

HOME

1,2,3-TRIAZOLES

1,2,4-TRIAZOLES

BASIC EXPLOSIVE

DADNE

DIAZO PRIMARIES

DPT

FURAZAN

NHN

NITROALKANES

NITROCUBANE

NITROGUANIDINE

NITROLIC ACIDS

PERCHLORATES

PYRAZOLE

TETRAZENE

TETRAZOLE

TRINITROMETHANE

STEMAP

trinitromethane

Physical Properties

Trinitromethane melts at 15°C, and begins slowly decomposing above 25°C. At room temperature nitroform is a colorless, or slightly yellow, oily liquid.

Trinitromethane can form salts with a base, such as methylamine or ammonia, or it can dissolve in hydrocarbons (although this can be very dangerous).

Chemical Properties

Trinitromethane can form salts with a base, such as methylamine or ammonia, or it can dissolve in hydrocarbons. It can be mixed with either nitro methane or nitro ethane, to form a powerful explosive binary mixture. The one with EtNO2 is somewhat more powerful, but it also requires a higher ratio of HC(NO2)3, so if nitromethane is easily available in large quantities it may be preferable. (the 'E' means the –CH2CH3 group)

Salts of trinitromethane are more stable (and somewhat less energetic) than perchlorates, although trinitromethane itself is fairly sensitive. The C(NO2)3(-) anion is very stable because of the resonances, there being four additional electrons to resonate around the six oxygen atoms. These salts are also known as nitroformates and are bright yellow in color. Trinitromethane oxidizes ferrous ions (Fe+2) to ferric (Fe+3). Dinitromethane can also oxidize the Fe+2 ion, but only if an alkaline solution of dinitromethane is added to an acidified solution of a ferrous salt. This is because the transient "aci-form" tautomer O2NCH=NO2H, which only exists for a few seconds, is more reactive.

Toxicity

Trinitromethane, while still giving off mildly poisonous fumes, is far less toxic than tetranitromethane. You would be well advised to avoid ever preparing tetranitromethane, which was once considered for use as a chemical weapon. Trinitromethane is somewhat poisonous: 800 mg/m3/2 hour Inhalation Mouse LC50, compare this with 12300ppm (for 36min, LC50) for tetranitromethane. It can be seen that tetranitromethane is far more toxic (it is highly recommended that the synthesis of this compound never be attempted), but nitroform should still be assumed to give off toxic vapor, and so should be handled outdoors or behind a windowed hood. The boiling point is 175.1 °C so at least it is much less volatile than tetranitromethane. Moderately toxic by inhalation. Irritating to skin, eyes; and mucous membranes. Inhalation can cause headache and nausea. Causes mild necrosis.

Explosion Hazard

A very dangerous explosion hazard; explodes when heated rapidly. Dissolution is exothermic and solutions of more than 50% can explode. Mixtures of 90% trinitromethane + 10% isopropyl alcohol in polyethylene bottles have exploded. Frozen mixtures with 2-propanol (10%) explode when thawed. Can explode during distillation. Mixtures with divinyl ketone can explode at 4°C. Trinitromethane itself is sensitive (about as much as picric acid), and mixtures of it and other hydrocarbons are more sensitive than the dangerous nitrate esters. Such mixtures are thermally unstable, quickly decomposing above 100degC, such decomposition can lead to detonation.

Salts of Trinitromethane

Ammonium nitroformate is much more stable than the sodium salt. Silver nitroformate slowly decomposes at room temperature, and is a very sensitive explosive. The potassium salt, KC(NO2)3 is a lemon yellow crystalline solid that decomposes slowly at room temperatures and explodes above 95 °C. Ammonium nitroformate deflagrates or explodes above 200 °C. Hydrazinium nitroformate is thermally stable to above 125 °C. Most salts of trinitromethane derive from the aci-form. However, the silver and mercuric salts exist in two forms: colourless and yellow. This may indicate that two forms of these salts - nitro and aci - can exist.

Preparation

There are several routes to prepare trinitromethane.

