The yield of both reactions is 65–70%. According to Aubertein [78] substance (I) may be prepared in a yield 84% of theoretical.

The explosive properties of this compound (I) may be of particular interest.

Trimethylenetrinitrosamine

Physical properties. The specific gravity of the substance is 1.508. It is sparingly soluble in water. Šimeček and Doležel [82] report the following figures for its solubility, expressed as the amount in grammes dissolved per 100 g of solvent (Table 22):

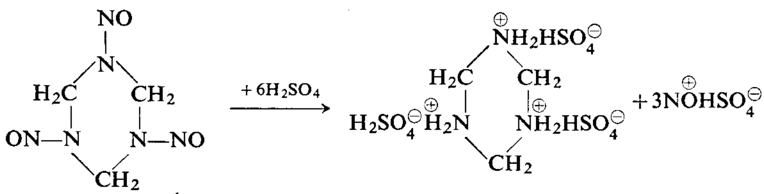
TABLE 22

	20°C	40°C	60°C
Water	0.2	0.3	0.6
Ethyl ether	0.8	1.2 at 34°	—
Toluene	1.4	2.3	4.4
Methyl alcohol	4.3	7.7	18.1
Acetone	68.5	139.7	254.5

According to Médard and Dutour [83] when molten the substance mixes with trinitrotoluene and gives an eutectic consisting of 58% of trinitrotoluene and 42% of trimethylenetrinitrosamine. The eutectic melts at about 55°C.

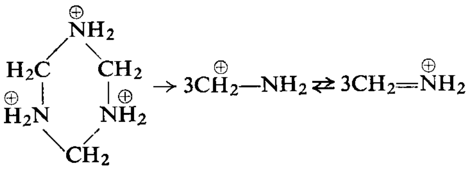
The thermochemical properties of this compound are of great interest. As early as 1896 Delépine [84] determined its heat of formation ($-\Delta H_f$) and found it to be negative. This observation was confirmed in later work by the same author and by Badoche [85] as well as in more recent experiments by Médard and Thomas [86]. According to the latter the heat of combustion of the compound (I) $-\Delta H_v = 557.17$ kcal/mole, hence its heat of formation is $-\Delta H_f = 71.1$ kcal/mole, i.e. 408 kcal/kg. The heat of detonation was found to be 850 kcal/kg.

Chemical properties. Trimethylenetrinitrosamine (I) decomposes explosively under the influence of concentrated sulphuric acid at room temperature. At a low temperature it is hydrolysed to form trimethylenetriamine sulphate (III)



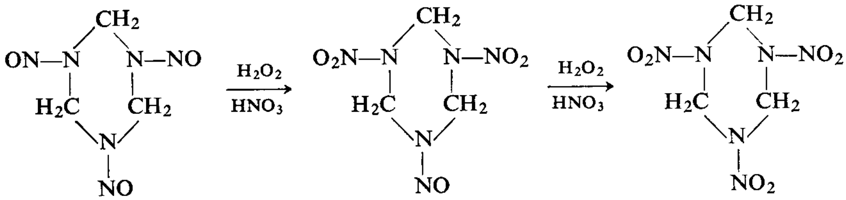
I III

According to Šimeček [87] trimethylenetriamine undergoes further decomposition to a Schiff's base:



Sodium hydroxide causes slow decomposition in the cold and rapid in the hot, with evolution of formaldehyde, nitrogen and ammonia. Rapid decomposition also occurs in boiling water and slow decomposition occurs in water at room temperature.

Oxidation of (I) leads to cyclonite. According to the work of Brockmann, Downing and Wright [12] oxidation with a solution of hydrogen peroxide (30%) in nitric acid (99%) in the ratio of 1 mole (I) to 82 moles of nitric acid, 3 moles of H_2O_2 and 3.7 moles of H_2O, at $-40°C$, gives dinitro-nitrosamine (IV) as an intermediate:



I IV

The yield of cyclonite in this reaction is 74%.

Explosive properties. The apparent density od trimethylenetrinitrosamine (I) is 0.84, according to Médard and Dutour [83]. The same authors give the following relationship between density and the compressing pressure:

pressure kg/cm^2	density
170	1.10
340	1.23
680	1.37
1020	1.44
1700	1.525
2380	1.57
3000	1.59

Complete detonation is obtained:

at a density of 0.85 by 0.30 g of mercury fulminate
at a density of 1.20 by 0.40 g of mercury fulminate
at a density of 1.40 by 0.50 g of mercury fulminate
at a density of 1.57 by 2.5 g of mercury fulminate

According to these authors sensitiveness to impact is of the same order as that of trinitrotoluene.

Šimeček and Šramek [88] give the following table for sensitiveness to impact in the drop test, using a 5 kg weight:

Weight falling from a height of cm	% of explosions
20	0
30	30
40	67
50	100

The value of the heat of detonation was reported earlier (p. 120).

According to Médard and Dutour the lead block expansion is 125.5 (taking picric acid as 100). The rate of detonation at a loading diameter of 30 mm is as follows:

Density	Rate m/sec
0.85	5180
1.00	5760
1.20	6600
1.40	7330
1.50	7600
1.57	7800

Charges of molten and solidified material at a density of 1.42 give a rate of detonation of between 7000 and 7300 m/sec.

In air the substance takes fire fairly easily and burns regularly.

The same authors examined the rate of detonation of a molten and solidified eutectic comprising 58% of trinitrotoluene and 42% of substance (I), and obtained a value of approximately 7000 m/sec.

Médard and Dutour [83] made a detailed investigation of the stability of the substance (I). At room temperature test samples of the substance remained apparently unaffected for 6 years. Marked decomposition occurred with rising temperature, beginning at about 150°C; at 160°C nitric oxides are evolved. Rapid heating causes immediate decomposition at 300°C and at 200°C decomposition occurs after 2 minutes.

The substance is exceptionally sensitive to the action of acids. When mixed with picric acid, for example, it undergoes violent decomposition after 2 hours' heating at 60°C. At 100°C decomposition ensues in 10–15 minutes. A mixture with trinitrotoluene is decomposed at 85°C.

The molten substance may react with such metals as iron, copper, aluminium. Thus, despite the fact that substance (I) is a powerful explosive, only slightly sensitive to impact, its low stability even in the presence of traces of substances with an acid reaction gives little promise for its practical use.

Dinitrosopentamethylenetetramine

Dinitrosopentamethylenetetramine (II) is used as a gasifiable product for the production of porous plastics and rubber (e.g. Unical ND, Vulkacel BN).