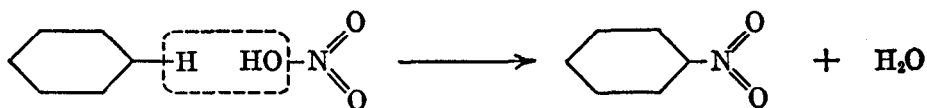# CHAPTER IV

AROMATIC NITRO COMPOUNDS

Aromatic nitro compounds are generally stable but are frequently reactive, especially if they contain groups other than nitro groups in the *meta* position with respect to one another. As a class they constitute the most important of the military high explosives. They are also used as components of smokeless powder, in compound detonators, and in primer compositions. Liquid nitro compounds, and the mixtures which are produced as by-products from the manufacture of pure nitro compounds for military purposes, are used in non-freezing dynamite and other commercial explosives. The polynitro compounds are solvents for nitrocellulose.

The nitro compounds are poisonous. Nitrobenzene, known also as "oil of mirbane," is absorbed through the skin and by breathing its vapors, and has been reported to cause death by the careless wearing of clothing upon which it had been spilled. The less volatile polynitro compounds, like trinitrotoluene, are absorbed through the skin when handled, and may cause injury by the inhalation of their dust or of their vapors when they are melted. Minor TNT sickness may manifest itself by cyanosis, dermatitis, nose bleeding, constipation, and giddiness; the severer form, by toxic jaundice and aplastic anemia.[1] One of the nitro groups is reduced in the body, and dinitrohydroxylaminotoluene may be detected in the urine. Trinitrobenzene is more poisonous than trinitrotoluene, which, in turn, is more poisonous than trinitroxylene, alkyl groups in this series having the same effect as in the

[1] J. W. Schereschewsky, "Trinitrotoluol, Practical Points in Its Safe Handling," U. S. Pub. Health Service, Reprint 434 from *Pub. Health Repts.,* Nov. 16, 1917, pp. 1919-1926. C. Voegtlin, C. W. Hooper, and J. M. Johnson, "Trinitrotoluene Poisoning—Its Nature, Diagnosis and Prevention," U. S. Pub. Health Service, *Hyg. Lab. Bull. 126,* 1920. A. Hamilton, "Trinitrotoluene as an Industrial Poison," *J. Ind. Hyg.,* 3, 102-119 (1921). A. L. Leigh Silver, "Treatment and Prevention of Industrial Diseases in Filling Factories," *J. Roy. Army Med. Corps,* July, 1938, pp. 87-96.

phenols, cresol, xylenol, etc., where they reduce the toxicity of the substances but increase their antiseptic strength.

In the manufacture of explosives the nitro groups are always introduced by the direct action of nitric acid on the aromatic substances. The simple reaction involves the production of water and is promoted by the presence of sulfuric acid which thus functions as a dehydrating agent. We shall later see cases in which sulfuric acid is used as a means of hindering the introduction of nitro groups. In consequence of the reaction, the nitrogen

$$\text{benzene}\!-\!\!\left[H \quad HO\right]\!-\!N\!\!\begin{array}{c}O\\\\O\end{array} \longrightarrow \text{benzene}\!-\!N\!\!\begin{array}{c}O\\\\O\end{array} + H_2O$$

atom of the nitro group becomes attached to the carbon atom of the aromatic nucleus. Nitro groups attached to the nucleus, unless *ortho* and *para* to other nitro groups, are not affected by sulfuric acid as are nitro groups attached to oxygen (in nitric esters) and to nitrogen (in nitroamines), or, ordinarily, by hydrolytic agents as are nitro groups attached to oxygen. Nitric acid is a nitrating agent both at low and at elevated temperatures; its vigor in this respect depends upon the concentration. But it is an oxidizing agent even in fairly dilute solution, and becomes more vigorous if the temperature is raised. Further, it decomposes when heated to produce nitrous acid, which is also a powerful oxidizing agent and may reduce the yield of the desired product. Nitrous acid present in the nitrating acid may also result in the formation of nitrophenols from aromatic amines. Aromatic nitro compounds, such as TNT and picric acid, on refluxing for some hours with nitric acid (*d.* 1.42) and then distilling the mixture, yield appreciable quantities of tetranitromethane, formed by the rupture of the ring and the nitration of the individual carbon atoms. The nitro group "strengthens" the ring against attack by acid oxidizing agents, but makes it more accessible to attack by alkaline ones. The polynitro compounds are destroyed rapidly by warm alkaline permanganate yielding oxalic acid. They combine with aniline, naphthylamine, etc., to form brightly colored molecular compounds. All aromatic nitro compounds give colors, yellow, orange, red, even purple, with alkaline reagents.

The position which the nitro group takes on entering the aromatic nucleus and the ease with which the substitution is

on the nucleus. We are accustomed to speak of the orienting or directing effect of the groups already present and of their influence in promoting or inhibiting further substitution. The two simple rules which summarize these effects have important implications and wide applications in the chemistry of aromatic substances.

Effect of Groups on Further Substitution

1. ORIENTING EFFECT. *The Modified Rule of Crum Brown and Gibson.* If the atom attached to the aromatic nucleus is attached to some other atom by an unsaturated linkage (i.e., by any bond which we commonly write as double or triple), then the next entering group takes the *meta* position; otherwise it takes the *ortho* and *para* positions.

The rule relieves us of the necessity for remembering which groups orient *meta* and which *ortho-para*; we may write them down on demand, thus: the —NO$_2$, —NO, —CO—, —COOH, —CHO, —SO$_2$—OH, —CN groups orient *meta*; and the —NH$_2$, —NHR, —NR$_2$, —OH, —OR, —CH$_3$, —CH$_2$—CH$_3$, —Cl, —Br groups orient *ortho-para*. It is necessary, however, to take note of three or four exceptions, only one of which is important in the chemistry of explosives, namely, that the azo group, —N=N—, orients *ortho-para*; the trichloromethyl group, —CCl$_3$, *meta*; that such conjugate systems as occur in cinnamic acid, —CH=CH—CO—, orient *ortho-para*; and further that a large excess of strong sulfuric acid reverses to a greater or less extent the normal orienting effects of the methoxy and ethoxy groups, of the amino group wholly and of the monosubstituted and disubstituted amino groups in part.

In all discussions of the application of the rule we make reference to the principal products of the reaction; substitution occurs for the most part in accordance with the rule, or with the exceptions, and small amounts of other materials are usually formed as by-products. In the mononitration of toluene, for example, about 96 per cent of the product is a mixture of *o-* and *p-*nitrotoluene, and about 4 per cent is the *m-*compound. Under the influence of *ortho-para* orienting groups, substitution occurs in the two positions without much preference for either one, but it appears to be the case that, when nitro groups are introduced, low temperatures favor the formation of *p-*compounds. The effect

of temperature on sulfonations appears to be exactly the opposite.

2. Ease of Substitution. *Ortho-para* orienting groups promote substitution; *meta* orienting groups hinder it and make it more difficult. The rule may be stated otherwise: that substitution under the influence of *ortho-para* orienting groups occurs under less vigorous conditions of temperature, concentration of reagents, etc., than it does with the unsubstituted aromatic hydrocarbon itself; under the influence of *meta* orienting groups more vigorous conditions than with the unsubstituted hydrocarbon are necessary for its successful accomplishment. The rule may also be stated that *ortho-para* substitution is easier than *meta*. In this last form it fails to make comparison with substitution in the simple hydrocarbon, but does point clearly to the implication, or corollary, that the orienting effect of an *ortho-para* orienting group dominates over that of one which orients *meta*. To the rule in any of these forms, we must add that, when more than one group is already present on the nucleus, the effect of the groups is additive.

Toluene nitrates more easily than benzene; aniline and phenol more easily still. Higher temperature and stronger acid are needed for the introduction of a second nitro group into benzene than for the introduction of the first, for the second is introduced under the influence of the *meta*-orienting first nitro group which tends to make further substitution more difficult. The inhibitory effect of two nitro groups is so great that the nitration of dinitrobenzene to the trinitro compound is extremely difficult. It is more difficult to nitrate benzoic acid than to nitrate nitrobenzene. The common experience of organic chemists indicates that the order of the groups in promoting substitution is about as follows:

$$-OH > -NH_2 > -CH_3 > -Cl > -H > -NO_2 > -SO_2(OH) > -COOH$$

Any one of these groups makes substitution easier than the groups which are printed to the right of it.

Xylene nitrates more easily than toluene. Two methyl groups promote substitution more than one methyl group does, and this appears to be true whether or not the methyl groups agree among themselves in respect to the positions which they activate. Although a nitro group may be said to "activate" a particular position, inasmuch as it points to that position as the one in which substitution will next occur, it nevertheless makes substitution more difficult in that position, as well as in all other positions on

the nucleus. The nitroanilines are more difficult to nitrate than aniline because of their inhibiting nitro group, and more easy to nitrate than nitrobenzene because of their promoting amino group. In o- and p-nitroaniline the amino and nitro groups agree in activating the same positions, and both substances yield 2,4,6-trinitroaniline when they are nitrated. In m-nitroaniline, the nitro group "activates" the 5-position, while the amino group activates the 2-, 4-, and 6-positions. Nitration takes place under the influence of the *ortho-para*-orienting amino group, and 2,3,4,6-tetranitroaniline results.

Utilization of Coal Tar

The principal source of aromatic compounds is coal tar, produced as a by-product in the manufacture of coke. Gas tar, of which much smaller quantities are produced, also contains these same materials. Aromatic hydrocarbons occur in nature in Borneo and other petroleums, and they may be prepared artificially by stripping hydrogen atoms from the cycloparaffins which occur in Caucasus petroleum and elsewhere. They are also produced from paraffin hydrocarbons by certain processes of cracking, and it is to be expected that in the future aromatic compounds will be produced in increasing quantity from petroleum which does not contain them in its natural state.

Coal yields about 6 per cent of its weight of tar. One ton of tar on distillation gives:

Light Oil—yielding about 32 lb. of benzene, 5 lb. of toluene, and 0.6 lb. of xylene.

Middle Oil—yielding about 40 lb. of phenol and cresols, and 80-120 lb. of naphthalene.

Heavy Oil—yielding impure cresols and other phenols.

Green Oil—yielding 10-40 lb. of anthracene.

Pitch—1000-1200 lb.

Naphthalene is the most abundant pure hydrocarbon obtained from coal tar. It takes on three nitro groups readily, and four under vigorous conditions, but ordinarily yields no product which is suitable by itself for use as an explosive. Nitrated naphthalenes, however, have been used in smokeless powder and, when mixed with ammonium nitrate and other materials, in high explosives for shells and for blasting.

The phenol-cresol fraction of coal tar yields phenol on distillation, which is convertible to picric acid, and the cresols, of which

m-cresol is the only one which yields a trinitro derivative directly. Moreover, synthetic phenol from benzene, through chlorobenzene by the Dow process, is purer and probably cheaper in times of stress.

Of the hydrocarbons toluene is the only one which nitrates sufficiently easily and yields a product which has the proper physical and explosive properties. Trinitrotoluene is the most widely used of the pure aromatic nitro compounds. It melts at such temperature that it can be loaded by pouring. It is easily and surely detonated, and is insensitive to shock, though not insensitive enough to penetrate armor-plate without exploding until afterwards. It is powerful and brisant, but less so than trinitrobenzene which would offer certain advantages if it could be procured in sufficient quantity.

Of the xylenes, the *meta* compound yields a trinitro derivative more readily than toluene does, but trinitro-*m*-xylene (TNX) melts somewhat higher than is desirable and is not quite powerful enough when used alone. It has been used in shells in mixtures with TNT and with ammonium nitrate. The other xylenes yield only dinitro derivatives by direct nitration. A mixture of *o*- and *p*-xylene may be converted into an explosive—an oily mixture of a large number of isomers, which has been used in the composition of non-freezing dynamites—by chlorinating at an elevated temperature in the presence of a catalyst (whereby chlorine is substituted both in the side chain and on the nucleus), then nitrating, then hydrolyzing (whereby both chlorines are replaced by hydroxyl groups, the nuclear chlorine being activated by the nitro groups), and finally nitrating once more.
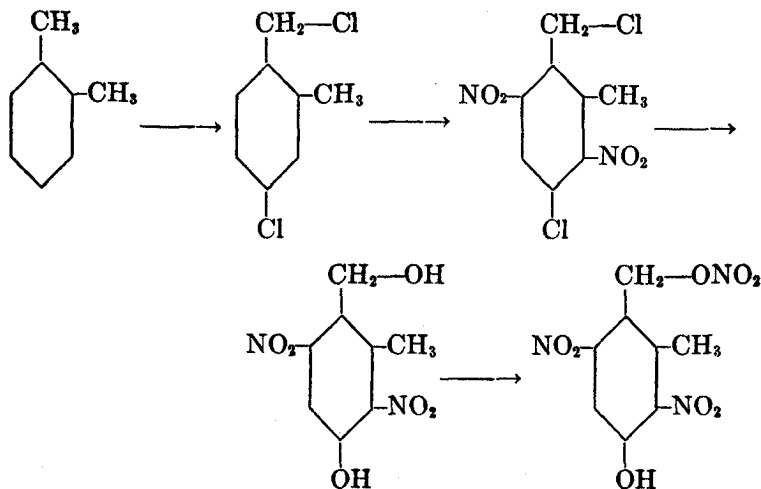
In each step several isomers are formed—only one of the possibilities in each case is indicated above—and the *ortho* and *para* compounds both go through similar series of reactions. The product is too sensitive and in the wrong physical state (liquid) for use as a military explosive. In short, for the manufacture of

FIGURE 45. Marius Marqueyrol, Inspecteur-Général des Poudres, France, 1919. Author of many researches on aromatic nitro compounds, nitrocellulose, smokeless powder, stabilizers and stability, chlorate explosives, etc.—published for the most part in the *Mémorial des poudres* and in the *Bulletin de la société chimique de France*.

military explosives toluene is the most valuable of the materials which occur in coal tar.

In time of war the industries of a country strive to produce as much toluene as possible. The effort results in the production also of increased quantities of other aromatic hydrocarbons, particularly of benzene, and these become cheaper and more abundant. Every effort is made to utilize them profitably for military purposes. As far as benzene is concerned, the problem has been solved through chlorobenzene, which yields aniline and phenol by the Dow process, and hence picric acid, and which gives dinitrochlorobenzene on nitration which is readily convertible, as will be described later, into picric acid and tetryl and several other

explosives that are quite as necessary as TNT for military purposes.

Effects of Substituents on Explosive Strength

Bomb experiments show that trinitrobenzene is the most powerful explosive among the nitrated aromatic hydrocarbons. One methyl group, as in TNT, reduces its strength; two, as in TNX, reduce it further; and three, as in trinitromesitylene, still further yet. The amino and the hydroxyl groups have less effect than the methyl group; indeed, two hydroxyl groups have less effect than one methyl—and trinitroresorcinol is a stronger explosive than TNT, though weaker than TNB. TNT is stronger than trinitrocresol, which differs from it in having an hydroxyl group. The figures given below were determined by exploding the materials, loaded at the density indicated, in a small bomb, and measuring the pressure by means of a piston and obturator. *Density of loading* is grams of explosive per cubic centimeter of bomb capacity.

	Pressure: Kilograms per square centimeter		
Density of loading:	0.20	0.25	0.30
Trinitrobenzene................	2205	3050	4105
Trinitrotoluene................	1840	2625	3675
Trinitro-*m*-xylene	1635	2340	2980
Trinitromesitylene.............	1470	2200	2780
Trinitrophenol (picric acid)......	2150	3055	3865
Trinitroresorcinol (styphinic acid)	2080	2840	....
Trinitroaniline (picramide)......	2080	2885	3940
Trinitro-*m*-cresol............ ...	1760	2480	3360
Trinitronaphthalene............	....	2045	2670

Similar inferences may be made from the results of lead block tests. Fifteen grams of the explosives produced the expansions indicated below, each figure representing the average from twenty or more experiments:

Trinitrobenzene.......... 480 cc.
Trinitrotoluene.......... 452 cc.
Picric acid.............. 470 cc.
Trinitrocresol........... 384 cc.
Trinitronaphthalene...... 166 cc.

Mono- and Di-Nitrobenzene

Nitrobenzene is a pale yellow liquid, b.p. 208.0°, which is poisonous and has an almondlike odor closely resembling that of benzaldehyde (which is not poisonous). It is used as a component of certain Sprengel explosives and as a raw material for the preparation of aniline and of intermediates for the manufacture of dyestuffs and medicinals. Its preparation, familiar to every student of organic chemistry, is described here in order that the conditions for the substitution of one nitro group in benzene may serve us more conveniently as a standard for judging the relative ease and difficulty of the nitration of other substances.

Preparation of Nitrobenzene. One hundred and fifty grams of concentrated sulfuric acid (*d.* 1.84) and 100 grams of nitric acid (*d.* 1.42) are mixed in a 500-cc. flask and cooled to room temperature, and 51 grams of benzene is added in small portions at a time with frequent shaking. Shaking at this point is especially necessary lest the reaction suddenly become violent. If the temperature of the mixture rises above 50-60°, the addition of the benzene is interrupted and the mixture is cooled at the tap. After all the benzene has been added, an air condenser is attached to the flask and the material is heated in the water bath for an hour at 60° (thermometer in the water). After cooling, the nitrobenzene (upper layer) is separated from the spent acid, washed once with water (the nitrobenzene is now the lower layer), then several times with dilute sodium carbonate solution until it is free from acid, then once more with water, dried with calcium chloride, and distilled (not quite to dryness). The portion boiling at 206-208° is taken as nitrobenzene.

m-Dinitrobenzene, in accordance with the rule of Crum Brown and Gibson, is the only product which results ordinarily from the nitration of nitrobenzene. Small amounts of the *ortho* and *para* compounds have been procured, along with the *meta*, from the nitration of benzene in the presence of mercuric nitrate.[2] Dinitrobenzene has been used in high explosives for shells in mixtures with more powerful explosives or with ammonium nitrate. Its use

[2] Davis, *J. Am. Chem. Soc.*, 43, 598 (1921).

as a raw material for the manufacture of tetranitroaniline is now no longer important.

Preparation of Dinitrobenzene. A mixture of 25 grams of concentrated sulfuric acid (*d.* 1.84) and 15 grams of nitric acid (*d.* 1.52) is heated in an open flask in the boiling water bath in the hood, and 10 grams of nitrobenzene is added gradually during the course of half an hour. The mixture is cooled somewhat, and drowned in cold water. The dinitrobenzene separates as a solid. It is crushed with water, washed with water, and recrystallized from alcohol or from nitric acid. Dinitrobenzene crystallizes from nitric acid in beautiful needles which are practically colorless, m.p. 90°.

