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(U) SYNTHESIS OF A NEW HIGH-ENERGY SOLID PROPELLANT OXIDIZER

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C.S. McDOWELL
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TECHNICAL REPORT AFRPL-TR-69-174

SEPTEMBER 1969

AIR FORCE ROCKET PROPULSION LABORATORY
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
EDWARDS, CALIFORNIA

C70-743

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SYNTHESIS OF A NEW HIGH-ENERGY SOLID PROPELLANT OXIDIZER (U)

C. S. McDowell
C. I. Merrill
M. W. Barnes

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FOREWORD

The work reported herein was performed under Project
314801ACL and covers the period 1 October 1967 through
30 May 1969.

Principal investigator during the initial synthesis
was Capt C. S. McDowell. Project Engineer for synthesis
and scale-up operations was Dr. C. I. Merrill and Task
Scientist for the synthesis project was Dr. F. Q. Roberto.

Evaluation of DOAP as a propellant ingredient is being
accomplished under AFRPL In-House Project 314801ACP.
Project Engineer is Capt C. S. McDowell, Task Scientist,
Dr. F. Q. Roberto.

Reviewed and approved for publication by:
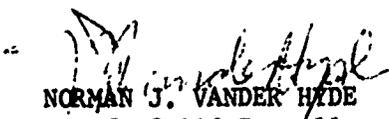
NORMAN J. VANDER HYDE
Chief, Solid Propellant Branch
Propellant Division
Air Force Rocket Propulsion Laboratory

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CONFIDENTIAL ABSTRACT

(C) Two new propellant ingredients, methylene-
dioxyamine (DO), a new monopropellant, and methylenedioxy-
ammonium diperchlorate (DOAP), a new solid propellant
oxidizer, have been synthesized at AFRPL using a five-step
sequence of reactions. The reaction sequence, for producing
DO in an overall yield of 51% or DOAP in an overall yield
of 25-30%, is presented in detail. A synopsis of the
experimental work leading to the successful synthesis cf
these new propellant ingredients is given.

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A. INTRODUCTION

(C) Performance studies, relative to new concepts in advanced ballistic missile systems have continually pointed out the need for improvement in the performance capability of composite solid propellants. Many approaches to improving the delivered performance of solid propellants are under study at the Air Force Rocket Propulsion Laboratory. This report documents one of these efforts, i.e., the successful synthesis of a new high-energy oxidizer code-named DOAP (methylenedioxyammonium diperchlorate).

(C) An initial interest in the oxyamine (-ONH$_2$) functional group as a precursor through fluorination to the oxydifluoramine (-ONF$_2$) group[1], led to studies on the possible synthesis of a homologous series of -ONH$_2$ substituted methanes and their perchlorate salts. As monopropellants and solid oxidizers respectively, these compounds held promise as new propellant ingredients. Preliminary calculations on the performance of some of these hypothetical propellant ingredients confirmed the desirability of synthesizing these compounds. The following compounds were of interest: Methoxyamine (MOA) and its perchlorate salt (MOAP); methylenedioxyamine (DOA) and its diperchlorate salt (DOAP); trioxyaminomethane (TROA) and its corresponding triperchlorate salt (TROAP); and tetraoxyaminomethane (TOA) and its tetraperchlorate salt (TOAP).

(C) The primary objective of this work was improvement of solid propellant performance with the advanced perchlorate oxidizers. The preparation of the monopropellants (free amines) was considered as a secondary objective. Thus the syntheses were planned as preparations of

perchlorate salts, i.e., new solid oxidizers.

(C) Beginning with the simplest of the homologous series, MOAP was prepared as a model compound from commercially available methoxyamine hydrochloride. MOAP itself was of little interest as an oxidizer in aluminized composite propellants because it lacks sufficient oxygen to function as an oxidizer in a non-oxidizing binder. However, a brief look at the properties of MOAP, i.e., melting point, hygroscopicity and thermal stability, suggested that one might expect the higher homologs to have reasonable propellant properties.

(C) In choosing one of the three oxyammonium perchlorates for attempted synthesis, several factors, including theoretical performance and simplicity of synthesis, were considered. Methylenedioxyammonium diperchlorate (DOAP) was chosen as the best candidate for synthesis based on its calculated performance in a baseline aluminized composite propellant and because stereochemically it appeared to be the easiest of the homologous series to synthesize.

(C) The theoretical performance of DOAP (270 sec) in a baseline aluminized composite propellant was compared with ammonium perchlorate (263 sec), hydroxylammonium perchlorate (268 sec), and with other members of the homologous oxyamine perchlorate series. Theoretical propellants containing the more complex trioxyaminomethane triperchlorate salt (TROAP) or tetra-oxyaminomethane tetraperchlorate salt (TOAP), did yield slight increases (1 and 2 sec, respectively) in specific impulse over the corresponding DOAP propellant. The anticipated greater difficulty of synthesizing these

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compounds, however, overshadowed the small potential increase in energetics.[*]

(C) Finally, theoretical performance calculations using DOAP as an oxidizer in advanced propellants containing aluminum hydride and/or domino (NF_2) ingredients indicated that DOAP provided a specific impulse comparable to HAP, (290 vs 289 sec., respectively) in an optimized NF binder using a realistic aluminum hydride loading.

(U) Subsequently, in October 1967 an investigation of the synthesis of DOAP was undertaken. The first DOAP was isolated in late March of 1968 and the characterization of DOAP including X-ray diffraction[2] and the determination of the thermal decomposition mechanism[3] of DOAP, was completed in May 1969. A series of synthesis scale-up runs was completed in June 1969.

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[*] (C) There are other potential gains to be derived from the synthesis of TROAP and TOAP in the properties that are important to rocket propulsion. These are a probable increase in density and melting point, and a possible decrease in solubility in binder materials. Additional benefits may be derived from the preparation of the diperchlorate of trioxyaminomethane or the diperchlorate of tetraoxyaminomethane. These compounds should be less acidic, less chemically reactive, and more thermally stable than DOAP. Preliminary calculations indicate that the free oxyamine functional group is energetic and contributes to increased performance.

(C) The aspects of using mixed oxyamine-oxyammonium perchlorate substituted methanes with oxidizing binders is attractive in terms of performance, but discussion of all the possibilities and ramifications of the use of oxyamine derivatives as propellant ingredients is beyond the scope of this report.

These runs provided a total of 11 lbs of the free amine (DOA) which will be used in part for the preparation of DOAP and the remainder for the evaluation of DOA as a monopropellant. Of the 11 lbs currently available, approximately 9 pounds were prepared in two and a half months, using large-scale (50 liter) laboratory equipment. Preparation of DOAP has not kept pace with preparation of DOA because of the hazards involved in handling large quantities of this material in the laboratory, the need for additional process development on the conversion of the free amine to the perchlorate and problems associated with the autocatalytic decomposition of DOAP on long-term storage.

B. HISTORY

(C) A number of compounds containing the oxyamine functionality were found in the literature. None of these included a geminal oxyamine grouping of the type desired in methylenedioxyamine (DOA) and methylenedioxyammonium diperchlorate (DOAP). Consequently, no information on the synthesis or stability of this type molecular structure was available.

C. PREPARATIVE ROUTES TO OXYAMINES

(C) Several general preparative routes to the synthesis of oxyamines have been outlined by Smith in his review of The Chemistry of Open Chain Organic Nitrogen Compounds.[4] The O-alkylation of the anions of oximes,[5] hydroxamic acids,[5, 6] N-hydroxyurethanes[7] and ethyl acethydroximate,[8] is followed by acid hydrolysis of the carbon-nitrogen bond(s). The resultant products include the oxyamine salt and the by-product ketone, acid, alcohol or ester, respectively (Equations I and II). The second possible preparative route [4] involves alcoholysis of chloramine[9] or hydroxylamine-O-sulfonic

acid,[10] and is illustrated in Equation III. Synthesis of DOA or DOAP by the second preparative route is impractical because of the instability of methanediol, the required intermediate for the alcoholysis of chloroamine or hydroxylamine-O-sulfonic acid. Therefore, the first preparative route was utilized.

$$(I) \quad RR'C=NOH + CH_2X_2 \xrightarrow{NaOH} NaX + (RR'C=NO)_2CH_2$$

$$X = I, \ Br, \ Cl$$

$$(II) \quad (RR'C=NO)_2CH_2 \xrightarrow{H^\ominus \ (H_2O)} RR'C=O + CH_2(ONH_2)_2 \cdot 2H^\oplus$$

$$(III) \quad NF_2X + HOR \xrightarrow{Base} X^\ominus + NH_2OR$$

$$X^\ominus = Cl, \ -SO_3H$$
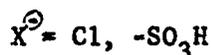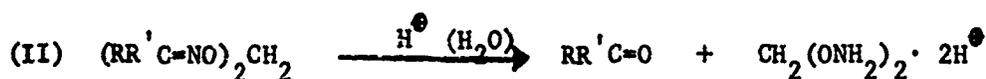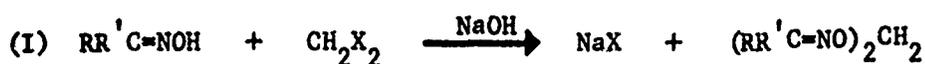
D. ATTEMPTED PREPARATIONS OF GEMINAL DIOXYAMINE

(U) Benzophenone oxime (1) was selected for the first attempt at the synthesis of the bis adduct because it is a cheap and commercially available chemical. Reaction of sodium benzophenone oximate with methylene iodide in acetonitrile at room temperature for 24 hours gave the desired adduct methylene-O, O'-bisbenzophenonoxime (80%) as identified by infrared spectra, nuclear magnetic resonance spectra (nmr) and elemental analysis (2) (Equation IV).

(IV)   2 $\emptyset_2C=NOH$ + CH_2I_2 $\xrightarrow[\text{Acetonitrile}]{\text{NaOH}}$ $(\emptyset_2C=N-O)_2\,CH_2$

              (1)   (2)
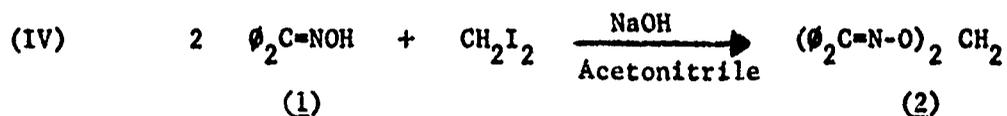
(U) Attempted hydrolysis of the oxime adduct 2, with hydrochloric acid gave ammonium chloride and hydroxylammonium chloride but none of the desired compound. Perchloric acid hydrolysis of the oxime adduct was also unsuccessful.

(U) The reaction of the sodium salt of N-benzyloxycarbonylhydroxylamine (3) with methylene iodide in refluxing acetonitrile (Equation V) gave a small yield of a material tentatively identified as methylene-0,0'-bis-N-benzoyl-oxycarbonylhydroxylamine (4). Attempted acid hydrolysis of 4 in ether with aqueous hydrochloric acid gave no detectable quantity of the desired compound, DOACl.

$$(V)\quad 2\emptyset CH_2O\overset{\overset{\text{O}}{\|}}{C}-\overset{\overset{\text{H}}{|}}{N}-OH \;+\; CH_2I_2 \;\xrightarrow[\text{Acetonitrile}]{\text{NaOH}}\; (\emptyset CH_2-O\overset{\overset{\text{O}}{\|}}{C}-\overset{\overset{\text{H}}{|}}{N}-O)_2CH_2$$

                    (3)   (4)
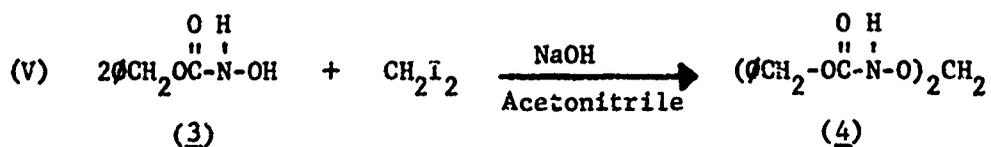
(U) The reaction of the sodium salt of acetoxime with methylene iodide was unsuccessful and a brief effort using N-hydroxyphthalimide (5) gave no reasonable yield of methylene-0,0'-bis-N-hydroxyphthalimide (6), Equation VI.

(VI)

(5) + CH$_2$I$_2$ $\xrightarrow[\text{NaOH}]{\text{CH}_3\text{C=N}}$ (6)
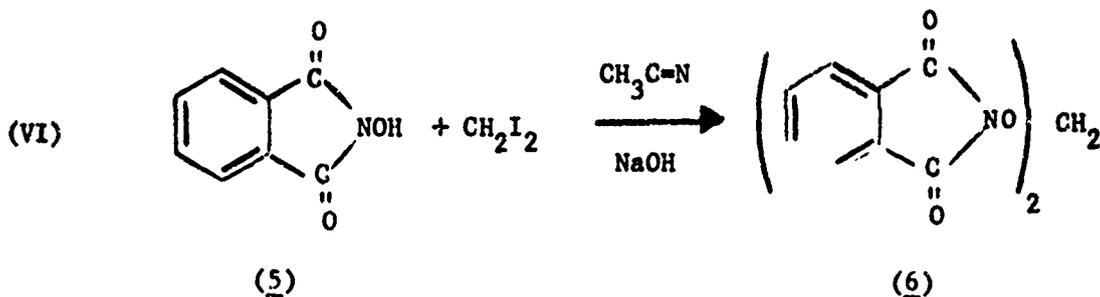
E. SUCCESSFUL SYNTHESIS OF METHYLENEDIOXYAMMONIUM DIPERCHLORATE

(C) Having found reference in the literature[8] to the facile hydrolysis
of O-substituted ethyl acethydroximate derivatives, the reaction of the
sodium salt of ethyl acethydroximate (7) with methylene iodide was attempted.
The reaction proceeded smoothly and rapidly in refluxing acetonitrile to
give a product identified by infrared, nmr and elemental analysis as
methylene-O,O'-bis(ethyl acethydroximate) (8), Equation VII. Hydrolysis of
the bis adduct 8, as illustrated in Equation VIII, in an ether solution
with aqueous hydrochloric acid resulted in the immediate formation of a
white precipitate. This material was identified by infrared, nmr and
elemental analysis as methylenedioxyamine dihydrochloride (DOACl)(9).

