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# EXPLORATORY RESEARCH, TASKS A, B, C, AND D

By: Robert L. Simon, Clifford L. Coon,
Michael Cowperthwaite, and Eugene Sincich

Prepared for:

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Livermore, California 94550

Attention: Raymond R. McGuire, L-402

Contract No. EY-76-03-0115
Project Agreement No. 106
Modification No. A001

SRI Project PYD-5058

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Approved:

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CONTENTS

## ILLUSTRATIONS



## TABLES

## PREFACE

This report summarizes the work conducted under Contract No. EY-76-03-0115, Project Agreement No. 106, Modification No. A001. Research on Task A of this project was performed by Michael Cowperthwaite of the Poulter Laboratory, Research on Tasks B, C, And D was performed by Robert L. Simon, Clifford L. Coon, and Eugene Sincich, respectively, of the Organic Chemistry Group, Chemistry Laboratory.

The authors express their appreciation to Milton Finger, Eugene Bissel, and Raymond McGuire of Lawrence Livermore Laboratory for their many helpful discussions and suggestions concerning this work.

# I INTRODUCTION AND SUMMARY

SRI International has conducted research on the upgrading of computerized thermo-hydro code calculations and the synthesis of energetic materials. This project comprised four tasks, as follows.

Task A included (1) formulating routines for inverting the $P = P(T,V)$ and $V = V(T,P)$ equations of state when isotherms exhibit a van der Waals' loop; (2) incorporating these routines into the TIGER code so V and T can be used as independent variables in computing thermodynamic functions of of liquids exhibiting a van der Waals' loop; (3) using these routines to incorporate into TIGER the prototype equation of state for liquids formulated at LLL by Dr. E. L. Lee; and (4) modifying TIGER routines to perform thermodynamic calculations when the concentrations of the gaseous species become zero.

In task B, a homopolymer of fluorodinitroethyl vinyl ether was obtained as a white, cotton-like material by bulk cationic polymerization. Work was begun on solution polymerization of fluorodinitroethyl vinyl ether.

During Task C, studies were conducted on the synthesis of energetic compounds, especially hexanitrobenzene (HNB). The following areas were investigated: (1) nitration of phloroglucinol trioxime, (2) reaction of nitroaromatics with hydroxylamine, (3) oxidation of triaminotrinitrobenzene (TATB) with nitric acid, (4) oxidations with trifluoroperacetic acid, (5) oxidations with ozone, and (6) oxidations with chromic anhydride under anhydrous conditions.

In Task D, known literature syntheses were examined and applied to the synthesis of new polymeric binders. An attractive scheme for the synthesis and polymerization of 2,3-disubstituted oxetanes is reported.

## II DISCUSSION

### A. Task A: Thermo-Hydro Code Development

During this task, we attempted to incorporate the Lawrence Livermore Laboratory (LLL) equation of state for water into the TIGER code. This equation of state expresses the Helmholtz free energy (A) as a function of the temperature (T) and the volume (V), and it was formulated by Dr. E. L. Lee as a prototype equation of state for liquids. The equation of state is complete because the pressure (P) and the entropy (S) are given by the thermodynamic identities $P = -(\partial A/\partial v)_T$ and $S = -(\partial A/\partial T)_V$.

Problems with the LLL equation of state arise in TIGER for the following reasons:

- The routines for computing thermodynamic functions of liquids in TIGER were formulated with T and P as independent variables.
- Thermodynamic calculations with the LLL equation of state in certain domains of the mixed-phase region are difficult because the isotherms exhibit a van der Waals' loop.

Both of these problems were addressed first outside TIGER. The routine EDLLEE was written to calculate pressure from the P = P(V,T) equation of state. The routines EDLEEH, EDLEEL, and EDLEEB for handling a van der Waals' loop were written and combined with EDLEE to form the routine EDLEEZ for first computing V as a function of T and P, and then computing the other thermodynamic functions of liquids needed in TIGER as functions of T and V. The routine EDLEEZ for computer thermodynamic functions of liquids as functions of T and V was then incorporated into TIGER through a routine called LEECON.

In addition, a function of temperature was added to the LLL equation of state to obtain a better description of water in the mixed-phase region.

