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Investigation of 3-methyl-2-penten-4-yne-l-ol (cis form)

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INVESTIGATION OF 3-METHYL-2-PENTEN-4-YNE-1-OL
(CIS FORM)

BY

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A THESIS
SUBMITTED TO THE FACULTY OF
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OF
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NEWARK, NEW JERSEY

1955

ABSTRACT

The isomerization of 3-methyl-1-penten-4-yne-3-ol into *trans*-3-methyl-2-penten-4-yne-1-ol and an isomer assumed to be the *cis* form has been studied. The problem of determining whether or not the arbitrarily assumed isomer is a geometrical isomer or an ordinary isomer has been brought forward in industry in the course of a synthesis of Vitamin A.

Qualitative tests on the questionable isomer were without result because of the activity that the unsaturated bonds exhibited when reagents were used to test it. All possible isomers of the compound were reviewed and the following chemical means were employed to prove that the isomer was the geometric one.

A total hydrogenation of both isomers was carried out which, in both cases, gave 3-methyl-1-pentanol. The 3,5-dinitro benzoate derivatives of both isomers were made, which proved that the structures were similar. The isomer possibility was thus limited to two forms.

The structure of the geometrical isomer was shown by adding one mole of hydrogen to *cis*-3-methyl-2-penten-4-yne-1-ol which produced 3-methyl-2,4-pentadien-1-ol. This resultant diene was reacted with maleic anhydride and the adduct formed was recrystallized from water to give a gamma lactone.

As further proof, the same diene was reacted with acetylene dicarboxylic ester. The adduct was oxidized with chloranil and the product was further oxidized with potassium permanganate. This yielded a compound containing a benzene ring with two carboxylic groups and one anhydride group:(3,6-dicarboxy phthalic anhydride).

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

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NEWARK, NEW JERSEY

MAY, 1955

ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor James A. Bradley, of Newark College of Engineering, and to Doctor Peter I. Pollak, of Merck and Co., Inc., for their assistance and tireless efforts throughout the investigation.

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INTRODUCTION

This paper represents work that has been carried out on the identification of an unknown compound formed when 3-methyl-1-penten-4-yne-3-ol (I) is isomerized under acidic conditions.

When the isomerization takes place, a trans isomer, 3-methyl-2-penten-4-yne-1-ol (II) is formed and its cis compound (III) is also formed. These two compounds may be separated by means of a vacuum fractional distillation which will be explained later.

The trans isomer (II) is used in the synthesis of Vitamin A and its structure has been verified. The cis isomer has not been demonstrated and some evidence is at hand to cast doubt on the assumption. The cis isomer will not pass through subsequent reactions in the Eisler synthesis to produce Vitamin A. It has been impossible to intra-convert the compounds even with treatment by iodine, light, and other means.(1)

The object of the present investigation was to determine whether or not these two compounds are geometric isomers (2). If the proof can be shown, industry will be able to benefit by it. The assumed cis compound is a by product of Vitamin A. If the cis compound exists there should be some means of converting it to the trans form and by doing this, the yields of the isomerization of 3-methyl-1-penten-4-yne-3-ol (I) could be increased by about five to ten percent. On a yearly basis, this could assure a very considerable monetary gain. Therefore the object of this work is prastical as well as academic.

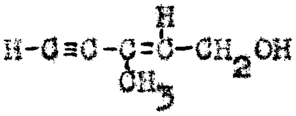
EXPERIMENTAL PROCEDURE

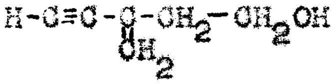
Pure trans-3-methyl-2-penten-4-yne-1-ol (II) is obtained by refractionating the factory production batch in the laboratory. The equipment set up for high vacuum distillation consisted of a one-liter, three-neck flask, equipped with a nitrogen inlet, thermometer, and a twenty six plate stainless steel column. The column was four feet high and it measured two inches in diameter. The rest of the equipment consisted of a reflux-splitter, reflux-timer, condensing product collector, monostat, manometer, and a vacuum pump. A one-liter mantle and powerstat were used for the heating source.

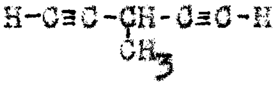
The equipment was charged with 673 grams of (II) and fractionated. The results are listed in table I and figures 1 and 2.

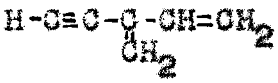
Pure cis-3-methyl-2-penten-4-yne 1-ol (III) may be obtained by fractionating the lean tail cuts of a factory production batch and the same procedure as the one used for the trans form was used for this one also. The results are listed in table II and figures 1 and 2. The two isomers were thus obtained in pure form and the next step was to hydrogenate the compounds completely and find out how many moles of hydrogen were absorbed.

study the final products to see if the same hydrogenated product was formed. This study will also tell us if (IV), (V), or (VI) has been formed.

