SYNTHESIS AND PROPERTIES OF SOME CYANURIC CHLORIDE DERIVATIVES

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FOREWORD

This report combines a summary of significant accomplishments of foundational research task assignments of the Fundamental Processes Division during the period from September 1959 to September 1961.

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## CONTENTS

<table>
<thead>
<tr>
<th>Heading</th>
<th>Page no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foreword</td>
<td>iii</td>
</tr>
<tr>
<td>Abstract</td>
<td>vi</td>
</tr>
<tr>
<td>Historical</td>
<td>1</td>
</tr>
<tr>
<td>Discussion</td>
<td>3</td>
</tr>
<tr>
<td>Experimental Details</td>
<td>10</td>
</tr>
<tr>
<td>References</td>
<td>19</td>
</tr>
</tbody>
</table>
ABSTRACT

Cyanuric chloride was reacted with several negatively substituted primary alcohols with fluoro, bromo, nitro, or nitroxy groups as electronegative substituents. Completely substituted reaction products were obtained with trifluoroethanol, tribromoethanol, pentaerythritol trinitrate, and pentaerythritol dinitrate. Di- and tri-substituted products were obtained with 2-methyl-2-nitro-1-propanol which has a tertiary nitro group, whereas alcohols with primary and secondary nitro groups did not react. The reaction with the potassium salt of nitroform gave a product which gradually decomposed on standing. The monoperchlorate salt of trihydrazino-s-triazine was obtained, but attempts at the preparation of perchlorate derivatives of aminozido-s-triazines were unsuccessful. Sensitivity and stability data are reported on some of the products.
SYNTHESIS AND PROPERTIES OF SOME CYANURIC CHLORIDE DERIVATIVES

A project involving the synthesis of cyanuric chloride derivatives was undertaken with the purpose of preparing heat-stable materials which might be useful as propellant ingredients. Because of certain similarities in structure between cyanuric chloride and trimeric phosphonitrilic chloride, an investigation of the reactions with these two compounds was undertaken concurrently. The study with trimeric phosphonitrilic chloride will appear in a later report.

Reactions of cyanuric chloride (2,4,6-trichloro-s-triazine) with hydroxyl compounds to give alkoxy-s-triazines and aryloxy-s-triazines have been studied extensively by F. C. Schaefer's group at American Cyanamid Company.\(^{(1,2)}\) However, reactions with alcohols and alkanes containing nitroxy or nitro groups have not to our knowledge been reported. Therefore, as part of our study we undertook acquiring information on the reactivity of negatively substituted alcohols and alkanes with cyanuric chloride. Azido and hydrazino derivatives of cyanuric chloride proved of sufficient interest in gas-generator applications to warrant their inclusion in this investigation.

HISTORICAL

Cyanuric chloride has been known since 1827,\(^{(3)}\) although for some time it was considered to be the trichloride of cyanogen. Liebig\(^{(4)}\) determined its composition after preparing the compound by passing chlorine over dry potassium thiocyanate.

Impure cyanogen chloride was converted to cyanuric chloride with sunlight by Serullas.\(^{(3)}\) However, the product was believed for many years to be an isomer rather than the trimer of cyanogen chloride. As late as 1867,\(^{(5)}\) the trimer to monomer relationship of cyanuric chloride and cyanogen chloride was not clearly understood. Infrared and ultraviolet spectra\(^{(6)}\) now support the triazine
structure and indicate that the chlorines are located on the carbon atoms.

Cyanuric chloride is readily hydrolyzed by water vapor to cyanuric acid and hydrochloric acid. Treating cyanuric chloride with hot alcohols produces cyanuric acid and the corresponding alkyl halide with almost no esterification. Mono-, di-, and tri-alkyl esters of cyanuric acid have been made by reacting cyanuric chloride with alkaline earth alkoxides or with alcohols in the presence of basic acceptors. To carry out a stepwise substitution, the preferred base is either sodium carbonate or sodium hydroxide.

