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AN IMPROVED PROCESS FOR THE PREPARATION OF

2,2,2-TRINITROETHANOL, TNEOH (U)

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U. S. NAVAL ORDNANCE LABORATORY

WHITE OAK, MARYLAND

NAVORD Report 6752

AN IMPROVED PROCESS FOR THE
PREPARATION OF 2,2,2-TRINITROETHANOL, TNEOH

Prepared by:

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ABSTRACT: An improved process for the preparation of 2,2,2-
trinitroethanol, without isolation of intermediates, is
described. Tetranitromethane, I, is reduced to sodium nitroform,
II, which then is simultaneously acidified and formylated by a
solution of paraformaldehyde in hydrochloric acid. The crude
trinitroethanol, III, separates in 80-85% yield as an oil which
can be stored safely. Pure crystalline trinitroethanol is
obtained from chlorinated solvent solutions of the oil dried by
azeotropic distillation.

$$(NO_2)_4C \xrightarrow[\text{NaHCO}_3]{\text{NaNO}_2} (NO_2)_3CNa \xrightarrow[\text{HCl}]{\text{HCHO}} (NO_2)_3CCH_2OH$$

$$\quad\text{I}\qquad\qquad\qquad\qquad \text{II}\qquad\qquad\qquad\qquad \text{III}$$
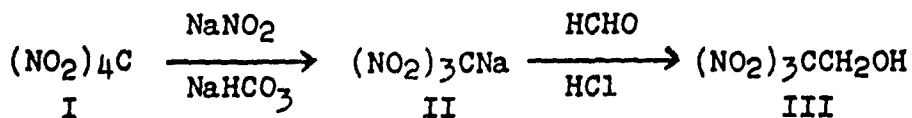
CHEMICAL RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, SILVER SPRING, MARYLAND

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This report describes the development of an improved
process of preparation of 2,2,2-trinitroethanol which was
carried out under Task 301-664/43006/08, Explosives
Applied Research. Because trinitroethanol is a primary
intermediate, the work was undertaken in connection with
the study of the synthesis of the oxygen-rich explosive
compounds trinitroethyl orthocarbonate, TNEOC;
bis(trinitroethyl) carbonate, BTNEC; and bis(trinitroethyl)
formal, TEFO.

JOHN A. QUENSE'
Captain, USN
Acting Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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INTRODUCTION

2,2,2-Trinitroethanol, TNEOH, has long been an important intermediate in the preparation of aliphatic polynitro compounds, since it affords one of the easiest means of introducing the trinitro group into an organic compound. The current interest in the oxygen rich explosive compounds, 2,2,2-trinitroethyl orthocarbonate, TNEOC, bis(2,2,2-trinitroethyl) carbonate, BTNEC, and bis(2,2,2-trinitroethyl) formal, TEFO, has focused attention on trinitroethanol since it is the basic intermediate in their preparation. The present study has been carried out in an attempt to improve the laboratory procedure for the preparation of trinitroethanol and also to collect information from scattered sources on its physical properties and characteristic reactions.

A review of the early history of nitroform and 2,2,2-trinitroethanol, with references, has been compiled by the Aerojet-General Corporation (1) and will only be supplemented and not be repeated here.

DISCUSSION AND RESULTS

Synthesis of 2,2,2-Trinitroethanol, TNEOH

A. **Historical.** The synthesis of 2,2,2-trinitroethanol, TNEOH, II, is according to the following equation:

$$H^+ + (NO_2)_3C^- + HCHO \rightleftharpoons (NO_2)_3CCH_2OH$$
$$I \qquad\qquad\qquad\qquad II$$
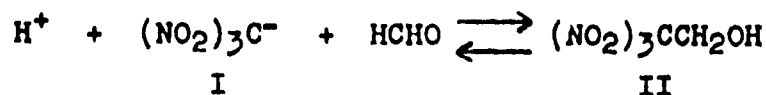
This is an equilibrium reaction, and the extent of formation of trinitroethanol is determined primarily by the pH of the reaction mixture. Above a pH 5.5 trinitroethanol largely exists in solution as its components, nitroform ion, I, and formaldehyde (2,23).

It is thus readily seen that the synthesis of trinitroethanol depends on the availability of nitroform.

