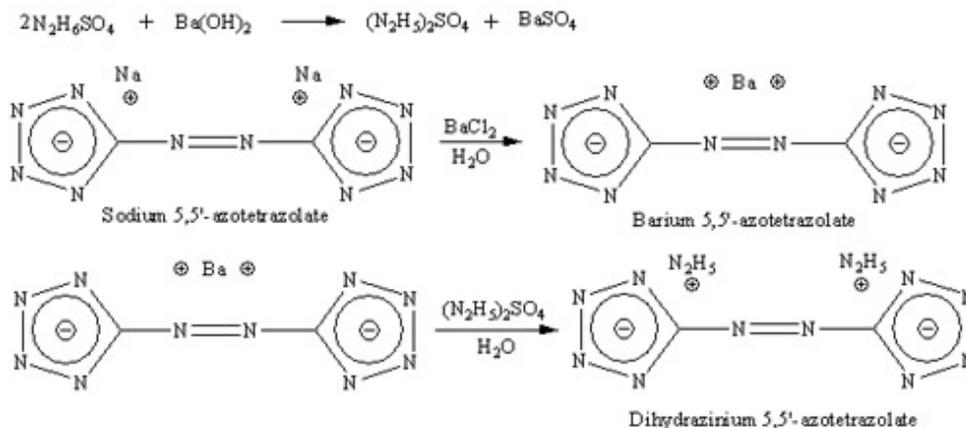




Reaction scheme:



[Edited on 14-9-2007 by Engager]

The_Davster - 11-9-2007 at 12:13 AM

Quote:

Originally posted by Engager

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

What is the reference for this procedure? I have not come across it, and I have read much of the azotetrazolate literature.

Quote:

Originally posted by franklyn

It too would be interesting to see if a polymer resin can be formed with formaldehyde.

If the chemistry is analogous to that of nitrotetrazole, an alcohol will be formed, in the case of nitrotetrazole $\text{NO}_2\text{CN}_4\text{CH}_2\text{OH}$ is formed

[Edited on 10-9-2007 by The_Davster]

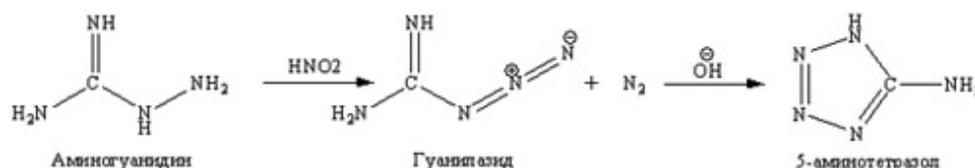
Engager - 11-9-2007 at 12:45 AM

Synthesis of 5-Aminotetrazole (ATZ)

Thiele method. 34g aminoguanidine-bicarbonate is dissolved in 217 ml of 15% nitric acid (36ml of 70% HNO_3 + 185 ml water). Mixture is stirred until CO_2 evolution stops and all solid dissolved. Resulting solution is

diazotized by solution of 17.2g sodium nitrite in 35 ml of water. Nitrite solution is added slowly with stirring, while reaction mixture is cooled on ice bath, temperature must all times kept below 20-25C. Diazotation is proceeding smoothly with negligible evolution of NOx, if mixture is foaming (result of HNO2 decomposition), addition must be paused and mixture must be well stirred to stop foaming, before new portions of nitrite added. Addition takes time about 10-15 minutes. After addition of nitrite is completed, mixture is allowed to sit for 20 mins at room temperature, and 29g of Na2CO3 (or 46g of baking soda) is added by portions with mixing. Mixture is stirred until CO2 evolution stops and all excess of bicarbonate fully dissolves. Mixture is placed to round bottom flask with attached reflux condenser and boiled for 4 hours. Resulting solution of 5-aminotetrazole is acidified by 30% H2SO4 to pH=4, and left to cool to room temperature. Usually crystallization of product starts around 40C, but solution has great tendency to supersaturate. If after cooling to room temperature crystallization is not started, seed crystal of aminotetrazole is introduced (made by placing glass rod with drop of solution to alcohol), or inner side of flask (below solution of course) is rubbed with glass rod with intense friction. After crystallization is started solution is left at room temperature for 12 hours, and cooled to 10C in freezer. Crystals of 5-aminotetrazole are filtered, slightly washed with ice cold water and dried at room temperature. Yield is 13.6g (64%). Photo of product will be shown at bottom of post.

Reaction scheme:



Schtolle method. **Warning!!!** This method includes work with extremely dangerous, explosive and highly toxic hydrogen azide. Concentration of its solution must be kept below 20% all the times because of severe explosion hazard (<20% are explosion safe). All work must be done with good ventilation, and fumes must not be inhaled in any circumstances (HN3 is very volatile, and is effective protoplasmic poison, causes blood cells decomposition and severe headaches). Never add sodium azide to cold acids solutions - it may result in condensation of drops rel. conc. HN3 on cold walls of flask, and can explode with extreme violence. Method of synthesis is optimized for maximum safety, but precautions must be remembered all times. Dissolve 10.5g of dicyandiamide and 16.25g of sodium azide in 250 ml of water heated to 50C. Mixture is stirred until all solid dissolves, and 2.15 ml of 36% HCl is added dropwise with stirring, mixture is left at room temperature for 12 hours, then, after heating to 50C 4.3 ml of 36% HCl is added in same way, mixture is left for 6 hours, next 6.45 ml and 2-3 hours, and finally remaining 8.6 ml of 36% HCl. After addition is completed mixture is left standing at room temperature for 1 week, white crystals of 5-aminotetrazole must appear, but solution again may be supersaturated and no crystals are precipitated - in this case crystallization must be started as written in Thiele method above. Yield depends of standing time and purity of reagents, I have ~50% (10.5g) yield after 2 weeks of standing, but literature sources show yields up to 97% after longer standing. Pure snow white crystals of 5-aminotetrazole are filtered off, washed with ice cold water and dried at room temperature.

Reaction scheme:



Photos of products are shown below. Left photo is ATZ made by Thiele's method, and right one is photo of ATZ made by Schtolle's method:



[Edited on 11-9-2007 by Engager]

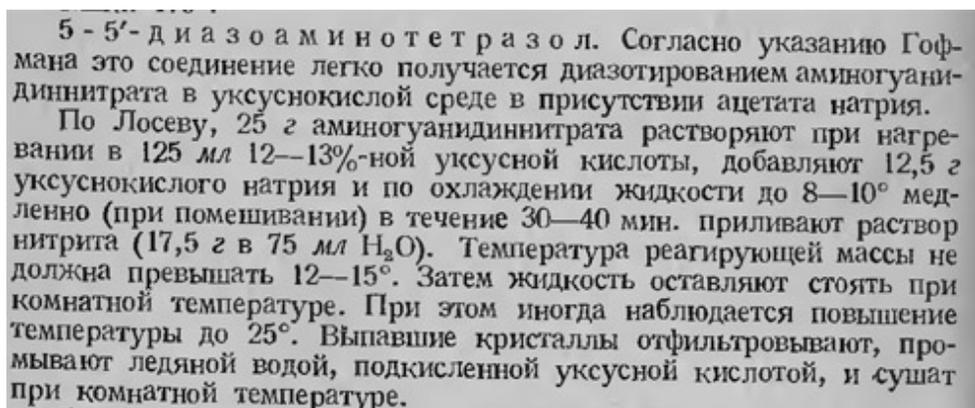
Engager - 11-9-2007 at 01:02 AM

Quote:

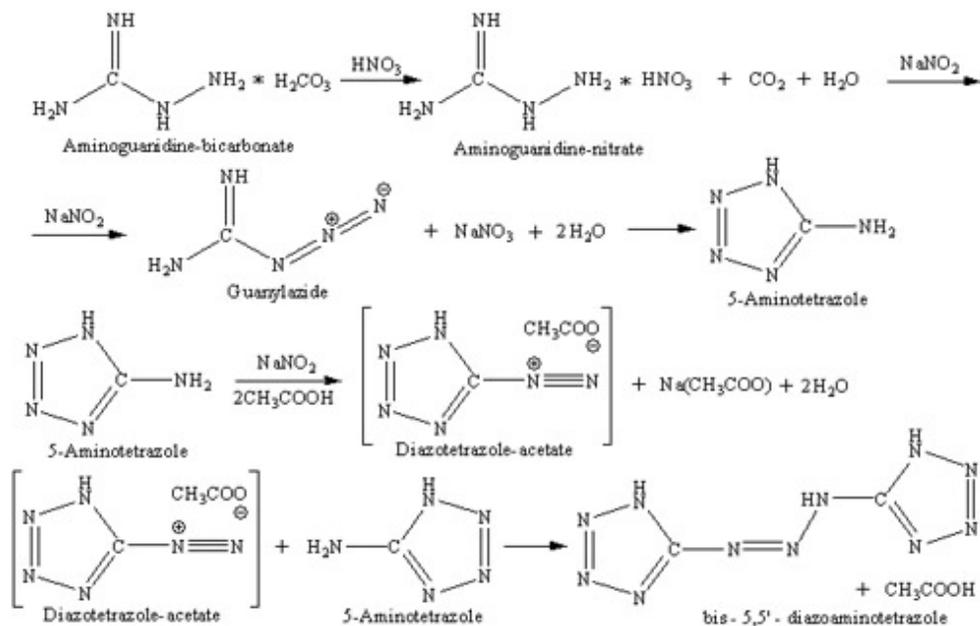
Originally posted by
The_Davster

What is the referance for this procedure? I have not came across it, and I have read much of the azotetrazolate literature.

Reference is russian book: Бубнов П.Ф. Иницирующие взрывчатые вещества и средства инициирования (часть 1). М., 1940. [P.F.Bubnov "Primary explosives and prime devices(part 1)" Moscow, 1940.] page 316



Original method uses aminoguanidine nitrate as starting material, i have modified it to generate it in situ from aminoguanidine bicarbonate. Method was tested by me with success, photo is evidence if you don't believe. Also i want to post reaction mechanism so no further explanation will be required:



[Edited on 11-9-2007 by Engager]

Engager - 11-9-2007 at 01:54 AM

Somebody interested in synthesis procedures for BNCP [Tetraamino-cis-bis(5-nitro-2H-tetrazolato-N2) cobalt (III) perchlorate] and NH₄CuNT [5-nitro-1H-tetrazolato-N2 cuprate (II)], both newest edge priming explosive materials?

[Edited on 11-9-2007 by Engager]

artem - 12-9-2007 at 09:22 AM

Quote:

[quote/]

..dihydrazinium salt [N₂H₅]₂:[N₄C-N=N-CN₄]. Heat of formation is + 1147 kcal/kg one of the highest ever reported...