Trinitrobenzene

1,3,5-Trinitrobenzene (*sym*-trinitrobenzene, TNB) may be prepared only with the greatest difficulty by the nitration of *m*-dinitrobenzene. Hepp[3] first prepared it by this method, and Hepp and Lobry de Bruyn[4] improved the process, treating 60 grams of *m*-dinitrobenzene with a mixture of 1 kilo of fuming sulfuric acid and 500 grams of nitric acid (*d.* 1.52) for 1 day at 100° and for 4 days at 110°. Claus and Becker[5] obtained trinitrobenzene by the action of concentrated nitric acid on trinitrotoluene. Trinitrobenzoic acid is formed first, and this substance in the hot liquid loses carbon dioxide from its carboxyl group.
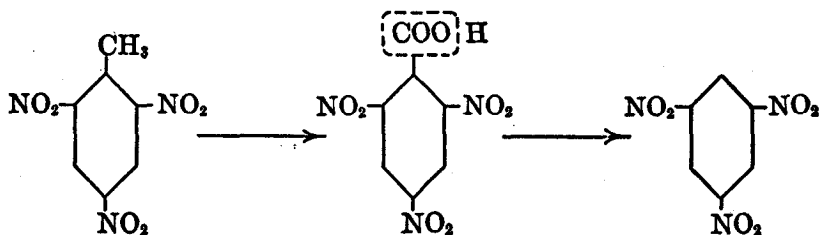
For commercial production the Griesheim Chem. Fabrik[6] is reported to have used a process in which 1 part of TNT is heated at 150-200° with a mixture of 5 parts of fuming nitric acid and 10 parts of concentrated sulfuric acid. In a process devised by J. Meyer,[7] picryl chloride (2,4,6-trinitrochlorobenzene) is reduced by means of copper powder in hot aqueous alcohol. The reported details are 25 kilos of picryl chloride, 8 kilos of copper

[3] *Ber.,* **9,** 402 (1876); *Ann.,* **215,** 345 (1882).
[4] *Rec. trav. chim.,* **13,** 149 (1894).
[5] *Ber.,* **16,** 1597 (1883).
[6] Ger. Pat. 77,353, 77,559 (1893); 127,325 (1901).
[7] Ger. Pat. 234,726 (1909).

powder, 250 liters of 95 per cent alcohol, and 25 liters of water, refluxed together for 2 hours and filtered hot; the TNB crystallizes out in good yield when the liquid is cooled.

The nitration of m-dinitrobenzene is too expensive of acid and of heat for practical application, and the yields are poor. Toluene and chlorobenzene are nitrated more easily and more economically, and their trinitro compounds are feasible materials for the preparation of TNB. Oxidation with nitrosulfuric acid has obvious disadvantages. The quickest, most convenient, and cheapest method is probably that in which TNT is oxidized by means of chromic acid in sulfuric acid solution.

Preparation of Trinitrobenzene. A mixture of 30 grams of purified TNT and 300 cc. of concentrated sulfuric acid is introduced into a tall beaker, which stands in an empty agateware basin, and the mixture is stirred actively by means of an electric stirrer while powdered sodium dichromate ($Na_2Cr_2O_7\cdot 2H_2O$) is added in small portions at a time, care being taken that no lumps are formed and that none floats on the surface of the liquid. The temperature of the liquid rises. When it has reached 40°, cold water is poured into the basin and the addition of dichromate is continued, with stirring, until 45 grams has been added, the temperature being kept always between 40° and 50°. The mixture is stirred for 2 hours longer at the same temperature, and is then allowed to cool and to stand over night, in order that the trinitrobenzoic acid may assume a coarser crystalline form and may be filtered off more readily. The strongly acid liquid is filtered through an asbestos filter; the solid material is rinsed with cold water and transferred to a beaker in which it is treated with warm water at 50° sufficient to dissolve all soluble material. The warm solution is filtered, and boiled until no more trinitrobenzene precipitates. The crystals of TNB growing in the hot aqueous liquid often attain a length of several millimeters. When filtered from the cooled liquid and rinsed with water, they are practically pure, almost colorless or greenish yellow leaflets, m.p. 121-122°.

Trinitrobenzene is only moderately soluble in hot alcohol, more readily in acetone, ether, and benzene. Like other polynitro aromatic compounds it forms colored molecular compounds with many aromatic hydrocarbons and organic bases.[8] The compound

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[8] Compare Hepp, *Ann.*, **215**, 356 (1882); Sudborough, *J. Chem. Soc.*, **75**, 588 (1889); **79**, 522 (1901); **83**, 1334 (1903); **89**, 583 (1906); **97, 773** (1910); **99**, 209 (1911); **109**, 1339 (1916); Sachs and Steinert, *Ber.*, **37**, 1745 (1904); Nölting and Sommerhoff, *ibid.*, **39**, 76 (1906); Kremann, *ibid.*, **39**, 1022 (1906); Ciusa, *Gazz. chim. ital.*, **43**, II, 91 (1913); Ciusa and

with aniline is bright red; that with naphthalene, yellow. The compounds with amines are beautifully crystalline substances, procurable by warming the components together in alcohol, and are formed generally in the molecular proportions 1 to 1, although diphenylamine and quinoline form compounds in which two molecules of TNB are combined with one of the base.

Trinitrobenzene gives red colors with ammonia and with aqueous alkalies. On standing in the cold with methyl alcoholic sodium methylate, it yields 3,5-dinitroanisol by a metathetical reaction.[9]
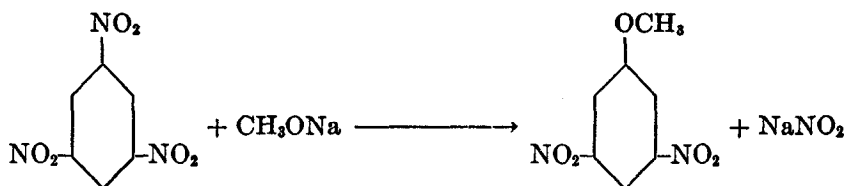
On boiling with alcoholic soda solution it undergoes a partial reduction to form 3,3',5,5'-tetranitroazoxybenzene.[10]
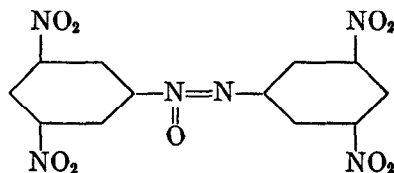
The first product, however, of the reaction of methyl alcoholic caustic alkali on TNB is a red crystalline addition product having the empirical composition $TNB \cdot CH_3ONa \cdot \frac{1}{2}H_2O$, isolated by Lobry de Bruyn and van Leent[11] in 1895. The structure of this substance has been discussed by Victor Meyer,[12] by Angeli,[13] by Meisenheimer,[14] and by Schlenck,[15] and is probably best represented by the formula which Meisenheimer suggested. It is thus

Vecchiotti, *Atti accad. Lincei,* 20, II, 377 (1911); 21, II, 161 (1912); Sastry, *J. Chem. Soc.,* 109, 270 (1916); Hammick and Sixsmith, *J. Chem. Soc.,* 972 (1939).

[9] Lobry de Bruyn, *Rec. trav. chim.,* 9, 208 (1890).

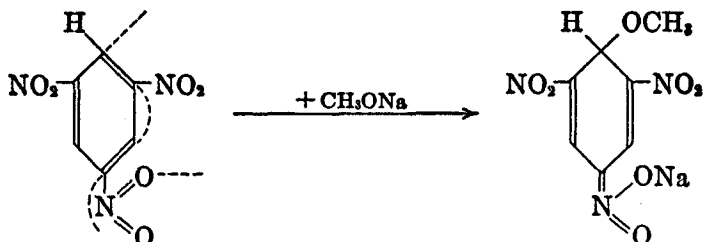[10] Lobry de Bruyn and van Leent, *ibid.,* 13, 148 (1894).

[11] *Ibid.,* 14, 150 (1895).

[12] *Ber.,* 29, 848 (1896).

[13] *Gazz. chim. ital.,* 27, II, 366 (1897). Compare also Hantzsch and Kissel, *Ber.,* 32, 3137 (1899).

[14] *Ann.,* 323, 214, 241 (1902).

[15] *Ber.,* 47, 473 (1914).

probably the product of the 1,6-addition of sodium methylate to the conjugate system which runs through the ring and terminates in the oxygen of the nitro group. Busch and Kögel[16] have prepared di- and tri-alcoholates of TNB, and Giua[17] has isolated a compound of the empirical composition TNB·NaOH, to which he ascribed a structure similar to that indicated above. All these compounds when dry are dangerous primary explosives. They are soluble in water, and the solutions after acidification contain red, water-soluble acids which yield sparingly soluble salts with copper and other heavy metals, and the salts are primary explosives. The acids, evidently having the compositions TNB·CH$_3$OH, TNB·H$_2$O, etc., have not been isolated in a state of purity, and are reported to decompose spontaneously in small part into TNB, alcohol, water, etc., and in large part into oxalic acid, nitrous fumes, and colored amorphous materials which have not been identified. All the polynitro aromatic hydrocarbons react similarly with alkali, and the use of alkali in any industrial process for their purification is bad practice and extremely hazardous.

Trinitrobenzene reacts with hydroxylamine in cold alcohol solution, picramide being formed by the direct introduction of an amino group.[18]
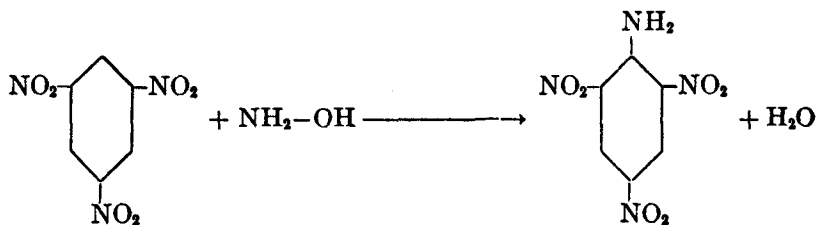
Two or three nitro groups on the aromatic nucleus, particularly those in the 2,4-, 2,6-, and 2,4,6-positions, have a strong effect in increasing the chemical activity of the group or atom in the

[16] *Ber.*, **43**, 1549 (1910).

[17] *Gazz. chim. ital.*, **45**, II, 351 (1915).

[18] Meisenheimer and Patzig, *Ber.*, **39**, 2534 (1906).

1-position. Thus, the hydroxyl group of trinitrophenol is acidic, and the substance is called picric acid. A chlorine atom in the same position is like the chlorine of an acid chloride (picryl chloride), an amino group like the amino of an acid amide (trinitroaniline is picramide), and a methoxy like the methoxy of an ester (trinitroanisol has· the reactions of methyl picrate). In general the picryl group affects the activity of the atom or group to which it is attached in the same way that the acyl or R—CO— group does. If the picryl group is attached to a carboxyl, the carboxyl will be expected to lose CO_2 readily, as pyruvic acid, CH_3—CO—COOH, does when it is heated with dilute sulfuric acid, and this indeed happens with the trinitrobenzoic acid from which TNB is commonly prepared. TNB itself will be expected to exhibit some of the properties of an aldehyde, of which the aldehydic hydrogen atom is readily oxidized to an acidic hydroxyl group, and it is in fact oxidized to picric acid by the action of potassium ferricyanide in mildly alkaline solution.[19] We shall see many examples of the same principle throughout the chemistry of the explosive aromatic nitro compounds.

Trinitrobenzene is less sensitive to impact than TNT, more powerful, and more brisant. The detonation of a shell or bomb, loaded with TNB, in the neighborhood of buildings or other construction which it is desired to destroy, creates a more damaging explosive wave than an explosion of TNT, and is more likely to cause the collapse of walls, etc., which the shell or bomb has failed to hit. Drop tests carried out with a 5-kilogram weight falling upon several decigrams of each of the various explosives contained in a small cup of iron (0.2 mm. thick), covered with a small iron disc of the same thickness, gave the following figures for the distances through which the weight must fall to cause explosion in 50 per cent of the trials.

	CENTIMETERS
Trinitrobenzene	150
Trinitrotoluene	110
Hexanitrodiphenylamine ammonium salt	75
Picric acid	65
Tetryl	50
Hexanitrodiphenylamine	45

[19] Hepp, *Ann.,* 215, 344 (1882).

According to Dautriche,[20] the density of compressed pellets of TNB is as follows:

PRESSURE: KILOS PER SQUARE CENTIMETER	DENSITY
275	1.343
685	1.523
1375	1.620
2060	1.641
2750	1.654
3435	1.662

The greatest velocity of detonation for TNB which Dautriche found, namely 7347 meters per second, occurred when a column of 10 pellets, 20 mm. in diameter and weighing 8 grams each, density 1.641 or 1.662, was exploded in a paper cartridge by means of an initiator of 0.5 gram of mercury fulminate and 80 grams of dynamite. The greatest which he found for TNT was 7140 meters per second, 10 similar pellets, density 1.60, in a paper cartridge exploded by means of a primer of 0.5 gram of fulminate and 25 grams of dynamite. The maximum value for picric acid was 7800 meters per second; a column of pellets of the same sort, density 1.71, exploded in a copper tube 20-22 mm. in diameter, by means of a primer of 0.5 gram of fulminate and 80 grams of dynamite. The highest velocity with picric acid in paper cartridges was 7645 meters per second with pellets of densities 1.73 and 1.74 and the same charge of initiator.

Velocity of detonation, other things being equal, depends upon the physical state of the explosive and upon the nature of the envelope which contains it. For each explosive there is an optimum density at which it shows its highest velocity of detonation. There is also for each explosive a minimum priming charge necessary to insure its complete detonation, and larger charges do not cause it to explode any faster. Figures for the velocity of detonation are of little interest unless the density is reported or unless the explosive is cast and is accordingly of a density which, though perhaps unknown, is easily reproducible. The cordeau of the following table[21] was loaded with TNT which was subsequently pulverized *in situ* during the drawing down of the lead tube:

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[20] *Mém. poudres*, **16**, 28 (1911-1912).
[21] Desvergnes, *Mém. poudres*, **19**, 223 (1922).

	METERS PER SECOND
Cast trinitrobenzene.................	7441
Cast tetryl.........................	7229
Cast trinitrotoluene.................	7028
Cast picric acid.....................	6777
Compressed trinitrotoluene (d. 0.909) ..	4961
Compressed picric acid (d. 0.862)......	4835
Cordeau............................	6900

Nitration of Chlorobenzene

The nitration of chlorobenzene is easier than the nitration of benzene and more difficult than the nitration of toluene. Trinitro-chlorobenzene (picryl chloride) can be prepared on the plant scale by the nitration of dinitrochlorobenzene, but the process is expensive of acid and leads to but few valuable explosives which cannot be procured more cheaply and more simply from dinitro-chlorobenzene by other processes. Indeed, there are only two important explosives, namely TNB and hexanitrobiphenyl, for the preparation of which picryl chloride could be used advantageously if it were available in large amounts. In the laboratory, picryl chloride is best prepared by the action of phosphorus pentachloride on picric acid.

During the early days of the first World War in Europe, electrolytic processes for the production of caustic soda were yielding in this country more chlorine than was needed by the chemical industries, and it was necessary to dispose of the excess. The pressure to produce toluene had made benzene cheap and abundant. The chlorine, which would otherwise have become a nuisance and a menace, was used for the chlorination of benzene. Chlorobenzene and dichlorobenzene became available, and dichlorobenzene since that time has been used extensively as an insecticide and moth exterminator. Dinitrodichlorobenzene was tried as an explosive under the name of *parazol*. When mixed with TNT in high-explosive shells, it did not detonate completely, but presented interesting possibilities because the unexploded portion, atomized in the air, was a vigorous itch-producer and lachrymator, and because the exploded portion yielded phosgene. The chlorine atom of chlorobenzene is unreactive, and catalytic processes[22] for replacing it by hydroxyl and amino groups had

---

[22] Steam and silica gel to produce phenol from chlorobenzene, the Dow process with steam and a copper salt catalyst, etc.

not yet been developed. In dinitrochlorobenzene, however, the chlorine is active. The substance yields dinitrophenol readily by hydrolysis, dinitroaniline by reaction with ammonia, dinitromethylaniline more readily yet by reaction with methylamine. These and similar materials may be nitrated to explosives, and the third nitro group may be introduced on the nucleus much more readily, after the chlorine has been replaced by a more strongly *ortho-para* orienting group, than it may be before the chlorine has been so replaced. Dinitrochlorobenzene thus has a definite advantage over picryl chloride. It has the advantage also over phenol, aniline, etc. (from chlorobenzene by catalytic processes), that explosives can be made from it which cannot be made as simply or as economically from these materials. Tetryl and hexanitrodiphenylamine are examples. The possibilities of dinitrochlorobenzene in the explosives industry have not yet been fully exploited.

Preparation of Dinitrochlorobenzene. One hundred grams of chlorobenzene is added drop by drop to a mixture of 160 grams of nitric acid (*d.* 1.50) and 340 grams of sulfuric acid (*d.* 1.84) while the mixture is stirred mechanically. The temperature rises because of the heat of the reaction, but is not allowed to go above 50-55°. After all the chlorobenzene has been added, the temperature is raised slowly to 95° and is kept there for 2 hours longer while the stirring is continued. The upper layer of light yellow liquid solidifies when cold. It is removed, broken up under water, and rinsed. The spent acid, on dilution with water, precipitates an additional quantity of dinitrochlorobenzene. All the product is brought together, washed with cold water, then several times with hot water while it is melted, and finally once more with cold water under which it is crushed. Then it is drained and allowed to dry at ordinary temperature. The product, melting at about 50°, consists largely of 2,4-dinitrochlorobenzene, m.p. 53.4°, along with a small quantity of the 2,6-dinitro compound, m.p. 87-88°. The two substances are equally suitable for the manufacture of explosives. They yield the same trinitro compound, and the same final products by reaction with methylamine, aniline, etc., and subsequent nitration of the materials which are first formed. Dinitrochlorobenzene causes a severe itching of the skin, both by contact with the solid material and by exposure to its vapors.

Trinitrotoluene (TNT, trotyl, tolite, triton, tritol, trilite, etc.)

