POTASSIUM t-BUTOXIDE-INITIATED ELIMINATION ON SUBSTRATE 1,1,2-TRIMETHOXYETHANE

BY

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FACULTY COMMITTEE

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ABSTRACT

1-bromo-2,2-dimethoxyethane (I) was prepared in 68% yield from the addition of bromine to a solution of vinyl acetate and methanol. A Williamson ether synthesis, using sodium methoxide in methanol and I, gave 1,1,2-trimethoxyethane (II) in 48% yield. The compound (II) was the desired substrate for elimination reactions because it contains poor leaving alkoxide groups.

Many different reactions were investigated to convert II into 1,2-dimethoxyethylene. Among these were pyrolysis, acid catalyzed eliminations, and base initiated elimination reactions.

Best results were obtained using a bomb reactor, compound II as substrate, and potassium t-butoxide as the base. From this reaction, tertiary-butyl methyl ether, tertiary-butanol, cis-1,2-dimethoxyethylene and trans-1,2-dimethoxyethylene were isolated by preparative gas chromatography and identified as end products.

A combination of elemental analysis, chemical tests, infrared spectroscopy, analytical gas chromatography, and nuclear magnetic resonance spectroscopy, prove conclusively and unambiguously the structures of the final products.

An interesting analogy of the NMR spectra of cis-and-trans-1,2-dimethoxyethylene is made with the NMR spectra of cis-and-trans-1,2-difluoroethylene.

ACKNOWLEDGEMENT

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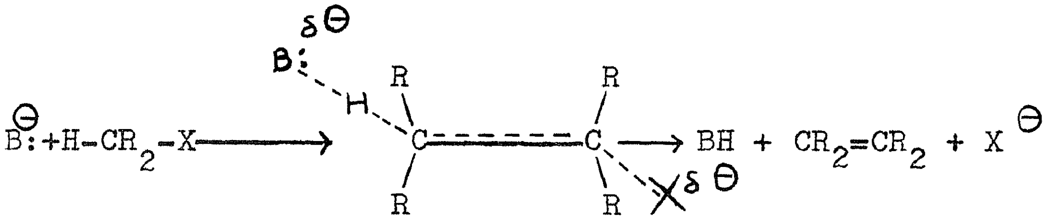
INTRODUCTION

Base-initiated elimination reactions are generally *trans*-eliminations in which the activated complex in the reaction adopts a conformation with the departing nucleophile as far removed as possible from the proton being abstracted by the base.



where R = H, alkyl, etc.

The overwhelming predominance of *trans*-eliminations is not completely understood. Electrostatic effects, energy effects, and eclipsing effects are sometimes given as an explanation.(46)

In order to verify experimentally whether an elimination reaction has proceeded by a *cis*-or *trans*-mechanism, the substrate under consideration must have two adjacent asymetric carbon atoms and therefore exist in the optically active *d*, *l*, or *meso*-form. *Threo*-and *erythro*-modifications will also suffice.

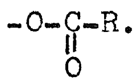
There has been some interesting work done(15,16,44) on optically active tosylates, quaternary ammonium salts, and ketones which showed that the bimolecular elimination reactions investigated proceeded via a trans-elimination mechanism.

Some cis-elimination reactions have also been studied. They usually involve a cyclic carbanion mechanism.(13,58) In non cyclic systems, cis-elimination was observed in most ester and xanthate substrates(17,18) which underwent vapor phase elimination reactions during pyrolysis.(20) In the pyrolytic cis-eliminations the mechanism is believed to involve an intramolecular cyclic transition state.(7,26)

1,1,2-trimethoxyethane was prepared to investigate the elimination reaction of a substrate with poor leaving methoxide groups. One of the products of the elimination reaction, 1,2-dimethoxyethylene, is an important intermediate for the preparation of 1,2-dideutero-1,2-dimethoxyethane. This optically active substrate can be used for investigating stereoselective elimination reactions.

THEORY & BACKGROUND

Elimination reactions can be classified into two groups known as alpha-and beta-eliminations. In alpha-eliminations the proton and leaving group (X) are detached from the same carbon atom. In the far more usual beta-elimination reactions, atoms are lost from adjacent carbons. The substituent X (leaving group) is usually a halide ion, water, $-NR_3$, $-SR_2$ or



$-O-\overset{}{\underset{\underset{O}{\|}}{C}}-R$.

The kinetics and mechanisms of elimination reactions are well defined in the literature.(6,24,35,38) Elimination reactions are usually unimolecular or bimolecular. The symbolism used to denote the different types of eliminations was founded by Ingold in 1927, when he initiated the mechanistic study of elimination reactions.(32)

Many acid-catalyzed dehydrations of alcohols proceed by a unimolecular elimination designated as E1. In 1935, Hughes(36) found the rate determining step to be the ionization of the substrate to form a carbonium ion followed by a rapid removal of the proton.

Bimolecular base-initiated eliminations can proceed by two mechanisms designated as E1cB and E2. The E1cB mechanism is very uncommon. It involves the conjugate base of the substrate.(6) The rate determining step is the abstraction of a proton by a base. The more common E2 mechanism is consistent with second order kinetics (first order in substrate and first order in base). The usual steric requirement for E2 reactions is that the electrons from the beta-carbon-hydrogen bond should enter the octet on the alpha-carbon on the opposite side to the leaving group electrons.(12,59) This minimizes the repulsion energy between the electron pairs (in a manner analogous to that occurring in the Walden Inversion) and results in a trans-elimination. A cis-elimination may appear in acyclic structures when the trans-conformation for E2 reactions cannot be attained owing to steric hindrance caused by large, bulky groups.

Many of the conditions which favor bimolecular elimination also promote bimolecular nucleophilic substitution reactions; thus the reactions often occur together. However, by a proper choice of reaction conditions one process can be favored almost to the exclusion of the other. For instance, when the activation energy is greater for E2 reactions than SN2 reactions, higher temperatures favor the elimination. This is the case for primary halides. However, for tertiary halides the reverse is true. They do not react at all by SN2 processes because the energy of activation is too high.

Bimolecular elimination is facilitated at the expense of substitution by: a) branching at either the alpha-or *beta*-carbon atom, b) the action of strong bases at high concentration, c) nonpolar solvents and, d) high temperatures.

EXPERIMENTAL

I. Preparation of 1-Bromo-2,2-Dimethoxyethane (I) by Liquid Addition of Bromine.(30,45)

Bromine was diluted with chloroform to stop the bromine from freezing in the dropping funnel since the reaction was carried out at -40°C. The volume of chloroform used was approximately 2.5 times the volume of bromine. The quantities were:

1.5g-moles of bromine= 240 grams = 77cc bromine
200cc chloroform
1.5g-moles of vinyl acetate = 129 grams
7.4g-moles of methanol = 300cc

Vinyl acetate and methanol were added to a three neck one liter reaction flask. A bromine solution was added dropwise over a three-hour period with constant stirring. The reaction mixture was kept at -40°C during the bromine addition by immersing the flask in a Dry Ice-acetone Dewar. After the addition was complete the reaction mixture was allowed to stand 4-5 days before it was worked up.

After the reaction mixture stood 5 days, the contents were poured into an equal volume of ice water. If an emulsion forms at this time, hydrated sodium sulphate is added (188 grams per liter of ice water).

The product separated as an oil. The water layer was extracted several times with small quantities of ether (approximately 1/5 volume of ether per volume of water).

The ether solution was washed twice with cold water (60cc of water per mole of reactant). It was then washed with cold sodium carbonate solution (8-10%) until the ether layer showed no acidity to moist litmus paper. It was then treated with a final cold water wash to remove salt impurities.

The two fractions were added together and dried twice over anhydrous calcium chloride for 30 minute periods. Five grams of calcium chloride were used per mole of reactant.

The final product was purified by distillation on a Todd column. A low boiling azeotrope (29°C/760mmHg) of methylacetate and diethylether was removed first. Chloroform, diethylether and methanol were all removed at atmospheric pressure whereas the final acetal was fractionated under vacuum (15-20mmHg) at a 25 to 1 reflux ratio.

Purified I boils at 49.5°C/18mmHg. The yield was 134 grams or 53% of theory based on vinyl acetate.

Other runs were performed in the same way and yields as high as 68% were obtained.

An alternate method in the preparation of I was used.

This incorporated the addition of bromine vapor directly which eliminated the dilution with chloroform and therefore simplified the purification.

Bromine was added as a vapor diluted in dry air which was pulled over with an aspirator. A two liter three neck flask was employed with an adapter. The vessel was stirred and contained a gas inlet, gas outlet, and thermometer. The quantities were:

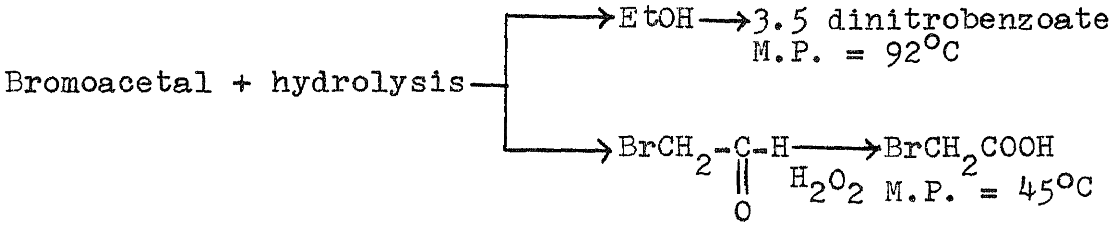
4g-moles of bromine = 640 grams = 205cc
4g-moles of vinyl acetate = 344 grams
20g-moles of methanol = 810cc

The bromine froze in the gas sparger when the reaction mixture was kept at $-40^{\circ}C$; therefore, the temperature was maintained between -5° to $-10^{\circ}C$ which allowed the bromine to go in freely.

The addition time took 13 hours to vaporize all of the bromine. The reaction mixture was allowed to stand five days and was worked up as described previously. A 50% yield based on vinyl acetate was obtained.

Bromoacetal (I) is a strong lachrymator and was handled in a hood at all times.

The acetal can be characterized by hydrolysis and the end products identified.



$$\text{Bromoacetal + hydrolysis} \begin{cases} \rightarrow \text{EtOH} \rightarrow \text{3.5 dinitrobenzoate, M.P.} = 92^{\circ}\text{C} \\ \rightarrow BrCH_2\text{-}\underset{\overset{\|}{O}}{C}\text{-}H \xrightarrow[H_2O_2]{} BrCH_2COOH \quad \text{M.P.} = 45^{\circ}\text{C} \end{cases}$$

II. Preparation of 1,1,2-Trimethoxyethane (II)(55)

Sodium was added slowly to absolute methanol under a nitrogen atmosphere to give the desired sodium methoxide. The quantities were:

200 grams of bromodimethylacetal = 1.185g-moles

31.4 grams of sodium = 1.365g-atoms (15% excess)

280cc of methanol = 6.8g-moles

A 5:1 molar ratio of methanol to sodium was used. Lower ratios were tried but the reaction was too slow and not all of the $NaOCH_3$ went into solution.

An excess of $NaOCH_3$ was used to insure 100% conversion of I, since unreacted bromoacetal would have to be treated with sodium and refluxed to destroy the bromo compound.

The reaction was performed in a three neck flask with stirring and with a constant flow of nitrogen flowing through the system to maintain dryness. The nitrogen rate was determined by a bubble counter.

Bromoacetal was added dropwise to a methanol-sodium methoxide solution. The mixture was refluxed slowly for

48-72 hours.

The reaction mixture was worked up as follows: The organic liquid was decanted from the sodium bromide. The sodium bromide was dissolved in water and extracted 4-5 times with ether to take out the residual organic which adhered to the sodium bromide.

The ether portions were added to the organic layer and dried with two portions of anhydrous calcium chloride for 1-2 hours. The mixture was distilled at atmospheric pressure to remove diethyl ether and methanol. The remaining liquid was fractionated under vacuum on a Todd column with a 10:1 reflux ratio. The boiling point of the purified 1,1,2-trimethoxyethane was 39°C/22mm Hg. A yield of 68 grams was obtained which is 48% of theory based on bromoacetal (I). The product (II) was stored over sodium ribbon for future use.

