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General Aniline and Film Corporation
Central Research Laboratory
Easton, Pennsylvania

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April 1, 1954

Final Report

SUBJECT: Synthesis of Nitroalkyl Vinyl Ethers

CONTRACT: Nonr-846(00)

PERIOD COVERED: November 1, 1952 - April 1, 1954

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14,206 Synthesis of Nitroalkyl Vinyl Ethers. L. E. Craig, J. M.
Wilkinson. 55 pp., 5 tables, 1 figure. General Aniline and
Film Corp. Final Rept. of 1 April 1954 (Contract Nonr-846(00)).
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Aliphatic nitro compounds are unstable under the conditions usually used for vinylation of alcohols. Attempted vinylation of nitro alcohols at 150-160° C. with acetylene in the presence of alkaline catalysts were unsuccessful. A small amount of 2, 2-dinitropropane prevented the normal vinylation of an alcohol, presumably by neutralization of the alkaline catalyst.

Attempts were made with no success to stop the acid-catalyzed addition reaction of alcohols and acetylene at the vinyl ether stage. Mercuric salts of ion-exchanged resins were investigated as catalysts.

2-Methyl-2-nitropropanol was added to one equivalent of glycol divinyl ether to give 2-(1, 3-dimethyl-3-nitrobutoxy)ethyl vinyl ether in 60% yield. This nitroalkyl vinyl ether was polymerized by boron trifluoride to a viscous syrup. An attempt was made to add nitroform to glycol divinyl ether, but an explosion occurred as the excess glycol divinyl ether was being removed. The explosion was probably due to vigorous polymerization of the glycol divinyl ether.

Polymeric material was obtained from the mercuric sulfate-catalyzed reaction of 4, 4-dinitroheptanediol and acetylene. Low-molecular-weight polymers with relatively high specific impulses might be made from polynitro glycols in this manner.

The addition of nitryl chloride to vinyl ethers was being studied when cessation of the investigations was necessary. Nitryl chloride was bubbled into chloroform solutions of vinyl ethers at ice-bath temperatures. Evaporation of the solvent left relatively non-volatile addition products in yields of about 50%, based on 1:1 addition products. The addition products were found to contain very labile chlorine atoms, but the chlorine contents were lower than theory for 1:1 addition products. The products gave solid derivatives with p-nitroaniline and 2, 4-dinitrophenylhydrazine, but it was not possible to obtain them in pure form. Attempts were made to identify the addition products and their derivatives, but such was not possible in the short time spend on them. It seems possible that telomers were obtained rather than 1:1 addition products.

Attempts were made to prepare nitroalkyl vinyl ethers by pyrolysis of nitroalkyl alkyl acetals. A number of catalysts for this purpose were screened with diethyl acetal, alumina pellets being the best found. Pyrolysis of unsymmetrical acetals showed that secondary and tertiary alkyl groups were cleaved to about four times the extent of primary alkyl groups. Pyrolyses of nitroalkyl alkyl acetals, however, resulted in extensive formation of oxides of nitrogen and no nitroalkyl vinyl ether was isolated.

Pyrolysis of acylal over sodium acetate supported on porous plate fragments gave ethyl vinyl ether in 30% conversions, whereas diethyl acetal was unchanged under the same conditions. This suggested that nitroalkoxyacetoxyethane could probably be converted to the nitroalkyl vinyl ether. However, no convenient method for preparing nitroalkyl acylals was found.

Attempts were made to convert crude alcohol-acetaldehyde-hydrogen chloride reaction products, presumably α-chloroethyl ethers, to vinyl ethers. However, the use of this crude reaction product was not successful.

A procedure for preparing vinyl ethers from alcohols and vinyl acetate at low temperatures was recently reported, the extent of vinyl ether formation being inferred from acetic acid titrations of the reaction product. This procedure was followed and similar acetic acid titrations were observed; however, attempts to isolate any vinyl ether were unsuccessful.

Attempts were made to introduce nitro groups into an existing polymeric material by esterifying PVM/MA with nitro-alcohols. Esterification, however, proceeded to at most 20% of theory for the half ester.

2-Methyl-2-nitropropyl esters of maleic and fumaric acids were prepared. The esters did not copolymerize with vinyl ethers.

Contents

Tables

Figures

Introduction

On June 1, 1952, General Aniline and Film Corporation was awarded Contract No. Nonr-846(00) by the Office of Naval Research. The contract called for investigations of possible syntheses of nitroalkyl vinyl ethers and polymers therefrom in connection with the extensive program being carried out on nitro polymers and their application to solid smokeless propellants. This report constitutes a final report on all investigations carried out by General Aniline and Film Corp.

Summary and Conclusions

A number of possible methods for synthesizing nitroalkyl vinyl ethers and several alternative methods for preparing nitro polymers were investigated. The more important results and conclusions are listed below.

[redacted] Aliphatic nitro compounds are unstable under the conditions usually used for vinylation of alcohols. Attempted vinylation of nitro alcohols at 150-160°C. with acetylene in the presence of alkaline catalysts were unsuccessful. A small amount of 2,2-dinitropropane prevented the normal vinylation of an alcohol, presumably by neutralization of the alkaline catalyst.

[redacted] Attempts were made with no success to stop the acid-catalyzed addition reaction of alcohols and acetylene at the vinyl ether stage. [redacted] Mercuric salts of ion-exchanged resins were investigated as catalysts.

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[redacted]) 2-Methyl-2-nitropropyl esters of maleic and fumaric acids were prepared. The esters did not copolymerize with vinyl ethers. End

Prior Art

The literature references cited throughout the Discussion and Experimental sections are listed at the end of the report.

Patent Action

No patent action has been taken. An application covering various nitroalkyl acetals was considered, but both symmetrical and unsymmetrical acetals from nitroalcohols have been disclosed in the literature. Acetals described herein would be isomeric or homologous to those reported in the literature and would undoubtedly be unpatentable in view of the lack of unexpected utility or properties.

Patent action was considered on the vinyl ether-nitryl chloride addition products. However, since the products were not characterized and some question about their identity exists, no patent action was taken.

Discussion

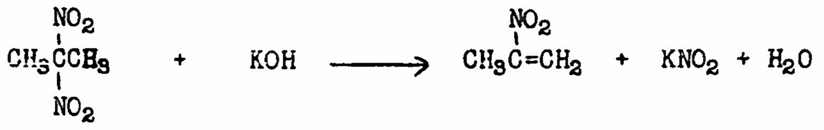
A. Vinylation of Nitroalcohols

1) With Alkaline Catalysts

The usual procedure for preparing vinyl ethers from alcohols and acetylene involves reactions at 150-165°C. with potassium hydroxide or the potassium alkoxide as catalyst /1/. Although the stability of the nitroalcohols under these conditions was questionable, it was felt that this approach should be investigated.

When 2-methyl-2-nitropropanol was heated in an autoclave at 160°C. with powdered potassium hydroxide, gaseous decomposition was indicated by a steady increase in pressure to 345 psig. Small samples of 4-methyl-4-nitropentanol, 4,4-dinitropentanol, 5,5-dinitro-2-hexanol, and 5,5-dinitro-2-ketohexanol, kindly supplied by Aerojet Engineering Corp., were treated with potassium <u>sec</u>.-butoxide in <u>sec</u>.-butanol. Exothermic reactions occurred in some cases at room temperature; decomposition was evident in all cases on heating.

<u>gem</u>-Dinitro compounds are considered to be the most stable of the nitroparaffins. However, the above observations indicated they are relatively unstable in the presence of alkali. It seems probable that the decomposition is due to the splitting out of a molecule of nitrous acid with formation of the nitroolefin as indicated in equation (1). To check this possibility,



$$CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_3 + KOH \longrightarrow CH_3\overset{NO_2}{C}{=}CH_2 + KNO_2 + H_2O \qquad (1)$$

2,2-dinitropropane was heated at reflux with 1.5 equivalents of sodium ethoxide in ethanol. The solid which separated was identified as sodium nitrite and 1.45 equivalents of the nitrite ion were cleaved. This suggests that the reaction proceeds farther than nitroolefin formation. It seems possible that the nitroolefin is formed, that ethanol then adds to the double bond, and that more nitrous acid is split out to give, probably, a vinyl alkyl ether.

In spite of the indicated instability of the nitroalcohols, a few attempts were made to carry out vinylations with alkaline catalysts. All were unsuccessful. Also, an attempt was made to vinylate 2-ethylhexanol under usual conditions in the presence of a small amount of 2,2-dinitropropane. No vinyl ether was produced. This approach to the synthesis of nitroalkyl vinyl ethers was, therefore, abandoned.

2) With Acid Catalysts

Alcohols add readily to the triple bond of acetylenic compounds in the presence of mercuric salts. However, the reaction does not stop at the vinyl ether stage, the alcohol adding to the vinyl ether to give the acetal as the final product. The addition of the alcohol to the vinyl ether is acid-catalyzed and is probably the more rapid reaction. As the acetylene is introduced as a gas, the alcohol concentration is always high. This also favors the second step in equation (2).

$$HC\equiv CH + HOR \xrightarrow{Hg^{++}} CH_2{=}CHOR \xrightarrow[H^+]{HOR} CH_3CH(OR)_2 \qquad (2)$$

British Patent 231 841 /2/ claims that the vinyl ether can be prepared from methanol and acetylene in ligroin with a mercuric phosphate catalyst, the vinyl ether being continuously swept out of the reaction with the excess acetylene. British Patent 156 121 /3/ and US Patent 1 436 288 /4/ disclose the preparation of vinyl ethers by adding acetylene to concentrated sulfuric acid and then treating the "vinyl sulfuric acid" with alcohols; yields of 55-80% are claimed. However, these reported methods were considered impracticable.

As the second step of equation (2) is acid-catalyzed and the first step is catalyzed by mercuric salts, the possibility of finding a mercuric salt which would allow the reaction to be stopped at the first step was considered. For this reason, ion-exchange resins of the sulfonic and carboxylic acid types were converted to mercuric salts and examined as catalysts in this reaction. The ion-exchange resin and alcohol were stirred while acetylene was introduced below the level of the liquid. The nature of the product was determined by analyzing for vinyl ether and acetal. Four catalysts were studied: 1) Dowex 50, a sulfonated aromatic hydrocarbon polymer, containing about 12% capacity of mercuric ions; 2) Dowex 50 containing 25% capacity of mercuric ions and 75% capacity of ferric ions; 3) Dowex 50 containing full capacity of mercuric ions; and 4) Amberlite IRC-50 (polyacrylic acid) containing about 50% capacity of mercuric ions.

The results of the experiments carried out are summarized in Table 1. Little or no vinyl ether was produced, the main product being the acetal.

Another possible method of stopping equation (2) at the first step would be to use a large excess of the acetylenic compound. Thus, if the alcohol could be added slowly to the acetylenic compound containing the mercuric catalyst, the first step would be favored. This method, of course, would be impractical with acetylene itself. For this purpose, methyl propargyl ether was prepared from propargyl bromide and methanolic potassium hydroxide. The properties of the product obtained agreed well with those reported and it was used in an experiment in which butanol was added slowly to it in the presence of mercuric sulfate.

The identity of the product obtained is unknown, although iodometric titration indicated that little or no vinyl ether was produced. This experiment was carried out before analyses on the methyl propargyl ether were obtained. A sample was sent to the analytical laboratory for assay by acetylenic hydrogen determination. Since the analytical results were low, the product was examined further, but the discrepancies could not be explained.

This approach to the synthesis of vinyl ethers from alcohols and acetylenic compounds still seems feasible, but it was not pursued further for the nitro polymer program. If acetylenic compounds other than acetylene must be used, the resulting added carbon and hydrogen atoms would make the preparation of nitro compounds with a high specific impulse difficult. Methoxyacetylene might be suitable for use as the acetylenic compound in this approach, but it was not available at the time this approach was being examined.

B. Addition of Nitroalcohols and Nitroform to Divinyl Ethers

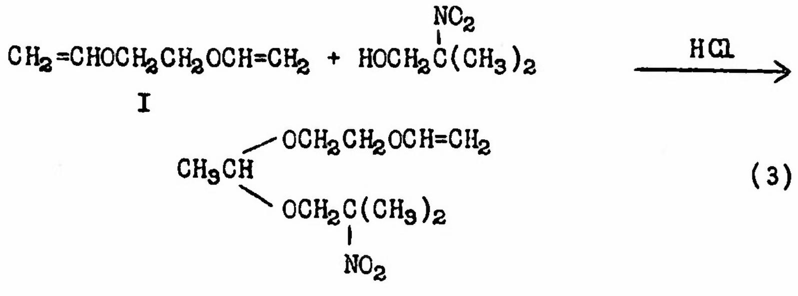
The addition of one equivalent of nitroalcohol or nitroform to one equivalent of a divinyl ether would result in a vinyl ether containing nitro groups. In the initial experiment of this approach, 2-methyl-2-nitropropanol was added to an excess of glycol divinyl ether (I) with a small amount of methanolic hydrogen chloride as catalyst. The desired product (II) was obtained in 60% yield. It was identified by elemental analysis.

