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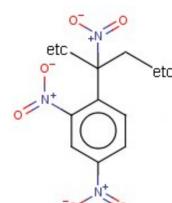
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Energetic Binders and Plasticizers

Polytetranitro-Styrene

It is well known that Styrofoam can actually be nitrated into Polydinitrostyrene. However, further nitration of this polymer is not straightforward, because the hydrocarbon polymer chain is vulnerable to destructive oxidation from nitration with concentrated acids. NitroPolystyrene can offers the opportunity for an energetic binder for compositions. However, the common less nitrated "dinitro-" version is not as energetic as the nitrate ester of cellulose.



PolyTriNitroStyrene

First bubble in nitrogen dioxide, then perform a cold nitration with 98% sulfuric acid and nitric acid. The nitration should not be longer than four to six minutes, otherwise the nitric acid will begin to attack the hydrocarbon chain. A polymer with the following structure will form

.....(NO2).....

 (NO2)2(C6H3)--C--CH2--etc

etc.....

It is soluble in acetone, forming a gunky paste that can be molded, and then dried and hardened into a plastic shape. The polymer has explosive properties similar to TNT. It can be used as the binder in "plastic-bonded" formulations, and it also performs well with potassium chlorate.

If a third nitro group is desired on the benzene ring, Cu(NO3)2 dissolved in Ac2O must be used. The nitric acid will sooner oxidize the hydrocarbon chain than put a 3rd nitro group on the ring. (Styrofoam can also be nitrated with more dilute acids (70%) if the left to boil for 1-2 hours, but that only forms mono-nitro phenol, and waste most of the nitric acid, giving off a lot of CO2 and NO2.)

When bubbling in the nitrogen dioxide, the reaction proceeds rapidly and with highest yield at 90 degrees Celsius, but the reaction will also happen at room temperature. The nitration with NO2 proceeds through the aromatic ring conducting an electron away from the methyl group, allowing an H+ ion to ionize off and leaving a radical. See the attachment below.

It might be desirable to conduct the initial reaction with NO2 in an organic solvent, such as benzene or CH2Cl2, plain water is not likely to fully penetrate into the polystyrene. For the subsequent nitration with mixed acids, a CH2Cl2 solvent might also be desirable. CH2Cl2 solvent during mixed acid nitration is frequently mentioned in the literature; presumably the aromatic ring gets nitrated at a much faster rate than the CH2Cl2 gets oxidized.

Dinitropolystyrene has a variable detonation velocity, depending on density and extent of nitration. At 0.25 g/cm3, the detonation velocity is 1510 m/sec. When the density is increased to 0.95 g/cm3, the detonation velocity increases to 2 km/s.

The density could probably be increased by squeezing in a vice. The styrofoam precursor used in both measurements was probably the foam form, which would explain why the nitrated products ended up with low measurements for density. However beginning with a denser form of polystyrene is likely to sterically hinder nitration to a greater degree, so for measurements of the denser forms of polynitrostyrene, it should be assumed that the polymer is not fully nitrated to the full theoretic dinitro ratio. This leaves unanswered the question of what the maximum theoretic detonation velocity would be of High-Density nitropolystyrene in a with a complete dinitro average ratio. It is very difficult to significantly increase the density of a low density polymer after it has formed. An idea would be to melt the polymer with a melt-castable filler, to fill in the "spaces" between the molecular chains.

Phenylnitromethane cannot be nitrated into "tetra-nitro toluene" because the nitromethyl group is vulnerable to disproportionation into a carboxyl group and hydroxylamine (which will quickly get oxidized) in acidic environments.

http://article.pubs.nrc-cnrc.gc.ca/p..._startPage=3483

There is an unlikely possibility that this "modified Meyer reaction" could be minimized if the temperature was kept far below room temperature. however, then the nitromethyl group would be likely to get nitrated to a trinitromethyl group, which would make the final product very sensitive and thermally unstable.

However, for nitro-polystyrene, where the nitro is on a carbon which is not bonded to a hydrogen atom, the Meyer disproportionation reaction is not possible, and neither is the formation of a vulnerable-to-nitration tautomer possible (such as the aci-form of nitromethane).

"Copper nitrate, in combination with acetic anhydride, is an effective reagent for nitration of aromatic compounds, under what are known as "Menke conditions", in honor of the Dutch chemist who discovered that metal nitrates are effective reagents for nitration." <http://webcache.googleusercontent.co...&ct=clnk&gl=us>

When using Cu(NO3)2 in Ac2O, "nitration of toluene . . . produces a mixture of at least 9:1 of 2,4- and 2,6-dinitrotoluene." Compare this with a ratio of " 8:2 when using mixed acid." Josef Meissner GmbH & Co., DE 2 921 487 (1979)

Phenylnitromethane has been prepared by the nitration of toluene with dilute nitric acid in a sealed tube. Konowalow, Ber. 28, 1860 (1895). (the sealed tube probably implies heating)