The function was constructed to obtain agreement between the calculated and experimental values of the chemical potential along the mixed-phase line. The chemical potential was standardized along the Clausius-Clapeyron line to improve phase-change calculations. For this reason also, TIGER was modified to perform thermodynamic calculations when the gaseous concentrations reach zero.

The new routines and the modified equation of state for liquid water were tested by performing a series of calculations using both the BKW and the JCZ3 equations of state to describe the gaseous phase. The first series of calculations showed that the new routines handle the phase-change along the one-atmosphere isobar. When the temperature along this isobar was decreased, the gas changed first to gas-liquid, and then to liquid; this sequence of steps was reversed when the temperature was increased. Successful calculations were also performed in the gaseous and mixed-phase regions at pressures of 4.1 and 16.3 atmospheres.

Problems encountered in the calculations, however, suggest that additional work is required before the new routines can be documented. The EDLEEZ procedure for inverting $P = P(V,T)$ into $V = V(T,P)$ does not converge in the neighborhood of the critical point, and the routine for performing calculations when no gas is present cannot be used with JCZ3. However, both of these incalculabilities are not considered to be major problems but rather iteration problems that can be readily solved.

## B. Task B: Synthesis of Fluoro-Nitro Aliphatic Compounds

The work for this task entailed an energetic polymer from 2,2,2-dinitrofluoroethyl vinyl ether for use as a binder in pressed explosives.

Adolph[1] reported the polymerization of 2,2-dinitropropyl and 2,2,2-dinitrofluoroethyl vinyl ethers. From 2,2,2-dinitrofluoroethyl vinyl ether he obtained a viscous brown oil (MW 1500) by free radical initiation, and from 2,2-dinitropropyl vinyl ether he obtained a white solid (MW 4000) by cationic initiation.

M. Coburn[2] improved the polymerization of 2,2-dinitropropyl vinyl ether (MW 20,000-100,000) by preparing the monomer by a route developed by Shakelford et al.[3] Coburn observed that the purity of monomer is crucial to the degree of polymerization obtainable.

For our study we adopted Coburn's procedure for the polymerization of 2,2-dinitropropyl vinyl ether. 2,2,2-Dinitrofluoroethyl vinyl ether was initially prepared by the method of Shackelford et al.[3] This is a one-step exchange reaction between divinyl ether and dinitrofluoroethanol:

$$CH_2=CHOCH=CH_2 + FC(NO_2)_2CH_2OH \xrightarrow{\text{Catalyst}} FC(NO_2)_2CH_2OCH=CH_2 \quad (1)$$

The crude product is purified by distillation and passing the distillate through alumina. The product is a colorless liquid that is pure by gc analysis. A number of cationic polymerizations were conducted using $SnCl_4$ or $BF_3$ etherate, in solution and in bulk. Solution polymerizations gave yellow oils of low viscosity. The bulk polymerizations gave polymers ranging from dark viscous oils to black putty-like materials. The degree of polymerization was unpredictable and varied considerably. Coburn also found this to be the case with the dinitropropyl vinyl ether. This erratic behavior might be attributable to undetectable impurities in the monomer. This inconsistency in polymer product led us to change the method of monomer synthesis.

Coburn[4] reported the preparation of nitro-containing vinyl ethers by the pyrolysis of the corresponding acetyaldehyde acetal. This synthesis does not use a volatile acid or alkaline catalyst, which might contaminate the monomer and affect the polymerization. Acetaldehyde bis(2,2,2-dinitrofluoroethyl)acetal was prepared by the following route:

$$CH_3COH + 2FC(NO_2)_2CH_2OH \xrightarrow{BF_3\text{-etherate}} CH_3CH[(OCH_2C(NO_2)_2F)]_2 \quad (2)$$

The crude bis-acetal was obtained in about 50% yield. The acetaldehyde bis(2,2,2-dinitrofluoroethyl)acetal was heated in the presence of anhydrous $NaHSO_4$ to 150-170°C at ∿1.5 mm of Hg, and 2,2,2-dinitrofluoroethyl vinyl ether and dinitrofluoroethanol were distilled off and collected. The two products were separated by careful fractional distillation and gave >99% 2,2,2-dinitrofluoroethylvinyl ether. The amount of high-purity dinitrofluoroethylvinyl ether was low (∿39%) because the center cut from the vinyl ether distillation had to be taken to avoid any contamination