Calculated value H=+1147kcal/kg (1105kJ/mole) is doubtful. Different estimations give no more than +715...750KJ/mole (743...779kcal/kg).

For example,

condensed polyacetylenes 2055kcal/kg(C₄H₂), 1570(C₄N₂)

azides 1467(HN₃), ~1490(C(N₃)₄), ~1400 for C₂N₄(N₃)₂, N₃CN₄H, 1100-1200(C₃N₃(N₃)₃).

tetrazole 817

Rosco Bodine - 13-9-2007 at 06:41 PM

It's nice to see interest in experimentation with these tetrazoles  Nice crystals 

Some thoughts ...

There are a few related things which may be worth looking into , which were mentioned on the preceding page .

There are possible shortcuts to aminoguanidine from reaction of any guanidine salt with hydrazine via hydrazine sulfate . See US5041661 . And also possibly dicyandiamide reaction with hydrazine sulfate may produce aminoguanidine . See US3285958 .

Guanylazide styphnate , and nitroguanylazide styphnate could also be very interesting 

As styphnic acid is a di-acid , the neutral salts would actually be (di)guanylazide styphnate , and likewise for the (di)nitroguanylazide styphnate salt . There probably would be a basic lead salt for the mono-guanylazide styphnate and also for mono-nitroguanylazide styphnate .

Also the synthesis of aminotetrazole might produce higher yield via tetracene intermediate .

[Edited on 14-9-2007 by Rosco Bodine]

Engager - 14-9-2007 at 06:37 AM

Synthesis of acid copper 5-Nitrotetrazolate (CuNT) from 5-aminotetrazole

Prepare solution 20.8g sodium nitrite and 11g of copper sulphate (CuSO₄*5H₂O) in 60 ml of hot water, resulting solution contains copper nitrite and has dark green color. Prepare solution of 10.3g aminotetrazole (ATZ) and 0.4g CuSO₄*5H₂O in 12.8 ml 70% nitric acid + 120 ml of water. Diazotetrazole is intermediate in nitrotetrazole synthesis, it can explode in solution if concentration will reach 2% from the slightest stimulus, even at 0C. Microexplosions are not dangerous but acting on nerves. To completely avoid them, slow addition, effective stirring and careful temperature control are essential. Small addition of copper sulphate to ATZ solution is essential to avoid microexplosions in drops, on contact with nitrogen oxides, escaping from reaction mixture. Copper nitrite solution is placed on ice bath and cooled to 5C, then solution of ATZ in nitric acid, is added slowly with stirring (perfectly drop by drop). During addition temperature of reaction mixture must be kept below 15C all times. If mixture begins to foam, addition is paused and mixture is well stirred until foam disappears before next portions of ATZ solution are added (foaming is result of HNO₂ decomposition to water and NO_x if it's concentration is too high). Reaction is proceeding smoothly, without microexplosions, with small evolution of NO_x, if conditions are carefully controlled. Whole addition process takes time about

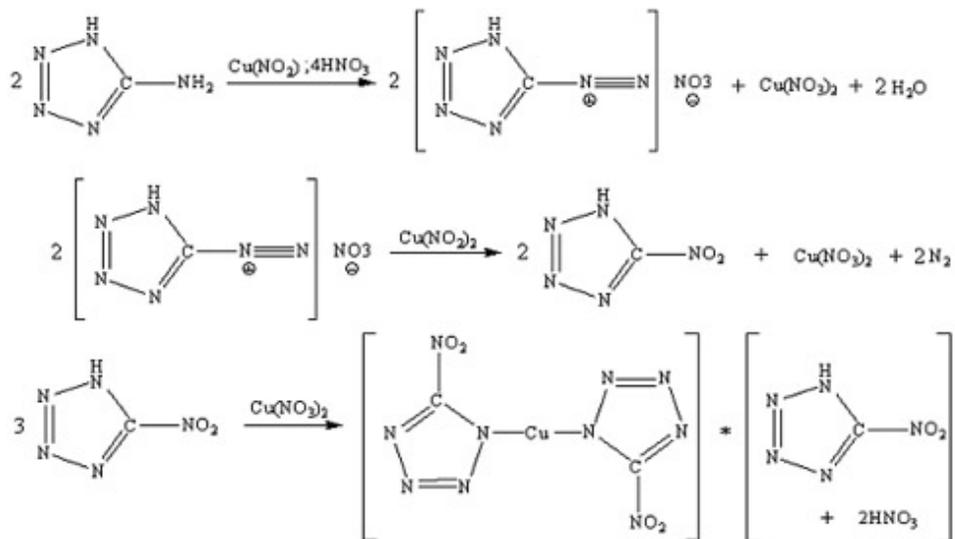
1.5 hours. Close to end of addition mixture becomes thicker, and changes color to green- blue (similar with homemade $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$). After addition is completed mixture is left to sit in ice bath for 15 minutes, after that 14 ml of 70% nitric acid + 6 ml of water is added with stirring. Reaction mixture is left for 1 hour, solid precipitate of acid copper salt of nitrotetrazole is filtered off, washed with 5.72 ml HNO_3 + 44 ml H_2O and with three portions of 50 ml H_2O . Yield is about 85%. Product is bluish - green crystals, almost insoluble in cold water.

Warning!!! Acid copper salt of nitrotetrazole is powerfull and sensitive explosive. It is almost completely safe then wet, but in dry state it can explode violently on friction, impact or heating. Safety precautions must be remembered all times.

Below are the photos of process. Left photo shows solutions of copper nitrite (left one) and ATZ in nitric acid with CuSO_4 added (right one). Photo in the middle shows ice bath with sitting reaction flask, and termocouple temperature control. Right photo shows reaction product on filter.



Reaction sheme:



Acid copper salt of nitrotetrazole can be easily converted to soluble salts of nitrotetrazole by heating in solution of corresponding hydroxides. For example solution of sodium 5-nitrotetrazolate can be prepared by boiling acid copper salt in NaOH solution: $\text{Cu}(\text{NT})_2 \cdot \text{HNT} + 3\text{NaOH} \Rightarrow 3\text{NaNT} + \text{CuO} + 2\text{H}_2\text{O}$. Solid black copper oxide is removed by filtering, pure solution of NaNT can be concentrated to separate solid salt, or can be used directly for further reactions.

[Edited on 14-9-2007 by Engager]

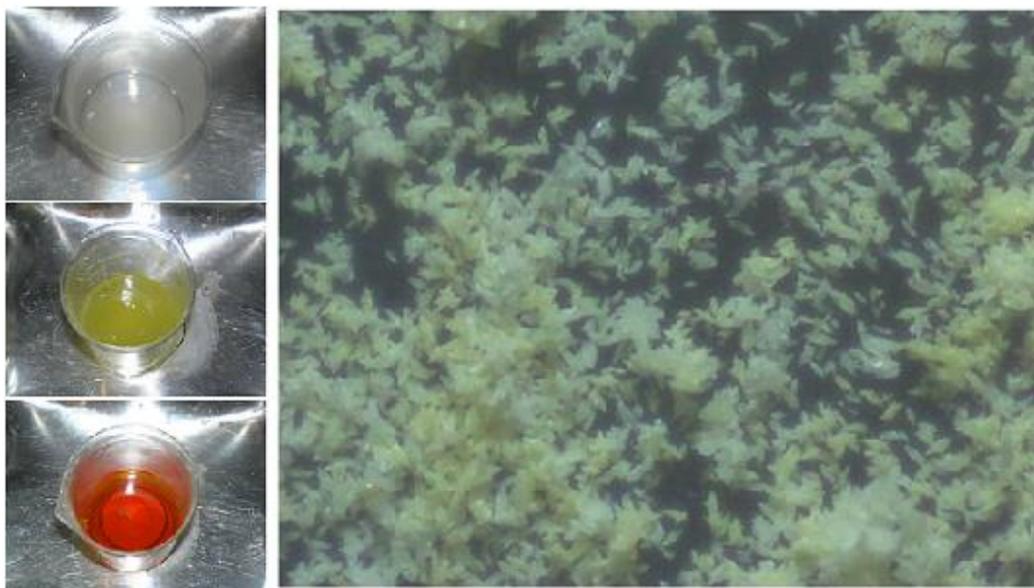
Axt - 28-9-2007 at 06:29 AM

Excellent posts Engager, but just a suggestion, dont use imageshack or other free hosts as inevitably within

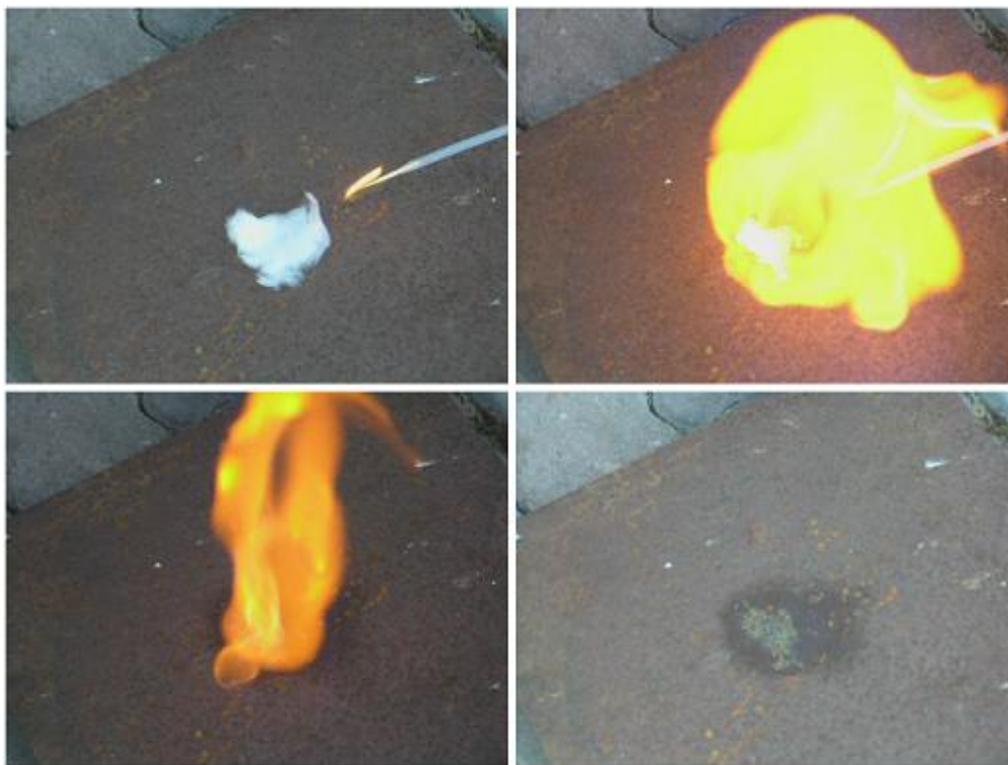
a month or two they will all end up dead links. Instead either attach them directly or to embed them in the text use the [forum pic ftp](#) setup specifically for this purpose. What program did you use to draw the reaction schematics?

