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SYNTHESIS OF BIS (TRINITROETHYL) FORMAL, TEFO (C)

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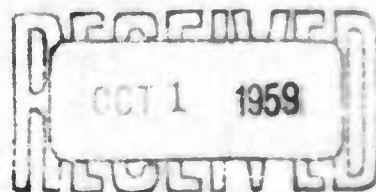
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NITROALCOHOL ACETAL PREPARATION IN
SULFURIC ACID, I. SYNTHESIS OF BIS
(TRINITROETHYL) FORMAL, TEFO (C)

Prepared by:

M. E. Hill
K. G. Shipp

Approved by: DARRELL V. SICKMAN, Chief
Organic Chemistry Division

ABSTRACT: A new synthetic method has been devised for the preparation of nitroalcohol acetals, principally bis(trinitroethyl) formal, III:



The compound, III, is prepared very easily by the reaction of 2,2,2-trinitroethanol, I, with formaldehyde, II, in strong sulfuric acid solution at room temperature. The crystalline product precipitates from solution and is isolated in 85-90% yields in less than an hour. Alternatively good yields are obtained by briefly emulsifying a solution of 2,2,2-trinitroethanol monohydrate in a chlorinated solvent with a sulfuric acid solution of formaldehyde at room temperature and isolating the product from the solvent phase.

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDINANCE LABORATORY
WHITE OAK, SILVER SPRING, MARYLAND

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1 May 1959

This report describes the preparation and properties of bis(trinitroethyl) formal, TEFO, a member of a family of trinitroethoxy compounds of unusual oxygen content of interest in both propellant and high explosive formulations. The work, in part a portion of a fundamental investigation of organic reactions in sulfuric acid, was largely supported by Task FR-44. The development of practical methods of making TEFO on a larger than laboratory scale was done under Task 301-664/43006/08 (Explosives Applied Research).

The work reported here is the basis for a patent application, and is for information only.

MELL A. PETERSON
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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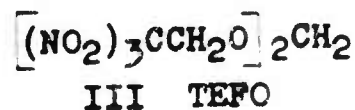
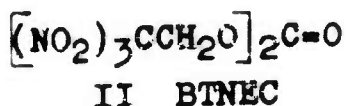
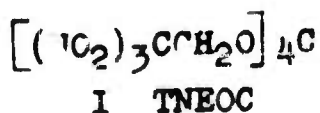
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NITROALCOHOL ACETAL PREPARATION IN
SULFURIC ACID, I. SYNTHESIS OF BIS
(TRINITROETHYL) FORMAL, TEFO (C)

INTRODUCTION

Energetic organic compounds having very high oxygen content are of considerable interest as components of explosive mixtures. Three structurally similar compounds, trinitroethyl orthocarbonate, I, bis(trinitroethyl) carbonate, II, and bis(trinitroethyl) formal, III, are unusually high



in oxygen content. About 62% of the molecular weight of the compounds consists of oxygen which is 20-30% in excess of that required for their own combustion to carbon dioxide and water.

As a group, these compounds are not usable in the conventional type of explosive formulation because of their sensitivity to impact. However, recently the Naval Ordnance Test Station and the Naval Ordnance Laboratory have observed that the compounds are soluble in polymers such as polymethylvinyltetrazole (1), nitrocellulose, and polynitrourethane (2). The solutions of the high oxygen compounds in a polymer are somewhat less sensitive than the pure dry explosive and constitute a new approach to utilizing these very high energy compounds in explosive and solid propellant compositions. These are being considered for further evaluation on a larger than laboratory scale (2).

Trinitroethyl orthocarbonate and bis(trinitroethyl) carbonate have been made by a new reaction of trinitroethanol with carbon tetrachloride catalyzed by ferric chloride (3). Initially, bis(trinitroethyl) formal was obtained as a by-product in the pre-pilot plant production of trinitroethyl orthocarbonate and in very small quantities in this laboratory in the course of the study of the reaction producing the orthocarbonate (3). Because the formal is a good plasticizer for nitropolymers and dissolves more readily in propellant polymers than either the orthocarbonate or bis

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carbonate, larger than laboratory research quantities were desired for further study. Since its synthesis was still unknown, a study was undertaken to prove its structure and in addition to find a procedure for making the compound by a method which could be used on a pilot plant scale.

