

May 18, 1954

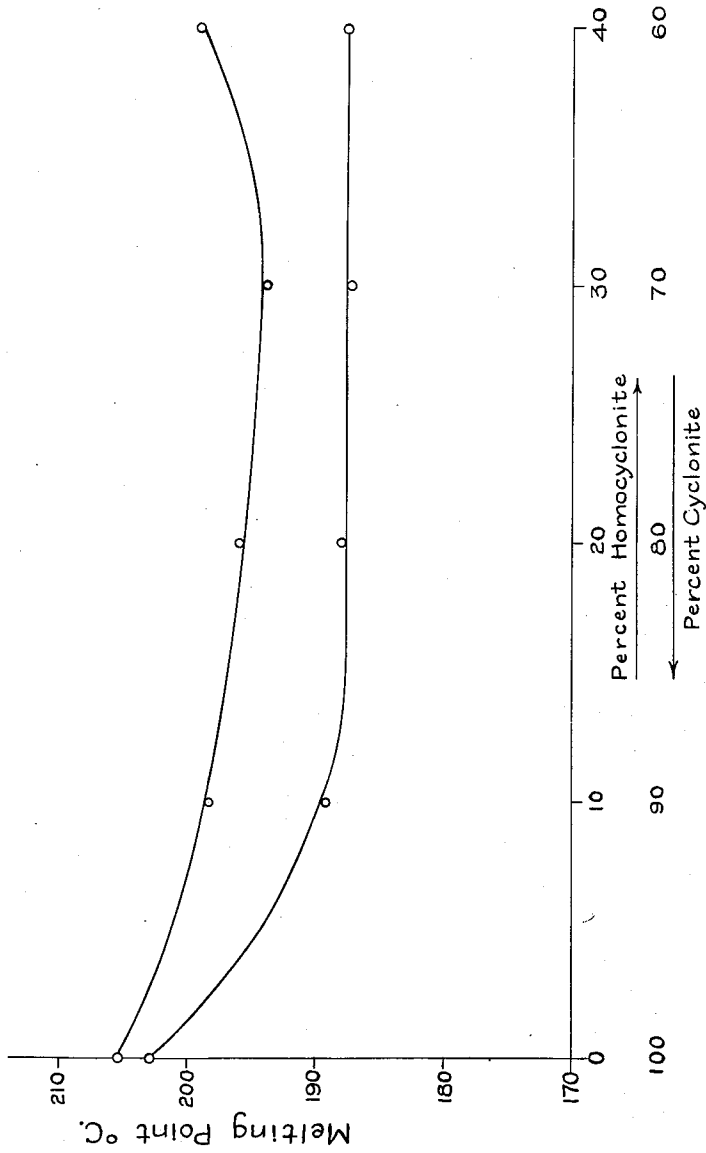
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2,678,927

NITRAMINES AND THEIR PREPARATION

Filed Oct. 27, 1944

PLATE III  
Mixed Melting Point Relations  
of Cyclonite and Homocyclonite  
up to 40% Homocyclonite



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# UNITED STATES PATENT OFFICE

2,678,927

## NITRAMINES AND THEIR PREPARATION

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Application October 27, 1944, Serial No. 560,704

2 Claims. (Cl. 260-248)

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The present invention relates to a new series of chemical compounds and methods of preparing the same. More particularly the invention is concerned with certain new nitramines and their preparation from readily available raw materials.

Broadly speaking, the object of the present invention is to provide a new series of polymethylene polynitramines suitable for various industrial purposes but of particular interest in connection with the production of military and industrial explosives.

A more particular object is the provision of a new cyclic polymethylene polynitramine having an eight-membered ring structure, said compound being equal to cyclonite in explosive power and brisance.

Another object is to provide a new and improved explosive of great power and brisance.

A further object is to produce a dinitro derivative of a bicyclic polymethylene polyamine and to convert this intermediate compound to various derivatives of interest as explosives, fuse powders and the like.

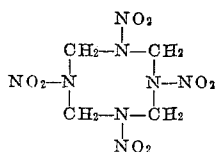
Another object is the provision of a number of alternative methods of preparing said bicyclic intermediate from various readily available raw materials.

Still another object is to provide a method of producing an explosive essentially comprising a mixture of cyclonite and an analogous, equally powerful polymethylene polynitramine having an eight-membered ring structure.

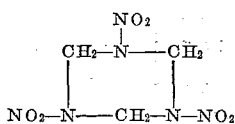
Other objects and advantages will become apparent as the invention is hereinafter more particularly described.

The subject matter of the present application is somewhat related to that of copending application Serial Number 444,254, filed May 23, 1942.

The novel cyclic polymethylene polynitramine with which the present invention is primarily concerned consists of cyclotetramethylenetetranitramine (I).



I (Homocyclonite)

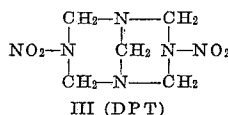


II (Cyclonite)

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In view of the close similarity of this new compound (I) to cyclonite (II), both in structure as well as in chemical and explosive properties, the eight-membered cyclic "homologue" (I) of cyclonite will hereinafter be designated by the trivial name "homocyclonite."

In accordance with one aspect of the present invention, homocyclonite (I) may be prepared by a variety of methods from an intermediate that is also a new chemical compound. The intermediate, in turn, may be prepared from readily available raw materials by a number of novel alternative methods to be described later. The intermediate in question consists of 3,7-dinitropentamethylenetetramine (III) (hereinafter referred to by the trivial designation, "DPT"), having the following probable structural formula:



This intermediate (DPT) may be converted either to homocyclonite, or to a mixture of cyclonite and homocyclonite or to certain linear polynitramines that are also of interest in the preparation of explosives of various types.

The various reactions involved in the preparation of the bicyclic intermediate (DPT), its conversion to the derivatives briefly mentioned above, and the properties of certain of the products will be hereinafter described with reference to the several plates attached hereto, wherein:

Plate I is a schematic representation of the reactions involved in the preparation of DPT;

Plate II is a schematic representation of the conversion of DPT to various end products, and

Plate III shown in the accompanying drawing is a plot of melting points versus composition, of a mixture of cyclonite and homocyclonite as produced in accordance with one aspect of the present invention.