(VII) $\quad$ 2 CH$_3$C=NOH $\quad$ + $\quad$ CH$_2$I$_2$ $\xrightarrow[\text{Acetonitrile}]{\text{NaOH}}$ (CH$_3$C=NO)$_2$CH$_2$

$\qquad$ OEt $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ OEt

$\qquad\quad$ (7) $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (8)Bis Adduct

(VIII) $\quad$ (CH$_3$C=NO)$_2$ CH$_2$ $\xrightarrow[\text{H}_2\text{O}]{\text{HCl(g)-Ether}}$ CH$_2$(ONH$_2$)$_2$·2 HCl $\quad$ + $\quad$ CH$_3$COEt

$\qquad\quad$ OEt $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ O

$\qquad\quad$ (8) $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ (9)
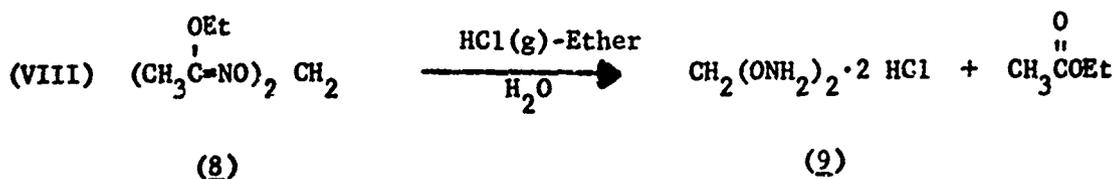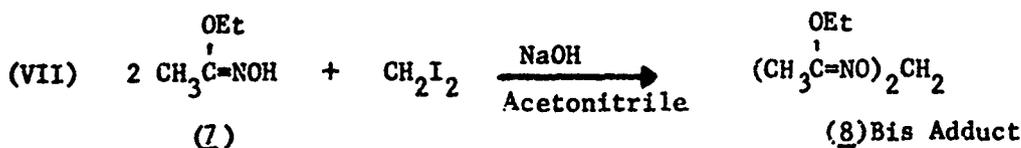
(C) Hydrolysis of the bis adduct 8 in nitromethane with concentrated
perchloric acid as shown in Equation IX gave a white crystalline material
(platelets), which after drying melted at 114°C. Characterization by
infrared, nmr and elemental analysis of this initial product and additional
perchlorate produced by perchloric acid titration of the free amine (prepared
from the dihydrochloride), identified it as methylenedioxyammonium diperchlorate
(10), DOAP. Thus the synthesis of DOAP had been achieved. Synthesis
scale-up and evaluation of DOAP was subsequently initiated.

$$\text{(IX)}\quad (CH_3\overset{OEt}{\underset{|}{C}}=NO)_2\,CH_2 \;+\; HClO_4 \;(aq) \xrightarrow{CH_3NO_2} CH_2(ONH_2)_2 \cdot HClO_4 + CH_3\overset{O}{\overset{\|}{C}}\text{-O-Et}$$
$$\underline{(8)}\qquad\qquad\qquad\qquad\qquad\qquad\qquad \underline{(10)}$$
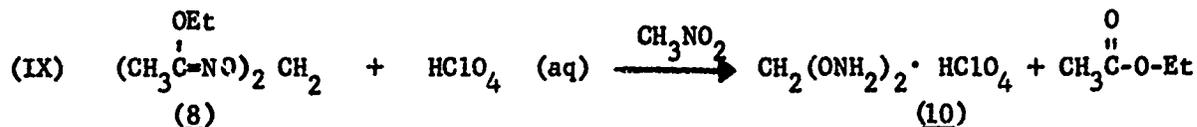
F. CONTINUING SYNTHESIS EFFORT

(C) The application of a similar preparative route to the synthesis
of trioxyaminomethane (TROA) and tetraoxyaminomethane (TOA) and their
corresponding perchlorate salts TROAP and TOAP constitute one of the major
efforts of the continuing in-house synthesis effort at AFRPL. Although
small quantities of material tentatively identified as the tris adduct
11 and tetrakis adduct 12 have been prepared according to Equations X and
XI, no firm conclusion on the future availability of TROAP or TOAP can be
made at the writing of this report.

$$\text{(X)}\quad CH_3\overset{OEt}{\underset{|}{C}}=NOH + CHI_3 \xrightarrow[\text{Acetonitrile}]{NaOH} (CH_3\overset{OEt}{\underset{|}{C}}=NO)_3CH + \text{elimination}$$
$$\underline{(11)}$$

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$$(XI) \quad \underset{\text{CHC=NOH}}{\overset{OEt}{|}} + CCl_3NO_2 \xrightarrow[\text{Acetonitrile}]{NaOH} \underset{(12)}{(CH_3\overset{OEt}{\underset{|}{C}}=NO)_4C} + \text{recovered starting material}$$
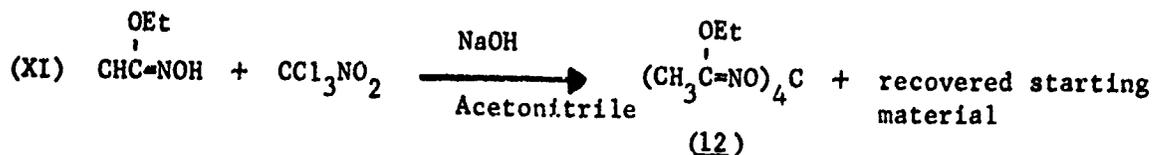
G. DESCRIPTION OF SYNTHESIS SEQUENCE

(C) The synthesis of DOA and DOAP can be divided into four or five reaction steps, respectively. Each of these steps is discussed briefly in this section giving an overall description of the entire reaction sequence as it evolved during the large-scale preparation of DOAP. Section H of this report will discuss the problems encountered in scaling the reactions from standard laboratory equipment (1-1. flasks) to large laboratory equipment (22 and 55 liter vessels). The six equations for the preparation of DOAP, which include the preparation sequence for DOA, are given below (Equations XII - XVII).

$$\underline{\text{STEP 1}} \quad (XII) \quad CH_3C\equiv N + EtOH \xrightarrow[\substack{4\% \text{ xs} \quad <10°C}]{HCl(g)} \underset{(12)}{CH_3\overset{NH\cdot HCl}{\overset{\|}{C}}OEt}$$

$$(XIII) \quad CH_3\overset{NH\cdot HCl}{\overset{\|}{C}}OEt + H_2NOH\cdot HCl \xrightarrow[\substack{\text{Ether}\\NaHCO_3}]{H_2O} CH_3\overset{N-OH}{\overset{\|}{C}}OEt + NH_4Cl \quad (7)$$

$$\underline{\text{STEP 2}} \quad (XIV) \quad 2 CH_3\overset{OEt}{\underset{|}{C}}=NOH + CH_2Br_2 \xrightarrow[\substack{KOH\\70°C\\-2 KBr}]{\text{Acetonitrile}} (CH_3\overset{OEt}{\underset{|}{C}}=NO)_2CH_2 \quad (8)$$

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STEP 3 (XV) $(CH_3\overset{OEt}{\underset{|}{C}}=NO)_2CH_2$ + 2 HCl(aq) $\xrightarrow[\substack{40\text{-}50°C \\ -2\ EtAc}]{\text{Ethanol}}$ $CH_2(ONH_2)_2 \cdot 2\ HCl$

(9)

STEP 4 (XVI) $CH_2(ONH_2)_2 \cdot 2\ HCl$ + 2 KOH $\xrightarrow[\substack{-2\ KCl \\ -2\ H_2O}]{\text{Ethanol}}$ $CH_2(ONH_2)_2$

(14)

STEP 5 (XVII) $CH_2(ONH_2)_2$ + 2 $HClO_4$(aq) $\xrightarrow[\substack{2.\ \text{Drierite}}]{1.\ \text{Ethanol}}$ $CH_2(ONH_2)_2 \cdot 2\ HClO_4$

(10)
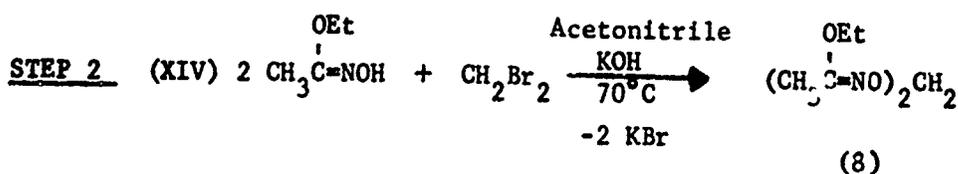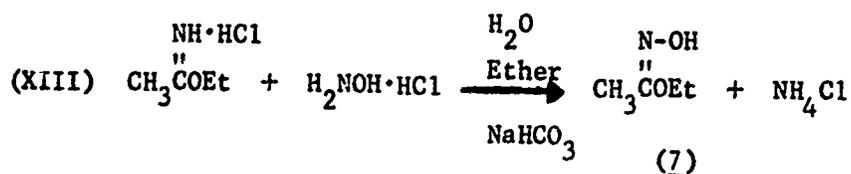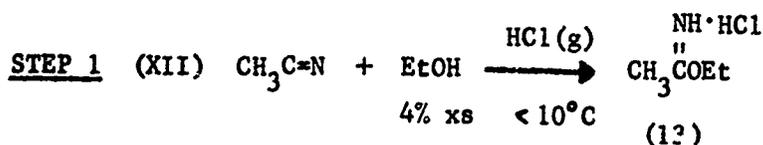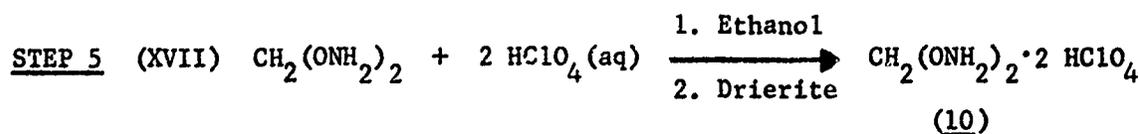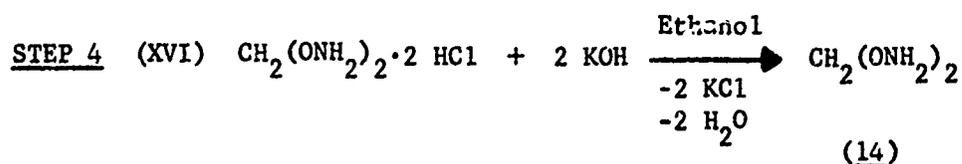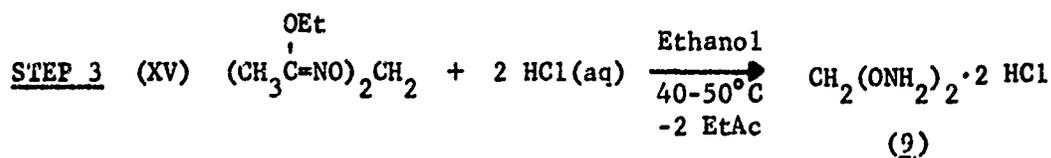
(C) STEP 1 - This involves the preparation of the key starting material for the synthesis of DOA and DOAP. Ethyl acethydroximate (7) was prepared in a two-reaction sequence which first required the addition of dry hydrogen chloride (46 moles) to a mixture of ethanol and acetonitrile (46 and 45 moles, respectively) at 0-10°C[11, 12] in a 22-liter flask. The resultant ethyl acetimide hydrochloride (13), which formed in 2-3 days, was slurried in ether, and then converted (via an AFRPL-developed modification of the literature[11, 12] procedure) to ethyl acethydroximate.

(C) Equivalent amounts of the imide hydrochloride 13, as the ether slurry, and hydroxylamine hydrochloride were dissolved in a minimum of cold water. Powdered sodium bicarbonate was added carefully to the water solution while the temperature of the reaction mixture was maintained at approximately 0°C. The rapid evolution of carbon dioxide aided in maintaining the reaction temperature at 0°C. As addition of the bicarbonate

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continued, product ethyl acethydroximate separated in solution with the ether (contained in the ethyl acetimide hydrochloride slurry) from the slowly stirring reaction mixture. This upper layer was removed intermittently during bicarbonate addition and the ether was replenished in the reaction vessel. After completion of bicarbonate addition, the aqueous layer was washed with ether and the ether wash was combined with the other product ether solutions.

(C) The accumulated ethyl acethydroximate-ether solution was dried over sodium sulfate and stripped on a rotary evaporator at 70 mm to give clear colorless ethyl acethydroximate containing 5-10% ether. This material was found suitable for direct application in Step 2 of the synthesis sequence.

(C) STEP 2 - The preparation of methylene-0,0'-bis(ethyl acethydroximate) (8) was accomplished in a 50-liter flask. Ethyl acethydroximate (60 moles) containing 8-10% ether was added to approximately four times its volume of dry acetonitrile. Powdered potassium hydroxide (stoichiometric for ethyl acethydroximate) was added with careful heating and temperature control to obtain a slurry of potassium ethyl acethydroximate in acetonitrile at $70°±1°C$. To this rapidly stirring mixture was slowly added an equivalent amount of methylene bromide (30 moles). The rate of addition of the halide was regulated carefully and external cooling of the flask used to prevent boil-over due to the very exothermic nature of this reaction. A temperature of at least 68°C was maintained during the entire addition, thus precluding problems of reaction runaway. The latter may occur if methylene bromide concentrations build up because the mixture temperature drops below

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the threshold reaction temperature (65°C) characteristic of this particular reaction.