Table 1

Addition of Ethanol to Acetylene in the Presence of Ion-Exchange Resin Catalysts

Exp. No.	Catalyst	Time	**Vinyl Ether**	Acetal		Acetaldehyde	
			Total Moles	Total Moles	% Yield[a]	Total Moles	% Yield[a]
3053-61	I	3	0	0.188	78	0.002	0.8
3053-63	I	7	0	0.714	85	0.048	5.7
3053-74	II	5	0	0.0088		0.0013	
3053-78	III	3		0.062		0.0024	
3053-71	IV	5		0.0064		0.0024	

[a] Based on approximate amount of acetylene absorbed.

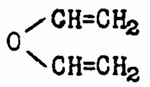


(3)

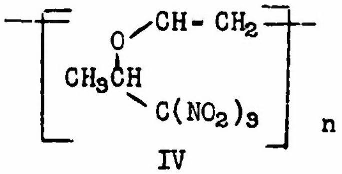
II

The addition of a few drops of boron trifluoride etherate to a benzene solution of II resulted in an exothermic reaction and an increase in viscosity. Removal of the benzene *in vacuo* left a viscous gummy polymer.

This reaction was considered as a possible route to compounds with high specific impulse only if divinyl ether (III) and nitroform or trinitroethanol could be used. Thus, the polymer (IV) from the divinyl ether-nitroform adduct would have a specific impulse of about 236.



III

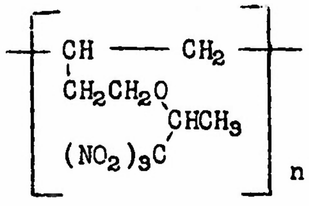


IV

Investigations at Aerojet Engineering Corp. and U. S. Rubber Co. had shown that divinyl ether does not react in the usual way. Rather, the product from divinyl ether and methanol was shown to give methyl vinyl ether and, presumably, acetaldehyde.

$$CH_2{=}CHOCH{=}CH_2 + CH_3OH \xrightarrow{BF_3} CH_3OCH{=}CH_2 + CH_3CHO \qquad (4)$$

Of the other available divinyl ethers, that of ethylene glycol (I) would introduce the fewest additional carbon and hydrogen atoms. The polymer from the hypothetical glycol divinyl ether-nitroform adduct (VI) would have a specific impulse of about 215.



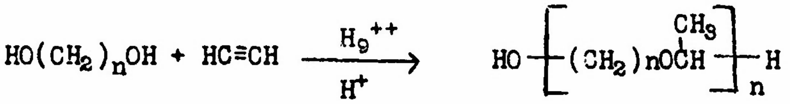
VI

An attempt was made to add one equivalent of nitroform to glycol divinyl ether. The addition was carried out and the solvent and excess divinyl ether were being removed when an explosion occurred. The explosion was probably due to violent polymerization of the divinyl ether. It was subsequently shown that nitroform catalyzes the polymerization of divinyl ether at elevated temperatures, and this polymerization is very violent.

Further work with nitroform and trinitroethanol was, therefore, not carried out. The use of other nitro alcohols was not considered because of the relatively low specific impulses which the resulting compounds would have.

C. Polymers from Nitroglycols and Acetylene

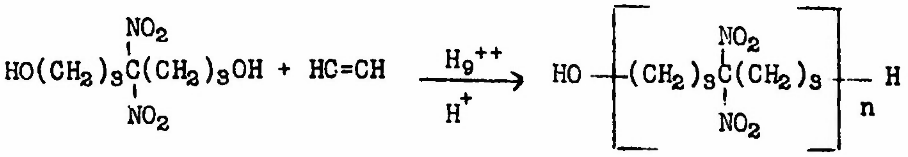
Acetylene can be considered as a bifunctional molecule as far as addition of alcohols are concerned. Addition reactions with glycols could, therefore, give rise to polymeric materials, as illustrated by equation (5). In order to avoid the formation of cyclic rather than linear acetals, a glycol with n greater than three should be used.



$$HO(CH_2)_nOH + HC{\equiv}CH \xrightarrow[H^+]{Hg^{++}} HO\left[(CH_2)_nO\overset{CH_3}{\overset{|}{C}}H\right]_nH \qquad (5)$$

1,4-Butanediol and 1,6-hexanediol were shown to give such polymeric acetals. Acetylene was bubbled into a dioxane solution of the glycol containing mercuric sulfate as the catalyst until no more was absorbed. Evaporation of the solvent left a viscous, non-volatile syrup.

A polymeric material was prepared similarly from 4,4-dinitroheptanediol, as illustrated in equation (6). Polymers prepared in this manner would probably never have particularly high molecular weights. Materials with fairly high specific impulses might be prepared from polynitro glycols. 2,2-Dinitropropanediol, which is available, would probably give rise largely to cyclic acetals. Polymeric materials such as VII might be useful as solvents and plasticizers for high energy propellants.

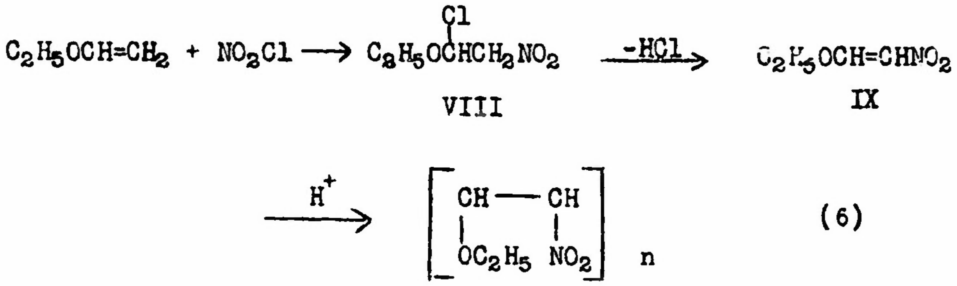


$$HO(CH_2)_3\underset{NO_2}{\overset{NO_2}{C}}(CH_2)_3OH + HC{=}CH \xrightarrow[H^+]{Hg^{++}} HO\left[(CH_2)_3\underset{NO_2}{\overset{NO_2}{C}}(CH_2)_3\right]_nH$$

VII

D. Addition of Nitryl Chloride to Vinyl Ethers

Equation (6) illustrates another possible route to nitroalkyl vinyl ethers and polymers thereof. The addition product (VIII) should



$$C_2H_5OCH{=}CH_2 + NO_2Cl \longrightarrow C_2H_5O\overset{Cl}{\overset{|}{C}}HCH_2NO_2 \xrightarrow{-HCl} C_2H_5OCH{=}CHNO_2$$

VIII IX

$$\xrightarrow{H^+} \left[\begin{array}{ccc} CH & — & CH \\ | & & | \\ OC_2H_5 & & NO_2 \end{array}\right]_n \qquad (6)$$

X

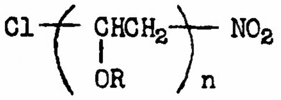
contain a very labile chlorine atom and dehydrohalogenation to IX should be possible. Polymer X represents the polymer with the highest specific impulse (185) that could be prepared in this manner. Compounds VIII or IX, however, might be valuable intermediates in the preparation of other high-energy materials. For example, either VIII or IX would be a convenient source of nitroacetaldehyde, which might be useful in a variety of condensation reactions.

Investigations with nitryl chloride were underway but not completed when it was necessary to discontinue the work. Nitryl chloride was added to vinyl ethers in chloroform solution at ice bath temperatures. Unstable products were obtained when an excess of the vinyl ether was used, but the addition product was stable when an excess of the nitryl chloride was used. The addition reaction is somewhat exothermic; in one case a mild explosion was encountered when nitryl chloride vapors came in contact with undiluted ethyl vinyl ether at room temperature.

The general procedure used was to bubble nitryl chloride into a stirred chloroform solution of the vinyl ether at ice bath temperatures. Ethyl vinyl ether was used for most of the work. An excess of nitryl chloride was introduced and the excess removed under a stream of nitrogen. Reduced pressure evaporation of the chloroform left light yellow residues which were not volatile at room temperature at 5-10 mm. pressure. The residues obtained represented yields of about 50%, based on 1:1 addition products.

Only about 25% of the residues so-obtained was volatile at room temperature at pressures of about 1 mm. This, plus the rather low active chlorine values, suggests that the product is not the simple 1:1 adduct.

Telomerization may have occurred with formation of adducts represented by XI.



$$Cl\left(\underset{\mid \atop OR}{CHCH_2}\right)_n NO_2$$

XI

The products did contain reactive chlorines, as indicated by the formation of voluminous precipitates upon shaking with aqueous silver nitrate. They gave solid derivatives with aniline, p-hydroxyaniline, p-nitroaniline, semicarbazide, phenylhydrazine, and 2,4-dinitrophenylhydrazines. These derivatives, however, were very difficultly purified. The derivatives with p-nitroaniline and 2,4-dinitrophenylhydrazine were the most stable. Attempts at purification by chromatography and by recrystallization were unsuccessful.

The derivatives with p-nitroaniline and 2,4-dinitrophenylhydrazine were dissolved in acetic acid and warm ethanol, respectively, filtered and reprecipitated by drowning in water. Attempts at slow reprecipitation (recrystallization) were unsuccessful. Elemental analyses and molecular weight determinations on the solid derivatives do not suit any reasonable product that has yet been considered. A higher state of purity of the derivatives will be necessary before elucidation of structures are possible.

Nitryl chloride was added to n-butyl and sec.-butyl vinyl ethers. The products gave derivatives similar to those obtained from the ethyl vinyl ether.

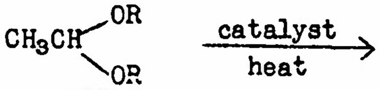
α-Chloroethyl ethers give acetals when heated with ethanol. If compound VIII is formed in the reaction, it should react with ethanol to give the diethyl acetal of nitroacetaldehyde. An ethyl vinyl ether-nitryl chloride product was heated with ethanol. Reduced pressure distillation of the product gave a small yield of product boiling in the range reported for the diethyl acetal of nitroacetaldehyde /5/. It gave a difficultly purified derivative with phenylhydrazine that melted near the reported melting point of the phenylhydrazone of nitroacetaldehyde /6/.

Unsuccessful attempts were made to dehydrohalogenate the ethyl vinyl ether-nitryl chloride addition products. Heating with dimethylaniline and ethylmethylpyridine resulted in very dark solutions but no separation of the amine hydrochlorides. Treatment with ethanolic sodium ethoxide gave an immediate white precipitate, but the product would undoubtedly be the diethyl acetal rather than IX.

E. Pyrolysis of Nitroalkyl Acetals

One of the reported methods for making vinyl ethers is the catalytic cleavage of acetals /1/. The reaction has been carried out, for the most part, in the vapor phase over supported nickel, palladium, platinum, etc., catalysts. Temperatures of 180-500°C. have been used. It is significant that the reaction will take place in the 180-250°C. range, and it was felt that nitro compounds might stand this temperature for very short contact times.

The course of the reaction is illustrated by equation (7). If the acetal (XII) is symmetrical, only one vinyl ether is obtained. If, however,


XII

$$CH_3CH(OR)_2 \xrightarrow[\text{heat}]{\text{catalyst}} CH_2{=}CHOR + HOR \qquad (7)$$

an unsymmetrical acetal is used, either or both alcohols might be cleaved to give two different vinyl ethers. For the preparation of nitroalkyl vinyl ethers, it would be desirable to have only one nitroalkyl group present as the acetal could be conveniently prepared by adding a nitroalcohol to a vinyl ether.

In order to study this method for preparing vinyl ethers, it was necessary to choose a catalyst. Unpublished information indicated that alumina-supported catalysts were used by German investigators. Palladium and nickel on alumina and palladium and platinum on silica gel were examined along with alumina alone, silica gel, porous plate, and acidic and basic materials supported on pulverized porous plate. A sample of 0.5% palladium on alumina seemed to be the best catalyst but it was little better than alumina alone. Another sample of 0.5% palladium on alumina, presumably the same catalyst, was obtained, but this sample was found to be inferior to alumina alone. The results of screening of several catalysts are summarized in Table 2. With alumina at 200°C., diethyl acetal was converted to ethyl vinyl ether in conversions of 37-39%.

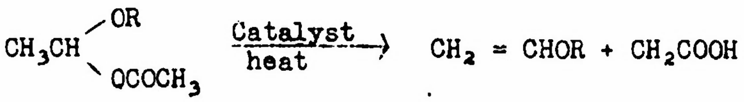
For the extension of this method to the preparation of nitroalkyl vinyl ethers from nitroalkyl alkyl acetals, it was desirable to know whether straight or branched chain alkyl groups are cleaved most readily. For this study, n-butyl ethyl acetal, *sec*.-butyl ethyl acetal, and *tert*.-butyl ethyl acetal were pyrolyzed over alumina. The results of these experiments (see Table 3) indicated that *sec*.-butyl alcohol and *tert*.-butyl alcohol are cleaved to about four times the extent of ethyl alcohol. As the conversion was higher in the case of the *sec*.-butyl vinyl ether, 45.7% as compared to 29.4%, and since vinyl ethers of secondary alcohols are more readily available, the use of isopropyl nitroalkyl acetal or *sec*.-butyl nitroalkyl acetal was indicated.

