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AFRPL-TR-69-85

(Unclassified Title)

NEW HIGH-ENERGY OXYGEN OXIDIZERS

Final Report

M. B. Frankel

W. Maya

E. F. Witucki

Rocketdyne, A Division of North American Rockwell Corporation
6633 Canoga Avenue, Canoga Park, California

TECHNICAL REPORT AFRPL-TR-69-85

March 1969

Group 4
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FOREWORD

- (U) The work performed herein was performed under Contract F04611-68-C-0059, and covers the period 1 April 1968 through 3 February 1969. This work will be continued under Contract F04611-69-C-0052. The program was monitored by Dr. Francisco Q. Roberto and Lt. Michael W. Barnes, AFRPL, Edwards Air Force Base, California.
- (U) The program manager for this contract is Dr. E. A. Lawton, Manager, Synthetic and Propellant Chemistry. The project scientist is Dr. M. B. Frankel, Principal Scientist of Advanced Solid Propellants and Explosives. Contributors to this research effort were Dr. W. Maya and Mr. E. F. Witucki. Technical support work was provided by Dr. N. N. Ogimachi and Mr. R. Rushworth. Microanalyses were by Mr. S. Gird.
- (U) This report has been assigned the Rocketdyne number R-7793.
- (U) This report has been reviewed and approved.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division

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CONFIDENTIAL ABSTRACT

- (C) Work is described toward the synthesis of cyanodinitromethyl compounds, in particular TENDE, 1,2-dicyanotetranitroethane, a potentially new, high-energy, solid oxidizer. Three approaches to the synthesis of TENDE were explored: the nitration of selected dicyano compounds, attempted dimerizations of cyanonitro compounds, and the dicyanation of appropriate nitro compounds.
- (C) The synthesis of the dinitronate salts of 2,3-dinitrosuccinonitrile, the direct intermediate to TENDE, has been successfully accomplished. The dipotassium salt of 2,3-dinitrosuccinonitrile has been synthesized through the base catalyzed nitration of succinonitrile by alkyl nitrates. From the potassium salt, silver and sodium salts have been made. The potassium and silver salts have been characterized by elemental analysis, ir and uv spectra. Attempted halogenation of the crude salts of 2,3-dinitrosuccinonitrile with chlorine and bromine were not successful in yielding a pure halo derivative for identification purposes.
- (U) The dioxime of succinonitrile, dicyanoglyoxime, was synthesized by the base catalyzed reaction of succinonitrile with alkyl nitrites. Nitration and halogenation attempts on the dioxime led mainly to the formation of dicyanofuroxan. Attempted oxidation of the dioxime with peroxytrifluoroacetic acid led to the formation of a new compound, 3-carbamyl-4-cyanofurazan-2-oxide, identified by its elemental analysis, ir and nmr spectra.
- (U) The addition of nitrogen tetroxide to fumaronitrile, dichlorofumaronitrile, and dichloromaleonitrile, did not yield the desired adducts.
- (U) Oxidative dimerization was tried on the anion of dinitroacetonitrile with potassium ferricyanide, potassium permanganate in acetone and in liquid ammonia, and with oxygen catalyzed by cuprous bromide. No reaction occurred under these conditions. With acidified 30-percent hydrogen peroxide, dinitroacetonitrile was oxidized to sodium nitrate. Oxidative dimerization

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was attempted on nitroacetonitrile, without success. When the oxidative dimerization was attempted on ethyl cyanoacetate, oxamide was the only product isolated. Reactions between cyanodinitroethyl chloride and potassium nitrite were not successful in forming nitronate salts. Cyanation reactions attempted with cyanogen chloride on dipotassium tetranitroethane and 1,2-dichlorotetranitroethane, and cyanation reactions employing sodium cyanide with 1,2-dichlorotetranitroethane, hexanitroethane, and fluorotri-nitromethane were not successful.

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INTRODUCTION

- (C) For many years ammonium perchlorate has remained the workhorse oxidizer for solid propellants. Despite intensive research, progress in the synthesis of new higher-energy solid oxidizers has been very slow. The emphasis in this work has been concerned principally with other perchlorate salts. In particular, a great deal of effort has been expended on nitronium perchlorate because of its high energy potential. However, the use of nitronium perchlorate in solid propellant systems does not appear feasible because of its undesirable properties (poor thermal stability, volatility, hygroscopicity, and reactivity with binder ingredients). The most promising new candidates that are currently being evaluated are hydroxyl-ammonium perchlorate and hydrazine dperchlorate. These perchlorate salts, intermediate in energy between ammonium perchlorate and nitronium perchlorate, possess some of the undesirable properties inherent with this class of compounds, namely, hygroscopicity, impact sensitivity, and chemical reactivity.
- (C) The need for new high-energy oxidizers with improved physical properties is readily apparent. An additional requirement, for application in smokeless solid propellants, is a halogen-free oxidizer. The requirements of a nonhygroscopic halogen-free oxidizer strongly suggest an organic covalent compound. Currently, the best candidates available in this field are HMX and RDX. The synthesis of halogen-free organic compounds, more energetic than HMX, poses a challenging problem.
- (Q) The most energetic halogen-free solid oxidizer candidate that has been prepared and evaluated, is hexanitroethane (HNE). HNE has the advantages of high energy, high melting point, high crystalline density, and nonhygroscopicity. The marginal thermal stability of HNE at temperatures near 70 C has precluded its use in solid propellants. Examination of a molecular model of HNE shows that there is considerable crowding because of the six nitro groups on two carbon atoms. Free rotation is markedly hindered and a strain is placed on the carbon-carbon bond as well as the carbon-nitrogen bond. To alleviate this strain and consequently improve the thermal

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stability of HNE type compounds it is necessary to replace one nitro group on each carbon atom with a smaller, less bulky group. However, this smaller group must retain the high energy, melting point, and density associated with the nitro group. The use of a cyano group substituent offers considerable promise toward meeting these stringent requirements.

