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The preparation, spectra, and conformations of cis, cis-, cis, trans-, and trans, trans- dipropenyl ethers

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THE PREPARATION, SPECTRA, AND CONFORMATIONS OF *CIS,CIS*-, *CIS,TRANS*-, AND *TRANS,TRANS*-DIPROPENYL ETHERS

BY

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APPROVAL OF THESIS

THE PREPARATION, SPECTRA, AND CONFORMATIONS OF <u>CIS</u>,<u>CIS</u>-, <u>CIS</u>,<u>TRANS</u>-, AND <u>TRANS</u>,<u>TRANS</u>-DIPROPENYL ETHERS

BY

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FOR

DEPARTMENT OF CHEMICAL ENGINEERING AND CHEMISTRY

NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

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ABSTRACT

Cis,*cis*-dipropenyl ether was prepared by potassium t-butoxide catalyzed rearrangement of diallyl ether in diglyme solution. Pyrolysis was used in an attempt to produce an isomeric dipropenyl ether mixture with a high percentage of the less stable *trans*,*trans* isomer; 21.6% *trans*,*trans*-dipropenyl ether was produced by pyrolysis at 395°C, but formation of an azeotropic byproduct in significant quantities negated the feasibility of this synthesis. A mixture of 45.7% *cis*,*cis*-, 43.6% *cis*,*trans*-, and 10.7% *trans*,*trans*-dipropenyl ether was produced by mercuric acetate catalyzed isomerization at 80°C, and the mixture was separated on a Nester/Faust spinning band column of two hundred theoretical plates.

Physical properties, including boiling point, density, index of refraction, and proton and carbon-13 chemical shifts were determined for all three isomers. Liquid-phase Raman spectra and liquid-phase, vapor-phase, and CCl_4 solution infrared spectra were taken on the three dipropenyl ethers and vibrational frequency assignments were made. Conformations have been established based on the vibrational and NMR spectra.

The most stable conformation for *cis*,*cis*-dipropenyl ether is the planar C_{2v} form, but a non-planar conformer

exists at higher temperatures, in the liquid-phase, and in solution. *Trans*,*trans*-dipropenyl ether is slightly more stable in the planar C_s conformation with the planar C_{2v} conformer present at a slightly lower population level. Two C_s conformations are found for *cis*,*trans*-dipropenyl ether; the linear coupled C_s planar form is more stable than the bent C_s planar conformation.

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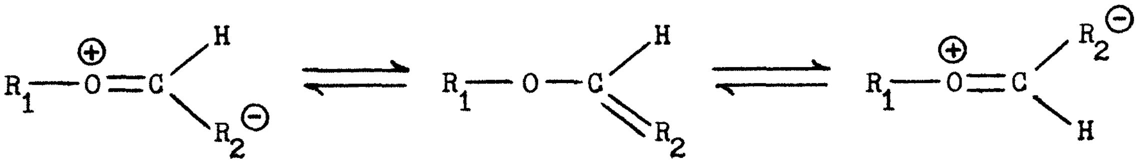
DEDICATION

To my husband, Leo

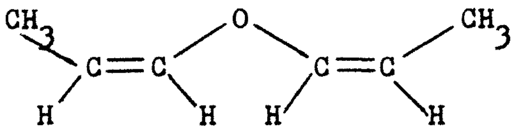
I. INTRODUCTION

Vinyl ethers display a number of interesting properties, including rotational conformations and vibrational coupling. Multiple bands in the infrared and Raman carbon-carbon double-bond stretching region are attributed to different conformations for methyl vinyl ether,(1) ethyl vinyl ether,(2) cis- and trans-1,2-dimethoxyethylene,(3) vinyl 2-ethylhexyl ether,(4) three vinyl β-fluoroalkyl ethers,(4) and divinyl ether.(5) These rotational conformations result from the partial double-bond character of the central carbon-oxygen bond:(6, 7)

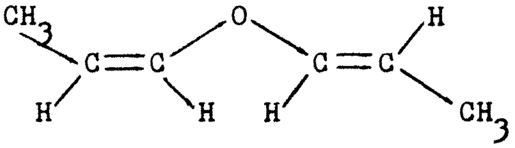


Vibrational coupling is found in ethers with two vinyl double bonds, such as divinyl ether and Z,Z-bis(1-propenyl)ether.(10) In the present work, the three isomers of bis(1-propenyl)ether were prepared and examined for the presence of rotational conformations.

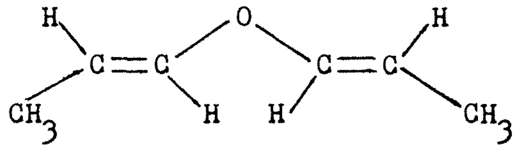
Z,Z-bis(1-propenyl)ether, commonly called cis,cis-dipropenyl ether, is reported to have a planar C_{2v} conformation with strong vibrational coupling between the double-bonds:(10)



Conformations have not been reported for the other two isomers. The other isomers are cis,trans-dipropenyl ether (E,Z-bis(1-propenyl)ether),



and trans,trans-dipropenyl ether (E,E-bis(1-propenyl)ether):



Planar conformations are shown for cis,cis-dipropenyl ether (ccDPE), cis,trans-dipropenyl ether (ctDPE), and trans,trans-dipropenyl ether (ttDPE). Rotation of the vinyl group around either or both of the carbon-oxygen axes leads to additional conformations for each molecule.

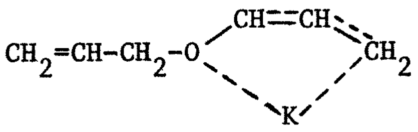
The infrared carbon-carbon double-bond stretching frequencies are reported to be 1656 cm^{-1}, 1662 cm^{-1}, and 1662 cm^{-1} for ccDPE, ctDPE, and ttDPE respectively; the Raman frequencies for ccDPE are reported at 1691 cm^{-1} and 1658 cm^{-1}. (8, 9) Gillis and Schimmel report characteristic infrared bands of 1653 cm^{-1} and 924 cm^{-1} for ttDPE, produced by trans-elimination of β,β'dichlorodipropyl ether.(11) In an attempt to duplicate this reaction, Tomalesky produced ccDPE.(12) The 1653 cm^{-1} band reported by Gillis and Schimmel(11) is definitely closer to the 1656 cm^{-1} band reported by Snyder(8) and verified in the present work for ccDPE, than to the ttDPE band. The physical properties that have been reported for ccDPE are a refractive index of 1.4318, a density of 0.803 g/ml, a molecular refractivity of 31.67 (all at 20°C), and a boiling point of 94.5 - 97°C.(8) A refractive index of 1.4173 and a density of 0.8012 g/ml at 25°C, and a boiling point of 118 - 122°C are reported for ttDPE.(11) The physical properties for ctDPE have not been reported. Complete spectra have not been published for any of the three dipropenyl ether isomers.

In order to determine the spectral and physical properties, and the conformations of the three dipropenyl ether isomers, pure samples of ccDPE, ctDPE, and ttDPE were required. The *cis,cis* isomer can be prepared by potassium t-butoxide catalyzed rearrangement of diallyl ether (*bis*(2-propenyl)ether).(8, 13) The other isomers can be prepared by mercuric acetate catalyzed isomerization of ccDPE. In previous work, micro-samples of ctDPE and ttDPE were collected in CS_2 solution by using gas chromatographic separation techniques with a column containing 25% THEED on Chromosorb.(8) Separation of the isomeric dipropenyl ether mixture was previously attempted on a Todd column of sixty theoretical plates.(12) In order to facilitate separation of ctDPE and ttDPE in the present work, pyrolysis was used in an attempt to synthesize a *trans* rich mixture and a Nester/Faust spinning band column of two hundred theoretical plates was used for the batch distillation.

II. PREPARATION OF THE DIPROPENYL ETHERS

A. Base-Catalyzed Rearrangement of Diallyl to Dipropenyl Ether

Potassium t-butoxide has been reported effective in the base-catalyzed rearrangement of allyl to propenyl ethers. Prosser used 2-15 wt% catalyst without solvent at temperatures of 150-175°C. He reported nearly complete conversions with initial catalyst concentration being the limiting parameter due to catalyst deactivation.(13) Snyder reported complete conversions using 52 wt% potassium t-butoxide to dipropenyl ether in diglyme solution at 60°C.(8) Complete conversion is important because diallyl ether boils at 94.3°C (between cis, cis- and cis,trans-dipropenyl ether), making distillative separation rather difficult. The propenyl ethers prepared by this method are essentially pure cis derivatives; this is explained by the formation of a stable cis-allylic carbanion as an intermediate:(13)



In the present work complete conversion was obtained by using 15 wt% catalyst to ether ratios (in diglyme solution). Visible evidence of catalyst decomposition consisted of the formation of solids in the reaction mixture--these solids were evidently insoluble organo-potassium salts. Potassium t-butoxide initiated elimination on the diglyme solvent explains both the solid formation and the formation of t-butanol as follows:(15)

(1) $(CH_3O\text{-}CH_2\text{-}CH_2)_2O \longrightarrow CH_3O\text{-}CH{=}CH_2 + HOCH_2\text{-}CH_2\text{-}OCH_3$

(2) $(CH_3O\text{-}CH_2\text{-}CH_2)_2O \longrightarrow CH_3OH + CH_2{=}CH\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OCH_3$

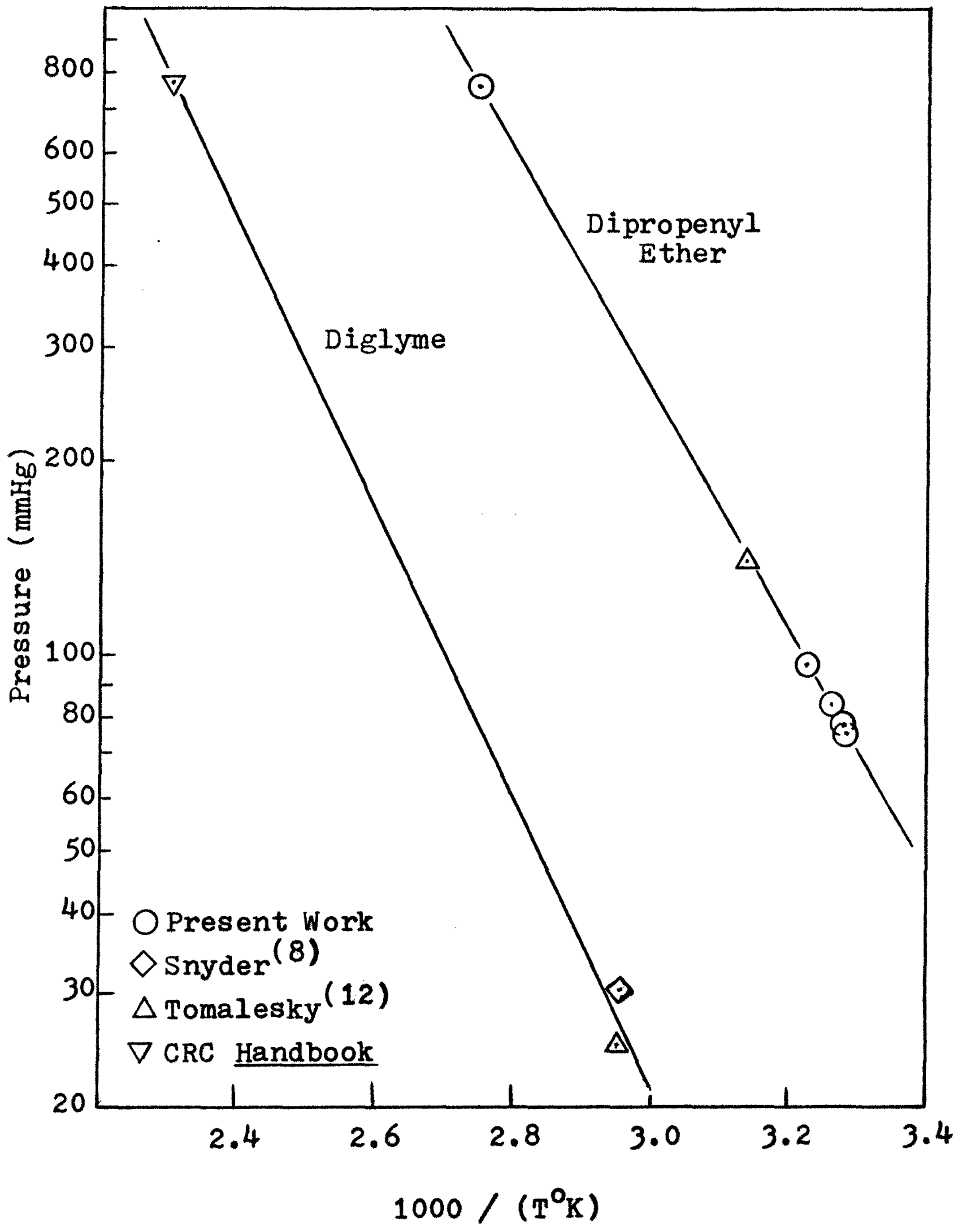
(3) $HOCH_2\text{-}CH_2\text{-}OCH_3 + KO\text{-}t\text{-}Bu \longrightarrow KOCH_2\text{-}CH_2\text{-}OCH_3 + t\text{-}BuOH$

(4) $CH_3OH + KO\text{-}t\text{-}Bu \longrightarrow KOCH_3 + t\text{-}BuOH$

Cis,cis-dipropenyl ether was recovered from the reaction mixture by vacuum distillation. The fractionation of ccDPE from diglyme is a clean separation, based on the difference in vapor pressures, as shown in Figure 1. GC analysis of the product ether, distilled from the reaction mixture, showed the major impurity in runs 1-4 to be 1.7%, 4.7%, 7.1%, and 4.8% t-butanol respectively. The t-butanol impurity was removed as an azeotrope by distillation on a Nester/Faust spinning band column of two hundred theoretical plates. A 99.9% pure sample of ccDPE (Figure 10) was collected at a temperature of 91.6± 0.3°C and a pressure of 756.4 mm Hg.

B. Isomerization and Fractionation of Dipropenyl Ether

Mercuric acetate isomerization of cis,cis-dipropenyl ether (ccDPE) at 80°C is reported to yield an equilibrium mixture of 41.9 ± 1.7% cis,cis-, 45.9 ± 1.3% cis,trans-, and 12.2 ± 0.8% trans,trans-dipropenyl ether.(12) A 10.10 g isomerized sample, prepared as a GC standard, contained 41.8% cis,cis-, 46.2% cis,trans-, and 12.0% trans,trans-dipropenyl ether as determined by relative peak areas on the GC (triangulation). High-temperature pyrolysis was used in an attempt to produce an ether mixture with about 20% trans,trans-dipropenyl ether (ttDPE) in order to facilitate fractionation. The pyrolysis experiments gave 14.3% ttDPE at 360°C and 21.6% ttDPE at 395°C, but the dipropenyl ethers comprised only 55% and 16% of the total product in these two runs. An unidentified

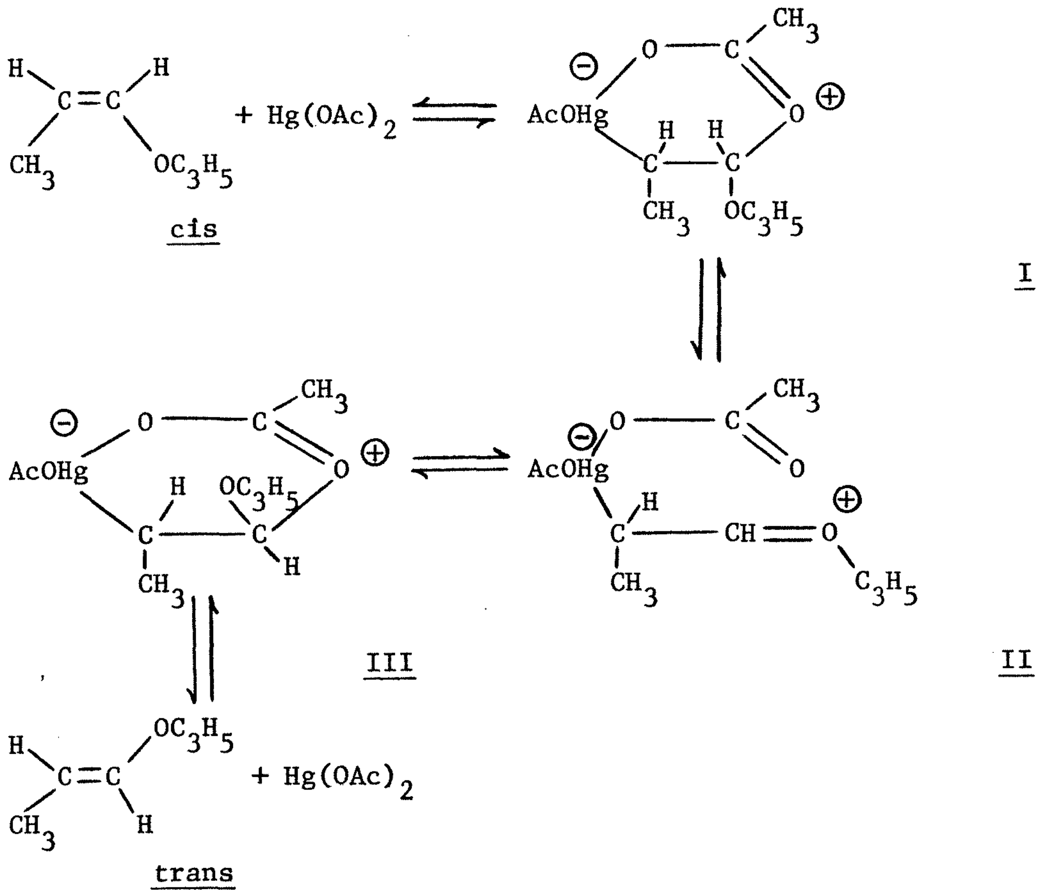


<u>FIGURE 1</u>

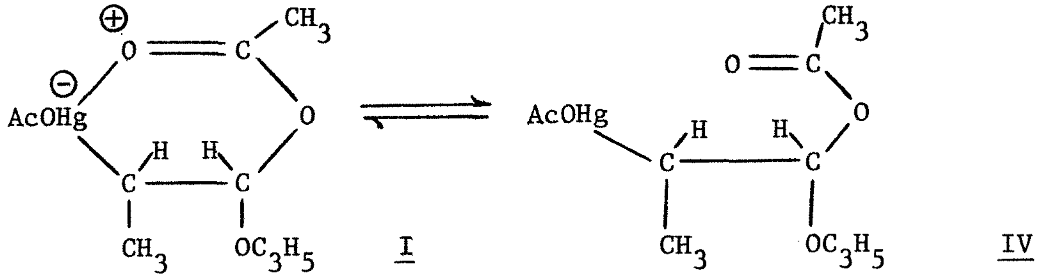
<u>Vapor Pressures of Dipropenyl Ether and Diglyme</u>

high-GC-retention time impurity was formed which azeotroped with the ethers. The mercuric acetate preparation was chosen since it gave a relatively clean product.

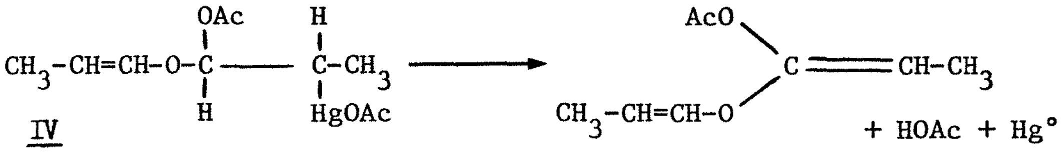
The reversible cis-trans isomerization of dipropenyl ether is postulated to proceed through a series of acetoxy-mercury intermediates as follows:(8)



Intermediates I or III are also posultated to give an organomercury intermediate IV.



Decomposition of IV should be analogous to the decomposition of 3-butenyl mercuric acetate. Free mercury, acetic acid, and butadiene plus 1.4% 3-butenylacetate were obtained on heating this compound to 150-200°C.(16) Acetic acid and metallic mercury were noted in the dipropenyl ether isomerization. The decomposition of intermediate IV explains these byproducts:



Foster and Tobler determined that the decomposition mechanism in unsaturated mercury compounds is dependent on the position of the double bond, relative to the mercuric acetate. α unsaturation leads to a different mechanism, β unsaturation gives a mixture of products, and γ unsaturation in 3-butenylacetate gives only 1.4% products from the second mechanism.(16) Therefore, the δ unsaturation in intermediate IV should dictate the mechanism above. This is an accepted mechanism for mercuric acetate catalytic decomposition,(17) which can be shown to lead to formation of propenyl acetate.

Mercuric acetate was used to isomerize ccDPE to a mixture of the three isomers. The dipropenyl ether mixture was separated on a Nester/Fanst spinning band column of two hundred theoretical plates. The boiling point of 99.9% pure ccDPE was 92°C. An 86% pure sample of ctDPE was collected at 98°C; the major impurity was 12% propenyl acetate which was not visible in the GC analysis (Figure 11). A 74% pure sample of ttDPE containing 19% propenyl acetate and 7% ctDPE was collected at 101°C.

The theoretical molecular refractivity for dipropenyl ether is calculated to be M_R = 30.77 (see calculations Appendix I). The index of refraction at 20°C was found to be 1.4307, 1.4316, and 1.4293 for ccDPE, ctDPE, and ttDPE respectively. The refractive indices for *cis*- and *trans*-propenyl acetate are 1.4130 and 1.4140 at 20°C.(16) The ctDPE and ttDPE values are probably both being lowered by the impurities. The densities at 25°C are 0.813 g/ml, 0.829 g/ml, and 0.835 g/ml for the three isomers, giving a M_R at 25°C of 31.10, 30.56, and 30.20 for ccDPE, ctDPE, and ttDPE respectively. The refractive indices are accurate to ± 0.0001 and the densities to ± 0.001. Previously reported values are a refractive index and density at 20°C of 1.4318 and 0.803 and a M_R of 31.67 for 95.5% pure ccDPE.(8) Also reported are a refractive index and density at 25°C of 1.4173 and 0.8012 for ttDPE.(11)

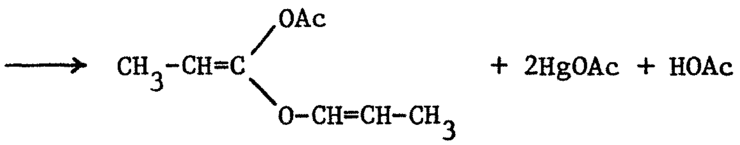
C. Propenyl Acetate Byproduct Formation and Removal

Cis- and *trans*-propenyl acetate are identified as the major impurities in *cis,trans*-dipropenyl ether (ctDPE) and *trans,trans*-dipropenyl ether (ttDPE). Physical evidence includes the characteristic sweet ester odor, the boiling points, and certain infrared and NMR spectral bands. In addition a plausible set of chemical reactions can explain byproduct formation of the propenyl acetates from decomposition of the mercuric acetate catalyst.

After the mercuric acetate catalyzed isomerization of ccDPE, metallic mercury was observed in the reaction flask along with a small amount of granular solids. The remaining solids were assumed to be either mercuric or mercurous acetate and were not analyzed. It should be noted, however, that the vinyl mercuric esters (the catalyst decomposition intermediates) are also crystalline solids.(16) The visible solids were filtered-out and the dipropenyl ether mixture was distilled under vacuum to remove any additional catalyst. A colorless, viscous substance remained in the reaction flash, and a small amount of yellow liquid remained in the distillation flask. The yellow liquid is a higher condensation product attributed to the lengthy heating period associated with the spinning band distillative removal of t-butanol. The metallic mercury and the clear viscous liquid are byproducts produced by catalyst decomposition.

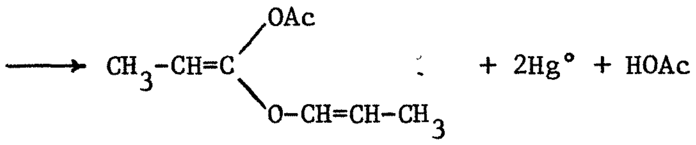
In reactions involving mercuric acetate where organo-mercury compounds are not isolated, the mercury (II) salt is reduced to either mercurous acetate or to elemental mercury.(18) Waldron reported trace amounts of metallic mercury formation in the dimethoxy ether isomerization reaction. The reduction to elemental mercury for the dipropenyl ether isomerization can be explained by the following reactions:(17)

(1) $CH_3\text{-}CH{=}CH\text{-}O\text{-}CH{=}CH\text{-}CH_3 + 2Hg(OAc)_2$



$$\longrightarrow \mathrm{CH_3{-}CH{=}C}\genfrac{}{}{0pt}{}{\diagup \mathrm{OAc}}{\diagdown \mathrm{O{-}CH{=}CH{-}CH_3}} + 2\mathrm{HgOAc} + \mathrm{HOAc}$$

(2) $CH_3\text{-}CH{=}CH\text{-}O\text{-}CH{=}CH\text{-}CH_3 + 2HgOAc$



$$\longrightarrow \mathrm{CH_3{-}CH{=}C}\genfrac{}{}{0pt}{}{\diagup \mathrm{OAc}}{\diagdown \mathrm{O{-}CH{=}CH{-}CH_3}} + 2\mathrm{Hg}^\circ + \mathrm{HOAc}$$

This mechanism for the catalyst decomposition is supported by experimental observations; trace amounts of acetic acid were identified by characteristic odor in several cuts from the spinning-band distillation. Also the observed propenyl acetate formation can be explained by the presence of acetic acid in the reaction mixture.

Vinyl transesterification of the dipropenyl ether isomers with acetic acid would yield propenyl acetate plus propionaldehyde as follows:(19,20)

(3) $CH_3\text{-}CH\text{=}CH\text{-}O\text{-}CH\text{=}CH\text{-}CH_3 + HOAc$

$\rightleftharpoons CH_3\text{-}CH\text{=}CH\text{-}OAc + CH_3\text{-}CH_2\text{-}CHO$

Mercuric salts of weak acids such as mercuric acetate are common catalysts for vinyl transesterification or vinyl transetherification.(18, 19) Propionaldehyde boils at 48.8°C; since the isomerization mixture was at 80°C, any propionaldehyde formed would boil-off driving the reaction to completion. Propionaldehyde was not identified in the GC analysis or in the spinning band distillation of the dipropenyl ether catalysis product. The limiting reagent in these reactions is the acetic acid; the amount of acetic acid present depends on the amount of catalyst used and the percentage decomposition of the mercuric acetate. Complete catalyst decomposition would give impurity levels comparable to those observed in the ctDPE and ttDPE products (see calculations Appendix I).

Infrared and NMR spectral evidence indicate the presence of both the cis and trans isomers of propenyl acetate. Foster and Tobler produced a mixture of 53% cis propenyl acetate and 47% trans-propenyl acetate from the reaction of propionaldehyde with acetic anhydride.(23) House and Kramer reacted propionaldehyde with acetic anhydride to produce 52% cis propenyl acetate and 48% trans-propenyl acetate.(24) Foster and Tobler found that the decomposition of cis-1-propenylmercuric acetate yielded 66.7% cis and 33.3% trans propenyl acetate, while the decomposition of cis-1-propenylmercuric acetate yielded 68.8% cis- and 31.2% trans-propenyl acetate.(23) Transesterification of propenyl acetate takes place only with cis-trans isomerization.(20,25) Henry obtained a mixture of 46% cis- and 54% trans-propenyl acetate after three hours in an exchange reaction between trans-propenyl acetate and deuterated acetic acid; he proved that each ester exchange occurred with a trans-cis or cis-trans isomerization.(20) Sabel et. al. obtained similar results in the transesterification of propenyl acetate with propionic acid.(31)

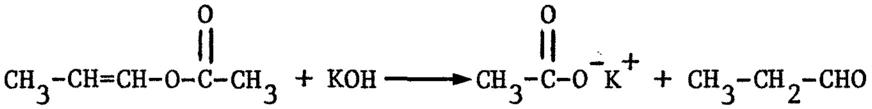
Distillation of propenyl acetate mixtures on a spinning band column of 65 theoretical plates gave a boiling point of 101°C for 85.4% cis-propenyl acetate and 103°C for 93.7% trans-propenyl acetate.(23) A boiling point of 98°C for 88% cis,trans-dipropenyl ether and 101°C for 81% trans,trans-dipropenyl ether were recorded using a Nester/Faust spinning band column in this work. Based on boiling points, propenyl acetate cannot be separated from the trans,trans-dipropenyl ether. The cis,trans-dipropenyl ether can probably be purified if a different GC column, which will separate the acetate and the ether, is used to monitor the samples from the spinning-band distillation.

Waldron found that mercuric salicylate and mercuric benzoate gave isomerization results comparable to mercuric acetate as enol ether catalysts.(17) Mercuric acetate had been used satisfactorily in previous work with dipropenyl ethers.(8, 12) In two preliminary isomerizations of 1.60 g and 10.10 g samples of impure ccDPE (containing 4.6% t-butanol), there was no visible evidence of mercury formation. Waldron correlated the catalytic decomposition of mercuric acetate in 1,2-dimethoxyethylene isomerization to the presence of impurities or to temperatures above 175°C.(17, 26) All three dipropenyl ether samples were isomerized at

80°C; the impure samples remained in contact with the mercuric acetate for ten to eleven days without mercury formation while the pure sample experienced mercury formation in less than two days. The decomposition of the mercuric acetate in the purified ccDPE is an enigma, but the problems associated with the decomposition byproducts can be avoided by using mercuric salicylate or mercuric benzoate. The corresponding byproduct esters, propenyl salicylate or propenyl benzoate, would have higher boiling points and could be separated by distillation.

An ester saponification reaction was used to remove the propenyl acetate impurity from ctDPE and ttDPE. The reaction of propenyl acetate with potassium hydroxide proceeds as follows:

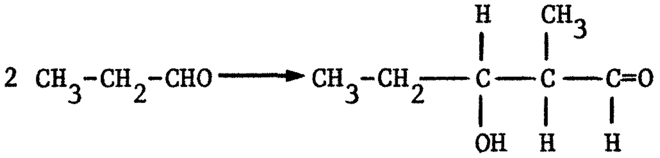
(4)



$$CH_3\text{-}CH{=}CH\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3 + KOH \longrightarrow CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^-K^+ + CH_3\text{-}CH_2\text{-}CHO$$

Aldol condensation of the propionaldehyde then yields the β-hydroxy-aldehyde, 3-hydroxy-2-methylpentanal:(27)

(5)



$$2\ CH_3\text{-}CH_2\text{-}CHO \longrightarrow CH_3\text{-}CH_2 - \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - \underset{\underset{H}{|}}{C}{=}O$$

This product undergoes further aldol condensation at the α-hydrogen to yield higher molecular weight products. The final products have a much higher melting point and a much lower vapor pressure than the ester and can therefore be separated from the cis,trans and trans,trans-dipropenyl ether, giving pure gas-phase spectra.

The infrared bands for cis- and trans-propenyl acetate are given in Table I.(16) Also noted are the bands which were removed from the

TABLE I

Propenyl Acetate Infrared Bands(16)

Cis Isomer[a]	Trans Isomer[a]	ctDPE Impurity	ttDPE Impurity
3067 cm^{-1}	3067 cm^{-1}		
	3021		
2933	2950		
2865			
1764	1764	{1776 cm^{-1} {1743	{1778 cm^{-1} {1740
1675	1684	1663[b]	
1445	1439		
1389			
1370	1372		
1357			
	1304		
	1282	1278[c]	1273[c]
1220	1220	1228	1226
1120	1124		
1098	1098		
1045	1044	1047	
	998		
987			
927	927	915[d]	923[d]
908	903		
740		720[d]	

Notes:

(a) The infrared spectra were determined in CS$_2$ and CCl$_4$ solution. The intensities are not given.

(b) Pure ctDPE has a doublet in this region which disappears in the presence of the impurity.

(c) Pure ctDPE and ttDPE have doublets in this region. In the presence of the impurity one peak of the doublet is enlarged and the other peak becomes a shoulder.

(d) These peaks of ctDPE and ttDPE are significantly increased in the presence of the impurity.

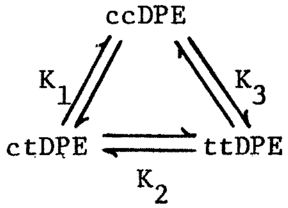
ctDPE and ttDPE gas-phase spectra. The impurity bands indicate that ctDPE contains both cis- and trans-propenyl acetate, while the major impurity in ttDPE is trans-propenyl acetate. This is consistent with production of a 50/50 mixture of cis and trans-propenyl acetate (see calculations Appendix I). If 0.98 g of trans propenyl acetate represents the ester impurity in ttDPE from complete catalyst decomposition, ctDPE would contain 1.34 g of cis-propenyl acetate plus 0.36 g of trans-propenyl acetate.

Significant bands removed are the vinyl ester C=O stretch at 1777 cm^{-1}, the asymmetric C-O-C stretch at 1220 cm^{-1}, and the symmetric C-O-C stretch at 1045 cm^{-1}. Decreased intensity is noted for the cis vinyl C-H out-of-plane bending at 740 cm^{-1} and the trans vinyl C-H out-of-plane bending at 927 cm^{-1}. Changes in the shapes of the C=C stretch at 1675 cm^{-1} and the vinyl C-H in-plane rock at 1282 cm^{-1} are also noted.