Isopropyl 4,4-dinitropentyl acetal, isopropyl 2,2-dinitropropyl acetal, and ethyl 2-methyl-2-nitropropyl acetal, prepared from the nitroalcohols and the appropriate vinyl ether, were passed over alumina at 200°C. under reduced pressure. Rather large amounts of nitrogen oxide fumes were obtained, particularly from the dinitro compounds. No significant quantity of nitroalkyl vinyl ether was isolated from the reaction.

A number of previously unreported nitro alkyl acetals were prepared for possible use in this reaction. They are summarized, along with their properties and elemental analyses, in Table 4.

F. Pyrolysis of Acylals

Another possible route considered for the preparation of nitro alkyl vinyl ethers involves pyrolysis of acylals, as indicated by equation (8). A single experiment indicated that acetic acid is split out of acylal when



$$CH_3CH\begin{matrix} \diagup OR \\ \diagdown OCOCH_3 \end{matrix} \xrightarrow[\text{heat}]{\text{Catalyst}} CH_2 = CHOR + CH_2COOH \qquad (8)$$

passed over sodium acetate supported on porous plate in a 30% conversion, whereas diethyl acetal was recovered unchanged.

The practicability of this method would depend on the ease with which acylals containing nitro alkyl groups could be prepared. Attempts were made to add alcohols to vinyl acetate with a variety of catalysts, but none were successful.

G. Reactions Involving α-Chloroethyl Ethers

Shostakovskii and Bogdanova /8/ describe the preparation of butyl vinyl ether from α-chloroethyl butyl ether. The α-chloroethyl ether and dimethylaniline were mixed and allowed to stand overnight at room temperature. The reaction was stated in the abstract to give "40% butyl vinyl ether and butanol, with 100% yield of dimethylaniline hydrochloride." It is not clear whether the yield of butyl vinyl ether was 40% of theory or whether the mixture of butanol and butyl vinyl ether represented a 40% yield. The α-chloroethyl ether was prepared by adding anhydrous hydrogen chloride to butyl vinyl ether and it was purified by distillation.

Shoemaker and Board /9/ describe a procedure for preparing α-chloroethyl ethers from alcohols, acetaldehyde, and hydrogen chloride gas in crude yields of 75-85%. Attempted purification by distillation was stated to be undesirable. If this crude material could be used in the dehydrohalogenation reaction, an acceptable procedure for preparing nitroalkyl vinyl ethers might result.

Several attempts were made to prepare α-chloroethyl ethers and vinyl ethers in this manner. Using the technique of Shoemaker and Board, acetaldehyde and n-butanol were reacted to give organic layers representing crude yields of 72-81%. A sample of this crude product and methanolic potassium hydroxide gave a trace of vinyl ether and a 66% yield of butyl methyl acetal, as determined by analysis of the reaction product.

Other samples of crude products were mixed with dimethylaniline, pyridine, and ethylmethylpyridine. In all cases, precipitates were obtained. The filtrates from removal of the solids, presumably the amine hydrochlorides, contained essentially no vinyl ethers, as indicated by iodometric titrations.

2-Methyl-2-nitropropanol and 2-nitrobutanol were reacted similarly with acetaldehyde and hydrogen chloride gas to give organic layers representing essentially quantitative yields. Treatment with tertiary amine bases, however, gave products containing little or no vinyl ether.

The Russian workers /8/ also disclosed the preparation of acylals by the reaction of distilled α-chloroethyl ethers with acetic acid and sodium acetate. Several attempts were made to convert the above crude α-chloroethyl ethers, including the nitroalkyl α-chloroethyl ethers, to the acylals in this manner. No acylals were isolated. The reaction products were washed with dilute potassium carbonate solutions to remove acidic materials. It is now known that acylals can be quantitatively titrated with 0.1 N sodium hydroxide, and it seems possible that acylals may have been produced but were hydrolyzed during the dilute potassium carbonate wash.

H. Attempted Syntheses of Vinyl Ethers from Vinyl Acetate

A paper /10/ describing the synthesis of vinyl ethers from alcohols and vinyl acetate at low temperatures with mercuric sulfate as catalyst recently appeared. The reported procedure involves adding an alcohol slowly at -30° to -20°C. to an excess of vinyl acetate containing mercuric sulfate catalyst. The reaction was believed to proceed according to equation (9), and

$$ROH + CH_2 = CHOCOCH_3 \xrightarrow{Hg^{++}} ROCH = CH_2 + CH_3COOH \qquad (9)$$

the conversions were determined by titration of the liberated acetic acid.

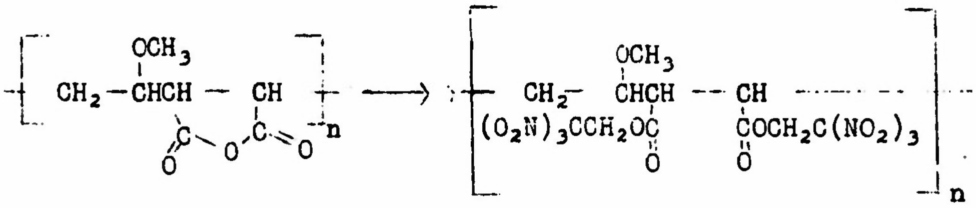
The reported procedure was followed with n-butanol. Titration of an aliquot of the reaction product indicated that 92.9% of one equivalent of acetic acid had been split out in the reaction. However, fractional distillation gave no butyl vinyl ether.

Titration of the liberated acetic acid, of course, does not indicate that butyl vinyl ether was formed. The formation of dibutyl acetal, which is known to occur at higher temperature, also results in the formation of acetic acid. Also, any acylal formed would be titrated.

Several reactions involving alcohols and vinyl acetate were carried out with a variety of catalysts. In no case was any appreciable amount of vinyl ether formed.

I. Attempted Esterification of PVM/MA with Nitroalcohols

Methyl vinyl ether-maleic anhydride copolymers (PVM/MA, (XIII) are available. Esterification of this copolymer with nitroalcohols would, of course, result in a polymer containing nitro groups. The diester with trinitroethanol (XIV), for example, would have a specific impulse of about 215. It seemed unlikely that the diester could be prepared, but preparation of the half ester seemed possible. Attempts at esterification with nitroalcohols were relatively unsuccessful, however, the extent of esterification being only about twenty percent in the best experiment. The esterification attempts are summarized in Table 5.


(10)

XIII XIV

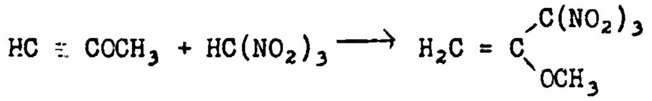
J. Preparation and Attempted Copolymerizations of Nitroalkyl Maleates and Fumarates

A polymeric material having the structure represented by XIV would result from the copolymerization of nitroalkyl maleates or fumarates with vinyl ethers. Di(2-methyl-2-nitropropyl) maleate and di(2-methyl-2-nitropropyl) fumarate were prepared by the procedure of Mighton /11/. Attempts at copolymerization with ethyl vinyl ether, however, were unsuccessful. It was subsequently learned that even the simple methyl maleates and fumarates copolymerize poorly with vinyl ethers.

K. Alkoxyacetylenes

Still another possible method for preparing nitroalkyl vinyl ether involves the addition of nitroparaffins, nitroform for example, to an alkoxyacetylene. Eglinton /12/ prepared alkoxy acetylenes from bromo- and chloroacetals by treatment with sodamide in liquid ammonia. Compound XV has a

$$ClCH_2CH(CCH_3)_2 \xrightarrow{NaNH_2} HC \equiv COCH_3 \qquad (11)$$



$$HC \equiv COCH_3 + HC(NO_2)_3 \longrightarrow H_2C = C\begin{matrix} C(NO_2)_3 \\ OCH_3 \end{matrix} \qquad (12)$$

XV

calculated specific impulse of about 250.

The initial attempt at preparing methoxyacetylene by Eglinton's procedure resulted in a fire. When, according to the reported procedure, the saturated sodium chloride solution was added to the product left from evaporation of the ammonia, a vigorously burning fire occurred.

The experiment was repeated with commercial sodamide in liquid ammonia and the product was decomposed with ethanol. No methoxyacetylene was produced. In the third experiment, sodamide prepared <u>in situ</u> was used and the product again decomposed with ethanol before water was added. An ethanol solution of methoxy-acetylene was obtained, the yield, based on acetylenic hydrogen determination of the solution, being about 38%.

The addition of a nitroparaffin to the methoxyacetylene in this ethanol solution was planned, but work was interrupted before this could be done.

Experimental

A. Attempted Preparations of Nitroalkyl Vinyl Ethers by Vinylation of Nitroalcohols with Alkaline Catalysts

1) Stability of Nitroparaffins Toward Alkali

a) 2-Methyl-2-nitropropanol and Potassium Hydroxide (3053-13)

A mixture of 35 g. of 2-methyl-2-nitropropanol and 1.75 g. of powdered potassium hydroxide was placed in a glass liner of an Aminco bomb and heated at 160°C. for 4 hr. A pressure rise was noted at about 100°C.; it rose to 230 psig. when the temperature reached 160°C. and steadily increased to 345 psig. This suggests gaseous decomposition or formation of volatile material. Material remaining in glass liner after cooling and venting was a very dark red-brown liquid containing brownish solid.

b) Nitroalcohols and Potassium sec.-Butoxide (3053-90)

Small samples of 4-methyl-4-nitropentanol (A), 4,4-dinitropentanol (B), 5,5-dinitro-2-hexanol (C), and 5,5-dinitro-2-ketohexanol (D), all obtained from Aerojet Engineering Corp., were placed in test tubes and a solution of potassium sec.-butoxide in sec.-butanol added to each. An immediate exothermic reaction and darkening occurred with C and D. In a few minutes, an exothermic reaction also occurred with B. The three solutions also became turbid. The four test tubes were immersed in an oil bath and the temperature raised slowly. Compounds B, C, and D continued to darken. At about 100°C., an exothermic reaction occurred in the test tube containing A. The temperature was taken to 145-50°C. and held for one hour. Dark reddish brown fluids containing solids were present in test tubes containing A, B, and C. In test tube D, hard black solid material was distributed up the walls. No fuming was noted at any time and moist starch iodide paper at the mouth of the test tubes showed no change in color.

c) 2,2-Dinitropropane and Ethanolic Sodium Ethoxide (3053-108)

A solution of 13.4 g. (0.1 mole) of 2,2-dinitropropane in 100 g. of 10% ethanolic sodium ethoxide (0.15 mole of alkoxide) was heated at reflux for 20 hr. A white precipitate bagan to form soon after heating was started. After cooling, the white solid was collected by filtration, washed with a little cold ethanol, and dried. The resulting solid weighed 10.0 g. Titration against sulfanilic acid indicated that it was sodium nitrite of 98.6, 100.3, 100.7% purity. The 10 g. represents 0.145 mole of sodium nitrite indicating 1.45 equivalents of nitrite ion had been formed from the 0.1 mole of dinitropropane. Addition of water to the filtrate followed by steam distillation gave 2.5 g. of organic product which solidified in condenser. This product melted at about 105-115°C. and was not identified.

2) Attempted Vinylations of Nitroalcohols

(3053-11). A mixture of 10.0 g. of 2-methyl-2-nitropropanol, 0.5 g. of powdered KOH, and 10 ml. of benzene were placed in a 43 ml. rocker-type bomb and agitated at 160°C. under 200 psig. of acetylene for 6 hr. The resulting dark brown solution gave no qualitative test for vinyl ether (no precipitate with 2,4-dinitrophenylhydrazine reagent).

(3053-5). A mixture of 5.95 g. of 2-methyl-2-nitropropanol, 0.12 g. of sodium methoxide, and 15 ml. of benzene was placed in rocker-type bomb, the temperature raised to 160°C., and nitrogen introduced to 60 psig. and acetylene introduced to a total pressure of 200 psig. After 4 hr. the reactants were cooled and removed from the bomb. The test for vinyl ether was negative.

(3053-1). A mixture of 5.95 g. of 2-methyl-2-nitropropanol, 0.12 g. of zinc naphthenate, and 15 ml. of benzene were heated at 125°C. under nitrogen-diluted acetylene at 200 psig. for 4 hr. The vinyl ether test was negative.

(3053-2). The above experiment was repeated at 160°C. for 4 hr. The vinyl ether test on the product was also negative.