As will be evident by reference to Plate I, DPT (III) may be prepared by neutralization of the mother liquors obtained in the nitrolysis of hexamine (IV). Alternatively, DPT may be prepared from hexamine dinitrate (V) by treatment with a carboxylic anhydride, or it may be produced synthetically by condensation of formaldehyde, nitramide (VI) and ammonia.

As indicated in Plate II, if the DPT obtained by any of the foregoing processes is treated with absolute nitric acid or with absolute nitric acid, ammonium nitrate and acetic anhydride, a novel explosive homocyclonite is produced, but with a solution of ammonium nitrate in concentrated nitric acid, a mixture of cyclonite (II) and homocyclonite (I) is produced. Moreover, if DPT is treated with a mixture of concentrated nitric acid and acetic anhydride an acetylated linear polynitramine (VIII) (hereinafter referred to by the trivial designation "AcAn") is formed. Furthermore, if DPT is treated with "106% nitric acid" (i. e., absolute nitric acid containing sufficient dissolved nitrogen pentoxide to titrate as apparently 106% acid), a linear polynitramine (VII) hereinafter designated by the trivial name "106" is formed. Lastly if 106 is treated with an alcohol, the nitroxy groups are replaced by alkoxy groups to form the corresponding ether (IX) which for convenience may be designated "106-E."

To summarize the foregoing reactions of DPT or its derivatives:

- (1)  $\text{DPT} + 98\% \text{HNO}_3 \rightarrow \text{Homocyclonite (I)}$
- (2)  $\text{DPT} + \text{HNO}_3 + \text{Ac}_2\text{O} + \text{NH}_4\text{NO}_3 \rightarrow \text{Homocyclonite (I)}$
- (3)  $\text{DPT} + \text{HNO}_3 + \text{NH}_4\text{NO}_3 \rightarrow \text{Homocyclonite (I) plus Cyclonite (II)}$
- (4)  $\text{DPT} + \text{HNO}_3 + \text{Ac}_2\text{O} \rightarrow \text{AcAn (VIII)}$
- (5)  $\text{DPT} + 106\% \text{HNO}_3 \rightarrow 106 \text{ (VII)}$
- (6)  $106 + \text{ROH} \rightarrow 106\text{-E (IX)}$
- (7)  $\text{AcAn} + \text{HNO}_3 \rightarrow 106 \text{ (VII)}$
- (8)  $106 + \text{HOAc} \rightarrow \text{AcAn (VIII)}$

In order more clearly to disclose the nature of the present invention, a number of specific examples will hereinafter be described in considerable detail. It should be clearly understood, however, that this is to be done solely by way of example and is not to be construed as a limitation upon the spirit and scope of the appended claims.

PLATE I

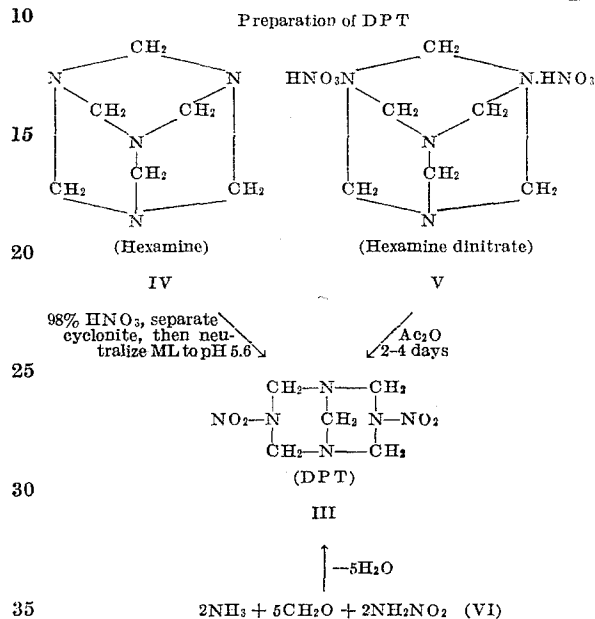
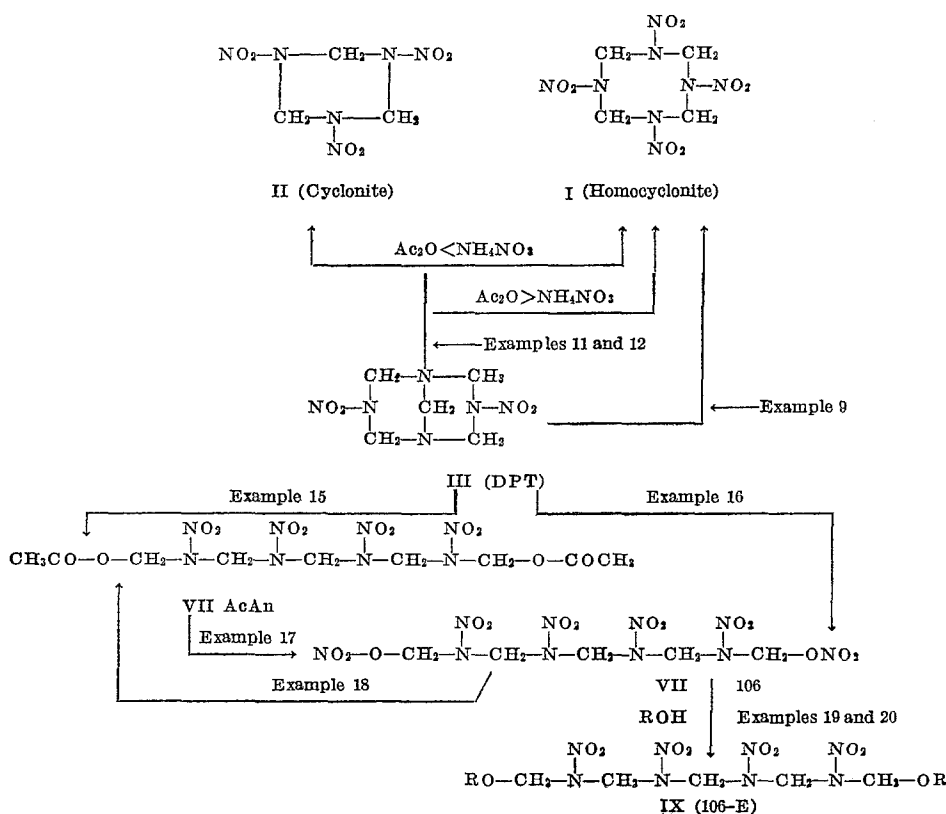


