



Pentryl, by AXT

This study was conducted to determine the easiest way to produce the explosive, pentryl, using backyard methods. It was also done to synthesize useful intermediates that could be used for other purposes. It was found that pentryl could be produced in five quite easy steps starting from sodium benzoate, which was decarboxylated to benzene. The benzene was then chlorinated to chlorobenzene and the chlorobenzene nitrated to 2,4-dinitrochlorobenzene. The fourth step was to condense 2,4-dinitrochlorobenzene with ethanolamine to produce 2,4-dinitrophenylaminoethanol which was then nitrated to pentryl.

All the precursors were purposefully sourced from readily available products available in supermarkets, hardware stores and farm supply merchants. The properties of the precursors and intermediates for the synthesis of pentryl are listed in tabular figures 1 and 2.

Figure 1: Properties of pentryl precursors

Formula	MW	Solubility H ₂ O	Density	MP	BP
C ₆ H ₅ COONa	144.11	63g @ 20°c	1.44g/cm ³	>300g	decomp.
NaOH	39.00	111g	2.10g/cm ³	318°C	1390°C
C ₃ H ₃ N ₃ O ₃		1.2g		249°C	
KNO ₃	101.10	35.7g	2.10g/cm ³	334°C	400°C
H ₂ SO ₄	98.08	miscible	1.84g/cm ³	10°C	337°C
H ₂ NCH ₂ CH ₂ OH	61.08	miscible	1.01g/cm ³	10.3°C	170°C

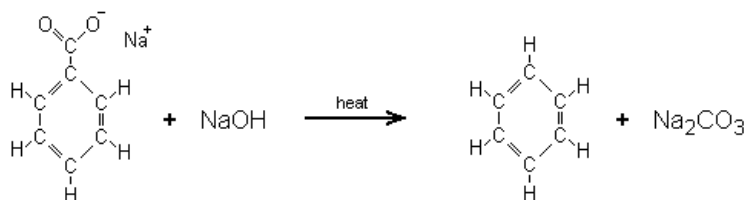
Figure 2: Properties of pentryl intermediates

Formula	MW	Solubility H ₂ O	Density	MP	BP
C ₆ H ₆	78.11	0.18 @ 25°C	0.88g/cm ³	5.5°C	80.1°C
C ₆ H ₅ Cl	112.56	low	1.11g/cm ³	-45°C	131°C
(NO ₂) ₂ C ₆ H ₃ Cl	202.56	insoluble	1.70g/cm ³	53.4°C	31.5°C
(NO ₂) ₂ C ₆ H ₃ NHC ₂ H ₄ OH	227.18			89.9°C	

Benzene

Benzene synthesis was studied in detail by other sciencemadness.org members[13]. Benzene is conveniently made by the decarboxylation of sodium benzoate with sodium hydroxide[1] (figure 3). The dry distillation was done using an apparatus made from copper plumbing pipe and fittings with a metal can (similar to a paint can) used for the heating vessel (figure 4). Within the can was placed a number of lengths of copper pipe to act as a conduction aid.

Figure 3: Decarboxylation of sodium benzoate to benzene



Precursors

The sodium benzoate was sourced from a food supply store and came in 1 kg bags. Sodium benzoate is used as a preservative for the prevention of yeast, bacteria and fungi. As an ingredient it's mainly used in baking powder, fruit esters, antiseptic, winemaking and effervescent beverages. Sodium hydroxide was purchased from the local hardware store in a 3 kg container under the name "caustic soda". Its main domestic use is as a drain cleaner where it's able to saponify the grease and decomposes the protein of hair to unblock drains.

Synthesis of Benzene

A powdered mixture comprised of 150 g sodium benzoate and 75 g sodium hydroxide was poured over and into the copper pipes in the metal can and attached to the distil-

Figure 4: Benzene distillation apparatus



lation apparatus. After about 10 minutes of strong heating on a gas burner, an orange distillate started to collect in the receiving flask. This was continued for about 45 minutes by which time 83 mL of crude benzene had been collected which is 90% of the theoretical yield. Redistilling the crude orange benzene by heating in a boiling water bath gave a clear distillate leaving behind a small quantity of an orange high boiling point product composed predominantly of biphenyl[1]. The final yield of clear benzene was 75 mL or 81% of theory.

Chlorobenzene

The chlorination of benzene using trichloroisocyanuric acid (TCCA) was first described by Juenge, Beal and Duncan[2]. It was found that in the presence of anhydrous ferric chloride or 50% sulphuric acid catalysts, benzene could be converted to chlorobenzene in high yield (based on TCCA used) with precipitation of cyanuric acid as a byproduct (figure 5). This is analogous to the reaction of benzene with molecular chlorine, which requires Lewis acid catalysis. I simplified and modified their procedure to provide a higher yield based on the benzene used.

