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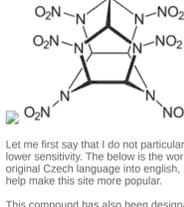
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## Nitramines

### 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW)



Let me first say that I do not particularly like this compound, there are several other compounds with similar power and lower sensitivity. The below is the work of "Nitro" and "Andrej". This site has gone to the trouble of translating it from its original Czech language into english, made more difficult by the Ruthenian dialect. Hopefully the addition of this section will help make this site more popular.

This compound has also been designated as CL-20.

Heat of formation (observed): +228 cal/g  
Detonation Velocity: 9.38 km/sec  
Density: 1.98 g/cm<sup>3</sup>  
Calculated detonation pressure: 428 kbar

The alpha crystal structure consists of rhombic prisms, while the beta consists of either colorless needles or chunky prisms.

Impact sensitivity: using 2.5 kg "hammer" to measure the drop height required to produce a 50% probability of detonation, the alpha form gave an average value of 17cm, while the beta form gave a value of 21cm. Compare this with a value between 23 and 25 cm for HMX.

A plasticized composition of 90% HNIW and a 10% mix of HTPB (used as solid rocket binder) and PL1 (plasticizer which is a 1:1 ratio copolymer of poly(3-butyl-co-3,4-dibutylthiophene and 3-butyl and 3,4-dibutyl thiophene) is recommended since CL-20 is somewhat more sensitive than HMX. This composition has measured VOD of 7.83 km/s, with calculated pressure of 330 kbar. So while HNIW seems to be powerful in its pure form, this pure compound is not very practical. The safer and easier to handle plasticized/castable composition of HNIW does not require less insensitive performance. There are several other highly energetic and more insensitive compounds that require less plasticizer and binder to be both tolerably resistant to impact and have desirable moldable/castable properties. Another thing to consider is that HNIW is significantly less dense (1.82 g/cm<sup>3</sup>) than the pure compound, whereas the other nitramines do not lose as much density when formed into compositions.

#### Synthesis:

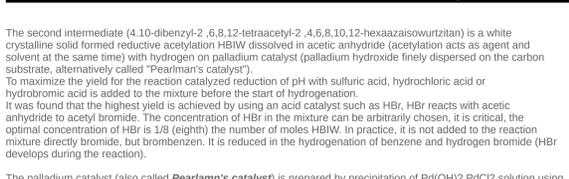
The starting materials for preparing the HNIW benzylamine and glyoxal, which together in an organic solvent condensed in the presence of a catalyst for HBW (2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane) . The second step is HBW (with catalyst) temperature-controlled fermentation acylated arises TAIW (4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane).

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In the last step TAIW debenzylate and nitration to form the desired HNIW. The first intermediate HBW there is condensation of benzylamine with hm: 40% aqueous glyoxal solution in an organic solvent (this may be a mixture of methanol or acetonitrile-water), catalyst reaction is formic acid.  
HBW greatest yield (81%) is achieved by slowly adding 1 mol-equivalent of an aqueous solution of glyoxal in a solution of (2mol-equivalents) of benzylamine and formic acid (0.2 mol equivalents) in acetonitrile.  
After mixing all the ingredients, the mixture is kept stirring at least 16 hours (overnight) at 25 ° C.

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Relatively long reaction time increases to a maximum yield of HBW, commonly HNIW precipitate forms within a few hours, but the interruption response after 5 hours we reach a somewhat lower yield.  
HBW with suction, washed with cold methanol and dried (in air). The yield achieved, as has been said 80-81%.  
Recrystallization from boiling acetonitrile obtained colorless crystals HBW with TT 153-157 ° C.  
The Organic Catalyst (formic acid) can be replaced by acetic acid. By heating the reaction time is reduced, but the yield has no effect. Addition of acetonitrile and methanol as solvents can be used similar substances (ethanol, propanol).



The second intermediate (4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane) is a white crystalline solid formed reductive acetylation HBW dissolved in acetic anhydride (acetylation acts as agent and solvent at the same time) with hydrogen on palladium catalyst (palladium hydroxide finely dispersed on the carbon substrate, alternatively called "Pearlman's catalyst").

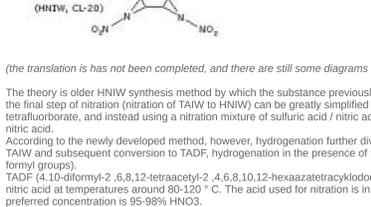
To maximize the yield for the reaction catalyzed reduction of pH with sulfuric acid, hydrochloric acid or hydrobromic acid is added to the mixture before the start of hydrogenation.