3) Attempted Vinylation of 2-Ethylhexanol in the Presence of 2,2-Dinitropropane (3053-99)

A mixture of 20 g. of 2-ethylhexanol, 1 g. of powdered KOH, and finely divided calcium carbide was warmed for several minutes until gas evolution had ceased. The mixture was filtered and a 15 g. sample of the filtrate and 1 g. of 2,2-dinitropropane were placed in the 43 ml. bomb. Vinylation was carried out with propane-diluted acetylene (70 psig. of propane) at 200 psig. at 150°C. for 8 hr. There appeared to be no acetylene pickup and the product contained, by analysis, less than 0.5% octyl vinyl ether and 93.0% octyl alcohol.

An experiment was previously carried out in this set-up in which 2-ethylhexanol was vinylated successfully (3053-92). In this case, the filtrate from the calcium carbide treatment was vinylated under the above-described conditions to give a product containing 86.3-86.6% octyl vinyl ether and 3.8% octyl alcohol.

B. Addition of Alcohols to Acetylene in the Presence of Acidic Catalysts

1) Preparation of Ion-Exchange Resin Catalysts

Catalyst I (3053-60). A 250 ml. sample of moist Dowex 50 (sulfonated aromatic hydrocarbon polymer) was stirred with a solution of 50 ml. of sulfuric acid in 950 ml. of water for one hour. The resin was placed in a 1" diameter column and washed with distilled water until the effluent water was free of sulfate ion. A solution of 20 g. of mercuric acetate (63 milliequivalents) of mercuric acetate in 500 ml. of water was passed slowly through the resin bed. No mercuric ions passed through the column as indicated by lack of precipitate with dilute sulfuric acid. The capacity of Dowex 50 is stated to be 2.2 millieq. of ion per ml. of moist catalyst; therefore the amount of mercuric salt used was about 11% of the capacity of the resin used. The resin bed was washed with twice the volume of water required above to remove all sulfate ions. The resin was pulled as free of water as possible in a Büchner funnel and dried completely at 70°C. in a vacuum oven (36 hr.). About 120 ml. of dry resin was obtained.

Catalyst II (3053-73). A 200 ml. sample of moist Dowex 50 (440 millieq. capacity) was converted to the free acid form with dilute sulfuric acid in the manner described above. It was then stirred for one hour in a solution of 17.5 g. (110 millieq.) of mercuric acetate and 29.7 g. (330 millieq.) of ferric chloride in 2 l. of water. The resin was then placed in a column and washed with distilled water until free of chloride ion. The resin was then dried in a vacuum oven as described above.

Catalyst III (3053-77). A 50 ml. sample of Dowex 50 in the acid form was placed in a column and treated with a dilute mercuric acetate solution until the effluent liquid had contained mercuric ions for a 1/2 hr. period. The resin was then washed with distilled water until the effluent contained no mercuric ions. The resin was pulled free of water and dried in a vacuum oven as described above.

Catalyst IV (3053-68). A 200 ml. bed of Amberlite IRC-50 (polyacrylic acid, capacity 4.2 millieq./ml.) in a 1" column was treated with a solution of 67 g. (210 millieq., 50% of the capacity of the resin bed) of mercuric acetate in 1500 ml. of water. The bed was then up-washed and down-washed with a total of 20 l. of distilled water. It was then washed with ethanol, after pulling as free of water as possible, and dried in a vacuum oven at 70°C.

2) Reaction of Ethanol and Acetylene in the Presence of Ion-Exchange Resin Catalysts

For the addition of ethanol to acetylene in the presence of the various ion-exchange resin catalysts, acetylene was bubbled into a stirred mixture of 100 ml. of absolute ethanol and 50 ml. of the dry catalyst in 250 ml. three-necked flasks. Acetylene was introduced at a rate of 0.1-0.2 mole per hr. at room temperature. The resin was removed by filtration and an aliquot of the filtrate was analyzed for vinyl ether, acetal, and acetaldehyde. The results of the experiments are summarized in Table 1.

3) Preparation of Methyl Propergyl Ether (3053-94)

A solution of 168 g. (3 moles) of flake potassium hydroxide in 600 ml. of CP methanol was heated at reflux while adding 238 g. (2 moles) of propargyl bromide over a 1 1/2 hr. period. After heating at reflux for another hour, the mixture (white solid present) was poured into cold water. The resulting mixture was extracted with high petroleum ether, the extracts dried over sodium sulfate, and the product isolated by distillation. After a 3 g. forerun, material was collected at 60-60.5°C., n_D^{25} 1.3911-1.3914, 56.6 g. (40.4% of theory). After standing a week, the combined product had n_D^{25} 1.3933 and analyzed as follows: Methanol, 0.2%; methyl propargyl ether (by acetylenic hydrogen method), 67.09%.

Another experiment (3053-98) was carried out under the same conditions to give a 55% yield, assuming the product to be the desired one, of material boiling at 60-62°C., n_D^{25} 1.3920-1.3932. This product analyzed as follows: Methanol, 1.6%; methyl propargyl ether, 63.61%. The product from both of these experiments was combined and redistilled (3053-120) at high reflux ratio through a column packed with protruded metal packing to give water-white material, 12 cuts being collected with following range of properties: b.p. 60-60.4°C., n_D^{25} 1.3913-1.3916. The following properties of methyl propargyl ether are recorded in the literature: b.p. 61-2°C., 63°C. (Beilstein, I, 454, /504/); b.p. 63-4°C., n_D^{19} 1.3975 /7/.

Still another experiment was carried out (3053-124) under the same conditions, 2380 g. (20 moles) of propargyl bromide being used. Five center cuts were collected, 487 g., b.p. 59-62.5°C., n_D^{25} 1.3916-1.3928, combined n_D^{25} 1.3916.

Anal. Calcd. for C_4H_6O: C, 68.54; H, 8.63. Found: C, 69.60, 69.56; H, 9.60, 9.51; methanol, <0.4%; water, 0.15% acetylenic hydrogen by silver method, 81.03, 80.68, 79.71%, calculated as methyl propargyl ether; acetylenic group by hydrogenation, 62.2, 64.3%, calculated as methyl propargyl ether.

The water layer from the petroleum ether extracts was examined to see if it contained any appreciable amount of product. About 75% of the water layer was distilled at high reflux ratio through a column packed with stainless steel protruded metal packing as follows:

Cut	B.P., °C.	Amt., G.	n_D^{25}	Anal.		
				Methyl Propargyl Ether[a]	Methanol	Water
1	55-7	224	1.3771	66.88	24.6	0.29
2	57-9	45	1.3650	48.65	44.3	0.21
3	59-63	58	1.3422	25.94	70.5	0.19
4	63-5	40	1.3288	6.60	92.0	0.11
5	65	49	1.3272	0.69	99.1	0.13

[a] This represents an acetylenic hydrogen determination, the calculation being based on methyl propargyl ether.

4) Addition of Butanol to Methyl Propargyl Ether (3053-121)

A 70 g. sample of methyl propargyl ether (3053-120) was placed in a flask and 0.96 g. (0.003 mole) of mercuric acetate and 0.1 ml. (*ca.* 0.0018 mole) of 100% sulfuric acid added. This mixture was stirred at room temperature while 15 g. (0.2 mole) of n-butanol was added dropwise over a 2 hr. period. The solution was stirred for another 3 hr., solid potassium carbonate added, and the mixture stirred for several minutes. Aqueous potassium carbonate was then added, the mixture was agitated, and the water layer discarded. The organic layer was washed with water, dried, and distilled. After collecting a forerun in five cuts (largely methyl propargyl ether) the following cuts were collected:

Cut	B.P.,°C.	Wt., G.	n_D^{25}
1	54-5/80 mm.	4.6	1.3930
2	55/80 mm.	0.5	1.3938
3	55/80 mm.-69/3 mm.	Few drops	
4	69-78/3 mm.	1.4	1.4146
5	78/3 mm.	2.5	1.4180
6	78/3 mm.	3.8	1.4178

All cuts gave a precipitate with 2,4-dinitrophenylhydrazine reagent. Following analyses were obtained:

Cut	% Butanol	Vinyl Ether, Moles/G.	Ketal, Moles/G.
1	29.8	0.0	0.0067
4	13.0	<.00001	0.0052
5	1.0	<.00004	0.0054
6	1.0	<.00005	0.0058

The following elemental analysis was obtained on cut 6: C, 66.21, 66.16; H, 11.89, 11.86. Calcd. for $C_{12}H_{27}O_3$: C, 65.8; H, 12.5.

C. Addition of Nitroalcohols to Divinyl Ethers

1) 2-Methyl-2-nitropropanol and Glycol Divinyl Ether (3053-28)

A solution of 114 g. (1 mole) of glycol divinyl ether in 100 ml. of anhydrous ether containing 1 ml. of 25% methanolic hydrogen chloride was stirred at 0-5°C. while 23.8 g. (0.2 mole) of 2-methyl-2-nitropropanol was added in small portions over a 1 hr. period. The solution was stirred for another hr. at 0-5°C. and allowed to stand at room temperature overnight. A few grams each of potassium carbonate and sodium methoxide were added and the mixture stirred for 2-3 hr. The solids were removed, the ether evaporated on a steam bath and the residue distilled through a protruded metal-packed column. After recovering 81 g. (71%) of glycol divinyl ether, 28 g. of product, b.p. 129-130°C. (4 mm.), n_D^{25} 1.4439-1.4443, d_4^{25} 1.0624, was collected. This represents a 60% yield.

Anal. Calcd. for $C_{10}H_{19}NO_5$: C, 51.49; H, 8.21. Found: C, 51.67; H, 8.35; N, 6.02.

2) Addition of Nitroform to Glycol Divinyl Ether (3053-47)

A solution of 57 g. (0.5 mole) of glycol divinyl ether (freshly distilled) in 50 ml. of anhydrous ether was stirred at 0-5°C. while a solution of 15 g. (0.1 mole) of freshly prepared nitroform in 103 g. of dioxane was added over a 1.5 hr. period. The solution was stirred for 1 hr. at this temperature and then allowed to warm up to room temperature. After stirring for several minutes with solid sodium carbonate and sodium methoxide and filtering, the solution was heated on a steam bath with the intention of removing the ether and dioxane by distillation at reduced pressure. When most of the solvents had been removed, an explosion occurred.

D. Polymers from Glycols and Acetylene

1) 1,4-Butanediol and Acetylene (3053-39)

A mixture of 2 g. of red mercuric oxide, 2 ml. of boron trifluoride etherate, and 2 ml. of methanol was warmed for a few minutes on a steam bath in a 500 ml. flask. After cooling, 59 g. (0.5 mole) of purified 1,4-butanediol and 200 ml. of dioxane were added. A current of acetylene was bubbled through the stirred mixture at a rate of about 0.15 mole/hr. A grey precipitate formed as soon as the acetylene was introduced. Acetylene absorption at this rate was essentially quantitative for about 1/2 hr. Absorption slowed considerably after about 3 hr. More catalyst was added and acetylene introduced for another 2 hr. The weight increase was 12 g. (theory = 13 g.). After stirring with several grams of potassium carbonate and sodium methoxide and filtering, the dioxane was stripped off under reduced pressure. The residue was a very viscous, clear syrup.

2) 4,4-Dinitro-1,7-heptanediol and Acetylene (3053-104)

A mixture of 1 g. of red mercuric oxide, 1 ml. of boron trifluoride etherate, and 1 ml. of CP methanol was stirred and warmed for a few minutes. A solution of 7.6 g. (0.36 mole) of 4,4-dinitro-1,7-heptanediol in 50 ml. of dry tetrahydrofurane was added to the flask and the mixture agitated while acetylene was bubbled in as above until no more was being absorbed. After stirring with solid potassium carbonate and filtering, the solvent was removed _in vacuo_. The residue was a viscous, amber syrup. A 1% solution in acetone had a specific viscosity of 0.079.

3) Attempted Preparation of Di(hydroxyethyl)nitramine (3053-203, 3053-205)

Diethanolamine nitrate was prepared by adding a solution of 23 g. (0.37 mole) of 100% nitric acid in 261 g. of chloroform to an ice-cold, stirred solution of 42 g. (0.4 mole) of freshly distilled diethanolamine in 260 g. of chloroform. The resulting mixture was allowed to warm slowly to room temperature and to stand overnight. The chloroform was decanted from a light orange, moist solid and the solid triturated with 250 ml. of ice-cold absolute ethanol. The solid was then collected and dried _in vacuo_ at room temperature. The product was a colorless, crystalline solid, 47 g., 76%, m.p. 92-4°C.

A solution of 4.2 g. of diethanolamine nitrate and 2 g. of anhydrous zinc chloride in 51 g. of acetic anhydride was heated at reflux for 2 hr. After cooling, it was poured with stirring into 500 ml. of ice water. Within a few minutes all had dissolved in the water.

This experiment was repeated twice, the first time (3053-222) the same quantities of material and reaction time were used but only 200 ml. of water was used in the drowning. Orange oily material separated at first, but it dissolved on continued stirring. In the last experiment (3053-223), 5 g. of zinc chloride was used. Again, no water-insoluble material separated.