- (C) It has been established that polycyano compounds are energetic yet thermally stable, high density solids (Ref. 1). A molecular model of 1,1,2,2-tetranitro-1,2-dicyanoethane (TENDE) showed that there was considerably less crowding and steric strain in the molecule. This is due to the fact that the cyano moiety is a small linear group which allows freer rotation of the two cyanodinitromethyl groups around the carbon-carbon bond, something that was not possible with the two bulky trinitromethyl groups on vicinal carbon atoms. Consequently, it is predicted that TENDE would be more thermally stable than HNE. Furthermore, the energy content of the cyanodinitromethyl group is quite comparable to that of the trinitromethyl group. The calculated heat of formation of TENDE is +105 kcal/mole compared to +28 kcal/mole for HNE. Performance calculations of TENDE and HNE propellant systems reveal that both oxidizers are comparable in energy.
- (C) The effort described in this report is mainly directed toward the synthesis of TENDE. The strategy adopted for its synthesis has been threefold: the nitration of selected dicyano compounds, the cyanation of appropriate nitro compounds, and attempts at the dimerization of cyanonitro compounds that would yield TENDE or compounds closely related to it.

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SUMMARY AND CONCLUSIONS

- (C) The potassium ethoxide catalyzed nitration of succinonitrile with alkyl nitrates has been successful in forming the desired dipotassium salt of 2,3-dinitrosuccinonitrile. The nitration of this salt by a variety of means is an attractive route to the target compound, TENDE, 1,2-dicyanotetranitroethane. Consequently, future experimental effort will be concentrated in this direction.
- (C) The approach toward the synthesis of TENDE by the nitration of the dioxime of succinonitrile (dicyanoglyoxime) led to the formation of dicyanofuroxan, as did the chlorination. Both of these synthetic methods may yet be successful if pursued further, because the formation of the furoxan should be highly dependent on the isomer of the glyoxime used. The oxidation of the dicyanoglyoxime by peroxytrifluoroacetic acid led to the formation of 3-carbamyl-4-cyanofurazan-2-oxide. This approach to 2,3-dinitrosuccinonitrile has been abandoned because the hydrolysis of the cyano groups under these conditions appears inevitable.
- (U) The nitration of the olefins fumaronitrile, dichlorofumaronitrile, and dichloromaleonitrile, by the addition of nitrogen tetroxide, did not lead to the formation of the corresponding dinitro compounds. This approach does not appear promising and will not be pursued further.
- (U) Oxidative dimerization was tried on the anion of dinitroacetonitrile employing potassium ferricyanide, potassium permanganate in acetone and in liquid ammonia, and with oxygen catalyzed by cuprous bromide-ammonium complex. No reaction occurred under these conditions. With acidified 30-percent hydrogen peroxide and acidified permanganate, the dinitroacetonitrile was oxidized to carbon dioxide and sodium nitrate. Under appropriate conditions, this reaction may be successful. The oxidizing agents employed so far bracket the conditions for either no reaction or complete oxidation. Oxidative dimerizations were also attempted on nitroacetonitrile and ethyl cyanoacetate, without success. The above comments for dinitroacetonitrile also apply in this case.

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- (C) Cyanation reactions attempted on dipotassium tetranitroethane, 1,2-dichlorotetranitroethane, and hexanitroethane with cyanogen chloride or sodium cyanide were unsuccessful. The availability of new cyanating agents would make this synthetic path to TENDE attractive again.

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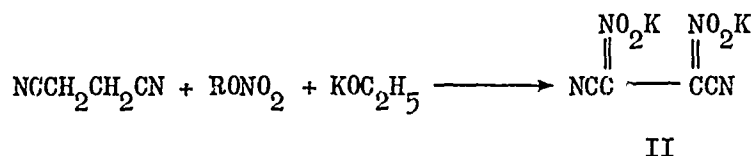
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DISCUSSION

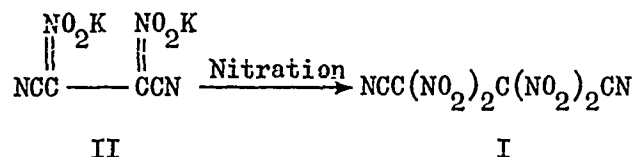
- (C) The purpose of this study was to develop a general method for the synthesis of cyanodinitromethyl compounds in general, and at the same time attempt the synthesis of the target compound, TENDE (I), 1,2-dicyanotetranitroethane. Three approaches to the synthesis of TENDE were explored: the nitration of selected dicyano compounds, the dimerization of cyanonitro compounds that would yield TENDE or compounds closely related to it, and the cyanation of appropriate nitro compounds.

NITRATION OF SUCCINONITRILE

- (C) The base catalyzed nitration of succinonitrile has proven to be a successful route to the synthesis of the dipotassium salt of 2,3-dinitrosuccinonitrile (II):



- (C) This salt is considered to be a very important intermediate for the synthesis of TENDE, because nitration by a number of routes should achieve this goal:



- (U) Base catalyzed nitration of nitriles was first reported by Wislicenus (Ref. 2) in which he showed that arylacetonitriles could be nitrated with ethyl nitrate. He later reported (Ref. 3) the synthesis of the dioxime of succinonitrile by the base catalyzed nitrosation of succinonitrile with alkyl nitrites; our study of this reaction, reported in a later section of this report, led to the present approach to the synthesis of II. Previous in-house work and our earlier studies of this reaction had shown that the more usual approaches to the synthesis of II, based on the work of Feuer

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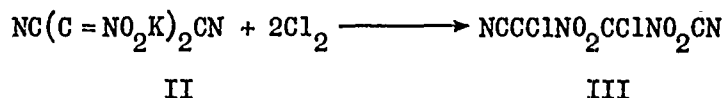
(Ref. 4 and 5), did not work. Reactions between succinonitrile and alkyl nitrates employing potassium tert.-butoxide (Ref. 4) in tetrahydrofuran or potassium amide in liquid ammonia (Ref. 5) led mainly to the formation of a black product containing mostly potassium nitrite.

