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A.C. 7791

Chem/Ex. 380
H.E.I. 442
R.D.X. 204

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MINISTRY OF SUPPLY

ADVISORY COUNCIL ON SCIENTIFIC RESEARCH AND TECHNICAL DEVELOPMENT

EXPLOSIVES RESEARCH COMMITTEE (CHEMISTRY)

SUB-COMMITTEE H.E.I.

R.D.X. RESEARCH PANEL

INDEX OF COMPOUNDS RELATED TO HEXAMINE AND TO R.D.X.

by

H. D. Springall, M.A., D. Phil.

Gloucester Branch, A.R.D.
Bristol Report No. 143

November, 1944

Received February 12th 19

CONTENTS

Para. 1

INTRODUCTION

It is hoped that this collection of data will serve as a guide to workers in RDX chemistry who are, not unreasonably, baffled by the strange assortment of initials by which many of the polymethyleneamine $(-CH_2-NH-)_x$ derivatives have come to be designated.

The collection is based on those British and Transatlantic reports which have been available and on conversations with members of the staffs of the A.R.D. and of various "out-stations".

Some related compounds, prepared long ago in early academic work on hexamine, and related topics, are included.

The treatment for each compound is as follows:- The "Initial" designation is given, followed by the structural formula, "short systematic name"*, m.p., solvent for recrystallisation, and references to methods of preparation. No direct consideration of the reactions of the compound is given, though most transformations are, automatically, included as preparative methods for other compounds, and from the paragraph index at the end of the work a list of the positive reactions of any given compound can be at once set down.

Wherever possible, reference to transatlantic work is made by

(a) the laboratory concerned in the work;

(b) The O.S.R.D. (U.S.A.) or C.E. or X.R. (Canada) number;

(c) The date of writing the report**;

(d) The S.R.7/number of the report.

British work is similarly treated for reference:

(a) the laboratory concerned in the work;

(b) the Laboratory Report number;

(c) the date of writing the report**;

(d) the A.C. number of the report.

Para. 2

For a more detailed review of the work up to October, 1943, the serial report on RDX research by Linstead, British Central Scientific Office, Washington, D.C., U.S.A., SR7/876 (to Oct. 1941); SR7/2600 (to Oct. 1942); M.O.S. London, A.C.5224 (to Oct. 1943) and the report by Haworth, Lamberton and Woodcock, Sheffield, A.C.5053, Oct. 1943, should be consulted.

There are several systems of nomenclature and numbering in use in this field. The system followed here is that treated in Bristol Br. Rep. 32, Nov. 1943, A.C.5403, in which the following typical compounds have the given systematic names and numbering, and convenient "short names". (p. 3).

A very similar system is now in use in Canada.

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* See below, pp. 2 and 3.

** The date on which the report was written is given as accurately as possible. Thus, for example, a progress report covering January, 1942, written during February, 1942, and received at the appropriate control office in March, 1942, would be quoted here as "Feb. '42." Some overlapping of work has resulted from the unavoidable delay in transmission of reports between Transatlantic and British workers, e.g. Toronto, X.R.16 Rep. 1 Sept. '44, SR7/44/3158 was received in Bristol on 27 Oct. '44.

C 13248 (1)

For convenience in discussion, the hexamine cage system is indicated by the short name "Hex."; similar short names used are "PT" for the pentamethylene tetramine cage.

"8-ring" for the cyclo-2:4:6:8-tetramethylene-1:3:5:7-tetramine ring.

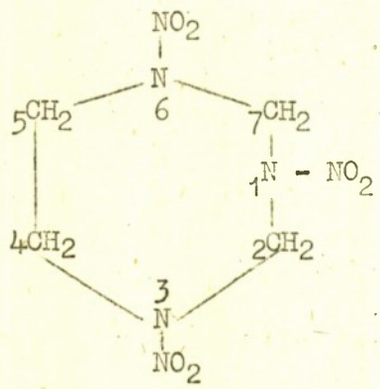
"6-ring" for the cyclo-2:4:6-trimethylene-1:3:5-triamine ring.

"7-chain" for the lin*-2:4:6-trimethylene-1:3:5:7-tetramine chain.

"5-chain" for the lin-2:4-dimethylene-1:3:5-triamine chain.

"3-chain" for the lin-2-methylene-1:3-diamine chain.

For related compounds not containing the simple alternating system N-C-N-C-N- the "aza" system, similar to that in use in Canada, is used here. For example,



1:3:6-trinitro-cyclo-1:3:6-azaheptane.

Yields of RDX are calculated on the basis $3CH_2O \longrightarrow$ 1 RDX represents a yield of 100%.

Para. 4

'HNO_3' means 98-100% HNO_3. The actual percentage of HNO_3 is given for more dilute acid.

'CH_2O' means paraformaldehyde.

'aq. CH_2O' means 40% formalin.

'Me-' means CH_3-

'Et' means C_2H_5-

'Ø'- means C_6H_5-

'Ac'- means CH_3-CO-

"P" - means paragraph

Following the Harvard and University of Pennsylvania workers, '$AcONO_2$' is used for the equimolecular mixture of HNO_3 and Ac_2O.

The general arrangement of the material is in order of increasing complexity of the parent structures.

A Table of Melting Points is given to assist in identification of compounds prepared in the laboratory.

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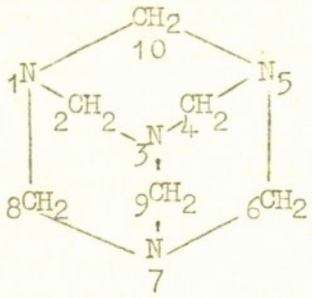
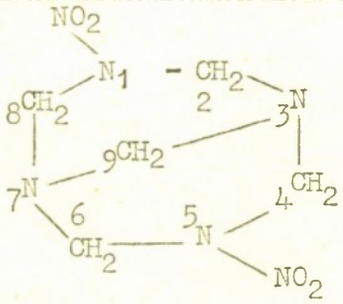
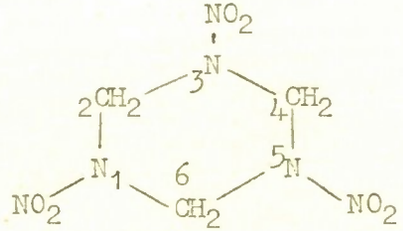
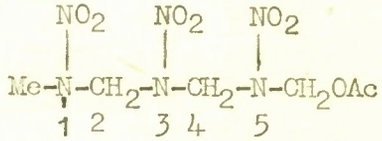
* The term "lin", which may be read "linear", is used to facilitate the recognition of the parent skeleton structures of the open chain compounds, just as the term "cyclo" is used for the ring compounds.

Para. 3

"Trivial name" or Initial Designation	Hexamine	D.P.T.	RDX	M.S.X.
Formula				
Systematic name	1:5-Endomethylene (10)-3:7-Endo-methylene(9)-cyclo-2:4:6:8-tetramethyl-ene-1:3:5:7-tetra-mine	1:5-Dinitro-3:7-endo-methylene(9)-cyclo-2:4:6:8-tetramethyl-ene-1:3:5:7-tetramine	1:3:5-Trinitrocyclo-2:4:6-trimethylene-1:3:5-triamine	1-Methyl-5-acetoxymethyl-1:3:5-trinitrolin- 2:4-dimeth-ylene-1:3:5-triamine
Short name	Hex.	1:5-Dinitro-(P.T.)	1:3:5-Trinitro-(6-ring)	1-Methyl-5-acetoxymethyl-1:3:5-trinitro-(5-chain)

Lists to facilitate "literature searching" are set out giving the British SR7/ reference numbers for the following Transatlantic serial reports:

(a) The Division 8 N.D.R.C. of O.S.R.D. Interim Reports "Studies on RDX and Related Compounds." R.R.C. 1 to 22 from Jan. 1943 - Oct. 1944.

(b) The Canadian Explosives Research Extramural Summaries from March 1942.

(c) The Reports of the U.S.A. - Canada RDX Committee Meetings from 4th September 1942.

British work is reviewed up to Oct. 1944 and Transatlantic work up to Sept. 1944.

Para. 7

NITROXY DERIVATIVES OF FORMALDEHYDE

Para. 8

P_1.

$NO_2.O - CH_2 - O.NO_2$.

Methylene dinitrate. b.p. 48°/15 mm.

Moreschi, Atti.R.Accad.Lincei, 1919, 28, 227; Chem.Abs., 1919, 13, 3519.

Houben and Pfankuch, Ber., 1926, 59, 86.

Travagli, Gazzetta chim.ital., 1938, 68, 718; Chem.Abs., 1939, 33, 2486.

For early A.R.D. work, see R.D. Rep. RDX 15 (? 1939).

Hex. normal nitrolysis,

then extract reaction system

$+ CCl_4 \longrightarrow$ mixture of P_1 and P_2

$CH_2O \xrightarrow[H_2SO_4]{HNO_3}$ mixture of P_1 and P_2

Separate by vac. distillation.

(Above structure accepted by A.R.D. and quoted in A.R.D. Exp. Rep. 591/44, June '44, A.C.6455).

Para. 9

P_2.

$$NO_2 - O - \underset{1}{CH_2} - O - \underset{2}{CH_2} - O - \underset{3}{CH_2} - ONO_2$$

1:3-Bis (nitroxymethyl) lin-1:3-dioxo-2-methylene.

b.p. 89°/9 mm.

Refs. as for P_1.

Prepared with P_1 and separated by vacuum distillation.

Para. 10

II

SOME SIMPLE MONONITRAMINES

Para. 11

Nitramine (Nitramide)

$$NH_2.NO_2$$

Ppt. from ether by light petroleum. m.p. 72-75°.

Thiele and Lachmann, Annalen, 1895, 288, 267.

Inorganic Syntheses. I. New York, 1939, p. 68.

$$NH_2CO_2Et \xrightarrow[H_2SO_4]{EtONO_2} NH(NO_2)-CO_2Et \xrightarrow{NH_3}$$

$$NH_4\{NO_2:N-CO_2Et \xrightarrow{KOH} K\{NO_2:N-CO_2Et \xrightarrow[H_2O]{H_2SO_4} NH_2.NO_2$$

Para. 12

Methylnitramine

$$CH_3NH.NO_2.$$

From ether. m.p. 38°.

Franchimont and Klobbie, Rec.Trav.Chim., 1888, 7, 355.

$$CH_3NH_2 + Cl.CO_2Et \longrightarrow CH_3-NH-CO_2Et \xrightarrow{HNO_3}$$

$$CH_3-N(NO_2)-CO_2Et \xrightarrow[\text{ether and pass in } NH_3]{\text{diss. in}} CH_3.NH.NO_2$$

Thiele and Lachmann, Annalen, 1895, 288, 291.-

$$NH_2CO_2Et \xrightarrow{EtONO_2} NH(NO_2)-CO_2Et \xrightarrow{Ag_2O} Ag\{N(NO_2)-CO_2Et \xrightarrow{MeI}$$

$$CH_3-N(NO_2)-CO_2Et \xrightarrow[\text{ether and pass in } NH_3]{\text{diss. in}} CH_3.NH.NO_2$$

Para. 12a

Methylolnitramine

$$HOCH_2-NH-NO_2$$

not isolated.

Postulated as possible by-product in hexamine nitrolysis system;

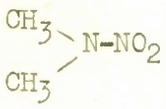
Bristol Res. Rep. 120, April '44; A.C.6302.

A.R.D. Exp. Rep. 591/44, May '44; A.C.6455.

Bristol Br. Rep. 43, Aug. '44; A.C.7119.

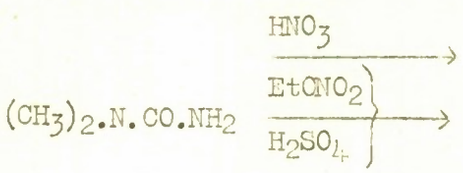
Para. 13

Dimethylnitramine

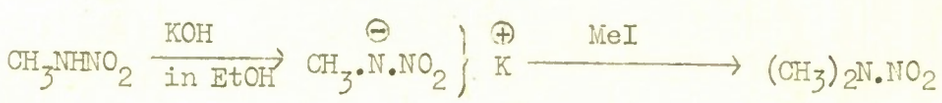


From ether. m.p. 57°.

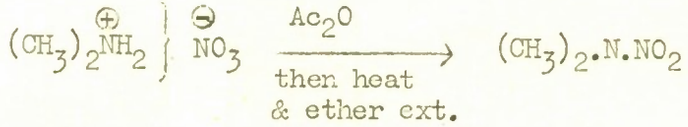
Franchimont, Rec. Trav. Chim., 1883, 2, 123.



Franchimont and Klobbie, Rec. Trav. Chim., 1888, 7, 355.

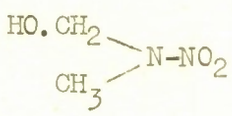


Bamberger and Kirpal, Ber., 1895, 28, 537.



Para. 14

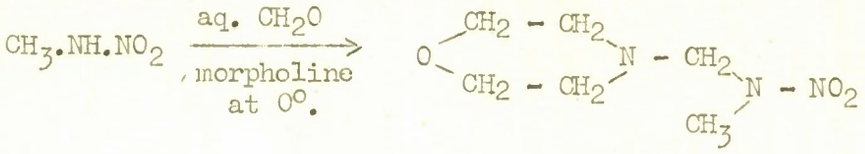
Methylmethylolnitramine



Not isolated.

Sheffield Rep. 43. May '44, A.C.6406.

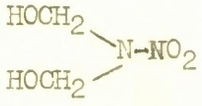
Morpholine derivative of methylmethylolnitramine prepared:-



m.p. 84-86°.

Para. 15

Bis methylolnitramine



Not isolated.

Toronto workers (X.R.16 Rep. 31, Jan. '44, SR7/44/984) consider the stabilisation of NH_2NO_2 by excess aq. CH_2O to be due to the formation of bismethylolnitramine.

Postulated as probable by-product in hexamine nitrolysis system:

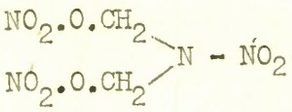
Bristol Res. Rep. 120, April '44; A.C.6302;

A.R.D. Expl. Rep. 591/44, May, '44; A.C.6455;

Bristol Br. Rep. 43, Aug. '44; A.C.7119.

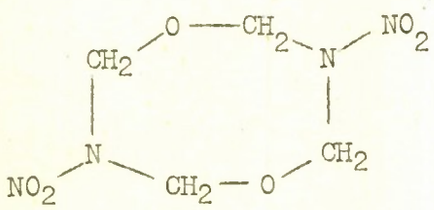
Para. 15a

Bis(nitroxymethyl)nitramine



From ether. m.p. 59-60°.

Toronto, X.R.16 Prog. Rep., 1 Sept. '44, SR7/44/3158.



$\xrightarrow[\text{7 mins. at 0° drown in slurry (ice + water)}]{20\ HNO_3}$ $(NO_2OCH_2)_2N.NO_2$ in 68% yield.

P.S.1.

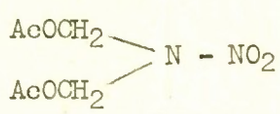
(see p. 203)

$(AcO.CH_2)_2N.NO_2 \xrightarrow{HNO_3} (NO_2OCH_2)_2N.NO_2$ (38 per cent).

see p. 15b

Para. 15b

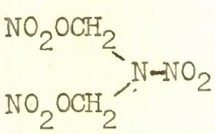
Bis(acetoxymethyl)nitramine



b.p. 153-156°/12 mm.

Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

Filtrate from Ross or Bachmann runs (see pp. 85, 86).
Evap. HOAc at 11 mm. Ether extract ——→ oil. Wash with H_2O (pH 8), ether extract, evap. and flash distil (12 mm., bath at 200-215°). Repeat washing and extraction, and distillation.

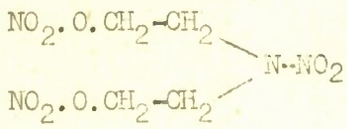


$\xrightarrow[\text{reflux:3 mins.}]{\text{HOAc:NaOAc}}$ bis acetoxymethyl deriv. (69%).

Hex. in HOAc $\xrightarrow[\text{5 } Ac_2O \text{ at 15-20°, heat to 75°, cool and neutralise with NaOH}]{4HNO_3}$ ppt. BSX (see p. 63) filtrate distilled at 12 mm. ——→ bisacetoxymethyl nitramine (39%).

Para. 16

DINA



Bis (β-Nitroxyethyl) nitramine.

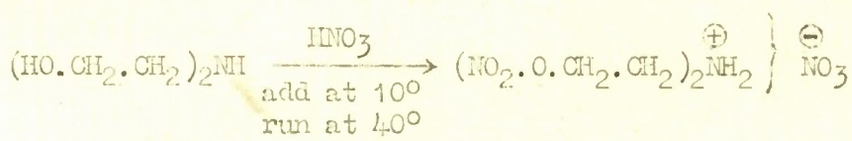
From AcMe or EtOH. m.p. 51-52°.

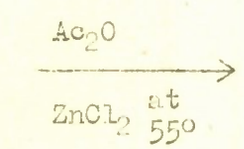
A review of the extensive and specialised literature devoted to DINA is outside the scope of this work: see Toronto X.R.19 Reports,

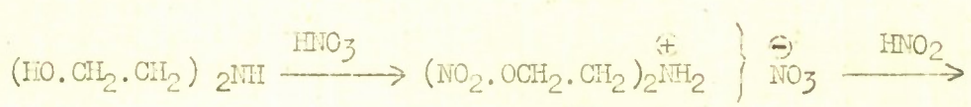
e.g. Toronto, X.R.19 Rep., June '43, SR7/4748.

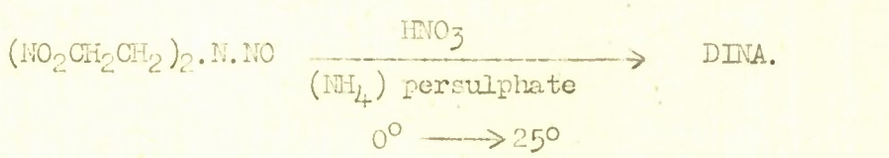
See also Cornell. Div.8.N.D.R.C. of O.S.R.D. Interim Rep. on Organic Development Problems. O.D.P.18. May '44, SR7/44/1872.

There are two standard preparations.









Para. 17 III

DERIVATIVES OF METHYLENEIMINE

$CH_2 = NH$

Para. 18

(a) $CH_2 = NH$ and (b) $HOCH_2 - NH_2$.

(a) Methylene imine and (b) Methyloamine.

Toronto workers, X.R.16 Rep., 31 Jan. '44; SR7/44/984, consider that "Henry's solution" (Henry, Bull.Acad.Roy.Belg., 1902,ii,721) consisting of an equimolecular mixture of aq. CH_2O and .880 aq. NH_3 "dried with K_2CO_3" probably contains $CH_2 = NH$ and/or $HOCH_2 - NH_2$ in equilibrium with cyclotrimethylene-triamine ("6-ring").

Para. 19

N-Methylolacetamide

$HO.CH_2.NHAc$.

Evap. AcMe solution. m.p. 54°.

Einhorn and Ladisch, Annalen, 1905, 343, 265.
Michigan, Div.8 Int. Rep., R.R.C.3, Feb.-March '43; SR7/4179.
Bristol Br. Rep. 27, Oct. '43; A.C.5051.

$AcNH_2$ + aq. CH_2O ⟶ $HOCH_2.NHAc$.

Para. 20

N-Methylolbenzamide

$HO.CH_2.NHCO\emptyset$.

From aq. EtOH. m.p. 108-110°.

Einhorn, Bischkopf and Szelinski, Annalen, 1905, 373, 223.
Bristol Br. Rep. 27, Oct. '43, A.C.5051.

$\emptyset CONH_2$ + aq. CH_2O ⟶ $HOCH_2NHCO\emptyset$

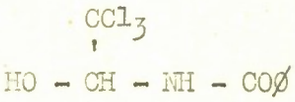
Characterised as N-Ø urethane.

Bristol Br. Rep., 27 Oct. '43, A.C.5051.

$\emptyset NH.CO_2.CH_2.NH.CO\emptyset$ m.p. 177°.

Para. 21

Chloral-benzamide



N(α-Hydroxy-β:β:β-trichloroethyl)-benzamide.

From EtOH. m.p. 150°.

Beilstein, 9, 209.

Jacobsen, Annalen, 157, 245.

Para. 22

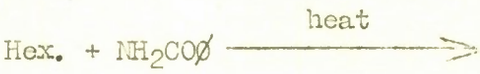
Tris(benzamidomethyl)amine

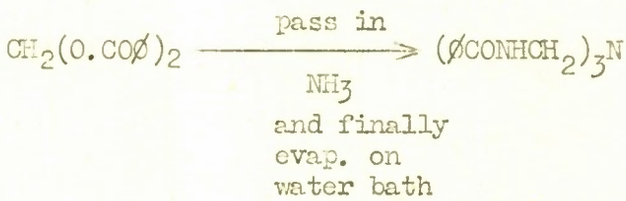
$(\text{ØCONHCH}_2)_3\text{N}$

From EtOH. m.p. 187°.

Beilstein, 9, 208.

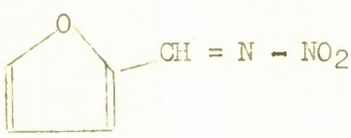
Descudé, Ann.Chim., [7], 29, 542; Comptes rendus, 1902, 135, 694.





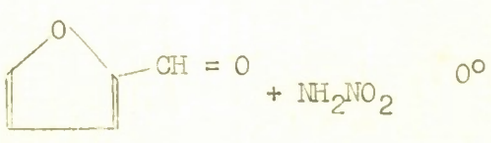
Para. 23

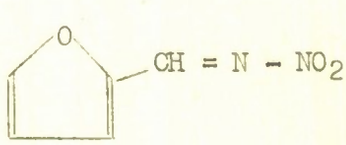
Furfurylidene nitramine



From ØH m.p. 116°.

Toronto, X.R.16. Rep., 31 Jan. '44; SR7/44/984.





(does not trimerise).

DERIVATIVES OF METHYLENE DIAMINE

lin-2-methylene-1:3-diamine

$$\underset{1}{NH_2} - \underset{2}{CH_2} - \underset{3}{NH_2}$$

MEDA or "3 - Chain" Series.

Para. 25

MEDNA

$$\underset{1}{NH}(NO_2) - \underset{2}{CH_2} - \underset{3}{NH}(NO_2)$$

1:3-Dinitro-(3-chain).

"Methylene dinitramine."

From ether and light petroleum. m.p. 103°.

Bristol Br. Rep. 28, Oct. '43; A.C.5058.

PCX (see p. 95) —NaOH aq, then acidify & extract with ether.→ MEDNA

Para. 26

MEDNA (Continued)

Sheffield Rep. 42, Fe. '44; A.C.5996.

$CH_2(NHAc)_2$ (See p. 36) —HNO_3, at -2^o, then cool to -15^o and add Ac_2O + $FeCl_3$ at 0^o, drown and neutralise.→ extract product with ether. → oil

→ $Ba(OH)_2$ → filter and add AcMe → $Ba\left[CH_2(N.NO_2)_2\right]$

↓ acidify as in Bristol Br. Rep. 28.

$CH_2(N\text{-}Ac)_2$ (NO$_2$) —$BaCl_2$ NaOH, and make acid→ MEDNA.

(private communication from Dr. Lamberton (Sheffield), June '44).

(See p. 29a).

Sheffield Rep. 44, March '44; A.C. 6045.

N:N'-Bis methylol-MEDNA (See p. 30). —Ac_2O, 70°→ MEDNA.

Bristol Res. Rep. 128, June '44; A.C. 6477.

DPT —HNO_3, -40^o, drown + ether (isolate via Ba salt).→ MEDNA. 0.7 mole.

MEDNA (Continued)

Bristol Res. Rep. 131, June '44.

HADN 10 g. (See p. 177) —(H_2SO_4; drown with ice, ether extract and purify via Ba salt.)→ MEDNA 0.2 g.

Hex. 20 g. —(H_2SO_4 60%, HNO_3 20%, H_2O 20%; drown and ether extract)→ MEDNA 1.5 g.

Methylolamine nitrate (See p. 202) —(H_2SO_4; drown and ether extract)→ MEDNA 10% yield.

Bristol Br. Rep. 28, Oct. '43; A.C.5058.

$CH_2(NHNO_2)_2$ ⟶ insoluble salts:-

Ba^{++}, $(Ag)_2$, unstable in alkali.

Pb^{++} salt, detonator props.

$(NH_4^+)_2$ m.p. ca 125° rapid decomp.

Morpholine salt of MEDNA.

Sheffield Rep. 44, March '44, A.C.6045.

MEDNA —(excess morpholine in EtOAc)→ $CH_2(\bar{N}NO_2)_2$ $[\overset{+}{N}H_2(CH_2CH_2OCH_2CH_2)]_2$

McGill, X.R.4 Prog.Rep., 1 July '44; SR7/44/2740.

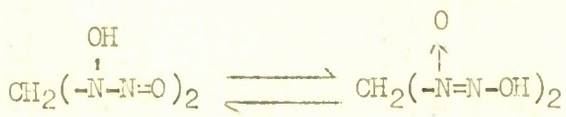
K_2 BSX —(+ HCl aq (2 equiv.); add AcMe to ppt. KCl. Extract filtrate with ether and evaporate; neutralise)→ MEDNA

$K(N(NO_2)-CH_2-N(NO_2)-CH_2-N(NO_2))K$

(See p. 48)

Para. 28

MEDNA is chemically and physically different from the isomeric product from the Traube Reaction on AcMe. This latter product is



and is only known in the form of its salts and esters.

For the Traube Reaction see Toronto X.R.20 Reports, particularly XR.20 Rep. May '43; SR7/4550.

For the constitutions of MEDNA and the Traube products see

Bristol, Res.Rep.110, Dec. '43; A.C.5602.

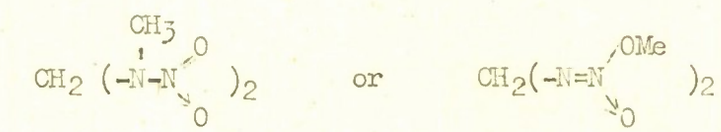
Queen's University, Kingston, X.R.13 Reps., (recently reviewed in Canadian Exp.Res.Extramural Summary 15 March to 15 April, 1944, S.R.7/44/1747).

University of Pennsylvania, O.S.R.D., 3565, May '44, SR.7/44/2002.

Bristol views accepted by U.S.A., Canada RDX Committee at meeting April '44; SR7/44/1594.

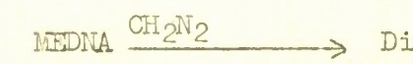
Para. 29

Methylene Dinitramine Dimethyl Ether



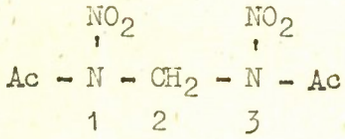
M.E.D.N.A. Dimethyl Ether. An oil.

Bristol Br. Rep. No. 28, Oct. '43; A.C.5058.



Para. 29a

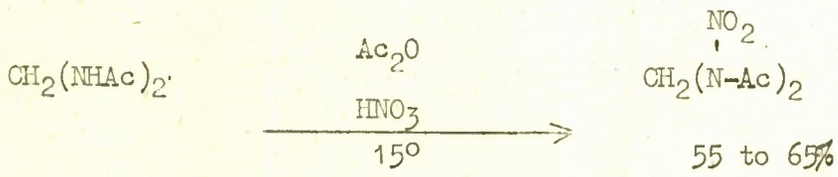
N:N'-Diacetyl-MEDNA



1:3-Diacetyl-1:3-dinitro-(3-chain).

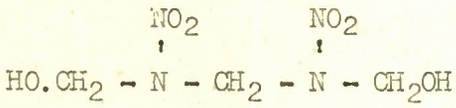
From aq. MeOH. m.p. 63°.

Sheffield, June '44 (Private communication from Dr. A. Lamberton).



Para. 30

N:N'-Bismethylol MEDNA

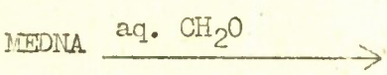


1:3-Bismethylol-1:3-dinitro(3-chain).

From ØH - AcMe. m.p. 68 - 72°.

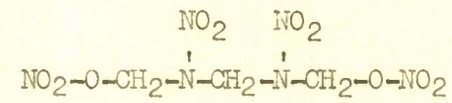
Sheffield Rep. 41, Feb. '44; A.C. 5995.

Sheffield Rep. 44, March '44; A.C. 6045.



Para. 31

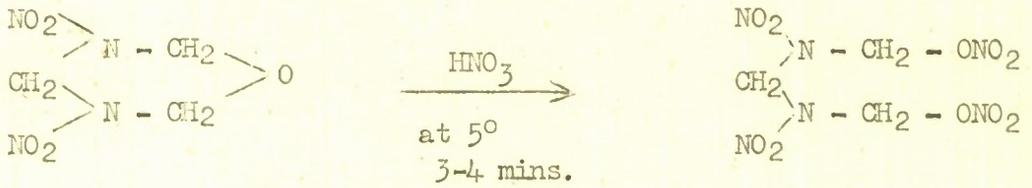
COX



1:3-Bisnitroxymethyl-1:3-dinitro-(3-chain).

Ppt. from HNO_3 by H_2O. m.p. 98-101°.

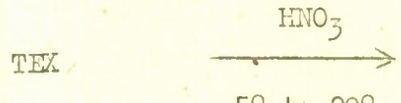
A.R.D. Prep. RDX(B). Prog.Rep.9; Exp.Rep.239/43, July '43; A.C.4628.



Cyclonite Oxide COX

(see p. 118)

Sheffield, Rep. 44, March '44; A.C.6045.

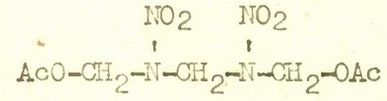


TEX 0.3 g. COX 0.2 g.

(see p. 32)

Para. 32

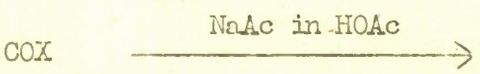
TEX



1:3-Bisacetoxymethyl-1:3-dinitro-(3-chain).

From reaction mixture. m.p. 103-104°.

(Postulated by Davy, RDX committee at Toronto, Dec. '42).
A.R.D. Prep. RDX(B) Prog. Rep. 9; Exp. Rep. 239/43, July '43; A.C.4628.

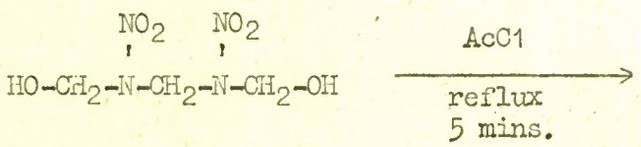


COX TEX

Para. 32 (Continued)

TEX (Continued)

Sheffield Rep. 44, March '44; A.C.6045.



N:N'-Bismethylol MEDNA
0.2 g.

0.26 g. crude
0.18 g. recryst.

Toronto, X.R.16, Canadian Exp. Res. Extramural Summary, April, '44, S.R.7/44/1747.

$NH_4NO_3 + CH_2O + HOAc + Ac_2O \longrightarrow$ TEX in small amount.
(+ DPT, 18%
+ RDX(B), 5%
+ BSX in small yield).

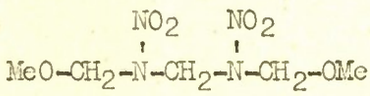
Toronto, X.R.16 Proj., RDX Committee (U.S.A. and Canada), 26 May '44; SR7/44/2801, See X.R.16 Rep. 1 Sept. '44; SR7/44/3158.

Ross reaction —25°, 19 hrs.→ 1.4% TEX.
(+ 5.2% RDX(B).
+ 18% DPT
+ 18% EDX)

MEDNA in 2 CH_2O aq. —2 NaOAc, 10 Ac_2O at 25°. Run at 95°, 1 hr. drown and neut. to pH 6.→ TEX, 9%
(+ EDX(A))

Para. 33

N:N'-Bismethoxymethyl-MEDNA



1:3-Bismethoxymethyl-1:3-dinitro-(3-chain).

From MeOH. m.p. 79-80°.

A.R.D. Prep. RDX(B) Prog. Rep. 9; Exp. Rep. 239/43, July '43, A.C.4628.

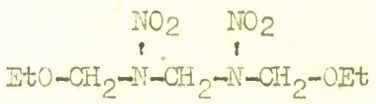
COX —Reflux + MeOH→ di MeO derivative.

Sheffield Rep. 44, March '44, A.C.6045.

Repeat preparation with COX from MEDNA.

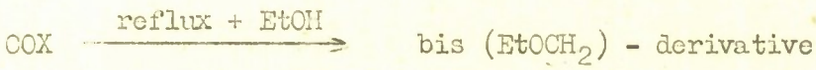
Para. 34

N:N'-Bisethoxymethyl-MEDNA



1:3-Bis(ethoxymethyl)-1:3-dinitro-(3-chain). "an oil".

A.R.D. Prep. RDX(B) Prog. Rep. 9; Exp. Rep. 239/43, July '43; A.C.4628.

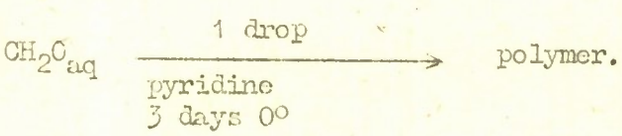


Para. 34a

(MEDNA - CH_2O) polymer

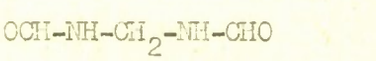
m.p. 219-230°.

Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.



Para. 35

Methylene bisformamide



1:3-Diformyl-(3-chain).

From $HCONH_2$. m.p. 142°.

Knudsen, Ber., 1914, 47, 2698.

Para. 36

H.7.

$AcNH-CH_2-NHAc$.

1:3-Diacetyl-(3-chain).

Methylene bisacetamide.

From EtOH. m.p. 197°.

Pulvermacher, Ber., 1892, 25, 310.

Beilstein's Handbuch, 2, 179.

$$NH_2Ac \xrightarrow[\text{trace HCl, many hours' shaking.}]{\text{Aq. } CH_2O} \text{H.7.}$$

Harvard, N.D.R.C., Rep., Oct. '42; SR7/3263.

$$\text{H.10 (see p. 37)} \xrightarrow[\text{aq. HOAc}]{\text{boil}} \text{H.7.}$$

Para. 37

H.10.

$Ac_2N - CH_2 - NAc_2$.

1:1:3:3-tetracetyl-(3-chain).

N:N:N':N'-tetracetylmethylenediamine.

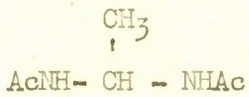
From acetone. m.p. 218-220°.

Harvard, N.D.R.C. Rep., Oct. '42; SR7/3263.

Preparation. Oily layer from prepn. (2) of H.6 (see p. 151), after separation of H.6 deposits crystals of H.10 ('comparatively high yield').

Para. 38

1:3-Diacetyl-2-methyl-(3-chain)



Ethylidene bisacetamide.

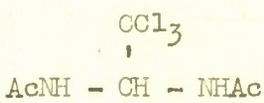
m.p. 169°.

Tawildarow, Ber., 1872, 5, 477.

$$CH_3CHO + NH_2Ac \xrightarrow[\text{tube heat}]{\text{sealed}} CH_3CH(NHAc)_2$$

Para. 39

1:3-Diacetyl-2(trichloromethyl)-(3-chain)



From HOAc. Sublimes.

Hepp, Ber., 1877, 10, 1651.

$$Cl_3C.CHO + NH_2Ac \xrightarrow{\text{heat}} Cl_3C.CH.(NHAc)_2.$$

Para. 40

Methylene bisbenzamide

$\emptyset.CO.NH-CH_2-NH-CO\emptyset$

1:3-Dibenzoyl-(3-chain).

Cryst. from EtOH. m.p. 224-226°.

Kraut and Schwartz, Annalen, 1884, 223, 47.

See Duden and Scharff, ibid., 1895, 288, 249.

$$\text{Hex.} \xrightarrow{\emptyset COCl} CH_2(NHCO\emptyset)_2.$$

Knudsen, Ber., 1914, 47, 2698.

$$CH_2(NHCHO)_2 \xrightarrow[\text{alkali}]{\emptyset COCl} CH_2(NHCO\emptyset)_2$$

Bristol Res. Rep. 112, Jan. 1944, A.C.5603.

$$HO-CH_2-NHCO\emptyset \xrightarrow[HOAc]{Ac_2O} CH_2(NHCO\emptyset)_2$$

Toronto, X.R.16. Rep., 31 Jan. '44; SR7/44/984.

NH_4Cl in H_2O + NaOH + CH_2O. $\xrightarrow[10°]{\emptyset COCl}$ crude product.

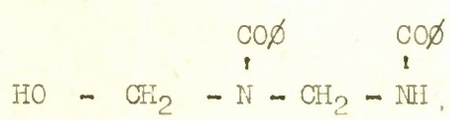
Digest with EtOH → cool filtrate → $CH_2(NHCO\emptyset)_2$ 12% yield on CH_2O

Digest with EtOH → residual solid = Tribenzoyl-6 Ring.

(See p. 109).

Para. 41

1-Methylol-1:3-dibenzoyl-(3-chain)



From EtOH. m.p. 182.5°.

Einhorn, Bischkopff and Szelinski, Annalen, 1905, 343, 225.

$$CH_2(NHCO\emptyset)_2 \xrightarrow{CH_2O} \text{Methylol dibenzoyl-(3-chain).}$$

Para. 42

Ethylidene bisbenzamide

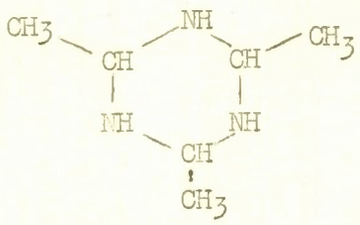
$$\begin{array}{c} CH_3 \\ | \\ \text{Ø.CO-NH-CH-NH-COØ} \\ 1\ \ 2\ \ 3 \end{array}$$

1:3-Dibenzoyl-2-methyl- (3-chain).

From EtOH. m.p. 202-4°. (187 - 8°*).

Limpricht, Annalen, 99, 119.

(Delepine, Comptes rendus, 1899, 128, 105).



$$\xrightarrow{\text{ØCOCl}} \quad CH_3CH(NHCO\text{Ø})_2$$

dehydrated "aldehyde ammonia".

(see p. 113)

Nencki, Ber., 1874, 7, 159.

$$CH_3CHO + NH_2CO\text{Ø} \xrightarrow[H_2SO_4]{\text{trace}} CH_3CH(NHCO\text{Ø})_2$$

See Beilstein, 9, 209.

---

* Henle and Schupp, Ber., 1905, 38, 1370 give this m.p.