"Nitrogen dioxide has been known to trap the benzyl radical more efficiently than molecular oxygen, thus favoring phenylnitromethane over benzaldehyde"

"To get phenylnitromethane, the reaction must be carried out at low temperature"

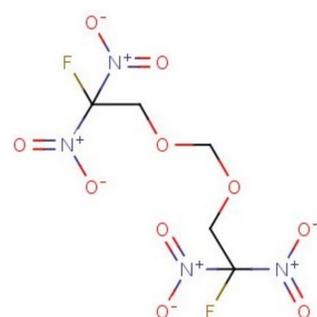
"nitration of toluene with nitrogen dioxide at a temperature between 20C to 95C yields a mixture of phenylnitromethane and phenyldinitromethane"

"synthesized phenyldinitromethane by treating phenylnitromethane with dinitrogen tetroxide in ether"

<http://onlinelibrary.wiley.com/doi/1...059364.ch1.pdf>

FEFO

FEFO, an acronym for bis(2-fluoro-2,2-dinitroethyl) formal, is an energetic plasticizer or binder, the synthesis can be found on rogue science, but here is the molecular structure:



The calculated detonation pressure for FEFO is 295 kbar, the calculated detonation velocity is 8.3 km/sec, and the calculated density is 1.75 g/cm3. The "LLNL -- Explosive Handbook: Properties of Chemical Explosives and Explosive Simulants" (1981) gives the measured detonation velocity as 7.5 km/sec, with an observed density of 1.607 g/cm3. FEFO is an oily liquid at room temperature, with a melting point of 14 degC. The compound is decently insensitive. It has been considered as a substitute for astrolite, since it is less sensitive, and has a calculated detonation velocity only 100 m/sec lower. The fluorine stabilizes the gem-dinitro groups, resulting in good thermal stability for the compound. FEFO is somewhat volatile and is highly toxic, easily absorbing through skin. Precautions need to be taken when handling the compound.

Preparation of 2,2-dinitro-2-fluoroethanol Precursor

Nitromethane and methyl nitrate react in the presence of a nitrite ion to form methanol and a psuedonitrosole R--CH(NO)(NO2):

R. K. Blackwood, N. Kornblum and D. D. Mooberry, J. Am. Chem. Soc., 1956, 78, 1501.

Dinitromethane reacts with CH2O in the presence of a base to form (NO2)2CHCH2OH. This can react with Iodine to form I(NO)2CHCH2OH.

However, unlike Rogue Science's synthesis, elemental fluorine need not be used. In the presrence of a base, 1,1-dinitroethane reacts with iodine to form 1-iodo-1,1-dinitroethane, which when dissolved in a ketone solvent, can then react with solid sodium fluoride to form 1-fluoro-1,1-dinitroethane, the sodium iodide byproduct being soluble in ketones. 2-hydroxy-1,1-dinitroethane can be formed by condensing dinitromethane with CH2O using a base.

2,2-dinitro ethanol can be fluorinated to 2-fluoro-2,2-dinitro ethanol with either F2 or ClO3F. The latter fluorinating agent can be prepared from Cl2O7 acting on NaF, the Cl2O7 being the product of the dehydration of perchloric acid using P2O5. Thus electric current is not necessary for preparation of the precursor. The fluorinating gas is diluted with nitrogen and fed into an aqueous alkaline solution (the sodium salt of dinitroethanol). Yields are typically 60%, although 70% is possible. Ethyl ether works well for extraction.

Alternatively the fluorination of nitroform gives 80-90% yields. The resulting FC(NO2)3 is reduced with an alkaline solution of H2O2 (at -5 degC) and simultaneously condensed with formadehyde to give 2,2-dinitro ethanol. (H2O2, although usually an oxidizer, can sometimes act as a reducing agent with the concurrent evolution of oxygen gas, for example it reduces hypochlorite to chloride).

Fluorodinitroethanol is a colorless liquid with a bp of 53 degC at 1mm Hg, density of 1.54 g/cm3 at 25 degC. It can be vaccum distilled with minimal decomposition.

Alternative Variations

Another variation would be to reflux 1,1-dinitroethylene with formaldehyde, which produces 1,1-dinitro,3-hydroxy propane,

The 1,1-dinitro,3-hydroxy propane could then possibly be reluxed with more 1,1-dinitroethylene, with iodine then being added into the reaction after the other two chemicals have already been mixed. This might produce a precursor with the structure:

(O2N)2(I)CCH2CH2OCH2C(I)(NO2)2, where the formula is C5H6N4O9I2. I think I read somewhere that an unsaturated hydrocarbon would condense with an alcohol in the presence of bromine to form a bromo-ester, someone please find out about this.

