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"IMPROVED METHOD FOR THE PREPARATION
OF ESTERS OF 2,2,2-TRINITROETHANOL"

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ABSTRACT: This report contains preliminary information on the use of anhydrous aluminum chloride to accelerate the reaction between organic acid chlorides and 2,2,2-trinitroethanol under mild conditions.

This reaction is a necessary step in the preparation of a new class of experimental high explosives under active development by the Bureau of Ordnance.

Explosives Research Department
U. S. Naval Ordnance Laboratory
White Oak, Maryland

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19 November 1951

This report is a description of the synthesis of esters of 2,2,2-trinitroethanol performed under Task NOL-Re2c-19-1-52. The reliability of the work and validity of the conclusions are the responsibility of the author and of the Chemistry Division, Explosives Research Department, of the Naval Ordnance Laboratory. This report is for preliminary information only.

W. G. SCHINDLER
Rear Admiral, USN
Commander



PAUL M. PYE, Department Chief
Explosives Research Department
By direction

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"IMPROVED METHOD FOR THE PREPARATION
OF ESTERS OF 2,2,2-TRINITROETHANOL"

INTRODUCTION

1. Esterification of organic acids with 2,2,2-trinitroethanol was first accomplished in 1943 by Dr. Rudolf Schenck and others of the State Institute for Metal Chemistry, Marburg, Germany (reference 1). In this country the Hercules Powder Company (reference 2) has repeated the preparation of most of the esters reported by Schenck and prepared additional ones. Some of the 2,2,2-trinitroethanol esters are of considerable interest as new high explosives because of their high oxygen content and good thermal stability. In addition certain of them have polymerization properties which are being investigated for propellant compositions and others may be useful as explosive waxes. Butestic formation by trinitroethyl 4,4,4-trinitrobutyrate and bis (trinitroethyl) succinate and excellent thermal stability at 120°C has led to further study of these two esters as new castable high explosives. They are now in pilot plant production by the Naugatuck Chemical Division of the United States Rubber Company under BuOrd contract (reference 3).

2. This report contains preliminary information on the accelerating effect of anhydrous aluminum chloride on the rate of reaction between 2,2,2-trinitroethanol and organic acid chlorides under mild conditions. This reaction is a necessary step in the preparation of such compounds, but has heretofore been carried out under difficult or dangerous conditions.

3. The reactive properties of the OH group in 2,2,2-trinitroethanol are greatly decreased by the trinitromethyl group. Consequently formation of its esters by the usual methods from organic acids or acid anhydrides is difficult and not generally applicable. Their preparation has usually been accomplished by heating trinitroethanol with an organic acid chloride without a solvent medium at temperatures ranging from 25°C to 135°C for several hours. Trinitroethanol esters prepared by the Hercules Powder Company (reference 2) by this method include the benzoate, acetate, cyanoacetate, acrylate, salicylate, malonate, succinate, glutarate, adipate,

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phthalate, 4-nitrophthalate, and terephthalate. The rate of reaction of trinitroethanol with acid chlorides decreased greatly when a solvent was used to dilute the reactants and few preparations have been successful when carried out in this manner. No product was obtained by the Aerojet Engineering Corporation (reference 4) when mesaconyl chloride was refluxed with trinitroethanol in methylene chloride or chloroform, and only a small amount of a product was obtained when xylene was used as a solvent. When fumaryl chloride was heated with trinitroethanol in tetrachloroethane at 141° for 2 hours, no reaction resulted (reference 5). However, the Naugatuck Chemical Division of the United States Rubber Company (reference 6) has obtained bis(trinitroethyl) succinate by dissolving succinyl chloride and trinitroethanol in benzene and refluxing for five hours with p-toluenesulfonic acid catalyst. Trinitroethyl acrylate has been prepared from acrylyl chloride and trinitroethanol by 16 hours refluxing in benzene with p-toluenesulfonic acid (reference 7).

The classical chemical method of simple esterification of free acids by alcohols, when attempted with trinitroethanol using mineral acid catalysts, requires very long reaction periods. The Aerojet Engineering Corporation (reference 8) has prepared trinitroethyl methacrylate in 56% yield by reacting trinitroethanol and methacrylic acid for 98 hours in refluxing benzene using sulfuric acid catalyst. The preparation of trinitroethyl acrylate in the same manner required five days and nights (reference 9). In this laboratory bis(trinitroethyl) succinate was obtained in 55% yield by direct esterification in refluxing benzene for 300 hours with p-toluenesulfonic acid catalyst added intermittently.

Previous work on the catalytic esterification of acids by trinitroethanol has been confined to the use of strong acids, such as sulfuric and p-toluenesulfonic acid as catalysts. These have been far from satisfactory from the standpoint of yield, reaction time and applicability to large scale production. Direct reaction of an acid chloride and trinitroethanol in the absence of a solvent at elevated temperatures makes even large scale laboratory preparation unfeasible because of the danger of explosion inherent in the method. Also none of the above methods was easily applicable to preparation of esters of alpha, beta unsaturated dicarboxylic acids. From this situation arose an interest in finding a catalytic method which would afford easier and safer laboratory preparation, which would extend esterification to previously unreactive acids and which would be applicable to pilot plant production. Consideration of a type of catalyst dissimilar to the strong acids but known for reactivity and complex formation led to the successful use of anhydrous aluminum chloride.