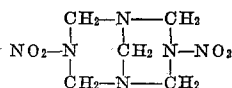
PLATE II

Reactions of DPT



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## PREPARATION OF DPT



## 1. BY NEUTRALIZATION OF MOTHER LIQUORS FROM THE NITROLYSIS OF HEXAMINE

*Example 1*

Hexamine was treated with a large excess of absolute nitric acid (from 20 to 25 moles of acid per mole of hexamine) according to the procedure described by Hale, Jour. Amer. Chem. Soc., 47, 2754 (1925). The hexamine (preferably admixed with Dry Ice) was added in small proportions to the concentrated nitric acid, the latter being stirred slowly but continuously and held below  $-25^\circ\text{C}$ . by means of an acetone-Dry Ice bath. Each portion was allowed to dissolve before the introduction of the next. The time of addition may vary from about 75 to 140 minutes, during which the reaction mixture is held at  $-25^\circ\text{C}$ .

After all the hexamine was added, the reaction mixture was poured over twice its weight of crushed ice and the resulting precipitate of cyclonite was immediately filtered from the mixture. The cold filtrate, which smelled strongly of formaldehyde, was then promptly but cautiously neutralized with aqueous ammonia to a pH of about 5.6 (solution barely blue to bromocresol green). After about 15 minutes precipitation was complete and the solution became more acid. The mixture was then filtered and the crude product (melting at about  $188$  to  $193^\circ\text{C}$ ., plus or minus 5 to  $10^\circ\text{C}$ .) was further purified by repeated recrystallization from nitromethane. The melting point of the purified product was thus raised to about  $205$  to  $206^\circ\text{C}$ .

The weight ratio of DPT to cyclonite produced by the foregoing process varied from about 1:5 to 1:6, although a 1:4 ratio was occasionally obtained. Generally speaking, it has been found that the optimum yields of DPT are obtained provided the reaction mixture resulting from the nitrolysis of hexamine is diluted with water as quickly as possible after the hexamine addition is complete. Furthermore it appears that the yield of DPT, in contrast to that of cyclonite, is inversely affected by the quantity of nitric acid used, within certain limits.

The neutralization of the nitrolysis mother liquors may be effected with any suitable alkali other than the ammonia employed in Example 1. This is illustrated in Example 2.

*Example 2*

The reaction mixture from 40 g. (0.285 mole) of hexamine and 180 cc. (4.28 moles) of 99.6% nitric acid was diluted with ice and water immediately after the addition of the hexamine was complete, and the cyclonite was promptly filtered from the mixture: 46.2 g. of cyclonite, or 73.19% of the theoretical yield, was obtained. The cold filtrate after the separation of the cyclonite was then neutralized with saturated aqueous sodium carbonate solution to a pH of 5.6. The yield was 6.43 g. of DPT, representing a 10.3% yield. A mixed melting point with a sample of DPT obtained as in Example 1 was not lowered.

The product obtained by the procedure described in Example 1 or 2 consists of 3,7-dinitropentamethylenetetramine (III) or DPT. This new compound melts with decomposition and

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sublimation at a somewhat indefinite temperature, particularly in the crude state. However, after repeated recrystallizations, the melting point of DPT may be raised to approximately  $204$  to  $205^\circ\text{C}$ ., using acetone, methyl ethyl ketone, nitromethane or any other suitable solvent for recrystallization. In this connection, it may be mentioned that DPT exists in two polymorphic modifications melting at  $222$  to  $223^\circ\text{C}$ . and  $204$  to  $205^\circ\text{C}$ ., respectively.

DPT is decomposed rapidly by boiling water and slowly by boiling 95% alcohol. It is decomposed easily by heat and darkens on melting; if heated at  $170^\circ\text{C}$ . for 16 to 18 hours it gives a mixed sublimate which apparently consists of paraformaldehyde and hexamine. The chemical properties of DPT will be discussed more fully hereafter under the heading of "Reactions of DPT."

*Analysis.*—Calc'd  $\text{C}_5\text{H}_{10}\text{N}_6\text{O}_4$ : C, 27.50; H, 4.58; N, 38.5. Found: C, 27.72; H, 4.48; N, 38.9.

2. BY TREATMENT OF HEXAMINE WITH  $\text{NH}_4\text{NO}_3\text{-HNO}_3$  SOLUTION

Hexamine may be converted to DPT (III) without the production of cyclonite by treatment at moderate temperature with nitric acid containing dissolved ammonium nitrate. This method is described in Example 3.

*Example 3*

To a solution of 20 cc. (0.48 mole) of 95% nitric acid and 17.2 g. (0.21 mole) of ammonium nitrate at room temperature was added 14 g. (0.10 mole) of hexamine. After four hours the resulting slurry set to a solid (hexamine dinitrate). After the reaction mixture had stood at room temperature for approximately two weeks, the solid was dissolved in 200 cc. of water; no insoluble residue remained and therefore no cyclonite was present. The resulting aqueous solution was neutralized with 28% aqueous ammonia to a pH of 5.6, producing 1.23 g. of DPT, corresponding to a yield of 5.6% of the theoretical. After recrystallization from methyl ethyl ketone, a mixed melting point of the resulting product with a sample of DPT prepared as in Example 1 was not lowered.

## 3. BY TREATMENT OF HEXAMINE DINITRATE WITH ACETIC ANHYDRIDE

Considerably better yields of DPT may be obtained by first converting hexamine (IV) to hexamine dinitrate (V) and then treating the latter compound with a carboxylic acid anhydride at moderate temperatures for a considerable period of time. The procedure, starting with hexamine dinitrate, is described in Example 4.