It was found that the highest yield is achieved by using an acid catalyst such as HBr. HBr reacts with acetic anhydride to acetyl bromide. The concentration of HBr in the mixture can be arbitrarily chosen, it is critical, the optimal concentration of HBr is 1/8 (eighth) the number of moles HBIW. In practice, it is not added to the reaction mixture directly bromide, but brombenzen. It is reduced in the hydrogenation of benzene and hydrogen bromide (HBr develops during the reaction).

The palladium catalyst (also called *Pearlman's catalyst*) is prepared by precipitation of Pd(OH)2 PdCl2 solution using lithium hydroxide in the presence of coal (resulting catalyst containing 10-20% palladium), quantity of catalyst is about one quarter the weight HBW.  
After hydrogenation, the mixture was cooled to 25°C and filtered off the precipitated catalyst with TAIW, TAIW separated from the catalyst by boiling in chloroform. The remaining solution is further extracted by shaking the proportion of acetonitrile. TAIW is a total yield of 60-65%.

The last part of the preparation of CL-20 is a precursor TAIW nitration in two steps to the maximum possible hexanitro derivative. The first part of the reaction involves a debenzylating nitration, performed at a temperature of 60 ° C, using nitrosyl tetrafluoroborate (NOBF4), which oxidizes the benzyl groups.

The second part is the nitration with nitronium tetrafluoroborate (NO2BF4) still at the same temperature of 60 ° C. The reaction product is very pure ammonium HNIW (yield 93-97% of TAIW).



(the translation is has not been completed, and there are still some diagrams to add)

The theory is older HNIW synthesis method by which the substance previously produced. According to a newer procedure, the final step of nitration (nitration of TAIW to HNIW) can be greatly simplified by replacing the carbon dioxide and tetrafluoroborate, and instead using a nitration mixture of sulfuric acid / nitric acid alone or, even easier using "anhydrous" nitric acid.

According to the newly developed method, however, hydrogenation further divided into two steps, namely preparing TAIW and subsequent conversion to TADF, hydrogenation in the presence of formic acid (benzene groups are replaced formyl groups).  
TADF (4,10-diformyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazatetracykloodekan) nitration with high concentrations of nitric acid at temperatures around 80-120 ° C. The acid used for nitration is in a concentration range of 90-98%, while the preferred concentration is 95-98% HNO3.

During nitration (as well as with other nitration reactions) there is a dilution of acid with water. When you reach a concentration of about 70% HNO3 decomposition occurs (which strongly supports the high temperature) reactant by-products, mainly oxo- and dioxo-substituted isowurtzitane. When sufficient acid is used in the nitration, net yield for HNIW very high, typically 90-99% of theory. The reaction must proceed at temperatures above 100 ° C, because if heated to only 80 ° C there will be up to 70% by-products, while at 115-120 ° C the byproduct contents will be below 2%.

In the laboratory it is possible to prepare HNIW by starting with TADF in cold nitric acid, and gradually heating the mixture up to 120 ° C for 4-5 hours.

The preceding HNIW is in the gamma crystal phase, which is subsequently reversed by crystallization from benzene to the alpha phase, or by newer methods of dissolving the epsilon gamma (or beta) crystal phase in the mixture acetic acid / ethyl acetate, and "seeding" the solution by adding several epsilon-phase crystals of HNIW, then adding hexane to the solution. The phase conversion is quantitative.

Preparation:

#### Step A (preparation HBW)

An accurate laboratory procedure for the preparation of HBW is in the lower section on this page.  
72.5 g 40% aqueous solution of glyoxal (FANDA RD procedure) added a solution of 118 grams of benzylamine and 57.5 g 88% formic acid in acetonitrile 1100 ml per hour. The temperature is always maintained below 20 ° C.  
After the addition of glyoxal Pour the mixture into 10 ml of water at a temperature of 25 ° C. The reaction mixture allowed to stand overnight (16-18 hours).

The precipitated product is filtered, washed with cold acetonitrile. Yield: 96.0 g HBW (91.3% theory), melting point 150-152 ° C. - Recrystallization from acetonitrile gave a colorless product tt 153-157 ° C. Formula: C48H48N8O4.