I recently prepared 5-nitraminetrazole. Its properties given in Chem. Mater. 2007, 19, 1731-1739 are quite remarkable, its density via gas pycnometry is 2.06g/cm which gives a calculated VOD of 10358m/s using the "Cheetah 4.0" program of LLNL. JACS, 73(5), 2327-2329 mentions that it is a sensitive explosive, though this is disputed by J. Org. Chem., 18(8), 941-945, saying that it won't explode when struck "very sharply" on an anvil with a hammer. Though they don't say if they were testing the sensitivity of the hydrated or anhydrous acid. That's another problem with nitraminetrazole, it retains solvent of crystallisation and water of hydration though this is said to be lost on standing at room temperature.

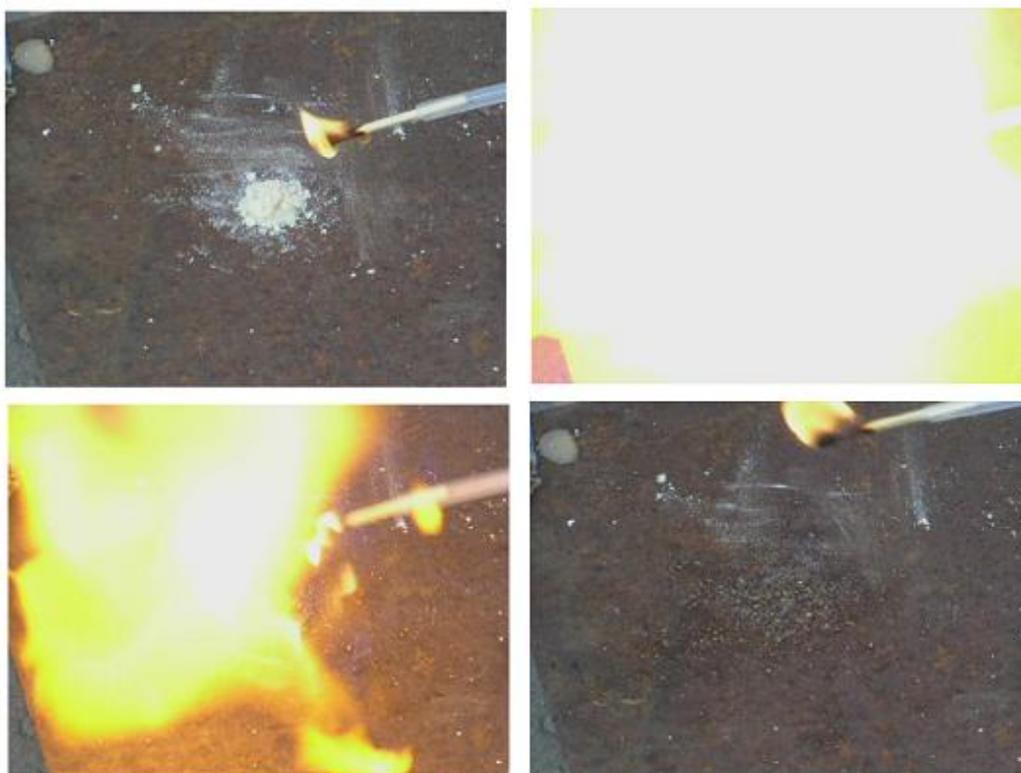
I prepared nitroaminoguanidine by condensing [nitroguanidine](#) with hydrazine hydrate via the method of JACS, 73, 474, this is said by the authors to give a purer product in higher yield than the method of JACS, 50, 2465-2470 that used hydrazine sulphate-ammonia mixture for the condensation. Below is the change in colour of the solution and the appearance of nitroaminoguanidine crystals under the microscope.



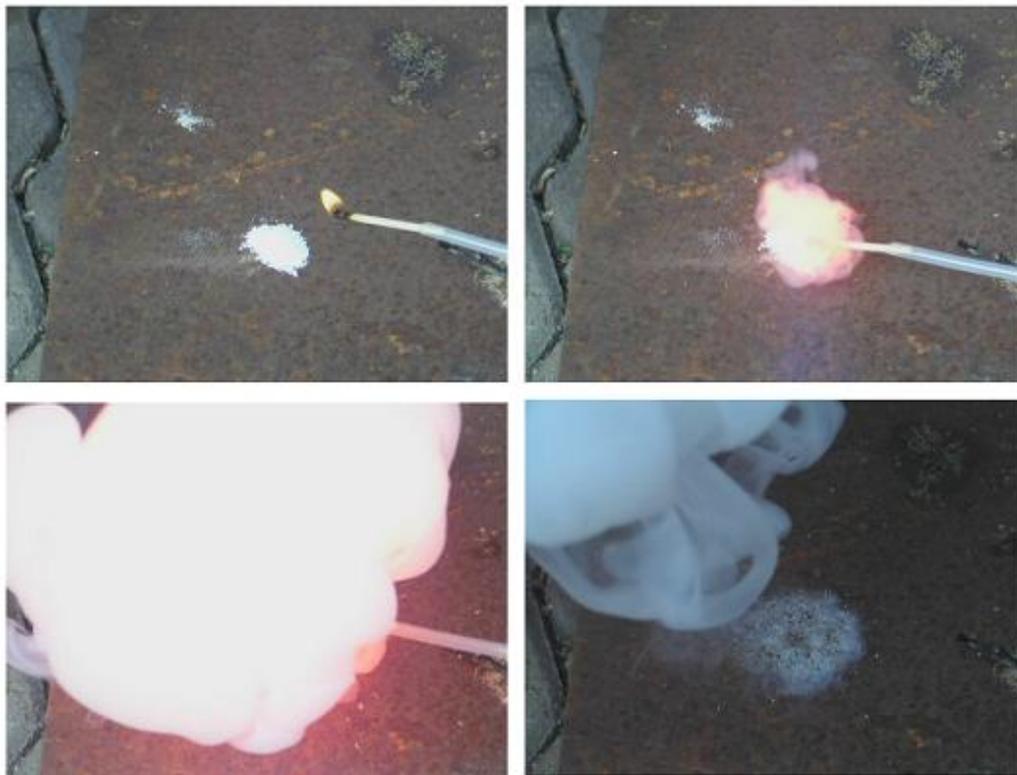
To see if this was indeed nitroaminoguanidine, the hydrazone derivative was produced by condensation with formaldehyde. On standing very long fine needles separated which meets the description in JACS, 50, 2465-2470. The precipitate resembled fiberglass or nitrocellulose and when ignited deflagrated vigorously with a large orange flame as shown below.



The nitrosation of nitroaminoguanidine was done following the experimental method "A" given in JACS, 73, 2327-2329, which uses a heated neutral solution of nitroaminoguanidine and potassium nitrite, though modified it to use sodium nitrite. Cooling the solution resulted in precipitation of the sodium nitraminotetrazolate but this was not isolated, rather HCl was added then it was extracted with ether, evaporation yielded ~5.5g of crude 5-nitraminotetrazole from 8g nitroaminoguanidine. Doing this probably resulted in some contamination with nitroguanylazide and its this contamination that J. Org. Chem., 18(8), 941-945 speculates to be the reason for an increased sensitivity. This crude product on drying for a number of days at room temperature exploded easily under the hammer on a rusty anvil and deflagrated in a flash on ignition as shown in the picture below.



A 1:1 molar aqueous mixture of AgNO₃ and nitraminotetrazole were combined which resulted in an immediate white precipitate of the acid silver salt. When dried this salt only "snapped" when held in a flame spreading the pile around but wouldnt sustain in the small quantities used. The literature does mention that salts of nitroaminotetrazole are not initiating explosives with the possible exception of the mercury salt. The potassium salt was also prepared by combining 1:2 molar ratio of nitraminotetrazole and potassium hydroxide in ethanol, again a white precipitate formed immediately which was filtered and dried. This only deflagrated on ignition as shown below.



[Edited on 1-10-2007 by Axt]

Engager - 30-9-2007 at 06:13 PM

Quote:

Originally posted by Axt

Excellent posts Engager, but just a suggestion, dont use imageshack or other free hosts as inevitably within a month or two they will all end up dead links. Instead either attach them directly or to imbed them in the text use the [forum pic ftp](#) setup specifically for this purpose. What program did you use to draw the reaction schematics?

[Edited on 28-9-2007 by Axt]

ChemDraw Ultra 8.0 from ChemOffice 2004 Suite. Thanks for the advice, next time i will attach images directly to posts. Now, getting back to topic. I've recently made silver salt of 5-nitrotetrazole, and conducted some tests on AgNTZ sensitivity. Here is a small detail about this interesting explosive material:

Silver nitrotetrazolate is white crystalline powder, stable to light and moisture, prepared by mixing soluble nitrotetrazole salt solution with silver nitrate. Compound is powerful primary explosive, heat of explosion 1.94 MJ/kg, initiating power is 0.005g vs tetryl (HgNTZ: 0.006g, Lead azide: 0.02g, Mercury Fulminate 0.2g). Silver 5-nitroterazolate is sensitive to shock and friction - slightly more than mercury fulminate. Can be overpressed.

Then wet it can detonate on contact with flame, but is much less sensitive to friction and shock, than in dry

state. I've made some friction and tests on dry salt. On intensive friction between paper and wooden rood, no explosion was encountered. However attempt of grinding in mortar, resulted in almost emidate violent explosion, with bright white flash. Sensivity to shock is very high, even slightest hits can cause violent detonation. In my personal oppinion, silver nitrotetrazolate can be handeled in safe manner with little risk when threated right, but extreme caution is advised.

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 $(\text{NH}_4)_2[\text{Cu}(\text{N}_4\text{C-NO}_2)_4(\text{H}_2\text{O})_2]$ - green primary (NH_4CuNT) ; 2. $(\text{N}_2\text{H}_4)_2(\text{N}_4\text{C-N=N-CN}_4)$ - dihydrazinium 5,5'-azotetrazolate (HZT) ; 3. $\text{Cu}_3(\text{N}_4\text{C-N=N-NH-CN}_4)_2$ - copper 5,5' diazoaminotetrazolate (CuDAT) ; 4. $\text{Cu}(\text{N}_4\text{C-NO}_2)_2 \cdot (\text{HN}_4\text{C-NO}_2)$ - acid copper salt of 5-nitrotetrazole (CuNT) ; 5. $\text{Ag}(\text{N}_4\text{C-NO}_2)$ - silver 5-nitrotetrazolate (AgNT) ; 6. $\text{Na}_3(\text{N}_4\text{C-N=N-NH-CN}_4)$ - sodium 5,5'-diazoaminotetrazolate (NaDAT) ; 7. $\text{Na}_2(\text{N}_4\text{C-N=N-CN}_4)$ - sodium 5,5'-azotetrazolate (NaAT) ; 8. $\text{HN}_4\text{C-NH}_2 \cdot \text{H}_2\text{O}$ - 5-aminotetrazole monohydrate (ATZ).