Para. 43

1:3-Dibenzoyl-2-(trichloromethyl)-(3-chain)

$$\begin{array}{c} CCl_3 \\ | \\ \text{Ø - CO - NH - CH - NH - COØ} \end{array}$$

Trichloroethylidene bisbenzamide.

From EtOH. m.p. 257°.

Hepp and Spiess, Ber., 1876, 9, 1428.

$$Cl_3C.CHO + 2NH_2CO\text{Ø} \xrightarrow[H_2SO_4]{\text{conc.}} \text{Dibenzoyl(trichloromethyl)-(3-chain).}$$

Para. 44

Methylene Bisurethane

$$EtO_2C - NH - CH_2 - NHCO_2Et.$$

1:3-Dicarbethoxy-(3-chain).

From EtOH. m.p. 131°.

Conrad and Hock, Ber., 1903, 36, 2206.

$$NH_2CO_2Et \xrightarrow[\text{conc. HCl}\\ \text{cold.}]{CH_2O\ aq} \text{Methylene bisurethane.}$$

Para. 45

Methylenediamine salts

$$CH_2(\overset{\oplus}{N}H_3)_2\ [\overset{\ominus}{X}]_2$$

Knudsen, Ber., 1914, 47, 2698.

$$CH_2(NHCHO)_2 \xrightarrow[12^o]{\text{fuming HCl at}} \text{di HCl.}$$

(Hygrosc. and decomp. by H_2O).

$$\xrightarrow{HNO_3} \text{di } HNO_3$$

(deflagrates on melting).

$$\xrightarrow{H_2SO_4} \text{sulphate.}$$

Sulphate also prepared by Toronto workers, X.R.16 Rep. Jan. '44, SR7/44/984.

43% Henry solution plus 60% H_2SO_4 $\longrightarrow$ $CH_2(\overset{\oplus}{N}H_3)_2SO_4$ =

Para. 45a

TEMD

$Et_2N - CH_2 - NEt_2$

1:1:3:3-Tetraethyl-(3-chain).

b.p./760 mm., 166-169°.

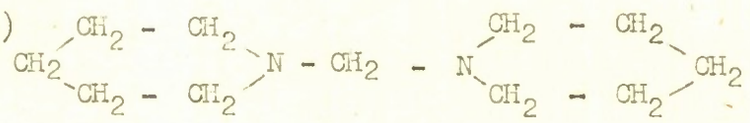
Beilstein's Handbuch, 1, 106.

Chicago, N.D.R.C. Div.8 Int. Rep. R.R.C.17, April-May '44; SR7/44/2047.

$$EtNH_2 + CH_2O_{aq} \longrightarrow Et_2NCH_2OH \xrightarrow{Et_2NH} Et_2N.CH_2.NEt_2.$$

Analogous compounds:-

(a) $Me_2N-CH_2-NMe_2$, Tetramethyl-(3-chain), b.p./760 mm., 85°.
Similarly prepared, Beilsteins Handbuch, 1, 54.

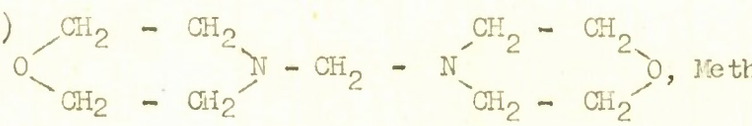
(b) 

Methylene bis piperidine, b.p./760°, 230°.

b.p./15°, 115°.

2-piperidine + 1 aq CH_2O ⟶ compd.

Beilsteins Handbuch, 20, 36.

(c)  , Methylene bis-morpholine.

Sheffield, preliminary communication to RDX Research Panel Meeting, London, 21 June '44.

DERIVATIVES OF lin-2:4-DIMETHYLENE-1:3:5-TRIAMINE

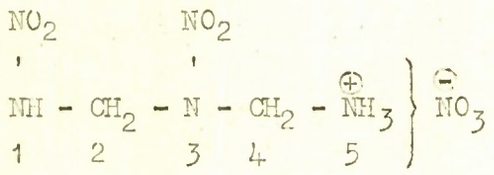
$$NH_2 - CH_2 - NH - CH_2 - NH_2$$

1 2 3 4 5

"5-Chain" Series.

Para. 47

1:3-Dinitro-(5-chain) - 5-nitrate



From EtOH, m.p. 129°.

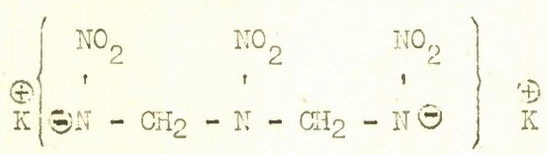
Bristol Br. Report No. 28, Oct. '43; A.C.5058.

H.A.D.N. —(HNO_3, -40° then dilute with ether.)→ precipitate —(cold EtOH, & filter. Evaporate filtrate.)→ above compound.

(See p.177)

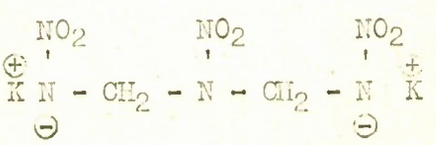
Para. 48

1:5-Dipotassio-1:3:5-trinitro-(5-chain) (K_2B SX)



McGill, X.R.4, Prog.Rep., 1 Mar. '44, SR7/44/1001.

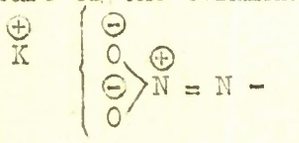
BSX —(4 KOH in MeOH)→



(See p.63)

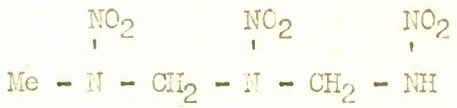
RDX —(2KOH (- CH_2O))→

The structure of the terminal grouping is probably



Para. 49

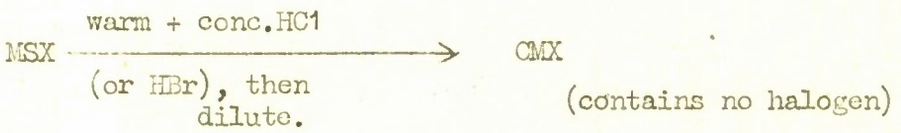
C.M.X.



1-Methyl-1:3:5-trinitro-(5-chain).

From C_6H_6-light petroleum. m.p. 130-131°

McGill, X.R.4.Prog.Rep., 1 Feb. '43; SR7/4036.

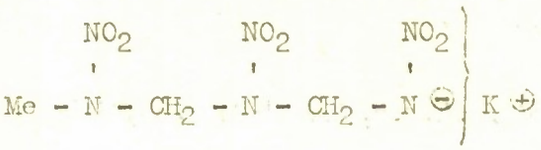


McGill, X.R.4.Prog.Rep., 1 Mar. '44; SR7/44/1001.

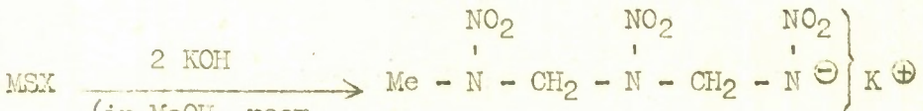
C, H, and N analysis and structure suggested.

Para. 50

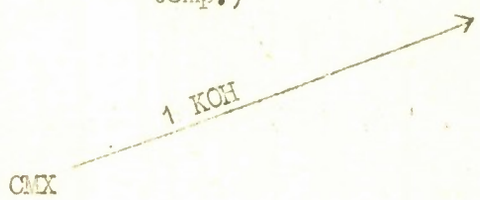
1-Methyl-5-potassio-1:3:5-trinitro-(5-chain) (KCMX)



McGill, X.R.4.Prog.Rep., 1 Mar. '44; SR7/44/1001.

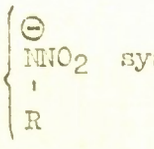
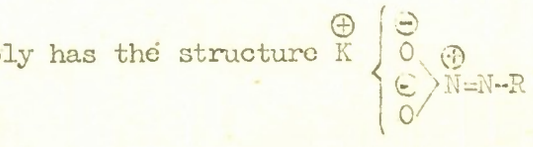


(See p.51)



K in this and similar compounds is very unreactive, but will give silver derivative.

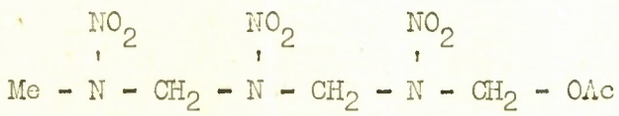
See also McGill, X.R.4 Prog.Rep., April '44; SR7/44/1308.

The  system probably has the structure 

Para. 51

M.S.X. (McGill).

H.21 (Univ. Penn.)

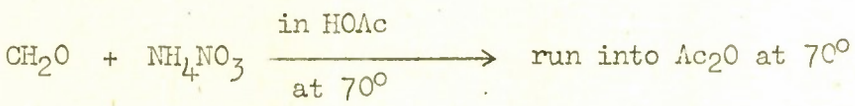


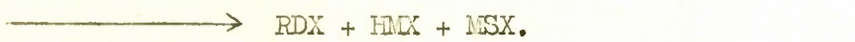
1-Methyl-5-acetoxymethyl-1:3:5-trinitro-(5-chain).

From $CHCl_3$ - AcMe or MeOH. m.p. 155°.

McGill. C.E.53 Prog.Reps., 1 Sept. '42: SR7/3042:

1 Nov. '42: SR7/3454.





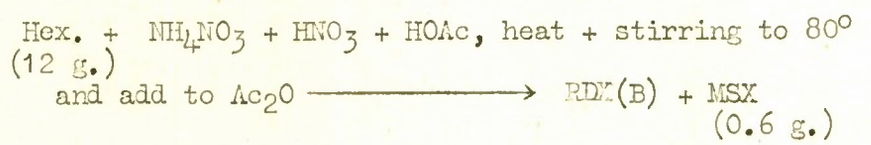
RDX + HMX + MSX.

Separate by fract. cryst. (see Cornell, Div. 8. Int.Rep.R.R.C.3, Mar. '43; SR7/4179, for working up).

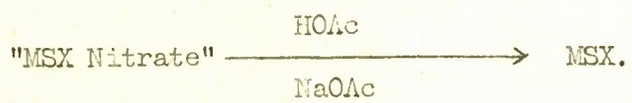
Checked by Penn. State, Div. 8 Int.Rep.R.R.C.5, May '43; SR7/4766

30 g. CH_2O ⟶ 0.99 g. pure M.S.X.

McGill X.R.4 Prog.Rep., 1 Feb. '43; SR7/4036.



McGill X.R.4 Prog.Reps., 1 Feb. '43 and Mar. '43; SR7/4036 and 4037.



(See p. 54)

Both checked by A.R.D. Prep. RDX(B) Prog.Rep.9, Expl.Rep. 239/43, July '43; A.C.4628.

MSX (Continued)

McGill X.R.4.Prog.Rep., 1 Mar. '43; SR7/4037.

$$\text{OFX} \xrightarrow[\text{HOAc}]{\text{NaOAc}} \text{MSX.}$$

(See p. 57)

University Penn., Div. 8. Int. Rep., R.R.C.5, May '43; SR7/4766.

$$\text{H.18} \xrightarrow[\text{AcONO}_2]{\text{4 moles}} \text{DPT} + \text{MSX.}$$

(Hex.methonitrate; see p. 164)

Separated by fractional cryst. from CH_3NO_2 + AcMe. (1 g. MSX from 18 g. H.18).

$$\text{H.18 (16 g.)} \xrightarrow[\text{AcONO}_2]{\text{13 moles}} \text{Crude MSX (14 g.)} \xrightarrow[\text{in HOAc}]{\text{NaOAc}} \text{MSX}$$

Crude MSX (14 g.) probably contains "MSX Nitrate" - see p. 54.

MSX 7-8 g. pure. Called H.21 until identified.

See also Univ.Penn., O.S.R.D., 1733 Rep., July '43; SR7/43/448.

$$\text{H.26} \xrightarrow{\text{AcONO}_2} \text{MSX.}$$

(Hex.nitrate, methonitrate, see p. 179)

McGill X.R.42 Rep. May and June '43; SR7/43/319.

Using $\left.\begin{matrix}\oplus \\ NH_3Me\end{matrix}\right\}\begin{matrix}\ominus \\ NO_3\end{matrix}$ for NH_4NO_3 in the Bachmann Combination RDX(B) process, got a mixture of MSX and BSX, m.p. 125°, difficult to separate by crystallisation.

Univ.Penn., Div. 8, Int. Rep. R.R.C.9, Sept. '43; SR7/43/924.

$$\underset{8\text{ g.}}{\text{PS.2.}} \xrightarrow{\text{EXCESS AcONO}_2} \underset{\text{ca 1 g.}}{\text{MSX}}$$

(Hexa methopicrate, see p. 166).

Para. 53

MSX (Continued)

Univ. Penn. Div. 8 Int.Rep. R.R.C.11, Nov. '43; SR7/44/70.

H.29 —($MeNH_3$ NO_3 / $AcONO_2$)→ product, m.p. 147-148°, which is probably a mixture of MSX + H.28. (see p. 58)

(Hex. ethonitrate, see p. 168)

H.18 —($EtNH$ NO_3 / $AcONO_2$)→ product, m.p. 147-148°, which is probably a mixture of MSX + H.28. (see p. 58)

Bristol Res. Rep. 131. June '44; A.C.6657.

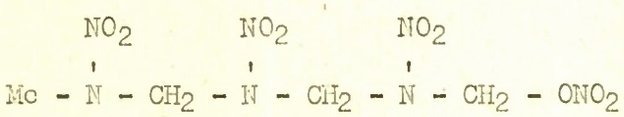
MEDNA + (CH_2O + $\overset{\oplus}{M}eNH_3$ $\overset{\ominus}{NO_3}$) —(Ac_2O, keep cool)→ MSX

(1 mole) (2 mols)

45% yield.

Para. 54

'M.S.X. nitrate'



1-Methyl-5-nitroxymethyl-1:3:5-trinitro-(5-chain).

Washed with water, m.p. 136-139°.

McGill, X.R.4 Prog.Reps., 1 Feb. and 1 March '43. SR7/4036 and 4037.

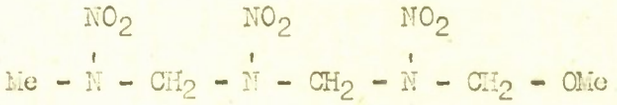
A.R.D., Prep.RDX(B) Prog.Rep.9, Exp.Rep.239/43, July '43, A.C.4628.

M.S.X. —(HNO_3)→ M.S.X. nitrate

(probably in good yield).

Para. 55

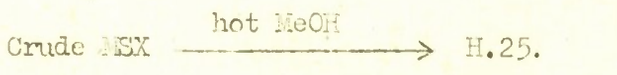
H.25. (MSX - Me).



1-Methyl-5-methoxymethyl-1:3:5-trinitro-(5-chain).

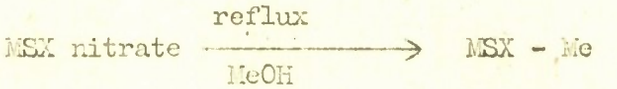
From MeOH. m.p. 102°.

Univ. Penn., Div. 8 Int.Rep. R.R.C.5. May '43. SR7/4766.



(from H.18 plus 13 moles $AcONO_2$).

A.R.D., Prep. RDX(B) Prog.Rep.9, Exp.Rep. 239/43, July '43; A.C.4628.



m.p. 114-115°.

Found: C, 23.45; H, 4.94%

$C_5H_{12}N_6O_7$ requires C, 22.4; H, 4.48; N, 31.3%.

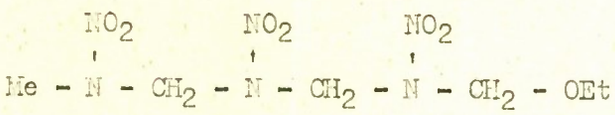
Univ.Penn., O.S.R.D. 1733 Rep., July '43; SR7/43/448;

States that the material m.p. 102° was impure.

Found: C, 22.9; 23.0; H, 4.56, 4.40; N, 31.0, 31.3%.

Para. 56

H.24 (MSX - Et)



1-Methyl-5-ethoxymethyl-1:3:5-trinitro-5(chain).

From EtOH, m.p. 109-110°.

Univ. Penn., Div. 8 Int.Rep., R.R.C.5, May '43; SR7/4766.

Crude MSX —Hot EtOH→ H.24.

(from H.18 plus

13 mols $AcONO_2$)

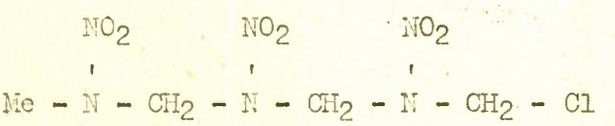
Univ. Penn, O.S.R.D. 1733 Rep., July '43; SR7/43/448.

Found: C, 25.1; H, 4.5; N, 29.8%.

$C_6H_{14}N_6O_7$ requires C, 25.5; H, 5.0; N, 29.8%.

Para. 57

OFX



1-Methyl-5-chloromethyl-1:3:5-trinitro-(5-chain).

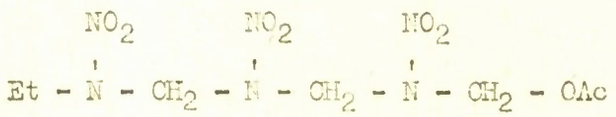
(from $CHCl_3$ + ligroin; m.p. 140.5-141.5°.

McGill X.R.4 Prog.Rep. 1 March '43; SR7/4037.

MSX —$CHCl_3$ sat. with HCl at -60°, sealed tube at 100° 1 hr.→ OFX (0.4 g.)

Para. 58

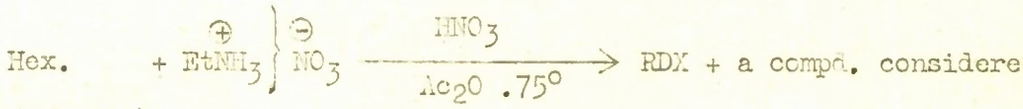
H.28



1-Ethyl-5-acetoxymethyl-1:3:5-trinitro-(5-chain).

From MeOH or HOAc m.p. 133-134°.

Penn.State, Div.8. Int.Rep., R.R.C.8, Aug. '43; SR7/43/391.

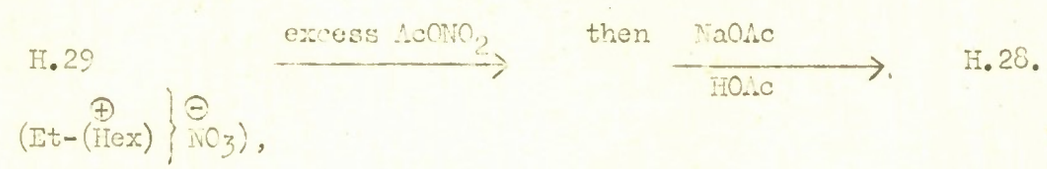


(Bachman Combination RDX(B) process with $EtNH_3\ NO_3$ for the NH_4NO_3).

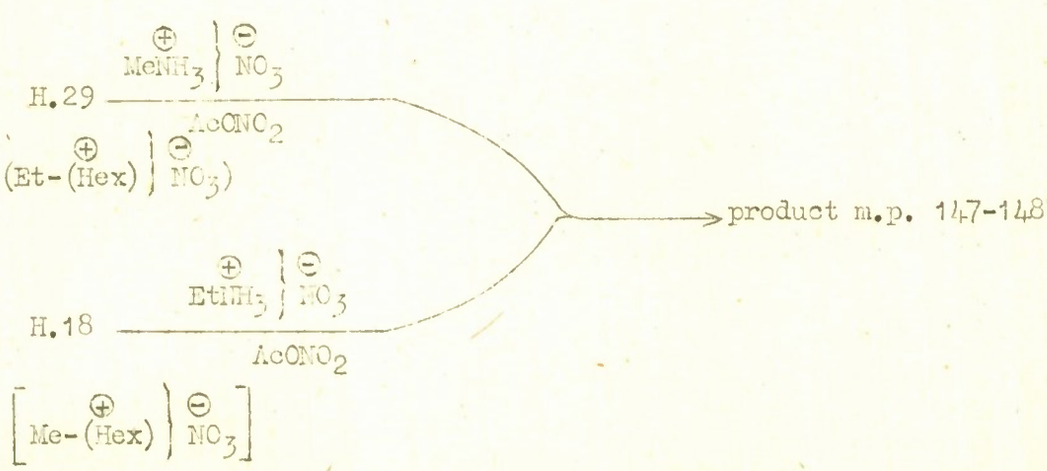
Univ.Penn., Div.8. Int.Rep. R.R.C.9, Sept. '43; SR7/43/924;
Div.8. Int.Rep. R.R.C.10, Oct. '43; SR7/43/925;
Div.8. Int.Rep. R.R.C.11, Nov. '43; SR7/44/70,

repeat above reaction and isolate (by separation via $CHCl_3$ and crystallisation from MeOH) the compound H.28 (1 g. from 25 g. hex.), which is very similar to MSX in many physical properties but is the EtN analogue of MSX.

Univ.Penn. in these three papers also report other preparations:



see p. 168)



Para. 59

H.28 (Continued)

See also U.S.A.-Canada-RDX Committee Rep., April '44;

SR7/44/1594.

Mixed m.p. of authentic (MSX + H.28) is 148-152°.

∴ probably above produet is MSX + H.28.

H.30 $\xrightarrow{\text{Excess } AcONO_2}$ H.28

(PS.2(Et))
$\left.\begin{matrix}\overset{\oplus}{\text{Et-(Hex.)}}\end{matrix}\right\}$ $\overset{\ominus}{\text{picrate}}$

see p. 169

Crystallographic evidence:-

Cornell. Div.8 Int.Rep.R.R.C.8, Aug. '43; SR7/43/391.

H.28 and MSX identical.

Univ.Penn.Div.8 Int.Rep.R.R.C.11, Nov. '43; SR7/44/70.

H.28 and MSX not identical.

McGill X.R.4 Prog.Rep., 1 Jan. '44; SR7/44/334.

H.28 and MSX not identical.

C. H, and N analysis and m.p. trends reviewed in Univ.Penn.Div.8 Int.Rep.R.R.C.11, Nov. '43; SR7/44/70, indicating that H.28 and derived compounds are Et-N derivatives.

Et-N identificd by HI distillation.

(Univ.Penn.Div.8 Int.Rep.R.R.C.13, Jan. '44; SR7/44/915.

Div.8 Int.Rep.R.R.C.14, Feb. '44; SR7/44/952).

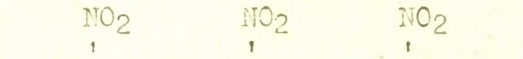
Bristol Res.Rep. 131, June '44; A.C.6657.

MEDNA + $\left.\begin{matrix}CH_2O + EtNH_3\end{matrix}\right\}NO_3$ $\xrightarrow{Ac_2O}$ H.28.

1 mole 2 moles 48% yield.

Para. 60

H.31



1-Ethyl-5-methoxymethyl-1:3:5-trinitro-(5-chain).

Cryst. from MeOH. m.p. 94.5-95.5°.

Univ.Penn.Div.8 Int.Rep.R.R.C.10; Oct. '43; SR7/43/925.

H.28 $\xrightarrow{HNO_3}$ and MeCH on product $\longrightarrow$ H.31

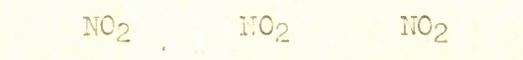
2 g. crude 0.7 g.

Univ.Penn.Div.8 Int.Rep.R.R.C.11, Nov. '43; SR7/44/70.

H.28 $\xrightarrow[\text{reflux}]{\text{MeOH}}$ H.31

Para. 61

H.32



1-Ethyl-5-ethoxymethyl-1:3:5-trinitro-(5-chain).

From EtOH. m.p. 87°.

Univ.Penn.Div.8 Int.Rep.R.R.C.11, Nov. '43; SR7/44/70.

H.28 $\xrightarrow[\text{reflux}]{\text{EtOH}}$ H.32

Para. 62

H.33

1-Ethyl-5-chloromethyl-1:3:5-trinitro-(5-chain).

From $CHCl_3$ reaction liq. by dilution with

light petroleum, m.p. 116-117°.

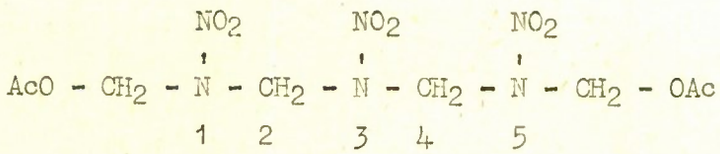
Univ.Penn.Div.8 Int.Rep.R.R.C.11, Nov. '43; SR7/44/70.

H.28 $\xrightarrow[\text{HCl}]{CHCl_3}$ H.33

sealed tube at 100°

Para. 63

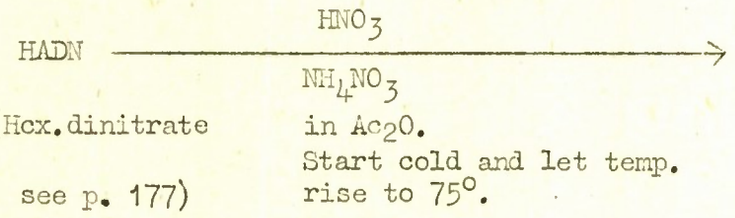
BSX



1:5-Bisacetoxymethyl-1:3:5-trinitro-(5-chain).

From AcMe or HOAc. m.p. 155-156°

Michigan N.D.R.C.Prog.Rep., 18 Oct. '41; SR7/874.



(Hex.dinitrate see p. 177)

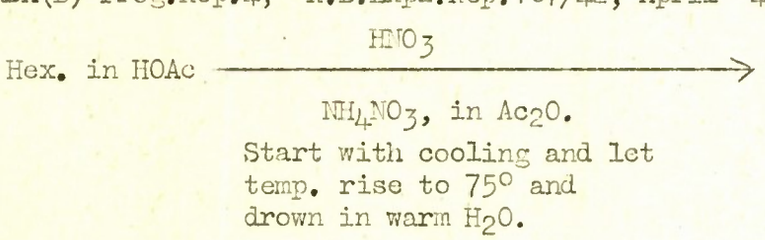
NH_4NO_3 in Ac_2O. Start cold and let temp. rise to 75°.

Toronto C.E.12 Prog.Rep., 1 March '42; SR7/1845,

isolated BSX as by-product in Bachmann Combination RDX(B) process.

(See pp. 86 and 88).

A.R.D. Prep.RDX(B) Prog.Rep.4; R.D.Expl.Rep.107/42, April '42.



NH_4NO_3, in Ac_2O. Start with cooling and let temp. rise to 75° and drown in warm H_2O.

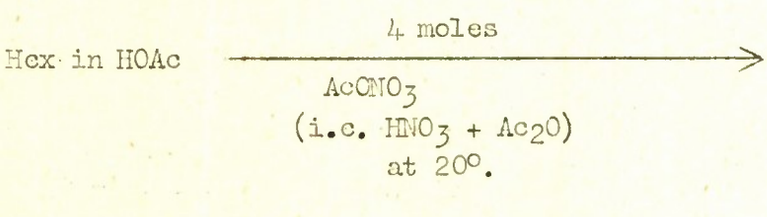
87% crude.

52% pure.

Michigan, N.D.R.C. Prog.Rep.B.M.324, 15 Nov. '42; SR7/3339,

(a) found heating to 75° in A.R.D. prep. unnecessary;

(b) found NH_4NO_3 unnecessary and use



(i.e. $HNO_3 + Ac_2O$) at 20°.

87% crude.*

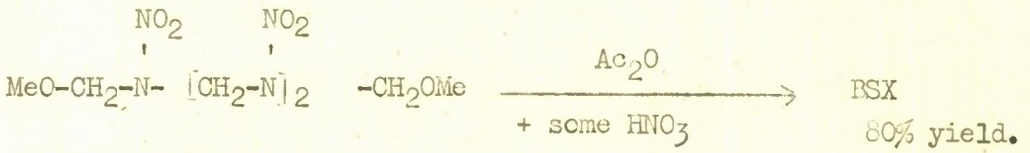
(See Univ.Penn., O.S.R.D., 1733 Rep., July '43; SR7/43/448).

* Toronto X.R.16 Rep., 1 Sept. '44; SR7/44/3158 show yield of BSX = 51% and isolate 39% bisacetoxymethylnitramine from filtrate (see p. 15b).

BSX (Continued)

Michigan, Div.8 Int.Rep.,R.R.C.12, Dec. '43; SR7/44/508, use this process with heating to 75° and then cool, seed, and stand for 12 hrs. BSX separates direct. Yield 51% after recrystallisation.

Toronto, C.E.12 Reps., 28 Feb. '42; SR7/1700; 1 Nov. '42, SR7/3466.

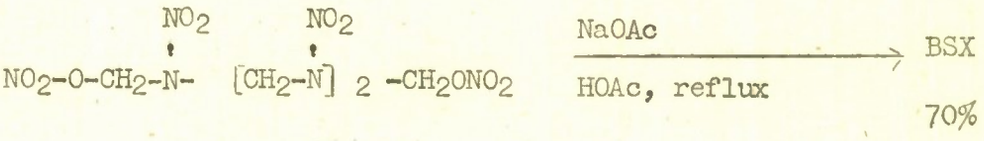


"104"

(see p. 67)

Toronto, C.E.12 Reps., 1 June '42; SR7/2350: 1 July '42, SR7/2558.

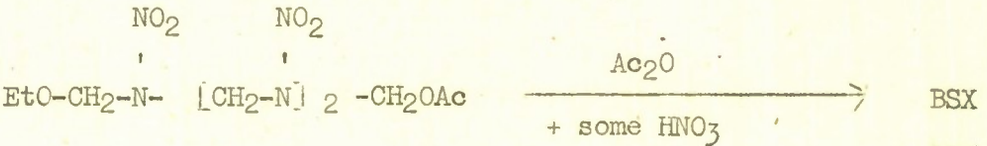
A.R.D. Prep.RDX(B) Prog.Rep.5, Expl.Rep., 254/42; Sept. '42.



ATX.

(see p. 66)

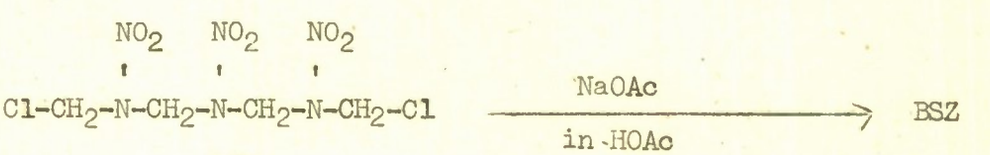
Toronto, C.E.12 Rep., 1 Nov. '42; SR7/3466.



"107"

(see p. 68)

McGill, X.R.4 Prog.Rep., 1 March '43; SR7/4037.



GSX

(see p. 70)

BSX (Continued)

McGill, X.R.42 Prog.Rep., May and June '43; SR7/43/319.

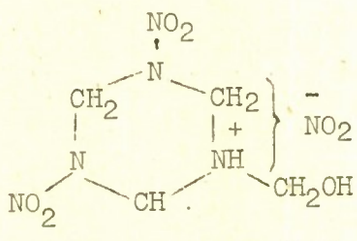
Used $MeNH_3NO_3$ for NH_4NO_3 in normal Bachmann Combination RDX(B) process (see p. 86) and got a mixture of BSX and MSX (see p. 52), m.p. 125°, and very difficult to separate by fractional crystallisation.

Bristol Br. Rep.26, Oct. '43; A.C.5049.

HAMN (Hex. mono-nitrate, see p. 159) —HNO_3, Ac_2O, -40°, (See p. 66)→ ATX (not isolated) + some RDX.

ATX —NaOAc, HOAc→ BSX

Dr. J. K. N. Jones (Bristol, private communication, June, '44).



Ac_2O, HNO_3, -40° → BSX

(see p. 205)

Toronto, X.R.16, Canadian Exp.Res.Extramural Summary, March-April '44; SR7/44/1747.

Ross Reaction[H] filtrates → 2.1% BSX.

[H] (see p. 85)

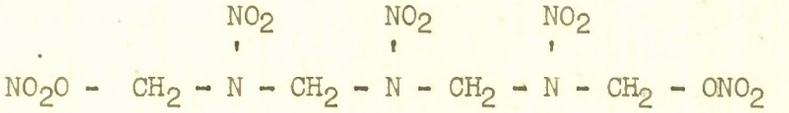
$NH_4NO_3 + CH_2O + HOAc + Ac_2O$ → BSX in small amt. (+ 18% DPT + 5% RDX(B) + TEX, small amount).

(See X.R.16 Rep., 1 Sept. '44; SR7/44/3158).

Para. 66

A.T.X. (Toronto)

N.B.S.X. (A.R.D.)

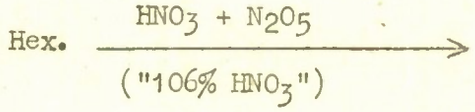


1:5-Bisnitroxymethyl-1:3:5-trinitro-(5-chain).

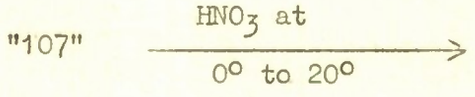
Ppt. from dioxan by CCl_4 or ppt. from AcMe by H_2O, and wash with cold EtOH, m.p. 154°.

(If crystallised from AcMe, ATX separates with solvent of crystallisation:- 2ATX.AcMe, m.p. 103°).

Toronto, C.E.12 Prog.Reps., 28 Feb. '42; SR7/1700; 1 Nov. '42; SR7/3466.



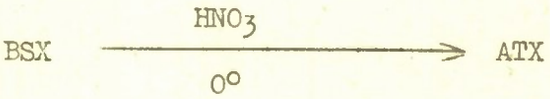
Toronto, C.E.12 Prog.Rep., 1 March '42; SR7/1845.



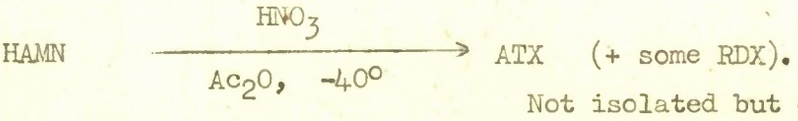
(See p. 68)

Toronto C.E.12 Prog.Reps. 1 June '42; SR7/2350; 1 July '42; SR7/2558: 1 Nov. '42; SR7/3466.

A.R.D. Prep.RDX(B) Prog.Rep.5, Exp.Rep.284/42, Sept. '42.

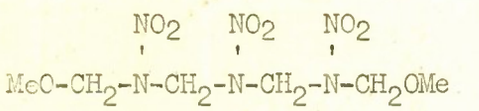


Bristol Br.Rep. 26, Oct. '43; AC.5049.



Para. 67

"104"



1:5-Bismethoxymethyl-1:3:5-trinitro-(5-chain).

From MeOH. m.p. 104°.

Toronto, C.E.12. Prog.Rep., 28 Feb. '42; SR7/1700.

Hex. $\xrightarrow[(\text{"106\% } HNO_3\text{"})]{HNO_3 + N_2O_5}$ RDX + DPT + ATX

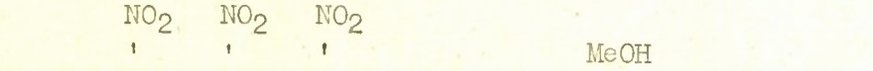
Extract with boiling MeOH, cool filtrate ⟶ "104".

Toronto, C.E.12. Prog.Rep., 1 Nov. '42; SR7/3466.

ATX $\xrightarrow[MeOH]{\text{reflux}}$ "104" 60.5% yield, pure.

(See p. 66)

McGill X.R.4 Prog.Rep., 1 Dec. '43; SR7/44/181.

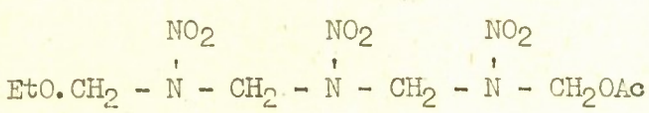


GSX

(see p. 70)

Para. 68

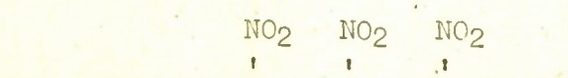
"107"



1-Ethoxymethyl-5-acetoxymethyl-1:3:5-trinitro-(5-chain).

From EtOH. m.p. 107°.

Toronto, C.E.12 Rep., 1 March '42; SR7/1845.

Hex $\xrightarrow[+\ Ac_2O,\ -25^\circ]{HNO_3}$ RDX + 

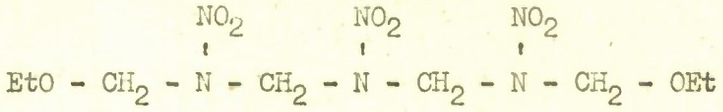
Extract with hot EtOH

↓

above ethoxymethyl-acetoxymethyl compound.

Para. 69

1:5-Bis(ethoxymethyl)-1:3:5-trinitro-(5-chain)



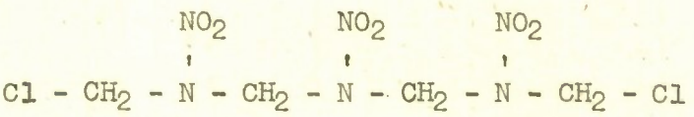
From EtOH, m.p. 80°.

Toronto, C.E.12. Prog.Rep., 1 Nov. '42; SR7/3466.

ATX —(EtOH; reflux (5 hrs.))→ bisethoxymethyl compound. 52% yield.

Para. 70

GSX



1:5-Bis(chloromethyl)-1:3:5-trinitro-(5-chain).

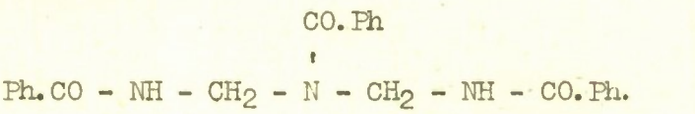
From $CHCl_3$. m.p. 145.5 - 146.5°C.

McGill, X.R.4 Prog.Rep., 1 March 1943; SR7/4037.

BSX —($CHCl_3$ satd. at -60° with HCl; in sealed tube at 100° for 1 hr.)→ GSX.

Para. 71

1:3:5-Tribenzoyl-(5-chain)



From EtOH, HOAc, or $CHCl_3$ with ether. m.p. 266-267°.

Duden and Scharff, Annalen, 1895, 288, 250.

Hex. —(NaOH; Ph.COCl)→ 1:3:5-tribenzoyl-6-ring (soluble in $Br.CH_2CH_2Br$) (see p. 109) plus 1:3:5-tribenzoyl-(5-chain) (insoluble in $BrCH_2CH_2Br$).