Primary and secondary amines, hydrazines, and related compounds react with cyanuric chloride in three steps. The oversimplified rule of thumb, expressed frequently in the literature, that the first chlorine atom is replaced at 0°C, the second at 30°C-50°C, and the third at 90°C-100°C cannot be used generally. This rule applies only to water solutions and not to other solvents. Some amines react to replace all three chlorine atoms at 0°C; others do not react at all, or react with the replacement of only one of the chlorines even at 100°C.

Certain mercaptans or their alkali metal salts react with cyanuric chloride indicating that the chlorine atoms are sufficiently active.

Cyanuric triazide is produced by the reaction of sodium azide and cyanuric chloride in aqueous acetone solution.

Cyanuric chloride has been reported to react vigorously with silver nitrate in acetonitrile solution to form a trinitro-s-triazine which has not been well characterized.

Alkyl Grignard reagents react with one of the chlorine atoms of cyanuric chloride, whereas, with some aryl Grignard reagents, two chlorine atoms undergo replacement. The products are 2-alkyl-4,6-dichloro-s-triazines and 2,4-diaryl-6-chloro-s-triazines, respectively.

Cyanuric chloride reacts with iodo- or bromobenzene or with bromophenetole and sodium to give mixtures of di- and tri-aryl-s-triazines. A mixture of cyanuric iodide and 2-chloro-4,6-dibromo-s-triazine is produced when a cold 56% hydroiodic acid solution is mixed with cyanuric chloride. This again is
essentially a simple exchange reaction wherein iodine replaces chlorine on the triazine ring.

Tris-(hydroxyaryl)-s-triazines(10) are formed by the reactions of phenols with cyanuric chloride in the presence of aluminum chloride catalyst. Cyanuric chloride reacts with sodium salts of organic carboxylic acids,(28) as well as with the free acids, to form sodium cyanurate and the corresponding acyl halides.

The active hydrogen of diethyl malonate reacts with one chlorine atom in cyanuric chloride(29) to form the (4,6-dichloro-s-triazinyl)-diethyl malonate. The primary reaction is base-catalyzed. In order to have a reaction with all three of the chlorines of cyanuric chloride at least three equivalents of sodium malonic ester and vigorous conditions are required.(29)

When cyanuric chloride is heated with benzamide, the cyanuric chloride is hydrolyzed to cyanuric acid as benzamide is dehydrated to benzonitrile.(28)

Cyanuric chloride is resistant to the action of most reducing agents. With lithium aluminum hydride in ether, Grundmann and Beyer(30) found only the inorganic products lithium chloride (LiCl), aluminum chloride (AlCl₃), and lithium aluminum cyanide (LiAl(CN)₄) in the reaction mixture; hydrogen was evolved during the reaction.

DISCUSSION

Cyanuric chloride, the starting material in the synthesis of s-triazine derivatives, is the acid chloride of cyanuric acid.
According to Pauling(31) the s-triazine ring is stabilized by a resonance energy of 82.5 kcal/mole compared to 39 kcal/mole for benzene. The high resonance energy is probably due to the six nonbonding electrons on the three ring nitrogens which contribute to the resonating system. Because of the high stability of the ring, much of the chemistry of s-triazines is simply the chemistry of the substituent groups. The ring is not often involved in the reactions except for its effect on the charge distribution.

This study was initiated with the purpose of synthesizing and determining the properties of nitro and nitroxy derivatives having the s-triazine nucleus. It was hoped that the reactivity of the chlorines in cyanuric chloride together with the high ring stability would result in the preparation of highly stable products. Halogen derivatives were included in the study because of the electron withdrawing properties (electronegativities) of the halogens which are similar to those of the nitro and nitroxy groups. Hydrazino and azido compounds were synthesized as potential gas generator ingredients.