from fluorodinitroethanol and low boiling impurities. After distillation and immediately preceding polymerization, the neat vinyl ether was passed through neutral alumina to remove any residual impurities present. A 1-g protion of the purified vinyl ether was placed into a 100-ml, three-neck, round-bottom flask equipped with a mechanical stirrer, a nitrogen flush, and an injector septum. The apparatus was completely flamed out to remove all traces of water before the monomer was added. The reacter was cooled to -78°C, whereupon the monomer solidified. A 4-µl portion of fresh $SnCl_4$ was added by syringe and the reactor was warmed to -15°C. In less than 30 minutes, the monomer changed to a colorless plastic solid. After several hours the reactor was warmed to ambient temperature and was left to stand overnight, during which time the product turned light yellow. The yellow material was dissolved in 5 ml of acetone and precipitated from 200 ml of water, giving a white thread-like solid. This experiment represents the first time the monomer polymerized to any extent at a temperature below ambient, and is also the first time that a white solid instead of a black putty or oil has been obtained. It is evident that the monomer must be extremely pure for it to polymerize under these conditions.

Using this new method of monomer synthesis, it might be possible to polymerize the vinyl ether in solution to gain the advantages of temperature control and mixing. At the time of this report, we were attempting to determine if solution polymerization is possible. If the polymer can be formed in solution, the next step would be to prepare at least 5 g for physical and chemical measurements.

## C. Task C: Synthesis of Polynitro Aromatic Compounds

Our efforts on this task were directed toward the synthesis of hexanitrobenzene (HNB) and, in part, were a continuation of work begun under earlier project agreements with LLL.

### 1. Nitration of Phloroglucinol Trioxime

The only route reported for HNB is through nitration of phloroglucinol trioxime and subsequent oxidation to HNB. This route has been studied by

several research groups in the United States, including ourselves, and in all cases extreme decomposition was noted during nitration. The Soviet and German allusions to this route give no data on the composition of the nitrating medium that was used, and hence we have studied a wide range of nitrating conditions. The research was discussed in detail in previous reports and will only be summarized briefly here.

Phloroglucinol trioxime (or its tautomer, 1,3,5-trihydroxylamino-2,4,6-trinitrobenzene, with which it is in equilibrium) should be very susceptible to oxidation and reactive toward nitrating species. We have studied the reaction of phloroglucinol trioxime with nitric acid concentrations ranging from 30% to 100% with nitric acid-sulfuric acid mixtures, with nitric acid-oleum mixtures, and with nitrate salt-oleum mixtures. All these reactions at either low or ambient temperature were characterized by the immediate appearance of a dark red-brown color upon the addition of the trioxime. Work-up of these reactions resulted in red-brown tars from which it was difficult to isolate products for characterization. Aromatic adsorptions were not present in the ir spectra of these tars, which were chiefly characterized by carbonyl and nitro (or nitrate) absorption. Elemental analyses of the tars usually showed a carbon/nitrogen ratio of from 6/4 to 6/5; this ratio was not attributed to a larger number of nitrogens attached to the aromatic nucleus, but rather to the presence of nitrated decomposition products.

We do not know how (or whether) the German or Soviet chemists prepared HNB, but it is possible that it might have been through the phloroglucinol route. However, in the extensive work we have carried out thus far, the nitration step has not yielded any products that appear promising enough to warrant continuing research on the phloroglucinol route to HNB.

2. Reaction of Nitroaromatics with Hydroxylamine

Hydroxylamine is an effective reagent for placing an amino group on a highly nitrated aromatic nucleus. For example, the reaction of 2,6-dinitrotoluene with hydroxylamine in base leads to the formation of 3-amino-2,6-dinitrotoluene in good yield. Recently, Grudtsyn and Gitic[5]

reported that either one or two hydroxylamine groups could be placed on 1,3,5-trinitrobenzene using hydroxylamine in $Me_2SO$-NaOMe or MeOH-NaOMe. We felt that this procedure might also be a way of placing a third hydroxylamine group on 1,3,5-trinitrobenzene, thus arriving at 1,3,5-tris(hydroxylamine)-2,4,6-trinitrobenzene, which is the desired, but allusive, product from the nitration of phloroglucinol trioxime. TATB was another possible product from the reaction of hydroxylamine with 1,3,5-trinitrobenzene.

