PREPARATION, PURIFICATION AND CIS-TRANS ISOMERIZATION OF 2-BUTENE-1,4-DIOL

by

Roman Stephan Slysh

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 Roman Slysh

Approved by William B. Martin, Jr.

May 12, 1955

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation and gratitude to Dr. William B. Martin, Jr. for his advice and guidance througout the preparation of this thesis.

I would also like to extend my thanks to Dr. Howard E. Sheffer for his helpful suggestions and interesting discussions.

Lastly, I would like to thank my wife, Irene, for the cheerful manner in which she typed these pages.

TABLE OF CONTENTS

INTRODUCTION

The preparation of cis- and trans-2-butene-1,4-diol has been reported in chemical literature by numerous workers. A well established procedure to obtain the cis isomer is to hydrogenate 2-butyne-1,4-diol at two to four atmospheres pressure in the presence of catalysts, such as Raney nickel or colloidal palladium. This reduction is selective and can be stopped easily at the ethylenic stage. The reaction has been studied by Lozac'h (1) who stated that the Raman spectrum of 2-butene-1,4-diol prepared in this way indicates the presence of the cis isomer only. Lozac'h does not mention the degree of purity of this product and nothing could be found about purity in other articles dealing with the preparation of cis-2-butene-1,4-diol.

It is reasonable to believe that in the preparation of this compound under ordinary laboratory conditions small amounts of 2-butyne- and/or butane-1,4-diol may be present. The boiling points of these two are close to the boiling point of the olefin and it would be very difficult to separate the latter from the others two by distillation.

Trans-2-butene-1,4-diol can be prepared by bromination of butadiene,followed by the conversion of the dibromide to the corresponding diacetate,and saponification of the latter with barium hydroxide. This method which is the only one mentioned in the literature is very long, and requires special precautions by the worker. A method which might utilize some stereochemical course for the reduction of the corresponding acetylene to the trans-2-butene-1,4-diol has not been reported.

In view of the preceding, it was desirable to work out a purification process for cis-2-butene-1,4-diol which would make it free from 2-butyne- and butane-1,4-diol. It was then thought to use this pure product for studying cis-trans isomeri,ation of this system using infrared spectra for comparisons. A further purpose of this study was to attempt to work out a shorter and simpler method for the preparation of trans-2-butene-1,4-diol which might replace the long and rather inconvenient one presently used.

HISTORICAL

A. SELECTIVE REDUCTION OF CARBON-CARBON TRIPLE BONDS AND THE STEREOCHEMISTRY OF THIS REDUCTION.

The methods used for the selective reduction of carbon-carbon triple bonds may be divided into three groups: chemical, electrolytic and catalytic.

The reducing agents used in the chemical reduction include the dissolving metal combinations, such as sodium in alcohol, sodium in liquid ammonia, sodium amalgam, zinc and tin in neutral, acid or basic media, zinc amalgam and aluminum amalgam. A large number of investigators have studied the chemical reduction of acetylenic bonds and consequently several theories have been advanced to explain its course. According to Campbell et al. (2), the oldest theory is that of Baeyer (3). He considered that the dissolving metal reacted with the solvent to liberate hydrogen atoms, and that these "nascent" hydrogen atoms then reacted with the organic compound before they could combine with each other to form molecular hydrogen. Willstätter et al. (4) and Kuhn et al. (5) rejected this mechanism as the result of careful studies of the course of reductions by sodium amalgam. Instead, they proposed that sodium amalgam reductions occur by the addition of metallic sodium to the carbon-carbon unsaturation followed by hydrolysis due to the solvent. According to this explanation the solvent takes no direct part in the reduction as it was proposed by Baeyer (3).

Several investigators have suggested an ionic mechanism to account for the reduction by chemical reducing agents. Burton and Ingold (6) were the most prominent advocators of this theory.

Although no agreement exists among investigators concerning the mechanism of the chemical reduction of acetylenic bonds it is generally accepted that the trans olefin configuration is obtained.

In 1937 Farkas (7) postulated that, since the reduction of an unsaturated linkage occurs by a stepwise mechanism, the intermediate fragment formed by addition of the first proton has time to adjust its substituents to a position of minimum potential energy before the second stage of the addition occurs. On this basis the selective chemical reduction of disubstituted acetylenes should yield the trans olefin. The work of Campbell and Eby (8,9) has given considerable support to the postulates of Farkas (7), for they have shown that dialkylacetylenes are selectively reduced to trans olefins by sodium in liquid ammonia. The Raman spectra obtained from products indicate that these trans olefins are free from their cis isomers. These configurations are further supported by freezing point and dipole moment data. Campbell and Eby (8,9) offer no explanation for this phenomenon, and the mechanism for the reaction is suggested by Greenlee and Fernelius (10). The concept of the course of the chemical reduction of acetylenic bond to give a trans configuration is also supported by Wheland (11) who stated that the predominance of trans over cis addition may be merely a direct consequence of the fact that, of the two possible stereoisomeric olefins, the trans form is usually the more stable.

Numerous investigators have reported trans olefins as products obtained from the reduction of acetylenes with chemical reducing agents. As early as 1889 Aronstein (12) obtained trans-cinnamic acid when phenylpropiolic acid was reduced by zinc dust and acetic acid. The same product was formed when phenylpropiolic acid was treated with sodium in methyl alcohol. Watt et al. (13) successfully prepared trans isomers of 3-hexene, 3-octene, 5-decene, 2-hexene and 2-octene by reducing the corresponding acetylenes with sodium in liquid ammonia.

Chemical reduction of tolane can give either the cis or trans form of stilbene, depending on the conditions used. According to Aronstein (12), with sodium in methyl alcohol, or zinc and acetic acid, the product is the trans form of stilbene. On the other hand cis-stilbene is formed when tolane is reduced with a zinc-copper couple in alcohol. Another exception to the rule that the controlled chemical reduction of the carbon-carbon triple bond gives trans olefin is the fact that cis-2-butene-1,4-diol has been obtained by the reduction of 2-butyne-1,4-diol with zinc and aqueous sodium hydroxide (14). No explanation has been given for these rather unusual phenomena.

Acetylenes can also be reduced electrolytically at cathodes of low overvoltage, such as iron, nickel, platinum and palladium. The reaction can be made selective and its course is very similar to that of catalytic hydrogenation. According to Campbell (2) there are many variables to be considered and therefore the results are not as susceptible to generalization as are those of chemical reduction and catalytic hydrogenation. This subject is discussed by Campbell and is beyond the scope of this paper.

A widely employed reduction of acetylenic compounds is that of catalytic hydrogenation. The acetylenic bond is readily attacked by hydrogen in the presence of a catalyst under mild conditions, and a wide variety of catalysts may be used. The two points of main interest in the catalytic hydrogenation of acetylenes are the selectivity of the process and, in case of disubstituted acetylenes, the stereochemical course of the reaction. The latter depends to a great extent on the nature of the catalyst used and to a smaller extent on the nature of the substituents. With platinum black the reaction is nonselective and cannot be stopped at the olefin stage. Sankichi (15), Zalkind (16), Lebedev (17) and others pointed out that apparently an olefin starts to undergo hydrogenation almost as soon as it is formed. One exception has been reported by Bogdanow (18) who pointed out that when an alcoholic solution of phenylacetylene was shaken with hydrogen and platinum black at 20°, the triple bond was reduced to the corresponding ethylene up to 97 per cent before the double bond was attacked.

With Raney nickel and colloidal palladium the reduction of acetylenic bonds is selective in the majority of cases studied. When equimolar equivalents of hydrogen have been added, the product is largerly or entirely the olefin (15,16,18,19,20,21,22).

An exception to this rule has been reported by Lai (23) who was unable to obtain the selective hydrogenation of acetylenic bromides of the type $RC{\equiv}CCH_2Br$; he found that the triple bond was always saturated.

Another useful catalyst is Raney iron which is as effective and selective as palladium or Raney nickel (24). Furthermore, Thompson (25) indicated that Raney iron shows a selectivity more marked than that of Raney nickel for in cases of some dialkylacetylenes the reduction proceeds to the olefin stage and stops there. The catalyst, however, is much less active than Raney nickel and requires higher temperatures.

As far as the stereochemistry of the selective catalytic reduction of the acetylenic bond is concerned, it has been shown by numerous authors that the reaction usually gives cis olefin. As early as 1909 Paal (26) indicated that the hydrogenation of phenylpropiolic acid and tolane by hydrogen in the presence of colloidal palladium led to the pure cis olefin, whereas reduction by chemical methods gave the trans isomers. Later work led by Zalkind (27) on acetylenic glycols and tolane seemed to show that the reaction was not simple and that various mixtures of cis and trans olefins were produced. Ott and Schröter (28) by using poisoned catalysts attempted to establish a relationship between the activity of the catalyst and the relative amounts of cis and trans isomers obtained. They finally concluded that the more active catalysts gave larger amounts of the cis form. Their somewhat improbable results were explained two years later by Bourguel (29) who suggested that the primary product in any catalytic hydrogenation of a disubstituted acetylene is always the cis form of the olefin, and that this might undergo stereochemical conversion to the trans form in the presence of the catalyst. Sherrill (30), Sheffer (31), Sankichi (15), Henne (20), Johnson (32) and many others have used colloidal palladium and they all obtained the cis olefin by hydrogenation of the corresponding acetylene. Sheffer (31) also used palladous oxide and showed that this catalyst gives cis-ethylcinnamate upon the reduction of ethyl ester of β-phenylpropiolic acid. Campbell and Eby (8,9), Valette (33), Yur'ev (34), Marvel (35), Lozac'h (1) and others used Raney nickel, and they all found that a cis olefin is formed when a corresponding acetylene is hydrogenated in the presence of this catalyst. The configurations of many of these olefins have been established by Raman spectra and dielectric constant measurements which indicate that the cis olefins so obtained are free from their trans isomers.

The mechanism of the catalytic reduction of acetylenic compounds has been suggested by Farkas (7) and is widely accepted. The occurrence of cis addition may be explained with the aid of two assumptions: first, that the organic molecule is adsorbed on the surface of the catalyst, and second that the two hydrogen atoms from the same hydrogen molecule approach the triple bond simultaneously and thereby add to the same side of the molecule. On this basis catalytic hydrogenation of disubstituted acetylenes should always yield the cis olefins.

B. CIS-TRANS ISOMERISM

It is well known that for cis-trans isomerization to occur, resistance of the double bond to free rotation must be overcome. In order to bring about this change, four distinct mechanisms have been suggested.

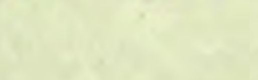
The first mechanism is associated with the simplest reaction, represented by homogeneous unimolecular rearrangement of maleic acid to fumaric in the liquid phase (36). Thermal isomerization of maleic acid has been studied by Höjendahl (36) who found the reaction to be unimolecular with an activation energy of 15,800 cal. The same mechanism may be assigned to the unimolecular isomerization of dimethyl maleate in the vapor phase (37) and the uncatalyzed liquid phase isomerizations of isostilbene and its α-chloroderivatives (38). A conversion of maleic acid into fumaric (39) by heating in an inert atmosphere, such as nitrogen or carbon dioxide, apparently belongs also to this simple type of rearrangement. A satisfactory explanation of the above mentioned conversions has not been given and it is assumed that these apparently depend on violent inelastic collisions which affect rotation about the double bond.

It has been known for some time that absorption of ultraviolet light can convert cis olefins into their trans isomers and vice versa (40,41). A good example of this type of geometrical rearrangement is the conversion of fumaric into maleic acid by ultraviolet radiation. Because of its effectiveness, this type of reaction is usually used for conversion of the stable trans isomer into the labile cis configuration. This second type of cis-trans isomerization caused by ultraviolet light has been studied by Olson (42) and Mulliken (43). Both men attempted to explain the mechanism of the rearrangement by the relative rotations of the CR'R" groups. According to Mulliken (43) the energy of certain excited states of ethylene and its derivatives caused by ultraviolet radiation, should be higher for the plane form of a molecule than for the perpendicular form when one CR'R" plane is rotated by 90 degrees. Hence the plane form should tend to go over spontaneously by rotation into the perpendicular form and, because of the momentum of rotation, on to the other plane form (180° rotation) after absorption of a suitable amount of ultraviolet light. In this way the cis form may rearrange into its trans isomer or vice versa.