Reactions of Cyanuric Chloride with Polyhalogen Alcohols:

Trifluoroethanol and tribromoethanol were reacted with cyanuric chloride. These alcohols were used to determine whether electron withdrawing halogen substituents affected the reactivity of the alcohol with cyanuric chloride or the stability of the final product. Both reactions proceeded smoothly to form the corresponding esters in good yields indicating that the electronegative groups did not hinder ester formation. The products appeared to be thermally stable up to and above 190°C.

\[
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Cl} \\
\text{Cl}
\end{array}
\quad + \quad \begin{array}{c}
\text{HOCH}_2\text{CX}_3 \\
\text{X}_3\text{CCH}_2\text{OC} \\
\text{COCH}_2\text{CX}_3
\end{array}
\rightarrow \begin{array}{c}
\text{C} \\
\text{OCH}_2\text{CX}_3 \\
\text{N} \\
\text{N} \\
\text{N}
\end{array}
\]

where \( X = \text{F} \) or \( \text{Br} \).
Reactions of Cyanuric Chloride with Nitroxyalcohols:

Reactions were carried out to determine whether nitroxy groups affected esterification or the subsequent stability of the products. Pentaerythritol trinitrate (PETrIN)\(^1\) and pentaerythritol dinitrate\(^2\) were the nitroxyalcohols used in these reactions. The cyanuric tri-ester was successfully obtained by the reaction of pentaerythritol trinitrate and cyanuric chloride in aqueous acetone solution with potassium hydroxide as the acid acceptor. This, to our knowledge, is the first nitrate ester reported in the \(s\)-triazine series.

\[
\begin{align*}
\text{Cl} & \quad \text{CH}_2\text{ONO}_2 \\
\text{N} & \quad \text{CH}_2\text{ONO}_2 \\
\text{N} & \quad \text{Cl} \quad \text{CH}_2\text{ONO}_2 \\
\text{N} & \quad \text{Cl} \quad \text{CH}_2\text{ONO}_2
\end{align*}
\]

Pentaerythritol dinitrate was reacted as above to form the corresponding tri-ester. The second hydroxyl group of pentaerythritol dinitrate underwent esterification as did the first hydroxyl group. Elemental analyses and molecular weight data indicate a reaction between two molecules of cyanuric chloride and three

\(^1\)2,2-Bis(nitroxymethyl)-3-nitroxy-1-propanol.
\(^2\)2,2-Bis(nitroxymethyl)-1,3-propanediol.
molecules of pentaerythritol dinitrate. A possible structure for the product is shown below.

\[
\begin{align*}
\text{Cl-} & \quad \text{C} & \quad \text{Cl} \\
\text{N} & \quad \text{N} & \quad \text{H} \\
\text{C} & \quad \text{C} & \quad \text{C} \\
\text{+ HOCH}_2\text{C}_{-}\text{CH}_2\text{OH} & \rightarrow \\
\text{CH}_2\text{ONO}_2
\end{align*}
\]

Reactions of Cyanuric Chloride with Mononitroalcohols and with Tri-nitroethanol:

Reactions with Mononitroalcohols: Reactions of cyanuric chloride with nitroethanol, 2-nitro-1-butanol, and 2-methyl-2-nitro-1-propanol were tried. Corresponding esters were not obtained by attempted reactions of nitroethanol (and 2-nitro-1-butanol) with cyanuric chloride, \(1\) in aqueous solution with an acid acceptor, \(2\) by suspension of potassium hydroxide in the nitroethanol with slow addition of cyanuric chloride, or \(3\) by fusion of nitroethanol and cyanuric chloride. However, 2-methyl-2-nitro-1-propanol did react in aqueous alkali solution to give the di- and the tri-esters in low yields.
The above may be at least partially explained on the basis of a tautomeric shift to the aci-form of primary and secondary nitro compounds. Nitroethanol with a primary nitro group and 2-nitro-1-butanol with a secondary nitro group can exist in both tautomeric forms. In basic solution the equilibrium shifts in the direction of the aci-form.

\[ \text{RCH}_2\text{NO}_2 \rightleftharpoons \text{RCH} = \text{NO}_2\text{H} \quad \text{KOH} \quad \text{RCH} = \text{NO}_2\text{K} \]

Under the reaction conditions used, the cyanuric chloride probably reacted with the aci-forms in these two instances to form the corresponding nitronic esters which then decomposed on attempted isolation. A tertiary nitro compound, such as 2-methyl-2-nitro-1-propanol, has no hydrogen alpha to the nitro group and, therefore, can have no aci-form. The reaction with cyanuric chloride would result in esterification through the alcohol group of the nitroalcohol.