*Example 4*

A mixture of 2220 cc. (20 moles) of acetic anhydride and 1330 g. (5 moles) of hexamine dinitrate was stirred for three days at room temperature. The resulting crystalline precipitate was then filtered from the reaction mixture. The product consisted of 125.6 g. of DPT melting at  $205\text{-}206^\circ\text{C}$ . Second and third crops of DPT were obtained by successive concentrations of the mother liquor. The total yield of DPT produced was 30.7% of the theoretical. A mixed melting point of the purified product with a sample of the DPT prepared as in Example 1 was not lowered.

## 4. BY TREATMENT OF HEXAMINE DINITRATE WITH SULFURIC ACID

Hexamine dinitrate may be converted to DPT by treatment with sulfuric acid in lieu of the acetic anhydride employed in Example 4. The sulfuric acid method is described in Examples 5 and 6.

*Example 5*

0.1 mole of hexamine dinitrate and 0.92 mole of 90% aqueous sulfuric acid were mixed together over a 30 minute period with proportionate addition of the reactants to the reaction vessel, and with efficient stirring. The reaction mixture was maintained at about 8 to 15° C. After the reactants had been added to the reaction vessel the mixture was stirred at about 15° C. for 45 minutes and then poured into 400 cc. of ice and water. After filtration, the filtrate was neutralized to a pH of 5.6 to 6.5 using 28% aqueous ammonia, producing 0.31 mole of DPT, corresponding to 31% of the theoretical yield.

*Example 6*

A solution of 13.3 g. (0.05 mole) of hexamine dinitrate and 34 g. (0.31 mole) of 90% aqueous sulfuric acid, prepared by proportionate addition at 8-15° C. over a thirty minute period, was subsequently stirred at 15° C. for 45 minutes after the addition was complete. The resulting mixture, if neutralized with ammonia as in Example 5, supra, would have given a 31% yield of DPT. Instead of following this procedure, however, the reaction mixture was poured into 55 cc. (1.24 mole) of well-stirred 99% nitric acid over an 8 minute period, the temperature of which was maintained at 10° C. The resulting reaction mixture was then stirred at 25° C. for a period of time indicated in Table I, infra, and then crowned in an ice-water mixture. The resulting cyclonite was filtered, dried, weighed in the crude state, fumed-off with 70% nitric, filtered, dried and again weighed. The filtrate from the initial separation of the cyclonite was cautiously neutralized with ammonia to a pH of 5.6, and the yield of DPT thus obtained was determined. The results are given in Table I.

TABLE I.—CYCLONITE-DPT YIELDS IN EXAMPLE 6

Stirring Time in HNO <sub>3</sub> ; min.	Cyclonite Yield and Quality				DPT Yield		
	Crude		Shrinks ° C.	Purified		Percent	M. P. ° C.
	Percent	M. P. ° C.		Percent	M. P. ° C.		
0.....	28	167-188	148	14	199-203	9	198-199
10.....	37	150-188	133	17	202-203	4	190-192
20.....	46	143-186	133	23	201-202	4	198.5-200
30.....	47	153-196	130	26	201.5-202.5	1.5	187-192

It will thus be apparent that under these reaction conditions the DPT yields vary approximately inversely with the cyclonite yields.

## 5. BY CONDENSATION OF FORMALDEHYDE, NITRAMIDE AND AMMONIA

The foregoing methods of preparing DPT all start with hexamine or one of its salts. DPT may also be produced by condensing about 10 to 12 moles of formaldehyde with about 2 moles of nitramide (VI) at about 0° to about 30° C. and then treating the reaction product with ammonia according to the procedure outlined in Example 7.

*Example 7*

0.062 g. (0.001 mole) of nitramide (Organic Syntheses, vol. 1, 68 (1939)) was mixed with 0.43 cc. (0.006 mole) of 40% formalin and the resulting solution was cooled to prevent gas evolution. After two minutes the solution was diluted with water and then cautiously neutralized to pH 5.6 with dilute ammonia. A precipitate slowly formed. The yield of DPT was 80 mg. corresponding to 73% of theoretical yield. The product was identified by mixed melting point with the DPT obtained in Example 1.

*Example 8*

DPT may also be prepared by reacting nitramide with formaldehyde and treating the resulting solution with methylenediamine sulfate (Knudsen, Ber. 47, 2700 (1914)). This reaction mixture on being neutralized to pH 7 with aqueous sodium carbonate yields DPT.

To a solution prepared by dissolving 0.10 g. (0.0016 mole) of nitramide in 0.12 cc. (0.0016 mole) of 40% formalin with cooling, was added 0.20 g. (0.0008 mole) of methylenediamine sulfate. The slurry was immediately diluted with 7.5 cc. of water and neutralized to pH 7 with aqueous sodium carbonate solution. The DPT which settled out slowly on keeping the reaction mixture at 0° C. for twenty minutes, weighed 78 mg. Yield of DPT calculated on the formaldehyde basis is 88%.

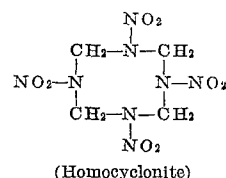
In view of the foregoing examples, it will be apparent that DPT may be formed by numerous alternative methods.

The chemical characteristics of DPT obtained by any of the foregoing procedures are of considerable interest and these will now be described.

## B. REACTION OF DPT

One of the most interesting and important properties of DPT resides in the fact that it may be converted in excellent yields to a new explosive compound, cyclotetramethylenetetranitramine or

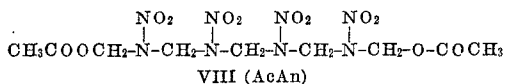
"homocyclonite," the probable structure of which is as follows:



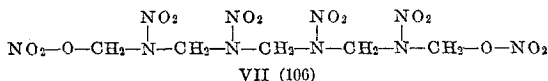
As previously indicated, homocyclonite is an explosive equal in ballistic strength and brisance to cyclonite, and has the same oxygen balance:

it is therefore an explosive of great power and brisance.