This report describes a rapid high yield synthesis of bis(trinitroethyl) formal, TEFO, by a new process which consists simply of the reaction of formaldehyde with trinitroethanol in a strong sulfuric acid solution at room temperature. The procedure is applicable to the preparation of other formals, such as bis(2,2-dinitropropyl) formal. Information concerning the theoretical aspects of this system and the study of the scope and mechanism of the reaction will follow as a separate report (4).

RESULTS AND DISCUSSION

Proof of Structure. Bis(trinitroethyl) formal was obtained in large quantities as a by-product in the pilot plant production of trinitroethyl orthocarbonate (5). In addition to the expected orthocarbonate a mixture of unknown composition, m.p. 55°-59°C, was isolated from the reaction mother liquors and sent to the Naval Ordnance Laboratory for identification of its components. Examination of the crude material showed that it was a mixture containing bis(trinitroethyl) carbonate and an unknown compound.

The assignment of structure of the unknown compound as being the bis(trinitroethyl) formal was based on physical evidence and was made tentative awaiting independent synthesis. The elemental analysis indicated empirical formulas of $C_8H_9N_9O_{22}$, FW 583, corresponding to $(TNEO)_3C_2H_3O$, and $C_5H_6N_6O_{14}$, FW 374, corresponding to $(TNEO)_2CH_2$ or bis(trinitroethyl) formal. Infrared analysis was inconclusive except to show that no OH groups were present. A molecular weight determination by the unit cell volume method gave a figure of 373 (6), which strongly indicated that the formal structure was probable. However, without independent synthesis of the compound the assignment of structure as the trinitroethyl formal was tenable only if it was assumed that the trinitroethoxy group remained intact in the reaction forming the by-product.

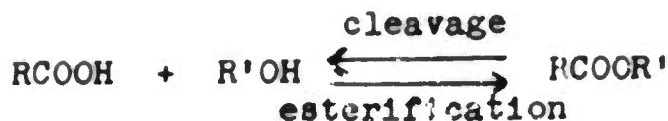
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Initially it was thought that a ferric chloride catalyzed reaction of trinitroethanol with formaldehyde impurity in the trinitroethyl orthocarbonate reaction system accounted for the formation of bis(trinitroethyl) formal. However only partial success was achieved in attempts to prepare the formal by the catalyzed reaction of formaldehyde with trinitroethanol in chlorinated solvents (7). Because trinitroethanol exhibited extreme unreactivity especially when diluted by solvents in some reaction systems, a fusion system was used to prepare the formal in order to establish definitely that the tentative assigned structure was correct and that indeed it could be formed from formaldehyde and trinitroethanol. In this procedure a solvent was not used and success depended upon the fact that the melting point of trinitroethanol was low enough to be depressed by paraformaldehyde and in effect act as its own solvent at reaction temperatures below its melting point. The ferric chloride dissolved in this oily mixture and served to catalyze the reaction as well as the depolymerization of the paraformaldehyde. In this manner, bis(trinitroethyl) formal was obtained in 20% yield and was identical with the product isolated from the pilot plant mixture. This result confirmed the assigned structure.

Although unadaptable to large scale preparations, the fusion method was investigated briefly in order to obtain knowledge of the reaction. The original reaction condition, 70°C for 6 hours was too drastic. Actually the formal was very easy to prepare and improvement was obtained by using milder conditions, particularly lower temperature and shorter reaction time. A larger quantity of catalyst than initially used increased the yields to 72% before other methods of preparation were investigated.

Preparation of Bis(trinitroethyl) Formal in Sulfuric Acid. In a previous study of synthetic methods of the preparation of esters of trinitroethanol, 100% sulfuric acid and fuming sulfuric acid had successfully been used as solvents for direct esterification and for transesterification, particularly in the preparation of trinitroethyl trinitrobutyrate, TNETB, from trinitrobutyric acid or its methyl ester and trinitroethanol (8,9). Although equilibria were set up in such systems, the formation of the least basic product was favored and the esterification reaction predominated over the opposing cleavage reaction:

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The ester grouping of TNETB was so weakly basic that the ester was un-ionized by sulfuric acid and precipitated as it was formed during the esterification reaction. By analogy on the basis that the trinitromethyl groups in the formal molecule would make the $-\text{OCH}_2\text{O}-$ group very weakly basic, it was thought that in sulfuric acid bis(trinitroethyl) formal formation would predominate over the cleavage reaction in a similar manner, notwithstanding the fact that strong acids were supposed to cleave acetals quantitatively.