[Edited on 1-10-2007 by Engager]



The_Davster - 30-9-2007 at 06:45 PM

Since I was feeling left out in my pet thread... 😊

I have been too busy to experiment! 😞

But when I have time, time for these guys, among other tetrazoles.

1) 2-hydroxymethyl-5-nitrotetrazole

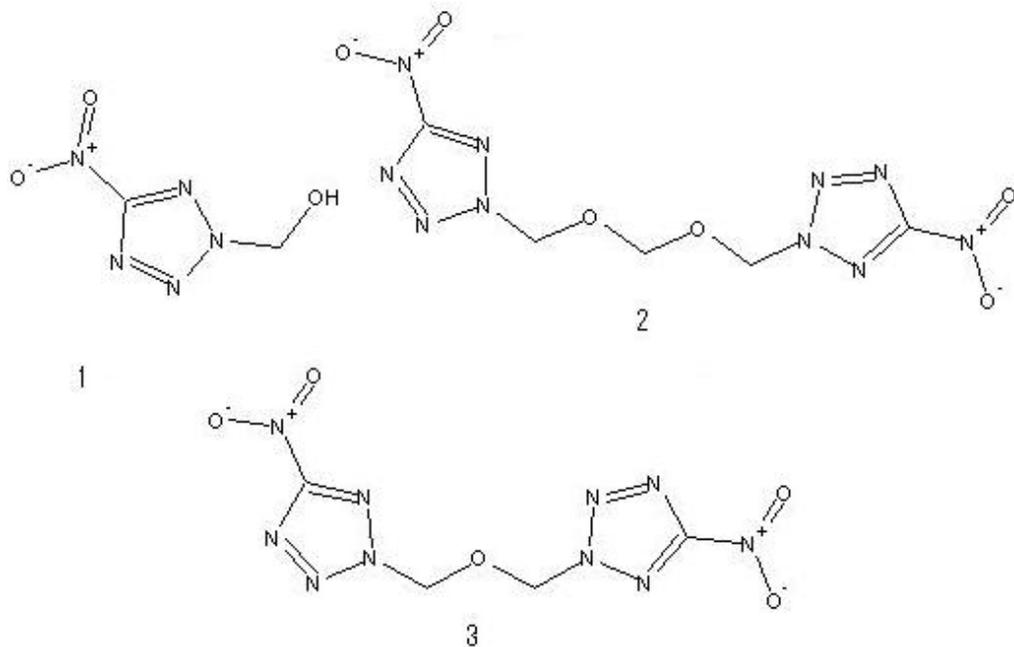
6.85g of sodium nitrotetrazole (hydrate) was dissolved in 50mL of water and 24.5mL of 20% sulfuric acid and 10mL of a 37% aqueous solution of formaldehyde were added with stirring at 5-10 C. The mixture was kept for 24h at 18-20C and extracted with ether(3x50mL) and the extract dried over magnesium sulfate and evaporated under reduced pressure to obtain 3.2g(67%) of compound 1 as a colorless crystalline substance, mp 63-64C

2) 2.6g of (1) was dissolved in 8mL of 101% sulfuric acid at 18-20C and 0.27g of paraform was added. The mixture was stirred for 1h at 35-40C, cooled to 5C, and poured into 50g of finely crushed ice. The precipitate was filtered off and washed with 50mL of ice water. Yield 4g(80%), colorless crystalline substance, mp157-158C

3)1.45g of (1) was dissolved in 20 mL of 101% sulfuric acid at 18-20C and the mixture was stirred for 2h at that temperature and poured into 100g of finely crushed ice. The precipitate was filtered off and washed with

50mL of ice water. Yield 0.5g(35%), colourless crystalline substance, mp 165-167C

[Edited on 30-9-2007 by The_Davster]



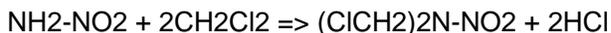
Engager - 7-10-2007 at 07:57 PM

I've found a very interesting nitrotetrazole based compound in my russian explosive related documents, called HT-1: 1,3-di(nitrotetrazolato-N2)-2-nitro-2-azopropane. Structural formula computed by RHF is attached below this message. HT-1 can be made by reaction of 1,3-dichloro-2-nitro-2-azopropane with silver nitrotetrazolate in organic solvent:

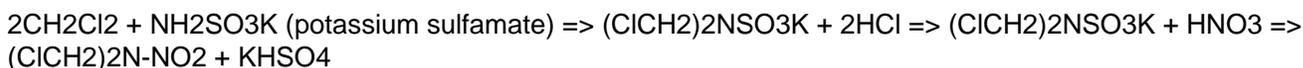


Some properties of HT-1. First time prepared in USSR in 1972, melting point 165C, density 1,90 g/cm³, heat of formation +476 ccal/kg (according different source 388 ccal/kg), heat of explosion 1430 ccal/kg, detonation velocity (density): 9350 m/sec (1.86), 9940 m/sec (1.90), critical diameter 0.82 mm. Thermal stability is acceptable.

I have fair ammount of Ag nitrotetrazolate, all that i need is to synthesis of 1,3-dichloro-2-nitro-2-azopropane. I had an idea to make this stuff through the nitramide, which i've made by hydrolisis of N,N'-dinitrourea in water (watch dinitrourea thread). Wonder if this will work:

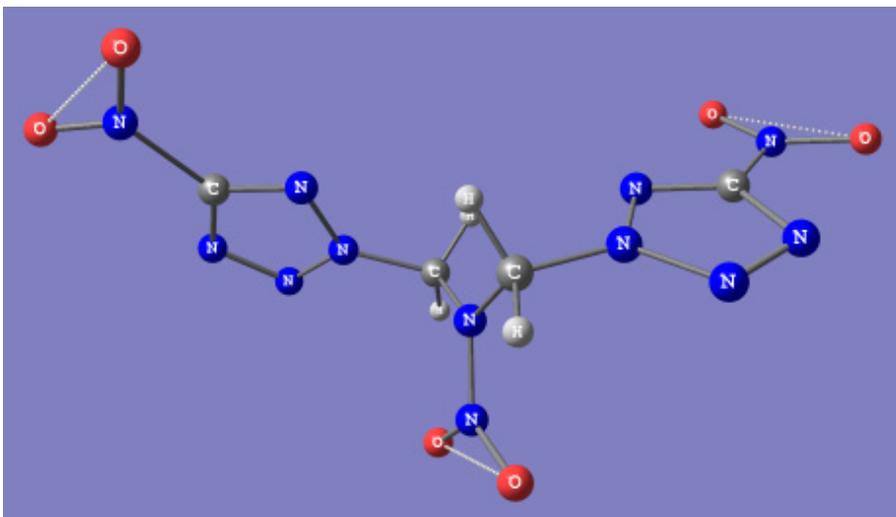


Other ideas:



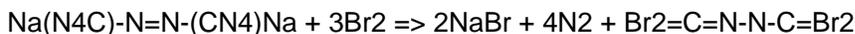
Someone have any ideas about how 1,3-dichloro-2-nitro-2-azopropane can be made?

[Edited on 8-10-2007 by Engager]

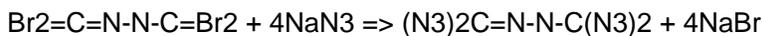


Engager - 7-10-2007 at 08:15 PM

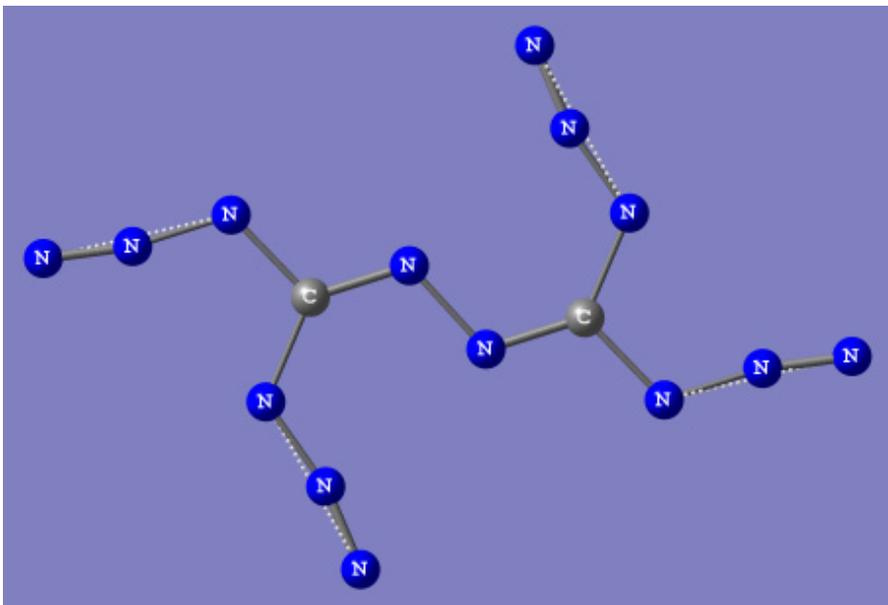
There is also an interesting route from 5,5'-azotetrazole (which is made by simple oxidation of aminotetrazole by KMnO_4 ; watch my post somewhere above) to isocyanogen tetrazide (watch US patent 2,990,412 for method details). Compound can be easily made from isocyanogen tetrabromide and solution of NaN_3 in acetone/water. Trick is that isocyanogen tetrabromide can be simply made with good yield by action of bromine (in form of bromine water) on solution of sodium azotetrazolate, nitrogen is evolved and product separates as black oily layer:



Action of sodium azide in acetone/water gives isocyanogen tetrazide with excellent yield:



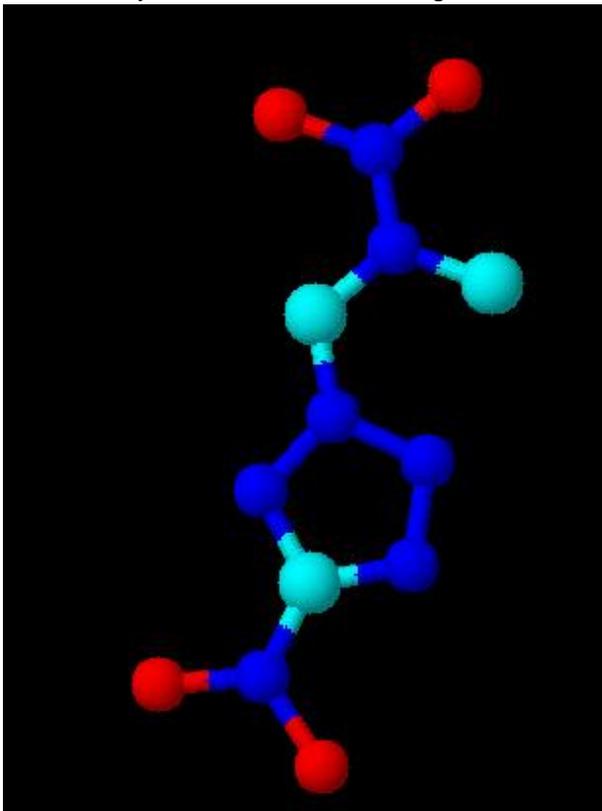
Not much digital data about explosive properties of compound exists, but it is certainly powerful explosive. Structural formula calculated by RHF is attached below this post. May be someone want to try this? This stuff is 100% real and excellently described in original work of Thiele and in US patent I've mentioned. Unfortunately I can't try this myself due to the lack of good place for such experimentation. Someone interested in trying this stuff?