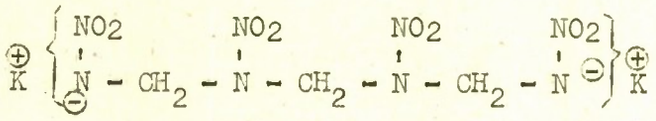
DERIVATIVES OF lin- 2:4:6-TRIMETHYLENE-1:3:5:7-TETRAMINE

$$NH_2 - CH_2 - NH - CH_2 - NH - CH_2 - NH_2$$
$$1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7$$

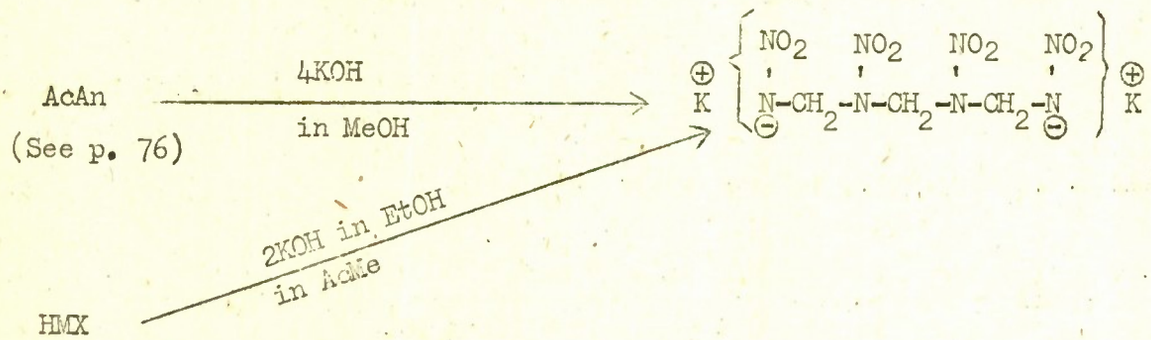
"7 - Chain" Series.

Para. 73

1:7-Dipotassio-1:3:5:7-tetranitro-(7-chain). (K_2AcAn)



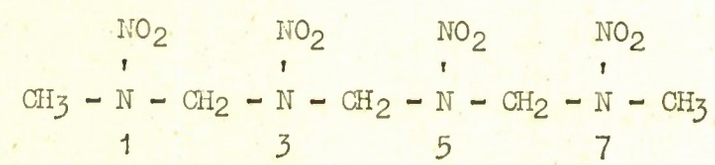
McGill, X.R.4 Prog.Rep., 1 March '44; SR7/44/1001.



(McGill, X.R.4 Prog.Rep., 1 April '44; SR7/44/1308).

Para. 74

DMTN



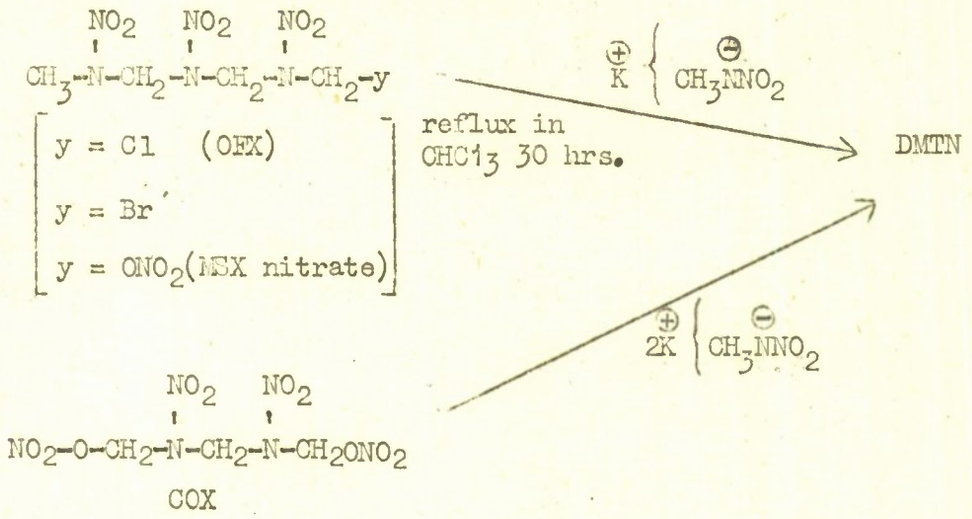
1:7-Dimethyl-1:3:5:7-tetranitro-(7-chain).

m.p. 244°.

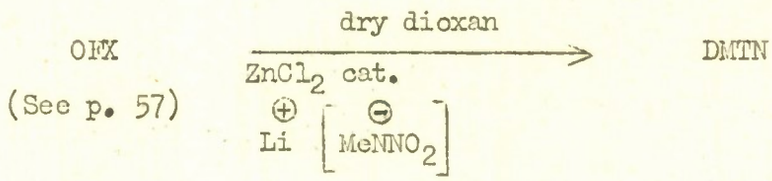
Para. 74 (Continued)

DMTN (Continued)

McGill, X.R.4 Prog.Rep., 1 Dec. '43; SR7/44/181.



Best prep. McGill, X.R.4 Prog.Rep., 1 Jan. '44; SR7/44/334.

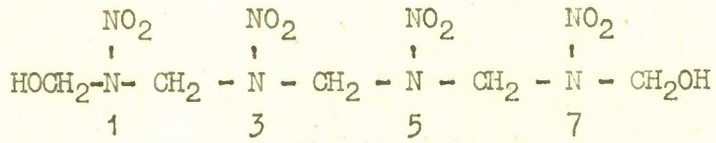


McGill, X.R.4 Prog.Rep., 1 March '44; SR7/44/1001.

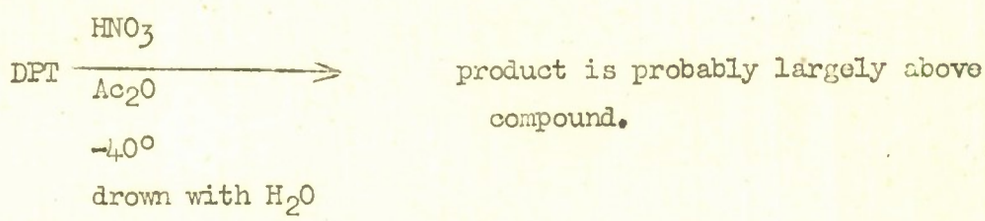
C, H, and N analysis.

Para. 75

1:7-Bis(methylol)-1:3:5:7-Tetranitro-(7-chain).

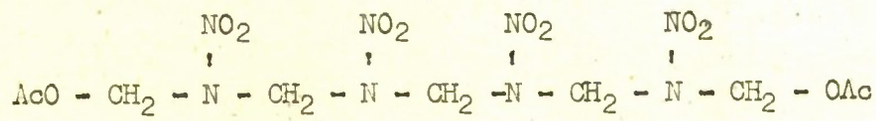


Bristol Res. Rep. 128, June '44; A.C.6477.



Paras. 76, 77

AcAn



1:7-Bis(acetoxymethyl)-1:3:5:7-tetranitro-(7-chain).

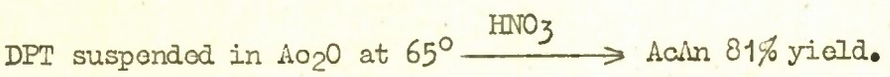
From AcMe or CH_3NO_2 m.p. 187°.

McGill, C.E.53 Prog.Rep., 1 Jan. '42, SR7/1436.

First prepared (impure)

Toronto C.E.12 Prog.Rep., 31 Jan. '42; SR7/1562.

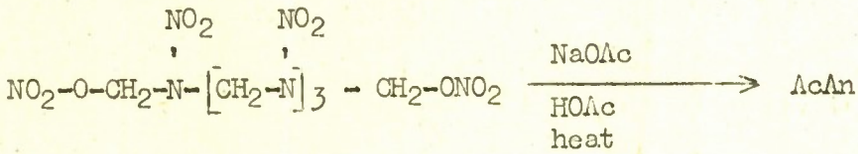
First prepared pure.



Toronto C.E.12 Prog.Rep., 28 Feb. '42; SR7/1700.

Above preparation runs better at 44°.

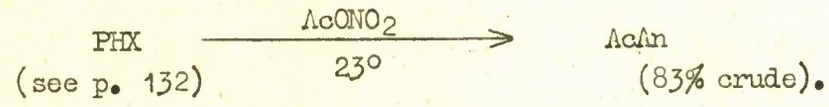
Toronto C.E.12 Prog.Rep., 1 June '42; SR7/2350.



"106"

(see p. 78)

Michigan, Div.8 Int.Rep.R.R.C.1, Jan. '43; SR7/3748.

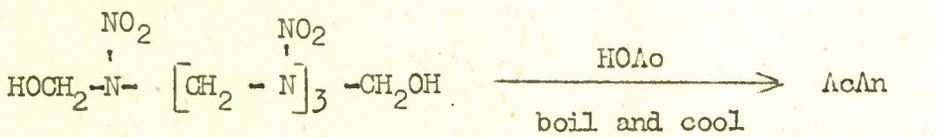


(see p. 132)

Checked by Cornell, Div. 8 Int. Rep. R.R.C.1, Jan. '43; SR7/3748.

Para. 77

Bristol Res.Rep. 128, June '44; A.C.6477.

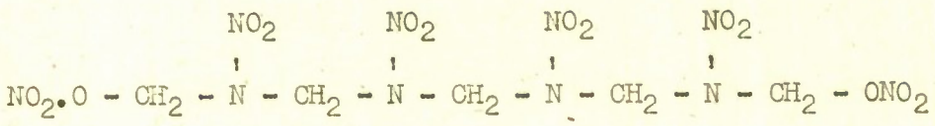


2 g. 1.2 g.

Cal.Tech., Div.8, Int.Rep. R.R.C.22, Oct. '44; SR7/44/3502

Chromatography of AcAn.

"106"



1:7-Bisnitroxymethyl-1:3:5:7-tetranitro-(7-chain).

From CH_3NO_2 m.p. 204.5-205°. (rapid heating).

Toronto, C.E.12 Prog.Rep., 31 Jan. '42; SR7/1562.

DPT —($HNO_3 + N_2O_5$ ("106% HNO_3") below 20° and drown out.)→ "106" 72% yield.

Toronto, C.E.12 Prog.Reps., 31 Jan. '42; SR7/1562; 1 June '42; SR7/2350: 1 July '42; SR7/2558.

pure AcAn —(HNO_3, 8°)→ "106" 80% yield.

Univ.Penn., Div.8 Int.Rep., R.R.C.1, Jan. '43; SR7/3748.

H.16 (see p. 82) 2.3 g. —(HNO_3, 0°, 45 mins.)→ "106" 0.3 g.

(See also Univ.Penn., O.S.R.D., 1733 Rep., July '43; SR7/43/448).

Toronto, X.R.16 Prog.Rep., 15 Jan. '43; SR7/3721.

Crude RDX from Hexamine nitrolysis contains a trace of "106" - identified as bisethoxymethyl derivative.

A.R.D. Exp.Rep. 505/44 Jan. '44; A.C.5605,

had indications of "106" in hexamine nitrolysis system (by CH_2O and HNO_3 analysis).

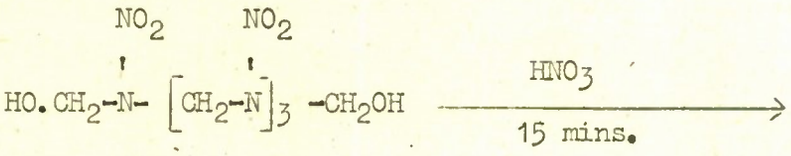
A.R.D. Exp.Rep. 591/44, May '44; A.C.6455

confirmed this by isolation of bis-methoxymethyl- and bis-ethoxymethyl- derivatives. (See pp. 80 and 81).

Para. 79

"106" (Continued)

Bristol Res.Rep.128, June '44; A.C.6477.



64% on DPT.

From DPT, Ac_2O, HNO_3

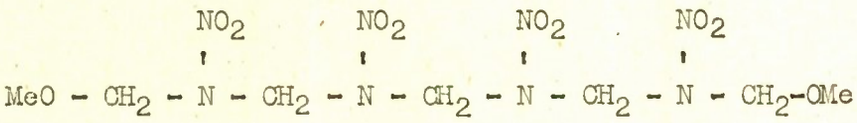
-40°

Univ. Penn., Div. 8 Int.Rep.R.R.C.8, August,'43; SR7/43/391.

(see p. 219)

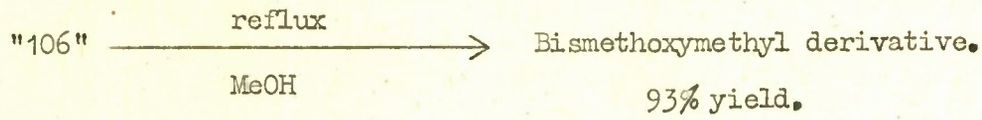
Para. 80

1:7-Bis(methoxymethyl)-1:3:5:7-tetranitro-(7-chain)



From MeOH. m.p. 182-183°.

Toronto C.E.12 Prog.Rep. 1 Nov. '42; SR7/3466.

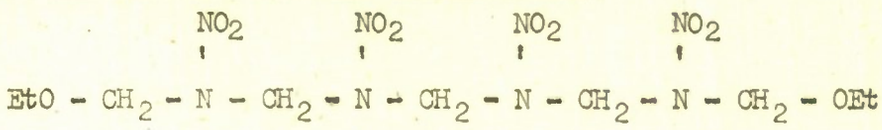


Similarly by

A.R.D., Exp.Rep.591/44, May '44; A.C.6455.

Para. 81

1:7-Bisethoxymethyl-1:3:5:7-tetranitro-(7-chain)



m.p. 166-167°.

Toronto C.E.12 Prog.Rep., 1 Nov. '42; SR7/3466.

"106" $\xrightarrow[EtOH]{\text{reflux}}$ Bisethoxymethyl derivative.

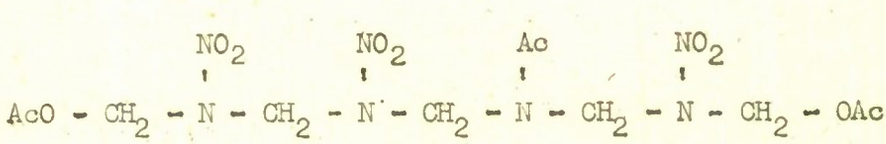
Also by

A.R.D., Exp.Rep. 591/44, May '44, A.C.6455.

Para. 82

H.16. (Univ. Penn.).

WRX. (McGill).



1:7-Bis(acetoxymethyl)-1:3:7-trinitro-5-acetyl-(7-chain).

From aq. AcMe or AcMe + EtOH. m.p. 157°.

Univ.Penn. Div.8 Int.Rep.R.R.C.1; Jan. '43; SR7/3748.

Hex. in HOAc $\xrightarrow[AcONO_2, \text{ at } 40^\circ]{\text{3 moles}}$ H.16 (11%).

Univ.Penn. Div.8 Int.Rep.R.R.C.3, March '43; SR7/4179.

H.2 (see p. 170) $\xrightarrow[(Ac_2O + HNO_3)\ \text{from 2 to 13 moles at } 4^\circ]{AcONO_2}$ H.16 (30%).

McGill X.R.4 Prog.Rep., 1 June '43; SR7/4908.

Hex. + NH_4NO_3 $\xrightarrow[HOAc + Ac_2O]{\text{large excess}}$ product called WRX.

McGill X.R.4 Prog.Rep., 1 July '43; SR7/43/298.

WRX identical with H.16.

DERIVATIVES OF lin- 2:4:6:8-tetramethylene-1:3:5:7:9-pentamine

$$\underset{1}{NH_2} - \underset{2}{CH_2} - \underset{3}{NH} - \underset{4}{CH_2} - \underset{5}{NH} - \underset{6}{CH_2} - \underset{7}{NH} - \underset{8}{CH_2} - \underset{9}{NH_2}$$

"9-chain" series.

Para. 82b

1:9-Bismethylol-1:3:7:9-tetranitro-5-methyl-(9-chain)

$$HOCH_2 - \overset{NO_2}{\underset{|}{N}} - CH_2 - \overset{NO_2}{\underset{|}{N}} - CH_2 - \overset{Me}{\underset{|}{N}} - CH_2 - \overset{NO_2}{\underset{|}{N}} - CH_2 - \overset{NO_2}{\underset{|}{N}} - CH_2OH$$

Fract. cryst. from EtOH - AcMe, m.p. 134-135°.

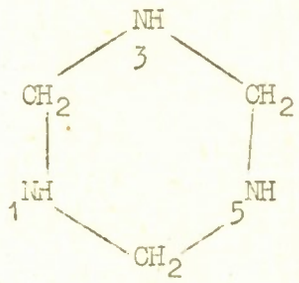
Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

$$\text{EDNA} \xrightarrow[0^\circ]{6\ CH_2O_{aq} + 2MeNH_2} \text{above 9-chain compd. + dinitro-dimethyl-(8-ring).}$$

(See p. 138a).

Separate by fract. cryst.

DERIVATIVES OF cyclo-2:4:6-TRIMETHYLENE-1:3:5-TRIAMINE

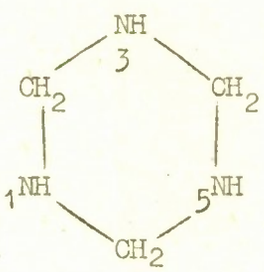


"6-Ring".

Section A: Derivatives not substituted on the C atoms.

Para. 84

Cyclo-2:4:6-Trimethylene-1:3:5-triamine

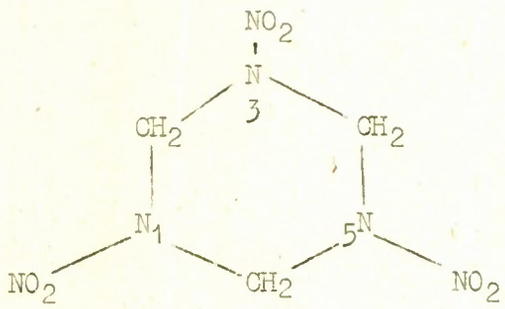


"6-ring".

Toronto workers, X.R.16 Rep., 31 Jan. '44; SR7/44/984, consider that "Henry's solution" (Henry, Bull.Acad.roy.Belg., 1902, 11, 721), consisting of an equimolecular mixture of aq. CH_2O and .880 NH_3 "dried with K_2CO_3" contains a high proportion of cyclotrimethylenetriamine (probably in equilibrium with CH_2 = NH and/or $HO.CH_2-NH_2$) but contains no hexamine.

Para. 85

RDX



1:3:5-Trinitro-(6-ring).

From AcMe m.p. 204.5-204.8°.

Henning, D.R.P. 104280 (June 1899).

See Hale, J.A.C.S., 1925, 47, 2754, for early work.

A.R.D. "Woolwich Process" or "Hex. nitrolysis".

Hexamine (or HADN, see p. 177) —HNO_3 in excess (ca 25 moles)→ RDX 40% yield.

McGill, C.E.53 Prog.Rep.1, 1 Nov. '40; SR7/33.

"Ross Reaction".

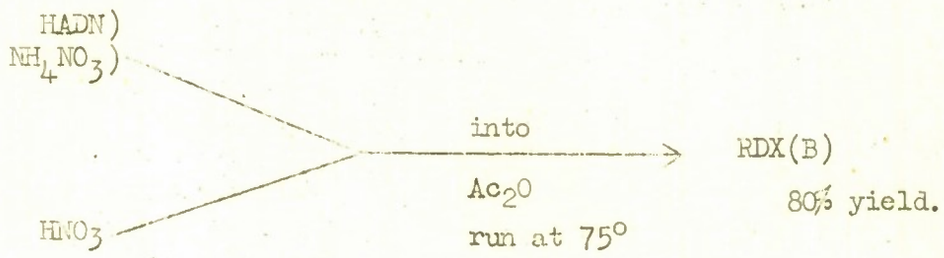
CH_2O —Ac_2O / NH_4NO_3→ RDX(B) 35 to 60% yield (yield somewhat capricious).

See McGill, C.E.53 Prog.Rep.9, 1 July '41; SR7/543, for review.
Best conditions Cornell, O.S.R.D.979 Rep. 30 July, '42; SR7/3333.

RDX (Continued)

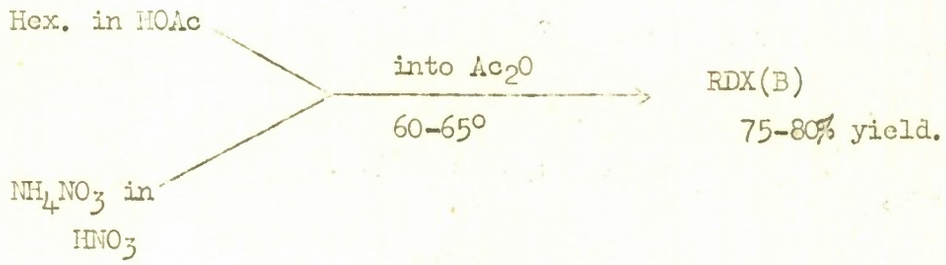
Michigan O.S.R.D.150 Rep. (to 15 Sept. '41) 8 Oct. '41; SR7/813. (1st reported at N.D.R.C. meeting May '41).

Bachmann Combination Process.

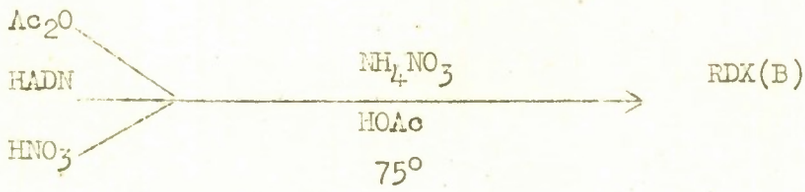


(Bachmann "C - 6 - C" procedure).

Toronto, C.E.12 Rep. 15 Aug. '41, SR7/643, added HOAc to Combination system, and C.E.12 Prog.Reps. 1 Sept. '41; SR7/689: 15 Sept. '41; SR7/749, used

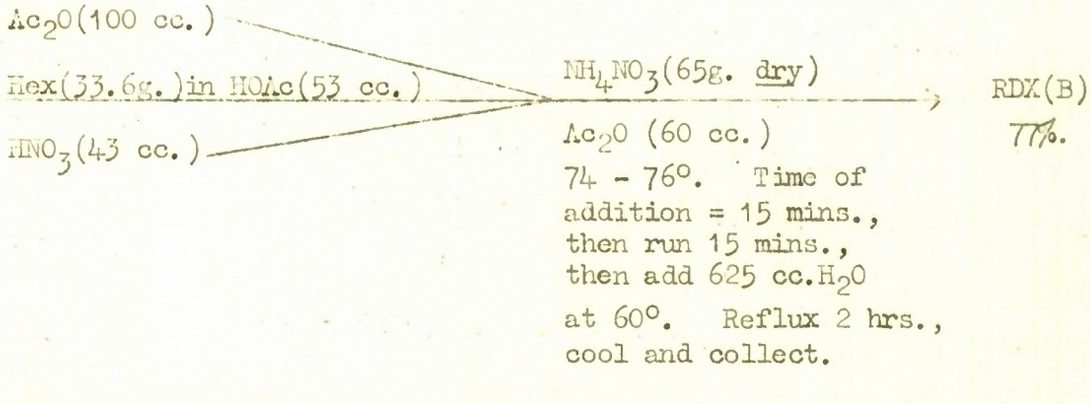


Michigan, Int.Prog.Rep. 19 Dec. '41; SR7/1330



(Bachmann's V-86 procedure).

Cornell, O.S.R.D.800 rep., up to 30 July '42; SR7/2856.



(Johnson's C.U.10 procedure).

Para. 87

RDX (Continued)

Michigan O.S.R.D. 820 Rep., 15 Aug. '42; SR7/2982.

Ac_2O(150 cc.)
Hex(33.6g.)in HOAc(56 g.)
NH_4NO_3(55g.)in HNO_3(75g.)
→ Ac_2O(30 cc.)
HOAc(30 cc.) at 75°
add 6 cc. of
(NH_4NO_3:HNO_3) first,
then rest during
13 mins., run 10 mins.;
add 600 cc. H_2O, cool
to 20° and collect.
→ RDX(B)
79%

(Bachmann's V-167 procedure).

Michigan, B.M.324, 15 Nov. '42; SR7/3339.

70% aq. HNO_3 plus Ac_2O, equiv. to the 30% H_2O, can be used for HNO_3 in Bachmann Combination RDX(B) Process, without loss of yield.

Toronto, X.R.16 Rep. 15 May '43; SR7/4549.

0.24 moles Hex
in 2.8 moles HOAc
0.61 moles NH_4NO_3
in 0.92 moles HNO_3
(NH_4NO_3:HNO_3 = 1:1.6)
→ Ac_2O
1.7 moles
68°
→ RDX(B)
80% yield.

A.R.D. investigated the preparation of RDX(B) by the process "nitration of hexamine in Ac_2O by the complex $2HNO_3.NH_4NO_3$". See Prep. RDX(B) Prog.Reps. Nos. 1 to 6 (from Oct. '41 to Dec. '42). These reports have not been circulated but a summary of the work is given in the review by Linstead "Chemistry of RDX and Related Compounds" (to Oct. '43), M.O.S. London, 31 Oct. '43; A.C.5224 (page 41). The term RSX was originally used for the crude RDX(B) obtained in this A.R.D. work.

Para. 88

RDX (Continued)

RDX prepared by "Hexamine nitrolysis" contains traces of HMX; (Toronto, X.R.16 Prog.Rep. May '43; SR7/4436: Bristol Br Rep. 23, May '43; A.C.4237: A.R.D.Exp.Rep. 256/43, Aug. '43; A.C.4629) and "106" (Toronto, X.R.16 Prog.Rep., 15 Jan. '43; SR7/3721: ARD, Exp.Reps. 505/44, Jan. '44; A.C.5605: and 591/44, May '44; A.C.6455).
"106" is destroyed by heating to 75° with aq. HNO_3 (50-70%).

RDX(B) prepared by the Bachmann Combination Process contains HMX (up to 10%; usually ca 3% by weight of RDX(B)). First found by Toronto workers, C.E.12 Prog.Reps., 1 Sept. '41; SR7/689: 15 Sept. '41; SR7/749, by fractional crystallisation of crude RDX(B) from dioxane:
BSX, Toronto C.E.12 Prog.Rep. 1 March '42; SR7/1845, and ARD (see Prep.RDX(B) Prog.Rep.4, April '42, Exp.Rep. 107/42). The BSX is destroyed by heating (75°) with aq. HNO_3 (50-70%).

Mother liquors after separation of RDX(B) contain small amounts of AcAn (see p. 76), QDX (see p. 130), TAX (see p. 98).

Toronto, C.E.12 Prog.Rep., 30 Sept. '41, SR7/840, can use phthalic anhydride for Ac_2O in Ross Reaction and still get some RDX.

Toronto, C.E.12 Prog.Reps., 30 Nov. '41; SR7/1173: 31 Dec. '41; SR7/1438.

1:3:5-Trinitroso-(6-ring) (see p. 106). $\xrightarrow[-40^\circ \text{ and warm to } 0^\circ]{HNO_3}$ RDX very pure.

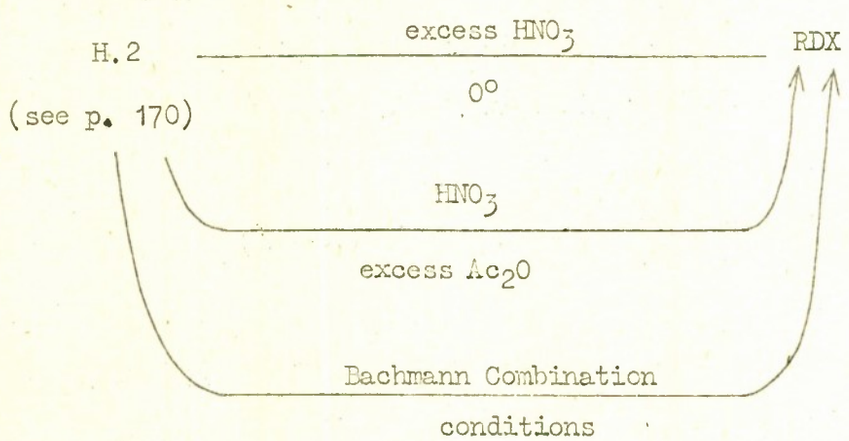
McGill, C.E.53 Prog.Rep., 1 Jan. '42; SR7/1426.

$CH_2(\overset{\oplus}{N}H_3\}\ \overset{\ominus}{N}O_3)_2 \xrightarrow[\pm\ CH_2O]{\text{heat}}$ RDX (small yield + some HMX)

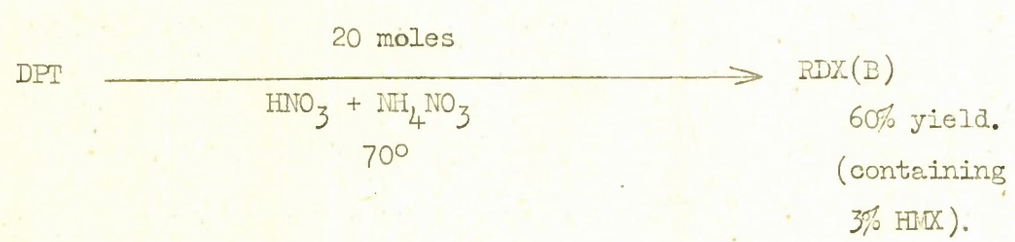
RDX (Continued)

Harvard, N.D.R.C.Rep., Oct. '42; SR7/3263.

Univ. Penn., Div.8 Int.Rep.R.R.C.3, March '43; SR7/4179.



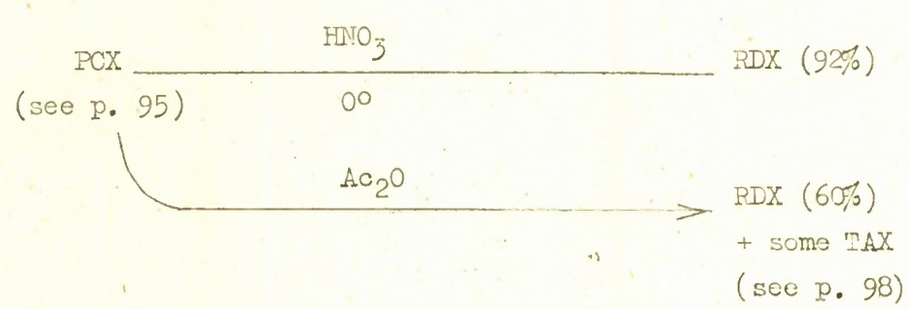
Toronto, X.R.16 Prog.Rep., 15 Jan. '43; SR7/3721.



McGill, X.R.6 Prog.Rep., April '43; SR7/4315:

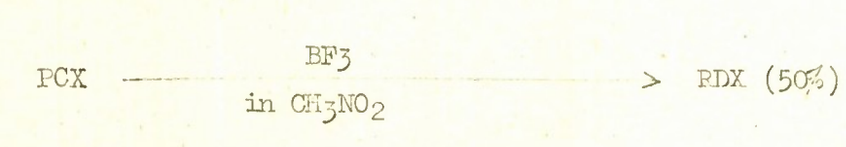
Bristol, Res.Rep.89, June '43; A.C.4417 and

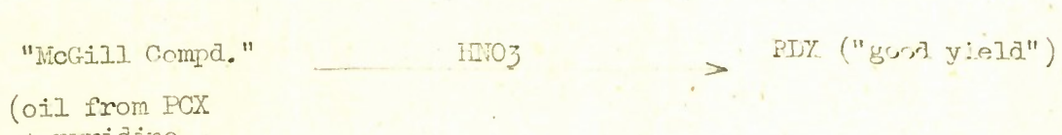
Bristol Br. Rep. 28, Oct. '43; A.C.5058



McGill, X.R.6, Canadian Exp.Res.Extram.Summary, Oct. '43;

SR7/43/848 and X.R.6.Prog.Rep., Feb. '44; SR7/44/578.





Para. 90

RDX (Continued)

Toronto, X.R.16 Reps., May '43; SR7/4549, July '43; SR7/43/303.

Bristol Br. Rep. 28, Oct. '43; A.C.5058.

TAX —(HNO_3 at 65°)→ RDX (40%).

(see p. 98)

Univ. Penn. Div.8 Int.Rep.R.R.C.6, June '43; SR7/4879:

R.R.C.8, Aug. '43; SR7/43/391

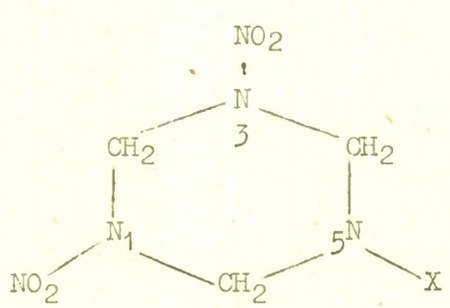
H.18 (Hex. methonitrate) 26 g. —(HNO_3, NH_4NO_3, Ac_2O . 75°. (Bachmann conditions))→ RDX (+ MSX) 18g. 8g.

H.29 (Hex.ethonitrate) —(Bachmann conditions)→ RDX (+ H.28)

McGill, X.R.4 Prog.Rep., Nov. '43; SR7/43/1057.

Checked H.18 in Bachmann ——→ RDX(B) + MSX. Sepd. by $CHCl_3$ boiling (MSX more soluble).

Bristol Br. Rep. 28, Oct. '43; A.C.5058.



X = NO or CH_2OH

(see pp. 96 & 100).

HNO_3 ——→ RDX 85%.

(McGill, X.R.6 Prog.Rep., Feb. '44; SR7/44/578, checked above for X = CH_2OH).

RDX (Continued)

Penn. State, Div.8.Int.Rep. R.R.C.11, Nov. '43; SR7/44/70.

P.S.1 (see p. 203) $\xrightarrow[HNO_3 \text{ at } 100^\circ]{NH_4NO_3}$ 21% yield RDX.

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984.

Henry solution (see p. 18) $\xrightarrow[-40^\circ \text{ (1 hr.)}\ 20^\circ \text{ (10 min.)}]{HNO_3}$ 44% yield RDX.

Bristol Res.Rep.117, March '44; A.C.6046.

H.2 $\xrightarrow[N_2O_4\ 0^\circ]{HNO_3}$ RDX (+ Nitroso-PCX).

Toronto, Canadian Exp.Res.Extram.Summary, April '44, SR7/44/1747.

$NH_4NO_3 + CH_2O + HOAc + Ac_2O \longrightarrow$ RDX(B) 5%. (+ DPT 18% + BSX & TEX in small amounts)

Bristol Res.Rep. 129, June '44; A.C.6486.

$NH_4OAc + CH_2O \longrightarrow$ clear solution $\xrightarrow[20^\circ\text{-}40^\circ]{HNO_3}$ RDX 28%

$NH_4(HCOO) + CH_2O \longrightarrow$ clear solution $\longrightarrow$ RDX 20%

NH_4NO_3 + aq. CH_2O $\xrightarrow[-40^\circ \text{ \& warm to } 20^\circ]{90\%\ HNO_3}$ RDX 6%

$(NH_4)_2CO_3$ + aq.CH_2O $\xrightarrow[-40^\circ \text{ \& warm to } 20^\circ]{90\%\ HNO_3}$ RDX 37%

Para. 92

RDX (Continued)

Dimethyl-(P.T.) picrate (2 g.) $\xrightarrow[NH_4NO_3 \ (\pm CH_2O) \text{ at } 40^\circ \text{ \& heat to } 70^\circ]{HNO_3}$ RDX 0.4 to 0.6g.

H.6 (2 g.) $\xrightarrow[NH_4NO_3 + CH_2O;\ \text{at } 40^\circ \text{ and heat to } 70^\circ]{HNO_3}$ RDX 0.4g. (m.p. 190-194°).

H.18 (2 g.) $\xrightarrow[NH_4NO_3 + CH_2O,\ 1 \text{ g.; at } 40^\circ \text{ and heat to } 70^\circ]{HNO_3}$ RDX 0.15g.

H.18 (5 g.) $\xrightarrow[NH\ NO \text{ at } 20^\circ \text{ \& heat to } 95^\circ]{HNO_3}$ RDX 3 g.

$(HNO_3:NH_4NO_3)$ + "stabiliser", m.p. 193° + CH_2O (2g.) $\xrightarrow{80^\circ}$ RDX 0.5g.

[$CH_2O + NH_4NO_3$ + ppt. + MeOH. See p. 180)]

liq. $(3CH_2O + NH_4NO_3)$ (24 g.) $\xrightarrow[NH_4NO_3, \text{ at } 20^\circ, \text{ \& run at } 95^\circ]{HNO_3}$ RDX 2 g.

Hex. + HNO_3 $\xrightarrow[\text{add } NH_4NO_3 \text{ and run at } 90^\circ \text{ for 30 mins.}]{\text{normal nitrolysis, at } 20^\circ; \text{ then}}$ RDX 51%

Hex. + HNO_3 $\xrightarrow[\text{"stabiliser, m.p. 193°", and run at } 90^\circ \text{ for 15 mins.}]{\text{normal nitrolysis at } 20^\circ; \text{ then add}}$ RDX 39%

Hex. + HNO_3 $\xrightarrow[\text{stabiliser} + NH_4NO_3 + CH_2O \text{ and run at } 90^\circ.]{\text{normal nitrolysis at } 20^\circ; \text{ then add}}$ RDX 57%

RDX (Continued)

Syrup from (1 $\overset{\oplus}{C}H_3NH_3\}\overset{\ominus}{NO_3}$. + $2CH_2O$ —(HNO_3; NH_4NO_3 at 20° & heat to 95° & add CH_2O.)→ RDX 7.5% (m.p. 190-202°).

Bristol Res. Rep. 130, June '44; A.C.6478.

CH_2O —(HNO_3; NH_4NO_3; at 90-95°.)→ RDX 25.8%.

CH_2O gas —(HNO_3; NH_4NO_3; at 120°.)→ RDX 9%.

Bristol Res.Rep. 131, June '44; A.C.6657.

Methylolamine nitrate —(Ac_2O; 60-80°)→ RDX Very small yield.

MEDNA + methylolamine nitrate —(Ac_2O - HOAc; 60-80°)→ RDX

1 g. 1.7 g. 0.5 g.

or —(HNO_3; NH_4NO_3)→

CH_2O added to (NH_4NO_3 + HNO_3) at 90° → RDX 38%.

Add MEDNA to above → RDX 47%.

A.R.D. Exp. Rep. 593/44; June '44; A.C.6456.