To determine if bis(trinitroethyl) formal would be stable in sulfuric acid, a small amount of the formal was placed in 100% sulfuric acid at room temperature. Upon finding that the formal was nearly insoluble and not easily cleaved, a successful exploratory preparation experiment was carried out in which a two molar solution of trinitroethanol in 100% sulfuric acid was heated at 60°C for two hours with an equivalent amount of paraformaldehyde. Although the yield was low in this initial attempt the process was studied further because of its theoretical significance. In addition its simplicity made plant production of large quantities feasible.

The preparation of trinitroethyl formal in sulfuric acid was very easy, requiring much milder conditions for high yields than were used in the original experiment. Subsequent investigation showed that one need only add paraformaldehyde to a solution of trinitroethanol in commercial concentrated sulfuric acid at room temperature. Precipitation of the product began almost immediately and the reaction was complete in about thirty minutes. The formal was isolated nearly pure in good yields by pouring the reaction mixture into ice and water, filtering and drying. One recrystallization from alcohol and water sufficed to purify the product. The following general observations on the reaction parameters were made during the study of the reaction:

(a) Acid strength had a marked effect on the amount of product obtained in the preparations. Optimum yields were obtained in 90-96% sulfuric acid, possibly as a result of greater insolubility of the formal in acid containing a

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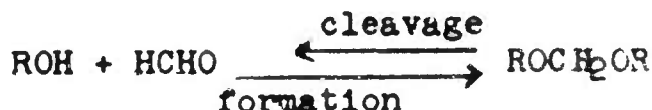
small amount of water, (Table I).

(b) Yields were optimum when the concentration of trinitroethanol in the acid was 4 molar. At lower concentration the yields dropped off rapidly. It was necessary to warm the alcohol-acid mixture to complete solution of the crystals at the higher concentrations and then cool to room temperature before adding paraformaldehyde.

(c) Hardly any exotherm was noted during the reaction. Some activity in the acid occurred when the paraformaldehyde was added, accompanied by a little discoloration during the reaction period. However, the precipitated product was of very good purity.

(d) A period of 30-60 minutes was found to be sufficient for virtual completion of the reaction. Prolonged reaction periods and heating the reaction solutions were ineffective in changing the yield appreciably.

Strong evidence has been obtained that this reaction, like transesterification, is also an equilibrium process and proceeds toward the formal product to a point at which the cleavage of the formal is in equilibrium with its formation:



The mechanism by which the "equilibrium point" is reached is discussed in more detail elsewhere (4).

Paraformaldehyde, $\text{HO}(\text{CH}_2\text{O})_n\text{H}$, was used almost exclusively as the source of anhydrous formaldehyde. As obtained commercially it contains more than 99% formaldehyde with perhaps a small amount of adsorbed water. The ease of weighing and handling the polymer and its rapid depolymerization in the sulfuric acid solutions made it ideal for obtaining exactly the amount of anhydrous formaldehyde desired. Methylal, $\text{CH}_3\text{OCH}_2\text{OCH}_3$, was tried without particular advantage as an alternative formaldehyde source by its degradation in acid to methanol and formaldehyde.

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TABLE I

Effect of Acid Strength and Alcohol
Concentration on Yields of TNE Normal

<u>Initial H₂SO₄ Acid Strength</u>	<u>% Yield <u>/a</u></u>
80%	50
90%	87
96% <u>/b</u>	89
100%	77
5% SO ₃ in H ₂ SO ₄	70
10% SO ₃ in H ₂ SO ₄	58

/a - Reaction in 4 molar TNEOH solution

/b - Commercial concentrated sulfuric acid

<u>Initial TNEOH Concentration in 96% H₂SO₄</u>	
2 Molar	67
4 Molar	89
5.5 Molar	86