When toluene is nitrated, about 96 per cent of the material behaves in accordance with the rule of Crum Brown and Gibson.
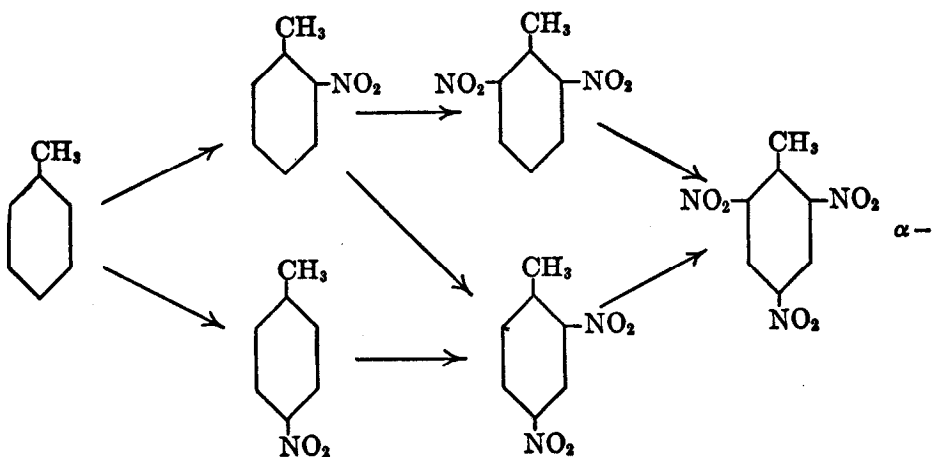
In industrial practice the nitration is commonly carried out in three stages, the spent acid from the trinitration being used for the next dinitration, the spent acid from this being used for the mononitration, and the spent acid from this either being fortified
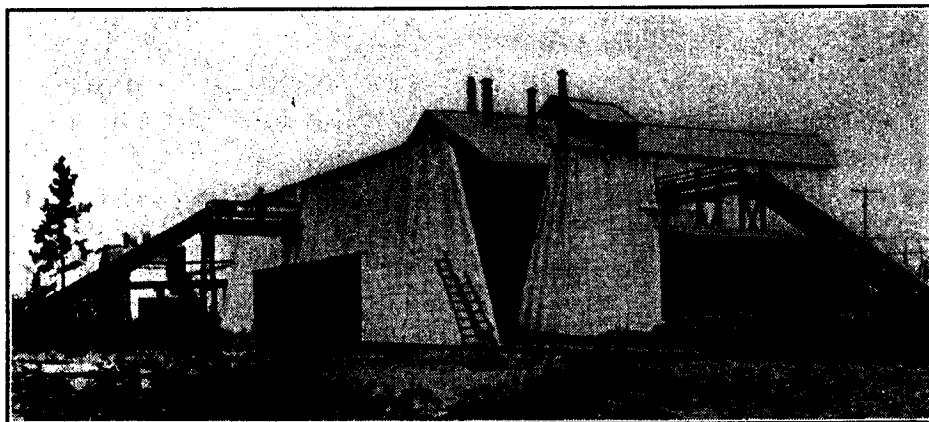

FIGURE 46. TNT Manufacturing Building, Showing Barricades and Safety Chutes. (Courtesy E. I. du Pont de Nemours and Company, Inc.)

for use again or going to the acid-recovery treatment. The principal products of the first stage are o- (b.p. 222.3°) and p-nitrotoluene (m.p. 51.9°) in relative amounts which vary somewhat according to the temperature at which the nitration is carried out. During the dinitration, the *para* compound yields only 2,4-dinitrotoluene (m.p. 70°), while the *ortho* yields the 2,4- and the 2,6- (m.p. 60.5°). Both these in the trinitration yield 2,4,6-trinitrotoluene or α-TNT. 2,4-Dinitrotoluene predominates in the product of the dinitration, and crude TNT generally contains a

small amount, perhaps 2 per cent, of this material which has escaped further nitration. The substance is stable and less reactive even than α-TNT, and a small amount of it in the purified TNT, if insufficient to lower the melting point materially, is not regarded as an especially undesirable impurity. The principal impurities arise from the *m*-nitrotoluene (b.p. 230-231°) which is formed to the extent of about 4 per cent in the product of the mononitration. We omit discussion of other impurities, such as the nitrated xylenes which might be present in consequence of impurities in the toluene which was used, except to point out that the same considerations apply to trinitro-*m*-xylene (TNX) as apply to 2,4-dinitrotoluene—a little does no real harm—while the nitro derivatives of *o*- and *p*-xylene are likely to form oils and are extremely undesirable. In *m*-nitrotoluene, the nitro group inhibits further substitution, the methyl group promotes it, the two groups disagree in respect to the positions which they activate, but substitution takes place under the orienting influence of the methyl group.
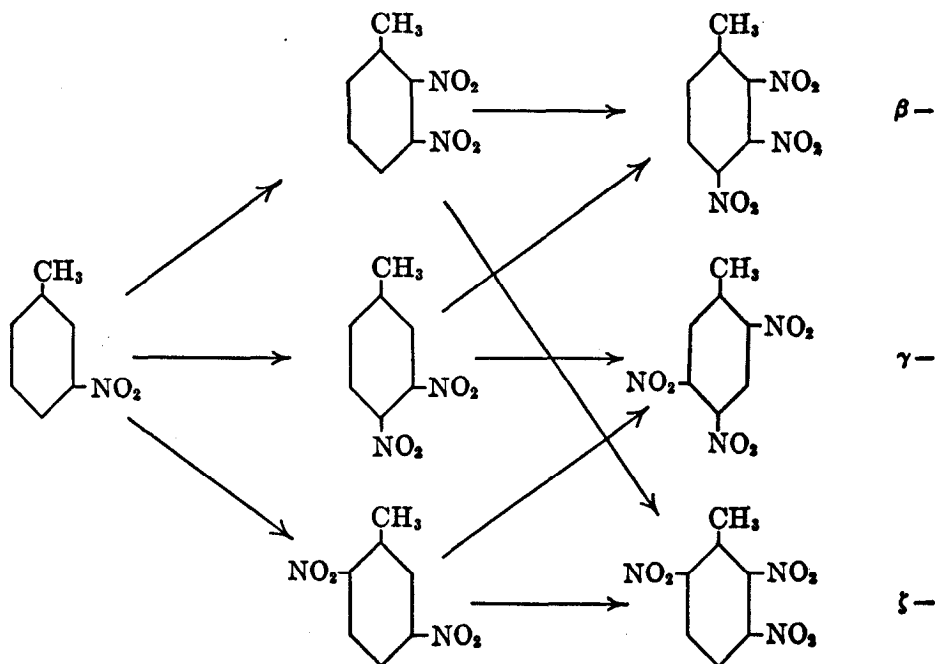
β-TNT or 2,3,4-trinitrotoluene (m.p. 112°) is the principal product of the nitration of *m*-nitrotoluene; γ-TNT or 2,4,5-trinitrotoluene (m.p. 104°) is present in smaller amount; and of ζ-TNT or 2,3,6-trinitrotoluene (m.p. 79.5°), the formation of

which is theoretically possible and is indicated above for that reason, there is not more than a trace.[23] During the trinitration a small amount of the α-TNT is oxidized to trinitrobenzoic acid, finally appearing in the finished product in the form of TNB, which, however, does no harm if it is present in small amount. At the same time some of the material is destructively oxidized and nitrated by the strong mixed acid to form tetranitromethane, which is driven off with the steam during the subsequent boiling and causes annoyance by its lachrymatory properties and unpleasant taste. The product of the trinitration is separated from the spent acid while still molten, washed with boiling water until free from acid, and grained—or, after less washing with hot water, subjected to purification by means of sodium sulfite.

In this country the crude TNT, separated from the wash water, is generally grained by running the liquid slowly onto the refrigerated surface of an iron vessel which surface is continually scraped by mechanical means. In France the material is allowed to cool slowly under water in broad and shallow wooden tubs, while it is stirred slowly with mechanically actuated wooden paddles. The cooling is slow, for the only loss of heat is by radiation. The French process yields larger and flatter crystals, flaky, often several millimeters in length. The crystallized crude TNT is of about the color of brown sugar and feels greasy to the touch. It consists of crystals of practically pure α-TNT coated with an oily (low-melting) mixture of β- and γ-TNT, 2,4-dinitrotoluene, and possibly TNB and TNX. It is suitable for many uses as an explosive, but not for high-explosive shells. The oily mixture of impurities segregates in the shell, and sooner or later exudes through the thread by which the fuze is attached. The exudate is disagreeable but not particularly dangerous. The difficulty is that exudation leaves cavities within the mass of the charge, perhaps a central cavity under the booster which may cause the shell to fail to explode. There is also the possibility that the shock of setback across a cavity in the rear of the charge may cause the shell to explode prematurely while it is still within the barrel of the gun.

The impurities may be largely removed from the crude TNT,

[23] 3,5-Dinitrotoluene, in which both nitro groups are *meta* to the methyl, is probably not formed during the dinitration, and δ- and ε-TNT, namely 3,4,5- and 2,3,5-trinitrotoluene, are not found among the final products of the nitration of toluene.

with a corresponding improvement in the melting point and appearance of the material, by washing the crystals with a solvent. On a plant scale, alcohol, benzene, solvent naphtha (mixed xylenes), carbon tetrachloride, and concentrated sulfuric acid have all been used. Among these, sulfuric acid removes dinitrotoluene most readily, and organic solvents the β- and γ-TNT,
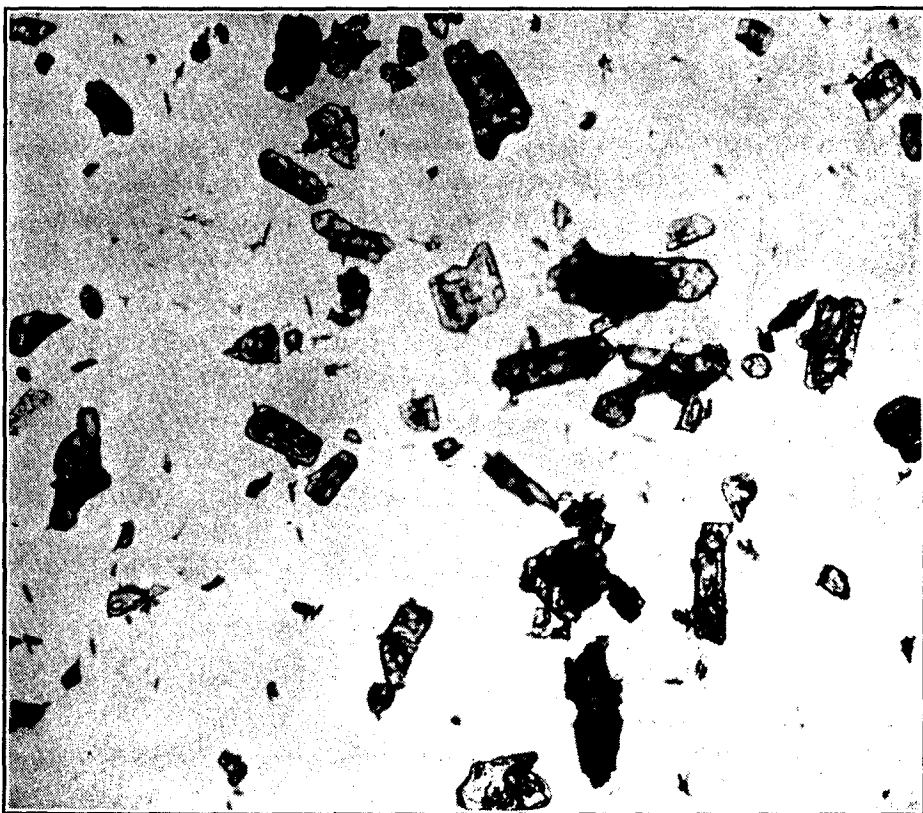

FIGURE 47. Commercial Sample of Purified TNT (25×).

but all of them dissolve away a portion of the α-TNT with resulting loss. The material dissolved by the sulfuric acid is recovered by diluting with water. The organic solvents are recovered by distillation, and the residues, dark brown liquids known as "TNT oil," are used in the manufacture of non-freezing dynamite. The best process of purification is that in which the crude TNT is agitated with a warm solution of sodium sulfite. A 5 per cent solution is used, as much by weight of the solution as there is of the crude TNT. The sulfite leaves the α-TNT (and any TNB, TNX, and 2,4-dinitrotoluene) unaffected, but reacts rapidly and completely with the β- and γ-TNT to form red-colored materials

which are readily soluble in water. After the reaction, the purified material is washed with water until the washings are colorless.

Muraour[24] believes the sulfite process for the purification of TNT to be an American invention. At any rate, the story of its discovery presents an interesting example of the consequences of working rightly with a wrong hypothesis. The nitro group in the *m*-position in β- and γ-TNT is *ortho*, or *ortho* and *para*, to two other nitro groups, and accordingly is active chemically. It is replaced by an amino group by the action of alcoholic ammonia both in the hot[25] and in the cold,[26] and undergoes similar reactions with hydrazine and with phenylhydrazine. It was hoped that it would be reduced more readily than the unactivated nitro groups of α- or symmetrical TNT, and that the reduction products could be washed away with warm water. Sodium polysulfide was tried and did indeed raise the melting point, but the treated material contained finely divided sulfur from which it could not easily be freed, and the polysulfide was judged to be unsuitable. In seeking for another reducing agent, the chemist bethought himself of sodium sulfite, which, however, does not act in this case as a reducing agent, and succeeded perfectly in removing the β- and γ-TNT.

The reaction consists in the replacement of the nitro by a sodium sulfonate group:
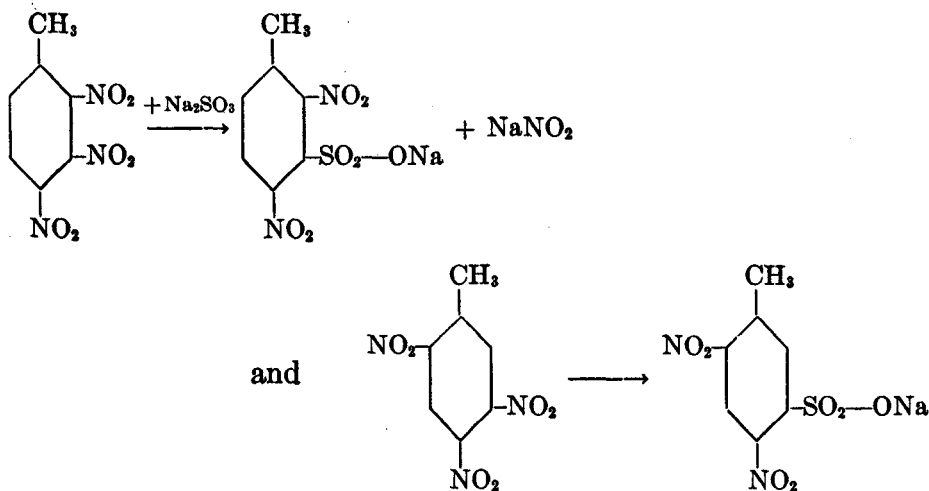


[24] *Bull. soc. chim.*, IV, **35**, 367 (1924); *Army Ordnance*, **5**, 507 (1924).
[25] Hepp, *Ann.*, **215**, 364 (1882).
[26] Giua, *Atti accad. Lincei*, **23**, II, 484 (1914); *Gazz. chim. ital.*, **45**, I, 345 (1915).

The soluble sulfonates in the deep red solution, if they are thrown into the sewer, represent a loss of about 4 per cent of all the toluene—a serious loss in time of war—as well as a loss of many pounds of nitro group nitrogen. The sulfonic acid group in these substances, like the nitro group which it replaced, is *ortho*, or *ortho* and *para*, to two nitro groups, and is active and still capable of undergoing the same reactions as the original nitro group. They may be converted into a useful explosive by reaction with methylamine and the subsequent nitration of the resulting dinitrotolylmethylamines, both of which yield 2,4,6-trinitrotolyl-3-methylnitramine or *m*-methyltetryl.
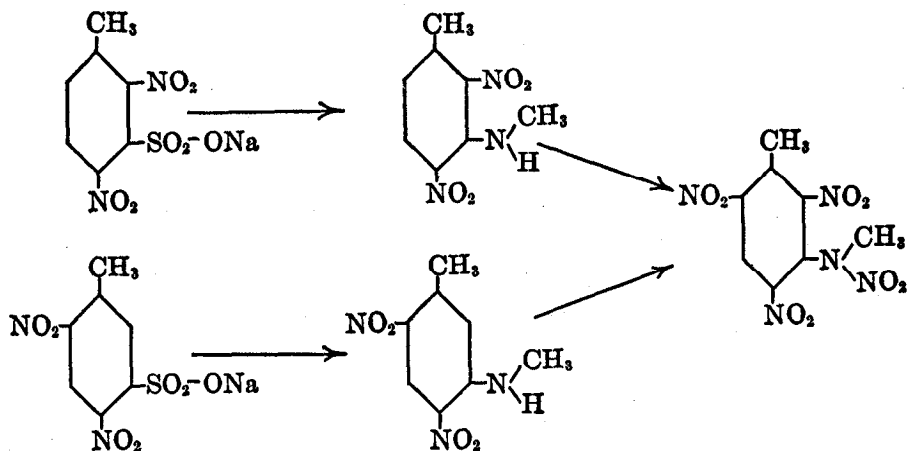
m-Methyltetryl, pale yellow, almost white, crystals from alcohol, m.p. 102°, was prepared in 1884 by van Romburgh[27] by the nitration of dimethyl-*m*-toluidine, and its structure was demonstrated fully in 1902 by Blanksma,[28] who prepared it by the synthesis indicated on the next page.

β- and γ-TNT lose their active nitro group by the action of aqueous alkali and yield salts of dinitro-*m*-cresol.[29] The mixed dinitro-*m*-cresols which result may be nitrated to trinitro-*m*-cresol, a valuable explosive. Their salts, like the picrates, are primary explosives and sources of danger. β- and γ-TNT react with lead oxide in alcohol to form lead dinitrocresolates, while α-TNT under the same conditions remains unaffected.

In plant-scale manufacture, TNT is generally prepared by a

[27] *Rec. trav. chim.*, **3**, 414 (1884).

[28] *Ibid.*, **21**, 327 (1902).

[29] Will, *Ber.*, **47**, 711 (1914); Copisarow, *Chem. News*, **112**, 283 (1915).
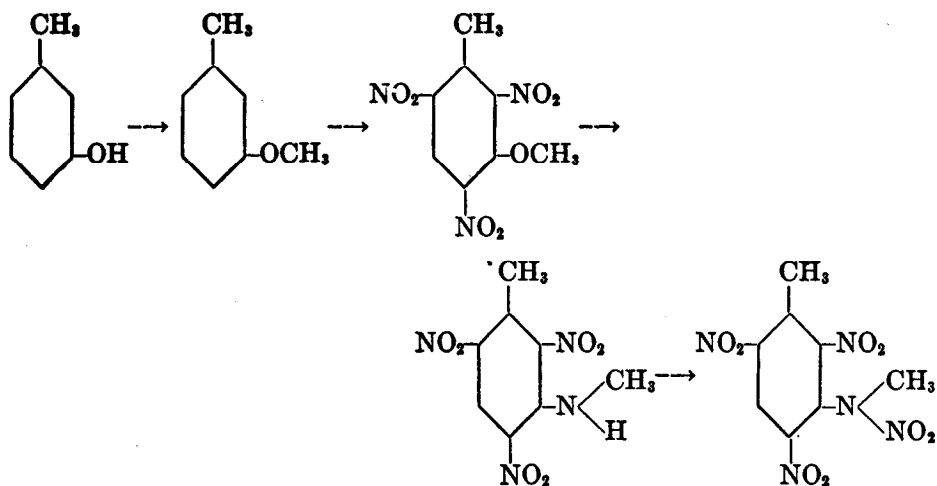
three-stage process, but processes involving one and two nitrations have also been used.

Preparation of Trinitrotoluene (Three Stages). A mixture of 294 grams of concentrated sulfuric acid (*d*. 1.84) and 147 grams of nitric acid (*d*. 1.42) is added slowly from a dropping funnel to 100 grams of toluene in a tall 600-cc. beaker, while the liquid is stirred vigorously with an electric stirrer and its temperature is maintained at 30° to 40° by running cold water in the vessel in which the beaker is standing. The addition of acid will require from an hour to an hour and a half. The stirring is then continued for half an hour longer without cooling; the mixture is allowed to stand over night in a separatory funnel; the lower layer of spent acid is drawn off; and the crude mononitrotoluene is weighed. One-half of it, corresponding to 50 grams of toluene, is taken for the dinitration.

The mononitrotoluene (MNT) is dissolved in 109 grams of concentrated sulfuric acid (*d*. 1.84) while the mixture is cooled in running water. The solution in a tall beaker is warmed to 50°, and a mixed acid, composed of 54.5 grams each of nitric acid (*d*. 1.50) and sulfuric acid (*d*. 1.84), is added slowly drop by drop from a dropping funnel while the mixture is stirred mechanically. The heat generated by the reaction raises the temperature, and the rate of addition of the acid is regulated so that the temperature of the mixture lies always between 90° and 100°. The addition of the acid will require about 1 hour. After the acid has been added, the mixture is stirred for 2 hours longer at 90-100° to complete the nitration. Two layers separate on standing. The upper layer consists largely of dinitrotoluene (DNT), but probably contains a certain amount of TNT. The trinitration in the laboratory is conveniently carried out without separating the DNT from the spent acid.

While the dinitration mixture is stirred actively at a temperature of about 90°, 145 grams of fuming sulfuric acid (*oleum* containing 15 per

cent free SO_3) is added slowly by pouring from a beaker. A mixed acid, composed of 72.5 grams each of nitric acid (d. 1.50) and 15 per cent oleum, is now added drop by drop with good agitation while the heat of the reaction maintains the temperature at 100-115°. After about three-quarters of the acid has been added, it will be found necessary to apply external heat to maintain the temperature. After all the acid has been added (during 1½ to 2 hours), the heating and stirring are continued for 2 hours longer at 100-115°. After the material has stood over night, the upper TNT layer will be found to have solidified to a hard cake, and the lower layer of spent acid to be filled with crystals. The acid is filtered through a Büchner funnel (without filter paper), and the cake is broken up and washed with water on the same filter to remove excess of acid. The spent acid contains considerable TNT in solution; this is precipitated by pouring the acid into a large volume of water, filtered off, rinsed with water, and added to the main batch. All the product is washed three or four times by agitating it vigorously with hot water under which it is melted. After the last washing, the TNT is granulated by allowing it to cool slowly under hot water while the stirring is continued. The product, filtered off and dried at ordinary temperature, is equal to a good commercial sample of crude TNT. It may be purified by dissolving in warm alcohol at 60° and allowing to cool slowly, or it may be purified by digesting with 5 times its weight of 5 per cent sodium hydrogen sulfite solution at 90° for half an hour with vigorous stirring, washing with hot water until the washings are colorless, and finally granulating as before. The product of this last treatment is equal to a good commercial sample of purified TNT. Pure α-TNT, m.p. 80.8°, may be procured by recrystallizing this material once from nitric acid (d. 1.42) and once from alcohol.

