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STUDIES OF REDUCTIONS OF UNSATURATED COMPOUNDS WITH LITHIUM ALUMINUM HYDRIDE

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by

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

By Robert William Barito

Approved By William B. Martin, Jr.

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HISTORICAL

Reactions involving the use of lithium aluminum hydride were first reported before the Symposium on Hydrides and Related Compounds at the Chicago meeting of the American Chemical Society, September 10, 1946. The paper which reported these reactions was a joint contribution by Finholt, Bond, and Schlesinger (1). The reactions of lithium aluminum hydride with organic compounds was presented in a series of three papers by Nystrom and Brown (2) (3) (4).

Lithium aluminum hydride, which has the formula $LiAlH_4$, is one of a group of complex metal hydrides. It has been described in the literature as a selective reducing agent for various polar functional groups. The following are some of the organic functional groups that are reduced by lithium aluminum hydride and the reduction products.

Functional Group	Product
Aldehyde	Primary Alcohol
Ketone	Secondary Alcohol
Quinone	Hydroquinone
Epoxide	Alcohol
Ester	Primary Alcohols
Lactone	Diol
Carboxylic acid	Primary Alcohol
Anhydride	Primary Alcohol

The reducing power of lithium aluminum hydride has been given the distinction of being called selective, since certain organic groups capable of reduction are not reduced under normal operating conditions. The following types are reduced either slowly or not at all: alcohols, ethers, ketals, carbon-carbon double and triple bonds, diaryl sulfones, and diakyl peroxides.

Reductions with lithium aluminum hydride are usually made in diethyl ether. Occasionally, when solids of limited solubility in diethyl ether are encountered, it is convenient to use solvents such as dioxane, tetrahydrofuran, or n-dibutyl ether. These higher boiling solvents also have been used to permit the operation of a particular reaction at temperatures above the boiling point of diethyl ether.

Reductions with lithium aluminum hydride closely resemble conventional procedures for syntheses using Grignard reagents. As in Grignard syntheses, the reactions usually give rise to intermediate metal alkoxides from which the desired products are liberated by hydrolysis. Reactions with the hydride usually proceed quite rapidly and are relatively free of side reactions. The principal limitation on yield is the loss entailed in the isolation of the product.

The structure of lithium aluminum hydride has never been determined. However, it can be assumed to have a structure similar to lithium borohydride since they closely resemble each other in properties and reactions. X-ray data on lithium borohydride indicate a polar structure consisting of lithium ions and borohydride ions (5). So, it is reasonable to assume that in ether solutions, lithium aluminum hydride exists as ionic groupings of highly solvated lithium ions and alumino hydride ions.

Reductions with lithium aluminum hydride usually proceed by displacement of a highly electronegative element (O, N, halogen, etc.) and then the acceptance of a hydrogen atom at the electron deficient center (6). Followed by coordination of the neutral aluminum hydride or the lithium ion with the nucleophilic fragment. So, it is reasonable to assume that hydrogen is transferred as hydride in a bimolecular nucleophilic displacement. The following is an illustration of the reduction of a ketone using lithium aluminum hydride as the reducing agent.

$$AlH_4^- + \overset{|}{\underset{|}{C}} = 0 \text{ — } AlH_3 + H\text{-}\overset{|}{\underset{|}{C}}\text{-}0^- \qquad I$$

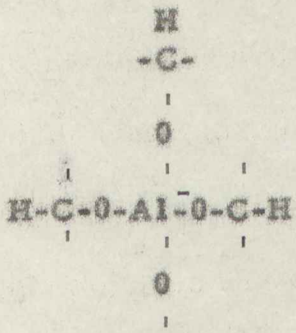
At this point in the reduction the alkoxide ion which has been formed can either combine with a lithium ion

$$H\text{-}\overset{|}{\underset{|}{C}}\text{-}0^- + Li^+ \text{ — } H\text{-}\overset{|}{\underset{|}{C}}\text{-}0^-\ Li^+ \qquad II$$

or coordinate with the neutral aluminum hydride and form a new ion.

$$H\text{-}\overset{|}{\underset{|}{C}}\text{-}0^- + AlH_3 \text{ — } H\text{-}\overset{|}{\underset{|}{C}}\text{-}0\text{-}\bar{A}lH_3 \qquad III$$

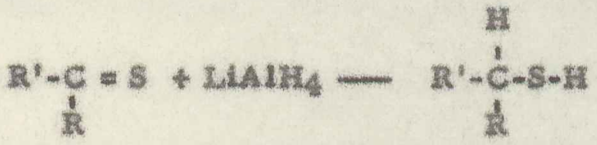
This new ion can, by a series of bimolecular reactions with additional molecules of the reactant, be converted as in equations I and II to the following:



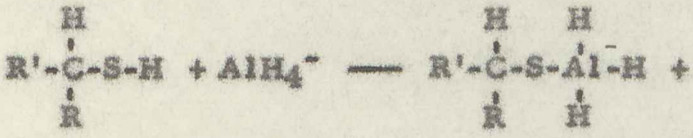
$$\begin{array}{c} H \\ \text{-}C\text{-} \\ | \\ 0 \\ | \\ H\text{-}\overset{|}{\underset{|}{C}}\text{-}0\text{-}Al^{-}\text{-}0\text{-}\overset{|}{\underset{|}{C}}\text{-}H \\ | \\ 0 \\ | \\ \text{-}C\text{-} \\ H \end{array}$$

However, it can not be stated with certainty that the aluminum hydride that is formed in the first step of this reaction coordinates with the anions formed and continues reducing other molecules of reactant by nucleophilic displacements. It has been observed in the reduction of certain alkyl halides that it is necessary to add one mole of lithium aluminum hydride per mole of alkyl halide since the reaction virtually stops after one of the four hydrogens of the original lithium aluminum hydride has reacted.

Reductions involving compounds containing nitro groups, sulfoxides, etc., proceed by a more complicated series of reactions. In these reductions there is an evolution of hydrogen gas. In reactions of this type a hydrogen atom combines with a sulfur atom or a nitrogen atom forming an active hydrogen atom, which is removed by further reaction with the metal hydride.



$$R'\text{-}\underset{R}{C}=S + LiAlH_4 \longrightarrow R'\text{-}\overset{H}{\underset{R}{C}}\text{-}S\text{-}H \qquad \text{IV}$$



$$R'\text{-}\overset{H}{\underset{R}{C}}\text{-}S\text{-}H + AlH_4^- \longrightarrow R'\text{-}\overset{H}{\underset{R}{C}}\text{-}S\text{-}\overset{H}{\underset{H}{Al^-}}\text{-}H + H_2 \qquad \text{V}$$

There is confusion in the literature concerning the reduction of carbon-carbon double bonds by lithium aluminum hydride. Nystrom and Brown cited the fact that the double bonds, in certain unsaturated compounds, were not reduced (2). In their paper they reported that crotonaldehyde was reduced to crotyl alcohol, methyl oleate was reduced to oleyl alcohol, and sorbyl chloride was reduced to sorbyl alcohol. In each of these cases the carbon-carbon double bond was not reduced. In another paper Nystrom and Brown stated that double bonds of aliphatic unsaturated acids, e. g., sorbic acid, were not affected by lithium aluminum hydride (4). Later, Hochstein and Brown reported the reduction of the double bond in allyl alcohol under forcing conditions (7). Likewise, upon prolonged refluxing, alpha-ethyl crotonamide was reduced to beta-ethyl butyl amine (8). However, cinnamic acid, cinnamyl alcohol and cinnamaldehyde were reduced by lithium aluminum hydride* to hydrocinnamyl alcohol. This product was obtained if the cinnamic acid, or cinnamyl alcohol, or cinnamaldehyde, in ether solution, was added to a solution of lithium aluminum hydride, even, if the reaction was started at room temperature and never exceeded the boiling point of the diethyl ether (34.6° C). However, reduction of the double bonds in these compounds could be avoided by mixing the reactants in the inverse order, operating the reaction at a lower temperature, and adding a minimum quantity of the hydride. It was suggested by Nystrom and Brown that it is characteristic of lithium aluminum hydride to reduce ethylenic nuclei that are substituted on one side by a phenyl group and on the other side by a reducible group (carboxyl, carbonyl, nitro, etc.) (4).

Benedict and Russell carried out the reductions of acetylene dicarboxylic, propiolic, acrylic and fumaric acids with lithium aluminum hydride at room temperature (9). According to their results, acids containing triple bonds such as acetylene dicarboxylic and propiolic were reduced to the corresponding ethylenic alcohols; acrylic and fumaric acids were reduced to allyl alcohol

*Sufficient $LiAlH_4$ was added to reduce the double bond.

and 2-butene - 1, 4 diol respectively. These results are in disagreement with the results obtained by Slysh (10). Slysh observed that upon reducing dimethylfumarate with lithium aluminum hydride, he obtained the completely reduced product, butane - 1, 4 diol. The reduction of dimethylfumarate with lithium aluminum hydride in ether and in tetrahydrofuran at room temperature and in tetrahydrofuran at ice temperature under nitrogen, resulted in butane - 1, 4 diol. Further, fumaric acid was reduced by lithium aluminum hydride in ether solution according to the procedure employed by Benedict and Russell. The reduction product in this experiment was not successfully isolated. This reaction was not repeated by Slysh. Again, fumaric acid was reduced by lithium aluminum hydride in tetrahydrofuran. The reaction was carried out in an ice-water bath. Care was taken to keep the temperature of the reaction mixture below 5° C. The reduction product from this experiment was identified as butane - 1, 4 diol.

Carbon-carbon double bonds have been reported to have been reduced by lithium aluminum hydride in molecules that do not contain polar functional groups. An example of this was the reduction of p-bromobenzylidenefluorene to p-bromobenzylfluorene, which has been reported by Lavie and Bergmann (11). Several other unsaturated fluorene compounds were reduced by Lavie and Bergmann. In some of the fluorene compounds which they investigated, there was conjugated carbon-carbon double bond unsaturation. With these compounds it was observed that one of the carbon-carbon double bonds was reduced and the other was not reduced. An example of this is the reduction of 9-cinnamylidenefluorene to 9- cinnamylfluorene.

Our work has involved the reduction of certain alpha-beta unsaturated carbonyl compounds and the reduction of two compounds that did not contain alpha-beta unsaturated carbonyls. These compounds that had alpha-beta unsaturation contained a conjugated carbonyl and carbon-carbon double bond. Following is a list of the compounds which we reduced:

dimethyl fumarate	alpha-beta unsaturation
diethylmaleate	
chalcone (Benzylidene acetophenone)	
4-phenyl - 3 butene - 2 - one (benzalacetone)	
methyl vinyl cyclo tetrasiloxane	no alpha-beta unsaturation
bicycloheptadiene	

The aim of this project was to determine the extent of the saturation of carbon-carbon double bonds; therefore, the evaporated concentrates were titrated for double bond content without attempting to isolate separate products; it was felt that Slysh might have obtained some butene-diol in his reduction of fumarates, but that his separation technique isolated only the saturated portion of the products.

EXPERIMENTAL

1. Grignard Reagent Used for the Production of Anhydrous Ether

A single neck, two liter flask, fitted with a ground glass stoppered refluxate take-off and a condenser, was charged with one mole of butyl bromide (137_g), an equal volume of diethyl ether, and .25 moles of magnesium (6_g) If the reaction was a little sluggish in starting some of the magnesium was broken under the liquid with a stirring rod. If the reaction still did not start heat was applied to the flask by means of a Glas-col heater. Once the reaction started an exothermic reaction ensued and it was necessary to cool the flask with a water bath. When the .25 moles of magnesium had completely reacted and the flask had cooled sufficiently, more magnesium was added. This process was continued until one mole of magnesium had been added to the flask. At this point diethyl ether was added to the flask until the flask was about three quarters full.

Whenever anhydrous ether was needed the flask was heated by means of a Glas-col heating mantle and the ether was distilled into an arm on the take-off and from there it was drained directly into the reaction flask. The take-off was positioned between the flask and the condenser.

As the ether in the flask was depleted, more ether would be added periodically to replenish the supply. When the Grignard reagent lost its characteristic gray color the solution was discarded and a new solution was prepared.