By direct substitution

Trinitroacethane has been obtained from iodopiricin I3CNO2 and silver nitrite AgNO2. Hantzsch, Chemische Berichte, 39, p2478, (year 1906) Such yields would be expected to be low, less than 11%, since nitrite substitution on secondary and tertiary haloalkanes gives successively lower yields than a primary haloalkane because a small proportion of nitrite gets substituted instead of nitro groups, which in this case would lead to degradation of the molecules with such undesirable substitutions. Bromopiricin could alternate be used, but the reaction rate for the substitution of chloropiricin would be far too slow to be practical (although there do exist room temperature catalysts to speed up such substitutions). Even with iodopiricin, the reaction will likely take several days for completion. Both starting chemicals must be first dissolved in appropriate solvents, for example benzene. Use of propylene carbonate as a solvent might possibly enable sodium nitrite to be used instead of silver nitrite.

By reducing tetranitromethane

Hantzsch and Rinckenberger obtained the ammonium salt of trinitromethane by treating tetranitromethane with aqueous ammonia. It is well known that trinitromethane can be reduced to nitroformate salts using an alkaline solution of hydrogen peroxide. This is the most usual route for preparing trinitromethane. Prepare a solution of 168 g of potassium hydroxide in 350 mL of water in a round-bottomed 1000-mL Florence flask, and cool to 5 °C with a salt-ice bath. While stirring, add 108 mL of 30% hydrogen peroxide to the solution. Next, add 117 mL of tetranitromethane at a rate which keeps the temperature at 20-25 °C, add while stirring. The temperature is then allowed to rise to 30 °C over 15 minutes. The bright yellow solid, that should have formed, is filtered to collect it using glass filter paper because of its high acidity, washed with anhydrous methyl alcohol, then anhydrous ethyl ether, and finally air (need to give 100% of the potassium salt of trinitromethane). The salt is suspended in anhydrous ethyl ether and anhydrous hydrogen chloride gas is exploded in a unit the yellow color disappears. The white precipitate of potassium chloride is filtered off and washed with anhydrous ethyl ether. The ethyl ether is evaporated from the filtrate and additional washings at reduced pressure give 85-90% of crude trinitromethane which can be purified by sublimation.

Although usually an oxidizer, in some reactions hydrogen peroxide can act as a reducing agent. For example, it reacts with hypochlorite to form chloride and oxygen gas. Similarly, an alkaline solution of H2O2 reduces Cl2 to Cl- ions.

From Trinitroacetone

Trinitroacetone can be synthesized by the nitration of cyanoacetic acid with a solution of sulfur dioxide and 98+% concentrated nitric acid in carbon tetrachloride, with 73-77% yields. The trinitroacetone can be stored as a solution in the carbon tetrachloride, and need not be isolated for further use on other reactions. NCC2HC(=O)OH + (3) HNO3 + (3)SO2 --> NCC(NO2)3 + CO2 + (3) H2SO4

Trinitroacetone is a colorless, camphor-like, crystalline compound melting at 41.5 °, and detonating violently at 220°. It hydrolyzes to carbon dioxide and the ammonium compound of nitroform by water or alcohol at ordinary temperatures.

"Nitroacetone has been prepared by treating methanoic acid with thionyl chloride SOCl2 in ether. That the compound so obtained is nitroacetone follows from the fact that it yields a nitroetherylamino-oxime with hydroxylamine, and gives the nitrolic acid reaction. Its formation from methanoic acid proves the correctness of the formula. (methanoic acid has the formula HON=NCH2CH2NO2, and is well discussed elsewhere on this forum). Nitroacetone, NCC2HNO2, is obtained as a fairly stable yellow oily liquid. When pure, it may be distilled under reduced pressure (boiling point 96 ° under 14mmHg reduced pressure). It does not seem to be explosive in unit the yellow color disappears. The white precipitate of potassium chloride is filtered off and washed with anhydrous ethyl ether. The ethyl ether is evaporated from the filtrate and additional washings at reduced pressure give 85-90% of crude trinitromethane which can be purified by sublimation.