The_Davster - 7-10-2007 at 09:22 PM

Engager, your posts in this thread are always a pleasure!

HT-1 is very similar to another energetic:



The preparation of which is in the attachment.

I know I came across the synthesis of 1,3-dichloro-2-nitro-2-azopropane while looking for the synthesis of 1-chloro-2-nitro-2-azopropane, I will use scifinder at Uni on tuesday to look it up again.

Attachment: [1nitrotetrazolato2nitro2azapropane.pdf](#) (113kB)

This file has been downloaded 287 times

Engager - 8-10-2007 at 09:28 AM

Quote:
*Originally posted
by The_Davster*
HT-1 is very similar to another energetic.

Yes i know this one, i asked for this article in References, section. Thiele work with isocyanogen is also available there by my request. I have description of manufacture 1,3-dichloro-2-nitro-2-azopropane from US patent 4,085,123 which is attached to the message. But unfortunately i haven't got acetic anhydride and high vacuum apparatus to perform such preparation. What's why i'm looking for simpler ways...

[Edited on 8-10-2007 by Engager]

The present invention relates to a novel azide plasticizer and to a process for producing same. The azide plasticizer of this invention can be prepared as follows:

A 12-liter, 3-necked flask, fitted with a mechanical stirrer, thermometer, and dropping funnel was charged with 3840 ml (40.7 moles) of acetic anhydride and cooled to 0°–10° C. Maintaining the temperature at 0°–10° C with external cooling, 1440 ml (34.3 moles) of 99% nitric acid was added in 30 minutes. A solution of 949 grams (6.77 moles) of hexamine in 1760 ml of glacial acetic acid was added in 1.5 hours at 5°–10° C. The mixture was stirred for additional five hours at ambient temperature, allowed to sit overnight. It was then filtered to separate a solid which was 1,7-diacetoxy-2,4,6-trinitrazaheptane.

The acid filtrate from the reaction mixture was diluted with 1500 ml of methylene chloride and washed with water, 16% sodium hydroxide, water, dried and concentrated to give a crude liquid residue consisting of 1,3-diacetoxy-2-nitrazapropane (DACNP) plus an unidentified polymeric material. It was found difficult to remove the DACNP by conventional distillation. However, utilizing a high vacuum, wiped film still, the DACNP was readily distilled at 121°C/0.3mm, n_D^{25} 1.4552. The yield of DACNP was 332.6 grams (35.1%), based on hexamine.

A solution of 238.3 grams (1.16 moles) of DACNP and 400 ml of dioxane was saturated with anhydrous hydrogen chloride gas at 5°–15° for 1.5 hours and stored in the refrigerator for 88 hours. The solution was concentrated and distilled to give 172.6 grams (93.6%) of colorless liquid, b.p. 64 C/0.4mm, n_D^{25} 1.5050. The product crystallized on standing and was identified as 1,3-dichloro-2-nitrazapropane (DCNP).

franklyn - 8-10-2007 at 08:14 PM

Quote:

Originally posted by Engager

Isocyanogen tetrazide easily made from isocyanogen tetrabromide and solution of NaN₃ in acetone/water

2,4,6-trichlorotriazine (Cyanuric trichloride) similarly serves as the precursor for 2,4,6-triazidotriazine, also made by metathetic action with NaN₃. (See page 432 Chemistry of Powder & Explosives by T. L. Davis.

2,4,6-triazidoborazine, sensitive to impact and friction, one of the very few known metastable boron compounds (all azides) is obtained from a 1 : 3 molar blend of trichloroborazine and trimethylsilylazide (Me₃SiN₃)

<http://www.sciencemadness.org/talk/viewthread.php?tid=1987&page=2&#...>

the resulting trimethylsilylchloride evaporates from the product.

[Edited on 14-2-2008 by franklyn]

Engager - 30-10-2007 at 05:22 AM

Here is synthesis of 2 copper-nitrotetrazole complexes, both are efficient primaries, and use soluble nitrotetrazole salts as precursors. This salts can easily be made dissolving acid copper nitrotetrazole salt (made

as described in posts above)in corresponding hydroxide, heating the solution and filtering off copper oxide. By weighting copper oxide, quantity of nitrotetrazole anion in solution is determined, this required to be known before any other transformations.

Synthesis of precursor nitrotetrazole salts:

Sodium nitrotetrazolate required for first complex is obtained by dissolving acid copper nitrotetrazolate in NaOH solution. Ammonium nitrotetrazolate is somewhat more difficult to produce because ammonium hydroxide can not be used directly (copper forms complexes with it). So to make ammonium tetrazolate acid copper nitrotetrazole salt is dissolved in barium hydroxide, solution is heated to complete exchange and destroy $\text{Cu}(\text{OH})_2$, black copper oxide is filtered off, and weighted to determine quantity of nitrotetrazolate ion in solution. Then ammonium sulphate is added in stoichiometrical amount to initial barium hydroxide, this results in formation of ammonium nitrotetrazolate and insoluble barium sulphate, while excess of barium hydroxide is also destroyed to form some ammonia and barium sulphate. Solution is filtered from BaSO_4 and boiled to remove residual ammonia, resulting in pure NH_4NT solution.

Synthesis of mono-(5-nitro-H-tetrazolato-N)triammine copper(II) perchlorate (MNCuP):

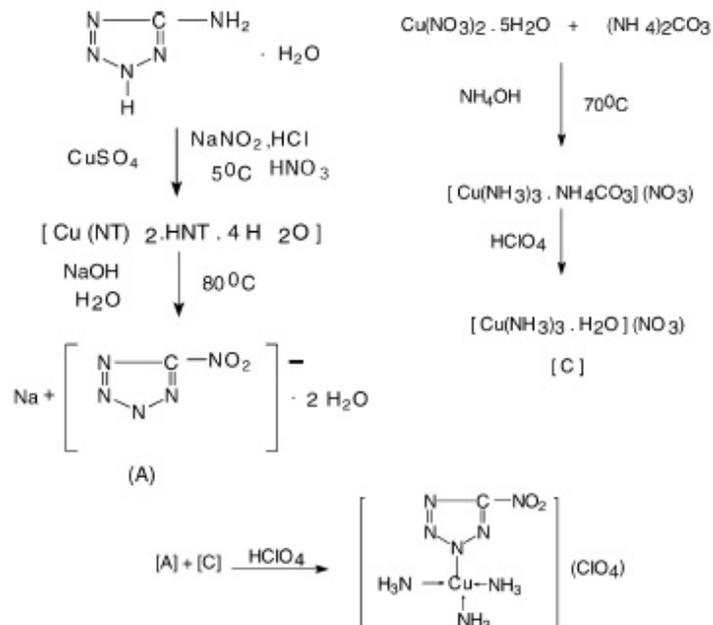
Prepare solutions 10g copper nitrate trihydrate (0.041 mol) in 50 ml of warm water, and 24g (0.25 mol) ammonium carbonate in 24 ml of 25% ammonia + 30 ml water. Solution of ammonium carbonate is added with stirring to solution of copper nitrate, resulting in intense blue/violet solution of copper-ammonia complex. Solution is placed on water bath and heated until thin light blue layer of copper basic carbonate ($\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$) begin to form at the bottom of reaction flask. During heating period 5g more ammonium carbonate is added in installments. Solution is filtered from any solid and then 3-4 volumes of alcohol is added. Complex compound is almost insoluble in alcohol and precipitates, solid is filtered off, washed with alcohol and dried. Product is blue/violet crystals of $[\text{Cu}(\text{NH}_3)_3 \cdot \text{NH}_4\text{CO}_3](\text{NO}_3)$. Yield is 75-80%.

To solution of 40 ml 70% HClO_4 in 100 ml of water, 3.5g (0.01379 mol) of carbonato triammine copper(II) nitrate in 30 ml of water is added with stirring. Deep blue color of copper carbonate complex quickly turns to transparent sky blue. Resulted mixture is heated to $60 \pm 10^\circ\text{C}$ and left to stand at this temperature for half of hour and heated to $\sim 80^\circ\text{C}$, then concentrated solution of sodium 5-nitrotetrazolate (0.00689 mol) is added by drops with stirring. Mixture is left to sit in boiling water bath for 4 hours, and cooled to room temperature. Product precipitates as sky blue solid, it is filtered off, washed with small amount of ice cold water and dried. Yield is about 85% of theory.