2. Reduction of Dimethylfumarate and Subsequent[*] Williamson Sythesis Attempt

A one neck flask that was fitted with a condenser and a magnetic stirrer was charged with .125 moles (14.5g) of dimethylfumarate. A sufficient quantity of anhydrous diethyl ether was added to dissolve it. In a separate container 0.187 mole (7.1g) of $LiAlH_4$ was weighed out and to it was added anhydrous ether. The suspension of $LiAlH_4$ in ether was added to the flask batchwise. The ether in the flask began refluxing everytime a batch of the $LiAlH_4$ suspension was added. After the addition of the last batch, the reaction was allowed to stir for 72 hours. Then 0.75 moles (106g) of methyl iodide was added to the reaction flask in 10 batches. After the addition of each batch of methyl iodide, the reaction flask was shaken. It was necessary to shake the flask since the solids formed in the reaction prevented the magnetic stirrer from agitating the mixture adequately. The ether in the flask refluxed with each addition of methyl iodide. However, when the last batch of methyl iodide was added, no refluxing was observed. The reaction was then permitted to stir for three days. The mixture was filtered under nitrogen and the filtrate was concentrated by distilling the ether. Only a fraction of a gram of materials remained behind. An infrared analysis was made on the crystalline product and the spectrum that was obtained indicated that no organic materials were present. This material melted at 70-71° C. A red flame test led to an investigation of lithium salts; it was found that $LiI \cdot 3H_2O$ melts at 73° C.

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[*] Prepared by R. Slysh in this laboratory; m.p. 102° C

The solid material was mixed with water in an attempt to find the organic products. This was then filtered and the filtrate was continually extracted with chloroform for three days. The chloroform was distilled from its extract solution and an infrared analysis made on the small fraction of a gram of the product. The product showed very little hydroxyl absorption. This spectrum lacked a strong OH^- absorption, but showed 2 carbonyl absorptions at 5. 64 microns and 5. 74 microns and ester absorptions at 8. 75 microns and 8. 54 microns.

3. Reduction of Cinnamaldehyde and Subsequent Williamson Synthesis Attempt

This reaction was carried out simultaneously with the one just described.

A one neck flask that was fitted with a condenser and a magnetic stirrer was charged with 0. 10 moles (13. 2g) of freshly distilled cinnamaldehyde. Anhydrous ether was added to the flask until the cinnamaldehyde was completely dissolved. In a separate container a slurry of 0. 050 moles (1. 9g) $LiAlH_4$ in ether was prepared. The suspension of $LiAlH_4$ was added to the flask batchwise. With each addition of $LiAlH_4$ a vigorous reaction followed. The reaction was stirred for 72 hours. After this period 0. 2 moles (28. 4g) of methyl iodide was added batchwise to the reaction flask. When the methyl iodide was added there was no apparent reaction. Again, it was necessary to shake the flask, since sufficient agitation could not be obtained with the magnetic stirrer. The reaction was filtered under nitrogen and then concentrated by distilling the ether. The weight of the ether-soluble material from this reaction was 10. 67g. The infrared spectrum showed some unreacted cinnamaldehyde to be present (greatly reduced C=O absorption at 5.95 microns). The other absorption peaks were generally similar to those of cinnamaldehyde with the exception of a strong OH^- absorption at 2.96 microns and a medium strength absorption at 9.17 microns.

4. Reduction of Dimethylfumarate

An apparatus was assembled which consisted of a 500 cc. three neck flask which was fitted with a mechanical stirrer, an extraction vessel in each of the side arms, with a condenser attached to each of the extraction vessels. Each of the extraction vessels contained a platform of sintered glass on which the $LiAlH_4$ or the material to be reduced could be placed.

One extraction vessel was charged with 0.125 moles (14.5g) of dimethylfumarate and the other extraction vessel was charged with 0.25 moles (9.5g) of $LiAlH_4$. The reaction flask was filled to about the half way mark with anhydrous ether and then the flask was heated causing the ether to reflux. It was observed after a few minutes that the ether was only refluxing in the extraction vessel containing the dimethylfumarate. The heating mantle was removed and the apparatus was disassembled. Examination of the extraction vessel containing the $LiAlH_4$ indicated that the sintered glass was being plugged with $LiAlH_4$ due to its limited solubility in ether.

In order to overcome this difficulty the reagents were transferred to two straight glass columns which were loosely plugged with glass wool at the bottom. The apparatus was reassembled with the glass columns in place of the extraction vessels and again the flask was heated. The refluxing ether brought the reactants into the reaction flask at about the same rate. After four hours the reactants were all in the reaction flask. The mixture was permitted to stand for 72 hours. Water was cautiously added to decompose the excess of $LiAlH_4$ and to hydrolyze the salts. The ether layer was carefully decanted and found to contain 2.7g of a material with a very disagreeable odor. The solids were mixed with more water and then filtered. The filtrate was an orange-brown color. After continuously extracting the aqueous solution for 10 hours with chloroform, it was found that only a fraction of a percent of product had been extracted. The aqueous solution was extracted several times with chloroform by shaking vigorously in a separatory funnel. Again, the combined chloroform extracts were found to contain only a fraction of a percent of product. The solids were then mixed with chloroform and permitted to stand for three days. The material was filtered and again the chloroform was found to have extracted only a fraction of a percent of product.

The aqueous solution was neutralized with dilute hydrochloric acid. Toluene was added and the entire mixture was placed in a distilling apparatus. After the water was completely removed by azeotropic distillation from the mixture, a sticky amorphous solid remained on the bottom of the flask. The amorphous solid was found to weigh 8.05g. The infrared spectrum on this material indicated the presence of butane - 1,4 diol and lithium or aluminum salts of carboxylic acids.

The product was redissolved in water and extracted with ethyl acetate. When the ethyl acetate was evaporated it was found to contain 0.17g of material. An infrared spectrum of this material matched the spectrum of butane- 1,4 diol fairly closely, the main difference being that of carbonyl peaks at 5.70 microns and 5.95 microns in this spectrum.

The aqueous solution was extracted with other solvents in an attempt to affect a better separation. Following is a list of the solvents used:

m-cresol
cyclohexane
petroleum ether
ethyl butyl ketone
methyl amyl ketone
isobutyl keptyl ketone
2, 4 pentandione

Nothing was extracted with any of these solvents.

The infrared spectrum of the aqueous concentrate showed absorption peaks found in butane - 1,4 diol (see reference infrared spectra in Union College Chemistry Department file). Besides these, absorptions were found at 6.2, 6.3 and 7.1 microns which are in accord with Bellamy's (13) (ref. - p. 149, 150) assignment for the carboxylate ions. A flame test on the aqueous solution confirmed the presence of lithium ions. Absorptions at 3.40 and 3.47 microns respectively indicate the presence of CH and CH_2 absorptions. Results of titration for unsaturation in this aqueous concentrate are found in table I.

5. Reduction of Diethylmaleate

A 500 cc three neck flask was fitted with a mechanical stirrer, a glass column in one of the side arms, which contained a soxhlet extraction tube, a condenser on top of the glass column, and a dropping funnel in the other side arm of the flask. The soxhlet extraction tube was filled with 0.25 moles (9.5g) of $LiAlH_4$ and the dropping funnel was charged with 0.125 moles (21.5g) diethylmaleate, sp. g. 1.0675, refractive index 1.4408 (values of 1.070 and 1.4407 respectively from Lange's Handbook). Anhydrous ether was added to the flask until it was about half full.

The flask was heated, by means of a heating mantle, causing the ether to reflux and extract the $LiAlH_4$. At the same time diethylmaleate was dripped into the flask. It was observed that as the diethylmaleate reacted with the $LiAlH_4$ sufficient heat was generated to cause the ether to reflux. So, the heating mantle was turned off. The reaction was stirred for two hours after all of the reactants were in the flask, and then permitted to stand for 72 hrs. Sufficient water was cautiously added next to decompose the excess $LiAlH_4$ and to hydrolyze the salts. The reaction was filtered. The filtrate was extracted, in a separatory funnel, several times with chloroform. The chloroform was evaporated and it was found that none of the product had been extracted.

The aqueous solution containing the product was placed in a one neck flask that was fitted with the necessary distillation equipment. Toluene was added to the flask and the flask was heated causing the toluene and water to azeotrope. As the toluene in the flask was depleted, the heating was stopped and the toluene that had been distilled was returned to the flask. This process was continued until about all of the water was removed from the product. It was observed that as the water was removed a relatively small amount of a crystalline solid was forming on the walls of the flask. This was assumed to be the water soluble LiOH. The reaction product was then vacuum filtered to remove the crystalline solid that was present. Then the filtrate was redissolved in distilled water and continuously extracted with ethyl acetate. The ethyl acetate was evaporated. A total of 1. 55g of product was extracted by ethyl acetate. This would correspond to a 14% yield, if it were pure butane 1, 4 diol. Its infrared spectrum indicated that it was almost entirely butane 1, 4 diol (Union College Infrared Spectrum #55-6). There was a trace of carbonyl absorption at 5. 81 microns.

In order to determine the amount of carbon-carbon double bond unsaturation remaining in the product, a method of titrating double bonds was adapted from Siggia (12). A summary of the results obtained for this titration, the titration of reaction products obtained in the subsequent experiments, and the titration of the unreduced parent compounds, will be found at the end of the experimental section in table I.

6. Reduction of Dimethylfumarate

Dimethylfumarate was again reduced in order to obtain enough of the reduction product for a titration to determine the percentage of remaining double bonds. The same amounts of reactants were used in this reaction as were used in the previous reduction of dimethylfumarate. Essentially the same apparatus and conditions were employed in this reduction as were used in the previous one. Results of the titration on the product of this reaction are tabulated at the end of the experimental section.

7. Reduction of Chalcone (Benzylidene Acetophenone)

A 500 cc., three neck flask fitted with a mechanical stirrer and a reflux condenser was charged with 0. 20 moles (41. 6g) of chalcone and sufficient ether to dissolve the chalcone. 0. 10 moles (3. 8g) of finely powdered $LiAlH_4$ was added to the reaction flask batchwise. As the $LiAlH_4$ was added, no refluxing of the ether was observed. The reaction was then permitted to stand for 72 hours. At this time, no visible changes seemed to have occurred.

A 25 cc. sample of the clear liquid was taken from the reaction flask. Enough water was added to the sample to decompose the excess $LiAlH_4$ and to hydrolyze the product. Dilute hydrochloric acid was added to neutralize the sample. The ether layer was decanted and the ether removed by evaporation. An infrared analysis and a titration for double bonds was made on the sample. These results will be recorded after the next paragraph.

The remainder of the mixture in the flask was refluxed for 36 hours. Sufficient water was then added to just decompose the excess $LiAlH_4$ and hydrolyze the salts. The contents of the flask were filtered. The filtrate was a pale yellow color. After evaporating the ether it was found that a nearly quantitative yield was obtained (41. 8g).

No differences at all were noted between the spectra of the early sample and the hydrolyzed end product. Both showed the strong OH^- absorption at 2. 9 microns. New absorptions appeared at 3. 41 and 3. 50 microns. The former absorption is due to CH_2 groups which result from reduction of the carbon carbon double bond. The original absorptions at 3. 26 and 3. 30 remain (trans and cis CH absorptions respectively at HC=CH double bond group in the commercial mixture of the two), indicating that double bond reduction is not complete. If the relative intensities of these two absorptions before and after reduction are significant, it would appear that the trans isomer is reduced at the double bond to a greater degree than the cis isomer. The new absorption at 3. 50 microns may be due to the secondary alcohol CH absorption at $\overset{\overset{H}{|}}{C}\text{-O-H}$.

An absorption also occurs at 5. 95 microns which is found as a shoulder in the parent chalcone. This is probably not a carbonyl absorption since the carbonyl abosrption of the parent compound occurs at 6. 01 microns. The C-O stretch of the alpha-beta unsaturated alcohol appears in the product at 9. 5 microns (Zeiss & Tsutsui (14)). A broad absorption shoulder for saturated alcohol C-O absorption occurs at 9. 0 microns.

Titration data for chalcone and the reduction products are to be found in table I at the end of this experimental section. Neither the parent compound nor its reduction product gave satisfactory titrations by Siggia's method, either with the $HgSO_4$ catalyst or without it.

8. Reduction of Benzalacetone (4-phenyl 3-buten 2-one)

A 500 cc., three neck flask fitted with a mechanical stirrer and a reflux condenser was charged with 0.20 moles (29.2g) of benzalacetone and sufficient ether to dissolve the benzalacetone. 0.10 moles (3.8g) of $LiAlH_4$ was finely powdered and added to the reaction batchwise. Each time a portion of $LiAlH_4$ was added, the ether refluxed for a few minutes. The reaction was then permitted to stand for 72 hours.