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Properties of Bis(trinitroethyl) Formal. The synthesis of bis(trinitroethyl) formal in sulfuric acid confirmed an early observation that the formal was quite stable under acidic conditions which would hydrolyze ordinary acetals. Several efforts were made earlier to hydrolyze the trinitroethyl formal under the usual hydrolytic conditions without effect. Under one extreme condition the formal was held at the reflux temperature of aqueous methanol saturated with hydrogen chloride for 100 hours, undergoing only a few percent loss (3). This unusual stability to acid originally cast some doubt on the reasonableness of the acetal grouping in the assignment of structure. Ostensibly normal acetals hydrolyzed quite easily by acid catalysis according to the literature. The trinitroethyl formal is not an exception to this assertion but is instead the first example of the reversal of the often discussed equilibrium between an acetal and its cleavage products.

Under basic conditions degradation of the trinitroethyl formal did take place, as have other nitroform derivatives, but apparently involved the nitro carbon groups rather than the acetal grouping. In aqueous alcoholic sodium hydroxide solution the typical intense yellow color of nitro alkane anions arose. Spectrophotometric measurements of the reaction solution indicated an absence of any appreciable quantity of trinitromethyl anion which would have been present if saponification followed by deformylation had occurred. Instead a maximum absorption was observed at 365 mμ, suggestive of a dinitroalkane anion. The products of the degradation have been identified for the reaction of the formal with base in the presence of hydrogen peroxide (10). In this system the acetal grouping apparently was unaffected also, and the corresponding dinitroethyl formal anion was formed by reduction of the terminal trinitromethyl groups. Bis(potassium dinitroethyl) formal was isolated from the reaction of the formal with alcoholic potassium hydroxide in the presence of hydrogen peroxide.

Bis(trinitroethyl) formal has shown unusual stability when subjected to the standard vacuum thermal stability test. The formal has not shown the instability sometimes exhibited by an explosive when heated above its melting point. At 100°C, 35° above its melting point, the formal evolved only 3.4 cc of gas per gram over a period of seven days, and only 1.6 cc of gas per gram at 90°C in six days. This unusual stability in the non-crystalline

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state probably accounts for the good thermal stability of the compositions in which it is dissolved. For instance, a composition containing 22.5% TEFO, 49.8% TNEOC and 23.7% guncotton, evolved 0.74 cc of gas per gram at 100°C in forty-eight hours (2).

The physical properties of trinitroethyl formal have been summarized in Table II.

TABLE II

Properties of Bis(trinitroethyl) Formal

Melting Point	65.3 - 65.4°C
Vacuum Stability	1.60 cc/g/6 days at 90°C
Impact Sensitivity (50% height, 2.5 kg weight, bare tools)	18 cm (number is dependent upon particle size; RDX=50 cm with bare tools) 269 cm (as 30% TEFO-alcohol solution) 210 cm (damp with water)
Crystal Density	1.72
Heat of Formation	-103 kcal/mole (RDX=+14 kcal/mole)
Solubility	Soluble: hexane, pentane Very soluble: chloroform, methanol