Photos of products are shown below, left one is carbonato triammine copper(II) nitrate ; right one mono-(5-nitro-H-tetrazolato-N)triamminecopper(II) perchlorate (MNCuP):



Reaction scheme:



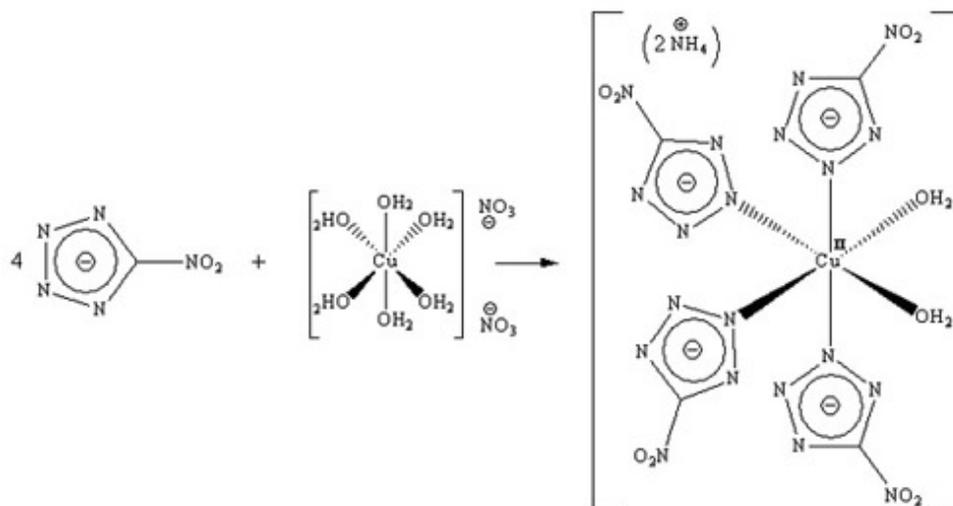
Synthesis of ammonium diaquatetrakis (5-nitro-1H-tetrazolato-N2) cuprate (II) (NH₄CuNT):

Solution of 5.5g ammonium 5-nitrotetrazolate (made by chain: CuNT => BaNT => NH₄NT) in 38 ml of water added with stirring to solution of 2.52g Cu(NO₃)₂·6H₂O in 110 ml of water. 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:



Reaction scheme:



Properties of complexes:

MNCuP: $[\text{Cu}(\text{NH}_3)_3(\text{NT})](\text{ClO}_4)$ - sky blue solid with bulk density about 0.65, irregular plate structure. Sensitive to impact and friction but less than conventional primaries (similar to BNCP). Digital data about explosive properties is unavailable now, and will be investigated by later research.

NH₄CuNT: $(\text{NH}_4)_2[\text{Cu}(\text{NT})_4(\text{H}_2\text{O})_2]$ 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 265°C, 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 $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ was unsuccessful, as I've mentioned in previous post. Attempt with $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ 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 30-10-2007 by Engager]

guanylazide 5,5'-Azotetrazolate (possible?)

Rosco Bodine - 30-10-2007 at 03:11 PM

Quote:

Originally posted by Engager

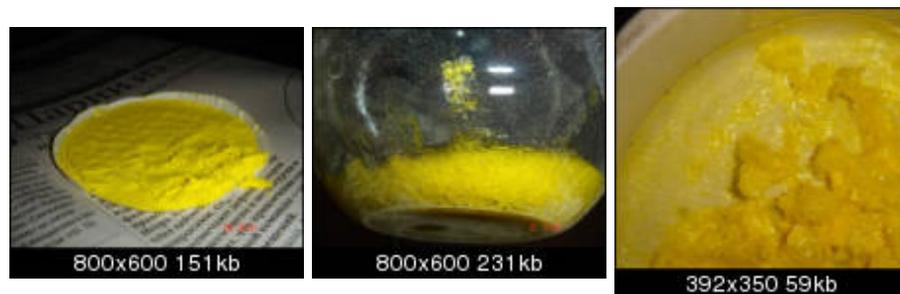
Synthesis of dihydrazinium 5,5'-Azotetrazolate (HZT)

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 10°C and filtered. Ba salt is washed with small amount of ice cold water and dried at room temperature. Yield is about 6.2g.

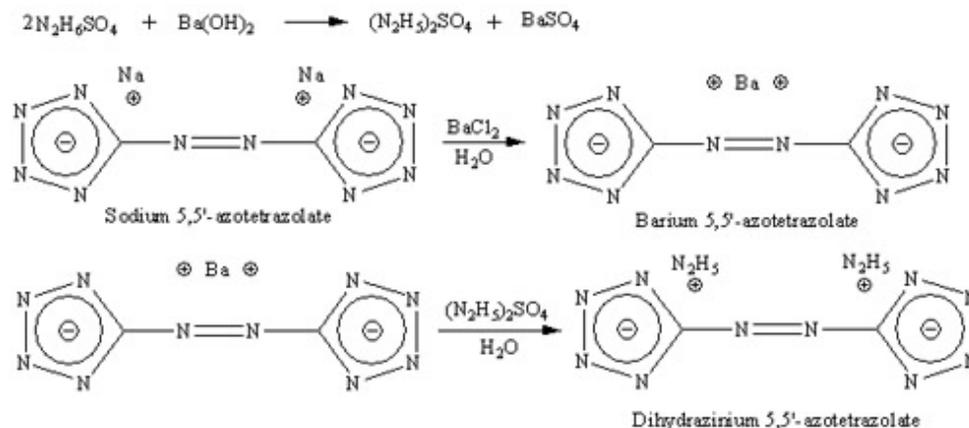
Make solution of 5.3g hydrazine sulphate ($\text{N}_2\text{H}_6\text{SO}_4$) in 155 ml of water, 6.44g of barium hydroxide is added with stirring, and after 6.2g of barium 5,5'-azotetrazolate is added. Mixture is well stirred for 1 hour, solid (BaSO_4) is filtered off and discarded, resulting in yellow 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 10°C. 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 100°C 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 azotetrazole (HZT):

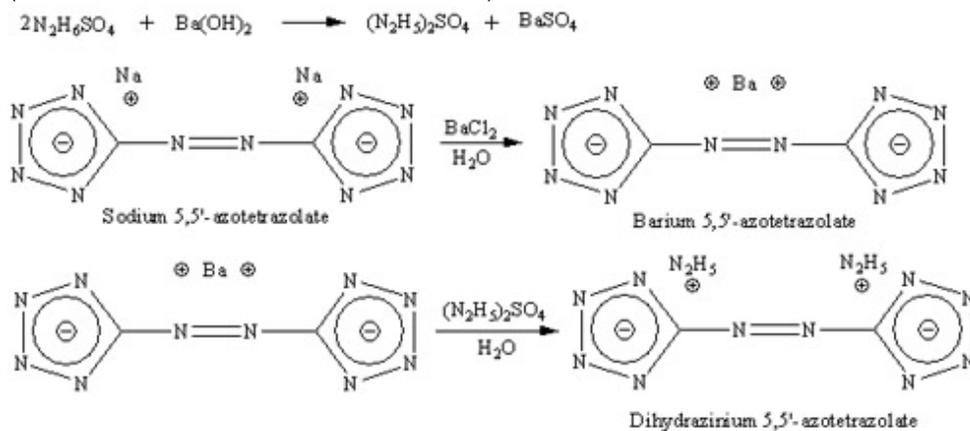


Reaction scheme:



[Edited on 14-9-2007 by Engager]

(reaction scheme stored on local server)



Sorry for not mentioning this earlier

It would seem that the guanylazide salt would have more interest in terms of an energetic material and could be made

by a parallel reaction , using (mono)guanylazide sulfate (exist?) substituted for the dihydrazine sulfate , the parallel reaction expected to follow the course of your last reaction shown above .

The predicted product would be
guanylazide 5,5'-Azotetrazolate .

The possible usefulness of guanylazide ,

and (though less convenient) nitroguanylazide ,
as well as triaminoguanidine , should not be overlooked
as possible "metal substitutes" in the formation of energetic salts derived from the various energetic acid tetrazoles .

I don't know of any references concerning such materials ,
so extreme caution would be prudent in experiments concerning such possible compounds .

P.S. As Axt pointed out earlier , you should upload , copy your attachments into the forum ftp , so they will
not become dead links and empty space , (lost data) later , but are safely archived and backed up here .

[Edited on 30-10-2007 by Rosco Bodine]

quicksilver - 12-1-2008 at 05:34 PM

Quote:

Originally posted by Rosco

Bodine

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 .

Does anyone know how the decomposition mechanism works within this chemical? I have seen this personally
in that after a period of weeks the tetrazene produced via the COPAE would no longer produce the black-
smoke deflagation it had previously. But in this case the exposure level was perhaps 40 C over the course of
weeks or months. Is tetrazene unstable @ room temp?

An addendum: it appears that 40C is not a contributor to instability but 30+ degree temp fluctuation may be.
The only accountable issue would be that or UV from a extremely low level source.

[Edited on 14-2-2008 by quicksilver]

The_Davster - 8-2-2008 at 09:01 PM

synthesis of azidotetrazole from cyanogen bromide:
(as requested)

Attachment: [cyanogen azide.pdf](#) (640kB)

This file has been downloaded 301 times

Engager - 20-2-2008 at 11:44 PM

Today i've made batch of acid copper nitrotetrazolate for fourth time. Unlike my previous experieces, this time
i have encountered "minor detonations" during same procedure as i've used before. These microdetonations
are caused by nitrogen oxide fumes from the reaction solution reacting with droplets of 5-AT on surfaces in
the reactor to form 5-diazotetrazole which may **spontaneously detonate in solution** when the
concentration exceeds 1%. Aside from being psychologically disturbing, these micro-detonations may be
strong enough to break glass and may result in release of the potentially explosive reaction mixture.
Detonations are accompanied by white flashes and loud report, you got to have a steel nerves to stay not
worried about such scary stuff, especialy then mixture is allmost full of precipitated acid copper 5-nitrotetrazole salt.

Reasons why this time they arrisen remain unclear, they seem to appear randomly, without any correlation
with reaction state. However i've found that in round bottom flask, they appear much more frequently, then in
flat bottom flask, and also depend from flask volume and neck width. This may be connected with
temperature gradients and vent efficiency inside reaction wessel.

Temperature also plays a role, surprisingly, when it is low microdetonation probability rises greatly, so it is

very important to keep temperature between 15 and 18C at ALL points of reaction mixture. This may be achieved by adjusting reagent addition rate and by effective stirring. Mixing rod edge must be round and smooth to produce minimal impact if it accidentally hits the bottom during stirring. At low temperature, glass stirring rod with relatively sharp edge, causes minor detonations at almost any accidental contact with flask bottom.

So there are some additional notes to procedure to avoid minor detonation problem. Reaction vessel must be flat bottom flask with large volume and wide neck, stirring rod should not have sharp or low area bottom edge to maximize impact area. Addition rate must be slower at least twice then 90 mins mentioned in literature, addition should be not more then 0.5 ml at one time, perfectly drop by drop. Efficient stirring and temperature control are essential, temperature during addition time must be kept strictly between 15 and 18C in all points of reaction mixture.

Don't bother literature sources say that minor detonations are relatively safe, they must be taken very serious!!! They still can do nasty damage to glassware, and may be even able to initiate explosion of whole mixture. This synthesis of 5-nitotetrazole must be taken as **hazardly dangerous**, and must be carried out only by experienced chemist, with all necessary safety measures.

[Edited on 21-2-2008 by Engager]

The_Davster - 23-2-2008 at 01:20 AM

Interesting to hear of your detonations, I have prepared the copper salt in small round bottom or erlenmeyer flasks with magnetic stirring 3 times now, and have never experienced this. Good to know it can happen even with copper present in the ATZ solution being added. I believe due to a too slow addition I went to 10C once without experiencing these microdetonations.

