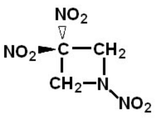
TNAZ



Trinitroazetidine (TNAZ) is unique in that it is based on a square ring. The strain from this configuration (which adds 37kcal/mol), as well as the high density from this geometric structure, lends increased power to the compound. It has a melting point of 101-103degC, and a density of 1.84 g/mL. The compound is considered melt-castable.

Sensitivity
TNAZ is more resistant to shock and impact than HMX, but the sensitivity is highly variable depending on the crystal grain size. Smaller grains (5.5 micrometers) have a 66cm sensitivity using the drop height test, while larger grains approach the 23cm sensitivity of HMX. TNAZ has a shock sensitivity of 4.3 kbar.

Performance
TNAZ has a detonation velocity between 8.6 and 8.85 km/sec, and generates a pressure of 372 kbar. One measured value for the detonation velocity was 8.73 km/sec. *"Characterisation of the Sensitivity and Performance Properties of 1,3,3-Trinitroazetidine (TNAZ)" Aubert, S.A. (1994).* TNAZ has 7.7% (or about 8%) more explosive power per unit of weight than HMX. (HMX has a higher detonation velocity of 9.1 km/sec because it has a higher density at 1.91 g/mL).

Thermal Stability
The compound begins to slowly decompose, releasing small ammounts NO2, above 180degC. Prolonged temperatures above 200degC can lead to explosion, but TNAZ can withstand a shorter duration of heating up to 240degC. The main difficulty of the synthesis is initial formation of the square azetidine precursor, which requires extensive knowledge in advanced organic chemistry.

Cost and Difficulty
The least expensive route utilizes Mitsunobu reaction. Assuming that the DEAD is recycled (by reoxidizing with chlorine), assuming that a cheaper substitute can be found for the Trifluoroacetic acid, and not counting the cost of the triphenyl phosphine (which could possibly be cheaply produced on site), the cost of the basic precursors is estimated to have a lower limit of 1 Euro (year 2000) per gram of TNAZ produced.

This is the only amateur/hobbyist source for how TNAZ can be made.

Synthesis 1:
CH_2=CHCH$_2$Cl + HOCl → HOCH$_2$CHClCH$_2$Cl mixed with ClCH$_2$CH(OH)CH$_2$Cl
The resulting mixture of alcohols is then treated with NaOH to form epichlorohydrin (with NaCl byproduct).
Epichlorohydrin is an epoxide of propanane with a chlorine atom.

Tert-butylamine, (formula [CH$_3$]$_3$CNH$_2$) and epichlorohydrin react to form 1-tert-butyl-3-hydroxyazetidine.
The 1-tert-butyl-3-hydroxyazetidine is then treated with Methanesulfonyl chloride CH3SO2Cl which forms an ester on the 3-position. This ester is then reacted with sodium nitrite, with a small ammount of 1,3,5-Benzenetriol (which is both the symetric tri-ketone of hexane, and tri-hydroxy benzene, because of tautomers) present. This forms 1-tert-butyl, 3-nitro azetidine. The 1,3,5-Benzenetriol helps to prevent nitrite esters from forming.
Sodium nitrite and sodium persulfate, with sodium ferricyanide present, oxidizes the mono-nitro to the di-nitro in 60% yield. Finally, the tert-butyl group is hydrolysed/oxidized off using acetic anhydride and nitric acid (in similar concentrations used for making other nitramines). This now leaves TNAZ. The net procedure gives a 17% yield. Most of the inefficiency comes during the formation of the square ring and then the reaction with nitrite. Other amines beside tert-butyl amine can probably be used instead, but likely will give lower yields.

Synthesis 2:
condensation of tris(hydroxymethyl)nitromethane with tert-butylamine and formaldehyde forms 3-tert-butyl-5-hydroxymethyl5-nitrotetrahydro-1,3-oxazine. This is treated with HCl acid solution to yield 2-tert-butylaminomethyl-2-nitro-1,3-propanediol hydrochloride which was cyclized (using Diethyl azodicarboxylate with triphenylphosphine which initiated a **Mitsunobu reaction**) to 1-tert-butyl-3-hydroxymethyl,3-nitroazetidine hydrochloride. The reaction is conducted at 0degC, and the ether solution of DE-azodicarboxylate added last, where it is very slowly added with stirring. This is allowed to warm to room temperature for 2 hours. Note that the DE-azodicarboxylate gets reduced during the reaction, and the Ph3P gets oxidized.