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From Nitric Acid and Isopropanol

A 250 ml three-necked flask was fitted with a mechanical stirrer, a thermometer and a dropping funnel. 140 ml (3.33 moles) of 98% nitric acid was introduced into the flask. The acid was warmed to about 60 degree. C. and 20 ml (0.26 mole) of isopropyl alcohol was added dropwise over a 10-minute interval. External cooling was used to maintain the temperature at 60°C. The solution was then heated to a temperature of about 70°C, and held at that temperature for 2 hours. Substantial quantities of brown gaseous fumes evolved during this nitration. The solution subsequently was cooled to ambient temperature and analyzed for nitroform content. The yield of nitroform was determined to be 9.8 gm (approximately a 25% yield). To obtain significant yields of the desired trinitromethane it is essential that the isopropyl alcohol be introduced into an excess of nitric acid. Thus, the molar ratio of nitric acid to isopropyl alcohol will be in excess of about 8:1. Too great an excess of nitric acid will, of course, increase the cost of the method, and will require an unnecessary amount of nitric acid to be distilled and recycled to the process. Thus, the molar ratio of nitric acid to isopropyl alcohol generally is maintained within a range of from about 10 to 25, and preferably within a range of from about 15:1 to 20:1. The reaction temperature is not particularly critical, provided, of course, that the temperature must be sufficiently high to maintain the mixture of reactants in a liquid phase. In addition, the temperature should not be too high, otherwise substantial gas evolution takes place with little or no formation of nitroform. Therefore, the temperature generally has been maintained within a range of from about 25° to 85° C, and preferably within a range of from about 40° to 70° C. The time required for the reaction will vary with temperature, pressure ratio of reactants, etc. Generally, a time of from about 1 to 5 hours is sufficient to react substantially all of the isopropyl alcohol to form the desired trinitromethane. Yields of up to 50-58% have been obtained from a modification of this procedure.

From 4,6-dihydroxypyrimidine

Nitration of 4,6-dihydroxypyrimidine using mixed nitric and sulfuric acids yielded nitroform as the sole product, although gas evolution was also observed.

Other Possible Methods

A mixture of nitromethane and NaOH will form the salt of nitromethane, sodium "nitromethanate". Bubble in nitrogen dioxide into a solution of this salt, and trinitromethane can be obtained, because the intermediate aci- form of nitromethane, which is vulnerable to oxidation, is formed. The aci-form is probably CH2=NO2H. Alternatively, bubble mixed nitric oxides into a solution of sodium nitrite and nitromethane (which is sparingly soluble in water), then bubble in only nitrogen dioxide. Sodium nitrate and trinitromethane will form in solution.

B G Gowenlock and I Batt

"The isomerisation of nitrosomethane to formaldoxime", Theochem-Journal of Molecular Structure, 454 1998: 103-4.

B G Gowenlock, B King, J Pfab and M Witanowski

"Kinetic studies of the reaction of some nitrosoalkanes with nitrogen dioxide", Journal of the Chemical Society, Perkin Transactions 2, 1998: 483-5.

Excess treatment with nitrogen dioxide would likely result in trinitromethane, as NO2 oxidizes nitroso.

"The oxidation of nitrosobenzene by nitrogen dioxide in carbon tetrachloride has been re-examined"

"There is an early report S that a small quantity of nitrosobenzene was formed when dry chloroform solutions of nitrogen dioxide and nitrosobenzene were allowed to stand at 22.8C for 39 h."

J. Chem. Soc., Perkin Trans. 2, 1997, 1793 - 1798, DOI: 10.1039/a700258k

Kinetics of the oxidation of aromatic C-nitroso compounds by nitrogen dioxide

Brian G. Gowenlock, Josef Pfab and Victor M. Young

"Formaldehyde, an intermediate in ammonia oxidation, reacts with formaldehyde to form formaldoxime" Methanol and Formaldehyde Oxidation by an Autotrophic Nitrifying Bacterium by PA Voysey - 1987

Thoughts about Producing Trinitromethane:

Nitromethane can act as an acid, even though it is not acidic, and can form salts. In a mixture of nitromethane and ammonia, some of the molecules ionize to form a salt. The "nitromethane" ion, CH2=NO2(-) is much more sensitive than nitromethane. Even though a mixture of ammonia and nitromethane is less powerful than pure nitromethane, it is much easier to detonate. It is virtually impossible to detonate pure nitromethane otherwise. Nitromethane also can form hydroxylamine, if it is heated with 30% H2SO4. This will form hydroxylamine sulfate that can be removed, then reacted with Ca(NO3)2. This will form insoluble CaSO4 and leave hydroxylamine nitrate in solution. Hydroxylamine nitrate is much more powerful than ammonium nitrate, but it is very difficult to dry. Also, acetic anhydride can react with chlorine gas (and a tiny bit of water added) to form chloro-acetic acid. This can be distilled with NaNO2, and then CH3NO2 can be distilled out. This happens at only 70degC so a plastic bottle might be able to be used.