**Reaction with Trinitroethanol**: Methods of carrying out the reaction of cyanuric chloride with trinitroethanol were limited because
of the decomposition of trinitroethanol in basic solution as well as at high temperatures. Hence, it was not possible to fuse the two components at elevated temperatures. Attempted fusion at a relatively low temperature yielded an oil which was probably a mixture of di- and tri-substituted derivatives. When ferric chloride (or aluminum chloride) was used as a catalyst in carbon tetrachloride solution, the main product was trinitroethyl orthocarbonate (TNEOC).

Reactions with Nitroalkanes:

Reactions with Nitromethane: The reactions were tried (1) in aqueous alkali solution, (2) in suspension of potassium hydroxide in nitromethane with addition of cyanuric chloride, and (3) in a refluxing mixture of cyanuric chloride and nitromethane. However, no expected product was obtained. Nitromethane, compared to other nitroparaffins, is uniquely sensitive to the action of alkali. Also, as in the case of the nitroalcohols, the formation of an unstable nitronic ester may have taken place when the reaction was carried out in alkaline solution. When cyanuric chloride was refluxed in nitromethane, the starting material was recovered almost quantitatively.

Reactions with Potassium Nitroform: An attempt was made to react potassium nitroform with cyanuric chloride according to the following reaction:

\[
\begin{align*}
\text{Cl-C} & + \text{KC(NO}_3\text{)Cl} \quad \rightarrow \\
\text{C(NO}_2\text{)_3} & + \text{KCl}
\end{align*}
\]

Based on the quantitative yield of KCl obtained, the reaction appeared to have proceeded smoothly. However, an accurate microanalysis was not obtained, probably due to instability of the product formed. Once again, the instability may be due to the formation of the nitronic ester which gradually decomposed following isolation.
On the other hand, if the reaction proceeded as given above, the instability of the product could be due to the electropositive nature of the ring carbon as well as the carbon with the three electron withdrawing nitro groups resulting in weak C-C linkages. Attempts at removing residual quantities of solvent from the n-hexane soluble portion of the reaction mixture proved difficult. Gradual decomposition was apparent from changing microanalysis on standing.

Reactions with Trihydrazino-s-triazine:

The trihydrazino-s-triazine was made with the hope that the triperchlorate could be prepared. However, the experimental results indicate that only the monoperchlorate was obtained. Trihydrazino-s-triazine did react with 3 moles of acetone to give the corresponding hydrazone derivative. Apparently, the trihydrazino-s-triazine was not basic enough to form the stable triperchlorate. Upon diazotization of trihydrazino-s-triazine, 2-azido-4,6-dihydrazino-s-triazine was isolated. (21)

\[
\begin{align*}
\text{H}_2\text{NHNC} & \quad \text{CNNH}_2 \\
\text{N} & \quad \text{N} \\
\text{C} & \quad \text{N} \\
\text{NHNH}_2 & \quad \text{NHNH}_2
\end{align*}
\]

\[
\text{H}_2\text{NHNC} \quad \text{CNNH}_2 + \text{HONO} \xrightarrow{\text{H}^+} \quad \text{N}_3\text{C} \quad \text{CNNH}_2 \\
\text{H}_2\text{O}, 0^\circ \text{C} \quad \text{NHNH}_2 + \text{H}_2\text{O}
\]

This compound decomposed upon addition of perchloric acid and therefore no perchlorate was obtained.