Nitroform was first discovered in 1857 by Schischkoff (3) but
it was in 1899 that it was prepared by Hantzsch and
Rinckenberger (4) by the reduction of tetranitromethane, TNM,
and since that time there has been extensive work on tetra-
nitromethane and its reduction to nitroform (5). Tetranitro-
methane is a good oxidant and many common reducing agents
have been used with it to produce nitroform, usually as the
potassium salt. Hantzsch and Rinckenberger (4) used
alcoholic potassium hydroxide, or "better potassium ethylate"
to prepare potassium nitroform from tetranitromethane. However,
somewhat later, Macbeth (6) warned against the use of sodium
ethylate in this reaction because of his experience with an
explosion in the laboratory. Macbeth and Orr (7) found glycerine
a convenient reducing agent with potassium hydroxide, and
glycerine was used in pilot plant production of potassium nitro-
form (8). Potassium sulfite, potassium ferrocyanide, arsenious
acid, potassium phosphite, ammonium sulfide and hydrazine have
all been used effectively to produce potassium nitroform from
tetranitromethane (9).

One of the better methods previously used for the pre-
paration of trinitroethanol from potassium nitroform is the pro-
cess developed from Schimmelschmidt's work (10) by Aerojet-
General Corporation (1), and later modified at the Naval
Ordnance Laboratory (11). The potassium nitroform is pre-
pared from tetranitromethane by reduction with hydrogen
peroxide and potassium hydroxide according to the following
equation:

$$C(NO_2)_4 + 2 \; KOH + H_2O_2 \longrightarrow (NO_2)_3CK + KNO_2 + O_2 + 2 \; H_2O$$
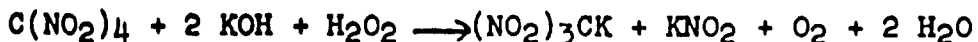
The potassium nitroform can then be acidified and the
resulting nitroform condensed with formaldehyde to produce
trinitroethanol in high yield. The over-all series of
reactions is:

$$(NO_2)_4C \longrightarrow (NO_2)_3CK \longrightarrow (NO_2)_3CH \longrightarrow (NO_2)_3CCH_2OH$$
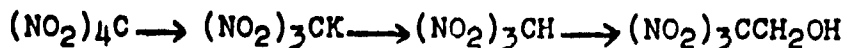
The reactions in the various steps proceed smoothly and the
yields are good, the only difficulty arising from the necessity
of handling the potassium nitroform. This intermediate has an
impact sensitivity of 44 cm (tetryl = 40 cm) and is unstable
in storage, even when stored under solvent (12). By using
potassium nitroform the same day it is isolated the danger is

minimized, but its use should be avoided if possible, and for large scale production of trinitroethanol would be very hazardous.

The use of potassium nitroform can be avoided by preparing the soluble sodium salt of nitroform by the Glover-Sickman reaction (13), which utilizes sodium nitrite and sodium bicarbonate for the reduction of tetranitromethane according to the following equation:

$$(NO_2)_4C + NaNO_2 + NaHCO_3 \longrightarrow NaC(NO_2)_3 + NaNO_3 + CO_2 + HNO_2$$
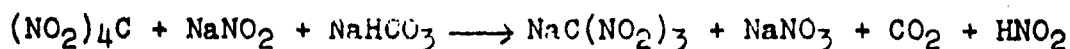
Dacons and Kamlet (14) studied this reaction rather extensively in preparing nitroform for the synthesis of 4,4,4-trinitrobutyric acid and established the conditions for good yields in the nitrite reduction of tetranitromethane. They then developed a "one-pot" synthesis of trinitroethanol (15) following the customary procedure of acidification of the alkali salt of nitroform and condensation of the free nitroform with 37% formalin solution to form trinitroethanol. They obtained dry trinitroethanol by adding methylene chloride to the reaction mixture and removing all of the water by azeotropic distillation.

The present authors have found that various simplifications of this method can be made, namely: the use of paraformaldehyde instead of formalin solution which obviates the necessity of analyzing the formalin and reduces the volume of water used; simultaneous acidification and formylation which shortens the reaction period appreciably; elimination of the heating period in the second step; and an improvement in the drying procedure for obtaining crystalline trinitroethanol or dry trinitroethanol in solution.