The theory of Mulliken is far from being satisfactory because it fails to explain the phenomenon quantitatively. According to modern theory (44) in olefinic compounds the two unsaturated carbon atoms exhibit the trigonal mode of hybridization and not the tetrahedral as postulated by van't Hoff. Thus there are three coplanar valencies, so-called σ-bonds, and the fourth, π-bond, at right angles to the trigonal hybrids. It is the overlap of the π-electrons which causes the resistance to rotation about the carbon-carbon double bond. Therefore in any process of isomerization that does not involve a complete rupture of the ethylene compound into radicals it is these electrons that are involved. According to the same reference the cis-trans isomerization caused by ultraviolet radiation is not fully understood.

A third type of mechanism for cis-trans interconversion is associated with catalysts which can donate protons or accept electron pairs. This type includes isomerizations caused by mineral acids, other Lewis acids, such as aluminum chloride, ferric chloride, zinc chloride, or boron trifluoride, primary and secondary amines. As early as 1889 Anschütz (45) found that the isomerization of maleic acid to fumaric could be catalyzed by inorganic acids and salts. This reaction was confirmed later by several investigators (46,47) who attempted to explain the course of this conversion. The mechanism of this reaction was for years a matter of controversy which finally seemed to vanish when in 1941 Nozaki and Ogg (48) proposed a new explanation. According to their suggestion, both a proton and an anion have to be considered and both take part in the rearrangement. The suggested mechanism for the isomerization of maleic acid catalyzed by mineral acids involves three steps. Step (a) involves the addition of a proton to the carbonyl oxygen of carbon 1, the addition of an anion to carbon 3, and the shift of the double bond from between carbons 2 and 3 to carbons 1 and 2.

Step (a)

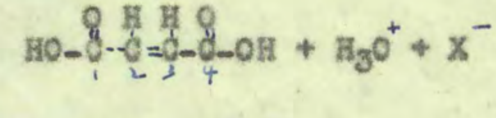


$(HO)_2C{=}CH{-}CHX{-}C(=O){-}OH$

where X represents an anion.

Nozaki and Ogg assumed that in the first process carbon 3 undergoes a "Walden inversion". This step is also considered to be a rate determining one for the isomerization. Step (b) is simply the reverse of step (a), i. e. maleic acid and the catalyst are regenerated. Carbon 3 is "reinverted".

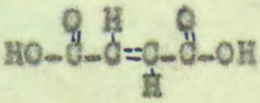
Step (b)



$$\mathrm{HO{-}\underset{1}{\overset{\overset{O}{\|}}{C}}{-}\underset{2}{\overset{H}{C}}{=}\underset{3}{\overset{H}{C}}{-}\underset{4}{\overset{\overset{O}{\|}}{C}}{-}OH + H_3O^+ + X^-}$$

Step (c) brings about isomerization to fumaric acid. It is a reaction in which the original bond between carbons 1 and 2 is broken, leaving a new bond between them. This is equivalent to a "Walden inversion" of carbon 2, and this inversion together with a second "inversion" of carbon 3 in step (b) gives an odd number of inversions of the two ethylenic carbons for steps (a) and (c).

Step (c)



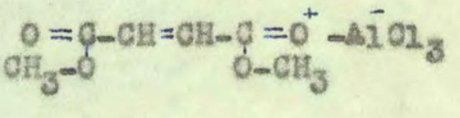
$$\mathrm{HO{-}\overset{\overset{O}{\|}}{C}{-}\overset{H}{C}{=}\underset{H}{C}{-}\overset{\overset{O}{\|}}{C}{-}OH}$$

It might be assumed from the above mechanism that equal quantities of maleic and fumaric acid should be obtained from decomposition of the intermediate. Practically, however, all of the maleic acid is rearranged because the regenerated acid in step (b) is again converted into the intermediate and eventually isomerised. On the other hand, fumaric acid is not affected, because the activation energy of step (a) for the formation of the intermediate from fumaric acid is about 7000 calories greater than from maleic acid.

The isomerizations catalyzed by salts, such as potassium thiocyanate or sodium bromide, proceed by the same mechanism except that in this case the protons are supplied by the ionization of other molecules of maleic acid. The proposed mechanism is applicable to the cis-trans isomerization of all α-β unsaturated carboxylic acids and their esters which are catalyzed by acids. This is also true for methyl maleate (49), isocrotonic acid (50), isocinnamic acid (51) and others.

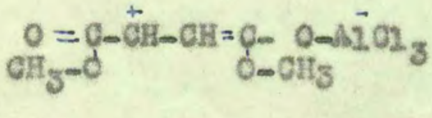
The mechanism proposed by Nozaki and Ogg is interesting, because it assumes the occurance of a Walden inversion of unsaturated carbon atoms when a shift of a pair of electrons takes place. It is well known that the Walden inversion is associated with carbon atoms of a tetrahedral structure and, since the two unsaturated carbon atoms exhibit the trigonal mode of hybridization rather than tetrahedral, it is questionable if a true Walden inversion takes place. It seems more likely that there is actually a rotation about a single bond in the complex, and it is felt that the term "rotation" would be more applicable to use than that of the Walden inversion.

Other Lewis acids besides the proton can catalyze cis-trans interconversions. Gilbert et al. (52) have shown that methyl maleate can be isomerized to methyl fumarate by aluminum chloride, ferric chloride, and zinc chloride. Wheland (11) stated, that these reactions, presumably, involve intermediates with charge distributions that are intermediate between the extremes represented by structures I and II:



$$O=\underset{CH_3-O}{C}-CH=CH-\underset{O-CH_3}{C}=\overset{+}{O}-\overset{-}{Al}Cl_3$$

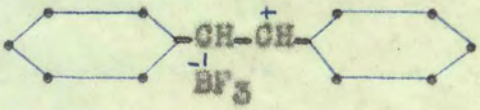
I



$$O=\underset{CH_3-O}{C}-\overset{+}{C}H-CH=\underset{O-CH_3}{C}-O-\overset{-}{Al}Cl_3$$

II

It should be pointed out, that not all strong Lewis acids are effective as catalyst. Price and Meister (53) found that boron trifluoride does not catalyze the isomerization of methyl maleate, but does catalyze that of cis-stilbene, possibly through the following intermediate



They suggest that the reason that methyl maleate does not isomerize is due to the fact that boron trifluoride associates readily with an unshared pair of electrons from the oxygen atoms in preference to a pair from the carbon-carbon double bond. Ester-boronfluorides so formed are quite stable and may be isolated.

Several investigators (54,55,56) have reported that ammonia, primary, and secondary amines bring about the isomerization of maleic acid and that of methyl maleate. Nozaki (57) studied the catalytic effect of various amines on the isomerization of diethyl maleate and suggested that the mechanism for these reactions is similar to that proposed for the isomerization catalyzed by inorganic acids and salts (48). Since amines could serve both as proton and electron donors, the suggestion of Nozaki seems to be quite reasonable. Nozaki concluded further that tertiary amines are not effective and that the more strongly basic amines are better catalysts.

A fourth type of mechanism for the cis-trans interconversion involves catalysts with two unpaired or an odd number of valence electrons. The catalysts include univalent atoms, free radicals, molecules with odd number of electrons and paramagnetic substances in general. A well known example of this type of isomerization is that of the catalytic effect of halogens in the presence of light. It has been known for some time that light and the presence of free halogens induce the isomerization of such compounds as maleic acid and cis-stilbene (58,59). Since halogen molecules dissociate into atoms in the presence of light (60), it is logical to conclude that these atoms are responsible for the isomerization. The mechanism for this reaction is given by Wheland (11).

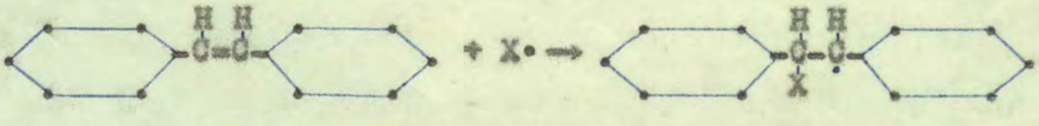
Step (a) involves the formation of halogen atoms by light. In step (b) one of these atoms adds to an unsaturated carbon atom thus forming an intermediate, which, like the original atom, is a free radical with a single unpaired electron. In step (c) the bromine atom is transferred from the free radical to a second molecule of cis-stilbene, while the original molecule of the intermediate is transformed into trans-stilbene. Thus the second molecule of cis-stilbene becomes a free radical intermediate equivalent to the one in the step (b). This chain of reactions can continue until with the aid of a single halogen atom a large number of molecules of cis-stilbene have been isomerized.

The following equations represent the three steps involved:

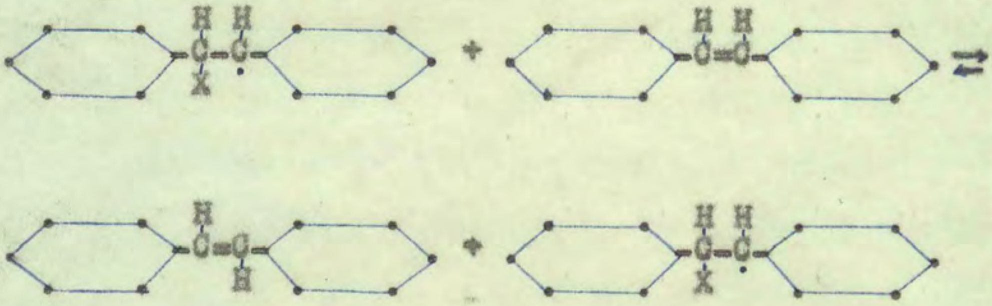
(a) X_2 + light ⇝ $2X\cdot$

where X_2 represents a halogen molecule.

(b)



(c)



Cis-stilbene can also be transformed into its trans isomer by hydrogen bromide if the reaction mixture is subjected to ultraviolet light, or if it contains traces of impurities, such as oxygen or benzoyl peroxide (59). The presence of small amounts of antioxidants, however, prevents isomerization completely. The above phenomena may be explained by assuming that this isomerization is a chain reaction initiated by bromine atoms. These are produced from hydrogen bromide by light, oxygen or benzoyl peroxide. The effect of the antioxidants is explained by the assumption that they react with, and destroy, either the bromine atoms or the intermediate free radicals.

It is interesting to note that while hydrogen bromide acts mainly as a source of bromine atoms in the isomerization of cis-stilbene, it acts as a proton donor in that of methyl maleate.

Cis-trans interconversions can frequently be catalyzed by other substances which are free radicals with unpaired electrons. An extensive work on the subject was performed by Kuhn (58), who concluded that substances which possess a permanent magnetic moment bring about this transformation. Kuhn's findings received considerable support by Selwood (61) and McConnell (62), who found that cis-trans isomerizations about the carbon-carbon double bonds are frequently catalyzed by paramagnetic substances such as oxygen, nitrous oxide, nitrogen dioxide, iodine, bromine, sodium, potassium, rubidium and cesium. Gilbert et al. (52), however, rejected Kuhn's hypothesis. According to their observations there is no direct correlation between the magnetic characteristic of a compound and its catalytic activity. Although they disaproved Kuhn's explanation of isomerization, the idea prevails that interconversions caused by paramagnetic substances involve the radical-chain mechanism (11,58,63).

A number of other catalysts have been found to induce cis-trans isomerization. Taube (64) reported that when a solution of sodium thiosulfate is added to a solution of maleic acid, fumaric acid is formed. The same reaction results in the presence of a mixture of sulfurous acid and hydrogen sulfide (58). Platinum black was found to be an effective catalyst in some cases (65), but no explanation of its action has been given.

EXPERIMENTAL RESULTS

A. PREPARATION OF:

1. Cis-2-butene-1,4-diol

This compound was prepared according to Valette (33). The 2-butyne-1,4-diol used in this preparation was received from General Aniline and Film Corporation. It was recrystallized from ether; m.p. 57-8°.

The reduction of 17.2 g (0.2 mole) of 2-butyne-1,4-diol in 100 ml. of ethyl alcohol was carried out in the Parr pressure reaction apparatus in the presence of 0.3 g of activated Raney nickel until the equivalent amount of hydrogen was used. The reaction required 25 minutes and the temperature rose from 21° to 38°. After removal of catalyst by filtration the crude products from five runs were combined and fractionated to give 63.3 g (74% yield) of cis-2-butene-1,4-diol; b.p. 120°/6 mm; n_D^{25}=1.4745.