Nitromethane can be made by the nitration of methane, but only when there is a big excess methane. This means that the nitration has to be performed at 400C when the nitric acid is vaporized into a gas. The reason that it is difficult to obtain nitromethane is that nitric acid reacts with nitromethane much faster than it does with methane. First, strongly acidic solutions decompose nitromethane into hydroxylamine and formic acid. Hydroxylamine is a reducing agent, and is easily oxidized by concentrated nitric acid. Bubbling Nitrogen dioxide into a solution of nitromethane. Therefore, the temperature generally has been maintained within a range of from about 25° to 85° C, and preferably within a range of from about 40° to 70° C. The time required for the reaction will vary with temperature, pressure ratio of reactants, etc. Generally, a time of from about 1 to 5 hours is sufficient to react substantially all of the isopropyl alcohol to form the desired trinitromethane. Yields of up to 50-58% have been obtained from a modification of this procedure.

Nitromethane has two forms: the regular form, and the "aci- form.

Reference: <http://pubs.acs.org/doi/abs/10.1021/ja00081a072>

"This acid form has a double bond on the carbon, that leaves the hydrogens more vulnerable to oxidation. This is known as an "unsaturated" molecule

Now, to quote: "Nitrations can also often be performed by addition reactions using unsaturated hydrocarbons with . . . nitrogen dioxide"

So to summarize, initially nitrating methane is difficult, but after the first nitro group, the others are much easier to add. According to Love to Know: 1911 Edition, "The hydrogen in the primary and secondary nitro compounds which is attached to the same carbon atom as the nitro group is readily replaced by bromine in alkaline solution." Note that bromine does NOT readily react with regular hydrocarbons (unless left in sunlight). This indicates that nitromethane behaves as an unsaturated hydrocarbon under alkaline conditions.

Nitrogen dioxide reacts at room temperature with unsaturated hydrocarbons. With ethylene (H2C=CH2) the main reaction (about 95%) is an addition reaction and so dinitro-ethane is formed. But a smaller reaction is an oxidative nitration reaction where one of the hydrogens get replaced by a nitro group, forming CH2=CH–NO2.

Reference: <http://pubs.acs.org/doi/abs/10.1021/ja00388a035>

However, with a double bond between a carbon and nitrogen atom, the addition reaction is not possible since the N has a positive charge on it in this resonance state.

Also, at 60 degrees Celsius, pure nitromethane can be detonated by a # 8 blasting cap. Nitroethane can only be detonated if heated near its boiling point under confinement. Nitroethane, by itself, cannot be detonated without confinement.

Hydroxylamine can be made by heating nitromethane with hydrochloric or sulfuric Acid.

(V. Meyer, Ann. (1876) p.663)

Extremely concentrated sulfuric acid >98% reacts with nitromethane to form hydroxylamine sulfate and carbon monoxide.

Trinitromethane can also be made by reacting (NO2)3C–CN with water.

(NO2)3C–CN can be made in 75% yield by doing a nitration on Methyl cyanide in a carbon tetrachloride solvent. Methyl cyanide can be made by dehydrating acetamide (CH3CONH2) with P2O5. Acetamide can be made by simply stirring ammonia and acetic acid (vinegar) in a sealed tube, this is well known to those that run a meth-lab.

BUT BE WARNED: methyl cyanide is very poisonous, a leak at a factory in India killed hundreds of people.

A relevant link to NO2 reactions with unsaturated hydrocarbons:

<http://pubs.acs.org/doi/abs/10.1021/ja00388a035>

Another quote, "In spite of . . . addition of two NO2 radicals in the reaction of nitrogen dioxide with allylbenzene and some other alkenes, kinetic studies indicate that both NO2 and NO2A are reactive species, each leading only to addition products." However, this is not quite entirely true. Russian researchers have shown that there is a small side reaction.