- (C) The reaction of succinonitrile, propyl nitrate and potassium ethoxide in an ethereal medium at 0 C overnight led to the formation of II in 15- to 20-percent yield. No effort has been made at maximizing the yield. The crude reaction product is a black deliquescent material which is highly impure. It has been only in the last month of this contract that a successful method of purification has been achieved, and that acceptable analytical data were obtained. Therefore, all the reactions attempted on II reported here were performed on impure material, and do not necessarily reflect the true chemical behavior of II. Future work on II will be performed and reported under contract F04611-69-C-0052. The identification of II rests on the elemental analyses of both II and of its derivative, the disilver salt of 2,3-dinitrosuccinonitrile. The disodium salt was also prepared by passing II through an ion exchange column, its direct preparation by employing sodium ethoxide in the synthesis was not successful.
- (C) All of the salts prepared (potassium, sodium, and silver) exhibit six major absorptions in the infrared in the ranges (in microns): 4.4-4.6, 6.8-7.2, 7.5-7.8, 8.5-8.7, 10.0-10.3, and 13.7-14.0. The absorption centered at 4.5 microns is clearly attributable to the CN group; the strong absorption centered at 7.0 microns is tentatively assigned to the nitronate group, which generally absorbs at 6.8 microns. The reason for this shift is not clear at this time. Ultraviolet spectra were also used for identification purposes and proved to be very useful. Kamlet (Ref. 6) has also found this to be true. The salts studied by Kamlet were gem dinitro anions and these were found to have an identifying peak in the range 320 to 380 mμ. Our salts, on the other hand, are vicinal dinitro anions and they all exhibit a major peak in the range 325 to 350 mμ.
- (C) The stability of these salts is also interesting. Although they burn very energetically, particularly the silver salt, they appear to be quite stable both to heat and shock. The silver salt explodes at 162 C and the potassium salt melts at 274 C with decomposition.

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Halogenation of II

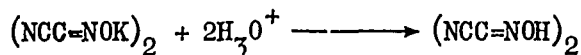
- (C) Both chlorination and bromination of crude II were attempted as a means of identification through the corresponding halo-nitrocompound:



- (C) The products of these reactions had an infrared spectrum consistent with the presence of the halo-nitrocompound III; however, they were contaminated with an impurity that possessed a carbonyl absorption in the ir. It was not possible to obtain a pure sample of III, although various means of purification were tried such as distillation, liquid chromatography and other conventional techniques. It was observed that the purer the starting salt II was, the purer was the product obtained. It is expected that with pure II an analytical sample of III might be obtained. A further complication is expected in that III may not be obtained as a crystalline material at first, because it is expected to exist as a mixture of meso, and d,l-isomers.

REACTIONS OF DICYANOGLYOXIME

- (U) Dicyanoglyoxime (the dioxime of succinonitrite) was first synthesized in 1909 (Ref. 3) by the base catalyzed reaction of succinonitrile with amyl nitrite:



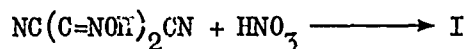
- (C) Because of the close structural relationship between the dioxime and TENDE, the reactions of this compound were studied in some detail. The above procedure for the synthesis of the dioxime affords the potassium salt, which must be neutralized in order to obtain the free dioxime. The yield of the

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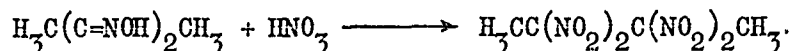
free dioxime, as the original workers remarked (Ref. 3), was very small. It was found that one reason for this was that the neutralization of the salt to the oxime proceeded in poor yield; therefore, many of the reactions described were attempted on the di salt. The disodium salt could be prepared by employing sodium ethoxide in the synthesis; however, the yields and purity of the salt were better when potassium was employed. Attempts at the formation of the dioxime by a conventional (cf. Ref. 7) acid nitration of succinonitrile failed.

Nitration of Dicyanoglyoxime

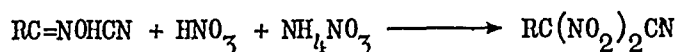
- (C) The nitration of the dicyanoglyoxime, if successful, would yield TENDE directly:



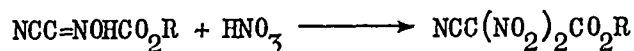
- (U) The nitration of oximes to dinitro compounds is a recognized method of synthesis, as, for instance, the nitration of dimethylglyoxime to tetranitrobutane (Ref. 8):



the nitration of α -oximinonitriles to cyanodinitromethyl compounds (Ref. 9)



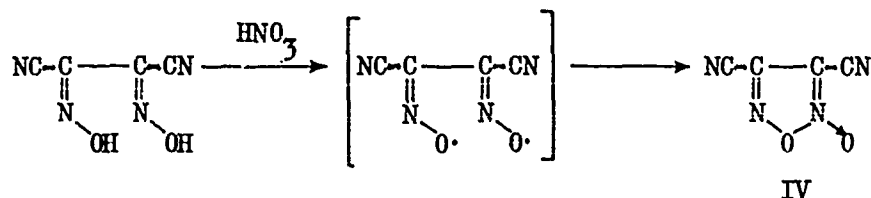
and the nitration of oximinocyanoacetates to dinitrocyanoacetates (Ref. 7)



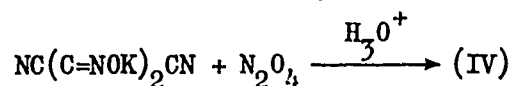
- (U) The free dicyanoglyoxime was nitrated at low temperatures with a mixture of sulfuric acid and 100-percent nitric acid. The main product obtained was dicyanofuroxan (IV), identified by its infrared spectrum (Ref. 10),

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along with an unidentified minor product that possessed both carbonyl and nitro groups:



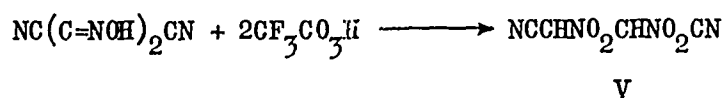
- (U) Compound IV was thought to arise by the oxidation of the dioxime in the nitrating medium. The attempted nitration of dichloroglyoxime similarly afforded dichlorofuroxan (Ref. 11). Dicyanofuroxan, along with free unreacted dioxime, was also obtained by the nitration of the dipotassium salt of dicyanoglyoxime by nitrogen dioxide at 0 C, another known nitrating procedure (Ref. 12).



- (C) Attempts to nitrate the salts of dicyanoglyoxime directly with nitric acid resulted in deflagrations even at -30 C. A procedure was adopted patterned after the synthesis of hexanitroethane from dipotassium tetranitroethane (Ref. 13), in which the free glyoxime was generated in situ, by adding cold sulfuric acid to a suspension of dioxime salt in methylene chloride at -10 to -15 C, and then treating with a nitrating mixture of sulfuric acid and anhydrous nitric acid in the cold. By this means, a yellow oil was obtained that had an infrared spectrum which contained absorptions attributable to nitro and cyano groups. However, all attempts at purification failed, and a pure compound was not isolated. This approach, although promising, was held in abeyance to explore other routes to TENDE.

