as styphnic acid could bond with *two* of the guanylazide groups and unless it tended towards formation of a hydrate , it should be more powerful than the picrate . It would also seem possible the formation of a basic lead guanylazide styphnate , and also possible though perhaps less likely , a sort of double salt or complex salt of normal lead styphnate and guanylazide styphnate .

The nitroguanylazide is interesting too , but I have not found any reference describing its explosive properties , except that it is explosive . Whether or not the nitroguanylazide forms stable explosive salts similarly as does

the guanylazide is unclear .

Linked below are some other threads which contain information relevant to this thread with regards to precursors and intermediates , particularly of interest being methods based on OTC materials . This list will be lengthened here and/or further along in this thread as time passes .

OTC Cyanamide

<https://sciencemadness.org/talk/viewthread.php?tid=825>

Guanidine

<https://sciencemadness.org/talk/viewthread.php?tid=1469>

Cyanuric Acid

<https://sciencemadness.org/talk/viewthread.php?tid=8160>

[Edited on 25-3-2007 by Rosco Bodine]

Attachment: [US2125462 Guanylazide Picrate Base Charge.pdf](#) (120kB)

This file has been downloaded 450 times

Referring to "Green primaries 1"

pdb - 29-3-2007 at 09:39 AM

I am considering preparing some of the primaries listed in the "Green primaries 1" paper available upper in this thread. However, I have two questions before going further:

- the ferrous complex requires $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$: I have been searching chem databases for a while, and I didn't find this 6-hydrate chloride, but the 4-hydrate form only. And I don't think it's a typo in the article. If the molar ratio is respected, do you think it could make a difference ?
- is it known if such green primaries are unequivocal ?

Rosco Bodine - 29-3-2007 at 10:58 AM

I could be wrong but I would expect that any soluble Iron compound could be substituted in these syntheses , and also for the copper and ammonium variants . I see no reason why such substitutions would cause any problem .

I would avoid the acetates and other organic acid salts completely if possible ☹ Nitrates would be my first choice .

I believe there is something in the articles which mentioned about a hundredfold variation in the explosiveness , dependant upon the substituents for the complex . I'd have to go back and read it again but I'm sure it is there because I wondered what would be the effect of a potassium substituent on the level of hydration , and couldn't find anything . I figured it was something that they were looking at also within the experiments that are no doubt still a work in progress .

[Edited on 29-3-2007 by Rosco Bodine]

The_Davster - 13-6-2007 at 12:42 AM

A previous limitation in the prep of nitrotetrazoles from 5-ATZ was the nature of the acid copper nitrotetrazolate salt, $\text{Cu}(\text{NT})_2\text{HNT}$, $(\text{NT}=\text{CN}_5\text{O}_2^-)$

This patent here: <http://www.freshpatents.com/Primary-explosives-dt20060209ptan20060030715.php> mentions: "Ammonium nitrotetrazolate was prepared by diazotization of 5-aminotetrazole in the presence of excess nitrite followed by extraction as the tri-laurylamine salt and displacement by ammonia. Upon addition of stoichiometric amount of ammonium hydroxide, sodium nitrotetrazolate forms quantitatively and is

analytically pure."

I have seen nothing in the literature on such a synthesis, I wonder if it is some sort of in-house method at LANL or something?

Axt - 13-6-2007 at 01:46 AM

I've tried to find a detailed direct prep. and isolation for the sodium salt before but was met with much frustration as no authors give details, rather refer it off to the attached article, which refers it off to the unobtainable reference:

Gilligan, W. H., and Kamlet, M. J., Technical Report 76-146 (1976), Naval Surface Weapons Centre, White Oak Labs, Silver Spring, Md, U.S.A. [Microfiche AD A036 0861.

Some info can be gleaned from the attachment though.

"1 H-Tetrazol-5-amine monohydrate was converted into sodium 5-nitrotetrazolate dihydrate by diazotization in the presence of excess nitrite according to the method of Gilligan and Kamlet."