Several of the molecular compounds of TNT with organic bases are listed below.[30] TNT and diphenylamine give an orange-brown color when warmed together or when moistened with alcohol, and the formation of a labile molecular compound of the two substances has been demonstrated.[31]

The compound of TNT with potassium methylate is a dark red powder which inflames or explodes when heated to 130-150°, and has been reported to explode spontaneously on standing at ordinary temperature. An aqueous solution of this compound, on the addition of copper tetrammine nitrate, gives a brick-red precipitate which, when dry, detonates violently at 120°. Pure TNT

[30] See references under TNB.
[31] Giua, *Gazz. chim. ital.*, **45**, II, 357 (1915).

MOLECULAR PROPORTIONS	M.P.	DESCRIPTION
TNT: Substance		
1 : 1 Aniline.....................	83–84°	Long brilliant red needles.
1 : 1 Dimethylaniline..............	...	Violet needles.
1 : 1 o-Toluidine.................	53–55°	Light red needles.
1 : 1 m-Toluidine...............	62–63°	Light red needles.
1 : 1 α-Naphthylamine...........	141.5°	Dark red needles.
1 : 1 β-Naphthylamine...........	113.5°	Bright red prismatic needles.
1 : 1 β-Acetnaphthalide..........	106°	Yellow needles.
1 : 1 Benzyl-β-naphthylamine......	106.5°	Brilliant crimson needles.
1 : 1 Dibenzyl-β-naphthylamine....	108°	Deep brick-red needles.
2 : 1 Benzaldehydephenylhydrazone	84°	Dark red needles.
1 : 1 2-Methylindole.............	110°	Yellow needles.
3 : 2 Carbazole.................	160°	Yellow needles.
1 : 1 Carbazole.................	140–200°	Dark yellow needles.

explodes or inflames when heated to about 230°, but Dupré[32] found that the addition of solid caustic potash to TNT at 160° caused immediate inflammation or explosion. A mixture of powdered solid caustic potash and powdered TNT inflames when heated, either slowly or rapidly, to 80°. A similar mixture with caustic soda inflames at 80° if heated rapidly, but may be heated to 200° without taking fire if the heating is slow. If a small fragment of solid caustic potash is added to melted TNT at 100°, it becomes coated with a layer of reaction product and nothing further happens. If a drop of alcohol, in which both TNT and KOH are soluble, is now added, the material inflames within a few seconds. Mixtures of TNT with potassium and sodium carbonate do not ignite when heated suddenly to 100°.

Since the methyl group of TNT is attached to a picryl group, we should expect it in some respects to resemble the methyl group of a ketone. Although acetone and other methyl ketones brominate with great ease, TNT does not brominate and may even be recrystallized from bromine. The methyl group of TNT, however, behaves like the methyl group of acetone in certain condensation reactions. In the presence of sodium carbonate TNT condenses with p-nitrosodimethylaniline to form the dimethylaminoanilide of trinitrobenzaldehyde,[33] from which trinitrobenzaldehyde and N,N-dimethyl-p-diaminobenzene are produced readily by acid hydrolysis.

[32] "Twenty-eighth Annual Report of H. M. Inspector of Explosives," 1903, p. 26.

[33] Sachs and Kempf, Ber., 35, 1222 (1902); Sachs and Everding, ibid., 36, 999 (1903).
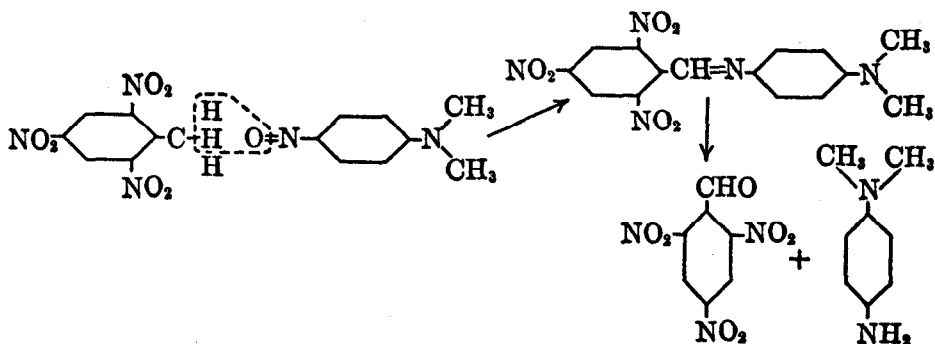
If a drop of piperidine is added to a pasty mixture of TNT and benzaldehyde, the heat of the reaction is sufficient to cause the material to take fire. The same substances in alcohol or benzene solution condense smoothly in the presence of piperidine to form trinitrostilbene.[34]
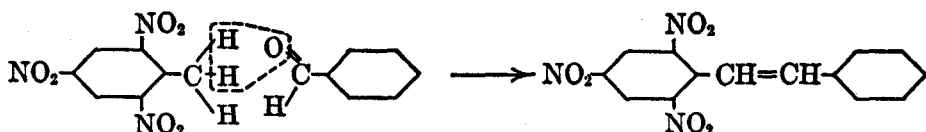
Preparation of Trinitrostilbene. To 10 grams of TNT dissolved in 25 cc. of benzene in a 100-cc. round-bottom flask equipped with a reflux condenser, 6 cc. of benzaldehyde and 0.5 cc. of piperidine are added, and the mixture is refluxed on the water bath for half an hour. The material, while still hot, is poured into a beaker and allowed to cool and crystallize. The crystals, collected on a filter, are rinsed twice with alcohol and recrystallized from a mixture of 2 volumes of alcohol and 1 of benzene. Brilliant yellow glistening needles, m.p. 158°.

Trinitrotoluene, in addition to the usual reactions of a nitrated hydrocarbon with alkali to form dangerous explosive materials, has the property that its methyl group in the presence of alkali condenses with aldehydic substances in reactions which produce heat and which may cause fire. Aldehydic substances from the action of nitrating acid on wood are always present where TNT is being manufactured, and alkali of all kinds ought to be excluded rigorously from the premises.

Giua[35] reports that TNT may be distilled in vacuum without the slightest trace of decomposition. It boils at 210-212° at 10-20 mm. When heated for some time at 180-200°, or when exposed to

[34] Pfeiffer and Monath, *Ber.,* **39,** 1306 (1906); Ullmann and Geschwind, *ibid.,* **41,** 2296 (1908).

[35] Giua, "Chimica delle sostanze esplosive," Milan, 1919, p. 248.

sunlight[36] in open tubes, it undergoes a slow decomposition with a consequent lowering of the melting point. Exposure to sunlight in a vacuum in a sealed tube has much less effect. Verola[37] has found that TNT shows no perceptible decomposition at 150°, but that it evolves gas slowly and regularly at 180°. At ordinary temperatures, and even at the temperatures of the tropics, it is stable in light-proof and air-tight containers—as are in general all the aromatic nitro explosives—and it does not require the same surveillance in storage that nitrocellulose and smokeless powder do.

The solubility[38] of trinitrotoluene in various solvents is tabulated below.

SOLUBILITY OF TRINITROTOLUENE

(Grams per 100 grams of solvent)

Temp.	Water	CCl₄	Benzene	Toluene	Acetone	95% Alcohol	CHCl₃	Ether
0°	0.0100	0.20	13	28	57	0.65	6	1.73
5°	0.0105	0.25	24	32	66	0.75	8.5	2.08
10°	0.0110	0.40	36	38	78	0.85	11	2.45
15°	0.0120	0.50	50	45	92	1.07	15	2.85
20°	0.0130	0.65	67	55	109	1.23	19	3.29
25°	0.0150	0.82	88	67	132	1.48	25	3.80
30°	0.0175	1.01	113	84	156	1.80	32.5	4.56
35°	0.0225	1.32	144	104	187	2.27	45	...
40°	0.0285	1.75	180	130	228	2.92	66	...
45°	0.0360	2.37	225	163	279	3.70	101	...
50°	0.0475	3.23	284	208	346	4.61	150	...
55°	0.0570	4.55	361	272	449	6.08	218	...
60°	0.0675	6.90	478	367	600	8.30	302	...
65°	0.0775	11.40	665	525	843	11.40	442	...
70°	0.0875	17.35	1024	826	1350	15.15	...	...
75°	0.0975	24.35	2028	1685	2678	19.50	...	...
80°	0.1075	...	...	...	...	...	...	...
85°	0.1175	...	...	...	...	...	...	...
90°	0.1275	...	...	...	...	...	...	...
95°	0.1375	...	...	...	...	...	...	...
100°	0.1475	...	...	...	...	...	...	...

[36] Molinari and Quartieri, "Notizie sugli esplodenti in Italia," Milan, 1913, p. 157.

[37] *Mém. poudres,* **16**, 40 (1911-1912).

[38] Taylor and Rinkenbach, *J. Am. Chem. Soc.,* **45**, 44 (1923).

Dautriche found the density of powdered and compressed TNT to be as follows:

Pressure: Kilos per Square Centimeter	Density
275	1.320
685	1.456
1375	1.558
2060	1.584
2750	1.599
3435	1.602
4125	1.610

Trinitrotoluene was prepared by Wilbrand[39] in 1863 by the nitration of toluene with mixed acid, and in 1870 by Beilstein and Kuhlberg[40] by the nitration of o- and p-nitrotoluene, and by Tiemann[41] by the nitration of 2,4-dinitrotoluene. In 1891 Haussermann[42] with the Griesheim Chem. Fabrik undertook its manufacture on an industrial scale. After 1901 its use as a military explosive soon became general among the great nations. In the first World War all of them were using it.

Trinitroxylene (TNX)

In m-xylene the two methyl groups agree in activating the same positions, and this is the only one of the three isomeric xylenes which can be nitrated satisfactorily to yield a trinitro derivative. Since the three isomers occur in the same fraction of coal tar and cannot readily be separated by distillation, it is necessary to separate them by chemical means. When the mixed xylenes are treated with about their own weight of 93 per cent sulfuric acid for 5 hours at 50°, the o-xylene (b.p. 144°) and the m-xylene (b.p. 138.8°) are converted into water-soluble sulfonic acids, while the p-xylene (b.p. 138.5°) is unaffected. The aqueous phase is removed, diluted with water to about 52 per cent acidity calculated as sulfuric acid, and then heated in an autoclave at 130° for 4 hours. The m-xylene sulfonic acid is converted to m-xylene, which is removed. The o-xylene sulfonic acid, which remains in solution, may be converted into o-xylene by autoclaving at a higher temperature. The nitration of m-xylene is conveniently carried out in three steps. The effect of the two methyl

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[39] *Ann.*, **128**, 178 (1863).
[40] *Ber.*, **3**, 202 (1870).
[41] *Ber.*, **3**, 217 (1870).
[42] *Z. angew. Chem.*, 1891, p. 508; *J. Soc. Chem. Ind.*, 1891, p. 1028.

groups is so considerable that the introduction of the third nitro group may be accomplished without the use of fuming sulfuric acid. Pure TNX, large almost colorless needles from benzene, melts at 182.3°.

Trinitroxylene is not powerful enough for use alone as a high explosive, and it does not always communicate an initial detonation throughout its mass. It is used in commercial dynamites, for which purpose it does not require to be purified and may contain an oily mixture of isomers and other nitrated xylenes. Its large excess of carbon suggests that it may be used advantageously in conjunction with an oxidizing agent. A mixture of 23 parts of TNX and 77 parts of ammonium nitrate, ground intimately together in a black powder mill, has been used in high-explosive shells. It was loaded by compression. Mixtures, about half and half, of TNX with TNT and with picric acid are semi-solid when warm and can be loaded by pouring. The eutectic of TNX and TNT contains between 6 and 7 per cent of TNX and freezes at 73.5°. It is substantially as good an explosive as TNT. A mixture of 10 parts TNX, 40 parts TNT, and 50 parts picric acid can be melted readily under water. In explosives such as these the TNX helps by lowering the melting point, but it also attenuates the power of the more powerful high explosives with which it is mixed. On the other hand, these mixtures take advantage of the explosive power of TNX, such as that power is, and are themselves sufficiently powerful and satisfactory for many purposes—while making use of a raw material, namely *m*-xylene, which is not otherwise applicable for use in the manufacture of military explosives.

Nitro Derivatives of Naphthalene

Naphthalene nitrates more readily than benzene, the first nitro group taking the α-position which is *ortho* on one nucleus to the side chain which the other nucleus constitutes. The second nitro group takes one or another of the expected positions, either the position *meta* to the nitro group already present or one of the α-positions of the unsubstituted nucleus. The dinitration of naphthalene in actual practice thus produces a mixture which consists almost entirely of three isomers. Ten different isomeric dinitronaphthalenes are possible, seven of which are derived from α-nitronaphthalene, seven from β-nitronaphthalene, and four

from both the α- and the β-compounds. After two nitro groups have been introduced, conflicts of orienting tendencies arise and polynitro compounds are formed, among others, in which nitro groups occur *ortho* and *para* to one another. Only four nitro groups can be introduced into naphthalene by direct nitration.

The mononitration of naphthalene takes place easily with a mixed acid which contains only a slight excess of one equivalent of HNO_3.
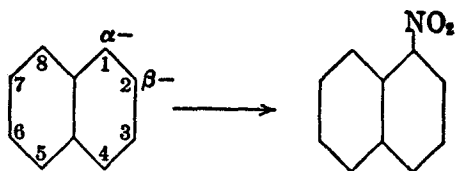
For the di-, tri-, and tetranitrations increasingly stronger acids and higher temperatures are necessary. In the tetranitration oleum is commonly used and the reaction is carried out at 130°.

The nitration of α-nitronaphthalene[43] (m.p. 59-60°) yields a mixture of α- or 1,5-dinitronaphthalene (silky needles, m.p. 216°), β- or 1,8-dinitronaphthalene (rhombic leaflets, m.p. 170-172°), and γ- or 1,3-dinitronaphthalene (m.p. 144-145°).
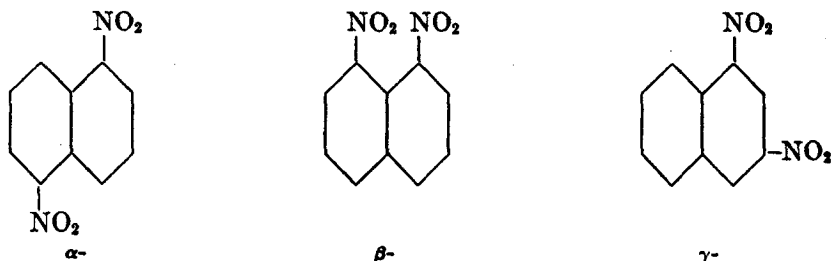
The commercial product of the dinitration melts at about 140°, and consists principally of the α- and β-compounds. The nitration of naphthalene at very low temperatures,[44] −50° to −60°, gives good yields of the γ- compound, and some of this material is undoubtedly present in the ordinary product.

The nitration of α-dinitronaphthalene yields α- or 1,3,5-tri-nitronaphthalene (monoclinic crystals, m.p. 123°), γ- or 1,4,5-

[43] Roussin, *Comp. rend.*, 52, 796 (1861); Darmstädter and Wickelhaus, *Ann.*, 152, 301 (1869); Aguiar, *Ber.*, 2, 220 (1869); 3, 29 (1870); 5, 370 (1872); Beilstein and Kuhlberg, *Ann.*, 169, 86 (1873); Beilstein and Kurbatow, *Ber.*, 13, 353 (1880); *Ann.*, 202, 219, 224 (1880); Julius, *Chem. Ztg.*, 18, 180 (1894); Gassmann, *Ber.*, 29, 1243, 1521 (1896); Friedländer, *ibid.*, 32, 3531 (1899).

[44] Pictet, *Comp. rend.*, 116, 815 (1893).

trinitronaphthalene (glistening plates, m.p. 147°), and δ- or 1,2,5-trinitronaphthalene (m.p. 112-113°). The nitration of β-dinitronaphthalene yields β- or 1,3,8-trinitronaphthalene (monoclinic crystals, m.p. 218°), and the same substance, along with some α-trinitronaphthalene, is formed by the nitration of γ-dinitronaphthalene.
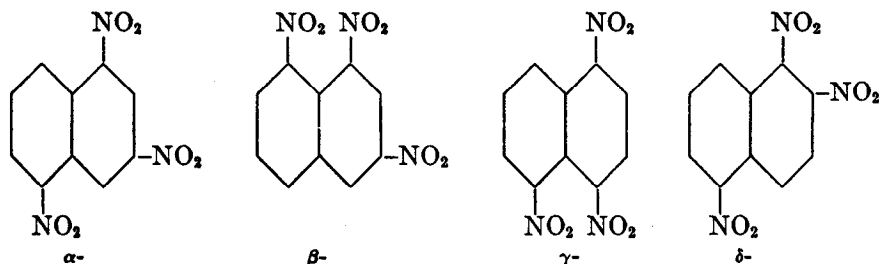
All these isomers occur in commercial trinitronaphthalene, known as *naphtite*, which melts at about 110°.

The nitration of α-, β-, and γ-trinitronaphthalene yields γ- or 1,3,5,8-tetranitronaphthalene (glistening tetrahedrons, m.p. 194-195°). The nitration of the β-compound also yields β- or 1,3,6,8-tetranitronaphthalene (m.p. 203°), and that of the δ-trinitro compound yields δ- or 1,2,5,8-tetranitronaphthalene (glistening prisms which decompose at 270° without melting), a substance which may be formed also by the introduction of a fourth nitro group into γ-trinitronaphthalene. The nitration of 1,5-dinitronaphthalene[45] yields α-tetranitronaphthalene (rhombic crystals, m.p. 259°) (perhaps 1,3,5,7-tetranitronaphthalene), and this substance is also present in the crude product of the tetranitration, which, however, consists largely of the β-, γ-, and δ-isomers.
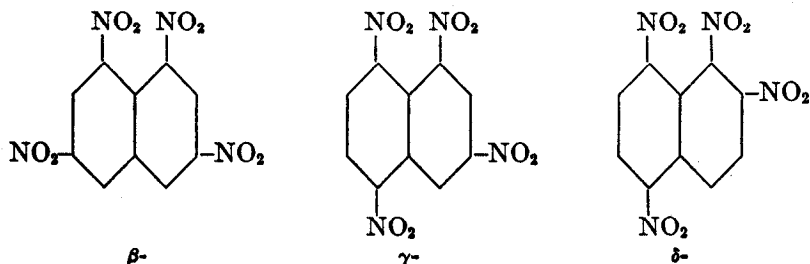
The crude product is impure and irregular in its appearance; it is commonly purified by recrystallization from glacial acetic acid

[45] Aguiar, *Ber.*, **5**, 374 (1872).

The purified material consists of fine needle crystals which melt at about 220° and have the clean appearance of a pure substance but actually consist of a mixture of isomers.