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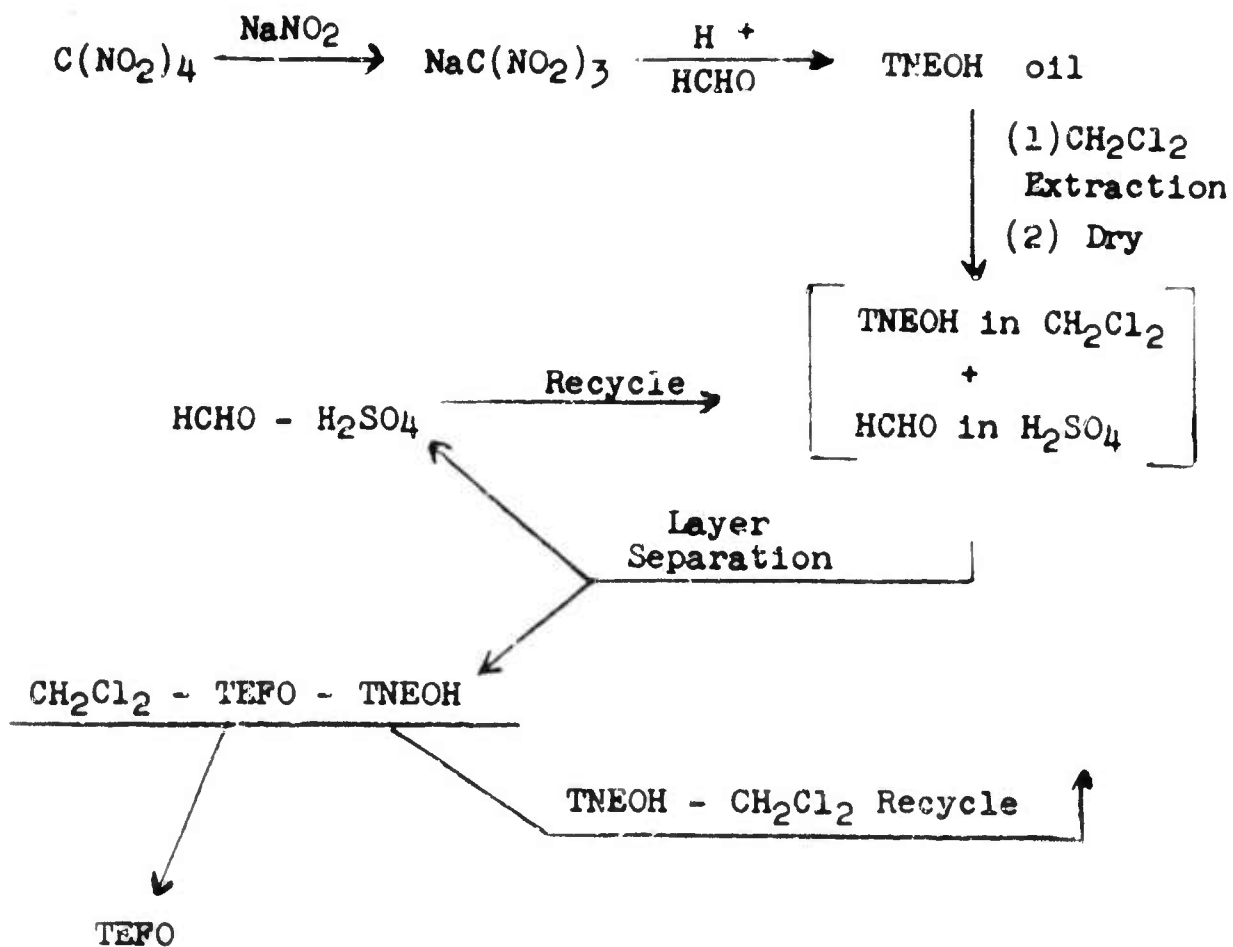
Process Development. Trinitroethanol was prepared by simultaneous acidification and formylation of sodium nitroform in methanol-water solution. The crude alcohol separated as an oil which was a mixture of the alcohol monohydrate with some methanol, water and other impurities (11). Normally the trinitroethanol oil had to be dried before it could be used for succeeding syntheses. Therefore in order to eliminate the drying step, several efforts were made with only partial success to utilize the oil directly by the addition of the crude oil to a strong fuming sulfuric acid solution of paraformaldehyde.

As an alternative, a two phase system was investigated consisting of an alcohol-solvent phase and a sulfuric acid-paraformaldehyde phase. Such a system was designed to serve three purposes: (1) it provided a means of overcoming the equilibrium by continual extraction of the product from the sulfuric acid reaction medium by the organic solvent; (2) the alcohol could be completely or partially dried in the solvent and used without isolation; (3) the system was adaptable to continuous processing of the reaction components and products. In an initial experiment the crude trinitroethanol oil dissolved in a chlorinated organic solvent was slurried with a solution of paraformaldehyde in 5% fuming acid which functioned both as a drying agent and reaction medium. The product was isolated from the organic phase with the sulfuric acid retaining very little of the formal. The yields were still unsatisfactory possibly because of residual water and methanol not separated from the chlorinated solvents. However, trinitroethanol monohydrate prepared by adding water to dry trinitroethanol worked well in a two phase system in which the monohydrate in methylene chloride was slurried vigorously with 5% fuming sulfuric acid for 15 minutes. The recrystallized yield was 76% compared with 80% yield from a similar system in which dry trinitroethanol in methylene chloride was slurried with 100% sulfuric acid. These yields were about 9% below the maximum obtainable and may be improved with further experimentation.