Reaction of Cyanuric Chloride with Ammonia Followed by Sodium Azide:

Cyanuric chloride was reacted with ammonia to give 2-amino-4,6-dichloro- and 2-chloro-4,6-diamino-s-triazine by varying the conditions according to Thurston, Dudley, Kaiser, Hechenbleikner, Schaefer, and Holm-Hansen. (33) Treating sodium azide with 2-amino-4,6-dichloro-s-triazine produced 2-amino-4,6-diazido-s-triazine which was identical with an authentic sample synthesized by another route (passing ammonia gas into an ether solution of cyanuric triazide).
This former route for making 2-amino-4,6-diazido-s-triazine was less hazardous than the latter. Attempts at making the perchlorate of the 2-amino-4,6-diazido-s-triazine were unsuccessful and only starting material was recovered in all cases. Treatment of 2-chloro-4,6-diamino-s-triazine with sodium azide gave none of the corresponding azide. The limited solubility of the 2-chloro-4,6-diamino-s-triazine in common organic solvents might explain this.

EXPERIMENTAL DETAILS

2,4,6-Tris(trifluoroethoxy)-s-triazine:

A suspension of 0.85 g (0.015 mole) of potassium hydroxide in 10 ml of trifluoroethanol was stirred at room temperature while 0.9 g (0.005 mole) of cyanuric chloride was added gradually; the reaction temperature was held at 30°-35° C. After all the cyanuric chloride was added, the mixture was refluxed for 5 hours. A solid (potassium chloride) was separated by filtration. The filtrate was washed with water, and the excess trifluoroethanol removed by distillation. The residue was washed with water and then dried. Recrystallizations from petroleum ether gave colorless crystals; mp 45°-46° C; yield 1.2 g (64%).

1 All melting points are uncorrected.
Anal for \( C_9H_4Br_3N_3O_3 \):

<table>
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<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>F</th>
<th>N</th>
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<td>1.60</td>
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<td>11.20</td>
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<td>Found</td>
<td>28.96</td>
<td>1.54</td>
<td>45.67</td>
<td>11.60</td>
</tr>
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Ignition temperature: 325°+ (slight fuming 192°-290° C).

**2,4,6-Tris(tribromoethoxy)-s-triazine:**

A solution of 0.9 g (0.005 mole) of cyanuric chloride in 15 ml of acetone was mixed with 4.4 g (0.015 mole) of tribromoethanol in 15 ml of acetone. A solution of 0.85 g (0.015 mole) of potassium hydroxide in 10 ml water was then added slowly in order to keep the reaction temperature around 45° C. After all the solution was added, the mixture was stirred for 20 min. The solid was separated by filtration and washed with water, alcohol, and then acetone. Repeated recrystallizations from methylene chloride and n-hexane yielded the pure product weighing 4.0 g (86%); mp 280°-281° C (d).

Anal for \( C_9H_4Br_3N_3O_3 \):

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<td>Found</td>
<td>11.57</td>
<td>0.57</td>
<td>4.64</td>
<td>78.38</td>
</tr>
</tbody>
</table>

**Tripentyl cyanurate (or 2,4,6-tris[2,2,2-tris (nitroxy methyl) ethoxy]-s-triazine):**

A solution of 3.0 g (0.011 mole) of PETriN in 5 ml of acetone and 10 ml of 5% potassium hydroxide solution was stirred at room temperature. The mixture was added to a solution of 0.7 g (0.00379 mole) of cyanuric chloride in 10 ml of acetone. There was an immediate rise in temperature up to 45° C. Stirring was continued for 20 min. The mixture was then placed under an air stream to evaporate the acetone. Upon removal of the acetone the aqueous solution was decanted. The residue was washed with portions of water, alcohol, and benzene, and then recrystallized from acetone and alcohol to form small needles; mp 131°-132° C; yield 3.0 g (0.00337 mole, 88%).