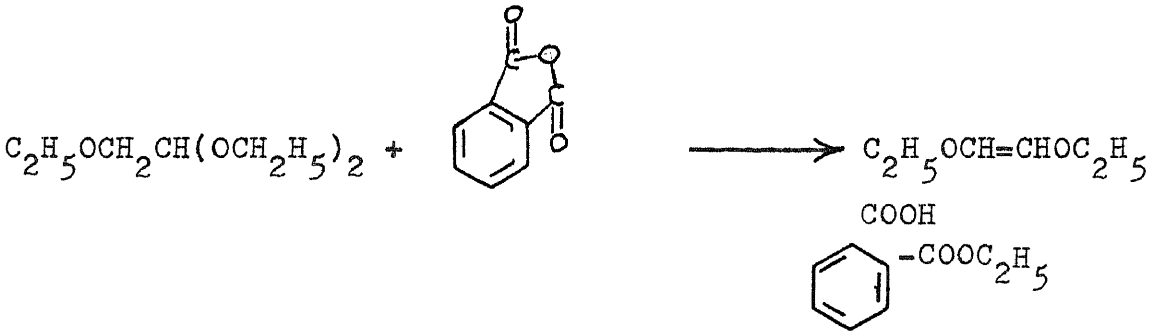
A Beilstein copper wire halogen test (green flame) was used for the final product and was negative. Since I was not found in the distillate, refluxing with sodium was unnecessary.

Gas chromatography showed that the purity was greater than 99%. Three other runs were made with the same results as given above. Commercially available sodium methoxide was used as an alternative but was found to be ineffective and impure.

III. Attempted Synthesis of 1,2-Dimethoxyethylene Using Alkoxyacetal Substrates.

After obtaining 1,1,2-trimethoxyethane (II) the next step involved the preparation of the olefin, 1,2-dimethoxyethylene. The first paths chosen were based on Scheibler's work.(52) The ethyl derivative of the acetal, 1,1,2-triethoxyethane was also used because it has a higher boiling point (185°C/760mm Hg) and could be used in a slightly different manner.

A. Reaction between phthalic anhydride and 1,1,2-triethoxyethane (II). A quantity of 20 grams of II was



added to 25 grams of phthalic anhydride. The stirred reaction vessel was immersed in an oil bath at 160°-170°C at which point the phthalic anhydride melted and went into solution. The temperature of the reaction was above the boiling point of the olefin; therefore, the olefin, if formed, could come over as the distillate leaving the unreacted acetal behind. The apparatus was fitted with a condenser for partial take-off. Over a 24 hour period 10cc were collected. No olefin was isolated. The 1,1,2-triethoxyethane distilled over as unreacted material. Three other attempts were made with the same results. A Dry Ice-acetone trap was also used to insure against loss of any noncondensibles. An infrared spectrum was taken of the distillate. It showed a strong O-H stretching vibration at 3650 cm^{-1} and another absorption at 1740 cm^{-1}.

B. <u>Acid catalyzed elimination of 1,1,2-trimethoxyethane</u>(52). The reaction is as follows:

$$CH_3OCH_2\text{-}CH(OCH_3)_2 \xrightarrow{H+} CH_3OCH{=}CHOCH_3 + CH_3OH$$

A quantity of 13.4 grams of 1,1,2-trimethoxyethane was heated with a catalytic amount of phosphoric acid in the presence of 0.5 grams of quinoline. According to Scheibler, a crude distillate would be formed which would yield, after distillation from potassium carbonate, 70% 1,2-dimethoxyethylene. The reaction was carried out at different temperatures and with total reflux, reflux with a partial take-off, and total take-off. The same conditions were also tried with the ethoxy derivative. What was found was unreacted starting materials and minute amounts of polymerized products. An infrared spectrum was taken of the distillate and it showed essentially the same spectra as the unreacted 1,1,2-trimethoxyethane with the exception of very small absorption bands at 1740 cm^{-1} and 1710 cm^{-1}.

C. Pyrolysis of acetals.(4) The apparatus used was a slight modification of that described by Flaig.(22) Both 1,1,2-trimethoxyethane and 1,1,2-triethoxyethane were pyrolyzed in an upright furnace by using a dropping funnel with a nitrogen inlet. The acetals were passed down the pyrolysis tube at rates between 1 ml to 5 ml per minute. The products were collected in two Dry Ice-acetone receivers to guard against any loss due to entrainment in the nitrogen stream. The pyrolysis tube contained porcelain Raschig rings and was maintained at desired temperatures.

Eight runs were made at temperatures between 300° to 650°C. Half of the runs were done with a ceric oxide catalyst which adhered to the porcelain Raschig rings.(3,4,5) At the low temperatures the acetals went through the tube essentially unreacted. As the temperature was increased, some decomposition products were collected. However, no olefin was isolated as any of the products. Carbon dioxide and possibly some carbon monoxide were given off. The only identifiable products were aldehydes and unreacted starting material. This was verified from the infrared spectra of the components which were separated individually by preparative gas chromotography and dissolved in CCl_4. A characteristic absorption band for aldehydes at 1740 cm^{-1} was found in one of the minor products.(21,53) Decomposition products in the form of smoke also formed but could not be condensed.

D. Potassium t-butoxide initiated elimination of 1,1,2-trimethoxyethane. The reaction is as follows:

$$CH_3OCH_2\text{-}CH(OCH_3)_2 + K^+t\text{-}BuO^- \longrightarrow CH_3OCH{=}CHOCH_3 + t\text{-}BuOH + KOCH_3$$

Potassium t-butoxide was prepared by direct cleavage of di-t-butyl peroxide.(54) Di-t-butyl peroxide was distilled

$$2K + (CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_3 \longrightarrow 2K^+O^-\text{-}C(CH_3)_3$$

from a two liter flask at 90-100mm Hg. The pot temperature was not allowed to exceed 70°C. The solvent used for the preparation of potassium t-butoxide was dimethoxyethane. Potassium was cut into small cubes and added to dimethoxyethane which was previously dried by distillation from lithium aluminum hydride. The temperature was raised in order to form a melted potassium suspension in the solvent. At this point, freshly distilled di-t-butyl peroxide was added dropwise. The peroxide was added slowly in order to keep the cleavage reaction under control. An excess of potassium was used to insure complete conversion of the peroxide. The quantities employed were:

165 grams of potassium (4.22 moles)
1575cc of dimethoxyethane
273g of di-t-butyl peroxide (1.88 moles)

Potassium t-butoxide was recovered in its solid state by vacuum evaporation while maintaining a dry, inert nitrogen atmosphere. The potassium t-butoxide was found to be 98% pure by titration with HCl. (Appendix A)

Reactions were performed using both 1,1,2-trimethoxyethane and the 1,1,2-triethoxyethane. The initial reactions were run in a stirred, three neck flask, fitted with a reflux condenser and nitrogen inlet, at atmospheric pressure, and at the boiling point of the acetal. The system was kept dry at all times by a constant stream of nitrogen through the apparatus. The reactions with 1,1,2-trimethoxyethane were kept between 125° to $130^{\circ}C$, while the reactions with 1,1,2-triethoxyethane were maintained at 180° to $185^{\circ}C$. Total reflux was employed for periods up to 48 hours.

When the reaction mixture was distilled there was no trace of olefin. The reaction with 1,1,2-trimethoxyethane did show that some substitution took place at the lower temperature. Tertiary butyl methyl ether was identified by infrared spectroscopy. The amount formed, less than 0.5%, was negligible. Reactions with 1,1,2-triethoxyethane yielded trace amounts of t-BuOH as product. This was verified by infrared spectroscopy and gas chromotography.

The products of a reaction carried out on a 0.08 molar scale (1/1 ratio of base to substrate) were methylated with 0.08 moles of methyl iodide (12.2 grams) in 35cc absolute ethanol. The quantity of methyl iodide was based on a complete conversion to ethoxide ion. Analysis of the methylated products by gas chromatography showed methyl t-butyl ether and 1,1,2-triethoxyethane as the major products. Minor side products were also present but they constituted approximately one per cent of the total volume. A method for calculating the reaction time necessary to insure complete methylation is given in Appendix A.

IV. 1,2-Dimethoxyethylene Synthesis Employing Bomb Reactor.

The same base-catalyzed elimination reactions were performed in a reaction bomb. The reaction of 1,1,2-trimethoxyethane and potassium t-butoxide was run in a reaction bomb immersed in an oil bath at 150-200°C. The bomb was initially purged with nitrogen to maintain an inert, dry atmosphere. All manipulation and handling were done in a glove bag under a nitrogen atmosphere in order to keep the system completely dry. An oxygen-free dry atmosphere is essential when working with an extremely strong base such as potassium t-butoxide.

A few trial runs were performed to determine the optimum reaction conditions such as temperature, reaction time and reactant ratios. The bomb capacity was 45cc which allowed the reactants to occupy approximately 35cc, leaving a 10cc vapor space. One is forced to use a small amount of potassium t-butoxide since it is not very soluble in 1,1,2-trimethoxyethane. Approximately a 3:1 mole ratio of the acetal to the potassium t-butoxide was used which still left a large excess of undissolved potassium t-butoxide.

However, at higher temperatures the solubility of the alkoxide increases. It was found from the foreruns that temperatures below 150°C left essentially unreacted material while temperatures exceeding 180°C formed low boiling liquids and dark brown to black products in the solid phase. The dark colored solids are very likely high molecular weight aldol polymers.

The oil bath temperature was maintained at 165°C and the reaction was allowed to proceed until the pressure reached approximately 250 psig. This pressure was chosen since this is greater than the vapor pressures of t-butanol and t-butyl methyl ether, both of which were end products identified in the foreruns. Two experiments were performed at the same conditions to check the consistency of the results.

The 1,1,2-trimethoxyethane was freshly distilled in a Todd column at 50:1 reflux ratio (b.p. 126.1°C/760mm Hg) and stored over sodium ribbon. Potassium t-butoxide purchased from M.S.A. Research Corporation was used since it assayed 99.0% purity by titration with 0.0992N HCl (0.0898g consumed 8cc of acid). A Fisher Hi-Temp oil bath was used in which the bomb reactor was submerged for the duration of the run. The quantities and conditions used in the two runs are described as follows:

RUN I

23.5g 1,1,2-trimethoxyethane (0.196 moles)

7.1g potassium t-butoxide (0.0635 moles)
30.6g total

Oil bath temperature : 165°C

Reaction time : 30 hours

Final pressure reading: 200 psig

Final solid products : 6.0g

Final liquid products : 23.4g
29.4g total

Per cent losses = $\frac{1.2}{30.6}$ = 3.92%

RUN II

25.1g 1,1,2-trimethoxyethane (0.209 moles)

7.2g potassium t-butoxide (0.0643 moles)
32.3g total

Oil bath temperature : 165°C

Reaction time : 33 hours

Final pressure reading: 220 psig

Final solid products : 6.1g

Final liquid products : 24.9g
31.0g total

Per cent losses = $\frac{1.3}{32.3}$ = 4.03%

Both experiments were worked up in the same manner. The liquid and solid products were transferred to a small flask in a dry bag and the liquid was removed under vacuum in a rotary evaporating apparatus. The liquid products from both runs were analyzed by gas chromatography. The product distributions in both runs were essentially identical. Five peaks were found which were resolved on a 1/8" x 10' column (20% carbowax 20M chromosorb W). Peaks 1,2 and 5 were identified in the foreruns to be t-butyl methyl ether, t-butanol, and unreacted 1,1,2-trimethoxyethane. This was determined by reinjection of the pure samples and by infrared analysis of the separate peaks and pure samples. Peaks 1,3 and 4 were isolated by preparative gas chromatography and identified unambiguously as t-butyl methyl ether (Peak I), *trans*-1,2-dimethoxyethylene (Peak 3), and *cis*-1,2-dimethoxyethylene (Peak 4). The product distribution was as follows:

Products	Mole %[d]	Wt. %	Yield (g)
t-BuOMe	2.910 ±.03	2.220	0.520
t-BuOH	7.230 ±.03	4.650	1.090
trans-DME[a]	1.030 ±.03	.785	0.184
cis-DME[b]	2.150 ±.03	1.650	0.386
TME[c]	86.670 ±.07	90.695	21.220
	100.000	100.000	23.400

[a] *trans*-1,2-dimethoxyethylene [b] *cis*-1,2-dimethoxyethylene
[c] 1,1,2-trimethoxyethane [d] Quantitative gas chromatographic analysis was made by weighing the peaks. A synthetic mixture consisting of 3 mole per cent t-BuOMe, 7 mole per cent of t-BuOH, and 90 mole per cent TME was made for

comparison of reaction products. The detector sensitivity was identical.