(C) After two-thirds of the methylene bromide had been added to the reaction mixture, an additional quantity (20% of stoichiometry) of powdered potassium hydroxide was added. Methylene bromide addition was then continued to completion.

(C) The methylene-O,O'-bis(ethyl acethydroximate) acetonitrile solution was filtered to remove potassium bromide and other solid impurities. The bulk of bis adduct 8, was obtained by stripping the acetonitrile at 50 mm in a rotary evaporator and washing the resultant óil with water.

(C) By-product acetamide from hydrolysis of acetonitrile solvent and decomposition of the bis adduct as well as ethyl acethydroximate constituted the principal impurities in the crude product. The acetamide is removed by water washing and ethyl acethydroximate is removed by fractional distillation at 2 mm through a 1-inch-ID spinning-band column. A more detailed discussion of the bis adduct recovery procedure can be found in the experimental reaction section (K) of this report. Overall yields of 75-80% of the clear colorless isomeric mixture (trans-and anti-oxime structure) of methylene-O, O'-bis(ethyl acethydroximate) were obtained in a series of these large-scale reactions.

(C) STEP 3 - Hydrolysis of methylene-O,O'-bis(ethyl acethydroximate) (8) to methylenedioxyamine dihydrochloride (9) is a simple reaction. The purified bis adduct 8 (10.5 moles) was taken up in approximately six times its own volume of absolute ethanol in a 22-liter flask. To this room-temperature mixture was added, with stirring, 10% in excess of two

equivalents of concentrated hydrochloric acid. The addition of the acid
results in a temperature increase to approximately 50°C. The resultant
white slurry of dihydrochloride 9 and ethanol was stirred overnight. The
precipitated product was filtered, washed with ether and dried. The ethanol
mother liquor was concentrated and a second crop of dihydrochloride collected.
Yields of the fluffy white crystalline salt, m.p. 154-155°C, were generally
greater than 95%.

(C) STEP 4 - Preparation of methylenedioxyamine 14 is carried out on
a somewhat smaller scale than the previous preparations.

(C) Although the shock sensitivity (60 Kg-cm, Closed Cup, Olin
Mathieson Tertia) of methylenedioxyamine is such that a detonation from
shock is a remote possibility, fire or rapid decomposition from an
inadvertently overheated sample of the free amine is a very real danger.

(C) One mole of methylenedioxyamine dihydrochloride was slurried
in a 500 ml of ethanol and a freshly prepared ethanolic-potassium hydroxide
solution (two equivalents) was added carefully with constant stirring until
a pH of eight was indicated by Hydrion paper. The reaction was rapid and
after stirring for a short time, the mixture was filtered, stripped of
ethanol in a rotary evaporator at reduced pressure and fractionally
distilled at minimum pot temperatures through a Spinning Band column at
< 0.3 mm. Methylenedioxyamine, a clear, colorless and somewhat viscous
liquid, was obtained in purities of 99% or better and in yields of 82-86%.

(C) STEP 5 - The preparation of methylenedioxyammonium diperchlorate
(10) is the most hazardous of the synthesis sequence steps.

(C) Methylenedixoyammonium diperchlorate is shock sensitive (E_{50} = 100 Kg-cm). In ethanol solution it also presents a substantial fire hazard. The diperchlorate 10 was prepared in one-pound batches. A solution of methylenedioxyamine (1.63 moles) in 500 cc of absolute ethanol, was cooled while stirring in an ice bath. Concentrated perchloric acid (3.42 moles, 5% excess) was added slowly to maintain the temperature at less than 5°C. The DOAP solution was then transferred to a four-liter erlenmeyer flask containing "Drierite" which had previously been saturated with ethanol. The flask was sealed and the erlenmeyer flask was placed in an ice bath. After standing two hours with intermittent shaking, the DOAP-Drierite mixture was filtered under dry nitrogen and 0.15% by weight of anhydrous sodium perchlorate in solution with absolute ethanol was added to the mixture. The clear DOAP-ethanol solution was partially stripped of ethanol on a rotary evaporator. The stripping operation was stopped at the first signs of crystallization. The remaining ethanol was then allowed to evaporate slowly from the DOAP solution under a blanket of dry nitrogen over a period of 3-5 weeks, while crystallization occurred.

(C) Filtration and ether washing of the resultant crystals under dry nitrogen gave white crystalline DOAP (monoclinic crystals of mixed sizes, some as large as 1/8" x 1/8" x 1") in yields of 50% or 1/2-pound size batches. A second crop of a poor quality DOAP (contained impurities and had decreased thermal stability) could be obtained if the DOAP-ethanol mother liquors were further evaporated under nitrogen. Total yields of 70% could thus be obtained.

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H. DISCUSSION OF SYNTHESIS SCALE-UP

(U) The following discussion includes considerable detail on the problems and solution to the problems for each step as they were encountered in scaling the synthesis sequence from small laboratory equipment to the large laboratory scale process described in Section G and the Experimental Section K.

(U) STEP 1. The synthesis of ethyl acethydroximate (7) can be found in the literature [11], [12] and involves a two-step reaction sequence. During initial preparation of this material on a small scale, a 50-60% overall yield could be realized, although the literature procedure was cumbersome. After the successful synthesis of DOAP and during subsequent scale-up of the synthetic intermediates, it became apparent that the procedure was unsatisfactory for the preparation of ethyl acethydroximate on a large scale.

(U) Several problems were associated with the preparation:

a. The procedure required the isolation and storage of ethyl acetimide hydrochloride (13). This material is bulky and, on a large laboratory scale, was difficult to isolate, dry and store. It is also sensitive to hydrolysis and is hygroscopic.

b. The second part of Step 1, the preparation of ethyl acethydroximate (7), proved very difficult to scale-up because of the heterogeneous nature of the reaction mixture. The mixture consisted of ether, hydroxylamine hydrochloride (solid), ethyl acetimide hydrochloride (solid) and pyridine/pyridine hydrochloride (a heavy sludge), plus the reaction products. The viscosity of the sludge which formed during the reaction made efficient

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stirring of the reaction impossible. An ARC Model 1200 propellant mixer was
used for the reaction during the first large scale-up, and stirring efficiency
was still poor. Temperature control during the reaction was difficult, and
it was later shown that temperatures greater than $0^{\circ}C$ were detrimental to the
reaction. Temperatures encountered in the propellant mixer frequently ranged
as high as $25-30^{\circ}C$.

(U) As a result of inefficient mixing and poor temperature control,
the overall yields of ethyl acethydroximate dropped to 40% during the first
scale-up operation. This fact coupled with the very laborious procedure
led to a process development study.

(U) In an effort to simplify the procedure for making the hydroxi-
mate, it was desirable to rform the preparation of ethyl acetimide hydro-
chloride (13) and the com on of it to hydroximate in the same reaction
vessel. If the heterogeniety of the second reaction mixture could be
eliminated and better temperature control instigated, the yields might be
expected to increase.

(U) The use of ether as solvent by earlier workers[11, 12] reflects
their thoughts on the sensitivity of ethyl acetimide hydrochloride to
hydrolysis. In view of the merits of using water as the solvent, it seemed
reasonable to attempt the reaction in that medium, anticipating that the
rate of hydrolysis might be slower than the rate of hydroximate formation.
In addition, the use of pyridine[9] as the base seemed undesirably messy and
sodium bicarbonate was chosen instead. Potassium carbonate was used by
Houben and Schmidt in 1913.[12]

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(U) Based on these conditions a series of reactions using water as a solvent with only a small amount of ether present were accomplished for the purpose of studying the order of addition of the reaction components and the effect of potassium versus sodium carbonates or bicarbonates. The conclusions were as follows:

1. Hydroximate formation at temperatures 5°C is faster than hydrolysis under acidic conditions.

2. The weaker the base the better the yield, sodium bicarbonate being best.

3. The base should be added last and in the solid phase, incrementally for best yields.

4. A minimum of water as required to dissolve the ethylacetimide and hydroxylamine hydrochlorides should be used. Ethyl acethydroximate is partially soluble in water and it may be partially hydrolyzed or otherwise destroyed under the reaction conditions in the presence of an excess of water. Limiting the quantity of water gives a saturated salt solution which decreases the hydroximate solubility problem. An added advantage of minimizing the quantity of water used is an increase in reaction size in a given size flask.

(C) Confining the two reactions to the same vessel was not a difficult task. The first reaction is carried out quite normally[7, 10] in a 22-liter flask (45 moles). The dry hydrogen chloride gas is added rapidly to the ethanol-acetonitrile solution, as fast as is permitted while maintaining the temperature at $<$ 10°C with a trichloroethane dry-ice bath. The mixture is allowed to stir at 10°C for 4 hours and a 5-liter portion of ether is then added and the mixture stirred for 48-72 hours at room temperature.

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The purpose of the ether is to slurry the ethylacetimide hydrochloride as it begins to precipitate from the reaction mixture. In the absence of ether, the reaction mixture solidifies to an unworkable mass in 48-72 hours.

(C) A cold aqueous solution of hydroxylamine hydrochloride is added to the stirred ethyl acetimide hydrochloride-ether slurry and to this mixture is added incrementally the requisite amount of powdered sodium bicarbonate. The evolution of CO_2 is rapid, after a slight induction period, and the cooling effect of gas generation is sufficient to maintain the temperature of the stirred solution at $0°C$ or below. The stirring rate of this reaction mixture should be very low. Experience has indicated that best yields are obtained if the ether product layer is not dispersed into the aqueous layer. The ether product layer is separated from the aqueous layers at regular intervals during bicarbonate addition in an effort to further minimize the contact of the acidic-aqueous hydrochloride layer with the easily hydrolyzed hydroximate.

(C) The ether-hydroximate solution is dried and stripped of ether to give ethyl acethydroximate containing 5 to 10% ether which is suitable for direct use in Step 3 of the DOAP synthesis sequence. The purity of the final product which permits direct use of the hydroximate-ether mixture in Step 3, is of considerable benefit to the overall yield of the synthesis sequence. Distillation of highly impure ethyl acethydroximate was tedious and frequently disastrous in that catalytic decomposition of the material occurred at elevated pot temperature ($>80°C$). In addition, during one distillation, 5 liters of 90% product was lost with violent

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gassing over a period of 2-3 minutes, when upon observation that catalytic decomposition and gassing was occurring, the vacuum was broken and air entered the system.

(C) <u>STEP 2</u> - The success which was associated with the first attempt at preparation of methylene-0,0'-bis(ethyl acethydroximate), Section E, predicted a minimum of difficulty in scaling up this reaction. On a larger scale, however, several problems were revealed which were readily solved but were critical in terms of obtaining satisfactory yields.

(C) The reaction of potassium hydroxide with ethyl acethydroximate is slow at room temperature, probably because of the low solubility of the potassium salt in acetonitrile. To speed the process of salt formation, the acetonitrile was heated slowly while the powder potassium hydroxide was being added. As the temperature of the acetonitrile mixture approaches 50°C, the rate of formation of the potassium ethyl hydroximate increases and the resultant exotherm can cause boil-over of the reaction mixture. Caution must be exercised in performing this reaction and provisions for both heating and cooling the acetonitrile reaction mixture must be at hand. One convenient method of cooling the reaction mixture contained in a 50-liter four-neck flask, was to pass trichloroethylene from a dry-ice bath through a cold finger immersed in the stirring mixture.

(C) A second problem, requiring the use of good temperature control, in the preparation of methylene-0,0'-bis(ethyl acethydroximate) was encountered at a point later in the reaction procedure.

(C) The reaction of methylene bromide with potassium ethyl

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acethydroximate has an inherent induction period at temperatures below 68°C. Consequently it is necessary to maintain a temperature of no less than 68°C in the reaction mixture. At temperatures below this, an accumulation of methylene bromide may lead to a runaway reaction, since, once initiated, the displacement reaction is very rapid and exothermic. External cooling of the reaction mixture to maintain a temperature below 78°C (b.p. of acetonitrile) on the other hand, is necessary, if a satisfactory rate of addition of methylene bromide is to be maintained.

(C) The reaction mixture workup presented no problem on a very small scale. Filtration of the inorganics and purification of the crude product by distillation gave excellent yields. With scale-up to the 5-mole level, problems developed as follows. Distillation of the crude methylene-O, O'-bis(ethyl acethydroximate) at 2-3 mm and 66-70°C led to decomposition of the product to form acetamide. Acetamide distills at slightly lower temperatures than the desired material and solidifies in the condenser and receiver of the distillation apparatus.

(C) The problem was corrected by washing the crude methylene-O, O'-bis(ethyl acethydroximate) as an ether solution after removal of the acetonitrile. This presumably removed potassium bromide and potassium hydroxide as well as any acetamide (water soluble) which might have been formed during the reaction at 70°C.

(C) On a still larger scale (30 moles) the presence of acetamide was more pronounced. Upon stripping the acetonitrile from the filtered reaction mixture, a two-phase liquid system was obtained. The upper pale

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yellow layer was product while a lower dark brown layer was identified by infrared spectra as acetamide with some impurities.

(C) Purification of the bis adduct from large scale reactions required a phase separation of the two liquid phases followed by water washing of the product layer to remove dissolved inorganic materials and acetamide. Distillation, provided a thorough water washing has been accomplished, provides a pure product. A fore cut, of unreacted ethyl acethydroximate, is usually obtained followed by the desired material.

(C) Methylene-0,0'-bis(ethyl acethydroximate) is a colorless liquid having a strong sickening odor. A well-ventilated work area and good hood facilities are recommended while handling this material as it can cause headaches, stomach upset and temporary amnesia.

(C) STEP 3. The hydrolysis of methylene-0,0'-bis(ethyl acethydroximate) (8) with concentrated hydrochloric acid in ethanol to give methylenedioxyamine dihydrochloride (9) is a clean reaction. Diglyme or glyme have been used, and facilitate the hydrolysis to some extent. However, these solvents are difficult to remove from methylenedioxyamine dihydrochloride (9) (DOACl) and interfere with the Step 4 preparation of methylenedioxyamine (14).