In a second preparation an 86% yield of cis-2-butene-1,4-diol was obtained; b.p. 121-122°/7mm; n_D^{25}=1.4744. A third reduction of 2-butyne-1,4-diol gave 80% of the theoretical amount of cis-glycol; b.p. 134-135°/15mm; n_D^{25}=1.4765.

2. Cis-2-butene-1,4-diol Dibenzoate

a. Schotten-Baumann Reaction:

To a mixture of 62.5 g (0.71 moles) of cis-2-butene-1,4-diol in 300 ml. of 20% aqueous sodium hydroxide in a one liter round bottom flask 210 g (1.5 moles) of benzoyl chloride was added a little at a time while vigorously shaking and cooling the flask.

A brown paste was obtained which was filtered and recrystallized three times from ethyl alcohol. The yield of slightly brown crystalls of cis-2-butene-1,4-diol dibenzoate, m.p. 65-66°, was 62 g (30%).

b. Pyridine Method (66):

To a solution of 38.5 g (0.44 moles) of cis-2-butene-1,4-diol and 100 ml. of pyridine in a 500 ml. round bottom flask 140 g (1 mole) of benzoyl chloride was added a little at a time while vigorously shaking the flask. After the initial reaction had subsided the flask was heated over a low flame for a minute. The mixture was then poured into a beaker containing 300 ml. of ice cold water and was placed in an ice box for 15 minutes. After filtering and recrystallizing the solid three times from 80% ethyl alcohol, 98 g (77% yield) of white cis-2-butene-1,4-diol dibenzoate, m.p. 65-66°, was obtained.

In a second run an 81% yield of white dibenzoate crystalls, m.p. 65-66°, was obtained.

B. PURIFICATION OF CIS-2-BUTENE-1,4-DIOL:

1. Hydrolysis of Cis-2-butene-1,4-diol Dibenzoate

a. By Sodium Hydroxide:

A mixture of 100 g (0.34 moles) of cis-2-butene-1,4-diol dibenzoate, 80 ml. of ethyl alcohol and 400 ml. of 10% solution of sodium hydroxide was refluxed for two hours. The clear yellowish liquid was neutralized by adding an equivalent amount of concentrated hydrochloric acid. Benzoic acid so formed was filtered off and to the clear filtrate a few drops of 10% sodium hydroxide solution were added in order to keep the mixture slightly alkaline. Excess alcohol and water were removed by distillation and the inorganic solids were filtered off and washed with a small amount of cold alcohol. The filtrate was concentrated again in order to precipitate more sodium chloride. After three successive processes of distilling and filtering off the solid material, the remaining liquid was treated with ethyl acetate in order to extract the cis-2-butene-1,4-diol. The oily liquid changed to a white precipitate immediately upon adding an excess of ethyl acetate. This new material burned in a flame and left a fair amount of black residue which turned moisten litmus paper blue. This indicates that the material might be an organic salt. The material remained unmelted even at 300 degrees.

b. Hydrolysis by Water:

Twenty grams (0.07 moles) of cis-2-butene-1,4-diol dibenzoate was dissolved in a little hot alcohol and was refluxed for 24 hours with a large amount of water. White crystalls were formed upon cooling the mixture. They melted at 65-66° and did not produce a melting point depression when mixed with equal quantities of cis-2-butene-1,4-diol dibenzoate.

c. Hydrolysis by Acetic Acid:

A solution of 20 g (0.07 moles) of cis-2-butene-1,4-diol dibenzoate in 300 ml. of 80% acetic acid was refluxed for 25 hours.

After cooling and adding water, white solid formed which melted at 65°. A mixed melting point with cis-2-butene-1,4-diol dibenzoate produced no melting point depression.

d. Hydrolysis by Sodium Hydroxide followed by the removal of Ions by Ion exchange columns:

A solution of 88.7 g (0.3 moles) of cis-2-butene-1,4-diol dibenzoate and 65 ml. of alcohol was refluxed with 350 ml. of a 10% solution of sodium hydroxide for six hours. The yellow solution was neutralized with concentrated hydrochloric acid. Benzoic acid was filtered off and the clear filtrate was made slightly alkaline with 10% sodium hydroxide. The filtrate which contained water, cis-2-butene-1,4-diol, sodium chloride and a small amount of sodium hydroxide was allowed to pass through anion and then through cation exchange columns. Amberlite IR-4B and IR-100H were used as the anion and cation exchange resins respectively. The aqueous layer was concentrated and the remaining liquid distilled under reduced pressure. Its boiling point went as high as 70° at 30 mm. The refractive index at 25° was found to be 1.3320, which is very close to that of water (1.3325). No cis-2-butene-1,4-diol could be identified in this fraction.

2. Reduction of Cis-2-butene-1,4-diol Dibenzoate by Lithium Aluminum Hydride

A suspension of 15.2 g (0.4 mole) of lithium aluminum hydride in 700 ml. of tetrahydrofuran was placed in a two liter three-necked flask equipped with reflux condenser, dropping funnel, mechanical stirrer, and protected from atmospheric moisture by calcium chloride tubes. Through the dropping funnel, a solution of 59.2 g (0.2 mole) of cis-2-butene-1,4-diol dibenzoate in 300 ml. of tetrahydrofuran was added at such a rate as to produce gentle reflux. Fifteen minutes after the addition had been completed water was added cautiously to decompose excess hydride cooling and stirring the contents meanwhile. A solid white material was filtered off and the tetrahydrofuran was distilled off from the filtrate. The remaining liquid was distilled under reduced pressure using a 30 cm fractionating column (Snyder condenser). Twenty five grams of benzyl alcohol, b.p. 93°/9 mm, was recovered. No glycol was found in this fraction.

The solid material (mainly aluminum and lithium hydroxides) was shaken with a 200 ml. portion of water in order to extract cis-2-butene-1,4-diol which was adsorbed by the aluminum hydroxide. The latter was filtered off and the alkaline filtrate was neutralized with a little hydrochloric acid. After boiling off water and tetrahydrofuran and distilling the mixture under reduced pressure, five more grams of benzyl alcohol, b.p. 93°/9 mm, and three grams of cis-2-butene-1,4-diol, b.p. 123-125/8 mm, n_D^{25}=1.4788, was recovered. The same solid material was then suspended in 20 per cent solution of sodium hydroxide and the mixture was extracted continuously with ether for 48 hours. After boiling off ether and distilling the high boiling mixture under reduced pressure, three more grams of benzyl alcohol and one gram of cis-2-butene-1,4-diol was obtained. The total amount of benzyl alcohol recovered was 33 g (77% yield) and that of glycol four grams (23% yield).

C. PREPARATION OF DIMETHYLFUMARATE

1. Methylation of Fumaric Acid with Diazomethane

Nitrosomethylurea was prepared according to Arndt (67). In a two liter round bottom flask was placed a solution of 202.5 g (3.3 moles) of methylamine hydrochloride in 200 ml. of water and concentrated hydrochloric acid until the solution was acid to methyl red; 575 ml. of water was added to bring the total weight to 1000 g; 600 g (10 moles) of urea was added and the solution was boiled gently under reflux for three hours and then vigorously for one-quarter hour. The solution was cooled to room temperature and 220 g (3 moles) of 95% sodium nitrite was added. The whole was cooled to zero degrees.

A mixture of 1200 g of ice and 200 g of concentrated sulfuric acid in a four liter beaker was surrounded by an ice-salt bath and the cold methylurea-nitrite solution was run in slowly with mechanical stirring at such a rate that the temperature did not rise above 5°. The nitrosomethylurea rose to the surface as a crystalline foamy precipitate which was filtered at once with suction and pressed well on the filter. The crystalls were stirred to a paste with about 100 cc of cold water, sucked as dry as possible on a filter and dried in a vacuum desiccator. The amount of nitrosomethylurea obtained was 250 g (81 % yield).

A mixture of 200 ml. of a 40% solution of potassium hydroxide and 300 ml. of ether was placed in a flask which was cooled in ice. Small portions of nitrosomethylurea were added to the mixture with vigorous shaking. After about 80 grams of nitrosomethylurea were added, the yellow ether layer containing diazomethane was decanted into another flask, cooled in ice, and dried over potassium hydroxide. This process was repeated twice, and the combined ether layers were placed in a distilling flask from which diazomethane and ether were codistilled cautiously.

To the cold ether solution of diazomethane, 26 g (0.22 moles) of fumaric acid in absolute methyl alcohol was added in small portions. After distilling off ether and methyl alcohol, the product was recrystallized three times from water; 28 g of white material, m.p. 97-98°, was obtained. A literature reference (68) gives 97° as the melting point of dimethyl-pyrazole-4,5-dicarboxylate, and an infrared spectrum and a positive nitrogen test after sodium fusion indicated that this pyrazole derivative was the product obtained.

2. Esterification of Fumaric Acid with Absolute Methyl Alcohol

A solution of 36 g (0.31 moles) of fumaric acid and 500 ml. of anhydrous absolute methyl alcohol saturated with dry hydrogen chloride was refluxed for 8 hours. After cooling and recrystallizing twice from a 40% solution of ethyl alcohol, 35 g (78% yield) of dimethylfumarate, m.p. 102-104°, was obtained.

3. Reflux of Maleic Anhydride in absolute Methanol

A solution of maleic anhydride in absolute methanol saturated with hydrogen chloride was refluxed for several hours. A solid material was formed rather rapidly. After two recrystallizations, 300 g of dimethylfumarate, m.p. 102-104°, was obtained.

D. METHODS FOR PREPARATION OF TRANS-2-BUTENE-1,4-DIOL

1. Reduction of Dimethylfumarate with Lithium Aluminum Hydride

a. In Ether:

The apparatus used in this reaction was about the same as that employed for the reduction of cis-2-butene-1,4-diol dibenzoate as described on pages 24 and 25. The apparatus differs from that described in that a continuous extractor was inserted between the flask and the reflux condenser. A suspension containing 15.2 g (0.4 mole) of lithium aluminum hydride in 500 ml. of anhydrous ether was placed in the flask, and 28.8 g (0.2 mole) of dimethylfumarate was placed in the extraction thimble. The solution was heated until all of the dimethylfumarate had been transferred to the reaction flask. The flask was then cooled and the excess hydride was decomposed by addition of water. The white solid material was filtered off and shaken with three 200 ml. portions of ethyl acetate in order to extract the glycol. After boiling off the ethyl acetate and distilling the high boiling liquid under reduced pressure, two grams (11% yield) of butane-1,4-diol, b.p. 120°/10 mm, was obtained. Its dibenzoate ester, recrystallized four times from ethyl alcohol, and once each from isopropyl alcohol, cyclohexane and a 50-50 mixture of tetrahydrofuran in water, melted at 82-83°. A mixture of this compound and authentic butane-1,4-diol dibenzoate produced no melting point depression.

b. Reduction in Tetrahydrofuran at Room Temperature

The apparatus used in this reduction was the same as that employed for the reduction of cis-2-butene-1,4-diol dibenzoate as described on pages 24 and 25. A suspension containing 15.2 g (0.4 mole) of lithium aluminum hydride in 800 ml. of tetrahydrofuran was placed in the flask, and a solution of 28.8 g (0.2 mole) of dimethylfumarate in 700 ml. of tetrahydrofuran was added dropwise from a separatory funnel. Fifteen minutes after the addition had been completed water was added coutiously to decompose excess hydride. White solid material was filtered off and after distilling off tetrahydrofuran from the filtrate, no liquid was left in the distilling flask. The solid separated by filtration was then shaken well with four 200 ml. portions of tetrahydrofuran. After boiling it off, no liquid was left in the flask again. This time a portion of 200 ml. of water was used to extract the glycol from the solid. The solid was filtered off and the filtrate was neutralized with a little concentrated hydrochloric acid. After distilling off the mixture of water and ethyl acetate, a small amount of the high boiling liquid remained in the flask. This liquid was treated with pyridine and benzoyl chloride to give the dibenzoate ester. After three recrystallizations from alcohol a white solid which melted at 81-82°C was obtained. A mixture of this solid with butane-1,4-diol dibenzoate melted also at 81-82°C. This fact proved that the reduction product was butane-1,4-diol.

c. Reduction in Tetrahydrofuran at Ice Temperature under Nitrogen

The apparatus used in this reduction was the same as described above. A suspension containing 8.4 g (0.22 moles) of lithium aluminum hydride in 350 ml. of tetrahydrofuran was placed in a flask, cooled in an ice-water bath, and kept under an atmosphere of dry nitrogen. A solution of 28.8 g (0.2 moles) of dimethylfumarate in 700 ml. of tetrahydrofuran was added slowly to the flask, keeping the temperature of the reaction mixture below five degrees. Addition of dimethylfumarate solution required three hours. After addition had been completed water was added to decompose excess hydride. The solid material was filtered off and the filtrate was heated until all tetrahydrofuran had distilled off. The remaining liquid was distilled under reduced pressure using a 50 ml. Claisen flask. Two grams (11% yield) of butane-1,4-diol, b.p. 120°/10 mm, was obtained. This was proved by the fact that a mixture of its dibenzoate ester with butane-1,4-diol dibenzoate produced no melting point depression.