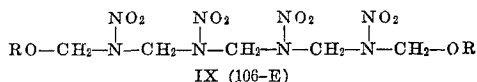
By still other reactions DPT may be converted to a substance (hereinafter identified by the trivial name "AcAn") which consists of 1,9-diacetoxypentamethylene-2,4,6,8-tetranitramine (VIII), having the following structure:



Furthermore, if DPT is treated with nitric acid containing sufficient dissolved nitrogen pentoxide to titrate as apparently "106% HNO<sub>3</sub>," there is obtained still another explosive compound (hereinafter designated by the trivial name "106") which consists of 1,9-dinitroxypentamethylene-2,4,6,8-tetranitramine (VII):



This latter compound is the nitroxy analog of the diacetoxypentamethylene compound, AcAn, and these two compounds are in fact interconvertible. Moreover, the dinitroxy compound (VII) may be converted by treatment with alcohol to a new series of ethers, viz., 1,9-dialkoxy-pentamethylene-2,4,6,8-tetranitramine (IX), these ethers (hereinafter designated as "106-E") having the probable formulae:



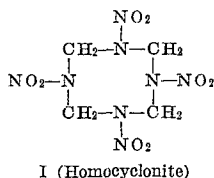
The reactions of DPT as diagrammatically indicated in Plate II are illustrated in the examples given below.

#### 1. CONVERSION TO HOMOCYCLONITE WITH CONCENTRATED NITRIC ACID

Homocyclonite may be obtained by treating DPT with concentrated nitric acid at about 0 to 30° C. This procedure is illustrated in Example 9.

##### Example 9

DPT was treated with 99.6% nitric acid at about 20° C. using 30 parts by weight of acid to one part by weight of DPT. The crude material thus obtained melted at about 230-262° C. The crude material was purified by digestion with aqueous ammonia which preferentially destroys any cyclonite contained in the crude product. Thereafter the material was digested with 70% nitric acid and finally recrystallized from nitromethane. The product melted at 279.5 to 280° C. corr. (with decomposition). It consists of cyclotetramethylenetetranitramine (I) having the probable structural formula:



**Analysis.**—Calcd for C<sub>4</sub>H<sub>8</sub>N<sub>8</sub>O<sub>8</sub>: C, 16.22; N, 37.84. Found: C, 16.4; N, 38.24. Molecular weight: Calc'd for C<sub>4</sub>H<sub>8</sub>O<sub>8</sub>N<sub>8</sub>, 296; Found, 296.

Homocyclonite is an explosive having properties similar to those of cyclonite (II). It has approximately the same power (i. e., about 150 compared to 100 to TNT) and brisance as cyclonite.

The solubility of homocyclonite, generally speaking, resembles but is somewhat lower than that of cyclonite. It is quite appreciably less soluble in many organic solvents, for example, acetic acid and dioxane. Homocyclonite may be conveniently recrystallized from any solvents including acetone, methyl ethyl ketone, acetic acid, nitromethane, dilute nitric acid and the like.

In regard to its chemical properties, homocyclonite is also similar to cyclonite. Thus it is as stable toward 70% nitric acid as cyclonite. Likewise it is decomposed slowly by concentrated nitric acid. However, homocyclonite is considerably more stable than cyclonite toward weak alkalis (e. g., aqueous ammonia or aqueous sodium bicarbonate), and this property provides a convenient method of preferentially destroying the cyclonite in cyclonite-homocyclonite mixtures in the preparation of pure homocyclonite.

It has been found that homocyclonite accompanies the cyclonite produced in the process described and claimed in the copending application of Scheissler and Ross (Serial No. 2,599, filed February 16, 1943), according to which a formaldehyde-producing substance (e. g., paraformaldehyde) is treated with ammonium nitrate in the presence of a carboxylic acid anhydride (e. g., acetic anhydride). Although the principal product of this reaction consists of cyclonite, a small proportion of homocyclonite usually accompanies the main product.

It has also been found that homocyclonite accompanies the cyclonite produced by the process described and claimed in the copending application of Bachmann (Serial No. 498,078, filed July 16, 1943). This latter process involves the treatment of hexamine or hexamine dinitrate with ammonium nitrate, also in the presence of a carboxylic acid anhydride, and as pointed out in said Bachmann application, the presence of homocyclonite in the product of the reaction is not objectionable from the viewpoint of explosive power and strength since the two components are substantially identical in their ballistic properties.

In view of the fact that homocyclonite and cyclonite are frequently produced in the same reaction, synthetic mixtures of these two explosives were prepared from the pure compounds and the melting points of the various mixtures were determined. The preparation of these mixtures is described in Example 10, infra, and the melting point data are given in Table II, infra. Plate III of the drawing represents a plot of melting point vs. composition, for cyclonite-homocyclonite mixtures containing from 0 to 40% homocyclonite. This plot enables a rough estimation of the percent homocyclonite in mixtures of these two explosives where the cyclonite component predominates.

##### Example 10

Crude homocyclonite was refluxed with ammonia and then with 70% nitric acid, after which it was recrystallized from nitromethane; melting point 279.5-280° C. corr. Cyclonite was prepared by the Hale procedure and recrystallized from nitromethane, dioxane and glacial acetic acid; melting point, 203.3-205° C. corr. Synthetic mixtures of cyclonite and homocyclonite were then prepared from the purified components and the melting points of the various mixtures were determined. The results are given in Table II.

TABLE II.—MELTING POINT OF CYCLONITE-HOMOCYCLONITE MIXTURES

Percent Homocyclonite in Composition	Melting Point, C.
0.....	203.3-205
1.....	200.8-204
4.....	196-203
10.....	188.5-193.5
20.....	189-193.5
30.....	187-193.5
40.....	187.5-193.5
60.....	185.5-239.5
70.....	222.5-260.5
80.....	264-270
100.....	279.5-280

In the case of the mixtures, the upper temperature indicated in the melting point spread (representing the temperature at which liquefaction was complete), was difficult to reproduce. Plate III represents a plot of percent composition against the lower temperature and the upper temperature of the melting "point" for mixtures containing from 0 to 40% homocyclonite. The melting "point" of cyclonite-homocyclonite mixtures therefore provides a rough indication of the percent composition within certain limits.