None of the nitrated naphthalenes is very sensitive to shock. α-Nitronaphthalene is not an explosive at all and cannot be detonated. Dinitronaphthalene begins to show a feeble capacity for explosion, and trinitronaphthalene stands between dinitrobenzene and dinitrotoluene in its explosive power. Tetranitronaphthalene is about as powerful as TNT, and distinctly less sensitive to impact than that explosive. Vennin and Chesneau report that the nitrated naphthalenes, charged in a manometric bomb at a density of loading of 0.3, gave on firing the pressures indicated below.[46]

	KILOS PER SQUARE CENTIMETER
Mononitronaphthalene.....	1208
Dinitronaphthalene........	2355
Trinitronaphthalene........	3275
Tetranitronaphthalene	3745

The nitrated naphthalenes are used in dynamites and safety explosives, in the Favier powders, *grisounites*, and *naphtalites* of France, in the *cheddites* which contain chlorate, and for military purposes to some extent in mixtures with ammonium nitrate or with other aromatic nitro compounds. Street,[47] who proposed their use in cheddites, also suggested a fused mixture of mononitronaphthalene and picric acid for use as a high explosive. *Schneiderite,* used by France and by Italy and Russia in shells during the first World War, consisted of 1 part dinitronaphthalene and 7 parts ammonium nitrate, intimately incorporated together by grinding in a black powder mill, and loaded by compression. A mixture (MMN) of 3 parts mononitronaphthalene and 7 parts picric acid, fused together under water, was used in drop bombs and was insensitive to the impact of a rifle bullet. A mixture (MDN) of 1 part dinitronaphthalene and 4 parts picric acid melts at about 105-110°; it is more powerful than the preceding and is also less sensitive to shock than picric acid alone. The

[46] Vennin and Chesneau, "Les poudres et explosifs et les mesures de sécurité dans les mines de houille," Paris and Liége, 1914, p. 269.

[47] *Mon. Sci.,* 1898, p. 495.

Germans used a mine explosive consisting of 56 per cent potassium perchlorate, 32 per cent dinitrobenzene, and 12 per cent dinitronaphthalene.[48] Their *Tri-Trinal* for small-caliber shells was a compressed mixture of 2 parts of TNT (*Tri*) with 1 of trinitronaphthalene (*Trinal*), and was used with a booster of compressed picric acid.

Trinitronaphthalene appears to be a genuine stabilizer for nitrocellulose, a true inhibitor of its spontaneous decomposition. Marqueyrol found that a nitrocellulose powder containing 10 per cent of trinitronaphthalene is as stable as one which contains 2 per cent of diphenylamine. The trinitronaphthalene has the further effect of reducing both the hygroscopicity and the temperature of combustion of the powder.

Hexanitrobiphenyl

2,2′,4,4′,6,6′-Hexanitrobiphenyl was first prepared by Ullmann and Bielecki[49] by boiling picryl chloride in nitrobenzene solution with copper powder for a short time. The solvent is necessary in order to moderate the reaction, for picryl chloride and copper powder explode when heated alone to about 127°. Ullmann and Bielecki also secured good yields of hexanitrobiphenyl by working in toluene solution, but found that a small quantity of trinitrobenzene was formed (evidently in consequence of the presence of moisture). Hexanitrobiphenyl crystallizes from toluene in light-yellow thick crystals which contain ½ molecule of toluene of crystallization. It is insoluble in water, and slightly soluble in alcohol, acetone, benzene, and toluene, m.p. 263°. It gives a yellow color with concentrated sulfuric acid, and a red with alcohol to which a drop of ammonia water or aqueous caustic soda has been added. It is neutral, of course, and chemically unreactive toward metals, and is reported to be non-poisonous.

Hexanitrobiphenyl cannot[50] be prepared by the direct nitration

[48] Naoum, "Schiess- und Sprengstoffe," Dresden and Leipzig, 1927, p. 62.

[49] *Ber.*, **34**, 2174 (1901).

[50] The effect may be steric, although there is evidence that the dinitrophenyl group has peculiar orienting and resonance effects. Rinkenbach and Aaronson, *J. Am. Chem. Soc.*, **52**, 5040 (1930), report that *sym*-diphenylethane yields only very small amounts of hexanitrodiphenylethane under the most favorable conditions of nitration.

of biphenyl. The most vigorous nitration of that hydrocarbon
yields only 2,2',4,4'-tetranitrobiphenyl, yellowish prisms from
benzene, m.p. 163°.

Jahn in a patent granted in 1918[51] states that hexanitrobi-
phenyl is about 10 per cent superior to hexanitrodiphenylamine.
Fifty grams in the lead block produced a cavity of 1810 cc., while
the same weight of hexanitrodiphenylamine produced one of 1630
cc. Under a pressure of 2500 atmospheres, it compresses to a
density of about 1.61.

Picric Acid (melinite, lyddite, pertite, shimose, etc.)

The *ortho-para* orienting hydroxyl group of phenol promotes
nitration greatly and has the further effect that it "weakens" the
ring and makes it more susceptible to oxidation. Nitric acid at-
tacks phenol violently, oxidizing a portion of it to oxalic acid,
and produces resinous by-products in addition to a certain
amount of the expected nitro compounds. The carefully con-
trolled action of mixed acid on phenol gives a mixture of *o*-nitro-
phenol (yellow crystals, m.p. 45°, volatile with steam) and
p-nitrophenol (white crystals, m.p. 114°, not volatile with steam),
but the yields are not very good. When these mononitrophenols
are once formed, their nitro groups "activate" the same positions
as the hydroxyls do, but the nitro groups also inhibit substitution,
and their further nitration may now be carried out more smoothly.
p-Nitrophenol yields 2,4-dinitrophenol (m.p. 114-115°), and later
picric acid. *o*-Nitrophenol yields 2,4- and 2,6-dinitrophenol (m.p.
63-64°), both of which may be nitrated to picric acid, but the
nitration of *o*-nitrophenol is invariably accompanied by losses
resulting from its volatility. The straightforward nitration of
phenol cannot be carried out successfully and with satisfying
yields. In practice the phenol is sulfonated first, and the sulfonic
acid is then nitrated. The use of sulfuric acid (for the sulfona-
tion) in this process amounts to its use as an inhibitor or mod-
erator of the nitration, for the *meta* orienting sulfonic acid group
at first slows down the introduction of nitro groups until it is
itself finally replaced by one of them.

[51] U. S. Pat. 1,253,691 (1918).
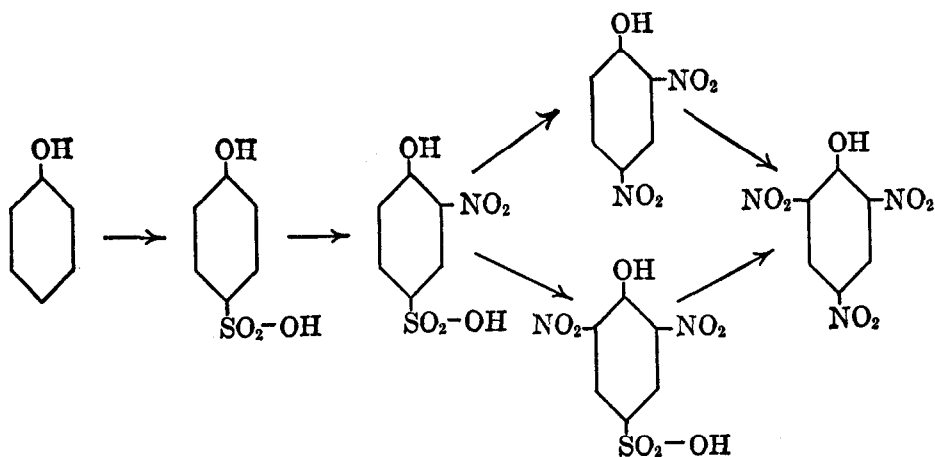
The sulfonation of phenol at low temperatures produces the
o-sulfonic acid, and at high temperatures the p-sulfonic acid
along with more or less of the di- and even of the trisulfonic acids
according to the conditions of the reaction. All these substances
yield picric acid as the final product of the nitration.[52]

Unless carefully regulated the production of picric acid from
phenol is accompanied by losses, either from oxidation of the
material with the production of red fumes which represent a loss
of fixed nitrogen or from over sulfonation and the loss of uncon-
verted water-soluble nitrated sulfonic acids in the mother liquors.
Olsen and Goldstein[53] have described a process which yields 220
parts of picric acid from 100 parts of phenol. In France, where
dinitrophenol was used during the first World War in mixtures
with picric acid which were loaded by pouring, Marqueyrol and
his associates[54] have worked out the details of a four-stage
process from the third stage of which dinitrophenol may be re-
moved if it is desired. The steps are: (1) sulfonation; (2) nitration
to the water-soluble mononitrosulfonic acid; (3) nitration to
dinitrophenol, which is insoluble in the mixture and separates out,
and to the dinitrosulfonic acid which remains in solution; and
(4) further nitration to convert either the soluble material or
both of the substances to picric acid. The process is economical
of acid and gives practically no red fumes, but the reported
yields are inferior to those reported by Olsen and Goldstein. The

[52] Cf. King, *J. Chem. Soc.*, 119, 2105 (1921).

[53] Olsen and Goldstein, *Ind. Eng. Chem.*, 16, 66 (1924).

[54] Marqueyrol and Loriette, *Bull. soc. chim.*, 25, 376 (1919); Marqueyrol
and Carré, *ibid.*, 27, 195 (1920).

dinitrophenol as removed contains some picric acid, but this is of no disadvantage because the material is to be mixed with picric acid anyway for use as an explosive.

Preparation of Picric Acid (Standard Method). Twenty-five grams of phenol and 25 grams of concentrated sulfuric acid (*d*. 1.84) in a round-
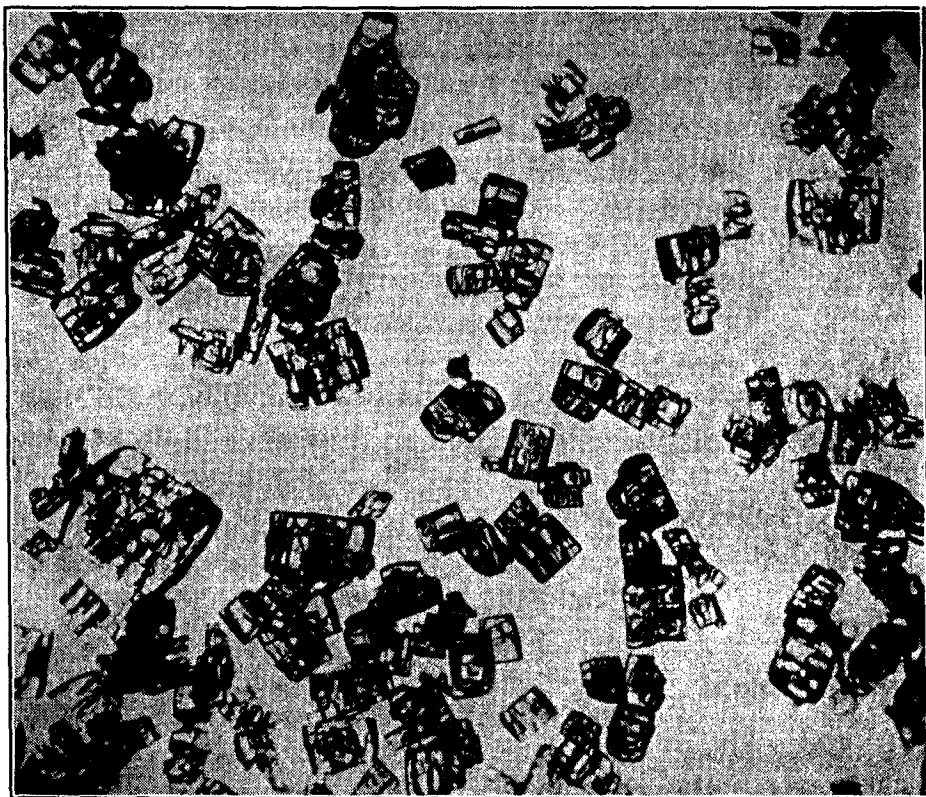

FIGURE 48. Commercial Sample of Picric Acid (25×).

bottom flask equipped with an air condenser are heated together for 6 hours in an oil bath at 120°. After the material has cooled, it is diluted with 75 grams of 72 per cent sulfuric acid (*d*. 1.64). To the resulting solution, in an Erlenmeyer flask in the hood, 175 cc. of 70 per cent nitric acid (*d*. 1.42) is added slowly, a drop at a time, from a dropping funnel. When all the nitric acid has been added and the vigorous reaction has subsided, the mixture is heated for 2 hours on the steam bath to complete the nitration. The next morning the picric acid will be found to have separated in crystals. These are transferred to a porcelain filter, washed with small portions of water until the washings are free from sulfate, and dried in the air. The crude product, which is equal in quality to a good commercial sample, is purified by boiling it

with water, in the proportion of 15 grams to the liter, filtering hot, and allowing to cool slowly. The heavy droplets of brown oil which dissolve only slowly during this boiling ought to be discarded. Pure picric acid crystallizes from water in pale yellow flat needles, m.p. 122.5°. It may be obtained in crystals which are almost white by recrystallizing from aqueous hydrochloric acid.

The best process for the production of dinitrophenol is probably the autoclaving of dinitrochlorobenzene with aqueous caustic soda. The product is obtained on acidification and is used as such, or is nitrated to picric acid for the commercial production of that material by the so-called synthetic process.

The "catalytic process" for the production of picric acid directly from benzene in one step by the action of nitric acid in the presence of mercuric nitrate has much theoretical interest and has been applied, though not extensively, in plant-scale manufacture. It yields about as much picric acid as is procurable from the same weight of benzene by the roundabout method of sulfonating the benzene, converting the benzene sulfonic acid into phenol, and nitrating the phenol to picric acid—and the benzene which is not converted to picric acid is for the most part recovered as such or as nitrobenzene. The first mention of the process appears to be in the patent of Wolffenstein and Boeters.[55]

Preparation of Picric Acid (Catalytic Process). Two hundred grams of benzene in a 2-liter round-bottom flask equipped with a sealed-on condenser is refluxed on the sand bath for 7 hours with 600 cc. of nitric acid (d. 1.42) in which 10 grams of mercuric nitrate has been dissolved. The material is then transferred to another flask and distilled with steam. Benzene comes over, then nitrobenzene, then finally and slowly a mixture of dinitrobenzene and dinitrophenol. The distillation is continued until all volatile matter has been removed. The liquid in the flask is filtered hot and allowed to crystallize. If the picric acid is not sufficiently pure, it is recrystallized from hot water.

Mercuric nitrate combines with benzene to form a deep-brown or black addition compound, the probable structure of which is indicated below. This material when warmed with nitric acid is oxidized with the production of red fumes and the formation of

[55] Wolffenstein and Boeters, Ger. Pat. 194,883 (1908); Ger. Pat. 214,045 (1909); Ramy, Brit. Pat. 125,461 (1918); MacDonald and Calvert, Brit. Pats. 126,062, 126,084, 126,675, 126,676 (1918); Brewster, Brit. Pat. 131,403 (1919).

a yellow nitrophenolate of mercuric nitrate. By the continued action of the acid this is nitrated to the trinitrophenolate and decomposed with the formation of picric acid and the regeneration of mercuric nitrate.[56]
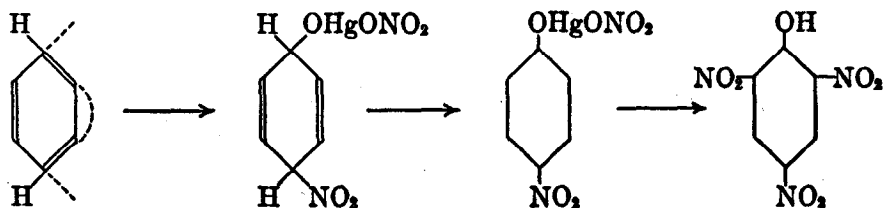
The addition of mercuric nitrate is here written as a 1,4-addition, but 1,2-addition would give the same final product, and there is no evidence in the facts concerning benzene which enables us to choose between the alternative hypotheses. Toluene yields trinitro-*m*-cresol by a similar series of reactions, and it is clear that the nitro group in the addition product of mercuric nitrate and toluene has taken either the 2-, the 4-, or the 6-position, that is, one or the other of the positions activated by the methyl group. In the addition of mercuric nitrate to naphthalene, the nitro group correspondingly may be supposed to go to the active α-position. If the addition is 1,2-, the product on oxidation will yield a derivative of β-naphthol. If it is 1,4-, it will yield a derivative of α-naphthol. The two possibilities are indicated below.
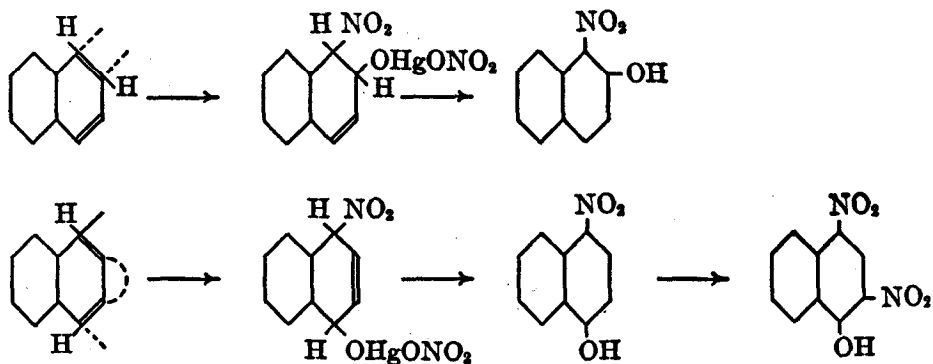
Gentle treatment of naphthalene with nitric acid containing mercuric nitrate yields, 2,4-dinitro-α-naphthol in conformity with the belief that the first addition product is 1,4- as represented by the second of the above formulations.

Picric acid was obtained in 1771 by Woulff, who found that

[56] Davis, Worrall, Drake, Helmkamp, and Young, *J. Am. Chem. Soc.*, **43**, 594 (1921); Davis, *ibid.*, **44**, 1588 (1922). Davis, U. S. Pat. 1,417,368 (1922).

the action of nitric acid on indigo yielded a material which dyed silk yellow. Hausmann[57] isolated the substance in 1778, and reported further studies upon it in 1788, noting particularly its bitter taste. Welter[58] in 1799 obtained picric acid by the action of nitric acid on silk, and the material came to be known generally as "Welter's bitter." Its preparation from indigo, aloes, resin, and other organic substances was studied by many chemists, among them Fourcroy and Vauquelin, Chevreul, Liebig, Wöhler, Robiquet, Piria, Delalande, and Stenhouse. Its preparation from oil of eucalyptus was suggested during the first World War. It was given the name of *acide picrique* by Dumas; *cf.* Greek πικρός = bitter, old English *puckery*. Its relation to phenol was demonstrated in 1841 by Laurent,[59] who prepared it by the nitration of that substance, and its structure was proved fully by Hepp,[60] who procured it by the oxidation of *sym*-trinitrobenzene.

Picric acid is a strong acid; it decomposes carbonates and may be titrated with bases by the use of sodium alizarine sulfonate as an indicator. It is a fast yellow dye for silk and wool. It attacks the common metals, except aluminum and tin, and produces dangerously explosive salts. *Cordeau Lheure*, which was long used extensively in France, was made by filling a tin pipe with fused picric acid and later drawing down to the desired diameter. It had the disadvantage that the metal suffered from the "tin disease," became unduly brittle, and changed to its gray allotropic modification. Picric acid and nitrophenols, when used in ammunition, are not allowed to come in contact with the metal parts. Shells which are to be loaded with these explosives are first plated on the inside with tin or painted with asphaltum varnish or Bakelite.

Dupré[61] in 1901 reported experiments which indicated that the picrates of calcium, lead, and zinc, formed *in situ* from melted picric acid are capable of initiating the explosion of that material. Kast[62] found that the dehydrated picrates are more sensitive than those which contain water of crystallization. The data tabulated

[57] *J. Phys.* **32**, 165 (1788).

[58] *Ann. chim. phys.*, I, **29**, 301 (1799).

[59] *Ann. chim. phys.*, III, **3**, 221 (1841).