Figure 5: Chlorination of benzene with TCCA

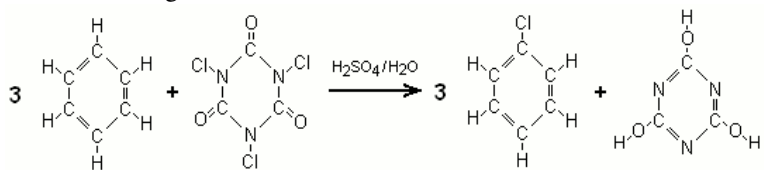


Figure 6: Chlorination of benzene with TCCA



Precursors

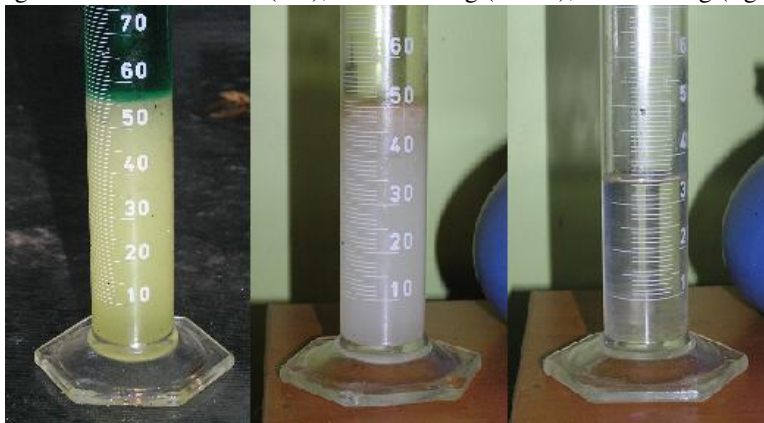
Trichloroisocyanuric acid (TCCA) also known as “symclosene” or “1,3,5-Trichloro-s-triazine-2,4,6(1H,3H,5H)-trione” was bought as swimming pool chlorinator tablets in a hardware store. It is used to reduce algae and other microorganisms in swimming pool water. The product used was sold under the name “HY-CLOR” and marked “850g/kg available chlorine present as trichloroisocyanuric acid”. Sulphuric acid is available at hardware stores as drain cleaner. I used a product called “Mo-Flo” that was marked “1835g/L sulphuric acid”.

Synthesis of Chlorobenzene

75 mL of benzene was added to 50 mL of water and 50 mL sulphuric acid in a 300 mL conical flask. 75 g of finely powdered TCCA was then swirled into the solution. The mixture was then heated to 60-80°C for 8 hours (figure 6).

The slurry was then cooled and transferred into a metal can for distillation, where it was heated at 130°C until the distillate stopped coming over. This gave 54 mL of a dense milky yellow organic layer (d. 1.14 g/cm³) underneath a green aqueous solution of copper chloride from the reaction of HCl and Cl₂ with the copper condenser

Figure 7: Crude distillate (left); after washing (centre); after boiling (right)



(figure 7). The organic layer was separated and washed with dilute sodium hydroxide to remove dissolved Cl_2 and HCl , then with water to give 48 mL of a milky white liquid (figure 7). The milky liquid was then quickly heated to 110°C where it boiled vigorously; temperature of the liquid was allowed to rise to 130°C then quickly cooled to yield 34 mL of clear chlorobenzene (figure 7), for a final yield of 40% of theory based on benzene used.

2,4-Dinitrochlorobenzene

Warning

2,4 dinitrochlorobenzene is genotoxic, mutagenic in the Ames assay, and a contact sensitizer in humans. Inhalation, ingestion, and skin contact with this compound should be scrupulously avoided.

The nitration of chlorobenzene yields 2,4-dinitrochlorobenzene (DNCB) (figure 8), a reactive intermediate to many explosives some of which have been adopted for military and civilian applications. Examples of other explosives that can be derived from DNCB are:

Tetryl: By condensing with methylamine followed by nitration in mixed acids.

Picramide: By condensing with ammonia, then nitration.

2,4-Dinitrobenzenediazonium Perchlorate: By condensing with ammonia followed by diazotisation then precipitation with perchloric acid.

Picric acid: By reacting with sodium hydroxide in methanol, then nitration.

Hexanitroazobenzene: By condensing with hydrazine, then nitration.

Hexanitrodiphenylamine: By condensing with aniline, then nitration.