This was then treated with sodium hydroxide and then nitrated (which also oxidized the molecule) to give 1-tert-butyl-3,3-dinitroazetidine. This was then reacted with NH4NO3 and acetic anhydride to give TNAZ. Based on the starting reactants in the procedure, this gives a 55% yield.

Alternatively,1-tert-butyl-3,3-dinitroazetidine reacts with benzyl chloroformate to yield 1-(benzyloxycarbonyl)-3,3-dinitroazetidine. The Benzyloxycarbonyl group has a structure of (C6H5)CH2OC(=O)R, where R would, in this case, be the Nitrogen atom on the dinitroazetidine ring. This Benzyloxycarbonyl group can easily be hydrolyzed off the square ring with NH4OH, leaving 3,3-dinitroazetidine.

If an acetyl group is on the nitrogen atom in the ring, this can be converted to the N-nitro by nitrating with 98% nitric acid, or using ammonium nitrate in acetic anhydride.

Oxidixing agents, such as pyridinium chlorochromate, can oxidize the hydroxyl group (in the 3-position on the ring) to the ketone, leaving the ring intact. The ketone of azetidine is known as azetidinone. From here, the oxime can be formed, and then a dinitro formed by bubbling in NO2, then treating with H2O2.

Synthesis 3:
CH2=CHCH2NH2 can be treated with Br2 and Et2O at 15C to form HBr.(NHC2H3)CH2Br. The group (NHC2H3) is a triangular ring, the CH2Br group is attached to a carbon atom on the ring, and the amine part of the ring has formed a hydrobromide salt.

Alternatively CH2=CHCH2NH2 can instead react with SO2Cl2 and CH2Cl2, by being heated, to form HCl.(NHC2H3)CH2Cl, which is the same compound above, except with chlorine replacing the bromine atoms.

The HCl.(NHC2H3)CH2Cl (or the one with bromine instead), thus formed is reacted with BuLi and THF at (minus) -78C to form "azabicyclo" propane, which is basically two triangles connected together, forming a square, with a nitrogen atom in the corner connected to all three carbon atoms. This is an unusual structure, and obviously the molecule is very strained.

Treatment of this molecule with formic acid and THF, then with HCl and methanol will form 3-hydroxy azetidine hydrochloride,
which has a formula of HCl.(NHC3H5)OH, where the group (NHC3H5) is a square ring. A group on the nitrogen would be considered in the 1-position, whereas a group on the carbon atom on opposite end of the ring would be in the 3-position. The hydrochloride salt converts to plain 3-hydroxy azetidine when it is neutralized by a weak base.

THF is just a type of cyclic ether. Regular ethyl ether can be used instead. BuLi can be prepared by reaction 1-bromo-butane with lithium metal, using a solvent such as Et2O or benzene. If 1-chloro-butane is used instead, a precipitate of LiCl will form, since this salt does not form a complex with the BuLi like LiBr does. Also 1-chloro propane could probably work instead.
(1-chloro propane can be formed by reacting acetone and a limited quantity of Cl2 at room temperature, forming chlroacetone, then reducing this ketone by using anhydrous Hydrogen Iodide). Note that ethers such as THF react with BuLi above (minus) -20degC, therefore the temperature must be kept below this the whole time. Dry ice with acetone "ice baths" achieve a -78C temperature.

As a side note, when BuLi is heated, it forms lithium hydride and gives of Butylene gas C4H8, obviously this is in the absence of air.

Diethyl azodicarboxylate is a reddish orange liquid, with a structure of CH3CH2OC(=O)N=NC(=O)OCH2CH3
Hydrazine condenses with ethyl chloroformate to form the the above compound, except with two hydrogen atoms on the two central nitrogen atoms. In the reaction, hydrazine is gradually added in small additions, and after each addtion, Na2CO3 is added to neutralize the resulting HCl that gets formed. The central hydrazine group --NHNH-- can be oxidized to the diazo group --N=N-- using chlorine to form the final diethyl azodicarboxylate. This chemical gives off very poisonous fumes, which is suggested by its acronym, DEAD, which is what you may be if you do not take proper precautions!

Ethyl chloroformate can be prepared in moderate yield by reacting a phosgene (COCl2) with excess pure ethanol.

An unusual reaction is: the Trioxane form of formaldehyde disproportionates, using a boric acid catalyst, to form methyl formate. Trioxane was heated with a minute quantity of boric acid at 250C for several hours, using a hydrocarbon solvent. This gave a 70% yield of methyl formate. If a sodium ethoxide catalyst is used instead, the mixture does not require heating.
"Boric acid catalyzed Tishchenko reactions", by Paul Stapp, Journal of Organic Chem.(1973)
The methyl formate can substitute for the ethyl formate, when making the azodicarboxylate ether, *Dimethyl* azodicarboxylate being formed instead.