E. Addition of Nitryl Chloride to Vinyl Ethers

1) Preparation of Nitryl Chloride (3053-207)

A nitryl chloride generator was set up in the following manner. In a 500 ml. 4-necked flask fitted with stirrer, thermometer, dropping funnel, and drying tube-vented air condenser was placed 150 g. of 90% nitric acid (2.14 moles of HNO_3, 0.8 mole of water). This was cooled in a dry ice-acetone bath and stirred while 335 g. of 20% oleum (0.84 mole SO_3) was added so that temperature remained below -10°C. To generate the nitryl chloride, this solution was stirred at about 10°C. while adding 33 ml. (58 g., 0.5 mole) of chlorosulfonic acid, the nitryl chloride being collected in a dry ice-acetone trap. About 40 g. (70%) of nitryl chloride was usually obtained. The generator could be used to prepare four such quantities of nitryl chloride.

2) Addition of Ethyl Vinyl Ether

(3053-209). A solution of 20 g. (0.28 mole) of ethyl vinyl ether in 50 ml. of chloroform was stirred in an ice bath under a dry ice-cooled condenser while 14 g. (0.16 mole) of nitryl chloride was introduced over a one-hour period. The nitryl chloride was introduced by allowing it to evaporate slowly into the system from the receiver in which it was collected from the generator. The receiver was cooled intermittently in an acetone-dry ice bath to control the rate of evaporation. A light green color developed in the chloroform solution as the nitryl chloride was added. The solution was stirred for another 30 min. and allowed to warm up to room temperature. Sometime after the ice bath was removed, a mild exothermic reaction occurred and most of the solution was lost by evaporation. The residue contained some insoluble, dark tarry material.

(3053-224). To 50 ml. of ethyl vinyl ether stirred in ice bath was added, in the manner described above, 7 g. of nitryl chloride over a one-hour period. Some reflux was noted on the dry ice condenser. The greenish-yellow solution was stirred for another hour after all had been added. Within a few minutes after the solution had reached room temperature, the solution became dark in color.

(3053-225). Using the general procedure as described above, 20 g. (0.25 mole) of nitryl chloride was added to 14.4 g. (0.2 mole) of ethyl vinyl ether in 25 ml. of chloroform over a 2-hr. period. The solution became greenish-yellow as the nitryl chloride was added and brownish-orange as an excess was added. The solution was warmed to room temperature and the excess nitryl chloride removed in a stream of nitrogen. The resulting light yellow solution did not darken, even on standing for several days. The chloroform was removed under reduced pressure at room temperature, a vacuum of 5 mm. being applied finally. The residue (16 g., 52% of theory for the 1:1 addition product) was a light yellow, medium heavy liquid with a faint but pungent odor.

Anal. Found: active Cl, 4.2%; mol. wt. 205, 225.

(3053-231). A solution of 24 g. (0.3 mole) of nitryl chloride in 50 ml. of chloroform was stirred in a bath at -20°C. under a dry ice-cooled condenser. The drop-wise addition of ethyl vinyl ether from a dropping funnel was started. At the third or fourth drop, a flash of flame occurred and the dropping funnel was blown from the flask. The reaction was not carried further.

(3053-232). The procedure of the above experiment was followed except that a chloroform solution of the ethyl vinyl ether was added. The reaction went smoothly. The solution was allowed to warm to room temperature and the excess nitryl chloride and chloroform removed as described above. The residue was a light yellow oil, active chlorine content, 3.6%.

(3053-235). A solution of 14.4 g. (0.2 mole) of ethyl vinyl ether, 0.1 g. of benzoyl peroxide, and 0.1 ml. of pyridine in 50 ml. of chloroform was stirred in an ice bath while 20 g. (0.25 mole) of nitryl chloride was added over a 2-hr. period. The product was isolated in the usual manner, the residue from removal of the chloroform being light yellow and amounting to 14.6 g. (28% of theory for the 1:1 adduct). Anal. active chlorine, 3.6%; mol. wt. 245.

3) Examination of Ethyl Vinyl Ether-Nitryl Chloride Reaction Products

The product from Experiment 3053-225 described above was examined qualitatively with a number of reagents. An immediate precipitate formed with aqueous silver nitrate. No solid derivative was obtained from dilute ethanolic sodium bisulfite. Addition of a sample to dilute ethanolic aniline hydrochloride gave a dark gum-like material within a few minutes.

A solution of a sample of the product and p-nitroaniline in acetic acid was allowed to stand for an hour or so and poured into cold water, a tan solid separating. In a similar manner, p-hydroxyaniline gave a dark brownish solid. A sample with aqueous 2,4-dinitrophenylhydrazine hydrochloride gave an immediate orange precipitate. Similarly, phenylhydrazine hydrochloride gave a tan solid which rapidly darkened and became black and oily.

Attempts at purification of these derivatives, both by crystallization and chromatography, indicated that derivatives with p-nitroaniline and 2,4-dinitrophenylhydrazine were the most stable. The products from aniline and phenylhydrazine were very unstable.

The p-nitroaniline derivative melted at about 135-148°C. The following elemental analysis was obtained on the crude derivative: C, 49.16; H, 3.67; N, 14.05; mol. wt. 355, 360. This corresponds to an empirical formula of $(C_{4.1}H_{3.6}NO_{2.1})_{3.6}$ or $C_{14.8}H_{13}N_{3.6}O_{7.6}$. A sample purified by dissolving in ethanol, filtering while hot, and reprecipitating with water had the following elemental analysis: C, 37.81; H, 2.96; N, 21.73, 21.84. It was said to be too insoluble for molecular weight determination. This analysis corresponds to an empirical formula of $(C_{2.08}H_{1.83}NO_{1.5})_n$.

The 2,4-dinitrophenylhydrazine derivative, purified by dissolving in warm ethanol, filtering, and reprecipitating with water, darkened and melted at ca. 135-140°C. Anal. found: C, 37.37; H, 2.96; N, 20.25, 20.29, mol. wt. 235, 240. This corresponds to an empirical formula of $(C_{2.14}H_{2.03}NO_{1.7})_{3.4}$ or $C_{7.3}H_{6.8}N_{3.4}O_{5.8}$.

The product from Experiment 3053-232 was also converted to derivatives with p-nitroaniline and 2,4-dinitrophenylhydrazine. The p-nitroaniline derivative had the following elemental analysis: C, 49.44; H, 3.56; N, 15.23; mol. wt. 280, 290. This corresponds to an empirical formula of $(C_{3.8}H_{3.3}NO_{1.8})_{3.1}$ or $C_{11.8}H_{10.2}N_{3.1}O_{5.6}$.

The 2,4-dinitrophenylhydrazine derivative, purified as described above, melted at 145-147°C. Anal. found: N, 21.35.

The product from Experiment 3053-235 was placed in a flask and a vacuum of ca. 0.2 mm. pulled on it at room temperature. Distillate was collected in a trap cooled to -20°C. About 3.6 g. was obtained. Both the residue and the distillate gave solid derivatives as above. The yellow 2,4-dinitrophenylhydrazine derivative of the distillate melted at 154-156°C. Anal. found: C, 37.71; H, 2.84; N, 21.39; mol. wt., 190. This corresponds to $(C_{2.05}H_{1.8}NO_{1.55})_{2.9}$ or $C_6H_{5.3}N_{2.9}O_{4.5}$. The orange p-nitroaniline derivative from the distilled material melted at 155-156°C. Anal. found: C, 37.63; H, 3.15; N, 18.77; mol. wt., 296. This corresponds to an empirical formula of $(C_{2.34}H_{2.33}NO_{1.89})_{3.95}$ or $C_{9.2}H_{9.2}N_{3.95}O_{7.5}$.

a) Preparation of the Diethyl Acetal of Nitroacetaldehyde (3053-210)

The nitryl chloride-ethyl vinyl ether addition product was made in the usual manner by adding 14 g. (0.16 mole) of nitryl chloride to 20 g. (0.28 mole) of ethyl vinyl ether in 50 ml. of chloroform. Before allowing the temperature to rise, 14 g. (0.32 mole) of absolute ethanol was added to the solution. The resulting solution stood overnight at room temperature. The solution was stirred with solid potassium carbonate, filtered, and the chloroform removed at reduced pressure. The residue weighed 19 g. (77% of theory). A 6.9 g. sample was distilled through a short, spiral wire-packed column, three small fractions (ca. 1 ml. each) being collected at 30°C. at 4-5 mm. Reported b.p. 84°C./14.5 mm. /5/. All three cuts gave solid derivatives with aqueous 2,4-dinitrophenylhydrazine. The phenylhydrazone was prepared and recrystallized twice from petroleum ether to give tan solid, m.p. 72-74°C. Reported for the phenylhydrazone of nitroacetaldehyde, m. 74-74.5°C. /6/.

b) Attempts to Dehydrohalogenate the Vinyl Ether-Nitryl Chloride Addition Products

(3053-212). Nitryl chloride (14 g., 0.16 mole) was added to a solution of 20 g. (0.28 mole) of ethyl vinyl ether in 50 ml. of chloroform in the usual manner. After stirring this solution for 1 hr. in the ice bath, 24 g. (0.2 mole) of ethylmethylpyridine was added slowly and the solution stirred for another hour. The dark solution stood at room temperature overnight. No solid separated.

One ml. samples of the product from 3053-227 were treated with 3-4 ml. amounts of dimethylaniline, ethylmethylpyridine, and ethanolic sodium ethoxide. No solids separated from the materials containing the tertiary amines after about a week at room temperature and after warming. An immediate precipitate occurred with ethanolic sodium ethoxide.

4) Addition to n-Butyl Vinyl Ether (3053-238)

A solution of 15 g. (0.15 mole) of n-butyl vinyl ether in 50 ml. of chloroform was stirred in an ice bath while 16 g. (0.2 mole) of nitryl chloride was added over a 1.75 hr. period in the usual manner. The excess nitryl chloride was removed with a stream of nitrogen and the chloroform by reduced pressure distillation. The residue weighed 19 g. (70% of theory for the 1:1 addition product.) When a vacuum of 3-4 mm. was pulled on the system, 5.5 g. of product was collected in a -20°C. trap. Both this distilled material and the residue gave derivatives with 2,4-dinitrophenylhydrazone and p nitroaniline. The derivative of the distillate with 2,4-dinitrophenylhydrazone was the same as that obtained from ethyl vinyl ether-nitryl chloride adduct. It melted at 147-9°C. and had the following elemental analysis: C, 38.44; H, 3.12; N, 21.36; mol. wt., 212. This analysis is essentially identical with those obtained on derivatives from ethyl vinyl ether. It suggests the following empirical formula: $(C_{2.1}H_{2.04}NO_{1.52})_{3.2}$ or $C_{6.7}H_{6.5}N_{3.2}O_{4.8}$. The p-nitroaniline derivative melted at 117-120°C. and had the following elemental analysis: C, 49.80; H, 3.75; N, 19.31; mol. wt. 209. This suggests $(C_{3.01}H_{2.70}NO_{1.23})_{2.9}$ or $C_{8.7}H_{7.8}N_{2.9}O_{3.6}$.

5) Addition to sec-Butyl Vinyl Ether (3053-240)

The same ratio of reactants and reaction conditions as described in the previous experiment were used with sec-butyl vinyl ether. Residue from removal of chloroform weighed 16.7 g. (62% of theory). About 3 g. of residue was volatile at room temperature at 3-4 mm., and both the residue and distillate gave derivatives with 2,4-dinitrophenylhydrazine and p-nitroaniline. These derivatives had solubility characteristics and broad, uncertain melting points similar to derivatives from ethyl vinyl ether and n-butyl vinyl ether.

F. Preparation of Vinyl Ethers by Pyrolysis of Acetals

1) Apparatus for Pyrolysis Experiments (3053-148)

The set-up for carrying out the vapor phase pyrolysis experiments with acetals is illustrated in Figure 1. The acetals were added from a constant bead dropping funnel, a slow current of nitrogen being introduced during the experiment. The temperature was indicated and controlled from a single point within the catalyst bed.

2) Screening of Catalysts (3053-151, 166)

A standard procedure was used for screening materials as catalysts for conversion of diethyl acetal to ethyl vinyl ether in the apparatus described above and illustrated in Figure 1. A 50 ml. catalyst bed was used. The glass beads below the bed occupied about 50 ml. and those above, which served to pre-heat the acetal vapors, occupied about 100 ml. The catalyst was placed in the tube and was given various pre-pyrolysis treatments, as indicated in Table 2. A 25 ml. sample of diethyl acetal was dropped from the constant bead dropping funnel at an approximate constant rate. The time for addition of the 25 ml. sample was recorded and the rate of addition was converted to l. of liquid acetal per l. of catalyst bed per hour. The volume of liquid collected in the -20° to -10°C. trap was recorded and the % recovery calculated. A 1 ml. aliquot of this material was removed and the vinyl ether determined iodometrically (Anal. Chem., 20, 762 (1948)). The catalyst screened, the conditions employed, and the results are summarized in Table 2. In the experiments listed consecutively with the same catalysts, the same catalyst bed was reused.