A brief study of this reaction showed that after acidification of the products from the reaction of hydroxylamine hydrochloride with 1,3,5-trinitrobenzene in either $Me_2SO$-NaOMe or MeOH-NaOMe, the main product was picramide. Picramide yields of as high as 80% were common. Many unsuccessful attempts were made to place a second amino group on the aromatic ring, but after acidification of the reaction mixture, picramide was the main product. When picramide was used as a starting material, a stable, water-soluble, orange solid could be isolated. Upon acidification, picramide was precipitated with an almost quantitative recovery.

Many researchers have studied the reactions of 1,3,5-trinitrobenzene with a variety of bases, and it is evident that substitutions, 1,3-additions, and both pi and sigma complex formations are possible. Further research in this area might be useful in the synthesis of energetic compounds, but we doubt that these reactions with hydroxylamine will lead to an HNB precursor and plan no further research in this area at this time.

3. Oxidation of TATB with Nitric Acid

Although TATB appears to be a logical precursor to HNB, its insolubility in most solvents and strong inter- and intra-molecular hydrogen bonding have made it less attractive as an HNB starting material. In addition, there is no reason to use TATB as a precursor for HNB when PNA is available. However, in the study of the oxidation of acetylated TATB (described below), the question arose concerning the products from the oxidation of TATB with 90% $HNO_3$. A brief study on this subject showed that TATB reacts rapidly with 90% nitric acid at 50°C to give a number of products. One of these products is trinitrophloroglucinol, which raises

the question of when displacement of the nitrogen-containing moiety by hydroxyl occurs. It is probable that under the highly oxidizing conditions, an amino group is converted to a nitro group, and then, aided by the activating effect of the adjacent nitro groups, is displaced by hydroxyl ion. Although it is doubtful that HNB is an intermediate in the conversion of TATB to trinitrophloroglucinol, this reaction indicates the need for an oxidizing medium that is free of nucleophilic ions.

4. Oxidation with Trifluoroperacetic Acid ($CF_3COOOH$)

We previously reported an extensive study on the attempted oxidation of HNB precursors to HNB using $CF_3COOOH$. Work was continued in this area using several substrates.

a. 1,3,5-Triazido-2,4,6-trinitrobenzene (TAzTNB). Although no conversions of an azido group to a nitro group have been reported, we felt that TAzTNB was a likely precursor to HNB, and carried out a brief study of its oxidation with $CF_3COOOH$. This work is summarized in Table 1.

TAzTNB does not react with $CF_3COOOH$ at 25°C, but it will react at reflux temperature (74°C) to give BTF and several unidentified by-products. The formation of BTF is probably not affected by the oxidizing medium, but BTF is the expected product from heating TAzTNB in an acidic medium. Several other by-products probably result from oxidization by $CF_3COOOH$ owing to their strong carbonyl absorptions. One by-product, which is soluble in hexane and melts at 106°C, appears to be an intermediate between TAzTNB and BTF. The ir spectrum of this by-product shows that an azide group is present but is not as strong as in TAzTNB. No carbonyl is present.

b. 1,3,5-Tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene. One reaction was done on the oxidation of 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene with $CF_3COOOH$. At ambient temperature, no reaction occurred. This reaction should be studied at elevated temperatures.

c. Acetylated Triaminotrinitrobenzene (TATB). TATB was acetylated in order to increase its solubility in the $CF_3COOOH$ oxidizing medium, for

Table 1

REACTION OF TAzTNB WITH $CF_3COOOH$

| Run No. | TAzTNB (g, mmol) | TFAA (ml) | 90% $H_2O_2$ (ml) | Time (min) | Temp. ($^oC$) | Results |
|---|---|---|---|---|---|---|
| 1 | 0.35, 1.0 | 9.6 | 1.42 | 60<br>720 | 25<br>74 | BTF main product; several unknowns, one with mp 106°C |
| 2 | 0.35, 1.0 | 9.6 | 1.42 | 60 | 25 | TAzTNB |
| 3 | 0.35, 1.0 | 9.6 | 1.42 | 240 | 25 | TAzTNB |
| 4 | 0.35, 1.0 | 9.6 | 1.42<br>1.42<br>1.42 | 60<br>60<br>60 | 25<br>25<br>25 | <br><br>TAzTNB |
| 5 | 0.35, 1.0 | 9.6 | 1.42 | 60 | 25 | TAzTNB, BTF; several unknowns, one with mp 106°C |