The reaction mixture was distilled on a Todd column at a 50:1 reflux ratio to increase the concentration of the *cis*-and-*trans*-olefins in the distillate, thereby facilitating preparative VPC. Complete separation was impossible since many azeotropes were formed. The *cis*-and-*trans*-olefins azeotroped with t-butanol and 1,1,2-trimethoxyethane. The t-butyl methyl ether also formed an azeotrope with the olefins and/or t-butanol. A few distillations did however succeed in increasing the concentration of olefins in the distillate. This made the preparative gas chromatographic separations more feasible since the concentration of the olefins in the original reaction mixture was less than 3.2 mole per cent.

Preparative gas chromatography was used to separate the liquid end products. Three columns were tried each using chromosorb W as the solid support. They were 20% XF-1150 which is a cyanosilicone fluid, 25% Theed which is tetrahydroxyethyl ethylenediamine, and carbowax 20M which is a polyglycol. The carbowax 20M gave the best separation whereas the other columns showed excessive tailing and poor separation.

A 1/4" and 20' column was used to isolate the products (30% carbowax 20M on chromosorb W, 60-80 mesh). A Varian

A700-A gas chromatograph was used. Injections of 100 microliters were made onto the column which was heated isothermally at 130°C. The flow rate of helium was 105cc per minute. The peaks were collected, isolated and identified by elemental analysis, infrared analysis and nuclear magnetic resonance. Each peak was reinjected after collection and found to be homogeneous. The spectra are described in the Discussion of Results.

The solid phase from the reaction mixture, after drying on the "Roto-Vaporator", was added to an excess of water and titrated with 1.007N H_2SO_4 to a pH of 7.0 on a Beckman Zeromatic pH meter. The solid from the first run (6.0 grams) took 5.65cc of 1.007N H_2SO_4 to neutralize 0.6991 grams, therefore 6.0 grams = 49.0 meq.

The second run (6.1 grams) took 5.47cc of 1.007N H_2SO_4 to neutralize 0.692 grams, therefore 6.1 grams = 48.6 meq. The significance of the titration will also be described in the Discussion of Results.

DISCUSSION OF RESULTS

I. The Synthesis and Related Syntheses of 1,2-Dimethoxyethylene.

1,1,2-trimethoxyethane was prepared by a two-step synthesis starting from vinyl acetate. The final product purity was greater than 99%, as determined by gas chromatography. It can also be prepared in 40% yield by the acid catalyzed addition of ethanol to ethoxyacetaldehyde.(33,41)

The reaction of 1,1,2-triethoxyethane and phthalic anhydride gave a crude distillate which showed essentially unreacted starting material by infrared absorption. However, carbonyl absorption (1740cm^{-1}) and hydroxy absorption (3650cm^{-1}) also appeared in the spectrum.(8) The mono ethyl ester of phthalic acid, which would be one of the reaction products, decomposes before it reaches a boiling point.

In the acid catalyzed elimination reaction of 1,1,2-trimethoxyethane there was formation of polymerized material. Quinoline was used to neutralize some of the acid, but it appears that as soon as any olefin was formed, it underwent acid catalyzed cationic polymerization which is typical of many vinyl ethers. Although Scheibler describes the preparation of 1,2-dimethoxyethylene from the acid catalyzed elimination reaction, his results could not be duplicated.(52)

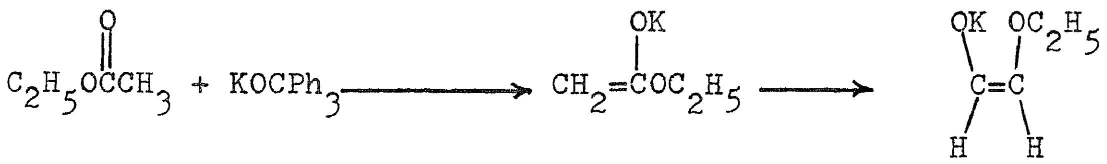
The results obtained by pyrolysis of both the 1,1,2-trimethoxyethane and the 1,1,2-triethoxyethane are more difficult to explain. A possible explanation lies in the relative stability of the acetal. Essentially the same results were obtained using either contact catalyst, ceric oxide, or no catalyst at all. The contact time of the acetal on the porcelain Raschig rings and the temperature were the controlling factors. When the contact times were 5 ml/per minute and the temperature maintained between 300° to 500°C, the acetals went through the pyrolysis tube essentially unreacted. With longer contact times (1 ml/per minute and higher temperatures (500° to 650°C) some decomposition products were collected. No olefins were isolated in any of the product fractions although Baganz discusses the formation of 1,2-dimethoxyethylene by pyrolysis of 1,1,2-trimethoxyethane at 290° - 300°C using a ceric oxide catalyst.(4) However, trace amounts of aldehydes were identified as products by infrared absorption and gas chromotography. Some of the decomposition products in the form of smoke could not be condensed.

Baganz obtained _cis_-and-_trans_- 1,2-dimethoxyethylene by the elimination of chlorine from 1,2-dichloro-1,2-dimethoxyethane with magnesium using tetrahydrofuran as a solvent.(3) The reported boiling points and refractive indices for the _cis_-and-_trans_-isomers are;(3) _cis_-isomer, b.p. 97°C/760mm Hg, n_D^{25} 1.4190; _trans_-isomer, b.p. 93°C/760mm Hg, n_D^{25} 1.4070.

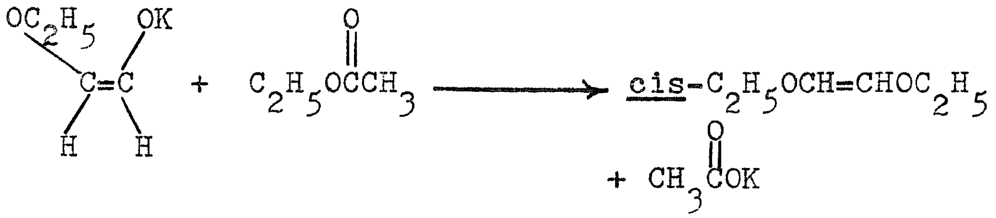
Scheibler discusses the formation of _cis_-1,2-diethoxyethylene from ethyl acetate and potassium tri-phenylmethoxide

(52)

using diethyl ether as a solvent. Normally, one would expect to produce the enolate ion which would condense with another molecule of ethyl acetate to produce the acetoacetic ester. Scheibler claims that the enolate ion undergoes intramolecular hydride transfer with an S_N1 displacement on ethoxide producing the cis-adduct.



This then acts as the nucleophile for an S_N2 displacement on the methylene carbon of ethyl acetate to produce the olefin and potassium acetate.



It appears extremely doubtful that the nucleophile displaces acetate ion instead of simply adding to the carbonyl group.

A novel approach to obtain the olefin was a base-initiated elimination reaction similar to the work previously done with diglyme (the dimethylether of diethylene glycol).(54) The difference between the diglyme elimination and the acetal elimination is the high stability of the acetal, making elimination reactions difficult except at severe conditions. When the acetal eliminations were run at atmospheric pressure in ordinary glass apparatus, the reaction temperature could not exceed the boiling point of 1,1,2-trimethoxyethane which was too low for the substrate to undergo elimination (127°C). Nitrogen was being swept through the systems in order to maintain a completely dry atmospere and although two Dry Ice-acetone traps were used to collect any carry over, the olefin if formed, could have been entrained in the nitrogen stream and lost. The reactions were refluxed from 2 to 5 days. Unreacted starting material and a trace amount of methyl t-butyl ether, a substitution product, were identified.

The same reaction (1,1,2-trimethoxyethane and potassium t-butoxide) performed in a bomb reactor at higher temperatures finally gave the desired _cis_-and-_trans_-1,2-dimethoxyethylene, and unreacted 1,1,2-trimethoxyethane. The results of two runs are shown in Table I.

TABLE I

PRODUCTS FROM ELIMINATION REACTION.

Run no.[a]	T, °C	t, hr.	Products, moles t-BuOMe	tBuOH	trans DME[b]	cis DME[c]
1	165±5	30	.00590	.01480	.00209	.00439
2	165±1	33	.00639	.01560	.00234	.00483

[a] experiment described on page 27, [b] _trans_-1,2-dimethoxyethylene

[c] cis-1,2-dimethoxyethylene

The ratio of _cis_-to-_trans_-isomer is 2.1/1 from run

No. 1 and 2.06/1 from run No. 2. This shows that *cis*-formation probably proceeds by a lower energy mechanism with one conformation of the substrate predominating. However, since the substrate does not contain asymmetric carbon atoms, it is impossible to ascertain the direction of the elimination because *cis*-elimination can lead to the *cis*-and-*trans*-isomers as can trans-elimination. The total conversion of potassium t-butoxide to the *cis*-and-*trans*-olefins and methyl-t-butyl ether for run No. 1 was 19.6% and for run No. 2 was 21.1%. The amount of low boiling side products formed was less than 0.1 gram and was therefore neglected. The low boiling fractions could be methoxyacetylene if 1,2-dimethoxyethylene eliminated CH_3OH

$$CH_3OCH{=}CHOCH_3 + KtBuO \longrightarrow CH_3OC{\equiv}CH + tBuOH{+}KOMe$$

or acetylene if 1,2-dimethoxyethylene was pyrolized at the temperatures used producing methyl vinyl ether which could then undergo elimination.

$$CH_3OCH{=}CHOCH_3 \xrightarrow{\text{pyrolysis}} CH_2{=}O + CH_3OCH{=}CH_2$$

$$CH_3OCH{=}CH_2 + KtBuO \longrightarrow CH{\equiv}CH + KOMe + tBuOH$$

The mechanism for the elimination and substitution reactions are very likely examples of E2 and S_N2 reactions involving both substrate and nucleophile in transition state. Non polar solvents and poor leaving groups also support this fact. Initial carbanion formation (E1CB mechanisms) is unlikely since methoxy groups are poor carbanion stabilizing groups.

II. Analysis and Spectra of Reaction Products.

Methyl t-butyl ether, t-butanol, *cis*-and-*trans*-1,2-dimethoxyethylene and unreacted 1,1,2-trimethoxyethane were isolated from the reaction mixture by preparative gas chromatography.

Elemental analysis of the *cis*-and-*trans*-1,2-dimethoxyethylene (purity greater than 99%) gave the following results:

cis-1,2-dimethoxyethylene	*trans*-1,2-dimethoxyethylene
Theory: C = 54.0%, H = 9.1%	Theory: C = 54.0%, H= 9.1%
Found : C = 53.97%,H = 8.1%	Found : C = 54.08%,H = 9.46%

The infrared spectra of each component was taken and checked with published spectra if these were available. Fig. 6 contains the published spectra of t-butanol and methyl t-butyl ether.(49) The spectrum of methyl t-butyl ether, obtained as a reaction product, is shown in Fig. I. The two spectra are identical. Likewise, Fig. 2 is the spectrum of t-butanol obtained as a reaction product which is also identical with the one in Fig. 6. All the infrared spectra were obtained using 5% solutions in CCl_4.