Just enough water was added to the reaction to decompose the excess $LiAlH_4$ and hydrolyze the salts. The reaction was filtered and the filtrate was concentrated by evaporating the ether. After weighing the product it was determined that nearly a quantitative yield (29.5g) was obtained. Titration data are to be found in table I at the end of this section of experimental work.

The infrared spectrum of the reduced mixture of benzal acetone indicated both trans and cis C-H stretching absorptions (3.36 and 3.40 microns respectively). The trans had been the stronger of the two peaks in benzal acetone, but this relationship was reversed in the reduction mixture. The C-O carbonyl absorption had disappeared. In the reduction product, carbinol was noted by O-H absorption at 2.96 microns and the two C-O stretch absorptions at 8.9 and 9.5 microns for a saturated secondary alcohol and the unsaturated allyl type alcohol respectively. Saturation of the double bond was indicated by absorption for CH_2 groups at 3.41 and 3.5 microns respectively.

9. Reduction of Methyl Vinyl Cyclotetrasiloxane

A 500 cc., three neck flask fitted with a mechanical stirrer and condenser was charged with 0.125 moles (43g) of methyl vinyl tetrasiloxane. Sufficient ether was added to dissolve it. 0.125 moles (4.7g) of $LiAlH_4$ was finely powdered and added to the flask batchwise. The ether did not reflux when the $LiAlH_4$ was added to the flask. However, it was noted that an odor reminiscent of a silane was given off by the reaction mixture when the $LiAlH_4$ was added. After the addition of the last portion of $LiAlH_4$ the reaction was permitted to stand for 72 hours.

When work was resumed on this reaction it was found that all of the ether had evaporated. The silicone product on the bottom of the flask was observed to be a waxy solid. Water was added to decompose the excess LiAlH4 and hydrolyze the salts. Toluene was added to dissolve the silicone. The entire mixture was then filtered. The toluene solution was shaken with several portions of water until the solution was neutral to litmus paper. The toluene solution was then transferred to a one neck flask fitted with a Snyder column, thermometer, and a condenser. After distillates boiling up to about 115° were removed, it was determined that 7.8g of product remained in the flask. This corresponds to an 18.1% yield. Data on the results of the titration of this product can be found at the end of the experimental section in table II. The infrared absorption spectrum of the reduced product shows only three peaks not found in the parent methyl vinyl cyclotetrasiloxane, and these are found to be the strongest peaks of toluene, so are apparently due to traces of toluene.

10. Reduction of Bicycloheptadiene

A 500 cc., three neck flask fitted with a mechanical stirrer and a condenser was charged with 0.25 moles (23g) of bicycloheptadiene. Sufficient ether was added to dissolve it. 0.125 moles (4.7g) of $LiAlH_4$ was finely powdered and added to the reaction flask batchwise. It was observed that the ether did not reflux when the $LiAlH_4$ was added, but that gas was evolved fairly rapidly at each addition. The reaction mixture was permitted to stand for 72 hours.

When work was resumed, water was cautiously added to the reaction flask. The reaction was then filtered and transferred to a one neck flask fitted with a packed column, a thermometer and a condenser. Xylene was added to the flask as a chaser for the distillation. The flask was heated and ether began distilling at 36° C. Following the distillation of the ether, four fractions were collected. The four fractions were collected over the following temperature ranges:

		Estimated Volumes
Fraction 1	41°C - 61°C	10cc
Fraction 2	64°C - 70°C	5cc
Fraction 3	87°C - 95°C	10cc
Fraction 4	110°C - 125°C	12cc

The boiling point of the pure bicycloheptadiene is 96° C.

Infrared data indicated the following:

Fraction 1: This fraction contained mostly ether, since all of the diethyl ether peaks were found to be present. In addition, none of the bicycloheptadiene peaks were missing, except peaks where ether absorptions covered the area and then lack of absorption might have been noted. Ether CH_2 absorptions obscured the presence or lack of reduction of double bonds in bicycloheptadiene.

Fraction 2: Again, ether absorptions were present, although diminished in intensity. And again, all parent absorptions were found present. The only new absorption noted, which was not found in the parent compound or ether, was one at 5.6 microns.

Fraction 3: Absorptions for ether were now largely lacking except for possibly trace amounts causing the absorption at 8.95 microns. Beyond the parent peaks, this fraction showed absorptions at 5.5, 6.18, 6.60, 7.42, 8.95 (possibly ether), 9.31, 9.66, 11.34, 13.04 and 14.5 microns.

Fraction 4: Rather than list absorptions, it might best be said that all absorptions fitted those for either the parent compound or xylene.

TABLE I
RESULTS ON TITRATION OF CARBON-CARBON DOUBLE BONDS

Sample	Wt. of sample, mg	M. moles of sample	Meq. of Br_2 avail.	Meq. of $Na_2S_2O_3$	Meq. Br_2 Consumed	Meq. of double bonds left	Double bonds/ mole
Dimethylfumarate	68.0	.472	.9050	.5324	.3726	.1863	.394
"	60.8	.422	.9110	.5460	.3650	.1825	.432
Reduction product of dimethylfumarate	65.0	.738	.8955	.7600	.1355	.0677	.092
" "	62.0	.704	.9172	.7533	.1639	.0820	.116
Diethylmaleate	54.5	.3168	.9080	.2817	.6263	.3131	.988
"	55.0	.3197	.9350	.3016	.6334	.3167	.990
Reduction product of diethylmaleate	61.0	.693	.9075	.7842	.1233	.0617	.089
" ' "	61.0	.693	.9111	.7872	.1239	.0619	.089
Chalcone	87.8	.422	.9013	.0530	.8483	.4242	1.005
(benzylidene	75.8	.364	1.986	1.329	.657	.329	.903
acetophenone)	93.0	.447	.8986	.3384	.5602	.2801	.627
Reduction product of chalcone (before refluxing)	52.3	.250	.9132	.5589	.3543	.1772	.709
" "	31.8	.152	.9095	.6032	.3063	.1532	1.007
Reduction product of chalcone (after refluxing)	110.6	.529	.8941	.5373	.3568	.1784	.337
" "	120.9	.578	.9038	.4552	.4486	.2243	.387
Benzalacetone	60.5	.414	.9034	.0512	.8522	.4261	1.03
"	31.0	.212	.9070	.4589	.4481	.2240	1.06
Reduction product of benzalacetone	66.1	.449	.8990	.3920	.5070	.2535	.564
" "	53.9	.367	.9095	.5400	.3695	.1848	.503