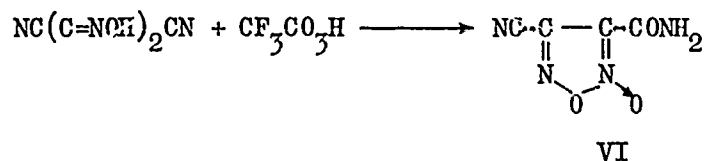
Oxidation of Dicyanoglyoxime

- (U) The oxidation of oximes to nitro compounds by means of peroxytrifluoroacetic acid is a reaction known to proceed in high yields (Ref. 14), and was attempted on dicyanoglyoxime as a route to 2,3-dinitrosuccinonitrile (V):

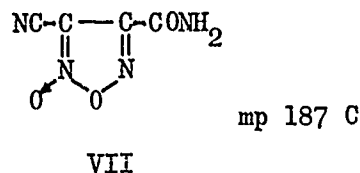


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- (U) When the free dioxime was treated with peroxytrifluoroacetic acid in acetonitrile, in the presence of sodium bicarbonate buffer, a solid was obtained that was identified as 3-carbamyl-4-cyanofurazan-2-oxide (VI), a new compound:

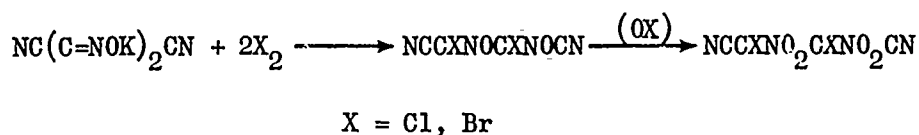


- (U) The identification rests on its elemental analysis, infrared and proton nmr spectrum. The nmr of the compound in acetonitrile showed only one very broad peak (50 Hz wide) at 9.5 δ . The broadness of the peak and its chemical shift show that all the protons are bound to nitrogen in an amide group. The isomer VII is a known compound (Ref. 15) and its melting point is reported at 187 C (dec.) as contrasted to the melting point for VI of 118 to 119 C:



Halogenation of Dicyanoglyoxime

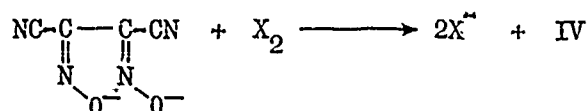
- (U) Exploratory work was done on the halogenation of the dipotassium salt of dicyanoglyoxime to attempt to obtain the corresponding gem-halo nitroso or nitro compounds:



- (C) Various synthetic routes could be used to convert the halo-nitro compound to I.

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- (U) Both bromination and chlorination of the potassium salt at low temperatures (5 C) afforded mainly dicyanofuroxan (IV). As in the cases described above, IV is thought to have arisen by the oxidation of the dioxime by the halogen:

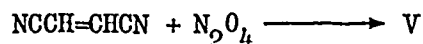


- (U) Two attempts were made to chlorinate the potassium salt in aqueous basic solutions at ice-bath temperature. In one case 1M KOH was employed, and in the other saturated NaHCO_3 was used. In both cases ill defined products were obtained, whose ir had unmistakeable absorptions due to carbonyl groups. The reactions were not pursued further.

NITRATION OF OLEFINS

Addition of N_2O_4 to Fumaronitrile

- (U) An attempt was made to synthesize 2,3-dinitrosuccinonitrile (V) by the addition of N_2O_4 to fumaronitrile:

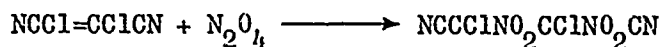


- (U) No way was found to accomplish the addition; either no reaction occurred or the nitrile was oxidized too vigorously. Additions were attempted at 0 C in ether and in methylene chloride in the presence of oxygen, according to well known procedures (Ref. 16), the fumaronitrile was recovered unreacted. In one case a fume off was experienced, but it may have been caused by the presence of inorganic nitrating species in the diethyl ether. No such incidents were observed when the reaction was performed in methylene chloride. When the addition was attempted in sealed Carius tubes at temperatures of 60 to 85 C, patterned after the successful addition of N_2O_4 to 2,3-dinitrobutene (Ref. 8), the reaction mixtures invariably exploded. Because there is reason to expect that 2,3-dinitrosuccinonitrile would be an unstable compound (Ref. 4) best handled at low temperatures, this approach was discontinued.

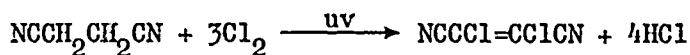
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Addition of N_2O_4 to Dichlorofumaronitrile and Dichloromaleonitrile

- (U) The addition of N_2O_4 was attempted on the above compounds because there is good evidence that this type of reaction has a higher probability of success when the olefin is electronegatively substituted (Ref. 17):



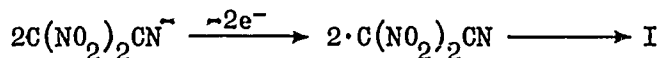
- (U) Both dichlorofumaro and maleo nitriles were synthesized by the chlorination of succinonitrile (Ref. 18):



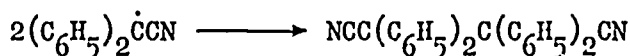
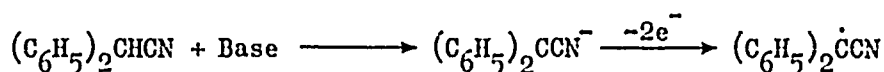
- (U) The nitration of these compounds was attempted both by the addition of N_2O_4 in stainless-steel bombs at temperatures ranging from 60 to 95 C for several days, and by reaction with mixtures of nitric and sulfuric acids. The results of these experiments were generally the same, about 40 to 60 percent of the starting material was recovered (a mixture of cis and trans isomers) and the balance of the material underwent degradative oxidation. In some of the experiments, a material was detected that had a band in infrared spectrum at 6.2 microns, indicative of an $N=C$, but the material was found to disappear on treatment with water. It is felt that the material was probably a trace of nitrate esters which was hydrolyzed by the water treatment. Work on this approach was suspended at this point.