B. Optimum Procedure. For laboratory purposes, therefore, the sodium nitrite-sodium bicarbonate reduction of tetranitromethane appears to be the best procedure to follow in order to obtain nitroform for the synthesis of trinitroethanol. This reduction is carried out by adding tetranitromethane to a slurry of sodium nitrite and sodium bicarbonate in 50% methanol-water and holding at 55°-60°C for two and a half to three hours. During this period the color deepens from the original yellow to a reddish brown and the heterogeneous mixture becomes an homogeneous solution. The use of a slurry of the inorganic salts keeps the volume of the reaction medium within practical handling limits. Methanol is essential in the reaction medium

to increase the solubility of the tetranitromethane since
otherwise the extreme insolubility of tetranitromethane in
water results in a very slow reaction rate. The tetranitro-
methane may be added to the slurry quite rapidly since there is
no apparent exothermic or other detrimental reaction at this
point. The reaction period of two and a half to three hours
is necessary to insure complete reduction of the tetrani-
tromethane.* The necessity of the long reaction period for the
reduction of tetranitromethane to nitroform is verified not only
by a lower yield realized from a shorter reaction period but by
calculations based on a kinetic study of the reaction in
aqueous medium by D. J. Glover (16).

The acidification of the basic reduction solution, and the
formylation of the nitroform ion with formaldehyde is carried
out in one step in the same container as was used for the
reduction of tetranitromethane. Paraformaldehyde offers a
convenient source of formaldehyde, easy to handle and readily
depolymerized in concentrated hydrochloric acid. Such a solu-
tion is added rapidly to the tetranitromethane reduction
solution after cooling the latter to room temperature. Some
brown fumes of oxides of nitrogen are evolved, but there is no
exothermic reaction beyond that expected from dilution of the
acid. There is an abrupt color change from orange to lemon
yellow when the solution becomes acid and a heavy lemon yellow
oil separates immediately. The trinitroethanol formation is
complete as soon as the acid-formaldehyde addition is complete
and the oil can be separated from the aqueous layer immediately.
Neither a prolonged reaction period nor a prolonged period at
an elevated temperature produces an appreciable additional
amount of product.

For laboratory purposes the aqueous layer can be discarded.
It has been shown by extraction of the mother liquor with
methylene chloride and isolation of crystalline trinitroethanol
from the extract that the aqueous layer contains only about 5%
of the total trinitroethanol obtained in the reaction, or
3.75% of the theoretical weight of trinitroethanol obtainable
based on the amount of tetranitromethane used. On a larger
than laboratory scale such extraction procedures would probably
be justified.

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* The preceding paragraph is essentially a repetition from
Dacons and Kamlet (14) and is included here for clarity and
completeness of discussion.

<u>Preparation of Dry Trinitroethanol</u>. The oil layer contains principally trinitroethanol hydrate, with methanol, water, and some impurities including inorganic salts dissolved in the water present. Isolation of crystalline trinitroethanol from the oil is accomplished by dissolving the oil in a chlorinated solvent such as methylene chloride, chloroform, or carbon tetrachloride, drying the resulting solution by azeotropic distillation to concentrate the solution, and chilling the concentrated solution to cause crystallization.

Ordinary drying agents such as Drierite or magnesium sulfate are not adequate for isolating crystalline trinitroethanol. Either the trinitroethanol does not crystallize at all or the crystalline product is sticky and low melting. After drying the solution by azeotropic distillation, however, the trinitroethanol crystallizes in well formed crystals from which the solvent evaporates readily, leaving dry crystals. Carbon tetrachloride is probably the best solvent from which to crystallize trinitroethanol because it is easier to dry its solutions of trinitroethanol and also because pure trinitroethanol is only slightly soluble in carbon tetrachloride. However, the trinitroethanol oil is not very soluble in carbon tetrachloride and although the two phase system of oil-carbon tetrachloride can be dried by azeotropic distillation, such a system might be hazardous, especially in large quantity. Since the trinitroethanol oil is miscible with methylene chloride it was found preferable to dry the oil by azeotropic distillation of the methylene chloride-trinitroethanol oil solution, then add carbon tetrachloride and strip off the methylene chloride. Trinitroethanol crystallizes from the chilled carbon tetrachloride solution and is filtered off and dried. A yield of 80-85% of theoretical, based on the amount of tetranitromethane used is obtained by this isolation procedure. The product is a white crystalline material which melts at 74°C.

Dry crystalline trinitroethanol is a sensitive compound. Danger of handling can be decreased by keeping the trinitroethanol in solution after drying since, for many purposes, it is not necessary to isolate crystalline trinitroethanol. Trinitroethyl orthocarbonate, TNEOC, (17), bis(trinitroethyl) carbonate, BTNEC, (18), and bis(trinitroethyl) formal, TEFO, (19), preparations are carried out by using carbon tetrachloride solutions of trinitroethanol. The concentration of trinitroethanol in the carbon tetrachloride or other solvent used can be determined by spectrophotometric measurement.