In principle these experiments established that the two phase system can be used but it may be necessary to dry the crude trinitroethanol oil in solution until at least the monohydrate stage of the alcohol is reached. The formal synthesis lends itself to adaptation as a continuous process.

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For instance, continuous addition of a methylene chloride solution of trinitroethanol monohydrate and sulfuric acid solution of paraformaldehyde into a reactor with continuous take off to a separator is feasible. Fortification and recycling of the acid and recycling of the methylene chloride mother liquors with additional trinitroethanol should permit efficient use of these components. In fact the entire synthesis from tetranitromethane is reasonably simple. The following reaction sequence incorporates the current experimental results:



EXPERIMENTAL

Typical experiments conducted during the study of the synthesis of bis(trinitroethyl) formal follow:

(A) Sulfuric Acid Method. A solution of 3.62 g (0.02 mole) trinitroethanol in 5 ml of concentrated (96%) sulfuric acid was prepared by warming and stirring in a small (25 ml) erlenmeyer flask. After cooling to room temperature 0.30 g (0.01 mole) of formaldehyde as paraformaldehyde was added with stirring. As the paraformaldehyde dissolved in the reaction mixture the temperature of the mixture rose to 35°C and a colorless oil formed on top of the solution. Within a few minutes this oil began to crystallize in glistening leaflets. The mixture was stirred for 30 minutes and then poured onto flaked ice. The precipitated white crystalline product was filtered off, washed well with water and dried. The yield was 3.36 g or 90% of the theoretical yield and had a melting point of 62-63°C. Recrystallization from 50% methanol-water gave a pure white crystalline product melting at 64-65°C.

The results of the study of the reaction parameters of this method are summarized in Table III.

(B) Two Phase System. A solution of 0.30 g (0.01 mole) formaldehyde as paraformaldehyde in 5 ml of 100% sulfuric acid was prepared in a 50 ml, 3-neck, round bottom flask fitted with a mechanical stirrer. To this solution was added a solution of 3.62 g (0.02 mole) of trinitroethanol in 10 ml of methylene chloride and the resulting mixture was stirred very rapidly for 15 minutes. At the end of that time the methylene chloride layer was separated from the sulfuric acid layer by means of a separatory funnel. The sulfuric acid layer was washed once with 5 ml of methylene chloride and this was added to the methylene chloride layer. The methylene chloride was then removed by evaporation under reduced pressure and the residue was washed with water, filtered and dried. The yield of crude product was 3.14 g or 84% of theory. The melting point of the crude material was 60-61.5°C. Recrystallization from methanol-water gave a pure product which melted at 64-65°C; total yield, 80%. No additional product was obtained by pouring the sulfuric acid layer into ice and water.

Additional experiments which were run utilizing "trinitroethanol oil" and trinitroethyl monohydrate are summarized in Table IV.

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TABLE III

Preparation of
Bis(trinitroethyl) Formal in Sulfuric Acid
Reaction: $2\text{TNEOH} + \text{HCHO} \longrightarrow \text{TNEOCH}_2\text{OTNE}$

Alcohol/HCHO Moles	Alcohol Conc., Molar	H ₂ SO ₄ Acid Strength	Reaction Period	Tempera- ture	Yield Mole %
.02 / .01	4	80%	1.0 hr. at	room	50
.02 / .01	4	90%	1.0 hr. at	room	91
.02 / .01	4	96%	15 min. at	room	87
.02 / .01	4	96%	2 hrs. at	45°C	83
.02 / .01	2	96%	30 min. at	room	67
.02 / .01	5.5	96%	30 min. at	room	86
.022 / .01 (10% xcs TNEOH)	4.4	96%	30 min. at	room	93
.2 / .1	4	96%	2 hrs. at	room	88
.2 / .1	4	96%	16 hrs. at	room	90
.02 / .01	4	100%	30 min. at	room	77
.04 / .01 (100% xcs TNEOH)	4	100%	30 min. at	room	98
.02 / .02 (100% xcs HCHO)	4	100%	30 min. at	room	81
.02 / .01 (400% xcs HCHO)	4	100%	30 min. at	room	77
.02 / .01	4	5% fuming	30 min. at	room	70
.034 / .01 (70% xcs TNEOH)	5.8	5% fuming	30 min. at	room	95
.02 / .01	4	10% fuming	30 min. at	room	58