2. Reduction of Fumaric-Acid by Lithium Aluminum Hydride

a. In Ether

This reduction was carried out according to Benedict and

Russell (69). The apparatus used was the same as that for the reduction of dimethylfumarate in ether as described on page 28. Nineteen and one half grams (0.5 mole) of lithium aluminum hydride was suspended in 750 ml. of anhydrous ether by stirring for three hours; 23.2 g (0.2 mole) of fumaric acid was placed in an extraction thimble and the mixture was refluxed gently for 20 hours. After this period of time, 5.7 g of fumaric acid remained still undissolved. The excess hydride was then cautiously decomposed with water and the solid material was dissolved in 20% sulfuric acid and extracted continuously with ether for 60 hours. After removing ether, the remaining liquid was distilled under reduced pressure. A fraction which boiled up to 90° at 20 mm was collected. (A considerable amount of tar-like material remained in the Claisen flask). No dibenzoate ester could be prepared after treating this fraction with benzoyl chloride and pyridine.

b. Reduction in Tetrahydrofuran

The apparatus used in this reaction was the same as that for the reduction of cis-2-butene-1,4-diol dibenzoate as described on pages 24 and 25. A suspension containing 15.2 g (0.4 mole) of lithium aluminum hydride in 750 ml. of tetrahydrofuran was placed in a flask which had been cooled in an ice-water bath. A solution of 23.2 g (0.2 mole) of fumaric acid in 700 ml. of tetrahydrofuran was added slowly, keeping the temperature of the reaction mixture slightly below five degrees. After the addition had been completed, the mixture was stirred continuously at room temperature for

8 hours. The excess hydride was then cautiously decomposed with water and the solid material was filtered off. After removing tetrahydrofuran from the filtrate, the remaining high boiling liquid was distilled under reduced pressure. A fraction which boiled at 124°/12 mm formed a dibenzoate ester when treated with benzoyl chloride. Its melting point was found to be 81-82°. A mixed melting point with butane-1,4-diol dibenzoate produced no depression. The reduction product was butane-1,4-diol.

3. Reduction of 2-Butyne-1,4-diol by Sodium in Liquid Ammonia

In a one liter three-necked flask equipped with a dry ice condenser with cooling mixture at -60° and a mechanical stirrer, 500 ml. of liquid ammonia was condensed. The cooling bath was a mixture of dry ice and acetone. Portions of metallic sodium followed alternately by small amounts of 2-butyne-1,4-diol were added into the flask while stirring constantly. After the addition of 17 g (.75g-atom) of sodium and 17.2 g (.2 mole) of 2-butyne-1,4-diol the stirring was continued for one and one-half hours longer. Ammonia was evaporated under reduced pressure and the intermediate was treated with a portion of 200 ml. of water. This solution was allowed to stand for ten days in the refrigerator. A dibenzoate ester of the glycol was obtained by adding 87.5 g (0.6 mole) of benzyol chloride a little at a time to the solution which contained glycol and large amounts of sodium hydroxide. A dark brown paste was formed which gave cream colored crystalls after recrystallization from ethyl alcohol. The material was recrystallized six times from ethyl alcohol, once from cyclohexane and once from isopropyl alcohol. Each time a melting point of 76-77° was observed. This compound proved to be 2-butyne-1,4-diol dibenzoate. The total amount of the material obtained after seven recrystallizations was 25 g which corresponds to 42.5% yield of the original 2-butyne-1,4-diol added.

After analyzing the combined filtrates from the seven recrystallizations it was found that they contained about five grams of benzoic acid and about one gram of sodium chloride.

4. Conversion of Butadiene to Trans-2-butene-1,4-diol

a. Trans-1,4-dibromobutene-2

This and following compounds were prepared according to the directions of Sheffer (31). A one liter three-necked flask was fitted with a mechanical stirrer, a dry ice condenser with cooling mixture at -35°, and a separatory funnel; 365 ml. of chloroform was placed in the flask. The cooling solution was a mixture of chloroform, carbon tetrachloride and dry ice. This mixture was kept at -35° by addition of pieces of dry ice. From a tank 108 g (2 moles) of butadiene was distilled into the reaction flask. From the separatory funnel 320 g (2 moles) of bromine was added dropwise as the solution was stirred. The addition of bromine required one hour. The chloroform was then removed under reduced pressure and the brown solid was recrystallized under the hood twice with petroleum ether. The melting point of the trans-1,4-dibromobutene-2 was 49-52°C.

b. Trans-1,4-diacetoxybutene-2

A solution of trans-1,4-dibromobutene-2 in 1000 ml. of absolute ethyl alcohol was placed in a two liter round bottom flask and 385 g (3.9 moles) of freshly fused potassium acetate was added. The mixture was refluxed for six hours. Potassium bromide was filtered off and the filtrate was heated in order to remove the alcohol. In the course of this process white solid precipitated (presumably potassium bromide and unreacted potassium acetate). It was filtered off and the filtrate was heated further. After a short period of time a precipitate formed again. The process of filtration and distillation was repeated two times more until about 150 ml. of liquid remained in the flask. This liquid was distilled under reduced pressure. Two fractions were collected: the first fraction boiled up to 110°/8 mm and amounted to 47 g. The second fraction boiled sharply at 108-110°/6 mm; $n_D^{25} = 1.4431$. This fraction was taken as pure 1,4-diacetoxybutene-2. The amount was 112 g (34% yield). The total amount of both fractions was 159 g which corresponds to a total yield of 45 per cent.

c. Trans-2-butene-1,4-diol and its Dibenzoate

A mixture of 100 g (0.58 moles) of trans-1,4-diacetoxy-butene-2 and 473 g (1.5 moles) of barium hydroxide was refluxed in 750 ml. of 95 per cent ethanol for 13 hours. Barium acetate was filtered off and washed with several small portions of cold alcohol. The alcohol was removed by heating and the high boiling liquid was distilled under reduced pressure. The yield of trans-2-butene-1,4-diol, b.p. 126°/6 mm, $n_D^{25}=1.4760$, was 32 g (63% yield).

A dibenzoate derivative was prepared and recrystallized twice from ethyl alcohol giving white crystalls which melted at 101-102°.

E. CIS-TRANS ISOMERIZATION OF 2-BUTENE-1,4-DIOL

1. Effect of Sunlight and Catalysts

A solution of ten ml. of cis-2-butene-1,4-diol in ten ml. of absolute ethyl alcohol was placed into each of seven different test tubes. Test tubes no. two, three and four contained 0.5 ml. of saturated alcoholic bromine solution, 0.15 ml. and 0.05 ml. of saturated alcoholic iodine solution respectively. The solutions in test tubes no. five, six and seven were treated with a little chlorine, hydrogen chloride and hydrogen bromide respectively. One test tube contained 15 ml. of cis-2-butene-1,4-diol and traces of bromine. All eight test tubes were allowed to stay in the bright sunlight for ten hours. After this period of time, all solutions were investigated for possible isomerization. This was achieved by preparing the corresponding dibenzoate esters and by taking their melting points, since cis- and trans-dibenzoates melt 35 degrees apart.

The dibenzoate esters were prepared as follows: alcohol was boiled off and the glycol was distilled under reduced pressure using 50 ml. Claisen flask. A solution of two ml. of glycol and five ml. of pyridine was treated with several ml. of benzoyl chloride. A white dibenzoate formed, and was poured into a beaker containing about 50 ml. of ice cold water. The mixture was then allowed to stand in an ice box for about 15 minutes. The dibenzoate was filtered off and washed thoroughly first with ten 10 ml. portions of water followed by the same amount of cyclohexane. After drying the material, all samples, except one containing hydrogen bromide, melted between 64 and 67 degrees. Cis-2-butene-1,4-diol treated with hydrogen bromide gave no dibenzoate. During the vacuum distillation sharp smelling vapors were evolved which could not be condensed. A dark residue boiling at 110°C at 20 mm remained behind. This material was not investigated further.

2. Effect of Ultraviolet Light and Catalysts

A solution of 15 ml. of cis-2-butene-1,4-diol in the same amount of absolute alcohol was placed into each of four different test tubes. The solutions contained traces of bromine, chlorine, hydrogen bromide and iodine respectively. Another test tube contained 15 ml. of the glycol alone and a different one contained a solution of equal amounts of trans-2-butene-1,4-diol and absolute ethyl alcohol. The six test tubes were irradiated with a source of ultraviolet light for six hours. All solutions were then analyzed for possible isomerization, as described in the preceding paragraph. All the dibenzoates prepared melted between 64 and 67 degrees, except that from the samples containing hydrogen bromide and trans-2-butene-1,4-diol. The dibenzoate ester of the latter melted at 99-101° and the sample containing hydrogen bromide gave no dibenzoate. This latter reaction behaved the same way as that treated with sunlight.

3. Effect of Heating

A sample of cis-2-butene-1,4-diol was refluxed for 17 hours. The dibenzoate ester melted at 65 degrees.

A second sample of cis-2-butene-1,4-diol was treated with 0.2 g of platinum dioxide and was refluxed for two hours. The dibenzoate ester of this sample melted also at 65 degrees.

4. Effect of Triphenylmethyl Free Radical on Isomerization

A solution of 20 ml. of triphenylmethyl radicals* in benzene was added to a solution of 30 ml. of cis-2-butene-1,4-diol and 30 ml. of dry tetrahydrofuran. The mixture was kept under an atmosphere of nitrogen and was allowed to stand for ten hours. The free radical was decomposed by passing air through the flask. The peroxide so formed was filtered off and the solution of benzene and tetrahydrofuran was removed by distillation. The high boiling liquid was distilled under reduced pressure. Its dibenzoate ester melted at 65 degrees.

---

* prepared by Mr. Robert Ballard in Chemistry 12b.

DISCUSSION

The purpose of this work was to prepare pure cis-2-butene-1,4-diol free from any 2-butyne- and/or butane-1,4-diol. The cis-glycol of high purity was desirable in order to study its cis-trans interconversions using infrared spectra for comparison. Pure trans-2-butene-1,4-diol was also needed for this purpose and a new rapid and simple method of preparing this isomer was a further objective of this study.

Numerous procedures have been published for the preparation of cis-2-butene-1,4-diol. Most of these methods utilize the stereochemical course of catalytic reduction of 2-butyne-1,4-diol and they differ only in the use of catalyst, solvent and pressure. A widely employed method to prepare the cis-glycol is that of Valette (33). He carried out the reduction of 2-butyne-1,4-diol at atmospheric pressure using Raney nickel as a catalyst and absolute ethanol as a solvent. This procedure with slight modifications was adopted by the author. This reduction was carried out at 4-5 atmospheres using the Parr pressure reaction apparatus, and 95% ethyl alcohol as solvent. Three separate preparations of cis-2-butene-1,4-diol gave yields of 74%, 86% and 80% respectively; the boiling points (uncorrected) were 120°/6 mm, 121-122°/7 mm and 134-135°/15 mm respectively; the respective indices of refraction at 25° were 1.4745, 1.4744 and 1.4765. The infrared spectrum of this compound is given in plate I.

These yields and boiling points check well with values reported in literature. Recorded indices of refraction at 25° range from 1.4710 up to 1,4776 with best values for 98-99% pure cis-diol between 1.4768 and 1.4773 as reported recently by General Aniline and Film Corporation (70).

It has been mentioned in the introduction part of this paper that in the preparation of the cis-glycol under ordinary laboratory conditions small amounts of 2-butyne- and/or butane-1,4-diol may be present. This is a reasonable assumption, because it was quite difficult to note when an exact equivalent of hydrogen had reacted due to slight variations in temperature, and the fact that the rate of reduction did not diminish after all the acetylenic glycol had been used up. Also the fact that any of the refractive indices of the cis-diol obtained was below the value reported by General Aniline and Film Corporation (70), may indicate the presence of some butane-1,4-diol, n_D^{25}=1.4442 (71). To separate the 2-butyne- and butane-1,4-diol from the cis-2-butene-1,4-diol by distillation would be very difficult, because their boilings points (32,71) are very close to that of the cis-diol. In order to remove these impurities, therefore, it was decided to convert the cis-2-butene-1,4-diol into its dibenzoate ester, followed by purification of the diester by recrystallization,and hydrolysis of the latter to the free glycol. This process of purification seemed to be quite promising, because the dibenzoate derivatives of 2-butyne- and butane-1,4-diol have different melting points than that of the cis-diol.