Back to info on the tetrazylazide as discussed on the first page of this thread:



Organic Derivatives of Azidotetrazole

Friederich (Refs 7 & 8) patented the prepn and use of expls prepd by action of alkali salts of tetrazylazide on organic chlorides or sulfates. Examples of these expl compds are given below:

1) Alkyltetrazylazides

Ethylenetetrazylazide. $C_3H_3N_7$; mw 137.10; N 71.53%; oily liq. It possesses extraordinary brisance and is easily ignited by sparks and flames. The azide gelatinizes NC and forms easily ignitable gelatines which have high shattering power. When absorbed in porous materials such as kieselguhr or cellulose paper, it becomes an excellent igniter for proplnts

Ethyltetrazylazide. See Vol 6, E331-R

According to Friederich's patents the organic tetrazylazides are more stable and less sensitive than the salts. He suggested that they be used, either alone or in various mixts, as ignition compns for percussion caps, detonators, electric primers, detonating fuses, etc. Suitable secondary charges are PETN, RDX, Tetryl or TNT

- Refs: 1) Beil 26, 347, (110) & [197]
 2) J. Thiele & H. Ingle, Ann 287, 238 (1895)
 3) K.A. Hofmann et al, Ber 43, 1091-93 (1910) & CA, not found 4) Ibid, 44, 2947 (1911) & CA, not found 5) H. Rathsburg, BritP 185555 (1922) & CA 17, 1147 (1923)
 6) Ibid, USP 1511771 (1924) & CA 19, 178 (1925) 7) W. Friederich, USP 2170943 (1939) & CA 34, 265 (1940) 8) W. Friederich,

The prepn of organic tetrazyl azides is accomplished by reaction of the azides' alkali or alkaline earth salts with organic chlorides, sulfates or nitrocompds in suitable solvent media. The compds so formed are reported to be remarkably stable and brisant expls. It is suggested in the referenced patents that these tetrazyl azides be used either alone or in combination with inert materials such as powdered glass, kieselguhr, Sb sulfide, etc, or other expls to form initiating or HE compns. Examples of organic tetrazyl azides are: **Acetone Mono- or Di-Tetrazylazide** (a solid); **Ethylene Di-Tetrazylazide** (v brisant; easily ignited); **Methyl Tetrazylazide** (a solid); **Picryl Tetrazylazide** $[(NO_2)_3-C_6H_2.CN_7]$; a solid less easily ignited than the others; suitable for use in detonators or fuses]; and **Trinitrophenylamino Tetrazylazide** $[(NO_2)_3-C_6H_2.NH.CN_7]$; a solid; prepn by reaction of tetranitroaniline with an alkali tetrazyl azide] Refs: 1) Beil 26, 347, (110) & [197 & 366] 2) W. Friederich, USP 2170943 (1939) & CA 34, 265 (1940) 3) Ibid, FrP 841768 (1939) & CA 34, 4574 (1940) 4) W. Friederich & K. Flick, USP 2179783 (1939) & CA 34, 1827 (1940) 5) W. Friederich, GerP 695254 (1940) & CA 35, 5318 (1941) 6) Ibid, BritP 519069 (1940) & CA 35, 7982 (1941) 6a) Blatt, OSRD 2014 (1944) 7) H. Ficherouille & A. Kovache, "Salts of Tetrazyl Azide", MP 41, 9-11 (1957)

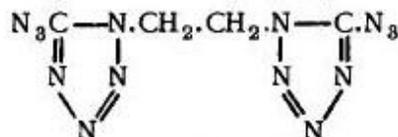
(1925) 7) W. Friederich, USP 2170943 (1939) & CA **34**, 265 (1940) 8) W. Friederich & K. Flick, USP 2179783 (1939) & CA **34**, 1827 (1940) 9) F.R. Benson, ChemRevs **41**, 8 (1941) & CA **41**, 6885 (1947) 10) Blatt, OSRD **2014** (1944) 11) E. Lieber & D.R. Levering, JACS **73**, 1313-17 (1951) & CA **45**, 9486 (1951) 11a) L.F. Audrieth & J.W. Currier, "Compounds of High Nitrogen Content - Derivatives of 5-Aminotetrazole", Final Report **B**, Univ of Ill, Urbana, Contract DA-11-022-ORD-33 (1954), 45-47 12) H. Ficherouille & A. Kovache, MP **41**, 9-11 (1959) & CA, not found 13) A.J. Baratt et al, "Some Reactions of the Azotetrazole Anion with Dilute Mineral Acids", ERDE-TN-44 (1971) & CA **78**, 124508 (1973)

9-11 (1957)

Ethyltetrazylazide, $C_3H_5N_7$; mw 139.12, 70.49%; crystals. Prep'd by reacting ethyl chloride or sulfate with an alkali salt of tetrazylazide. No props or structure are given; presumably it is the 1-ethyl-5-azido-1H-tetrazole, $N(C_2H_5)-N=N-N=CN_3$

Refs: 1) Beil, not found 2) W. Friederich, USP 2170943 (1939) & CA **34**, 265 (1940) 3) Ibid, BritP 510992 (1939) & CA **34**, 5664 (1940)

Ethyleneditetrazylazide,



mw 248.18, N 79.04%. It is a highly brisant comp'd which can be easily initiated by sparks or flame. When absorbed in a porous combustible material like cellulose or paper, it has still an excellent igniting power for expls. It gelatinizes NC, thus forming an easily ignited gelatin of high brisance

Friederich patented the comp'd for use in primers and detonators and as a core of detonating fuses

Refs: 1) Beil, not found 2) W. Friederich, USP 2170943 (1939) & CA **34**, 265 (1940)

Engager - 8-3-2008 at 01:02 AM

Russian references as i promised, sorry man, too large to attach, i had to place them on Rapidshare.

<http://rapidshare.com/files/97898324/Davster.rar.html>

oket - 8-3-2008 at 07:19 AM

"SOME REACTIONS OF THE AZOTETRAZOLE ANION WITH DILUTE MINERAL ACIDS"

5-Hydrasinotetrazole

To a solution of disodium asotestrazole pentahdrate (10.0 g) Tuspended in water (100 ml) was added hydrochloric acid (25 m1 5N). The solution was warmed on a water bath until the gas evolution finished, then was evaporated to dryness from water three times to remove the hydrochloric acid. The residue was dissolved in a minimum of hot water and a hot solution of sodium acetate (10.0 g) in water (10 ml) was added. The apparatus was flushed out with carbon dioxide and the solution allowed to cool to give 5-hydrasinotetrasole as white prisms with a yield of 2.5 g# mp 195 - 8°0 (lit 199d).

Engager - 10-3-2008 at 11:10 PM

Bis-(5-nitrotetrazolato-N2) cobalt (III) perchlorate (BNCP).

Orange-red needle-shaped crystals insoluble in cold water. Density 2.05 g/cm³, thermally stable below 200°C, decomposes at 269°C. Heat of explosion 3.32 MJ/kg, detonation velocity 8100 m/sec (at 1.97 g/cm³), deflagration - detonation transition takes about 10-11 microseconds, minimal initiating charge vs RDX is 0.05g. Non toxic, not hygroscopic, sensitive to fire, relatively insensitive to impact and friction (on secondary explosive level). Gives 50% explosions in drop test with 2.5 kg weight and 17 cm drop altitude (PETN - 12 cm), insensitive to electrostatic discharge. Ignite from Nd laser beam (wavelength 1.06 micrometers, impulse time 1 msec, beam diameter 0.5 mm, impulse energy ~ 1.5J). Can be used as primary in detonators without secondary - booster charge. Has optimal density interval, if density is too low burns - without detonation, if too high - becomes overpressed. Used in safe electric detonators and futuristic light ignition detonator systems.

Synthesis of BNCP

1. Preparation of [Co(NH₃)₄CO₃]₂SO₄·3H₂O complex. 47g CoSO₄·7H₂O is dissolved in 125 ml of water and is added to solution of 100g (NH₄)₂CO₃ in 500 ml H₂O + 250 ml 25% ammonia solution. Resulted dark violet solution is oxidised by addition of 14 ml of 30% hydrogen peroxide. Solution is allowed to sit for 30 minutes, after that period it is placed on boiling water bath and is evaporated to 300 ml volume. During course of the concentration process, solid ammonium carbonate (25 g) was added in installments. Solution is filtered from insignificant amount of precipitated black cobalt oxide and is further concentrated to 200 ml volume. Solution is slowly cooled to room temperature, product precipitates as small deep-red prisms. They are filtered out from the solution and allowed to dry at room temperature. Yield is 16 g of pure product, mother liquor can be further concentrated with addition of ammonium carbonate to get more 16 g of complex, but it is less pure.
2. Preparation of [Co(NH₃)₄CO₃](ClO₄) complex. 16g of complexed synthesised on first step is dissolved in 320 ml of water. Solution is filtered and 16g of sodium perchlorate in 40 ml of water is added with stirring. Mixture is cooled on ice (or in freezer) for 3-4 hours. Product precipitates as small, lustrous, sharp violet prisms. Crystals are filtered off, washed with small amount of ice cold water and dried at room temperature. Yield is about 14 grams.
3. Preparation of BNCP. 14g [Co(NH₃)₄CO₃](ClO₄) is dissolved in 140 ml 10% perchloric acid, and solution of 26.5g of sodium 5-nitrotetrazolate dihydrate in 450 ml of water is added with stirring. Solution is placed on boiling water bath, and allowed to sit there for 4 hours. Solution is slowly cooled to room temperature and then cooled in freezer to 10°C, precipitated crystals of BNCP are filtered off, washed with cold water, and recrystallised from 1% perchloric acid. Yield is 12.9g.

Photos of reaction products: first is tetraminocarbonato cobalt (III) sulphate trihydrate (product 1), second is tetraminocarbonato cobalt (III) perchlorate (product 2), third is crystals of BNCP.