Alternative preparation of 2,2-dinitro-2-fluoroethanol precursor

The nitration (using a 65:85 ratio of pure HNO3 and 30% concentrated oleum, respectively) of 1,2-dichloro-1,2-difluoro ethylene, ClFC=CFCl, gives chlorofluoronitroacetic acid (40% yield), with a formula HOC(=O)CFCl(NO2).

Chlorofluoronitroacetic acid reacts with red fuming nitric acid (HNO3 / NO2) to give chlorofluoronitronitrosomethane, with a formula O=N-CFCI(NO2), and which possesses a deep blue color. *I.V. Martynov, Y.L. Kruglyak, S. Markarov. Zh Obshch. Khim. volume 33, p3385. (1963)*

This latter compound was then oxidized to dinitrofluorochloromethane, using HNO3 / H2O2, and next reduced (using potassium iodide) to dinitrofluoromethane, and simultaneosly reacted with formaldehyde (in a single step) to give 2,2-dinitro-2-fluoroethanol, with a formula HOCH2CF(NO2)2.

1,2-difluoro-tetrachloroethane can be reduced to CFCl=CFCl using Zn in 80% yield, other isomers are also formed and are difficult and impractical to remove before subsequent nitration. **1,2-dichloro-1,2-difluoro ethylene could be prepared by reacting NaOH with 1,2,3-dichloro-1,2-difluoro ethane. This latter compound could be made by burning the refrigerant "R-1112a" with a limited ammount of chlorine. Warning: do not use any trivalent phosphorus compounds in any reaction with the above precursors; this could result in an extremely deadly vapor, with acetylcholine blocking properties. Even a personal protective respirator, in addition to a fully contained fume hood would be completely inadequate for protection.**

Synthesis:

Into a 100-mL 3-necked round-bottomed flask equipped with a magnetic stir bar, thermometer, and drying tube prepare a mixture of 15.3 g of 2,2-dinitro-2-fluoroethanol in 30.6 mL of ethylene chloride. Immerse the flask in a cold water bath. Slowly add, while stirring, 16.8 mL of 96% sulfuric acid over a 5 minute period. The temperature of the reaction should be kept between 20-25 C during the addition. Add 1.5 g of paraformaldehyde to the mixture in one portion and stir for 100 minutes. Place the mixture in a separatory funnel and remove the acid layer. The organic layer is washed with four portions of 15 mL of 1.25N sodium hydroxide solution and four portions of 15 mL of water. The washed organic layer is filtered to remove any impurities and heated at 50 C under reduced pressure to remove the solvent. Final yield of liquid FEFO is 11.7 g. (about 75% yield) NOTE: If the fluorine atom where replaced by a methyl group, sulfuric acid would then be too strong of a dehydrating agent for this type of reaction, and a BF3 catalyst would then need to be used instead.

The methylene chloride solution used to prepare the energetic plasticizer FDNE is concentrated to 500 mL. Add to this a mixture of 21 g of paraformaldehyde dissolved in 225 mL of concentrated sulfuric acid. Stir the mixture for 3 hours at room temperature to fully convert it to FEFO. Place the mixture in a separatory funnel and remove the acid layer. The organic layer is washed with four portions of 15 mL of 1.25N sodium hydroxide solution and four portions of 15 mL of water. The washed organic layer is filtered to remove any impurities and heated at 50 C under reduced pressure to remove the solvent.

The washed crystals of bis(potassium-2,2-dinitroethyl)formal as prepared here are suspended in a solution of 10 g of sodium carbonate (or sodium bicarbonate) in 500 mL of water and heated at 50 C to concentrate the mixture to 400 mL. A steady flow of a mixture of fluorine and nitrogen gas in a ratio of 1:3.75 is bubbled into the mixture through a bubbler. The reaction is kept at 23-25 C, through the use of an ice bath, and will require about 100 minutes to complete. By the end of the reaction the mixture will be milky white in appearance. The mixture is cooled to 5 C and extracted with three 100 mL portions of chloroform. The extracts are combined and washed with 5% sodium hydroxide solution followed by water. The washed extract is gently heated under reduced pressure to remove the solvent leaving behind pure FEFO. Final yield is a little over 14 g or 55%.

Into a 20-mL Erlenmeyer flask prepare a solution of 9.0 g of 2-fluoro-2,2-dinitroethanol in 5 mL of 90% sulfuric acid. Cool the solution in an ice bath to below 5 C and rapidly add 1.8 g of paraformaldehyde with stirring. The mixture is stirred for 1 hour at room temperature. Pour the mixture into a beaker containing an excess of crushed ice. An oily layer will form which is decanted off and dissolved in a minimum of ether. The ether solution is washed with four portions of 10 mL of 5% sodium hydroxide solution and with four portions of cold water. The washed ether is then dried over anhydrous magnesium sulfate. The ether is removed by gently heating at 50 C under reduced pressure leaving behind pure FEFO.



[phenylnitromethane.bmp](#) (434k)

Anders Hoveland, Nov 2, 2010, 7:13 PM

v.1



Comments