COUPLING REACTIONS

- (C) This approach was prompted by the ready availability of the salts of dinitroacetonitrile (Ref. 10). Oxidative coupling of the anion of dinitroacetonitrile would yield TENDE directly:



- (U) A direct analogy to this reaction is the known coupling of diphenylacetonitrile by oxidizing agents in basic solutions (Ref. 19 and 20):



- (U) Diphenylacetonitrile has been coupled in basic solution in nearly quantitative yield to tetraphenylsuccinonitrile by the action of a variety of oxidizing agents, including ferricyanide in methanol (Ref. 19), permanganate in acetone (Ref. 19) and in liquid ammonia (Ref. 20), and oxygen in the presence of cuprous bromide complexed with amines (Ref. 19). The analogy is considered particularly apt because the coupling of diphenylacetonitrile occurs despite the steric constraint of bringing together two pairs of phenyl groups in the transition state, and despite the energy required to localize the lone electron on the central carbon atom of the intermediate radical in the transition state.
- (U) To become familiar with the procedures involved, the coupling of diphenylacetonitrile was repeated employing two different methods. In one method, the coupling was effected with potassium ferricyanide in a medium of methanol and concentrated aqueous ammonia (Ref. 19), and in the other the diphenylacetonitrile was treated with potassium amide in liquid ammonia and oxidized with potassium permanganate (Ref. 20). Both methods afforded tetraphenylsuccinonitrile in excellent yields.

Attempted Coupling of Dinitroacetonitrile

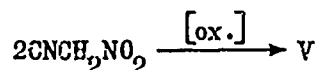
- (U) The repetition of the above procedures employing dinitroacetonitrile in the place of diphenylacetonitrile led to no reaction. The following conditions were tried: ferricyanide in methanol, permanganate in acetone and in liquid ammonia, and oxygen catalyzed by cuprous bromide complexed with aqueous ammonia. The lack of reaction is thought to arise from the probable difference in oxidation potentials between the anions of dinitro

and diphenylacetonitrile; that is, it is expected that the work of pulling an electron away from the anion of dinitroacetonitrile will be much greater than from diphenylacetonitrile.

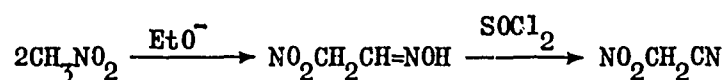
- (U) Attempts to use stronger oxidizing agents were not examined in depth. Acidified 30-percent hydrogen peroxide and acidified permanganate were employed and resulted in complete degradation of the dinitroacetonitrile. Presumably oxidizing agents of intermediate strength might effect dimerization but this approach was deferred for future studies.

Attempted Coupling of Nitroacetonitrile

- (U) The coupling of nitroacetonitrile was examined as a way to the synthesis of the intermediate 2,3-dinitrosuccinonitrile (V):



- (U) The nitroacetonitrile was synthesized by a two step reaction from nitromethane (Ref. 21):



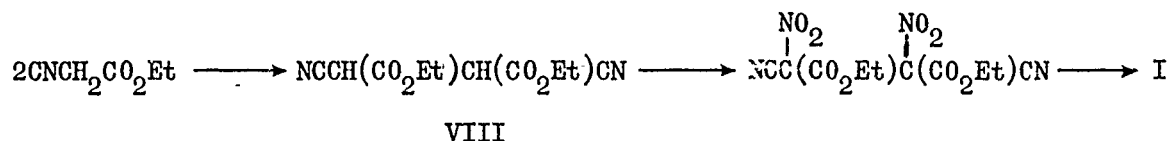
- (U) The nitroacetonitrile was characterized by its ammonium salt, mp 134 to 135 C (Ref. 22). Several exploratory attempts were made to couple it patterned after the procedures described above. Reactions employing potassium ferricyanide as the oxidizing agent resulted in the recovery of the unreacted nitroacetonitrile. When oxygen was employed, with cuprous bromide catalysis, a product was obtained whose infrared spectrum was very similar to that of starting material. The material resisted all efforts at purification to obtain an analytical sample, and was not pursued further.
- (U) The ammonium salt of nitroacetonitrile was dissolved in liquid ammonia and treated with potassium amide and potassium permanganate. A liquid product

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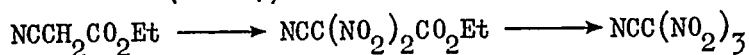
was obtained whose infrared spectrum showed the presence of NO_2 and CN groups, and a band at 3.0 microns indicative of an amide group. Efforts to purify this material through the formation of the ammonium salt failed, and efforts on this approach were suspended.

Attempted Coupling of Ethyl Cyanoacetate

- (C) An attempt was made to couple ethyl cyanoacetate to 1,2-dicarbethoxysuccinonitrile (VIII), an intermediate to I:



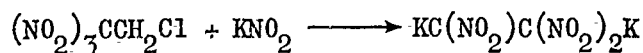
- (C) The product (VIII) would have been nitrated to the nitroester, which could be decarboxylated and nitrated further to give I, much as ethyl cyanoacetate has been nitrated to trinitroacetoneitrile via the intermediate ethyl dinitrocyanoacetate (Ref. 7):



- (U) Classical methods of coupling malonic acid derivatives, i.e., treatment of the anion with free halogen, do not work for cyanoacetates (Ref. 23). Oxidative coupling conditions for ethyl cyanoacetate were examined with the following oxidizing agents: $\text{K}_3\text{Fe}(\text{CN})_6$, KMnO_4 , and O_2 catalyzed by CuBr . In all cases, a solid was recovered that was identified as oxamide by its infrared spectrum.

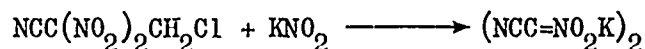
Attempted Coupling of Cyanodinitroethyl Chloride

- (U) The mechanism of the conversion of trinitroethyl chloride to the dipotassium salt of tetranitroethane by the action of potassium nitrite (Ref. 13) is unknown:



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- (U) If it involved the rupture of the C-C bond followed by a dimerization to yield the product, then it should be possible to perform a similar reaction with cyanodinitroethyl chloride:



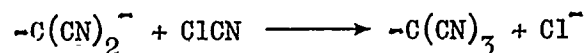
- (U) Therefore, cyanodinitroethyl chloride was synthesized from cyanodinitroethanol, employing conditions similar to those used in the conversion of the corresponding trinitroethyl compounds (Ref. 13). Cyanodinitroethyl chloride is a new compound, and its ir spectrum and physical properties were consistent with the structure, however, a pure sample was not obtained. Previous workers did not obtain an analytical sample of cyanodinitroethanol (Ref. 24) either, and the impurity in the alcohol, paraformaldehyde, apparently was carried on to the chloride. The reaction of cyanodinitroethyl chloride with potassium nitrite did not lead to the formation of nitronate salts, and this approach was not pursued further.