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Discussion

4. The use of small amounts of anhydrous aluminum chloride with an acid chloride and 2,2,2-trinitroethanol permits the reaction to proceed rapidly under mild conditions either with or without a solvent. Good yields have been obtained in short reaction periods and the method seems to be generally applicable. However, many aspects of the process have not been investigated as yet and the information contained in this report should be considered preliminary.

The preferred procedure for carrying out the reaction is to add slowly a solution of organic acid chloride to a mixture of 2,2,2-trinitroethanol and a small amount of aluminum chloride in the presence of a solvent such as carbon tetrachloride or chloroform at temperatures ranging from 40°C to the reflux temperature of the solvent. Evolution of hydrogen chloride gas is vigorous and maintains a fair rate until the reaction is complete. Alternatively, 2,2,2-trinitroethanol and an acid chloride may be dissolved in a solvent and powdered aluminum chloride added at room temperature. If necessary this reaction mixture may then be warmed to such temperature that vigorous evolution of hydrogen chloride gas occurs and, after this evolution subsides, ending with a short reflux period to complete the reaction. The crude product obtained after filtration is washed with iced dilute hydrochloric acid to remove aluminum chloride and recrystallized.

In the absence of a solvent, the esterification reaction proceeded vigorously at room temperature in most cases in the presence of aluminum chloride. In the preparation of bis(trinitroethyl) succinate, the reaction proceeded so rapidly that the reactant mixture set to a solid mass of precipitated product within two minutes. By themselves fumaryl chloride and trinitroethanol did not react at an appreciable rate below 100°C, but did react completely at room temperature with five minutes after aluminum chloride was added (reference 5). Trinitroethyl 4,4,4-trinitrobutyrate was prepared from 4,4,4-trinitrobutyryl chloride by this method in 87% yield after recrystallization.

So far the optimum amount of aluminum chloride to use has not been determined. The quantities which were used varied with the conditions of experiment and with the reactivity of the acid chlorides. For experiments where no

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solvent was used quantities of aluminum chloride equal to 10-20% of the molar quantities of the acid chlorides gave satisfactory results, and for experiments using a solvent medium, quantities up to 50% molar ratio were used. Reactant concentration was 0.4 mole of acid chloride per liter of solvent, either carbon tetrachloride or chloroform, with trinitroethanol in 10-20% excess. The rate of reaction of the components was followed by leading the hydrogen chloride gas evolved into a solution of silver nitrate or a standard solution of sodium hydroxide.

Plans have been made to determine the relative effect of other Friedel-Craft type catalysts (of which aluminum chloride is only one example) on the esterification reaction and to determine the applicability of the method to other polynitro alcohols. From this work some information on the mechanism of the reaction may be obtained. Patent application has been submitted covering this process.

Experimental

Results and information on the conditions used in the experiments conducted so far are summarized in Table I.

Acknowledgement

The helpful suggestions of Dr. O. H. Johnson are acknowledged. Mr. J. D. Upton assisted in experimental work.

Table I

Ester	Moles Acid Chloride	Moles TBE	Moles AlCl ₃	Solvent	Method /1	Reaction Temperature /2	Reaction Time /3	Yield Re'x'd	M.P. °C.
1. Succinate	0.010	0.022	0.002	none	--	20°	5 min	70	125.5-126
2. Succinate	0.010	0.022	0.002	4 ml CCl ₄	A	45°	15 min	93	125.5-126
3. Succinate	0.010	0.021	0.002	20 ml CCl ₄	A	50°	1 1/2 hrs	68	125 - 126
4. Succinate	0.010	0.021	0.009	20 ml CCl ₄	A	50°	1 hr	69	125.5-126
5. Succinate	0.020	0.048	0.010	50 ml CCl ₄	B	70°	1 hr	75	125 - 126
6. Succinate	0.020	0.048	0.009	50 ml CCl ₄	B	61°	1 hr	74	125 - 126
7. Trinitrobutyrate /2	0.002	0.0021	0.0008	none	--	25°	7 min	87	91 - 92
8. Trinitrobutyrate /2	0.020	0.024	0.009	50 ml CCl ₄	B	61°	1 1/4 hrs	82	92.5-93
9. Fumarate	0.010	0.021	0.002	none	--	20-25°	5 min	80	152
10. Fumarate	0.020	0.045	0.006	40 ml CCl ₄	A	70°	9 hrs	69	151 - 152
11. Fumarate	0.040	0.096	0.020	100 ml CCl ₄	B	61°	3 hrs	74	152
12. Itaconate	0.006	0.013	0.002	none	--	45°	25 min	78	74 - 76
13. Phthalate	0.010	0.024	0.003	30 ml CCl ₄	A	30°	1 hr	90	128 - 129
14. Acetate	0.020	0.024	0.002	40 ml CCl ₄	A	25°	3/4 hr	80	30
15. Benzoate	0.020	0.022	0.010	40 ml CCl ₄	B	60°	35 min	88	76 - 77

/1_ Method

A - Reactants mixed with solvent, aluminum chloride added, and then mixture warmed to reaction temperature; after reaction subsided, refluxed to complete reaction.

B - Trinitroethanol was dissolved in solvent, aluminum chloride added, and then the acid chloride was added dropwise at the optimum reaction temperature.

/2_ from trinitrobutyryl chloride prepared from trinitrobutyric acid and PCl₅.

/3_ Reaction time: Time elapsed from beginning of acid chloride addition or AlCl₃ addition until HCl gas evolution virtually ended.

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