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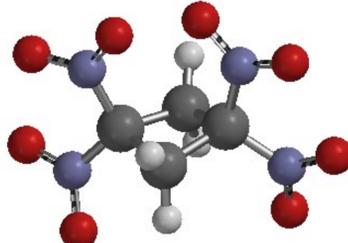
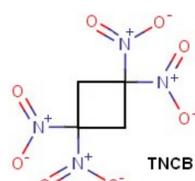
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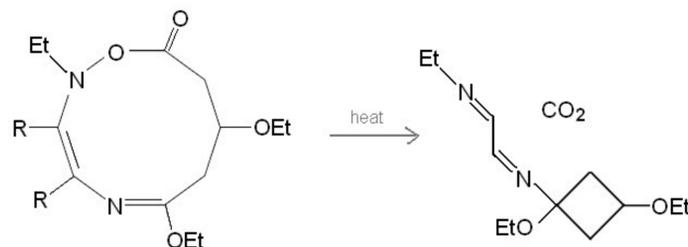
TNCB

1,1,3,3-tetranitro-cyclobutane



Detonation Pressure: between 372 - 400 kbar
Density: 1.83 g/mL.
Melting Point: 165 degC (not considered melt-castable, significant decomposition)
TetraNitro Cyclobutane is more powerful than HMX.

Below is my idea:
The OEt hydrolyzes off with conc HCl solution



The product of the above reaction reacts with concentrated HCl solution to form 3-hydroxy cyclobutanone. This can be selectively oxidized to O=(C4H4)=O, then condensed with hydroxylamine in alkaline solution, then NO₂ bubbled in, then treatment with dilute H₂O₂ will form 1,1,3,3-tetranitro cyclobutane

TNCB

synthesized **trans-1,2,3**-tris(nitramino)cyclopropane by the nitration of **1,2,3**-tris(acetamido) cyclopropane with Ac₂O with HNO₃ or TFAA and HNO₃, followed by ammonolysis of the amide groups, and subsequent acidification of the tris ammonium salt

In the attachment below, the resulting 1,3-dinitro cyclobutane can be easily nitrated to 1,1,3,3-tetranitro cyclobutane (TNCB).

See the section "TNAZ", which, for the procedures in the final steps, discusses applicable chemical reactions for TNCB.

1,1,3,3-tetranitrocyclobutane

1,3-dinitropropane would probably react with methylene bromide, CH₂Br₂, in the presence of a non-nucleophilic base. This could be a mild base such as sodium acetate, but another interesting choice could be *1,8-Bis(dimethylamino)naphthalene*, sold as "Proton Sponge". The compound has an extreme affinity for hydrogen ions, yet is not nucleophilic (it is not a source of basic anions that could substitute off the bromine atoms in CH₂Br₂). This would form, besides from some unwanted polymerized byproducts, 1,3-tetranitrocyclobutane.

1,3-tetranitrocyclobutane could be nitrated to **1,1,3,3-tetranitropropane**. For example, oxidative nitration of N-tert-butyl-3-nitroazetidine to N-tert-butyl-3,3-dinitroazetidine can be done in 60% yield with a mixture of sodium nitrite and sodium persulfate in the presence of potassium ferricyanide, or in 39% yield with a mixture of sodium nitrite and silver nitrate. This oxidative nitration with persulfate and ferricyanide is probably similar to the type of procedure below:
Quote:

To a stirred solution of 2.66 g (66.5 mmoles) of sodium hydroxide in 15 ml of water at 20° was added 5.0 g (66.5 mmoles) of nitroethane. When all the nitroethane dissolved, the solution was cooled to 5°-7° in an ice-water bath. The sodium salt of nitroethane was prepared as above. To the stirred solution was added a solution of 20 g (288 mmoles) of sodium nitrite in 50 ml of water, followed by a solution of 4.4 g (13.4 mmole) of potassium ferricyanide in 25 ml of water. Finally, 16.0 g of solid sodium persulfate (67 mmoles) was added all at once. The reaction temperature, moderated by an ice-water cooling bath, increased to 50°. The orange mixture was stirred at 25° for 1 hour and then cooled to 10°. Urea, 20 g (0.33 mole), was added, followed by 10 ml of glacial acetic acid. The mixture was extracted with three 25 ml portions of ether and the combined extracts were washed with brine and dried. The crude product was distilled to give 4.2 g (52% yield) of 1,1-dinitroethane, b.p. 87°-89° (16 mm), identified by its nmr spectrum. *Patent 4910322*

Another variation of the reaction may be possible. If 1,1,3,3-tetranitropropane was used instead in the reaction with CH₂Br₂ and base, then the **1,1,3,3-tetranitropropane** could potentially be directly formed, without the need for subsequent nitration.