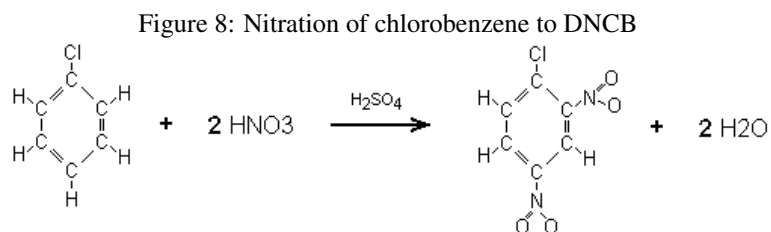


Figure 9: Nitration of chlorobenzene (left); washing of dinitrochlorobenzene (right)



Precursors

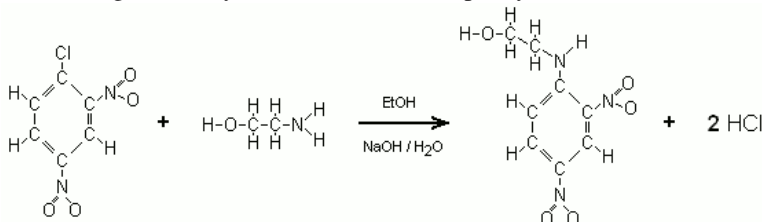
Potassium nitrate was obtained from an agriculture supply store as fertilizer, the product came in a 25 kg bag marked “K-Nitrate” and coded 13-0-38.

Synthesis

The synthesis is described by Davis[3] which I adapted to use mixed $\text{KNO}_3/\text{H}_2\text{SO}_4$ acids instead of the concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$. The nitration mixture was made by combining 80.9 g (0.8 mol) potassium nitrate with 130 mL 98% sulphuric acid, which was dissolved then cooled to 25°C. With rapid stirring 20.4 g (0.2 mol) chlorobenzene was then added in small portions, making sure to keep the resultant exotherm from heating the mixture over 50°C. After the DNCB was added the temperature was slowly raised to 95°C and stirred at this temperature for 2 hours.

Once taken off the heat the DNCB separated as a light yellow upper layer (figure 9), which solidified after cooling. The nitration mixture was then stirred into 1 litre of cold water which separated the DNCB as chunks that fell to the bottom (figure 9). The acidic aqueous solution was then decanted and replaced with 750 mL water, which was boiled to melt the DNCB; this was rapidly stirred to wash the DNCB of any remaining acids. The water was then decanted and the DNCB powdered and dried. Yield was 32 g or 79% of theory.

Figure 10: Synthesis of 2,4-Dinitrophenylaminoethanol



2,4-Dinitrophenylaminoethanol

DNCB condenses readily with ethanolamine to yield 2,4-Dinitrophenylaminoethanol (figure 10). This condensation step has been studied and published by a number of workers such as Clarke[4], and Kremer[9], who studied the condensation of mononitrochlorobenzenes with ethanolamine and also some analogous reactions[10].

Precursors

Ethanolamine was available in a product called “Selleys BBQ Kleen” and is an ingredient in many grease cleaners; BBQ Kleen was 10.5% ethanolamine though it also contained polyoxyethylene lauryl ether as a detergent, dispersant and surfactant[8]. The impurities were removed by boiling the solution until the temperature rose to the boiling point of ethanolamine. The ethanol used was “methylated spirits” bought from a hardware store as a 95% solution.

Synthesis

Into 145 g ethanol was added 8.6 g ethanolamine and 28.4 g DNCB. The solution was then heated with stirring to 70°C until the DNCB dissolved, the solution turning orange. With rapid stirring 5.7 g sodium hydroxide in 8.5 g water was added slowly whereby the solution turned dark cherry red and a sodium chloride precipitate formed. The solution was left at 70°C for 30 minutes then filtered. The precipitate was kept as it contained bright yellow bis(dinitrophenyl)aminoethanol.

The filtrate was boiled down to 50 mL and let stand. Orange crystals formed, the supernatant liquid was decanted, and the orange crystals of 2,4-dinitrophenylaminoethanol were flushed with cold ethanol then dried (figure 11). Yield was 15 g (47% of theory).

Figure 11: Crystals of 2,4-dinitrophenylaminoethanol



Figure 12: Precipitate of bis(dinitrophenyl)aminoethanol



The original precipitate that formed was then stirred into 400 mL water, dissolving the sodium chloride leaving the bright lemon yellow byproduct of bis(dinitrophenyl)aminoethanol (figure 12), which was filtered and dried.