Hex. + HNO_3

1 pt. 10.3 pts. —(Normal nitrolysis at 20°; then add NH_4NO_3, 4.2 parts, and heat to 85° for 3 mins.)→ RDX 53.5%.

(CH_2O also added at 95°, then yield is 59.5%).

Hex. + (NH_4NO_3:$2HNO_3$)

1 pt. 50 pts. —(start at 20° and run for 30 mins. at 95°)→ RDX 67.5%.

Para. 94

RDX (Continued)

A.R.D. Exp.Rep. 594/44, June '44, A.C.6457.

$$\underset{1\text{ pt.}}{CH_2O} + \underset{48\text{ pts.}}{(NH_4NO_3:2HNO_3)} \xrightarrow[30\text{ mins.}]{95^\circ} \text{RDX } 37.7\%.$$

A.R.D. RDX Res.Panel, London, 21 June '44.

RDX obtained in yields varying from about 30 to about 60% by adding x to $(NH_4NO_3:2HNO_3)$ either at 95° or at 20° and heat to 95°.

x = CH_2O gas.

CH_2O.

$P_1 + P_2$.

Cyclonite Oxide.

BSX.

AcAn.

DPT.

(all probably acting as sources of CH_2O).

Bristol, June '44; private communication from Dr. A. Carruthers.

$$PCX \xrightarrow[\text{system}]{\text{in Hex. nitrolysis}} \underset{100\%}{RDX}$$

Toronto, X.R.16 Proj., Canadian E.R.Extram.Summary 20, May-June '44; SR7/44/2426 (following A.R.D.).

Compd. (1 part) + $HNO_3:NH_4NO_3$ (75:60 parts) at 100°.

Compound	% RDX *
Hexamine	136
DPT	117
Cyclonite Oxide	69
COX	64
TEX	64
BSX	81
AcAn	97
106	79
H.16	90

*% Calc. on basis: 1 mole. Compd. ⟶ 1 mole RDX = 100%.

Para. 94a

RDX (Continued)

RDX Committee (U.S.A. and Canada) Meeting, 26 May '44; SR7/44/2801: (Toronto, X.R.16 Proj.).

P.S.1 $\xrightarrow[\text{excess } HNO_3 \text{ at } 100^\circ \text{ for } \frac{1}{2} \text{ hour.}]{\text{excess } NH_4NO_3}$ RDX (72 per cent).

Ross Reaction $\xrightarrow[19 \text{ hrs.}]{25^\circ}$ 5.2 per cent RDX(B).
+ 1.4% TEX
+ 18% DPT
+ 18% EDX.

Toronto X.R.16 Rep., 1 Sept. '44; SR7/54/3158.

EDX $\xrightarrow[\text{at } 100^\circ]{\text{excess } (NH_4NO_3 - HNO_3)}$ RDX

(see p. 223)

Crude product, m.p. 154-162° (see p. 103a) $\xrightarrow{HNO_3}$ RDX

Michigan, N.D.R.C. Div.8 Int. Reps.; R.R.C.21, Sept. '44; SR7/44/3207.
R.R.C.22, Oct. '44; SR7/44/3502.

Latest work on the Bachmann Combination Process.

"Run A - 248"

Initial Stage. NH_4NO_3 (9 g.) + HOAc (25 cc.) in 1 litre. 5-necked flask at 75°. Run in Ac_2O (3 cc.). Cool bath to 60°. When flask contents at 70° run in [HNO_3 + NH_4NO_3 : 53% : 45%] (0.8cc.)

Reaction Stage

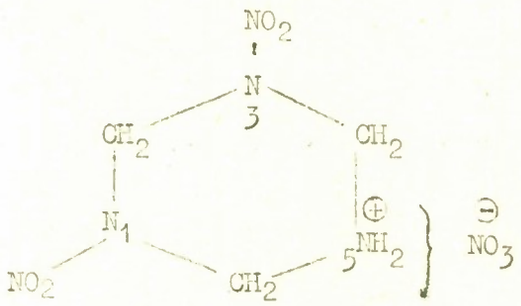
[HNO_3 + NH_4NO_3] (74.4 cc.)
Ac_2O (167 cc.)
[HOAc + Hex] (71 cc.)
(38.1% Hex)
→ Flask containing initial system. Run at 65° during addition time (25 mins.) and ageing time (30 mins.); heat to 79°: cool to 76°: add 10 cc. H_2O; temp. rise 10.8°; simmer over-night, cool and filter; air dry. RDX(B), 85.4 g. = 85.4 per cent.

Contour plots are given showing the effect on RDX(B) yield of variation of Ac_2O and HNO_3. Optimum yield, 86.7 per cent using Ac_2O (6.7 moles), HNO_3(4.4 moles) to Hex (1 mole).

Para. 95

PCX (McGill)

HCX (Davy)



1:3-Dinitro-(6-ring) - 5-nitrate.

ppt. from HNO_3 at -20° by ice + H_2O ——→ cryst. material, m.p. 98-99°.

McGill, X.R.6 Prog.Rep., April, '43; SR7/4315.

HADN —(HNO_3; -40° for 45 secs., dilute + H_2O; at low temp.)→ PCX

Bristol Res.Rep. 89, June '43; A.C.4417:

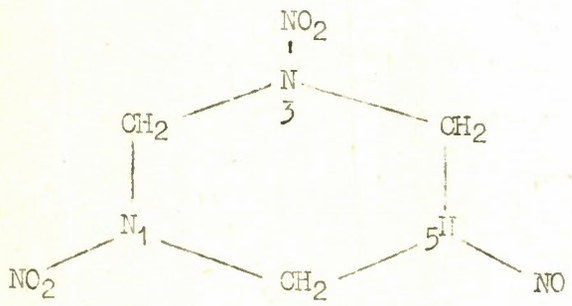
Bristol Br. Rep. 28, Oct. '43; A.C.5058, confirm preparation and determine structure.

See also McGill, X.R.6 Prog.Rep., Feb. '44; SR7/44/578.

This compound was postulated by Davy (U.S.A.-Canada-RDX Committee Meeting, Dec. '42) under the name of "HOX" as an intermediate in the Bachmann Combination RDX(B) process.

Paras. 96, 97

"NITROSO-PCX"

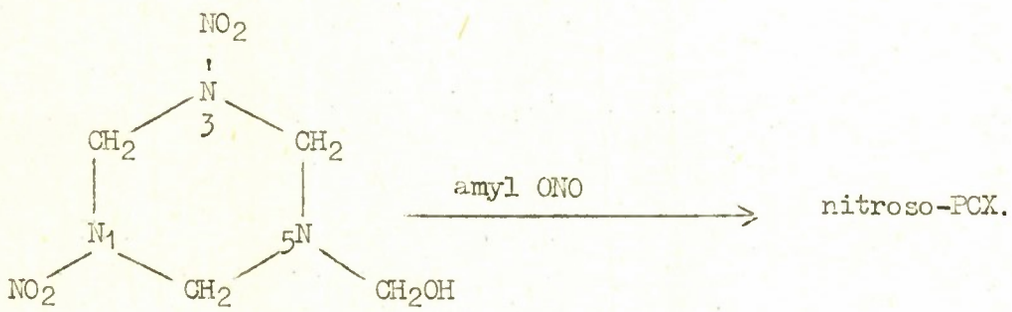


1:3-Dinitro-5-nitroso-(6-ring).

From MeOH. m.p. 168°.

Bristol Br. Rep. No. 28, Oct. '43; A.C.5058.

PCX —($NaNO_2$ plus H_2O / or amyl ONO)→ nitroso-PCX.



(see p. 100).

Bristol Res.Rep. 117, March '44; A.C.6046.

Hex. 5 g. —(HNO_3 / N_2O_3 . 0°)→ nitroso-PCX 2.7 g.

or —(HNO_3 / N_2O_4 . 0°)→ nitroso-PCX.

H.2 —(HNO_3 / N_2O_4 . 0°)→ nitroso-PCX (+ RDX)

McGill, X.R.4 Project C.E.R.Extram.Summary, 20, May-June '44; SR.7/44/2426.

PCX in HOAc, Ac_2O suspension. —(aq. $NaNO_2$ / or AcBr)→ nitroso-PCX in 20% yield.

Para. 97

"NITROSO-PCX" (Continued)

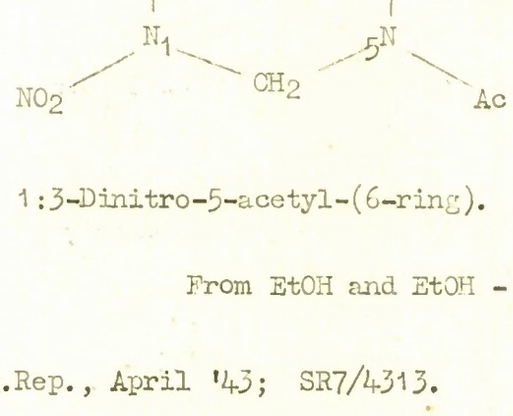
Add AcBr, aq. $NaNO_2$ or HCl to Bachmann Combination Process reaction system ⟶ yellow crystals "in good yield".

purify ↙

nitroso-PCX

Paras. 98, 99

TAX



1:3-Dinitro-5-acetyl-(6-ring).

From EtOH and EtOH - AcMe. m.p. 156°.

Toronto, X.R.16 Prog.Rep., April '43; SR7/4313.

Isolated TAX as a by-product in the Bachmann Combination RDX(B) process, using excess Ac_2O. Neutralised filtrate and separated resulting BSX, AcAn, QDX (see p. 130) and TAX by fractional crystallisation (0.3 g. TAX from 33.6 g. Hex.).

A.R.D., Prep.RDX(B) Prog.Rep. 8, Expl. Rep./173/43, May '43;

A.C.4293: and Prog.Rep.9, Exp.Rep. 239/43, July '43; A.C.4678.

Isolated TAX from mother liquor from normal Bachmann Combination RDX(B) run.

Toronto, X.R.16 Prog.Rep., May '43; SR7/4549.

Dissolve NH_2Ac (1 mole) in usual Hex.-HOAc solution (1 mole Hex.) for normal Bachmann Combination RDX(B) run. TAX isolated from product in yield 3.5%.

Toronto, X.R.16 Prog.Rep., July '43; SR7/43/303.

$$\text{PCX} \xrightarrow[\text{NaOH}]{Ac_2O} \text{TAX.}$$

(Repeated independently, Bristol Br.Rep.28, Oct. '43; A.C.5058).

Para. 99

TAX (Continued)

Bristol Br.Rep.28, Oct. '43; A.C.5058.

"Nitroso-PCX" (Dinitro-nitroso-(6-ring)) —AcCl→ TAX

"Methylol-PCX" (Dinitromethylol-(6-ring)) —Ac_2O, 80°; 4 hrs.→ TAX

Toronto, X.R.16, Canadian Exp.Res.Extram.Summary, April '44; SR7/44/1747:

X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

TAX isolated in 1.1% yield from Ross Reaction filtrates.

University Penn., RDX Committee (U.S.A. and Canada) Meeting, 26 May '44;

SR7/44/2801.

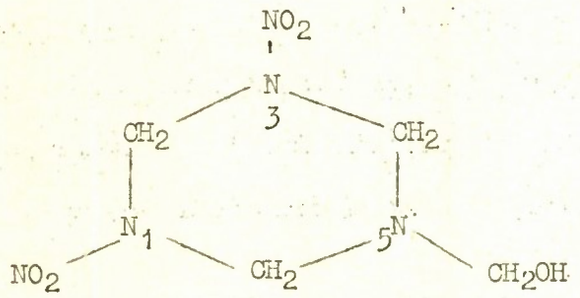
Nitroso-PCX —AcCl→ TAX.

Reaction needs a few drops of water.

Para. 100

"METHYLOL-PCX" (Bristol)

PCX(A) (McGill)



1:3-Dinitro-5-methylol-(6-ring).

From anhydrous AcMe plus ether. m.p. 136°.

Para. 100 (Continued)

"METHYLOL-PCX" (Continued)

Bristol Br. Rep. No. 28, Oct. '43; A.C.5058.

Crude PCX —(triturate with H_2O; collect insoluble residue)→ DPT plus above $-CH_2OH$ compd. plus unidentified products —(fract. crystn.)→ Above $-CH_2OH$ compd.

McGill, X.R.6 Prog.Rep., Feb. '44; SR7/44/578.

PCX + alkali ——→ PCX(A). m.p. 133°.

(For preliminary work, see McGill, X.R.6, Canadian Exp.Res.Extram.Summary, May '43, SR7/4547).

Reaction goes better in AcMe suspension.

4 g. PCX ——→ 0.8 g. PCX(A).
(after rinsing with EtOH and ether).

McGill PCX(A) is probably identical with Bristol Methylol-PCX.

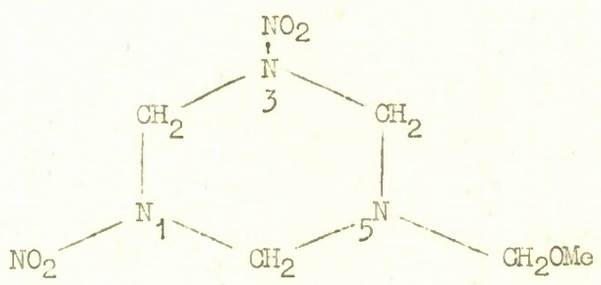
Toronto, U.S.A. and Canada RDX Committee Meeting, April '44; SR7/44/1594:

X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

PCX —(CH_2O; NaOH in AcMe)→ Methylol-PCX (6% yield) + DPT (18% yield).

Para. 101

1:3-Dinitro-5-methoxymethyl-(6-ring)



From MeOH. m.p. 128°.

Bristol, June '44; Dr. J. K. N. Jones, private communication.

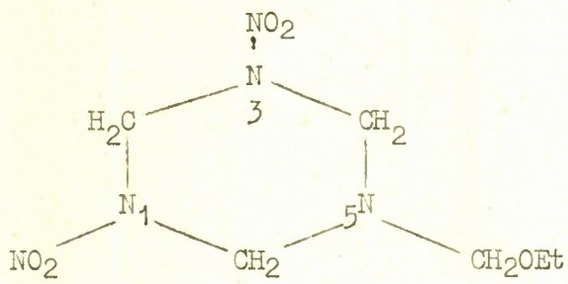
Compd. $C_4H_{10}N_6O_7$ —(MeOH; (loss of HNO_2 & methylation))→ Dinitromethoxymethyl-(6-ring).

(see p. 205)

Probably dinitro-methylol-(6-ring) nitrate.

Para. 102

1:3-Dinitro-5-ethoxymethyl-(6-ring)



From EtOH. m.p. 114°.

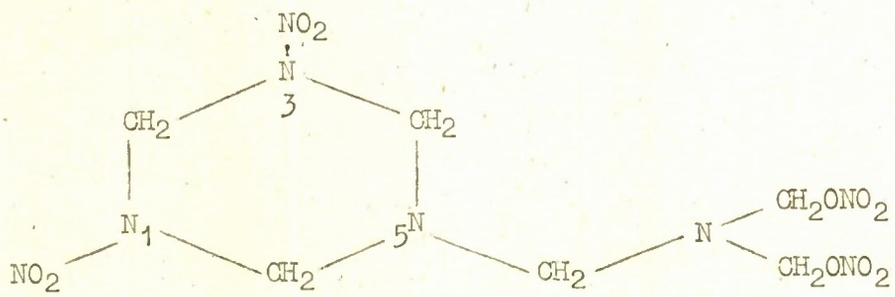
Bristol Br. Rep. 28. Oct. '43; A.C.5058.

HADN —(HNO_3; -40° then dilute with ether)→ precipitate —(cold EtOH & filter collect)→ ppt. of above $-CH_2OEt$ compound.

Para. 103

P. P.C.X. (Bristol)

P.3. (A.R.D.)



Not isolated.

1:3-Dinitro-5-bis(nitroxymethyl)aminomethyl-(6-ring).

Bristol, Br. Rep. 28, Oct. '43; A.C.5058.

Postulated as precursor of PCX.

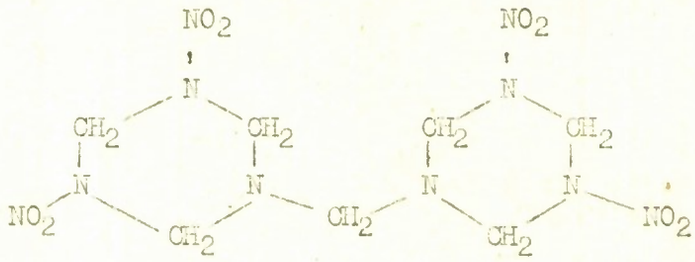
See also Bristol Res.Rep.120, April '44; A.C.6302:

A.R.D. Exp.Rep. 591/44, May '44; A.C.6455.

See Toronto X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

Para. 103a

Methylene bis (1:3-dinitro-(6-ring)-5-)



Not purified yet.

Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

MEDNA + 3 CH_2O_{aq} + 1 NH (10% aq.) ⟶ crude product

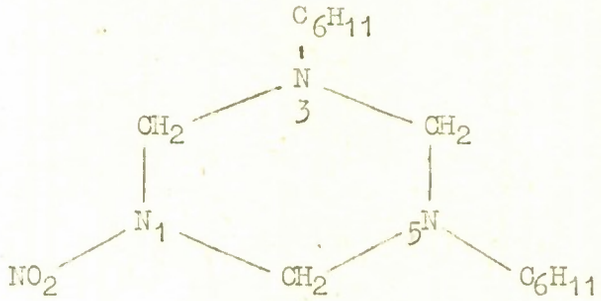
m.p. 154-162° (shrinkage at 79°) probably containing above compd.

EtOH
EtOAc
AcMe
"purif."

DPT + amorphous insoluble compd., m.p. 141°

Para. 104

1-Nitro-3:5-dicyclohexyl-(6-ring)



Cryst. from AcMe(25° - 0°) m.p. 99°.

Toronto, X.R.16 Rep. 31 Jan. '44; SR7/44/984.

NH_2NO_2 in aq. CH_2O + $C_6H_{11}NH_2$ ⟶ 1-Nitro-3:5-dicyclohexyl-6-ring.

Hexamine nitrolysis system: collect ppt. RDX:

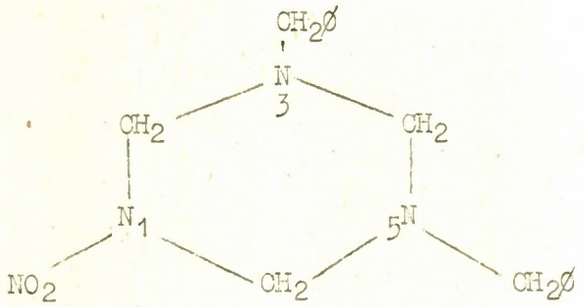
(Hex:HNO_3 = 1:4.5 by wt.)

adjust filtrate to pH 2: ether extract: ext. into H_2O;

neutralise to pH 6.5 with $C_6H_{11}NH_2$ ⟶ 1-Nitro-3:5-dicyclohexyl-6-ring.

Para. 105

1-Nitro-3:5-dibenzyl-(6-ring)



Decomp. in hot solvents: ppt. from cold AcMe by H_2O (see below).

m.p. 109°.

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984.

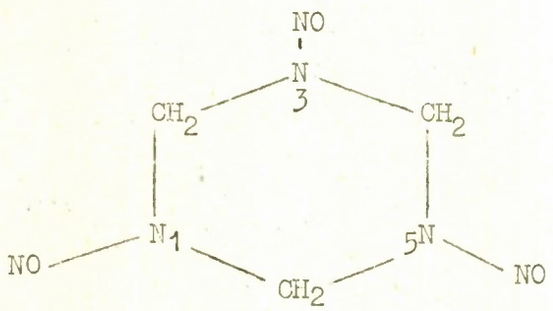
NH_2NO_2 in soln. in CH_2.aq $\emptyset CH_2.NH_2$ ⟶ 1-Nitro-3:5-dibenzyl-6-ring. (+ 1:5-Dinitro-3:7-dibenzyl- 8-ring).

(see p. 139.)

Mixt. separated by dissolving in min. AcMe at 25°; cool to 0°. 8-ring compd. separates. 6-Ring compd. from filtrate by 1:1 H_2O dilution.

Para. 106

1:3:5-Trinitroso-(6-ring)



(From EtOH or AcMe by H_2O addition). m.p. 105-106°.

Griess and Harrow. Ber., 1888, 21, 2737.

Mayor. Ber., 1888, 21, 2883.

Duden and Scharff, Annalen, 1895, 288, 218 et seq.

Hex. in very dilute HCl $\xrightarrow{NaNO_2}$ trinitroso-(6-ring)

Michigan, Div.8 Int.Rep.R.R.C.13: Dec. '43-Jan. '44; SR7/44/915.

HNO_2 on Hex. $\xrightarrow{pH = 1}$ trinitroso-6-ring.

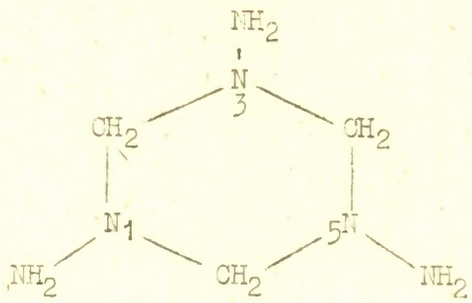
Knudsen, Ber., 1914, 47, 2700.

$CH_2(\overset{\oplus}{N}H_3\ \overset{\ominus}{C}l)_2 \xrightarrow{NaNO_2}$ trinitroso-6-ring.

In preliminary work in Bristol in 1939, attempts to repeat this conversion failed.

Para. 107

1:3:5-Triamino-(6-ring)



Not isolated.

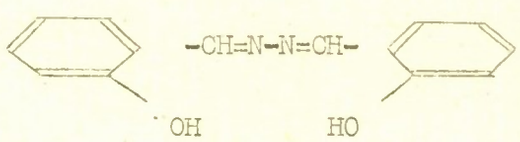
Duden and Scharff, Annalen, 1895, 288, 218.

Trinitroso-(6-ring) $\xrightarrow[\text{cold water}]{\text{Na/Hg}}$ triamino-(6-ring),

isolated as tris(-o-hydroxybenzylidene)- derivative, m.p. 139-140° (from $CHCl_3$ - ether).

Bristol, M.O.S. Paper, Dec. '39; A.C.14:

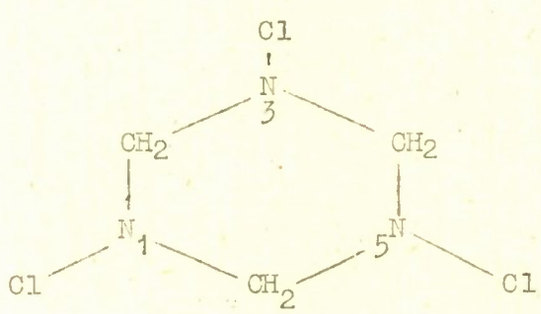
(a) repeated this Na/Hg reduction and (b) reduced RDX similarly. The only product isolated was the



o:ó -Dihydroxybenzalazine, from $CHCl_3$, m.p. 162°, of Curtius and Lublin, Ber., 1900, 33, 2463.

Para. 108

1:3:5-Trichloro-(6-ring)



m.p. decomp. 78°.

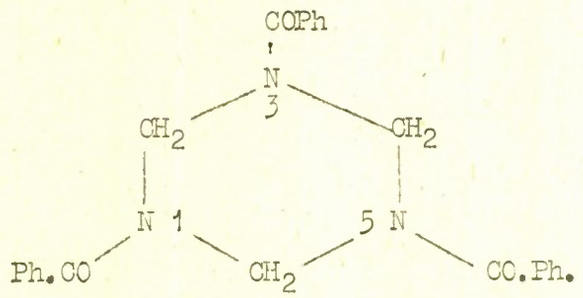
Delépine: Bull.soc.Chim., 1911 (4), 9, 1025.

Dichloro-(P.T.) in HOAc $\xrightarrow[\text{water}]{\text{dilute with}}$ Trichloro- (6-ring).

(See p. 149).

Para. 109

1:3:5-Tribenzoyl-(6-ring)



From $Br.CH_2CH_2Br$, or $CHCl_3$

by ppt. + ether) m.p. 220-221°.

Duden and Scharff, Annalen, 1895, 288, 248.

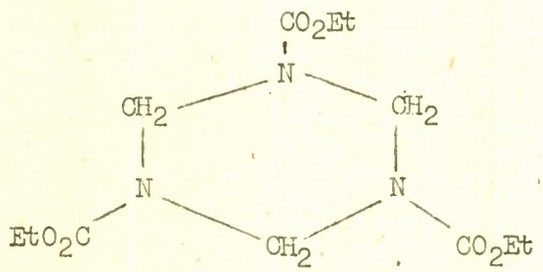
Hex. $\xrightarrow[Ph.COCl]{NaOH}$ 1:3:5-tribenzoyl-6-ring.
(soluble in $BrCH_2CH_2Br$)
+
1:3:5-tribenzoyl(5-chain)
(insoluble in $BrCH_2CH_2Br$;
see p. 71).

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984.

Henry solution $\xrightarrow{PhCOCl}$ tribenzoyl-(6-ring)
(See p. 18) (13% yield).

Para. 110

1:3:5-Tricarbethoxy-(6-ring)



m.p. 102°.

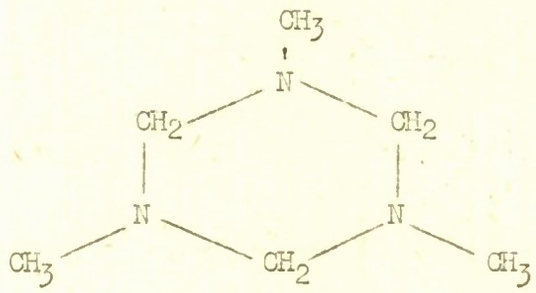
Bischoff and Reinfeld, Ber., 1903, 36, 39.
Conrad and Hock, Ber., 1903, 36, 2206.

NH_2CO_2Et $\xrightarrow[HCl;\ 100°\ in\ sealed\ tube]{aq.\ CH_2O}$ tricarbethoxy-(6-ring).

Originally reported as $(CH_2\text{-}N\text{-}CO_2Et)_n$, with n = 2. n = 3 much more likely and the compound actually is as above; private communication from Professor R. P. Linstead, F.R.S.

Para. 111

1:3:5-Trimethyl-(6-ring)



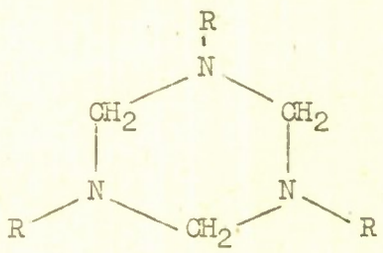
b.p./760 mm. 166°.

Henry, Bull Acad.roy.Belg., 1893, [3], 26, 200; ibid, 1895, [3], 28, 359. Cambier and Brochet, Comptes rendus, 1895, 120, 450; Bull.soc.chim., 1895, [3], 13, 392.

$$33\%\ \text{aq. } CH_3NH_2 \xrightarrow[\text{cold and add KOH}]{\text{aq. } CH_2O} \text{Trimethyl-(6-ring).}$$

Gives a picrate m.p. 127° (Duden and Scharff, Ber., 1895, 28, 936).

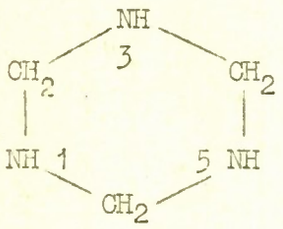
For other derivatives of the general type,



see Beilsteins Handbuch, 26, 1. System No. 3194-3196.

For R = Ø see Miller and Wagner, J.A.C.S., 1932, 54, 3698.

Para. 112 DERIVATIVES OF cyclo-2:4:6-TRIMETHYLENE-1:3:5-TRIAMINE

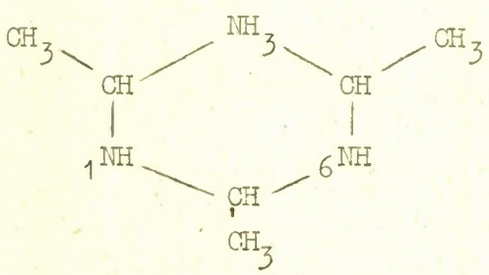


"6-Ring".

Section (B). Derivatives substituted on the C atoms.

Para. 113

2:4:6-Trimethyl-cyclo-2:4:6-trimethylene-1:3:5-triamine

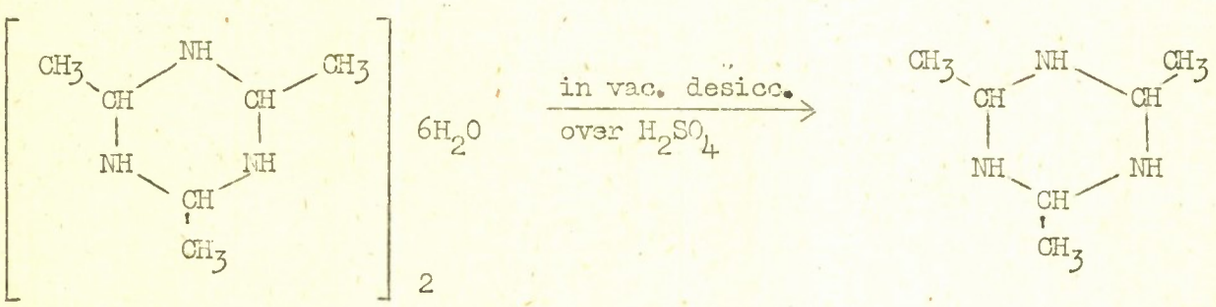


2:4:6-Trimethyl-(6-ring)

From $CHCl_3$. m.p. 85°.

Delépine, Comptes rendus, 1897, 125, 952; ibid, 1899, 128, 105.

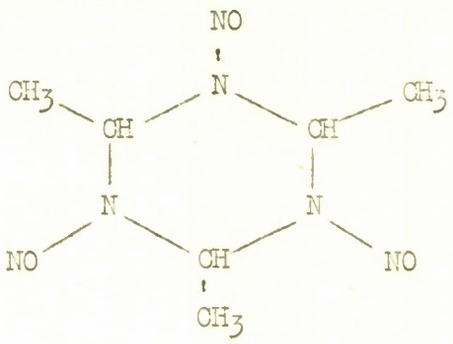
"Aldehyde Ammonia".



(See Moerman, Z.Krist., 1938, 98, 447, for structure of "aldehyde ammonia").

Para. 114

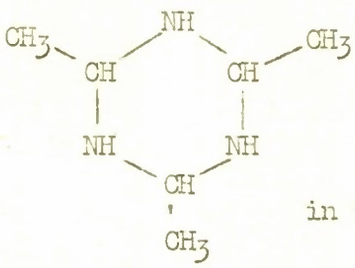
1:3:5-Trinitroso-2:4:6-trimethyl-(6-ring)



m.p. 161°

From EtOH, C_6H_6 or $CHCl_3$.

Delépine, Comptes rendus, 1907, 144, 853.



5 g.

N_2O_3 at -23° in $CHCl_3$ →

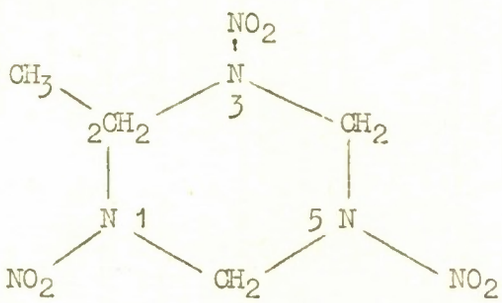
in $CHCl_3$

1:3:5-Trinitroso-2:4:6-Trimethyl-6-Ring.

0.3 g.

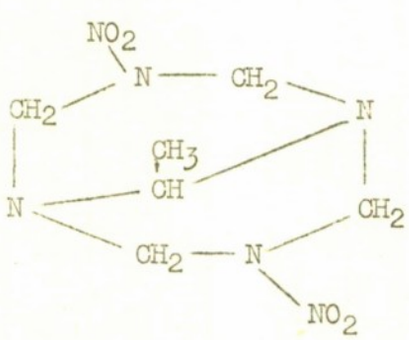
Para. 115

1:3:5-Trinitro-2-methyl-(6-ring)



m.p. 175-185°.

Toronto workers (U.S.A. - Canada RDX Committee Meeting, April '44; SR7/44/1594) suggest this may be the structure of the unstablo by-product of the roaction,



HNO_3 →

HMX

+

unstable compound

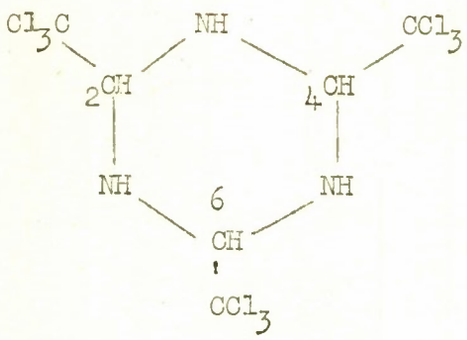
m.p. 175-185°.

(See p. 147)

See Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

Para. 116

2:4:6-Tris(trichloromethyl)-(6-ring)



From $CHCl_3$ or NH_2CHO

α stereoisomer, m.p. 105-106°.

β stereoisomer, m.p. 150-155°.

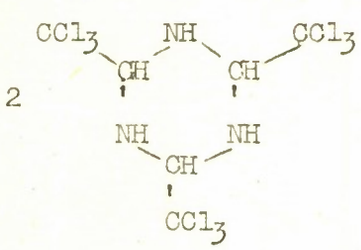
Meyer-Jacobson, Lehrbuch, I. 2, 873.

Delépine, Bull.Soc.chim., 1896, [3], 19, 171.

Orndorff and White, Amer.Chem.J., 1894, 16, 67.

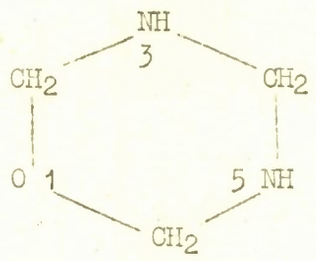
Chloral-Ammonia $\xrightarrow[\text{in } CHCl_3 \text{ or } NH_2CHO]{100^\circ}$ tris(trichloromethyl)-(6-ring).

(probably



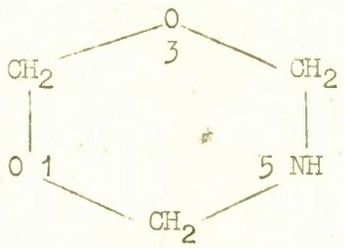
$6H_2O$)

Para. 117 DERIVATIVES OF cyclo-1-OXO-2:4:6-TRIMETHYLENE-3:5-DIAMINE



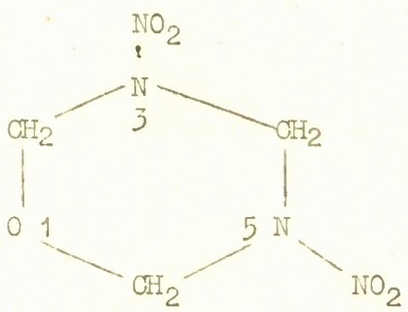
and

Cyclo-1:3-DIOXO-2:4:6-TRIMETHYLENE-5-AMINE,



Paras. 118, 119

"Cyclonite Oxide"



3:5-Dinitrocyclo-1-oxo-2:4:6-trimethylene-3:5-diamine.

From H_2O, MeOH, $CHCl_3$ or C_6H_6, m.p. 97-99°.

A.R.D. RDX Rep. 2.

Hex. nitrolysis + fume off; mother liquor evaporated to small bulk ⟶ "Cyclonite Oxide" in very small yield.

Para. 118 (Continued)

"Cyclonite Oxide" (Continued)

Toronto; C.E.12 Prog.Rep., Jan. '41; SR7/72: C.E.12 Prog.Rep., 30 Nov. '41; SR7/1173.

Isolated cyclonite oxide from hexamine recovered from Toronto modification of ARD process. (CH_2O recovery as hexamine). This hexamine contains 5% "cyclonite oxide", separated by flotation with $CHCl_3$.

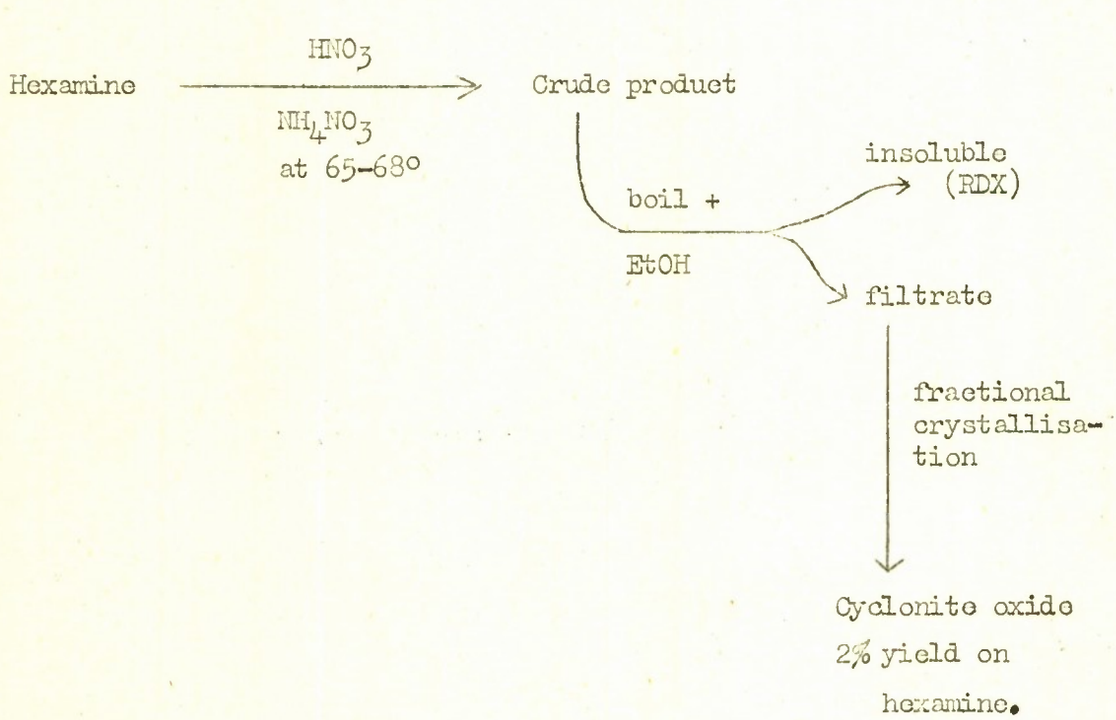
ARD, Prep. RDX(B) Prog.Rep.5, Exp.Rep.28/4/42, April '42,

isolated cyclonite oxide from mother liquors from Combination Process using "slurry technique" (i.e. add slurry of (Hex. + NH_4NO_3: $2HNO_3$) to Ac_2O). Not found in mother liquors from Combination Process using "Liquid Feed Technique" (i.e. (Hex. in HOAc) + (NH_4NO_3: $2HNO_3$) + (Ac_2O)).