which $CH_2Cl_2$ or $CHCl_3$ is used as a solvent. TATB is easily acetylated with refluxing acetic anhydride that contains a small amount of sulfuric acid. This reaction was first run by M. Coburn at LASL, who isolated the tri-acetylated product by quenching the reaction in water and collecting the product by filtration. We found that a mixture of the hexa- and penta-acetyl derivatives of TATB can be isolated by removing the solvent after acetylation and that they can be separated by column chromatography. Both the hexa- and the penta-acetyl TATB can be converted into the triacetyl derivative if they are stirred with water.

Oxidation of tri-, penta-, and hexa-acetyl TATB with $CF_3COOOH$ was done with the objective of obtaining HNB. With tri-acetyl TATB essentially no oxidation occurred, and all the starting material was isolated. Penta- and hexa-acetyl TATB were converted to tri-acetyl TATB by the reaction medium.

5. Oxidation with Ozone

Ozone has been used extensively for the oxidation of carbon atoms to form ozonides, alcohols, aldehydes, and acids. There are no reports of ozone oxidation of the azide or amino groups to form nitro groups. We have briefly studied the reaction of ozone with 1,3,5-triamino-2,4,6-trinitro-benzene (TATB), and pentanitroaniline. These studies are summarized in Table 2.

a. TATB and Pentanitroaniline (PNA). In general, these reactions were unsuccessful and only starting material or uncharacterized products of oxidation were isolated. However, two reactions led to results that are worth noting in this summary. First, treatment of TAzTNB with ozone gave small quantities of BTF and possibly an intermediate product between TAzTNB and BTF. This latter product could be of interest as a CNO explosive. These results are similar to those obtained from the aforementioned reaction of TAzTNB with 90% $H_2O_2$ in $Ac_2O/AcOH$.

Secondly, oxidation of PNA with ozone in methylene chloride gave a $CCl_4$-soluble product that had an ir spectrum substantially different

Table 2

OXIDATION OF HNB PRECURSORS WITH OZONE

| Compound (g, mmoles) | Ozone[a] (mmol) | Solvent | Reaction Time (min) | Results |
|---|---|---|---|---|
| TAzTNB[b] (0.28, 0.83) | 9.8 | $CCl_4$ | 14 | Mixture of TAzTNB, BTF, and possibly an intermediate |
| TAzTNB (0.28, 0.83) | 21.0 | $CCl_4$ | 30 | Mixture of TAzTNB, BTF, and oxidized by-products |
| TAzTNB (0.28, 0.83) | 42.0 | TFAA | 60 | N.R. |
| TAzTNB (0.28, 0.83) | 42.0 | TFAA/TFA | 60 | N.R. |
| TAzTNB (0.28, 0.83) | 52.0 | $ClCH_2CH_2Cl$ (40°C) | 75 | Mixture of TAzTNB, BTF, oxidized by-products, and $ClCH_2COOH$ |
| TATB[c] (0.4, 1.55) | 10.5 | $CCl_4$ | 15 | TATB; $CCl_4$-soluble oxidation product |
| TATB (0.4, 1.55) | 21.0 | $ClCH_2CH_2Cl$ (40°C) | 30 | TATB; $CCl_4$-soluble oxidation product |
| TATB | 28.0 | $CH_3COOH$ (40°C) | 40 | N.R. |
| TATB (0.4, 1.55) | 168.0 | $ClCH_2CH_2Cl$ (50°C) | 240 | TATB, $CCl_4$-soluble oxidation product |
| PNA[d] (0.2, 0.61) | 7 | $CCl_4$ | 10 | N.R. |
| PNA (0.2, 0.61) | 35 | $CCl_4$ | 50 | N.R. |
| PNA (0.4, 1.22) | 10.5 | EtOCa | 15 | Mainly PNA; some oxidation evident |
| PNA (0.4, 1.22) | 52.5 | EtOAc | 75 | Mainly PNA; highly oxidized by-products evident |
| PNA (0.4, 1.22) | 10.5 | $CH_2Cl_2$ | 15 | Mainly PNA; trace of an interesting $CCl_4$-soluble product isolated |
| e (0.20, 0.51) | 84.0 | $CCl_4$ | 120 | N.R. |