2,4,6-Trinitrophenylnitraminoethyl Nitrate (Pentryl)

Pentryl is a powerful explosive, first produced by Moran[6] by the nitration of 2,4-dinitroaminoethanol (figure 13). Another route was also patented by von Herz[7], using the nitration of phenylaminoethanol obtained by reacting aniline with ethylene oxide or ethylene glycol chlorohydrin. Pentryl is of novel interest due to it containing the three major energetic moieties – the nitro, nitrate and nitramine groups – on a single molecule.

Synthesis

A nitration mixture was made by dissolving 54.6 g (0.54 mol) potassium nitrate into 100 mL sulphuric acid then cooling to 25°C. 13.6 g (0.06 mol) 2,4-dinitrophenylaminoethanol was then dissolved with rapid stirring into the nitration mixture which rose in temperature to 50°C then suddenly solidified as the pentryl precipitated from the solution.

Figure 13: Nitration of 2,4-dinitroaminoethanol

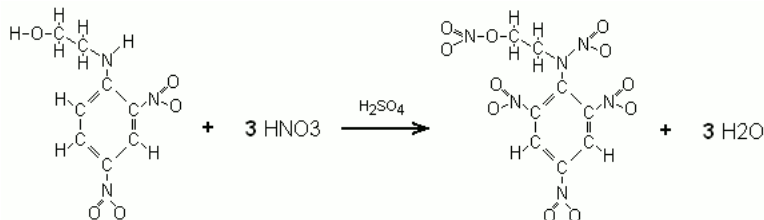
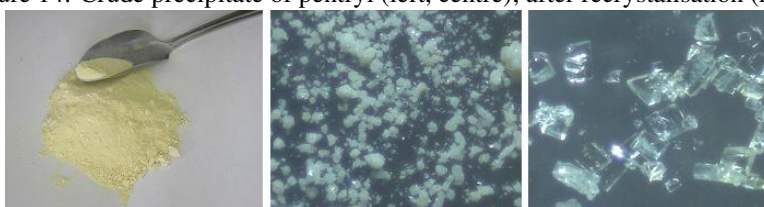


Figure 14: Crude precipitate of pentryl (left, centre); after recrystallisation (right)



The pasty mixture was stirred into 1 litre of cold water, filtered, and washed with more water. It was then washed with dilute sodium bicarbonate solution, then given a final wash with more water. The product was a fine cream coloured powder. Recrystallisation from acetone/ethanol yielded clear-yellow crystals (figure 14). Final yield of pentryl was 18.2 g or 84% of theory.

Explosive Properties

The explosive properties of pentryl rate it highly in the family of aromatic explosives containing the trinitrobenzene moiety; comparative properties are listed in tabular figure 15. The pentryl made in this study was pressed into a drinking straw and detonated against an aluminium plate (figure 16). Lead block compression tests were conducted by Clarke[4] (figure 17).

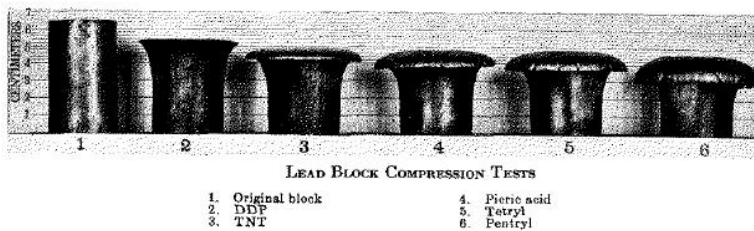
Figure 15: Properties of aromatic explosives

	Impact sensitivity 2kg weight (cm)	min. lead azide sensitivity (g)	Sand crushed <30 mesh (g)	Sm. trouze block (ml)	Ignition temperature (°C)	Crystal density (g/cm ³)	Velocity of detonation (m/s)
Pentryl	30cm	0.025	55.8	15.8	235°C	1.82	7300 @ 1.6
HNDPAEN	35	0.05	51.1	16.3	490°C	1.69	
Tetryl	27.5	0.03	54.2	13.8		1.73	7830 @ 1.71
Picric acid	42.5	0.12	45.3	12.4		1.76	7260 @ 1.71
TNT	>100	0.16	43.6	12.2		1.65	6930 @ 1.64

Figure 16: Detonation of pentryl against aluminium plate



Figure 17: Lead block compression tests



Bis(2,4,6-trinitrophenyl)aminoethyl nitrate (HNDPAN)

The byproduct of the DNCB/ethanolamine condensation, bis(dinitrophenyl)aminoethanol, can be nitrated to the explosive bis(2,4,6-trinitrophenyl)aminoethyl nitrate (figure 18).