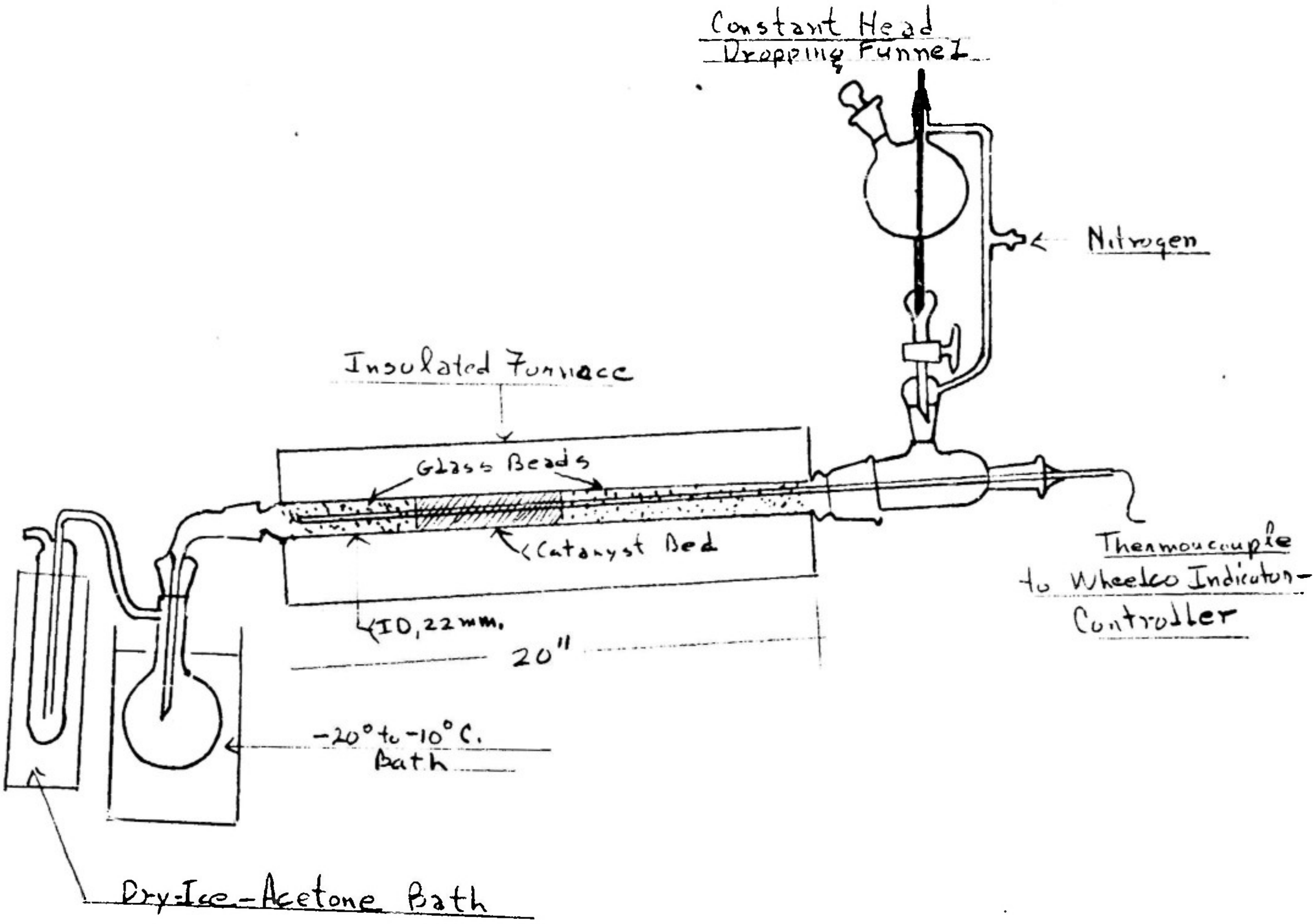


Figure 1
Furnace for Pyrolysis of Acetals

Table 2

Screening of Pyrolysis Catalysts

					Vinyl Ether	
Catalyst	Pre-pyrolysis Treatment	Temp., °C.	Rate of Addition, l./l./hr.	Recovery, %	Total Moles	Conversion, %
0.5% Pd on Alumina (1/8" Pellets)	2 hr. at 200°C. under H_2	200	--	--	0.0299	17.1
0.5% Pd on Alumina (1/8" Pellets)	2 hr. at 200°C. under H_2, 1 hr. at 250°C. under N_2	250	0.652	88	0.0340	19.4
0.5% Pd on Alumina (1/8" Pellets)	2 hr. at 200°C. under H_2, 1 hr. at 250°C. under N_2	300	0.625	88	0.0504	28.8
0.5% Pd on Alumina (1/8" Pellets)	2 hr. at 200°C. under H_2, 1 hr. at 300°C. under H_2	300	0.612	96	0.0770	44.0
Pulverized Porous Plate	2 hr. at 300°C. under N_2	300	0.657	100	0.0413	23.6
Silica Gel	2 hr. at 300°C. under N_2	300	0.625	94	0.00608	3.5
Aniline Sulfate on Porous Clay Plate	2 hr. at 200°C. under N_2	200	0.577	100	0.0483	27.7
Aniline Sulfate on Porous Clay Plate (3053-154)	2 hr. at 200°C. under N_2, 1 hr. at 300°C. under N_2	300	0.577	96	0.0587	33.5
Sodium Acetate on Porous Clay Plate (3053-155)	2 hr. at 200°C. under N_2	200	0.625	100	0.00171	0.98
Sodium Acetate on Porous Clay Plate	2 hr. at 200°C. under N_2, 1 hr. at 300°C. under N_2	300	0.652	96	0.00136	0.77

(Continued)

Table 2 (Continued)

Catalyst	Pre-pyrolysis Treatment	Temp., °C.	Rate of Addition, 1./1./hr.	Recovery, %	Vinyl Ether Total Moles	Vinyl Ether Conversion, %
$KHSO_4$ on Porous Clay Plate	2 hr. at 200°C. under N_2	200	0.612	100	0.00232	1.33
Alumina, 1/8" Pellets	2 hr. at 200°C. under N_2	200	0.652	100	0.0651	37.2
Alumina, 1/8" Pellets	2 hr. at 200°C. under N_2, 1 hr. at 200°C. under N_2	300	0.657	96	0.0488	27.9
0.3% Pd on Silica Gel	2 hr. at 300°C. under N_2	300	0.657	92	0.0575	32.9
0.8% Pd on Silica Gel	2 hr. at 300°C. under N_2, 1 hr. at 300°C. under H_2	300	0.652	100	0.0638	36.5
0.3% Pt on Silica Gel	2 hr. at 300°C. under N_2	300	0.657	84	0.00934	5.34
0.3% Pt on Silica Gel	2 hr. at 300°C. under N_2, 1 hr. at 300°C. under H_2	300	0.657	96	0.0445	25.4
H_3PO_4 on Puralox (1117-122)	2 hr. at 200°C. under N_2	200	0.657	92	0.0119	6.83
5% Ni on Alumina (1/8" Pellets) (3053-147)	2 hr. at 250°C. under N_2, 8 hr. at 200°C. under N_2	200	0.784	98	0.0286	16.0
0.5% Pd on Alumina[a] (1/8" Pellets) (3053-197)	6 hr. at 300°C. under H_2	300	0.657	20	--	--
0.5% Pd on Alumina[a] (1/8" Pellets) (3053-197)	6 hr. at 300°C. under H_2	200	0.544	92	0.034	19.5

(Continued)

Table 2 (Continued)

Catalyst	Pre-pyrolysis Treatment	Temp., °C.	Rate of Addition, l./l./hr.	Recovery, %	Vinyl Ether Total Moles	Vinyl Ether Conversion, %
0.5% Pd on Alumina[a] (3053-197)	6 hr. at 300°C. under H_2	250	0.657	80	0.0213	12.5
Alumina, 1/8" Pellets[a] (3053-198)	6 hr. at 400°C. under N_2, 4 hr. at 250°C. under N_2	250	0.460	92	0.0434	25.4
Alumina, 1/8" Pellets[a] (3053-198)	6 hr. at 400°C. under N_2, 4 hr. at 250°C. under N_2	200	0.214	100	0.0680	38.9

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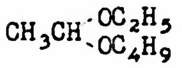
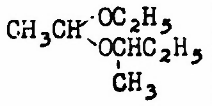
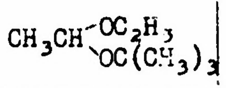
[a] These experiments were run with different lots of catalysts to recheck values obtained previously and listed above in this same table.

3) Pyrolysis of Unsymmetrical Acetals (3053-169, 170, 171)

In the reactor described in Figure 1, a 100 ml. bed of alumina (Harshaw Puralox, 1/8" pellets) was placed below about 50 ml. of glass beads. The catalyst was heated several hours at 400°C. under a current of nitrogen. This catalyst bed was then used for the pyrolysis of n-butyl ethyl acetal, sec.-butyl ethyl acetal, and tert.-butyl ethyl acetal at 250°C. Half-mole quantities of the acetals were passed through the reactor over 2.5 hr. periods (rate = ca. 290 g. of acetal per l. of catalyst bed per hr.) at 250°C. under a slow stream of nitrogen. The condensate was collected in an ice bath and weighed to get the total recovery. Iodometric titration of an aliquot gave the total moles of vinyl ether produced from which the % conversion was calculated. A 60 g. aliquot was dissolved in ether and extracted with dilute potassium carbonate and then water. The ether layer was collected, dried, and subjected to an efficient distillation to remove the ethyl vinyl ether (b.p. 35-36°C.) formed in the reaction. Arbitrarily, distillation was carried out until material was distilling at about 60°C. (b.p. of the butyl vinyl ethers 75-90°C.). An aliquot of the still pot residue was titrated iodometrically to determine the butyl vinyl ether. The moles of the butyl vinyl ether, obtained in this manner, less the total moles of vinyl ether produced were assumed to represent the amount of ethyl vinyl ether produced. The results with the three acetals are presented in Table 3.

Table 3

Pyrolysis of Unsymmetrical Acetals

Acetal	Vinyl Ether, Total Moles	Conversion, %	Moles of the Butyl Vinyl Ether	Molar Ratio, Ethyl Vinyl Ether to Butyl Vinyl Ether
 $CH_3CH\begin{smallmatrix}OC_2H_5\\OC_4H_9\end{smallmatrix}$	0.197	39.4	0.0791	1.49
 $CH_3CH\begin{smallmatrix}OC_2H_5\\OCHC_2H_5\\CH_3\end{smallmatrix}$	0.229	45.7	0.0478	3.77
 $CH_3CH\begin{smallmatrix}OC_2H_5\\OC(CH_3)_3\end{smallmatrix}$	0.147	29.4	0.0291	4.07

4) Pyrolysis of Nitroalkyl Acetals

a) Ethyl 2-Methyl-2-nitropropyl Acetal (3053-175)

Ethyl 2-methyl-2-nitropropyl acetal (25 ml.) was passed over 50 ml. of alumina (Harshaw Puralox, 1/8" pellets) at 250°C. under a slow stream of nitrogen. There was an exothermic reaction in the catalyst bed with the temperature rising to 275°C. Flow of the acetal was stopped until temperature returned to 250°C. After another such exothermic reaction, when a few drops of the acetal had been added followed by cooling, the remainder was passed through at 250°C. over a 35-min. period. The collected liquid amounted to 23 ml. (92%). It was present in two phases, the lower reddish layer amounting to _ca_. 3 ml. Iodometric titration indicated the presence of 0.0361 mole of vinyl ether in the upper layer and 0.0012 mole in the lower (28.3% conversion). Water pump vacuum was applied to the total distillate at room temperature until nothing was distilling. The few grams of dark residue left contained little or no vinyl ether.

b) Isopropyl 4,4-Dinitropentyl Acetal (3053-199)

A solution of 20 g. of the acetal in 20 g. of cyclohexane was passed over a 100 ml. bed of alumina at 200°C. at 20 mm. pressure. It was passed through over a 1.5 hr. period and another 20 g. of cyclohexane was passed through to sweep out the system. Condensate was collected over solid potassium carbonate in a -10°C. trap. The odor of oxides of nitrogen were detectable, the gases evidently passing through a dry ice acetone trap, a soda lime trap, and the vacuum pump. The condensate contained 0.0212 mole of vinyl ether. Extraction of the condensate solution with aqueous potassium carbonate, followed by drying and concentrating under water pump vacuum left less than 1 g. of dark orange oil which appeared not to decolorize the iodine solution.