(C) The purification of the dihydrochloride prepared from reasonably pure methylene-0,0'-bis(ethyl acethydroximate) is unnecessary unless higher boiling solvents such as diglyme or glyme are used. DOACl is readily recrystallized from water if necessary and material of high purity can be readily obtained.

(C) STEP 4. The preparative procedure for methylenedioxyamine is critical and must be followed specifically. The addition of the ethanolic

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potassium hydroxide solution to the methylenedioxyamine dihydrochloride-
ethanol slurry must be done with vigorous stirring and careful monitoring
of the pH with Hydrion paper to prevent addition of an excess of base.
If these precautions are not observed and an excess of base used or pellets
added inst~ . . ~ ethanolic potassium hydroxide, the yield of DO is reduced
substantially.

(C) Methylenedioxyamine is isolated from the ethanol-potassium chloride
slurry by filtering and stripping the ethanol at reduced pressure. The crude
product thus obtained is then distilled carefully at less than 0.3 mm
through a Spinning Band distillation column or through a large-bore (1 inch)
Vigreaux column.

(C) Distillation of crude methylenedioxyamine is difficult if
certain precautions are not taken. The free amine will decompose slowly
with off-gassing, during distillation, due to the catalytic effect of
impurities in the crude material. Maintaining a low pot temperature during
distillation will curtail this decomposition. This, in turn, requires a
good vacuum in the pot. A large-bore distillation column (1 inch, ID) helps
to minimize the pressure differential between the pot and top of the
distillation column. A 5/8-inch Spinning Band distillation column slightly
modified to improve vacuum in the pot (large vacuum takeoff on head and
additional holes in drip tip at bottom of column) was also used with success.

(C) Best yields of methylenedioxyamine were obtained when the
distillation was carried out slowly (very little reflux) with pot

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temperatures below 70°C.

(C) STEP 5. In carrying out the preparation of methylenedioxyammonium perchlorate (10) according to the procedure as described in Sections E and K of this report, caution must be exercised in adding the concentrated perchloric acid to the methylenedioxyamine-ethanol solution. Considerable heat is evolved in this process and aside from the explosive nature or fire hazards of the mixture, excess heat is detrimental to the quality of perchlorate eventually isolated. It is also of considerable importance that the heat generated during the drying process with "Drierite" be removed by cooling the mixture in an ice bath. In general, the perchlorate-ethanol solution should not be exposed to elevated temperature ($> 20°C$). At temperatures above this and even at lower temperatures, a yellow coloration of the solution develops, signifying decomposition of the perchlorate and/or dehydration of the solvent ethanol.

(C) The process of drying the methylenedioxyammonium diperchlorate-ethanol mixture with Drierite is troublesome (difficulty is encountered in filtering the mixture) and costly (7.5 lbs of Drierite per pound batch of DOAP). The choice of calcium sulphate as the drying agent seems poor in terms of the weight-to-weight efficiency of water absorbed (6 g H_2O/ 100 g $CaSO_4$). Its effectivenss in removing water, however, is demonstrated by the anhydrous nature of ethanol stripped from the perchlorate-ethanol product mixture after drying ($< 0.05\%$ water by Carl-Fisher Reagent analysis). Several drying agents ($MgSO_4$, $CaCl_2$) were considered but the probable solubility of these in the DOAP-ethanol solution discouraged their use.

One other drying agent was tested. Sodium sulfate was used in a manner similar to the "Drierite". The resultant DOAP was of fair quality, being obtained in unusually large crystals, and it appeared to be less hydroscopic than previous DOAP samples. Analysis indicated the absence of sulfate ion, but approximately 0.48% of sodium ion was present in the material, presumably as sodium perchlorate. It was subsequently found that the addition of 0.02 - 0.4% of anhydrous sodium perchlorate resulted in increased growth and a more rapid growth of relatively large crystals, when compared to those obtained from a non-sodium-perchlorate-treated, ethanol solution of DOAP.

(C) Although the mechanism through which sodium operates to a¹⁺ in crystal growth is not understood, the DOAP obtained is of better quality (high m.p., better long-term storage stability and less hygroscopic). It is currently standard procedure to add 0.15% by weight of anhydrous sodium perchlorate to the ethanol-DOAP solution just prior to the stripping operation.

(C) The crystallization of DOAP from the ethanol solution even when sodium perchlorate has been added, is rather slow (1 month under a slow stream of nitrogen) if larger size crystals are desired. The use of methanol as a crystallizing solvent is currently under study and results are not particularly encouraging. Lack of sites for dehydration in methanol as opposed to ethanol is preferable in view of the acidic nature of the DOAP solution. Higher yields of DOAP resulting from a more stable solvent system (i.e., less water and organic impurities to complicate the crystallization process) might be expected with decreased crystallization time

because of methanol's higher volatility. However, the solubility of DOAP in methanol is greater than in ethanol and crystallization is not as complete.

(U) In view of the difficulties with ethanol and methanol, a few other solvents were studied for the crystallization of DOAP. Nitromethane containing 5% methanol was thought, at one point, to be an excellent solvent for the crystallization of DOAP. It was later found that the DOAP was obtained as a 1:1 adduct with nitromethane. The nitromethane was quite easily removed in vacuo from the perchlorate but the DOAP remaining was amorphous and very sensitive to moisture and autocatalytic decomposition.

(U) 3,3,3-Trifluoroethanol was used as a solvent without success, but an adduct with DOAP was observed at temperatures below $0°C$.

(C) The quality (m.p., stability and hydroscopicity) of DOAP obtained by the current method is difficult to control and depends heavily on the stoichiometry of methylenedioxyamine perchloric acid titration. Under-titration of the DO-ethanol solution, as a result of perchloric acid lost on "Drierite", or to dehydration and reaction with ethanol, results in the contamination of the product with the monoperchlorate of methylenedioxyamine. This is turn causes fluctuations in melting point, hygroscopicity and stability. In general, slight under-titration tends to produce a higher melting DOAP which is generally more stable than stoichiometrically titrated DOAP.

(C) An increased stability in monoperchlorate-contaminated diperchlorate is not unexpected if the autocatalytic decomposition of DOAP

is considered. The decomposition is initiated by loss of perchloric acid [3] and continues to the formation of foramide. This process is observed as a wetting of the DOAP crystals and a cohesive appearance of the solid. The decomposition rate increases rapidly once the solid becomes sticky. It is reasonable to assume that the presence of methylenedioxyamine mono-perchlorate would serve to scavenge perchloric acid to some extent and thus slow the overall decomposition of DOAP (See Section J, Page 27).

(C) Step 5 will require some process development study before a uniform quality of DOAP can be regularly produced. Process improvement might include any or all of the following: a new solvent for the crystalli-zation of DOAP, a new method of removing water from the titration solution, a more rapid crystallization process which will still provide larger crystals, a reasonable explanation of the effects of sodium perchlorate or finally a new method of preparation such as a metathesis reaction to prepare methylenedioxyammonium diperchlorate.

I. CHARACTERIZATION OF METHYLENEDIOXYAMINE

(C) Physical Properties - Methylenedioxyamine is a slightly viscous liquid with a refractive index $n_D^{28} = 1.4625$, which is thermally stable when pure to 170°C. At temperatures above 170°C, detonation can occur. Its melting point is approximately 0°C, however, it tends to form a viscous liquid or glass when cooled below that temperature and it usually crystallizes only if considerable effort is expended to induce crystallization. The free amine, which has a slight musty odor, can be distilled (b.p. 47-50°C at 0.3 mm) if the distillation is carried out at minimum pot temperature ($< 70°C$).

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Inorganic impurities present in the crude amine and possibly metals such as monel or platinum will catalyze its decomposition in the distillation apparatus as evidenced by an inability to maintain a low pressure (i.e., slow gassing).

(C) Hazardous Properties. Methylenedioxyamine is a monopropellant and burns in the atmosphere with a nearly invisible blue flame leaving no residue. It is shock sensitive, detonating in a close cup at an E_{50} of approximately 60 Kg-cm. With certain precautions, this material can be safely prepared and stored in the laboratory. These precautions include: (1) careful control of distillation pot temperature, i.e., the temperature of the distillation pot should never exceed 75°C; (2) a hot distillation pot should never be exposed to the atmosphere as fire can result from such exposure.

(C) At present methylenedioxyamine holds promise as a new energetic monopropellant. A program for its evaluation is currently being planned In-House at AFPPL.

(C) Heat of Formation. The heat of formation of methylenedioxyamine was originally estimated as -20 Kcal/mole. Experimental determination of this number by Dow Chemical Company under Contract F04611-67-C-0025 in their Thermochemical Laboratory placed it at -22 Kcal/mole.

5. CHARACTERIZATION OF METHYLENEDIOXYAMMONIUM DIPERCHLORATE (DOAP)

(C) Physical Properties. Methylenedioxyammonium diperchlorate is a white crystalline solid with a density of 2.00, which melts (or decomposes?) when pure at 113-115°C. It melts with decomposition to hydroxyammonium

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perchlorate and formamide[3] giving a clear liquid which does not solidify
on cooling. The temperature at which the perchlorate melts or decomposes
is thought to be dependent on the presence of methylenedioxyammonium mono-
perchlorate. Diperchlorate samples melting as high as 128°C and as low as
107°C have been obtained. The carbon, hydrogen, nitrogen and perchlorate
elemental analyses for these materials were within reasonable experimental
error for the diperchlorate, however, the samples low in perchlorate content
usually corresponded to higher melting diperchlorate samples, while high or
correct perchlorate analysis tended to give lower melting solids.

(C) The melting point of a material identified by analysis as the
monoperchlorate salt of methylenedioxyamine was 134°C. This, coupled with
the observation that a low perchlorate content in the diperchlorate salt
corresponds to a higher melting point, suggests that the presence of the
monoperchlorate in the crystal lattice of the diperchlorate increases the
thermal stability of the diperchlorate. In view of the proposed decomposition
mechanism[3] (Equation XVIII) of the diperchlorate, it is likely that this is
true. The perchloric acid liberated in the first step of the decomposition
should be less available for catalysis of the internal displacement-
rearrangement step of the decomposition, if additional basic groups are
present in the crystal lattice.

(C) (XVIII) <u>PROPOSED THERMAL DECOMPOSITION MECHANISM OF DOAP.</u>
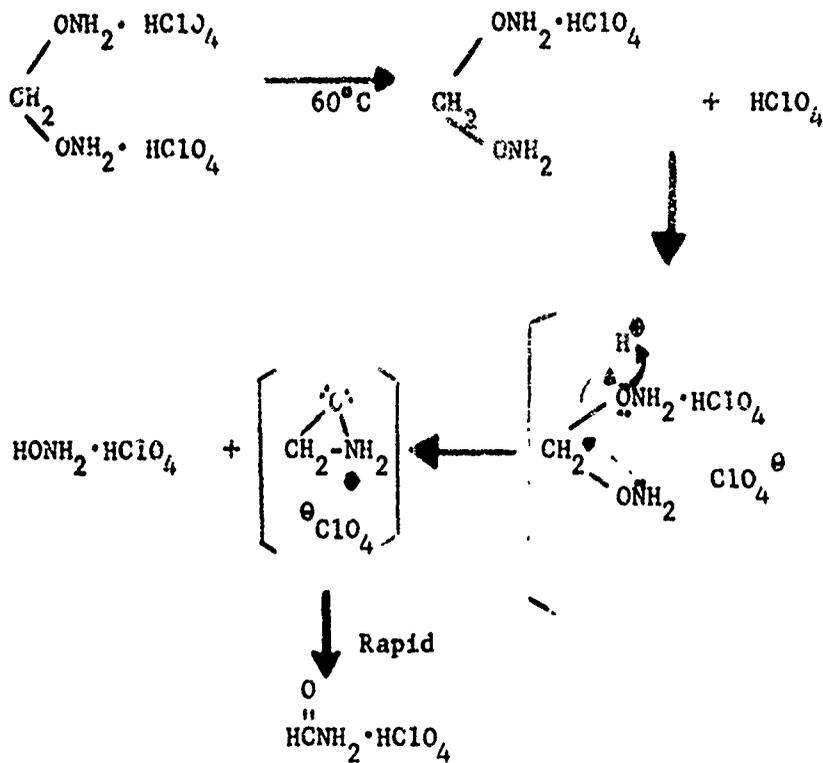
(C) The X-ray structural analysis of methylenedioxyammonium diperchlorate

has been completed [2] pending further refinement of the structure using

new equipment. The perchlorate crystallizes in a single form, monoclinic,

with a Space Group $P2_{1/N}$. A stereographic view of the structure as

determined to date is shown in Figure 1.
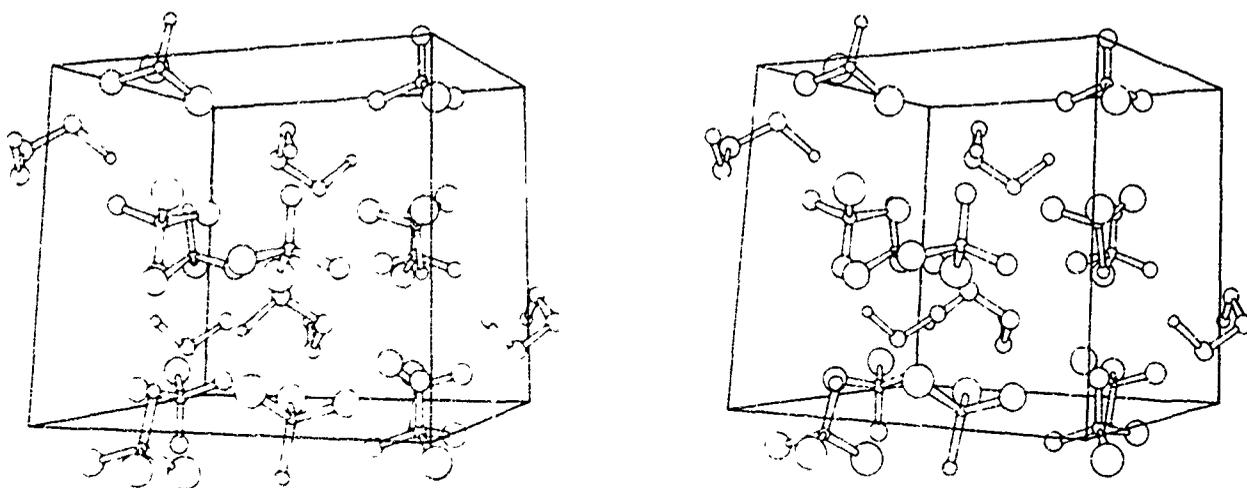
(C) FIGURE 1. Stereographic View of the Crystal Structure
of Methylenedioxyammonium Diperchlorate

(C) <u>Thermal Stability</u>. A differential thermogram of methylenedioxy-

ammonium diperchlorate is shown in Figure 2. As previously discussed,

decomposition occurs during or shortly after the solid-liquid transition.