The crystallographic and impact sensitivity properties of homocyclonite are more particularly described in the copending application of Johnson, Blonquist, and McCrone, Serial No. 495,081, filed July 16, 1943, wherein it is pointed out that the homocyclonite which accompanies the cyclonite produced by the Bachmann process may exist in any one of several polymorphic forms or modifications that are characterized by widely different impact sensitivities, approximately of the following order of magnitude:

Beta homocyclonite, ca. 33 cm.  
 Alpha homocyclonite, ca. 12 cm.  
 Gamma homocyclonite, ca. 7 cm.  
 Delta homocyclonite, ca. 5 cm.

These data were determined on a testing machine which gave a sensitivity reading of ca. 43 cm. for pure cyclonite. Because of the relatively high sensitivity of the alpha, gamma and delta polymorphic modification of homocyclonite, in the manufacture of cyclonite by the Bachmann or by the Schiessler and Ross processes, provision is desirably made in order to ensure that the homocyclonite present in the final product exists in the least sensitive or beta polymorphic modification. The above indicated Johnson et al. application describes and claims a method of purifying cyclonite compositions containing homocyclonite, in order to ensure that this condition is obtained. The same application also describes the technique of producing and isolating any desired polymorphic modifications of homocyclonite and its transformation into any other desired modification. Reference may be had to the Johnson et al. application for a more detailed description of homocyclonite polymorphism and the control thereof during manufacture of composition containing this interesting new explosive.

Because of its great explosive power and brisance, generally speaking, homocyclonite may be substituted for cyclonite as its substantial equivalent in the preparation of various commercial or military explosives. Thus it may be mixed with molten TNT to form a castable slurry suitable for shell loading. Likewise homocyclonite may be phlegmatized (e. g., for press loading) by incorporating therewith a small proportion of beeswax or polymorphous hydrocarbon wax, as described

in the copending application of Kistiakowsky et al., Serial No. 495,085, filed July 16, 1943. If so desired, homocyclonite may be substituted for cyclonite in the preparation of a plastic explosive such as that described and claimed in the copending application of Kistiakowsky et al., Serial No. 495,086, filed July 16, 1943. It will thus be apparent that homocyclonite is a new explosive compound of wide utility for military and commercial purposes, and of equal power and brisance to the most powerful explosive heretofore known.

## 2. CONVERSION TO HOMOCYCLONITE WITH ACETIC ANHYDRIDE AND AN AMMONIUM NITRATE-NITRIC ACID SOLUTION

The yield of homocyclonite per mole of DPT may be increased by about 65% by treating DPT at about 50 to 100° C. (preferably 60-75° C.) with a solution consisting of ammonium nitrate dissolved in nitric acid (in lieu of nitric acid alone), together with acetic anhydride. This process is illustrated by Example 11.

### Example 11

A mixture of 10 g. (0.046 mole) of DPT and 45.2 cc. (0.394 mole) of acetic anhydride was placed in a reaction vessel and stirred at 60 to 70° C. while a solution of 11.1 g. (0.138 mole) of ammonium nitrate in 13.4 cc. (0.319 mole) of 99.6% nitric acid was added over a 15 minute period. During the addition the suspension (DPT in anhydride) dissolved and a new precipitate appeared before the addition was complete. Thereafter the reaction mixture was stirred for 22 minutes at 62° C. and then for 10 minutes at 25° C. The reaction mixture was then poured into 400 g. of ice-water mixture. The solid was filtered and washed with 200 to 300 cc. of water. The product was suspended in 200 cc. of 70% nitric acid and heated until strong evolution of brown fumes ceased (hereinafter referred to as the "fume-off"). The reaction mixture was then immediately cooled and 2000 cc. of water was added. The mixture was filtered and the precipitate dried at 70° C. The yield was 8.88 g. of homocyclonite, corresponding to 65.5% of the theoretical; melting point of the crude material, 267 to 238° C. A mixed melting point of the purified material with the homocyclonite obtained in Example 9 was not lowered.

A modification of the procedure described in Example 11 is given in Example 12. In this modification the fume-off is avoided and the crude material is digested with water to destroy hydrolyzable impurities.

### Example 12

A solution of 44 g. of ammonium nitrate in 47 cc. of 93% nitric acid was prepared and allowed to stand until it became colorless and ceased gassing. In a two-liter, three-necked flask equipped with a thermometer and a mechanical stirrer was placed 100 g. of DPT and 460 cc. of acetic anhydride. The slurry was heated to 60° C. by means of a water bath and the nitric acid-ammonium nitrate solution was then added over a period of 10 minutes, the temperature being held at 60 to 65° C. during the addition. During the first five minutes of the addition, the reaction was highly exothermic and it was necessary to keep the bath at about 20 to 30° C. However, during the last five minutes of addition a bath temperature of around 40° C.

afforded sufficient cooling. When the addition was half complete it was observed that the reaction mixture had become a clear solution and no solid DPT remained. However as the addition continued the mixture became opaque.

After the addition the mixture was stirred at 60 to 65° C. for one hour. The first crystals of homocyclonite were observed about three minutes after the completion of the addition. Heat was evolved for some five to ten minutes after the addition had ceased and care was therefore taken in raising the temperature of the water bath. At the end of the hour the bath was removed and the mixture allowed to cool. When the temperature of the reaction mixture reached 50° C., 450 cc. of cold water was rapidly added with stirring. As the water was added, the temperature fell to about 40° C. and then rose to about 90° C. The crude homocyclonite was heated in the dilute mother liquor for 12 hours on a steam bath under a reflux condenser. During this period considerable gas was evolved, much of it consisting of formaldehyde. The reaction mixture was then cooled and filtered. Yield, 102 g.; melting point 272 to 278° C. (corr.). Recrystallization from acetone gave about 80 g. (first and second crops); melting point (first crop), 279–280° C. and (second crop), 278–279° C. (corr.). If exceptionally pure homocyclonite is desired it may be further purified by recrystallization from nitromethane, acetone or other suitable solvents.