The pyrolysis of isopropyl 4,4-dinitropentyl acetal was repeated (3053-217) under the same conditions. The condensate contained 0.022 mole of vinyl ether. Washing and concentration _in vacuo_ as above again left less than 1 g. of reddish-orange oil which appeared to contain little or no vinyl ether.

c) Isopropyl 2,2-Dinitropropyl Acetal (3053-218)

A solution of 20 g. of the acetal in 50 ml. of cyclohexane was passed over a 100 ml. bed of alumina at 200°C. at 20 mm. pressure over a 1.5 hr. period. Considerable gaseous decomposition occurred and oxides of nitrogen came through vacuum pump. Treatment of condensate as described in preceding experiment left less than 1 g. of dark orange residue.

5) Preparation of Acetals

The acetals used in the experiments described above were prepared by adding the appropriate alcohol to the appropriate vinyl ether with a small amount of hydrogen chloride as catalyst. The general procedure used was to place the vinyl ether, with or without ethyl ether as a solvent, in a flask fitted with stirrer and dropping funnel. A few ml. of ethanolic hydrogen chloride was added, the solution stirred in an ice bath at 0-10°C., and the alcohol, in ether solution if it was a solid, added slowly from the dropping funnel. After all had been added, the solution was stirred for 2-3 hr. in the ice bath and then allowed to warm to room temperature. The solution was stirred for *ca.* 1 hr. with solid potassium carbonate and sodium methoxide, filtered, the solvent removed under reduced pressure, and the residue fractionally distilled.

Another procedure was used in a few cases. The alcohol and a few drops of concentrated sulfuric acid were stirred at 0-10°C. while the vinyl ether was added slowly over a 1-2 hr. period.

The acetals prepared, the yields obtained, and the properties are summarized in Table 4.

Di(2,2-dinitropropyl) acetal (3053-196) was prepared by adding 3.6 g. (0.05 mole) of ethyl vinyl ether in 25 ml. of ethyl ether to a stirred solution of 15 g. (0.1 mole) of 2,2-dinitropropanol in 75 ml. of ethyl ether containing 10 drops of boron trifluoride etherate at 0°C. The solution was allowed to stand overnight at room temperature. It was then extracted with dilute aqueous potassium carbonate to remove any unreacted dinitroalcohol and to destroy the catalyst. After drying, the solvent was removed and the residue distilled under reduced pressure. Material distilling at 68-69°C. (0.02 mm.), n_D^{25} 1.4431, amounted to 7.1 g. It was probably about 50% desired product, the remainder being largely ethyl 2,2-dinitropropyl acetal. Anal. found: C, 32.32; H, 5.44; N, 14.47. Calcd. for $C_8H_{14}N_4O_{10}$: C, 29.45; H, 4.33; N, 17.18. Calcd. for $C_7H_{14}N_2O_6$: C, 37.84; H, 6.35; N, 12.6.

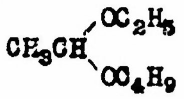
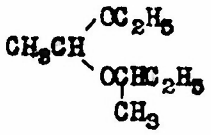
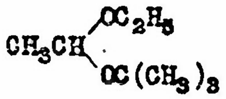
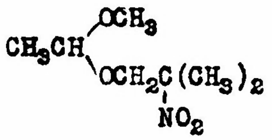
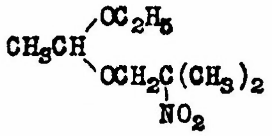
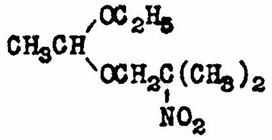
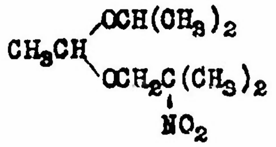
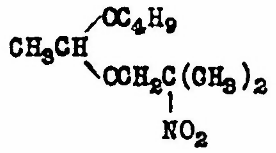
G. Preparation of Vinyl Ethers by Pyrolysis of Acylals

1) Preparation of 1-Acetoxy-1-ethoxyethane (3053-163)

Ethyl vinyl ether (396 g., 5.5 moles) containing 5 ml. of ethanolic hydrogen chloride was stirred at 0-5°C. while 300 g. (5 moles) of glacial acetic acid was added over a 2 hr. period. After standing for 48 hr. at room temperature, the solution was stirred for 1 hr. with potassium carbonate and sodium methoxide, filtered, and distilled. Product was collected at 74-75°C. (99-101 mm.), n_D^{25} 1.3882-1.3888; assay, 99.9% by hydroxylamine hydrochloride method, 97.9% by titration with base.

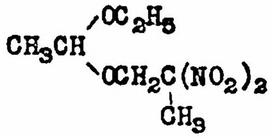
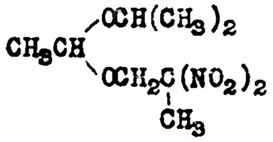
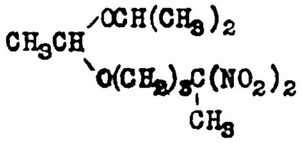
Table 4

Acetals

Acetal and Experiment No.		Vinyl Ether, Moles	Alcohol, Moles	Ethyl Ether, Ml.	Yield, %	B.P., °C.	n_D^{25}	d_4^{25}	Other Products Formed, (Yield, %)	Elemental Analyses					
										C, %		H, %		N, %	
										Calcd.	Found	Calcd.	Found	Calcd.	Found
$CH_3CH(OC_2H_5)_2$	(3053-150)	5.5	5	0	82[a]	103-103.5	1.3778- 1.3780	--							
$CH_3CH(OC_2H_5)_2$	(3053-162)	5.5	5	0	88[b]	101-102	1.3780- 1.3788	--							
 $CH_3CH(OC_2H_5)(OC_4H_9)$	(3053-132)	4.4	4	0	48.5[c]	98-98.8 (162 mm.)	1.3945- 1.3950	0.8257	diethyl acetal (46.5) dibutyl acetal (44.5)	65.71	65.72	12.40	12.23		
 $CH_3CH(OC_2H_5)(OCH(CH_3)C_2H_5)$	(3053-130)	4.4	4	0	54.3[d]	90-91 (160 mm.)	1.3925- 1.3929	0.8252	diethyl acetal (51) di(*sec*-butyl) acetal (32)	65.71	65.85	12.40	12.39		
 $CH_3CH(OC_2H_5)(OC(CH_3)_3)$	(3053-131)	4.4	4	0	65.0[e]	81-81.5 (151 mm.)	1.3911- 1.3915	0.8204		65.71	65.71	12.40	12.51		
 $CH_3CH(OCH_3)(OCH_2C(CH_3)_2NO_2)$	(3053-22)	5	0.75	1000	86	74 (4 mm.) 68 (3 mm.)	1.4236 1.4231	--		47.44	47.45	8.53	8.45	7.91	7.68
 $CH_3CH(OC_2H_5)(OCH_2C(CH_3)_2NO_2)$	(3053-16)	1.1[f]	1	150	45.4	60-60.5 (1 mm.)	1.4226- 1.4228	1.0176	di(2-methyl-2-nitropropyl) acetal	50.24	50.38	8.96	9.17	7.33	7.56
 $CH_3CH(OC_2H_5)(OCH_2C(CH_3)_2NO_2)$	(3053-24)	2.2	2	200	91.6	83-84 (3.5 mm.)	1.4227	--							
 $CH_3CH(OCH(CH_3)_2)(OCH_2C(CH_3)_2NO_2)$	(3053-133)	2.04	2	0	51[g]	70 (1.7 mm.)	1.4230- 1.4232	0.9953		52.66	52.68	9.33	9.19	6.82	6.67
 $CH_3CH(OC_4H_9)(OCH_2C(CH_3)_2NO_2)$	(3053-18)	1.1[f]	1	200	36.4	114 (6 mm.)	1.4270	0.9861	dibutyl acetal	54.77	54.73	9.65	9.56	6.39	6.26

(Continued)

Table 4 (Continued)

Acetal and Experiment No.	Vinyl Ether, Moles	Alcohol, Moles	Ethyl Ether, Ml.	Yield, %	B.P., °C.	n_D^{25}	d_4^{25}	Other Products Formed, (Yield, %)	Elemental Analyses C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
 $CH_3CH(OC_2H_5)(OCH_2C(NO_2)_2CH_3)$ (3053-165)	0.6	0.5	200	77	52 (0.2 mm.)	1.4320	--		37.84	38.23	6.35	6.22	--	--
 $CH_3CH(OCH(CH_3)_2)(OCH_2C(NO_2)_2CH_3)$ (3053-188)	0.6	0.5	100	67	59.5-66 (0.1 mm.)	1.4334	--		--	--	--	--	--	--
 $CH_3CH(OCH(CH_3)_2)(O(CH_2)_3C(NO_2)_2CH_3)$ (3053-195)	0.45	0.4	0	73.5	95 (0.2 mm.) 83 (<0.1 mm.)	1.4410- 1.4413	--		--	--	--	--	--	--

---

[a] Anal. Found: diethyl acetal, 99.6%; ethanol, 0.1%; acetaldehyde, <0.1%.

[b] Anal. Found: diethyl acetal, 99.1%; ethanol, <0.00002 mole/g.

[c] Elemental analysis determined on center cut; blend of cuts analyzed 98.6% as n-butyl ethyl acetal. Reported properties for n-butyl ethyl acetal: b.p. 58-60°C./28 mm., 148-9°C./760 mm.; n_D^{20} 1.3975-1.3993.

[d] Assay on blend of cuts, 97.2%.

[e] Assay on blend, 99.3%.

[f] The alcohol, ethyl ether, and 1 g. of conc. H_2SO_4 were placed in flask and the vinyl ether added.

[g] Assay on blend, 99.86%.

2) Pyrolysis of 1-Acetoxy-1-ethoxyethane

A 25 ml. sample of 1-acetoxy-1-ethoxyethane was passed over a 50 ml. bed of sodium acetate on porous plate at 200°C. at a rate of about 0.6 liter per liter of catalyst bed per hour. A 30% conversion to ethyl vinyl ether was obtained.

3) Attempted Preparation of Acylals by Addition of Alcohols to Vinyl Acetate

Experiment 3053-134. Freshly distilled vinyl acetate (344 g., 4 moles) containing 2 g. of 100% sulfuric acid was stirred at room temperature while butanol was added from a dropping funnel. The alcohol was inadvertently added over a 15 min. period. Cooling was applied to keep temperature at 25-30°C. The solution stood overnight at room temperature. The catalyst was neutralized by stirring with solid potassium carbonate and the vinyl acetate removed at reduced pressure; 178 g. (51.7 %) was recovered. The residue was distilled rapidly at reduced pressure to give 178 g. of distillate. This material was fractionally distilled through a protruded metal-packed column. The only plateaus observed in the distillation curve were at 51-4°C. (47-53 mm.) and 81-4°C. (19 mm.), n_D^{25} 1.4058-1.4062. These materials were probably butyl acetate (reported b.p., 124-6°C.; estimated b.p. at 50 mm., 50°C.) and dibutyl acetal (reported, b.p. 75°C. (14 mm.), n_D^{20} 1.4080, n_D^{25} 1.4045). The amounts obtained indicated that butyl acetate was obtained in 49.3% yield, based on the butanol used, and dibutyl acetal, in ca. 7% yield.

Experiment 3053-136. A mixture of 5 g. of red mercuric oxide, 2 ml. of boron trifluoride etherate, and 2 ml. of butanol was stirred and heated on a steam bath for several minutes. After cooling, 344 g. (4 moles) of vinyl acetate was added to the flask containing the catalyst and the mixture stirred at room temperature (some intermittent heating required) while 148 g. (2 moles) of n-butanol was added over a 2 hr. period. After sitting overnight at room temperature, the catalyst was neutralized with solid potassium carbonate and the vinyl acetate removed at reduced pressure (62 g., 18%). Residue also distilled rapidly at 10 mm. to 1 mm. pressure; 144 g. was collected, residue, 90 g. of black viscous material. The material was fractionally distilled. The only isolable products were 1-acetoxy-1-butoxyethane, ca. 20 g., 6.3% of theory, and dibutyl acetal, ca. 10 g., 3% of theory. Considerable polymerization and/or condensation occurred.

Experiment 3053-156. A mixture of 344 g. (4 moles) of freshly distilled vinyl acetate, 2 g. of hydroquinone, and 5 g. of freshly precipitated and dried mercuric sulfate was stirred at -30 to -20°C. while

9.2 g. (2 moles) of absolute ethanol was added over a 2 hr. period. The solution was stirred another hour and poured quickly into an ice-cold solution of 138 g. of potassium carbonate (1 mole) in 1.5 l. of water. The mixture was well agitated, the organic layer collected, dried, and fractionally distilled through a protruded metal-packed column. After removing the vinyl acetate (147 g., 43%) at atmospheric pressure, about 40 g. (15% yield) of 1-acetoxy-1-ethoxyethane was collected at 73-74°C. (100 mm.).