Cis-2-butene-1,4-diol dibenzoate was prepared by two different procedures. The Schotten-Baumann reaction produced slightly brown crystalls even after three recrystallizations, and the procedure using pyridine, as given by Shriner and Fuson (66), gave colorless crystalls of the cis-diol dibenzoate ester. Both kinds of crystalls, however, melted at 65-66° as reported in literature (35). The infrared spectrum of this compound is given in plate IV.

The hydrolysis of pure, sharp melting cis-2-butene-1,4-diol dibenzoate to free glycol was carried out in 10% solution of sodium hydroxide. After acidification and removal of benzoic acid by filtration, a solution was obtained which contained cis-diol, water, small amounts of alcohol, sodium hydroxide, and a fair amount of sodium chloride. The problem was to separate the glycol which is highly water- and alcohol-soluble and insoluble in ether, chloroform, benzene, and carbon/tetrachloride. It was thought that isolation of the cis-glycol could be achieved by distillations of water with alcohol followed by filtrations of inorganic solids and the extraction of diol with ethyl acetate. This operation, however, proved to be a failure, because of the following reasons:

a. The cis-glycol was strongly adsorbed by inorganic solids and successive washings with cold alcohol dissolved not only the glycol but small amounts of inorganic solids as well.

b. Excessive heating of the mixture, probably, caused some reaction among its contents which formed a white insoluble solid when treated with large amounts of ethyl acetate.

The white solid burned in a flame, leaving a black residue which turned moisten litmus paper blue. It reacted with bromine and potassium permanganate and did not melt even at 300 degrees. These facts indicate that the material was, probably, an unsaturated organic salt.

The formation of this salt upon treatment of the solution of cis-glycol and small amounts of inorganic salts and base with an excess of ethyl acetate is not understood. It seems possible that the cis-glycol had formed a salt when heated in presence of sodium hydroxide, but why it precipitated after the addition of ethyl acetate, can not be explained.

Attempts to bring about the hydrolysis of cis-2-butene-1,4-diol dibenzoate by refluxing it with large amounts of water and with 80% acetic acid were also unsuccessful. After a 24 hours reflux time, dibenzoate ester reprecipitated upon cooling the flask.

After these trials, it was decided to return to the alkaline hydrolysis using a 10% solution of sodium hydroxide. This time, however, instead of removing inorganic salts by successive distillations and filtrations followed by extraction of cis-glycol with a proper solvent, it was decided to remove the salts by ion exchange columns. Amberlite IR-4B and IR-100H were used as the anion and cation exchange resins respectively. After passing a solution containing cis-glycol, water, sodium chloride, a little sodium hydroxide, and alcohol through the anion and then through the cation exchange columns and after distilling off water, no glycol could be found in the flask. With its relatively strongly polar molecules with two functional groups, the glycol was probably adsorbed by the respective phenolic resins. The columns used were 2¼" in diameter and 20" in height. These volumes of resins provided enough surface area for contact between resin and glycol which resulted in the complete adsorption of the latter.

The actual adsorption of cis-glycol by the cation exchange resin was tested by allowing a 50 ml. portion of 1:3 ratio of cis--diol with water to pass through a small column (1" x 12"). The refractive index of the original solution was 1.3660 and the last drops of this solution showed an index of 1.3412 after being in contact with the resin. This fact indicates that the glycol was adsorbed almost completely by the resin.

After two unsuccessful attempts to isolate pure cis-2-butene--1,4-diol from products of its dibenzoate ester hydrolysis with sodium hydroxide, it was decided to carry out the reduction of the cis-glycol dibenzoate by lithium aluminum hydride. This reduction proved successful and four grams (23% yield) of cis-2-butene-1,4--diol, b.p. 123-125/8mm, $n_D^{25} = 1.4788$, was recovered. The infrared spectrum of this glycol is given in plate II.

Comparing the physical properties of this product with the cis-glycol before its purification it can be seen that they differ slightly. The boiling points are the same, but the refractive index of the former is appreciably higher. The value of 1.4788 is higher than any of the reported values in the literature. This may be explained by the fact that the cis-glycol before purification contained some butane-1,4-diol whose refractive index is appreciably lower than that of the olefin. The infrared spectrum of the glycol before purification indicates also the presence of small amounts of "impurities". A marked absorption at 8.9 µ is completely absent in the purified diol. The spectrum of the former also shows a rather broad minimum at 10.7-10.9 µ, which is absent in the purified fraction. The latter, however, absorbs more strongly at 10.2-10.3 µ.

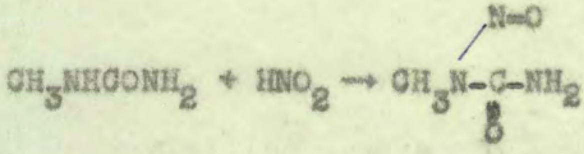
The rather low yield of cis-glycol recovered from the reduction of its dibenzoate ester may be explained by the fact that the cis-diol is strongly adsorbed by the aluminum hydroxide which is formed by decomposition of lithium aluminum hydride with water. Only by shaking the hydroxide with portions of water could small amounts of glycol be dissolved. Continuous extraction of a suspension of this aluminum hydroxide-glycol mixture in 20% aqueous sodium hydroxide for 48 hours with ether increased the yield of cis-diol by $^1/_3$ of the amount obtained previously.

The next step in the work presented in this paper was to prepare trans-2-butene-1,4-diol. Several references for preparing this compound have been found. All are about the same and are based on the conversion of butadiene to the trans-glycol. This procedure, however, is somewhat long; it involves three different steps of preparation, and requires special precautions by the worker. It was an aim, therefore, to work out a short and simple procedure for the preparation of the trans-glycol. Since lithium aluminum hydride proved to be a convenient and rather selective reducing agent, it was decided to carry out the reduction of dimethylfumarate with this reagent.

In order to obtain dimethylfumarate, fumaric acid was treated with diazomethane which was prepared according to the following equations:

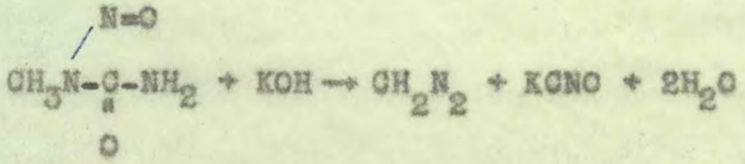
(a) $CH_3NH_3Cl + H_2NCONH_2 \rightarrow CH_3NHCONH_2 + NH_4Cl$

(b)



$$CH_3NHCONH_2 + HNO_2 \rightarrow CH_3\overset{N=O}{N}-\underset{\overset{\|}{O}}{C}-NH_2$$

(c)



$$CH_3\overset{N=O}{N}-\underset{\overset{\|}{O}}{C}-NH_2 + KOH \rightarrow CH_2N_2 + KCNO + 2H_2O$$

After fumaric acid had reacted with diazomethane, a white solid, m.p. 97-98°, was isolated which proved to be the dimethyl-pyrazole-4,5-dicarboxylate. It was thought that diazomethane would add to the carboxylic groups with evolution of nitrogen. Actually it reacted not only with the two carboxylic groups but also with the double bond as well, forming a pyrazole ring. Such double bond additions were not entirely unexpected, since it is known, that diazomethane does add to double bonds (68).

Dimethylfumarate was successfuly prepared by esterification of fumaric acid with absolute methanol. Its amount, however, was not adequate to give sufficient quantities of trans-2-butene-1,4-diol, and therefore more dimethylfumarate was made by rapid reaction between maleic anhydride and absolute methanol which was saturated with hydrogen chloride.

Reduction of dimethylfumarate with lithium aluminum hydride in ether gave butane-1,4-diol in 11% yield. This was proved by the following facts:

a. The melting point of the dibenzoate ester of the product was the same as that of the authentic butane-1,4-diol dibenzoate.

b. A mixture of its dibenzoate ester with equal quantities of the authentic butane-1,4-diol dibenzoate produced no melting point depression.

c. The infrared spectrum of the dibenzoate ester of the product was exactly the same as that of the authentic butane-1,4-diol dibenzoate (Plate VI).

Low yield (11%) was again caused by the difficulty in isolating the glycol which is apparently strongly adsorbed by the aluminum hydroxide formed by the reaction of the reduction mixture with water.

Reduction of the double bond by lithium aluminum hydride as in the above reaction is a very interesting phenomenon, because this hydride was considered to be a selective reducing agent which does not usually attack the double bond at ordinary temperatures (72). In view of this fact, the reduction of another portion of dimethylfumarate was carried out, using tetrahydrofuran as a solvent, because dimethylfumarate was quite insoluble in ether. Butane-1,4-diol was again isolated as a final product, which was proved by the same methods as in the previous reduction.

A third reduction of dimethylfumarate was performed. This time only 10% excess over the theoretical amount of the hydride needed was used, and the reaction was carried out at about 0° under an atmosphere of nitrogen. The product of this reduction was again butane-1,4-diol.

It can be seen from the above reductions, that lithium aluminum hydride does not always serve as a selective reducing agent. Since it did not react with the double bond in the reduction of cis-2-butene-1,4-diol dibenzoate, it is logical to conclude that conjugation of the double bond with a carbonyl group was responsible for its reduction. Brown (72) has also mentioned this possibility, but confined it only to aromatic systems containing the structural grouping $\mathrm{Ar}\underset{|}{\mathrm{C}}=\underset{|}{\mathrm{C}}\mathrm{CO}$ or $\mathrm{Ar}\underset{|}{\mathrm{C}}=\underset{|}{\mathrm{C}}\mathrm{N}<$. According to the same reference, among purely aliphatic compounds, reduction of the double bond by lithium aluminum hydride has been observed only with allyl alcohol and with α-ethylcrotonamide, which was reported to yield α-ethylbutylamine. Mićović and Mikhailović (73) studied the reduction of acetylenic acids of the type $\mathrm{RC{\equiv}CCOOH}$ with lithium aluminum hydride and they obtained in all cases a corresponding ethylenic alcohol. Benedict and Russell (69) carried out the reductions of acetylenedicarboxylic, propiolic, acrylic and fumaric acids with lithium aluminum hydride at room temperature. According to their results, acids containing triple bond were reduced to the corresponding ethylenic alcohols and acrylic and fumaric acids gave allyl alcohol and 2-butene-1,4-diol respectively.

It is possible that a triple bond (in conjugation with a double one) is attacked first by lithium aluminum hydride, but it is difficult to understand why in case of acrylic and fumaric acids the double bond which is also in conjugation with a carbonyl group is not reduced by the hydride. The results of Benedict and Russell are different from those obtained by this author and they also contradict the statement of Brown (72). Although Benedict and Russell did not specify which isomer of 2-butene-1,4-diol they obtained, it was decided to follow their procedure, expecting to obtain the trans-glycol. Using ether as a solvent, as they specified, proved to be very inconvenient, because fumaric acid is quite insoluble in ether and after 20 hours refluxing only 17.5 g (0.15 moles) of fumaric acid had dissolved. Treatment of the reaction mixture with a 20% solution of sulfuric acid after excess hydride has been decomposed was also not a very desirable, because 2-butene-1,4-diol might rearrange in an acidic medium. This mixture was continuously extracted with ether as specified, but no glycol could be identified after distilling off ether. Instead, a considerable amount of tar-like material was noticed in the flask.

Since no glycol was found after following the procedure of Benedict and Russell (69), the reduction of fumaric acid with lithium aluminum hydride was repeated using tetrahydrofuran as a solvent and omitting the treatment with sulfuric acid. Dibenzoate ester of the product produced no melting point depression when mixed with equal quantities of authentic butane-1,4-diol dibenzoate and its infrared spectrum was exactly the same as that of the butane-diol dibenzoate (Plate VI). These facts prove that butane-1,4-diol was the product of the reduction of fumaric acid.