CYANATION REACTIONS

- (C) Cyanation reactions, i.e., the introduction of cyano groups to the already preformed nitro compounds, is an attractive route to a general synthesis of cyanodinitromethyl compounds and to TENDE itself. The cyanation of the derivatives of tetranitroethane would provide an attractive route to TENDE because of their ready availability (Ref. 13).

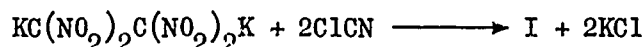
Reactions with Cyanogen Chloride

- (U) The introduction of the CN group was attempted through the use of cyanogen chloride, ClCN , by analogy to its use for the conversion of dicyanomethyl groups to tricyanomethyl (Ref. 25 and 26):

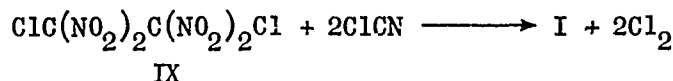


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- (C) Previous in-house work at Rocketdyne has shown that the dipotassium salt of tetranitroethane failed to undergo CN substitution with cyanogen chloride in ether type solvents, the conditions used in the above references. Therefore, a reaction was attempted in water, a solvent in which both reactants have moderate solubility and which might facilitate the reaction because of its highly polar character:



- (U) A slow reaction did take place at ambient temperature as indicated by the evolution of CO_2 and N_2O , but no organic soluble fraction was produced in this reaction. Apparently, under these conditions, the salt preferentially oxidized the CN groups rather than undergoing substitution.
- (C) A series of reactions were attempted involving dichlorotetranitroethane (IX) and cyanogen chloride:



- (U) The Cl in compound IX is polarized in a positive direction because of the heavy substitution by NO_2 groups; it was thought that the formation of Cl_2 might be favored because the Cl in ClCN is known to be polarizable both as a positive or a negative Cl, depending on the demands imposed on it by its environment (Ref. 27).
- (U) A reaction between IX and ClCN in ether at ambient did indeed produce Cl_2 , along with NO and NOCl . However, the CCl_4 soluble fraction revealed in the infrared only starting material and an unidentified substance absorbing at 6.3 microns, no evidence was found for any CN substituted products (expected absorption around 4.4 microns). At 0 C, IX was soluble in ClCN and no evidence for reaction was observed in 48 hours; the same reaction performed in the presence of mercury led to reaction with the formation of N_2O and mercury salts, presumably HgCl_2 , but no evidence was found for CN substituted products.

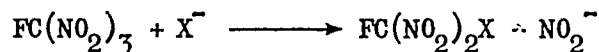
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Reaction With Sodium Cyanide

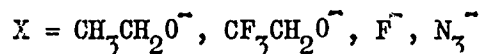
- (U) The displacement of chlorine from dichlorotetranitroethane (IX) was attempted employing sodium cyanide.
- (U) The compound IX was found to be incompatible with dimethylsulfoxide, and the reaction was attempted in dimethylformamide. A vigorous reaction took place at 0 C, with evolution of gas, and the products were all found to be water soluble and insoluble in chlorinated hydrocarbons. No further work was attempted on this system, as apparently the nitro compound oxidized the cyanide ion.

DISPLACEMENT OF NITRO GROUPS

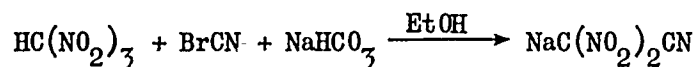
- (U) The attempt to displace a nitro by a cyano group from a trinitromethyl compound could be classified under a cyanation reaction; however, the unusualness of the approach was felt to merit its own heading. The possibility was suggested by the work of Adolph and Kamlet at the Naval Ordnance Laboratory (Ref. 28), who were able to effect a displacement of the nitro group in fluorotrinitromethane by a series of nucleophiles:



where

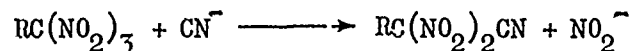


- (U) It seemed reasonable that the nucleophilic cyano group should be able to function in like manner, in view of a report of a similar reaction in which a nitro group from nitroform was replaced by a cyano group (Ref. 29):



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- (U) This approach, had it proved successful, would have provided a general route to the synthesis of cyanodinitromethyl compounds through reactions based on the accessible trinitromethyl compounds:



Reaction With Fluorotrinitromethane

- (U) Fluorotrinitromethane was utilized as a model compound to evaluate the feasibility of this approach; the expected product, fluorodinitroacetonitrile, is well characterized and would have been recognized if formed:



- (U) A series of eight experiments were performed between $FC(NO_2)_3$ and cyanide ion. The reactions were carried out at -10 to 0 C, in the solvents dimethylformamide, dimethylsulfoxide and aqueous ethanol, employing both sodium and potassium cyanide. In most instances a vigorous reaction took place, particularly in dimethylsulfoxide and dimethylformamide, with darkening and evolution of gas. However, none of the cyano compound was found either by infrared spectroscopy or gas chromatography. Some of the fluorotrinitromethane was recovered, and among the gases evolved CO_2 and N_2O were identified by their infrared spectra. The reaction products were not analyzed further once the absence of $FC(NO_2)_2CN$ was ascertained. Additional reactions were tried between $FC(NO_2)_3$ and $CuCN$, without solvent, in analogy to well known reactions where $CuCN$ is often successful in replacing halogens by the CN group. No reaction was observed after 1 week at 25 C.

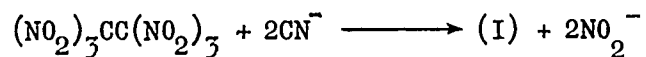
- (U) No reactions were observed between $FC(NO_2)_3$ and $BrCN$, both neat and in ethanol solution with $NaHCO_3$ present.

Reaction With Hexanitroethane

- (C) Because the above preliminary results indicated that much effort would have to be spent in finding conditions for converting fluorotrinitromethane to

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fluorodinitroacetonitrile, and because the conditions might not be strictly applicable to other trinitromethane compounds, the reaction was attempted on hexanitroethane itself. If successful, this reaction would have yielded TENDE directly:



- (U) Hexanitroethane was found to undergo a vigorous reaction with sodium cyanide in dimethylsulfoxide, but all the products were water soluble and could not be extracted from the water layer. It was concluded that again the oxidation of the cyanide ion had taken place.