Anal for \( C_{18}H_{24}N_{12}O_9 \):

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<tr>
<td>Found</td>
<td>24.30</td>
<td>2.89</td>
<td>18.79</td>
</tr>
</tbody>
</table>
Ignition temperature: 175° C  
Vacuum stability: 0.34 cc gas at 100° C for 40 hours  
Heat of combustion at constant volume at 25° C: 2437 cal/g

Reaction of cyanuric chloride with pentaerythritol dinitrate:

A solution of 0.9 g (0.005 mole) of cyanuric chloride in 20 ml of acetone and 3.4 g (0.015 mole) of pentaerythritol dinitrate was stirred at room temperature. A solution of 0.9 g of potassium hydroxide in 10 ml of water was added dropwise to the mixture while keeping the temperature at approximately 45° C. When all the aqueous solution had been added the mixture was continuously stirred at 45° C for 30 minutes and then at room temperature for 15 minutes. After evaporating the solvent, the oily residue was washed with water several times and then evaporated to dryness. The oily material was crystallized from n-butanol; yield 1.1 g (0.0011 mole, 22%); mp 94°-95° C. The crystallized material was assumed to have 1 mole of residual butanol.

Anal for C21H24N12O24 • C4H10O:

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<td>Found</td>
<td>32.88</td>
<td>3.98</td>
<td>17.52</td>
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Recrystallization from dioxane and methanol yielded a white solid in which a mole of methanol was retained; mp 185°-186° C (d).

Anal for C21H24N12O24 • CH4O:

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<td>Found</td>
<td>31.05</td>
<td>3.62</td>
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</table>

The pentaerythritol dinitrate was made by conversion of pentaerythritol dibromide to the dinitrate according to Cragle and Pistera. (34)

Reactions of cyanuric chloride with 2-methyl-2-nitro-1-propanol:

A solution of 1.8 g (0.01 mole) of cyanuric chloride and 3.7 g (0.03 mole) of 2-methyl-2-nitro-1-propanol in 30 ml of acetone was
slowly added to a solution of 1.7 g of KOH in 15 ml of water keeping the temperature at approximately 45° C. After the addition was completed, the mixture was stirred continuously for 30 minutes. Evaporation of the acetone yielded a solid which was recrystallized from methanol–water mixture; mp 103°–104° C. Analysis indicated that 2 moles of the alcohol reacted with 1 mole of cyanuric chloride to form the disubstitution product, 2-chloro-4,6-di(2-methyl-2-nitropropoxy)-s-triazine, yield 0.6 g (0.0017 mole, 17%).

Anal for $C_{14}H_28N_5O_6Cl$:

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<tr>
<td>Calcd</td>
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<td>Found</td>
<td>38.16</td>
<td>5.27</td>
<td>20.33</td>
<td>10.52</td>
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</table>

A solution of 1.8 g (0.01 mole) of cyanuric chloride and 3.7 g (0.03 mole) of 2-methyl-2-nitro-1-propanol in 30 ml of acetone was added to a solution of 1.7 g of KOH in 15 ml of water. The temperature rose immediately to 55° C, and then the mixture was allowed to reflux for 1-1/2 hours. Evaporation of the acetone gave a white solid which was recrystallized from nitromethane–methanol mixture; mp 248°–249° C. Analysis indicated the formation of the triester, 2,4,6-tris(2-methyl-2-nitropropoxy)-s-triazine, yield 0.7 g (0.0015 mole, 16%).

Anal for $C_{15}H_{24}N_6O_3$:

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<tr>
<td>Found</td>
<td>41.98</td>
<td>5.65</td>
<td>19.85</td>
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**Attempted reactions of cyanuric chloride with nitroethanol and 2-nitro-1-butanol:**

The attempted reactions of cyanuric chloride with nitroethanol and 2-nitro-1-butanol were carried out as above. Cyanuric acid was the only product isolated.

**Attempted reactions of cyanuric chloride and trinitroethanol:**

(a) A mixture of 0.7 g of cyanuric chloride and 2.2 g of trinitroethanol was placed in a flask and allowed to stand at room temperature for 3 days. When the trinitroethanol was extracted with water cyanuric chloride was recovered almost quantitatively.
To a solution of 0.5 g of cyanuric chloride in 10 ml of acetone was added 2.0 g of trinitroethanol and 10 ml of 10% K$_2$CO$_3$. After stirring at 30°-35° C for 20 minutes the mixture was evaporated to dryness and the residue extracted with ethyl acetate. The ethyl acetate insoluble material was a mixture of potassium nitroform and potassium chloride. When the ethyl acetate solution was added to p-ether, a yellow solid was obtained which decomposed upon standing. An accurate analysis on this material was not obtained.