In the presence of oxygen, nitrogen dioxide reacts with unsaturated hydrocarbons to form nitro-nitrates, and nitro-nitrates, in addition to plain double nitro compounds. "alkyl radicals later react with nitric dioxide and nitroalkanes are generated"

Effect of copper and oxygen on the yields of individual nitroalkanes in the vapour phase nitration of paraffin hydrocarbons, Ivan Mladenov, Pepa Toromanova-Petrova

This event indicates that nitrogen dioxide will not react with a plain alkane, such as ethane, an alkyl RADICAL is required. There are also numerous mention in patents to mixtures of hydrocarbons and NO2. However, I will concede that in some situations, NO2 can react.

It is mentioned in a certain source that, "toluene can be nitrated with nitrogen dioxide at only 20 degrees Celsius under phenyl-nitromethane", with a formula (C6H5)CH2NO2.

Here is a quote from researchers in St.Petersberg Russia;

"reaction of nitroethane salt with sodium nitrite . . . 1,1-dinitroethane formed in a high yield."

I.V.A. Petrova, Zhurnal Organicheskoi Khimii Volume 43, # 5, p. 653-656. (2007)

As can be inferred, this is directly relevant to nitrogen dioxide reacting with nitromethane, because "nitrite" is basically a form of nitrogen dioxide under alkaline conditions.

(2)NO2(-) + (2)H(+)-> NO2 + NO + H2O (2)NO2 + (2)OH(-) -> NO3(-) + NO2(-)

from wikipedia: "Nitrates of the alkali metals can be synthesized by reacting a mixture of nitrogen monoxide (NO) and nitrogen dioxide (NO2) with a corresponding metal hydroxide solution"

Here is the reference for nitromethane an methyl nitrate reacting in the presence of a nitrite ion to form methanol and a pseudonitrosole R–CH(NO)NO2)

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

Haloforn Reaction?

I have been thinking... could something similar to the haloforn reaction be done by bubbling NO2 into acetone?

Obviously the solution could not be alkaline, since the nitrite that would form is not a reactive oxidizer, but the solution should not be too acidic: either because a Meyer reaction on the nitroalkane would be undesirable.

I think, it should be possible in the presence of Cu(2+) catalyst. There is a reaction of halogenation of acetone with CuX2 salt. I believe, the mechanism is radical: one Cu2+ ion is coordinated with enolate or enol of acetone(with oxygen center), another Cu2+ is coordinated with X, then synchronously both copper atoms are reduced to Cu(I) with synchronous homolytic coupling of two radicals(not formed as free radicals, they form and couple synchronously)

I suppose same thing might happen with NO2 because it is a radical particle, and Cu2+ coordinated with enolate. NO2 can then oxidize Cu(I) to Cu(II), but this will result in formation of NO2-. that is a strong ligand and it may(not sure) occupy all copper 2+ and will lose its catalytic activity, so oxidation of Cu(I) to Cu(II) should not be done with NO2.

Why not Ag(+)- enolate reacting with NO2 ?

AgO(Cu)CH3=CH2, NO2 -> Ag .O=C(CH3)CH2NO2

I do not know whether silver hydroxide, solubilized in an ammonia solution, and with some acetone mixed in, would work. Do you have a reference to that reaction in which acetone is halogenated using CuCl2 ? I believe the presence of halogen ions changes the reduction potentials by coordinating to the copper ion, making Cu(+1) more favorable than otherwise. Indeed, iodide ions are known to reduce Cu(+2) ions to form a CuI precipitate and elemental iodine in solution.

Yes, I've seen at least two references, one with chlorination of Cu+2, another with bromination. If you so, I can provide them (I've not time to find them). Cl can make reaction different due to some reasons (like formation of stable CuX) so I am not sure about reaction with NO2 yet, because there is no Cu(I) formation. On the other hand, it is possible to add some lithium chloride into solution, not sure that it can help though

Also, it is possible that this route would require absence of water (otherwise, NO2 can react with water to form HNO3 and HNO2, and HNO2 can nitrosate acetone into isonitrosoacetone), so a Cu2 based catalyst should be soluble in pure acetone (maybe some fatty acid salt?). Also even if final reaction with nitroacetone is possible, after that many side reactions can occur, like further nitration of the same position of nitroacetone, or catalyst inactivation because obviously nitroacetone, rather than chloroacetone or acetone, would form enolate and coordinate with copper ion (because it may possess chelating properties)...