[60] Hepp, *loc. cit.*

[61] *Mém. poudres*, **11**, 92 (1901).

[62] *Z. ges. Schiess- u. Sprengstoffw.*, **6**, 7, 31, 67 (1911). See also Will, *ibid.*, **1**, 209 (1906); Silberrad and Phillips, *J. Chem. Soc.*, **93**, 474 (1908).

below have been published recently by J. D. Hopper.[63] Explosion temperature was determined as the temperature necessary to cause ignition or explosion in exactly 5 seconds when a thin-walled copper shell containing a few milligrams of the explosive was dipped into a molten metal bath to a constant depth. The minimum drop test was taken as the least distance through which a 2-kilogram weight must fall, in a standard apparatus,[64] to produce detonation or ignition in one or more instances among ten trials.

SUBSTANCE	DEGREE OF HYDRA-TION	TEMPERA-TURE OF DRYING, °C.	MINIMUM DROP TEST 2-KILO WEIGHT, INCHES	EXPLO-SION TEMPERA-TURE, °C.
Mercury fulminate	Anhydrous	...	2	210
Tetryl	Anhydrous	...	8	260
TNT	Anhydrous	...	14	470
Picric acid	Anhydrous	...	14	320
Ammonium picrate	Anhydrous	...	17	320
Sodium picrate	1 H_2O	50	17	360
Sodium picrate	Anhydrous	150	15	...
Sodium dinitrophenolate	1 H_2O	100	16	370
Sodium dinitrophenolate	Anhydrous	150	15	...
Copper picrate	3 H_2O	25	19	300
Copper picrate	Anhydrous	150	12	...
Zinc picrate	6 H_2O	25	34	310
Zinc picrate	Anhydrous	150	12	...
Cadmium picrate	8 H_2O	25	35	340
Cadmium picrate	Anhydrous	150	12	...
Nickel picrate	6 H_2O	25	26	390
Nickel picrate	....	100	9	...
Nickel picrate	Anhydrous	150	4	...
Aluminum picrate	10 H_2O	25	36	360
Aluminum picrate	2 H_2O	80	16	...
Aluminum picrate	....	100	16	...
Chromium picrate	13 H_2O	25	36	330
Chromium picrate	....	80	10	...
Chromium picrate	1 H_2O	100	8	...
Ferrous picrate	8 H_2O	25	36	310
Ferrous picrate	....	100	14	...
Ferric picrate	x H_2O	25	36	295
Ferric picrate	....	80	8	...
Ferric picrate	....	100	7	...
Ferric picrate	....	150	6	...

[63] *J. Franklin Inst.*, **225**, 219 (1938).
[64] H. S. Deck, *Army Ordnance*, **7**, 34 (1926).

Cast picric acid has a density of about 1.64. The density of pellets of compressed picric acid, according to Dautriche, is as follows.

PRESSURE: KILOS PER SQUARE CENTIMETER	DENSITY
275	1.315
685	1.480
1375	1.614
2060	1.672
2750	1.714
3435	1.731
4125	1.740

The use of picric acid as an explosive appears to have been suggested first in 1867 by Borlinetto,[65] who proposed a mixture of picric acid 35 per cent, sodium nitrate 35 per cent, and potassium chromate 30 per cent for use in mining. Sprengel in 1873 reported that picric acid in conjunction with suitable oxidizing agents is a powerful explosive. In 1885 Turpin[66] patented its use, both compressed and cast, in blasting cartridges and in shells, and shortly thereafter the French government adopted it under the name of *mélinite*. In 1888 Great Britain commenced to use it under the name of *lyddite*. Cast charges require a booster, for which purpose compressed picric acid or tetryl is generally used. The loading of picric acid into shells by pouring is open to two objections, which, however, are not insuperable, namely, the rather high temperature of the melt and the fact that large crystals are formed which may perhaps cause trouble on setback. Both difficulties are met by adding to the picric acid another explosive substance which lowers its melting point. Mixtures are preferred which melt between 70° and 100°, above 70° in order that exudation may be less likely and below 100° in order that the explosive may be melted by hot water. The mixtures are not necessarily eutectics. Two of the favorite French explosives have been DD 60/40, which consists of 60 parts picric acid and 40 parts dinitrophenol; and *crésylite* 60/40, 60 parts trinitro-*m*-cresol and 40 parts picric acid. Others are MDPC, picric acid 55 parts, dinitrophenol 35, and trinitro-*m-cresol* 10; and MTTC, which has the same composition as MDPC except that TNT is used instead of dinitrophenol. All these mixtures melt between

[65] Giua, *op. cit.*, pp. 287, 296.
[66] Fr. Pat. 167,512 (1885).

80° and 90° and are prepared by putting the materials together under water in wooden tanks and blowing in live steam. The water is sometimes acidulated with sulfuric acid to insure the removal of all metallic picrates. An explosive made by mixing 88 parts of picric acid with 12 parts of melted paraffin or stearic acid, and then rolling and graining, gives a compact charge when loaded by compression. It is nearly as powerful and brisant as picric acid, and responds satisfactorily to the impulse of the detonator, but is distinctly less sensitive to mechanical shock.

Ammonium Picrate

Ammonium picrate is less sensitive to shock than picric acid. It is not easily detonated by fulminate, but is commonly used with a

FIGURE 49. Commercial Sample of Ammonium Picrate (25×).

booster of powdered and compressed picric acid or tetryl. The pure substance occurs in two forms, a stable form which is of a

bright lemon yellow color and a meta-stable form which is a brilliant red. These differ slightly in their crystal angles but show no detectable difference in their explosive properties. Thallium picrate similarly exists in two forms.

Ammonium picrate is prepared by suspending picric acid in a convenient quantity of hot water, adding strong ammonia water until everything goes into solution and a large excess of ammonia is present, and allowing to cool. The crystals which separate are the red form. A dry sample of this material in a stoppered bottle will remain without apparent change for many years. In contact with its saturated aqueous solution it changes to the yellow form during several months. The yellow form of ammonium picrate is best procured by recrystallizing the red form several times from water.

Pure ammonium picrate melts with decomposition at 265-271°. It is more soluble in warm alcohol than guanidine picrate is, and more soluble in acetone than in alcohol, but it goes into solution very slowly in alcohol and crystallizes out again very slowly when the liquid is allowed to stand.

SOLUBILITY OF AMMONIUM PICRATE

(Grams per 100 cc. of solution)

Temperature, °C.		Ethyl Acetate	Ethyl Alcohol
0	......	0.290	0.515
10	......	0.300	0.690
20	......	0.338	0.850
30	......	0.380	1.050
40	......	0.420	1.320
50	......	0.450	1.890
60	......	0.500	2.165
70	......	0.540	2.760
80	......	0.560	3.620

Guanidine Picrate

Guanidine picrate is procured as a yellow, finely crystalline precipitate by mixing warm solutions of guanidine nitrate and ammonium picrate. It is even less sensitive to blow and to shock than ammonium picrate; it is not detonated by fulminate and is used with a picric acid booster. The pure material, recrystallized from alcohol or from water, in both of which solvents it is sparingly soluble, melts with decomposition at 318.5-319.5°.

SOLUBILITY OF GUANIDINE PICRATE

(Grams per 100 cc. of solution)

Temperature, °C.	Water	Ethyl Alcohol	Acetone
0	0.005	0.077	0.455
10	0.038	0.093	0.525
20	0.070	0.122	0.605
30	0.100	0.153	0.695
40	0.150	0.200	0.798
50	0.230	0.255	0.920
60	0.350	0.321	1.075
70	0.480	0.413	...
80	0.700	0.548	...
90	1.010	...	...
100	1.380	...	...

Trinitrocresol (cresylite)

This explosive is prepared from *m*-cresol by a process entirely similar to that by which picric acid is prepared from phenol. The pure material is readily soluble in alcohol, ether, and acetone, soluble in 449 parts of water at 20° and in 123 parts at 100°, yellow needles from water, m.p. 107°. The ammonium sa't, which is sparingly soluble in water, has been used in the composition of certain ammonium nitrate explosives, and it was adopted by the Austrian monarchy under the name of *ecrasite* as an explosive for shells of large caliber.

Trinitroresorcinol (styphnic acid)

Resorcinol nitrates readily to the trinitro compound, yellow prisms from water or alcohol, m.p. 175.5°. Styphnic acid is more expensive and less powerful than picric acid. Liouville[67] found that styphnic acid exploded in a manometric bomb, at a density of loading of 0.2, gave a pressure of 2260 kilos per sq. cm., whereas picric acid under the same conditions gave a pressure of 2350 kilos per sq. cm. It did not agglomerate to satisfactory pellets under a pressure of 3600 kilos per sq. cm. It is a fairly strong dibasic acid, and its salts are notably more violent explosives than the picrates. Lead styphnate has been used to facilitate the ignition of lead azide in detonators.

Trinitroanisol and Trinitrophenetol

2,4,6-Trinitroanisol (2,4,6-trinitrophenyl methyl ether, methyl picrate) has explosive properties comparable with those of picric

[67] *Mém. poudres*, **9**, 139 (1897-1898).

acid and trinitrocresol, but it contains no hydroxyl group and does not attack metals readily with the formation of dangerously explosive salts. In actual use, however, it reacts slowly with moisture and yields some picric acid. It has been colloided with nitrocellulose in the form of a strip powder, flashless and of low hygroscopicity, but the powder in the course of time developed enough picric acid to stain the fingers and to give a yellow solution with water. Its relatively low melting point, 67-68°, gives it an advantage over picric acid for certain purposes. Methyl alcohol is needed for its synthesis, and the present availability of this substance cheaply from high-pressure synthesis further commends it. While anisol is an expensive raw material, and has the further disadvantage that its direct nitration is dangerous, trinitroanisol may be prepared, without it, economically and easily from benzene through the use of dinitrochlorobenzene.

Trinitroanisol was prepared by Cahours[68] in 1849 by the direct nitration of anisol, and the same process has been studied more recently by Broadbent and Sparre.[69] The strongly *ortho-para* orienting methoxy group promotes substitution greatly, the first products of the nitration are explosive, and the temperature of the reaction mixture during the first stages ought never to be allowed to rise above 0°. A small drop of anisol, or of phenetol or other aromatic-aliphatic ether, added to 10 cc. of nitric acid (*d.* 1.42) in a test tube and shaken, causes a remarkable series of color changes; the liquid turns yellow, then green, then blue, and finally reddish purple. A batch of anisol which was being nitrated at ordinary temperature in the author's laboratory detonated without warning and without provocation while showing a bluish-purple color. Small pieces of the 2-liter flask which had contained the mixture were propelled so violently that they punctured the plate-glass windows of the laboratory without, however, breaking or cracking them.

Trinitroanisol may also be prepared by the interaction of methyl iodide and silver picrate, and by the nitration of anisic acid, during which the carboxyl group is lost, but the most convenient method appears to be that of Jackson[70] and his collaborators by which a methoxy group is substituted for chlorine in a nucleus already nitrated. A methyl alcohol solution of picryl

[68] *Ann.,* **69,** 236 (1849).
[69] *Eighth Intern. Congr. Appl. Chem.,* **4,** 15 (1912).
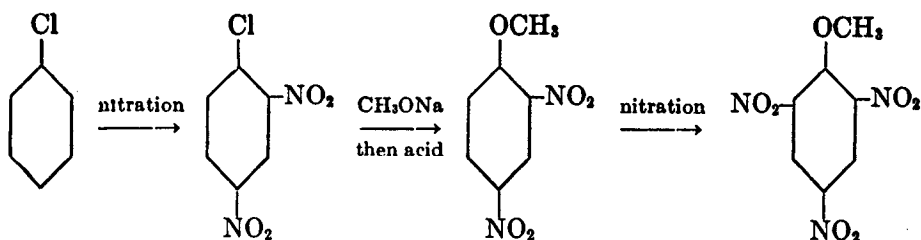[70] *Am. Chem. J.,* **20,** 448 (1898); **23,** 294 (1901).

chloride, treated with an excess of sodium methylate or of strong caustic soda solution, turns dark red and deposits handsome brilliant red crystals of the empirical composition, trinitroanisol·NaOCH$_3$. The probable constitution of these crystals is indicated below. On treatment with acid the substance yields trinitroanisol.
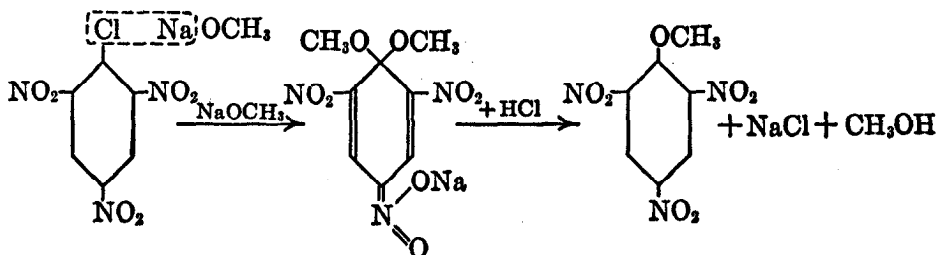
The red material is sparingly soluble in alcohol and in water, and is easily decomposed by aqueous acids. It is a primary explosive, stable to moderate heating but decomposing at 165° and exploding violently when introduced into a flame. It is not altered by dry air, but water decomposes it slowly to form first trinitroanisol and later picric acid. On boiling with ethyl alcohol, it yields the sodium ethylate addition product of trinitrophenetol—an interesting reaction analogous to the *ester interchange* in the aliphatic series.

Preparation of Trinitroanisol. Thirty-five grams of picryl chloride is dissolved in 400 cc. of methyl alcohol with warming under reflux, and the solution is allowed to cool to 30-35°. A solution of 23 grams of sodium hydroxide in 35 cc. of water is added slowly through the condenser, while the liquid is cooled, if need be, to prevent it from boiling. The mixture is allowed to stand for an hour or two. The red precipitate is filtered off, washed with alcohol, and stirred up with water while strong hydrochloric acid is added until all red color has disappeared. The slightly yellowish, almost white, precipitate, washed with water for the removal of sodium chloride, dried, and recrystallized from methyl alcohol, yields pale yellow leaflets of trinitroanisol, m.p. 67-68°. From anhydrous solvents the substance separates in crystals which are practically white.

Since the methoxy group exercises a greater effect in promoting substitution than the chlorine atom does, it is to be expected that dinitroanisol would take on a third nitro group more easily than dinitrochlorobenzene (to form picryl chloride), and with less expense for acid and for heat. The reactions indicated below are probably the best for the large-scale commercial production of trinitroanisol.

$$\text{Cl} \xrightarrow{\text{nitration}} \text{Cl, NO}_2, \text{NO}_2 \xrightarrow[\text{then acid}]{\text{CH}_3\text{ONa}} \text{OCH}_3, \text{NO}_2, \text{NO}_2 \xrightarrow{\text{nitration}} \text{OCH}_3, \text{NO}_2, \text{NO}_2, \text{NO}_2$$

During the first World War the Germans used a mixture of trinitroanisol and hexanitrodiphenyl sulfide in bombs.[71]

Trinitrophenetol or ethyl picrate, m.p. 78°, is prepared by the same methods as trinitroanisol. The explosive properties of the two substances have been studied by Desparmets and Calinaud, and by Desvergnes,[72] who has reported the results of the earlier workers together with data of his own and discussions of methods of manufacture and of the explosive properties of mixtures with picric acid, ammonium nitrate, etc. Drop test with a 5-kilogram weight were as follows:

	HEIGHT OF DROP, CENTIMETERS	PER CENT EXPLOSION
Picric acid........	30	50
Trinitroanisol......	100	20
Trinitroanisol......	110	30
Trinitrophenetol....	100	10
Trinitrophenetol....	110	10

Velocities of detonation (densities not reported) were trinitroanisol 7640 meters per second, trinitrophenetol 6880, and, for comparison, TNT 6880 meters per second. Pellets of the compressed explosives fired in the manometric bomb gave the results tabulated below.

	DENSITY OF LOADING	PRESSURE: KILOS PER SQUARE CENTIMETER
Picric acid..........	0.20	2310
Picric acid..........	0.20	2350
Picric acid..........	0.20	2210
Trinitroanisol.......	0.20	2222
Trinitroanisol.......	0.20	2250
Trinitroanisol.......	0.20	2145
Trinitrophenetol......	0.20	1774
Picric acid..........	0.25	3230
Trinitroanisol.......	0.25	2850
Trinitrophenetol......	0.25	2490
Trinitrophenetol......	0.30	3318

[71] Desvergnes, *Mém. poudres,* 19, 283 (1922).
[72] *Ibid.*

Both trinitroanisol and trinitrophenetol were found to be as satisfactory as compressed TNT for use as a booster charge in 75-mm. shells loaded with *schneiderite*.

Trinitroaniline (picramide)

2,4,6-Trinitroaniline, orange-red crystals from alcohol, m.p. 186°, has but little interest as an explosive for the reason that other more powerful and more valuable explosives may be prepared from the same raw materials. It may be prepared by nitrating aniline in glacial acetic acid solution or by the use of mixed nitric-sulfuric acid in which no large excess of sulfuric acid is present. The presence of nitrous acid must be avoided, as this attacks the amino group, replaces it by hydroxyl, and results in the formation of picric acid. The nitration of aniline in the presence of a large amount of concentrated sulfuric acid yields *m*-nitroaniline[73] and later the nitro compounds which are derived from it.

Tetranitroaniline (TNA)

2,3,4,6-Tetranitroaniline, discovered by Flurscheim,[74] has interesting explosive properties but is such a reactive chemical substance that, when all things are considered, it is unsuitable for use. It was used to some extent during the first World War and was studied very thoroughly at that time.

Flurscheim prepared TNA by a one-stage nitration[75] of *m*-nitroaniline sulfate, that substance being procured by the reduction of *m*-dinitrobenzene with sodium polysulfide. The nitration proceeds smoothly, and the entering groups take the positions indicated by the strongly ortho-para orienting amino group. The yield is about 120 per cent of the weight of the *m*-nitroaniline.

[73] van Duin, *Rec. trav. chim.*, 37, 111 (1917).

[74] *Chem. News*, 1910, 218; Brit. Pats. 3224, 3907 (1910); Ger. Pats. 241,697, 243,079 (1912); U. S. Pat. 1,045,012 (1912); Z. *ges. Schiess- u. Sprengstoffw.*, 1913, 185; *Mon. Sci.*, 1914, 490.