The method depends on alkaline extraction of the trinitro-
ethanol from the solvent and the fact that in alkaline medium
trinitroethanol is quantitatively decomposed to its components,
nitroform and formaldehyde. Measurement of the absorbency at
350 mμ, characteristic of the nitroform ion, is used to
determine the molar concentration of nitroform, and hence of
trinitroethanol.

Other Methods of Preparation of Trinitroethanol. The above
optimum process is adaptable to production on a large scale,
but the long reaction period required in the reduction of
tetranitromethane makes a continuous production method less
feasible than desired. Other reducing agents, notably sodium
sulfite and hydrazine, have been reported (9) as reducing
tetranitromethane to nitroform rapidly and without detrimental
side reactions. The work reported, however, involved the
preparation of the insoluble potassium salt of nitroform and
the use of alkaline solutions throughout, conditions which
probably prevented secondary action of the reducing agent.
These and other reducing agents were adapted to the "one-pot"
synthesis as described above and it was found that the reaction
time for the reduction of tetranitromethane could be shortened
considerably. In fact the reduction was complete almost as fast
as tetranitromethane was added to the reagent, but other con-
siderations nullified the gain. Either serious side reactions,
such as further reduction of the nitroform to the dinitro
compound, or precipitation of side products as in the case of
ferrous chloride, interfered in the reaction. In addition, the
volume of solvent had to be increased so that in no case was
the trinitroethanol obtained as an oil as it is in the sodium
nitrite-sodium bicarbonate reduction method, and extensive
extraction procedures were required to isolate crystalline
trinitroethanol.

Large scale production of trinitroethanol, i.e. pilot plant
or larger, will undoubtedly use nitroform produced by nitra-
tion of acetylene:

$$5\ C_2H_2 + 35\ HNO_3 \longrightarrow 3\ HC(NO_2)_3 + 21\ H_2O + 26\ NO_2 + 7\ CO_2$$
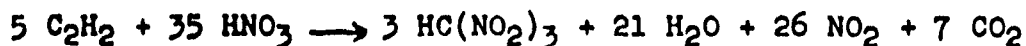
A feasibility study on an operation by this method at a rate
of five tons per day was made at the Naval Ordnance Laboratory
by Raymond W. Southworth (20). Production at the rate of one
kilogram per hour has been in operation, and a plant designed
to produce ten kilograms per hour is now being constructed (21).

Wetterholm and Nilsson (22) patented a two step distillation process for obtaining an aqueous solution of nitroform from the reaction mixture in the acetylene nitration. First 98% nitric acid is distilled off under reduced pressure to minimize further nitration of the nitroform to tetranitromethane until the nitric acid-water ratio approaches that of the azeotropic mixture. Water is then added to the residue until the nitric acid concentration is reduced to about 60%. Distillation of this mixture (also under reduced pressure) gives an aqueous solution of nitroform containing 44.3% of nitroform, 55.2% of water and 0.5% of nitric acid. That trinitroethanol can be prepared from such a solution has been demonstrated by a brief study. A solution of pure nitroform and aqueous nitric acid of the composition given above was prepared and 37% formalin was added to the solution. A lemon yellow oil formed and by following the customary extraction and drying procedures a 77% yield of crystalline trinitroethanol was isolated from this reaction.

Physical Properties of Trinitroethanol. Pure trinitroethanol crystallizes from methylene chloride in massive transparent rods having a melting point of 73.5-74°C. The alcohol is stable in storage at room temperature either in crystalline form or as the crude oil. The crystalline material sublimes very slowly at atmospheric pressure and ambient temperatures of storage, depositing trinitroethanol elsewhere in the storage vessel over a period of time. Also on long standing the crystals have a tendency to cake but are easy to handle under normal laboratory conditions.

Various laboratories have reported that trinitroethanol is very hygroscopic. Experience has shown, however, that the pure crystals do not readily take up water. On days of relatively low humidity, typical of the winter months, recrystallized trinitroethanol can be "bench dried" successfully and handled without extreme precaution against atmospheric moisture. Crystals of the pure alcohol appear to sublime into the air, at least partially accompanied by a reversion to formaldehyde and nitroform which are easily detected in the space above the crystal surfaces. Even in a humid atmosphere, water take-up is rather slow if the compounds is pure, but quite rapid if the recrystallized material contains impurities such as nitroform, formaldehyde, or water.