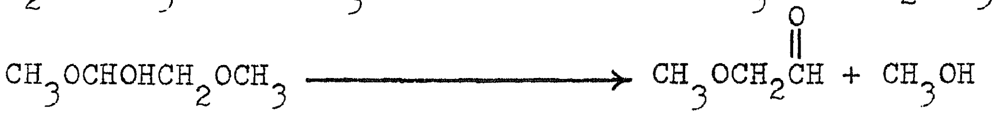
In Fig. 1, methyl t-butyl ether shows the characteristic asymmetrical C-O-C skeletal vibration at 1200cm^{-1} and

108cm.$^{-1}$(21,53) The characteristic t-butyl C-H bending doublet is observed at 1390cm.$^{-1}$ and 1365cm.$^{-1}$

In Fig. 2, t-butanol shows the O-H stretching absorption at 3590cm.$^{-1}$(8) The O-H bending appears at 1325cm.$^{-1}$(21)

In Fig. 3, the characteristic absorptions of <u>cis</u>-1,2-dimethoxyethylene are shown. The vinyl ether C=C-OCH$_3$ skeletal vibrations are observed at 1220cm^{-1} and 1120cm.$^{-1}$(53) The C=C stretching vibrations appear at 1670cm^{-1} and 1710cm.$^{-1}$(8) This appears to be an aldehyde carbonyl absorption, but it is definitely not. However, if one is not careful and gets moisture into the olefin, it will react and show a definite carbonyl absorption at 1740cm.$^{-1}$ This is shown in Fig. 5. A hydroxyl absorption is also noticeable at 3590cm.$^{-1}$ This is probably due to methoxyacetaldehyde and methanol which form as follows:

$$H_2O + CH_3OCH{=}CHOCH_3 \longrightarrow CH_3OCHOHCH_2OCH_3$$



$$CH_3OCHOHCH_2OCH_3 \longrightarrow CH_3OCH_2\overset{\overset{\displaystyle O}{\|}}{C}H + CH_3OH$$

A slight shoulder at 3020cm^{-1} in Fig. 3 is characteristic of the C=C-H stretching vibration for <u>cis</u>-olefins.(8) The weak band at 1425cm^{-1} is characteristic of the C=C-H in-plane bending vibration while the band at 718cm^{-1} is characteristic of C=C-H out-of-plane bending vibration for <u>cis</u>-olefins.(8) This is absent in the <u>trans</u>-olefin.

Fig. 4 is the infrared spectrum of trans-1,2-dimethoxyethylene. The vinyl ether C=C-OCH_3 skeletal vibrations are observed at $1220cm^{-1}$, $1170cm^{-1}$ and $1140cm.^{-1}$(8,53) This is a slightly different pattern than the cis-case. The C=C stretching vibration is observed as a weak band at $1670cm.^{-1}$(21) A sharp shoulder at $3020cm^{-1}$ is characteristic of the C=C-H stretching vibration.(53) The strong band at $960cm^{-1}$ is the out-of-plane bending vibration of C=C-H, which is characteristic of trans-olefins.(8)

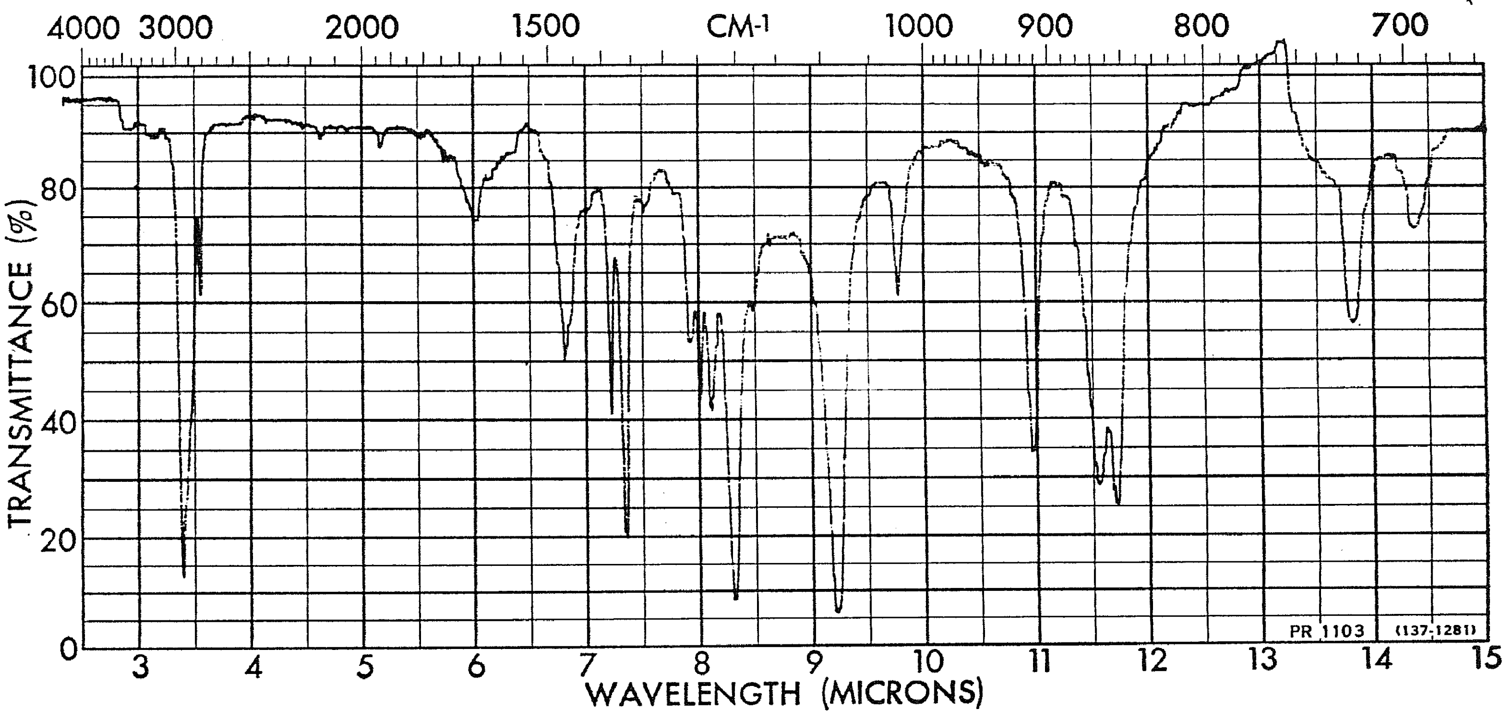
1,1,2-trimethoxyethane is shown in Fig. 7. The characteristic C-O-C stretching vibrations appear at $1195cm^{-1}$ and $1120cm.^{-1}$(8,21) This shows that vinyl ethers absorb at a slightly higher frequency than aliphatic ethers.

The absorption frequencies found for cis-and-trans-1,2-dimethoxyethylene agree with the literature values which are $1220cm^{-1}$ for the C=C-OCH_3 skeletal vibration and 1680-$1730cm^{-1}$ for the C=C stretching vibration.(3)

Nuclear magnetic resonance spectra were obtained on a Varian A-60-A spectrometer. All delta values were measured downfield from tetramethyl silane, (T.M.S.) and are therefore negative. T.M.S. has a delta value of zero. The isolated products were dissolved in CCl_4. The concentrations were high enough to produce a good signal to noise ratio thereby keeping the noise level at a minimum.