When a mixture of 1.0 g of trinitroethanol and 0.3 g of cyanuric chloride was heated slowly in an oil bath at 130°-135° C, the evolution of brown fumes was observed. After heating for 1 hour, cyanuric acid was the only product isolated.

A mixture of 4.5 g of trinitroethanol and 0.9 g of cyanuric chloride and 0.45 g of anhydrous ferric chloride was heated to 75°-80° C for 13 hours followed by 85°-90° C for 1 hour, 95°-100° C for 2 hours, and finally 95°-100° C for an additional 8 hours. The mixture was cooled and washed with dilute HCl and then with H$_2$O. Only a yellow oil was obtained. Attempts at crystallization were not successful. The crude oil was washed with H$_2$O until the yellow color disappeared. It was then dried in a vacuum desiccator. Assuming a mononitroform adduct to cyanuric acid, the following analysis was obtained:

$$\text{Anal for } C_4H_4H_4O_8:$$

<table>
<thead>
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<td>Calcd</td>
<td>18.46</td>
<td>1.54</td>
<td>24.61</td>
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<tr>
<td>Found</td>
<td>18.47</td>
<td>1.72</td>
<td>24.56</td>
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To a suspension of 0.9 g of cyanuric chloride and 2.8 g of trinitroethanol in 30 ml of CCl$_4$ was added 0.3 g of anhydrous FeCl$_3$. The mixture was heated in an oil bath at 75°-80° C for 20 hours. Upon cooling, a solid separated. The solid was washed with dilute HCl and H$_2$O and then recrystallized from aqueous alcohol. The major product was identified as TNEOC by a mixed melting point with an authentic sample.

2,4,6-Tris-(trinitromethyl)-s-triazine:

A solution of 1.84 g (0.01 mole) of cyanuric chloride and 5.7 g (0.03 mole) of freshly made potassium nitroform, prepared according to MacBeth and Orr (35) in 50 ml of acetonitrile, was heated gently for about 30 minutes and then allowed to cool to room temperature.
The suspended insoluble material (KCl) was separated by filtration, 1.69 g (0.0262 mole, 87%). The filtrate was evaporated under vacuum. The residue was extracted with n-hexane and dried with anhydrous sodium sulfate. The n-hexane solution was allowed to stand in a dry ice acetone bath overnight. A solid separated; mp 75°-89° C. After recrystallization from n-hexane the product was immediately sent for microanalysis without trying to remove residual n-hexane.

Anal for C₆N₁₂O₁₈:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
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<tbody>
<tr>
<td>Calcd</td>
<td>13.64</td>
<td>31.81</td>
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Anal for C₆N₁₂O₁₈ • 1/2C₆H₁₄:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
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<tr>
<td>Calcd</td>
<td>18.91</td>
<td>1.22</td>
<td>29.42</td>
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<tr>
<td>Found</td>
<td>19.43</td>
<td>1.23</td>
<td>28.10</td>
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</tbody>
</table>

Analysis after drying in a vacuum desiccator for 2 hours gave the following results: C, 19.78; H, 1.39.

Analysis after storing in an ice box for 1 week gave the following results: C, 20.57; H, 1.49; N, 30.53.

2,4,6-Trihydrazino-s-triazine perchlorate:

To a solution of 1.7 g (0.01 mole of trihydrazino-s-triazine in 15 ml of acetic acid was slowly added 1N perchloric acid. After standing at room temperature for a few minutes, the mixture upon addition of ether gave a white solid which was recrystallized from alcohol and dried in a desiccator: mp 170°-175° C (d). The analytical results suggest that only the monoperchlorate was formed.