See also ARD, Prep.RDX(B) Prog.Rep. 9, Exp.Rep.293/43, July '43, A.C.4628.

Para. 119

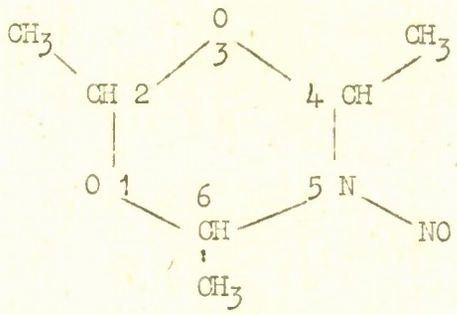
Toronto, X.R.16 Prog. Rep., 15 Jan. '43; SR7/3721.



See Cal. Tech., Div. 8 Int.Rep.R.R.C.21, Aug.-Sept. '44; SR7/44/3207; for chromatographic purification of crude cyclonite oxide.

Para. 120

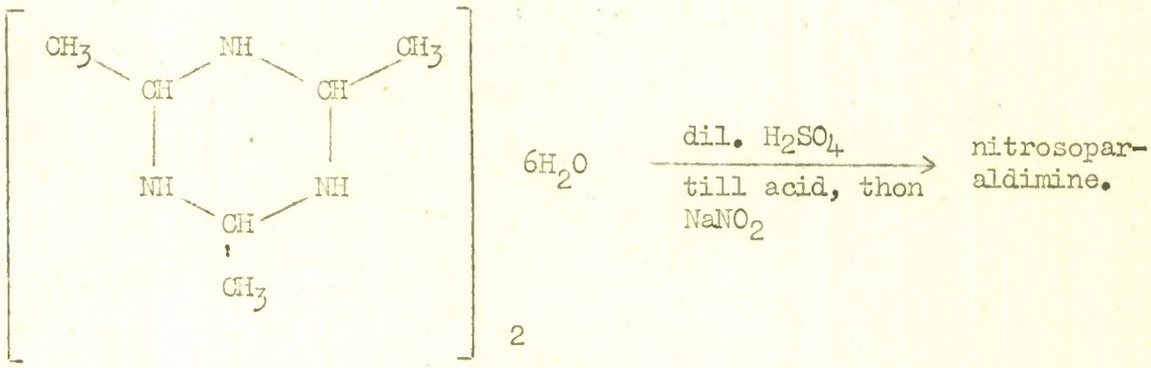
Nitrosoparaldimine



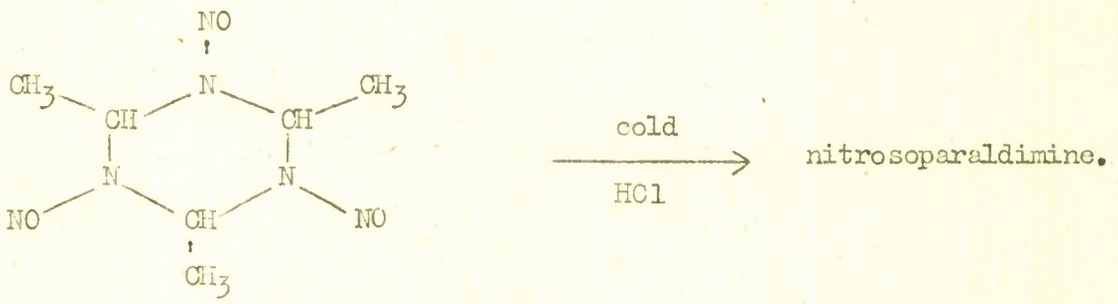
5-Nitroso-2:4:6-trimethylcyclo-1:3-dioxo-2:4:6-trimethylene-5-amine.

Yellow oil, b.p. 95°/35 mm.

Curtius and Jay, Ber., 1890, 23, 744.

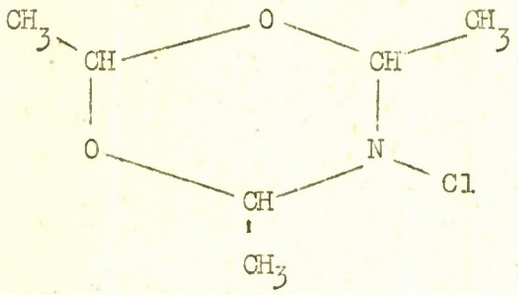


Delépine, Comptes rendus, 1907, 144, 853.



Para. 121

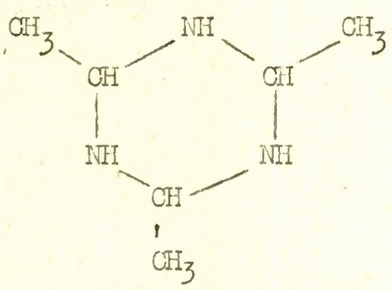
5-Chloro-2:4:6-trimethylcyclo-1:3-dioxo-2:4:6-trimethylene-5-amine



Very unstable.

Deflagrates on drying.

Delépine, Comptes rendus, 1899, 128, 105.



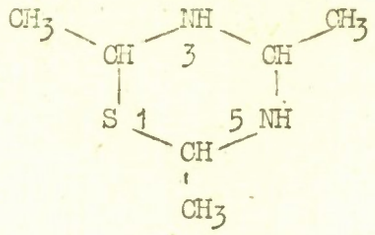
in HOAc

$\xrightarrow[H_2O]{NaOCl}$

above N - Cl compound.

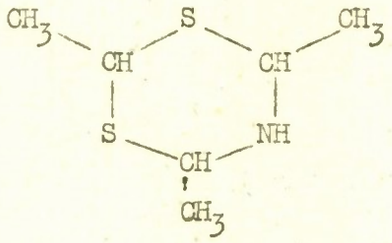
Para. 122

2:4:6-Trimethyl-cyclo-1-thio-2:4:6-trimethylene-3:5-diamine,



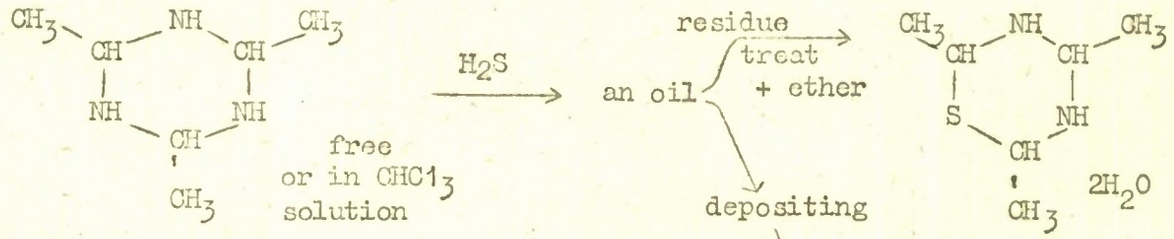
(m.p. of hydrate, + $2H_2O$, 70°).

and 2:4:6-Trimethyl-cyclo-1:3-dithio-2:4:6-trimethylene-5-amine (thialdine)

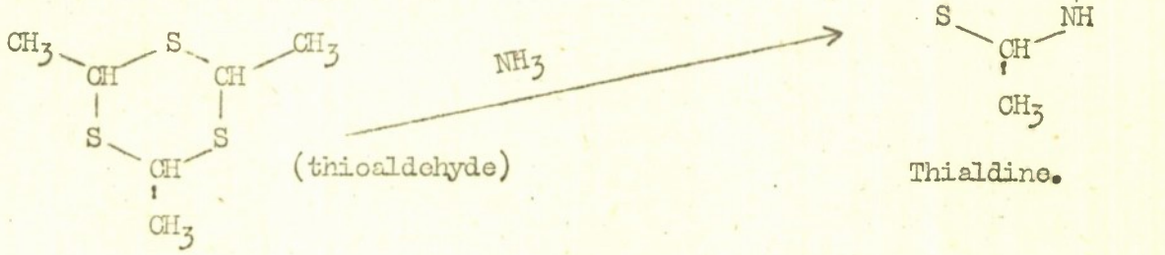


are known.

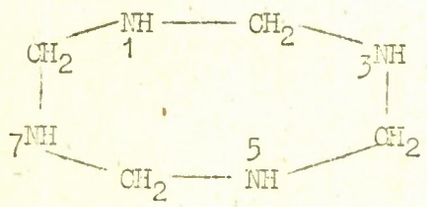
Delépine, Comptes rendus, 1899, 128, 105.



Markwald, Ber., 1896, 19, 1827.



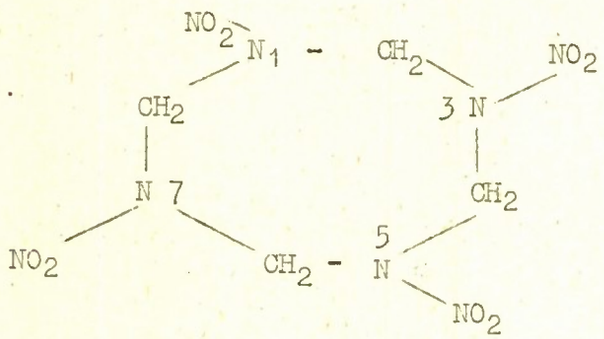
Para. 123. DERIVATIVES OF Cyclo -2:4:6:8-TETRAMETHYLENE-1:3:5:7-TETRAMINE



"8-Ring"

Para. 124

HMX



1:3:5:7-Tetranitro - (8-ring).

From AcMe, HOAc, dil. HNO_3, CH_3NO_2; m.p. 281-282°.

Toronto, C.E.12 Prog. Rep., Jan. '41; SR7/72.

DPT $\xrightarrow[\text{at } 20°]{HNO_3}$ HMX (34%).

Toronto, C.E.12 Prog. Rep., Nov. '41; SR7/1172.

DPT in Ac_2O $\xrightarrow[HNO_3 \text{ at } 65\text{-}70°]{NH_4NO_3}$ HMX (up to 65%).

Toronto, C.E.12 Prog.Rep., Aug. '41; SR7/643.

Hex. + NH_4NO_3 $\xrightarrow[Ac_2O]{HNO_3}$ Small yield HMX. No RDX.

Toronto, C.E.12 Prog. Rep., Aug. '41; SR7/643:
C.E.12 Prog. Rep., Sept. '41; SR7/689.

Michigan, N.D.R.C.Prog.Rep., Oct. '41; SR7/874.
HMX is present in RDX(B) (up to 10%, usually about 3%).
Separated by (a) difficult fractional crystallisation;
(b) fractional hydrolysis in alkali (RDX decomposed, HMX stable). See O.S.R.D. Rep. 1711, August '43, SR7/43/450, for a review of the methods of analysing HMX-RDX mixtures.

Para. 124 (Continued)

HMX (Continued)

Toronto, C.E.12 Prog.Rep., Sept. '41; SR7/689.
Ross reaction RDX contains some HMX.

Para. 125

Michigan Div.8 Int.Reps., R.R.C.3, March '43; SR7/4179.
Int.Reps., R.R.C.4, April '43; SR7/4180.
Int.Reps., R.R.C.6, June '43; SR7/4879.
Int.Reps., R.R.C.7, July '43; SR7/43/197.
Int.Reps., R.R.C.9, Sept. '43; SR7/43/924.

Modifications of Bachmann Combination RDX(B) process to give product containing high percentage of HMX. For example (from above reps. R.R.C.3 and 4),

Process (1)

1st Stage:

Hex. (33.6 g.) in HOAc(55 g.)
Ac_2O(150 cc.) + HOAc(100 cc.)
33 cc. of a solution of
(NH_4NO_3(75 g.) in HNO_3(102 g.)

→ Ac_2O(50 cc.)
HOAc(15 cc.)
at 45° during
4-5 mins.;
age at 45°
for 13 mins.

2nd Stage:

Then heat fast to 65° and add remaining 50 cc. of (NH_4NO_3(75 g.) in HNO_3(102 g.)) fast, cooling to keep at 65-70°.

Cool, add 500 cc. H_2O: simmer 4-5 hrs. Destroy RDX by boiling with pH 9 borax buffer.

Yield, 30-40% pure HMX.

(Crude product usually contains 50-60% HMX).

Process (2) (Above Ref. R.R.C.6).

1st Stage:

Hex. (336 g.) in HOAc(550 g.)
Ac2O (1500 cc.)
350 cc. of a solution of
(NH_4NO_3(550 g.) in HNO_3(750 cc.))

→ Ac_2O (100 cc.)
HOAc(1000 cc.)
in 12-litre
flask at 45°.
Add during 25 mins.
and age for 15 mins.

2nd Stage:

500 cc. of above
NH_4NO_3 - HNO_3 solution
Ac2O (1000 cc.)

→ above reaction system
at 45°. 25 mins. for
addition; age 45 mins.

Para. 125 (Continued)
HMX (Continued)

Pour into 22-litre flask containing 6 litres of water and simmer overnight. Cool, collect, wash and dry at 65° overnight. Product, 511 g., contains 85% HMX (61% overall yield of HMX on hexamine).

A.R.D. Prep. RDX(B) Prog.Reps. 3, Exp.Rep. 4490/41; and 4, Exp. Rep. 107/42, Jan. '42.

Hexamine in HOAc $\xrightarrow[\text{at } 65°\text{-}70°]{NH_4NO_3 . 2HNO_3}$ HMX 14%.

Para. 125a

Toronto, X.R.16 Rep., May '43; SR7/4436.

Bristol, Br. Rep. 23, May '43; A.C.4237.

ARD, Exp.Rep. 256/43, Aug. '43; A.C.4629.

RDX from Hexamine nitrolysis contains traces of HMX. HMX isolated from mother liquors of the hexamine nitrolysis process (HMX:RDX in process = 1:3000).

(ARD; Exp.Rep. 183/43, May '43; A.C.4231).

McGill, C.E.53, Prog.Rep., 1 Jan. '42; SR7/1436.

$CH_2(NH_2NO_3)_2 \xrightarrow[\pm\ CH_2O]{\text{heat}}$ HMX (little) + RDX.

Harvard N.D.R.C.Rep., Oct. '42; SR7/3263.

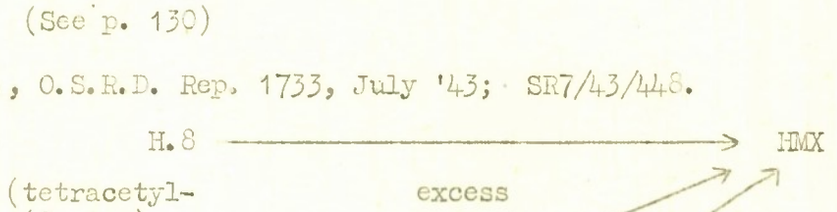
H.6 (diacetyl(PT) see p. 151) $\xrightarrow[HNO_3\ Ac_2O]{NH_4NO_3}$ HMX in poor yield.

Michigan, Div.8 Int.Rep. R.R.C. 1, Jan. '43, SR7/3748.

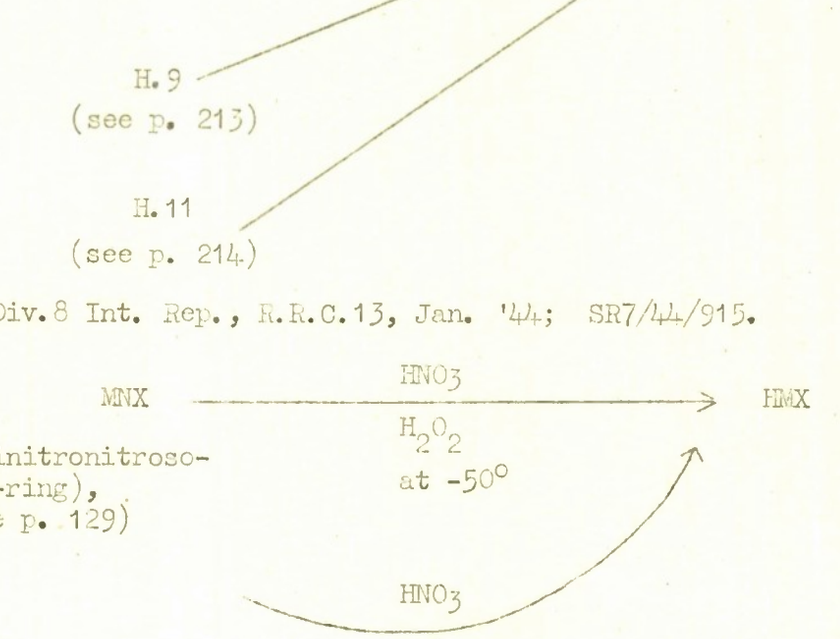
PHX (Trinitroacetoxy methyl-(8-ring), see p. 132). $\xrightarrow[HNO_3]{NH_4NO_3}$ HMX in good yield

HMX (Continued)

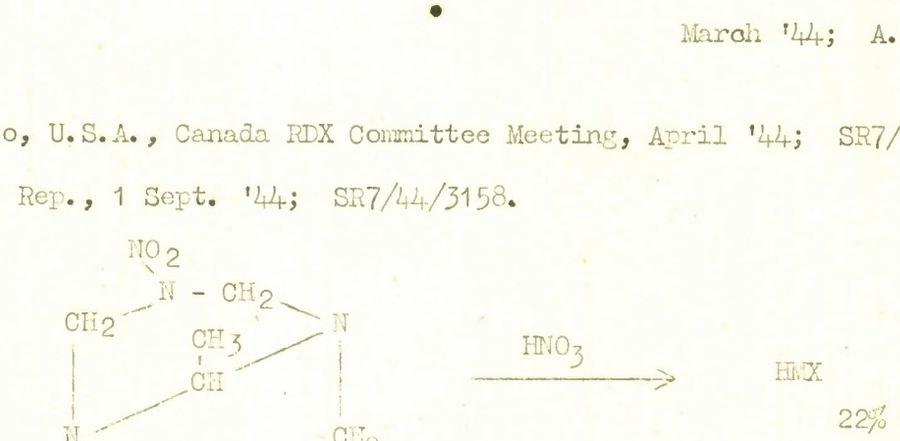
Toronto X.R.16. Prog.Rep. 15 April '43; SR7/4313.
X.R.16. Prog.Rep. July '43; SR7/43/303.



Univ. Penn., O.S.R.D. Rep. 1733, July '43; SR7/43/448.

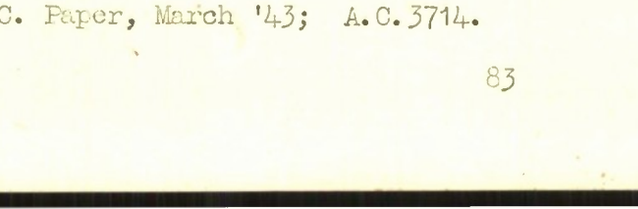


Michigan, Div.8 Int. Rep., R.R.C.13, Jan. '44; SR7/44/915.



Bristol Res.Rep.117; March '44; A.C.6046.

Toronto, U.S.A., Canada RDX Committee Meeting, April '44; SR7/44/1594;
X.R.16 Rep., 1 Sept. '44; SR7/44/3158.



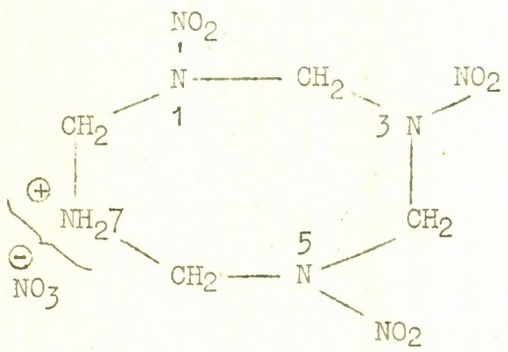
22% yield
+ unstable compound which may be 1:3:5-trinitro-2-methyl-(6-ring).

(see p. 147)

For the complicated polymorphism of HMX see Cornell, O.S.R.D., Rep. 1227: Feb. '43; SR7/3858: O.S.R.D. Rep. 3014, Aug. '44; SR7/44/2863.
ARD. S.A.C. Paper, March '43; A.C.3714.

Para. 128

1:3:5-Trinitro-(8-ring)-7-nitrate



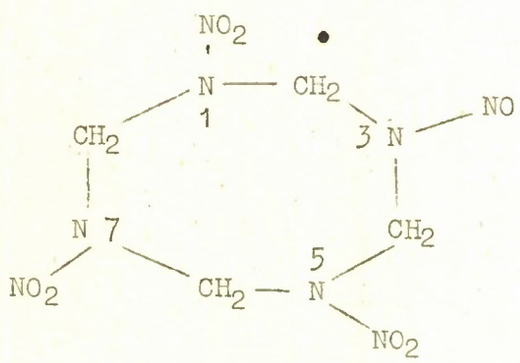
Bristol Res. Rep. 128, June '44; A.C.6477.

DPT —(HNO_3, -40°, and drown out)→ small yield of material, probably containing trinitro-(8-ring)-nitrate.

Para. 129

MNX (Michigan)

Nitroso-HMX (Bristol)



1:5:7-Trinitro-3-nitroso-8-ring.

From AcMe + EtOH. m.p. 236° (up to 243°).

Para. 129 (Continued)

MNX (Continued)

Michigan, Div. 8 Int.Rep. R.R.C.13, Jan. '44; SR7/44/915.

PHX —(NOCl, Ac_2O, 0°)→ MNX

(trinitro-acetoxymethyl-(8-ring), see p. 132)

Bristol Res. Rep. 117, March '44; A.C.6046.

DPT —(HNO_3, N_2O_3, 0°)→ MNX

2.5 g. 1.1 g.

Bristol Res. Rep. 128, June '44; A.C.6477.

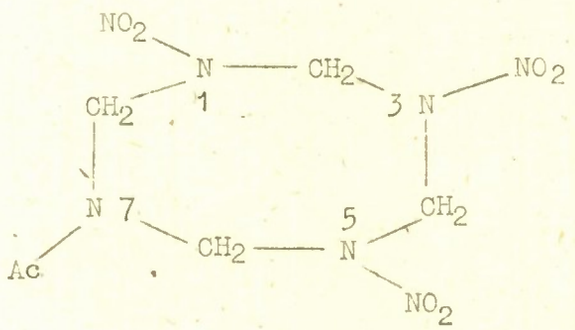
DPT —(HNO_3, −40°, drown)→ [trinitro-(8-ring) nitrate in small yield, not isolated] —($NaNO_2$, aq.)→ MNX

DPT —(HNO_3 at −40° and drown with aq. $NaNO_2$)→ MNX in 60% yield.

Paras. 130, 131

QDX (Toronto)

SEX (Penn. State).



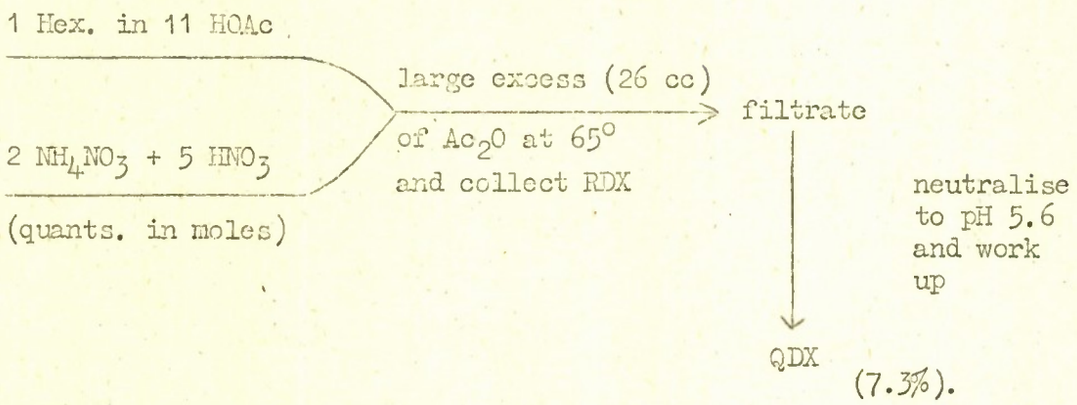
1:3:5-Trinitro-7-acetyl-(8-ring).

From AcMe and CH_3NO_2. m.p. 224-225°.

Penn. State, N.D.R.C., Prog.Reps., Sept. '42; SR7/3046:
Dec. '42; SR7/3673.

Filtrate from RDX(B), Bachmann Combination run, treat with NH_3 to pH 2 and work up by fraction crystallisation from AcMe → SEX (in small amount).

Para. 130 (Continued)
QDX (Continued)
Toronto, X.R.16 Prog.Rep., April '43; SR7/4313.



ARD Prep.RDX(B) Prog.Rep.8, Exp.Rep.173/43, May '43, A.C.4293 and Prog.Rep.9, Exp.Rep.239/43, July '43, A.C.4628, isolated and identified QDX from RDX(B), Bachmann Combination run, by dilution, neutralisation and fractional precipitation and crystallisation.

Para. 131

Toronto, X.R.16 Prog.Rep., May '43: SR7/4549.

Add 1 mole NH_2Ac per mole Hexamine to Hex - HOAc solution and do normal Bachmann Combination run: crude solid product contains RDX, HMX, QDX and TAX. QDX isolated in yield 8%.

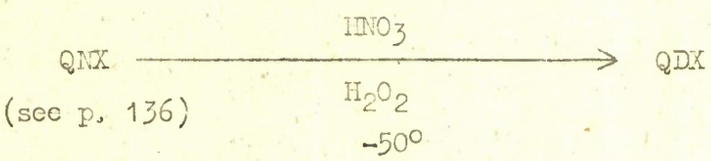
Penn. State. Div.8 Int.Rep., R.R.C.2, Feb. '43; SR7/3867; and
Cornell O.S.R.D.Rep.1227, Feb. '43; SR7/3858,

show by mixed m.p. and crystallography that QDX is identical with SEX.

Torohto X.R.16 Prog.Rep., July '43; SR7/43/303.

ARD, Prep.RDX(B) Prog.Rep.9, Exp.Rep.239/43, July 43; A.C.4628 showed constitution of QDX.

Michigan, Div.8 Int.Rep. R.R.C13, Jan. '44; SR7/44/915.

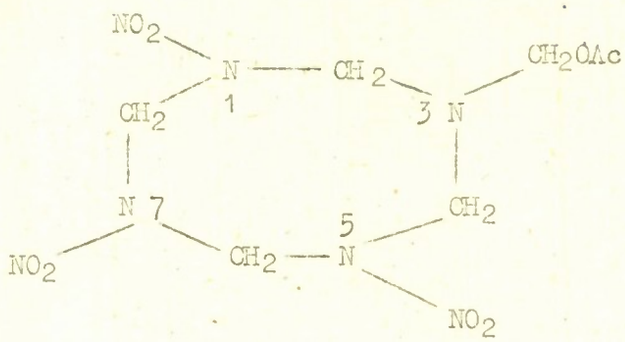


Toronto, X.R.16 Rep. 1 Sept. '44; SR7/44/3158.

Ross Reaction filtrates ⟶ QDX (2.8%).

Para. 132

PHX



1:5:7-Trinitro-3-acetoxymethyl-(8-ring).

From reaction mixture (slowly decomposed by organic solvents). m.p. 156-157°.

Michigan, N.D.R.C., Prog.Rep. B.M.372, Dec. '42; SR7/3676:

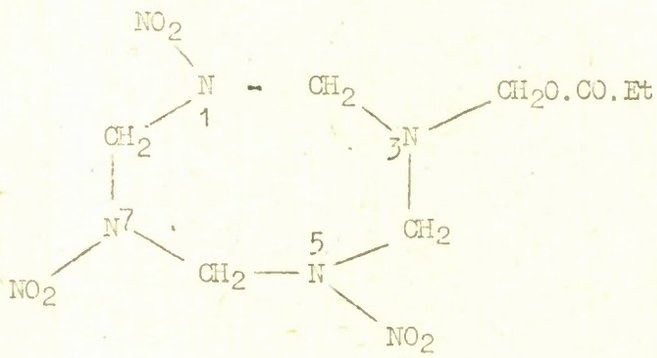
Div.8 Int.Rep.R.R.C.1, Jan. '43; SR7/3748.

Div.8 Int.Rep.R.R.C.2, Feb. '43; SR7/3867.

$$\text{DPT} \xrightarrow[Ac_2O]{\text{1 mole } HNO_3} \text{PHX}$$

Para. 132a

P2HX



1:5:7-Trinitro-3-propionoxymethyl-(8-ring) m.p. 120°.

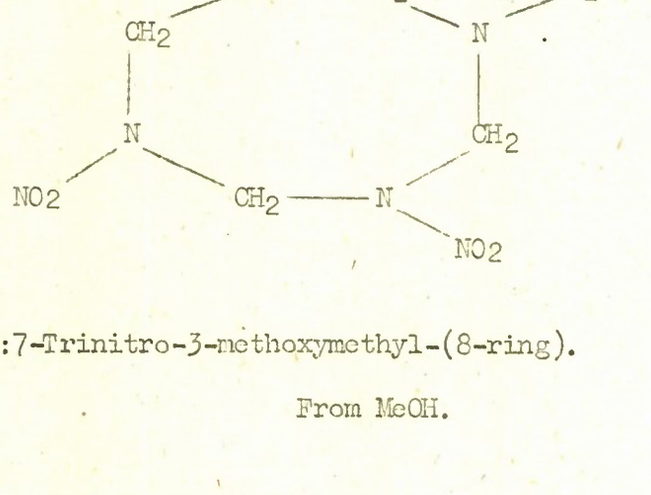
Preparation indicated on diagrammatic representation of Hex, RDX, etc. interactions:- "Compounds related to RDX, derived from Hexamine". "Revision of 2-10-44" (received London O.S.R.D. office, 25 Feb. '44).

No solvents or conditions.

$$\text{DPT} \xrightarrow[(EtCO)_2O]{HNO_3} \text{P2HX.}$$

Para. 133

MeHX



1:5:7-Trinitro-3-methoxymethyl-(8-ring).

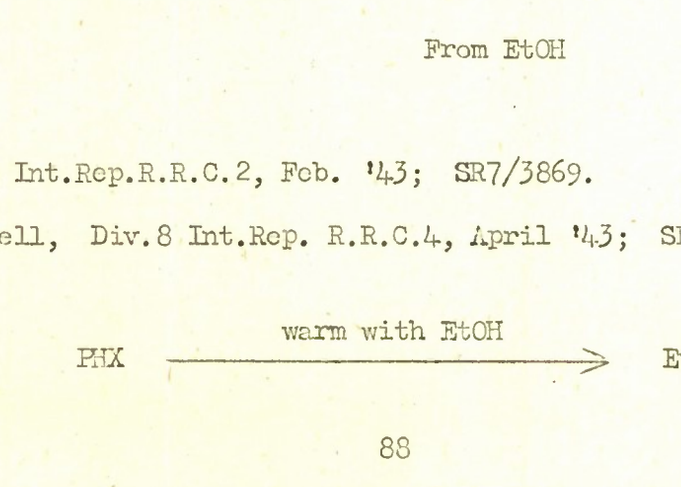
From MeOH. m.p. 138-139°.

Michigan, Div.8 Int.Rep., R.R.C.2, Feb. '43; SR7/3867.
(Checked by Cornell, Div.8 Int.Rep., R.R.C.4, April '43; SR7/4180).

PHX —(warm with dry MeOH and cool)→ MeHX

Para. 134

EtHX



1:5:7-Trinitro-3-ethoxymethyl-(8-ring).

From EtOH m.p. 115°.

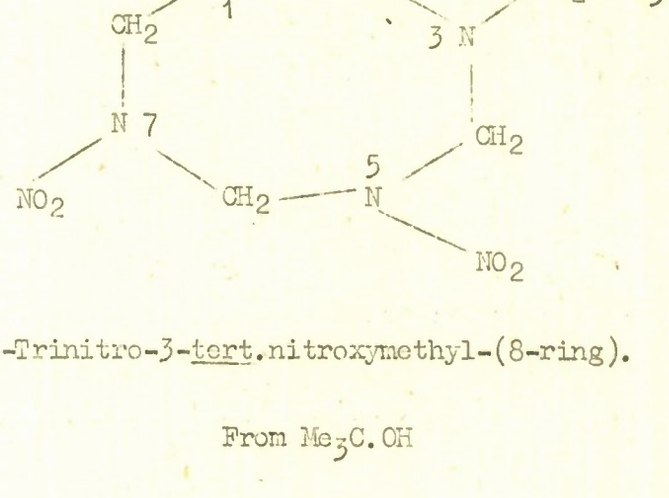
Michigan, Div.8 Int.Rep.R.R.C.2, Feb. '43; SR7/3869.

Checked by Cornell, Div.8 Int.Rep. R.R.C.4, April '43; SR7/4180.

PHX —(warm with EtOH)→ EtHX.

Para. 135

Tertiary Butyl HX



1:5:7-Trinitro-3-tert.nitroxymethyl-(8-ring).

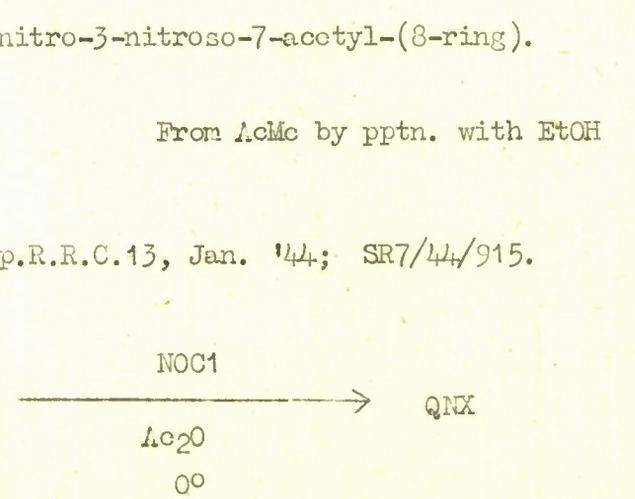
From $Me_3C.OH$ m.p. 129°.

Michigan, Div.8 Int.Rep.R.R.C.2, Feb. '43; SR7/3867.

PHX $\xrightarrow[Me_3C.OH]{\text{warm}}$ Tert. butyl HX.

Para. 136

QNX



1:5:Dinitro-3-nitroso-7-acetyl-(8-ring).

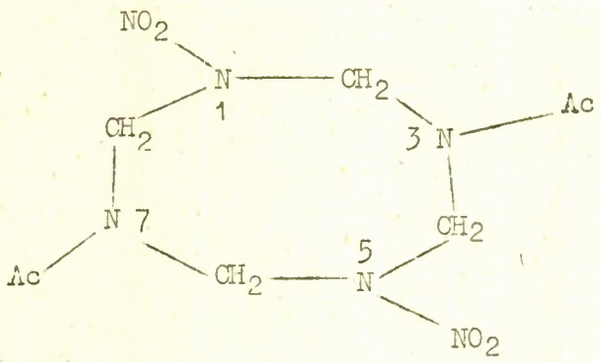
From AcMe by pptn. with EtOH m.p. 181°.

Michigan Div.8 Int.Rep.R.R.C.13, Jan. '44; SR7/44/915.

DPT $\xrightarrow[Ac_2O,\ 0°]{NOCl}$ QNX

Para. 137

H.12



1:5-Dinitro-3:7-diacetyl (8-ring).

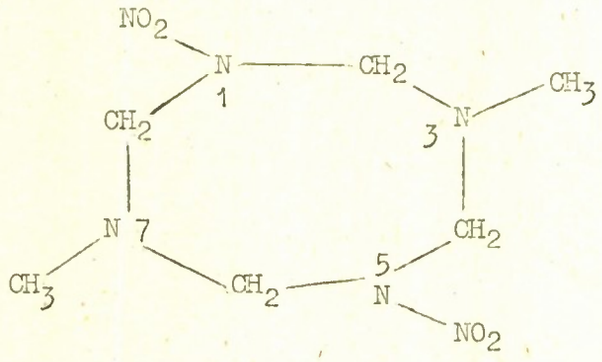
From CH_3NO_2 m.p. 257°.

Univ. Penn., O.S.R.D. 1733 Rep., July '43; SR7/43/448.

DPT $\xrightarrow[\text{reflux 40 mins. in dioxan}]{Ac_2O + AcCl}$ H.12 in very small yield

Para. 138

1:5-Dinitro-3:7-dimethyl-(8-ring)



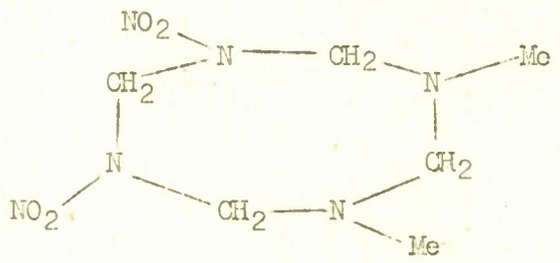
Unstable in hot solvents: cryst. from AcMe, (25° to -40°).
m.p. 124°

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984.

NH_2NO_2 in aq. CH_2O $\xrightarrow{CH_3NH_2}$ 1:5-dinitro-3:7-dimethyl-(8-ring).

Para. 138A

1:7-Dinitro-3:5-dimethyl-(8-ring)



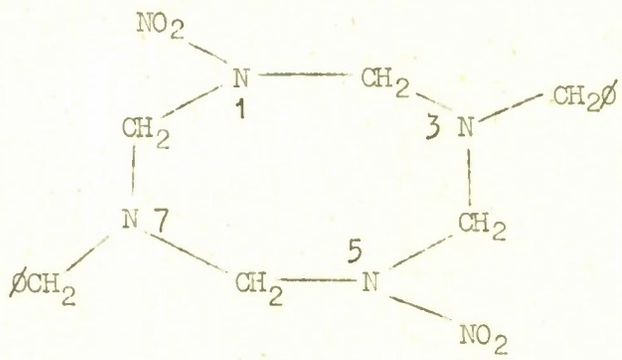
Fract. cryst. from EtOH-AcMe m.p. 108°.

Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

MEDNA $\xrightarrow[0°]{6CH_2O_{aq} + 2MeNH_2}$ Dinitrodimethyl-(8-ring) 25% + bismethyloltetranitro-methyl-(9-chain), 30% (see p. 82b). Separate by fract. cryst.

Para. 139

1:5-Dinitro-3:7-dibenzyl-(8-ring)



m.p. 150.5°.

Unstable in hot solvents: cryst. from cold AcMe.