The two bands in the 1700 region are probably due to different conformers of propenyl acetate. A number of substituted ethyl acetates have two carbonyl absorptions due to cis and gauche conformations.(28) A planar cis conformation is reported to be the most stable form of cis-propenyl acetate.(37) The less stable gauche conformer for a number of carboxylic esters is reported to be stabilized in solution.(29) The 1742 cm^{-1} infrared band is attributed to the propenyl acetate impurity since the band is significant, the band is removed with the propenyl acetate, and there is no evidence for another major impurity.

III. PYROLYSIS OF CIS,CIS-DIPROPENYL ETHER

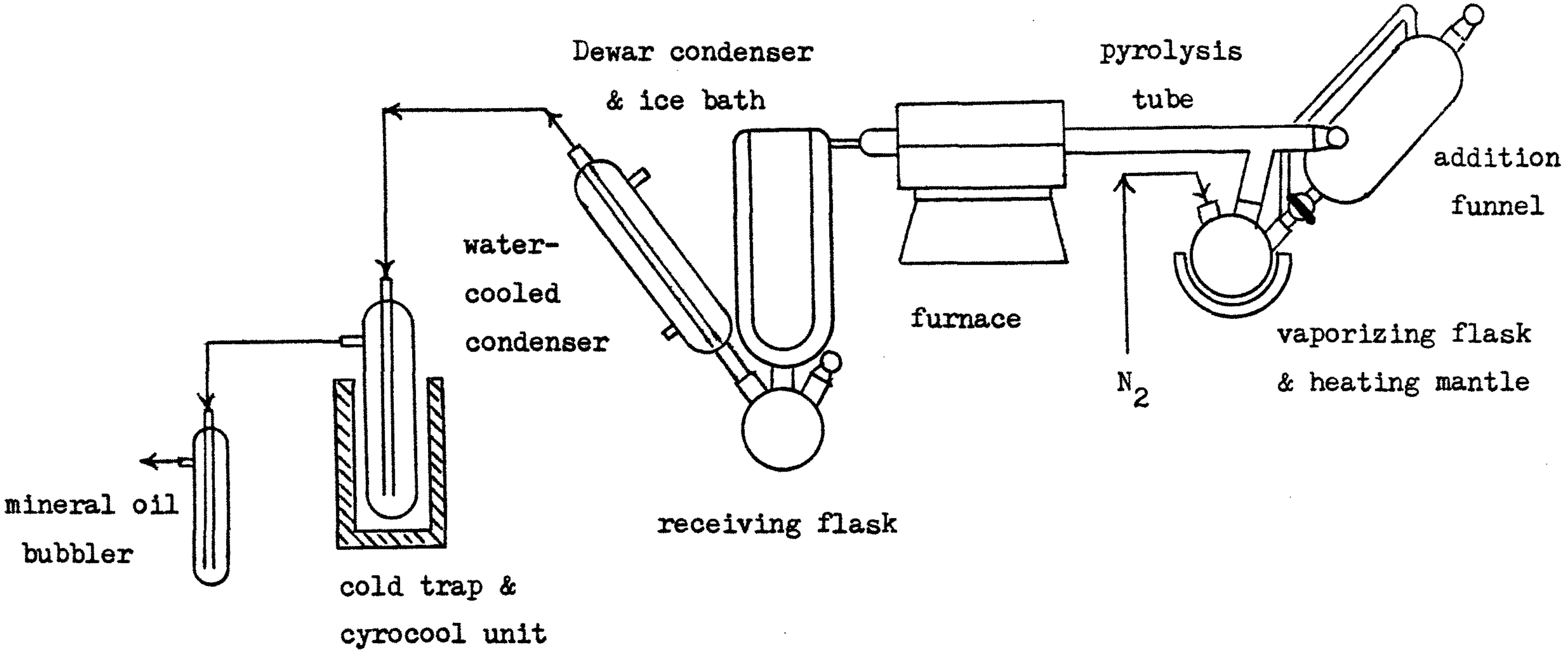
Cis,cis-dipropenyl ether (ccDPE) was passed over base-washed activated alumina, in a tube furnace set-up as shown in Figure 2, in an attempt to effect rearrangement to the thermodynamically less stable isomers. Equilibrium data taken at 80-130°C(12) was extrapolated to higher temperatures as shown in Figure 3, in order to predict the conditions necessary to produce a mixture containing approximately 20% trans,trans-dipropenyl ether (ttDPE). The trans,trans isomer is present in the equilibrium mixture in the smallest percentage and is also the highest-boiling fraction, making isolation by batch distillation difficult. The equilibrium constants, K_1, K_2, and K_3, are defined as follows:(12)



where: K_1 = ctDPE/ccDPE
K_2 = ttDPE/ctDPE
K_3 = ttDPE/ccDPE

Since only two of these equilibrium constants are independent, three values for the equilibrium percentages could be determined at each temperature. Details of the calculations are given in Appendex I. An average equilibrium value of 20% ttDPE was predicted to require a temperature of 367°C (see Figure 4).

Unsaturated compounds can be polymerized by pyrolysis, but need relatively low temperatures (below 250°C) and long residence times. Polymerization in high-temperature pyrolysis is attributed to secondary causes.(30) In the present work the formation of acetylene or acrolein is evidently **the cause of** formation of higher molecular weight compounds. Decomposition should be the primary reaction at high temperatures.(30)



<u>FIGURE 2</u> <u>Pyrolysis Experimental Set-Up</u>(33)

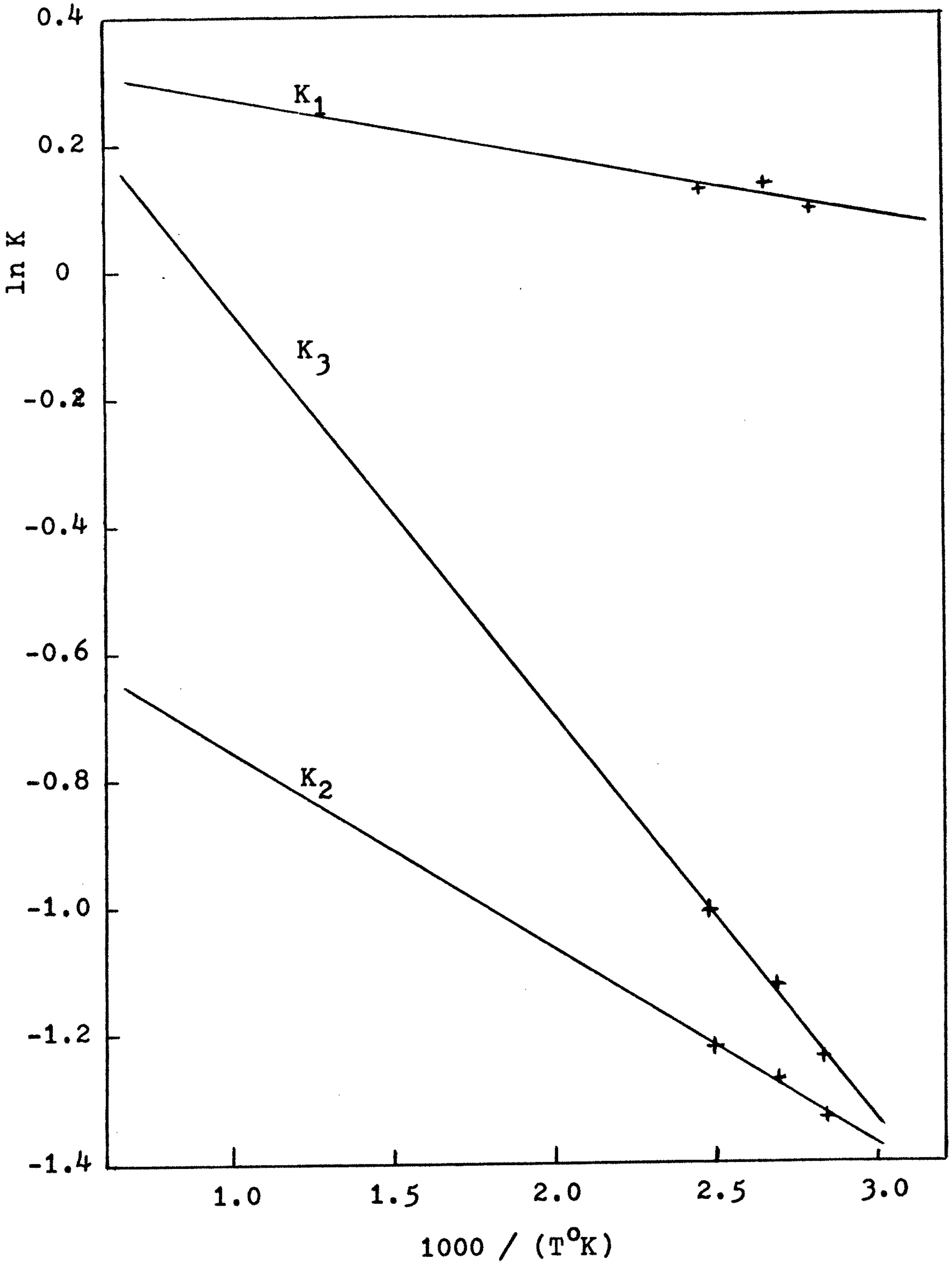


FIGURE 3

Equilibrium Constants for Dipropenyl Ether(5)

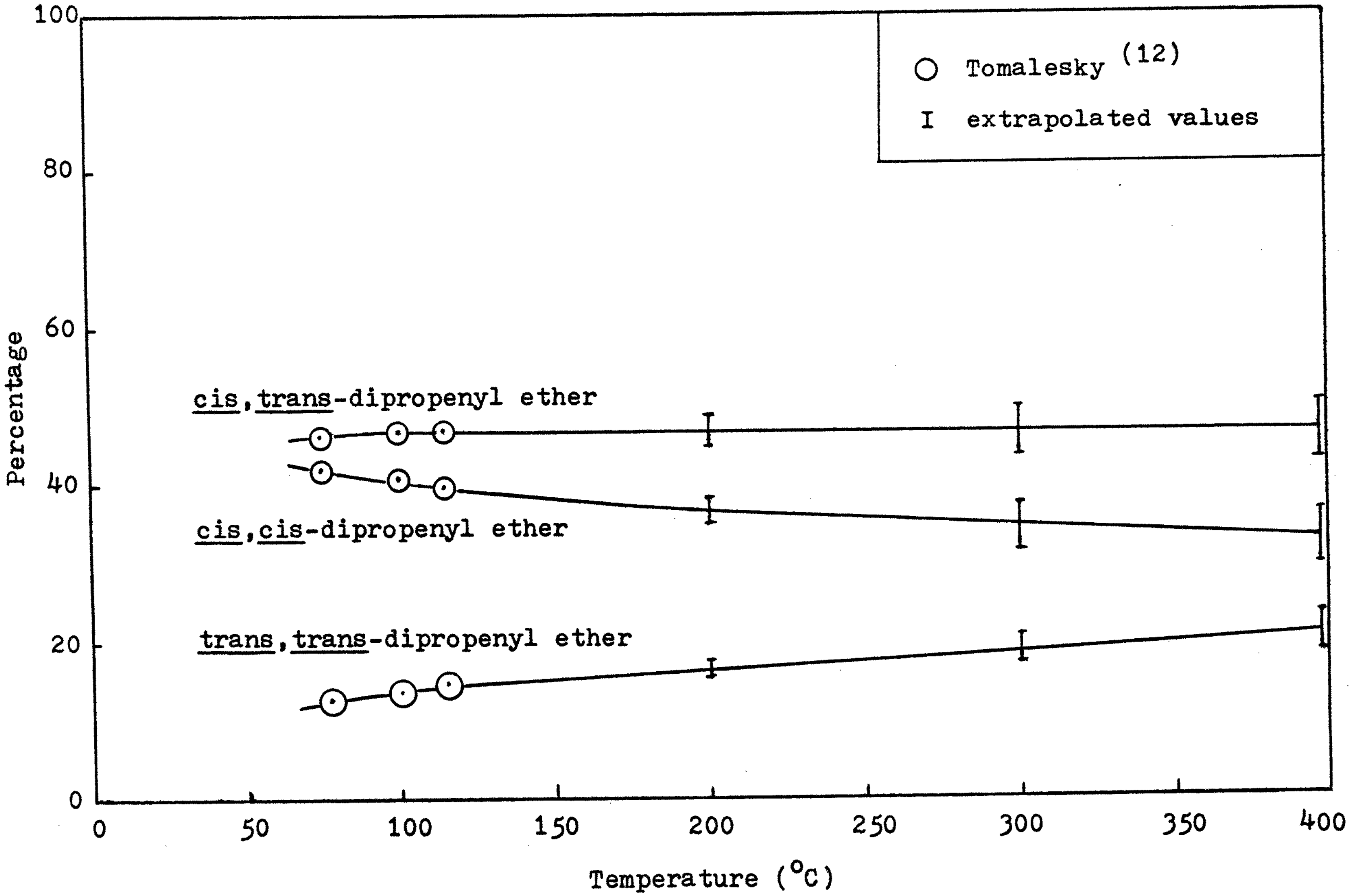
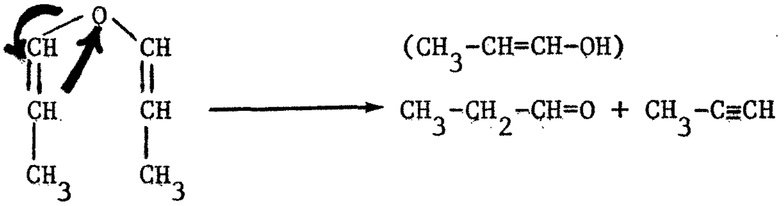


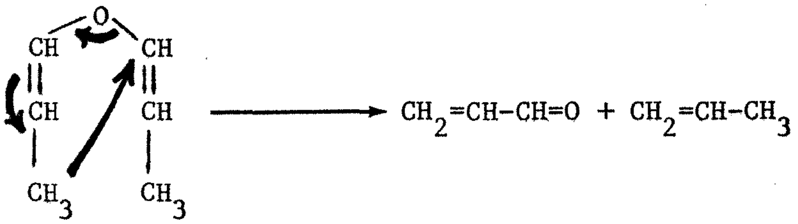
FIGURE 4 Dipropenyl Ether Equilibrium Compositions

Pyrolysis of vinyl ethers takes place with alkyl-oxygen cleavage yielding aldehydes and unsaturated hydrocarbons.(31) Three mechanisms for the decomposition of dipropenyl ether are proposed; the products are either propionaldehyde and methyl acetylene, propylene and acrolein, or isobutyraldehyde and acetylene:

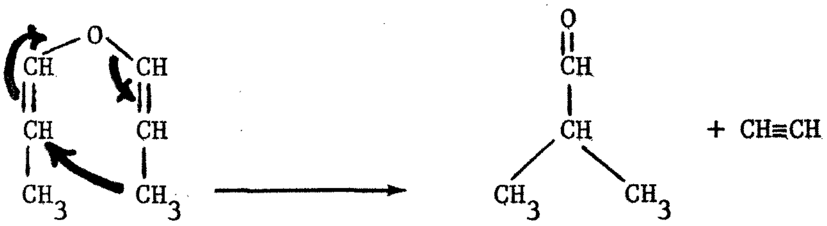
(1)



(2)



(3)



Acetylene boils at -83.6°C, so it would not be condensed in the pyrolysis experimental setup. Methyl acetylene boils at -23.3°C and should be collected in the cold trap. In Run #9 the entire contents of the cold trap evaporated instantaneously on attempting to bottle the sample, giving some evidence for the presence of methyl acetylene. Propionaldehyde boils at 48.8°C, acrolein at 53.7°C, and isobutraldehyde at 61.5-63.5°C. Propionaldehyde was tentatively identified by boiling point and odor in the spinning-band distillation of Runs #5 and 6. Acrolein polymerizes very readily,(32) and higher molecular weight material was identified in all of the pyrolysis samples.

Pyrolysis of propionaldehyde yields carbon monoxide and ethane which further decomposes to give ethylene and hydrogen:(30)

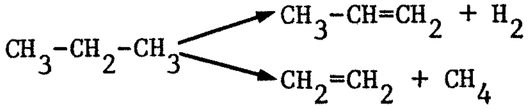
(4) $CH_3\text{-}CH_2\text{-}CH=O \longrightarrow CH_3\text{-}CH_3 + C\equiv O$

(5) $CH_3\text{-}CH_3 \longrightarrow CH_2=CH_2 + H_2$

Ethane boiling at -88.63°C and ethylene boiling at -103.71°C are both noncondensible in the pyrolysis system.

Pyrolysis of isobutyraldehyde yields carbon monoxide, hydrogen, methane, ethane, ethylene, and propylene:(30)

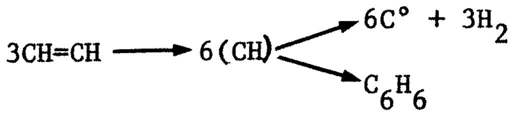
(6) $(CH_3)_2\text{-}CH\text{-}CH=O \longrightarrow CH_3\text{-}CH_2\text{-}CH_3 + C\equiv O$

(7) 

$$CH_3\text{-}CH_2\text{-}CH_3 \begin{array}{l} \nearrow CH_3\text{-}CH=CH_2 + H_2 \\ \searrow CH_2=CH_2 + CH_4 \end{array}$$

Propane boiling at -42.07°C and propylene boiling at -47.4°C are also noncondensible since the cryocool cold trap temperature was around -42°C throughout the pyrolysis experiments.

Pyrolysis of acetylene yields benzene, toluene, naphthalene, and polymeric compounds in addition to carbon, hydrogen, ethylene, ethane, and methane. Temperatures above 480°C favor polymerization. The postulated intermediate is (CH) which can decompose into carbon and hydrogen or polymerize or add to other compounds. These intermediates also combine to form benzene and other aromatic compounds.(30)

(8) 

$$3CH{=}CH \longrightarrow 6(CH) \begin{array}{l} \nearrow 6C^\circ + 3H_2 \\ \searrow C_6H_6 \end{array}$$

Blackened alumina, particularly in the center of the pyrolysis tube, is probably due to polymer formation. The products from Runs #1-8 all contained a water layer attributed to the alumina not being bone-dry. All of the runs also contained higher molecular weight material which increased in proportion to the ttDPE isomerization ratio. The product from Runs #5 and 6 contained ttDPE as 14.3% of total ethers and 8% of the condensible product; the high-GC-retention time impurities totalled 32%. The product from Runs #7 and 8 contained ttDPE as 21.6% of total ethers and 4% of condensible product; the high-retention time impurities totalled 52%. The 14.3% sample was yellow and the 21.6% sample was greenish-black. Divinyl ether is reported to form a black polymer with acid.(11) In Run #9 where the alumina was absolutely dry, ttDPE is only 1% of the total product while the high-retention impurities represent 96% of the condensible product. The formation of higher-molecular weight compounds can be attributed to polymerization of acrolein or to addition of acetylene radicals to dipropenyl ether.

The pyrolysis equipment was originally set-up as described by Waldron(33), and modified in later runs as shown in Figure 2. The nine pyrolysis runs are summarized in Table II. At 300°C, 18.9% ttDPE was predicted from the equilibrium curves (Figure 4), but only 3.4% ttDPE was produced. The temperatures were increased in other runs in an attempt to increase the rate of reaction and reach equilibrium at the residence time fixed by the experimental set-up. The approach to equilibrium with increasing temperature is shown in Figure 5.

The composite sample from Runs #7 and 8 contained 36.9% ccDPE, 41.4% ctDPE, and 21.6% ttDPE, which is close to the extrapolated equilibrium percentages. Figure 6 shows the GC analysis of this product. A

TABLE II

Pyrolysis Optimization Runs

Run #	Alumina, g	Feed, g	X feed	Q, g/hr	T, °C[a]	Product, g	Ether Composition[b]
1	102.18	16.49	95.4% cc	21.99	300	6.95	74.8% cc, 21.7% ct, 3.4% tt
2	80.17	15.38	95.4% cc	30.76	325	10.41	65.8% cc, 28.7% ct, 5.5% tt
3	132.40	16.35	70.4% cc[b]	21.80	340	6.28	49.7% cc, 38.6% ct, 11.7% tt
4	c	15.54	95.4% cc	17.92	340	12.97	55.8% cc, 35.5% ct, 8.7% tt
5	c	218.13	95.4% cc	29.73	370	-	41.1% cc, 42.4% ct, 16.5% tt
					370	-	54.7% cc, 36.2% ct, 9.1% tt
					390	-	53.6% cc, 37.3% ct, 9.1% tt
					390	-	56.0% cc, 35.0% ct, 9.1% tt
					410	-	55.7% cc, 35.4% ct, 8.9% tt
					410	-	54.9% cc, 35.8% ct, 9.2% tt
	(composite sample)				400	170.62	54.8% cc, 35.9% ct, 9.2% tt
6	123.01	64.84	54.5% cc[b]	18.79	390	-	32.9% cc, 41.7% ct, 25.4% tt
					390	-	33.5% cc, 41.7% ct, 24.8% tt
					360	-	39.9% cc, 44.6% ct, 15.5% tt
					350	-	43.4% cc, 43.2% ct, 13.4% tt
	(composite sample)				350	41.75	42.4% cc, 43.3% ct, 14.3% tt
7	137.03	35.18	95.4% cc	11.73	395	-	41.3% cc, 41.1% ct, 17.6% tt
					395	-	34.1% cc, 43.3% ct, 22.6% tt
					405	d	33.7% cc, 43.3% ct, 22.9% tt
8	130.52	38.55	95.4% cc	6.70	380	-	39.9% cc, 36.9% ct, 23.2% tt
					380	-	34.9% cc, 33.3% ct, 31.9% tt
					380	-	49.5% cc, 39.4% ct, 11.2% tt

TABLE II (continued)

Run #	Alumina, g	Feed, g	X feed	Q, g/hr	T, °C[a]	Product, g	Ether Composition[b]
8	(continued)				390	-	39.5% cc, 44.0% ct, 16.5% tt
					400	-	36.4% cc, 43.0% ct, 20.6% tt
					400	-	39.4% cc, 42.2% ct, 18.4% tt
	(composite Runs #7 and 8)					51.42	36.9% cc, 41.4% ct, 21.6% tt
9	125.49	5.25	99.9% cc	31.52	395	0.24[e]	26.6% cc, 32.6% ct, 40.8% tt

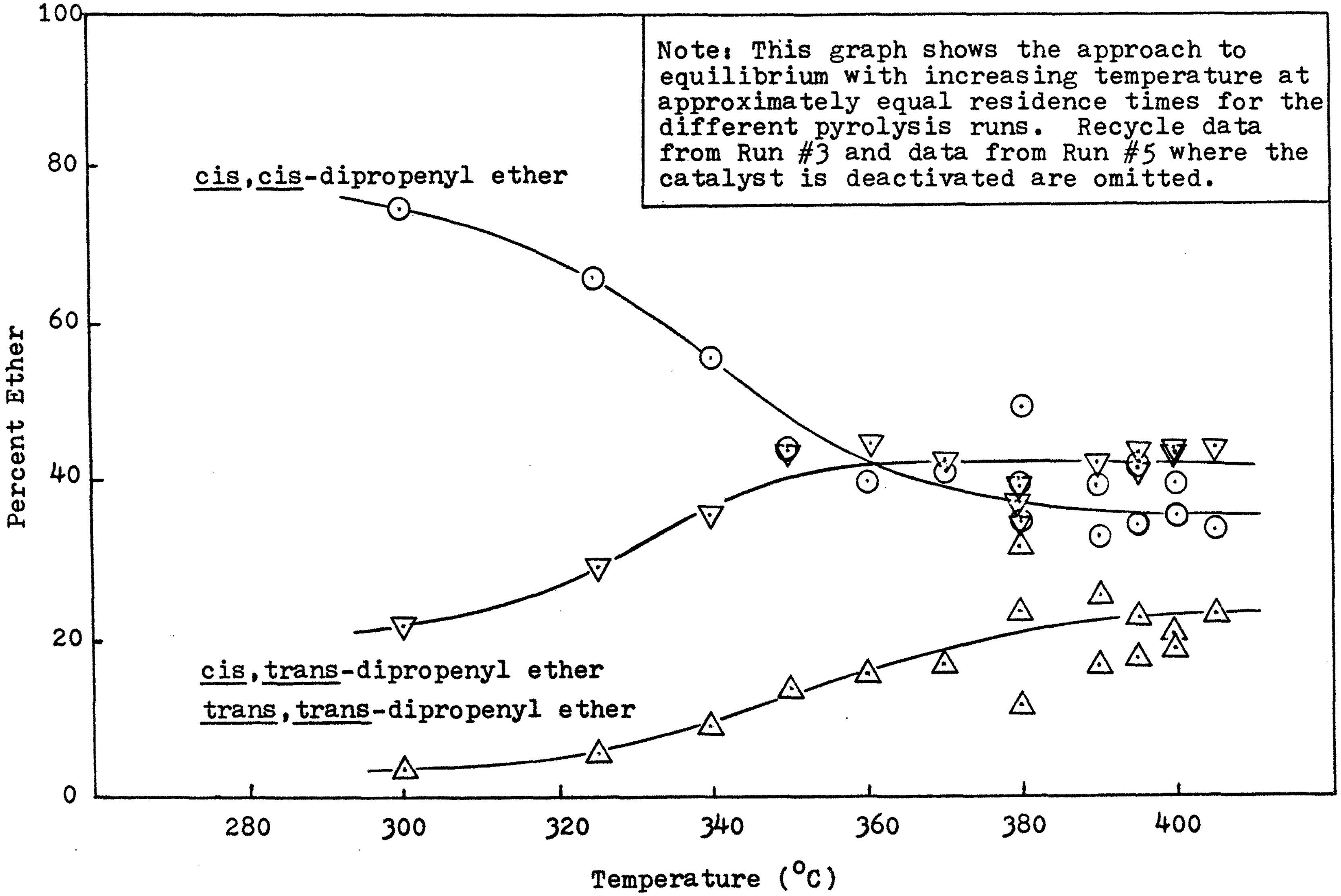
Notes: (a) Waldron determined a long time lag between the oven temperature and the oven pyrometer.(33) When the temperature was changed during a run, the average between the old temperature and the pyrometer reading is reported.

(b) The GC was run at 120°C to force high-molecular weight materials through. Percentages determined by peak height. All other percentages by peak area.

(c) Alumina from the previous run was reused.

(d) Product combined with Run #8.

(e) Low recovery due to leak in system.



Note: This graph shows the approach to equilibrium with increasing temperature at approximately equal residence times for the different pyrolysis runs. Recycle data from Run #3 and data from Run #5 where the catalyst is deactivated are omitted.

FIGURE 5 Pyrolysis: Dipropenyl Ether Compositions

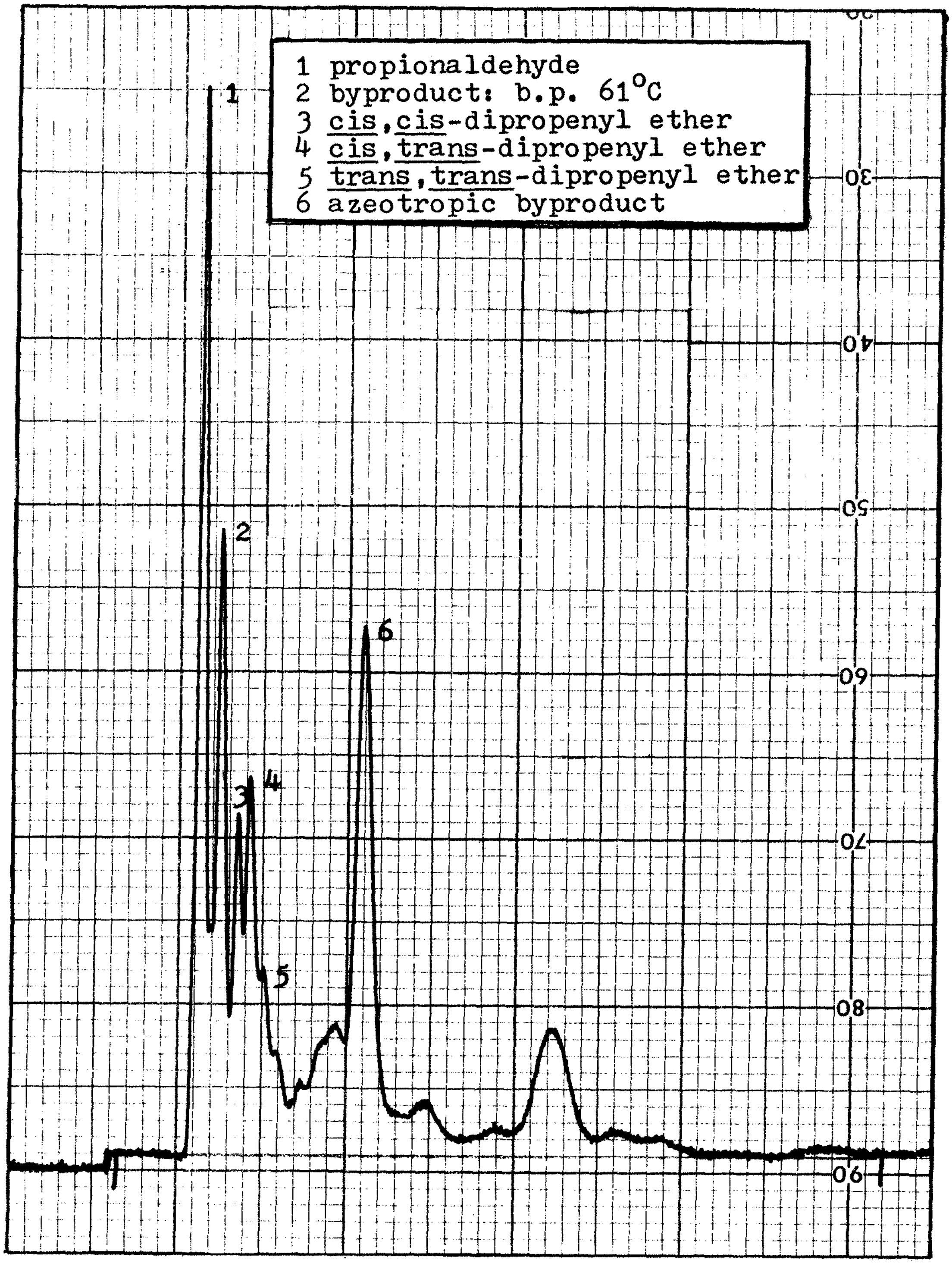


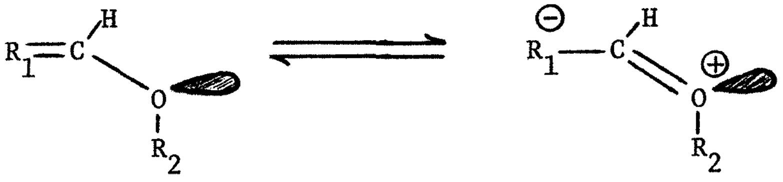
FIGURE 6

Equilibrium Pyrolysis Product Distribution large propionaldehyde peak (#1) may be attributed to water from the alumina reacting with ccDPE. A final run was made with catalyst which had been dried for eleven days. Peaks #1 and 2 of Figures 6 were much smaller, but many new high-retention time GC peaks appeared indicating a much larger percentage of polymer formation. Fractionation of the pyrolysis sample from Runs #5 and 6 was attempted, but pure dipropenyl ether samples could not be collected because of the presence of an azeotropic impurity. Pyrolysis was abandoned and mercuric acetate catalyzed isomerization was chosen as a preparative method for ctDPE and ttDPE because the product is much cleaner.