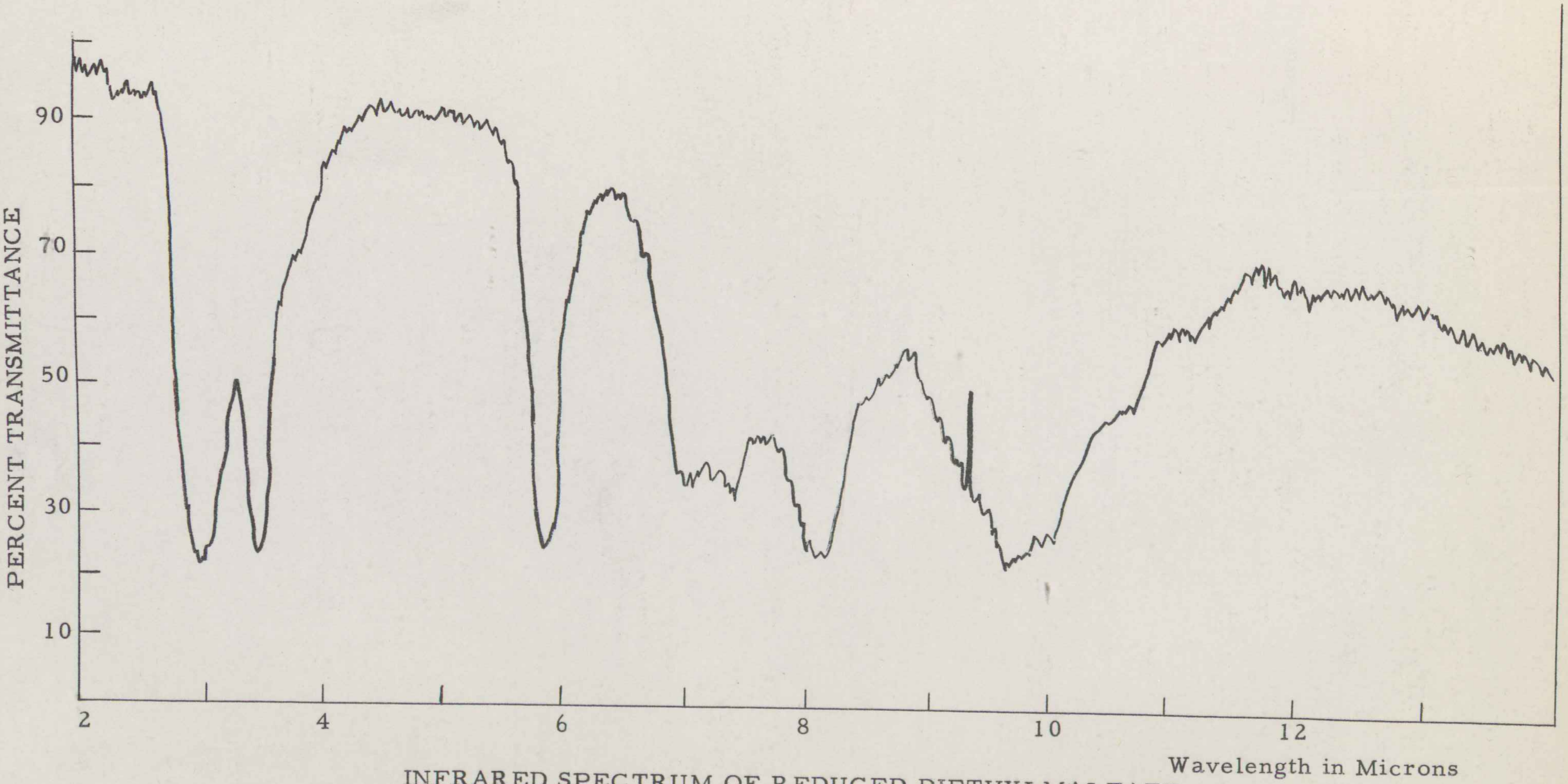
TABLE II

RESULTS ON TITRATION OF CARBON-CARBON DOUBLE BONDS

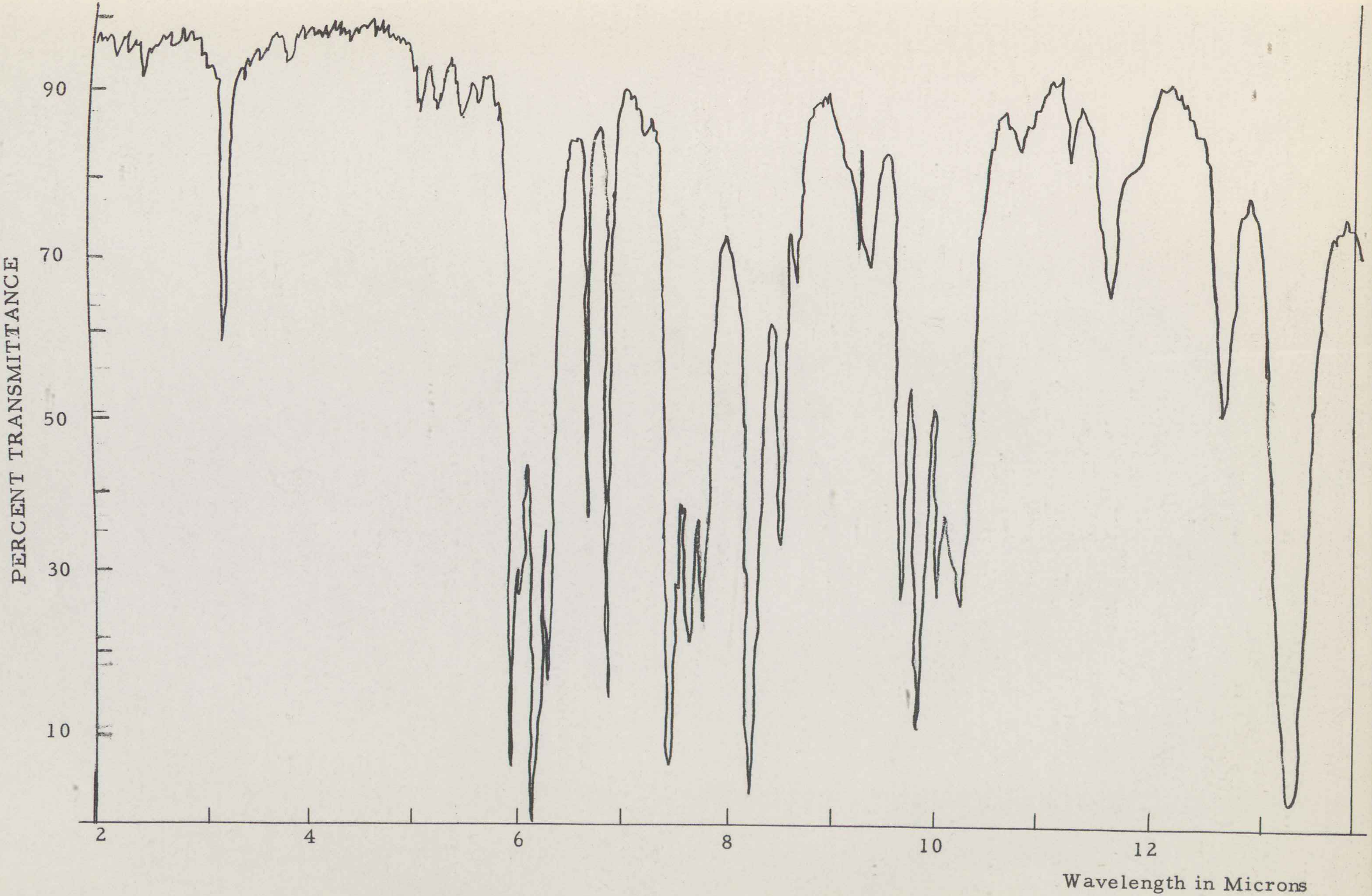
Sample	Wt. of sample, mg	M. moles of sample	Meq. of Br_2 avail.	Meq. of $Na_2S_2O_3$	Meq. Br_2 Consumed	Meq. of double bonds left	Double bonds/ mole
Methyl vinyl Tetrasiloxane*							1.00± .02
Reduction product							
of methyl vinylcyclotetra-	38.3	.435	.9110	.0784	.8326	.4163	.957
siloxane	37.8	.429	.9130	.0628	.8502	.4251	.990
Bicycloheptadiene	18.8	.204	.8960	.3310	.5650	.2825	1.384
"	23.4	.254	.8820	.1370	.7450	.3725	1.466
"	25.5	.266	.9510	.1740	.7770	.3885	1.460
Reduction product of bicycloheptadiene							
Fraction 1	28.4	.308	1.1590	.9911	.1679	.0839	.272
" "	63.8	.693	.9007	.5740	.3267	.1634	.236
Fraction 2	54.2	.589	.9000	.0105	.8895	.4448	.755
" "	49.5	.538	1.1720	.0718	1.1002	.5501	1.022
Fraction 3	20.8	.226	.9060	.3525	.5535	.2768	1.224
" "	53.8	.584	.9330	.0431	.8899	.4449	.762
Fraction 4	39.2	.426	.8945	.2270	.6675	.3338	.783
" "	81.3	.883	1.2010	.2526	.9484	.4742	.537

***Results obtained by Dr. W. B. Martin at the G. E. Silicone Plant, Waterford, New York**

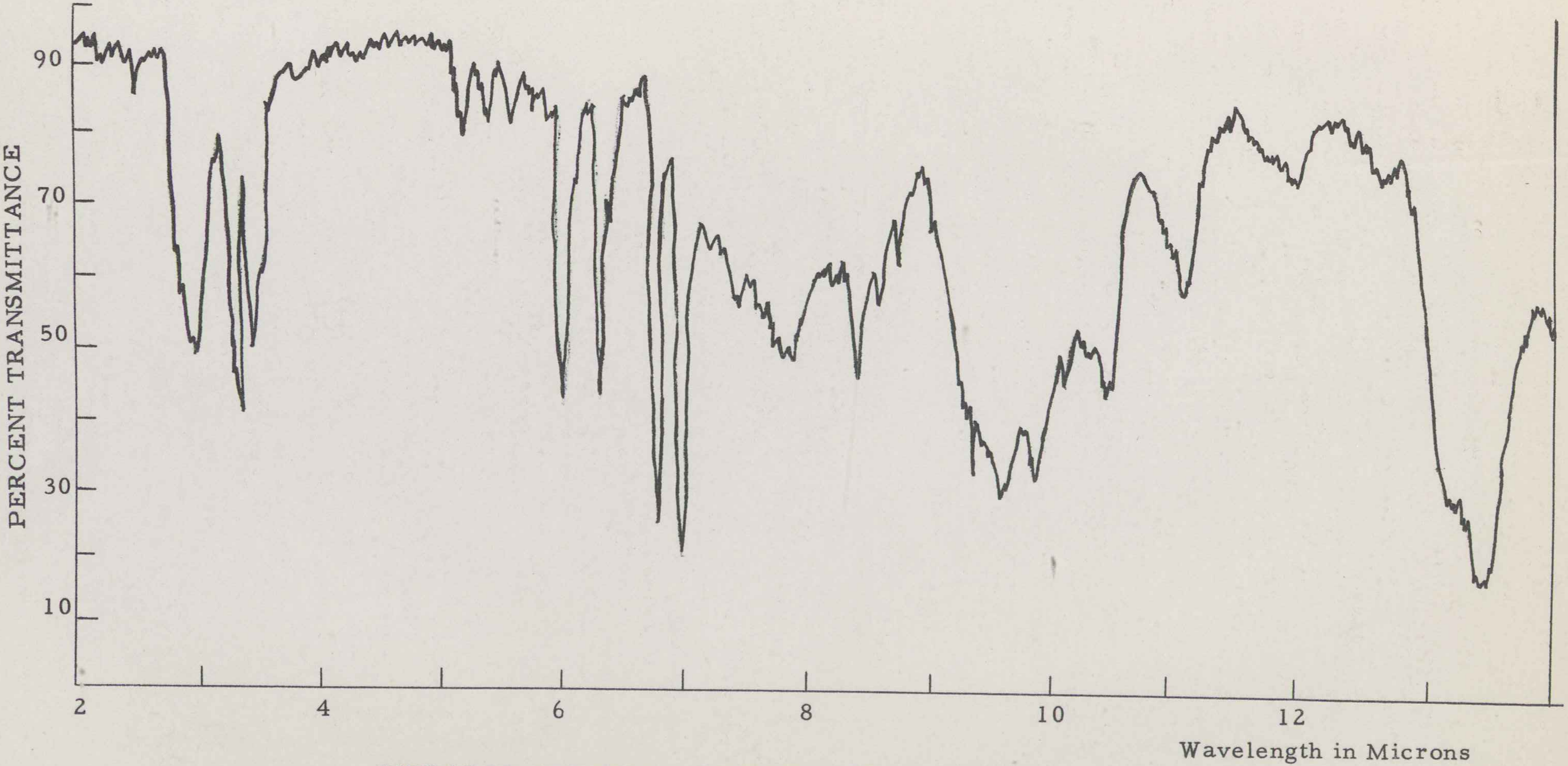
Concentration of KBrO3 was .1202N and $Na_2S_2O_3$ was .025N



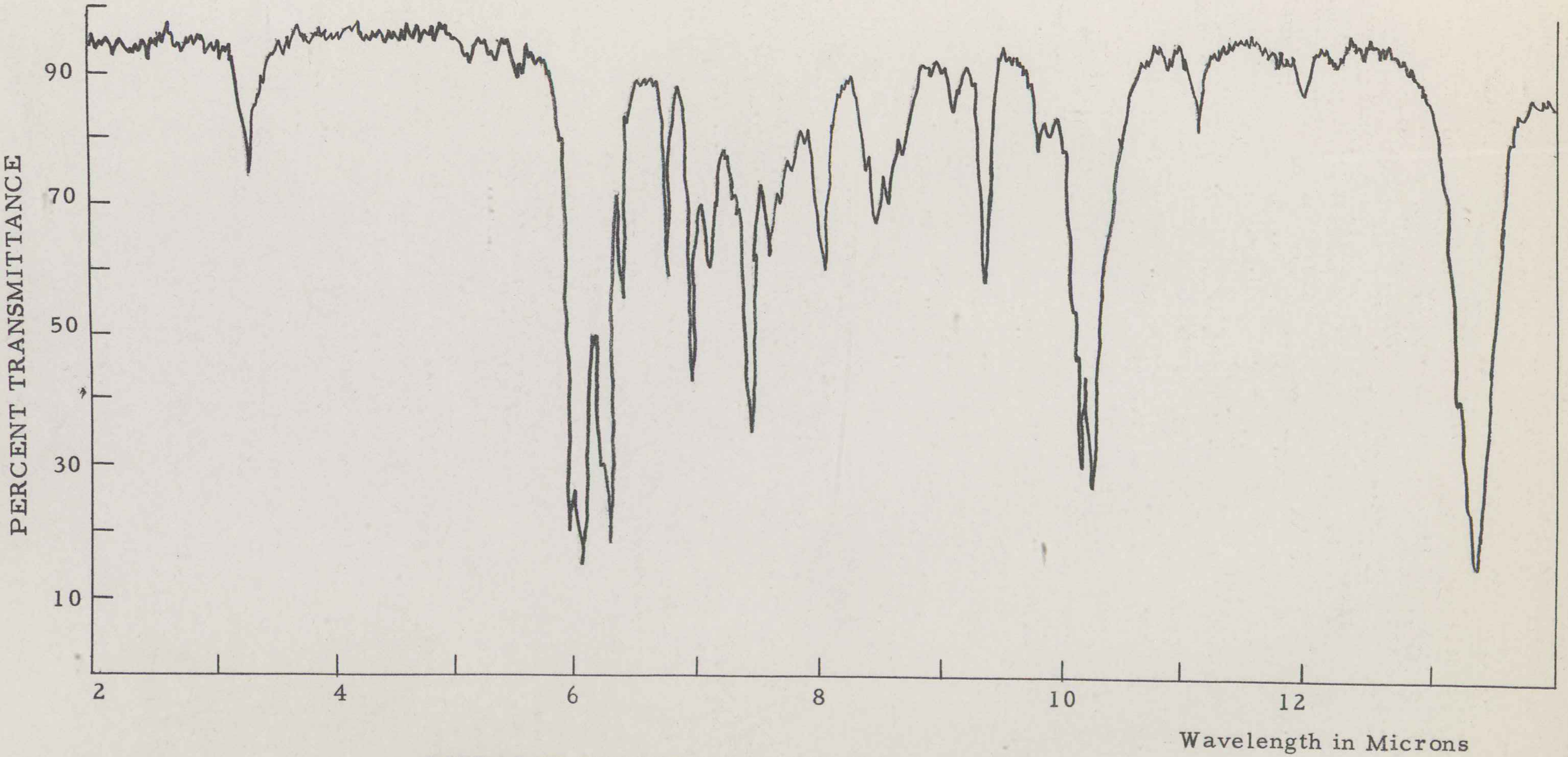
INFRARED SPECTRUM OF REDUCED DIETHYLMALEATE
(Ethyl Acetate Extract)
Plate I