On occasion, pure trinitroethanol which had "oiled" by absorbing water was observed to crystallize again to crystals

having a lower melting point. This observation, plus the
ineffectiveness of common adsorbents for drying trinitro-
ethanol oil solutions, indicated that the alcohol existed in
the crude oil as the hydrate and that the low melting "pure
trinitroethanol" reported by previous laboratories was really
the crystalline monohydrate. Ostensibly the crude oil con-
tained 20-30% water but all but a few per cent of the oil could
be dissolved in carbon tetrachloride or methylene chloride,
either of which could be an effective solvent for the mono-
hydrate of trinitroethanol, but not for water. Further
evidence on this point was obtained in one instance when it
was observed that, after ordinary drying procedures were
followed, azeotropic distillation removed the exact equivalent
of one mole of water for the amount of crystalline trinitro-
ethanol present in solution. It was then determined that well
formed, but "soft" or "sticky" long needles can be obtained
from dry crystalline trinitroethanol plus one mole of water.
The trinitroethanol dissolved with endothermic heat of solution
on addition of the water, but upon chilling or seeding the
solution becomes a solid mass of beautiful long needles.
Similar crystals can be obtained by evaporation of the residual
mother liquor from the trinitroethanol oil, or from a methylene
chloride solution of the oil. The melting point of the crystals
from the three sources was the same, 60-62°C. However, crystals
of the hydrate as obtained above were allowed to stand in the
open overnight in an atmosphere of low humidity and the next
day the melting point was 52°C and quite sharp at that point.
This observation seems to indicate that the crystalline
hydrate may vary in water content. It is also assumed that
the fact that trinitroethanol forms hydrated crystals probably
accounts for the different melting points, 30°C to 74°C,
reported for "pure trinitroethanol" by various authors.
Table I summarizes the general physical properties of trini-
troethanol.

TABLE   I

Physical Properties of Trinitroethanol

Melting Point	73.5-74°C
Crystal Density	1.70
Impact Sensitivity (50% Height, 2.5 kg weight)	11 cm (pure crystals RDX=24 cm)
	25 cm (wet with CCl_4)
	22 cm (monohydrate)
	86-101 cm (as crude production oil)
Vacuum Stability	Sublimes easily under reduced pressure
Solubility (room temperature)	Soluble in water, chloroform, methanol, methylene chloride Very soluble in glacial acetic acid Slightly soluble in hexane, carbon tetrachloride (v.s. hot)
Equilibrium Constant	1.4×10^{-5} (TNEOH $\xrightarrow{H_2O}$ HCHO + $HC(NO_2)_3$

(ref. 23)

Chemical Reactions of Trinitroethanol. Trinitroethanol deriv-
atives have been among the most important compounds evaluated
during the new explosives program. Nitro groups constitute
76% of the trinitroethanol molecule and for aluminized com-
positions trinitroethanol is one of the most efficient inter-
mediates for introducing oxygen into an explosive compound.

Although trinitroethanol has the structure of an alcohol,
the polar effect of the nitro groups decreases the reactivity
of the hydroxyl group to a very great degree. Esterifications,
acetal formation and other reactions which involve the basic
properties of the hydroxyl group are difficult to carry out
under normal conditions. Processes which proceed through a
carbonium ion intermediate are unknown. Ether formation via
the alkoxide or any reaction requiring basic conditions cannot
be realized because of the dissociation of the alcohol at
higher pH's. For reactions which occur under acidic conditions
several unusual methods are being used to circumvent the un-
reactivity of trinitroethanol.

Some of the most recently studied reactions of trinitro-
ethanol are discussed briefly below and others are outlined
in Table II.

1. Esterification. The very weak basicity of the
hydroxyl group of trinitroethanol was quite evident when
attempts were made to esterify the alcohol with aliphatic or
aromatic acids by the usual classical methods. Even with acid
chlorides long reaction periods were required in most cases to
obtain low yield of ester. Since organic esters are an
important class of compounds for evaluation as explosives,
several processes were devised which greatly speeded up the
esterification of trinitroethanol. An unusual method of
direct esterification, most useful for the preparation of
trinitroethyl trinitrobutyrate, TNETB, consisted of employing
100% sulfuric acid as solvent (24). The product precipitated
from the sulfuric acid and was easily isolated in high yield.
Fuming sulfuric acid was used for the transesterification of
methyl trinitrobutyrate (25) with trinitroethanol as an
alternative process. The sulfuric acid method was limited
to the reaction of trinitroethanol with strong organic acids
in order to get a favorable equilibrium between the formation
of the product and the opposing cleavage reaction. A more
general procedure for the preparation of trinitroethanol esters
consisted of the reaction of acid chlorides with the alcohol
in the presence of catalytic amounts of metal halides. High

yields were obtained at reaction rates several hundredfold
faster than previously realized (26). Trifluoroacetic anhy-
dride (27) was also used successfully as a solvent for
direct esterification.