When DPT is treated in the presence of acetic anhydride with ammonium nitrate dissolved in nitric acid according to the procedure described in Examples 11 and 12, the product predominantly consists of homocyclonite although a small proportion of cyclonite is also usually produced. However, by varying the amount of acetic anhydride, and/or the amount of ammonium nitrate employed in the foregoing examples, the relative proportion of cyclonite to homocyclonite in the product may be considerably varied. Thus if the anhydride is greatly reduced or omitted entirely, the relative proportion of cyclonite in the product is increased over that given in the foregoing examples. Moreover, if the amount of ammonium nitrate employed per mole of DPT is decreased, the relative proportion of homocyclonite in the reaction product increases. The concentration effects are illustrated in Example 13.

#### Example 13

A mixture of 0.05 mole of ammonium nitrate, 0.16 mole of acetic anhydride and 0.3 mole of acetic acid was stirred at 65 to 70° C., while 0.05 mole of DPT and 0.99 mole of 99% nitric acid were added alternately in 20 portions over a 20 minute period, the nitric acid addition being made in all cases about 15 seconds before the corresponding DPT addition. After the addition was complete, the reaction mixture was heated gradually to 90° C. over a 15 minute period. Thirty-five cc. of hot water was then added and the resulting solution stirred at 90° C. for 30 minutes. After cooling the reaction mixture to 20° C. it was filtered and the melting point and weight of the dried precipitate were determined.

A portion of the product was fumed off with 70% nitric acid and the thus-purified material was then dissolved under reflux in 85 to 100% acetone. When all the material was in solution, water was added until crystallization just began (70 to 75% acetone). Thereafter the

resulting suspension was refluxed for one hour and then further diluted by the addition of water to form a 50% acetone solution, the water being added slowly over a 30 minute period. Thereafter the acetone was distilled until only 10% of it remained in the residue, which was then refluxed one hour, after which the residual acetone was removed and the solution cooled. This procedure of purification results in the conversion of the homocyclonite to a crystalline form most suitable for the mechanical separation described below.

The filtered, carefully purified precipitate was centrifuged in 15 g. of iodobenzene. The homocyclonite-rich fraction settled to the bottom of the iodobenzene while the cyclonite-rich fraction accumulated on the surface. Based on this method of separation it was found that the product consisted of approximately 22% cyclonite and about 78% homocyclonite.

In a comparable run in which the amount of ammonium nitrate was doubled the product was found to consist of about 55% cyclonite and about 45% homocyclonite.

Summarizing the results obtained in the experiments described in Example 13: if 1 mole of ammonium nitrate is employed per mole of DPT, the reaction mixture consists predominantly of homocyclonite (ca. 22% cyclonite, 78% homocyclonite); if, on the other hand, 2 moles of ammonium nitrate are employed per mole of DPT the product consists predominantly of cyclonite (ca. 55% cyclonite, 45% homocyclonite). Example 13 therefore illustrates the control over the composition of the product that may be effected by variations in the proportions of the reactants.

#### 3. CONVERSION TO CYCLONITE AND HOMOCYCLONITE BY SULFURIC ACID TREATMENT FOLLOWED BY NITROLYSIS OF THE REACTION MIXTURE

##### Example 14

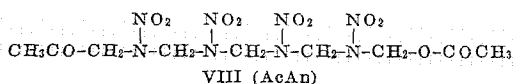
1.0 g. (0.0046 mole) of DPT was dissolved in 4.5 cc. (0.07 mole) of 86% sulfuric acid at 0° C. over a ten minute period. The solution was then added over a three minute period to 11.8 c. c. (0.28 mole) of 99% nitric acid at 0° C. The resulting clear solution was stirred 30 minutes at 25° C., then drowned in 120 cc. of ice and water. The crude cyclonite thus produced weighed 0.44 g. (43% of the theoretical yield, based on one mole cyclonite per mole of DPT) when fumed off with 4 cc. of 70% nitric acid gave an 80% recovery of cyclonite-homocyclonite mixture, M. P. 194–198° C., softening at 193° C. Based on the melting diagram (Fig. 1) the product contains about 5% homocyclonite. When the filtrate remaining after the separation of the crude cyclonite was neutralized with ammonia, no DPT could be recovered.

#### 4. CONVERSION OF DPT TO ACAN

In Example 11 supra the conversion of DPT to a mixture of cyclonite and homocyclonite by means of acetic anhydride and a solution of ammonium nitrate in nitric acid is described. If this procedure is followed except that the ammonium nitrate is entirely omitted, homocyclonite is not produced. Instead a compound, 1,9-diacetoxypentamethylene - 2,4,6,8-tetranitramine (VIII) (herein designated by the trivial name "AcAn") is produced to the extent of about 80%



of the theoretical yield. This compound has the probable structure.



The preparation of AcAn is described in Example 15.

#### Example 15

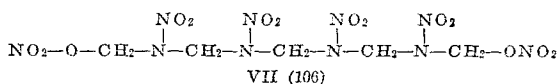
0.2 g. (0.0009 mole) of DPT is suspended in 4.07 cc. (0.043 mole) of acetic anhydride maintained at 65° C. by means of a water bath, while 1.3 cc. (0.31 mole) of 99.6% nitric acid is added with stirring. Vigorous bubbling occurs with the evolution of brown fumes. Within three minutes a precipitate appears. After 16 minutes at 65° the reaction mixture was poured on ice; yield, 0.239 g. of a solid melting at 182.3° C., softening at 179.2° C. This compound gave a positive Franchimont nitramine test, was not very sensitive to shock, and was completely destroyed by heating with 70% nitric acid. After three recrystallizations from nitromethane and one from acetone the melting point was raised to 186.5 to 187.2° C.

*Analysis.*—Calc'd for  $\text{C}_9\text{H}_{16}\text{N}_8\text{O}_{12}$ : C, 25.2; H, 3.76; N, 26.2;  $\text{CH}_3\text{CO}$ , 19.8. Found. C, 25.3; H, 3.93; N, 26.2;  $\text{CH}_3\text{CO}$ , 20.6, 20.3.