"Sodium 5-nitrotetrazolate dihydrate was prepared from tetrazol-5-amine hydrate according to the method of Gilligan and Kamlet. The product was purified by dissolution in the minimum of boiling acetone followed by filtration and precipitation by addition of an equal volume of hexane. The solution was allowed to cool and the product filtered under suction. Compound was obtained as irregular, chunky white crystals; ignition temp. 202°, 210°, 214° (lit. 202°)."

So, anyway. The action of sodium nitrite on the intermediate diazonium salt. It seems like no copper ion needed.

[Edited on 13-6-2007 by Axt]

Attachment: [Studies of stab initiation. Sensitization of lead azide by energetic sensitizers.pdf](#) (633kB)

This file has been downloaded 390 times

Microtek - 13-6-2007 at 04:05 AM

I converted the copper salt to the sodium salt by dissolving it in warm water (it is quite soluble at elevated temps) and adding a stoichiometric amount of NaOH soln to precipitate Cu(OH)₂. Then I kept the suspension at 80-90 C until the hydroxide had decomposed to the oxide to facilitate filtering. Gentle evaporation of the filtrate gave the hydrated sodium nitrotetrazolate.

The_Davster - 13-6-2007 at 08:49 AM

Quote:

Originally posted by Axt

The action of sodium nitrite on the intermediate diazonium salt. It seems like no copper ion needed.

I find that rather odd, the copper ions are added to prevent detonations from diazotetrazole formed from small droplets of the acidic 5-ATZ solution on the walls of the reaction vessel from reacting with the NO_x given off by the reaction and forming the diazotetrazole in percents greater than 2 which spontaneously explode in solution. I wonder what they use to prevent this?

US patent 4093623 and an older, unimproved version, 2006954, detail the process of producing the copper nitrotetrazolate, and from it the sodium salt.
from 4093623;

"During initial experimentation with the von Herz procedure by the U.S. Navy, several problems were encountered. First, during the diazotization there was a continuous series of minor detonations, which while not harmful in themselves, were psychologically disturbing and did on occasion break glassware. Moreover, there was the possibility that the potentially dangerous (in the dry state) acid copper 5-nitrotetrazole salt would be spilled over adjacent surfaces as a result of these detonations. Second, upon completion of the diazotization,

the acid copper salt was present as a voluminous gel-like precipitate which required long periods (6 hours or longer) to separate by filtration and to wash free of impurities. This would seriously hamper scale-up operations where large quantities would have to be processed."

Also, as I found a few days ago, the gel like nature of the copper salt can be reduced by doing the addition of 5-ATZ, acid, and trace copper over 3h or so, as opposed to 1.5h as detailed in the patent.

Interesting note at being unable to find synthesis refs Axt, I also been finding that there are often voids of information about these types of compounds.

[Edited on 13-6-2007 by The_Davster]

Nick F - 17-7-2007 at 09:13 AM

I can't remember if I've mentioned this before (and this connection is too slow for me to bother looking), but I have a fair amount of 5-aminotetrazole. I'd be happy to sell/trade some to anyone who's interested...

JohnWW - 17-7-2007 at 11:25 AM

How are you going to be able to legally send such an highly explosive compound through the post? BTW How did you acquire or make the stuff?

Nick F - 17-7-2007 at 01:28 PM

It seems fairly benign to me. If you heat it on a spoon for example it will decompose slightly energetically, but I certainly wouldn't call it explosive. The nitrate salt is pretty cool, if you powder it (probably not very safe!) and soak a bit of NG into it then it's impressive, to say the least... As for how I acquired it, well, that's a secret 😊.

The_Davster - 17-7-2007 at 07:42 PM

lol I remember from an old post on roguesci how you got it...you trickster you 😊. 1kg yes?

Aminotetrazole is non explosive, it decomposes non-explosively at around 205 C IIRC.

I have a hundred or so grams of aminoguanidine, so I am happy, I doubt I will ever need more for the small scale experiments I do.