IV. CONFORMATIONS OF ENOL ETHERS AND ESTERS

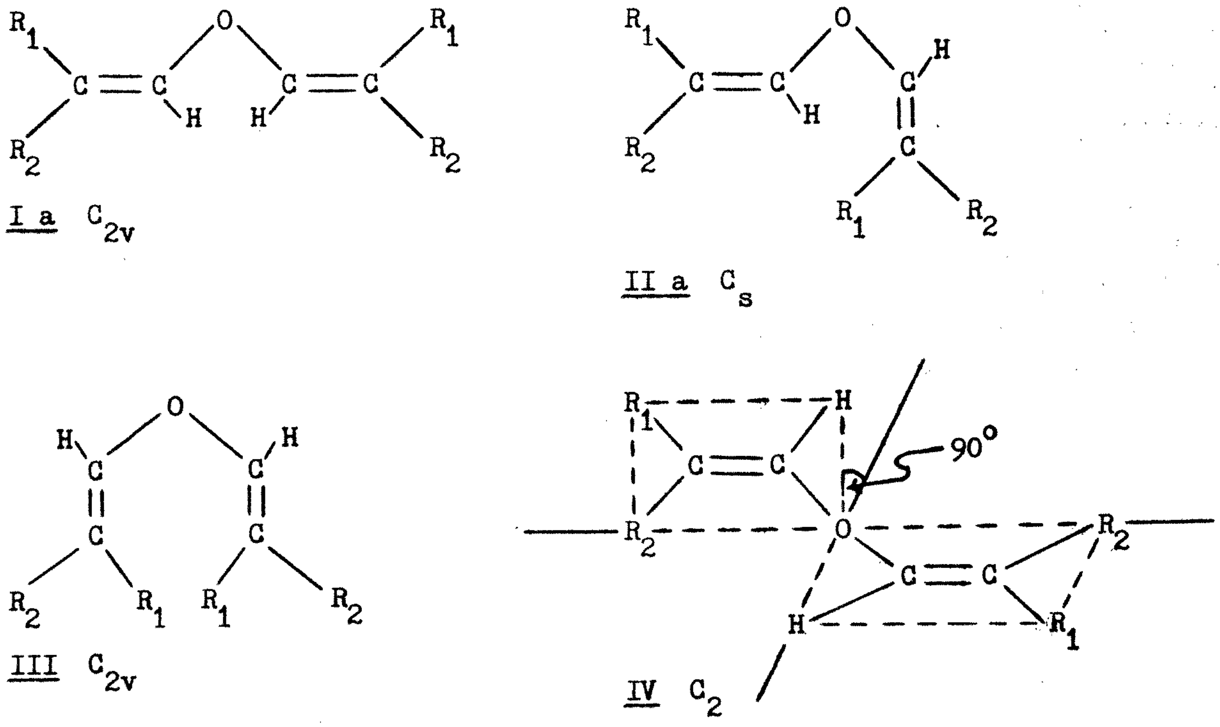
In the dipropenyl ether molecules, there exist two axes of rotation with respect to the central oxygen atom. All of the possible symmetric conformations due to rotation around these axes are shown in Figure 7. Conformation III is prohibited for all three isomers by steric hindrance. Conformation IIa is prohibited by steric hindrance for cis,cis-dipropenyl ether (ccDPE). The possible conformations for ccDPE are, therefore, a planar C_{2v}, a non-planar C_2, or a non-symmetrical C_1 form. The possible conformations for trans,trans-dipropenyl ether (ttDPE) are a planar C_{2v} or C_s, a non-planar C_2, and a C_1 form. Cis, trans-dipropenyl ether (ctDPE) has two possible planar conformations Ib and IIb, both of C_s symmetry. The linear coupled C_s conformer (Ib) is similar to the C_{2v} conformations of ccDPE and ttDPE, while the bent C_s conformer (IIb) is similar to the C_s conformation of ttDPE. IIb arises from rotation of the trans propenyl group around the carbon-oxygen axis; rotation of the cis propenyl group to the same position is sterically hindered.

The appearance of rotational conformers of alkyl esters, enol esters, alkyl vinyl ethers, and divinyl ethers may be attributed to steric hindrance to free rotation and to the partial double-bond character of the C-O bond.(6, 7) Sp^2 hybridization of the central oxygen atom is consistent with the resonance structures contributing to the partial double-bond character.



Cis,Cis-Dipropenyl Ether ($R_1 = CH_3$, $R_2 = H$)

Trans,Trans-Dipropenyl Ether ($R_1 = H$, $R_2 = CH_3$)

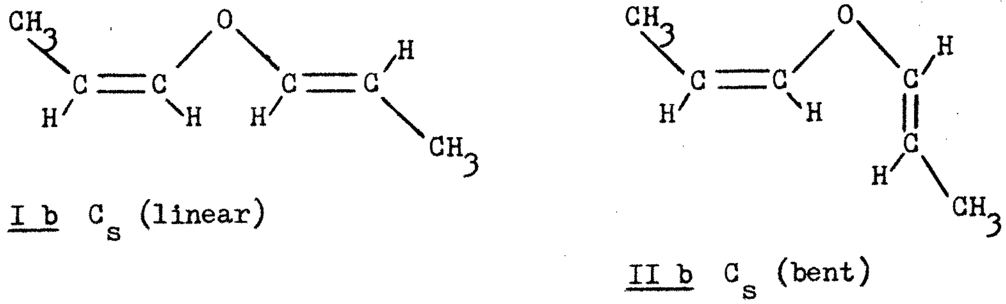

I a C_{2v}

II a C_s

III C_{2v}

IV C_2

Cis,Trans-Dipropenyl Ether


I b C_s (linear)

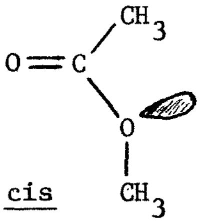
II b C_s (bent)

FIGURE 7

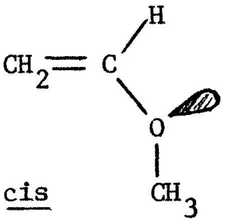
Conformations of Cis,Cis-, Cis,Trans- and Trans,Trans-Dipropenyl Ether

This hybridization gives either a planar <u>trans</u> or a planar <u>cis</u> conformation of the double bond with respect to the central oxygen atom.(1)

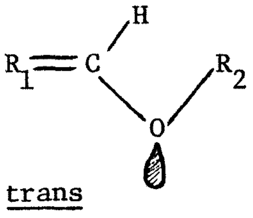
Methyl formate and methyl acetate were shown to exist in the planar <u>cis</u> conformation.(34) Two conformers are reported for methyl vinyl ether and ethyl vinyl ether with the more stable one being the planar <u>cis</u> conformation and the other conformer being non-planar.(1, 2, 35)



cis



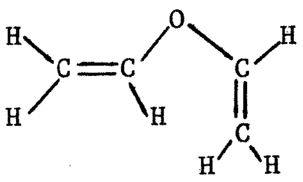
cis



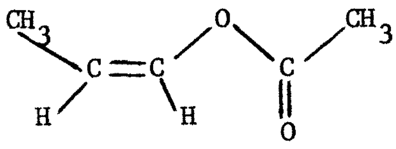
trans

The stability of the <u>cis</u> conformation in methyl vinyl ether is attributed to a nonbonded attraction between the methyl group and the double bond.(36)

Steric hindrance generally prohibits molecules with double-bonds on either side of the central oxygen atom from taking a conformation with both double-bonds <u>cis</u> with respect to the central oxygen atom. Divinyl ether, vinyl acetate, and <u>cis</u>-propenyl acetate are most stable in the planar conformation which has one double-bond <u>cis</u> and the other double-bond <u>trans</u> with respect to the central oxygen atom.(5, 37)



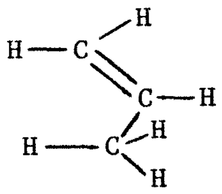
divinyl ether

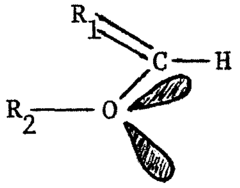


<u>cis</u>-propenyl acetate

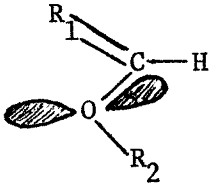
The C_{2v} conformation (Ia), which corresponds to both double-bonds being <u>trans</u> relative to the central oxygen atom, is reported as the conformation of *cis,cis*-dipropenylether and as a less stable conformation for divinyl ether.(5)

In propylene, the methyl protons take a staggered position relative to the adjacent vinyl proton. The analogous conformations of the enol ethers and of carboxylic esters would again be a planar *cis* form relative to the central oxygen atom, plus two gauche forms corresponding to a 120° rotation around the carbon-oxygen axis in either direction.(1)





cis



gauche

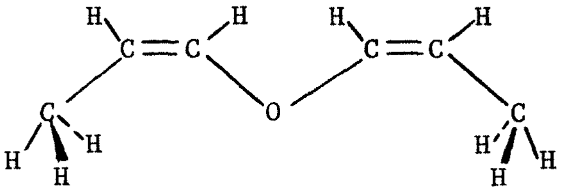
This sp^3 hybridization is used to account for the gauche conformers of methyl vinyl ether and of ethyl vinyl ether.(1) In isopropenyl acetate, which is sterically hindered from taking a planar conformation, the acetate group is rotated 110° with respect to the plane of the isopropenyl group.(37) The gauche conformer of divinyl ether, however, has a total angle of rotation of only 40°.(5) The C_2 conformer in Figure 7 represents a rotation of 90° around the central axis. This is not consistent with either sp^2 or sp^3 hybridization.

The appearance of multiple bands in the C=C stretching region of vinyl ethers is generally accepted as evidence of rotational isomerism.(1, 5) Fermi resonance of the C=C stretch fundamental with the overtone of the vinyl CH_2 wag, which is an additional source of multiple bands in many vinyl ethers,(1) may be ruled out by the molecular structure in the case of dipropenyl ethers. Coupling of the two double-bonds in divinyl or dipropenyl ether also leads to multiplicity of bands in the 1600 cm^{-1} region.(10) Observation of two or three Raman lines in this region is typical. Specifically, this multiplicity has been correlated with rotational isomerism in three β-fluoroalkyl ethers(4), *cis*- and *trans*-1,2-dimethoxyethylene,(3) ethyl vinyl ether,(2) and divinyl ether.(5)

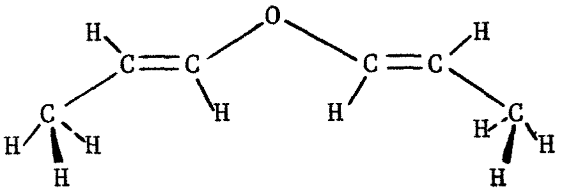
V. RAMAN AND INFRARED SPECTRAL ANALYSIS

A. Cis,Cis-Dipropenyl Ether

Dipropenyl ether is a non-linear molecule composed of seventeen atoms and, therefore, has a maximum of 3n-6 = 45 vibrational modes. The highest symmetry for the cis,cis or trans,trans isomer is a C_{2v} conformation:



cis,cis-dipropenyl ether (C_{2v})



trans,trans-dipropenyl ether (C_{2v})

The proton NMR coupling constants indicate rapid rotation of the methyl groups around their three-fold symmetry axis yielding a time-averaged dihedral angle of 0° (48) relative to the adjacent vinyl proton, as shown above. An equivalent heavy atom C_{2v} conformation can be drawn with both methyl groups rotated 180° from the positions shown above. The other C_{2v} conformation shown in Figure 7 is prohibited by steric hindrance.

The dipropenyl ether C_{2v} conformation has eight infrared-inactive frequencies of the A_2 symmetry series. If the terminal methyl groups are considered as point masses, 27 vibrational modes are calculated including four infrared-inactive A_2 modes. There are, therefore, a maximum of eight infrared-inactive vibrational frequencies for the C_{2v}

conformer with four of these modes attributable to the C-H bonds (see calculations, Appendix I).(38) Vibrations from identical bonds which do not couple would be expected to give accidentally degenerate vibrations, for example, the two identical methyl groups should have only nine vibrational modes two of which are infrared inactive, instead of eighteen vibrational modes. The nine methyl vibrations are a symmetric stretch, two asymmetric stretches, a symmetric deformation, two assymmetric deformations, a methyl torsion, and two methyl rocks. In conformations of less than C_{3v} symmetry, the asymmetric vibrations will have slightly different frequencies.(39)

A better prediction of the number of non-degenerate vibrational frequencies is obtained by considering the dipropenyl ether molecule as consisting of two CH_3-CH=CH-O- groups. This gives twenty-one bands from this group plus three additional bands due to the C-O-C linkage.(5) (Note: (2 x 21) + 3 = 45). Addition of bands due to coupling of the C=C stretches and the C-O stretches, plus subtraction of the vinyl torsion band at 85 cm^{-1} (5) which is out of the range of the equipment used, and of the C-C-C and C-C-O skeletal deformations which mix with the C-O-C skeletal deformation,(40) gives a total of 23 vibrational modes for the C_{2v} conformer of dipropenyl ether. Thirty-two bands are observed for cis,cis-dipropenyl ether. The additional bands are attributed to other conformations or to weak summation bands or overtones. All bands in the other conformations are both infrared and Raman active.

The infrared spectra for cis,cis-dipropenyl ether (ccDPE) are shown in Figures 19, 20, and 21 and the Raman spectra are shown in Figures 28 and 29. The infrared and Raman vibrational bands along with the corresponding frequency assignments for ccDPE ether are given in Table III. The assignment of band intensities is as follows: very strong, 90-100%, strong, 70-90%, medium, 30-70%, weak, 10-30%, and very weak, 0-10%.(60) The strongest band is assigned a value of 100% in all the spectra except for the Raman spectra of ccDPE. The ccDPE Raman band at 1691 cm^{-1} is three times the intensity of any other band in this spectra and has been given a special assignment of very very strong with the second strongest band assigned as the 100% value. This makes the Raman intensity assignments for ccDPE more consistent with the assignments for the cis, trans and trans,trans isomers.

The C-H stretching modes for enol ethers are similar to those for other alkenes; these vibrations are very weak in the infrared but fairly strong in the Raman spectra.(9) The $R_1CH=CHR_2$ stretch is predicted at 3020 cm^{-1}.(47) The band at 3057 cm^{-1} for ccDPE, the only strong Raman band in this region, is assigned to the vinyl C-H stretch. Colthup reports a range of 3500-3000 cm^{-1} for the vinyl C-H stretch.(39)

For methyl groups, the asymmetric C-H stretch is found at approximately 2972-2952 cm^{-1} and the symmetric C-H stretch at 2882-2862 cm^{-1}.(39) The Raman bands at 2921 cm^{-1} and 2866 cm^{-1} are assigned to the asymmetric and symmetric C-H stretches respectively. The weak bands at 2982 cm^{-1} and the shoulder at 2890 cm^{-1} may be the asymmetric and symmetric C-H stretches of another conformer. The frequencies of the C=C and the C-O-C stretches for the C_{2v} and the non-planar conformer are also widely separated. An additional very weak band at 3027 cm^{-1} may be due to the

TABLE III

Vibrational Frequencies and Assignments for Cis-Cis Dipropenyl Ether

Infrared (cm^{-1})[b]			Raman (cm^{-1})[b]	
Vapor (CsI)	Liquid (NaCL)	CCl_4 Solution	Liquid	Assignment[b]
			3102 vw	
3053 w	3039 w	3043 vw	3057 s 3027 vw	=C-H stretch
2980 vw	2988 vw	2977 vw	2982 w	CH_3 asym. stretch
2938 w		2940 (sh)	2936 (sh)	1691 + 1255
	2920 w	2920 w	2921 vs	CH_3 asym. stretch
2882 vw			2890 (sh)	
			2867	
	2863 vw	2860 vw	2865 m	CH_3 sym. stretch
			2823 vw	
			2772 vw	2 x 1386
			2728 vw	2 x 1362
1763 vw				
1726 vw	1724 vw			
1690 vw			1691 vvs[(a)]	C_{2v} sym C=C stretch
1668 1663 s 1658	1660 1654 s	1653 s	1654 vs	C_{2v} asym C=C stretch
1583 vw		1588 vvw		
1630 sh	1640 sh		1638 vw	C_1 C=C stretch
			1463 (sh)	HCH sym. deformation
	1444 vw	1443 w	1442 w	CH_3 asym. scissors
1403 sh	1398 sh		1406 w	
1395 m	1389 m	1389 m	1386 w 1362 w	CH_3 sym scissors
1356 m	1353 s	1353 s		
			1255 s	vinyl =C-H IP rock
1253 s	1253 s	1252 s		C_1 C-O-C asym. stretch
1138 vs	1129 vs	1132 vs	1133 vw	C_{2v} C-O-C asym. stretch
1082 w	1078 m	1079 m	1028 vw	C_1 C-O-C sym. stretch
	971 vw	972 w	967 vw	
			946 m	C_{2v} C-O-C sym. stretch
928 vw	926 vw	927 w	897 w	
794 vw				
718 m	720 m	712 m	728 vw	C_{2v} cis vinyl =C-H
705 sh	690 w	687 w	694 vw	C_1 o.o.p. bending
		667 w		
	603 vw		596 m	cis C-C=C skeletal def. + C-O-C def. + CCO
444 w	440 vw	430 m	441 m	cis C-C=C skeletal def.
			338 m	skeletal def.
			234 vw	asym. methyl torsion

Note: (a) This band is twice the intensity of the C=C in either of the other isomers and three times the intensity of the other bands in this compound.

TABLE III (continued)

Note: (b) Abbreviations used: s, strong; m, medium; w, weak; sh, shoulder; v, very; IP, in-plane; o.o.p., out-of-plane; sym, symmetric; asym, asymmetric; def, deformation.

vinyl C-H stretch of the second conformer.

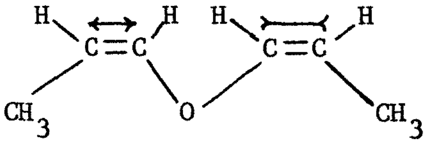
The remaining bands in the 3123-2643 cm^{-1} region for ccDPE are attributed to summation bands or overtones. These bands are relatively common in the infrared, but are rarely observed in the Raman.(41) The weak band at 2936 cm^{-1} is attributed to a combination of the exceptionally strong band at 1691 cm^{-1} plus the strong band at 1255 cm^{-1}. The other bands are very weak, as seen in Figure 28.

In vinyl ethers the C=C stretch is greatly intensified by the proximity to the oxygen atom.(39) Delocalization of the oxygen lone pairs into the double bond tends to decrease the vibrational frequency, while the field effect of the oxygen tends to increase the frequency. These two effects tend to cancel making the double-bond stretching frequencies of enol ethers similar to alkenes.(9) The C=C stretching frequency for <u>cis</u> $R_1CH=CHR_2$ bonds is predicted at 1660 cm^{-1}.(47) The carbon-oxygen bond in vinyl ethers is stiffened by resonance while the carbon-carbon double bond is weakened:

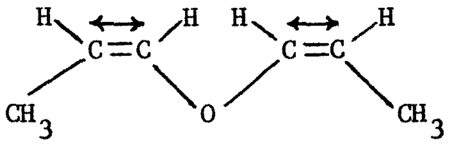
$$-CH=CH-O-CH= \rightleftharpoons -\overset{\ominus}{C}H-CH=\overset{\oplus}{O}-CH=$$

This tends to give a higher C=C stretching frequency and a lower C-O-C stretching frequency.(39) The two C=C stretches at 1691 & 1663 cm^{-1} average 1677 cm^{-1}, which represents a frequency increase, relative to the alkenes (47) or to divinyl ether(5). The 1138 cm^{-1} C_{2v} asymmetric C-O-C stretch is decreased compared to the average divinyl ether value of 1196 cm^{-1}.(5) Evidently the resonance structures make a larger contribution in ccDPE than in divinyl ether. The gauche C=C stretch is given as 1660-1635 cm^{-1} (39); a very weak Raman band at 1638 cm^{-1} and an infrared shoulder at 1630-1640 cm^{-1} are attributed to a non-planar conformer.

The strong infrared band at 1663 cm^{-1} and the exceptionally strong Raman band at 1691 cm^{-1} have previously been assigned to the coupled asymmetric and symmetric C=C stretches of the C_{2v} conformer of ccDPE:(10)



asymmetric



symmetric

Similar coupling has been reported for divinyl ether(10) and 1,4-pentadiene(5). The C_{2v} conformer of trans,trans-dipropenyl ether and the structurally similar C_s conformer of cis,trans-dipropenyl ether are also expected to have coupled C=C stretching vibrations. The carbon-13 NMR spectra indicate vibrational coupling for all three isomers.

The asymmetric C-O-C strech which is the strongest infrared band for vinyl ethers, appears around 1203 cm^{-1}.(39) Two bands in divinyl ether are reported at 1205 cm^{-1} (C_s) and 1186 cm^{-1}.(10) The bands in cis-dimethoxyethylene are reported at 1220 cm^{-1} and 1120 cm^{-1}, and the bands in trans-dimethoxyethylene at 1215 cm^{-1} and 1170 cm^{-1}.(3) The averages for these three compounds are 1196 cm^{-1}, 1170 cm^{-1}, and 1193 cm^{-1}. ccDPE has two infrared C-O-C asymmetric stretch bands at 1138 cm^{-1} and 1253 cm^{-1} giving an average value of 1196 cm^{-1}, identical to divinyl ether. The very strong band at 1138 cm^{-1}, the lower frequency, is assigned to the C_{2v} conformer; the frequency is lowered by resonance. This band is very weak in the Raman.

A strong Raman band at 1255 cm^{-1} is attributed to the vinyl C-H in-plane rock; this vibration generally gives a strong to medium intensity Raman vibration around 1295 cm^{-1}.(40) This band should be weak in the infrared and the strong C-O-C infrared band at the same wavelength should be very weak in the Raman. The only reasonable explanation for this band being strong in both spectra is accidental degeneracy of two vibrations. A similar degeneracy is reported for the C-O-C stretch and the CH_3-O rock at 1248 cm^{-1} in methyl acetate.(34) Two very strong, polarized Raman bands at 1299 cm^{-1} and 1323 cm^{-1} in divinyl ether are attributed either to two conformations or to coupling of the vinyl C-H wags.(5) Since only one strong band appears in ccDPE, the appearance of multiple bands in this region for divinyl ether, cis,trans-dipropenyl ether, and trans,trans-dipropenyl ether can be attributed to different conformations.

Additional bands expected in the 1700-1200 cm^{-1} region are the CH_3 asymmetric scissors at 1470-1435 cm^{-1} and the CH_3 symmetric scissors at 1385-1370 cm^{-1}.(39) In ethers, the methyl H-C-H symmetric deformation at 1480-1470 cm^{-1} appears superimposed on the high frequency side of the broad band due to the usual methyl deformation at 1460-1450 cm^{-1}.(40) The shoulder in the Raman at 1463 cm^{-1} is assigned to the H-C-H symmetric deformation. The broad Raman band at 1442 cm^{-1} is assigned as the asymmetric scissors and the bands at 1386 cm^{-1} and 1362 cm^{-1} to the symmetric scissors for the two conformations.

The characteristic cis vinyl C-H out-of-plane wagging vibration occurs at medium to strong intensity at 730-650 cm^{-1} in the infrared and is very weak in the Raman.(39) A medium intensity band at 718 cm^{-1} in ccDPE with a shoulder at 705 cm^{-1} in the vapor-phase separates into two distinct bands at 720 cm^{-1} and 690 cm^{-1} in the liquid-phase. The 720 cm^{-1} band is attributed to the C_{2v} conformer because of its relative size. The 690 cm^{-1} peak is attributed to a non-planar conformer. The gauche conformer of a number of carboxylic esters has been shown to be solvent stabilized due to the greater dipole moment.(29) The out-of-plane C-H deformations are usually strong enough for their overtone bands to be substantial.(51) The 1403 cm^{-1} infrared band could be an overtone of the 690-720 cm^{-1} band, but it is stronger than the lower frequency band in the Raman.

The other two characteristic ether bands are the C-O-C symmetric stretch and the C-O-C symmetric deformation. The symmetric C-O-C stretch appears as an intense Raman band at 930-830 cm^{-1} for n-alkyl ethers(40) or at 1075-1020 cm^{-1} in aryl and vinyl ethers.(27) For symmetrical di-ethers, this band is infrared-inactive.(44, 51) The 946 cm^{-1} band in ccDPE occurs at medium intensity and is infrared-inactive; this band is assigned to the C_{2v} C-O-C symmetric stretch. A very weak Raman band at 1028 cm^{-1} was chosen as the C-O-C symmetric stretch for the less stable conformer based on a correlation by Kimmel et. al.(3)

The C-O-C symmetric deformation appears at 500-400 cm^{-1} and mixes with the C-C-C and C-C-O skeletal deformations.(40) The skeletal bending modes are generally expected in the region below 650 cm^{-1}.(5) Cis alkenes generally give two strong bands at 588-571 cm^{-1} and at 488-465 cm^{-1}

for the C=C-C skeletal bending modes. The C-O-C bending vibration of dimethyl ether is found at 412 cm^{-1}. Bands at 250 and 241 cm^{-1} in dimethyl ether have been assigned to the asymmetric methyl torsion vibrational mode.(42) On this basis the 596 cm^{-1} band for ccDPE is assigned to the C=C-C skeletal deformation, the 441 cm^{-1} band to a combination of the C=C-C, C=C-O, and C-O-C skeletal deformations, and the 234 cm^{-1} band to the asymmetric methyl torsion. A 355 cm^{-1} band in divinyl ether is assigned as a combination or overtone band.(5) The 338 cm^{-1} band in ccDPE cannot be similarly assigned because of the absence of a band around 180 cm^{-1}; it must be another skeletal deformation.

B. Trans,Trans-Dipropenyl Ether

The infrared and Raman vibrational bands and the frequency assignments for trans,trans-dipropenyl ether (ttDPE) are given in Table IV. The infrared and Raman spectra are shown in Figures 22, 23, 24 and 30. The expected frequencies are the same as for cis,cis-dipropenyl ether (ccDPE) except for the trans $R_1CH=CHR_2$ stretch at 1675 cm^{-1} (47) and the trans vinyl C-H out-of-plane wag at 940-920 cm^{-1}.(9) In addition the skeletal deformations for trans alkenes appear as a medium to strong band at 455-379 cm^{-1} and sometimes an additional band at 667-455 cm^{-1}.(42) Additional bands appear in the Raman spectra of ttDPE; these bands may be attributed to an impurity as well as to additional conformers.

The vinyl C-H stretch in ttDPE is assigned to a medium intensity band at 3043 cm^{-1}. The asymmetric alkyl C-H stretch at 2933 cm^{-1} is increased in intensity in the Raman by the propenyl acetate impurity.

TABLE IV

Vibrational Frequencies and Assignments for Trans-Trans Dipropenyl Ether

Infrared (cm^{-1})			Raman (cm^{-1})	
Vapor (CsI)	Liquid (NaCl)	CCl_4 Solution	Liquid	Assignments
			3078 vw	
3058 w	3058 w		3048 (sh)	=C-H stretch
	3042 w	3033 w	3043 m	=C-H stretch
			3047 (sh)	
			3015 w	
		2960 m	2965 w	
2940 m	2948 m	2944 m	2942 (sh)	CH_3 asym. stretch
	2922 m	2922 m	2933 vs	CH_3 asym. stretch propenyl acetate
2902 w			2902 m	Fermi Resonance 2 x 1452
	2883 w	2890 w	2878 (sh)	CH_3 sym. stretch
2873 w	2859 w	2860 w	2871 m	CH_3 sym. stretch
			2760 w	
1763 vw	1762 m	1763 m		PA impurity
1742 vw	1742 w	1739 w		impurity
1717 vw				
		1690 vw	1698 s	C_{2v} C=C sym stretch
1690 vw				
	1673 (sh)	1674 sh		
1669 1662 m	1666 1660 s 1653	1668 1659 s	1677 s	C_s C=C stretch
			1657 m	C_{2v} C=C asym stretch
	1648 (sh)		1644 vw	
	1639 (sh)		1635 vw	
1460 vw	1454 w	1457 w	1452 w	CH_3 asym. scissors
	1439 w	1445 sh	1438 (sh)	PA impurity
1367 vw	1382 1369 w	1382 1369 w	1383 w	CH_3 sym. scissors
1339 w	1339 w	1338 w	1338 w	170 + 383 + 790 = 1351
	1307 vw		1313 w	
			1289 (sh)	PA impurity
1278 1271 m			1277 m	=C-H IP rock
	1268 m	1270 m	1264 w	=C-H IP rock
			1250 (sh)	cc or ct impurity
	1220 m	1222 m	1225 vw	PA impurity
1198 vs	1182 vs	1185 vs		C-O-C asym. stretch
1135 vw	1120 vw			cc impurity
			1117 vw	
1103	1103 1095 w	1103 w	1104 vw	
1039 w		1041 w	1049 vw	
1030 w	1033 w	1030 sh	1033 vw	

TABLE IV (continued)

Infrared (cm^{-1})			Raman (cm^{-1})	
Vapor (CsI)	Liquid (NaCl)	CCl_4 Solution	Liquid	Assignments
			996 vw	
923 m	920 m	927 m	924 vw	*trans* =C-H o.o.p. wag
			908 vw	C-O-C sym. stretch
793 w	783 vw	760 vw	790 w	
	725 vw	730		
	634 vw		636 vw	*trans* C=C-C def.
	611 vw		523 vw	
475 w	493 vw		495 vw	
			474 vw	C-O-C plus C=C-O def.
355 w			383 w	*trans* C-C=C def.
			329 vw	
~250 vw			286 vw	
			~178 w	skeletal def. C_5

Note: Abbreviations used; s, strong; m, medium; w, weak; sh, shoulder; v, very; IP, in-plane; o.o.p., out-of-plane; sym, symmetric; asym, asymmetric; def, deformation.

The symmetric C-H stretch is assigned as the 2871 cm^{-1} band. These three bands for the other conformer are located at 3048 cm^{-1}, 2942 cm^{-1}, and 2879 cm^{-1}. The intensity of the band at 2902 cm^{-1} is probably due to Fermi resonance with the overtone of the 1452 cm^{-1} asymmetric CH_3 scissors. In polar molecules interactions are commonly observed between the three fundamental C-H stretching modes previously discussed, and the overtones of the methyl deformation bands. The resulting series of bands between 2980 cm^{-1} and 2700 cm^{-1} vary in position and intensity depending on the position of the overtone absorption.(43)

The three Raman bands in the C=C stretch region of ttDPE are assigned to the coupled C_{2v} vibrations and to a C_s vibration. The symmetric C_{2v} C=C stretch appears as a strong Raman at 1698 cm^{-1} and a very weak infrared band at 1690 cm^{-1}. The asymmetric C_{2v} C=C stretch appears as the lower frequency part of a medium doublet at 1662 cm^{-1} in the infrared and as a medium Raman band at 1657 cm^{-1}. These bands average 1677 cm^{-1}, the same as the ccDPE C=C stretch bands. The third and strongest Raman band for ttDPE at 1677 cm^{-1} is assigned to the uncoupled C_s conformer. The two bands in divinyl ether which fall between the coupled C_{2v} vibrations are assigned to C_1 and C_s conformers;(5, 10) the C_s conformer for divinyl ether is the most stable. The sum of the intensities of the three Raman bands in ttDPE approximately equals the intensity of the dominant band in ccDPE.

The C-O-C asymmetric stretch in ttDPE appears as a very strong infrared band at 1198 cm^{-1}. This band has a broad triangular shape indicating the presence of more than one conformer. The C_s conformer for divinyl ether is reported to have a C-O-C asymmetric stretch of 1218 cm^{-1}, and the average of the two C-O-C bands for divinyl ether is 1198 cm^{-1}.(5) This band should appear as a weak band in the Raman; the only Raman band in this region is a very weak vibration at 1139 cm^{-1}, which may be caused by a ccDPE or ctDPE impurity. Since the asymmetric C-O-C stretch for ttDPE is similar to the C_{2v} C-O-C vibration for ccDPE, the symmetric vibrations should also be similar. The band in the Raman at 908 cm^{-1} is assigned to the symmetric C-O-C stretch for ttDPE.

A doublet at 1271 and 1278 cm^{-1} in the infrared and two bands at 1264 and 1277 cm^{-1} in the Raman are assigned to the vinyl C-H in-plane rock for the two different conformations of ttDPE. Note that the sum of the relative intensities of these bands is approximately equal to the intensity of the one Raman band in this region in the ccDPE spectra.

The bands for the CH_3 asymmetric and symmetric scissors in ttDPE are located at 1452 cm^{-1} and 1383 cm^{-1}. The characteristic trans vinyl C-H out-of-plane wagging vibration appears at 923 cm^{-1} in the infrared. The strongest band in the skeletal deformation region is the trans C-C=C band at 383 cm^{-1}. The second strongest band at 178 cm^{-1} is comparable to a band in divinyl ether at 180 cm^{-1} which is attributed to a C_s skeletal deformation.(5) The Raman band at 474 cm^{-1} can be assigned to the combination C-O-C plus C=C-O deformation. The other four bands in this region may be either additional deformation bands due to different conformations or impurity bands.

C. Cis,Trans-Dipropenol Ether

The infrared and Raman vibrational bands and frequency assignments are given in Table V for cis,trans-dipropenyl ether (ctDPE). The infrared and Raman spectra are shown in Figures 25, 26, 27, and 31. Since ctDPE is unsymmetrical, it is expected to have the largest number of vibrational frequencies or a maximum of forty-five bands plus additional bands for added conformations. The cis and trans vibrations given for the other two isomers are both expected to appear in this molecule. In the proton and carbon-13 NMR spectra both of these vibrations were observed.

The three bands assigned to the vinyl C-H stretch, the CH_3 asymmetric stretch, and the CH_3 symmetric stretch are located at 3055 cm^{-1}, 2926 cm^{-1}, and 2865 cm^{-1}. These bands are comparable to the bands observed in ccDPE. Shoulders appear on these bands at about half the intensities at 3041 cm^{-1}, 2936 cm^{-1}, and 2871 cm^{-1}. These vibrations are comparable to those observed for ttDPE. These pairs of bands are, therefore, attributable to the different environments existing in the cis and trans half of the ctDPE molecule.