(C) <u>Hazards</u>. Methylenedioxyammonium diperchlorate is shock sensitive

and friction sensitive. The E_{50} value for the diperchlorate as determined

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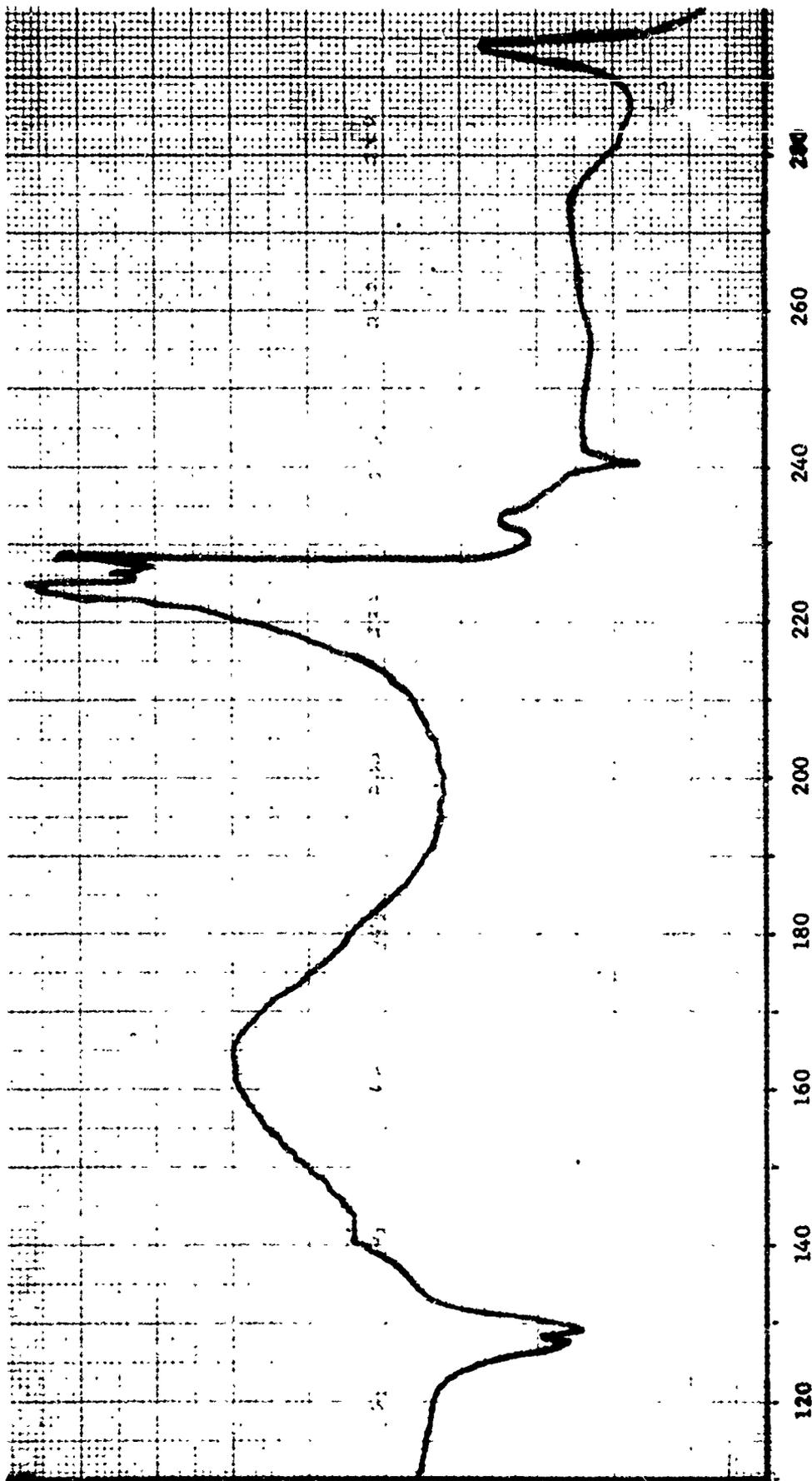
Figure 2. Differential Thermal Analysis Trace for DOAP. ΔT 1°C/in; Rate 10°C/min.

on an Olin Mathieson Impact Tester was 110 Kg-cm. The Esso Screw Type
Friction Tester gave a negative test with silicon carbide and an intermittent
positive test with diamond grit.

(C) A somewhat better indication of the shock-friction sensitivity
characteristics of the diperchlorate obtained when it was ground with a mortar
and pestle, porcelain on porcelain.   Frequent local detonations occurred
under these conditions with a pop or snap. The detonations were usually
small and did not propagate through the bulk of material. If a teflon
pestle was substituted for the porcelain pestle, no detonations were
observed even under adverse conditions, i.e., dropping the pestle from a
height of one to two feet into the mortar or grinding vigorously.

(C) In general DOAP can be handled in the laboratory. Care must be
exercised to minimize the hazards of fire and the solid material should not
be exposed to such things as ground-glass stoppers.

(C) <u>Heat of Formation</u>. The heat of formation of methylenedioxy-
ammonium diperchlorate was estimated for purposes of theoretical Isp
calculations as approximately -100 Kcal/mole. This value has since been
determined as -103 Kcal/mole by Dow Chemical Company under Contract F04611-
67-C-0025   at their Thermo Chemical Laboratory.

K. <u>EXPERIMENTAL PROCEDURES</u>

(C) Infrared spectra (ir) were obtained on a Beckman IR-5A spectrometer.
Nuclear magnetic resonance (nmr) spectra were recorded using a varian
DA-60-IL spectrometer. Differential thermal analysis was accomplished
using a DuPont Model 900 Differential Thermal Analyzer. Gas chromatographic

analyses of samples were performed on a Beckman/GC2A, using a 1/4-inch teflon column 18 inches in length and packed with 5% 9N9 Dowfax on Fluoro Pak-80 (20-40 mesh) at designated temperatures. Microanalyses were performed by the Chemical and Materials Branch (RPCC) of AFRPL using a Perkin Elmer 240 Elemental Analyzer. Perchlorate analyses were performed by titanium hydride reduction[13] or potentiometric titration with tetraphenylarsonium chloride[14]. Melting points were taken on a Thomas-Hoover melting point apparatus.

(C) Ethyl Acethydroximate. The following experimental descriptions are for typical reactions as performed for the laboratory scale-up project. In a 22-1, three-necked, round-bottomed flask equipped with a mechanical stirrer, gas inlet tube, and a thermometer were placed 1845 g (45 moles, 2350 cc) of dry acetonitrile (Note 1) and 2148 g (46.7 moles, 2736 cc) absolute ethanol. The mixture was cooled to -5°C and 1722 g (47.2 moles) gaseous hydrogen chloride was added as rapidly as possible (approximately two hours) while maintaining the temperature of the reaction mixture below 10°C. The reaction mixture was allowed to stir for 4 hours at 10°C. Five liters of anhydrous ether was added and stirring continued for 48 hours at 10°-25°C (Note 2) during which time white crystalline ethyl acetimide hydrochloride precipitated. Overall yields of ethyl acethydroximate improved if this reaction was allowed to stand for a total of 72 hours. To the ether slurry of ethyl acetimide hydrochloride was added a 0°C solution of 3158 g (45.5 moles) hydroxylamine hydrochloride in 6750 cc water. To this two-phase mixture was then added portionwise with gentle stirring 4158 g (39.5 moles) of powdered sodium bicarbonate, at such a rate that the mixture did not foam out of the

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flask while maintaining the temperature at $0°C$ (Note 3). At periodic
intervals during the addition, part of the top ether layer was drawn off;
any aqueous solution that was inadvertently transferred with the ether
layer was separated and returned to the reaction flask. Fresh ether was
then added to the reaction mixture and addition of bicarbonate was continued.
After the addition was complete (approximately 2 1/2 hours), the water layer
was extracted with five 800-cc portions of ether, and the ether solutions
were combined and dried over anhydrous sodium sulfate. Ether was removed
(Note 4) in vacuo at 70 mm on a rotary evaporator to give 4179 g of product
mixture which was 91% (82% overall yield) ethyl acethydroximate and 9% ether
by gas chromatographic analysis. This material was suitable enough for use
in Step 2 without further purification. For infrared and nmr spectra of
purified samples, see Appendix.

NOTES: 1. Analytical reagent material from Matheson, Coleman and
Bell was suitable.

2. If stirring was continued for only 24 hours, the yield was
reduced 10%.

3. The evolution of CO_2 was usually sufficient to maintain
the temperature at $0°$ without external cooling. If the reaction was
allowed to proceed at $10-15°$, the yield was decreased by 10%.

4. This ether was recycled in subsequent preparations.

(C) <u>Methylene-0,0'-bis(ethyl acethydroximate)</u> - To a 50-1, four-
necked, round-bottom flask (equipped with a mechanical stirrer, two cold
fingers that extended nearly to the bottom of the flask, a thermometer and

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an addition funnel with pressure equalizing side arm) were added 8 gallons of acetonitrile and 6840 g of a 90.5% ether solution of ethyl acethydroximate (60 moles). To this stirred mixture was added 3950 g of 85% powdered potassium hydroxide (60 moles) and the mixture heated carefully to 68°C (Note 1). At this point heating was discontinued and 5836 g (33.4 moles) methylene bromide were added with rapid stirring at such a rate as to maintain a temperature of 70±1°. The reaction was quite exothermic and it was necessary to keep a continuous flow of 0°C freezing mixture through the immersed cold fingers in order to maintain a satisfactory addition rate of methylene bromide. After about two-thirds of the methylene bromide had been added, an additional 600 g (9.1 mole, 15% excess) powdered 85% potassium hydroxide were added and the addition of methylene bromide continued. After the addition was complete, (approximately 4 hours), stirring was continued for one hour and then the acetonitrile solution was removed by vacuum transfer through a fritted gas dispersion tube. The remaining solids were dissolved in 14 liters water and the solution extracted with five 750 ml portions of ether; the ether solutions were combined, dried over sodium sulfate, and set aside. Acetonitrile from the reaction solution was removed _in vacuo_ at 50 mm with the aid of a rotary evaporator (Note 2) to give an oily product which separated into a lower layer of dark brown oil that solidified rapidly. (This lower layer was assumed to be mainly by-product acetamide (Note 3) and an upper yellow oil assumed to be mostly desired product. The upper layer was dissolved in an equal volume of ether and extracted with three portions of water (approximately 800 ml water per

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wash per 4.5 l total ether solution). The combined water washes were extracted with two portions of ether (approximately 600 cc ether per wash per 4 l water). The bottom dark layer was dissolved in 4 to 5 times its volume of water and extracted 3 times with ether (approximately 600-800 cc per wash per 4.5 l of solution). All of the ether solutions were combined, dried over sodium sulfate and the ether was removed _in vacuo_ at approximately 70-100 mm with the aid of a rotary evaporator (Note 2) to give 5935 g of a light yellow oil (Note 4) that was 88.1% product and 10% ethyl acethydroximate by gas chromatographic analysis at $130^\circ C$ for a total overall yield of 80%. Several runs were combined and fractionated _in vacuo_ removing a forerun of ethyl acethydroximate to give a 75% isolated yield of isomeric product boiling between $66-70^\circ$ @ 2 mm: $\lambda_{max}^{film} \mu$ 6.11 (s), 11.35 (s); nmr ($CDCl_3$) τ 8.77 and 8.70 (overlapping triplets, 6H, $-CH_2C\underline{H}_3$), 5.97 and 5.89 (overlapping quartets, 4H, $-C\underline{H}_2-CH_3$), 4.72 and 4.69 (singlets, 2H, $-OCH_2O-$). See Appendix for spectra. Anal. Calculated for $C_9H_{18}N_2O_4$: C, 49.53; H, 8.31; N, 12.83; Found: C, 49.0; H, 8.3; N, 12.8.

NOTES - 1. Powdered potassium hydroxide could be conveniently prepared by grinding the commercial pellets in a Waring commercial blender at high speed for no more than 30 seconds and sieving through a Number 10 sieve. All operations were carried out in a nitrogen dry box. Addition of the potassium hydroxide powder and subsequent heating of the reaction mixture must be accomplished with care to avoid overheating (boiling) the reaction mixture, due to the exothermic nature of the potassium salt formation.

2. A Buchi rotary evaporator, through the condenser of which

was circulated a freezing mixture of trichloroethylene-dry ice (for ether) or ice water (for acetonitrile), was found to be most convenient for this operation.