#### Step B (preparation of TAIW, hydrogenation)

A mixture of 150 g HBW, 500ml of acetic anhydride, 37.5 g palladium Pearlman catalyst (containing 20 grams of palladium per 100 g dry catalyst) and 4.2 g bromobenzene stirred in a 2.5 liter container. Note: *Pearlman's catalyst* is composed of solid palladium hydroxide which has been deposited onto carbon, more specifically activated charcoal. In a typical procedure, palladium(II) chloride and hydrochloric acid are added to activated carbon which has been previously washed with nitric acid.

The closed apparatus (autoclave) at 25 ° C brings the hydrogen bomb to achieve 50PS pressure. Over the next 30 minutes exothermic reactions the autoclave should be cooled with water maintained at 50 ° C. Approximately 1 hour, when the temperature of the mixture drops to 40-35 ° C, we start again in the apparatus to bring hydrogen to be consumed during the reaction (approximately half of the consumption) and let react at temperature of approximately 19-20 hours. The total consumption of hydrogen is 130% of the theoretical amount.

After the reaction contents cooled to 25 ° C, the precipitated products along with the catalyst is filtered, TAIW is extracted with boiling chloroform.  
The remaining filtrate was concentrated under vacuum, further excluded share TAIW filters. TAIW yields from both units is 69.0 g (63.2% theory), melting point 315-325 ° C. Recrystallization from acetonitrile gave small colorless crystals with a melting point of 322-323 ° C, with a composition/formula of C28H32N6O4.

Preparation can be done without using an autoclave, but with a much larger surplus of hydrogen at higher temperatures.

#### Nitration with NOBF4, NO2BF4 (preparation HNIW)

(Here is the method described earlier, which is now in use. NOBF4 newer method instead NO2BF4 and uses carbon dioxide or better on its own nitration with nitric acid concentration above 90% (usually 95-99%) at temperatures between 110-120 ° C)

A mixture of 15.5 g TAIW, 1 ml water and 300 ml sulfolane is added under cooling in a 30-minute periods a total of 14 grams NOBF4 in such portions that the temperature does not exceed 25 ° C. After adding **nitrosium tetrafluoroborate** stirring the mixture for 1 hour (25 ° C) and another hour at 55-60 ° C.

The resulting clear yellowish liquid (not to be cloudy, after the next hour) was cooled to 25 ° C and added at 47.8 g NO2BF4 (**nitronium tetrafluoroborate**), the mixture has cooled. In a similar manner promíchávámě mixture of 2 hours (25 ° C) for 2 hours at 55-60 ° C. The resulting suspension of white NOBF4 the yellow-colored liquid, cooled in an ice bath to 5 ° C is slowly added 4.5 liters of ice water, increasing temperature may not exceed 25 ° C. During the addition of water the color of the solution gradually turns to green, then white and brown fumes are released. Another 10 hours, constantly stirring the contents of the container, the temperature still maintained at 25 ° C. The resulting white precipitate was filtered and washed several times with water.

Yield: 12.78 g after drying Hexanitrohexaazaisowurtzitane amorphous, purity more than 99%. After crystallization from ethyl acetate receive rhombic white crystals of density 1.98 g/cm<sup>3</sup>.

updates:

#### Preparation of TADF

Do autoklávu objemu 320-350ml se předloží 85g surové směsi TAIW s katalyzátorem získané hydrogenací HBW (katalyzátor se neodděluje, pouze se směs získaného TAIW s katalyzátorem promyje ethanolom a vysuší) a 220g kyseliny mračené. The autoclave volume of 320-350 ml to provide 85 g crude mixture with a catalyst obtained by TAIW HBW hydrogenation (catalyst is not separated), only the mixture obtained TAIW catalyst washed with ethanol and dried) and 220 g formic acid. Obsah nádoby se nasýtí vodíkem a teplota udržuje na 50°C stejně jako při syntéze TAIW. Contents of the vessel becomes saturated with hydrogen and the temperature maintained at 50 ° C as well as the synthesis TAIW. Dále se postupuje zcela shodně (jako u TAIW). Proceed exactly the same (as with TAIW). Celková spotřeba vodíku: 130% teorie, výtečkem je 5.7g TADF (86% teorie). The total hydrogen consumption of 130% of theory yield is 5.7 g TADF (86% theory). Nitrate TADF pomocí kyseliny dusičné (gamma-HNIW novější metodou); TADF Nitration with nitric acid (gamma-HNIW newer method);

Do baňky ponorené v olejové lázni, opatřené magnetickým míchadlem a teploměrem nalijeme 30ml 95-98%ní HNO3, kyselina má mít laboratorní teplotu. The flask immersed in an oil bath, equipped with magnetic stirrer and thermometer, pour 30 ml 95-98% of her HNO3, acid has a room temperature. Zapneťme míchadlo a po malých dávkách přidávame celkem 10,0g TADF takovou rychlostí, aby teplota směsi nepřesáhla 20-25°C. We turn on the blender in small batches and add a total of 10.0 grams TADF such speed that the temperature does not exceed 20-25 ° C.