Double-bonds in different environments in a molecule frequently show different C=C stretching and C-H deformation frequencies. Conjugation of double bonds is minimized when the axes of the double bonds are at right angles to each other.(58) The C=C stretching frequency of the pure vapor-phase IR sample of ctDPE appears as a doublet at 1666 cm^{-1} and 1661 cm^{-1}. The 1661 cm^{-1} band is due to the asymmetric C=C stretch for the coupled vibration of a C_s conformer which is structurally similar to the C_{2v} conformers of ccDEP and ttDPE. The

TABLE V

Vibrational Frequencies and Assignments for Cis-Trans Dipropenyl Ether

Infrared (cm^{-1})			Raman (cm^{-1})	
Vapor (CsI)	Liquid (NaCl)	CCl_4 Solution	Liquid	Assignment
			3099 vw	
		3061 w	3055 m	*cis* =C-H stretch
3043 w	3042 w	3044 w	3041 w	*trans* =C-H stretch
		3029 w	3023 w	
			3002 vw	
			2979 w	
2957 w	2962 (sh)	2958 w	2959 w	
		2942 w		
2933 w	2923 m	2922 w	2936 (sh)	PA impurity *trans* C-H asym. stretch
			2926 vs	*cis* C-H asym. stretch
2894 w	2886 w	2883 w	2896 m	
2871 w	2860 w	2861 w	2871 (sh)	*trans* C-H sym. stretch
			2865 m	*cis* C-H sym. stretch
			2749 vw	
	1769 m	1759 m	1758 vw	PA impurity
1685 vw			1694 s	C_s C=C sym stretch
1666 } s			1666 m	C_s stretch
1661 }	1659 vs	1659 s		C_s C=C asym stretch
			1643 vw	
1633 (sh) vw			1627 vw	
			1459 w	
1450 vw	1444 m		1448 (sh) }	CH_3 asym. scissors
1419 (sh)	1416 (sh)		1440 (sh) }	
1399 m	1395 m		1397 w	
1374 w		1360 (sh)	1382 w }	CH_3 sym. scissors
1356 (sh)	1359 w	1353 w	1360 vw }	
	1337 vw	1349 w	1330 vw	
1323 w	1320 w		1318 w	
1281 } w	1276 s	1278 m	1279 (sh) }	*trans* vinyl =C-H IP rock
1273 }		1268 (sh)	1253 (w) }	
1248 m	1246 s	1243 m	1249 w	*cis* vinyl =C-H IP rock
	1221 m	1222 m		PA impurity
1176 vs	1168 vs	1179 vs	1161 vw	C-O-C asym. stretch
1137 w	1133 s	1137 m	1131 vw	C-O-C asym. stretch
			1113 vw	
	1111 w		1110 vw	
1095 w			1098 vw	
	1042 w		1042 vw	PA impurity
			1031 vw	
993 w	996 w			
		983 w	985 vw	
	979 w			
923 w	930 w (sh)	933 (sh)	937 vw	*trans* =C-H o.o.p. wag

TABLE V (continued)

Infrared (cm^{-1})			Raman (cm^{-1})	
Vapor (CsI)	Liquid (NaCl)	CCl_4 Solution	Liquid	Assignment
	918 m	917 m		PA impurity
910 (sh)			913 vw	C-O-C sym. stretch
			904 w	C-O-C sym. stretch
795 vw	794 vw		788 vw	
710 vw	723 w	713 w	682 vw	*cis* =C-H o.o.p. wag
567 vw			637 vw	*cis* C-C=C skeletal def.
460 vw			467 vw	
			445 vw	*cis* C-C=C plus C-O-C + C-C-O skelatal def.
			424 vw	
370 vw			353 vw	*trans* C-C=C def.
			280 vw	
250 vw			230 vw	asym. methyl torsion

Note: Abbreviations used; s, strong; m, medium; w, weak; sh, shoulder; v, very; IP, in-plane; o.o.p., out-of-plane; sym, symmetric; asym, asymmetric; def, deformation.

strong Raman band at 1694 cm^{-1} and the very weak infrared band at 1685 cm^{-1} is assigned to the symmetric C=C stretch for the same conformer. The Raman band at 1666 cm^{-1} as seen in Figure 8 is noticeably skewed on both shoulders. The average for the C_{2v} asymmetric Raman band and the C_s Raman band in this region for ttDPE is 1667 cm^{-1}. The skewed band C=C stretch band in ctDPE may be accounted for by an unresolved combination of three bands, one due to the asymmetric C=C stretch of the linear coupled C_s conformer, and the other two due to different C=C stretching frequencies of the cis and trans in the C_s conformer which has the axes of the double-bonds at right angles to each other.

The carbonyl absorption for the propenyl acetate impurity is seen in the Raman spectra of ctDPE at 1758 cm^{-1}. The relative intensity of the C=C stretch to the C=O stretch in conjugated carbonyl compounds is five to one.(57) The propenyl acetate C=C stretch at 1675-1684 cm^{-1} (16) may be affecting the shape of the ctDPE skewed band in this region in the Raman spectra, but would not be nearly strong enough to account for it. (A single band in the gas-phase infrared spectra of impure ctDPE became a doublet when the sample was purified.)

The vinyl C-H in-plane rock appears as three bands in ctDPE. The band at 1248 cm^{-1} in the Raman is comparable to the vibration observed in ccDPE. The doublet at 1281 cm^{-1} and 1273 cm^{-1} in the infrared is not completely resolved in the Raman because of interfering bands from the impurity. These two bands are comparable to the two bands observed for ttDPE and indicate two different trans vibrations and, therefore, two different conformations involving the trans bonds. The sum of the

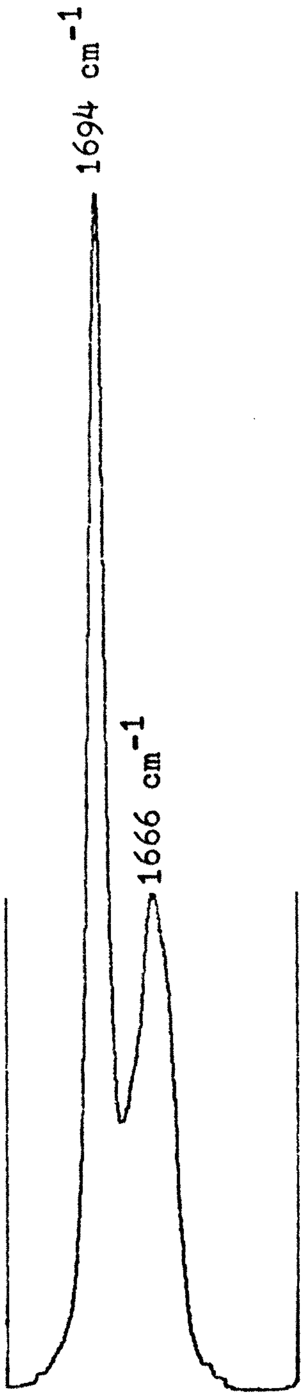


FIGURE 8

Raman C=C Stretching Region

for Cis,Trans-Dipropenyl Ether

intensities of the two trans vibrations approximately equals the intensity of the one cis vibration in the pure infrared sample.

The C-O-C asymmetric stretches are assigned to the bands at 1176 cm^{-1} and 1137 cm^{-1} in ctDPE. The C-O-C symmetric stretches are assigned to bands at 913 cm^{-1} and 904 cm^{-1}, again giving values comparable to those observed for both ccDPE and ttDPE.

The trans vinyl C-H out-of-plane wag in ctDPE is identified at 923 cm^{-1}, and the cis vinyl C-H out-of-plane wag at 710 cm^{-1}. In addition the cis and trans C-C=C skeletal deformations are assigned at 637 cm^{-1} and 353 cm^{-1} respectively.

VI. NUCLEAR MAGNETIC RESONANCE SPECTRA

A. Proton NMR Chemical Shifts

Rotational conformers are indicated for all three dipropenyl ether isomers in the Raman and infrared vibrational spectra. However, the nuclear magnetic resonance studies show only one set of coupled peaks for each of the three distinct types of protons in the cis, cis and trans, trans isomers, and a set of coupled peaks for each of the six types of protons in cis, trans-dipropenyl ether. In Raman and infrared spectroscopy, vibrational lifetimes as small as 10^{-11} to 10^{-13} seconds can be observed, while nuclear transitions of 10^{-2} to 10^{-5} seconds are observed in NMR spectroscopy.(44) The various vinyl ether conformers evidently have lifetimes falling between these two limits, because conformational isomers are only observed in vibrational spectroscopy.(1, 6)

Feeney, Ledwith, and Sutcliffe studied 2-ethylhexyl vinyl ether over a temperature range of +100°C to -100°C, finding no proton NMR evidence for rotational isomers. They postulate that -100°C is low enough to observe the barrier to interconversion; therefore, the two known conformers of 2-ethylhexyl vinyl ether must be shielded identically.(6) Owen and Sheppard studied the proton NMR for methyl vinyl ether at -100°C and also observed no spectral separation of the two known conformers. They calculate a maximum potential energy barrier of 10 kcal/mole at -100°C, but state that vinyl ethers have a resonance energy of only 3 kcal/mole due to the small degree of double-bond character of the C-O bond.(1) The appearance of conformational isomers is attributed to the partial double-bond character of the C-O bond as well as to steric hindrance of free rotation.(6, 7) Owen and Sheppard, therefore, postulate the rapid interconversion of vinyl ethers, even at -100°C.

The NMR spectra for the propenyl ethers were run at about 20°C thus eliminating any possibility of separate conformations. Two possibilities remain--equal population of all conformers due to very rapid rotation, or an unequal population of conformers at some intermediate rate of rotation.(7, 45) Tonnard, Odiot, and Martin were able to assign planar cis and trans, and nonplanar conformations for a number of vinyl ethers;(46) this indicates that the rate of interconversion for vinyl ethers is high enough to given an average proton signal corresponding to the average of the chemical shifts for the various conformations, but low enough to favor the chemical shift of the most stable conformation.

The proton NMR shifts and coupling constants for cis, cis-dipropenyl ether (ccDPE), cis, trans-dipropenyl ether (ctDPE), and trans, trans-dipropenyl ether (ttDPE) are given in Table VI. The chemical shift of the vinyl proton next to the oxygen, i.e., the α vinyl proton, for ccDPE (Figure 13) is 6.18 ppm. This signal is split into eight peaks by a coupling constant of 6.2 Hz for the adjacent vinyl proton and a long-range coupling constant of 1.7 Hz for the three methyl protons. The two center peaks overlap and the downfield peak appears as a shoulder giving a pattern of 1:3:3:2:3:3:1. The chemical shift for the α vinyl proton of ttDPE (Figure 14) is 6.16 ppm with J values of 12.7 Hz for the adjacent vinyl proton and 1.4 Hz for the terminal methyl protons. Two of the eight peaks appear as shoulders giving the expected pattern of 1:3:3:1:1:3:3:1. The α vinyl proton of ctDPE (Figure 15) has a cis chemical shift of 6.04 ppm

TABLE VI

Proton NMR Shifts (δTMS)

Compound	CH_3-CH=CH*-O-	CH_3-CH*=CH-O-	CH_3*-CH=CH-O-
Cis, Cis-Dipropenyl Ether	6.08 ppm, J = 6.2 Hz J = 1.7 Hz	4.45 ppm, J = 6.7 Hz J = 6.7 Hz	1.58 ppm, J = 6.8 Hz J = 1.5 Hz
Cis, Trans-Dipropenyl Ether	6.04 ppm, J = 6.4 Hz 6.19 ppm, J = 12.7 Hz (impurity = 6.99 ppm, J = 6.2 Hz)	4.45 ppm, J = 6.6 Hz J = 6.6 Hz 4.98 ppm, J = 6.5 Hz (13.0 Hz)	1.54 ppm, J = 5.8 Hz J = 1.8 Hz 1.49 ppm, J = 5.7 Hz J = 1.6 Hz (impurity = 1.98 ppm)
Trans, Trans-Dipropenyl Ether	6.16 ppm, J >12.3 Hz J > 1.4 Hz (impurity = 7.05 ppm, J = 12.3 Hz)	4.97 ppm, J = 6.5 Hz (13.0 Hz)	1.51 ppm, J = 6.6 Hz J = 1.4 Hz (impurity = 1.96 ppm)
Cis-Propenyl Acetate(24)	7.02 ppm, J = 7&2 Hz	4.71 ppm, J = 7&7 Hz	1.56 ppm, J = 7&2 Hz (acetate = 1.72 ppm)
Trans-Propenyl Acetate(24)	7.06 ppm, J = 12.5 Hz J = 2 Hz	5.30 ppm, J = 12.5 Hz J = 7 Hz	1.38 ppm, J = 7&2 Hz (acetate = 1.69 ppm)
Cis, 1-Ethoxy Propene(46)	5.83 ppm	4.26 ppm	
Trans, 1-Ethoxy Propene(46)	6.10 ppm	4.61 ppm	
Cis, 1-Ethoxy Butene(24)	5.70 ppm, J = 6&1 Hz	4.31 ppm, J = 6&6 Hz	
Trans, 1-Ethoxy Butene(24)	6.15 ppm, J = 12 Hz	4.69 ppm, J = 12&7 Hz	

with J = 6.4 Hz and a trans chemical shift of 6.19 ppm with J = 12.7 Hz. The center peaks overlap giving a 1:2:1 pattern. The long-range methyl coupling is not resolved but is indicated by peak broadening.

The chemical shift for the vinyl proton next to the methyl group, i.e., the β vinyl proton for ccDPE is 4.45 ppm with J = 6.7 Hz for the four adjacent protons giving five peaks with relative intensities of 1:4:6:4:1. The corresponding chemical shift for ttDPE is complicated by unequal coupling constants of 6.5 Hz for the adjacent vinyl proton and approximately 13 Hz for the adjacent methyl protons. If the J values are in a two to one ratio, the total number of peaks will be greater than the equally coupled case (5 peaks) but less than the unequally coupled case (8 peaks).(7) Six peaks are observed centered at 4.97 ppm for the β vinyl protons of ttDPE. The β vinyl protons of ctDPE have a cis chemical shift of 4.45 ppm with J = 6.6 Hz and a trans chemical shift of 4.98 ppm with J = 6.5 and 13 Hz. The five cis peaks and the six trans peaks overlap in the center, as seen by the increased intensity of the central peak, to give a total of ten peaks.

A non first order spectra appears for the vinyl protons of ttDPE (Figure 14) with the interior peaks of the two chemical shifts enlarged due to the shift difference being less than six times the coupling constant. This leads to the observation of decreased J values(47) as indicated in Table VI.

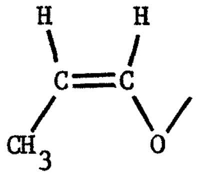
The methyl protons of ccDPE have a chemical shift of 1.58 ppm with J = 6.8 Hz for the adjacent β vinyl proton and J = 1.5 Hz for the α vinyl proton, yielding the expected four peaks. The shift for the ttDPE methyl protons is 1.51 ppm with J values of 6.6 Hz and 1.4 Hz giving four peaks. Downfield shoulders on the ttDPE methyl peak indicate a cis impurity, either cis-propenyl acetate or ctDPE or both. The eight peaks for the methyl ctDPE shift are not completely resolved so the precision is less for both the α vinyl coupling constant (± 1.7 Hz) and the chemical shift (± 0.03 ppm). A cis shift of 1.54 ppm with J's of 5.8 Hz and 1.8 Hz, and a trans shift of 1.49 ppm with J's of 5.7 Hz and 1.6 Hz are observed for the methyl protons of ctDPE.

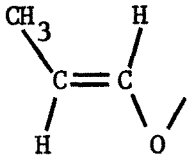
The spin-spin coupling constant for a freely rotating methyl group showing an average dihedral angle of 0° can be estimated from a modified Karplus curve to be 6.7 Hz for the adjacent vinyl proton and 1.4 Hz for the other vinyl proton.(48) The observed values of 6.5 - 6.8 Hz for the ccDPE and ttDPE adjacent vinyl coupling constants agree well with the predicted values. The trans coupling constant for the other vinyl proton is generally larger than the cis coupling constant, but Jackman and Wiley found equal coupling constants for a series of cis and trans 2-substituted propenes.(47) The observed long-range coupling constants of 1.4 - 1.8 Hz correspond to the predicted value of 1.4 Hz within the experimental error of ± 0.3 Hz. At room temperature, the rate of rotation of a methyl group around its three-fold symmetry axis is generally fast enough to equalize the environments of the three protons.(49) The NMR data indicate freely rotating methyl groups for the dipropenyl ethers.

The values for the proton spin-spin coupling constants across double bonds vary over a wide range, but generally Jtrans/Jcis equals two.(45) House and Kramer found J*trans* of 12 - 12.5 Hz and J*cis* of 6 - 7 Hz for a number of enol acetates and enol ethers.(24) These values compare favorably with J*trans* of 12.3 - 13.0 Hz and J*cis* of 5.7 - 6.8 Hz found for the dipropenyl ethers.

The chemical shifts for the α vinyl protons of ccDPE, ctDPE, and ttDPE are comparable to the observed shifts for the corresponding alkyl vinyl ethers listed in Table VI.(24, 46) Feeney, Ledwith, and Sutcliffe found that the β vinyl protons in a number of alkyl vinyl ethers were shifted 0.33 - 0.50 ppm upfield from the corresponding alkenes, because resonance decreased the double-bond character of the vinyl bond in the alkyl vinyl ethers.(46) The chemical shifts for the β vinyl protons of ccDPE, ctDPE, and ttDPE, however, are 0.19 - 0.37 ppm downfield from the corresponding alkyl vinyl ethers in Table VI. The dipropenyl ethers evidently have less resonance and more double-bond character for the vinyl bond than the alkyl vinyl ethers.

Examination of the configurations of the *cis* and *trans* propenyl ether bonds shows that the β vinyl protons should be shifted downfield for the *trans* configuration while the methyl protons should be shifted downfield for the *cis* configuration due to their proximity to the oxygen atom.


cis


trans

The observed shift difference for the β vinyl protons of the *trans* configuration is 0.52 ppm downfield compared to the *cis* β vinyl protons.

The shift difference for the methyl protons is 0.05 - 0.07 ppm downfield for the cis configuration compared to the trans methyl protons. The differential shielding of the cis and trans methyl protons for 2-butene is 0.00 ppm,(45) so the observed downfield shifts of the cis propenyl methyl protons must be due to the presence of the oxygen atom.

The major impurity in both ctDPE and ttDPE is identified as cis- and/or trans-propenyl acetate. The peaks observed at 7 ppm match the expected chemical shifts for the vinyl proton next to the oxygen in propenyl acetate. These peaks are missing in ccDPE and the different J values indicate cis-propenyl acetate to be the major impurity in ctDPE and trans-propenyl acetate to be the major impurity in ttDPE. The intensity of the 7 ppm peaks is comparable to that of spinning side bands so their significance is questionable.

The expected peaks in ctDPE and ttDPE due to the other vinyl protons in propenyl acetate are obscured by the propenyl ether shifts. The integrations for both the cis,trans and trans,trans isomers are slightly improved if corrections are made to these peaks and to the methyl peaks for the propenyl protons of the assumed impurity. The shifts for the acetate methyl protons are expected as a singlet at 1.69 and 1.72 ppm(24) (Table VI), but appear at 1.96 - 1.98 ppm. Solvent shifts of +0.23 - 0.31 ppm are common for the methyl protons of acetates.(50) The shifts due to the methyl carbon and the carbonyl carbon in propenyl acetate are completely overpowered by the acetone solvent shifts in the carbon-13 NMR spectra; therefore no impurity peaks appear in Figures 13, 14, and 15. This can be taken as further evidence for identification of the impurity as propenyl acetate.

Trace amounts of an unidentified aldehyde are also present in ttDPE as evidenced by tiny peaks at 2.26 ppm and 9.55 ppm. This impurity was probably introduced in the final crude distillation. These bands correspond to a RCHO proton shift of 9.6 ppm and a RCH_2*-CHO proton shift of 2.2 ppm.(51) Another trace impurity appears at 3.25 ppm. The relative intensity of these peaks in the NMR spectra is not comparable to the relative intensity of the infrared bands in the 1700 cm^{-1} region previously attributed to propenyl acetate.

B. Carbon-13 Chemical Shifts

The carbon-13 spectra in Figures 16, 17, and 18 show three distinct shifts for the three types of carbon atom in dipropenyl ether. As discussed in the proton NMR analysis, peaks due to different conformers are not evidenced because the lifetime of a particular conformation at room temperature is very small compared to the nuclear transitional lifetimes.(44) There are three peaks in the *cis,cis*-dipropenyl ether (ccDPE) spectra and three peaks in the *trans-trans* dipropenyl ether (ttDPE) spectra, one peak for each set of two equivalent nuclei. The spectra for *cis,trans*-dipropenyl ether (ctDPE) contains three doublets, each correlatable to a *cis* and *trans* shift for a particular type of carbon atom.

Two hundred scans were run on ccDPE at a repetition time of 3.50 seconds. The three peak heights are markedly different due to the nuclear Overhauser effect. If the repetition time is less than the spin-lattice relaxation time, the C^{13} nuclei will stay at a higher energy level and give a decoupled peak which is a maximum of 2.988

times the intensity of the undecoupled peak. If the repetition time is greater than the spin-lattice relaxation time, the C^{13} nucleus with the most protons, directly attached or adjacent, will be relaxed the most.(52)

The methyl carbon is relaxed by three directly attached protons and one adjacent proton and is therefore by far the smallest peak in the ccDPE spectra. The vinyl carbon next to the oxygen is relaxed by one directly attached proton and only one adjacent proton and, therefore, has a slightly larger peak than the vinyl carbon next to the methyl group, which has one directly attached proton plus three adjacent protons. The ctDPE and ttDPE samples were run at a repetition time of 2.00 seconds for five thousand and six thousand scans respectively. Evidently the scan time was small enough to prevent complete relaxation because the methyl carbon peak is only fractionally smaller than the other peaks.

Dorman, Jautelat, and Roberts developed a correlation for the carbon-13 shifts in substituted alkenes based on least-squares solutions of the observed shifts for fifty-two unsaturated hydrocarbons. The correlations fit well except for compounds with heteroatoms or coupled bonds. The coupling effects were examined in ten dienes.(53) Maciel examined the chemical shifts of twenty different substituents on monosubstituted alkenes, including the methoxy group.(54) These two correlations were combined to predict C^{13} shifts for the propenyl ether _cis_ and _trans_ groups in Table VII. The shift parameters and appropriate calculations are given in Appendix I. The observed C^{13} shifts for ccDPE, ctDPE, and ttDPE are also given in Table VII.

TABLE VII

Carbon-13 NMR Shifts (δTMS)

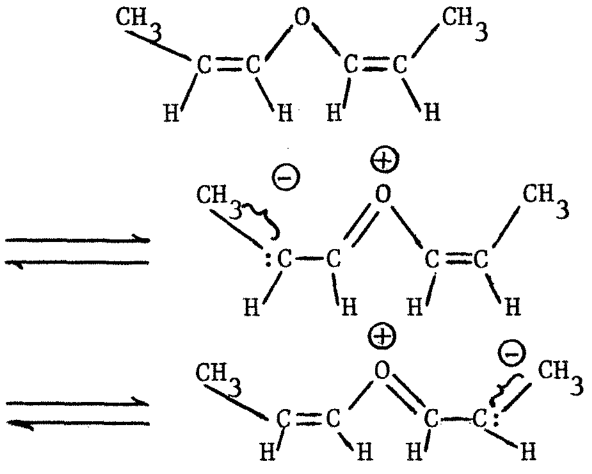
ATOM	CIS		TRANS	
Predicted Values (Appendix I)				
$C=\overset{*}{C}-O$	142.9	Δ = 45.3	144.0	Δ = 45.3
$C-\overset{*}{C}=C$	97.6		98.7	
$\overset{*}{C}-C=C$	12.2		17.5	
Cis, Cis-Dipropenyl Ether				
$C=\overset{*}{C}-O$	144.5	Δ = 41.7		
$C-\overset{*}{C}=C$	102.8			
$\overset{*}{C}-C=C$	9.4			
Cis,Trans-Dipropenyl Ether				
$C=\overset{*}{C}-O$	143.4	Δ = 40.4	145.8	Δ = 42.4
$C-\overset{*}{C}=C$	103.0		103.6	
$\overset{*}{C}-C=C$	8.9		12.2	
Trans,Trans-Dipropenyl Ether				
$C=\overset{*}{C}-O$			144.8	Δ = 40.8
$C-\overset{*}{C}=C$			104.0	
$\overset{*}{C}-C=C$			12.2	

The predicted values of 142.9 ppm (cis) and 144.0 ppm (trans) for the vinyl carbon next to the oxygen proved the efficacy of the calculation procedure, coming within 1.3% of the observed values. All of the observed values are slightly higher than predicted--the downfield shift indicating slightly greater deshielding than expected. The ccDPE shift is 144.5 ppm, the ttDPE shift is 144.8 ppm, and the two ctDPE shifts are 143.4 ppm and 145.8 ppm respectively. The cis bonds have a shift relative to the trans bonds of -0.3 ppm and -2.4 ppm versus the literature value of -1.11± 0.06 ppm.(53)

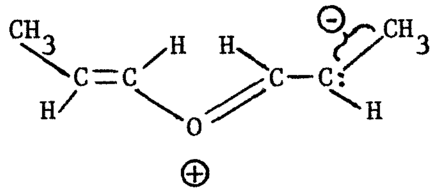
Dorman et. al. found that conjugation of double bonds in dienes had a "leveling effect" which tended to bring the chemical shifts of the two vinyl carbons closer together than predicted by their correlations.(53) The downfield shift relative to the predicted values for the vinyl carbon next to the methyl group in all three isomers can therefore be explained by coupling. 97.6 ppm is predicted for the cis bond and 98.7 ppm for the trans bond. The observed ccDPE shift is 102.8 ppm, the ttDPE shift is 104.8 ppm, and the ctDPE shifts are 103.0 ppm and 103.6 ppm respectively. The predicted shift difference between the two vinyl carbons is 45.3 ppm; the observed differences range from 40.4 ppm to 42.4 ppm. The observed shift difference was lowered 24% (6.6/27.2) by vibrational coupling in 1,3-butadiene, 13% (3.2/24.6) in 1,4-pentadiene, and 6% (1.4/24.6) in 1,5-hexadiene.(53) The observed shift differences are 8% lower than predicted in ccDPE, 10% lower in ttDPE, and 6-11% lower in ctDPE. If the general shift parameters are used in the calculations (Appendix II) instead of the α and α' for propene, the predicted delta is 47.1 ppm and the deltas for the propenyl ether isomers are 10-14% lower than predicted. This is indicative of vibrational coupling similar to 1,4-pentadiene.

The two vinyl carbons are shifted downfield from the predicted values while the methyl carbon is shifted upfield. The methyl shifts of 9.4 ppm for ccDPE, 12.2 ppm for ttDPE, and 8.9 ppm and 12.2 ppm for ctDPE are significantly lower than the shifts normally observed for either saturated or unsaturated hydrocarbons.(53) Shielding is attributable to a paramagnetic effect, a diamagnetic effect, and a steric contribution. The major factor in carbon-13 shifts is the diamagnetic term which is associated with electron-withdrawing factors such as charge polarization and variation in bond order.(55) In unsaturated molecules, atoms can withdraw or donate electron density over several bonds.(52) The C^{13} chemical shifts of all three dipropenyl ether isomers imply increased electron density for the methyl groups.

Resonance stabilization similar to that given for the alkyl vinyl ethers(6) can be hypothesized to account for the increases C^{13} shielding of the methyl carbons in ccDPE:



Similar resonance structures can be written for ctDPE and ttDPE. The methyl carbons are shifted upfield relative to the predicted values by 23% in ccDPE, 27% to 30% in ctDPE, and 30% in ttDPE. The greater resonance in the ttDPE molecule may be explained by comparing the structure of ttDPE to ccDPE:



Evidently the proximity of the oxygen atom to the methyl group in ccDPE limits the resonance; this may be attributed to nonbonded repulsion of electrons away from the methyl group by the oxygen atom. The decreased resonance for ccDPE indicates greater double-bond strength for the <u>cis</u> propenyl group. The resonance is greater for the <u>cis</u> propenyl group in ctDPE than in ccDPE. The largest resonance effect occurs in the <u>trans</u> propenyl group, which has the same chemical shift in both ctDPE and ttDPE.

Disubstituted alkenes with electronegative groups such as 1,2-dichloroethylene, 1,2-difluoroethylene, and 1,2-dimethoxyethylene are more stable in a <u>cis</u> configuration.(17, 26) Pitzer and Hollenberg have postulated that charge polarization similar to that shown for the resonance structures of the dipropenyl ethers dictates a stable <u>cis</u> configuration.(63) Waldron and Snyder state that the postulated resonance arguments are not sufficient to explain the greater stability of the gauche conformation relative to the <u>trans</u> conformation of 1,2-difluoroethane and 1,2-dimethoxyethane. They postulate that the adjacency of the two electronegative groups in the <u>cis</u> configuration of 1,2-dimethoxyethylene and in the gauche conformation of 1,2-dimethoxyethane pushes electron density into the central carbon-carbon bond in each case and strengthens that bond.(26)

The carbon-13 NMR chemical shifts indicate that the same argument holds for the cis propenyl groups in ctDPE and ttDPE. Snyder reports that cis-propenyl n-hexyl ether, cis-propenyl phenyl ether, and cis-propenyl t-butyl ether are more stable than the corresponding trans isomers.(8) Fueno, Furukawa, and Okuyama report that cis-propenyl ethyl ether, cis-propenyl isopropyl ether, cis-propenyl isobutyl ether, cis-propenyl t-butyl ether, and trans-propenyl methyl ether are more stable than the corresponding trans or cis isomers.(61) The equilibrium mixture for the dipropenyl ethers at 80°C contains 41.9% ccDPE, 45.9% ctDPE, and 12.2% ttDPE.(12) The ratio of the cis to trans bonds in this mixture is 1.8 to 1. The arguments stated above explain the greater stability of the cis bonds in dipropenyl ether, but do not explain the higher percentage of the cis,trans isomer in the dipropenyl ether equilibrium mixture.

VII. CONFORMATIONS OF THE DIPROPENYL ETHER ISOMERS

A. Cis,Cis-Dipropenyl Ether

The exceptionally strong Raman band at 1691 cm^{-1} and the very weak Raman band at 1654 cm^{-1}, which appears as a strong infrared band, are the coupled symmetric and asymmetric C=C stretches for the C_{2v} isomer of *cis,cis*-dipropenyl ether (ccDPE).(10) Four to eight infrared inactive bands from the A_2 symmetry series should be observed for a C_{2v} conformation of ccDPE. Some breakdown of the basic symmetry rules takes place in complex molecules, i.e., complex compared to carbon dioxide.(57) Coriolis forces are related to the coupling between rotational and vibrational modes of a molecule. When allowed and forbidden vibrations have similar frequencies, Coriolis interactions can excite the normally inactive infrared vibrations. For the C_{2v} conformation, the vibrational species which may interact are (a_1e), (a_2e), (a_1a_2) and (ee). When the forbidden A_2 bands appear, they are generally very weak.(58) In the case of ccDPE and ttDPE, it is also possible for an infrared band to appear at a forbidden C_{2v} vibrational frequency due to the presence of another conformation. The only band which is positively identified as belonging to the A_2 symmetry series of the C_{2v} conformation of ccDPE is the medium intensity Raman band corresponding to the C-O-C symmetric stretch at 946 cm^{-1}.(44, 51) This band is infrared-inactive. More conclusive evidence for the C_{2v} conformation is obtained from the observation of the strong coupling of the C=C stretches as evidenced in both the vibrational and the carbon-13 NMR spectra. The only conformation consistent with the observed coupling is the C_{2v} conformation.

A weak to medium shoulder in the C=C stretch region at 1630 cm^{-1} to 1640 cm^{-1} in the vapor-phase and liquid-phase infrared spectra is attributed to a second conformer of ccDPE. This conformer is either of C_1 or C_2 symmetry (see Figure 7). Evidence favors the non-symmetrical (C_1) conformation, but the C_2 conformer cannot be completely ruled-out. The more polar gauche conformer is favored in the liquid-phase.(29) The shoulder is more prevalent in the liquid-phase and a shoulder on the cis vinyl C-H out-of-plane wagging mode at 705 cm^{-1} in the vapor-phase splits into a distinct band in the liquid-phase at 690 cm^{-1}. The C_2 conformer is not consistent with either sp^2 or sp^3 hybridization of the central oxygen atom. Electron diffraction measurements of the rotational angle would be necessary to support a C_2 conformation. The 1640 cm^{-1} vibrational band is not evidenced in trans,trans-dipropenyl ether (ttDPE), and there is no feasible explanation for the appearance of a C_2 conformation for ccDPE and not for ttDPE. The second conformation of ccDPE is definitely non-planar and is probably of C_1 symmetry.

The Raman spectra taken at room temperature (about 20°C) show the band at 1638 cm^{-1} as a very weak vibration. For molecules of low symmetry, the intensity of the Raman and infrared bands should be similar.(44) The matching band in the infrared spectra is stronger, but this is probably due to a temperature effect. The less stable conformer should be a more stable at higher temperatures. Evaporation was a problem in determining the infrared spectra, indicating heat. The gas cell was noticeably warm to the touch (about 40°C) after making several repeat IR spectral determinations. As shown in Figure 9, the intensity of the shoulder increased with time and presumably with temperature in repeat runs.