This is the video of deflagration-detonation transition of BNCP in paper tube. Sorry i know i have to attach this file to post, but it seems to be too large, i tried 2 times with no result. So i have to place it on rapidshare:

[DDT of BNCP video](#)

[Edited on 11-3-2008 by Engager]

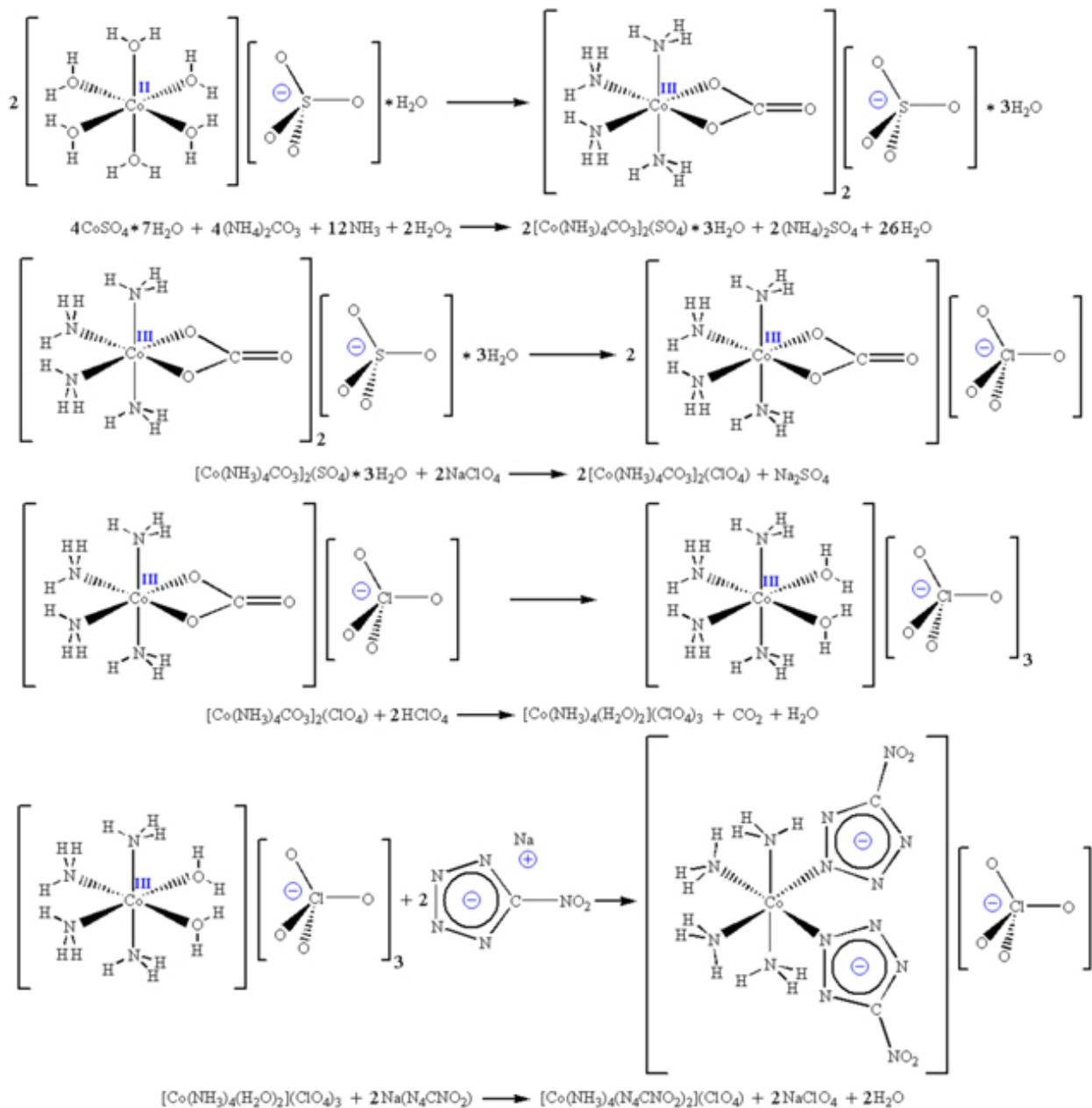
chemoleo - 11-3-2008 at 08:12 PM

Hello Engager, very very nice! Inorganic syntheses of beautiful compounds, yet with such interesting properties! Recrystallised from 1% HClO₄, is the compound unstable or why is this necessary? Did you base your synth on a published report (if so, pls say) or work it out yourself? I imagine the former as you also cite a lot of det data.

I was wondering whether you would upload the video to utube, it's likely to last longer there, and at least I can download it there!

Engager - 12-3-2008 at 04:40 AM

Recrystallization is for purification, it is not necessary but can be done if needed. And i forgot to post reaction schematic:



References are on Russian language, i attached them to the bottom of this post.

[Edited on 12-3-2008 by Engager]

Attachment: [BNCP Russian References.rar](#) (188kB)

This file has been downloaded 192 times

Rosco Bodine - 12-3-2008 at 10:46 AM

I would have guessed a different outcome for that last reaction which would essentially be a mixed salt of the

cation tetrammine Co dihydroxide complex , with one nitrotetrazolate anion and one ClO4 anion .

The same reactions should probably occur for copper and probably also for nickel .

I wonder , and have some skepticism 😬 actually , about the need for the "carbonato transition" shown . It seems the entire carbonate intermediate is unnecessary .

The reaction scheme seems so closely parallel to the reaction where tetrammine copper (di)perchlorate is precipitated from the double decomposition reaction of concentrated copper nitrate solution added to a warm NH4OH solution of NH4ClO4 .

What I see as more likely for Cobalt compound III , is that central two hydrogens on the extreme right , which are associated with the hydroxyls , are *not* supposed to be there 😬 at allbut simply the two hydroxyls which define the dibasic structure of the tetrammine cobalt "dihydroxide" base . It is a base , *not* a dihydrate as shown .

The subcase "3" for the ClO4 group in the last line should be 2 not 3 as shown .

And the final molecule should have the ClO4 group substituted for the lower nitrotetrazolate inside the bracketed larger structure , with a subcase of *2* outside the bracket .

That's the way I see it as more plausible anyway .

And one last thing , it doesn't seem possible that this substituted tetrammine cobalt perchlorate would be stable in neutral or acidic aqueous solution , but only in an ammoniacal solution of mixed ammonium nitrotetrazolate and ammonium perchlorate . In aqueous solutions otherwise it should decompose via hydrolysis , the same as does tetrammine copper perchlorate .

Being structured and reportedly behaving so differently from what would be expected , it is certainly anomalous in many ways if all of this is not true .

[Edited on 12-3-2008 by Rosco Bodine]

Engager - 12-3-2008 at 11:00 AM

Yea, this all is not my invention, read refs i provided. Cobalt with ammonia forms Co(NH3)6 and NH3 can not be substituted with 5-nitrotetrazole, carbonate is only a "protective" group, which is finally destroyed on final stage of synth to free 2 coordination places for NT. Tetramine complex is stable in acid even in 30% HClO4 you can make it for yourself to see this is true, so all is correct, read more about cobalt complexes before making your statements. You are denying practically observed and documentaly patented way of synth, may be you just go on and got top Nobell chemistry award if you are so clever.

[Edited on 12-3-2008 by Engager]

oops !

Rosco Bodine - 12-3-2008 at 12:45 PM

Pardon my brain fart above . I just went back and reread the text description and equations and saw the use of H2O2 to change the valency of the Co +II to Co +III in the first reaction which then changes everything to follow . The +III valency I was simply reading as "compound #3" and not paying attention it was the valency designation for the Co .

My Nobel prize will have to wait until I clean my glasses and have another cup of coffee ☹️

Interesting compound , and the reactions do make a lot more sense now .

Edit: I still have my reservations about the hydroxyls .

With a Co+III complex , should not we see a hexammine cobalt trihydroxide as the base ?

[Edited on 12-3-2008 by Rosco Bodine]

hokk - 20-3-2008 at 02:23 AM

Quote:

Originally posted by Engager

Synthesis of BNCP

I don't know if these are stupid questions or not, but anyways:

Could I use CoCl_2 instead of CoSO_4 without any problem? (changing the added mass of course)

Could I also use $(\text{NH}_4)\text{HCO}_3$ instead of $(\text{NH}_4)_2\text{CO}_3$ if I add more of the $(\text{NH}_4)\text{HCO}_3$?

Thanks!

[Edited on 20-3-2008 by hokk]

Engager - 20-3-2008 at 06:10 AM

No, you can't use CoCl_2 because it will form complex with different properties and structure. Synth of Werner complexes is quite delicate and require good replication of synth procedure. You can use NH_4HCO_3 , but procedure have to be modified. This synth is taken from literature, but if you modify it to use NH_4HCO_3 it can work but also may fail because a different solubilities/concentrations, so tryout is needed.

Rosco Bodine - 20-3-2008 at 03:41 PM

Cobalt nitrate and ammonium carbonate might work okay .

As for substituting the bicarbonate , it seems like that should work okay if you add extra NH_4OH sufficient for conversion of the acid carbonate to the normal carbonate .

Hmmm....according to this article attached , the chloride does form the analogous carbonatotetrammine cobalt (III) chloride , as part of a series of analogous salts derived from different cobalt salts used as the starting material .

The efficiency for conversion to the perchlorate would be solubility related .

But it doesn't appear structure would be any issue .

Engager is likely incorrect about the chloride not being workable .

[Edited on 20-3-2008 by Rosco Bodine]

Attachment: [Carbonatotetrammine cobalt \(III\) nitrate.pdf](#) (91kB)

This file has been downloaded 183 times

carbonatotetrammine cobalt (III) chloride

Rosco Bodine - 20-3-2008 at 11:10 PM

There is a preparation of the chloride analogue described in the attached article where it is an intermediate used in further synthesis .

Attachment: [carbonatotetrammine cobalt \(III\) chloride intermediate.pdf](#) (124kB)

This file has been downloaded 186 times

Engager - 23-3-2008 at 12:21 AM

Recently i've got interesting idea how bis-tetrazole can be made without use of dicyan as starting product. I found reaction in Elderfield book of heterocyclic chemistry, there was a reaction of HN₃ with oximes, it yielded corresponding tetrazole, so i thought to use this scheme to generate bis-tetrazole from glyoxime. Starting products will be glyoxal and hydroxylamine, they condense readily to form glyoxime, which is then reacted with 2 moles of HN₃ to yield 5,5'-bistetrazole:



However i have not found this synth in literature, but i think it can work. Literature methods use Mn to precipitate insoluble Mn bis-tetrazole salt, but case above this can not be made because one don't want to allow Mn azide to form. Excess of azide can be destroyed by using acidic nitrite solution on boiling, this will destroy azide: $\text{HN}_3 + \text{HNO}_3 = (\text{boiling}) \Rightarrow \text{N}_2 + \text{N}_2\text{O} + \text{H}_2\text{O}$

Also there is one problem - low solubility of glyoxime in cold water, this forces to preform reaction in hot solution - this will generate a lot of fumes of volatile hydrogen azide, what is dangerous.

Somobody got any ideas about this? Will this synth work, and how to rise solubility of glyoxime in cold water?

[Edited on 23-3-2008 by Engager]

convergence of earlier posts

Rosco Bodine - 23-3-2008 at 10:02 AM

Quote:

Originally posted by Engager

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: