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A NEW REACTION OF NITROALCOHOLS WITH HALOGEN COMPOUNDS

I. ORTHOESTERS

15 AUGUST 1955



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A NEW REACTION OF NITROALCOHOLS WITH HALOGEN COMPOUNDS
I. ORTHOESTERS

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ABSTRACT: A new reaction has been discovered between aliphatic polynitroalcohols and polyhalogen compounds catalyzed by ferric chloride. In this reaction the halogens are removed as hydrogen halide and replaced by the polynitroalkyl group. It has been successfully employed to prepare the stable, new high explosive compounds; trinitroethyl orthocarbonate, trinitroethyl orthoformate, and trinitroethyl orthobenzoate from trinitroethanol and carbon tetrachloride, chloroform, and benzotrichloride, respectively. With less acidic alcohols such as dinitropropanol the reaction produced normal carbonates instead of orthocarbonates. The scope of the reaction has been given a preliminary examination, and some discussion of a possible mechanism is reported.

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This is the first of a series of reports on the preparation of condensation products of nitroalcohols with halogen compounds using ferric chloride as catalyst. The work was performed under Task B2c-19-1-55 and is preliminary. The conclusions therefore are necessarily tentative and are subject to change as a result of new experimental work. The reliability of the work is the responsibility of the author and of the Explosives Chemistry Division.

Inasmuch as information reported herein forms the basis of a patent application this report is for information only.

JOHN T. HAYWARD
Captain, USN
Commander


JAMES E. ABLARD
by direction

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A NEW REACTION OF NITROALCOHOLS WITH HALOGEN COMPOUNDS
I. ORTHOESTERS

INTRODUCTION

During the summer of 1953 this laboratory was engaged in process development on the synthesis of the experimental high explosive, trinitroethyl trinitrobutyrate, TNETB. Because of the potential economy of the process, the transesterification of methyl trinitrobutyrate with trinitroethanol was investigated. As part of this study, there was tried, with partial success, an aluminum chloride catalyzed transesterification of methyl trinitrobutyrate with trinitroethanol in refluxing carbon tetrachloride. In an experiment in which anhydrous ferric chloride was substituted for aluminum chloride, some crystals different from the expected TNETB were isolated. They were explosive, and their melting point, 157°C, indicated that a new compound had been formed. In the course of determining the origin of the new compound, an experiment was carried out in which the methyl trinitrobutyrate was omitted. Again the same product was obtained but in improved yield. Ignition of the product by an open flame left no ash, which indicated that it was not an iron compound. The lack of a positive chlorine test after a sodium fusion, showed that the compound did not arise from partial substitution of the carbon tetrachloride. It was concluded then, that a new explosive had been formed by a new condensation reaction of trinitroethanol. Therefore, the reaction was studied more intensively to determine the structure of the new compound and to improve its preparation. It proved to be trinitroethyl orthocarbonate. Over a pound was prepared by the Naugatuck Chemical Division of the U. S. Rubber Company on a Bureau of Ordnance Contract (1) even before its proof of structure was completed.

This report covers the preparation and properties of trinitroethyl orthocarbonate, orthoformate, and orthobenzoate by the ferric chloride catalyzed reaction of trinitroethanol with carbon tetrachloride, chloroform, and benzotrichloride. In addition, results are given of the general study of the reaction of trinitroethanol and some other negatively substituted alcohols with other polyhalogen compounds. This report confirms, and in some respects alters, tentative information given at various symposia.

RESULTS AND DISCUSSION

A. Formation and Properties of Trinitroethyl Orthocarbonate TNEOC, and By-products. Optimum preparations of trinitroethyl orthocarbonate, TNEOC, also known as Compound "X" until a structure was assigned, consisted simply of refluxing for 16-24 hours a 1.5 molal solution of dry trinitroethanol in carbon tetrachloride in the presence of a catalytic amount of anhydrous ferric chloride. Hydrogen chloride, and phosgene, as by-products, were evolved steadily during the reaction period. The product began to form within 1-2 hours, and precipitated nearly quantitatively from the reaction mixture. After isolation of the crude material and recrystallization from chloroform, yields of 75-80% of trinitroethyl orthocarbonate, mp. 163°C (dec) were obtained. Varying amounts of bis(trinitroethyl) carbonate, BTNEC, also were obtained, depending upon the presence of moisture and upon other conditions which are discussed below. The physical properties of trinitroethyl orthocarbonate are given in Table I. Dependent upon successful desensitization, the high crystal density, oxygen content, and stability of the compound indicate that it may be useful explosive in compositions with aluminum and other explosives.

TABLE I

Properties of TNEOC

Formula	$C [OCH_2C(NO_2)_3]_4, C_9H_8N_{12}O_{28}$
Molecular Weight	732
Melting Point	163°C dec
Vacuum Stability	0.85 cc of gas/g in 6 days at 100°C
Impact Sensitivity	7 cm (some samples 14-20 cm)
Crystal Density	1.84
Oxygen Content	61.18% (= 0.1 g of oxygen per cc)
Solubility	Insol. in water Very slightly soluble in carbon tetrachloride, hexane, soluble in methanol, chloroform, ether

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Trinitroethyl orthocarbonate, unlike the normal alkyl orthocarbonates, is very stable to acid hydrolysis. Nearly quantitative recoveries were made after prolonged refluxing in strong aqueous or methanolic solutions of hydrogen chloride. On the other hand it was readily hydrolyzed by alkaline solutions to carbon dioxide, nitroform, and unidentified products. It was decomposed also by alcoholic ammonia to an unstable unidentified compound.

The formation of trinitroethyl orthocarbonate was very sensitive to the conditions of the reaction. If the reaction solution was more dilute than 1.6 millimoles per cubic centimeter the yield of product was decreased and a higher percentage of uncrystallizable oils was obtained. These oils contained partially substituted intermediates, one of which was identified as trinitroethyl chlorocarbonate. By keeping the reaction period between 16-24 hours the formation of the by-product bis(trinitroethyl) carbonate was minimized. The ferric chloride was found to be definitely catalytic in action. Very little difference in yield was obtained when 4, 10, 25, or 50 mole % of the catalyst was used. Some of the catalyst in each case was essentially deactivated by being completely enclosed by product crystals. The catalyst maintained its original appearance throughout the reaction, and several attempts to find any reduced ferrous chloride failed. For best results in the preparation of the orthocarbonate, strictly anhydrous ferric chloride was necessary. The presence of moisture in any of the components of the system increased the proportion of BTNEC which was formed. However, the ferric chloride would dry itself by hydrolysis of the carbon tetrachloride to phosgene and hydrogen chloride. A literature search indicated that hydrolysis of carbon tetrachloride by water to phosgene and hydrogen chloride in the presence of anhydrous ferric chloride had not been previously observed.

1. Assignment of Structure. When trinitroethyl orthocarbonate was first prepared, attempts to definitely establish its structure gave equivocal results. The fact that ferric chloride was used only in catalytic amounts, and that there was no ash left after ignition, indicated that the ferric chloride was not a reactant. The lack of chlorine in the structure indicated either a catalyzed condensation of trinitroethanol with itself in some manner, or complete substitution of the chlorines of the carbon tetrachloride. A condensation of trinitroethanol with itself to an acetal, or some other compound involving the alpha carbon, seemed highly unlikely and was not seriously considered. The known ability of metal halides to form

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complexes with halogen compounds led to consideration of a catalyzed reaction of trinitroethanol with the carbon tetrachloride. The elemental analysis of the compound and calculated empirical formulas were:

	Found Analysis	Calc. for $C_5H_4N_6O_{15}$	Calc. for $C_7H_7N_9O_{21}$	Calc. for $C_9H_8N_{12}O_{28}$
C	15.03	15.47	15.20	14.76
H	1.10	1.04	1.27	1.10
N	23.05	21.65	22.79	22.96
		MW 338	MW 583	MW 732

Other empirical formulas calculated from the analysis contained N atoms in numbers which were not a factor of 3. Since it was considered unlikely that the trinitromethyl would be altered these formulas were not considered further.

The first formula corresponds to bis(trinitroethyl) carbonate, BTNEC. The new compound was not a different crystalline form of BTNEC because the latter was formed as a by-product, was separable from the new compound by recrystallization, and was a melting point depressant for the unknown compound. The next corresponds to trinitroethyl orthoformate, tris(trinitroethoxy) methane. It would be difficult to account for the formation of this compound from carbon tetrachloride because of hydrogen atom on the methane carbon. That the unknown was not the orthoformate was definitely established when a new and totally different product was obtained by the reaction of chloroform and trinitroethanol using ferric chloride catalyst. The third formula corresponds to trinitroethyl orthocarbonate which seemed to be the likeliest structure. Efforts to establish a definite structure followed two lines, chemical degradation by base (2) and molecular weight determination (3).

Base degradation of trinitroethyl orthocarbonate theoretically should give 4 moles of nitroform to 1 mole of carbon dioxide. However, solutions of TNEOC which had been decomposed in alkaline aqueous dioxane solutions of various strengths, analyzed for about 30% more carbon dioxide than calculated from theory. Also the ultraviolet absorption spectra of the solutions did not have the correct maximum peak for nitroform. In order to determine if the base decomposition of various other examples of this type of compound occurred in the same manner as the orthocarbonate, bis(trinitroethyl) carbonate and trinitroethyl orthoformate were decomposed and they too gave more carbon dioxide than expected. These results indicated that the trinitromethyl

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group was undergoing decomposition. However, decomposition of both compounds in dilute alkali in aqueous methanol in the presence of hydrogen peroxide gave the calculated amount of nitroform and avoided the decomposition of the latter.

Determination of the molecular weight by freezing point depression measurements of the compound in solution in dioxane or nitrobenzene gave unreproducible results. However, using X-ray diffraction for the measurement of the unit cell volume and calculation of the molecular weight a figure of 740 was obtained. This figure is very close to the calculated molecular weight of 732 for TNEOC. On the basis of this molecular weight determination, elemental analysis, quantitative decomposition to nitroform and the elimination of other possible structures, the new compound was considered to be trinitroethyl orthocarbonate.

2. Formation of By-Product BTNEC. By the addition of enough water to the system the product ratio was reversed, and BTNEC was the principal product. The yields were not high from these systems, but, should large quantities of BTNEC be desired, the method could undoubtedly be successfully developed as a simple process for BTNEC preparation. With hydrated ferric chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and trinitroethanol in refluxing carbon tetrachloride, a yield of 47 percent of a mixture of products was obtained, of which less than half was the orthocarbonate. The ferric chloride hydrate at first melted and then gradually turned into black particles as the hydrolysis reaction dried it. The presence of a very large amount of water was detrimental as shown by the addition of 20% water to the trinitroethanol. With hydrated ferric chloride and trinitroethyl dichloroaluminate heated in a closed system only BTNEC and trinitroethyl chlorocarbonate were produced.

In the nearly anhydrous system, BTNEC originated as the initial product in the reaction mixture, rather than arising from a hydrolysis reaction of partially substituted carbon tetrachloride during the work-up. This was shown by mechanical separation of a mixture of needles, BTNEC, and equant crystals from the reaction mixture which had a particularly well formed crystalline product. In general, the normal carbonate was isolated during the workup as a mixture with the orthocarbonate, mp. 109-113°C. Repeated recrystallization raised the melting point to 113-114°C, as compared to 116 to 116.5°C for pure BTNEC. The mixed melting point of this product with authentic BTNEC was not lowered. In an attempt to find a solvent to separate the two compounds, a sample of the mixture having a constant melting point,

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113-114°C, was recrystallized from hot methanol. A large weight loss occurred and 20% of the original sample weight was recovered as trinitroethyl orthocarbonate. From the recrystallization mother liquor an additional product, mp. 36-37°C, was isolated. Since the melting point was so close to that of methyl trinitroethyl carbonate, a mixed melting point was taken with authentic material and no depression was observed. Its identity as methyl trinitroethyl carbonate was further confirmed by a comparison of their X-ray diffraction patterns which were identical. For the mixed carbonate to be formed a previously unobserved transesterification reaction between the BTNEC and methanol in the mixture must have occurred. Consequently pure BTNEC was refluxed in dry methanol for 1-1/4 hours. The BTNEC was converted to the mixed carbonate in 93% yield. If water was added to a hot methanol solution of BTNEC complete hydrolysis to water soluble products occurred. By the use of aqueous alcoholic solutions for recrystallization, BTNEC thereafter was removed selectively from mixtures with TNEOC.

3. Isolation of "Trinitroethyl Formal". Several pounds of trinitroethyl orthocarbonate were made at the Naugatuck Chemical Division of the U. S. Rubber Company based on an earlier small scale procedure furnished by this Laboratory (1). It differed from the NOL preparations in that crude trinitroethanol oil was dried in carbon tetrachloride with sulfuric acid and that a reflux period of 69 hours was used instead of 24 hours in a less dilute solution. Besides the expected orthocarbonate and BTNEC - orthocarbonate mixture a new third product, melting point 55-57°C, was isolated from the carbon tetrachloride mother liquor. Samples of the product were sent to this laboratory for examination.

Recrystallization of the crude material from chloroform-hexane mixtures raised the melting point to 57-58°C. Further recrystallization from aqueous methanol gave a nicely formed crystalline product, mp. 65°C, which constituted about 70% of the weight of the mixture sample. The filtrate from this recrystallization was intensely yellow indicating the presence of nitroform from the decomposition of BTNEC or similar compound in the mixture. The mixed melting point of known BTNEC with the new product was 57.5-60.5°C. Recrystallization of a sample of the original mixture from saturated solutions of hot chloroform successfully isolated BTNEC itself, thus establishing it as a component of the mixture. The new product was recrystallized from methanol, ethanol, and chlorinated solvents in various ways to determine if it also might be a mixture. No separation was achieved.

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The compound was very resistant to prolonged refluxing (100 hours) in strong methanolic hydrogen chloride. It was also isolated in this laboratory on two occasions but in such small amounts that identification could not be completed.

The physical properties of "trinitroethyl formal" are given in Table II.

TABLE II
Properties of "Trinitroethyl Formal"

Melting Point	65.3 - 65.4°C
Vacuum Stability	1.60 cc of gas/g at 90° for 6 days
Impact Sensitivity	7 cm
Crystal Density	1.72
Solubility	Soluble in methanol, ethanol, chloroform, hexane

Two possible empirical formulas were obtained by calculation from the elemental analysis: (A) $C_8H_9N_9O_{22}$, FW 583; and (B) $C_5H_6N_6O_{14}$, FW 374. If one assumed that trinitroethoxide ion would stay intact under the reaction conditions then formula (A) would correspond to a compound of the nature of $[(NO_2)_3CCH_2O]_3C[CH_3O]$. It seems unlikely that the residual CH_2O formed a methyl ether link judging from the nature of the reaction system. That it was not CH_2OH was shown by the absence of the OH absorption peak in the infra red spectrum. Formula (B) could correspond to $[(NO_2)_3CCH_2O]_2CH_2$ or trinitroethyl formal. A molecular weight determination by the unit cell volume method gave a figure of 373, constituting strong evidence that formula (B) may be the correct one.

Formal formation from formaldehyde and alcohols in the presence of acidic catalysts has long been a preparative method for this type of compound. Ferric chloride itself has been used to catalyze formal formation from paraformaldehyde and alcohols (4). The slow decomposition of trinitroethanol to formaldehyde and nitroform in refluxing carbon tetrachloride has been observed in this laboratory on various occasions. Prolonged heating in sulfuric acid also has decomposed trinitroethanol. Thus the presence of formaldehyde in trinitroethanol solutions that have been undergoing prolonged reflux in the preparation of the orthocarbonate is understandable. With the necessary catalyst present slow

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formation of a formal of trinitroethanol could take place. However, two attempts to make the compound from paraformaldehyde or trioxane in the presence of ferric chloride in carbon tetrachloride solution gave a low yield of a mixture of products, melting point about 55°C. Since independent synthesis of the formal has not yet been successful, the assignment of trinitroethyl formal as the structure of the pilot plant by-product is only tentative.

B. Preparation and Properties of Trinitroethyl Orthoformate. TNEOF, the formation of a product by heating trinitroethanol in chloroform in the presence of ferric chloride proceeded much slower than did the reaction of carbon tetrachloride. A good yield was not obtained until a particularly prolonged reflux period was used (120 hours). It was found that it was a new and different compound than trinitroethyl orthocarbonate and was probably the expected orthoformate. It depressed the orthocarbonate melting point and had a different X-ray diffraction pattern. Elemental analysis of the compound gave values for C, H, N very close to theory for TNEOF. Table III summarizes the physical properties of the compound.

TABLE III

Properties of TNEOF

Melting Point	127.6 - 128°C
Impact Sensitivity	7 cm
Vacuum Stability	0.50 cc of gas/g after 48 hours at 100°C
Crystal Density	1.80
Solubility	Soluble in methanol, chloroform, carbon tetrachloride; insoluble in water, hexane

Successive experiments were made varying conditions, principally the reflux period. As with trinitroethyl orthocarbonate, a highly concentrated reaction solution was desirable. Unlike the orthocarbonate preparation, no by-products were found, though it might be expected that the "trinitroethyl formal" would be formed during such long reaction periods although the reaction temperature was lower. A summary of experimental data is given later. The chemical reactions of trinitroethyl orthoformate will be reported in a subsequent report.

C. Preparation and Properties of Trinitroethyl Orthobenzoate. In analogy to the reactions in excess chloroform and carbon tetrachloride, an attempt was made to make trinitroethyl orthobenzoate by the reaction of trinitroethanol with excess benzotrichloride. Instead of the expected product trinitroethyl benzoate was obtained in 75% yield. Since the workup involved an aqueous extraction step, apparently only one chlorine atom had substituted and the other two were hydrolyzed. Consequently, the reaction was run with trinitroethanol in excess at 60°C using tetrachlorethylene as solvent. The hydrogen chloride which was evolved was swept out by nitrogen and measured by a method previously reported (5). Each equivalent of hydrogen chloride was evolved at a different rate. In a run in which 21 millimoles of hydrogen chloride was expected, the first equivalent evolved at a rate of 1 millimole per 2.3 minutes, the second at a rate of 1 millimole per 33 minutes, and the third at a rate of 1 millimole in 130 minutes. The reaction mixture was warmed to 90°C and held for 16 hours longer. Though the third equivalent hydrogen chloride had been evolved by the end of this period, only a 16% yield of trinitroethyl orthobenzoate, mp. 115.5-116°C, plus 25% yield of a mixture of the orthobenzoate and benzoate ester was obtained.

The physical properties of trinitroethyl orthobenzoate are given in Table IV.

TABLE IV

Properties of Trinitroethyl Orthobenzoate

Melting Point	115.5 - 116°C
Impact Sensitivity	16 cm
Vacuum Stability	0.40 cc of gas/g after 5 days at 100°C
Crystal Density	1.62

D. Attempted Reaction with other Polyhalogen Compounds. Methyl chloroform underwent a dehydrohalogenation reaction catalyzed by ferric chloride instead of forming the expected trinitroethyl orthoacetate. At temperatures of 30° to 50°C 1,1-dichlorethylene was formed in nearly quantitative yield. A patent issued to Hill and Dance (6) describes the preparation of 1,1-dichloroethylene under

precisely the same conditions. The reverse reaction of adding hydrogen chloride to 1,1-dichloroethylene in the presence of ferric chloride under slight super atmospheric pressure, was patented by Nutting and Huscher (7). In order to prevent the preferred dehydrochlorination, the orthoester preparation was attempted in a pressure reaction vessel at 68°C with methyl chloroform in excess. Only an uncrystallizable black oil was obtained.

Neither tetrachloroethylene nor tetrachlorethane underwent reaction with trinitroethanol in the presence of ferric chloride on prolonged heating at 90-100°C for 24 hours. Because these two tetrachloro compounds were unreactive in this system, they were useful as solvents for other systems. No reaction was obtained with 1,1,2-trichlorethane during 20 hours at 100-103°C. Chloro and bromopicrin and carbon tetrabromide dissolved in tetrachloroethylene did not react under similar conditions. Gas evolution occurred during the reaction of bromotrichloromethane, but no product was obtained and the ferric chloride was reduced to ferrous chloride. The latter was isolated from an ether solution of the reaction mixture by filtration, and identified by a color reaction with dimethylglyoxime (8). Trinitroethyl orthocarbonate was obtained in 43% yield from dichlorodibromomethane. Some of the ferric chloride was reduced in this experiment also.

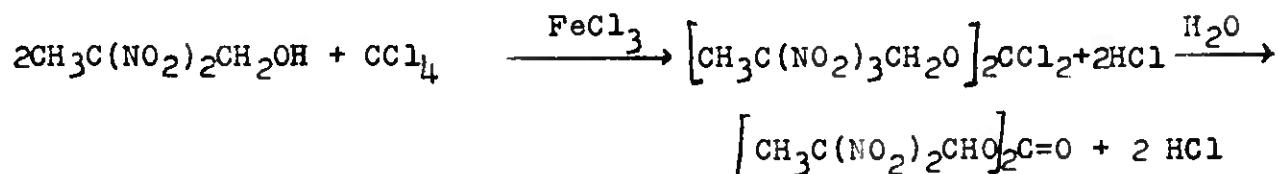
n-Butyl chloride was dehydrochlorinated by the ferric chloride. Its products formed black tars within a few hours. Other monohalogen compounds failed to react (9).

E. Preparation of Bis(dinitropropyl) Carbonate. In reactions analogous to the trinitroethanol - carbon tetrachloride system, 2,2-dinitropropanol was converted in 40-55% yields to bis(dinitropropyl) carbonate (mp. 121°C) instead of to the expected orthocarbonate. Elemental analysis of the product when first prepared, as in the case of the product obtained from trinitroethanol, was of little help in choosing a possible structural formula from the calculated elemental percentages. On the assumption that the dinitropropyl group would not hydrolyze to carbon dioxide, a sample of the product was decomposed in basic aqueous dioxane and analyzed for carbon dioxide. The amount found was, within experimental error, exactly the amount of carbon dioxide expected to be released from bis(dinitropropyl) carbonate (2). The melting point of the product was not lowered when it was mixed with known bis(dinitropropyl) carbonate prepared from phosgene and dinitropropanol using aluminum chloride catalyst (11). The

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bis(dinitropropyl) carbonate made in the ferric chloride condensation reaction had the same X-ray diffraction pattern as that prepared by the phosgene reaction, thereby confirming its identity.

The reaction of dinitropropanol with carbon tetrachloride was much faster than the reaction of trinitroethanol. The evolution of hydrogen chloride was essentially complete after a two hour reflux period. In analogy to the formation of BTNEC in the trinitroethanol system, the following equation represents the overall reaction:



A compound qualitatively identified as the intermediate bis-(dinitropropyl) dichloromethane, was isolated from the reaction solvent. Its melting point, about 96-100°C, varied with the length of exposure during handling. When slurried in water for a few hours, filtered and dried, the melting point was raised to 120-121°C, and the aqueous filtrate copiously precipitated silver chloride when silver nitrate was added. Bis(dinitropropyl) carbonate, itself, also was found in the reaction mixture.

When carbon tetrachloride was used as a reactant only, instead of reactant and solvent, no reaction could be obtained in tetrachloroethylene solution with dinitropropanol in excess. Only after enough carbon tetrachloride was added to make it the excess reactant was any hydrogen chloride evolved. Further experiments concerning the mechanism of this reaction are needed to determine why there is an apparent requirement for excess carbon tetrachloride, and no formation of the orthocarbonate.

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TABLE V

Properties of DNPC

Melting Point	120-121°C
Impact Sensitivity	73 cm
Vacuum Stability	0.51 cc of gas per gram in 48 hrs at 100°C
Crystal Density	1.63
Solubility	Soluble in chloroform, methanol, ether. Insoluble in water, hexane.

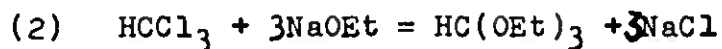
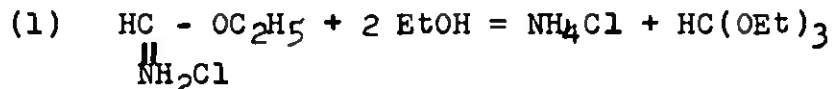
Unlike BTNEC, bis(dinitropropyl) carbonate would not transesterify with methanol or ethanol.

F. The Reaction of Other Acidic Alcohols with Carbon Tetrachloride. The catalyzed reaction of other "acidic" alcohols, such as 2,2,2-trichloroethanol and 2,4,6-trichlorophenol, with carbon tetrachloride occurred in a different manner than did the reaction of trinitroethanol with carbon tetrachloride. Instead of the ferric chloride remaining unchanged during the reaction, it was quantitatively reduced to ferrous chloride. The product of the reaction of trichloroethanol with carbon tetrachloride had an elemental analysis that corresponded to bis(trichloroethyl) carbonate. The trichlorophenol product was extremely difficult to purify and as yet its structure is not known. The study of the reaction of these alcohols and of similar alcohols with polyhalogen compounds will be continued and reported later.

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MECHANISM

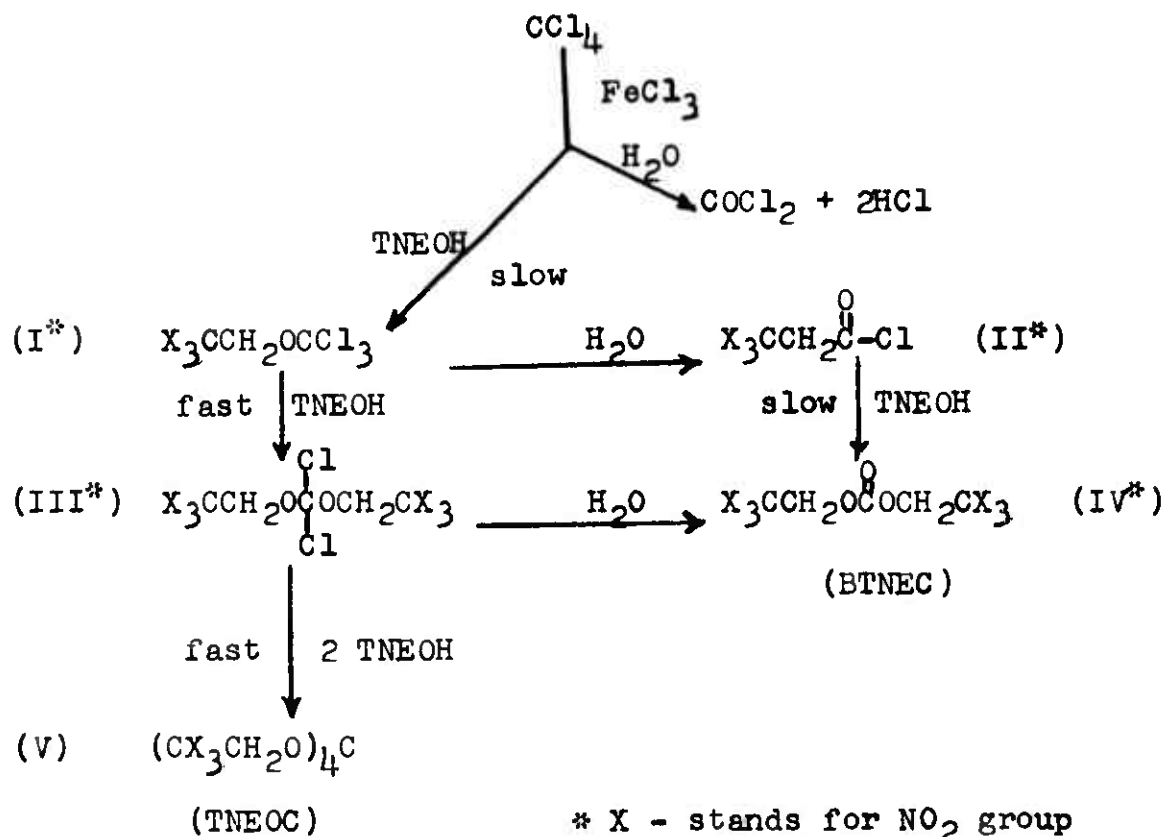
Orthoesters of alcohols such as methanol and ethanol have been made principally by two general reactions: (1) by action of an alcohol on an imidoester hydrochloride (equation 1) or (2) by alkali alkoxide reaction with a polyhalogen compound with three halogen atoms on the same carbon (equation 2).



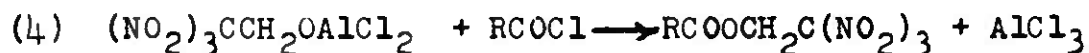
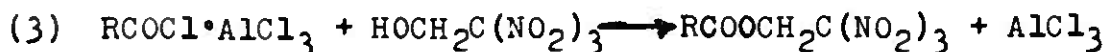
The latter reaction, a Williamson synthesis, can be used to prepare orthoformates, orthobenzoates, orthoacetates, etc. The alkyl orthoformate was always obtained when a carbon tetrahalide was used. Orthocarbonates can be prepared by the reaction of chloropicrin with a metal alkoxide (10). So far as can be determined the reaction described herein is the first example of Lewis acid catalyzed orthoester formation and the first example of an orthocarbonate being made from carbon tetrachloride.

The experimental work which has been done so far, has not given much evidence of the mechanism of the orthoester formation. Any mechanism would have to account for the facts that the orthocarbonate and orthoformate arise from excess reactant, that the reaction is catalytic, and that the catalyst appears not to undergo a change during the reaction. The following overall equations account for the observed products and identified intermediates:

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Since the carbon tetrachloride was in excess the intermediate products would have to be more reactive than the initial components. The role of the ferric chloride in catalyzing the reaction is not apparent. Because of the simplicity of the system the ferric chloride had only the halogen compound or the alcohol to activate by complex or compound formation. In the aluminum chloride catalyzed reaction of trinitroethanol with acid chlorides evidence for two principal mechanisms was obtained (equations 3 and 4).

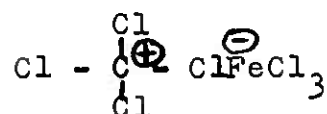


By a hypothetical analogy which is at present without evidence, the role of the ferric chloride could be to form a complex with the halogen compound, $\text{Cl}_3\text{CCl} \cdot \text{FeCl}_3$. Alternatively a

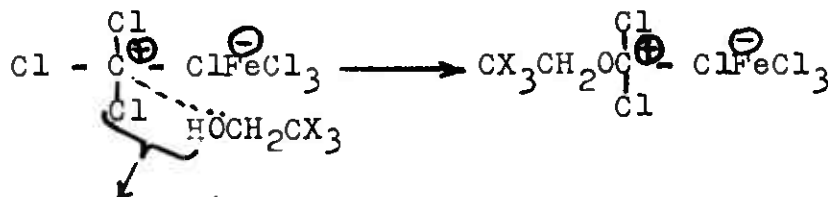
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highly reactive trinitroethyl dichloroferrate could be formed momentarily. And thirdly both types of reactive components might be formed. No dichloroferrate formation was observed in an experiment in which ferric chloride and trinitroethanol in nitrobenzene were heated at 100°C. It appears then that the reaction occurs because of the ability of ferric chloride to cause a disproportionation in the polyhalogen molecule either by a small amount being in solution or by surface catalysis. It is immaterial in the following considerations whether the ferric chloride action is by solution or surface catalysis.

If it is assumed then that ferric chloride complexes with carbon tetrachloride it appears reasonable to assume that the complex gives the central carbon a positive character:



One result of such a complexing action would be to force the atoms of the CCl₃ moiety toward co-planarity. Given such a condition of co-planarity and the carbonium ion character of the carbon atom then trinitroethanol, which is basic relative to that carbon atom and nucleophilic, could easily approach the carbon atom, form a partial bond and split out hydrogen chloride:



The result then would be an intermediate of more reactive character because of a stabilization of the carbonium ion character of the central carbon by the trinitroethoxy oxygen atom in analogy to the high reactivity of alpha halo ethers. Thus a faster reaction than before would ensue. The same assumptions would account for the subsequent substitutions and final regeneration of ferric chloride.

A particularly valid objection to the above reasoning for the first substitution would be: why does not the chlorine remain more tightly bonded than before and not come off the carbon atom with its electrons? If it is agreed that the carbon atom has positive character enough to allow partial bond

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formation with the poor nucleophile, trinitroethanol, it would follow that an equilibrium could be set up between the formation of the oxygen carbon bond and the re-formation of the chlorine carbon bond by the nucleophilic chlorine ion. This equilibrium is analogous to the mechanism postulated for trinitroethyl dichloroaluminate formation in the synthesis of BTNEC (12). That this equilibrium cannot exist long is evident because of the aprotic character of the solvent, and of the driving force of both the removal of the hydrogen chloride formed and of the nearly quantitative precipitation of the final product. Once one molecule of the substituted intermediate is formed the course of the reaction is set even though the chlorine atoms are tightly bonded. The foregoing mechanism is of course without evidence for the specific occurrences postulated.