Jakmile se přidá veškerý TADF, začne míchadlo odpojovat lázeň tak, aby teplota směsi rychlostí přibližně 5-10°C/min. Once you add all TADF, begin heating the oil bath so that the temperature rising rate of approximately 5-10 ° C / min. až na 115-120°C. up to 115-120 ° C.

Během reakce můžeme v baňce pozorovat srážení bílého produktu, HNIW. During the reaction flask can be seen in the precipitation of white product, HNIW.  
Při dosažení požadované teploty 115-120°C necháme reakci probíhat cca 4hodiny. Po skončení nitrace ochladíme baňku nejprve pod tekoucí vodou na laboratorní teplotu a pak celý obsah vyklopíme na 100g rozdroceného ledu. When you reach the desired temperature of 115-120 ° C, we let the reaction run about four hours. Nitration cool things down after the end of the first flask under running water to room temperature and then the entire HT content port period of time, the temperature should change from green to yellow, some brown fumes may be evolved. Maintain the temperature at 25 ° C with continuous stirring for 18 hours, a white precipitate should form. Filter to collect this crude HNIW, and wash several times with water to yield about 12 g of hydrated product. To purify the HNIW, dissolve it in 40 mL of **ethyl acetate**, chromatographically filter the solution through a short column of silica gel, and wash with ethyl acetate. Pour the filtered solution into 500 mL of chloroform to precipitate the HNIW in its anhydrous beta form. The chromatographic filtration can be skipped. If pale yellow crystals are obtained as the crude product, it is the wrong stuff. Heat these crystals in 15 mL of water per 1 g of product at 95 ° C with stirring for 10 minutes, then cool to 0 ° C. After standing for 6 hours, filter and wash the crude product as above, it should be HNIW now. You will need a graduated cylinder for measuring liquids, a stirring rod or magnetic stirrer for mixing, and a thermometer to monitor the temperature.

Výtečkem je velmi čistý gama-HNIW, v přepočtu na množství použitého TADF se výteček pohybuje mezi 90 až 99%. Yield is very pure gamma-HNIW with high purity. The amount of TADF the yield is between 90-99%.

Ještě roku 1992 se CL-20, připravovaný původním postupem podle Nielsena přes TAIW a fluoroboráty prodával za cenu kolem 400-450\$/kg. Still in 1992, CL-20, prepared by the original procedure according to Nielsen through fluoroboráty TAIW and sold at a price around \$ 400-450 per kg.

#### Selected Literature:

G. Jacobs a kol. "Chem. and polymorphic charact. of CL-20", France G. Jacobs et al., "Chem. Polymorphic and charact. of CL-20, France

Here is the synthesis from rogue science to compare:

Prepare a solution of 129 mL of **N,N-dimethylformamide** [ HC(=O)N(CH3)2 ] and 65 mL of **acetic anhydride** in a round-bottomed **500-ml Florence flask**. Add to the flask, with stirring, 43.2 g of **HBW**, 0.8 mL of **bromobenzene**, and 4.7 g of **Pearlman's catalyst**. Purge the flask by bubbling hydrogen gas in the liquid. This will displace the air. Continue to bubble hydrogen gas into the flask and stir. After the addition, maintain a pressure of 50 psi. Over a short period of time, the temperature may rise to about 50 °C, at this temperature begin cooling the flask with a cold water or salt-ice bath to keep it under 50 °C. The total reaction time needed is 24 hours. Since it is undesirable to bubble hydrogen gas through the flask for this length of time, as much water will be wasted, a pressure is maintained. During the reaction, stop cooling if the temperature drops below 35 °C, always below approximately half of the consumption of the flask for the entire 24 hours. Purge the flask by bubbling **nitrogen** gas into it to displace any remaining hydrogen. Filter the contents of the flask to collect the solid material and the catalyst. Wash with 130 mL of denatured **ethyl alcohol**, this should leave behind a gray solid of Pearlman's catalyst and TADF. The TADF can be separated from the catalyst by dissolving the solid in boiling **chloroform**, and filtering to remove the remaining solid catalyst. Boil the chloroform down to recrystallize the TADF. The yield is about 85%.