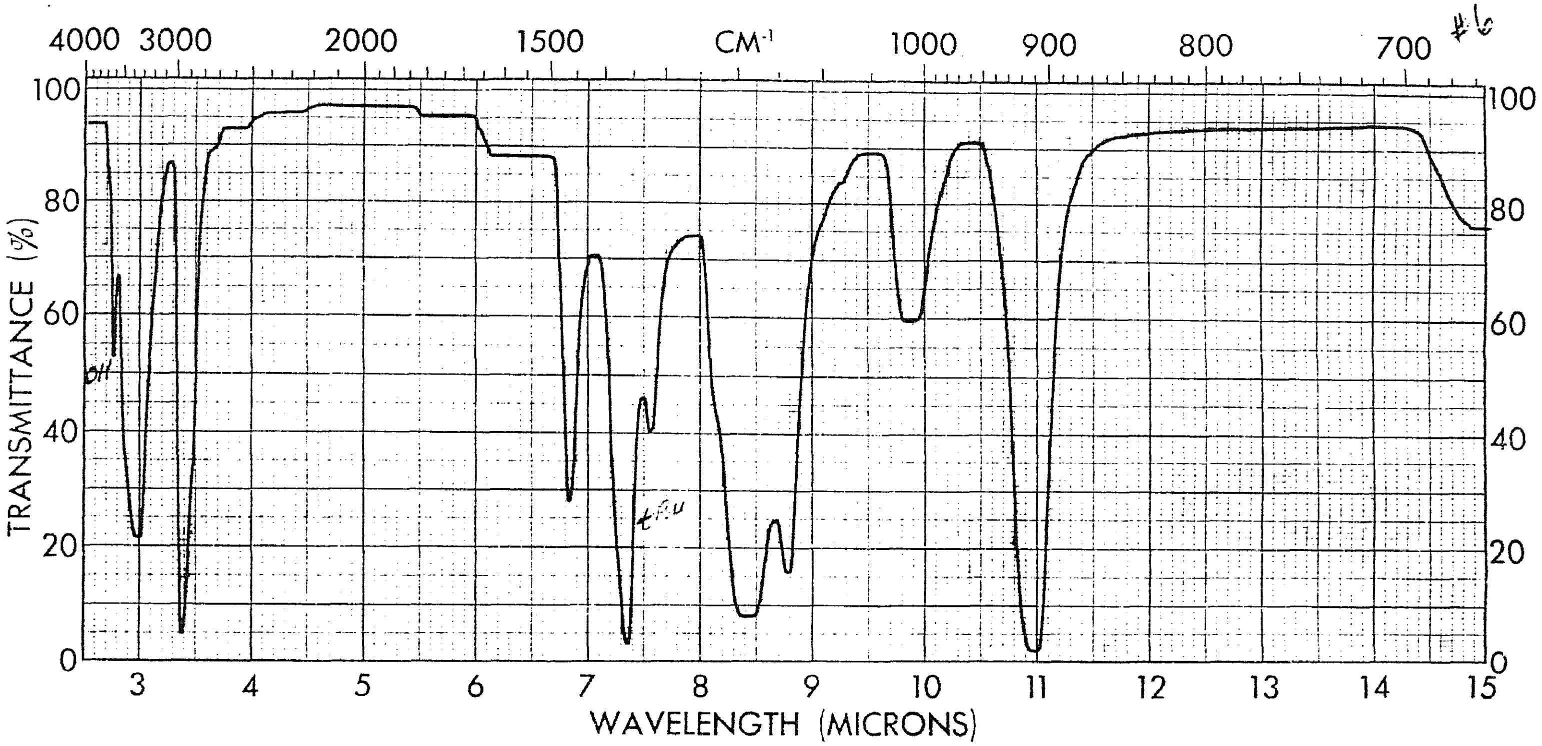
#5

FIGURE I



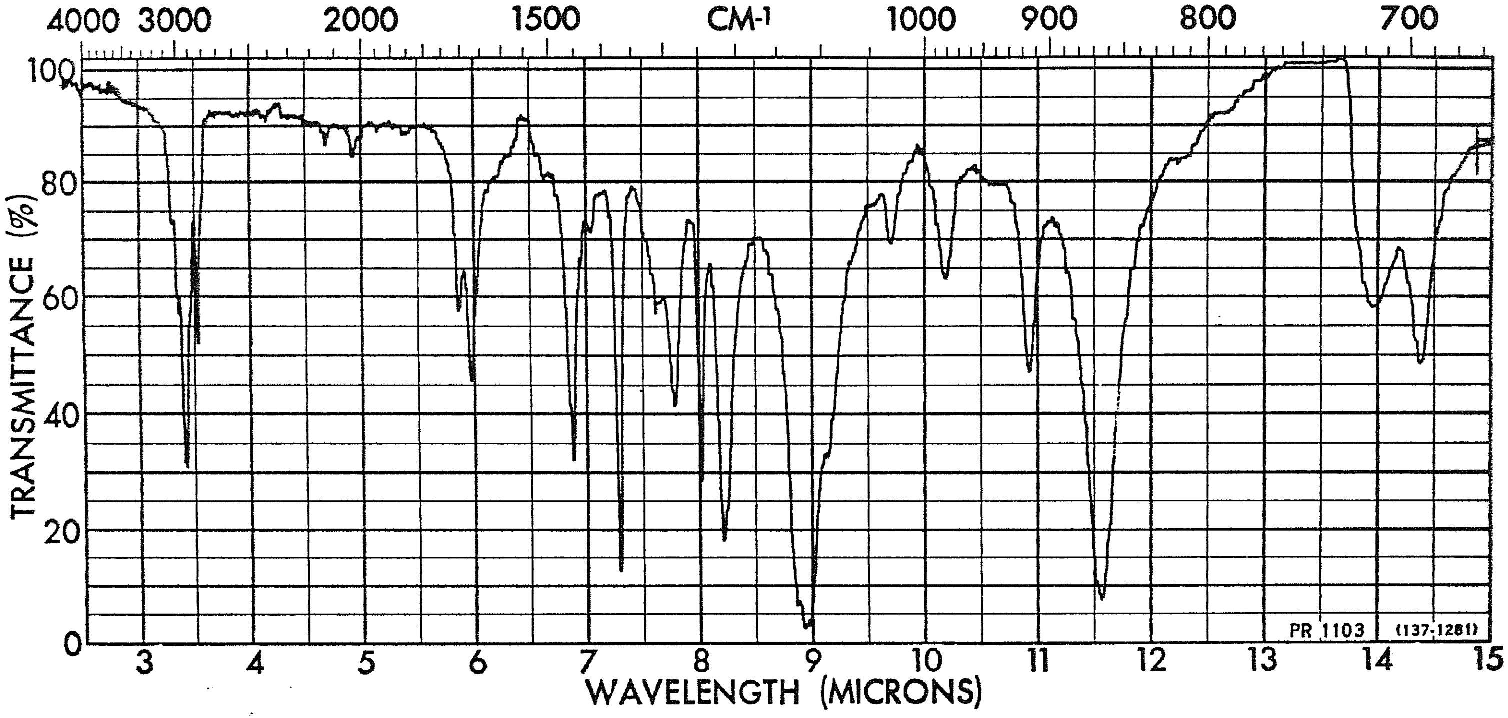
METHYL t-BUTYL ETHER

FIGURE 2



t-BUTANOL

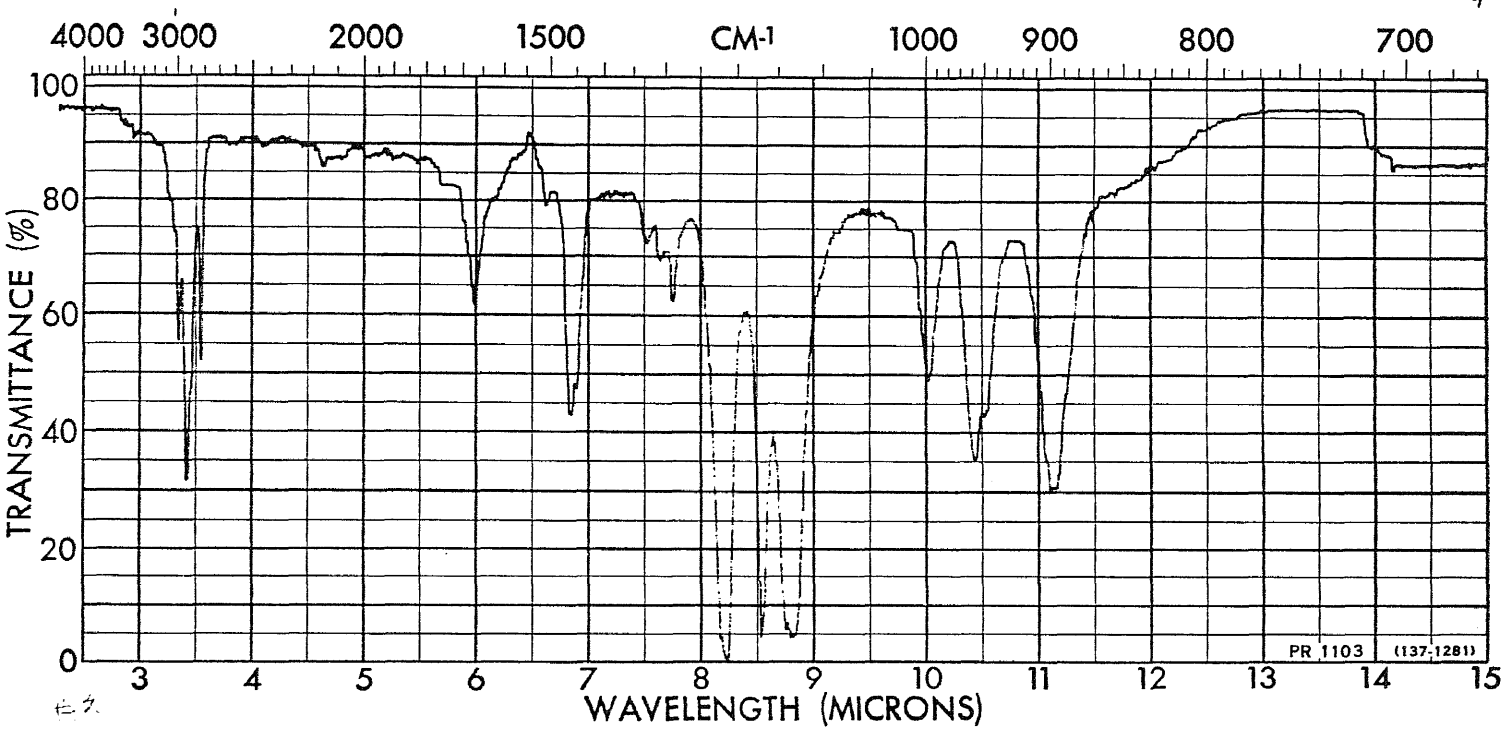
FIGURE 3



cis-1,2-DIMETHOXYETHYLENE

FIGURE 4

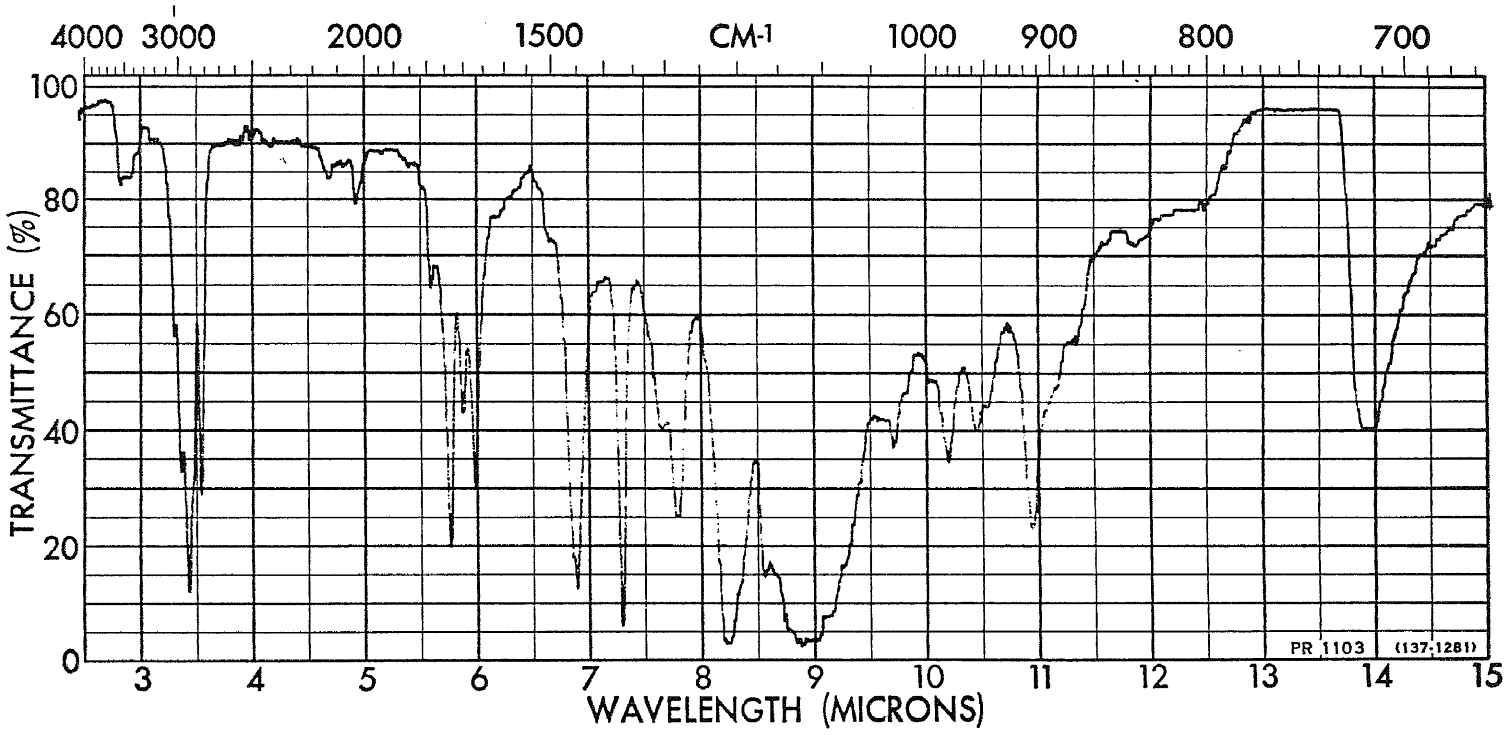
#8



trans-1,2-DIMETHOXYETHYLENE

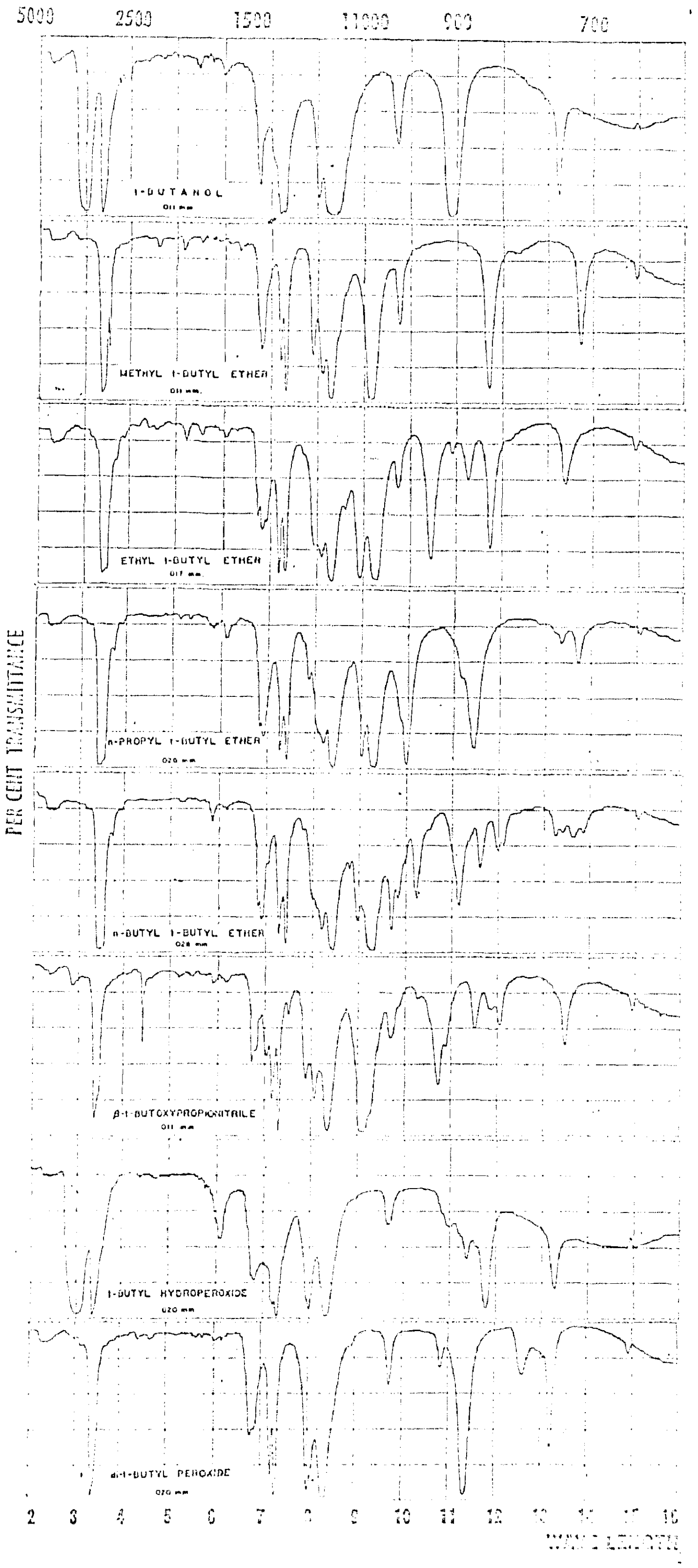
FIGURE 5

#9



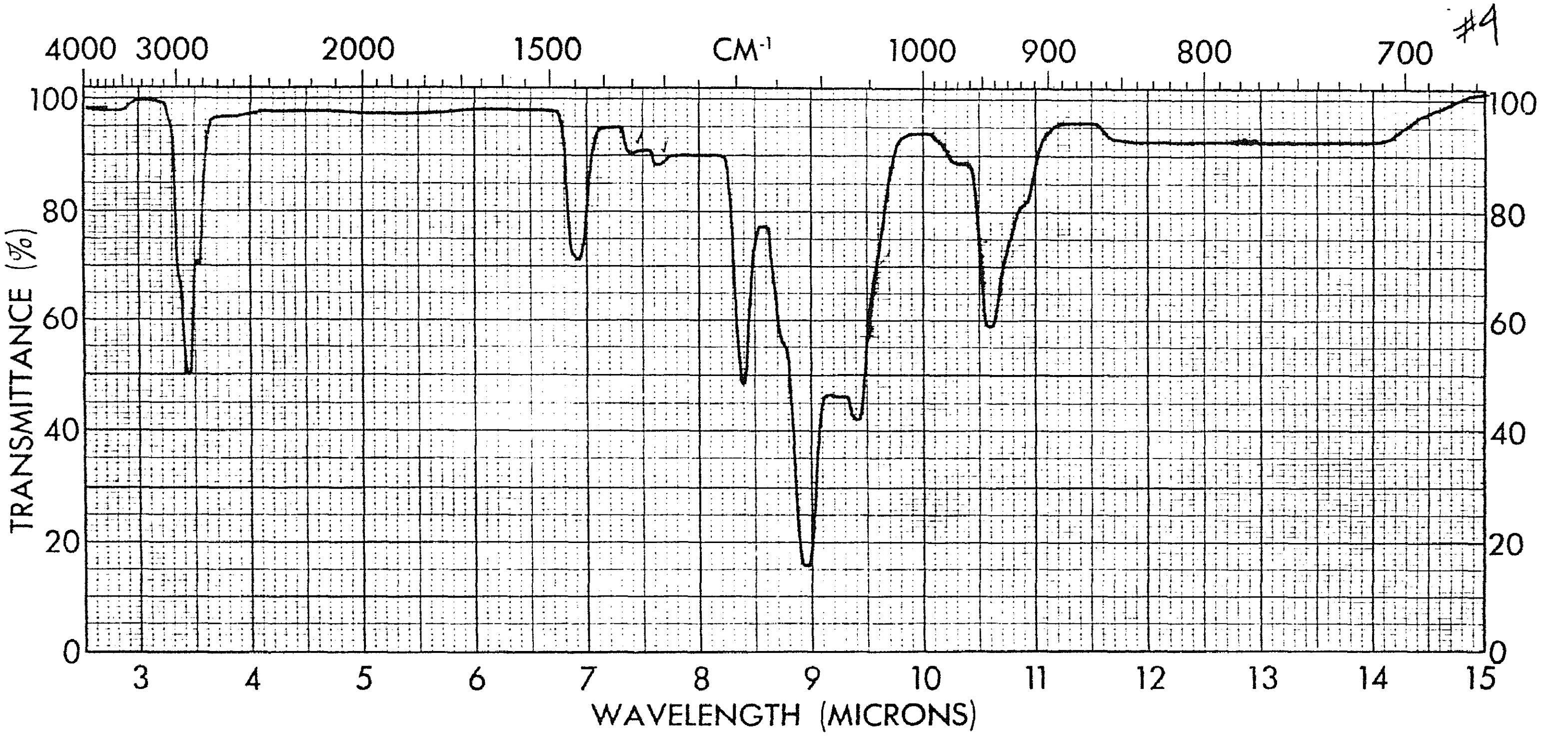
REACTION PRODUCT OF cis-1,2-DIMETHOXYETHYLENE AND WATER

FIGURE 6



PUBLISHED SPECTRA (49)

FIGURE 7



1,1,2-TRIMETHOXYETHANE

The following proton absorptions are characteristic of the type of proton environment.(11,21,39,50)

methyl protons on a t-butyl group: $\delta = 0.85-1.3$
methoxy protons : $\delta = 3.3-4.0$
acyclic vinyl protons : $\delta = 5.1-5.9$
aldehyde protons : $\delta = 9.3-10$
where $\tau = 10 - \delta$ (ppm)

Methyl t-butyl ether isolated from the reaction shows methoxy proton absorption at $\delta = 3.12$ and methyl proton absorption at $\delta = 1.13$. Both peaks are singlets. The relative peak areas are 10:31 = 1:3.1. (Theoretical 1:3) This is shown in Fig. 8.