2. <u>Acetal Formation</u>. The formation of acetals of
trinitroethanol by the usual methods has not been particularly
successful. Recently, however, high yields of formals have
been obtained by the reaction of trinitroethanol and some
other nitro alcohols with paraformaldehyde using strong
sulfuric acid as solvent at room temperature (19). The
product, bis(trinitroethyl) formal, precipitated from the
sulfuric acid solution.

3. <u>Orthoester Formation</u>. A new reaction of poly-
halogen compounds, $RCCl_3$, with trinitroethanol in the
presence of ferric chloride has provided a family of ortho-
esters of trinitroethanol which are unusually high in
oxygen content. One of these, trinitroethyl orthocarbonate,
$(TNEO)_4C$, was obtained in high yield from carbon tetra-
chloride, trinitroethanol and ferric chloride under strictly
anhydrous conditions (17). In a modification of this re-
action, the system was kept moist by the addition of water
in order to obtain trinitroethyl chlorocarbonate by
hydrolysis of the partially substituted carbon tetrachloride
intermediate. The chlorocarbonate was then converted to
bis(trinitroethyl) carbonate by reaction with trinitro-
ethanol in a separate step using metal halide catalysis (18).

4. <u>Urethane Formation</u>. After lack of success early in
the program in preparing trinitroethyl urethanes from iso-
cyanates, ferric acetyl acetonate was found to be a good
catalyst for the reaction of trinitroethanol with various
isocyanates (28).

TABLE II

Reactions of Trinitroethanol

TNEOH Reaction with:	Conditions	Product	
1. Acids	a) 100% H_2SO_4, 50°C b) $(CF_3CO)_2O$	TNE esters TNE esters	(24) (27)
2. Esters	Fuming H_2SO_4	TNE esters	(25)
3. Acid chlorides	$AlCl_3$ catalyst	TNE esters	(28)
4. Formaldehyde	Concentrated H_2SO_4, 25°C	Bis(TNE) formal	(19)
5. $RCCl_3$ compounds	a) Anhydrous $FeCl_3$ b) H_2O-$FeCl_3$-$RCCl_3$	a) TNE orthoesters b) TNEOĈR	(17) (17)
6. Ammonia	H_2O solution	Bis(TNE) amine	(29)
7. Isocyanates	Ferric acetyl acetonate catalyst	TNE Urethanes	(28)
8. RNHĈCl	Fusion	TNE Urethanes	(29)
9. $(RNH)_2C=O$	MeOH	TNE substituted Ureas	(29)
10. RSO_2NH_2	Fusion	TNE sulfonamides	(29)
11. HNO_3	H_2SO_4	$TNEONO_2$	(29)
12. PCl_5	HCl catalyst	TNE chloride and TNE phosphate	(30)
13. $SOCl_2$	CCl_4	$(TNEO)_2SO$	(31)
14. $AlCl_3$	CCl_4	TNEOH Cl_2	(26)

ACKNOWLEDGMENT

EXPERIMENTAL

Synthesis of Trinitroethanol Oil

A. By sodium nitrite-sodium bicarbonate reduction of tetra-
nitramethane (optimum procedure). A slurry of 78 g (1.15 mole)
of sodium nitrite and 95 g (1.15 mole) of sodium bicarbonate
(Note 1), 190 ml of methanol and 190 ml of distilled water
was heated to 55°C in a 2 liter, 3-neck, round bottom flask
fitted with a thermometer, mechanical stirrer and a Claisen
adapter with a Friedrich condenser and dropping funnel.
With vigorous stirring, 125 ml (1.0 mole) of tetranitro-
methane was added over a period of 10 minutes (Note 2).
The temperature was maintained at 55-60°C for two and a half
to three hours after the addition of the tetranitromethane
was completed (Note 3). The reaction mixture was then
cooled to room temperature and a solution of 36 g (1.2 mole)
of paraformaldehyde dissolved in 125 ml (1.25 mole) of con-
centrated hydrochloric acid was added fairly rapidly (Note 4).
The mixture was stirred for 15 minutes to insure complete
reaction and then transferred to a separatory funnel and the
trinitroethanol oil was separated from the supernatant
aqueous layer (Note 5). The oil weighed 250 g. It can be
stored safely or used for the preparation of dry crystalline
trinitroethanol.