Nick F - 17-7-2007 at 07:55 PM

Wow, I'd almost forgotten about roguesci! I remember that when I got the stuff I was wondering if I could do a decyclisation to get an azide. But then I got myself some of that, too. Scamming became almost an addiction at one point! 😊

(2kg 😊)

Engager - 17-8-2007 at 11:44 PM

Quote:

*Originally posted by
The_Davster*

A previous limitation in the prep of nitrotetrazoles from 5-ATZ was the nature of the acid copper nitrotetrazolate salt, $\text{Cu}(\text{NT})_2\text{HNT}$, ($\text{NT}=\text{CN}_5\text{O}_2^-$)

This patent here: <http://www.freshpatents.com/Primary-explosives-dt20060209ptan20060030715.php> mentions: "Ammonium nitrotetrazolate was prepared by diazotization of 5-aminotetrazole in the presence of excess nitrite followed by extraction as the tri-laurylamine salt and displacement by ammonia. Upon addition of stoichiometric amount of ammonium hydroxide, sodium nitrotetrazolate forms quantitatively and is analytically pure."

I have seen nothing in the literature on such a synthesis, I wonder if it is some sort of in-house method at LANL or something?

I've made NH₄NTZ solution in such method: dissolve Cu salt with excess of Ba(OH)₂ in water, boil until CuO settles down, filter it off and measure weight to calculate amount of nitrotetrazole ion in solution. After this add solution of (NH₄)₂SO₄ (1 mole for 1 mole initial Ba(OH)₂), filter insoluble BaSO₄ and you have NH₄ salt solution with some dissolved ammonia, which is removed by boiling. Although i'm not isolated NH₄ salt i found that it is very soluble. Also i found that conditions on which NH₄NTZ and Fe salts are mixed, are important. After addition of FeCl₂ and 2h boiling i got no preprecipitate. But then i dissolved CoSO₄ or CuSO₄ in sample taken from solution, i got pink or blue precipitate of corresponding nitrotetrazolate. On addition of K₂CO₃ to sample and slight heat i got ammonia smell. So i concluded that solution contains NH₄ nitrotetrazolate, so my reagents are ok. Some special conditions are needed to form NH₄FeNT salt. I'm sure in that. Also i found that in patent they use Fe(ClO₄)₂ instead of FeCl₂ used in green primaries article. Perchlorate anion very unlikely goes to inner sphere of complex compound, so this change may have some reason, may be to assist complex formation or to minimize side reactions, but i am not sure.

[Edited on 11-9-2007 by Engager]

Engager - 26-8-2007 at 01:48 AM

I have succeeded making 5-nitotetrazole - ammonium complex NH₄CuNT. Compound formula (NH₄)₂[Cu[NTZ] 4(H₂O)₂]. I've made it by following method: Solution of 5.5g ammonium 5-nitrotetrazolate in 38 ml of water added with stirring to solution of 2.52g Cu(NO₃)₂·6H₂O in 110 ml H₂O. A small quantity of blue precipitate is formed immediately. Solution was heated on boiling waterbath for 4 hours, solution becomes transparent blue. It's slowly cooled to room temperature and after to 10C in freezer. Large quantity of blue "snowy" precipitate is formed, solid is filtered off, washed with ice cold water and with small portion of ice cold alcohol. Product was air dried. Photo of product shown below:



According to patent data, density is 1.94 g/cm³, detonation velocity 7390 m/sec (at 1.71 g/cm³). Insensitive to spark up to 0.36 J (human activity generates up to 0.25 J), sensitive to shock 23 cm (vs 9.6 PbN₃ and 14 PETN), slightly sensitive to friction 0.6 kg (vs 0.01 PbN₃ and 5.8 for PETN). Thermally stable up to 265C, detonation products volume is about 750 l/kg, products of explosion: N₂, CO₂, H₂O, ~2% NO₂, ~3% CO. Oxygen balance (CO) is zero. Substance is stable on air, light and moisture. Almost completely safe then wet, even with open flame. In dry state flame contact takes DDT (deflagration-detonation transition).

I've also tried Fe and Co complexes. Attempt with FeCl₂·6H₂O was unsuccessful, as i've mentioned in previous post. Attempt with Co(ClO₄)₂·6H₂O gave success but yield was low. I guess there are some special conditions that need to be satisfied then making Fe and Co complex 5-nitrotetrazolates.

[Edited on 26-8-2007 by Engager]

Engager - 26-8-2007 at 02:15 AM

Quote:

Originally posted by Rosco

Bodine

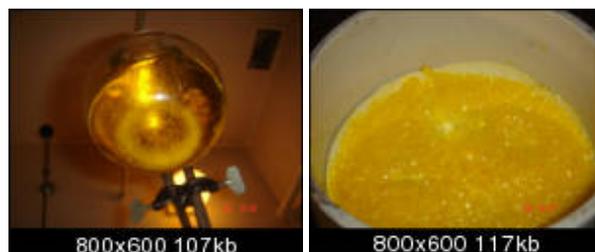
See PATR , Vol.1 , A-569

The sodium salt is produced in 76% yield from a solution of 5-aminotetrazole in 15% NaOH at 50C by oxidation with KMnO₄ solution added dropwise . Unreacted KMnO₄ is decomposed with alcohol , and the solution is refluxed for 1 hour at 100C . On cooling the sodium salt is obtained as crystals .

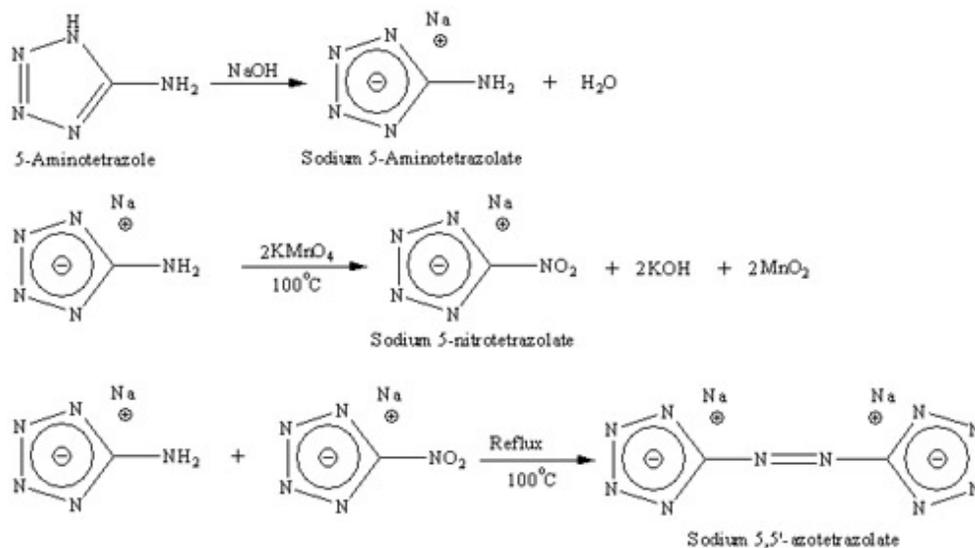
Synthesis of Na-5,5'-Azotetrazolate

Method was tested with success. 5-Aminotetrazolate monohydrate (10 g) was dissolved with stirring in 40 ml

of 15% aqueous NaOH solution at 50°C (dissolves almost permanently, solution is colorless). Another solution of 10 g of KMnO₄ in 50 ml of hot distilled water was prepared. The aqueous KMnO₄ solution was then added slowly into the stirred aqueous NaOH solution of 5-aminotetrazolate monohydrate (small gas evolution and heating were observed). Resulting solution is dark green with some brown precipitate. Into this mixture 10 ml of ethanol was added to react with excess KMnO₄, solution color is turned to brown/black. Then, the reaction solution was refluxed at 100° C. for 1 h. The resulting reaction mixture was then filtered. Upon cooling, yellow crystals of sodium 5,5'-azotetrazolate dihydrate (SZT) crystallized from the filtrate gradually. The crude product was recrystallized and dried to give 9.13 g (76.4%) of pure SZT. Photo of product crystallizing under mother liquor, and solid product on filter shown here:



Reaction scheme:



[Edited on 11-9-2007 by Engager]

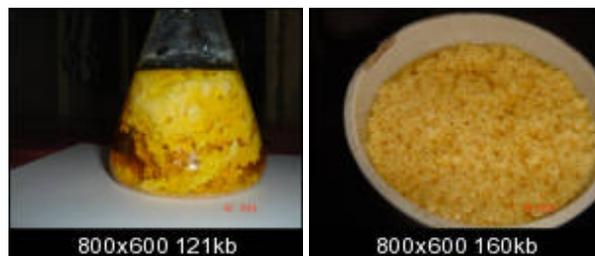
Engager - 10-9-2007 at 02:47 AM

I've also made two other tetrazole-based energetic compounds. Diazoaminotetrazole and dihydrazinium 5,5'-azotetrazolate (mentioned as substance with highest known positive heat of formation).

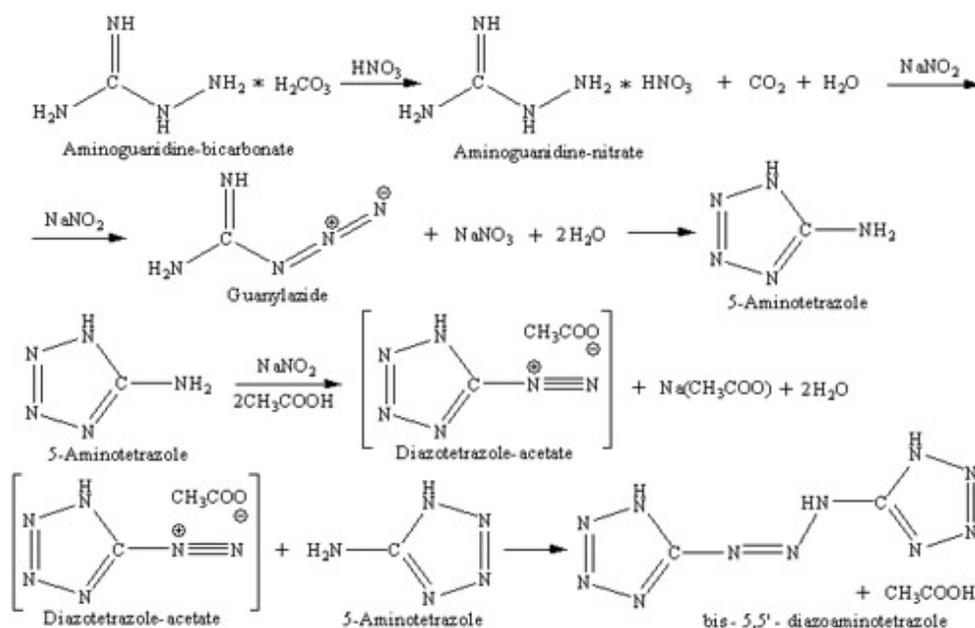
Synthesis of sodium bis-5,5'-diazoaminotetrazolate from aminoguanidine bicarbonate

Prepare mixture of 11.5 ml 70% nitric acid with 100 ml of water, add by portions with stirring 24.8g aminoguanidine bicarbonate. Stir mixture until CO₂ evolution stops and then add 20.4 ml 70% acetic acid. Mixture is stirred and slightly heated until all solid dissolves. The resulting clear yellow solution is solution of aminoguanidine nitrate in 12-13% acetic acid. This solution is cooled in freezer to 3-4C, well mixed and placed on ice bath. Slowly, with stirring, by small portions at time ice cold solution of 17.5g sodium nitrite in 75 ml of water is added. While addition, temperature must be all times kept below 12C, perfectly in interval of 5-7C, process takes about 30-40 minutes. After diazotation is finished mixture is removed from ice bath and left to stand at room temperature for 24 hours. Some time after removal from ice bath slow evolution of

nitrogen begins, and mixture can heat up to 25C, this is ok, so don't worry, and after about 12-16 hours of standing evolution of nitrogen stops and large amount of diazoaminotetrazole precipitates. Solid is filtered off, washed with ice cold water slightly acidified with acetic acid and left to dry at room temperature. Yield is about 50% of pure mono-sodium salt of diazoaminotetrazole. Photos of product shown below:



Reaction scheme:



[Edited on 11-9-2007 by Engager]

franklyn - 10-9-2007 at 10:36 AM

Ooh very nice , this one is certainly worth pursuing. Azotetrazolate is a dianion , its salts can have two cations or ligands. It too would be interesting to see if a polymer resin can be formed with formaldehyde.