This *cis*-1,2-dimethoxyethylene has a characteristic methoxy proton absorption at $\delta = 3.52$ and a vinyl proton signal at $\delta = 5.12$. Both peaks are singlets, as shown in Fig. 9.

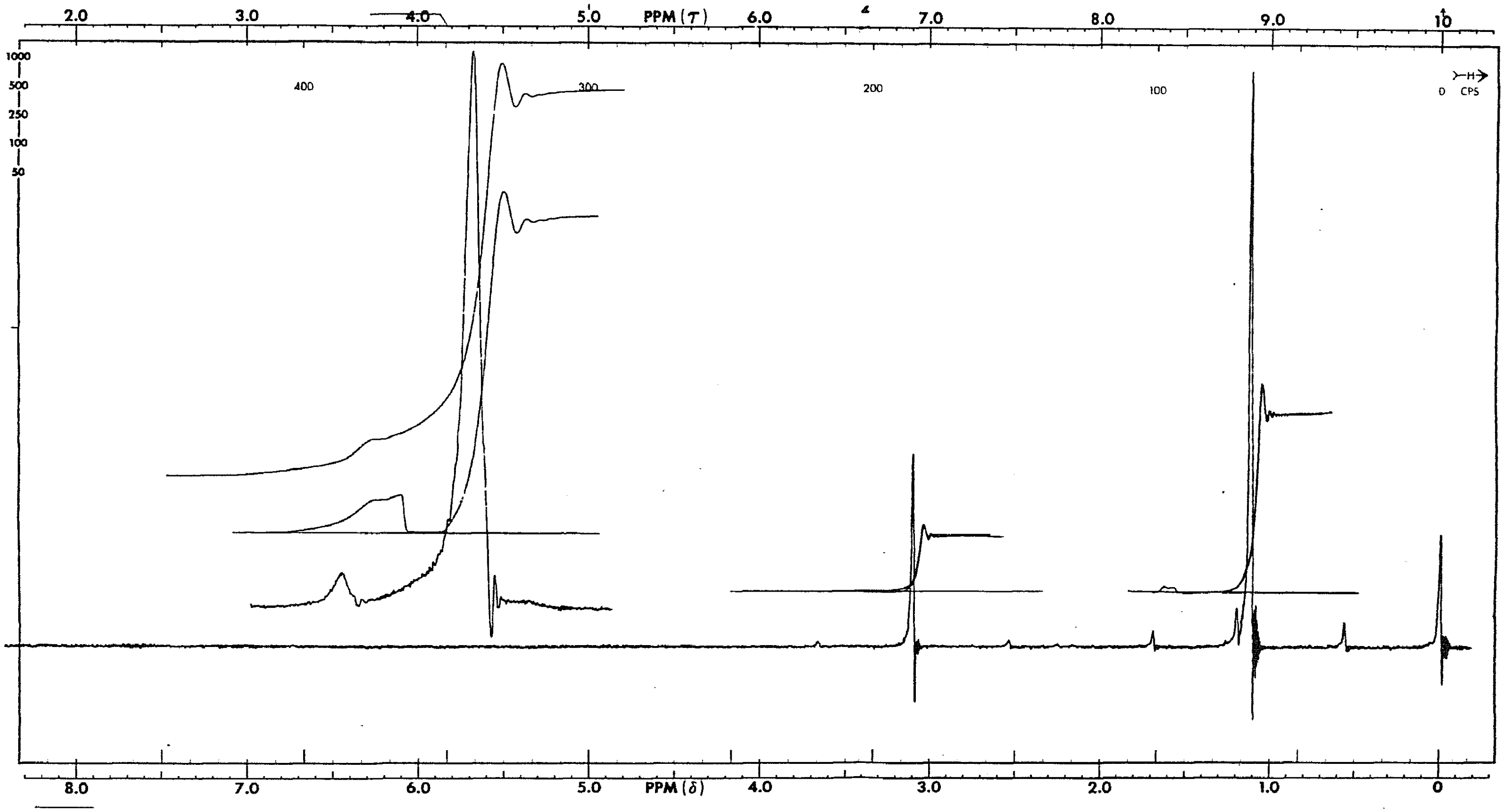
One may expect a vinyl doublet caused by spin-spin splitting, but since the molecule is symmetrical with identical groups, the spin-spin coupling constant for each vinyl hydrogen is identical. This reduces the doublet to a sharp singlet. The relative peak areas are 17.0:51 = 3.0:1.0 (Theoretical 3:1).

Trans-1,2-dimethoxyethylene has a characteristic methoxy proton absorption at $\delta = 3.40$ and vinyl proton absorption at $\delta = 6.15$ (Fig. 10). As in the *cis*-case, both peaks are singlets. The relative peak areas are 13:30 = 2.92:1 (Theoretical 3:1).

In each of the above cases, the spectrum was determined by sweeping from left to right (lower field to higher field), first with a sweep width of 1000 cps set at a high amplitude ratio to determine if any aldehyde protons were present as minor side products, then recorded at a sweep width of 500 cps which includes delta values from 0 ppm to 8.4 ppm, (Range of major proton absorptions). There were no aldehydes present in any sample.