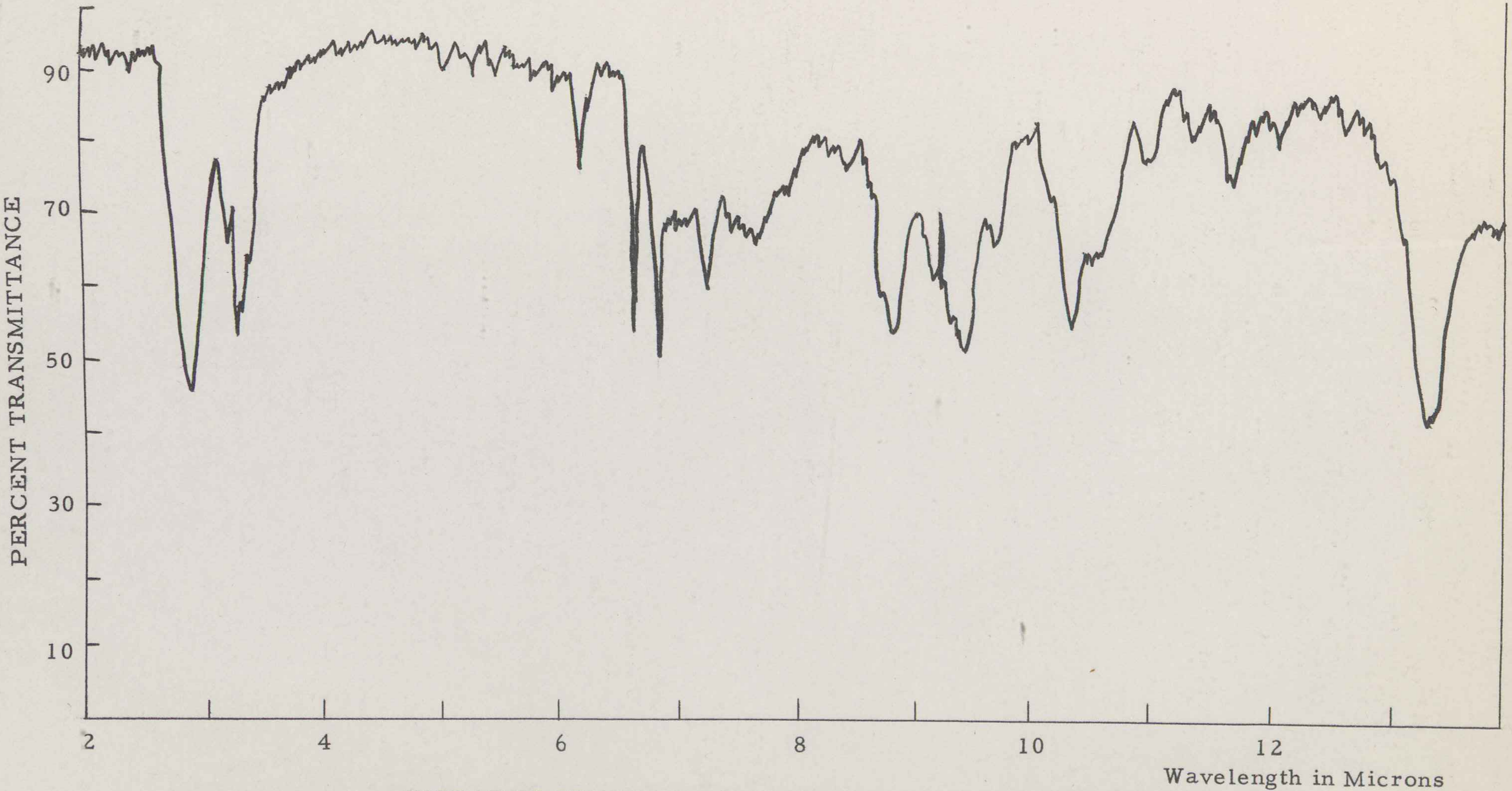
INFRARED SPECTRUM OF CHALCONE
Plate II



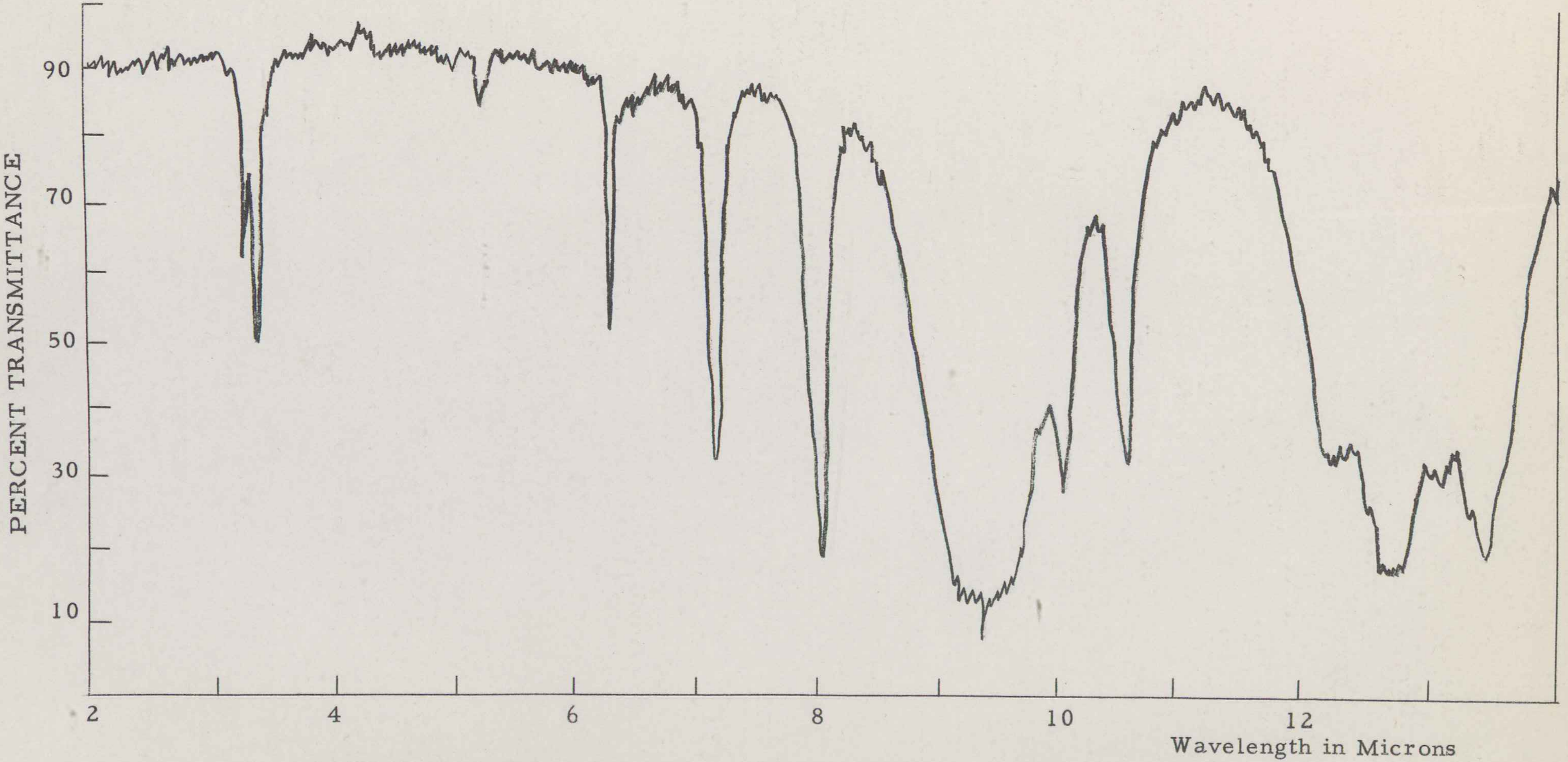
INFRARED SPECTRUM OF REDUCED CHALCONE
(Before Refluxing)
Plate III



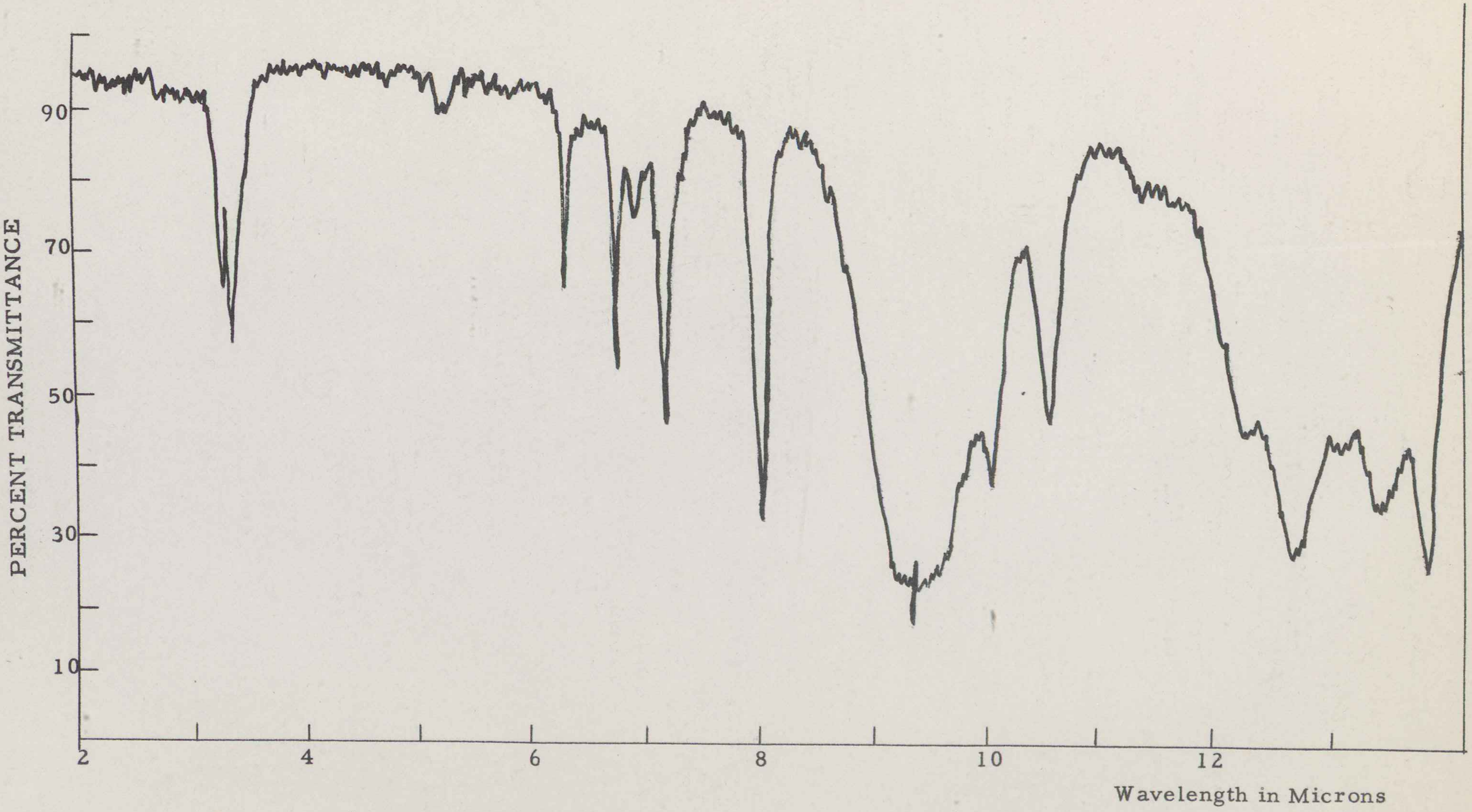
INFRARED SPECTRUM OF BENZALACETONE
Plate IV