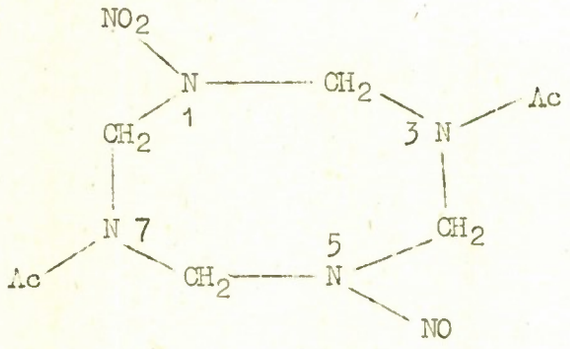
Toronto X.R.16 Rep., 31 Jan. '44; SR7/44/984.

NH_2NO_2, aq. CH_2O, $\emptyset CH_2NH_2$ ⟶ 1:5-Dinitro-3:7-dibenzyl(8-ring) + 1-Nitro-3:5-dibenzyl-(6-ring).

Separated by AcMe solution; see p. 105.

Para. 140

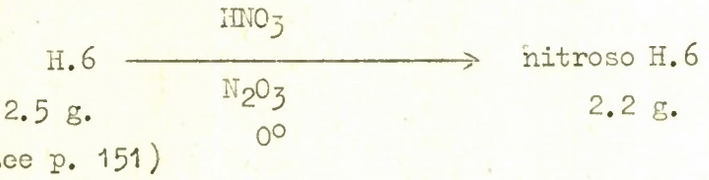
"Nitroso-H.6"



1-Nitro-5-nitroso-3:7-diacetyl-(8-ring).

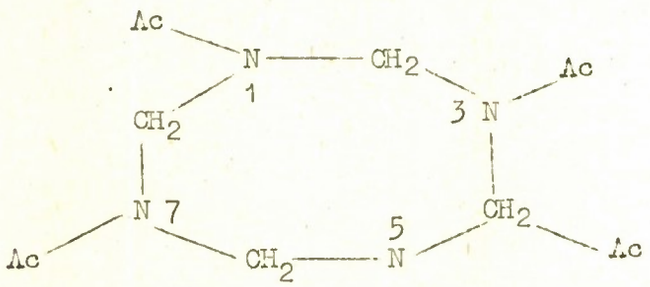
From CH_3NO_2; m.p. 224°.

Bristol Res.Rep.117, March '44; A.C.6046.



Para. 141

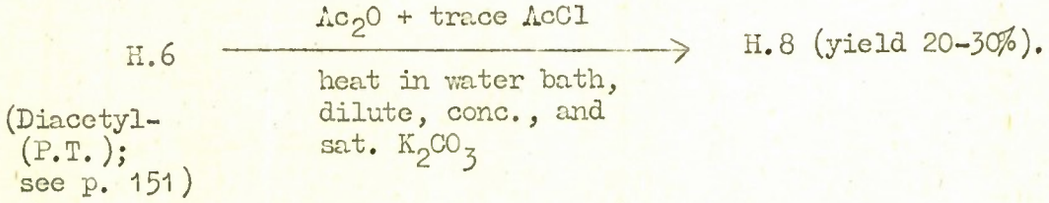
H.8



1:3:5:7-Tetracetyl-(8-ring).

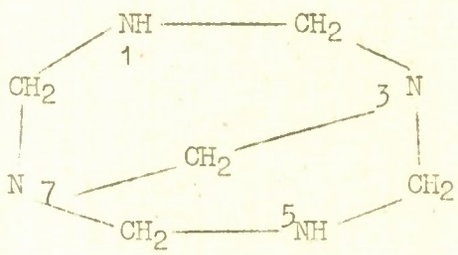
From EtOH. m.p. 157°.

Harvard, N.D.R.C. Rep., Oct. '42; SR7/3263.

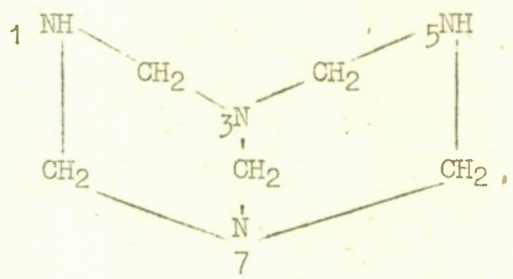


Goes better in $CHCl_3$ solution.

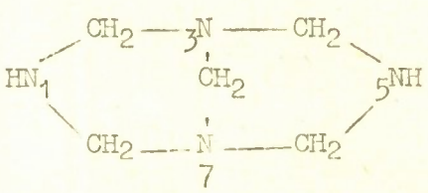
DERIVATIVES OF 3:7-ENDOMETHYLENEcyclo-2:4:6:8-TETRAMETHYLENE-1:3:5:7-TETRAMINE, ("PENTAMETHYLENETETRAMINE"; "PT")



Also drawn in the projections:-



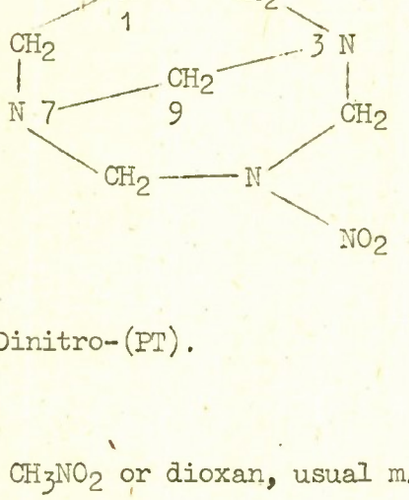
and



Para. 143

DPT (Toronto)

DNPT



1:5-Dinitro-(PT).

From AcMe, AcEt, CH_3NO_2 or dioxan, usual m.p. 203-206°

(Compound dimorphous: α m.p. 223-224°. (Stable at low temp.)

β m.p. 200°

(Cornell, Div.8 Int.Rep. R.R.C.1, Jan. '43; SR7/3748)

Toronto, C.E.12 Prog.Rep., Feb. '41.

Prog.Rep., Nov. '41; SR7/1173.

Hexamine nitrolysis, collect RDX and neutralise mother liquor to pH 5.6

(first used ammonia for neutralisation, but any alkali will do)

——————→ DPT

(up to 20%)

Toronto, C.E.12 Prog.Rep., 31 Dec. '41; SR7/1438:

X.R.16 Prog.Rep., 15 Jan. '43; SR7/3721.

NH_2NO_2	dissolved in aq. CH_2O	neut. with NH_3 to pH	DPT
(1 mole)	(CH_2O, 6 moles)	5.6	up to 73%.

Toronto C.E.12 Prog.Rep. Nov. '41; SR7/1173.

HADN	Ac_2O 4 days ca 30° watch temp. because may get out of hand.	DPT
(Hex.dinitrate		30%

(Checked by Penn.State, N.D.R.C.Rep.274, June '42; SR7/2440).

DPT (Continued)

McGill, C.E.53 Prog.Rep. 1 Jan. '42; SR7/1436.

HADN —(Ac_2O + NH_4NO_3)→ DPT

better yield but more difficult to purify than by Toronto method.

Harvard, N.D.R.C. Prog.Reps. Aug. '42 and Oct. '42; SR7/3263.

HADN (1 mole) —(mixture: 2 Ac_2O + 2 HOAc; plus trace of HCl or AcCl; 7 hrs. at 30°)→ DPT 35%.

(See also Univ.Penn. C.S.R.D.Rep. 1733, July '43; SR7/43/448).

Harvard, N.D.R.C.Prog.Rep., Nov. '42; SR7/3342.

H.2 (See p. 170) —(2 moles $AcONO_2$; -35°)→ DPT 30%.

Toronto, X.R.16 Prog.Rep., 15 Jan. '43; SR7/3721.

HADN —(aq. H_2SO_4 (92%); at 8-15°; drown and neutralise with ammonia to pH 6.)→ DPT 31%.

HADN + 92% aq. H_2SO_4 → RDX (14 per cent) + DPT (35 per cent).

Cornell, Div.8 Int.Rep. R.R.C.3, March '43; SR7/4179.

PHX (See p. 132) —(slow evaporation of EtOH solution (14 days))→ DPT (24%).

Cornell, Div.8 Int.Rop., R.R.C.4, April '43; SR7/4180.

MeHX (See p. 133) —(slow evaporation of MeOH solution)→ DPT

DPT (Continued)

$$\text{EtHX} \xrightarrow[\text{of EtOH solution}]{\text{slow evaporation}} \text{DPT}$$

Univ.Penn., Div.8 Int.Rep., R.R.C.5, May '43; SR7/4766.

$$\text{H.18} \; (\text{Hex.-Me}\}\overset{\oplus}{\text{N}}\overset{\ominus}{\text{O}}_3, \text{ see p. 164}) \xrightarrow[\text{AcONO}_2]{\text{4 moles}} \text{DPT}$$

in low yield + MSX.

Bristol Br.Rep. 28, Oct. '43; A.C.5058.

$$\text{Crude PCX} \xrightarrow[\text{water; collect inert residue and fract. cryst.}]{\text{triturate with}} \text{DPT}$$

$$\text{Methylol PCX} \xrightarrow{\text{heat}} \text{DPT}$$

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984.

$$\text{aq. } CH_2O + NH_2NO_2 + CH_2(\overset{\oplus}{N}H_3)_2\overset{=}{S}O_4 \longrightarrow \text{DPT}$$

97% yield.

Sheffield Rep. 44, March '44; A.C.6045.

$$\text{MEDNA} + CH_2O \text{ aq} \xrightarrow[NH_4NO_3]{NaHCO_3} \text{DPT}$$

1.3 g. — room temp. for 17 hrs. — 0.7 g. crude. 0.3 g. recryst.

$$\text{MEDNA} \xrightarrow[\text{2N } NH_4OH \text{ aq.}]{\text{dissolve in}} \text{DPT}$$

0.3 g. — ○ 0.03 g.

Crude PCX (1.3 g.), shake with H_2O and filter;

$$\text{filtrate} + NaHCO_3 \longrightarrow \text{DPT}$$

0.2 g. crude.

Para. 146

DPT (Continued)

Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

$$\text{MEDNA} + 3CH_2O + NH_3 \xrightarrow[\text{treat crude prod. with EtOH-AcMe.}]{H_2O \text{ at } 0^\circ} \text{DPT} \quad * \qquad 55\% \text{ yield.}$$

(Done independently by Sheffield workers: see Sheffield Rep. 44).

$$\text{PCX} \xrightarrow[NaOH]{3CH_2O\text{aq.}} \text{DPT (18\% yield)} + \text{methylol-PCX (6\%).}$$

(see Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158).

Toronto, X.R.16, Canadian Exp.Res.Extram.Summary, April '44; SR7/44/1747.

$$NH_4NO_3 + CH_2O + Ac_2O + HOAc \longrightarrow \text{DPT (18\%)} + \text{small amts. RDX(B), BSX and TEX.}$$

Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

$$\text{HADN} \xrightarrow[75 \text{ parts } HNO_3 \text{ at } 70^\circ \text{ for 168 hrs.}]{60 \text{ parts } NH_4NO_3} \text{ppt. P.S.1.Neut.filtrate} \longrightarrow \text{DPT (38\%).}$$

$$\text{Ross Reaction} \xrightarrow[19 \text{ hrs.}]{25^\circ} \text{18\% DPT. + 1.4\% TEX. + 5.2\% RDX(B). + 18\% RDX.}$$

$$(NO_2OCH_2)_2NNO_2 + NH_4NO_3 \xrightarrow[\text{neut. to pH 8 } (Na_2CO_3)]{2CH_2O_{aq}} \text{DPT (60\%).}$$

Cal.Tech., Div.8 Int.Rep.R.R.C. 22, Oct. '44; SR7/44/3502.
Chromatography of DPT.

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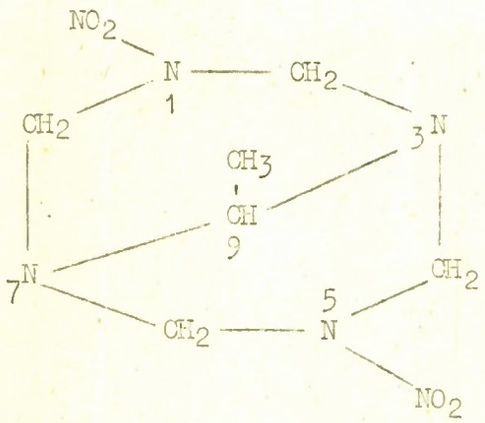
* Crude product probably contains methylene bis (3:5-dinitro-(6-ring)-1-). Treated with EtOH-AcMe ⟶ conversion to DPT and leaves amorphous residue, m.p. 141° (see p. 103a).

Para. 147

1:5-Dinitro-3:7-endoethylidene-(8-ring)



1:5-Dinitro-9-methyl-(P.T.)

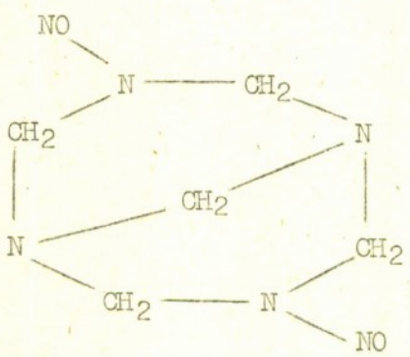
From EtOAc, m.p. 175°. (residue remains at 245°).

Toronto, X.R.16 Reps., 31 Jan. '44; SR7/44/984: 1 Sept. '44; SR7/44/3158.

NH_2NO_2
aq. CH_3CHO (70%)
aq. NH_3 (10%)
→ aq. CH_2O → 1:5-dinitro-3:7-endoethylidene-(8-ring).

Para. 148

1:5-Dinitroso-(P.T.)



m.p. 207°.

Griess and Harrow. Ber., 1888, 21, 2737.

Mayer. Ber., 1888, 21, 2883.

Duden and Scharff. Annalen, 1895, 288, 218 et seq.

Duden and Scharff.

Add excess NH_3 aq. to CH_2O aq. and treat with 2 moles $NaNO_2$ and HOAc.

Michigan, Div.8 Int.Rep., R.R.C.13, Jan. '44; SR7/44/915.

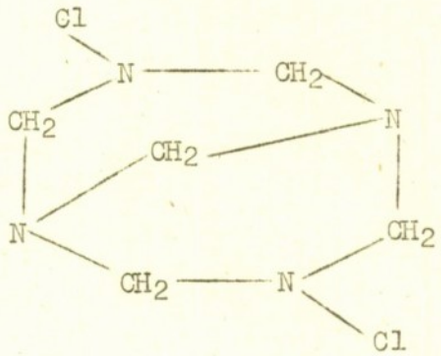
Hex. —HNO_2 / pH 3 to 5→ dinitroso (P.T.)

Bristol Res.Rep.129, June '44; A.C.6486.

NH_4NO_3 + $NaNO_2$ + aq. CH_2O —vigorous reaction→ dinitroso-(P.T.) in small yield.

Para. 149

1:5-Dichloro-(P.T.)



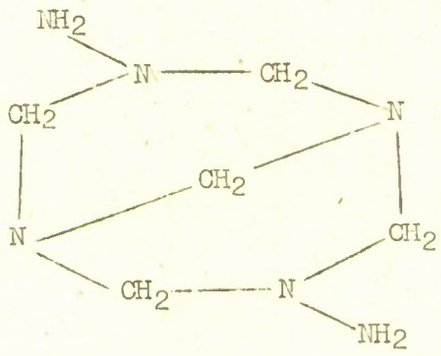
From H_2O and ether, m.p. 78°.

Delepine: Bull.soc.chim., 1911, (4), 9, 1025.

Hexamine in H_2O $\xrightarrow{NaOCl}$ Dichloro P.T.

Para. 150

1:5-Diamino-(P.T.)



Not isolated.

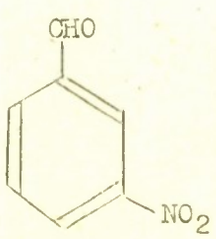
Duden and Scharff, Annalen, 1895, 288, 218.

Dinitroso-(P.T.) $\xrightarrow[\text{cold } H_2O]{Na/Hg}$ Diamino-(P.T.),

isolated as (a) dibenzylidene derivative, from EtOH. m.p. 226-7°;

(b) bis-o-hydroxybenzylidene derivative, from $CHCl_3$-ether. m.p. 213°.

Also made derivatives from



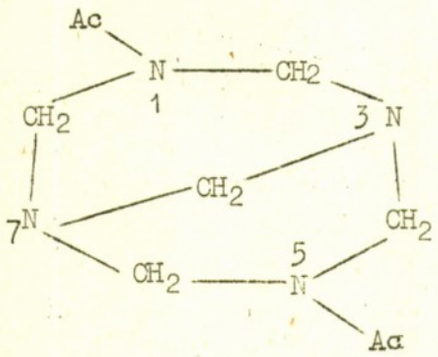
From EtOH, m.p. 134°.

and Ø-CH=CH-CH=O. From EtOH, m.p. 207°.

Para. 151

H.6

(DAPT)



1:5-Diacetyl - (P.T.).

From EtOH, m.p. 191°.

Harvard, N.D.R.C.Rep., Oct. '42; SR7/3263.

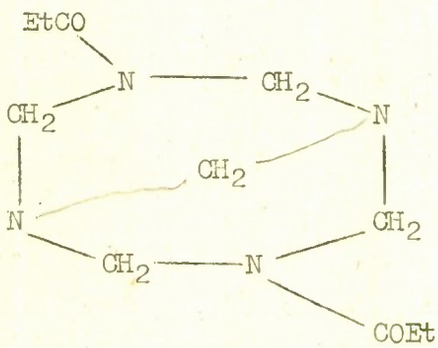
Hex. in $CHCl_3$ (boiling) $\xrightarrow[\text{reflux}]{Ac_2O\ (2.5\ \text{moles})}$ H.6 (14%).

Hex. in 2 parts Ac_2O, 2 hrs.' standing, then add 5 vols. ether. Lower oily layer deposits H.6 (10%).

Compound prepared by Dominikiewiez (Chem.Abs., 1936, 30, 1029) by Ac_2O on Hex. is probably H.6.

Para. 152

H.17



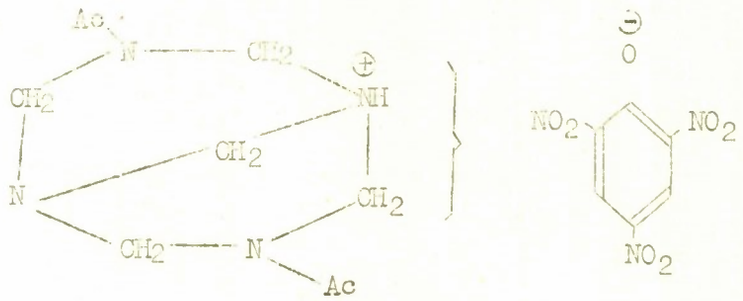
1:5-Dipropionyl-(P.T.). m.p. 133°.

Univ.Penn., Div.8 Int.Rep., R.R.C.8, Aug. '43; SR7/43/391, refer to this compound, which presumably was made earlier, probably by a method analogous to H.6 preparation (p. 151).

H.17 does not yield a picrate.

Para. 152A

H.6 Picrate



1:5-Diacetyl-(P.T.)-3-picrate.

From reaction mixture and washed with hot EtOH. m.p. 135°.

Bristol (private communication from Messrs. T. H. Bevan, M. E. Foss, N. H. Woodbury), Oct. '44.

H.6 in hot EtOH —(hot sat. EtOH solution of picric acid: cool slowly)→ H.6 picrate. (purify by extraction with hot EtOH).

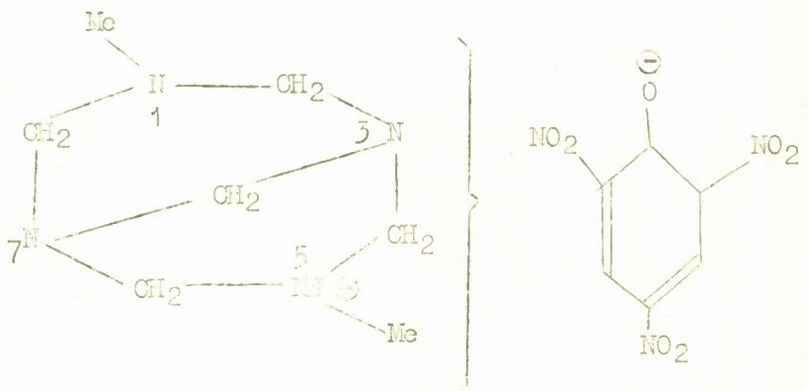
Found: C, 40.4; H, 4.27; N, 21.0.

$C_{15}H_{19}N_7O_9$ requires: C, 40.7; H, 4.31; N, 22.2%.

See p. 216 for other products from H.6 and picric acid reaction.

Para. 153

1:5-Dimethyl-(P.T.) picrate



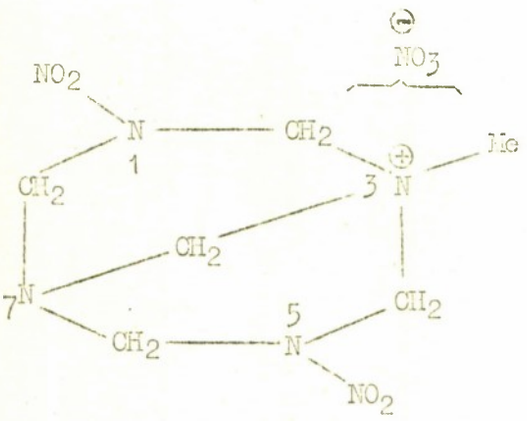
From AcOH, m.p. 195°.

Knudsen, Ber., 1914, 47, 2694.

$(NH_4)_2SO_4$ + aq. CH_2O —(picric acid)→ above picrate.

Para. 154

H.19



1:5-Dinitro-3-methyl-(P.T.)-3-nitrate.

Washed with water, EtOH, ether. m.p. 142-143°.

Univ.Penn., Div.8 Int.Rep., R.R.C.5, May '43; SR7/4766.

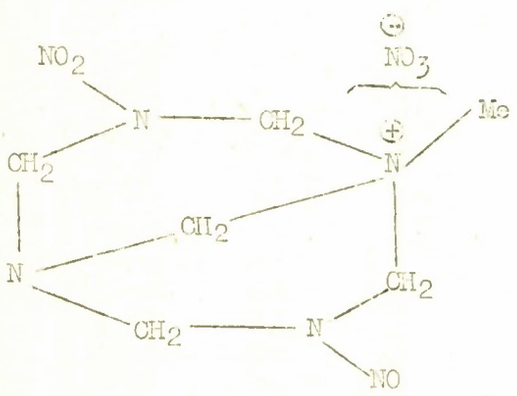
U.S.A.-Canada RDX Committee Meeting, June '43; SR7/4956.

H.18 (Hex.Metho-nitrate). (See p. 164) $\xrightarrow[-10^\circ \longrightarrow -15^\circ]{HNO_3}$ H.19. (Yield, 66 per cent).

See also, Univ.Penn.O.S.R.D. 1733 Rep., July '43; SR7/43/448.

Para. 155

Nitroso-H.19



1-Nitro-5-nitroso-3-methyl-(P.T.)-3-nitrate,

(not recryst., wash + H_2O, MeOH and ether, m.p. 128-130°).

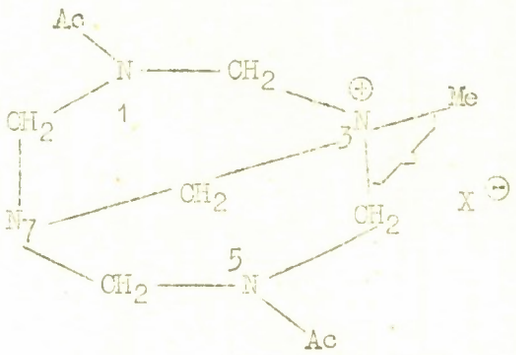
Bristol Res. Rep. 117, March '44; A.C.6046.

H.18 (See p. 164) $\xrightarrow[N_2O_4]{HNO_3}$ nitroso H.19.

0°

Para. 155A

H.6 Metho-salts



1:5-Diacetyl-3-methyl-(P.T.)-3-salts.

Bristol, (private communication from Messrs. T. H. Bevan, M. E. Foss, N. H. Woodbury), Oct. '44.

X = I.

From MeOH m.p. 180-1°.

H.6 + MeI $\xrightarrow[\text{MeOH}]{\text{reflux in}}$ H.6 methiodide.

X = NO_3

From MeOH m.p. 181-2°.

H.6 methiodide $\xrightarrow[\text{in MeOH}]{AgNO_3}$ H.6 methonitrate.

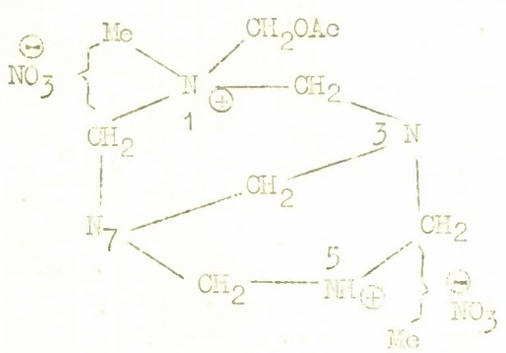
X = picrate.

From H_2O m.p. 199°.

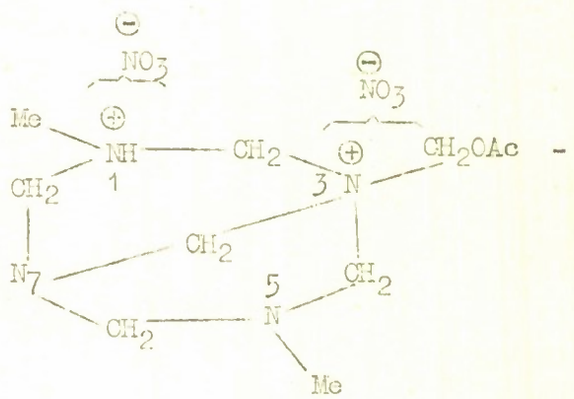
H.6 methiodide or metho-nitrate $\xrightarrow[\text{add sat. aq. picric acid}]{\text{in } H_2O}$ H.6 metho-picrate.

Para. 156

H.23



or



1:5-Dimethyl-1-acetoxymethyl-(P.T.)-1:5-dinitrate

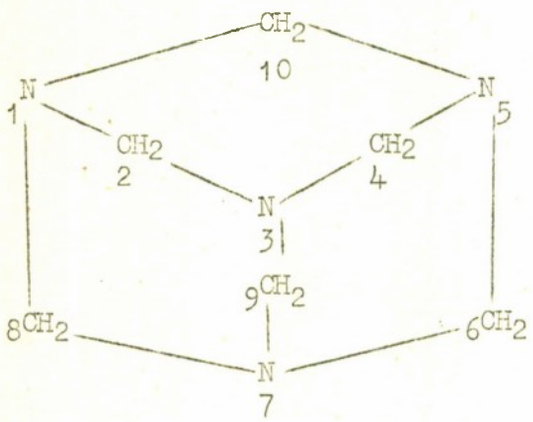
or 1:5-Dimethyl-3-acetoxymethyl-(P.T.)-1:3-dinitrate.

Dissolve in H_2O and ppt. with HOAc. m.p. 192°.

Univ.Penn., Div.8 Int.Rep.R.R.C.5, May '43; SR7/4766, and
Univ.Penn., Div.8 Int.Rep.R.R.C.6, June '43; SR7/4879.
See also Univ.Penn., O.S.R.D.Rep.1733, July '43; SR7/43/448.

H.18(12 g.) (Hex.-Me NO_3 see p. 164) $\xrightarrow[\text{at } 18°]{\text{2 moles } AcONO_2}$ H.23. 3.6 g. (crude). 1.5 g. (pure)

DERIVATIVES OF HEXAMETHYLENE TETRAMINE



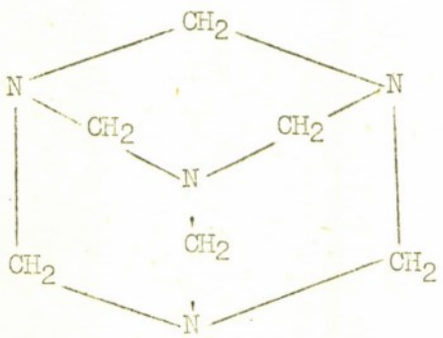
"Hex."

Para. 158

"Hexamethylene tetramine"

"(Hexamine)"

"Hex."



Sublimes with partial decomp.

on heating.

From water or ethyl alcohol.

Beilsteins Handbuch, I, 584.

See particularly Duden and Scharff, Annalen, 1895, 288, 218 for chemistry.

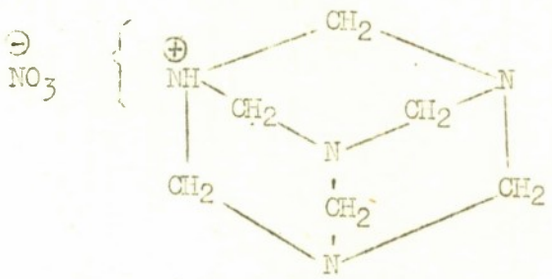
$$\text{aq. } CH_2O \xrightarrow{NH_3} \text{Hexamine.}$$

Dickinson and Raymond, J.A.C.S., 1923, 45, 22 and Wyckoff and Corey, Zeit.Krist., 1934, 89, 462 for X-ray crystal analysis giving proof of structure.

Para. 159

HAMN.

Hexamine mononitrate



Hex-1-nitrate

m.p. 158-168°, according to rate of heating.

Cambier and Brochet, Bull.soc.chim., 1895,(3), 13, 392.

Harvard, N.D.R.C.Rep., Oct. '42; SR7/3263.

$$\text{Hex. in water} \xrightarrow[\text{cold}]{\text{1 equiv. 70\% } HNO_3} \text{HAMN.}$$

(1st. Harvard prep. in May '42).

Michigan, Div.8 Int.Rep. R.R.C.12, Dec. '43; SR7/44/508.

$$\underset{14\text{ g.}}{\text{Hex.}} + \underset{8\text{ g.}}{NH_4NO_3} \xrightarrow[\text{HOAc and cool}]{\text{diss. in warm}} \underset{1.8\text{ g.}}{\text{HAMN}}$$

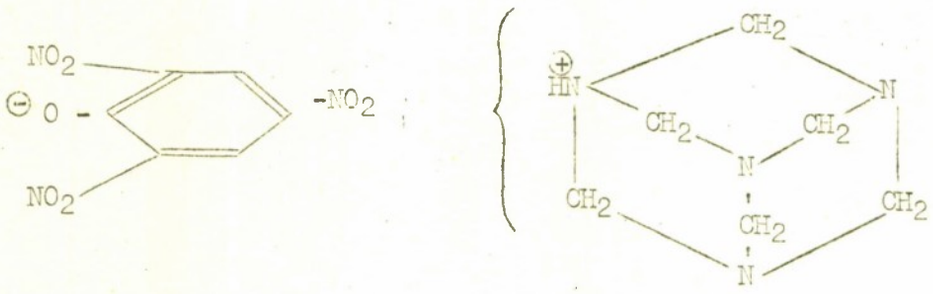
Bristol Res.Rep.113, Jan. '44; A.C.5739.

$$\text{Hex.} \xrightarrow[CHCl_3]{N_2O_3} \underset{14\% \text{ yield}}{\text{HAMN}}$$

(probably not a primary product)

Para. 160

Hexamine Picrate



m.p. 178-179°

Moschatos and Tollens, Annalen, 1893, 272, 285.

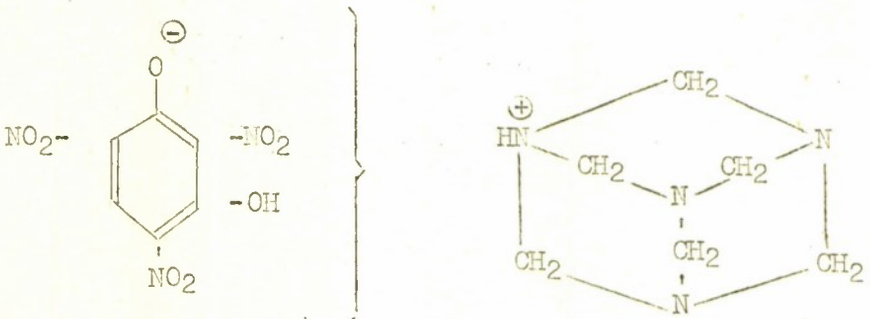
Hex. —(aqueous / picric acid)→ Hex. picrate.

Harvard, N.D.R.C. Rep., Oct. '42; SR7/3263.

H.3 —(boil with / EtOH)→ Hex. picrate.

Para. 161

Hexamine Styphnate



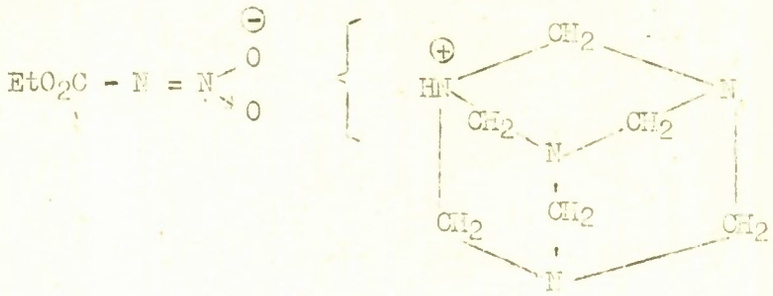
From CH_3NO_2 m.p. 197°

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984.

Hex. —(aq / styphnic acid (1 equiv.))→ Hex. Styphnate. 100% yield.

Para. 162

Hexamine Nitrourethane



From EtOH. m.p. 136-138°

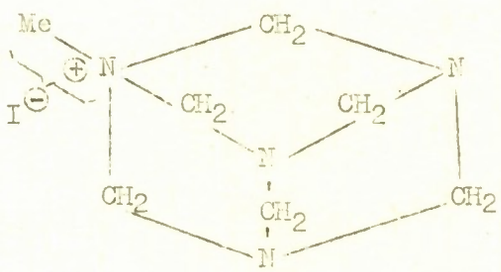
Bristol Br. Rep. 29, Oct. '43; A.C.5039.

$$NO_2\text{-}NH\text{-}CO_2Et \text{ in aq. } CH_2O \xrightarrow{NH_3} \text{Hex. nitrourethane.}$$

$$\text{Hex.} + NO_2.NH.CO_2Et \xrightarrow[\text{and evap.}]{\text{aq.}} \text{Hex. nitrourethane.}$$

Para. 163

Hexamine Methiodide



1-Methyl-(Hex.)-1-iodide.

From EtOH m.p. 190°

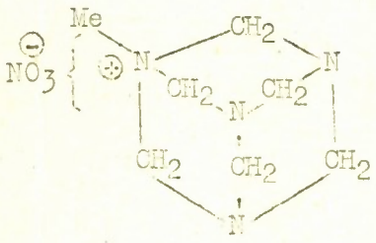
Wohl, Ber., 1886, 19, 1843.

Univ.Penn.Div.8 Int.Rep. R.R.C.5, May '43; SR7/4766.

$$\text{Hex.} \xrightarrow[MeI + MeOH]{\text{reflux}} \text{Hex. methiodide.}$$

Paras. 164, 165

H.18, (H.20), (H.1)



1-Methyl-(Hex.)-1-nitrate

"Hex-methonitrate"

From EtOH. m.p. 190°

Hahn and Walter, Ber., 1921, 54, 1531.

Univ.Penn., Div.8 Int.Rep.R.R.C.4, April '43; SR7/4180.

$$\text{Hex} + MeONO_2 \longrightarrow \text{H.18}$$

$$\text{Hex} + \text{DPT} \xrightarrow{\text{HOAc}} \text{H.18}$$

Univ.Penn., Div.8 Int.Rep.R.R.C.5, May '43; SR7/4766.

$$\text{Hex. in boiling MeOH} \xrightarrow[\text{then } AgNO_3]{MeI} \text{H.18}$$

(Best laboratory preparation).

$$\text{H.19} \xrightarrow[\text{hot } CH_3NO_2]{\text{dissolve in hot HOAc or}} \text{H.20} + CH_2O$$

H.20 forms a picrate, m.p. 205°.

Mixed m.p. H.20 - H.18, no depression.

Mixed m.p. H.20 picrate - P.S.2, no depression.

H.20 is H.18. (U.S.A., Canada RDX Committee Meeting, June '43, SR7/4956).

(See also Univ.Penn.Rep. O.S.R.D. 1733, July '43, SR7/43/448).

Cornell, Prog.Rep. O.S.R.D. 1803, Sept. '43, SR7/43/876.

$$\text{H.19} \xrightarrow{\text{HOAc}} \text{H.18}$$

Para. 165

H.18 (H.20, H.1) (Continued)

Bristol Prog.Rep. Sept. '43.

Bristol Br. Rep. 36, Jan. '44; AC.5725.

Bristol Res. Rep. 129, June '44; AC.6486.

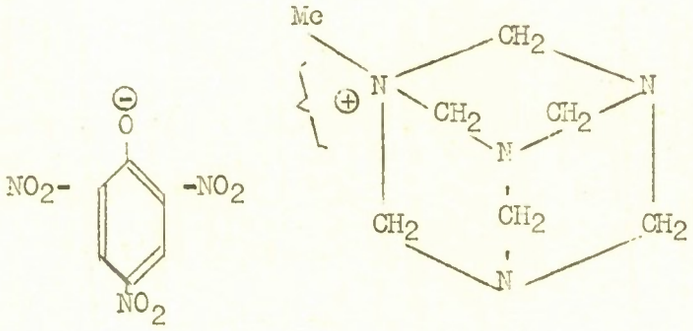
HADN $\xrightarrow[H_2O \text{ or MeOH or EtOH or isobutyl OH.}]{\text{reflux with}}$ H.18

HADN $\xrightarrow[CHCl_3 \text{ extraction}]{}$ H.1 identical with H.18

Univ. Penn. Rep. O.S.R.D. 1733, July 1943; SR7/43/448.

Para. 166

P.S.2

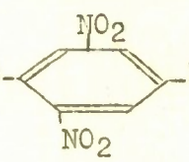


1-Methyl-(Hex)-1-picrate.

"Hex.-methopicrate"

m.p. 210-215°

Hahn and Walter, Ber. 1886, 19, 1510

Hex. + MeO-  $\longrightarrow$ compd. m.p. 210°.

Penn. State, Div.8 Int.Rep.R.R.C.2, Feb. '43; SR7/3867.

DPT $\xrightarrow{\text{picric acid}}$ P.S.2

Univ.Penn., Div.8 Int.Rep.R.R.C.4, April '43; SR7/4180.