N.R. =

a. 4% $O_3$ in $O_2$ added at a rate of 2 g $O_3$ per hr.
b. 1,3,5-Triazido-2,4,6-trinitrobenzene.
c. 1,3,5-Triamino-2,4,6-trinitrobenzene.
d. Pentanitroaniline.
e. 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene.

from PNA and consistent with that expected for HNB. This material represented only a small percentage of the reaction product and has not been characterized further.

b. Preparation of Pentanitroaniline (PNA). PNA is the most likely precursor for the synthesis of HNB. It is prepared in low to moderate yield by the nitration of dinitroaniline with mixed acids.[6] Over several years of working with PNA and from the comments of others, we have noted that results in the synthesis of PNA are inconsistent, with yields ranging from 0% to 40%. Our experience has shown that yields of around 30% can be obtained consistently if the nitration reaction is kept small. Yields from 1.5 g, 4.0 g, and 19 g of starting material were 45%, 30%, and 0%, respectively. In addition, PNA should be stored in a dry, cool location, because it decomposes slowly at ambient temperature and in the presence of moisture.

3,5-Dinitroaniline (3,5-DNA) can be purchased but it is relatively expensive and is often subject to backordering. It is best prepared by the method of Lathrop et al.,[7] using 3,5-dinitrobenzoic acid as starting material. Because we had some 1,3,5-trinitrobenzene on hand, we used it as starting material and followed the reduction procedure given in Hickenbottom[8]. From experience, we have learned that the reported ratio of 4.6:1 for reducing reagent to substrate is much too high and should be about 3:1. The reported ratio gave large quantities of 1,3-diamino-5-nitrobenzene while the latter gave an excellent yield of the desired 3,5-DNA, containing only trace amounts of 1,3-diamino-5-nitrobenzene.

6. Oxidation with Chromic Anhydride ($CrO_3$)

Chromic anhydride is commonly used for the oxidation of double bonds, alkyl substituents on aromatic rings, and alcohols to ketones. Although $CrO_3$ has never been reported to oxidize amino or azido groups to nitro groups, we studied it for this purpose because it is a powerful oxidizing agent that can be used under anhydrous conditions.

The reaction of $CrO_3$ with 1,3,5-triazido-2,4,6-trinitrobenzene (TAzTNB) was examined briefly using anhydrous acetic acid as solvent.

TATNB dissolved readily in the reaction medium, which changed from a dark blue-green color to light brownish-green during the course of the reaction, indicating that oxidation had occurred. Isolation of organic products proved to be a problem since we were trying to work under anhydrous conditions. The best procedure we developed was to pass the reaction solution through a neutral alumina column using dry methylene chloride as an eluant. Methylene chloride-soluble organic products could be isolated by this procedure. TAzTNB was the main constituent, but other products could also be isolated. They are characterized by strong carbonyl absorptions and a lack of aromatic character in their ir spectra. There was no evidence of the presence of HNB, pentanitroazidobenzene, or 1,3,4,5-tetranitro-2,6-diazidobenzene.

Research should be continued in this area to (1) study the oxidation of pentanitroaniline or TATB, (2) study the oxidation of TAzTNB under milder conditions for longer periods of time, and (3) examine the use of $CrO_3$ in other solvents such as DMF, acetic anhydride, and HMPA.

## D. Task D: Investigation of Poly-fluoro Binder Materials for BTF Application

The investigation of new compatible binder materials has led to the possibility of synthesizing totally new energetic binders for pressed explosives. Therefore, in this task we attempted to develop possible routes for such binders.

The most attractive route involves the ring-opening polymerization of oxetanes. Many 3,3-disubstituted oxetanes are known, as well as polymers prepared from these oxetanes. However, the resulting polymers are almost invariably high melting, crystalline materials. Accordingly, we investigated possible preparative routes for 2,3-disubstituted oxetanes in an effort to obtain a candidate material whose polymer would be an amorphous material possessing a low glass transition temperature ($T_g$).