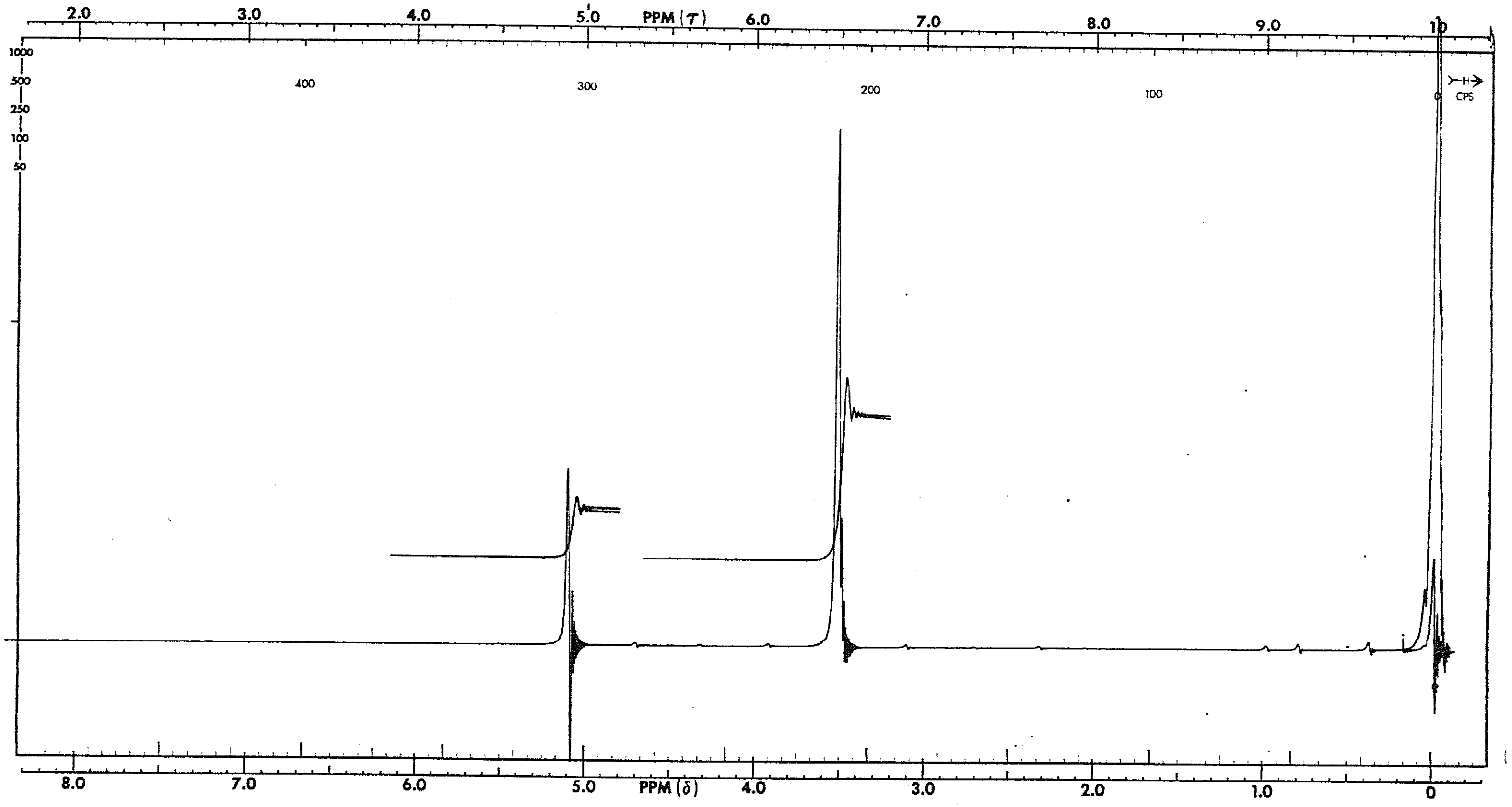
Published spectra for *cis*-and-*trans*-1,2-dichloroethylene indicate the vinyl proton in the *trans*-case appears further upfield ($\delta = 6.23$) than the *cis*-vinyl proton ($\delta = 6.28$).(60) This infers that the *trans*-protons are more effectively shielded than the *cis*-protons although the difference is negligible. However, when one observes the difference in *cis*-and-*trans*-1,2-dimethoxyethylene, the results are more drastic and are also reversed. In this case, the *trans*-vinyl protons are much more deshielded ($\delta = 6.15$) than the *cis*-protons ($\delta = 5.12$) since the *trans*-protons absorb further downfield from TMS. The difference in chemical shift is 1.03 ppm. This is also true for 1,2-difluoroethylene. The published spectra indicate the *cis*-vinyl proton absorbs at $\delta = 6.2$ ppm and the *trans*-vinyl proton at $\delta = 7.2$ ppm measured downfield from TMS.(23,56)

FIGURE 8



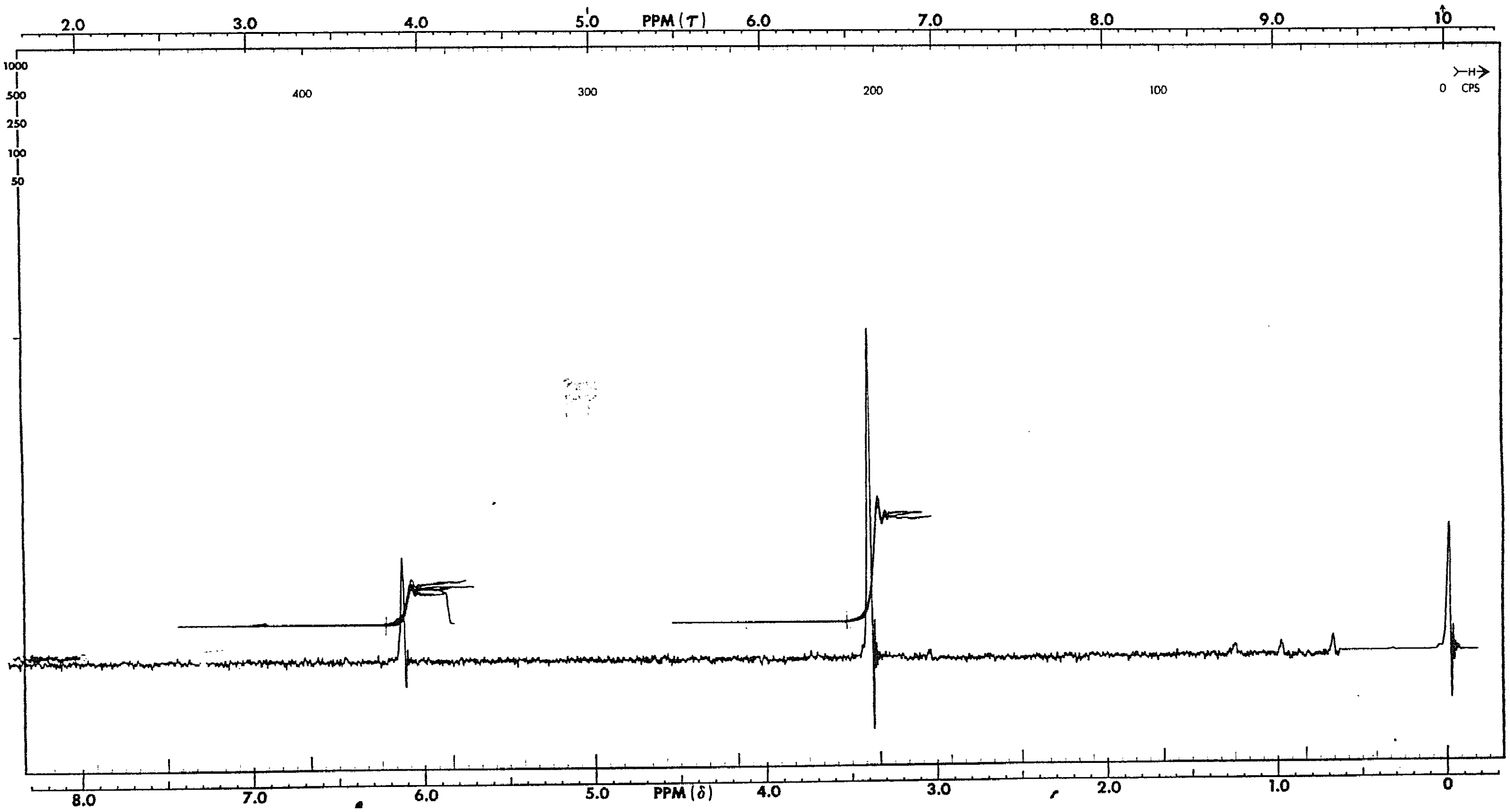
METHYL t-BUTYL ETHER

FIGURE 9



<u>cis</u>-1,2-DIMETHOXYETHYLENE

FIGURE 10



trans-1,2-DIMETHOXYETHYLENE

Normally, electron withdrawing groups attached to an olefin exert a more pronounced deshielding effect in the cis-isomer than in the trans-isomer as was shown above for 1,2-dichloroethylene. This is not true for methoxy and fluorine substituted olefins. Oxygen and fluorine have similar electronegativities which are higher than chlorine. Therefore, in the cis-isomer, the electron density is large enough near the substituents to produce an electronic field effect which can act in the opposite direction to an electron withdrawing effect. This causes electron density to be moved closer to the double bond, therefore, creating a larger deshielding effect in the trans-isomer than in the cis-isomer. This is exactly what was found in the dimethoxyethylene and difluoroethylene cases as shown above.

Another effect known as diamagnetic anistropy can take place in alkoxy substituted olefins.(11,39,50) The P-orbitals around oxygen create induced magnetic currents causing electronic circulation effects.(39) A conjugation effect also increases the electron density around the protons but is less important for the cis-isomer than the trans-isomer.

III. Discussion of Reaction Products

The conditions of the reaction (strong base at high concentration, high temperatures, non polar solvent, branching at alpha and beta carbon) would definitely seem to favor an elimination process and not nucleophilic substitution.(28) However, methyl t-butyl ether, a product of the reaction, did form by a substitution process. Three possible reactions for the formation of methyl t-butyl ether are shown below:

Reaction A:

III

$$CH_3OCH_2CH(OCH_3)_2 + KOC(CH_3)_3 \longrightarrow CH_3OCH_2CHOCH_3\text{-}OK + CH_3\text{-}O\text{-}C(CH_3)_3$$

Reaction B:

IV

$$CH_3OCH_2CH(OCH_3)_2 + KOC(CH_3)_3 \longrightarrow KO\text{-}CH_2CH(OCH_3)_2 + CH_3\text{-}O\text{-}C(CH_3)_3$$

Reaction C:

$$CH_3OCH_2CH(OCH_3)_2 + KOC(CH_3)_3 \longrightarrow CH_3OCH{=}CHOCH_3 + (CH_3)_3COH$$

V

$$CH_3OCH{=}CHOCH_3 + KOC(CH_3)_3 \longrightarrow KOCH{=}CHOCH_3 + CH_3\text{-}O\text{-}C(CH_3)_3$$

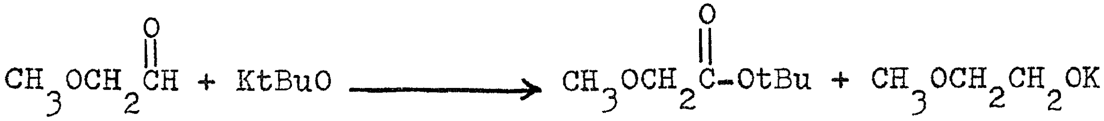
Reaction A is more likely to proceed than reaction B because of a 2 to 1 statistical factor favoring the hydrogens on carbon two.(57)

If III formed, a multitude of products would be expected. Product III could eliminate methoxide ion forming methoxyacetaldehyde, as in a Claisen condensation.(29)

$$CH_3OCH_2CHOCH_3OK \longrightarrow CH_3OCH_2\overset{O}{\overset{\|}{C}}H + KOMe$$

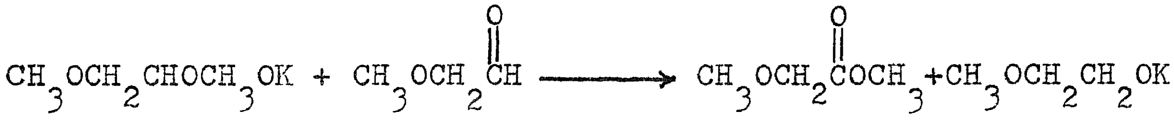
With a strong base such as potassium methoxide or potassium t-butoxide, the aldehyde can now undergo aldol condensation producing high molecular weight aldol products. This however would produce an equivalent amount of potassium methoxide equal to the methoxyacetaldehyde formed. A base-catalyzed elimination of hydroxide ion from the aldol product, a known reaction, would produce KOH.(2,31) A Cannizzaro reaction on methoxyacetaldehyde is now possible which would produce carboxylate ion in the solid residue. The solid residue showed an absorption at 1600cm^{-1} of moderate intensity indicating the presence of some carboxylate ion.(8)

Potassium t-butoxide can also add to the carbonyl group of methoxyacetaldehyde to affect a Tischenko reaction.(14,40) This product can then transfer a hydride ion to another molecule of methoxyacetaldehyde to produce the t-butyl ester of methoxyacetic acid and the potassium salt of methoxyethanol.



$$CH_3OCH_2\overset{O}{\overset{\|}{C}}H + KtBuO \longrightarrow CH_3OCH_2\overset{O}{\overset{\|}{C}}\text{-}OtBu + CH_3OCH_2CH_2OK$$

Mixed esters can also form. However, none of these products were observed. It might be conceivable for anion III, produced from reaction A, to transfer a hydride ion to methoxyacetaldehyde thus forming the potassium salt of methoxyethanol and methyl methoxyacetate.