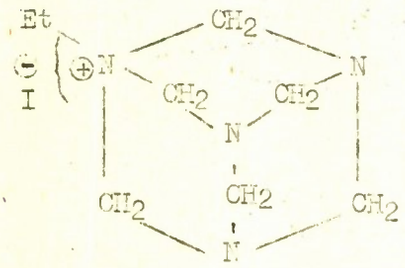
H.18 $\xrightarrow{\text{picric acid}}$ P.S.2

Univ.Penn., O.S.R.D.Rep. 1733, July '43; SR7/43/448.

P.S.2 is Hex-methopicrate.

Para. 167

Hexamine Ethiodide



1-Ethyl-(Hex.)-1-iodide.

m.p. 141-143°

Wohl, Ber., 1886, 19, 1844 gives m.p. 133°

Delépine, Bull soc.chim., [3], 13, 358 gives m.p. 146°

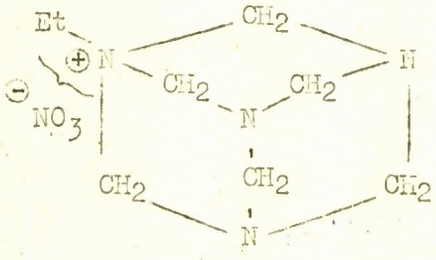
Univ.Penn., Div.8 Int.Rep. R.R.C.10, Oct. '43; SR7/43/925.

$$\text{Hex.} + \text{EtI} \xrightarrow[\text{MeOH}]{\text{boiling}} \text{Et-(Hex)}^{\oplus}\ \}\ \text{I}^{\ominus}$$

Second crop ⟶ m.p. 154-156°
and is different compound,
not identified.

Para. 168

H.29. "Hexamine Ethonitrate"



1-Ethyl-(Hex.)-1-nitrate

Usually just ether washed, m.p. 135°
but can be crystd. from
MeOH.

Univ.Penn., Div.8 Int.Rep. R.R.C.9, Sept. '43; SR7/43/924.

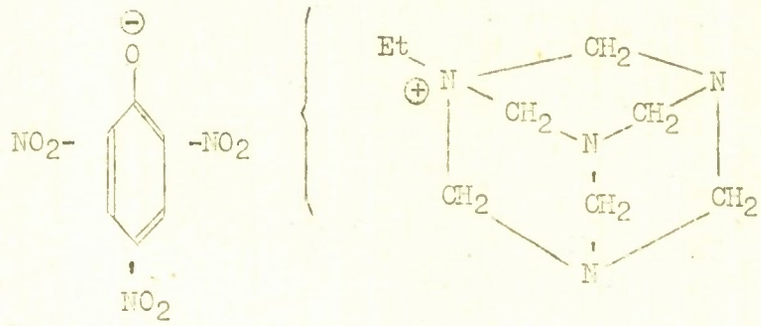
$$\text{Hex.} + \text{EtI} + \text{AgNO}_3 \xrightarrow[\text{ppt. with ether}]{\text{in EtOH, and}} \text{Et-(Hex.)}^{\oplus}\ \}\ \text{NO}_3^{\ominus}$$

(as for H.18)

Para. 169

H.30

PS.2 (Et)



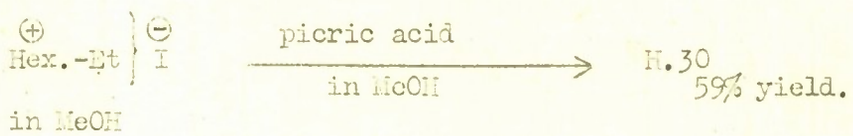
1-Ethyl-(Hex.)-1-picrate.

"Hexamine ethopicrate"

From MeOH m.p. 166-168°

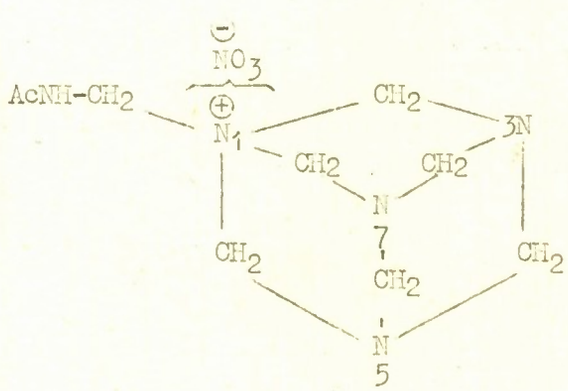
Univ.Penn., Div.8 Int.Rep.R.R.C.9, Sept. '43; SR7/43/924.

Div.8 Int.Rep.R.R.C.10; Oct. '43; SR7/43/925.



Paras. 170, 171

H.2



1-Acetamidomethyl-(Hex.)-1-nitrate.

Diss. in equal weight of H_2O and add

4 vols. of EtOH ——————→ cryst. m.p. 168-183° according to rate of heating

Para. 170

H.2 (Continued)

Harvard N.D.R.C.Rep. May '42;

N.D.R.C.Rep. Oct. '42; SR7/3263.

$$\text{HAMN} \xrightarrow[\text{room temp.}]{Ac_2O} \text{H.2 (small yield)}$$

$$\text{Hex. in boiling } CHCl_3 \xrightarrow[1.5 \text{ moles } Ac_2O]{1 \text{ mole } HNO_3} \text{H.2(30\%)}$$

Michigan, Div.8 Int.Rep.R.R.C.3, March '43; SR7/4179.

$$\text{HAMN*} + CH_2O + NH_2Ac \longrightarrow \text{H.2 (57\%)}.$$

(* or Hex. in HOAc and add 70% aq. HNO_3 in HOAc)

$$\text{HAMN} + HOCH_2.NHAc \longrightarrow \text{H.2 (60-70\%)}.$$

$$\text{HAMN} + \text{PHX*} + NH_2Ac \longrightarrow \text{H.2}$$

(* presumably acting as source of CH_2O).

$$\text{H.2 Cl} \xrightarrow{AgNO_3} \text{H.2 (quant.)}$$

(see p. 172)

Univ.Penn. Div.8 Int.Rep.R.R.C.3, March '43; SR7/4179

$$\text{H.6} + \text{HADN} \longrightarrow \text{H.2 (125\% on HADN)}.$$

(See Univ.Penn., O.S.R.D.Rep.1733, July '43; SR7/43/448, for review).

Para. 171

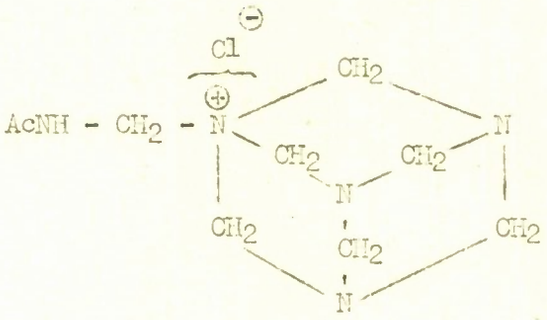
Michigan, Div.8 Int.Rep.R.R.C.12, Dec. '43; SR7/44/508.

$$\underset{(28 \text{ g.})}{\text{Hex.}} + \underset{(16 \text{ g.})}{NH_4NO_3} \text{ in HOAc (200 cc. soln.)} \xrightarrow[\text{at } 35^\circ, 5 \text{ mins.}]{Ac_2O (45 \text{ cc.})}$$

$$\underset{(32 \text{ g.})\ 68\%}{\text{ppt. H.2}} \xrightarrow{\text{cryst.}} \underset{(21 \text{ g.})\ 45\%}{\text{H.2}}$$

Para. 172

H.2 Cl



1-Acetamidomethyl-(Hex)-1-chloride.

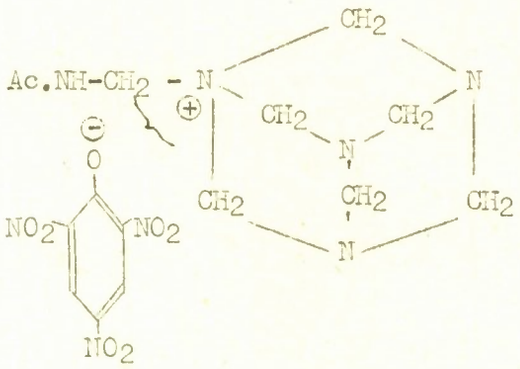
From EtOH m.p. 188-189°

Michigan, Div.8 Int.Rep.R.R.C.3, March '43; SR7/4179.

H.2 —(nitron Cl)→ H.2 Cl (quant.)

Para. 173

H.3



1-Acetamidomethyl-(Hex)-1-picrate.

m.p. 190°

(Cannot be recrystallised because

H.3 —(boiling EtOH)→ Hex. picrate)

Harvard, N.D.R.C.Rep., Oct. '42; SR7/3263.

Michigan, Div.8 Int.Rep.R.R.C.3, March '43; SR7/4179.

H.2 —(picric acid in aq. EtOH)→ H.3

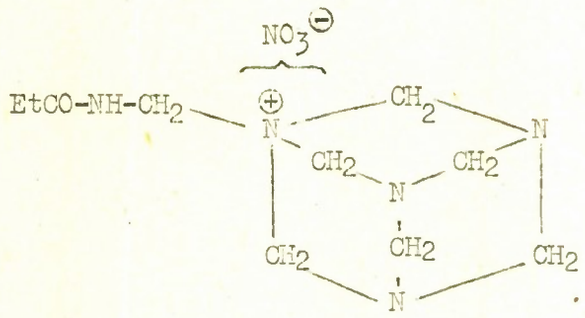
Univ.Penn., Div.8 Int.Rep.R.R.C.3, March '43; SR7/4179.

H.2 Cl —(picric acid)→ H.3

Para. 174

H.5 (Harvard)

Propionic H.2 (Michigan)



1-Propionamidomethyl-(HCl)-1-nitrate.

From EtOH. m.p. 160° (1st prep. Harvard)

"180° or higher" (Michigan prep.).

Harvard, N.D.R.C.Rep., Oct. '42; SR7/3263.

HAMN $\xrightarrow[\text{2 hrs. at } 50^\circ]{(EtCO)_2O}$ H.5 (small yield)

Michigan, Div.8 Int.Rep., R.R.C.3, March '43; SR7/4179.

Hex. in propionic acid $\xrightarrow[CH_2O]{EtCO.NH_2}$ H.5 (63%).

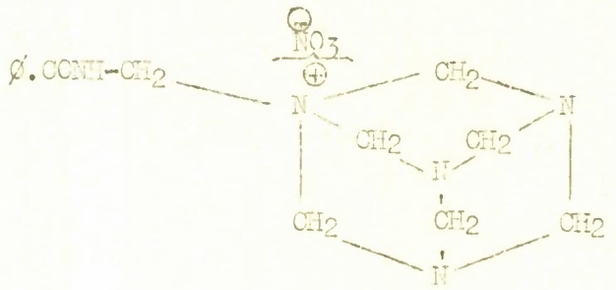
$\xrightarrow[\text{stand.}]{\text{HAMN} + EtCONH_2 + CH_2O;\ \text{all in aq. soln.;}}$ H.5 (40%)

Univ.Penn., O.S.R.D.Rep. 1733, July '43; SR7/43/448.

Hex. $\xrightarrow{EtCO.ONO_2}$ H.5

Para. 175

Benzoic H.2



1-Benzamidomethyl-(Hex)-1-nitrate.

From 90% aq.EtOH, m.p. 158-159°.

Bristol Res.Rep.96, June '43; A.C.4540.

$$\text{Hex. in } CHCl_3 \xrightarrow[20\text{-}30^\circ C.]{\emptyset.CO.ONO_2} \text{Benzoic H.2.}$$

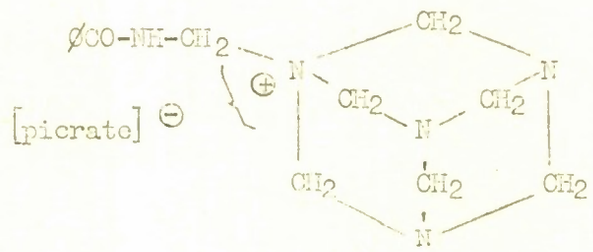
$$\text{Hex.mononitrate in HOAc} \xrightarrow{HO.CH_2.NH.CO.\emptyset} \text{Benzoic H.2.}$$

Univ.Penn., Div.8 Int.Rep., R.R.C.15, March '44; SR7/44/1236.

In first method of preparation, the yield of Benzoic - H.2 was dependent on EtOH content of $CHCl_3$.

Para. 176

Benzoic H.3



1-Benzamidomethyl-(Hex)-1-picrate.

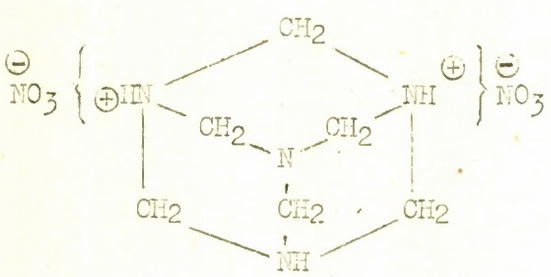
From EtOH, m.p. 157-158°.

Bristol, Res.Rep. 96, June '43, A.C.4540.

$$\text{Benzoic H.2} \xrightarrow[\text{picric acid}]{\text{alcohol}} \text{Benzoic H.3.}$$

Para. 177

HADN



Hex.-1:5-dinitrate.

m.p. 162°

Hale, J.A.C.S., 1925, 47, 2754,

Hex. in H_2O —(2 equivs. 70% HNO_3, at 0°)→ HADN

Michigan, O.S.R.D.Rep. 820, 15 Aug. '42; SR7/2982.

Hex. in aq. (25.5%) —(19% excess 60% aq. HNO_3, temp. < 15°)→ HADN 93% yield.

McGill, X.R.6 Prog.Rep., May '43; SR7/4435.

$CH_2O + NH_4NO_3$ —(in HOAc at 35°)→ HADN (85%).

Bristol, Br.Rep. 36, Jan. '44; A.C.5725.

Hex. —(70% aq. HNO_3 or HNO_3 HOAc)→ HADN (97% yield).

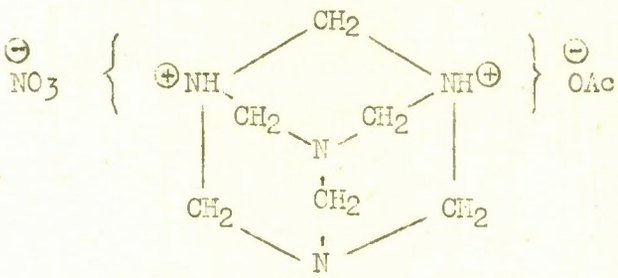
Bristol, Res.Rep. 129, June '44, A.C.6486.

NH_4OAc + aq. CH_2O —(70% aq. HNO_3)→ HADN

$NH_4NO_3 + CH_2O$ —(in HOAc)→ HADN

Para. 178

Hexamine nitrate acetate



Hex-1-nitrate-5-acetate.

Dry at room temp.

Warming ⟶ loss of HOAc ⟶ HAMN.

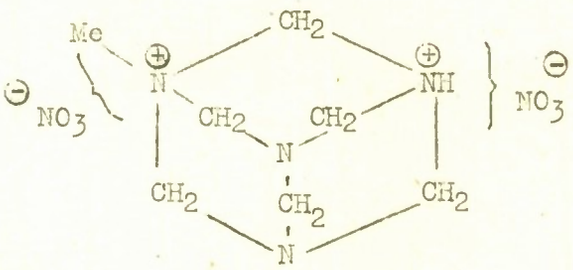
Michigan, Div.8 Int.Rep. R.R.C.12, Dec. '43; SR7/44/508.

$$\text{Hex.} + NH_4NO_3 \xrightarrow[\text{keep overnight}]{\text{excess HOAc}} \text{Hex., } HNO_3\text{, HOAc}$$

separates cryst.

Para. 179

H.26



1-Methyl-(Hex.)-1:5-dinitrate.

Product washed with HOAc and ether but not recryst. m.p. 150°

Univ.Penn., Div.8 Int.Rep.R.R.C.5, May '43; SR7/4766.

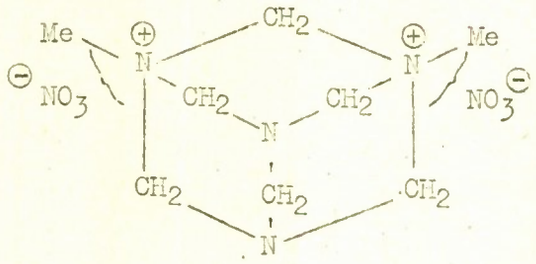
$$\text{H.18} \xrightarrow[\text{in HOAc}\ 20^\circ]{HNO_3} \text{H.26.}$$ 100% yield. (H_2O soluble).

(See Univ.Penn., O.S.R.D.Rep. 1733, July '43; SR7/43/448).

Para. 180

BCX (McGill)

Stabiliser Compound (Bristol)



1:5-Dimethyl-(Hex.)-1:5-dinitrate.

ppt. from 70% HNO_3aq + MeOH, m.p. 193° (Bristol)

m.p. 188-189° (McGill)

McGill, X.R.4 Prog.Report, 1 June '43; SR7/4908.

Hex. + $\left.\begin{matrix}\oplus\\ MeNH_3\end{matrix}\right\}\overset{\ominus}{NO_3}$ in HOAc. Add $(EtCO)_2O$, then HNO_3.

Start at room temp. Temp. rises to 45°. Ppt. collected after 1 hr.

(10 g. from 14 g. Hex.).

McGill, X.R.4 Prog.Rep., 1 May '44; SR7/44/

C, H, and N analysis, and suggest structure.

Bristol, Res.Rep. 129, June '44; A.C.6486.

Methylolamine Nitrate $\xrightarrow[MeOH]{\text{ppt. with}}$ "Stabiliser compound"

1:3:5-Trimethyl-(6-ring) $\xrightarrow[NH_4NO_3]{CH_2O}$ "Stabiliser compound" 28%

Then add 70% aq. HNO_3

Formula $\left[CH_3(CH_2)_3\overset{\oplus}{N}_2\right\}\overset{\ominus}{NO_3}\Big]_x$ suggested from C, H, N and $\overset{\ominus}{NO_3}$ analysis.

Suggest x = 2; compound is probably 1:5-dimethyl-(Hex.)-1:5-dinitrate.

Compound gives a picrate, m.p. 211-213° (1:5-Dimethyl-(Hex.)-1:5-dipicrate)

McGill, X.R.4 Prog.Rep., 1 July '44; SR7/44/2740.

H.18 + $MeNH_3NO_3$ $\xrightarrow[10\text{ cc. HOAc}]{20\text{ cc. }(EtCO)_2O}$ BCX

1 g. 0.5 g. at 45-50° for 45 mins. 82%

Para. 180A

BCX (Continued)

X.R.4 Proj., C.E.R. Extramural Summary 21, June-Aug. '44; SR7/44/3156.

$$\text{H.18} \xrightarrow[\text{in EtOH}]{\text{MeI}} \text{1:5-Dimethyl-(Hex.)-1-nitrate-5-iodide}$$

(m.p. 197-202°).

$$\xrightarrow[\substack{\text{aq.}\\ \text{EtOH}}]{AgNO_3} \text{BCX} \xrightarrow[\text{acid}]{\text{picric}} \text{BCX picrate.}$$

(These reactions are under independent investigation in Bristol).

McGill, X.R.4 Prog.Rep., 1 Sept. '44; SR7/44/3596

The picrates made by the 3 methods are identical (X Rays).

DERIVATIVES OF ETHYLENEDIAMINE

$$NH_2 - CH_2 - CH_2 - NH_2$$

Para. 182

EDNA

$$\begin{matrix} NO_2 & & NO_2 \\ | & & | \\ NH - CH_2 - CH_2 - NH \end{matrix}$$

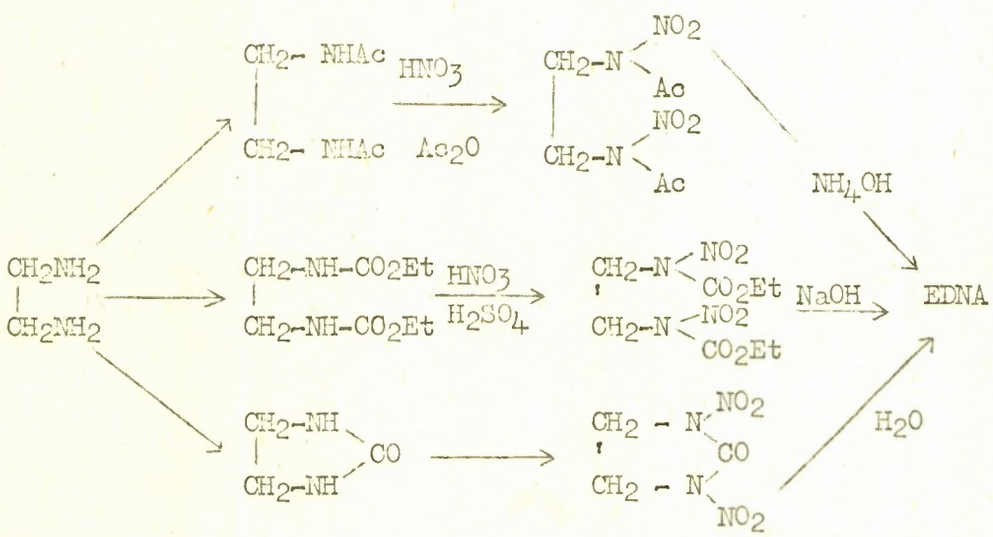
N:N'-Dinitroethylenediamine.

Ethylenedinitramine.

m.p. 177-179°

A review of the very extensive and specialised literature devoted to EDNA is outside the scope of this work.

Three methods of preparation from ethylene diamine are indicated by Haworth, Lamberton and Woodcock in their review (A.C.5053), Sheffield, Oct.'43.



Para. 183

N-Acetyl EDNA

$$\begin{matrix} & NO_2 & & NO_2 & \\ & | & & | & \\ Ac - N - CH_2 - & & CH_2 - & & NH \end{matrix}$$

Toronto, X.R.16, Canadian Exp. Res. Extramur. Summary, April '44;

SR7/44/1747.

$$EDNA + \text{aq. } CH_2O + NH_2Ac \xrightarrow{Ac_2O} \text{N-acetyl EDNA}$$

Para. 184

N.Hydroxymethyl-EDNA

$$HOCH_2 - \overset{NO_2}{\overset{|}{N}} - CH_2 - CH_2 - \overset{NO_2}{\overset{|}{N}}H$$

N-methylol-N:N'-dinitroethylenediamine.

N-Methylol-EDNA.

Cryst. from reaction mixt. m.p. 127-129°

(Hot organic solvents ——→ EDNA)

Can cryst. from AcMe-petrol.

Michigan, O.S.R.D. Rep. 820, 15 Aug. '42; SR7/2982.

Sheffield, Rep. 41, Feb. '44; A.C.5995.

$$EDNA \xrightarrow[100^\circ]{\text{aq. } CH_2O} \text{Methylol EDNA.}$$

(Characterised in Sheffield as morpholine derivative).

(From EtOAc, m.p. 128-130°).

Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

$$EDNA + \text{aq. } CH_2O + NO_2NH_2 \xrightarrow[\& \text{ cool}]{0^\circ} \text{methylol EDNA} \quad 67\%.$$

(The NH_2NO_2 is not necessary for this preparation).

Para. 185

N:N'-Bismethylol-EDNA

$$HOCH_2 - \overset{NO_2}{\overset{|}{N}} - CH_2 - CH_2 - \overset{NO_2}{\overset{|}{N}} - CH_2 - OH$$

Sheffield Rep. 41, Feb. '44, A.C.5995.

Not isolated from EDNA + CH_2O aq. but:-

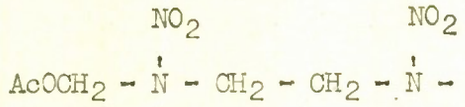
Dimorpholine derivative isolated; m.p. 170-171°(from EtOAc).

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984, considers this compound as an intermediate in the preparations on pp. 186 to 190.

e.g. the preparation of Homo RDX.

Para.186

N:N'-Bis(acetoxymethyl)-EDNA



From EtcH - Petrol. m.p. 83°.

Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

EDNA + aq. CH_2O + NH_2NO_2 —(15 Ac_2O; start at 25°; let temp. rise)→ N:N'-Bisacetoxymethyl-EDNA. 33%.

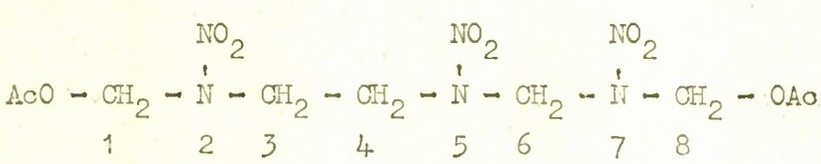
(the NH_2NO_2 is not necessary for this preparation).

(Called "bisacetoxymethylene EDNA" in Canadian Rep.).

EDNA + $2CH_2O_{aq}$ —(Ac_2O; NaOAc; 65°; 1 hr. Stand for 12 hrs. at 25°)→ Bisacetoxymethyl-EDNA. 61%.

Para.187

1:8-Diacetoxy-2:5:7-trinitro-2:5:7-triazaoctane

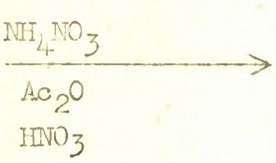


m.p. 98°

Ppt. from AcMe by Petrol.

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984.

Methylene-bis-(3:6-dinitro-1:3:6-triazacycloheptane) (sup. 190)



above compd. + "homo RDX"

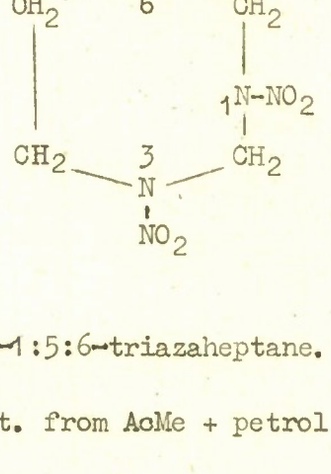
(see p. 188)

Separation by fractional pptn.

Para.188

Homo-RDX

Hepta-RDX



1:3:6-Trinitrocyclo-1:5:6-triazaheptane.

Ppt. from AcMe + petrol m.p. 165°

Toronto, X.R.16 Rep., 31 Jan. '44, SR7/44/984.

Methylene-bis-(3:6-dinitrocyclo-1:3:6-triazaheptane) (see p. 190)

$\xrightarrow[HNO_3 \text{ at } 0^\circ]{20 \text{ moles}}$ Homo RDX.

Also from same starting material, using

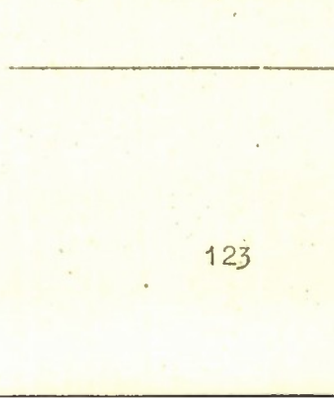
$NH_4NO_3 + Ac_2O + HNO_3 \longrightarrow$ Homo RDX +

1:8-Diacetoxy-2:5:7-trinitro-2:5:7-triazaoctane

(see p. 187)

Para.189

3:6-Dinitro-1-methylcyclo-1:3:6-triazaheptane



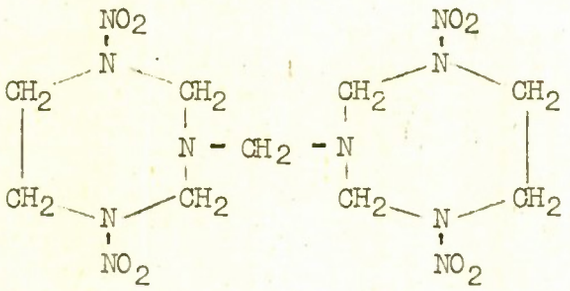
From EtOAc, m.p. 159°

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984.

EDNA + aq. $CH_2O + CH_3NH_2 \longrightarrow$ above compd. in 83% yield on EDNA (presumably via 1:4-Bismethylol-EDNA)

Para.190

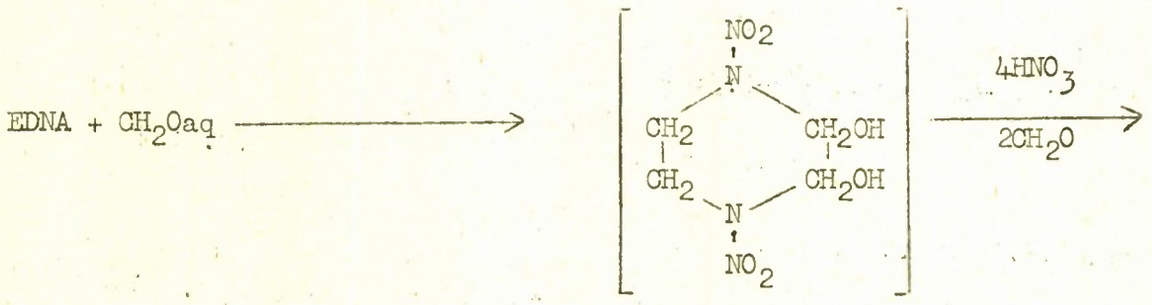
Methylene-bis-(3:6-dinitrocyclo-1:3:6-triazaheptane)



m.p. 205°

Ppt. from AcMe by petrol.

Toronto, X.R.16 Rep., 31 Jan. '44, SR7/44/984.



(presumed, not isolated)

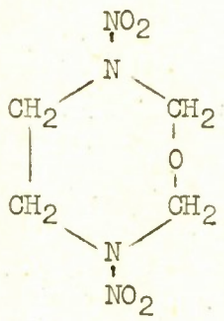
methylene-bis-(3:6-dinitrocyclo-1:3:6-triazaheptane)

63 per cent yield on EDNA.

Para.190A

3:6-Dinitrocyclo-1-oxa-3:6-diazaheptane

Homo-Cyclonite Oxide



From AcMe - petrol. m.p. 154-155°

Sheffield, Rep. 41, Feb. '44; A.C.5995.

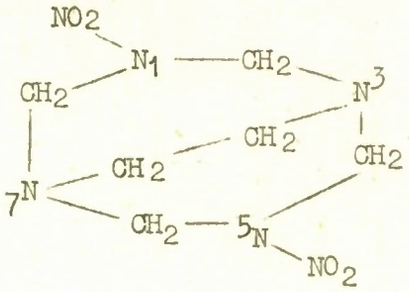
Methylol-EDNA 5 g. —heat, 140-145°, 1 hr.→ above compd. 0.9 g.

Toronto, X.R.16 Rep., 1 Sept. '44; SR7/44/3158.

EDNA + aq. CH_2O (+ NH_2NO_2) —run at 25° and add 15 Ac_2O, digest at 165° (20 mins.) and dilute.→ above compd. 23%

Para.191

1:5-Dinitro-3:7-endoethylene-(8-ring)



m.p. 140°

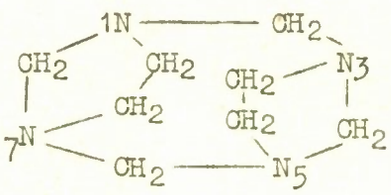
From AcMe.

Toronto, X.R.16 Rep., 31 Jan. '44; SR7/44/984

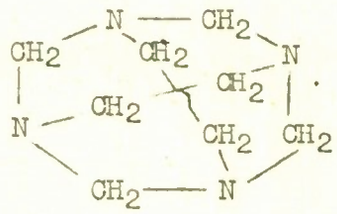
Solution of $NH_2.NO_2$ in CH_2O aq $\xrightarrow{NH_2CH_2CH_2NH_2}$ 1:5-dinitro-3:7-endoethylene-8-ring. 45% yield.

Para.192

OMTA



or



"Octamethylene tetramine"

(1:7)-(3:5)-or (1:5)-(3:7) - Bisendoethylene-(8-ring).

m.p. 196°

Bischoff, Ber., 1898, 31, 3254.

Cornell, Div.8 Int.Rep.R.R.C.16, April '44; SR7/44/1543.

Ethylenediamine + CH_2O ⟶ OMTA.

Para. 193

DERIVATIVES OF TRIMETHYLENE DIAMINE

$NH_2 - CH_2 - CH_2 - CH_2 - NH_2$

Para. 194

TMDNA

$NO_2 \quad\quad\quad\quad NO_2$

$NH - CH_2 - CH_2 - CH_2 - NH$

Trimethylene dinitramine.

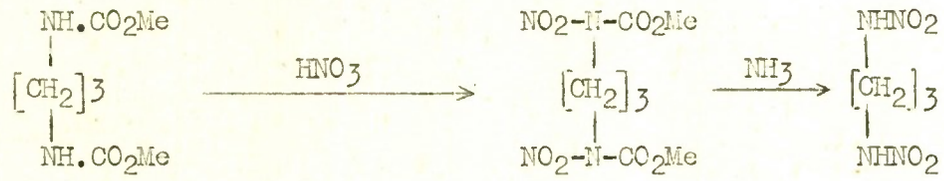
N:N'-Dinitrotrimethylenediamine.

Cryst. from H_2O or (ether + MeOH + petrol) m.p. 67°

Franchimont and Klobbie, Rec.Trav.chim., 1888, 7, 347.

Michigan, O.S.R.D. Rep. 820; 15 Aug. '42; SR7/2982.

Sheffield, Rep. 41, Feb. '44, A.C.5995.



Para. 195

N:N'-Bismethylol-TMDNA

$HOCH_2 - N(NO_2) - CH_2 - CH_2 - CH_2 - N(NO_2) - CH_2OH$

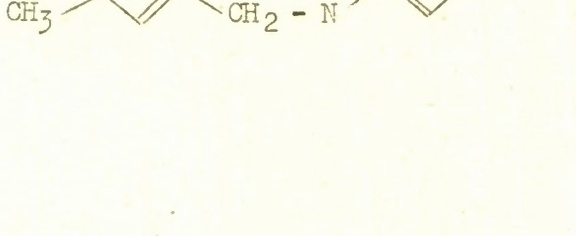
Cryst. from reaction mixture. m.p. 88-92°.

Sheffield, Rep. 41, Feb. '44; A.C.5995.

TMDNA + warm aq. CH_2O ⟶ N:N'-Bismethylol-TMDNA.

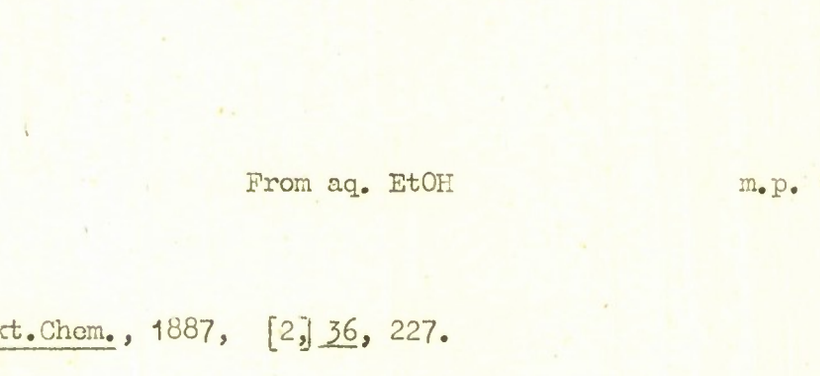
Dimorpholine derivative (from EtOAc), m.p. 130-132°.

DERIVATIVES OF TRÖGER'S BASE



Para. 197

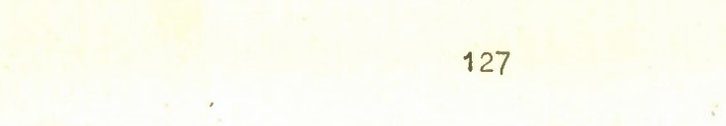
Tröger's Base



From aq. EtOH m.p. 135-136°

Tröger, J.prakt.Chem., 1887, [2] 36, 227.

Spielman, J.A.C.S., 1935, 57, 583.

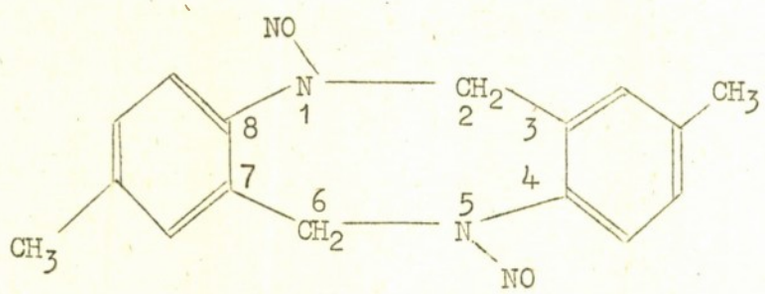


Tröger's Base

Tröger's Base gives a picrate (from EtOH), m.p. 188-9°.

Para. 198

"Dinitroso - Tröger's Base"



1:5-Dinitroso-(3:4)-(7:8)-Bis(1'-methylbenzo-4':5')cyclo-1:5-diazaoctane.

From HOAc or $\emptyset CH_3$ m.p. 254-5°

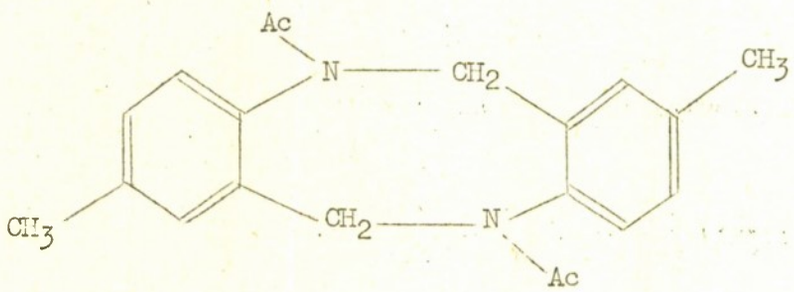
Tröger, loc. cit. see p. 197

Spielman, loc. cit. see p. 197

Tröger's Base in dil.HCl $\xrightarrow{NaNO_2}$ Dinitroso derivative.

Para. 199

"Diacetyl-Tröger's Base



ppt. from HOAc by H_2O. m.p. 286-8°

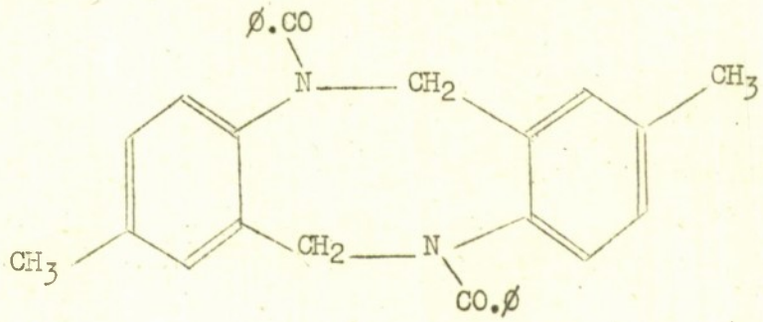
Tröger, loc.cit. see p. 197

Spielman, loc.cit. see p. 197

Tröger's Base $\xrightarrow[\text{boil}]{Ac_2O}$ di-Ac derivative.