I was thinking rather that the nitroacetone would continue to be attacked, adding more nitro groups, until a nitroformate (-C(NO2)3 is able to ionize off.

Thus **trinitromethane**, not nitromethane should be the product. However, the (-)CH2NO2 intermediate is far more stable than the (-)CH2H2, so I do not know if nitroacetone would easily hydrolyze to acetic acid and nitromethane before further attack by NO2. However this is so might not matter, as the aci-form of nitromethane CH2=NO2(-) is quite vulnerable to being oxidized, but this is usually only under alkaline conditions.

This seems surprising:

"Ethyl nitrolic acid (C2N2O3H4) was prepared by the action of potassium hydroxide and sodium nitrite on nitroethane" (Meyer & Constanm, 1882).

As for possible nitrosation of the acetone,

nitrogen dioxide can oxidize organic nitroso compounds.

Nitrosobenzene is oxidized to nitrobenzene, whereas nitrosoalkanes are typically oxidized to pseudonitrosites (with a nitro and nitroso on the same carbon). Thus CH3C(=O)C(=NOH)NO2 (acetylmethylnitrolic acid) may likely form.

I will save you the trouble of doing a search,

(the below has already been extensively discussed elsewhere in this forum)

"was prepared by mixing acetone with nitric acid (of 24% concentration) and a little fuming HNO3 and allowing the mixture to stand for 8 days at room temperature. An ether extraction gave an evaporation some acetylmethylnitrolic acid Beil 3.621 and R. Behrend & H. Tzylar, Ann283,221- 3(1894)

"... right after the strong oxidation left behind was a clear, thick yellow oil of a pungent odor. According to Jahresbericht über Fortschritte der Chemie (1902), Behrend and Tzylar, p. 1075-77 this oil contained one-third to half acetylmethylnitrolic acid (CH3.CO.C(NOH).NO2) (cryst., mp. 62 deg., very decomposable) and other byproducts..."

I do of course wonder if further nitrogen dioxide could react with acetylmethylnitrolic acid to form the intermediate CH3C(=O)C(NO2)3, since oximes are known to be oxidized by NO2 to pseudonitrosites. Such an intermediate would quickly hydrolyze to acetic acid and trinitromethane.

Nitroform (Trinitromethane), CH(NO3)3, is obtained in the form of its ammonium salt by the decomposition of trinitroacetone with water." (L. Schischkoff, Ann., 1857, 10 3, p. 364).

It is a colorless crystalline solid which melts at 15 °C and has the properties of a strong acid. ERICH SCHMIDT, RICHARD SCHUMACHER, HANS KÜHLMANN (Ber., 1921, 54, [8], 1483–1484). Potassium Nitroformate is prepared by the gradual addition of a solution of potassium ethoxide to an ice-cold solution of nitroform in alcohol; the product is filtered and washed with alcohol and ether.

The potassium salt is formed by the action of potassium ethylate on Tetranitromethane (A. **Hantzsch**, Ber., 1899, 32, p. 631). It is a deep yellow coloured solid, which is readily soluble in water. It explodes when heated. The silver salt, obtained by shaking an ether solution of nitroform with freshly prepared, slightly moist silver oxide, reacts with methyl iodide to form Trinitroethane, a crystalline solid which melts at 56 °C Concentrated caustic potash decomposes the salt completely, forming the potassium salt of dinitroethane, CH3 C(NO2)2K. Tetranitromethane, C(NO2)4, obtained by adding Nitroform to a hot mixture of nitric and sulphuric acids, is a crystalline solid which melts at 13° C.

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Hantzsch, Chemische Berichte, 39, p2478, (year 1906)

(such yields would be expected to be low, less than 11%, since nitrite substitution on the secondary and tertiary haloalkanes gives successively lower yields than a primary haloalkane because a proportion of the substitutions are nitrite esters rather than addition of nitro groups)

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