    3. Acetamide had been separated and characterized from previous small-scale preparations.

    4. All operations involving the product, methylene-0,0'-bis (ethyl acethydroximate) should be carried out in good ventilation. Even a brief exposure to its vapors may produce a noticeable feeling of lethargy and nausea. On one occasion one experimenter suffered a temporary amnesia after a prolonged exposure.

    (C) <u>Methylenedioxyamine dihydrochloride</u> - To a 22-1 three-necked flask equipped with a mechanical stirrer and thermometer were added 13.7 1 of absolute ethanol and 2290 g (10.5 moles) of methylene-0,0'-bis(ethyl-acethydroximate). To the stirred reaction mixture were added, in a thin stream, 1830 cc (22 moles, $\approx 10\%$ excess) concentrated hydrochloric acid. The addition was accompanied by a temperature rise to 50°C. The mixture was allowed to stir overnight, and the precipitated product then filtered, washed with 2 gallons absolute ether and dried in air, to give 1446 g of product as a white powder, m.p. 154-155°C. An additional 116.5 g of product precipitated from the filtrate on standing to give an overall yield of 97.5%: λ_{max}^{KBr} μ 3.82(s), 10.02(s); nmr (H$_2$O)Υ 4.95 (singlet, 6H, -ONH$_3^+$), 5.57 (singlet, 2H, -OCH$_2$O-). See Appendix. Anal. Calculated for CH$_8$N$_2$O$_2$Cl$_2$: C, 7.95; H, 5.30; N, 18.55; Found: C, 8.28; H, 5.08; N, 18.30.

(C) <u>Methylenedioxyamine</u> - To a 2-1 beaker were added 137.1 g (0.91 mole) of methylenedioxyamine dihydrochloride and 500 ml of absolute ethanol. To this stirred slurry an ethanol-potassium hydroxide solution (freshly prepared from 132 g of 85% (2.0 mole) potassium hydroxide and 500 ml of absolute ethanol) was added until a pH of eight was indicated by Hydrion paper. (Note 1). The reaction mixture was filtered and ethanol removed <u>in vacuo</u> using a rotary evaporator. The residue was distilled <u>in vacuo</u> through a Spinning Band to give 60.3 g (84.6%) of a pure (99.1%, glc.), colorless product, b.p. 47-50°C @ 0.3 mm (Note 2): $\lambda_{max}^{film}\mu$ 6.31 (s), 10.05 broad (s); nmr (DMSO-d_6) τ 4.65 (singlet, 2H, -CH$_2$-), 6.08 (singlet, 4H, -ONH$_2$). See Appendix for complete spectra. Anal. Calc'd for C CH$_6$N$_2$O$_2$: C, 15.4; H, 7.59; N, 35.9; Found C, 15.6; H.8; N, 35.7.

<u>NOTES</u> 1. The order of addition is very important and the potassium hydroxide must be totally dissolved. Any variation from this procedure gives much reduced yields.

2. Some difficulty was encountered in achieving rapid reflux and the best yields were obtained if the distillation was carried out slowly at minimum pot temperatures and pressures. Also there was a variation in head temperature with distillation rate. However, analyses for various lots of product were satisfactory in every case.

(C) <u>Methylenedioxyammonium diperchlorate</u> - To 500 cc of anhydrous ethanol were added 127 g (1.63 moles) of methylenedioxyamine (99% pure by g.l.c.) and the mixture was cooled to 0°C. To this mixture were added dropwise over a 1-hour period, 486 g of 70% perchloric acid (3.42 moles,

5% excess). The temperature of the reaction mixture was maintained at

5°C during the addition of perchloric acid. A white precipitate, formed

during the initial stages of addition, dissolves slowly giving a clear

solution after the addition is complete. The resultant "wet" ethanol

diperchlorate mixture was then poured into a 4-1 erlenmeyer flask cooled

in an ice bath and containing 7.5 lbs of Drierite previously saturated with

anhydrous ethanol. This Drierite product mixture was allowed to stand in

an ice bath for 2 hours during which time it was shaken 2-3 times. Filtration

of the mixture under N_2 and filtration of the Drierite wash (2-1000 ml

portions of anhydrous ethanol) gave approximately 3.1 l of clear, pale

yellow diperchlorate ethanol solution. To this solution was added 0.05%

by weight of anhydrous sodium perchlorate in solution with 10-15 cc of

absolute ethanol. (Note 1). The resultant solution was partially stripped

in vacuo at room temperature to give a pale yellow slightly viscous solution

which contained just a few crystals of methylenedioxyammonium diperchlorate.

(Note 1). The solution was placed (all handling done under GN_2) in a

crystallizing dish and partially covered with a sheet of polyethylene to

control the evaporation rate. The dish was placed in a dry-nitrogen purged

glove bag and stirred infrequently (once every 2-3 days).

(C) The resultant crystals were filtered from the mother liquor after

3-6 weeks and washed with ether. After drying, 229 g (50%) white crystalline

methylenedioxyammonium diperchlorate was obtained, m.p. 119-124°C (Note 2);

$\lambda \, _{K_{Br}}^{max} \, \mu$ 5.4 (m), 11.42 (s); nmr (DMSO-d_6)γ 5.37 (singlet, 2 H, -OCH$_2$O-),

9.03 (singlet, 6H, -ONH$_3$ClO$_4$). Anal: Calculated for CH$_8$O$_{10}$N$_2$Cl$_2$; C, 4.31;

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H, 2.87; N, 10.03; Cl⁻, 25.4. Found: C, 4.61; H, 274; N, 10.14; Cl⁻, 27.9.

(C) Further recrystallization of the mother liquor gave a poor quality diperchlorate but increased the yield of crystalline material to 70%.

NOTE: 1. The addition of sodium perchlorate appears to aid (through some unknown mechanism) the growth, growth rate and stability of diperchlorate crystals.

2. If stripping is carried beyond the formation of just a minimal number of crystals, the resultant crystallization will be too rapid and the crystal size of the diperchlorate will be unsatisfactorily small.

3. The melting point of methylenedioxyammonium diperchlorate which approaches theoretical perchlorate content is approximately 113-115°. The presence of the monoperchlorate of methylenedioxyamine in the diperchlorate generally results in a higher melting material (116-128°). Since the monoperchlorate is also an energetic material, the presence of some of this material is not necessarily detrimental and may even be of considerable benefit, resulting in decreased acidity, increased melting point and improved compatibility and stability.

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APPENDIX

INFRARED AND NUCLEAR MAGNETIC

RESONANCE SPECTRA
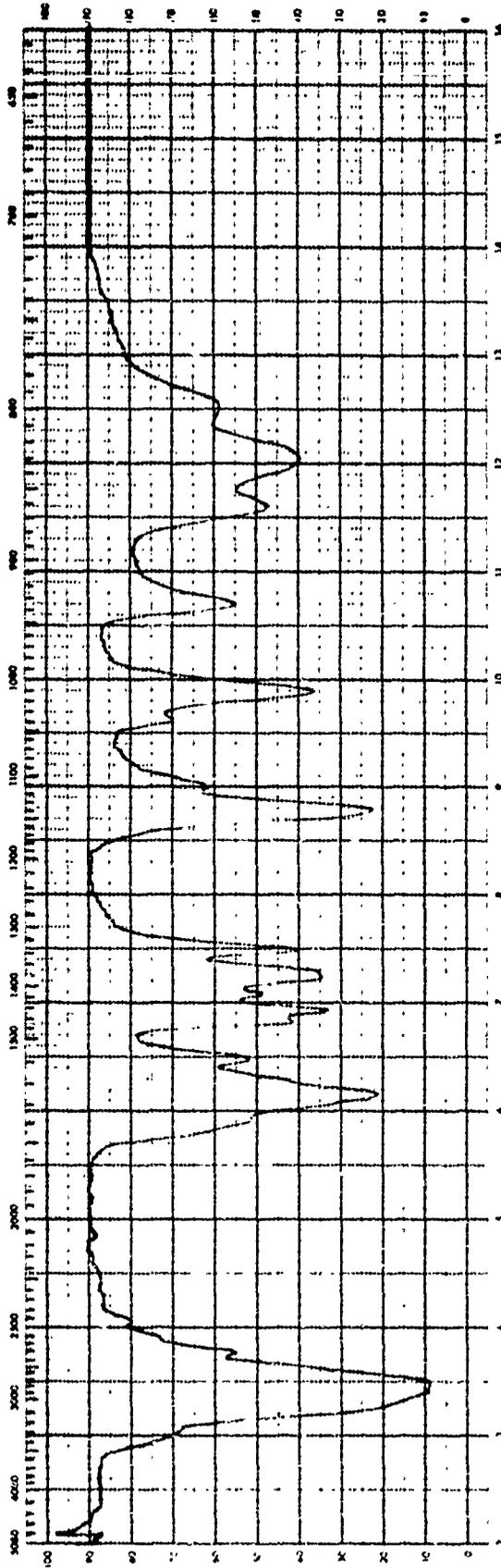
Figure 3. Ethylacetimide Hydrochloride
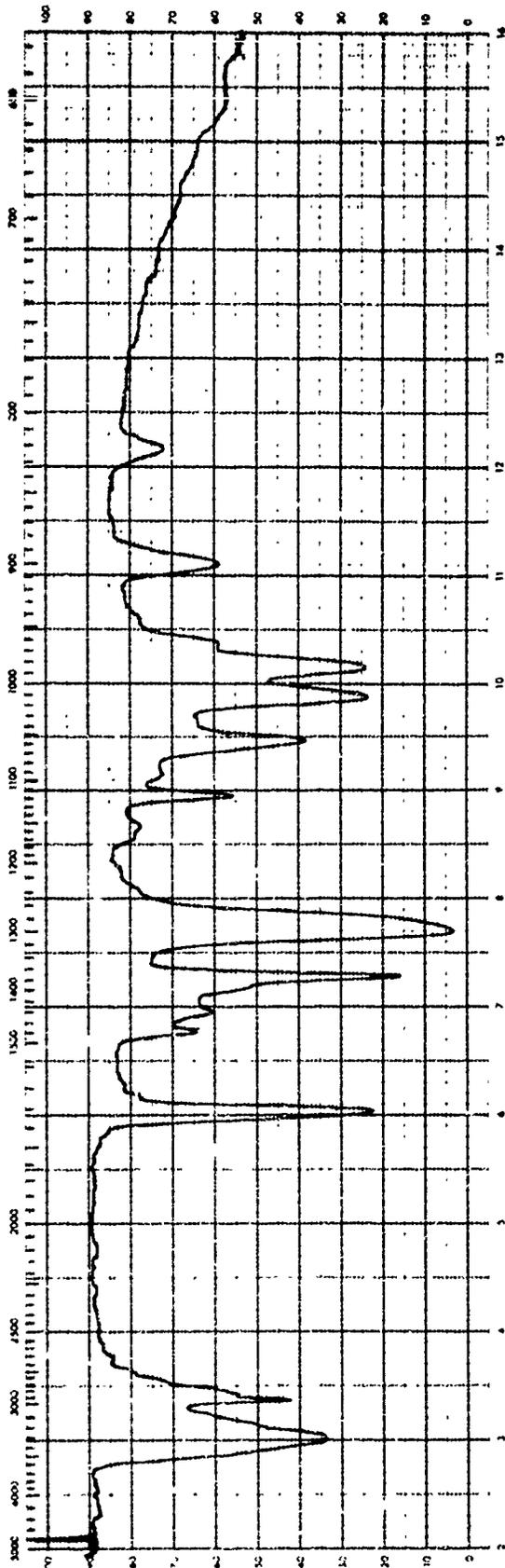
Figure 4. Ethyl Acethydroximate
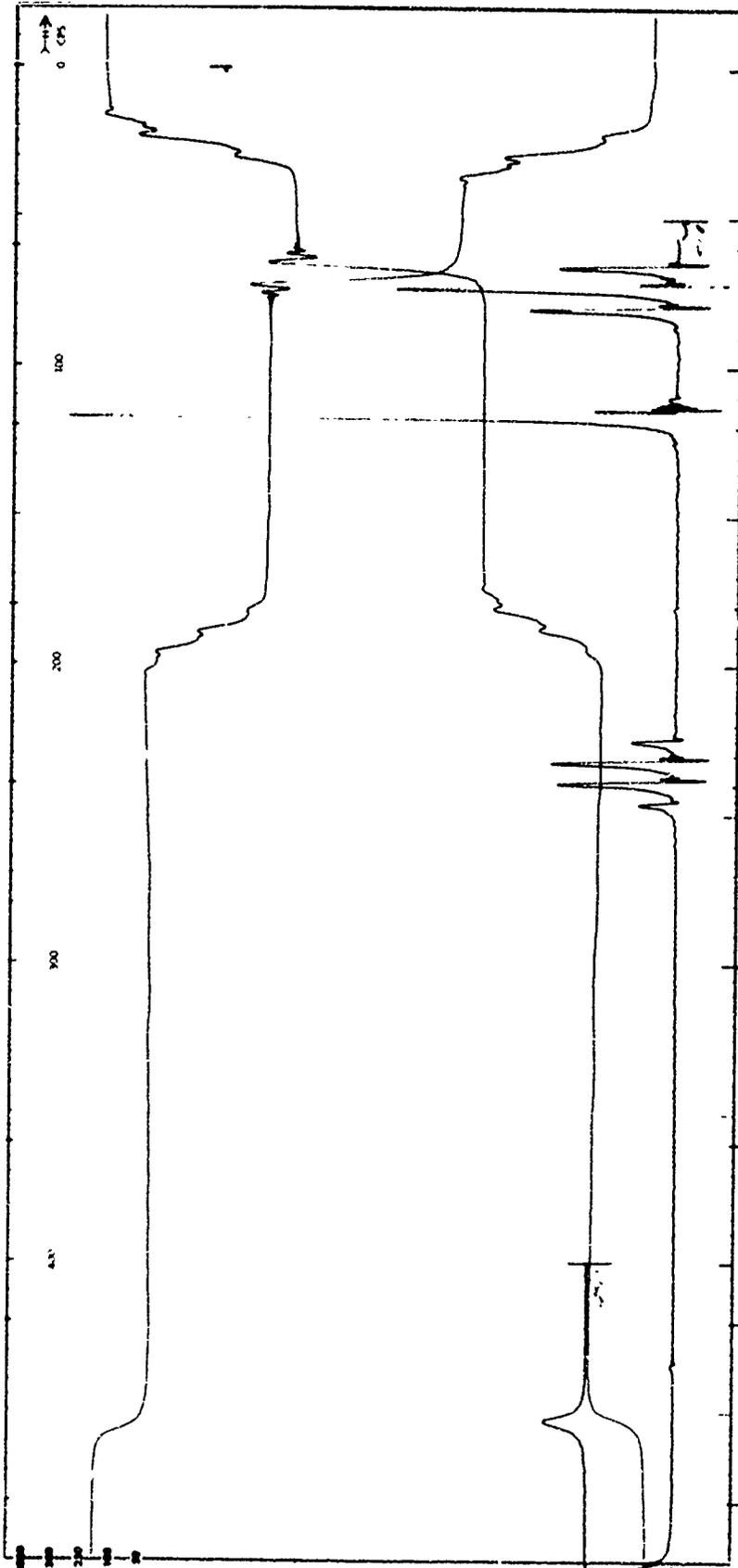
Figure 5. Ethyl Acethydroximate