[75] Other studies on the nitration: Stettbacher, Z. *ges. Schiess- u. Sprengstoffw.*, 11, 114 (1916); van Duin, *loc. cit.* A laboratory method for the preparation of TNA direct from aniline is described in Stettbacher's book, *op. cit.*, p. 201.
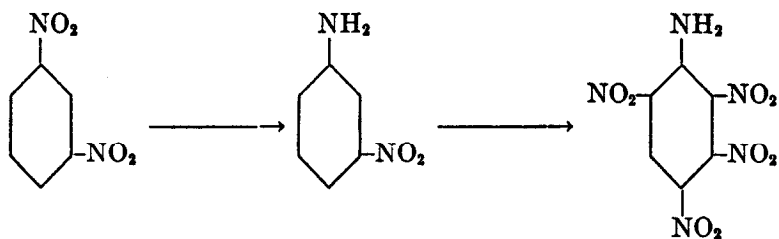
Pure TNA, yellowish-brown or greenish-brown crystals from acetone, melts with decomposition at about 210° and deflagrates at about 226°. It is soluble in glacial acetic acid (1 part in 24 at boiling temperature), readily in acetone (1 in 6 at boiling temperature), and sparingly in benzene, ligroin, and chloroform. If a small amount of water is added to an acetone solution of TNA and the liquid is refluxed, the nitro group in the 3-position, having other nitro groups *ortho* and *para* to it, is replaced rapidly by hydroxyl. The resulting trinitroaminophenol, m.p. 176°, is capable of attacking metals to form dangerous explosive salts which are similar to the picrates. If TNA is boiled with aqueous sodium carbonate or bicarbonate both the amino group and the nitro group in the 3-position are hydrolyzed, and trinitroresorcinol is formed.
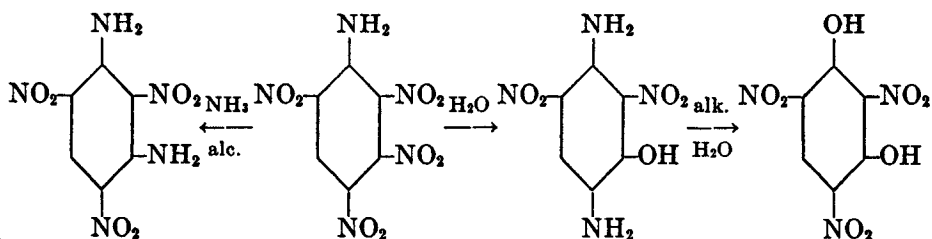
With alcoholic ammonia TNA yields trinitro-*m*-phenylenediamine, m.p. 288°. Its nitro group in the 3-position reacts with primary and secondary amines, with sodium acid sulfite, etc., in the same way that the *meta* nitro groups of β- and γ-trinitrotoluene do. Marqueyrol found that TNA is attacked rapidly by boiling water, about half of it being converted into trinitroaminophenol, the other half being destroyed with the evolution of gases, largely carbon dioxide and nitrogen along with smaller quantities of carbon monoxide, hydrocyanic acid, and nitric oxide. At 75° the reaction between water and TNA is complete after 4 days; at 60° it is about half complete after 7 days; at 40° it is appreciable after 10 days. Any decomposition of this sort, of course, is too much for an explosive intended for military use.

TNA shows about the same sensitivity as tetryl in the drop test. Lead block experiments have been reported which showed that 10 grams of TNA produced a net expansion of 430 cc., TNT 254 cc., picric acid 297 cc., tetryl 375 cc., guncotton 290 cc., and 75 per cent dynamite 300 cc.[76] Experiments with the manometric bomb gave the results indicated below.

	DENSITY OF LOADING	PRESSURE: KILOS PER SQUARE CENTIMETER
TNA................	0.20	2356
TNA................	0.25	3110
Tetryl..............	0.20	2423
Tetryl..............	0.25	3243

Since these data show that tetryl is slightly more powerful than TNA, the superiority of TNA in the lead block test must be interpreted as indicating that TNA has the higher velocity of detonation.

Tetryl (tetralite, pyronite)

Tetryl or 2,4,6-trinitrophenylmethylnitramine was first described by Michler and Meyer[77] in 1879, and was studied soon thereafter by van Romburgh[78] and by Mertens.[79] Van Romburgh proved its structure by synthesizing it from picryl chloride and potassium methylnitramine.
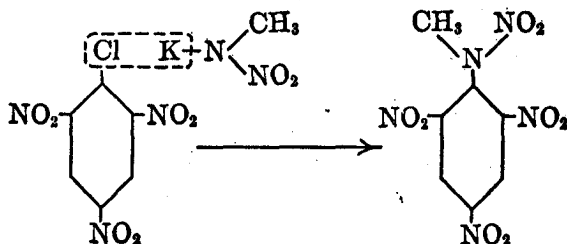
In the early literature of the subject, and to some extent at present, the substance is wrongly designated as tetranitromethyl-aniline. It results from the nitration of monomethyl- and of

[76] From the pamphlet "Tetra-Nitro-Aniline 'Flurscheim,'" Verona Chemical Company, sole licensed manufacturers for the United States, North Newark, New Jersey, 1917(?), p. 4. Giua, *op. cit.*, p. 317, states that the force of TNA measured in the lead block is 420 compared with picric acid 297.

[77] *Ber.*, **12**, 1792 (1879).

[78] *Rec. trav. chim.*, **2**, 108 (1883); **8**, 215 (1889).

[79] *Ber.*, **19**, 2126 (1886).

dimethylaniline, and is prepared industrially by the nitration of the latter. The course of the reactions is first the introduction of two nitro groups in the nucleus, then the removal of one of the
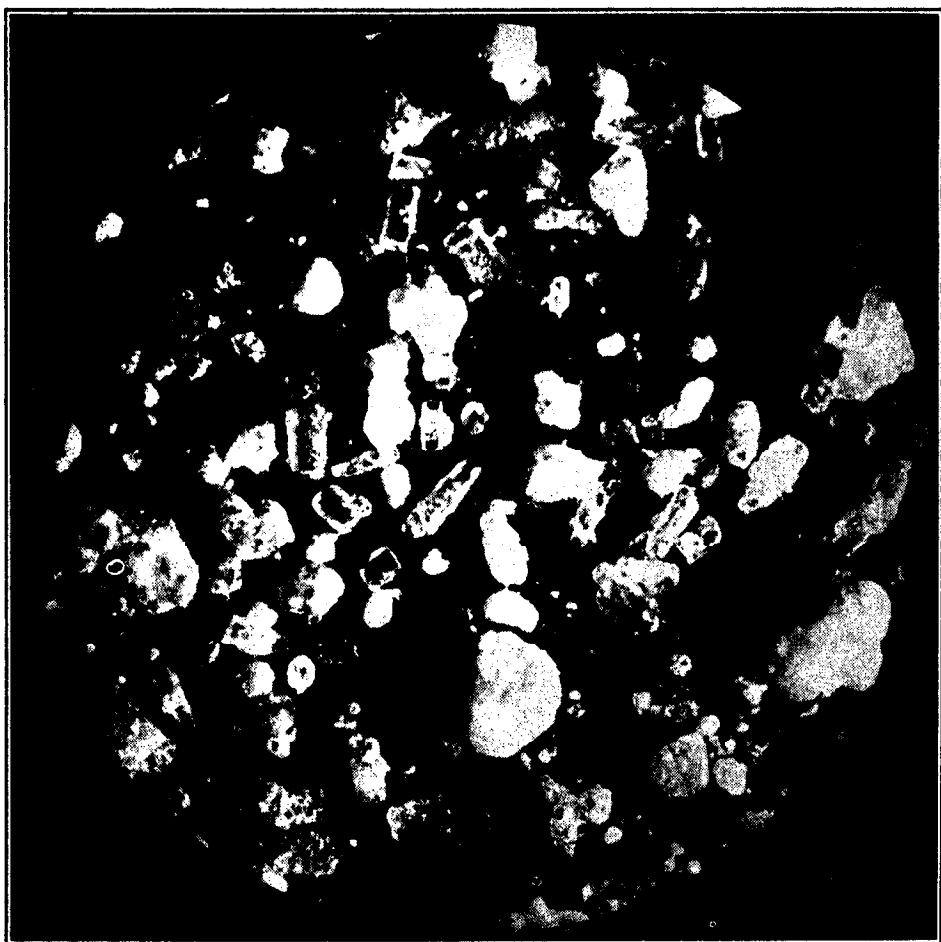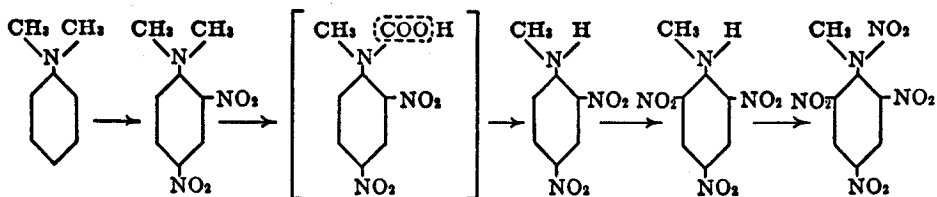

FIGURE 50. Commercial Sample of Tetryl (20×). Material crystallized in this form pours easily and may be made into pellets by machinery.

methyl groups by oxidation, then the introduction of a third nitro group in the nucleus, and finally the replacement of the amino hydrogen by a nitro group.

All the above-indicated intermediates have been isolated from the reaction. The last step is interesting because it is a reversible nitration. If tetryl is dissolved in concentrated (95 per cent) sulfuric acid and allowed to stand, the nitro group on the nitrogen is replaced by hydrogen, and nitric acid and trinitromethylaniline (methylpicramide), m.p. 111.8-112.4°, are formed.[80] Tetryl accordingly gives up this nitro group, and only this one, in the nitrometer. In the industrial preparation of tetryl, the usual method is to dissolve the dimethylaniline in concentrated sulfuric acid and then to carry out all the reactions in one stage. The process has been the subject of many careful studies, among which those of Langenscheidt,[81] van Duin,[82] Knowles,[83] Wride,[84] Desvergnes,[85] and Bain[86] are especially to be noted. The crude tetryl contains impurities which must be removed by boiling the finely comminuted substance in water, and by dissolving the crude material in benzene and filtering for the removal of insoluble materials. For the industrial crystallization of tetryl, either acetone or benzene is commonly used.

Preparation of Tetryl. Twenty grams of dimethylaniline is dissolved in 240 grams of concentrated sulfuric acid (*d.* 1.84), the temperature being kept below 25°, and the solution is allowed to run from a separatory funnel drop by drop into 160 grams of 80 per cent nitric acid (*d.* 1.46), previously warmed to 55° or 60°, while this is stirred continuously and kept at a temperature between 65° and 70°. The addition requires about an hour. After all has been added, the stirring is continued while the temperature of the mixture is maintained at 65° to 70°. The material is allowed to cool; the solid matter is collected on an asbestos filter, washed with water, and boiled for an hour with 240 cc. of water while further water is added from time to time to replace that which boils away. The crude tetryl is filtered off, ground under water to pass a 150-mesh sieve, and boiled twice for 4 hours each time with 12 times its weight of water. The solid is dried and treated with benzene sufficient to dissolve all readily soluble material. The solution is filtered and allowed to evaporate spontaneously, and the residue is recrystal-

[80] Davis and Allen, *J. Am. Chem. Soc.,* **46,** 1063 (1924).
[81] *Z. ges. Schiess- u. Sprengstoffw.,* **7,** 445 (1912).
[82] *Rec. trav. chim.,* **37,** 111 (1917).
[83] *J. Ind. Eng. Chem.,* **12,** 247 (1920).
[84] *Arms and Explosives,* 1920, 6.
[85] *Mém. poudres,* **19,** 217 (1922).
[86] *Army Ordnance,* **6,** 435 (1926).

lized from alcohol. Pure tetryl melts at about 129.4°; a good commercial sample, at about 128.5°.

The nitration of aniline in the presence of a large amount of strong sulfuric acid results wholly in the formation of m-nitroaniline, but the similar nitration of dimethylaniline gives principally a mixture of the *ortho*- and *para*-derivatives. Monomethylaniline stands between aniline and dimethylaniline in respect to the orienting effect of its amino group; it yields a considerable amount of the m-nitro- compound—and dimethylaniline is preferred for the preparation of tetryl. Commercial dimethylaniline contains a certain amount of monomethylaniline, from which it is extremely difficult to free it, and this in the manufacture of tetryl is converted in part into 2,3,4,6-tetranitrophenylmethylnitramine, or m-nitrotetryl, pale yellow, almost white, crystals from benzene, m.p. 146-147.°[87]
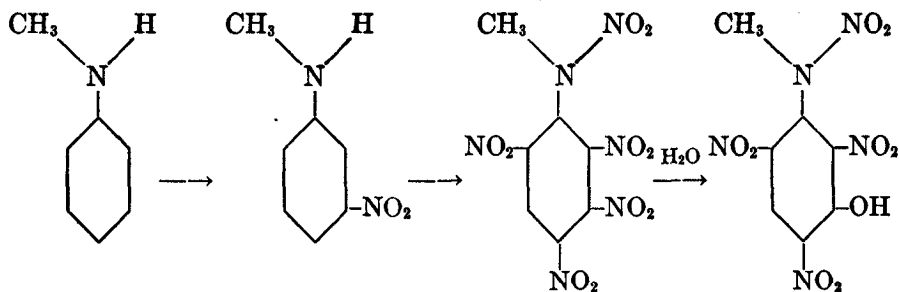

No m-nitrotetryl is produced if pure dimethylaniline is used in the usual process for the manufacture of tetryl. The amount of this impurity in the usual process depends upon the amount of monomethylaniline which may be present. A large excess of sulfuric acid tends toward the production of m-nitro compounds, but a reduction in the amount of sulfuric acid is not feasible for this increases the amount of benzene-insoluble material. m-Nitrotetryl reacts with water, as TNA does; the nitro group in the 3-position is replaced by hydroxyl, and m-hydroxytetryl or 2,4,6-trinitro-3-methylnitraminophenol, yellow crystals from water, m.p. 183°, is formed. This substance resembles picric acid and forms explosive salts. It is readily soluble in water, and

[87] Van Romburgh, *Rec. trav. chim.*, **8**, 274 (1889). Van Romburgh and Schepers, *Versl. Kon. Akad. Wetenschapen*, **22**, 293 (1913), also prepared this substance by the nitration of dimethylaniline (in 20 times its weight of concentrated sulfuric acid).

m-nitrotetryl is effectively removed from crude tetryl by boiling the finely powdered solid with water.

Crude tetryl commonly contains a small quantity of amorphous-appearing, buff-colored material of high melting point which is insoluble in benzene. The amount of this material is increased by the presence of larger amounts of water in the nitrating acid. Michler and Pattinson[88] found that tetramethyl-benzidine is produced when dimethylaniline is heated with concentrated sulfuric acid. The same material is evidently formed during the preparation of tetryl and gives rise to the three substances indicated below, which constitute the benzene-insoluble impurity.

I

II

III
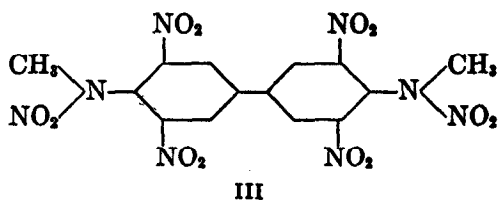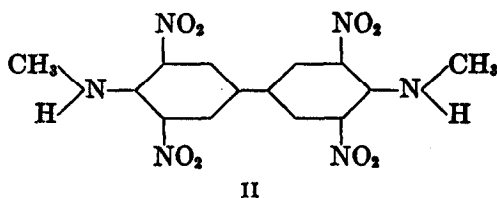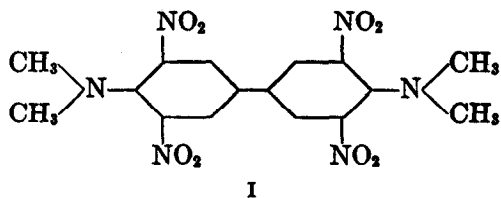
These substances were prepared by Mertens[89] in 1886 by the action of nitric acid on dimethylaniline (I, II, and III) and on monomethylaniline (II and III). Van Romburgh[90] in the same year proved them to be derivatives of benzidine, and at a much later time[91] summarized the work which had been done upon them and synthesized the substances in such manner as to prove the position of the nitro groups.

[88] *Ber.*, **14**, 2161 (1881).
[89] *Loc. cit.*
[90] *Rec. trav. chim.*, **5**, 240 (1886).
[91] *Ibid.*, **41**, 38 (1922).

If the benzene-insoluble material from crude tetryl is dissolved in hot fuming nitric acid and allowed to cool, glistening yellow crystals are procured. These, recrystallized from nitric acid and then from acetone with the addition of two volumes of ligroin, yield cream-colored small crystals of the third of the above-indicated substances, 3,3′,5,5′-tetranitro-4,4′-di-(methyl-nitramino)-biphenyl, or 3,3′,5,5′-tetranitrodimethylbenzidinedini-tramine. The material decomposes with foaming at 229-230° if its temperature is raised at the rate of 6° per minute. If it is heated more slowly, at 2° per minute, it melts partially and decomposes at 222° with preliminary softening and darkening. Like tetryl and other nitroamines, it gives a blue color with the diphenylamine reagent. Although Willstätter and Kalk[92] have found that monomethylaniline is not convertible into a benzidine derivative by Michler's method, it is nevertheless true that the benzene-insoluble by-products are produced during the preparation of tetryl from monomethylaniline, as indeed Mertens first procured them by the action of nitric acid on that substance.

The usual process for the preparation of tetryl from dimethyl-aniline has the disadvantage that the by-products, namely, the *m*-nitrotetryl and the benzene-insoluble material, necessitate a rather elaborate purification, and it has the further disadvantage that one of the methyl groups of the dimethylaniline is destroyed by oxidation (expense) with the production of red fumes (nuisance) and the consequent loss of valuable combined nitrogen. All these disadvantages find their origin at points in the reaction earlier than the formation of dinitromonomethylaniline. 2,4-Dinitromonomethylaniline, orange-yellow crystals, m.p. 174°, nitrates smoothly to form tetryl without the production of by-products or red fumes. Synthetic methyl alcohol is now available cheaply and in a quantity which is limited only by the will of the manufacturers to produce it. It reacts with ammonia (from the fixation of nitrogen) at elevated temperatures in the presence of a thorium oxide catalyst to form methylamine,[93] and methylamine reacts with dinitrochlorobenzene to form dinitromono-methylaniline. There seems every reason to believe that tetryl in the future will be manufactured chiefly, or wholly, from dinitro-chlorobenzene.

[92] *Ber.*, **37**, 3771 (1904).
[93] Davis and Elderfield, *J. Am. Chem. Soc.*, **50**, 1786 (1928).

The solubility of tetryl in various solvents is tabulated below.

SOLUBILITY[94] OF TETRYL

(Grams per 100 grams of solvent)

Temperature, °C.	Water	95% Alcohol	Carbon Tetrachloride	Chloroform	Carbon Disulfide	Ether
0	0.0050	0.320	0.007	0.28	0.0090	0.188
5	0.0058	0.366	0.011	0.33	0.0120	0.273
10	0.0065	0.425	0.015	0.39	0.0146	0.330
15	0.0072	0.496	0.020	0.47	0.0177	0.377
20	0.0075	0.563	0.025	0.57	0.0208	0.418
25	0.0080	0.65	0.031	0.68	0.0244	0.457
30	0.0085	0.76	0.039	0.79	0.0296	0.493
35	0.0094	0.91	0.048	0.97	0.0392	...
40	0.0110	1.12	0.058	1.20	0.0557	...
45	0.0140	1.38	0.073	1.47	0.0940	...
50	0.0195	1.72	0.095	1.78	...	...
55	0.0270	2.13	0.124	2.23	...	...
60	0.0350	2.64	0.154	2.65	...	...
65	0.0440	3.33	0.193	...	...	...
70	0.0535	4.23	0.241	...	...	...
75	0.0663	5.33	0.297	...	...	...
80	0.0810	...	...	...	...	...
85	0.0980	...	...	...	...	...
90	0.1220	...	...	...	...	...
95	0.1518	...	...	...	...	...
100	0.1842	...	...	...	...	...

Tetryl is hydrolyzed rapidly by boiling aqueous sodium carbonate to form sodium picrate, sodium nitrite, and methylamine which escapes. It is not affected by prolonged boiling with dilute sulfuric acid. It reacts with aniline in benzene solution at ordinary temperature; red crystals of 2,4,6-trinitrodiphenylamine, m.p. 179.5-180°, separate after the liquid has stood for a few hours, and extraction of the liquid with water yields an aqueous solution of methylnitramine.
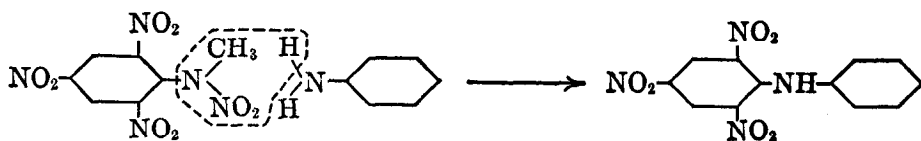
By heating tetryl alone, Farmer[95] and Desvergnes[96] obtained picric acid, and by heating tetryl in high-boiling solvents Mer-

[94] Taylor and Rinkenbach, *J. Am. Chem. Soc.*, **45**, 104 (1923).