The compound was destroyed slowly by refluxing with 28% aqueous ammonia (82% in 68 minutes). It is stable to 35% nitric acid at 25° C. for five hours but is decomposed by 70% warm nitric acid. Absolute nitric acid at 0° C. converts it to "106," infra.

#### 5. CONVERSION OF DPT TO "106"

As above pointed out, when DPT is treated with absolute nitric acid as in Example 9, homocyclonite is produced. However, if DPT is treated at about 0–30° C. (preferably below 20° C.) with "106% nitric acid" (i. e., absolute nitric acid containing sufficient dissolved nitrogen pentoxide to titrate as apparently 106% acid), a 72% yield of a new linear compound melting at 204.5 to 205° C. is obtained, rather than homocyclonite. This product obtained with "106% nitric acid" (for which reason it is herein designated by the trivial name "106") is the dinitroxy analogue of AcAn, and has the following probable structure (VII):



The preparation of "106" is described in Example 16.

#### Example 16

10 g. (0.046 mole) of DPT was added to 63 cc. (1.6 mole) of "106% nitric acid" over a 35 minute period. The temperature of the reaction mixture was maintained below 20° C. and provision was made to ensure anhydrous conditions in the reaction mixture. A precipitate formed before the addition of the DPT was complete. Following the addition, the reaction mixture was stirred at room temperature for 15 minutes and then poured into ice-water mixture, filtered and the solid material washed with water and air-dried. The yield was 13.4 g. (72% of the theoretical) of a compound melting in the crude state at 191.5 to 193° C. (corr.), softening at 189.5° C. This crude material was recrystallized from hot nitromethane, which raised its melting point to 204.5 to 205° C.

*Analysis.*—Calc'd for  $\text{C}_5\text{H}_{10}\text{N}_{10}\text{O}_{14}$ : C, 13.8; H, 2.30; N, 32.3.

Found:

	C, 13.7;	H, 2.52;	N, 31.7
	14.0	2.40	31.7
	13.5	2.42	33.0
	13.8	2.40	

The product ("106") was destroyed rapidly when heated with 70% nitric acid or when boiled for 50 minutes with water. It was insoluble in cold butanol, not very soluble in acetone, ethyl acetate, ethanol or benzene but fairly soluble in pyridine and toluene.

It was detonated easily and violently and gave a positive Franchimont nitramine test. It is indeed an explosive of abnormal power and sensitivity. Its sensitivity is 12 times that of TNT and at a density of 0.69 it has a Trauzel block expansion of 588 cc. compared to 256 cc. for TNT.

"AcAn" (VIII) and "106" (VII) are interconvertible. Thus, if "AcAn" is treated with absolute nitric in the cold (e. g., at 0° C.), "106" is obtained. On the other hand, if "106" is treated with sodium acetate and acetic acid at an elevated temperature (e. g., at the boiling point) "AcAn" is obtained. The interconversion of these two compounds is illustrated in Examples 17 and 18, respectively.

#### Example 17

30 g. of AcAn was added over a 30 minute period to 205 cc. of stirred 99.3% nitric acid maintained at 8° C. by means of an ice bath. After the addition was complete, the ice bath was removed and the reaction mixture was stirred for 20 minutes after which it was poured into 200 g. of ice-water mixture. The solid was filtered, washed with water and then washed with methanol. The yield of "106" was 30 g. or 98.3% of the theoretical. The melting point was 204.5 to 205° C. A mixed melting point with a sample of "106" prepared as in Example 16 was not lowered.

#### Example 18

To a solution of 0.23 g. of sodium acetate in 5 cc. of acetic acid was added 0.3 g. of "106." The mixture was heated to boiling for three minutes and then cooled and filtered. The solid material was washed with water, leaving 0.20 g. of material melting at 183° C. A mixed melting point with "AcAn" prepared as in Example 15 was not lowered. *Analysis:* Calc'd for  $\text{C}_9\text{H}_{16}\text{N}_8\text{O}_{12}$ : N, 26.4. Found, N, 26.5.

The nitroxy groups in 106 may readily be replaced by alkoxy groups by treating 106 with an alcohol at the boiling point. Examples 19 and 20 illustrate the preparation of the new dimethoxy- and the diethoxy-pentamethylene-2,4,6,8-tetra-nitramines (IX), respectively, by this type of reaction. These compounds are of interest because of their relative stability compared to 106.

#### Example 19

0.2 g. ( $4.6 \times 10^{-4}$  mole) of compound 106 in 10 cc. of absolute methanol was refluxed for ten hours. After cooling, the crystalline deposit was filtered and washed with methanol. M. P. 182–3° C. (soft 177° C.). Yield 0.16 g. After two recrystallizations from 1:1 dioxane-methanol, it melted at 182–183° C. *Analysis:* Calc'd for  $\text{C}_7\text{H}_{16}\text{N}_8\text{O}_{10}$ : C, 22.6; H, 4.32; N, 30.8. Found: C, 22.6; H, 4.27; N, 30.7.

## Example 20

Diethoxypentamethylene - 2,4,6,8 - tetranitramine was prepared in a manner similar to that used in Example 19, except that 95% ethanol was used in place of methanol. A 43% yield of a product melting at 166-167° C. was obtained. Analysis: Calc'd for  $C_9H_{20}N_8O_{10}$ : C, 27.0; H, 5.04; N, 28.0. Found: C, 27.4; H, 4.94; N, 28.2.

It will be apparent to those skilled in the art that many variations may be made in the foregoing procedure without departing from the spirit and scope of the invention. We therefore intend to be limited only in accordance with the following patent claims.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:

1. A method of preparing 3,7-dinitropentamethylenetetramine which comprises treating hexamine with concentrated nitric acid, sepa-

rating the cyclonite thus produced from the nitrolysis mother liquor, adjusting said mother liquor to a pH of about 5.6 to precipitate 3,7-dinitropentamethylene-tetramine and removing the precipitate from the liquor.

2. A method as defined in claim 1 wherein the precipitate is treated with nitromethane and recrystallized.

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