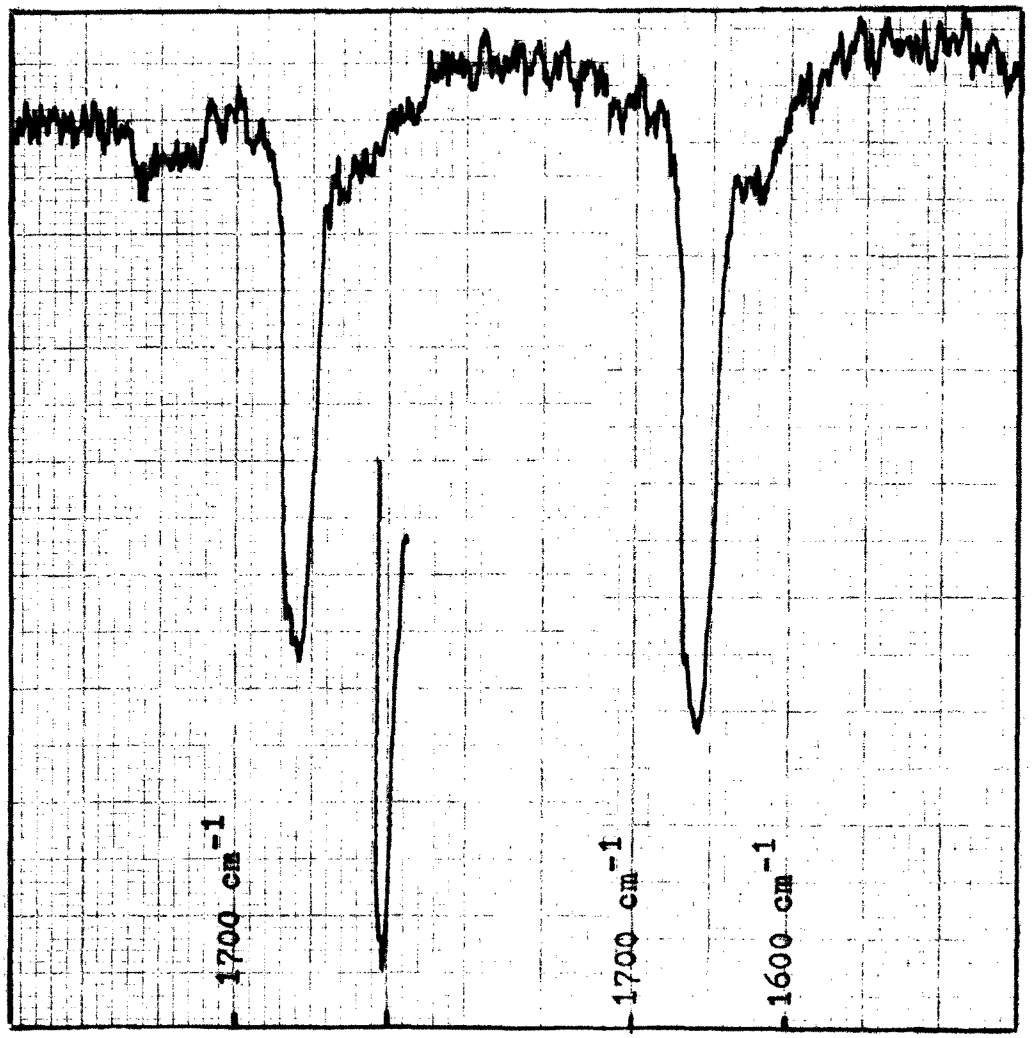


FIGURE 9

Infrared C=C Stretching Region

for Cis,Cis-Dipropenyl Ether

Supporting bands can be assigned for the two conformations of ccDPE in other regions, but in most cases the band for the C_{2v} conformer is dominant while the band for the non-planar conformer is almost insignificant. The C-O-C asymmetric stretch bands in the 1200 cm^{-1} region provide additional evidence for the two conformations. The very strong band at 1138 cm^{-1} in the infrared appears as a very weak band at 1133 cm^{-1} in the Raman spectra. The low frequency of this band is consistent with the expected resonance in the C_{2v} planar structure. The second strong band at 1253 cm^{-1} in the infrared also appears as a strong band at 1255 cm^{-1} in the Raman spectra where the C-O-C vibration should be weak. This is the only strong band below 1600 cm^{-1} in the Raman and must be assigned to the vinyl C-H in-plane rock, but this band should be weaker than the <u>cis</u> vinyl C-H out-of-plane vibration in the infrared. These two vibrations are apparently accidentally degenerate. The relatively high frequency of the 1253 cm^{-1} C-O-C asymmetric vibration is consistent with a non-planar structure exhibiting little resonance. The relatively low frequency of the 1638 cm^{-1} C=C stretch of the second conformer is also consistent with a non-resonance, non-planar structure.

B. Trans,Trans-Dipropenyl Ether

The presence of three Raman bands in the C=C stretching region for <u>trans,trans</u>-dipropenyl ether (ttDPE) indicates the presence of at least two conformers. The Raman samples contained an impurity, but the C=C stretch band for the impurity should be much weaker than the observed bands. The C=C infrared band of the pure ttDPE vapor-phase gas sample appears as a doublet indicating two conformations. The

C-O-C asymmetric stretch at 1198 cm^{-1} and the trans vinyl C-H out-of-plane wag at 924 cm^{-1} appear as broad triangular shaped bands also indicating the presence of more than one conformation. The vinyl C-H in-plane rock which appears as a single strong band in ccDPE appears as a doublet in both the pure infrared and the Raman spectra of ttDPE. The relative intensities of two peaks of this doublet in the Raman are comparable to the relative intensities of the two stronger peaks in the 1600 region.

Resonance is indicated for ttDPE by the carbon-13 NMR spectra. This resonance is consistent with sp^2 hybridization of either a C_s or a C_{2v} conformation for ttDPE. The strongest Raman C=C stretch band appears at 1677 cm^{-1}. No comparable band exists in the ccDPE spectra and the C_s conformation is the only symmetrical species which is possible for ttDPE but not for ccDPE. The C_s conformation would be expected to be the most stable for ttDPE based on studies of divinyl ether and other similar compounds.(5, 37) The vibrational frequency of this band is equal to the average of the two coupled frequencies for ccDPE and to the average for the other two C=C stretch bands in ttDPE. The planar C_s structure should have resonance structures and frequencies comparable to the planar C_{2v} conformers, due to sp^2 hybridization and the resultant partial double bond structure of the central oxygen bond.

Vibrational coupling of the two double-bonds is indicated for ttDPE by both the carbon-13 NMR spectra and the vibrational spectra. A C_{2v} conformation for ttDPE is consistent with the observed coupling. The relative intensity of the Raman bands indicates that the C_{2v} conformer is only slightly less stable than the C_s conformer. The strong

Raman band at 1698 cm^{-1} is assigned to the symmetric C=C stretch and the medium intensity infrared band at 1662 cm^{-1} is assigned to the asymmetric C=C stretch. Additional supporting bands for the second conformer appear in the C-H stretch region.

C. Cis,Trans-Dipropenyl Ether

The carbon-13 and proton NMR for cis,trans-dipropenyl ether (ctDPE) show that the chemical shifts for the cis and trans propenyl groups are comparable to the shifts observed for cis,cis-dipropenyl ether (ccDPE) and trans,trans-dipropenyl ther (ttDPE). The vibrational spectra show comparable sets of cis and trans frequencies. The conformations should also be similar. The vinyl C-H in-plane rock for ccDPE appears as one band at 1255 cm^{-1}. The vinyl C-H in-plane rock for ttDPE appears as two bands at 1278 cm^{-1} and 1271 cm^{-1}. All three of these bands appear in the ctDPE spectra falling at 1281 cm^{-1}, 1273 cm^{-1}, and 1248 cm^{-1}. Examination of the two C_s conformers for ctDPE in Figure 7 shows that the cis propenyl group is in the same position relative to the oxygen in both conformations. The trans propenyl group, however, is in a different position in the two planar conformations. These two structures are therefore compatible with the observation of one cis vibration and two weaker trans vibrations for the vinyl C-H in-plane rock.

The strong doublet in the infrared C=C stretch region at 1666 cm^{-1} and 1661 cm^{-1} provides additional evidence for two conformers of ctDPE. The 1661 cm^{-1} band is assigned to the asymmetric C=C stretch in the linear coupled C_s conformer. The coupled C=C symmetric stretch appears as a strong Raman band at 1694 cm^{-1} and a very weak infrared band at 1685 cm^{-1}. The 1694 cm^{-1} band is the strongest one in the 1600 region indicating that the linear coupled C_s conformer is the most stable form of ctDPE. The 1666 cm^{-1} bond is close to the frequency of the infrared bond assigned to the C_s conformer of ttDPE and is assigned as the bent C_s conformer of ctDPE. In this conformation the axes of the double-bonds are at right angles to each other, so the bonds may have different vibrational frequencies. The skewed Raman band at 1666 cm^{-1} is equal to the average value of the two bands in ttDPE from the C_s and the asymmetric C=C stretch vibrations. The 1666 cm^{-1} band is interpreted as an unresolved combination of the two nondegenerate C=C stretch vibrations from the bent C_s conformer of ctDPE and the asymmetric C=C stretch from the linear C_s conformer. The other bands in the ctDPE spectra confirm the different vibrations for the cis and trans portions of the molecule but give no additional evidence of multiple conformations.

VIII. EXPERIMENTAL

A. Potassium t-Butoxide Rearrangement of Diallyl Ether

Potassium t-butoxide was previously prepared in dimethoxyethane solution by reaction of di-t-butyl peroxide with potassium metal.(14) Potassium t-butoxide was recovered from solution using a rotovap at 25 mm Hg. An amount equivalent to 114.80 g (1.023 moles) was recovered and redissolved in 400 ml of diglyme yielding a 2.56 M solution. This solution was used to isomerize 627.9 g of diallyl ether (15 wt% catalyst to ether ratio) in four different batches. Complete rearrangement was obtained using an 80°C constant temperature bath for twenty-four hours. A 12 wt% catalyst ratio was tried but this percentage gave incomplete rearrangement due to limiting catalyst decomposition.

The *cis,cis*-dipropenyl ether was separated from the diglyme mixture by vacuum distillation using a 13-1/2 in. by 3/4 in. fractionating column filled with 1/4 in. glass helices. A Flexopause automatic reflux controller was used to set the reflux ratio, and a Thermowatch controller was attached to the overhead thermometer to prevent temperature overshoot. A Manowatch vacuum pressure regulator was used to hold the pressure constant at 74-75 mm Hg, 95-97 mm Hg, 77 mm Hg, and 83.5 mm Hg for the four runs; the corresponding boiling points for the four runs are 30-32°C, 36-38°C, 31.5°C, and 34°C. The head temperature went immediately to the boiling point of *cis,cis*-dipropenyl ether and stayed at this temperature, within the precision of the pressure regulator, until this cut was finished. As the pot temperature neared the boiling point of diglyme, the head thermometer went dry and the distillation was stopped before the next fraction could move up the column. A total of 482.2 g of cis,cis-dipropenyl ether were recovered giving a 77% composite recovery, which is comparable to previous work.(8)

A 23.53 g sample of cis,cis-dipropenyl ether was purified by distillation on a Nester/Faust spinning band column of two hundred theoretical plates. The t-butanol impurity was removed as an azeotrope at 80°C. The Nester/Faust Reflux Controller was used to read and control the head pot, and three column temperatures. A Leeds and Northrup 8691-2 millivolt potentiometer was calibrated with ice water and boiling water and used in conjunction with the Nester/Faust thermocouples and a barometer to obtain accurate boiling points. 6.08 g of 99.9% pure cis,cis-dipropenyl ether, containing a trace light impurity, as shown in Figure 10, were collected at a 100:1 reflux ratio. The boiling point at 756.4 mm Hg was found to be 91.6 ± 0.3°C. The bottoms from the distillation run were analyzed by GC peak area and found to contain 79.3% cis,cis-, 19.1% cis,trans-, and 0.8% trans,trans-dipropenyl ether plus 0.8% of the light impurity. This proves that the base-catalyzed rearrangement of the diallyl ether was complete, and that the shoulder on the cis,cis peak was due to small amounts of the other isomers. The remaining ether was a faint yellow color, as was acetone in an earlier test run.

A 99.45 g sample of cis,cis-dipropenyl ether was purified on a spinning band column in order to obtain a t-butanol free sample for isomerization. The first few milliliters of distillate formed a two-phase mixture, possibly due to methanol from the potassium t-butoxide decomposition reactions. A total 21.21 g azeotropic cut containing 41.7%

t-butanol and 58.3% dipropenyl ether was collected at 80°C. Mass balance gives 4.4% original t-butanol concentration which agrees with the 4.6% average for the four runs. GC samples were taken every fifteen minutes during the 7.50 hour run in order to monitor distillate composition. The distillation was stopped when the first pure ether sample was collected; the 75.59 g of ether remaining in the pot analyzed pure on the GC, but had a faint yellow color.

B. Mercuric Acetate Isomerization of Cis,Cis-Dipropenyl Ether

Mercuric acetate catalyzed isomerization was used to prepare the cis,trans and trans,trans isomers. A 50.31 g sample of the purified cis,cis-dipropenyl ether were isomerized with 9.83 g of mercuric acetate. The reaction mixture was placed in an 80°C constant temperature bath for thirty-nine hours. A dull metallic oblate spheroid, identified as impure free mercury, formed in the bottom of the reaction flask. Only a small amount of granular solids assumed to be mercuric or mercurous acetate remained in the flask. The reaction mixture was filtered into a flask in an ice bath to remove the solids and quench the reaction. A colorless, viscous substance coated the reaction flask; this substance was insoluble in both water and acetone and had to be removed with hydrofluoric acid. The reaction mixture was evaporated through a condenser into a cold trap in an ice bath and a cold trap at -42°C, under full vacuum, to remove any remaining dissolved solids. Wet solids plus a few drops of a yellow sweet-smelling substance remained in the distillation flask. 41.22 g of 45.7% cis,cis-, 43.6% cis,trans-, and 10.7% trans,trans-dipropenyl ether were collected giving an 87% recovery. Evaporation of the larger volume in this run probably allowed time for some reverse isomerization, explaining the lower cis,trans and trans,trans-dipropenyl ether percentages.

C. Fractionation of the Dipropenyl Ethers

The dipropenyl ether mixture was separated on the Nester/Faust spinning band column at a 100:1 reflux ratio over a period of 22.1 hours. The distillate composition was monitored by GC analysis at twenty minute intervals. The first three cuts boiling at 86-91°C analyzed as pure cis,cis-dipropenyl ether (ccDPE), but were discarded because of a distinctive acetic acid smell plus the low boiling point. An additional 4.25 g of pure ccDPE were collected giving a total 10.33 g. This heart cut is small compared to the total amount of ccDPE in the mixture. Various reflux and temperature adjustments were tried with no improvement. The large intermediate fractions between the pure heart cuts are evidently due to the similarities in the properties (such as activity coefficients) of the three isomers.

4.40 g of cis,trans-dipropenyl ether were collected with a boiling point of 97.8°C at 755.8 mm Hg. Shortly after the collection of pure ctDPE was started, trans,trans-dipropenyl ether (ttDPE) began appearing in trace amounts. The separation was improved slightly by lowering the column temperature, but quality had to be sacrificed for quantity. The ctDPE sample, as shown in Figure 11, contained 0.2% ccDPE and 2.3% ttDPE impurities. Unfortunately an additional impurity, identifed from the IR and NMR spectra as cis-propenyl acetate was also present in the magnitude of 12%. Ethyl acetate was tested on the GC column and found to give a sharp peak between the ctDPE and ttDPE peaks. The retention time of propenyl acetate should be increased by molecular weight and decreased by the vinyl bond. Evidently cis-propenyl acetate has a retention time similar to ctDPE. The irregular shape of the ctDPE peak in Figure 12 is cited as evidence for this assumption. The ctDPE sample was, therefore, only 86% pure and had to be further purified for the infrared spectra.

If the spinning band column is operated dry, there is a danger of breaking the teflon band. At a head temperature of 101°C, the band started making a loud abrasive noise indicating that some part of the column was dry. The distillation was stopped and a GC test made on the bottoms. The pot contained several grams of approximately 93% pure ttDPE ether. The possibility of distilling-over the ttDPE by adding a higher boiling compound to the still was rejected because previous heart cuts had been small anyway. The most obvious impurity was the yellow color of the sample. A thermometer and condenser were added to the pot and the remaining liquid distilled at 101°C. The product as shown in Figure 12 was analyzed on the GC and calculated to contain 0.2% ccDPE and 7.1% ctDPE impurities. IR and NMR analysis indicate an additional 19% trans-propenyl acetate impurity. The ttDPE sample was, therefore, only 74% pure and had to be further purified for the infrared spectra; the ether was colorless but had a very sweet odor. Evidently trans-propenyl acetate has a retention time similar to trans,trans-dipropenyl ether. A total ttDPE sample of 2.96 g was collected.

D. Gas Chromatographic Analysis

The ethers were analyzed on a Model A-700 "Autoprep" Gas Chromatograph. A 1/4 in. by 10 ft. aluminum analytical column was filled with 25% THEED on 60/80 Chromosorb W. The dipropenyl ether from the diallyl ether rearrangement was 95+% pure *cis,cis*-dipropenyl ether with a *cis, trans*-dipropenyl ether shoulder. A high-retention time impurity was identified as t-butanol by comparison to the retention time of that of pure t-butanol. Traces of dimethoxyethane solvent were identified the same way. An unidentified low-retention time impurity (not propionaldehyde) was also present in trace amounts. For analysis of the high-retention time impurities, the GC was operated at 120°C and 120 ml/min. helium flow. For separation of the isomeric dipropenyl ethers, the GC was operated at 70-80°C and 40 ml/min. helium flow. The peaks in order of increasing retention time are *cis,cis*-, *cis,trans*-, and *trans, trans*-dipropenyl ether; the peak for diallyl ether falls between the *cis,trans*- and *trans,trans*-dipropenyl ether peaks.

E. Determination of the Infrared Spectra

The infrared spectra were determined on a Perkin-Elmer 457 spectrophotometer (4000-250 cm^{-1}). A 10 cm cell with cesium iodide windows was used for the gas-phase spectra; all the gas-phase spectra represent pure compounds. The liquid-phase spectra were taken as a thin film between sodium chloride discs. Evaporation was evident in the liquid-phase IR spectra; so the intensities for the liquid-phase IR bands were taken from a Beckman 33 spectrometer which takes less time and, therefore, allows less evaporation. Infrared spectra were also taken in CCl_4

solution using 0.2 cm cells with Irtran windows. The quality of the solution spectra is very poor, but later attempts to redo these spectra using potassium bromide cells were equally unrewarding. Multiple spectra were run at different gas pressures, film thicknesses, and concentrations in order to pinpoint both the strong and the weak bands. All of the spectra were consulted in constructing the tables of data (Tables III, IV, and V) and the most legible spectra were chosen for Figures 19-27.

The liquid-phase spectra were run at fast scan speed from 4000 to 3200 cm^{-1} and from 2800 to 1800 cm^{-1} and at a medium scan speed elsewhere in order to minimize evaporation. All other spectra were run at medium scan speed. Random oscillations associated with power oscillations due to starting and stopping of machinery in adjacent laboratories plagued the spectral determinations. These occurred too frequently to obtain reasonable spectra using a slow scan speed. Moving the spectrometer to a location away from the chemical engineering laboratories helped somewhat.

In order to fill the cell for the gas phase infrared spectra, the dipropenyl ether sample was cooled in a dry ice/acetone bath to -78°C, the system evacuated, and the sample allowed to warm-up at ambient temperatures until a pressure of 4 mm Hg was reached. The <u>cis</u>,<u>cis</u>-dipropenyl ether was 99.9% pure. By trial and error, spectra were obtained for <u>cis</u>,<u>trans</u>-dipropenyl ether (ctDPE) and <u>trans</u>,<u>trans</u>-dipropenyl ether with the propenyl acetate impurity concentrations significantly reduced. This effect was attributed to a higher melting point for the ester. The liquid remaining after filling the gas cell had a characteristic sweet ester odor and increased infrared carbonyl absorbtion.

In further experimentation, a method based on ester saponification reaction plus aldol condensation was developed to completely remove the ester from the vapor-phase spectra. Five drops of ctDPE or ttDPE were added to a small flask containing ten potassium hydroxide pellets and sealed under nitrogen for one to two hours until the KOH pellets turned white to yellow to dark orange. The flask was then attached to the high-vacuum system and the gas cell filled as before. Pure gas-phase infrared samples for ctDPE and ttDPE were then obtained. The bands removed from the spectra of these two samples, when purified, correspond to the literature values of several bands in propenyl acetate.(16)

F. Determination of the Raman Spectra

The Raman spectra were determined in the liquid-phase using a Jarrel Ash 400 laser spectrometer at Rutgers University, Newark. An argon laser with an excitation of 19435 wavenumbers was used as the source. The samples were contained in sealed capillary tubes and the attenuation was changed to get the peaks on scale in the different regions. The initial and final readings were calibrated using neon and argon, and the intermittent readings were interpolated using a scale with sixty divisions per inch. The *cis,cis*-dipropenyl ether sample was 99.9% pure. The *cis,trans* and *trans,trans*-dipropenyl ether samples contained propenyl acetate impurities; the contribution of these impurities was determined by comparison of the pure gas-phase and the impure liquid-phase infrared spectra with the literature values for the propenyl acetate infrared bands.(16) The Raman spectra are shown in Figures 28-31; and the frequencies are listed in Tables III, IV, and V.

G. Determination of the Proton NMR Spectra

The proton NMR samples were analyzed on a Hitachi Perkin Elmer R-24A high resolution spectrophotometer as liquids (neat) using TMS as an internal reference. The cis,cis-dipropenyl ether was 99.9% pure as determined by gas chromatograph and reaffirmed by the proton NMR spectra. The cis,trans- and trans,trans-dipropenyl ethers contained propenyl acetate, a catalytic reaction byproduct, in the amounts of 12 mole% and 19 mole% respectively. Integration of the methyl peaks was used to calculate the percent acetate impurity. This analytical technique has been proven effective when the two methyl concentrations are below 36-40 mole%.(60) Since the propenyl ether concentrations are higher than this, the impurity percentages are approximate. Chemical shift values were measured to a precision of ± 0.005 ppm and spin-spin coupling constants to ± 0.3 Hz (60 x 0.005) using a scale with sixty divisions per inch.

H. Determination of the Carbon 13 NMR Spectra

Decoupled carbon-13 NMR samples were analyzed at Rutgers University, Newark, using a JEOL JNM-PS-100 spectrometer with internal deuterium lock. Cis,cis-dipropenyl ether was analyzed as a concentrated solution in deuterated acetone. The other two isomers were in very dilute solutions. TMS was used as an internal standard. The TMS signal was strong enough for computer analysis in only one sample, the dilute solution of the trans,trans isomer. The shift to the center methyl carbon peak in acetone for this sample was used to standardize the shifts for the other two isomers. The literature references use cyclohexane, benzene, acetone, or CS_2 (53, 54, 59) as internal standards; these were converted to TMS shifts for the calculations in Appendix I.

The center methyl carbon peak of acetone registered at 29.801 ppm. This represents a solvent shift of +0.6 ppm from the literature value for deutero-acetone of 29.2 ppm. Maciel and Ruben report a solvent shift of -2.0 ppm for acetone in diethyl ether.(59) The acetone shift is listed as 30.4 ppm, so the 29.801 value is reasonable to use. Since the solvent shift is also a function of concentration, the acetone-TMS shifts were measured in Figures 16, 17, and 18 using a scale with sixty divisions per inch. The measured solvent shifts were equal for all three isomers. Three of the six peaks for the cis,trans isomer were not recorded on the computer tape. All six cis,trans peaks were measured, and the measured peaks compared within ±0.1 ppm of the recorded peaks. The shifts for all three isomers are rounded-off to this precision.

I. Pyrolysis

Nine pyrolysis runs were made over a temperature range of 300-400°C at varying feed rates in an attempt to optimize the reaction conditions. The pyrolysis equipment was initially set-up as described by Waldron.(33) The cis,cis-dipropenyl ether (ccDPE) was vaporized by dropwise addition from an equalizing-arm separatory funnel into a preheated 250 ml three-necked flask. The vapor passed through a 1 in. o.d. by 2 ft. long pyrolysis tube filled with base-washed alumina and heated by Lindberg Hevi-Duty tube furnace. The product vapor was condensed by passage through an air-cooled and a water-cooled Allihn condenser and a Dewar condenser filled with dry ice/acetone at -78°C, into a 250 ml three-necked receiving flask in an ice bath. The noncondensible vapor passed through a cold trap cooled by a cryocool unit at -42°C and exited through a mineral oil bubbler used to measure nitrogen flow rate. The product vapor condensed in the air-cooled Allihn condenser in the first run; the second run used only one Allihn condenser which was water cooled. The product again condensed in the Allihn condenser. In the third run the product vapors were passed directly into the Dewar condenser and the water-cooled condenser was placed downstream of the receiving flask; the product froze in the Dewar condenser. For runs #4-9 the Dewar condenser was cooled by ice water which allowed the product to drip into the receiving flask as it was cooled so that intermittent gas chromatograph samples could be taken. This set-up is shown in Figure 2. The exposed tubing between the vaporization flask and the pyrolysis furnace was wrapped with heating tape.

In the thermal demethanolization of 1,1,2-trimethoxy ethane, the optimum pyrolysis temperatures were 300-320°C. Blackened, deactivated catalyst was noted above 360°C, along with decreased olefin yields and increased degradation products.(17) In the present work, the desired 20% trans,trans-dipropenyl ether (ttDPE) equilibrium value indicated a temperature of 367°C (see Figure 4). Run #1 was made at 300°C where the predicted equilibrium value of ttDPE was 18.9%; only 3.4% ttDPE was produced. Evidently the residence time was too short to reach equilibrium at that temperature. For an increase of 10°C the reaction rate approximately doubles or the equilibrium residence time should be approximately halved. Runs were made at successively higher temperatures in order to attempt to reach equilibrium conversions. The rate of reaction was fast enough to reach equilibrium at 380-400°C, using the existing equipment. Unfortunately catalyst deactivation occurs above 360°C. To compensate for this, periodic GC samples were taken during Runs #5-8, and the furnace temperature raised to compensate for the decreased catalyst activity. When the alumina was significantly blackened and the activity noticeably decreased, the run was stopped and the catalyst changed.

The possibility of increasing residence time by recycle was tested is Run #3. Water was removed from the products of Runs #1 and 2, and the organic layer containing 70.4% ccDPE was used as feed for Run #3. The product contained 49.7% of ccDPE, giving a conversion of 20.7%. Run #4 was made at 340°C, the same temperature as #3, but the feed was 95.4% and the product 55.8% ccDPE, giving a conversion of 39.6%. The conversion rate is a function of concentration and decreases as the equilibrium concentration is approached. The products in Runs #1 and 2 were yellow, the product in Run #4 was green, and the product in Run #3 was dark green. The darker-colored samples contained a higher percentage of higher-molecular-weight materials in the GC analyses. The darker color is attributed to polymerization products from competing side reactions, and is evidently a function of the feed conversion or approach to equilibrium rather than the temperature. Since it was assumed that light or heavy products could be separated from the dipropenyl ethers, the percentages are based on total ethers rather than on total product unless stated otherwise.

A 218.13 g sample was pyrolyzed in Run #5. The initial conversion rates gave 16.5% ttDPE at 370°C, but even with increasing temperature the composite sample contained only 9.2% ttDPE. The product was separated by vacuum distillation and the distilled fraction used as feed for Run #6. The composite product from this run contained 14.3% ttDPE and was a golden yellow. The mean temperature for Run #6 was 360°C.

A higher conversion was achieved in Runs #7 and 8 without recycle by increased average temperature and a decreased feed rate. In previous runs nitrogen gas was used as an inert carrier throughout the experiments. In Runs #7 and 8 the nitrogen flow was discontinued as soon as vaporization was started and the ether allowed to flow through by its own vapor pressure. Run #7 was discontinued when the alumina blackened, the catalyst was changed, and the remaining feed put through Run #8. The water layer was separated from the two composite samples and the organic layer dried with calcium hydride. The composite sample from Runs #7 and 8 contained 21.6% ttDPE and was dark green. This sample achieved the desired equilibrium conditions; the gas chromatograph is shown in Figure 6. The dipropenyl ether peaks plus peaks identified in the fractionation of Runs # 5 and 6 are noted. Analysis by weight of peak areas gives 16.4% ethers and 52.4% high-retention byproducts. The 27.9% polymeric material removed in the vacuum distillation of Run #5, which contains 9.2% ttDPE, indicates that this percentage is reasonable.

The Nester/Faust spinning band column was used for the fractionation of the composite sample from Runs #5 and 6. The column was run at a 100:1 reflux ratio for a total of 12.5 hours. A nasty-smelling substance which boiled at 48°C was tentatively identified as propionaldehyde (b.p. 48.8°C). A substance boiling at 61°C was tentatively identified as isobutyraldehyde (b.p. 61.5-63.5°C). These peaks are marked in Figure 6. The pyrolysis feed contained about 5% t-butanol. (The magnitude of this impurity was not realized until the pyrolysis runs were well underway, since the original GC column was not functioning properly.) The unreacted t-butanol azeotroped with ccDPE isomer at 78-81°C. A sweet-smelling, high-retention time impurity azeotroped with the cis,trans and trans,trans isomers. The last 0.25 g of ttDPE showed a decreased amount of the azeotropic material. Since the sample from Runs #7 and 8 contained a much larger ratio of the azeotropic material, fractionation of this product was not attempted.

Run #9 was made on 99.9% pure ccDPE in order to verify the conclusions made in the previous runs. Pyrolysis of t-butanol produces isobutylene and water.(27) The water reacts with the dipropenyl ether to produce propionaldehyde. The fraction of water observed was too large to be due solely to the t-butanol. The alumina was dried in the oven prior to filling the pyrolysis tube and dried in the furnace prior to starting the reaction. Additional drying time in Runs #7 and 8 produced less water so some of the water was evidently coming from the alumina. The catalyst was heated in the oven at 200°C for four days and heated in the pyrolysis furnace at 400°C for seven days. The cold trap kept freezing-up from the water. The nitrogen was therefore vented directly into the oil bubbler, the oil changed periodically, and the heating continued until no further water layer formed. The alumina had a few gray spots but did not turn black, indicating that the black catalyst deactivation is due to the formation of polymeric materials. The stop-cock grease on one of the joints dried-out during the long catalyst drying period, causing a leak during the run. The product collected was water-free, but contained a much higher concentration of byproduct polymers along with a significant reduction in the propionaldehyde concentration. A colorless liquid which was collected in the cold-trap vaporized instantaneously on attempting to pour the liquid into a bottle. This byproduct may be methyl acetylene which boils at -23.3°C or propylene which boils at -47.4°C. The pyrolysis of ccDPE was proven to be non-feasible as a synthesis for ttDPE, so further work to positively the byproducts was not undertaken.

IX. CONCLUSIONS

Pure cis,cis-dipropenyl ether may be prepared by potassium t-butoxide catalyzed rearrangement of diallyl ether, followed by fractionation to remove the t-butanol impurity. Pyrolysis is effective in isomerizing cis,cis-dipropenyl ether (ccDPE) to cis,trans-dipropenyl ether (ctDPE) and trans,trans-dipropenyl ether (ttDPE), but competing side reactions severely limit the yields and formation of an azeotropic byproduct prevents fractionation. Mercuric acetate catalyzed isomerization is still the preferred preparation for ctDPE and ttDPE, but mercuric salicylate or mercuric benzoate are probably better catalyst choices. The three dipropenyl ether isomers can be separated on the Nester/Faust spinning band column, but large quantities are needed to obtain reasonable quantities of the pure heart cuts.

Pure ccDPE (99.9%) has a boiling point of 92°C, an index of refraction at 20°C of 1.4307 ± 0.0001, a density at 25°C of 0.813 ± 0.001 g/ml, and a molecular refractivity of 31.10 (theoretical = 30.77). ctDPE has a boiling point of 98°C, and ttDPE has a boiling point of 101°C. The liquid samples of ctDPE and ttDPE were impure, so the values determined for their densities and refractive indices are only approximate. The impurity was identified as cis- and/or trans-propenyl acetate based on the proton NMR and the infrared spectra. The impurity was removed from the vapor-phase IR spectra by saponification with solid potassium hydroxide. Accurate proton and carbon-13 NMR spectra were obtained for all three dipropenyl ether isomers; ccDPE was pure and the impurity peaks did not interfere with the ctDPE or ttDPE chemical shifts. Vibrational spectral bands and frequency assignments are reported for all three isomers.