Anal for C₁₅H₁₈N₁₉O₄Cl:

<table>
<thead>
<tr>
<th></th>
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<th>N</th>
<th>Cl</th>
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<tr>
<td>Calcd</td>
<td>13.26</td>
<td>3.68</td>
<td>46.40</td>
<td>12.70</td>
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<tr>
<td>Found</td>
<td>13.23</td>
<td>4.20</td>
<td>45.99</td>
<td>13.13</td>
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</table>

Attempted preparation of the triperchlorate by using 70% perchloric acid or by prolonged standing of the mixture was unsuccessful.
Reaction of 2,4,6-trihydrazino-s-triazine with acetone:

A solution of 1.7 g (0.01 mole) of trihydrazino-s-triazine and 17.4 g (0.3 mole) acetone in 7 ml of acetic acid was heated gently for 15 minutes. Upon cooling to room temperature a solid separated which was filtered and recrystallized from methanol; mp 163°-164° C.

Anal for C_{12}H_{21}N_{8}·2H_{2}O:

<table>
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<th></th>
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<th>H</th>
<th>N</th>
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<tr>
<td>Calcd</td>
<td>44.03</td>
<td>7.67</td>
<td>38.53</td>
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<tr>
<td>Found</td>
<td>44.35</td>
<td>6.75</td>
<td>38.82</td>
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Diazotization of 2,4,6-trihydrazino-s-triazine:

The diazotization of 2,4,6-trihydrazino-s-triazine was carried out according to Ott and Ohse. (21)

2-Amino-4,6-dichloro-s-triazine and 2-chloro-4,6-diamino-s-triazine:

These compounds were made according to Thurston, Dudley, Kaiser, Hechenbleikner, Schaefer, and Holm-Hansen. (33)

2-Amino-4,6-diazido-s-triazine:

A solution of 0.7 g (0.002 mole) of 2-amino-4,6-dichloro-s-triazine in 10 ml of acetone was added to a solution of 0.2 g (0.003 mole) of sodium azide in 5 ml of water. The mixture was stirred for 30 minutes at room temperature. Evaporation of the acetone yielded a white solid which gave the same physical properties as the product prepared from the treatment of cyanuric triazide with ammonia.

Attempted synthesis of 2-amino-4,6-diazido-s-triazine perchlorate:

A suspension of 0.36 g (0.002 mole) of 2-amino-4,6-diazido-s-triazine in alcohol was added to 1N perchloric acid at 0° C. No reaction was observed. The mixture was allowed to stand at room temperature for several hours, but still no reaction was observed. Upon evaporation of the solvent the starting material was recovered. When acetic acid was used instead of alcohol as a solvent, no perchlorate was obtained.

Attempted synthesis of 2-azido-4,6-diamino-s-triazine:

A suspension of 2.9 g (0.02 mole) of 2-chloro-4,6-diamino-s-triazine and 1.95 g (0.03 mole) of sodium azide in 100 ml of dioxane...
was heated to reflux for 3 hours. No 2-azido-4,6-diamino-s-triazine was obtained. The solvent was changed from dioxane to o-xylene, but still no azide was formed.

**Cyanuric triazide:**

Cyanuric triazide was made according to Ott and Ohse. (21)
Ignition temperature: 182° C.
Vacuum stability at 80° C for 24 hours: 0.57 cc gas
40 hours: 0.58 cc gas.
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(11) H. Fries, Ber., 19: 2056 (1886).
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(21) E. Ott and E. Ohse, Ber., 54B: 179-86 (1921).

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(26) F. Kraftt, Ber., 22: 1759 (1889).


(28) A. Senier, Ber., 19: 311 (1886).


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163-167
<table>
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<td><strong>tribromoethanol, pentaerythritol trinitrate</strong>, and pentaerythritol dinitrate produced completely substituted reaction products. Di- and tri-substituted products were obtained with 2-methyl-2-nitro-1-propanol with its tertiary nitro group, but none from alcohols with primary and secondary nitro groups. The product from the reaction with the potassium salt of nitroform gradually decomposed. The monoperchlorate salt of trihydrazino-s-triazine was obtained, but no perchlorate derivatives of aminoazido-s-triazines.</td>
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