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EXPERIMENTAL

- (U) Only those experiments will be described that led to products that were identified. Descriptions of ir spectra and other data are given for new compounds and, also, for known ones where such data are not available in the literature.

NITRATION OF SUCCINONITRILE

Dipotassium Salt of 2,3-Dinitrosuccinonitrile

- (C) Potassium ethoxide (0.256 mole) was formed in situ from 10 g (0.256 g atom) of potassium and 75 ml of ethanol. Ether (120 ml) was added during this step to help solubilize the ethoxide. To this solution was added dropwise at 0 C succinonitrile (10.2 g, 0.128 mole), and n-propyl nitrate (29.4 g, 0.28 mole) in benzene (100 ml). The reaction mixture was then stirred at 0 C overnight. The resulting brown slurry was filtered and the solid was dried in vacuo over P_2O_5 to yield 8 g of crude dipotassium 2-3-dinitrosuccinonitrile. Addition of ether to the filtrate yielded 3 g more of crude material (somewhat less pure than the original solid). All operations were carried out in a nitrogen atmosphere.
- (C) The crude, hygroscopic material was partially purified by washing repeatedly with methanol and acetone, it was then dissolved in water and treated three times with activated charcoal. Upon evaporation of the aqueous solution, there was obtained 3 g (10-percent yield) of the pure salt II, m.p. 274 (dec.).

Analysis calculated for $C_4N_4O_4K_2$: C, 19.51; H, 0.00; N, 22.76;

Found: C, 19.73; H, 0.51; N, 22.71.

- (C) The ir spectrum of the potassium salt (KBr pellet) had the following absorptions (in microns): 4.45 s*, 7.2 s, 7.6 s, 8.6 to 8.7 doublet, 10.2 s 13.75 m triplet.

*Abbreviations used in reporting ir spectra: s = strong, m = medium, and w = weak.

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Disilver Salt of 2,3-Dinitrosuccinonitrile

- (C) The disilver salt was formed by adding an excess of silver nitrate to an aqueous solution of the dipotassium salt. The yellow-orange disilver salt was nonhygroscopic; it did not melt, but rather exploded at 162 C. The yield was quantitative.

Analysis calculated for $C_4N_4O_4Ag_2$: C, 12.50; H, 0.00; N, 14.58; O, 16.67;

Found: C, 13.06; H, 0.35; N, 14.02; O, 16.02.

- (C) The ir spectrum of the silver salt (KBr pellet) was as follows (in microns): 4.5 s, 6.9 shoulder, 7.2 vs, 7.9 s, 8.7 m, 10.3 s, 13.7 w, 14.1 w.

Disodium Salt of 2,3-Dinitrosuccinonitrile

- (C) The disodium salt was formed by passing an aqueous solution of the dipotassium salt through an ion exchange column (Dowex 50 W-X8 in the sodium form). The disodium salt (obtained as the hydrate as evidenced by ir) was isolated by evaporating the eluate and drying in vacuo over P_2O_5 . The yield in this case was also quantitative. The sodium salt was never obtained in high purity, because high purity potassium salt was not available at the time of this preparation.

Chlorination of the Salts of 2,3-Dinitrosuccinonitrile

- (C) Both the potassium and sodium salts were examined in this reaction, neither salt had been obtained pure at the time these reactions were conducted. The impurities in the salt gave rise to an impurity in the chlorinated product that had a strong absorption in its ir spectrum at 5.7 microns, indicative of a carbonyl group. This carbonyl impurity could not be eliminated by washes with sodium bisulfite, high vacuum distillation or by liquid chromatography.
- (C) The dipotassium salt (1.0 g) was suspended in 50 ml of anhydrous ether in an ice bath. Chlorine was slowly bubbled in until the salt was decolorized

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and the solution turned yellow. The mixture was filtered, and the ether and chlorine removed under water aspirator pressure. A yellow oil (about 0.6 g) was obtained, with the following ir (in microns). The bands thought to belong to impurities are marked imp.: 4.4 w, 5.7 m imp, 6.2 s, 7.7 m, 9.3 imp, 9.7, 11.1 m, 11.4 imp, 12.5 s, 13.1 m.

- (C) One attempt was made to conduct the chlorination at 5 C in aqueous media; similar results were obtained except with lower yields.

PREPARATION AND REACTIONS OF DICYANOGLYOXIME

Preparation

- (U) The butyl nitrite (Eastman) was distilled before use. From 100 g of starting material, only 5 $\frac{1}{2}$ g of butyl nitrite was obtained, bp 35 to 40/200 mm, n_D^{25} 1.3755.
- (U) Potassium metal (33 g; 0.84 g-atom) was dissolved in chunks into absolute ethanol (250 ml) at reflux. Toward the end of the addition, the minimum amount of ethanol necessary to dissolve any remaining potassium was added. The mixture was cooled in an ice bath and diethyl ether (1 liter) was added. When the temperature of the reaction mixture was 5 C, a mixture of benzene (40 ml), butyl nitrite (86 g; 0.83 mole) and succinonitrile (33 g; 0.41 mole) was added gradually. The reaction mixture was allowed to warm to 25 C after the addition, and was stirred for an additional 3 hours. Diethyl ether (500 ml) was added, and the reaction mixture filtered. The filtrate was washed thoroughly with ether, and dried overnight in a vacuum desiccator. The dipotassium salt of dicyanoglyoxime (46 g) was obtained in a 76 percent yield based on the butyl nitrite employed. The ir spectrum of the salt was taken in a KBr pellet, absorptions given in microns: broad 3.0 s (indicative of hydrate), 4.5 s, 6.1 m (hydrate), 7.1 s, 7.4 shoulder, 8.7 vs, 9.4 m, 10.2 s.

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- (U) The free dioxime was obtained by the procedure of Wislicenus and Grutzner (Ref. 3), which consisted in acidification of aqueous solutions of the K salt, followed by extraction and recrystallization of the dioxime from water. The yield by this method was very low, of the order of 1 to 2 g of the free dioxime, from 46 g of salt.

Nitration

- (U) The nitrations were carried out by standard procedures, as described in the discussion section. The nitrations were all attempted at ice bath temperatures or below, with anhydrous nitric acid, or mixtures of nitric and sulfuric acid. The resultant dicyanofuroxan was obtained after quenching the reaction mixture in ice, extracting with methylene chloride, drying the organic layer with magnesium sulfate, and evaporating to dryness under reduced pressure. The dicyanofuroxan obtained was impure, and was obtained as a yellow oil, and identified by its ir spectrum (Ref. 10). Pure dicyanofuroxan is reported to be a solid, mp 42 C (Ref. 10).