Para. 200

"Dibenzoyl-Tröger's Base"



From $ØCH_3$ - EtOH, m.p. 290-1°

Tröger, loc.cit. see p. 197

Spielman, loc.cit. see p. 197

Tröger's Base in pyridine $\xrightarrow{ØCOCl}$ Di-ØCO derivative.

MISCELLANEOUS SUBSTANCES OF UNCERTAIN CONSTITUTION

Para. 202

"Methylolamine nitrate"

Possibly a mixture of $HOCH_2-\overset{\oplus}{N}H_3\ \}\ \overset{\ominus}{N}O_3$ + $(HOCH_2)_2\overset{\oplus}{N}H_2\ \}\ \overset{\ominus}{N}O_3$ +

$(HOCH_2)_3\overset{\oplus}{N}H\ \}\ \overset{\ominus}{N}O_3$ + $CH_2(\overset{\oplus}{N}H_3\ \}\ \overset{\ominus}{N}O_3)_3$

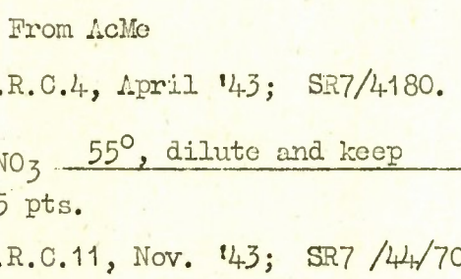
Bristol, Res.Rep.129, June '44; A.C.6486.

CH_2O + solid NH_4NO_3 ⟶ clear liquid "methylolamine nitrate"

Paras. 203, 204

P.S.1

Probably



3:7-Dinitrocyclo-1:5-dioxo-2:4:6:8-tetramethylene-3:7-diamine

m.p. 259-264° (Penn.State).
263-264° (Toronto).

From AcMe

Penn.State, Div.8 Int.Rep.R.R.C.4, April '43; SR7/4180.

Hex. + NH_4NO_3 + HNO_3 —55°, dilute and keep⟶ P.S.1.
60 pts. 75 pts.

Penn.State, Div.8 Int.Rep.R.R.C.11, Nov. '43; SR7 /44/70.

HADN —HNO_3, NH_4NO_3 at 30°; keep at 15°-20° for 168 hrs., then drown out.⟶ P.S.1.

14.5 g./m.Hex.

Analysis suggests $(CH_2 - \overset{NO_2}{\overset{|}{N}} - CH_2 - O)_x$

Toronto; U.S.A.-Canada-RDX Committee Meeting, April '44; SR7/44/1594.

$CH_2(NHNO_2)_2$ —aq. CH_2O⟶ white amorphous material, probably having constitution:-

MEDNA

$$HN(NO_2) - CH_2 - N(NO_2) - CH_2\left[O - CH_2 - N(NO_2) - CH_2 - N(NO_2) - CH_2\right]_n - OCH_2 - N(NO_2) - CH_2 - NH(NO_2)$$

$0 < n < 1$

Toronto, X.R.16 Project, Canadian Exp.Res.Extram.Summary 20, May-June '44, SR7/44/2426.

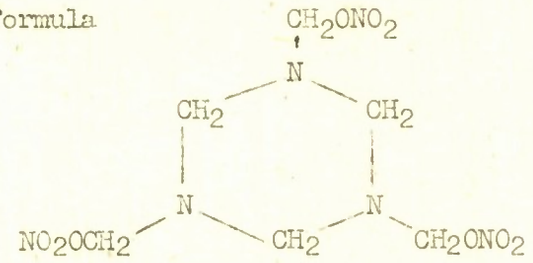
Regard (1) Above compound ≡ P.S.1 and
(2) above constitution as wrong.

Para. 204

P.S.I. (Continued)

Toronto, X.16 Proj., RDX Committee (U.S.A. and Canada) Meeting 26 May, '44; SR7/44/2801.

Suggest formula



Toronto, X.R.16 Prog.Rep., 1 Sept. '44; SR7/44/3158, abandon above and suggest much more likely structure, 3:7-Dinitrocyclo-1:5-dioxo-2:4:6:8-tetramethylene-3:5-diamine.

HADN $\xrightarrow[9.5\ HNO_3;\ 70^\circ \text{ for } 168 \text{ hrs.}]{6NH_4NO_3}$ P.S.1. (16%). (40% DPT by neut. of aq. filtrate).

$NH_2NO_2 + 2CH_2O$ aq. at 0°, then evap. at 12 mm. and heat at 100° at 12 mm. ⟶ P.S.1. (16%).

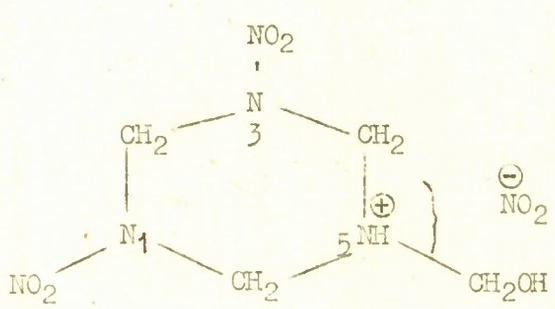
DPT $\xrightarrow[50^\circ \text{ for } 5 \text{ mins.}\ 11^\circ \text{ for } 11 \text{ days. Drown.}]{6NH_4NO_3;\ 10\ HNO_3}$ P.S.1. (12%).

Para. 205

$C_4H_{10}N_6O_7$

"Methylol-PCX-nitrite"

Probably



1:3-Dinitro-5-methylol-(6-ring)-5-nitrite.

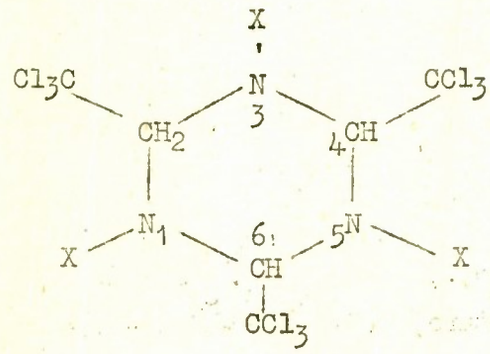
From reaction mixture. m.p. 168°.

Bristol, June '44, Dr. J. K. N. Jones, private communication.

Nitroso-PCX (Dinitronitroso-(6-ring)) $\xrightarrow{Cl.CH_2OMe}$ $C_4H_{10}N_6O_7$.

Para. 206

1:3:5-Tri(X)-2:4:6-Tris(trichloromethyl)-(6-ring)



X = CO_2Et, m.p. 143°.

X = CHO, m.p. 193°.

X = Ac, m.p. 207°.

X = CØ, m.p. 142°.

The compounds prepared by Moscheles, Ber., 1891, 24, 1803, from "chloral-ammonia" and recorded as Cl_3C-CH-N-X probably have the above constitution.

Para. 207

"Bristol Chloro-Compound"

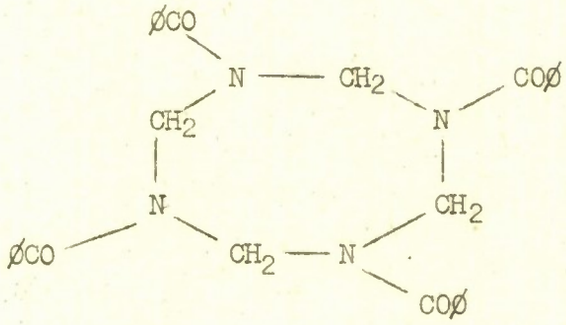
From HOAc. m.p. 218°.

Bristol, July '44 (Dr. J. K. N. Jones, private communication).

ØCOCl on Hex., pH 1.5 ⟶ compd. $(ØCO\text{-}N\text{-}CH_2)_x$ (sol. in MeOH) + Cl containing compd. (insol. in MeOH).

Para. 208

1:3:5:7-Tetrabenzoyl-(8-ring) ?



From MeOH. m.p. 225°.

Bristol, July '44 (Dr. J. K. N. Jones, private communication).

ØCOCl on Hex. at pH 1.5 ⟶ above compd. + chlorocompd. sepd. by MeOH extraction, which dissolves above compd.

Not triØCO-(6-ring).

Certainly analysis fits $(ØCO\text{-}N\text{-}CH_2)_x$.

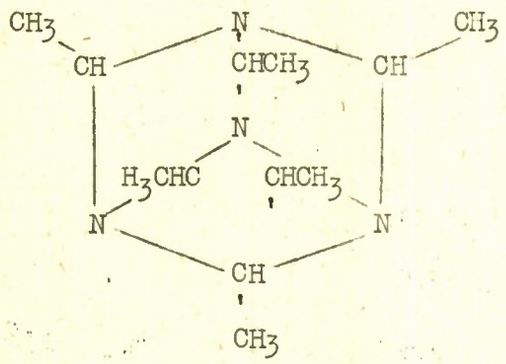
From M.W. in camphor, x = 2.

Para. 209

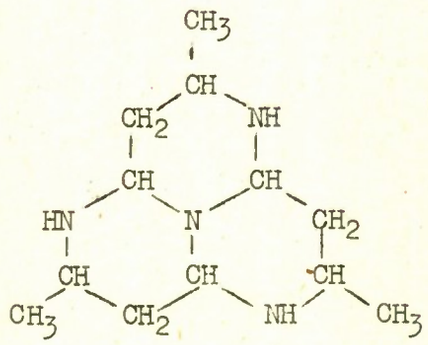
"Hexaethylidenetetramine"

or Tricrotonylidenetetramine

$C_{12}H_{24}N_4$



or, more probably



(Kudernatsch, Monatsh., 1900, 21, 137).

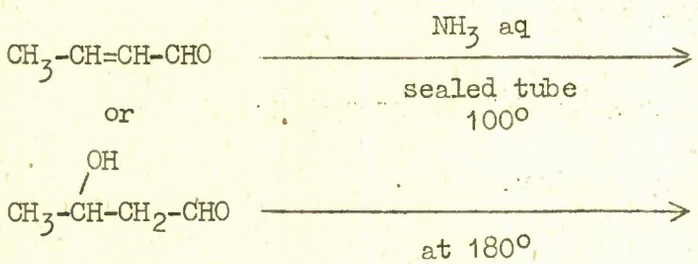
Cryst. from H_2O (+ $3H_2O$)

m.p. 96°

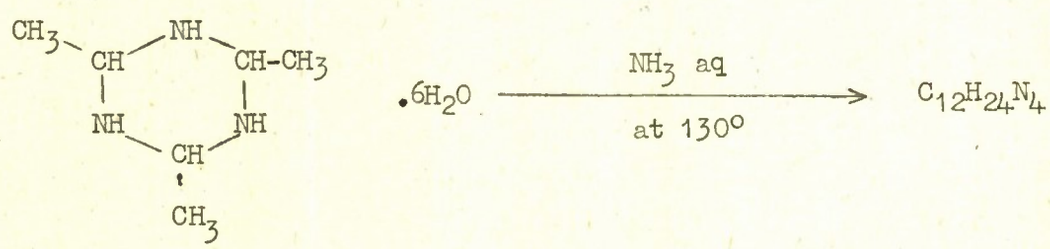
(Delépine, Comptes rendus, 1907, 144, 855: Bull. Soc.chim., [4], 1, 594.)

Loses $3H_2O$ and solidifies at 100°. m.p. (anhydrous) 102°.

Würtz., Comptes rendus, 1879, 88, 1154: Bull.Soc.chim., [2], 34, 486.



Kudernatsch, loc.cit.

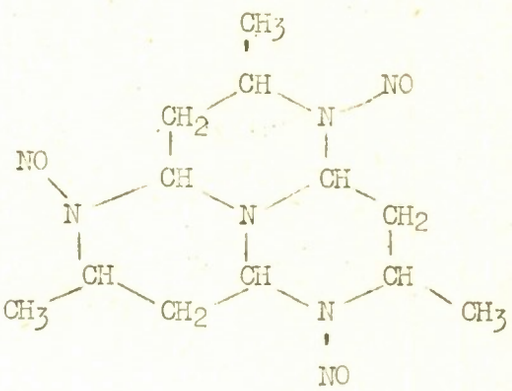


(See Bristol Res. Rep. 134, Aug. '44; A.C.6871).

Para. 210

$C_{12}H_{21}O_4(NO)_3$

Probably



m.p. 210-212°.

Kudernatsch, Monatsh., 1900, 21, 137.

Delépine, Comptes rendus, 1907, 144, 855.

$$C_{12}H_{24}N_4 \xrightarrow[HCl]{NaNO_2} C_{12}H_{21}N_4(NO)_3$$

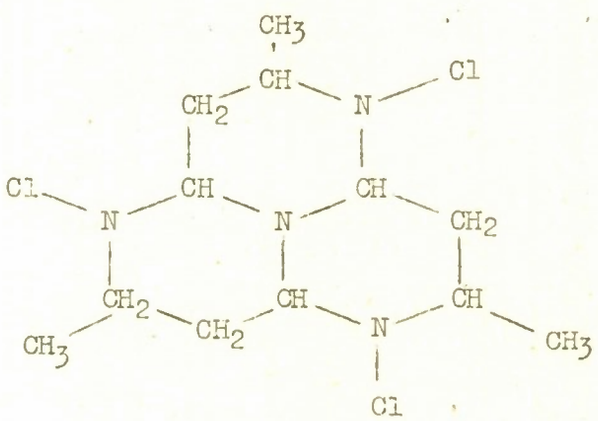
(either by Würtz
or Kudernatsch prepn)

Bristol, Res. Rep. 134, Aug. '44; A.C.6871: checked preparation and analysis.

Para. 211

$C_{12}H_{21}N_4Cl_3$

Probably



Detonates at 70°.

Delépine, Comptes rendus, 1907, 144, 855.

$$C_{12}H_{24}N_4 \xrightarrow{NaOCl} C_{12}H_{21}N_4Cl_3$$

Para. 212

H.4

See Univ.Penn., O.S.R.D.Rep.1733, July '43; SR7/43/448.

$$\text{H.2} \xrightarrow[\text{then picric acid}]{\text{alc. KOH}} \text{H.4}$$

(See p. 170)

H.4 is probably a mixture of H.3 (See p. 173) and potassium picrate.

Para. 213

H.9

m.p. 233-238°.

Harvard, N.D.R.C.Rep., Oct. '42; SR7/3263.

$$\text{H.8} \xrightarrow[0^\circ \rightarrow 25^\circ]{HNO_3 - Ac_2O \text{ at}} \text{H.9}$$

(See p. 141)

H.9 is very probably a mixture of intermediates in the exchange of 4 Ac of H.8 for the 4 NO_2 of HMX. (Univ.Penn.O.S.R.D.1733 Rep., July '43; SR7/43/448).

Para. 214

H.11

m.p. 225-244°.
'not identical with H.9'.

Harvard, N.D.R.C.Rep., Oct. '42; SR7/3263.

$$\text{H.9} \xrightarrow{HNO_3} \text{H.11 (looks as if one} > \text{N-Ac gives one} > \text{N-NO}_2\text{)}.$$

(See p. 213)

H.11 is probably a mixture like H.9, but richer in NO_2 groups.
(Univ.Penn.O.S.R.D.Rep.1733, July '43; SR7/43/448).

Para. 215

H.13

'an intractable oil'.

See Univ.Penn.O.S.R.D.1733 Rep., July '43; SR7/43/448.

H.6 in $CHCl_3$ $\xrightarrow[\text{with ether}]{AcONO_2;\ \text{reflux and drown}}$ H.13

(See p. 151)

H.13 ⟶ a picrate similar to H.3 (p. 173) but probably not identical with H.3.

Para. 216

H.14

H.6 P.

m.p. 164-165°.

Univ.Penn., O.S.R.D., Rep.1733, July '43; SR7/43/448.

H.6 $\xrightarrow[\text{picric acid}]{\text{EtOH}}$ H.14

(See p. 151)

C and H analysis indicates that the compound is not a simple picrate of H.6, but is derived from fragments of H.6 plus picric acid: Found, C, 35.5; H, 3.5; picryl, 74.6; Ac, 11.2%.

(Compare

DNPT $\xrightarrow{\text{picric acid}}$ P.S.2 ($Me - (\overset{\oplus}{Hex})$ picrate$^{\ominus}$)

(See p. 166).

Para. 217

H.15

'a solid'.

See Univ.Penn. O.S.R.D.1733 Rep. July '43; SR7/43/448.

$$\text{H.6} \xrightarrow[\text{in boiling } CHCl_3]{AcONO_2} \text{H.15 in small amount.}$$

(See p. 151)

Might be a nitrate analogue of H.13. (p. 215). Not investigated.

Para. 218

H.22

From HOAc, m.p. 181-182°.

Univ.Penn., Div.8 Int.Rep., R.R.C.5, May '43; SR7/4766.

$$\underset{(7\text{ g.})}{\text{H.18}} \xrightarrow[\text{at } 18^\circ]{1 \text{ mol } AcONO_2} \underset{(1.8\text{ g.})}{\text{H.22 + small amt. DPT.}}$$

(See p. 167)

Structure still unknown, Univ.Penn., O.S.R.D.Rep.1733, July '43; SR7/43/448.

Para. 219

H.27

Ppt. by H_2O from reaction mixture. m.p. ca 140°.

Univ.Penn.Div.8 Int.Rep.R.R.C.8, August '43; SR7/43/391.

$$\text{Hex. in HOAc} + \xrightarrow[1 \text{ mole } NH_4NO_3]{3 \text{ moles } AcONO_2} \text{H.27.}$$

Not stable and not yet purified.

Constitution still unknown, Univ.Penn., Div.8 Int.Rep. R.R.C.11, Nov. '43; SR7/44/70.

Para. 220

L.M.X.

McGill X.R.4 Prog.Report, June '43; SR7/4908.

Repeat BCX preparation (p. 180) using NH_4NO_3 for $MeNH_3NO_3$ ⟶ unstable low melting material, soluble in AcMe, called L.M.X. (9 g. from 14 g. hex.).

Para. 221

I.S.X.

m.p. 156-158°.

McGill X.R.4 Prog.Rep. June '43; SR7/4908.

$$\text{L.M.X.}(5.5\text{ g.}) \xrightarrow[\text{solution}]{\text{boil acetone}} CH_2O + \text{I.S.X.}\ (2.5\text{ g.})$$

I.S.X. insoluble in AcMe, Ph.H, ether, dioxan, MeOH, EtOH, $CHCl_3$.

Para. 222

McGill compound

Wash with ether. Yellow viscous oil.

McGill, X.R.6 Rep.; 1 Feb. '44; SR7/44/578.

$$\text{PCX} \xrightarrow[\text{and cool to } -40^\circ;\ \text{filter at } < 0^\circ]{\text{pyridine, add at } 20^\circ} \text{filtrate = yellow oil.}$$

Para. 223

EDX

White amorphous solid. m.p. 225°.

RDX Committee (U.S.A. and Canada) Meeting, 26 May '44; SR7/44/2801:

(Toronto, X.R.16 Rep. 1 Sept. '44; SR7/44/3158).

Ross Reaction —(25°, 19 hrs.)→ 18% EDX. + 18% DPT. + 1.4% TEX. + 5.2% RDX(B).

EDX —(boiling Ac_2O)→ Residue → EDX(A), m.p. 281-296°. ($C_{11}H_{24}N_{15}O_{16}$).

EDX —(boiling Ac_2O)→ Cool filtrate → EDX(B), m.p. 232-234°. ($C_3H_6N_3O_4$).

MEDNA in $2CH_2O_{aq}$ —(2 NaOAc; 10 Ac_2O; start at 25°, run at 95° for 1 hr., cool, drown and neut. to pH.6.)→ EDX(A) (+ TEX)

Para. 224

Hex. Ethiodide By-Product

From MeOH. m.p. 154-156°.

Univ.Penn.Div. 8 Int.Rep. R.R.C.10, Oct. '43; SR7/43/925.

Hex. + EtI —(boiling MeOH)→ first crop Et - (Hex)$^{\oplus}$ $I^{\ominus}$ m.p. 141-3°.

second crop m.p. 154-6°.

(See p. 167).

MELTING POINT IDENTIFICATION LIST

The "melting-points" recorded for many of the compounds in the Hexamine - RDX series are decomposition points and are, to some extent, functions of the rate of heating. Moreover, it is not always clear whether reported m.p.'s are corrected or not*. Nevertheless, the melting point of a member of the series, determined in the usual way, is often a very useful guide to the identification of the compound.

A list is, therefore, given of the compounds treated in this review, in order of rising melting point. The arrangement is in three columns and is such that one may read off the m.p., the description of the compound, and the paragraph of the review dealing with the compound.

Melting points listed with large ranges, and marked with an asterisk, indicate that the given substance melts (or decomposes) fairly sharply at some specific temperature within the range, this temperature being a function of the rate of heating.

Melting points listed with short ranges (and not marked by an asterisk) indicate that the substance melts over the range in question.

The following compounds are liquids at room temperatures.

Boiling point (°C)	Designation of Compound	Para.
48°/15 mm.	P.1	8
85°/760 mm.	Tetramethyl-(3-chain)	45a
89°/9 mm.	P.2	9
95°/35 mm.	Nitrosoparaldimine	120
115°/15 mm.	Methylene bis piperidine	45a
153-156°/12 mm.	Bisacetoxymethylnitramine	15b
166°/760 mm.	1:3:5-Trimethyl-(6-ring)	111
166-169°/760 mm.	TEMD	40a
———	N:N'-Bisethoxymethyl-MEDNA	34
———	Dimethylether of MEDNA	29
———	H.13	215
———	LMX	220
———	Methylolamine nitrate	202
———	McGill compound	223

* It is obviously desirable that recorded melting points should be corrected by standardisation of the thermometer and for "emergent column error". The use of the Thiele-Hershberg m.p. apparatus (Ind.Eng.Chem.(Anal.), 1936, 8, 307) with short range, Ansehutz type, thermometers, is to be recommended.

Solids at room temperatures

A. Melting points up to 100°

Melting point (°C)	Designation of Compound	Para.
38	Methyl nitramine	12
43	Thialdine	122
51-2	DINA	16
54	Methylolacetamide	19
57	Dimethylnitramine	13
59-60	Bisnitroxymethylnitramine	15a
63	Diacetyl-MEDNA	29a
67	TMDNA	194
68-72	Bismethylol-MEDNA	30
70	Trimethylcyclo-1-thio-2:4:6-trimethylene-3:5-diamine:$2H_2O$	122
70 (detonation)	$C_{12}H_{21}N_4Cl_3$	211
72-75	Nitramine	11
78	Dichloro-(P.T.)	149
78	Trichloro-(6-ring)	108
79-80	Bismethoxymethyl-MEDNA	33
80	Bisethoxymethyltrinitro-(5-chain)	69
83	Bisacetoxymethyl-EDNA	186
84-6	Morpholine derivative of methylmethylol-nitramine	14
85	2:4:6-Trimethyl-(6-ring)	113
87	H.32	61
88-92	Bismethylol TMDNA	195
94-96	H.31	60
96	$C_{12}H_{24}N_4 \cdot 3H_2O$	209
97-9	Cyclonite Oxide	118
98	Diacetoxytrinitrotriazaoctane	187
98-99	PCX (HOX)	95
98-101	COX	31
99	Nitrodicyclohexyl-(6-ring)	104

(B) Melting points 100°-150°

Melting point (°C)	Designation of Compound	Para.
102	Tricarbethoxy-(6-ring)	110
102	MSX-Me (H.25) (Univ. Penn.)	55
102	$C_{12}H_{24}N_4$	209
102	2ATX:AcMe	66
103	MEDNA	25
103-4	TEX	32
104	"104"	67
105-6	-tris(trichloromethyl)-(6-ring)	116
105-6	Trinitroso-(6-ring)	106
107	"107"	68
108	1:7-Dinitro-3:5-dimethyl-(8-ring)	138a
108-110	Methylolbenzamide	20
109	Nitrodibenzyl-(6-ring)	105
109-110	MSX-Et (H.24)	56
114	Dinitroethoxymethyl-(6-ring)	102
114-115	MSX-Me (H.25) (A.R.D.)	55
115	EtHX	134
116	Furfurylidenenitramine	23
116-117	H.33	62
120	P.2.HX	132a
124	Dinitrodimethyl-(8-ring)	138
125	MSX + BSX mixture	52 & 65
ca 125	Diammonium salt of MEDNA	27
127-9	Methylol-EDNA	184
128	Dinitromethoxymethyl-(6-ring)	101
128-130	Morpholine deriv. of Methylol-EDNA	184
128-130	Nitroso H.19	155
129	Dinitro-(5-chain)nitrate	47
129	Tert. butyl HX	135
130-1	CMX	49
130-2	Dimorpholine deriv. of Bismethylol-TMDNA	195
131	Methylene bisurethane	44

(B) Melting points 100°-150° (Contd.)

Melting point (°C)	Designation of Compound	Para.
133	H.17	152
133-4	H.28	58
134	Bis(m-nitrobenzylideneamino)-(P.T.)	150
134-5	Bismethyloltetranitromethyl-(9-chain)	82b
135	H.6 picrate	152a
135	H.29	168
135-6	Tröger's Base	197
136	Methylol-PCX (PCX(A))	100
136-8	Hex. nitrourethane	162
136-9	MSX nitrate	54
138-9	MeHX	133
139-140	Tris(salicylideneamino)-(6-ring)	107
140	Dinitroendoethylene-(8-ring)	191
140-2	OFX	57
ca 140	H.27	219
141-3	Hex. ethiodide	167
142	Methylene bisformamide	35
142	1:3:5-Tribenzoyl-2:4:6-tris(trichloro-methyl)-(6-ring)	206
142-3	H.19	154
143	1:3:5-Tricarbethoxy-2:4:6-Tris(trichloro-methyl)-(6-ring)	206
145-7	GSX	70
147-152	MSX + H.28 mixture	53, 58, 59

(C) Melting points, 150-200°

Melting point (°C)	Designation of Compound	Para.
150	Chloralbenzamide	21
150	H.26	179
150-1	Dinitrodibenzyl-(8-ring)	139
150-5	β Tris(trichloromethyl)-(6-ring)	116
154	ATX (NBSX)	66
154-5	Dinitrocyclooxodiazaheptane	190a
154-5	Unidentified by-product in Hex. ethiodide preparation	167 & 224
154-162	Crude Methylene bis(dinitro-(6-ring))	104a
155	MSX (H.21)	51
155-6	BSX	63
156	TAX	98
156-7	PHX	132
156-8	ISX	221
157	H.16 (WRX)	82
157	H.8	141
157-8	Benzoic H.3	176
158-9	Benzoic H.2	175
158-168*	HAMN	159
159	Dinitromethylcyclotriazaheptane	189
160-180*	H.5	174
161	Trinitrosotrimethyl-(6-ring)	114
162	HADN	177
164-5	H.14 (H.6 P)	216
165	Homo-RDX	188
166-7	Bisethoxymethyltetranitro-(7-chain)	81
166-8	Hex. ethopicrate (P.S.2(Et))	169
168	Nitroso-PCX	96
168	Methylol-PCX nitrite	205
168-183*	H.2	170
169	Ethylidene bisacetamide	38

(C) Melting points, 150-200° (Contd.)

Melting point (°C)	Designation of compound	Para.
170-1	Dimorpholine derivative of bismethylol-EDNA	185
175 (leaves residue)	Dinitroendoethylidene-(8-ring)	147
175-185	Trinitromethyl-(6-ring)	115
177	Ø-urethane of methylolbenzamide	20
177-9	EDNA	182
178-9	Hex. picrate	160
180-1	H.6 methiodide	155a
181	QNX	136
181-2	H.6 methonitrate	155a
181-2	H.22	218
182-3	Bismethoxymethyltetranitro-(7-chain)	80
182-3	Methyloldibenzoyl-(3-chain)	41
187	AcAn	76
187	Tris(benzamidomethyl)amine	22
187-8	Ethylidene bisbenzamide (also given as m.p. 202-4°)	42
188-9	H.201	172
188-9	Troger's Base picrate	
188-9	BCX (stabiliser compound) McGill m.p. (Bristol m.p. 193°)	180
190	H.3	173
190	H.18 (H.20) (H.1)	164
190	Hex. methiodide	163
190-200	Crude RDX(B)	85
191	H.6 (DAPT)	151
192	H.23	156
193	Triformyltris(trichloromethyl)-(6-ring)	206
193	BCX (stabiliser compound) Bristol m.p. (McGill m.p. 188-9°)	180
195	Dimethyl-(PT) picrate	153
196	OMTA	192
197	H.7	36
197	Hex. styphnate	161
199	H.6 methopicrate	155a

(D) Melting points over 200°

Melting point (°C)	Designation of Compound	Para.
200-3°	Crude RDX	85
202-4	Ethylidene bisbenzamide (m.p. also given as 187-8°)	42
203-6	DPT	143
204-5	106	78
204-5	Pure RDX	85
205	Methylene-bis(dinitrocyclotriazaheptane)	190
207	Bis(cinnamylideneamino)-(PT)	150
207	Dinitroso-(P.T.)	148
207	Triacetyltris(trichloromethyl)-(6-ring)	206
210-2	$C_{12}H_{21}H_4(NO)_3$	210
210-5	P.S.2	166
211-2	"Stabiliser compound" picrate (BCX picrate)	180
213	Bis(salicylideneamino)-(P.T.)	150
218	"Bristol Chloro Compound"	207
218-20	H.10	37
219-230	MEDNA-CH_2O polymer	34a
220-1	Tribenzoyl-(6-ring)	109
220-230	P.S.1 Toronto m.p. (Penn.State m.p. 259-64°)	203
224	Nitroso-H.6	140
224-5	QDX (SEX)	130
224-6	Methylene bisbenzamide	40
225	EDX	223
225	Tetrabenzoyl-(8-ring) (?)	208
225-44*	H.11	214
226-7	Bis(benzylideneamino)-(P.T.)	150
232-4	EDX(B)	223
233-8	H.9	213
236-43*	MNX	129
244	DMTN	74

(D) Melting points over 200° (Contd.)

Melting point (°C)	Designation of Compound	Para.
254-5	"Dinitroso-Tröger's Base"	198
257	H.12	137
257	Trichloroethylidenebisbenzamide	43
259-64	P.S.1. Penn. State m.p. (Toronto m.p. 220-30°)	203
266-7	Tribenzoyl-(5-chain)	71
281-2	HMX	124
281-296	EDX(A)	223
286-8	"Diacetyl-Tröger's Base"	199
290-1	"Dibenzoyl-Tröger's Base"	200

The following solid compounds have been isolated, and are discussed in the review, but, for the reasons indicated, the melting point data have not yet been recorded.

Compound	Behaviour	Para.
Acetyl-EDNA	No data yet	183
Bismethyloltetranitro-(7-chain)	Not yet specified; compd. unstable	75
Chlorotrimethylcyclodioxo-trimethyleneamine	Very unstable, deflagrates on drying	121
Diacetyltrichloromethyl-(3-chain)	Sublimes	39
H.15	No data yet	217
Hexamine	Sublimes	158
Hex:nitrate:acetate	Decomps. on warming ⟶ HAMN	178
K_2AcAn	No data recorded	73
K_2BSX	No data recorded	48
K CMX	No data recorded	50
MEDA salts	Hygrosc. and decomp. by H_2O (dinitrate deflagrates)	45
Methylenebismorpholine	No data yet	45a
Trinitro-(8-ring)-nitrate	No data yet	128

MONTHLY INTERIM REPORTS TO DIVISION 8, N.D.R.C. of O.S.R.D.

"Studies on RDX and Related Compounds"

These reports, covering the chemical work carried out in the U.S.A., have the (U.S.A.) designation R.R.C., followed by a serial number. The British "S.R.7" numbers are:-

R.R.C. No.	Date	SR7/ No.
1	Dec. '42 to Jan. '43	3748
2	Jan. to Feb. '43	3867
3	Feb. to March '43	4179
4	March to April '43	4180
5	April to May '43	4766
6	May to June '43	4879
7	June to July '43	43/197
8	July to Aug. '43	43/391
9	Aug. to Sept. '43	43/924
10	Sept. to Oct. '43	43/925
11	Oct. to Nov. '43	44/70
12	Nov. to Dec. '43	44/508
13	Dec. '43 to Jan. '44	44/915
14	Jan. to Feb. '44	44/952
15	Feb. to March '44	44/1236
16	March to April '44	44/1543
17	April to May '44	44/2047
18	May to June '44	44/2254
19	June to July '44	44/
20	July to Aug. '44	44/2833
21	Aug. to Sept. '44	44/3207
22	Sept. to Oct. '44	44/3502

CANADIAN EXPLOSIVES RESEARCH EXTRAMURAL SUMMARIES

(Research Projects of the Research and Development Sub-committee, Associate Committee in Explosives, National Research Council, Canada).

These give a clear review of the Canadian work and though, in the text of this Index, reference has been made rather to the University Progress Reports, the Extramural Summaries are probably the best means of tracking down work for which the direct Progress Report reference is not available.

Canadian Serial No.	Date	SR7/ No.
3	March to June '42	2349
4	June to Nov. '42	3608
5	Nov. to Dec. '42	3719
6	Dec. to Jan. '43	4309
7	Jan. to Feb. '43	4032
8	Feb. to March '43	4312
9	March to April '43	4546
10	April to May '43	4547
11	June to Sept. '43	43/774
12	Sept. to Oct. '43	43/848
13	Oct. to Nov. '43	43/1148
14	Nov. to Dec. '43	44/135
15	Dec. '43 to Jan. '44	44/
16	Jan. to Feb. '44	44/679
17	Feb. to March '44	44/1376
18	March to April '44	44/1747
19	April to May '44	44/2112
20	May to June '44	44/2426
21	June to August '44	44/3156

U.S.A. and Canada RDX Committee Meetings

The dates of the meetings since September 1942 and the SR7/numbers of the reports covering the meetings are

Date of meeting	SR7/number
4 Sept. '42	3319
1 Nov. '42	3440
19 Dec. '42	3665
10 April '43	4306
3 June '43	4956
7 Aug. '43	43/210
30 Sept. '43	43/1059
4 Dec. '43	44/299
5 Feb. '44	44/765
1 April '44	44/1594
26 May '44	44/2801
9 Sept. '44	44/

INDEX

This is a "Subject-Index". Each compound is listed under

(a) its "initial-designation";

(b) its popular or trivial name;

(c) its short systematic name.

It may be desirable to repeat that the "short systematic names" may be converted into the "full systematic names" by the following list of equivalents.

(3-chain) = lin-2-methylene-1:3-diamine = $\overset{1}{NH_2}$ - $\overset{2}{CH_2}$ - $\overset{3}{NH_2}$

(5-chain) = lin-2:4-dimethylene-1:3:5-triamine

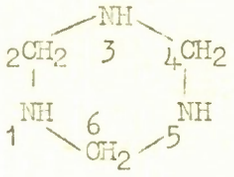
= $\overset{1}{NH_2}$ - $\overset{2}{CH_2}$ - $\overset{3}{NH}$ - $\overset{4}{CH_2}$ - $\overset{5}{NH_2}$

(7-chain) = lin-2:4:6-trimethylene-1:3:5:7-tetramine

= $\overset{1}{NH_2}$ - $\overset{2}{CH_2}$ - $\overset{3}{NH}$ - $\overset{4}{CH_2}$ - $\overset{5}{NH}$ - $\overset{6}{CH_2}$ - $\overset{7}{NH_2}$

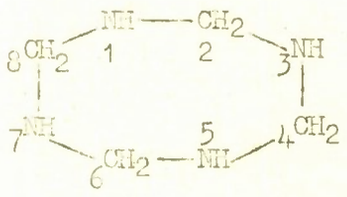
(6-ring) = cyclo-2:4:6-trimethylene-1:3:5-triamine

=

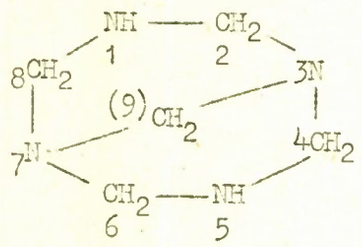


(8-ring) = cyclo-2:4:6:8-tetramethylene-1:3:5:7-tetramine

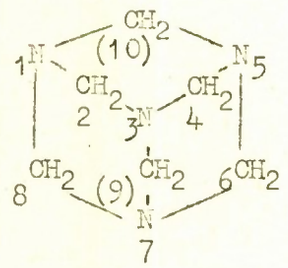
=



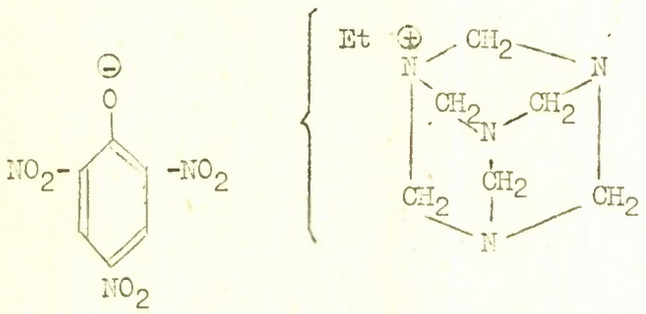
(P.T.) ≡ 3:7-endomethylene(9)cyclo-2:4:6:8-tetramethylene-1:3:5:7-tetramine ("pentamethylenetetramine")

≡ 

(Hex.) ≡ 1:5-endomethylene(10)-3:7-endomethylene(9)-cyclo-2:4:6:8-tetramethylene-1:3:5:7-tetramine. ("Hexamine").

≡ 

Thus the compound:-



is listed under the headings H.30; P.S.2(Et); "Hexamine Ethopicrate"; 1-ethyl-(Hex.)-1-picrate.

Under each of the names of a given compound is recorded (a) a list of all the other names of the compound (b) a full set of para. references. The paragraph number underlined is the main reference, being that of the paragraph dealing with the structure, physical properties and preparation of the compound: the other references are to paragraphs in which transformations of the compound are discussed.

Tröger's Base picrate; 197.

W

WRX; (H.16; 1:7-Bis(acetoxymethyl)-1:3:7-trinitro-5-acetyl-(7-chain));

78, 82, 94.

-

"104"; (1:5-Bis(methoxymethyl)-1:3:5-trinitro-(5-chain));

64, 67.

"106"; (1:7-Bis(nitroxymethyl)-1:3:5:7-tetranitro-(7-chain));

76, 78, 79, 80, 81, 88, 94.

"107"; (1-Ethoxymethyl-5-acetoxymethyl-1:3:5-trinitro-(5-chain));

64, 66, 68.

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Covering dates 1944
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