The preparative routes suggested are shown in Scheme 1. The starting material is tertiary amylene, which is commercially available from Shell, and a one-quart sample has been obtained. It can be brominated with NBS, followed by treatment with diborane and peroxide to form the alcohol. The ring-closing step with potassium hydroxide yields the 2,3-bis(bromomethyl oxetane). That material can then be nitrated and fluorinated to

form high energy 2,3-disubstituted oxetanes. The monomers are expected to readily polymerize cationically.

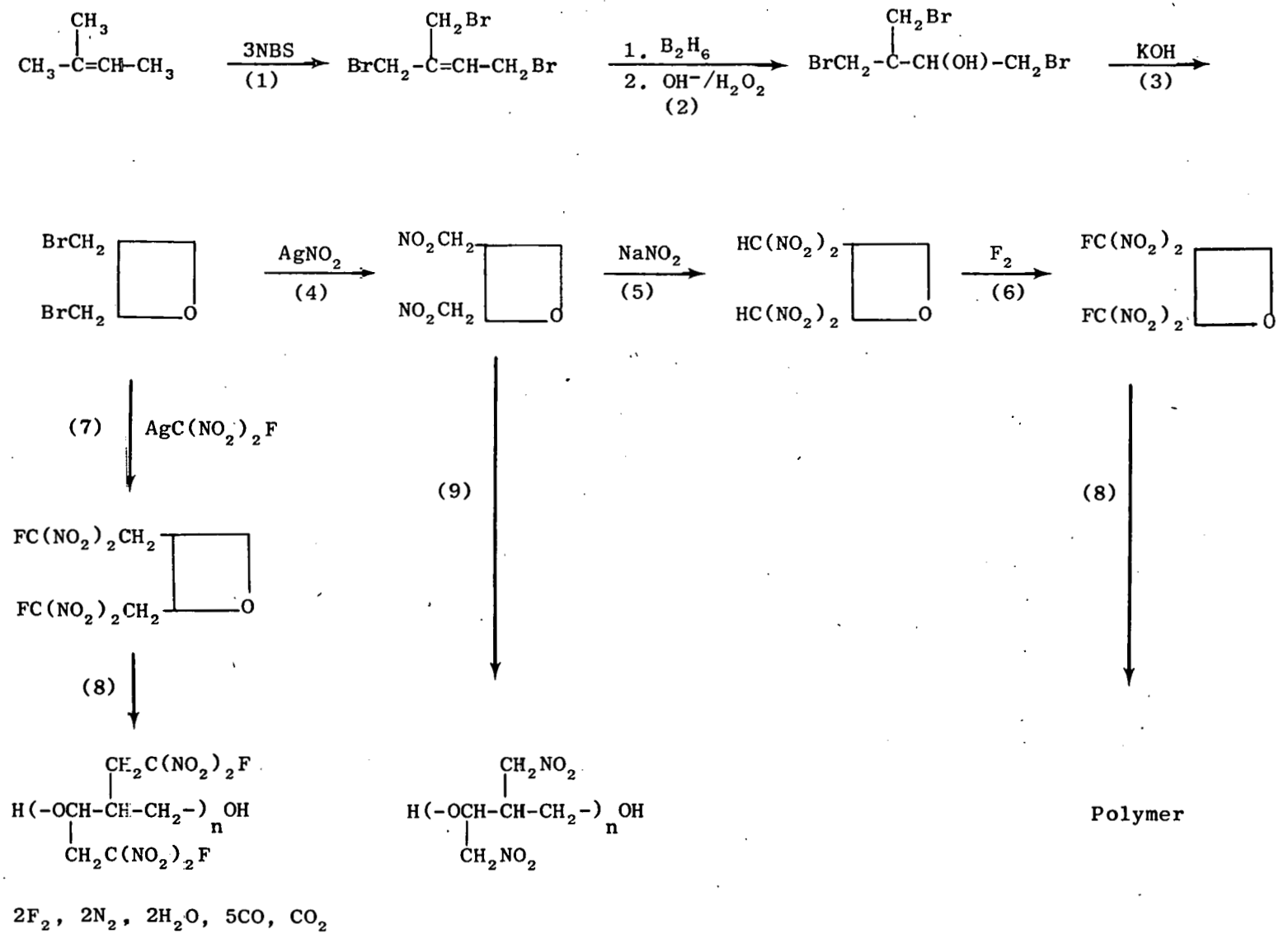


Figure 1. Proposed Synthesis of Energetic Oxetanes and their Polymers

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