Oxidation

- (U) A suspension consisting of acetonitrile (20 ml), urea (0.2 g), NaHCO_3 (4.6 g; 55 mmole) and dicyanoglyoxime (0.68 g; 10 mmole) was brought to reflux. A solution was added that consisted of acetonitrile (5 ml), trifluoroacetic anhydride (3.4 ml; 24 mmole) and 90-percent H_2O_2 (0.55 ml, 20 mmole) over a 25-minute period. The white suspension changed from white to light blue, to green, to gold, and finally to a light yellow. After refluxing for 1 hour, the reaction was quenched in ice and extracted with 5 portions of 60 ml of CH_2Cl_2 , the organic layer was washed with sodium bicarbonate and dried overnight with MgSO_4 . Evaporation of the solvent yielded 0.24 g of yellow solid, mp 115 to 118 C (equivalent to 31-percent yield, if pure, of cyanoamidofuroxan). Recrystallation from water gave 0.19 g of a yellow solid, mp 118 to 119 C. Proton nmr in acetonitrile solution showed only one very broad peak, 50 Hz wide, at 9.5 δ . The ir spectrum taken in KBr pellet had the following absorptions, reported in

microns: 3.1 s and broad, 6.1 s, 6.8 and 7.0 s doublet, 7.3 m, 7.6 m, 8.5 m, 9.2 w, 10.0 w, 11.1 vw, 12.2 s, 13.1 m.

Analysis calculated for $C_4H_2N_4O_3$: C, 31.15; H, 1.30; N, 36.35;

Found: C, 31.28; H, 1.39; N, 36.88.

Halogenation

- (U) The halogenations were all carried out at ice bath temperatures by standard techniques. The solvents employed were either diethyl ether or methylene chloride, the chlorine was bubbled in slowly to avoid a temperature rise, while in the case of brominations, the bromine was first dissolved in carbon tetrachloride before addition. After conventional workup, the dicyanofuroxan was obtained as a yellow liquid, as described above in the nitration case. In no case was any transient blue color observed in the course of these reactions, as might be expected if a nitroso compound had been produced.

NITRATION OF OLEFINS

- (U) The fumaronitrile (Aldrich Chemical Co.) was sublimed before use. The procedures used in the attempted nitrations were identical with those of Baldock et al. (Ref. 16), and Gabriel et al. (Ref. 8). The perchlorinated fumaro and maleonitriles were synthesized by the procedure of Eldred and Young (Ref. 18). The following was the ir of dichlorofumaronitrile taken as a molten film on NaCl plates, absorptions given in microns: 4.4 w with shoulder spike at 4.45, 6.4 w, 8.45 m, 8.75 w, 9.3 s, 9.7 m, 11.75 s center of broad band, 11.45 and 12.1 spikes on the 11.75 band. The dichloro-maleonitrile was not obtained pure and, therefore, its spectrum can not be given with confidence: 3.3 w (CH impurity), 4.4 w, 6.3 w and 6.4 m doublet, 8.5 s, 9.35 s, 11.5 s, 11.8 s and broad.

COUPLING REACTIONS

2,2-Dinitro-2-Cyanoethanol

- (U) To a solution of sodium dinitrocyanomethide (20 g; 0.13 mole) in 75 ml of 37-percent formalin was added dropwise concentrated sulfuric acid (7.25 ml; 0.13 mole). The temperature was maintained at 20 to 25 C during this addition. The reaction mixture was then stirred at room temperature for 5 days. The resulting clear yellow solution was extracted with four 20 ml portions of ether. The ether extracts were dried over magnesium sulfate and the ether was removed in vacuo. The resulting yellow liquid was then pumped under high vacuum removing several milliliters of water and depositing considerable paraformaldehyde. Ether was added and the paraformaldehyde was removed by centrifugation. The ether solution was washed with three 10 ml portions of 10-percent sodium bisulfite and then dried with magnesium sulfate. The ether was removed in vacuo yielding crude 2,2-dinitro-2-cyanoethanol (12 g; 57 percent yield), n_D^{25} 1.4585. Distillation through a small molecular still yielded several cuts of product of varying purity. The purest fraction (~4 g) was a colorless liquid, bp 67 C/0.05 mm, n_D^{25} 1.4574. The ir spectrum exhibited major absorptions (in microns) at 2.7, 4.25, 6.1, 7.4 and 7.6 (doublet), 9.1, 9.5, 11.85, and 12.55.

Analysis calculated for $C_3H_2N_2O_5$: C, 22.36; H, 1.86.

Found: C, 24.34; H, 2.41.

2,2-Dinitro-2-Cyanoethyl Chloride

- (U) To a solution of 8 g (0.05 mole) of 2,2-dinitro-2-cyanoethanol in 20 ml of thionyl chloride was added portion wise 0.14 g of anhydrous pyridine hydrochloride at reflux. The reaction mixture was refluxed for 4 hours and then stirred at room temperature overnight. Excess thionyl chloride was removed in vacuo and the residue was dissolved in methylene chloride.

The methylene chloride solution was extracted with water and then dried over magnesium sulfate. The solvent was removed in vacuo to yield crude 2,2-dinitro-2-cyanoethyl chloride (4.66 g; 52-percent yield), $n_D^{25} 1.4700$. Distillation through a small Vigreux column yielded a main fraction (~1 g) of colorless liquid, bp 35 C/0.05 mm, $n_D^{25} 1.4608$. The ir spectrum exhibited major absorptions (in microns) at 4.25, 6.1, 7.4 and 7.65 doublet, 8.85, 11.85, 12.55, and 13.0.

Analysis calculated for $C_3H_2N_2O_4Cl$: C, 20.11; H, 1.12;

Found: C, 22.65; H, 2.16

Reaction of 2,2-Dinitro-2-Cyanoethyl Chloride

With Potassium Nitrite

- (U) A solution of 2,2-dinitro-2-cyanoethyl chloride (1 g; 5.6 mmole) and potassium nitrite (3.8 g; 45 mmole) in 20 ml of 60-percent aqueous methanol was stirred at room temperature overnight. The reaction mixture at this point was a clear orange solution. Addition of ether to this solution did not yield a solid precipitate. The reaction was not worked up further.

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