Note 1. Greater quantities of sodium bicarbonate, 1.5 moles
and 2.0 moles, were used in different preparations. The
yield of crystalline trinitroethanol was not changed appre-
ciably by using a larger quantity of sodium bicarbonate and
handling difficulties were increased.

Note 2. The mixture became yellow immediately upon
addition of tetranitromethane.

Note 3. During the heating period the color deepened from
yellow to reddish orange. The inorganic salts dissolved
completely after about 45 minutes and the solution became
completely homogeneous, i.e. no visible droplets of tetra-
nitromethane, before the end of the reaction period.

Note 4. Brown fumes of oxides of nitrogen were always evolved
during the first part of this addition, but no exotherm
beyond that expected by dilution of the concentrated hydro-
chloric acid was noted, or other indication of detrimental
reaction. The color of the solution lightened from reddish

orange to orange during the addition of the acid-formaldehyde mixture and there was an abrupt change from orange to lemon yellow when the solution became sufficiently acid, accompanied by the formation of droplets of a lemon yellow oil.

Note 5. The aqueous layer has been shown to contain only about 5% of the trinitroethanol produced in the reaction and may be discarded or, if so desired, the trinitroethanol may be extracted with methylene chloride.

B. By sodium sulfite reduction of tetranitromethane. A slurry of 19.0 g (0.075 mole) of sodium sulfite ($Na_2SO_3.7H_2O$), 8.4 g (0.10 mole) of sodium bicarbonate, 50 ml methanol and 50 ml of distilled water was heated to 50°C in a 500 ml, 3-neck, round bottom flask fitted with a thermometer, mechanical stirrer and a Claisen adapter with a Friedrich condenser and a dropping funnel. External heating was discontinued during the addition of 6 ml (0.05 mole) of tetranitromethane, the temperature being maintained during the ten minutes of addition by the exotherm of the reaction. Heating was then resumed and continued for one hour. After cooling to room temperature the solution was acidified by the addition of 20 ml of concentrated hydrochloric acid containing 1.75 g (0.05 mole) of paraformaldehyde. The resulting lemon yellow solution was filtered from a small amount of inorganic salt and extracted with five 25 ml portions of methylene chloride. The methylene chloride solution was dried by azeotropic distillation with a reverse Dean-Stark trap and the methylene chloride was removed by evacuation in vacuo. The residue was dissolved in 20 ml of carbon tetrachloride and the solution was chilled. The crystalline product which formed weighed 6.1 g or 67.4% of theoretical yield, m.p. 73.5-74°C.

The reduction of tetranitromethane was followed by spectrophotometric measurements on samples withdrawn from the reaction mixture 5 minutes, 8 minutes and 15 minutes after the addition of tetranitromethane was completed. These analyses indicated that reduction of the tetranitromethane was complete within a few minutes.

However, it was found that, whereas the maximum absorbency for nitroform should be at 350 mμ, in these solutions the maximum was shifted toward 360 mμ, the peak for

dinitromethane. By calculating from known constants for nitroform and dinitromethane it was estimated that 6.6% of the total reduction product of TNM in the mixture was di-nitromethane rather than nitroform.

C.   By hydrazine reduction of tetranitromethane. The preparation was carried out as with sodium sulfite-sodium bicarbonate only using hydrazine sulfate and sodium bicarbonate at room temperature. In alkaline solution hydrazine is known to reduce tetranitromethane only as far as nitroform (9). Acidification as in the second stage of the TNEOH synthesis, however, produced a solution of intense orange color instead of the usual lemon yellow. Spectophotometric measurements showed a shift in the maximum absorbency from 350 mu, maximum for nitroform, toward 360 mu, maximum for dinitromethane. By calculations based on known constants for nitroform and dinitromethane it was estimated that 20% of the reduction product formed in this reaction was the di-nitro compound.

D.   By hydrogen peroxide and sodium hydroxide reduction of tetranitromethane. The formation of the sodium salt of nitroform was carried out with sodium hydroxide and hydrogen peroxide, duplicating the procedure for potassium nitroform (11). Acidification and formylation as in the synthesis from the sodium nitrite-sodium bicarbonate reduction above produced no oil, but a 50% yield of crystalline trinitro-ethanol was isolated from the reaction solution by extraction with methylene chloride.

E.   Ferrous chloride reduction of tetranitromethane. A small scale, test tube, experiment using ferrous chloride and sodium bicarbonate for the reduction of tetranitromethane showed that tetranitromethane was indeed reduced by ferrous chloride in alkaline solution as determined by spectrophoto-metric measurement of the nitroform in the solution. When the preparation was scaled up to 0.05 mole, however, the ferric hydroxide present in the alkaline mixture formed a thick gel which presented such difficulty in filtering that the method was considered impractical and not developed further.