Prepare a solution of 15.5 g of the above prepared TADF, 1.1 mL of water, and 300 mL of **sulfolane** in a round bottomed 500-ml Florence flask on a salt-ice bath. Add 10.0 g of **nitrosyl tetrafluoroborate** to the flask over a period of 30 minutes, keeping the temperature below 25 °C. After the addition, stir the mixture for 1 hour at 25 °C, then 1 hour at 55-60 °C. Allow the solution, which should be a yellow-orange color, to cool to 25 °C. After cooling, rapidly add 47.8 g of nitrosyl tetrafluoroborate, keeping the temperature below 25 °C. Stir the mixture at 25 °C for 2 hours, then at 55-60 °C for 2 hours. Cool the mixture to below 10 °C with a salt-ice bath, then dump the contents, solid precipitate and all, into a large bucket. Slowly add 4.5 L of water to the mixture in the bucket, keeping the temperature below 25 °C. The color of the solution should change from green to yellow, some brown fumes may be evolved. Maintain the temperature at 25 °C with continuous stirring for 18 hours, a white precipitate should form. Filter to collect this crude HNIW, and wash several times with water to yield about 12 g of hydrated product. To purify the HNIW, dissolve it in 40 mL of **ethyl acetate**, chromatographically filter the solution through a short column of silica gel, and wash with ethyl acetate. Pour the filtered solution into 500 mL of chloroform to precipitate the HNIW in its anhydrous beta form. The chromatographic filtration can be skipped. If pale yellow crystals are obtained as the crude product, it is the wrong stuff. Heat these crystals in 15 mL of water per 1 g of product at 95 °C with stirring for 10 minutes, then cool to 0 °C. After standing for 6 hours, filter and wash the crude product as above, it should be HNIW now. You will need a graduated cylinder for measuring liquids, a stirring rod or magnetic stirrer for mixing, and a thermometer to monitor the temperature.

#### Preparation of HBW Precursor

The procedure for making HBW (2,4,6,8,10,12-Hexabenzyl-2,4,6,8,10,12-hexaaza-tetracyklo [5.5.0.0.0] dodecane) stems from the publication of J. Org.Chem. (1990), 55, 1459. (1990), 55, 1459ff To verify only a slight adjustment of preparation was made. Diagram of reaction is shown here:



The reaction is very simple and is slowly added glyoxal solution to a solution of benzylamine in acetonitrile with water. The condensation is catalyzed by the presence of formic acid. As a solvent it is possible to use methanol, but the yields are lower and longer reaction time.

#### Experimental

A, From left to right in the picture: formic acid of 80-90% concentration, acetonitrile as solvent, 40% aqueous solution of glyoxal, and benzylamine.



B, The two-liter Erlenmeyer flask will present one liter of acetonitrile, 100 ml, 120 ml of benzylamine (117.9 g, 1.1 mol) and 4.8 ml 80-90% formic acid (5.76 g, 0.11 mol). Flask placed in a bath of ice and water and stir (preferably with a magnetic stirrer). Wait until the temperature drops below 15 °C.

C, To the solution slowly, stirring constantly, add Glyoxal 40% (72.5 g, 0.57 mol, 0.5 mol). The whole procedure should take about an hour. Adding either through a dropping funnel or better use a peristaltic pump. The temperature should not exceed 20°C. Shortly after beginning the addition of glyoxal in a solution of the product begins to appear as a white crystalline cavities, as shown on the left. When introduced into all the glyoxal reaction, remove the cooling bath and the solution for about 30 minutes stir.



D, then remove the stirrer, the flask cap permeable (eg aluminum foil) and place it in a dark place. Thus, the rest leave it at room temperature for 24 hours. During this time, will slowly change color from white to a mixture of yellow and orange:



E, Finally, crystals of the product, filtered and rinsed 2 x acetonitrile. The filtrate can stir aqueous acetonitrile and use it for the next reaction. In this case, has distilled all the liquid, but only 80-90% of the volume. Recrystallized thus obtained can be used for further condensation, it only add acetonitrile to volume of 1100 ml. You do not add water.



F, The product can be obtained by being recrystallized in acetonitrile, and can then be used without any purification for the next reaction. The product from this procedure should be around 90 g (0.12 mol, 76%) of HBW, you can see the final picture below. HBW is a slightly yellowish white solid with a melting point of 155-157 °C.



#### Comments