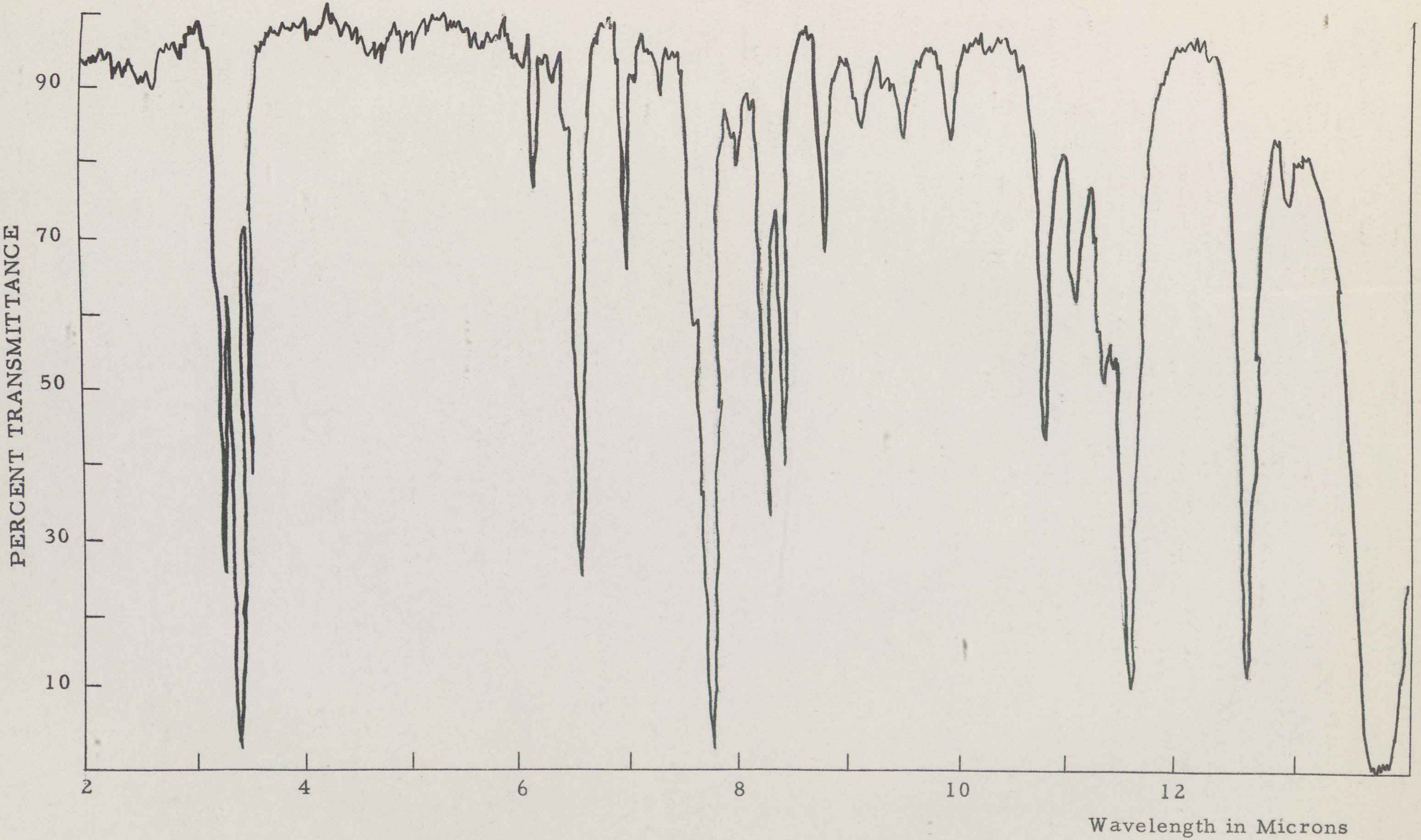
INFRARED SPECTRUM OF REDUCED BENZALACETONE
Plate V



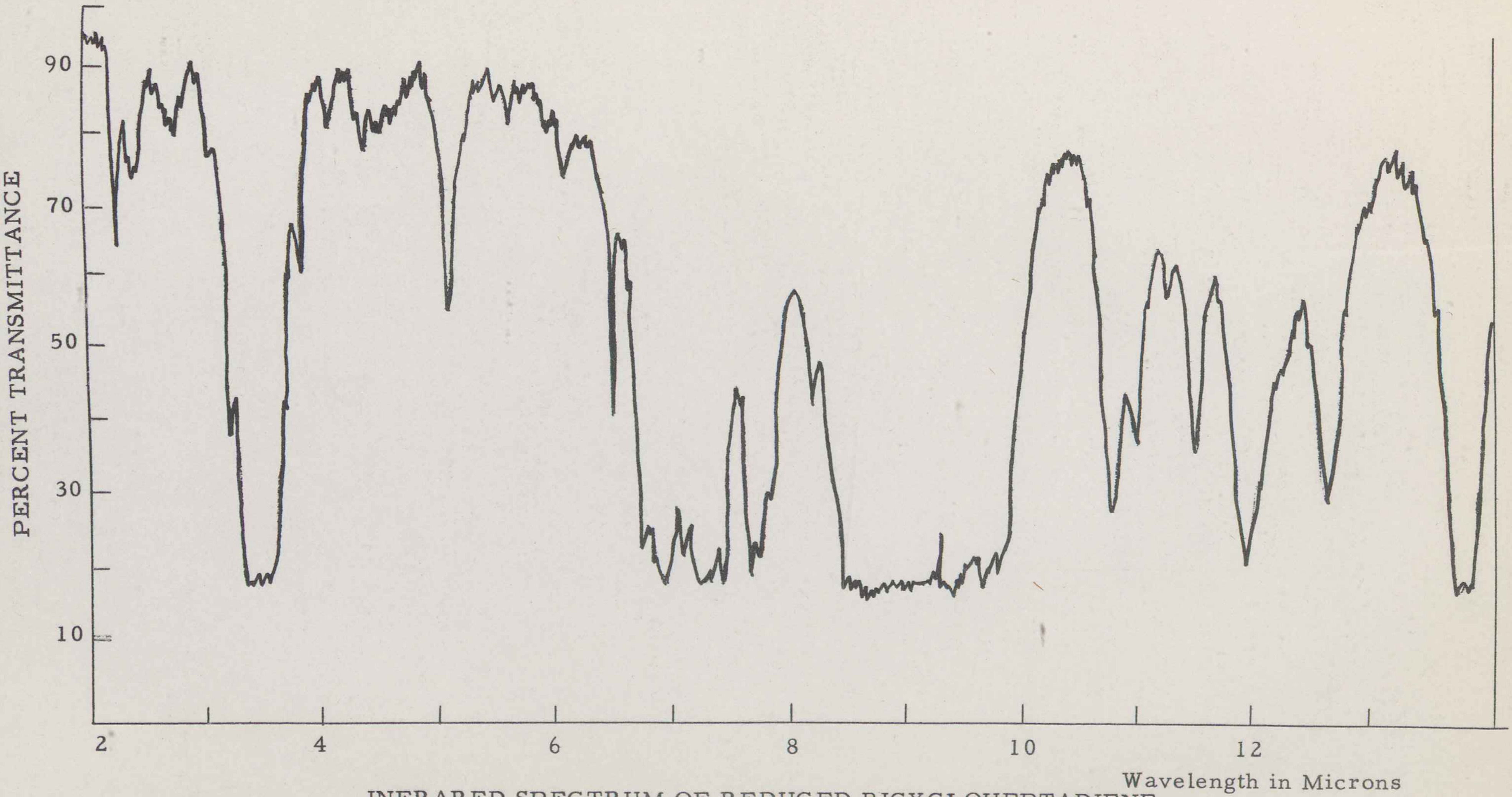
INFRARED SPECTRUM OF METHYLVINYLCYCLOTETRASILOXANE
Plate VI



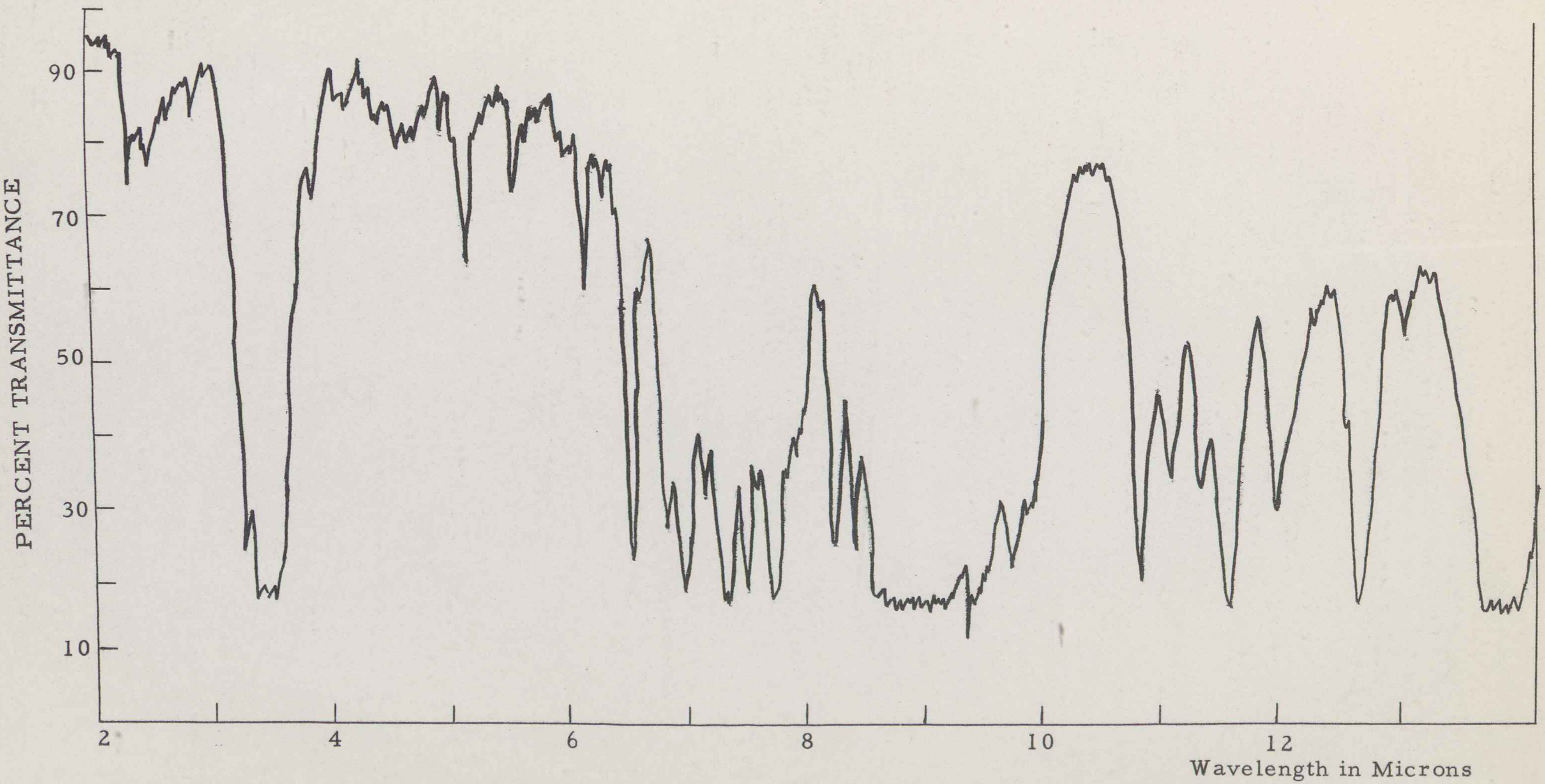
INFRARED SPECTRUM OF REDUCED METHYLVINYLCYCLOTETRASILOXANE
Plate VII



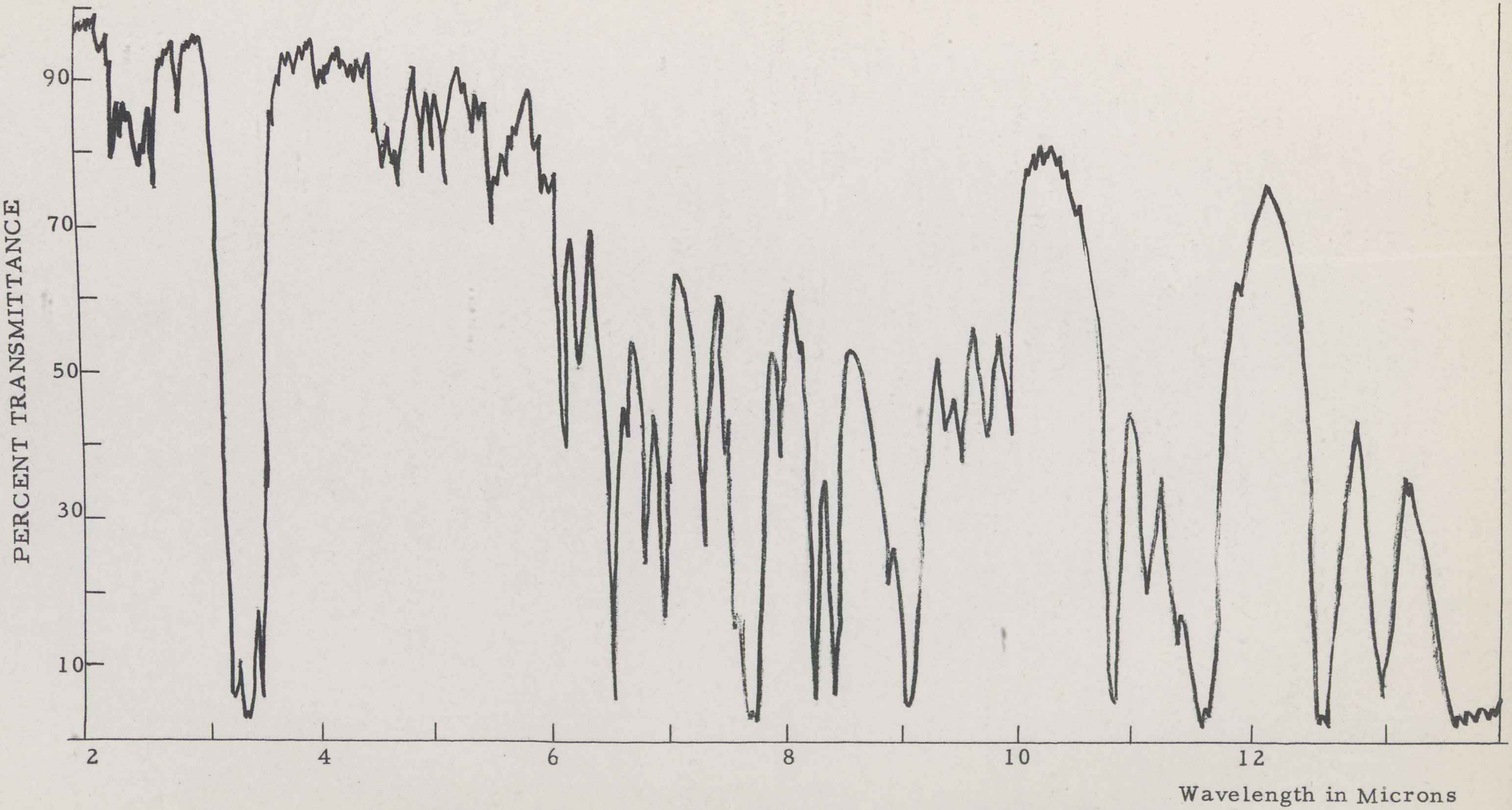
INFRARED SPECTRUM OF BICYCLOHEPTADIENE
Plate VIII