The statement of Brown (72) and results obtained by the author show that both the carbon-carbon double bond and the carbonyl unsaturation which are in conjugation with each other are reduced when treated with lithium aluminum hydride. In view of the results of Benedict and Russell (69), however, the above statement cannot be considered a law unless more extensive work will prove its validity.

After all reductions of dimethylfumarate and fumaric acid had proved unsuccessful for the preparation of trans-2-butene-1,4-diol, it was decided to make use of the stereochemical course of the chemical reduction of acetylenic glycols by reducing 2-butyne-1,4-diol with sodium in liquid ammonia. Unfortunately, this process had to be interrupted and only after 10 days of standing in refrigerator was it brought to completion. The final product was converted to its dibenzoate ester, m.p. 76-77°, which proved to be the 2-butyne-1,4-diol dibenzoate (32). The amount of the acetylenic glycol recovered was 42.5%.

It is interesting to note, that after 0.2 moles of 2-butyne-1,4-diol had been treated with 0.75 g.-atom of sodium, 0.085 moles of the former could be recovered. The specified amount of sodium had reacted with the glycol, because, after the addition of the two reactants the final solution was colorless. It might be asked at this point, what happened to the remaining 50% of 2-butyne-1,4-diol? Since 0.75 g.-atom of sodium definitely reacted with 0.2 moles of the acetylenic glycol, at least 0.35 g.-atom of sodium must have reacted with the triple bond. If the latter had been reduced to the double bond, 0.175 moles of ethylenic glycol should have been formed. If, on the other hand, the triple bond had been completely saturated, about 0.087 moles of butane-diol should have been formed. Actually, none of these, but 0.085 moles of 2-butyne-diol was identified in the final mixture. If 0.087 moles of butane-1,4-diol had actually been formed, no reason can be found for the fact that none of it reacted with benzoyl chloride. It is felt, therefore, that this compound was not formed at all. The fact, that about one half of the 2-butyne-1,4-diol added was the only product recovered after 0.75 g.-atom of sodium reacted with 0.2 moles of acetylene indicates, that the ethylenic glycol, if formed,probably "rearranged" on long standing in the strongly alkaline solution partially back to the acetylene and partially to some other material which did not form a derivative with benzoyl chloride.

This explanation is only a possibility of what might have occured, and in order to obtain more definite information, the reduction should be repeated. A time element prevented the author from repeating this reaction.

Rather interesting information concerning the chemical reduction of an acetylenic glycol has been found in literature.

According to Johnson (74), Bourguel prepared in 30% yield the true trans-2,5-dimethyl-3-hexene-2,5-diol by reducing the corresponding acetylenic diol with sodium in methanol. This trans-olefin has been examined by Zalkind and Bukhovets (75), who concluded that it was not an ethylenic derivative at all, but another crystalline form of the acetylenic glycol, 2,5-dimethyl-3-hexyne-2,5-diol. Later work of Johnson (76) confirmed Zalkind's statement, and he asserted that it is difficult to obtain an authentic trans form of the ethylenic glycol by the chemical reduction of 2,5-dimethyl-3-hexyne-2,5-diol. Since the structure of the latter is very similar to that of 2-butyne-1,4-diol it is probable that the latter might behave chemically similarly to the 3-hexyne-diol.

In order to be able to study the cis-trans isomerization of butene-diol in time, it was decided to discontinue new synthetic methods for preparing the trans-2-butene-1,4-diol and to make it according to the directions given by Sheffer (31). The trans-glycol, b.p. 126°/6 mm, n_D^{25}=1.4760 was finally obtained in 63% yield. Its dibenzoate ester melted at 101-102°, which checks well with the value reported by Marvel (35). Infrared spectra of the trans-2-butene-1,4-diol and its dibenzoate ester are given in plate III and plate V respectively.

The isomerization of 2-butene-1,4-diol proved to be more difficult than was originally anticipated. The physical properties of the two isomers are about the same and they both are oily liquids at room temperature. This makes their distinction and separation by ordinary means extremely difficult. It was thought that the differences in infrared spectra of the two would make a convenient way to study their cis-trans interconversions. Unfortunately, their spectra, as given in plates I-III, do not show a sufficient number of sharply marked maxima, but are rather broad, rounded-off curves which would not enable one to study accurately small changes of isomer contents after isomerization. Their infrared spectra were taken by using the corresponding neat liquids; it is possible that their solutions might give spectra which would be more satisfactory for comparisons. A proper solvent for making solutions which would not damage the sodium chloride cells could not be found, since either butene-1,4-diol is insoluble in chloroform, carbontetrachloride and carbondisulfide. Fortunately, the infrared spectra of the dibenzoate derivatives of both isomers show distinct differences in absorption and it was at first decided to use these in the study of the cis-trans isomerization of butene-glycol, although these later proved unnecessary.

It can be seen from plate IV that the cis-glycol dibenzoate absorbs quite strongly at 7.45 µ, whereas no absorption can be found here in case of the trans-isomer. The latter, however, (plate V) has a maximum of absorption at 10.2 µ and the cis does not . Except for these two frequencies, the infrared spectra of both isomers are almost identical.

The cis-trans interconversion was studied by subjecting the cis-glycol in the presence of various catalysts to the bright sunlight or to ultraviolet light. Bromine, chlorine, iodine, hydrogen chloride and hydrogen bromide were used as catalysts. After one set of solutions was irradiated with bright sunlight for 10 hours, and another set with ultraviolet light for six hours, their solutions were examined for possible isomerization by converting the glycols from each into their dibenzoate esters. In order to assure high purity of the diesters from non-ester impurities, the crude dibenzoate mixture was washed first with large amounts of water to remove pyridine, and then with the same amount of cold cyclohexane to remove excess benzoyl chloride. This operation proved to be satisfactory and produced white and sharply melting esters. All esters prepared in this way melted between 64 and 67 degrees. This shows that no isomerization has taken place, because 65° is the melting point of the cis-diol dibenzoate. Mixtures of cis- and trans-2-butene-1,4-diol dibenzoates containing 10, 20, 50 and 80 per cent of the latter melted at 70, 76, 86 and 93 degrees respectively, as indicated in the figure I. Esters of both isomers are insoluble in water and only sparingly soluble in cyclohexane. Since the cis-diol dibenzoate is almost twice as soluble in cyclohexane as the dibenzoate of the trans-isomer, the possibility that the latter could have been selectively washed out is excluded. The dibenzoate derivative from the solution of cis-glycol with hydrogen bromide could not be prepared, because the liquid decomposed while it was being distilled at 110° at 20 mm pressure. Heavy, sharp smelling vapors, which could not be condensed, were formed upon heating the liquid. This may be explained by the fact that hydrogen bromide, probably, reacted with the glycol to form the 1,4-dibromoderivative which would not give the dibenzoate ester when trated with benzoyl chloride and pyridine.

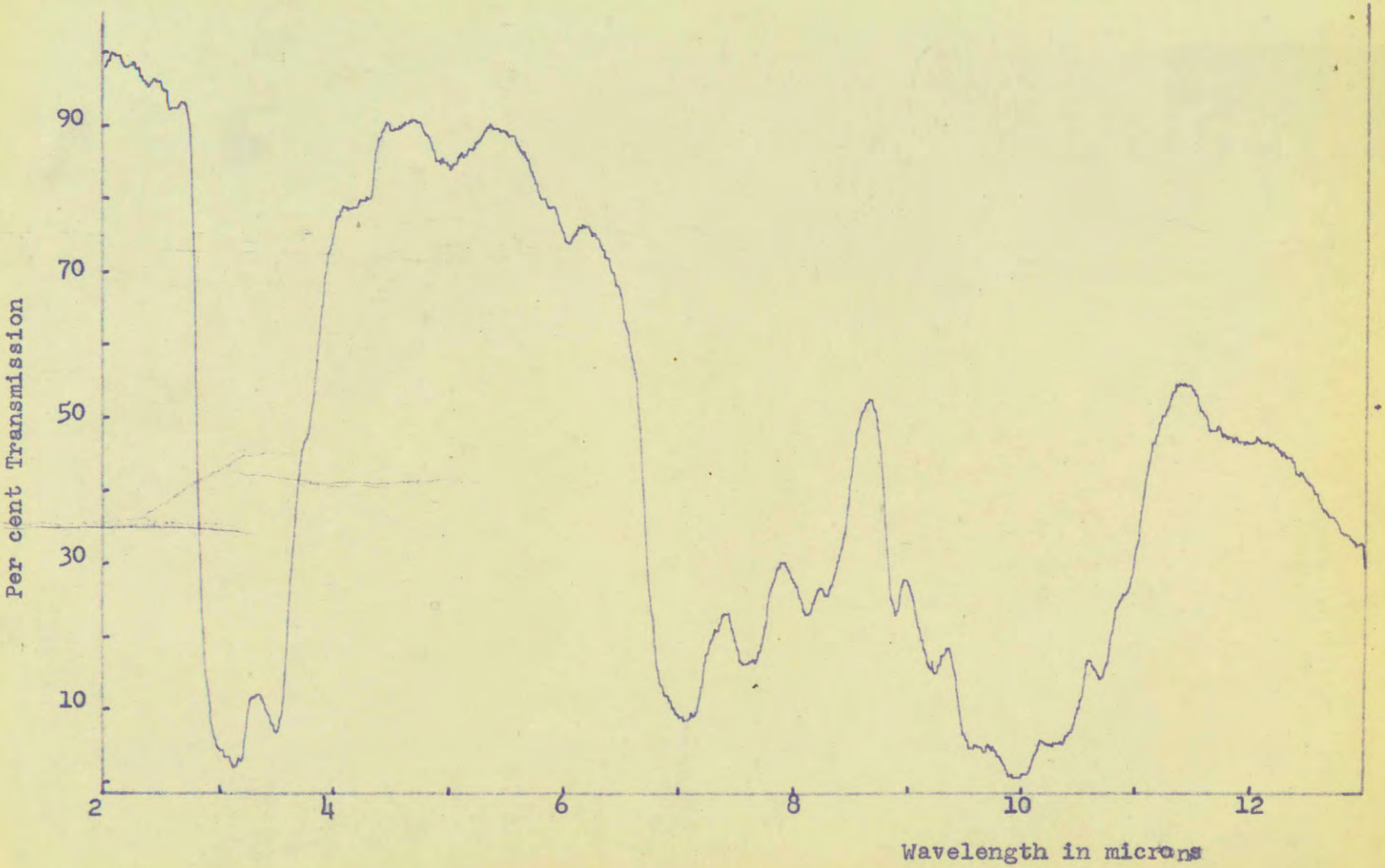
An attempt to bring about the isomerization of the cis-glycol by refluxing it for 17 hours and also by heating for two hours in the presence of a platinum catalyst proved fruitless as there was no change in the glycol. The dibenzoate esters prepared melted at 65° in both cases.

A final trial to achieve the isomerization was carried out with triphenylmethyl free radical, hoping that the free radical would start a chain reaction which would result in the complete conversion of cis-diol to its trans-isomer. The dibenzoate ester of the product also melted at 64-66 degrees.

It can be seen from the above results that the cis-glycol is extremely resistant to conversion into the trans-glycol by the usual methods. It seems possible that more drastic methods (such as elevated temperatures) or choice of a suitable catalyst might bring about isomerization of the cis-diol to its trans-isomer.