Information about tetranitropropane

1,1,1,3-tetranitropropane has a melting point around 50 degC. The solid is insoluble in both water and heptane, but soluble in toluene, methanol, acetic acid, and especially acetone. It has a density of 1.7g/cm³, acceptable thermal stability, and a detonation velocity around 6.75 km/sec.

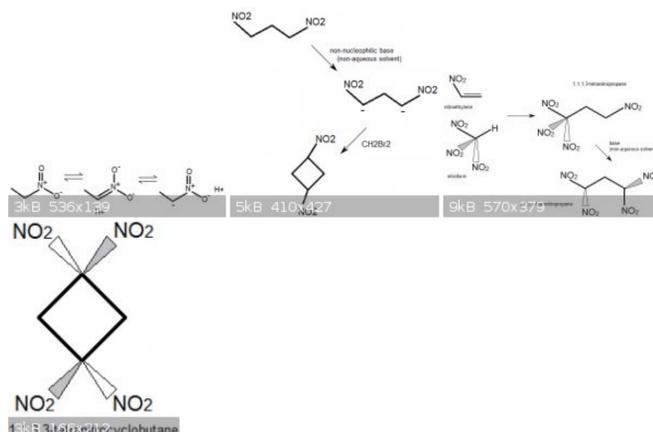
72g of Nitroethylene is condensed with 150mL trinitromethane, using 300mL methanol as a solvent at 0degC. Next the mixture is refluxed and the excess methanol is then distilled off with reduced pressure. The residue is dissolved in 0.75L glacial acetic acid, the product (1,1,1,3-tetranitropropane) then precipitates after addition of water.

In aqueous solutions of alkali or ammonium hydroxide 1,1,3,3-tetranitropropane isomerizes into 1,1,3,3-tetranitropropane (one of the nitro groups rearranges onto the other carbon). This reaction may seem inexplicable, but in alkanes with geminal or vicinal nitro groups, one of the nitro groups can potentially ionize off as nitrite. I can write a possible reaction mechanism diagram if anyone really wants to understand how this works. The reason the 1,1,3,3- isomer forms is probably that it is the most favorable. For example, nitroalkanes that do not have a hydrogen atom on the same carbon as the dinitro group require a higher temperature for thermal decomposition than those that have such a hydrogen (*P. S. DeCarli, D. S. Ross, Robert Shaw, E. L. Lee, H. D. Stromberg*).

1,1,3,3-tetranitrocyclobutane

Density: 1.83 g/mL. Melting Point: 165 degC (not considered melt-castable, significant decomposition)

This compound is probably more powerful than HMX.
Another explosive compound, TNAZ, for example, which also contains a geminal pair of nitro groups on a square ring, is *7.7% more energetic* than HMX. TNAZ, however, only has three nitro groups so its density is lower, and as a result its detonation velocity is slightly lower.



also to emphasise that tetranitrocyclobutane (TNCB) is probably *less* sensitive, and **more** stable than HMX. Although TNCB has been prepared, there finds not any information about its detonation velocity or sensitivity.

We can, however, probably get a good idea of these properties by looking at the properties of a structurally similar energetic compound, TNAZ, which has been researched in much more detail. As TNAZ contains structural elements of both TNCB and RDX, one would expect that the properties of TNAZ would lay between TNCB and RDX. In other words, if TNAZ is less sensitive than RDX, then TNCB should be even less sensitive.