[95] *J. Chem. Soc.*, **117**, 1603 (1920).

[96] *Loc. cit.*

tens,[96] van Romburgh,[96] and Davis and Allen[96] obtained methyl-
picramide. When refluxed in xylene solution, tetryl gives off
nitrous fumes and is converted into a tarlike mass from which
picric acid and methylpicramide may be isolated, along with a
third, unidentified, buff-colored finely crystalline substance which
melts at 240.5°. If pure tetryl is kept at 100°, it gives off nitrous
fumes and a small quantity of formaldehyde, and yields after 40
days a mass which remains semi-liquid at ordinary temperature.
By heating at 125° it is converted into a viscous liquid after
about the same number of hours.

At ordinary temperatures tetryl appears to be perfectly stable.
Current methods of purification insure the absence of occluded
acid. It is more powerful and more brisant than TNT and picric
acid, though distinctly more sensitive to shock, and is probably
the best of all the common explosives for use in boosters and
reinforced detonators. Koehler[97] reports pressures in the mano-
metric bomb (density of loading = 0.3) and temperatures pro-
duced by the explosions, as follows:

	PRESSURE: KILOS PER SQUARE CENTIMETER	TEMPERATURE, °C.
Tetryl.........	4684	2911
Picric acid......	3638	2419
TNT..........	3749	2060
TNB..........	3925	2356

Aranaz[98] reports that the explosion of tetryl produces a tempera-
ture of 3339°. Tetryl is slightly more sensitive than picric acid,
and considerably more sensitive than TNT, in the drop test. Ex-
perimenting with a 5-kilogram weight, Koehler found that a
drop of 150 cm. caused the detonation of tetryl 10 times out of
10 trials, a drop of 100 cm. 9 times out of 10, of 50 cm. 5 times
out of 10, and of 40 cm. 3 times out of 10. Martin[99] has deter-
mined the minimum charges of various primary explosives neces-
sary for the detonation of TNT and tetryl. The explosives were
loaded into detonator capsules, and the initiators were com-
pressed upon them at a pressure of 1100 kilos per square centi-
meter.

[97] Cited by Desvergnes, *loc. cit.*

[98] Aranaz, "Les nuevos explosives," Madrid, 1911, cited by Desvergnes.

[99] Martin, "Ueber Azide und Fulminate," Darmstadt, 1913, cited by Giua,
op. cit., p. 320.

	Minimum Charge for Detonation of	
	TNT	Tetryl
Mercuric fulminate.........	0.36	0.29
Silver fulminate............	0.095	0.02
Cadmium fulminate........	0.11	0.008
Mercurous azide...........	0.145	0.045
Silver azide...............	0.07	0.02
Lead azide................	0.09	0.025
Cadmium azide............	0.04	0.01

With each of the initiators which was tried, tetryl was more easily detonated than TNT. Taylor and Cope[100] have determined the minimum charges of fulminate-chlorate (90:10) necessary to cause the complete detonation of various mixtures of TNT and tetryl, as follows:

Mixture of TNT-Tetryl		Weight of Initiator, Grams
100	0	0.25
90	10	0.22
80	20	0.21
50	50	0.20
0	100	0.19

"Ethyl Tetryl." 2,4,6-Trinitrophenylethylnitramine

The ethyl analogue of tetryl was first prepared by van Romburgh,[101] who procured it both by nitrating monoethylaniline and by nitrating diethylaniline, and reported that it melts at 96°. The present writer has found that the pure material, recrystallized twice from nitric acid (d. 1.42) and once from alcohol, melts at 94°. It is comparable to tetryl in its chemical reactions and in its explosive properties.

"Butyl Tetryl." 2,4,6-Trinitrophenyl-n-butylnitramine

The n-butyl analogue of tetryl[102] has been prepared by two methods: (a) by condensing 2,4-dinitrochlorobenzene with n-butylamine to form 2,4-dinitro-n-butylaniline,[103] and by the nitration of this product; and (b) by the nitration in one step of n-butylaniline. The pure substance crystallizes from alcohol in

[100] *U. S. Bureau of Mines Technical Paper 145*, Washington, 1916.

[101] *Rec. trav. chim.*, **2**, 111 (1883).

[102] Davis, U. S. Pat. 1,607,059 (1926).

[103] Pure 2,4-dinitro-n-butylaniline crystallizes from alcohol in deep yellow or orange needles, m.p. 92.5-93.0°.

lemon-yellow plates which melt at 97.5-98.0°. It is readily soluble in benzene, ethyl acetate, alcohol and acetone, and is insoluble in petroleum ether. It yields sodium picrate when boiled with sodium carbonate solution.

Butyl tetryl is suitable for use in boosters, reinforced detonators, detonating fuse, primer caps, etc. For the detonation of 0.4 gram, it requires 0.19 gram of mercury fulminate. It has a slightly greater shattering effect than TNT in the sand test and shows about the same sensitivity as tetryl in the drop test. It explodes spontaneously at 210°.

Hexanitrodiphenylamine

2,2',4,4',6,6'-Hexanitrodiphenylamine (hexil, hexite, hexamin, etc.) is another explosive which can be prepared most conveniently from dinitrochlorobenzene. Its ammonium salt has been used under the name of *aurantia* as a yellow dye for silk and wool. It has valuable explosive properties but is more poisonous than nitroglycerin and attacks the skin, causing severe blisters which resemble burns. Its dust is injurious to the mucous membranes of the mouth, nose, and lungs. Mertens[104] in 1878 prepared hexanitrodiphenylamine by the nitration of diphenylamine with fuming nitric acid in concentrated sulfuric acid solution. Its behavior as a pseudo-acid has been studied by Alexandrov[105] and by Hantzsch and Opolski.[106] Hausermann[107] in 1891 reported upon its explosive power as compared with trinitrotoluene, and a patent granted in 1909 to Otto Freiherr von Schroetter[108] described an explosive consisting of 80 parts of hexanitrodiphenylamine and 20 parts of trinitrotoluene. The large-scale preparation by the direct nitration of diphenylamine was reported in 1910,[109] and the process from dinitrochlorobenzene, originally described in a patent to the Griesheim Chem. Fabrik,[110] was reported by

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[104] *Ber.*, **11**, 843 (1878). Austen, *ibid.*, **7**, 1249 (1874), reported the formation of the substance by the nitration of picryl-*p*-nitroaniline, and Gnehm, *ibid.*, **7**, 1399 (1874), by the nitration of methyldiphenylamine.

[105] *J. Russ. Phys. Chem. Soc.*, **39**, 1391 (1907).

[106] *Ber.*, **41**, 1745 (1908).
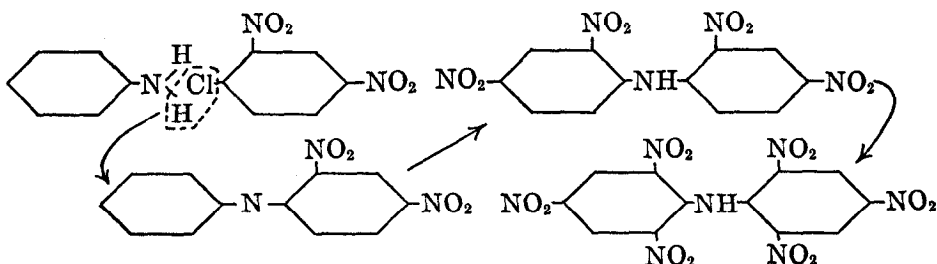
[107] *Z. angew. Chem.*, **17**, 510 (1891).

[108] U. S. Pat. 934,020 (1909).

[109] *Z. ges. Schiess- u. Sprengstoffw.*, **5**, 16 (1910).

[110] Ger. Pat. 86,295 (1895).

Carter[111] in 1913 and studied further by Hoffman and Dame[112] in 1919 and by Marshall[113] in 1920.

Dinitrochlorobenzene reacts with 2 equivalents of aniline, when the materials are warmed together in the absence of solvent or when they are stirred together vigorously with water 80-90°, to form dinitrodiphenylamine in practically quantitative yield, along with 1 equivalent of aniline hydrochloride. The use of the second molecule of aniline to combine with the hydrogen chloride involves unnecessary expense, and the same results may be accomplished by means of some mineral alkali or acid-neutralizing substance like sodium acetate or sodium or calcium carbonate. The product, which is insoluble in water, separates in bright red needles. Pure 2,4-dinitrodiphenylamine, recrystallized from alcohol or from benzene, melts at 156-157°. The crude product is nitrated in one or in two stages to the hexanitro compound.

Preparation of Hexanitrodiphenylamine (Two-Stage Nitration). Seventy grams of aniline and 32 grams of precipitated calcium carbonate are stirred up together with water in such manner as to form a homogeneous suspension, and the mixture is heated to about 60°. Dinitrochlorobenzene, 150 grams, previously melted, is poured in slowly in a fine stream while the stirring is continued and the mixture is heated gradually to about 90°, the rate of heating being regulated by the progress of the reaction. The product is washed with hydrochloric acid to free it from aniline and calcium carbonate, then with water until free from chlorides, and dried in the oven at 100°.

Fifty grams of finely powdered dinitrodiphenylamine is added in small portions at a time to 420 grams of nitric acid (*d*. 1.33), which is stirred vigorously while the temperature is maintained at 50-60°. The progress of the nitration is followed by observing the color change from

[111] *Z. ges. Schiess- u. Sprengstoffw.*, **8**, 205, 251 (1913).
[112] *J. Am. Chem. Soc.*, **41**, 1013 (1919).
[113] *J. Ind. Eng. Chem.*, **12**, 336 (1920).

the red of the dinitro compound to the yellow of the tetranitrodiphenylàmine. After all has been added, the temperature is raised to 80-90° and kept there for 2 hours longer while the stirring is continued. After the mixture has cooled, the product is filtered off directly, washed with water until free from acid, and dried in the air or in the oven at 100°.

Fifty grams of the tetranitrodiphenylamine is added slowly, with stirring, during an hour, to a mixture of 250 grams of nitric acid (d. 1.50) and 250 grams of sulfuric acid (d. 1.83). After all has been added, the mixture is allowed to stand for 3 hours at laboratory temperature, and is then drowned in ice water. The hexanitrodiphenylamine is filtered off, washed thoroughly with water, dried in the air, and recrystallized from acetone with the addition of petroleum ether.

Pure hexanitrodiphenylamine, small yellow needles, melts with decomposition at 243.0-244.5°. It is insoluble in chloroform, sparingly soluble in ether and in cold acetic acid, fairly soluble in alcohol, and readily soluble in cold acetone and in warm acetic and nitric acids.

Marshall[114] reports minimum priming charges of fulminate-chlorate (90:10) necessary for the complete detonation of the indicated explosives to be as follows:

|	GRAMS
Hexanitrodiphenylamine	0.18
Tetryl	0.20
Tetranitroaniline	0.20
Trinitrotoluene	0.25

He found hexanitrodiphenylamine to be slightly less sensitive in the drop test than tetryl and tetranitroaniline. When 1 pound of the explosive was loaded into a 3.5-inch cubical box of cardboard or tin and fired at with a U.S. Army rifle from a distance of 30 yards, hexanitrodiphenylamine gave no detonations in the cardboard boxes, and 7 detonations and 1 failure in tin; TNT gave no detonation in cardboard, fire and detonation in tin; and tetryl and tetranitroaniline gave detonations in every case with either kind of container. Marshall reported the velocity of detonation of hexanitrodiphenylamine to be 6898 meters per second at density 1.58, and 7150 meters per second at density 1.67. Pellets of the explosive, mixed with 1 per cent of stearic acid, compressed at 5000 pounds per square inch, had a density 1.43, at 10,000

[114] *Loc. cit.*

pounds per square inch, density 1.56; at 15,000 pounds per square inch, density 1.59; and at 20,000 pounds per square inch, density 1.60. The pellets which showed the best homogeneity and the least tendency to crumble were those of density 1.56.

Hexanitrodiphenyl Sulfide

$$NO_2 - \underset{NO_2}{\overset{NO_2}{\bigcirc}} - S - \underset{NO_2}{\overset{NO_2}{\bigcirc}} - NO_2$$
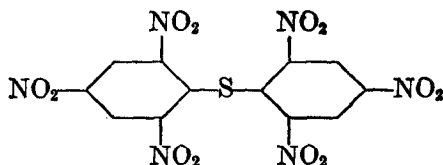
Hexanitrodiphenyl sulfide (picryl sulfide) is formed by the interaction of picryl chloride and sodium thiosulfate in alcohol solution in the presence of magnesium carbonate.[115] It is sparingly soluble in alcohol and ether, more readily in glacial acetic acid and acetone, golden-yellow leaflets from alcohol-acetone, m.p. 234°. It does not stain the fingers yellow and is said to be non-poisonous. Its explosive properties are comparable to those of hexanitrodiphenylamine. Its use in reinforced detonators has been suggested, and the fact that its explosion produces sulfur dioxide has commended it[116] for use in projectiles intended to make closed spaces, such as casemates, holds of ships, etc., untenable. During the first World War the Germans used drop bombs loaded with a mixture of equal parts of TNT and hexanitrodiphenyl sulfide.[117]

Hexanitrodiphenyl Sulfone

$$NO_2 - \underset{NO_2}{\overset{NO_2}{\bigcirc}} - SO_2 - \underset{NO_2}{\overset{NO_2}{\bigcirc}} - NO_2$$
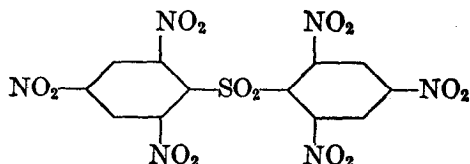
The action of nitric acid on hexanitrodiphenyl sulfide yields a substance, faintly yellowish crystals, m.p. 307°, which Stettbacher believes to be the sulfone, not the peroxide as the patent[118] states, for the reason that it is stable at elevated temperatures

[115] Ger. Pat. 275,037 (1912); Brit. Pat. 18,353 (1913).
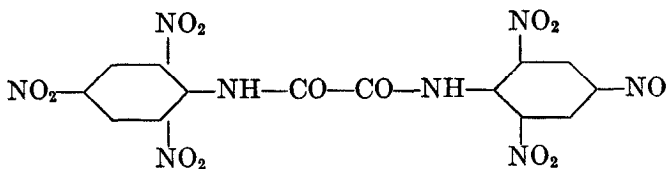
[116] Brit. Pat. 18,354 (1913).

[117] Alfred Stettbacher, "Die Schiess- und Sprengstoffe," Leipzig, 1919, p. 206.

[118] Ger. Pat. 269,826 (1913).

and is less sensitive to shock than the sulfide. It is a more powerful explosive than hexanitrodiphenyl sulfide.

Hexanitro-oxanilide

$$NO_2-\langle\ \rangle-NH-CO-CO-NH-\langle\ \rangle-NO$$

with NO_2 substituents on the rings

This substance, m.p. 295-300°, results from the direct nitration of oxanilide.[119] It is stable and about as powerful as TNT, and is reported to explode with the production of a temperature which is distinctly lower than that produced by many high explosives.

Hexanitrocarbanilide

$$NO_2-\langle\ \rangle-NH-CO-NH-\langle\ \rangle-NO_2$$

with NO_2 substituents on the rings
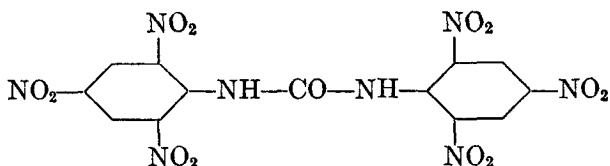
2,2',4,4',6,6'-Hexanitro-N,N'-diphenylurea (hexanitrocarbanilide or *sym*-dipicrylurea)[120] may be prepared by the nitration of carbanilide (*sym*-diphenylurea) in one, in two, or in three stages. It is of interest because of its explosive properties and because it supplies one way in which benzene may be converted into an explosive which is valuable both for military and for civil uses. Carbanilide may be prepared by the interaction of aniline and phosgene but is most conveniently and economically procured by heating aniline and urea together at 160-165°.

Preparation of Hexanitrocarbanilide (Two Stages). Forty grams of carbanilide is dissolved in 60 cc. of concentrated sulfuric acid (*d*. 1.84), and the solution is added drop by drop during 4 hours to 96 cc. of nitric acid (*d*. 1.51) while the mixture is stirred vigorously with a mechanical stirrer and its temperature is maintained at 35° to 40°. After all has been added, the stirring is continued and the temperature is raised to 60° during half an hour and maintained at 60° for another hour. The mixture is cooled to room temperature, allowed to stand over night, then treated with cracked ice and water, and filtered. The crude tetra-

[119] Fr. Pat. 391,106.
[120] Davis, U. S. Pat. 1,568,502 (1926).

nitrocarbanilide is washed thoroughly with water and allowed to dry in the air.

Ten grams of crude tetranitrocarbanilide is added to a mixture of 16 grams of concentrated sulfuric acid (d. 1.84) and 24 grams of nitric acid (d. 1.51), and the material is heated on the steam bath for 1 hour with constant stirring. The mixture, after cooling, is treated with cracked ice and water, and filtered. The product, washed with 500 cc. of cold water, then with 500 cc. of hot water, and dried in the air, is hexanitro-carbanilide of satisfactory quality for use as an explosive.

Pure hexanitrocarbanilide crystallizes from acetone-ligroin in pale yellow rosettes which soften and darken at 204° and melt at 208-209° with decomposition. It yields picric acid when warmed with dilute sulfuric acid, and trinitroaniline when boiled with strong ammonia water. A deep ruby-red color is developed when hexanitrocarbanilide is allowed to stand at ordinary temperatures in contact with strong ammonia water. Tetranitrocarbanilide, dinitroaniline, trinitroaniline, picric acid, and dinitrophenol do not give this color.

Hexanitrocarbanilide is a brisant high explosive suitable for use in boosters, reinforced detonators, detonating fuse, primer caps, etc. For the detonation of 0.4 gram, it requires 0.19 gram of mercury fulminate. It is slightly stronger than TNT in the sand test and of about the same sensitivity as tetryl in the drop test. It explodes spontaneously at 345°.

Hexanitroazobenzene

Hexanitroazobenzene may be prepared from dinitrochlorobenzene and hydrazine by the reactions indicated below:
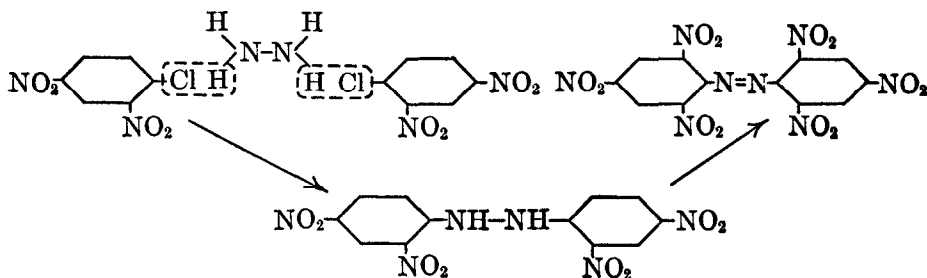
The first of these reactions takes place in hot-water suspension in the presence of sodium or calcium carbonate. The resulting tetranitrohydrazobenzene is both nitrated and oxidized by the mixed acid in the next step. Pure 2,2',4,4',6,6'-hexanitroazoben-

zene crystallizes from acetone in handsome orange-colored needles which melt at 215°. The explosive properties of the substance have not been reported in detail. The azo group makes it more powerful and more brisant than hexanitrodiphenylamine. The accessibility of the raw materials and the simplicity of its preparation commend it for use in boosters and compound detonators.