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(This page is unclassified)
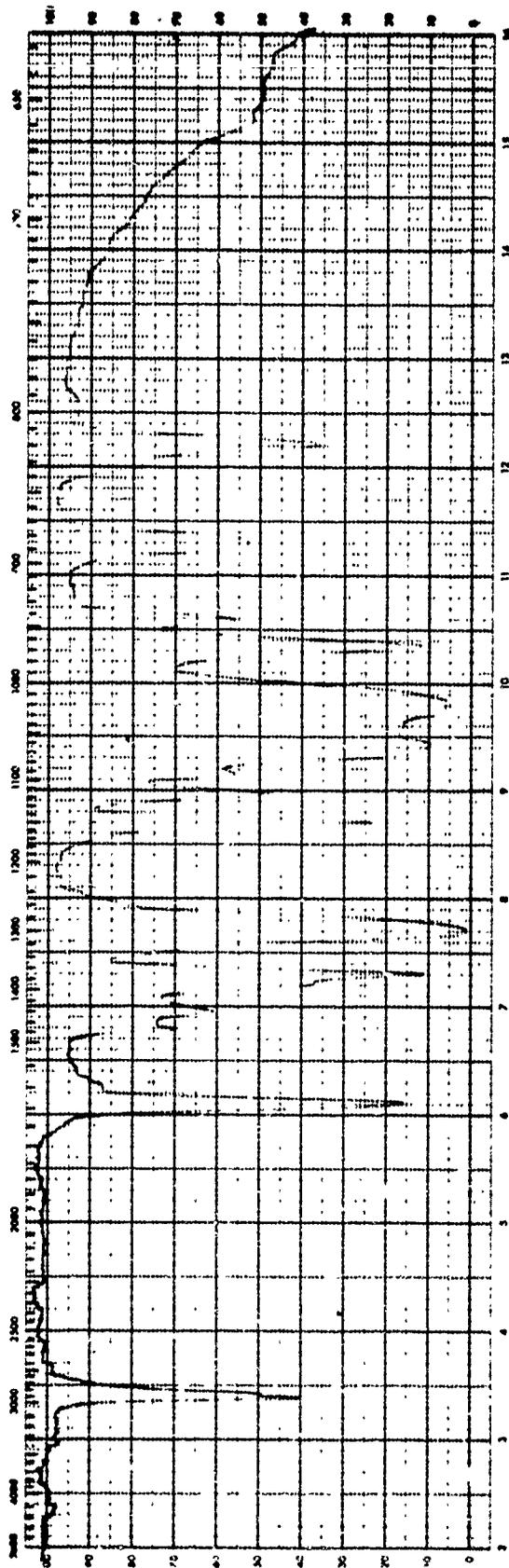
(C)   Figure 6.   Methylene-O,O'-bis(ethylacethydroximate)
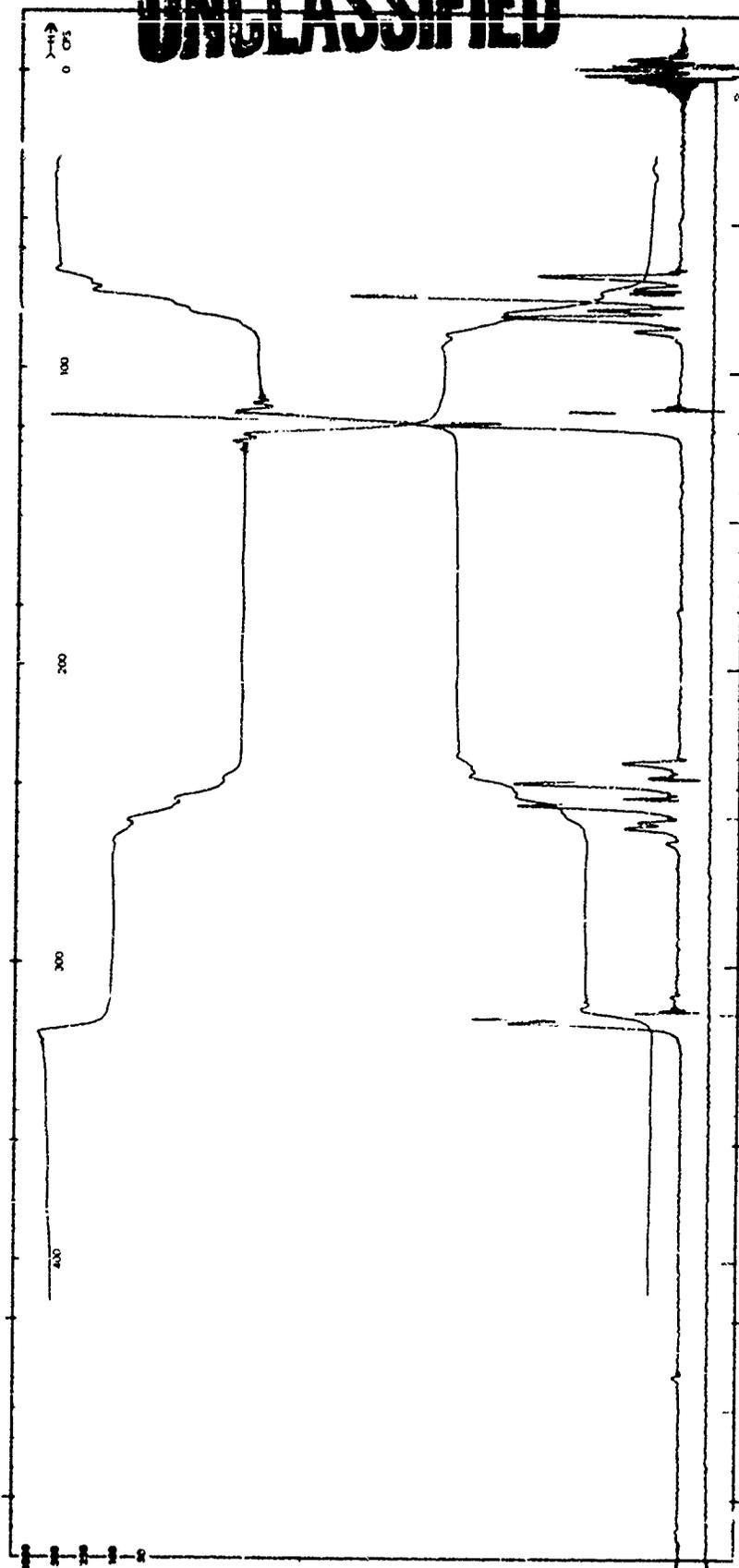
(C) Figure 7. Methylene-O,O'-bis(ethylacethydroximate)
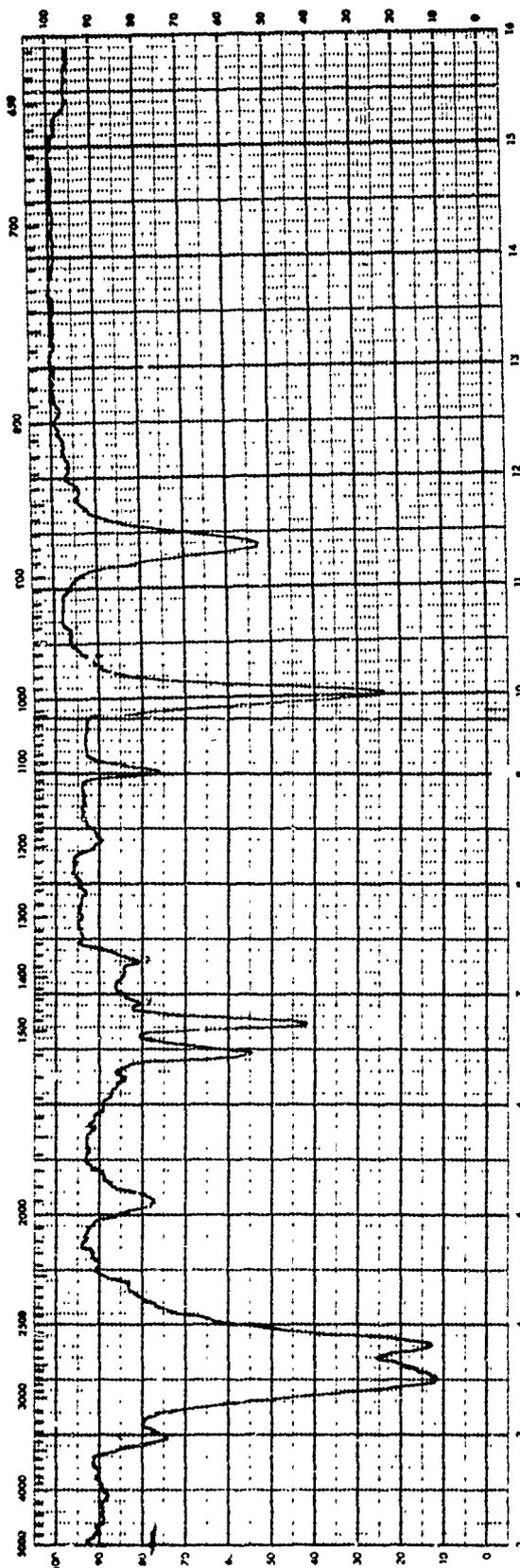
(C) Figure 8. Methylenedioxyamine Dihydrochloride