The carbon-13 NMR spectra show vibrational coupling for all three isomers. This is correlated with the C_{2v} conformers of ccDPE and ttDPE and with the linear coupled C_s conformer of ctDPE. The carbon-13 chemical shifts indicate increased electron density on the terminal methyl carbons, which may be correlated with charge-polarized resonance structures. The magnitude of the upfield shift relative to other unsaturated hydrocarbons indicates that resonance is greater for the trans configuration than for the cis configuration in the three dipropenyl ether isomers. The proton NMR chemical shifts indicate less resonance and more double-bond character for the dipropenyl ethers than for the alkyl vinyl ethers. Sp^2 hybridization of the central oxygen atom in either the C_{2v} or the C_s conformations is consistent with but not necessary for the observed resonance. Sp^2 hybridization is also consistent with the planar structure which is required to explain the exceptionally strong vibrational coupling in ccDPE.

The major conformation of ccDPE has been previously identified as a C_{2v} planar structure on the basis of the strong infrared-active C=C asymmetric stretch at 1656 cm^{-1} and the extremely strong Raman-active C=C symmetric stretch at 1691 cm^{-1}. (3) Additional bands attributed to this conformer are the vinyl C-H in-plane rock at 1255 cm^{-1}, the asymmetric C-O-C stretch at 1138 cm^{-1}, the C-O-C symmetric stretch at 946 cm^{-1}, and the cis vinyl C-H out-of-plane bend at 718 cm^{-1}. Another conformer of low symmetry is identified on the basis of a shoulder in the vapor-phase infrared which becomes a distinct band in the liquid-phase at 690 cm^{-1}, the cis vinyl C-H out-of-plane bending region. Supporting bands for the non-planar conformer are a shoulder in the infrared and a very weak band in the Raman at 1638 cm^{-1} (the C=C stretch), and the asymmetric C-O-C stretch at 1253 cm^{-1}. The vinyl C-H in-plane rock should be strong only in the Raman and the C-O-C asymmetric stretch should be strong only in the infrared. The fact that the 1253-1255 cm^{-1} band is strong in both is taken as evidence that these two vibrations are accidentally degenerate.

The planar C_s conformer is the most stable structure for ttDPE; this conformer is identified by the C=C stretch at 1677 cm^{-1}. The other two bands in this region are assigned to coupled C=C stretches of the C_{2v} conformer. The symmetric C_{2v} C=C stretch appears as a strong band in the Raman at 1698 cm^{-1} and a weak band in the infrared; the asymmetric C_{2v} C=C stretch appears as a strong band in the infrared at 1662 cm^{-1} and a medium band in the Raman. The vinyl C-H in-plane rock is a doublet in both the infrared and the Raman. Peak broadening in both the C=C and the C-O-C stretch regions is attributed to the presence of more than one conformer. The C=C peak of the pure vapor-phase ttDPE sample is a doublet with the 1669 cm^{-1} peak slightly larger than the 1662 cm^{-1} peak. The relative intensities in this doublet are comparable to the relative intensities of the C_s and the symmetric C_{2v} Raman vibrations. A very weak peak at 1646 cm^{-1} in the Raman spectra may indicate a low stability non-planar conformer, but there are no supporting bands and the impurity concentration makes it necessary to ignore shoulders like this.

The major conformer of ctDPE is identified as the linear coupled C_s

form, characterized by the strong C=C symmetric stretch at 1695 cm^{-1} in the Raman and the strong C=C asymmetric stretch at 1661 cm^{-1} in the infrared. A peak in the Raman at 1666 cm^{-1}, which is skewed on both sides, is interpreted as being a combination of the coupled asymmetric C=C stretch of the linear C_s conformer and two uncoupled _cis_ and _trans_ C=C vibrations of the bent C_s conformer. The vinyl C-H in-plane rock appears as a medium to weak band at 1249 cm^{-1} and a weak to very weak doublet at 1274 and 1282 cm^{-1}, the stronger band is attributed to the planar _cis_ vinyl C-H vibration and the doublet to the two planar _trans_ vinyl C-H vibrations of the two C_s conformations. The infrared C=C stretch also appears as a doublet. The assignment of the asymmetrical C-O-C stretch to the two conformers is not clear-cut; a very strong, slightly broadened peak appears at 1176 cm^{-1} and a weak band at 1137 cm^{-1}. In summation, two conformers have been identified for each of the dipropenyl ether isomers.

X. RECOMMENDATIONS

Mercuric salicylate or mercuric benzoate should be used as the catalyst for the isomerization of *cis,cis*-dipropenyl ether (ccDPE), rather than mercuric acetate. Catalyst screening studies with dimethoxyethylene indicate comparable effectiveness for these three catalysts in enol ether isomerizations.(17) Byproducts from decomposition of the higher molecular weight mercuric salts could be easily separated from *cis,trans*-dipropenyl ether (ctDPE) and *trans,trans*-dipropenyl ether (ttDPE). If mercuric acetate is used, the byproduct propenyl acetate should be removed from the isomerized ether by aldol condensation and rough distillation prior to the final ether fractionation.

Since propenyl acetate is present in the Raman samples of the ctDPE and ttDPE, the Raman bands for *cis*- and *trans*-propenyl acetate should be properly identified. The low symmetry of the propenyl acetate molecule dictates that all vibrational frequencies are both infrared and Raman active; however, the intensities aren't necessarily comparable. The effect of the impurity on the Raman spectra has been assumed, based on the known infrared bands of propenyl acetate. It is conceivable that an unidentified weak propenyl acetate infrared band may be stronger in the Raman spectra, and may be wrongly identified as a dipropenyl ether band.

The equilibrium kinetics for the dipropenyl ether isomers are based on a pure ccDPE feed at three temperatures, 80°, 100°, and 130°C, using mercuric acetate catalyst.(12) Complete kinetics should be determined with mercuric salicylate or mercuric benzoate over a more extensive temperature range. The presence of the propenyl acetate impurity makes the equilibrium data questionable since the data is based on GC analysis using a 25% THEED on Chromosorb W column and this column does not separate the impurity from ctDPE and ttDPE. Extrapolation of the equilibrium data to 395°C indicates that the ether composition should be 33.3 ± 3.4% ccDPE, 46.1 ± 3.8% ctDPE, and 20.7 ± 2.5% ttDPE. By comparison, the product ether composition from pyrolysis Runs #7 and 8 was 36.9% ccDPE, 41.4% ctDPE, and 21.6% ttDPE at an average temperature of 395°C. This agreement is excellent considering the magnitude of the extrapolation, however, the higher predicted ctDPE percentage may be due to the hidden propenyl acetate impurity. The equilibrium constants should be determined from alternate directions, by using ctDPE and ttDPE feeds. Pure heart cuts are difficult to obtain, but samples sufficiently rich in the cis,trans and trans,trans isomers can be isolated using the Nester/Faust spinning band column.

A number of propenyl ether compounds are reported to be more stable in the cis configuration. (8, 56) A notable exception is trans-propenyl methyl ether which is reported to be more stable than the corresponding cis isomer. (56) It may be worthwhile confirming the cis-trans equilibrium compositions for methyl propenyl ether.

XI. APPENDIX I - CALCULATIONS

A. Molecular Refractivities

The theoretical molecular refractivity is calculated by adding up the bond refractions at 20°C. The CRC Handbook refers to measurements by Vogel from 1948. More recent numbers by Vogel are used.(62)

Consider the dipropenyl ether molecule: $CH_3\text{-}CH{=}CH\text{-}O\text{-}CH{=}CH\text{-}CH_3$

$$
\begin{aligned}
\text{10 C-H bonds} &= 10 \times 1.676 = 16.76\\
\text{2 C-C bonds} &= 2 \times 1.296 = 2.592\\
\text{2 C=C bonds} &= 2 \times 4.17 = 8.34\\
\text{2 C-O (ether) bonds} &= 2 \times 1.54 = \underline{3.08}\\
\text{Total} &= 30.77 = M_R
\end{aligned}
$$

The actual molecular refractivity is calculated from the density, d, the molecular weight, M, and the refractive index, n, as follows:

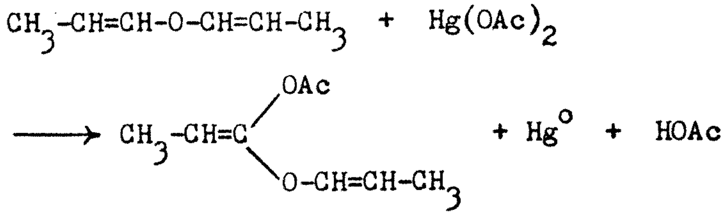
$$M_R = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}\ ,$$ where n and d are at the same temperature.

The values for the three dipropenyl ether isomers are as follows:

	n@20°C	n@25°C	d@25°C	M_R@25°C
cis,*cis*-dipropenyl ether	1.4307	1.4287	0.813	31.10
cis,*trans*-dipropenyl ether	1.4316	1.4296	0.829	30.56
trans,*trans*-dipropenyl ether	1.4293	1.4273	0.835	30.20

B. Maximum Propenyl Acetate Formation

The maximum propenyl acetate concentration may be calculated by assuming complete decomposition of the mercuric acetate catalyst which was used for the isomerization of *cis*,*cis*-dipropenyl ether. The reactions are as follows:

(1)


$$CH_3\text{-}CH\text{=}CH\text{-}O\text{-}CH\text{=}CH\text{-}CH_3 + Hg(OAc)_2 \longrightarrow CH_3\text{-}CH\text{=}C\begin{matrix} OAc \\ O\text{-}CH\text{=}CH\text{-}CH_3 \end{matrix} + Hg^o + HOAc$$

Compound	Reactants (1)		Products (1)	
	grams	moles	moles	grams
dipropenyl ether	50.31	0.513	0.482	47.30
mecuric acetate	9.83	0.0308	0	0
acetal			0.0308	4.81
acetic acid			0.0308	reacted
mercury			0.0308	solid

(2) $CH_3\text{-}CH\text{=}CH\text{-}O\text{-}CH\text{=}CH\text{-}CH_3$ + HOAc

$\longrightarrow CH_3\text{-}CH\text{=}CH\text{-}OAC + CH_3\text{-}CH_2\text{-}CHO\uparrow$

Compound	Reactants (2)		Products (2)	
	moles	grams	moles	grams
dipropenyl ether	0.482	47.30	0.451	44.26
acetic acid	0.0308	1.85	0	0
propenyl acetate			0.0308	3.08
propionaldehyde			0.0308	evaporated

The acetal is a higher boiling compound. Distillation of the isomerization mixture should yield 44.26 g of dipropenyl ether isomers plus 3.08 g of <u>cis</u>- and/or <u>trans</u>-propenyl acetate, giving a total of 47.34 g of impure ethers.

A 41.22 g sample of 45.7% cis,cis-dipropenyl ether (ccDPE), 43.6% cis,trans-dipropenyl ether (ctDPE), and 10.7% trans,trans-dipropenyl ether (ttDPE) was recovered after filtration and distillation to remove the solids. This represents an 87% recovery; the losses can be attributed to wetting of the filter paper, the catalyst, and the experimental apparatus, plus evaporative losses. Assuming the ethers and the acetate impurity suffer equal recovery losses, the mixture would contain:

45.7% ccDPE = 17.61 g
43.6% ctDPE = 16.81 g
10.7% ttDPE = 4.12 g
propenyl acetate = 2.68 g $\begin{cases} \sim 1.34 \text{ g } \underline{\text{cis}}\text{-propenyl acetate} \\ \sim 1.34 \text{ g } \underline{\text{trans}}\text{-propenyl acetate} \end{cases}$

The proton NMR indicates an impurity level of 19 mole% for ttDPE. This accounts for 0.98 g of propenyl acetate. The remaining 1.70 g of propenyl acetate would give a 9 mole% impurity for the ctDPE sample. This compares favorably with the 12 mole% observed for the heart cut of ctDPE. The propenyl acetate impurity levels are therefore directly correlatable to the observed formation of metallic mercury.

The equilibrium mixture of *cis*- and *trans*-propenyl acetate is approximately a 1 to 1 ratio.(23, 24) *Trans*-propenyl acetate boils at 103°C while the *cis* isomer boils at 101°C.(23) ttDPE boils at a higher temperature than ctDPE. It is therefore reasonable to assume that the 0.98 g of propenyl acetate in ttDPE is *trans*-propenyl acetate. This leaves 0.36 g of *trans*-propenyl acetate plus 1.34 g of *cis*-propenyl acetate in ctDPE, which correlates with NMR evidence showing *cis*-propenyl acetate to be the major impurity in ctDPE and *trans*-propenyl acetate to be the major impurity in ttDPE. The infrared studies indicate the presence of both impurities in ctDPE and only the trans impurity in ttDPE (Table I). The mass balance above is based on ttDPE because the boiling point of ttDPE is closer to that of the impurities, and because 72% of the ttDPE (2.96 g) was recovered versus only 26% of the ctDPE (4.40 g). The mass balance provides additional confirmation for the identification of the impurity.

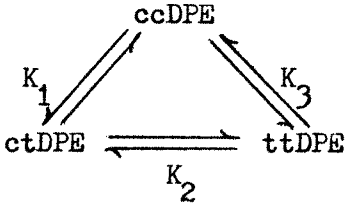
C. High-Temperature Ether Percentages

Let: cc = moles of cis,cis-dipropenyl ether (ccDPE) at equilibrium.

ct = moles of cis,trans-dipropenyl ether (ctDPE) at equilibrium.

tt = moles of trans,trans-dipropenyl ether (ttDPE) at equilibrium.

The equilibrium constants are defined as follows:(12)



where: $K_1 = ct / cc$

$K_2 = tt / ct$

$K_3 = tt / cc = \frac{tt / ct}{cc / ct}$

or $K_3 = K_1 K_2$

It is desired to derive equations for the mole fractions of each of the three isomers in terms of the equilibrium constants. Only two of the constants are independent, so three equations can be derived for each isomer.

Let: xcc = mole fraction of ccDPE at equilibrium.

xct = mole fraction of ctDPE at equilibrium.

xtt = mole fraction of ttDPE at equilibrium.

Then:
$$xcc = \frac{cc}{cc + ct + tt} = \frac{cc / cc}{\frac{cc}{cc} + \frac{ct}{cc} + \frac{tt}{cc}} = \frac{1}{1 + K_1 + K_3} = \frac{1}{1 + K_1 + K_1 K_2}$$
$$= \frac{1}{1 + (K_3 / K_2) + K_3}$$

Similarly:

$$xct = \frac{1}{(K_2 / K_3) + 1 + K_2} = \frac{1}{(1 / K_1) + 1 + K_2}$$

$$= \frac{1}{(1 / K_1) + 1 + (K_3 / K_2)}$$

$$xtt = \frac{1}{(1 / K_3) + (1 / K_2) + 1} = \frac{1}{(1 / K_1K_2) + (1 / K_2) + 1}$$

$$= \frac{1}{(1 / K_3) + (K_1 / K_3) + 1}$$

Using the constants determined by Tomalesky,(12) equations for K_1, K_2, and K_3 can be found by linear regression analysis:

$$\ln K_1 = -91.04 / T(^{\circ}K) + 0.3621$$

$$\ln K_2 = -310.3 / T(^{\circ}K) - 0.4428$$

$$\ln K_3 = -634.2 / T(^{\circ}K) + 0.5711$$

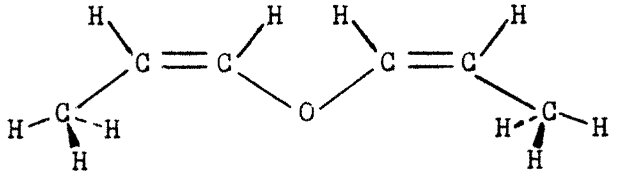
Using the equations for the equilibrium constants and the equations for the mole fractions, three values for the mole fraction of each isomer can be calculated at any temperature. For example the following values are calculated at 395°C:

	K_1 & K_2	K_2 & K_3	K_3 & K_1	Percentage
xcc	0.362	0.296	0.340	33.3 ± 3.4%
xct	0.454	0.502	0.427	46.1 ± 3.8%
xtt	0.184	0.203	0.233	20.7 ± 2.5%

This extrapolation technique indicates the error range, which increases as the magnitude of the extrapolation increases.

D. Infrared Inactive Bands

The A_2 symmetry series for the C_{2v} conformation of cis,cis-dipropenyl ether (ccDPE) and of trans,trans-dipropenyl ether (ttDPE) is inactive in the infrared vibrational spectra. The number of vibrations for each species of vibration, A_1, A_2, B_1, and B_2, are calculated as follows:(38)



Let: m = "the number of sets of equivalent nuclei not on any element of symmetry".

m_o = "the number of nuclei lying on all symmetry elements present".

m_{xz} and m_{yz} = "the number of sets of nuclei lying on the xz and yz plane respectively but not on any axes going through these planes".

n = the number of atoms in the molecule.

For either ccDPE or ttDPE: $m = 1$, $m_{xz} = 6$, $m_o = 1$, $m_{yz} = 0$

The appropriate equations are:(38)

$$A_1, \quad 3m + 2m_{xz} + 2m_{yz} + m_o - 1 = 15$$

$$A_2, \quad 3m + m_{xz} + m_{yz} - 1 = 8$$

$$B_1, \quad 3m + 2m_{xz} + m_{yz} + m_o - 2 = 14$$

$$B_2, \quad 3m + m_{xz} + 2m_{yz} + m_o - 2 = \underline{8}$$

$$\text{Total} = 3n - 6 = 3\,(17) - 6 = 45$$

There are, therefore, eight infrared-inactive vibrations of the A_2 symmetry series for the C_{2v} conformations of ccDPE or ttDPE.

Now consider the methyl groups as point masses not affecting the symmetry of the molecule:

$m = 0$, $m_o = 1$, $m_{xz} = 5$, $m_{yz} = 0$

A_2 vibrations: $3\ (0) + 5 + 0 - 1 = 4$

A_2 vibrations from C-H $= 8 - 4 = 4$

Total vibrations $= 3\ (11) - 6 = 27$

Total vibrations from C-H $= 45 - 27 = 18$

In summation, there are a maximum of 45 vibrations for the dipropenyl ether molecule. For the C_{2v} conformation of ccDPE or ttDPE, eight of these vibrations are inactive in the infrared spectrum and four of the inactive modes may be attributed to the C-H vibrations. For the C_s, C_2, or C_1 conformations, all the bands are active in both the Raman and the infrared.

E. Predicted Carbon-13 Chemical Shifts

The following shift parameters are taken from the paper by Dorman, Jautelat, and Roberts.(53) Starting with the C^{13} shifts for ethylene, the appropriate substituent parameter is added for each carbon atom in the chain disregarding any additional unsaturation.

$$C^{\delta}-C^{\gamma}-C^{\beta}-C^{\alpha}-C^{*}=C-C^{\alpha'}-C^{\beta'}-C^{\gamma'}-C^{\delta'}$$

$\alpha = +10.57 \pm 0.08$ ppm
$\beta = +7.15 \pm 0.08$ ppm
$\gamma = -1.47 \pm 0.05$ ppm
$\delta = +0.19 \pm 0.13$ ppm
$\alpha' = -7.94 \pm 0.08$ ppm
$\beta' = -1.64 \pm 0.08$ ppm
$\gamma' = +1.42 \pm 0.04$ ppm
$\delta' =$ negligible
cis $= -1.11 \pm 0.06$ ppm

Dorman et. al. note that the α shift for propene is exceptionally large. The following shift parameters are, therefore, used for the dipropenyl ethers for a slightly improved correlation:

$$\begin{aligned} \alpha &= +12.9 \pm 1.0 \text{ ppm} \\ \alpha' &= -7.4 \pm 1.0 \text{ ppm} \end{aligned}$$

The alkene shift parameters above do not account for substituents other than hydrogen. The vinyl carbon shifts determined by Maciel are used to account for the oxygen atom in the dipropenyl ethers.(54)

$C^1H_2{=}C^2H{-}X$, where X is OCH_3

$$\left.\begin{aligned} \delta C1 &= -44.1 \pm 0.8 \text{ ppm} \\ \delta C2 &= +24.2 \pm 0.8 \text{ ppm} \end{aligned}\right\} \text{relative to benzene}$$

The chemical shift for benzene is 128.5 ± 0.5 ppm.(55)

<u>Calculate $C{=}\overset{*}{C}{-}O$ trans:</u>

$$C^{\alpha'}{-}({-}C{=}C^2{-}O{-}C{-}){-}C^{\gamma}{-}C^{\delta}$$

$$\begin{array}{rlll}
\delta C2 = & \left\{\begin{array}{l} +128.5 \pm 0.05 \text{ ppm} \\ +24.2 \pm 0.8 \text{ ppm} \end{array}\right. & & \\
\alpha' = & -7.94 \pm 0.08 \text{ ppm} & \text{or} & -7.4 \pm 1.0 \text{ ppm (propene)} \\
\gamma = & -1.47 \pm 0.05 \text{ ppm} & & \\
\delta = & \underline{+0.19 \pm 0.13 \text{ ppm}} & & \\
 & 143.5 \pm 1.1 \text{ ppm} & \text{or} & 144.0 \pm 2.0 \text{ ppm}
\end{array}$$

<u>Calculate $C{=}\overset{*}{C}{-}O$ cis:</u>

$$\begin{array}{rlll}
\underline{\text{cis}} = & \underline{-1.11 \pm 0.06 \text{ ppm}} & & \\
 & 142.4 \pm 1.2 \text{ ppm} & \text{or} & 142.9 \pm 2.1 \text{ ppm}
\end{array}$$

<u>Calculate $C{-}\overset{*}{C}{=}C$ trans:</u>

$$C^{\alpha}{-}({-}C^1{=}C{-}O{-}C{-}){-}C^{\gamma'}{-}C^{\delta'}$$

$$\begin{array}{rlll}
\delta C1 = & +128.5 \pm 0.05 \text{ ppm} & & \\
 & -44.1 \pm 0.8 \text{ ppm} & & \\
\alpha = & +10.57 \pm 0.08 \text{ ppm} & \text{or} & +12.9 \pm 1.0 \text{ ppm (propene)} \\
\gamma' = & \underline{+1.42 \pm 0.04 \text{ ppm}} & & \\
 & 96.4 \pm 1.0 \text{ ppm} & \text{or} & 98.7 \pm 1.9 \text{ ppm}
\end{array}$$

Calculate $C-\overset{*}{C}=C$ cis:

cis = -1.11 ± 0.06 ppm

95.3 ± 1.0 ppm or 97.6 ± 2.0 ppm

Calculate $\overset{*}{C}-C=C$ trans:

shift in n-hexane = 13.7 ppm
shift in n-decane = 13.9 ppm (55)

trans 1,2-disubstituted methyl shift = +3.8 ± 0.3 ppm(53)

Total = 13.7 + 3.8 = 17.6 ppm

Calculate $\overset{*}{C}-C=C$ cis:

cis 1,2-disubstituted methyl shift = -1.5 ± 0.2 ppm(53)