Quote:

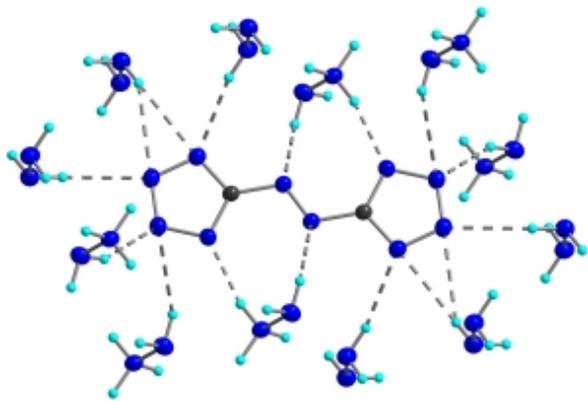
Dihydrazinium 5,5'-Azotetrazolate

Synthesis in water produces yellow needles of the dihydrazinium salt $[\text{N}_2\text{H}_5]_2:[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]$. Heat of formation is + 1147 kcal kg one of the highest ever reported. The compound is stable at

room temperature, almost insensitive to friction and impact, but detonates violently when the explosion is initiated, e.g., by rapid heating over the decomposition temperature or by using an initiator.

5,5'-azotetrazolate salts show the remarkable insensitivity to electrostatic discharge, friction and impact while having a very high heat of formation.

Dihydrazinium 5,5'-Azotetrazolate Dihydrazinate Complex



<http://pubs.acs.org/cgi-bin/abstract.cgi/inocaj/2001/40/i14/abs/ic0...>

US patent 5877300

Preparation of guanidinium 5,5'-azotetrazolate

Variations on tetrazolates _

[Ionic Liquids as Energetic Materials](#)

<http://stinet.dtic.mil/cgi-bin/GetTRDoc?AD=ADA464308&Location=U2&do...>

Engager - 10-9-2007 at 11:07 AM

I've already made dihydrazinium azotetrazolate. I can post method of synthesis with photos if somebody interested. It's yellow needle like solid, soluble in water.

[Edited on 11-9-2007 by Engager]

Engager - 10-9-2007 at 11:27 PM

Synthesis of dihydrazinium 5,5'-Azotetrazolate (HZT)

Prepare solution of 4.8g sodium 5,5'-azotetrazolate in 30 ml boiling water and 5.58g barium chloride dihydrate in 15 ml of boiling water. Solutions are mixed and stirred, precipitate of barium 5,5'-azotetrazolate forms immediately, solution is cooled to 10C and filtered. Ba salt is washed with small amount of ice cold water and dried at room temperature. Yield is about 6.2g.

Make solution of 5.3g hydrazine sulphate ($N_2H_6SO_4$) in 155 ml of water, 6.44g of barium hydroxide is added with stirring, and after 6.2g of barium 5,5'-azotetrazolate is added. Mixture is well stirred for 1 hour, solid ($BaSO_4$) is filtered off and discarded, resulting in yellow solution of dihydrazinium 5,5'-azotetrazolate. Solution of HZT is placed on boiling water bath and heated until most of water evaporate and first crystals of HZT form. Solution is then removed from water bath and cooled to room temperature and after in freezer to 10C. Mixture almost completely solidifies to form yellow needles of dihydrazinium 5,5'-azotetrazolate dihydrate. Crystals are filtered off and dried at room temperature. Yield is about 87%. Anhydrous salt may be obtained by drying dihydrate in vacuum exicator at 100C for 2 days.

I've already made dihydrazinium azotetrazolate. I can post method of synthesis with photos if somebody interested. It's yellow needle like solid, soluble in water. Photos shown below, left photo is barium azotetrazolate, two others are dihydrazinium azotetrazolate (HZT):