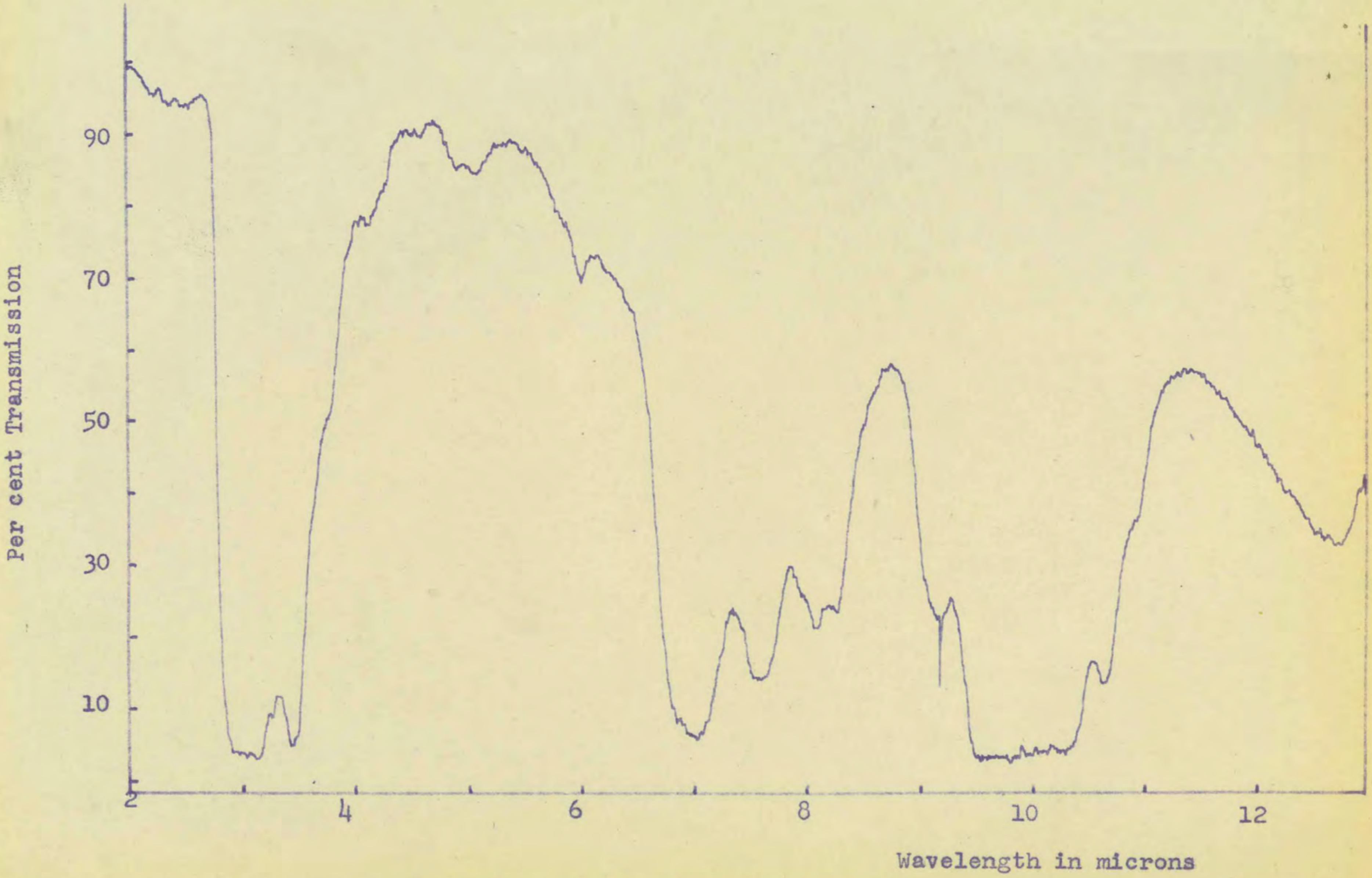
The results obtained by this author confirm the opinion of Dupont (77) that aliphatic cis-olefins are extremely difficult to isomerize to their trans-isomers and may contradict the conclusion reached by Valette (78) that in the dehydration of 2-butene-1,4-diol the cis-glycol isomerizes in part to its trans isomer. This conclusion was reached on the basis that dehydration of cis-glycol gave 35% 2,5-dihydrofuran and 65% crotonaldehyde which is also obtained by the dehydration of the trans-glycol. These results are inadequate to prove that the trans-glycol was actually formed, because it was not isolated before it rearranged further. The fact that crotonaldehyde was obtained does not necessarily mean that the trans-glycol was formed first. It might be possible that in the formation of crotonaldehyde the rotation about the carbon-carbon double bond occured only after the removal of the hydroxide group. It is felt by the author that as long as the mechanism of this dehydration has not been proved, no definite conclusions can be made about a possible cis-trans isomerization of 2-butene-1,4-diol.

An interesting fact concerning the cis-trans isomerization of a 2-butene-1,4-diol derivative has been reported by Valette (33). In the preparation of trans-2-butene-1,4-diol Valette claimed to have achieved the conversion of cis-1,4-dibromo-2-butene to the corresponding trans compound by heating the former on an oil bath for 2 hours at 120°. This is quite interesting, because the cis-glycol could not be converted to its trans isomer even after 17 hours of heating. It may therefore be concluded from the work of Valette and that of this author that substitution of hydroxide groups by bromine greatly facilitates the isomerization of the olefin.



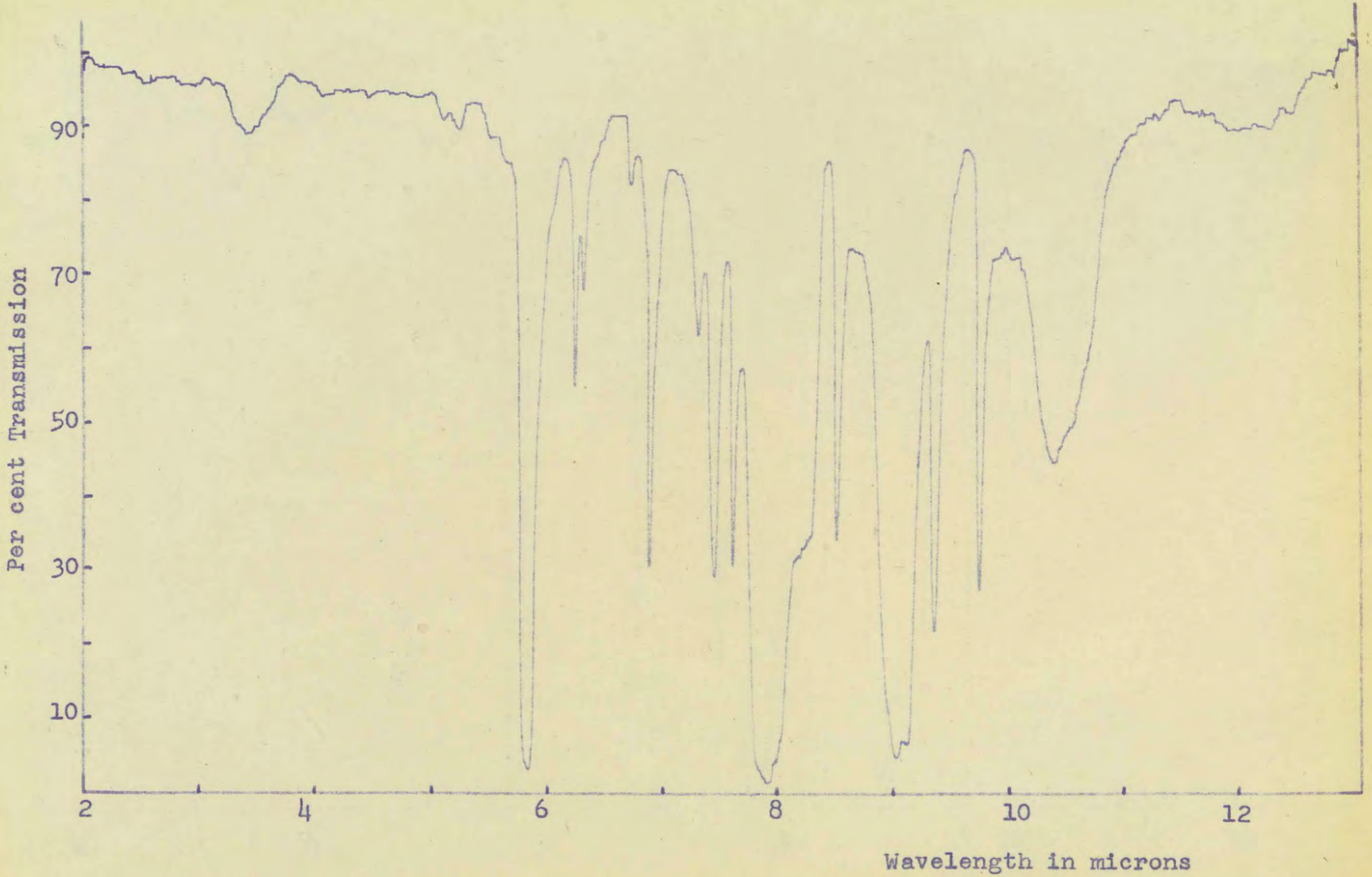
INFRARED SPECTRUM OF CIS-2-BUTENE-1,4-DIOL

PLATE I



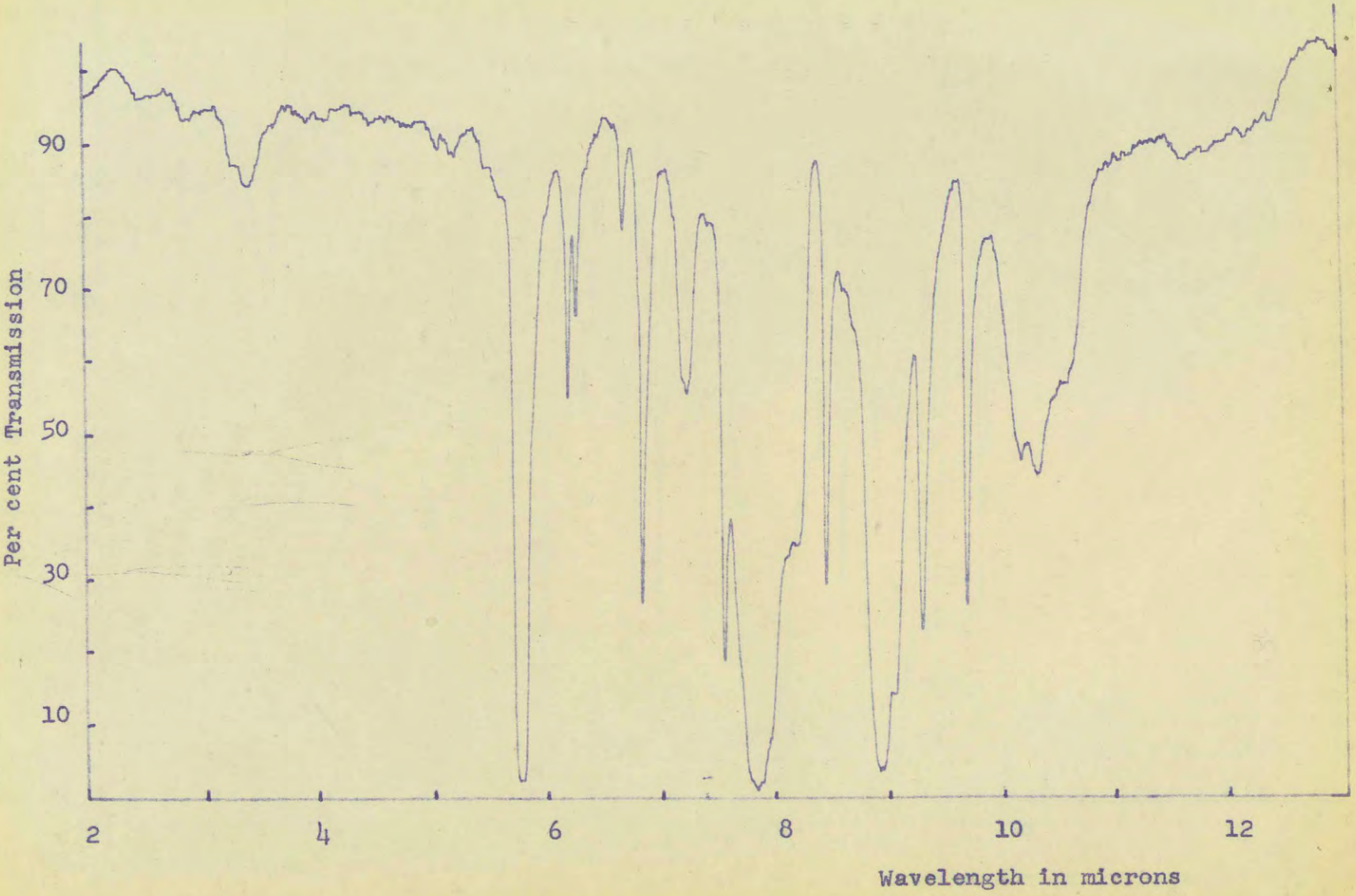
INFRARED SPECTRUM OF PURIFIED CIS-2-BUTENE-1,4-DIOL