TABLE IV
Preparation of Bis(trinitroethyl) Formal in 2-Phase Systems

Alcohol (plus equivalent HCHO)	Solvent Phase	Acid Phase	Reaction Period	Yield
10g "TNEOH oil"(6.3g TNEOH)	10 ml CH ₂ Cl ₂	8.6 ml 5% fuming H ₂ SO ₄	16 hr at room temp	67%
10g "TNEOH oil"(6.3g TNEOH)	10 ml CH Cl ₃	9.0 ml 96% H ₂ SO ₄	4 hr at room temp	53%
3.62g anhydrous TNEOH	10 ml CH ₂ Cl ₂	5.0 ml 100% H ₂ SO ₄	15 min at room temp	80%
3.62g TNEOH monohydrate	10 ml CH ₂ Cl ₂	5 ml 6% fuming H ₂ SO ₄	15 min at room temp	75%

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(C) Fusion Method. A mixture of 3.6 g (0.02 mole) trinitroethanol, 0.30 g (0.01 mole) formaldehyde as paraformaldehyde and 1.62 g (0.01 mole) anhydrous ferric chloride was placed in a large test tube and heated in a water bath at 60°C for one hour with magnetic stirring. The reaction mixture was then poured on flaked ice, a small amount (5 ml) of 6 N HCl added, and the resulting mixture stirred until the ferric chloride dissolved and the solid product was greyish white. The product was filtered off, washed well with water and dried. The yield was 2.7 g or 72% of theoretical. The product was recrystallized from methanol and water to give a beautiful white product, m.p. 64.5-65°C.

ACKNOWLEDGMENT

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NAVORD Report 6672

References

1. W. G. Pinnegan, L. A. Burkhart, R. A. Henry, and W. S. McEwan, "Preparation and Evaluation of Poly (1- and 2-Methyl-5-Vinyltetrazoles)", Bulletin of the Fourth Meeting, JANAF Solid Propellant Group, Vol. II, p. 139; Redstone Arsenal, Huntsville, Alabama, May 1958.
2. O. H. Johnson, NAVORD Report (NOL) 6677, in process, "High Explosive and Propellant Compositions Based Upon a New Class of Soluble Oxidants, I. Organic Oxidants Preliminary Report", 10 July 1959.
3. (a) M. E. Hill, NAVORD Report (NOL) 3915, "A New Reaction of Nitroalcohols with Halogen Compounds, I. Orthoesters", 15 August 1955.
AD-83188
(b) M. E. Hill and K. G. Shipp, NAVORD Report (NOL), in preparation, "A New Reaction of Nitroalcohols with Halogen Compounds, II. Synthesis of Nitroalcohol Chlorocarbonates and Bis Carbonates", 1959.
4. M. E. Hill and K. G. Shipp, NAVORD Report (NOL), in preparation, "Nitroalcohol Acetal Preparation in Sulfuric Acid, II. Study of the Reaction Mechanism and Factors Affecting the (Sulfuric Acid-Acetal) System", 1959.
5. U. S. Rubber Company, Naugatuck Chemical Division, Naugatuck, Connecticut; Progress Report, December 1954-January 1955, Contract NOrd 10,947.
6. J. R. Holden, U. S. Naval Ordnance Laboratory, unpublished information.
7. The preceding paragraphs were abstracted from Ref. 3a for completeness of this report.
8. U. S. Rubber Company, General Laboratories, Passaic, New Jersey; Quarterly Progress Report No. 23, 1 August 1953, Contract NOrd 10,129.

CONFIDENTIAL
NAVORD Report 6672

References
(cont'd)

9. M. E. Hill, NAVORD Report (NOL) 3655, "Transesterification by Trinitroethanol", 1 November 1953.
10. D. J. Glover, NAVORD Report (NOL) 4305, "Spectrophotometric Method for the Quantitative Analysis of Trinitromethyl Compounds", 29 May 1956. *DD-103725*
11. K. G. Shipp and M. E. Hill, NAVORD Report (NOL) in preparation, "Improved synthesis of 2,2,2-Trinitroethanol", 1959.