3-Chloro Propylene

this compound is difficult to prepare, one way is to pass chlorine gas, preheated to 400C, and react it with propylene gas, which is the product of isopropyl alcohol with concentrated H2SO4. If the chlorine gas has been preheated, the main reaction will be the formation of 3-Chloro Propylen, through a radical mechanism. Otherwise chlorine will just react to form the undesirable byproduct of 1-chloro propylene ClCH=CHCH3. This undesirable reaction even happens when the two a simply mixed without heating. A longer route exists is it is desired to work with lower temperatures.

Synthesis of 3-hydroxy propylene CH2=CHCH2OH

A mixture of 500g anhydrous oxalic acid and 500g of glycerol was heated under reduced pressure, using a hot water bath for at least 4 hours until formic acid ceases to distill over. The mixture was then gradually heated to 240degC (under normal pressure) the flask being fitted with a fractionating column. At 220-225degC carbon dioxide is given off and a mixture of approximately equal amounts of 3-hydroxy propylene and allyl formate distilled, leaving a residue in the distillation flask containing about half of the glycerol initially used. only minute traces of acrolein is produced in the reaction. The distillate was treated with 50g NaOH in 1L water to hydrolyze the formate). This is distilled after waiting 6 hours. The first 300 mL of distillate contained all the allyl alcohol, which after fractionation yielded 200g of a allyl alcohol/water mixture (bp 87-98C) which may be dehydrated using dry K2CO3, yielding approximately 150g of anhydrous **3-hydroxy propylene**.

The glycerol residue left can be resused if the procedure is repeated. The yield of allyl alcohol is nearly quantitative calculated on the amount of glycerol reacted. Note that formic acid is produced in the reaction. Alternatively, glycerin and formic acid may be used to **make 3-hydroxy propylene** instead, see the "organic precursors 2" section.

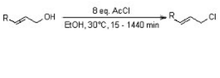
3-hydroxy propylene may be converted into **3-chloro propylene**, which can then be used in the TNAZ synthesis. This may be accomplished using acetyl chloride CH3C(=O)Cl, which can be prepared by reacting glacial acetic acid with SCl2.

SCl2 from buring sulfur in chlorine gas that has been dried by passing through baked CaCl2. Note that SCl2 reacts with water to form SO2, S, and HCl gas.

Acetyl Bromide could be used instead, forming 3-bromo ethylene, which can then react with anhydrous ammonia to form CH2=CHCH2NH2, with a NH4Br byproduct. This could be used as the starting precursor in synthesis 3.

Synthesis 4:
NH2C(CH2OH)3 was added to acetic acid using a chloroform and ethyl ether solvent, then anhydrous HBr and glacial acetic acid were added. The mixture was put into a sealed tube and heated to 155degC. This formed HBr.NH2C(CH2Br)3 in a 70% yield. This was then reacted with sodium hydroxide at 80degC under reduced pressure (10% of regular atmospheric). This formed BrCH2C{CH2}2N, where both the {CH2} groups, as well as the 2nd Carbon atom in the sequence are bonded to the Nitrogen atom. This is a "azabicyclo" compound again. It basically looks like two triangles put together to form a parallelogram. However the yields for this step are only around 10%. This is reacted with a solution of sodium nitrite and a solution of HCl to form 1-(NO),3-(NO2),3-(CH2Br)-azetidine. The structure can also be shown as O=N(NC3H2)(CH2Br)(NO2), where the last two groups are bonded to the same carbon on the opposite end of the square from the nitrogen atom. This compound has a nitrosamine group in it. This is then oxidized with nitric acid (optionally using trifluoroacetic acid solvent) at 0degC, then neutralized with boiling bicarbonate solution, and finally reacted with an alkaline solution of sodium nitrite with ferricyanide and persulfate. The compound formed is now TNAZ. This whole procedure gives very low yields, and so synthesis 4 is not suitable for making more than an extremely small quantity of TNAZ for studying. One added note, the neutralization with bicarbonate is very slow since the the intermediate ring compound is not soluble in water. Sodium Iodide forms a complex with the common solvent DMSO, and once the sodium ions are thus dissolved, sodium bicarbonate will also be sparingly soluble in the DMSO-NaI mixture. This side step is extra trouble, but allows the neutralization to procede rapidly without trouble.

For making the 3-chloro propylene from propylene alcohol,



Comments