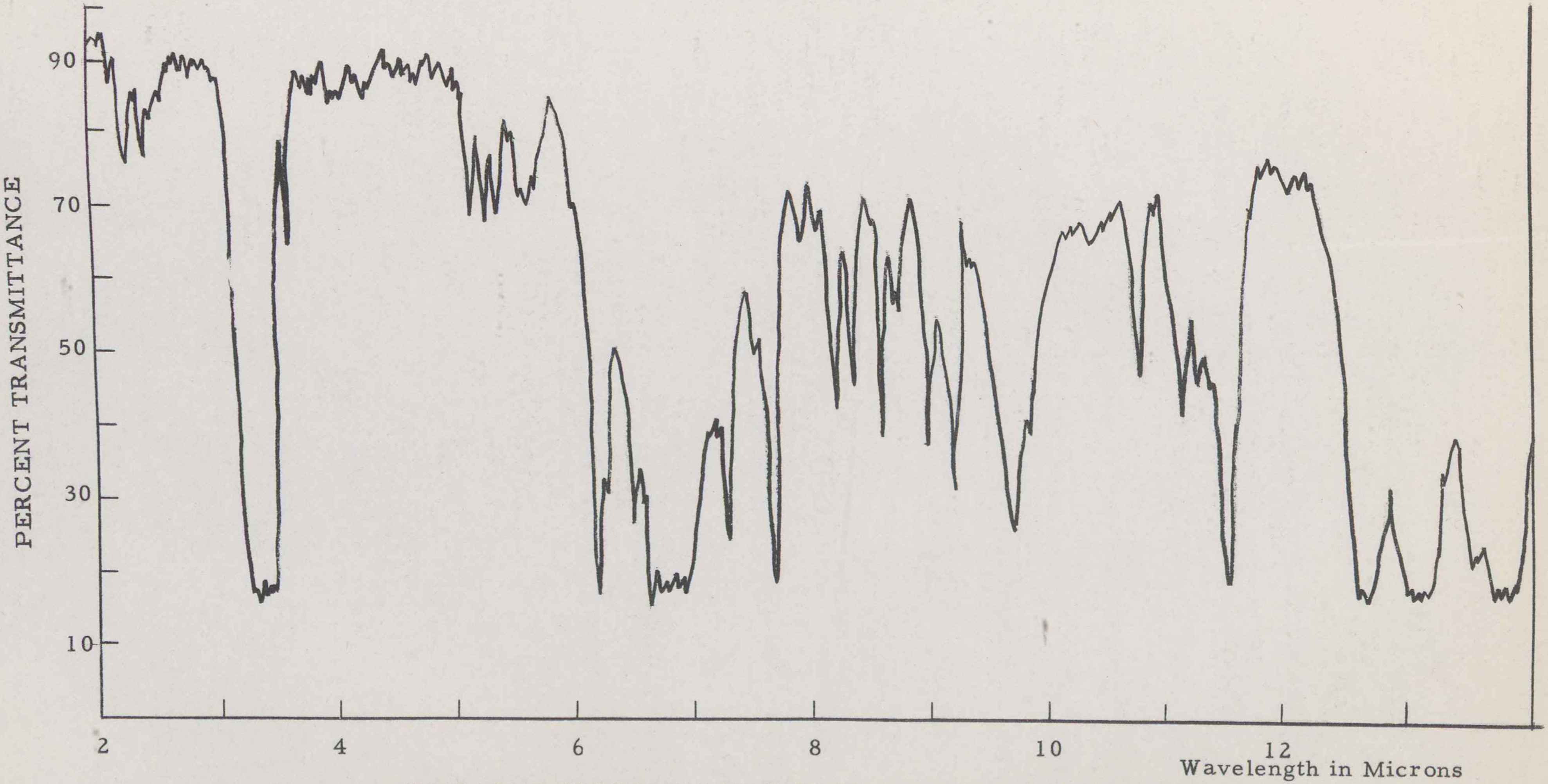
INFRARED SPECTRUM OF REDUCED BICYCLOHEPTADIENE
(Fraction #1)
Plate IX



INFRARED SPECTRUM OF REDUCED BICYCLOHEPTADIENE
(Fraction #2)
Plate X



INFRARED SPECTRUM OF REDUCED BICYCLOHEPTADIENE
(Fraction #3)
Plate XI

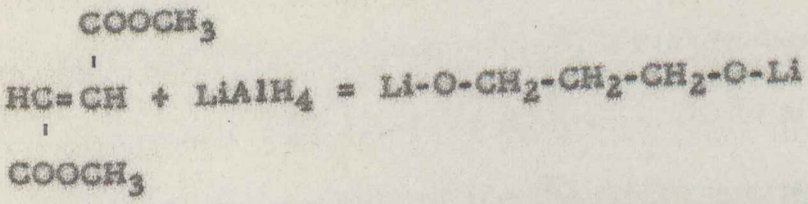


INFRARED SPECTRUM OF REDUCED BICYCLOHEPTADIENE
(Fraction #4)
Plate XII

DISCUSSION

The purpose of this work was to study the reductions of certain unsaturated organic compounds with lithium aluminum hydride. The majority of the compounds studied possessed a carbonyl with conjugated carbon-carbon double bond unsaturation. The other two compounds merely possessed carbon-carbon double bonds which could have been reducible with lithium aluminum hydride due to attached silicon or to steric strain.

From previous work done by Brown, by Slysh and by others it was found that when a diol resulted from the reduction of a particular compound with lithium aluminum hydride, separation of the diol was difficult. The poor yield obtained for these reactions has been attributed to the absorption of the diol on the surface of the $Al(OH)_3$. In an attempt to overcome this difficulty, a Williamson Synthesis was tried on the metal alkoxide intermediate of the reduced compounds. The following equations will serve to explain the aim of this trial:



$$\begin{array}{l} \quad\ \mathrm{COOCH_3} \\ \quad\ \ \vert \\ \mathrm{HC{=}CH + LiAlH_4 = Li\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}Li} \\ \ \vert \\ \mathrm{COOCH_3} \end{array} \qquad \mathrm{VI}$$

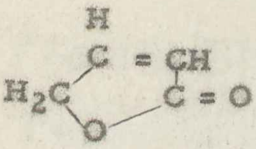
$$\mathrm{Li\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}Li + 2CH_3I = CH_3O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OCH_3 + 2LiI} \qquad \mathrm{VII}$$

Had the Williamson type Synthesis worked, this would have given a product that could have been easily extracted with ether. However, in the case of the reduction of dimethylfumarate and the subsequent Williamson-type Synthesis, a product was obtained that was not ether soluble; this fact suggested that the Williamson type synthesis had not occurred. The lack of ether solubility of this product pointed to the possibility that an intermediate different from the expected one, may have been formed. The following could have been a possible intermediate in this reaction:

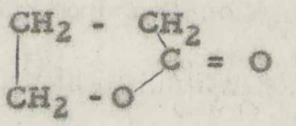
$$-\overset{|}{\underset{|}{Al}}\;{}^{-}O-CH_2-CH_2-CH_2-CH_2-O-\;{}^{-}\overset{|}{\underset{|}{Al}}-$$

This intermediate would undoubtedly have very little alkoxide nature to it and hence would not displace iodide ion from methyl iodide. Similarly, the lithium ion might have complexed strongly with the alkoxide ions, preventing an SN_2 displacement of iodide ion from methyl iodide by alkoxide ions. After failing to find any of the product in the ether layer, water was added to the reaction. The solids were extracted several times with water. Then the water solution was extracted with chloroform and a small amount of material was obtained. The infrared spectrum of this material indicated two new absorptions at 5.64 microns and 5.74 microns. Reference to Bellamy[13] (p 155 & 163) suggested the presence of two different types of esters. Also, two new absorptions were observed at 8.54 microns and 8.75 microns. These would be C-O stretch absorptions which would be consistent with the product containing 2 esters. However, these frequencies do not correspond to esters of maleic or fumaric acids. These ester absorptions seem to correlate better with the lactone frequency absorptions.

This suggests the possibility that the reaction produced a small amount of



and



These are not unlikely in small amounts if, for some reason, the $LiAlH_4$ was not present in excess or if the lactone or last of the $LiAlH_4$ became tied up in the precipitate and was not available for further reaction.

The Williamson Synthesis proceeds according to the following general equation:

$$RONa + R'I = ROR' + NaI$$

From this equation it might be speculated that had $NaBH_4$ been used to reduce the compound, the sodium alkoxide would have been formed, which upon subsequent treatment with methyl iodide would have undergone the Williamson Synthesis.

The reduced cinnamaldehyde contained monofunctional alcohols which would have been ether-soluble. The treatment of the reduction intermediate with methyl iodide was to check for ether formation. The infrared spectrum of the ether-soluble product had an absorption at 9.17 microns, which is near the aliphatic ether absorption wavelength (Bellamy(13) p. 100). Since absorptions (based on the spectrum of diethyl ether) have been found to be so very much stronger than any other peak, this rather weak absorption in the crude mixture could represent only very small amounts of methyl cinnamyl ether or methyl hydrocinnamyl ether.

Furthermore, the strong hydroxyl absorption at 2.96 microns indicates that the main products of this reaction contained alcohol functions. This led to an investigation of the spectrum for C-O absorption of primary alcohols. It was noted that the only new absorption was at 9.17 microns in the usual range of C-O stretch absorption. Thus, this absorption which might have been ascribed to ether seems more likely to have been due to alcohol. Together with the observations for dimethylfumarate, this would suggest that little, if any, Williamson type synthesis occurred in this reaction either. CH absorptions and C=C absorptions which might have indicated the degree of unsaturation in the reduced cinnamaldehyde were obscured by other absorptions.

In the reaction of dimethylfumarate with $LiAlH_4$ followed by hydrolysis the infrared spectrum of the aqueous concentrate seemed to have absorption peaks of butane - 1,4 diol. This is what Slysh found. However, an absorption at 3.40 microns (C-H groups) indicated the presence of some unsaturation. That this was due to butene-1, 4 diol seems unlikely since there was no characteristic absorption at 11.25 microns (butene-1, 4 diol; Union College Chemistry Dep't. Spectrum #55-5). Since there were carboxylate absorption peaks, it seems likely that some fumaric acid or gamma-hydroxy buten-2-oic acid was present. These could account for the C-H absorption at 3.40 microns.

Titration with bromine by the method of Siggia (2) was made on the aqueous concentrate and indicated that roughly one tenth of the double bonds still remained. The titration was performed on the second reaction of dimethylfumarate with lithium aluminum hydride. The two titrations of the aqueous solution agreed within ± .02. However, the parent compound, dimethylfumarate, indicated on two titrations that it had only about .4 double bonds per mole. Since the dimethylfumarate was of known origin and had very good physical constants, this casts some doubt on the validity of the titration of fumarate esters by this technique. This also leaves some serious doubt as to the validity of the titration of the reduction products. It was noted that the fumarate ester titration involved a heterogeneous mixture (this was not the case in the titration of diethylmaleate, which titrated well). The titration of the reduction product was on a water soluble material. At any rate, there definitely seemed to be some hydrogenation of the carbon-carbon double bond. The residual unsaturation was close to that found in the reduction product of diethylmaleate.