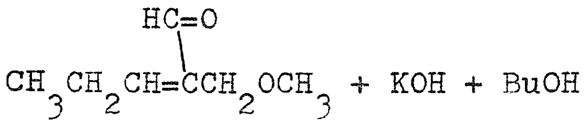


$$CH_3OCH_2CHOCH_3OK + CH_3OCH_2\overset{\overset{O}{\|}}{C}H \longrightarrow CH_3OCH_2\overset{\overset{O}{\|}}{C}OCH_3 + CH_3OCH_2CH_2OK$$

As before, none of these products formed. The solid residue from the reaction had a brown color. When the reaction was run for long periods of time at temperatures near 200°C, the solid was dark brown to black. However, at slightly milder conditions, similar to runs 1 and 2, the solid was colored light-medium brown. Trace amounts of aldol or Canizzaro products would explain the colored product.

Reaction B would produce anion IV $\left[KOCH_2CH(OCH_3)_2\right]$ which would not react any further. Two hypothetical calculations were made based on reaction A and reaction B.

The first calculation was based on reaction A only. The theoretical amount of methoxyacetaldehyde was calculated which could then undergo aldol condensation to produce:



$$CH_3CH_2CH{=}\overset{\overset{HC=O}{\backslash}}{C}CH_2OCH_3 + KOH + BuOH$$

The number of basic milliequivalents (meq.) was calculated (Appendix B), as was the number of grams of solid produced. The theoretical calculation resulted in 6.191 grams of solid containing 58.05 meq. of base (found: 6.0 grams of solid containing 49.0 meq. of base).

In the same manner, the theoretical number of milliequivalents along with the total weight of solid was calculated for reaction B. In this case, the anion does not undergo further reaction. The theoretical total weight was calculated to be 6.084 grams containing 55.09 meq. of base (found: 6.1 grams of solid containing 48.6 meq. of base).

Since the two different substitution paths do not produce a significant difference in the milliequivalents of base produced, the titration results, although closer to reaction B, are not very meaningful. This is especially true if one considers the low yields of products which were obtained (Table I). In considering the different substitution paths, the theoretical calculations were based on the formation of certain products to the exclusion of others. In reality, multi-type reactions are probably taking place, producing aldol products of various molecular weight, possibly Tischenko and Canizzaro products, enolate ion (V), and possibly some stable anion as in reaction B.

A low yield of olefin can also be explained by reaction C. In this reaction, dimethoxyethylene is consumed by potassium t-butoxide to form methyl t-butyl ether and the enolate ion (V). This reaction path is very possible due to the stability of enolate ion formation.

CONCLUSIONS

1) The bromination of vinyl acetate in methanol gave the desired bromodimethylacetal in 68% yield.

2) The methoxylation of bromoacetal gave methoxydimethylacetal in 48% yield.

3) Many different reactions were tried in order to obtain 1,2-dimethoxyethylene. The only successful reaction was the alkoxide initiated elimination of 1,1,2-trimethoxyethane in which t-butyl methyl ether, t-butanol, *cis*-1,2-dimethoxyethylene and *trans*-1,2-dimethoxyethylene were identified as products.

4) Since the *cis*-to-*trans*-ratio is 2.1:1, the cis-formation is thermodynamically favored under the reaction conditions used ($T = 160^{o}C$, $P = 200$ psi).

5) The delta values of the olefinic protons are 5.12 for the *cis*-isomer and 6.15 for the *trans*-isomer measured downfield from TMS. The *trans*-vinyl hydrogens are therefore more deshielded.

6) The number of moles of substitution product (methyl t-butyl ether) was approximately the same as the number of moles of olefin produced. This result is unusual because the reaction conditions (strong base, non polar solvent, high temperature) favor elimination processes over substitution reactions.

RECOMMENDATIONS

Due to the high stability of 1,1,2-trimethoxyethane, potassium t-butoxide can be prepared directly in the substrate instead of using another solvent such as dimethoxyethane. This eliminates vacuum evaporation of the solvent and avoids possible contamination to the base.

Further investigation for a different mode of reaction to obtain 1,2-dimethoxyethylene is definitely warranted. The base catalyzed elimination of 1,1,2-trimethoxyethane in a bomb reactor produces the olefin in poor yield. The yield may be increased by using stronger bases to abstract the proton. Bases such as phenyl lithium, phenyl sodium, ethyl lithium, etc., could be used.(42,43)

Also, in non polar solvents such as 1,1,2-trimethoxyethane, the base is essentially existing as an ion-pair.(19) Solvents such as dimethyl sulfoxide which will solvate the cation and leave the anionic portion alone will greatly increase the base strength. This should also facilitate the elimination.

Increasing the size of the cation should also increase base strength by increasing cation solvation. Benzyltrimethyl ammonium hydroxide is approximately 20 times more effective in promoting elimination than potassium t-butoxide.(9,10) Solutions of benzyltrimethyl ammonium t-butoxide are known to be at least 1000 times more basic than a solution of potassium t-butoxide of the same concentration.(10) The rate of (E2 type elimination reactions) conversion was also increased by factors of several thousand.

Different novel approaches to produce the olefin should also be considered. The reaction of sodium with glyoxal followed by methylation with methyl iodide is one example:

$$\mathrm{O{=}CHCH{=}O + 2Na \longrightarrow NaOCH{=}CHONa + 2CH_3I \longrightarrow CH_3OCH{=}CHOCH_3 + 2NaI}$$

The dehydrohalogenation of 1-chloro,-1,2-dimethoxyethane should also produce the desired olefin.

$$\mathrm{CH_3OCH_2CHClOCH_3 + KOtBu \longrightarrow CH_3OCH{=}CHOCH_3 + KCl + t\text{-}BuOH}$$

The chloro-derivative can be prepared by direct chloronation of dimethoxyethane under ultra violet light or by the addition of equal molar amounts of methanol and HCl to methoxyacetaldehyde.(34) Methoxyacetaldehyde can be prepared by oxidizing the mono-methyl ether of ethylene glycol using periodic acid, or by oxidation of 2-methoxyethanol using chromic acid.(33,37)

To make an optically active substrate deuteration is necessary. Deuteration of the olefin can be performed in a Parr apparatus at 50 psi. A liquid phase deuteration employing a 10% palladium on alumina catalyst should give *cis*-addition of the deuterium across the double bond.(47)

APPENDIX A

Analysis of Sodium Methoxide (Matheson, Collman & Bell).

108.9446g

108.5161g (tare)

0.4285g of $NaOCH_3$

$NaOCH_3$ (M.W. = 54.03

NaOH (M.W. = 40

HCl (.0970N)

phenolphthalein end point = 84.8cc

V X N = (.0848) (.0970) = .00821 Eq.

assume NaOH is present in methoxide, also assume no Na_2CO_3

therefore: $X(40) + y(54) = 0.4285$

$X + y = .00821$

where X = g moles of NaOH

y = g moles of $NaOCH_3$

$(.00821-y)40 + 54y = .4285$

$14y = .1005$

therefore: $y = .00715$

$x = .00106$

and $\frac{.3860}{.4285}$ = 90.2% $NaOCH_3$

$\frac{.0425}{.4285}$ = 9.8% NaOH

Titration of Potassium t-Butoxide Prepared by Peroxide Cleavage.

KtBuO (M. W. = 112.1)

A volume of 8.8 ml of 0.097N HCl was consumed to reach the end point.

$V \times N = (8.8)\ (0.0970) = 0.854$ meq.

$(0.854)\ (112.1) = 95.8$ mg

$$\frac{95.8 \text{ mg}}{98.4 \text{ mc}} \text{ sample} = 97.5\%\ \text{Kt}^{+}\text{-BuO}^{-}$$

Reaction Time Necessary for Methylation with $CH_3I^{(48)}$

$$\underset{(a)}{CH_3I} + \underset{(b)}{C_2H_5O^{-}K^{+}} \longrightarrow C_2H_5OCH_3 + Kl$$

in ethanol at 24°C

$$t \text{ (sec) } \frac{1}{k_2(a-b)} \quad \ln \frac{b(a-x)}{a(b-x)}$$

where:

$k_2 = 10^{-3}\ \text{sec}^{-1}\ \text{conc}^{-1}$

$b = 1.6$ (limiting)

$a = 3.2$

(a) and (b) = molecular conc (g moles/liter)

95% conversion $x = .95(1.6) = 1.520$

$$\text{therefore: } t = \frac{1}{1.6 \text{x} 10^{-3}} \ln \frac{(1.68)(1.6)}{(3.2)\ (.08)}$$

$$t = 1460 \text{ sec or } 25 \text{ min. } (95\% \text{ conversion})$$

(a) (b)

$CH_3I + CH_3O^-K^+ \longrightarrow CH_3OCH_3 + Kl$

in methanol at 27°C

$$t = \frac{1}{k_2(a-b)} \ln \frac{b(a-x)}{(a)\ (b-x)}$$

$$k_2 = A\ e^{E/RT}$$

where $A = 2.01 \times 10^{12}$ liters/mole -sec

$E = 21,940$ cal/mole

$T = 300°K$

$$k_2 = (2.01 \times 10^{12})\ e^{\frac{-21,940}{600}}$$

$$k_2 = (2.01 \times 10^{12})\ e^{-36.56} = (2.01 \times 10^{12})\ (1.26 \times 10^{-16})$$

$$k_2 = 2.54 \times 10^{-4}$$

therefore, for 95% conversion as before

$$t = \frac{1}{4.06 \times 10^{-4}} \ln \frac{(1.68)\ (1.6)}{(3.2)\ \ (.08)}$$

or t = 5790 sec = 96.5 min. for 95% conversion

APPENDIX B

Calculations for product distribution in potassium t-butoxide initiated elimination.

Products	VPC Area	Mol %	Wt. %	Yield (g)
tBuOMe	0.0153	2.910	2.220	0.520
t-BuOH	0.0381	7.230	4.650	1.090
trans-DME[a]	0.0054	1.030	0.785	0.184
cis-DME[b]	0.0114	2.160	1.650	0.386
TME[c]	0.4570	86.670	90.695	21.220
	0.5372	100.000	100.000	23.400

[a] *trans*-1,2-dimethoxyethylene [b] *cis*-1,2-dimethoxyethylene

[c] 1,1,2-trimethoxyethane (unreacted)

Start of Reaction: 7.1 KOtBu = 0.0634 moles

1.090g t-BuOH = 0.0148 moles

0.520g t-BuOMe = 0.0059 moles

therefore:

.0148 moles t-BuOH
.0059 moles t-BuOMe
.0207 moles

.0634 moles KOtBu
\- .0207 moles t-BuOH and T-BuOMe
.0427 moles of KOtBu remain unreacted

0.00209 moles *cis*-DME
+0.00439 moles of trans-DME
0.00648 moles of total olefin formed

Part A

Assume methyl t-butyl ether is formed exclusively by displacement on the methoxy carbon as in reaction A (Page 41) forming methoxy acetaldehyde, which is then assummed to produce an aldol product and KOH.

Therefore: moles of $KOCH_3$ = moles of olefin and moles of t-BuOMe

moles of KOH = 1/2 moles of t-BuOMe

moles of aldol product (M.W. = 128) = .00296 = 0.378g

t-BuOK = 42.70 meq. = 4.780g

KOMe = 12.39 meq. = 0.867g

KOH = $\underline{2.96 \text{ meq.}}$ .166g

58.05 meq.

$\underline{.378\text{g}}$ aldol

6.191g

Therefore: 6.0g = 56.3 meq. (Theory)

6.0 grams of solid obtained from the reaction was titrated as before and was found to contain 49.0 meq.

Part B

Assume methyl t-butyl ether is formed exclusively by reaction B (page 41) therefore producing no methoxyacetaldehyde.

Therefore: moles of KOCH = moles of olefin produced

moles of IV $KOCH_2CH(OCH_3)_2$ = moles of t-BuOMe formed.

KOtBu = 42.70 meq. = 4.780g

KOMe = 6.48 meq. = 0.453g

anion IV $\underline{5.91 \text{ meq.}}$ = $\underline{0.851\text{g}}$

55.09 meq. 6.084g

Therefore: 6.0g = 54.5 meq. (Theory)

6.0 grams of solid was obtained from the reaction and was titrated with 1.007N H_2SO_4. The product contained 49.0 meq.

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