PLATE II



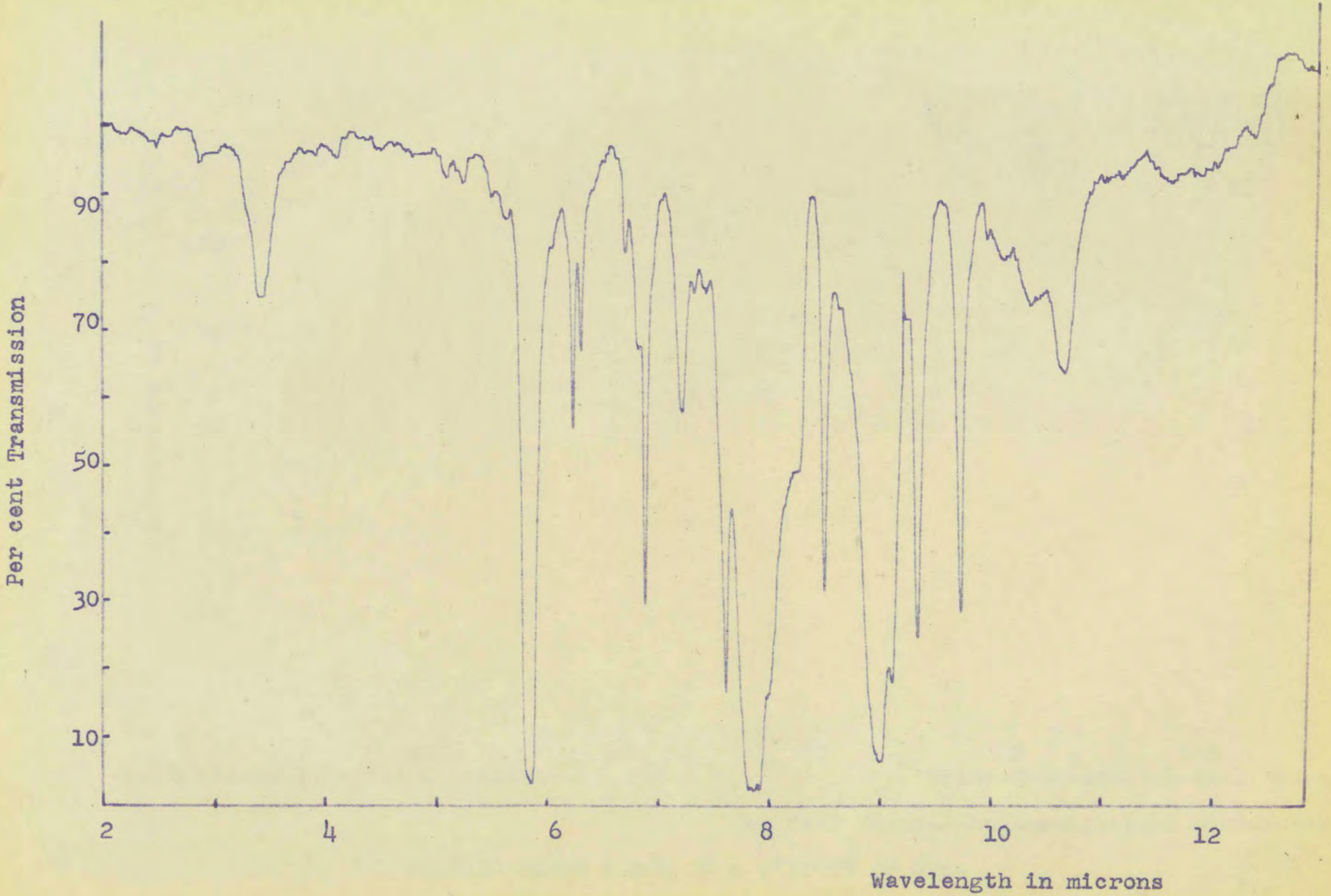
INFRARED SPECTRUM OF CIS-2-BUTENE-1,4-DIOL DIBENZOATE

PLATE IV



INFRARED SPECTRUM OF TRANS-2-BUTENE-1,4-DIOL DIBENZOATE

PLATE V



INFRARED SPECTRUM OF BUTANE-1,4-DIOL DIBENZOATE

PLATE VI

SUMMARY

1. Cis-2-butene-1,4-diol has been prepared by hydrogenating 2-butyne-1,4-diol in the presence of Raney nickel with ethanol as a solvent.

2. The cis-glycol has been purified by reducing its dibenzoate ester with lithium aluminum hydride.

3. Cis-2-butene-1,4-diol is strongly adsorbed by some inorganic solids and phenolic resins.

4. Trans-2-butene-1,4-diol cannot be prepared by reducing the dimethylfumarate or fumaric acid with lithium aluminum hydride. These reactions give butane-1,4-diol rather than the trans-glycol.

5. The reduction of 2-butyne-1,4-diol with sodium in liquid ammonia gives the same acetylenic glycol in 42.5% yield.

6. Trans-2-butene-1,4-diol has been prepared by converting the butadiene to the trans-glycol.

7. Cis-2-butene-1,4-diol cannot be isomerized to its trans isomer by usual methods under mild conditions.

8. Infrared spectra of both butene-diols, their dibenzoate derivatives and that of butane-1,4-diol dibenzoate are given.

BIBLIOGRAPHY

(1) N. Lozac'h, Bull. soc. chim. France 1949, 286; C.A. 43, 6162

(2) K.N. Campbell and B.K. Campbell, Chem. Revs. 31, 77 (1942)

(3) A. Baeyer, Ann. 269, 145 (1892)

(4) R. Willstätter, F. Seitz, and E. Bumm, Ber. 61, 871 (1928)

(5) R. Kuhn and M. Hoffer, Ber. 66, 1263 (1933)

(6) H. Burton and C.K. Ingold, J. Chem. Soc. 1929, 2022

(7) A. Farkas and L. Farkas, Trans. Faraday Soc. 33, 837 (1937)

(8) K.N. Campbell and L.T. Eby, J. Am. Chem. Soc. 63, 216 (1941)

(9) K.N. Campbell and L.T. Eby, J. Am. Chem. Soc. 63, 2683 (1941)

(10) K.W. Greenlee and W.C. Fernelius, J. Am. Chem. Soc. 64, 2505 (1942)

(11) G.W. Wheland, Advanced Organic Chemistry, John Wiley and Sons, New York, 2-nd Ed., 1953, Chapter 7

(12) L. Aronstein and A. Hollemann, Ber. 22, 1181 (1889)

(13) G.W. Watt, W.B. Leslie and T.E. Moore, Chem. Revs. 31, 525 (1942)

(14) I.G. Farbenindustrie A.-G. B.P. 508,543 June 29, 1939

(15) Sankichi Takei, C. A. 45, 4201 (1951)

(16) I. Zalkind, C. A. 38, 1470 (1944)

(17) S.V. Lebedev and V.Ya. Stern, C. A. 27, 266 (1933)

(18) I.F. Bogdanov, C. A. 36, 6882 (1942)

(19) B.P. 595,459, Dec. 5, 1947; C. A. 42, 4194 (1948)

(20) A.L. Henne and K.W. Greenlee, J. Am. Chem. Soc. 65, 2020 (1943)

(21) K.N. Campbell and M.J. O'Connor, J. Am. Chem. Soc. 61, 2897 (1939)

(22) I. Marszak, C. A. 45, 9474 (1951)

(23) T.Y. Lai, Bull. soc. chim. [4] 53, 1533 (1933)

(24) A.F. Thompson Jr. and E.N. Shaw, J. Am. Chem. Soc. 64, 363 (1942)

(25) A.F. Thompson Jr. and S.B. Wyatt, J. Am. Chem. Soc. 62, 2555 (1940)

(26) C. Paal, Ber. 42, 3930 (1909)

(27) I. Zalkind, C. A. 32, 2086 (1938)

(28) E. Ott and R. Schröter, Ber. 60, 624 (1927)

(29) M. Bourguell, Bull. soc. chim. [4] 45, 1067 (1929)

(30) M.L. Sherrill and E.S. Matlack, J. Am. Chem. Soc. 59, 2134 (1937)

(31) H.E. Sheffer, Ph. D. Thesis, Cornell University (1943)

(32) A.W. Johnson, J. Chem. Soc. 1946, 1009

(33) A. Valette, Ann. chim. [12] 3, 644 (1948); C. A. 43, 2577

(34) Yu.K. Yur'ev, I.K. Korobitsyna and E.K. Brige, C. A. 44, 7822 (1950)

(35) C.S. Marvel and C.H. Young, J. Am. Chem. Soc. 73, 1066 (1951)

(36) K. Höjendahl, J. Phys. Chem. 28, 758 (1924)

(37) M. Nelles and G.B. Kistiakowsky, J. Am. Chem. Soc. 54, 2208 (1932)

(38) T.W.J. Taylor and A.R. Murray, J. Chem. Soc. 1938, 2078

(39) U.S. 2,444,238 May 11, 1948; C. A. 42, 6377

(40) R. Stoermer, Ber. **42**, 4865 (1909)

(41) R. Stoermer, Ber. **44**, 637 (1911)

(42) A.R. Olson, Trans. Faraday Soc. **27**, 69 (1931)

(43) R.S. Mulliken, Phys. Revs. **41**, 751 (1932)

(44) I.L. Finar, Organic Chemistry, Longmans-Green and Co., London 1954, page 367

(45) T. Anschütz, Ann. **254**, 173 (1889)

(46) T. Michael, J. prakt. Chem. **52**, 323 (1895)

(47) E.M. Terry and L. Eichelberger, J. Am. Chem. Soc. **47**, 1402 (1925)

(48) K. Nozaki and R. Ogg Jr., J. Am. Chem. Soc. **63**, 2583 (1941)

(49) O. Simamura, Bull. Chem. Soc. Japan **14**, 22 (1939)

(50) J. Wislicenus, Ann. **248**, 341 (1888)

(51) C. Liebermann, Ber. **23**, 512, 2512 (1890)

(52) W.I. Gilbert, J. Turkevich and E.S. Wallis, J. Org. Chem. **3**, 611 (1939)

(53) C.C. Price and M. Meister, J. Am. Chem. Soc. **61**, 1595 (1939)

(54) Tanatar, J. Russ. Phys.-Chem. Soc. **43**, 1742 (1911)

(55) P. Pfeiffer, Ber. **47**, 1592 (1914)

(56) G.R. Clemo and S.B. Graham, J. Chem. Soc. **1930**, 213

(57) K. Nozaki, J. Am. Chem. Soc. **63**, 2681 (1941)

(58) R. Kuhn, see Freudenberg, Stereochemie, Leipzig 1933, page 913

(59) M.S. Kharash, J.V. Mansfield and F.R. Mayo, J. Am. Chem. Soc. **59**, 1155 (1937)

(60) D.H. Hey and W.A. Waters, Chem. Revs. **21**, 169 (1937)

(61) P.W. Selwood, Chem. Revs. 38, 41 (1946)

(62) H. McConnell, J. Chem. Phys. 20, 1043 (1952)

(63) F. R. Mayo and C. Walling, Chem. Revs. 27, 404 (1940)

(64) H. Taube, J. Am. Chem. Soc. 65, 526 (1943)

(65) B. Tamamushi, Bull. Chem. Soc. Japan 17, 321, 417 (1942)

(66) R.L. Shriner and R.C. Fuson, Identification of Organic Compounds, John Wiley and Sons, Inc., New York 1948, 3-rd Ed., page 164

(67) F. Arndt, Organic Syntheses, Collective volume II, John Wiley and Sons, Inc., New York 1943, 2-nd Ed., page 461

(68) H. von Pechmann, Ber. 27, 1890 (1894)

(69) G.E. Benedict and R.R, Russell, J. Am. Chem. Soc. 73, 5444 (1951)

(70) General Aniline and Film Corporation, Preliminary Data Sheet on 2-Butene-1,4-diol, No. A-109, February 1954

(71) Beilstein, Organische Chemie, Verlag von Julius Springer, Berlin 1941, Band I, Zweites Ergänzugswerk, page 545

(72) W.G. Brown, Organic Reactions, John Wiley and Sons, Inc., New York 1951, Volume VI, Chapter 10

(73) V.M. Mićović and M.Lj. Mikhailović, Glasnik Khem. Drushtva Beograd, 16, 19 (1951); C. A. 46, 8609

(74) J.R. Johnson and O.H. Johnson, J. Am. Chem. Soc. 62, 2615 (1940)

(75) I. Zalkind and S. Bukhovets, C. A. 32, 2086 (1938)

(76) J.R. Johnson, J. Am. Chem. Soc. 63, 2282 (1941)

(77) G. Dupont, Bull. soc. chim. [5] **3**, 1030 (1936)

(78) A. Valette, Compt. rend. **223**, 907 (1946); C. A. **41**, 1606