Total = 13.7 - 1.5 = 12.2 ppm

XII. APPENDIX II

Spectra

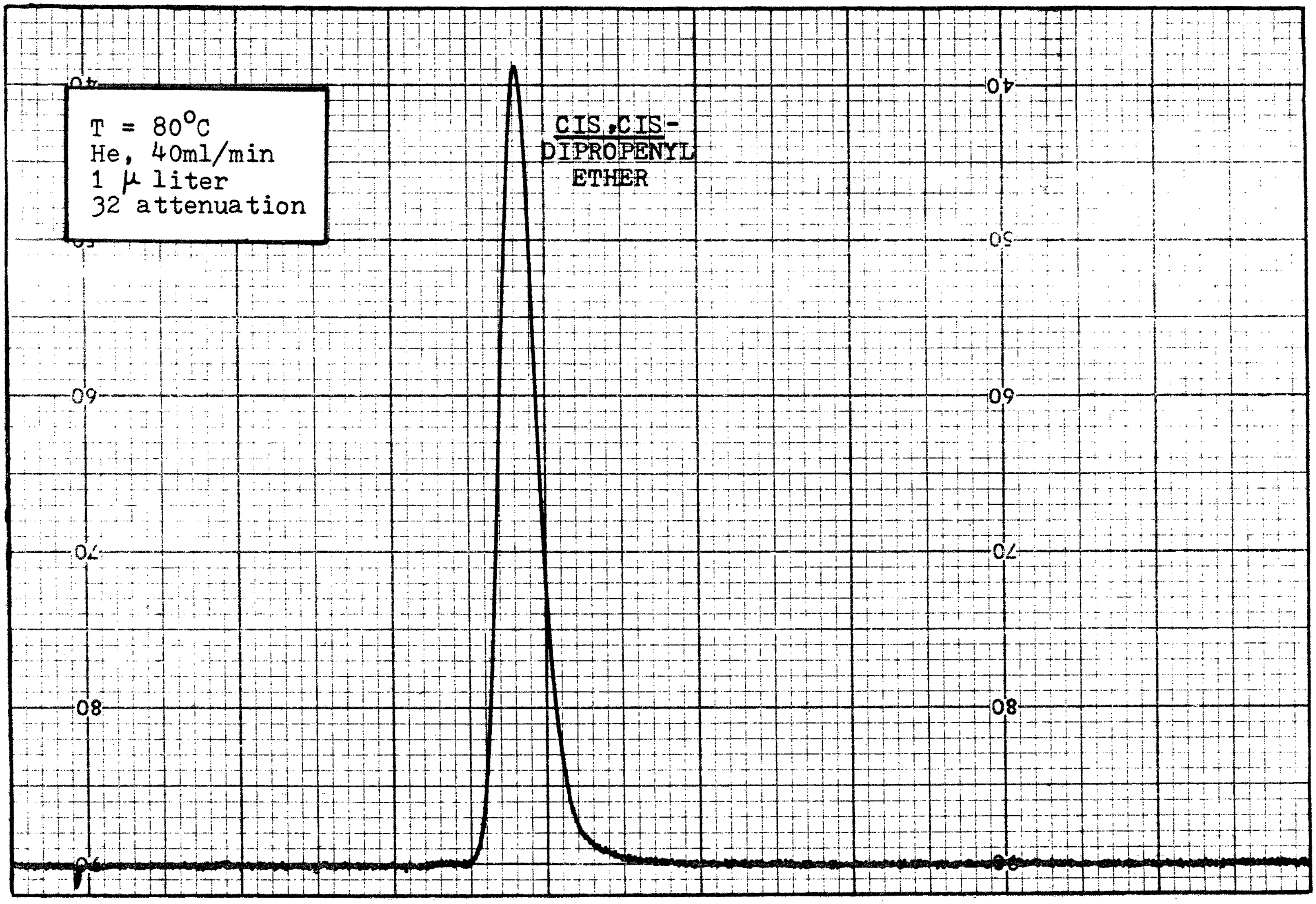


FIGURE 10 G.C. Analysis of Cis,Cis-Dipropenyl Ether

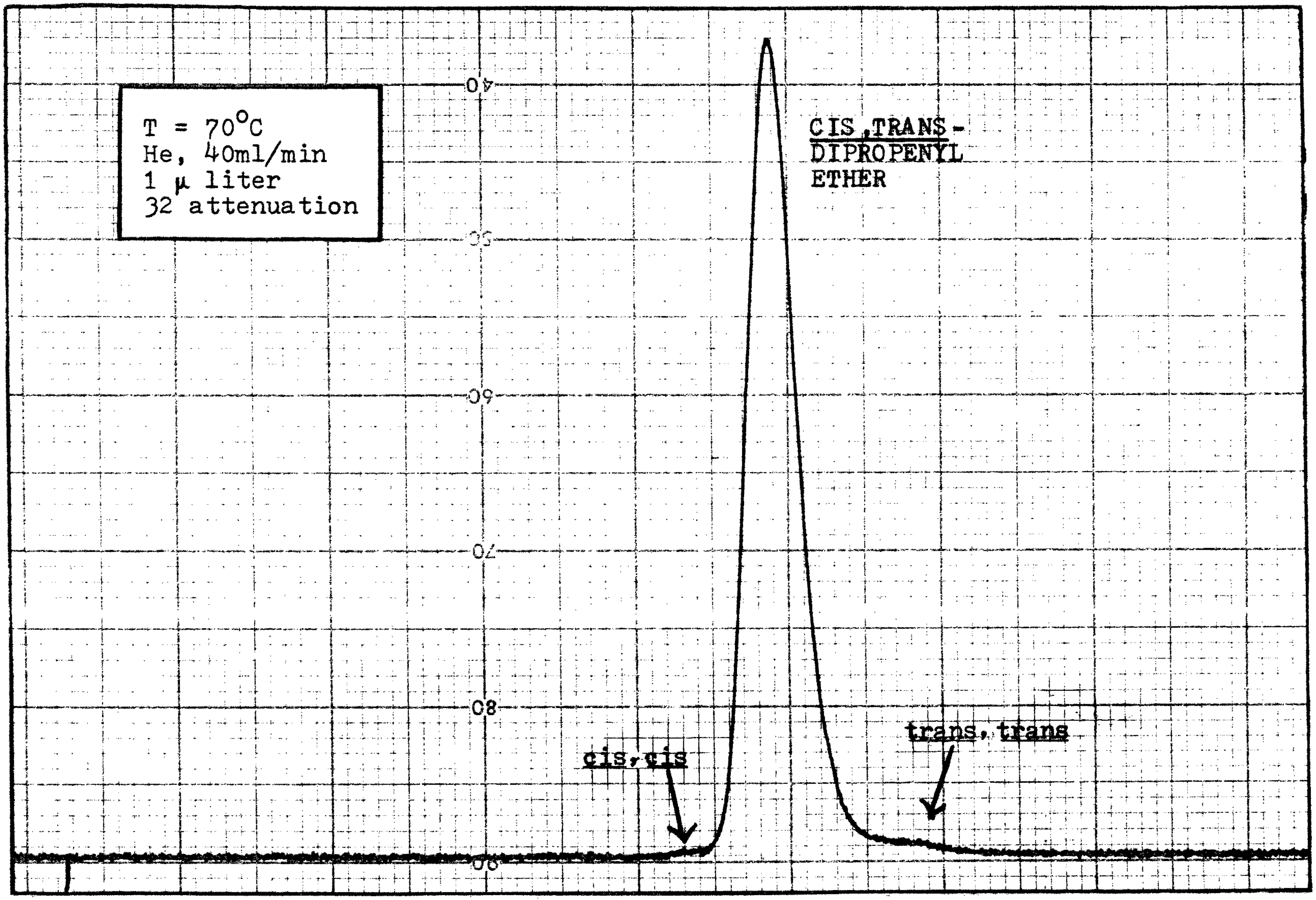


FIGURE 11 G.C. Analysis of Cis,Trans-Dipropenyl Ether

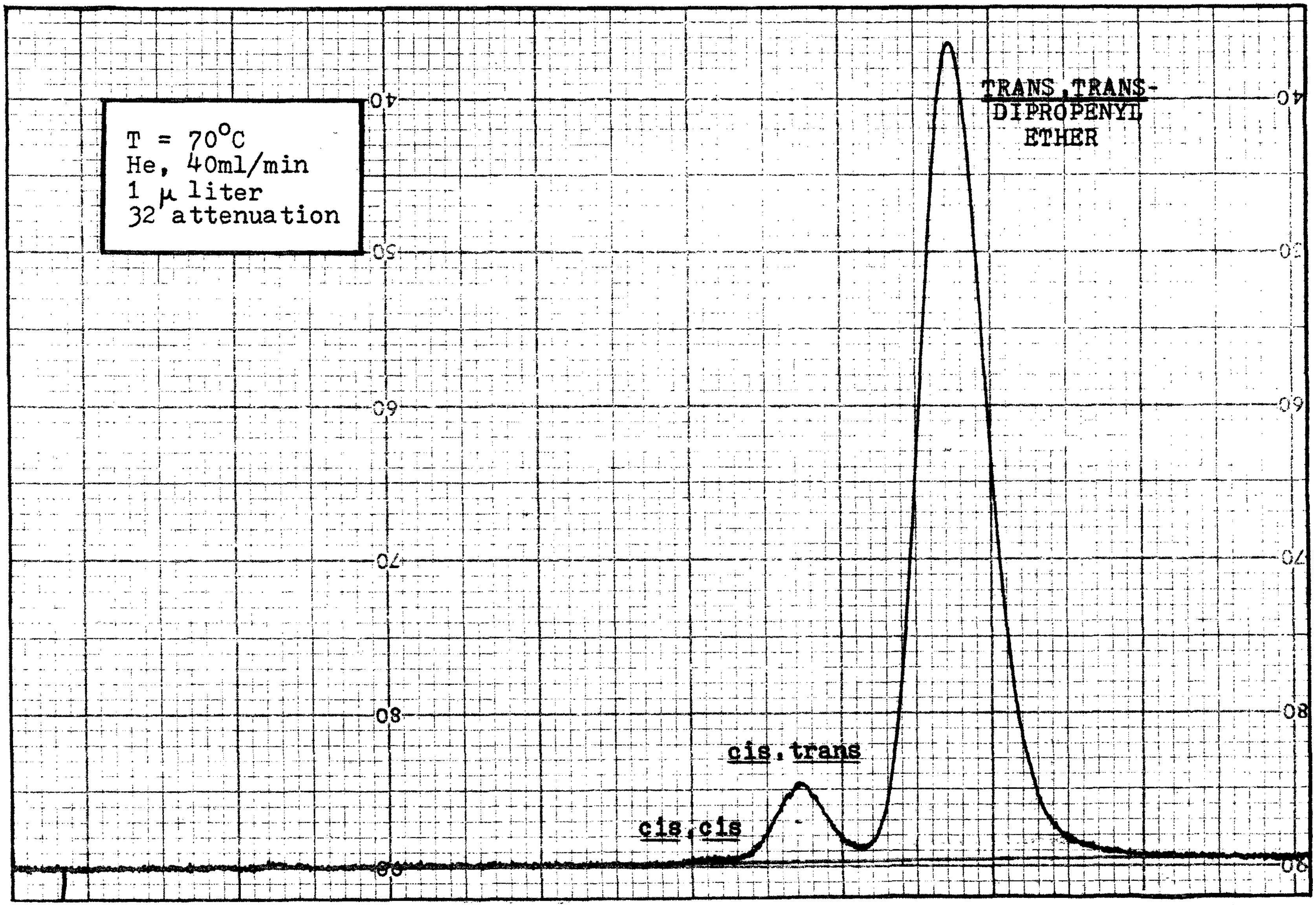


FIGURE 12 G.C. Analysis of Trans,Trans-Dipropenyl Ether

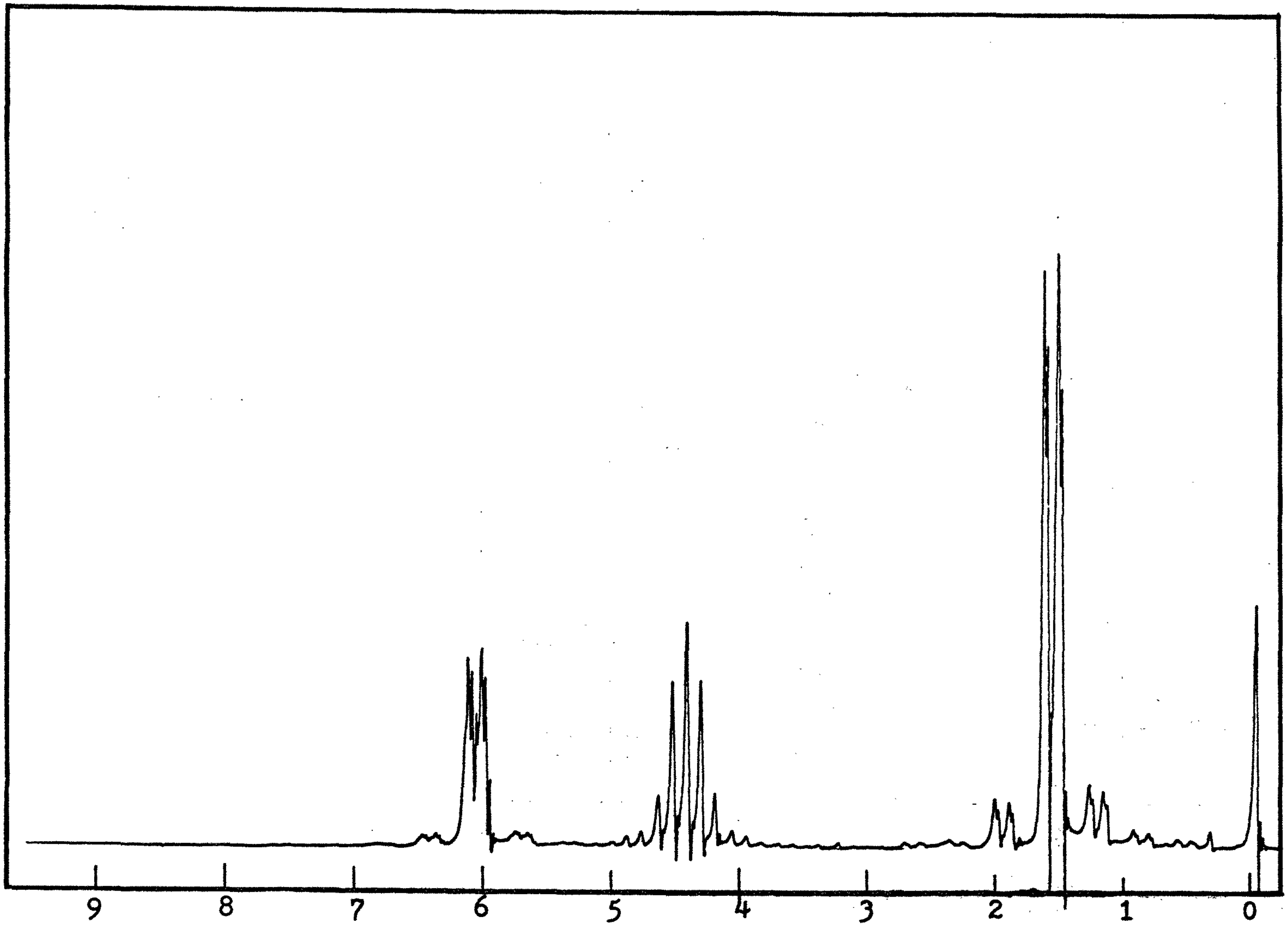


FIGURE 13 Proton NMR of Cis,Cis-Dipropenyl Ether

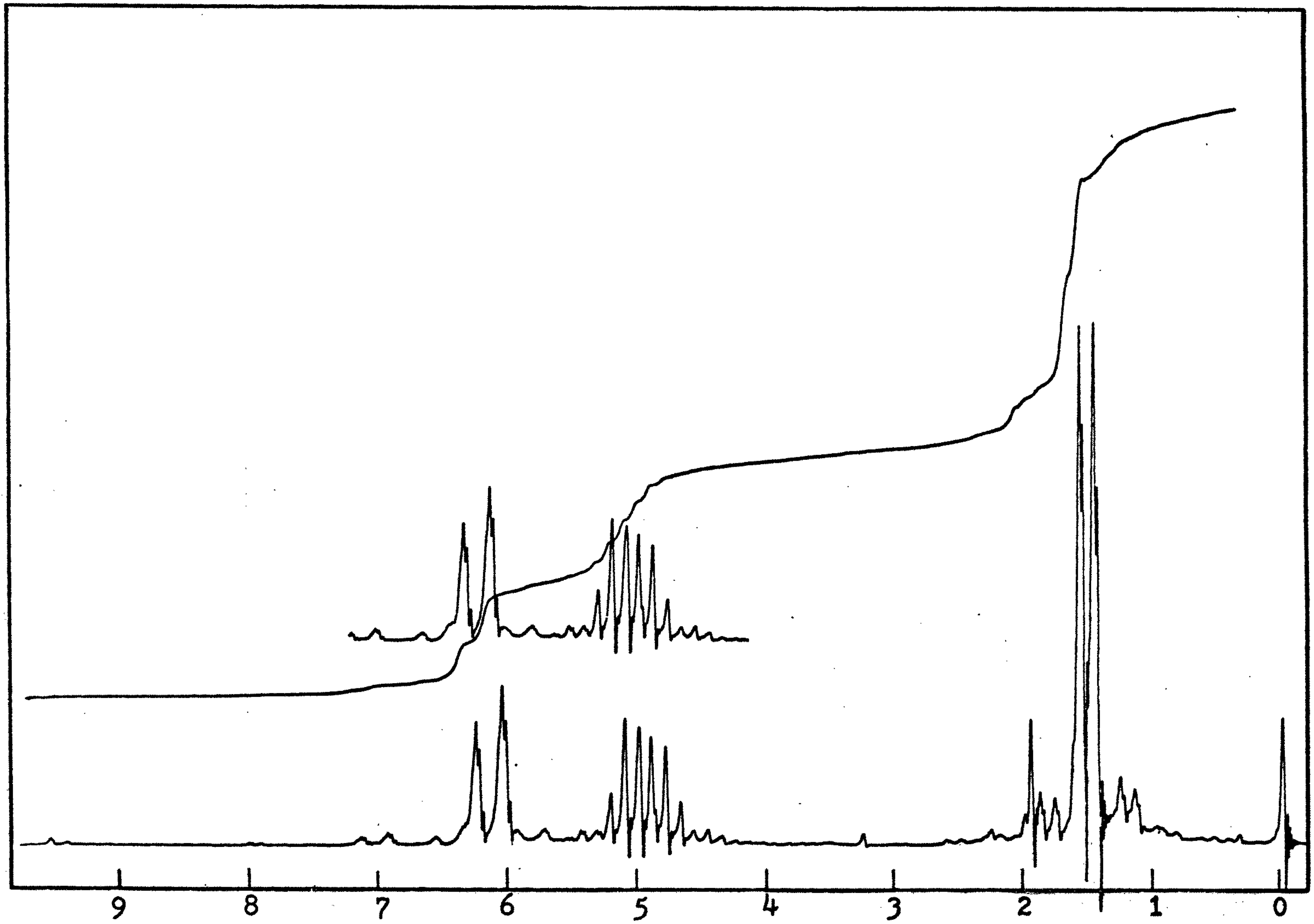


FIGURE 14 Proton NMR of Trans,Trans-Dipropenyl Ether

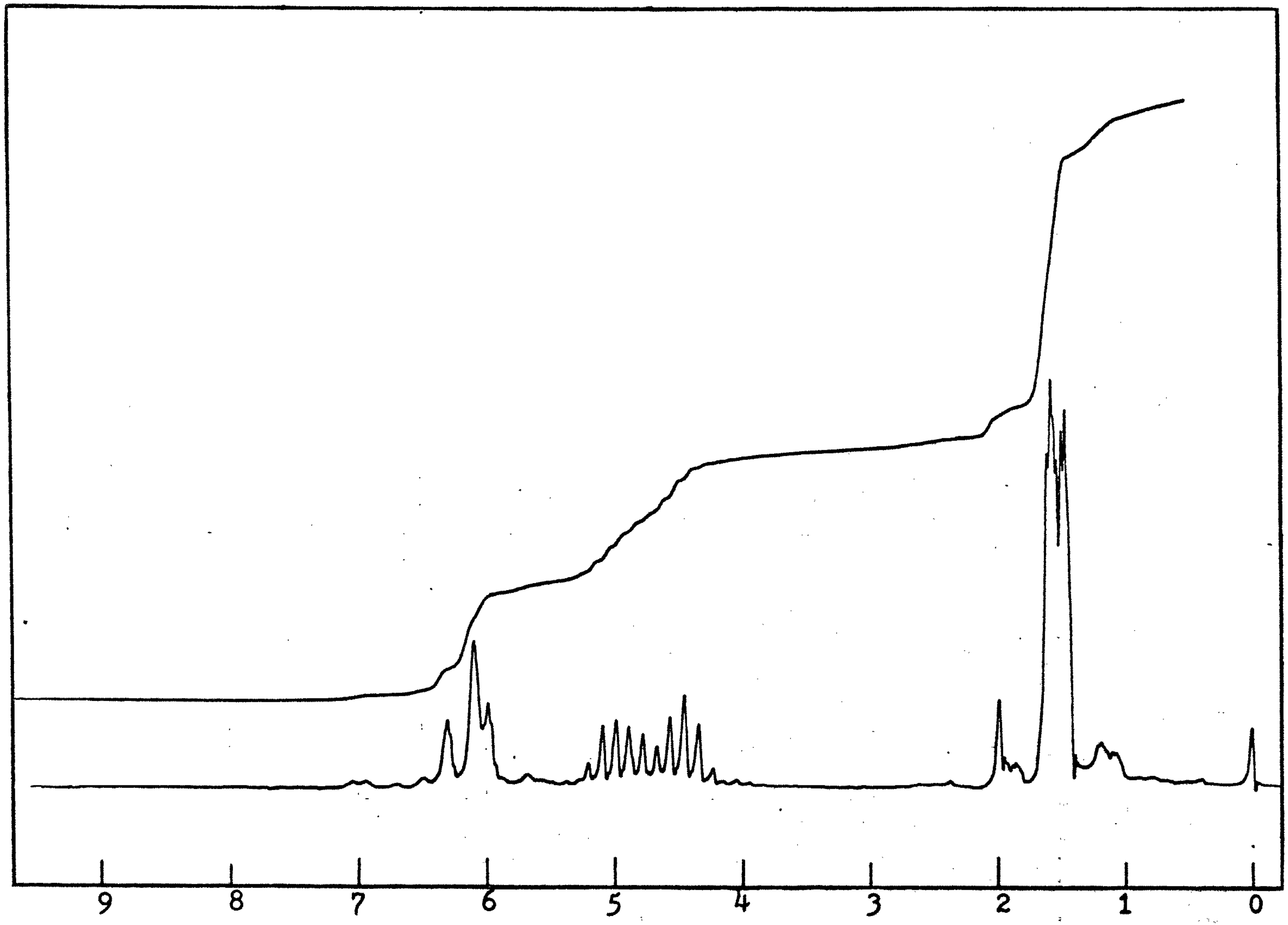


FIGURE 15 Proton NMR of Cis,Trans-Dipropenyl Ether

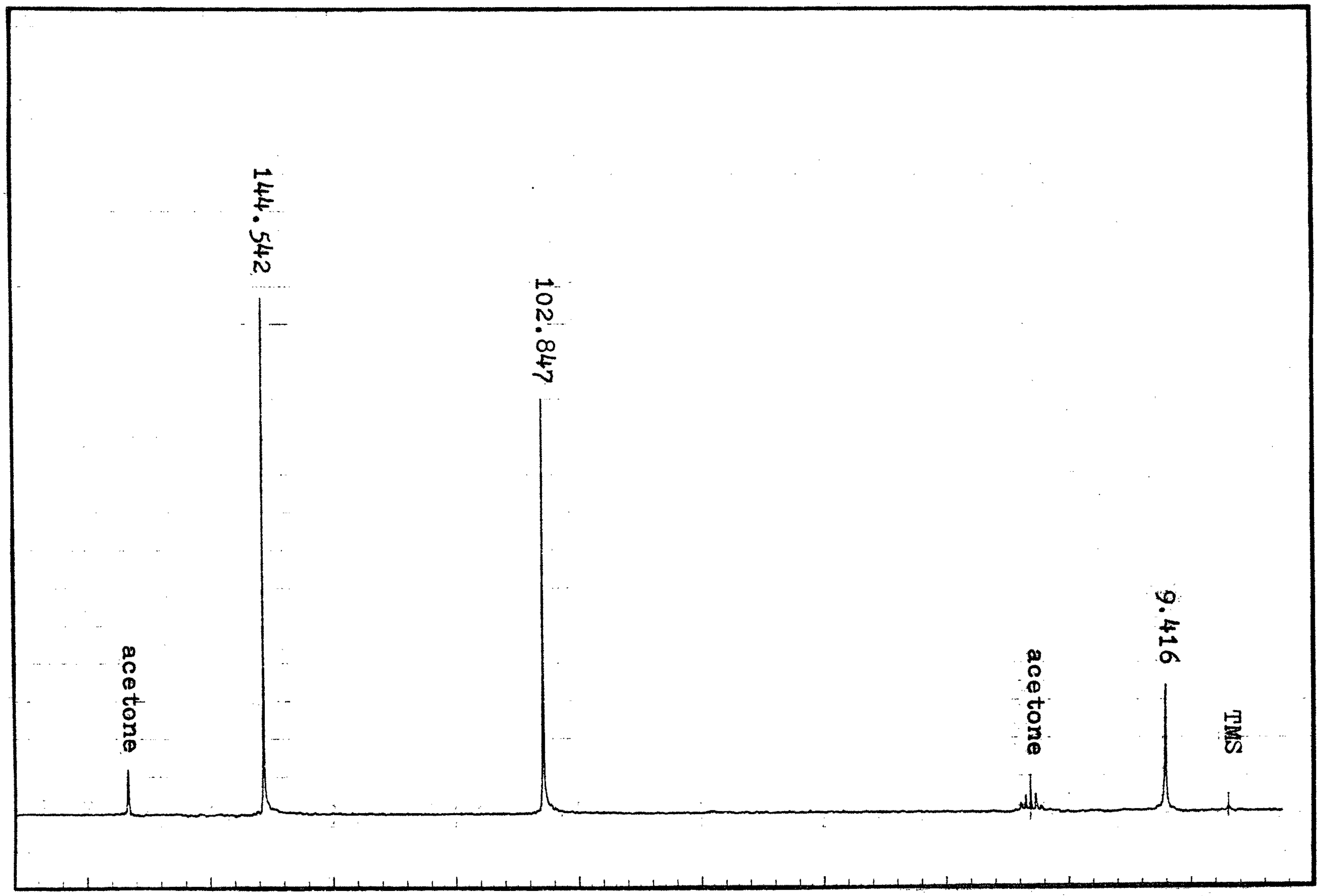


FIGURE 16 C^{13} NMR of Cis,Cis-Dipropenyl Ether

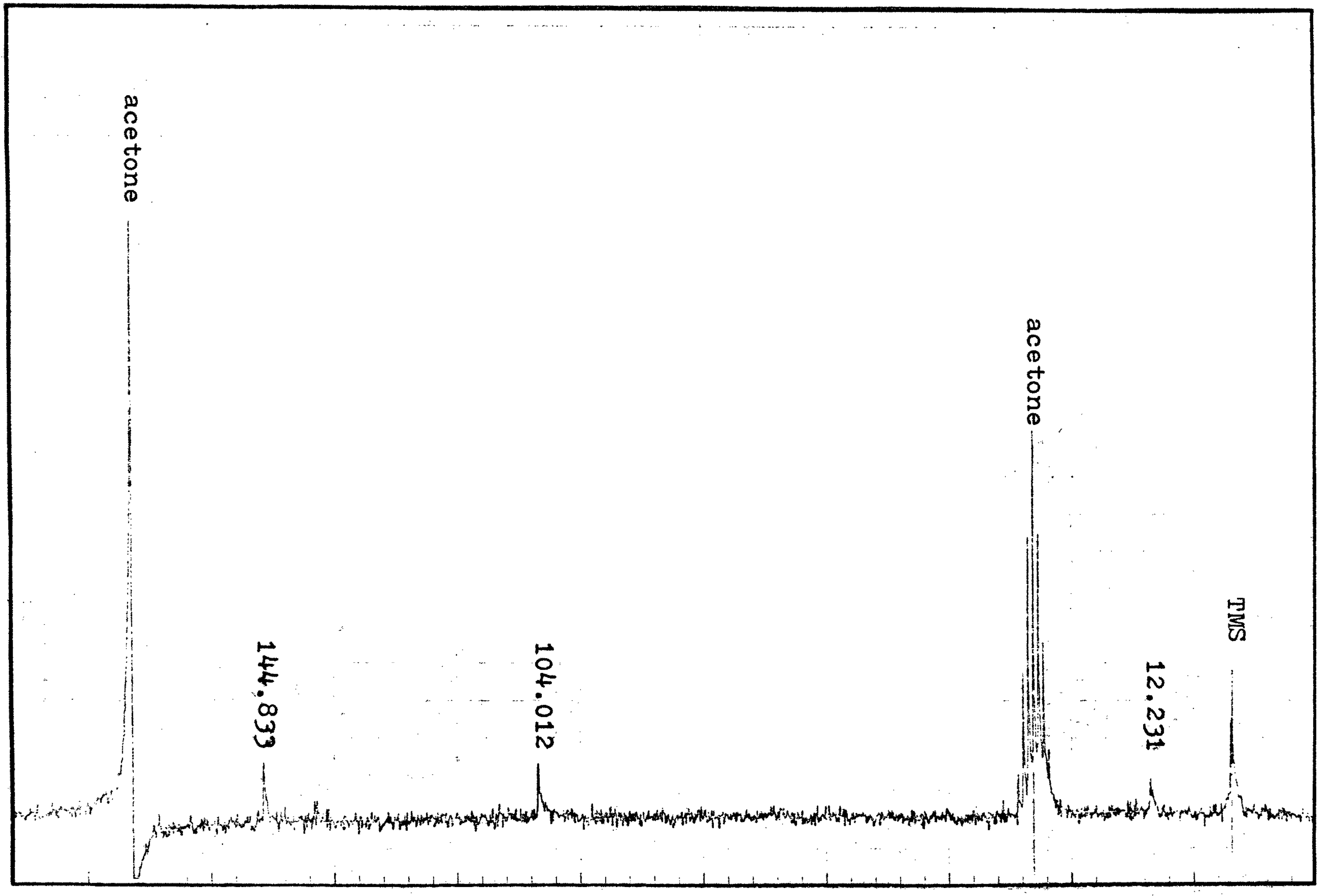


FIGURE 17 C^{13} NMR of Trans,Trans-Dipropenyl Ether

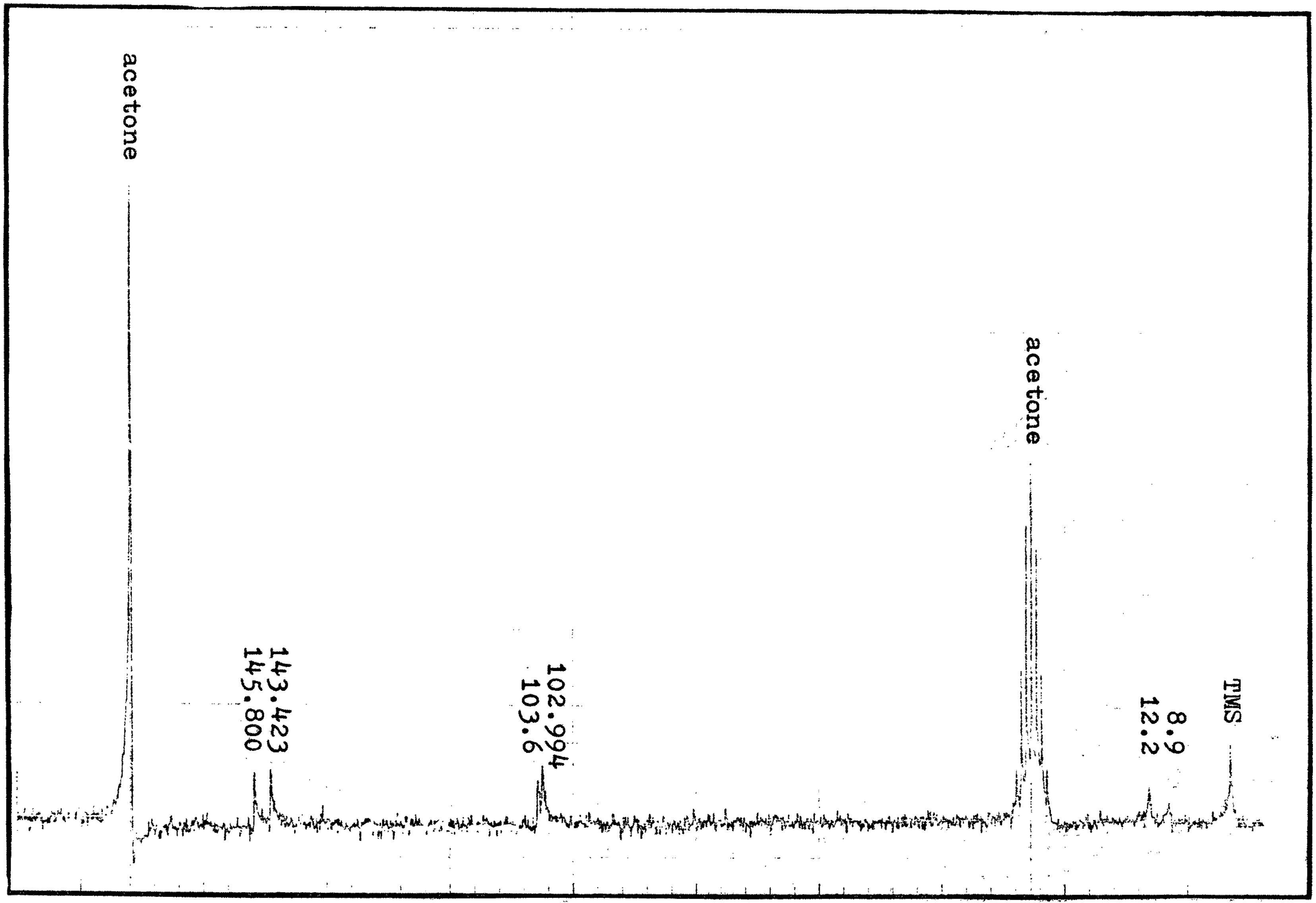
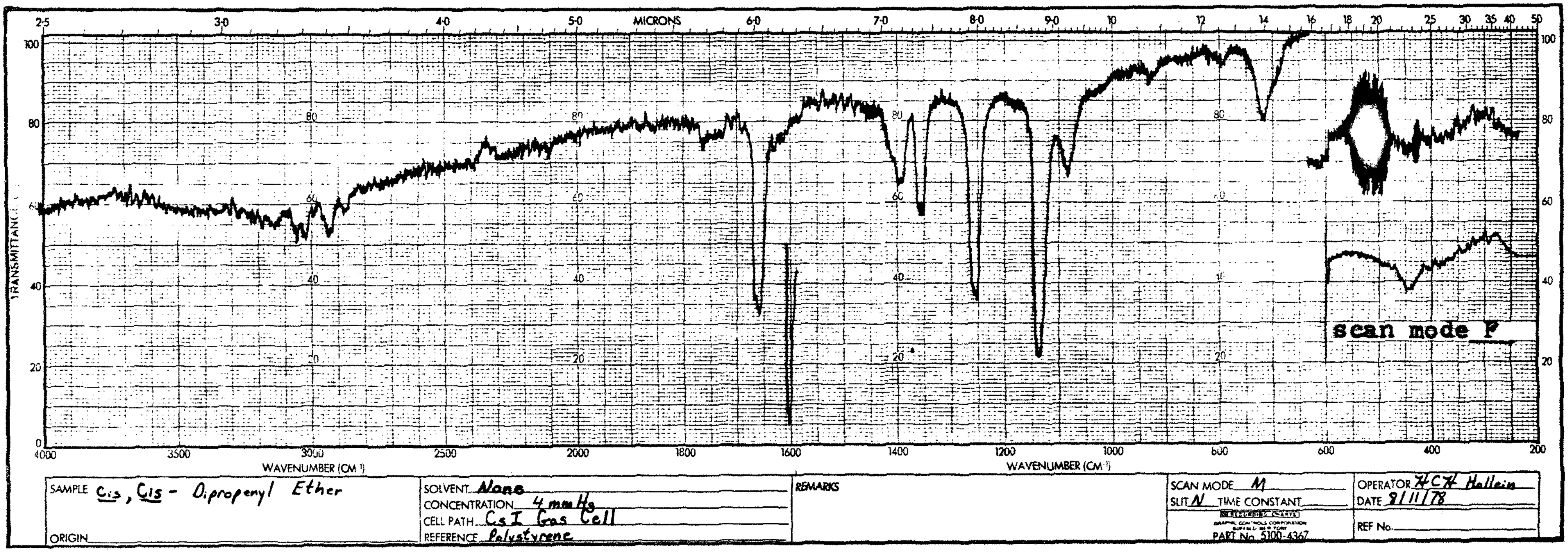


FIGURE 18 C^{13} NMR of Cis,Trans-Dipropenyl Ether



SAMPLE Cis, Cis - Dipropenyl Ether

ORIGIN

SOLVENT None

CONCENTRATION 4 mm Hg

CELL PATH CsI Gas Cell

REFERENCE Polystyrene

REMARKS

SCAN MODE M

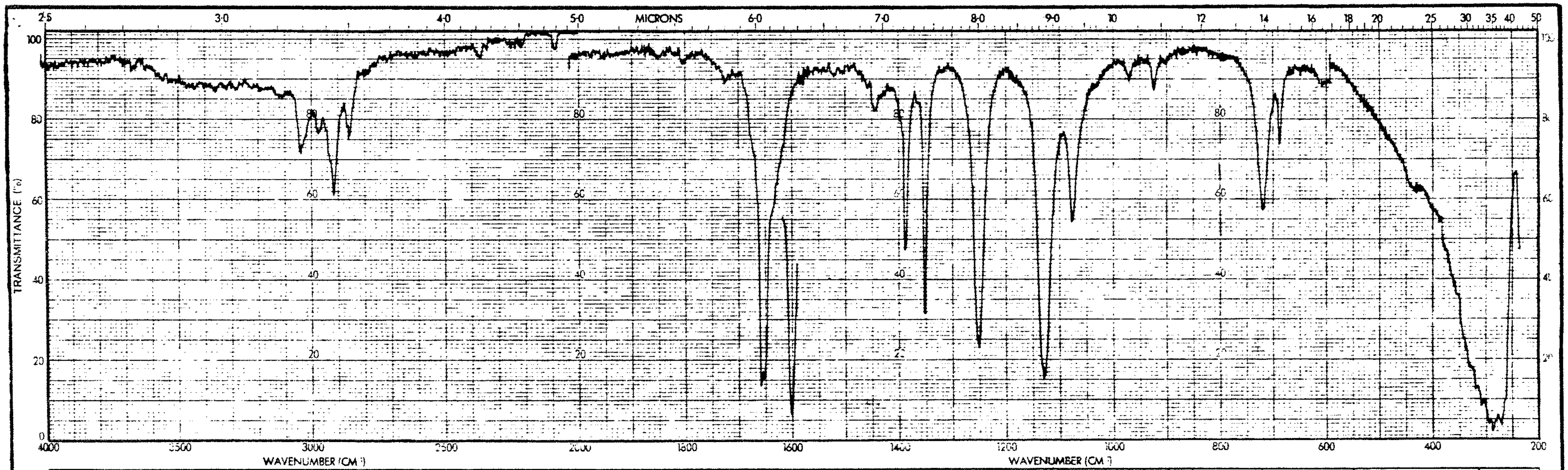
SLIT N TIME CONSTANT

OPERATOR HCH Hallein

DATE 9/11/78

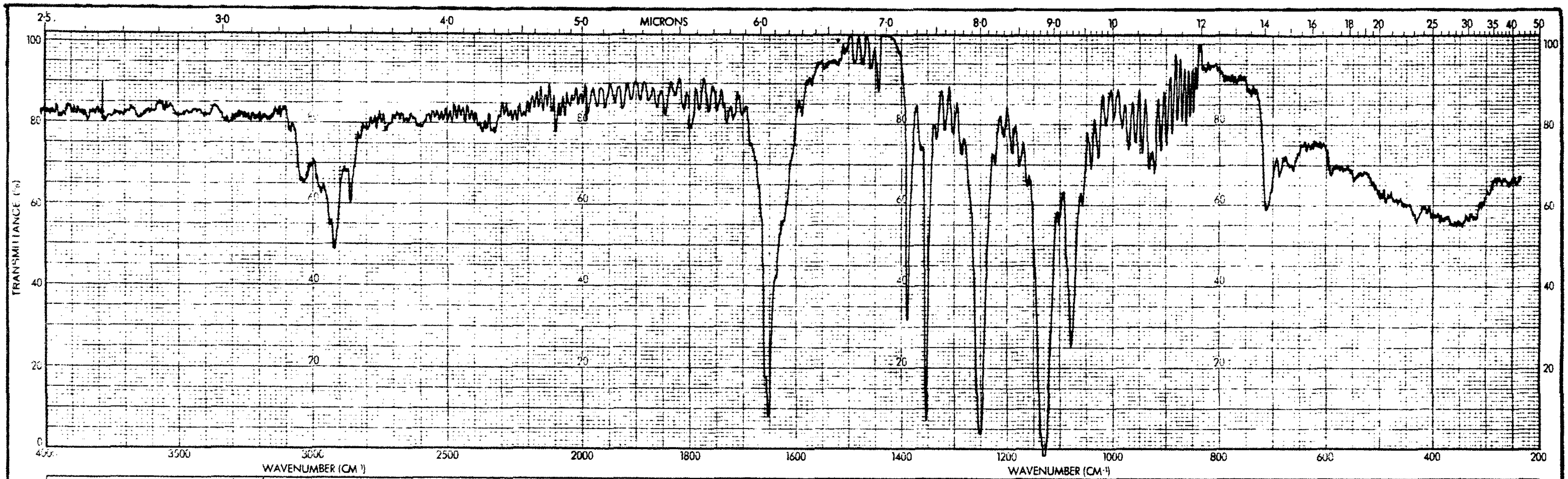
REF No.

FIGURE 19 Vapor-Phase IR Spectra of Cis,Cis-Dipropenyl Ether



SAMPLE *cis, cis - dipropenyl ether*
ORIGIN
SOLVENT *none*
CONCENTRATION
CELL PATH *NaCl crystals*
REFERENCE *Polystyrene @ 1601.8 cm⁻¹*
REMARKS *Polystyrene Correction (+1 cm⁻¹)*
Evaporation
SCAN MODE *Medium*
SLIT *N* TIME CONSTANT
RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO NEW YORK
PART No. 5100-4367
OPERATOR *H. C. Hollem*
DATE *8/9/78*
REF No.