Synthesis

Two solutions were made, one by dissolving 12 g (0.12 mol) potassium nitrate in 42 g sulphuric acid and another by dissolving 2 g (0.005 mol) bis(dinitrophenyl)aminoethanol into 20 g sulphuric acid. With both solutions cooled to 25°C they were slowly combined by pouring the bis(dinitrophenyl)aminoethanol solution into the potassium nitrate solution. A slight exotherm resulted and the solution thickened and turned from yellow to cream as the HNDPAN precipitated. The HNDPAN was stirred into 700 mL cold water then neutralized with dilute sodium bicarbonate solution. After a final wash with water it was filtered and dried to yield 2.31 g (86%) of HNDPAN.

Figure 18: Nitration of bis(dinitrophenyl)amino ethanol to HNDPAN

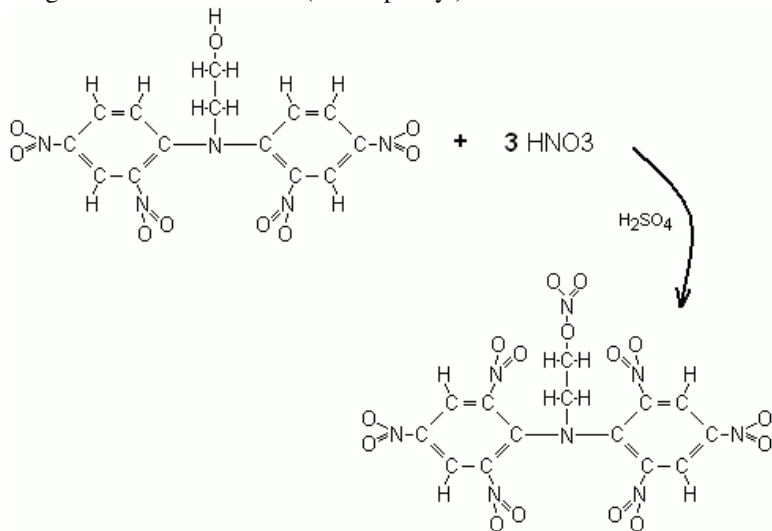


Figure 19: deflagration of HNDPAN



Explosive Properties

The explosive properties of HNDPAN are listed in tabular figure 15. That made in this study was not detonated, however when ignited it deflagrated very vigorously with a large orange flame and grayish smoke (figure 19).

References

- [1] J. F. Norris *Experimental Organic Chemistry*; 2nd edition; pg. 132; McGraw-Hill Book Company, New York & London. 1924.
- [2] E. C. Juenge, D. A. Beal & W. P. Duncan. "Chlorination of aromatic systems with trichloroisocyanuric acid under polar and free-radical conditions". *Journal of Organic Chemistry*; **35** (3); 719-722. (1970)

- [3] T. L. Davis, The Chemistry of Powder and Explosives Pg. 141; New York, John Wiley & Sons; London, Chapman & Hall. 1941.
- [4] Le Roy V. Clarke "Analogues of Tetryl I. Trinitrophenylnitraminoethyl Nitrate (Pentryl)". *Industrial and Engineering Chemistry*; **25** (12); pg. 1385-1390. (1933)
- [5] B.T. Fedoroff et. al. Encyclopedia of Explosives and Related Items. vol. 1; pg. A425. Picatinny Arsenal; New Jersey, USA. 1960.
- [6] R. C. Moran "Explosive and Process of Making Same" US patent #1560427 (1925)
- [7] E. von Herz "An Improved Method of Producing Explosives" British patent #367713 (1931)
- [8] "MSDS - Selleys BBQ Kleen" SH&E Shared Services, Orica; Australia.
- [9] C. B. Kremer "Alkanolamines. II. Reaction of the Chloronitrobenzenes with Monoethanolamine". *Journal of the American Chemical Society*; **59** (9); 1681-1682; (1937)
- [10] C. B. Kremer & M. Meltsner "Intermediates of Pentryl Analogs. Chloronitroanilino Alkanols". *Journal of the American Chemical Society*; **64** (6); 1285-1286; (1942)
- [11] Le Roy V. Clarke "Analogues of Tetryl. Hexanitrodiphenylaminoethyl Nitrate" *Industrial and Engineering Chemistry*; **26** (5); pg. 554-557; (1934)
- [12] Dobratz, B and Crawford, P. "LLNL Explosives Handbook - Properties of Chemical Explosives and Explosive Simulants". Lawrence Livermore National Laboratory. California. 1985.
- [13] Chromium, with contributions by IPN, Ordemblitz, S.C. Wack, and Organikum. "Preparation of Benzene" (online) http://www.sciencemadness.org/member_publications/benzene_production.pdf