Reduction of diethylmaleate produced ether insoluble products which gave about 14% of product soluble in ethylacetate, which was mostly butane-1, 4 diol as determined by comparison of its infrared spectrum with that taken on Slysh's butane- 1, 4 diol. The only other product probable in this reaction, according to the spectrum, seems to be some unreacted diethylmaleate (absorption at 5.81 microns); the weakness of the carbonyl absorption indicates that only very small amounts of ester are present. This yield of butane-1, 4 diol is in agreement with yields Slysh obtained from reductions of fumarates and maleates.

Titration of the aqueous phase after ether extraction suggested that the residual unsaturation in the reduction mixture approximated that left in corresponding mixtures from the reduction of dimethylfumarate. In this case, however, the titration results were in excellent agreement (see table I). Moreover, the parent compound, diethylmaleate, titrated close to one double bond per molecule (.99± .002). The better titration in this case than in the case with dimethylfumarate stems from the solubility of the former in the titration media whereas dimethylfumarate formed a separate phase.

Titrations on chalcone were found to consume too much bromine with mercuric sulfate catalyst; without it, results were too erratic to trust the titration of this product. It was felt that even though fairly good agreement was obtained on one set of two titrations, the lack of agreement of two titrations on the partial reduction mixture of chalcone throws out the validity of any determinations made on this reduction mixture. The lack of reproducibility may well stem from benzene-ring bromination in the reduction mixture, a substitution reaction of bromine rather than an addition reaction. However, the interpretation of the infrared leaves little doubt that unreduced double bonds were left; there were absorptions at 3.26 and 3.3 microns for CH stretching absorption, and a C-O stretch at 9.5 microns for an allyl type secondary alcohol. Also, indication of some reduction of the double bonds was found; absorption at 3.41 microns, is typical for CH_2 groupings; also, a saturated secondary alcohol absorption shoulder was found at 9.0 microns. An interesting fact is that little relative differences in sizes of these absorptions are to be found between spectra taken of the early sample of the chalcone reduction and the sample after complete reduction; reaction then must have been rapid between the chalcone and $LiAlH_4$, although it did not appear to have undergone any reaction. The relative sizes of the 3.26 and 3.30 absorptions for trans CH=CH and cis CH=CH shift during the course of the reduction, suggesting that trans has the more readily reduced double bond. This might have been due to some complexing of an intermediate in the reduction of the carbonyl with the pi electrons of the C=C double bond, with subsequent reduction of the double bond.

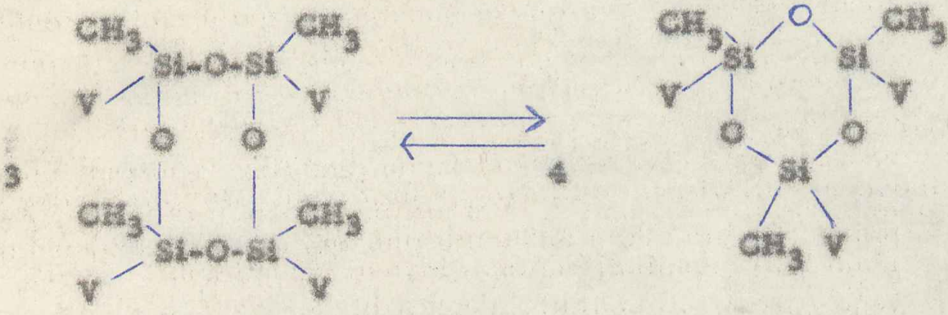
As was observed in the case of chalcone, the commercial mixture of cis and trans benzalacetone showed stronger trans absorption at 3.26 microns, but the reduction mixture showed stronger cis absorption at 3.33 microns. This again suggests that the carbon-carbon double bond is more readily reduced in the trans isomer. The CH_2 absorptions at 3.41 microns and 3.50 microns are enhanced in the reduced benzalacetone, the parent showed it because of the methyl group, but reduction of the double bond led to more CH_2 type stretching. No carbonyl absorption was left in the reduced mixture, and the strong OH absorption was found at 2.96 microns. That partial reduction of the carbon-carbon double bond had occurred was indicated by the C-O stretch of the alcohol at 8.9 microns; some double bond was left as indicated by the allyl type C-O stretch absorption at 9.5 microns.

Titration of benzal acetone gave good results for double bond content, but only when the catalyst, mercuric sulfate, was omitted; with catalyst, there was apparently substitution of bronime on the benzene ring. The reduced benzal acetone indicated that about $53^{\pm 3}$% of the double bonds remained or that about 47% saturation of the carbon-carbon double bond had occurred.

Meek, Lorenzi, and Cristol (15) have reported a quantitative yield when benzalacetone was reduced with lithium aluminum hydride. The product they obtained was identified as styrylmethylcarbinol. However, they did not perform any quantitative experiments to determine if any carbon-carbon double bonds in the compound had been reduced.

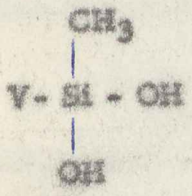
Titration of the reduction product of methylvinylcyclotetrasiloxane indicated that none of the carbon-carbon double bonds had been reduced. This reaction indicates that a vinyl group is not reduced by lithium aluminum hydride when it is bonded to a silicon atom. The infrared spectrum indicated that this was only unreacted methylvinylcyclotetrasiloxane. It is apparent from the yield and observations of this reaction however, that some reaction had occurred between the lithium aluminum hydride and methylvinylcyclotetrasiloxane. The cyclotetrasiloxane can depolymerize by base catalyst, and, at least in part, this had occurred.

On heating the toluene solution of the polymer, trimer could have been formed. An example of re-equilibration is:



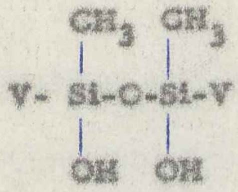
V= vinyl IX

However, lower fragments would have had hydroxyl groups were it a case of base hydrolysis when in contact with water. The likely products from this would be:



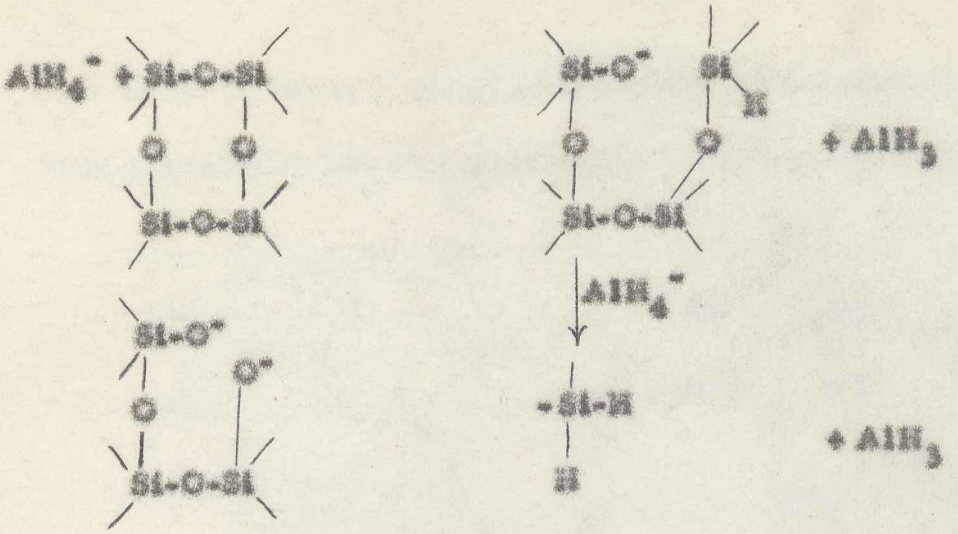
$$\mathrm{V{-}\overset{CH_3}{\overset{|}{Si}}{-}OH}\ \text{with OH below Si}$$

and



$$\mathrm{V{-}\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{Si}}}}{-}O{-}\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{Si}}}}{-}V}$$

However, all of these products would have boiling points well over 115°. To our knowledge, none of these azeotrope with toluene. This, coupled with odors of volatile silicone products during the reduction, makes it seem likely that some Si-H compounds of more volatile nature were formed, such as $\mathrm{CH_3{-}\underset{H}{\underset{|}{\overset{V}{\overset{|}{Si}}}}{-}H}$. These conceivably could have occurred by hydride displacement of a siloxy grouping:

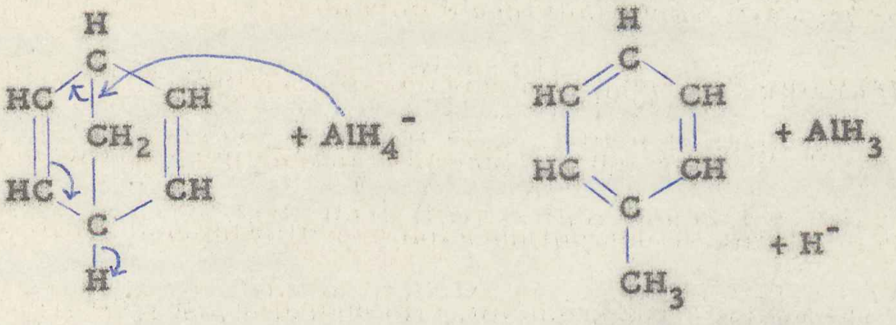


X

Unfortunately, the toluene distillate was discarded before an infrared spectrum was taken on it to check for Si-H absorptions. The $(MeVSiO)_n$ polymer itself can be converted back to tetramer by heating in toluene with a basic catalyst, conditions which may well have existed in distillation of the toluene.

In the reduction of bicycloheptadiene the infrared spectra on fractions 1 and 2 were of no value for interpretation because of the presence of diethyl ether. There was one absorption at 5.5 microns which could not be attributed to the parent compound or ether; however, this might have been due to toluene formed by rearrangement.

In fraction 3 a relatively strong absorption at 5.5 microns indicates that a vinyl group which could be the cause of this absorption is probably not the cause since, in the absence of ether absorption at 7.08 microns, the lack of a stronger absorption at this frequency precludes the presence of a vinyl group. All of the new absorptions in fraction could fit absorptions attributable to toluene; this suggest that toluene may be part of the mixture; it would even explain the absorption at 5.5 microns. Such a product might be possible by a rearrangement such as:



XI

The last fraction showed absorptions which fitted those of either the parent compound or xylene. It was, therefore to be concluded that the infrared spectra showed nothing definite, but suggested the presence of some toluene in fraction 3.

Titration data on bicycloheptadiene were very unsatisfactory for actual results, but gave very consistent results, indicating about 1.4 double bonds per molecule. It is suspected that this may be due to the impurity of the parent compound. Titration of the fractions was hampered by volatility of the compound--as regards both weighing of samples accurately and in titrating in a system under reduced pressure. The problem is made more difficult by the other solvents being present in unknown concentrations. The third fraction, which was largely free of either ether or xylene, gave divergent titration results, which were thus not to be trusted.

CONCLUSIONS

1. In the reduction of dimethylfumarate and cinnamaldehyde with lithium aluminum hydride followed by a Williamson type synthesis, it appears that the latter reaction does not occur. This possibly is due to the fact that an intermediate is formed which possesses little alkoxide nature.
2. Butane-1, 4 diol seems to have been formed in yields of about 15% by reduction of diethylmaleate with lithium aluminum hydride.
3. Reduction of double bonds did occur not only in dimethylfumarate, but also diethylmaleate. Reduction of olefin unsaturation was not complete in these two compounds, but seems to have been largely complete.
4. Reduction of the $C_6H_5\text{-}CH{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}$ system gave some reduction of double bonds as well as complete reduction of the carbonyl function--but olefin reduction was not complete. It appears that, in these commercial mixtures of cis and trans isomers, trans is slightly favored for reduction of the double bond.
5. Reaction occurred with methylvinylcyclotetrasiloxane and lithium aluminum hydride, but no reduction of carbon-carbon double bonds occurred. Loss of volatile portions suggests that some Si-H compounds may have been formed by reaction with lithium aluminum hydride and the siloxane system.

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