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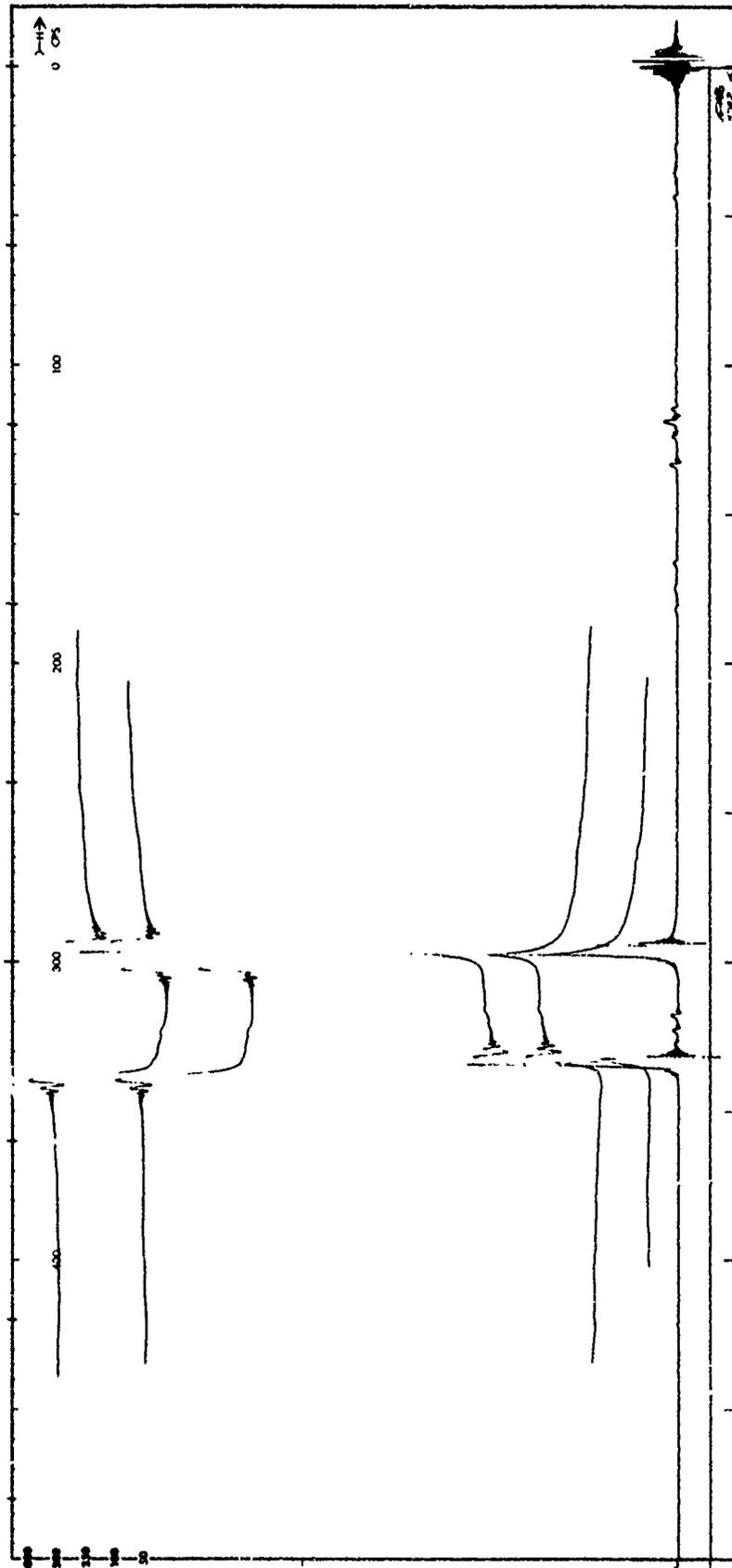
(C) Figure 9. Methylenedioxyamine Dihydrochloride
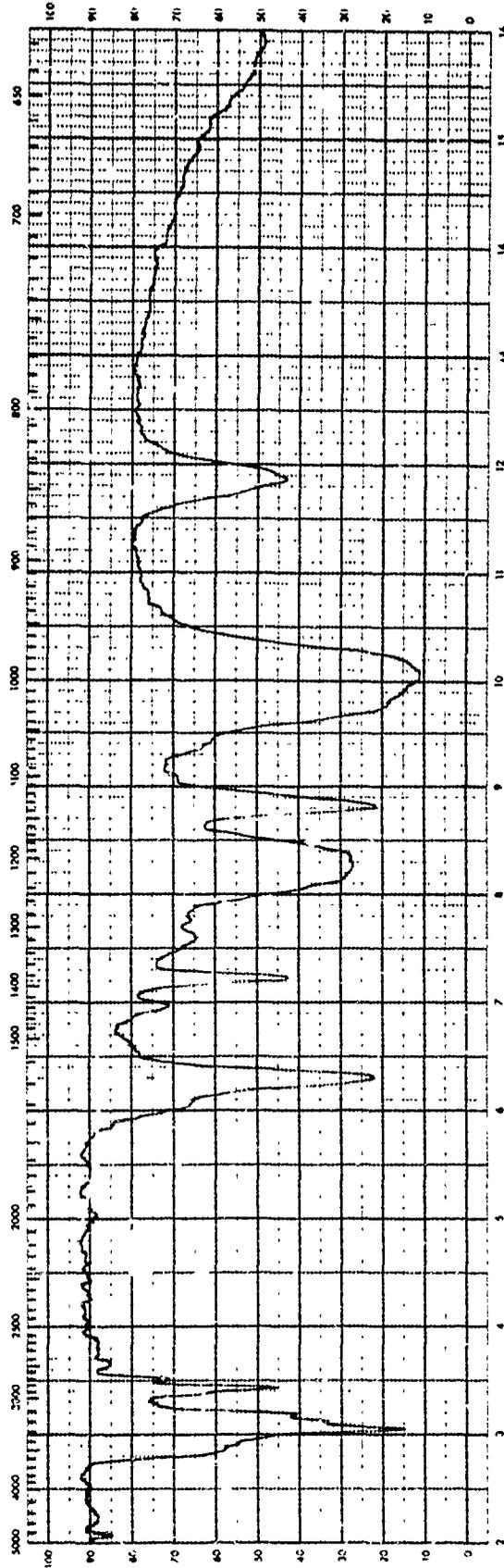
(C) Figure 10. Methylenedioxvamine
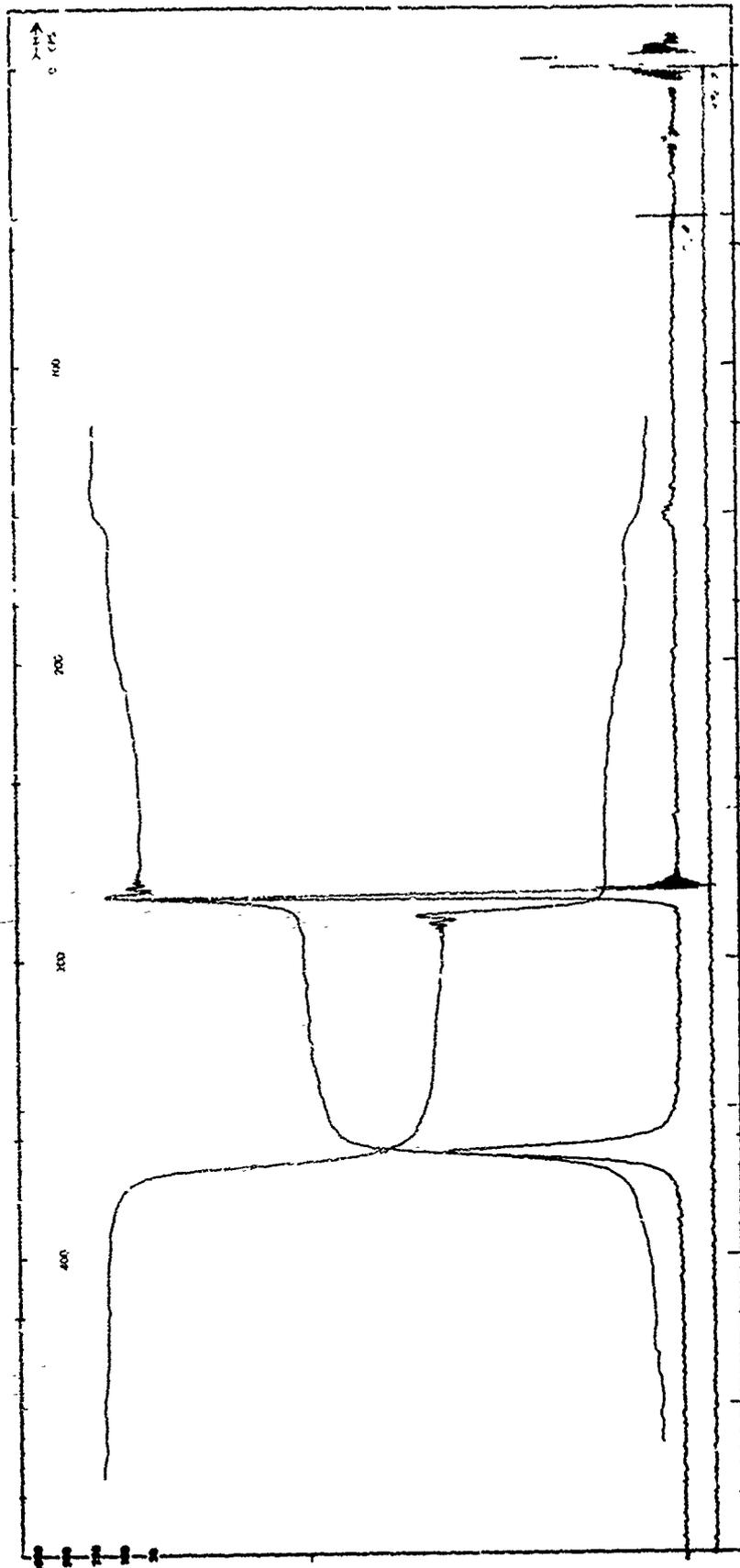
(C) Figure 11. Methylenedioxyamine

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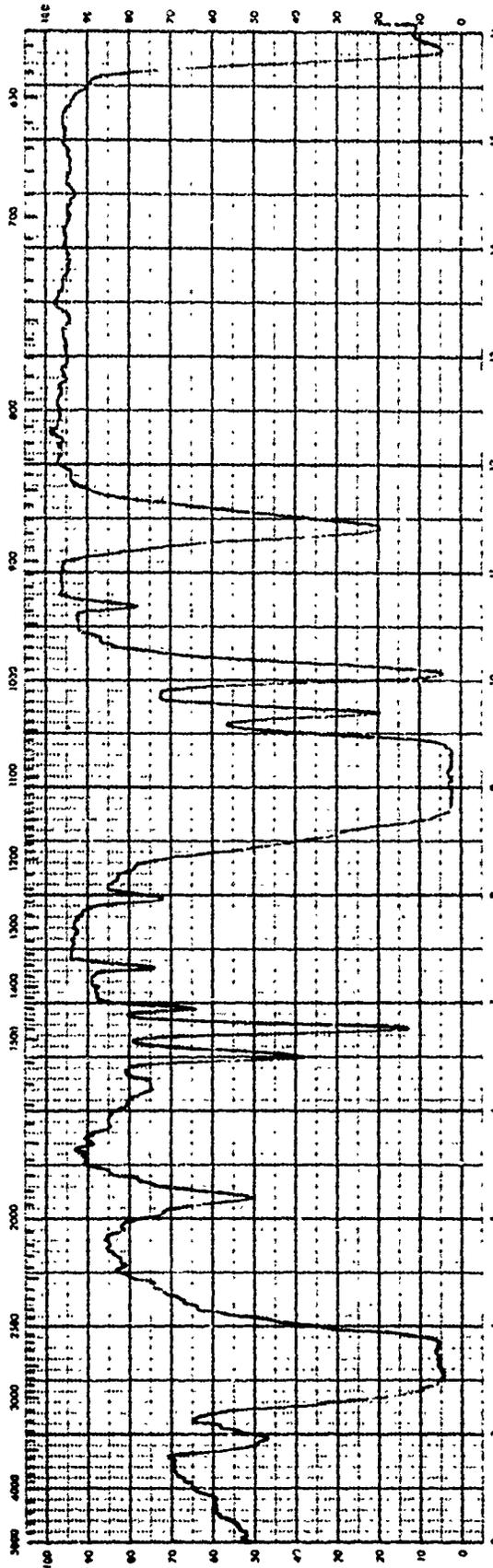
(C) Figure 12. Methylenedioxyamine Diperchlorate

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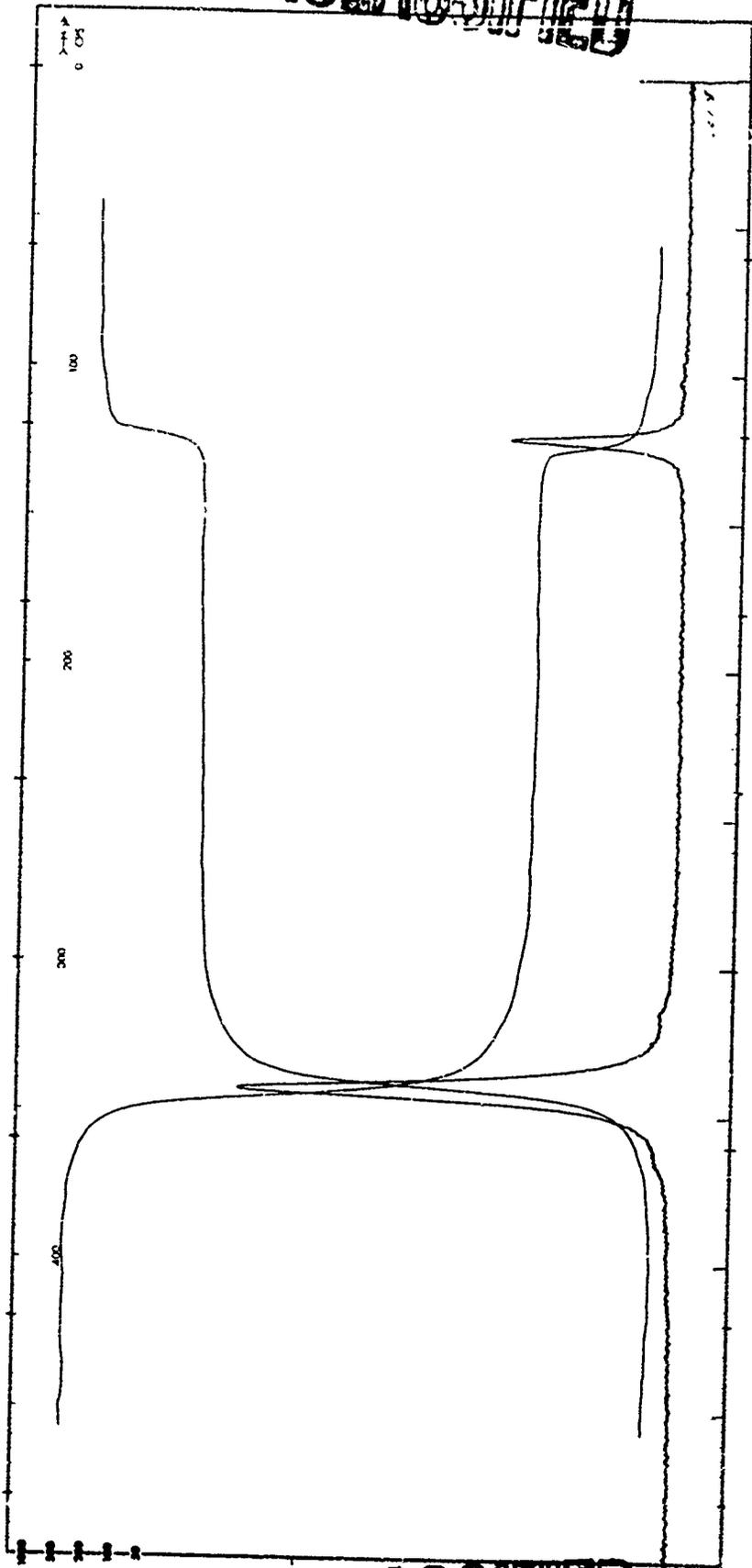
(C) Figure 13. Methylenedioxyamine Diperchlorate

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13. ABSTRACT

(C) Two new propellant ingredients, methylenedioxyamine (DO), a new monopropellant, and methylenedioxyammonium diperchlorate (DOAP), a new solid propellant oxidizer, have been synthesized at AFRPL using a five-step sequence of reactions. The reaction sequence, for producing DO in an overall yield of 51% or DOAP in an overall yield of 25-30%, is presented in detail. A synopsis of the experimental work leading to the successful synthesis of these new propellant ingredients is given.

DD FORM 1473

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Oxidizer (U); Solid Propellant (U); Oxyamine (U); Monopropellant (U); Perchlorate (U); Oxyamine Synthesis (U).						

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