<u>Experiment 3053-158</u>. A mixture of 5 g. of red mercuric oxide, 2 ml. of boron trifluoride etherate, and 2 ml. of absolute ethanol were warmed momentarily in a flask, cooled, and 344 g. (4 moles) of pre-cooled vinyl acetate containing 2 g. of hydroquinone was added. This mixture was stirred at -30° to -20°C. while ethanol was added over a 2 hr. period. The product was worked up in the manner described in the previous experiment. The distillation curve showed no plateaus; an inflection was present at about 75°C. (100 mm.) which could have been due to acetoxyethoxyethane.

H. Reactions Involving α-Chloroethyl Ethers

1) Preparation of 1-Chloroethyl Butyl Ether (3053-172)

A solution of 88 g. (2 moles) of paraldehyde and 148 g. (2 moles) of anhydrous butanol was placed in a short separatory funnel immersed in an ice-salt bath at -15° to -10°C. Dry hydrogen chloride gas was bubbled into the solution in a manner giving rise to very little agitation. Care was taken to avoid mixing of the two liquid phases which formed. When 76 g. (2.1 moles) had been added, the lower layer was withdrawn and discarded (110 g.). The upper layer was dried over calcium chloride under slight vacuum. The product weighed 196.6 g. (72% of theory for the α-chloroethyl ether).

<u>Anal</u>. Calcd. for $C_6H_{13}ClO$: Cl, 25.7. Found: Cl 19.43, 19.81.

This experiment was repeated (3053-177) with same quantities and conditions to give 221 g. of product (81.3% of theory). No chlorine analysis was carried out.

2) Attempted Preparations of Butyl Vinyl Ether from the α-Chloroethyl Ether

a) Alcoholic Potassium Hydroxide (3053-174)

A sample of the product from experiment 3053-172 (27.2 g.) was added slowly to a stirred solution of 4 g. of potassium hydroxide in 200 ml. of methanol. Solid, presumably potassium chloride, precipitated as the material was added. The mixture was stirred for 30 min. after addition was complete, then filtered to remove the solid. Analysis of an aliquot of the filtrate indicated the presence of 0.133 mole of acetal and 0.016 mole of vinyl ether.

b) Tertiary Amines (3053-179, 180, 181)

To each of three 41 g. (ca. 0.3 mole) samples of the product from 3053-177 above in 50 ml. of ether was added 0.35 mole quantities of dimethylaniline, pyridine, and ethylmethylpyridine. The ether solutions of the amine were cooled in an ice bath and the α-chloroethyl ether added in small portions. All were allowed to stand overnight at room temperature.

The reaction with dimethylaniline became very dark. The solid which formed was removed by filtration. Iodometric titration of the filtrate indicated the presence of very little, if any, vinyl ether. However, the dark nature of the product made the attempt at titration difficult.

The reaction with pyridine remained essentially colorless, a white precipitate forming. The precipitate was a moist slurry which did not filter well. Some of the liquid was decanted from the solid, but no vinyl ether could be detected.

With ethylmethylpyridine, the light tan precipitate which formed filled the flask and no liquid was apparent. The solid was extracted with ether as well as possible, the ether extracts concentrated, and the residue titrated iodometrically. No vinyl ether appeared to be present.

3) Attempted Preparation of Nitroalkyl Vinyl Ethers via α-Chloroethyl Ethers

a) 2-Methyl-2-nitropropanol (3053-183)

A solution of 133 g. (1 mole) of 2-methyl-2-nitropropanol and 44 g. (1 mole) of acetaldehyde in 220 g. of benzene was placed in a separatory funnel at -10°C. and dry hydrogen chloride introduced without agitation until 1.3 moles had been added. The lower layer, which was discarded, weighed 39 g., the upper, 404 g. (102% of theory). The upper layer was dried over calcium chloride and the excess hydrogen chloride removed under reduced pressure.

A 180 g. sample of this solution was mixed slowly with cooling with 60 g. of redistilled dimethylaniline (3053-189). The mixture was heated at reflux with stirring for 2 hr. The solid, presumably the amine hydrochloride, was removed by filtration, the benzene removed at reduced pressure, and the residue distilled at 0.1-0.2 mm. in a short-path distillation. The distillate did not decolorize the iodine reagent.

A solution of 180 g. of the reaction product from 3053-183 and 30 g. of glacial acetic acid was heated on a steam bath for 2 hr. The solution became very dark and hydrogen chloride was evolved. The dark solution was washed with cold, dilute aqueous potassium carbonate to remove all acidic materials. The organic layer was then placed over solid potassium carbonate. An exothermic reaction occurred, much product was lost by foaming, and a dark semi-solid mass resulted.

b) 2-Nitrobutanol (3053-184)

A solution of 95 g. (0.8 mole) of 2-nitrobutanol and 35 g. (0.8 mole) of paraldehyde was placed in a separatory funnel, cooled to -10°C., and hydrogen chloride added in the manner described above. The upper layer weighed 131 g. (118% of theory). It was dried in vacuo over calcium chloride.

A 110 g. sample of this product was mixed with 37 g. of glacial acetic acid and the solution heated on a steam bath for 2 hr. In attempting to wash the solution with dilute potassium carbonate, most of it was lost because of extensive foaming.

I. Attempted Synthesis of Butyl Vinyl Ether from n-Butanol and Vinyl Acetate (3053-111)

The procedure described by Adelman /10/ was used in an attempt to prepare butyl vinyl ether from vinyl acetate. In a flask immersed in a bath at -30° to -20°C. was placed 74 g. (1 mole) of butanol, 516 g. (6 moles) of freshly distilled vinyl acetate, 0.05 g. hydroquinone, 1.8 g. of mercuric acetate, and 0.8 g. of sulfuric acid in that order. After stirring 2 hr., titration of an aliquot indicated that 0.929 mole of acetic acid had been formed. The entire solution was poured quickly into a cold solution of 53 g. (0.5 mole) of sodium carbonate in 1 liter of water. The mixture was shaken well, the organic layer collected, dried over sodium sulfate and fractionally distilled. After removing the vinyl acetate, material distilled up to 90°C. (pot temp. 177°C.) with no levelling of the boiling point. At this point decomposition of the pot residue was apparent and acetic acid was coming off. No significant quantity of butyl vinyl ether was obtained.

J. Esterification of PVM/MA with Nitroalcohols

Attempts were made to esterify PVM/MA with nitroalcohols by heating various solutions at reflux. The products were isolated by pouring the solutions into carbon tetrachloride in a Waring blender. The resulting polymer was again dissolved in acetone and reprecipitated from carbon tetrachloride in the Waring blender. Nitrogen analyses were run on the resulting dried polymer. The experiments carried out are summarized in Table 5.

Table 5

Esterification of PVM/MA with Nitroalcohols

Experiment Number	Alcohol		PVM/MA, Moles	Solvent (Ml)	Time, Hr.	Nitrogen Content, %	Extent of Esterification, %
	Identity	Moles					
3053-15	2-Nitrobutanol	0.1	0.1[a]	Acetone (100)	3	1.0, 1.86[b]	19
3053-14	2-Methyl-2-nitropropanol	0.1	0.1[a]	Acetone (100)	3	trace, 1.05[b]	--
3053-36	2-Methyl-2-nitropropanol	0.2	0.2[c,e]	Acetone (300)	8	trace	--
3053-50	2-Methyl-2-nitropropanol	0.2	0.1[d]	Acetone (150)	6	trace	--
3053-51	2-Methyl-2-nitropropanol	0.2	0.1[d]	2-Butanone (150)	6	trace	--
3053-52	2-Methyl-2-nitropropanol	0.2	0.1[d]	Acetylacetone (150)	6	0.94	18
3053-53	2-Methyl-2-nitropropanol	0.2	0.1[d]	Cyclohexanone (150)	6	1.14	22
3053-55	2,2-Dinitropropyl	0.02	0.02[d]	Acetone (25)	6	trace	--

---

[a] Sample 2829-243, η^{25}_{sp} 1.06.

[b] The second values were obtained on insoluble, gel-like material which precipitated on sides of flask.

[c] Sample 2829-157, η^{25}_{sp} 0.55.

[d] Sample 2829-296, η^{25}_{sp} 0.41.

[e] p-Toluene sulfonic acid used as catalyst.

K. Nitroalkyl Maleates and Fumarates

1) Preparation of Di(2-methyl-2-nitropropyl) Maleate (3053-34)

A solution of 98 g. (1 mole) of maleic anhydride, 250 g. (2.1 moles) of 2-methyl-2-nitropropanol, and 5 g. of p-tolunene sulfonic acid in 200 ml. of toluene was stirred at reflux, water being removed azeotropically. After 6 hr. (14.9 ml. of water had been collected), another 120 g. of the nitroalcohol and 2 cc. of conc. sulfuric acid were added and the reaction continued for another 2 hr. (19.6 ml. of water collected). The cooled solution was poured into 2 liters of cold water and an excess of potassium carbonate added. The solid was collected by filtration and air-dried to give 383 g. (theory = 318 g.) of slightly moist tan solid. Recrystallization from ethanol with charcoal treatment gave 178 g. of soft colorless plates, m.p. 78.5-79.5°C. (Reported m.p. 78.5-79°C. /11/.) A second crop of crystals, 63 g., melted at 71.5-75°C. The total, 241 g., represents a 77% yield.

2) Preparation of Di-(2-methyl-2-nitropropyl) Fumarate (3053-35)

A solution of 116 g. (1 mole) of fumaric acid, 357 g. (3 mole) of 2-methyl-2-nitropropanol, and 10 g. of p-toluenesulfonic acid in 400 ml. of toluene was allowed to react in the manner described in the previous experiment. The theoretical amount of water was collected in about 16 hr. Most of the toluene was removed by distillation in vacuo and the residue cooled. The solid was collected and recrystallized from ethanol-benzene to give 163 g. (51% yield) of light tan solid, m.p. 129-130°C. (Reported m.p. 129.5°C. /11/)

3) Attempted Copolymerizations (3053-56, 3053-57)

Benzene solutions of 0.1 molar amounts of di(2-methyl-2-nitropropyl) maleate and di(2-methyl-2-nitropropyl) fumarate, 0.2 molar amounts of ethyl vinyl ether, and 0.5% by weight of benzoyl peroxide were heated at reflux for 8 hr. In neither case was any polymer precipitated by carbon tetrachloride, chloroform, acetone, or low-boiling petroleum ether. After adding more catalyst and heating at reflux for another 8 hr., no polymeric material was isolable.

L. Preparation of Methoxyacetylene

The procedure for preparing methoxyacetylene was taken from a thesis entitled "The Synthesis of Acetylenic Compounds" submitted to Victoria University of Manchester by Geoffrey Eglinton (October, 1951). In the first experiment (3053-213), sodamide was prepared from ca. 600 ml. of liquid ammonia and 35 g. (1.5 moles) of sodium with ferric nitrate being used as catalyst. To this stirred suspension, 62 g. (0.5 mole) of freshly distilled dimethyl chloroacetal was added dropwise over a 15 min. period. The ammonia was evaporated under a stream of nitrogen overnight. According to the procedure of Eglinton, the flask was immersed in a dry ice-acetone bath at -80°C. and 250 ml. of saturated sodium chloride solution pre-cooled to -20°C. was added rapidly. As soon as all had been added, a stopper was blown from one neck and a fire burned vigorously from this neck for 20-30 seconds.

In a second experiment, about 600 ml. of liquid ammonia was placed in a flask and 65 g. (1.67 moles) of commercial sodamide powder was added. This stirred mixture, 69 g. (0.65 mole) of dimethyl chloroacetal was added drop-wise and the ammonia evaporated overnight under a stream of nitrogen. The flask was immersed in dry ice-acetone bath and 100 ml. of ethanol added drop-wise. A saturated sodium chloride solution (250 ml.) was then added. While stirring, the flask was heated on a steam bath, distillation being carried out until only ethanol was distilling. The 141 g. collected had a faint odor of ammonia. The material was distilled through a packed column; no significant amount of product was obtained below 78°C. The original condensate and the distilled material gave no precipitate with Tollen's reagent, mercurous iodide reagent, or cuprous chloride reagent.

In a third experiment (3053-220), sodamide was prepared in liquid ammonia from 35 g. of sodium with ferric nitrate catalyst. Dimethyl chloro acetal (62 g., 0.5 mole) was added drop-wise and the ammonia allowed to evaporate overnight under a stream of nitrogen. The flask was cooled in a dry ice-acetone bath and 400 ml. of cold ethanol added with stirring. A cold saturated sodium chloride solution (250 ml.) was then added and stirring continued until all lumps had disappeared. Heat was applied and distillation carried out until only ethanol was distilling. The condensate, 141 g., gave voluminous precipitates with Tollen's, cuprous chloride, and mercurous iodide reagents. Determination of acetylenic hydrogen by the mercury method indicated that the methoxyacetylene concentration was 0.00133 mole/g. The total yield was 0.188 mole or 37.6% of theory. Several days later, analyses indicated the presence of 0.16 mole of methoxy acetylene. A week later, the concentration was 0.1 mole.

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