FIGURE 20 Liquid-Phase IR Spectra of Cis,Cis-Dipropenyl Ether



SAMPLE cis,cis-dipropenyl ether

ORIGIN

SOLVENT CCl4

CONCENTRATION 2%

CELL PATH

REFERENCE

REMARKS

SCAN MODE M

SLIT N TIME CONSTANT

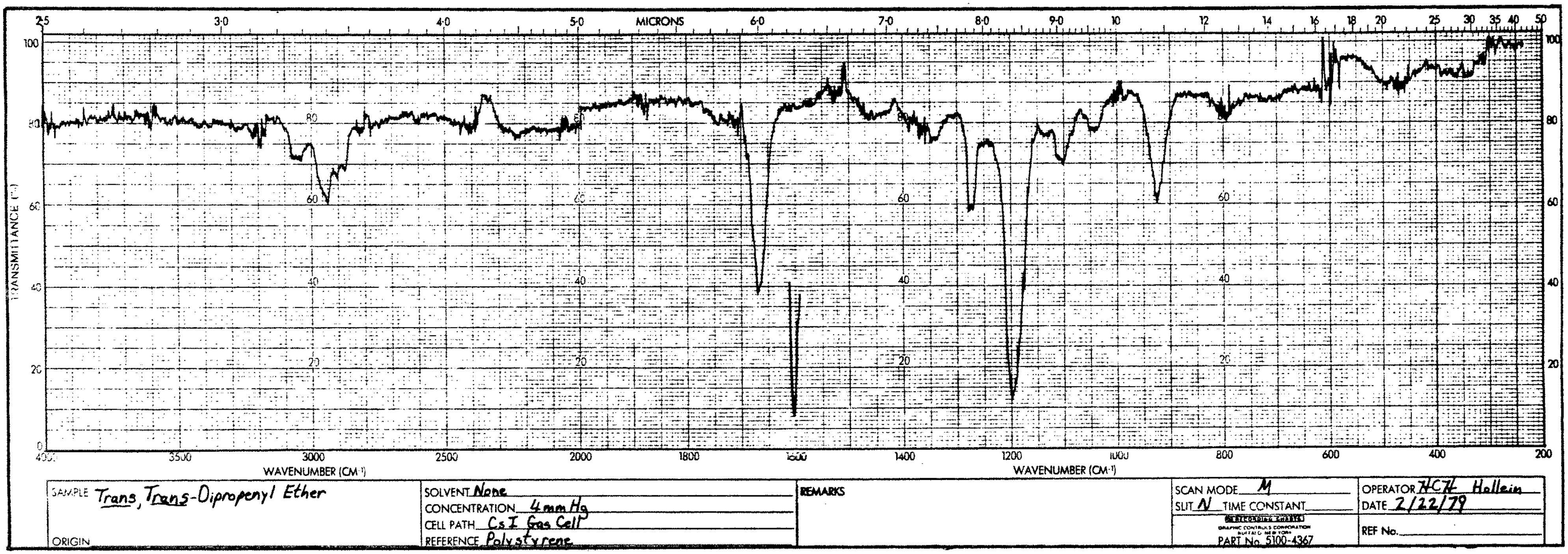
PART No. 5100-4367

OPERATOR HCH Hollein

DATE 8/10/78

REF No.

FIGURE 21 CCl_4 Solution IR Spectra of Cis,Cis-Dipropenyl Ether



SAMPLE Trans, Trans-Dipropenyl Ether

ORIGIN

SOLVENT None

CONCENTRATION 4 mm Hg

CELL PATH Cs I Gas Cell

REFERENCE Polystyrene

SCAN MODE M

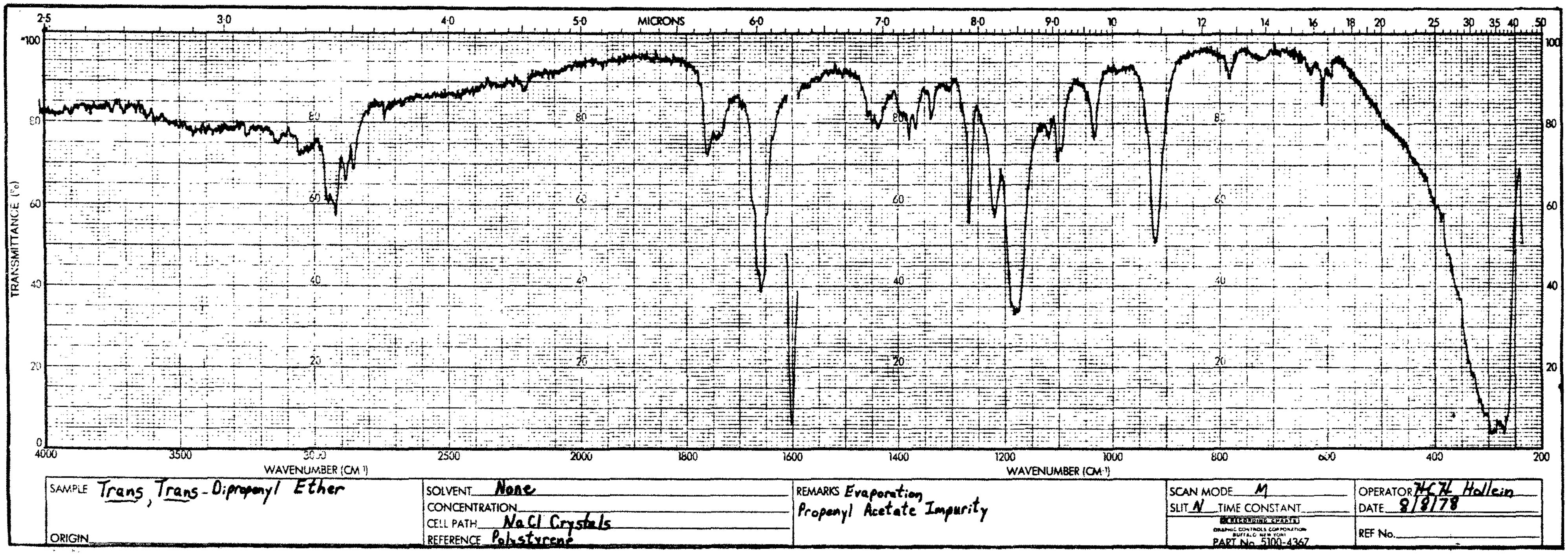
SLIT N TIME CONSTANT

OPERATOR HCH Hollein

DATE 2/22/79

REF No.

FIGURE 22 Vapor-Phase IR Spectra of Trans, Trans-Dipropenyl Ether



SAMPLE Trans, Trans-Dipropenyl Ether

ORIGIN

SOLVENT None

CONCENTRATION

CELL PATH NaCl Crystals

REFERENCE Polystyrene

REMARKS Evaporation
Propenyl Acetate Impurity

SCAN MODE M

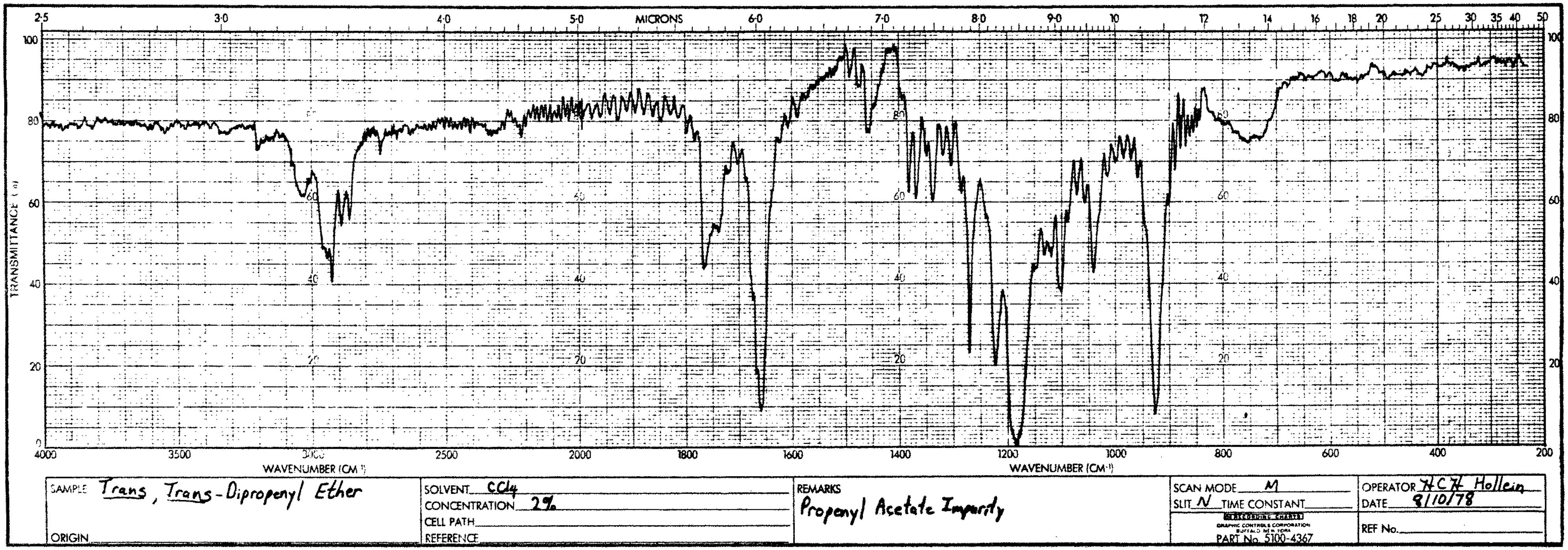
SLIT N TIME CONSTANT

OPERATOR HCH Hollein

DATE 8/8/78

REF No.

FIGURE 23 Liquid-Phase IR Spectra of Trans,Trans-Dipropenyl Ether



SAMPLE Trans, Trans-Dipropenyl Ether

ORIGIN

SOLVENT CCl_4

CONCENTRATION 2%

CELL PATH

REFERENCE

REMARKS Propenyl Acetate Impurity

SCAN MODE M

SLIT N TIME CONSTANT

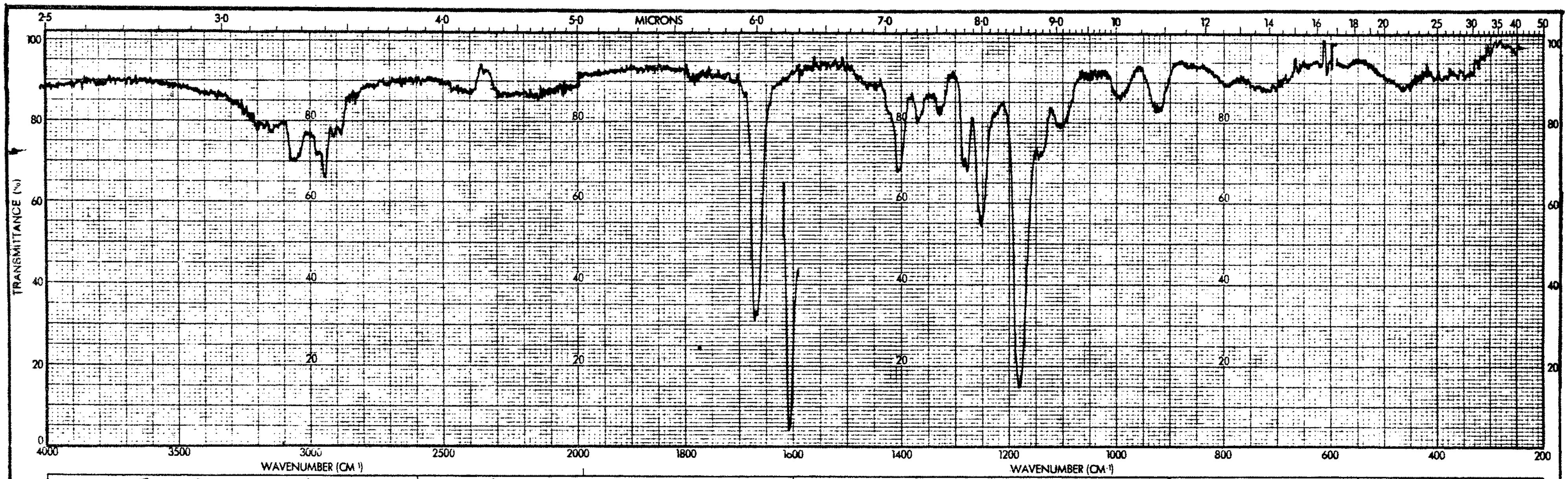
GRAPHIC CONTROLS CORPORATION BUFFALO NEW YORK PART No. 5100-4367

OPERATOR HCH Hollein

DATE 8/10/78

REF No.

FIGURE 24 CCl_4 Solution IR Spectra of Trans,Trans-Dipropenyl Ether



SAMPLE Cis, Trans-Dipropenyl Ether

ORIGIN

SOLVENT None

CONCENTRATION 4mm Hg

CELL PATH CsI Gas Cell

REFERENCE Polystyrene

REMARKS Polystyrene Correction (-5cm⁻¹)

SCAN MODE M

SLIT N TIME CONSTANT

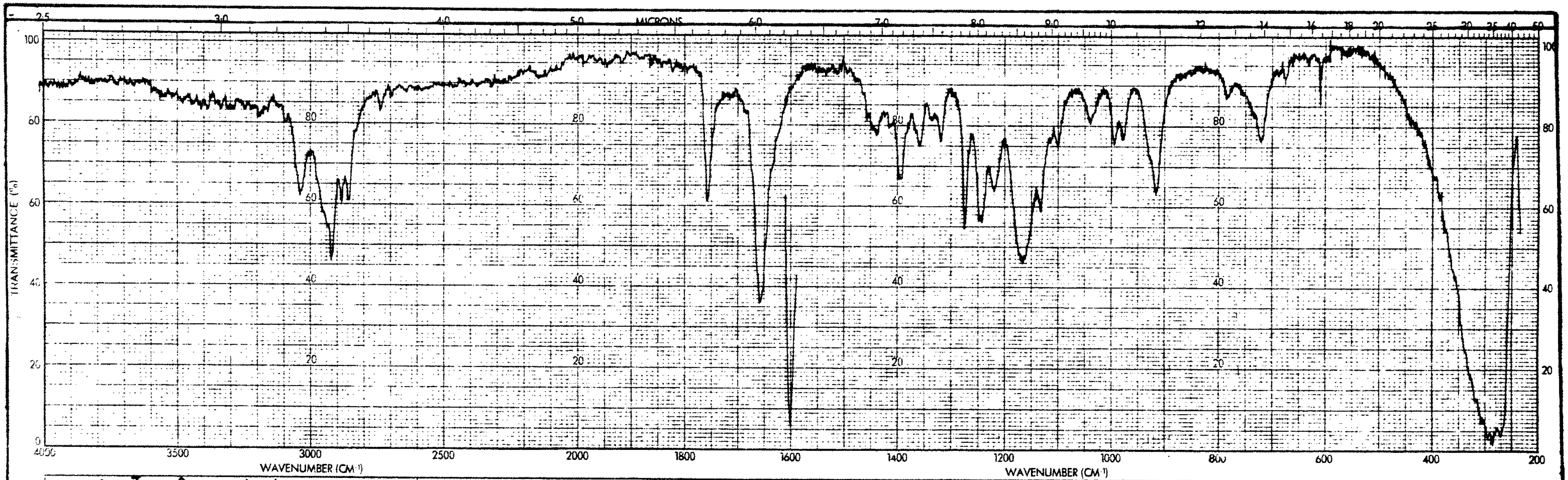
RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO NEW YORK
PART No. 5100-4367

OPERATOR HCH Hellein

DATE 2/16/79

REF No.

FIGURE 25 Vapor-Phase IR Spectra of Cis,Trans-Dipropenyl Ether



SAMPLE Cis, Trans-Dipropenyl Ether
ORIGIN

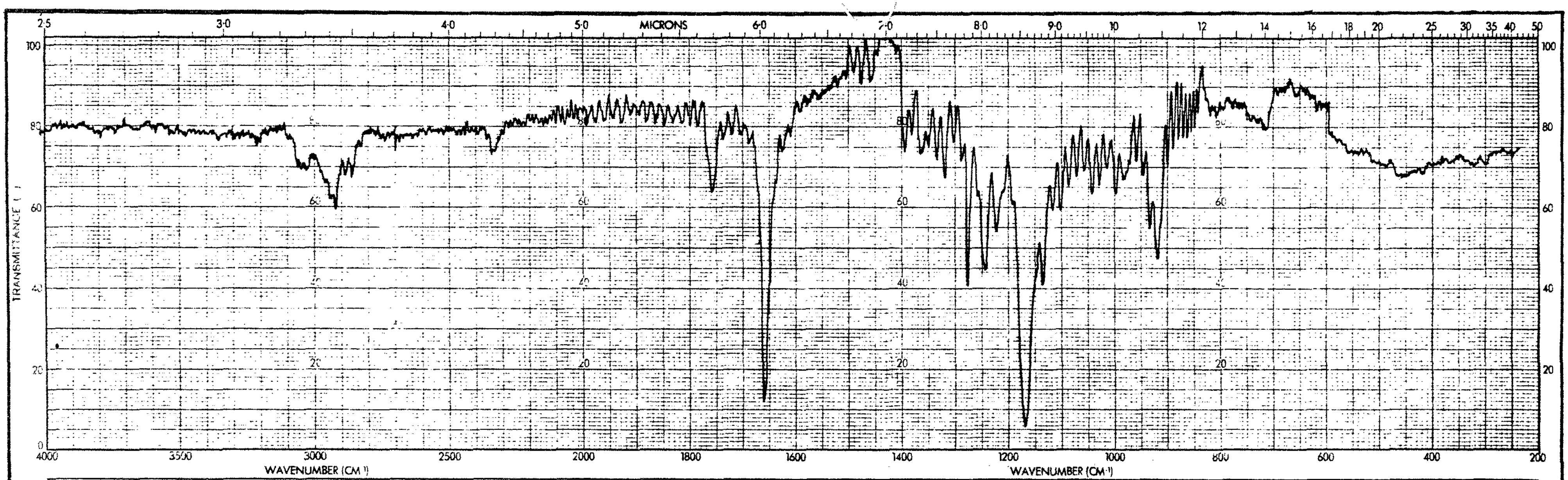
SOLVENT None
CONCENTRATION
CELL PATH Na Cl Crystals
REFERENCE Polystyrene

REMARKS Evaporation
Propenyl Acetate Impurity

SCAN MODE M
SLIT N TIME CONSTANT
RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO NEW YORK
PART No. 5100-4367

OPERATOR HCH Hollein
DATE 8/8/78
REF No.

FIGURE 26 Liquid-Phase IR Spectra of Cis,Trans-Dipropenyl Ether



SAMPLE *cis, trans-dipropenyl ether*
ORIGIN
SOLVENT *CCl4*
CONCENTRATION *2%*
CELL PATH
REFERENCE
REMARKS *Propenyl Acetate Impurity*
SCAN MODE *M*
SLIT *N* TIME CONSTANT
PART No. 5100-4367
OPERATOR *HCH Hollein*
DATE *8/10/78*
REF No.

FIGURE 27 CCl$_4$ Solution IR Spectra of Cis,Trans-Dipropenyl Ether

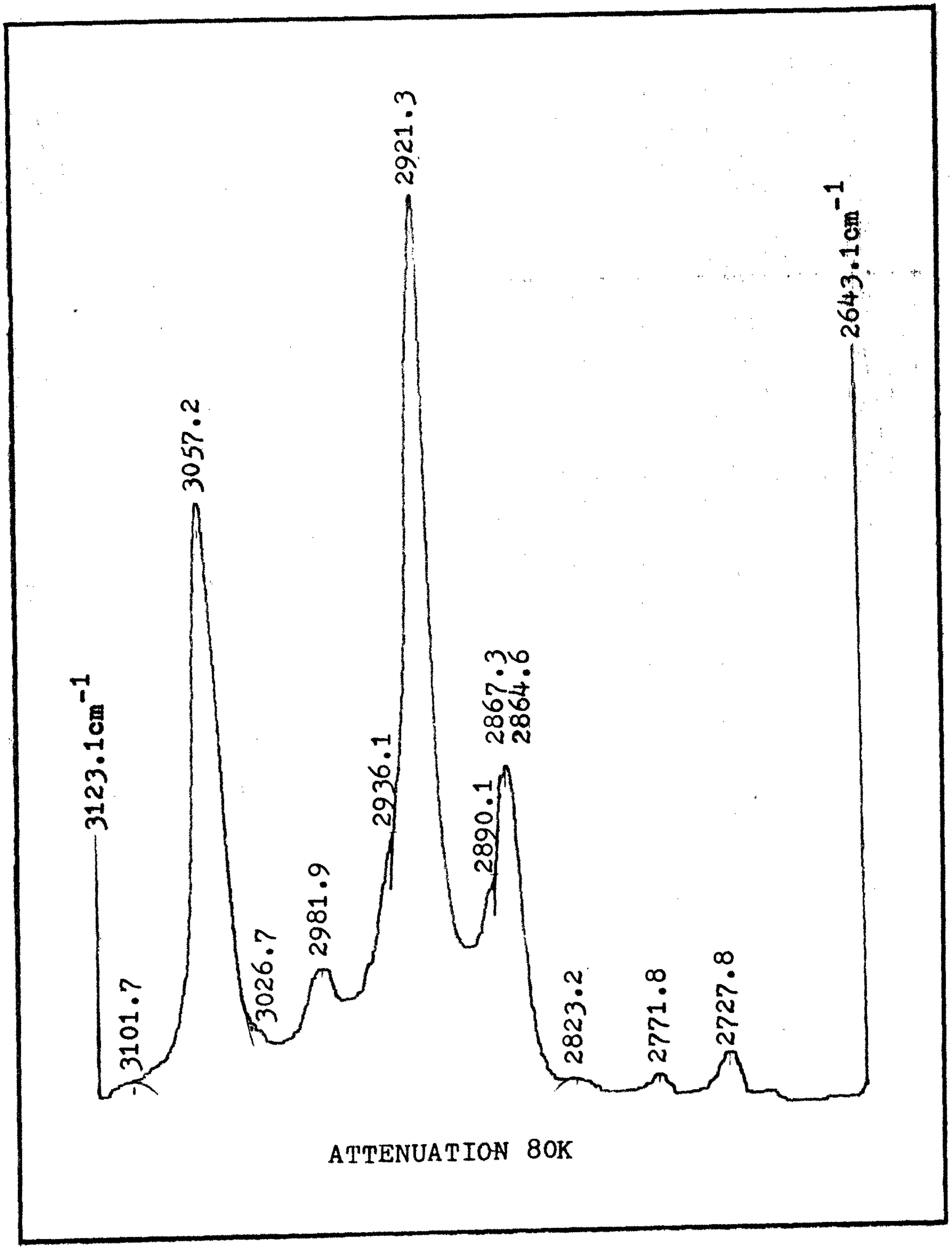


FIGURE 28

Raman C-H Stretching Region for Cis,Cis-Dipropenyl Ether

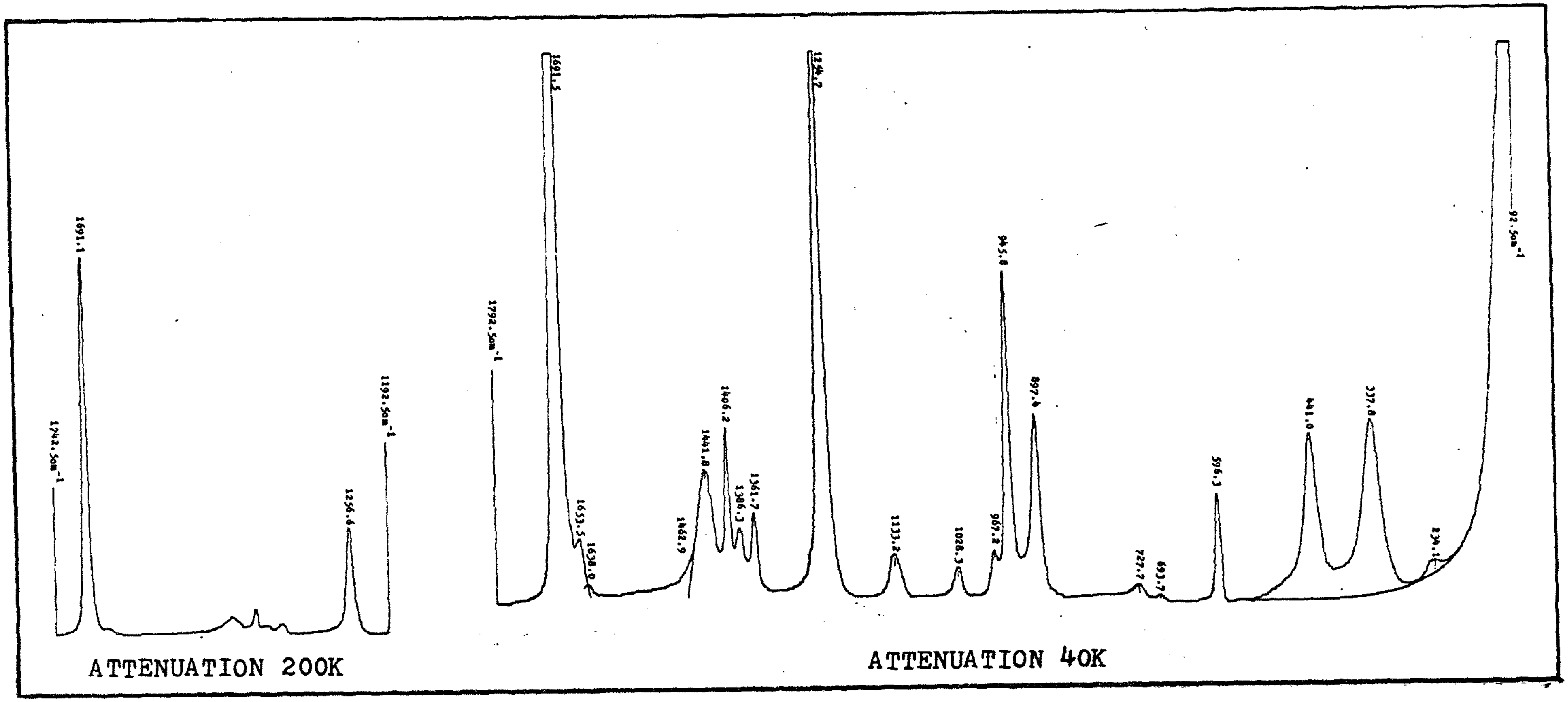


FIGURE 29 Raman Spectra of Cis,Cis-Dipropenyl Ether

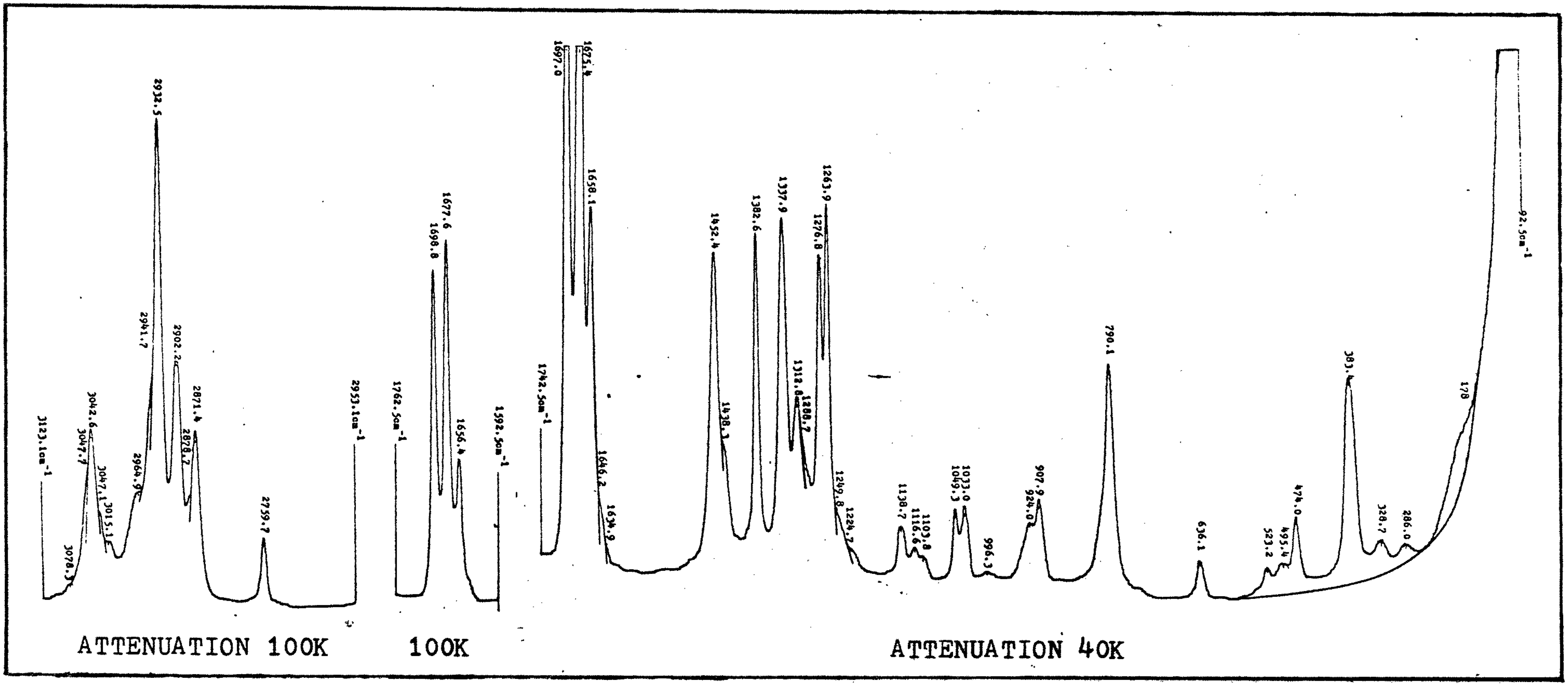


FIGURE 30 Raman Spectra of Trans,Trans-Dipropenyl Ether

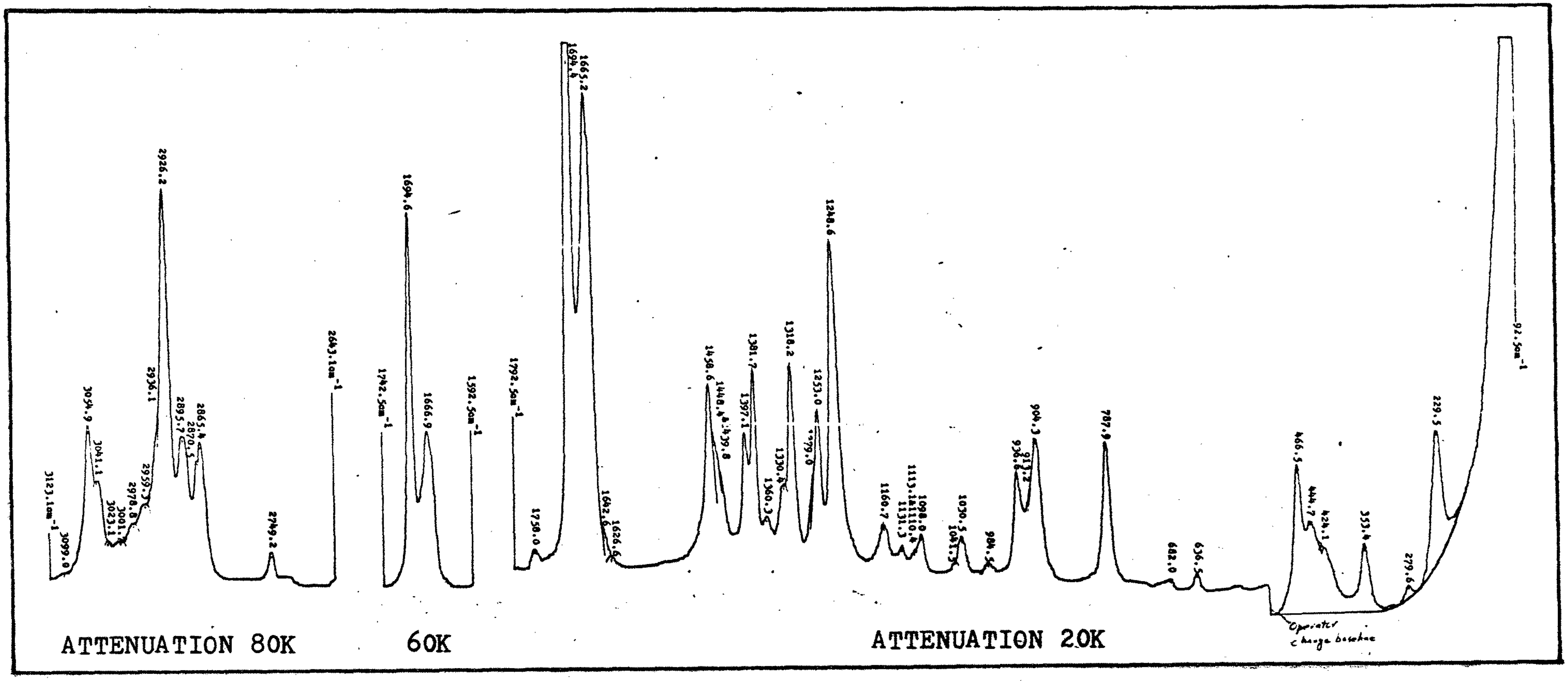


FIGURE 31 Raman Spectra of Cis,Trans-Dipropenyl Ether

XIII . REFERENCES

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