The formation of BTNEC and trinitroethyl chlorocarbonate can be accounted for by the hydrolytic action of small amounts of water on the intermediates postulated above, rather than by the reaction of phosgene with trinitroethanol. In the synthesis of BTNEC (12), no product could be obtained by reaction of phosgene with trinitroethanol when ferric chloride was used as catalyst. The low concentration of phosgene in a system at atmospheric pressure made carbonate formation from it unprobable in the ferric chloride carbon tetrachloride system. The amount of BTNEC formed in strictly anhydrous systems was virtually nil, while on the other hand, BTNEC could be obtained as the principal product with no ortho-carbonate formation, when water was deliberately added.

EXPERIMENTAL

Following are typical preparative procedures for the principal compounds covered by this report:

A. Preparation of Trinitroethyl Orthocarbonate, TNEOC.
Trinitroethanol (4.34 g, 24 mmol) and 0.40 g (10 wt %) of ferric chloride were placed in 10 cc of carbon tetrachloride with careful exclusion of moisture. The mixture was refluxed for 24 hours. Upon cooling, the carbon tetrachloride solution was decanted from the crystalline product and ferric chloride. Evaporation of the mother liquor left only a very small amount of an oil. The crystalline product and ferric chloride were freed of solvent in vacuo, and then added slowly to an iced dilute hydrochloric acid solution to dissolve the ferric chloride. Filtration and drying gave 3.67 g of crude product (84% conversion). By recrystallization of the crude material from chloroform (35 cc per gram), 3.50 g (80 mole %) of trinitroethyl orthocarbonate, mp. 161.5-162°C, was obtained in two crops. An additional 0.07 g of a mixture, mp. 107-110°C, of bis-(trinitroethyl) carbonate and trinitroethyl orthocarbonate was isolated. The results of varying experimental conditions are given in Table VI.

TABLE VI

Effects of Reaction Variables on Yield of TNEOC

Conc. Mmol TNE/cc CCl ₄	% FeCl ₃	Reflux Time	Yield Wt. %	
			TNEOC*	Mixture TNEOC/BTNEC
0.8	50	48 hrs.	53	9
1.0	50	72 hrs.	63	5
1.6	50	48 hrs.	72	4
2.4	50	48 hrs.	71	15
2.4	50	24 hrs.	73	4
2.4	25	24 hrs.	73	5
2.5	25	16 hrs.	73	1
2.5	25	8 hrs.	63	0
2.4	10	24 hrs.	80	2
2.4	4	24 hrs.	74	1
2.0	5	24 hrs.	80	3

* Mole % TNEOC = wt % x 0.963
1.0% of yield corresponds to about 0.1

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The reaction mixture was worked up by either of two methods. After cooling the reaction mixture, the solvent was removed by vacuum distillation, and the mixture of solids was poured into ice water. The crude material was filtered and dried. Alternatively, the entire reaction mixture was added to ether. After extraction by water, drying and removal of the ether, the crude product was recrystallized.

B. Preparation of Trinitroethyl Orthoformate (TOF).

With careful exclusion of moisture, 9.20 g (51 mmol) of trinitroethanol and 2.0 g (21 wt %) of ferric chloride were added to 20 cc of chloroform. The mixture was refluxed 120 hours. Upon cooling, the contents of the reaction vessel were poured into 200 cc of ether. The ether solution was extracted several times with water and dried. Removal of the solvent by distillation under vacuum, left a crude product which was recrystallized from a 50% mixture of chloroform and hexane. There was obtained 6.92 g (74%) of trinitroethyl orthoformate, mp. 127.6-128°C. The effect of varying conditions is given in Table VII.

TABLE VII

Preparation of Trinitroethyl Orthoformate

Conc. Mmol TNE/ml CHCl ₃	Mole % FeCl ₃	Reflux Period	Yield Mole % Recrystal
0.7	40	70 hrs.	10
0.8	50	46 hrs.	0
2.5	50	72 hrs.	43
2.1	30	89 hrs.	56
2.5	25	120 hrs.	74

C. Preparation of Bis(dinitropropyl) Carbonate. Dinitropropanol (4.50 g, 30 mmol) was added to a mixture of 1.0 g of ferric chloride in 12 cc of carbon tetrachloride. The mixture was slowly warmed to the reflux temperature over a period of 30 minutes, and then held at reflux temperature for 1.5-2 hours. After cooling, the solvent was removed by vacuum distillation. The vessel contents were dropped into iced dilute hydrochloric acid, and the mixture was allowed

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to stand several hours. The crude product was filtered off, dried, and recrystallized from chloroform-hexane. There was obtained 2.69 g of bis(dinitropropyl) carbonate, mp. 120.5-121°C (55%). The yields in other experiments ranged from 40-65%.

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