Isolation of Crystalline Trinitroethanol

A.   By drying a methylene chloride extract.

1.   From the crude trinitroethanol oil layer. The oil
layer from a 1.0 mole preparation of trinitroethanol,
252.7 g, was dissolved in 350 ml of methylene chloride.
The solution was dried by refluxing for 5-6 hours with a
reverse Dean-Stark trap. The dry solution was decanted
from the inorganic salts which separated from the solution
during drying, and chilled. The crystalline product which
formed was filtered off and dried. It weighed 107.5 g.
The filtrate was reduced to half volume by evaporation in
vacuo, then chilled, and the second crop of crystals was
filtered off and dried. This weight was 33.6 g. The com-
bined yield from the oil layer was 141.1 g, or 78% of
theoretical, m.p. 73-74° C.

2.   From the aqueous mother liquor. The aqueous
mother liquor from the same 1.0 mole preparation of tri-
nitroethanol as in 1, above, was extracted with five 25 ml
portions of methylene chloride. The combined methylene
chloride solutions were dried by azeotropic distillation,
the volume of the solution was reduced to about 25 ml by
evaporation in vacuo, and the solution was chilled. The
crystalline product which formed was filtered off and dried.
It weighed 6.8 g, 3.75% of theoretical, or 4.6% of the total
weight of trinitroethanol isolated from the reaction, m.p.
73-74°C. The combined yield from oil and aqueous layers as
crystalline trinitroethanol was 147.9 g or 83% of the
theoretical.

B.   By drying a carbon tetrachloride solution. A portion,
50 g, 20% of the oil obtained from a 1.0 mole preparation
of trinitroethanol, of trinitroethanol oil was added to
150 ml of carbon tetrachloride in a 300 ml round bottom
flask and the mixture was refluxed with a reverse Dean-
Stark trap to remove the water present. The dry carbon
tetrachloride solution was decanted from the inorganic salts
which separated during the azeotropic distillation and
chilled. The crystalline product which formed was filtered
off and dried. It weighed 29.1 g, m.p. 73.5-74°C. The
total yield of trinitroethanol on this basis would be 145.5
g, or 80.5% of the theoretical in the oil layer. Assuming

7.0 g in the aqueous layer as determined in A-2 above, the total yield of crystalline trinitroethanol would be 152.5 g, or 84.3% of theoretical.

C. By drying a methylene chloride-carbon tetrachloride solution. The mother liquor from a 1.0 mole preparation of trinitroethanol was extracted with six 50 ml portions of methylene chloride. This extract was added to the trinitroethanol oil, 247.3 g, formed in the preparation, to form 460 ml of solution. A portion of this solution, 100 ml, was added to 100 ml of carbon tetrachloride and the mixture was dried by azeotropic distillation with a reverse Dean-Stark trap for three hours. The dry solution was decanted from the inorganic salts which separated during the drying, the methylene chloride was stripped from the solution by distillation, the carbon tetrachloride solution was chilled and the white crystalline product which formed was filtered off and dried. It weighed 33.9 g, m.p. 73.5-74°C. The total weight of trinitroethanol on this basis would be 155.9 g, or 86% of the theoretical based on the weight of tetranitromethane used in the trinitroethanol preparation.

Preparation of Trinitroethanol Hydrate. Water, 0.5 g (0.0275 mole) was added to 5 g (0.0275 mole) of dry crystalline trinitroethanol in a 25 ml erlenmeyer flask. The trinitroethanol dissolved with endothermic heat of solution. Chilling the solution produced a solid mass of crystalline material, or a small amount of the solution on a watch glass crystallized to a solid mass of long needles when seeded with a crystal of the chilled product.

A small amount of trinitroethanol oil was allowed to stand in the open at room temperature in an atmosphere of low humidity. Long needle like crystals, similar in shape to those from dry crystalline trinitroethanol plus water formed. Similar crystals were also obtained by allowing a small amount of a methylene chloride solution of crude trinitroethanol oil to stand on a watch glass at room temperature in an atmosphere of low humidity.

Crystals from the three sources, crystalline trinitroethanol plus water, trinitroethanol oil, and a methylene chloride solution of trinitroethanol oil, melted at the same temperature on a hot stage, 60-62°C. After standing over night in an atmosphere of low humidity, however, the crystals melted sharply at 52°C.

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