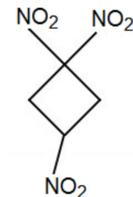
For thermal stability, although 1,1,3,3-tetranitrocyclobutane contains geminal nitro groups [two nitro groups on the same carbon atom], this should not be a problem. The strained square ring should prevent thermal instability. For example, TNAZ begins to slowly decompose, releasing small amounts NO₂, above 180degC. Prolonged temperatures above 200degC can lead to explosion, but TNAZ can withstand a shorter duration of heating up to 240degC. For comparison, RDX begins to decompose at 170 °C, (RDX and HMX are very similar chemically).

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.

So tetranitrocyclobutane should have ideal explosive properties.

1,1,3-trinitrocyclobutane

Although 1,1,3,3-tetranitro-cyclobutane is not considered melt-castable (there is significant decomposition at its 165 °C melting point), perhaps 1,1,3-trinitrocyclobutane *would* be melt-castable.



A structurally similar compound, 1,3,3-trinitroazetidine (TNAZ) is melt-castable, having a melting point of 101-103 °C.

Trinitrocyclobutane could potentially be a high-performance replacement for TNT. Just compare molecular formulas, C₄H₅(NO₂)₃ C₇H₆(NO₂)₃ for TNT

And unlike the synthesis for TNAZ, preparing cyclobutane derivatives could potentially be much more straightforward.

Partial condensation of formaldehyde with nitromethane under alkaline conditions to obtain 2-nitroethanol (note that 2-nitroethanol is toxic and can potentially be absorbed through skin contact). 2-nitroethanol then distilled with conc. H₃PO₄ and NaBr to give 1-nitro-2-bromoethane. This is then cyclized to 1,3-dinitrocyclobutane in a procedure similar the one used by Wade (synthesis trans-1,2-Dinitrocyclopropane (DNCP)). **2.6 Synthesis of Compound 6: trans-1,2-Dinitrocyclopropane (DNCP)**. *Wade and co-workers' procedure for the synthesis of trans-1,2-dinitrocyclopropane*

An oxidative nitration could then be done to add the third nitro group, 60% yield, using a mixture of sodium nitrite and sodium persulfate in the presence of potassium ferricyanide⁺, or in 39% yield with a mixture of sodium nitrite and silver nitrate.

In the second attachment

The Henry addition reaction between dinitroethane and glyoxime is not straightforward, and the yields are low. A great excess of dinitroethane must be used to prevent unfavorable further condensation products with the glyoxime. To increase dimer yields, a third inert solvent should be used, for example DMSO with NaI and NaOH dissolved in. The more polymerized condensation products will be much less soluble in ether, while once the amines are added, any residual octagonal rings will practically insoluble in alcohol.

The nitrogroups are disproportionated/hydrolyzed off by warming with acid, leaving ketones. This also forms hydroxylamine salt as a byproduct. (Meyer reaction). The two need not be separated, since they can react back together in the next step. The ketone is then condensed with hydroxylamine using a strong solution of NaOH to form the oxime (1,3-diamino, cyclobutane-2,4-dioxime) and this is then cold nitrated to 2,4-diamino-1,1,3,3-tetranitrocyclobutane, which should have a higher density and be more powerful and less sensitive than plain TNCB.

Dinitroethane is made by the spontaneous addition of nitrogen dioxide and ethylene. It is not very thermally stable, and is somewhat chemically reactive, so should be considered an intermediate precursor rather than a desired energetic compound.

In the presence of a base, it can react (Michael addition) with CH₂O to add four (CH₂OH) groups, the resulting compound can then be nitrated to give a melt castable (melting at only 85C) compound that is comparable to HMX in power. Because of the four methylene groups, this is an uncommon example of nitro groups withstanding mixed acid nitration. The compound has a decomposition point of 141degC. 1.915 g/ cm³ (see third attachment)

Further information, **Dihydroxyacetone and amines spontaneously react to form methylglyoxal CH₃C(=O)C(=O)OH**.

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Ĉ	cyclobutanereaction3.bmp (824k)	Anders Hoveland, Nov 1, 2010, 11:51 AM	v.1	d'
Ĉ	diaminocyclobutane.bmp (969k)	Anders Hoveland, Nov 8, 2010, 11:15 AM	v.1	d'

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