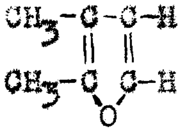
(a) 
$H\text{-}C\equiv C\text{-}\underset{CH_3}{C}=\overset{H}{C}\text{-}CH_2OH$ (*cis* or *trans*)

(b) 
$H\text{-}C\equiv C\text{-}\underset{\underset{CH_2}{\|}}{C}\text{-}CH_2\text{-}CH_2OH$

(c) 
$H\text{-}C\equiv C\text{-}\underset{CH_3}{CH}\text{-}C\equiv C\text{-}H$ (dehydration of (a))

(d) 
$H\text{-}C\equiv C\text{-}\underset{\underset{CH_2}{\|}}{C}\text{-}CH=CH_2$ (dehydration of (b))

(e) Ring structure of the type:



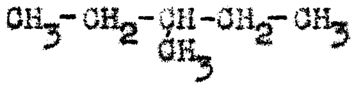
2-3-dimethyl-furan

A complete hydrogenation will show what structure exists above because (a) and (b) will absorb three moles of hydrogen and yield:


$CH_3\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}CH_2OH$

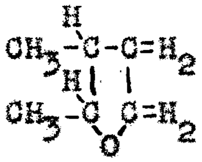
3-methyl-1-pentanol (IV)

(c) and (d) will absorb four moles of hydrogen and yield:


$CH_3\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}CH_3$

3-methyl-pentane (V)

(e) will absorb two moles of hydrogen and yield:

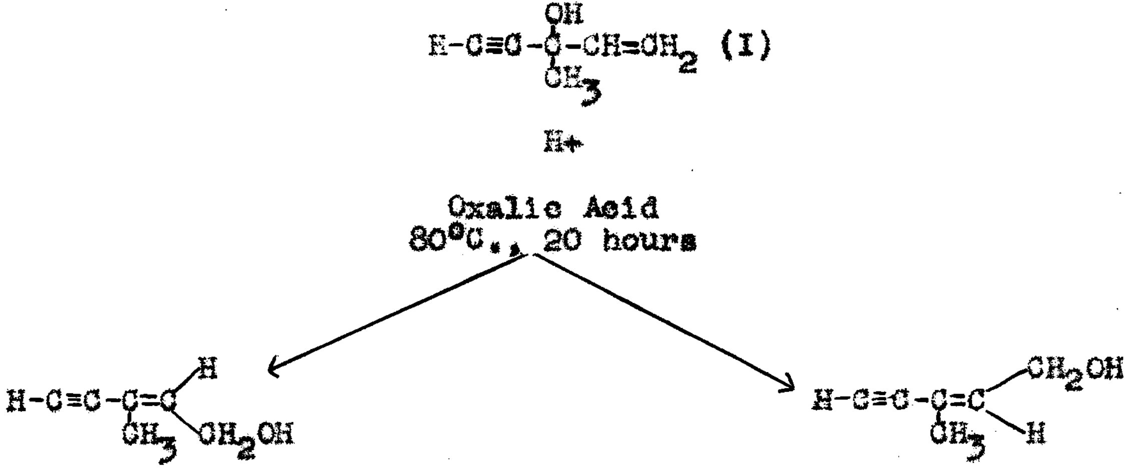


2,3-dimethyl tetrahydrofuran (VI)

No other isomers can exist. Therefore our next step is to completely hydrogenate the both compounds and then

DISCUSSION

In the isomerization of 3-methyl-1-penten-4-yne-3-ol:



Trans-3-methyl-2-penten-4-yne-1-ol (II)

Cis-3-methyl-2-penten-4-yne-1-ol (III)

The *trans* isomer is formed and another isomer which was arbitrarily named the *cis* form was also produced. The two isomers can be separated by means of a vacuum fractional distillation. The structure of (III) has not been proven. The object of this paper is to determine whether or not these two substances are geometric isomers or merely isomers.

Qualitative tests were run to determine certain groups in both compounds. The results were not conclusive because of the reactive acetylenic group. A study of the possible compounds containing the same groups was made. The following may be mentioned:

TABLE I

Distillation data of trans-3-methyl-2-penten-4-yne -1-ol

Time	Cut	(°C) Vapor Temp.	(°C) Still Temp.	(mm.) Vac.	(-°C) M.P.	N_D20	% HCH	(Gms.) Prod.
8:50	1	38	72	2.5	19.0	1.4810	.013	46.4
9:40	2	38	72	2.5	17.1	1.4812	.013	43.4
10:40	3	42	72	2.5	16.4	1.4820	.013	123.3
11:45	4	42	73	2.5	16.2	1.4820	.013	123.2
12:20	5	45	73	2.5	16.2	1.4820	.013	110.0
1:10	6	45	73	3.0	16.0	1.4820	.012	100.0
3:00	7	47	73	3.0	16.0	1.4820	.012	60.0
4:20	8	49	73	3.0	16.0	1.4820	.012	10.0
Shut down until the next day (Refluxed column one hour)								
8:00	-	47	74	3.0	--	---	--	--
9:25	9	47	74	3.0	16.1	1.4820	.015	10.0
11:50	10	47	74	2.5	16.1	1.4820	.015	10.0
12:00	11	47	74	2.5	16.1	1.4820	.015	10.0

Final product of trans-3-methyl-2-penten-4-yne 1-ol

M.P.	-16.1°C.
Purity	99.7%
N_D20	1.4820
$\%H_2O$	0.015
Sp.Gr.	0.922
B.P.	47°C(2.5-3.0 mm.)

TABLE II

Distillation data of *cis*-3-methyl-2-penten-4-yne-1-ol

Time	Cut	(°C) Vapor Temp.	(°C) Still Temp.	(mm.) Vac.	(-°C) M.P.	N_D20	% HOH	(Gms.) Prod.
9:00	-	30	42	3.5	-	-	-	-
11:00	1	48	88.0	3.5	-	1.4872	-	100.0
2.00	2	49	89.0	3.5	-	1.4890	-	100.0

Stopped the distillation until the next day

(Refluxed column one hour)

Time	Cut	(°C) Vapor Temp.	(°C) Still Temp.	(mm.) Vac.	(-°C) M.P.	N_D20	% HOH	(Gms.) Prod.
5:00	3	61	95.0	3.5	-	1.4919	-	10.0
6:00	4	61.2	97.0	3.5	-	1.4919	-	11.2
7:00	5	61.2	100.0	3.5	-	1.4920	-	10.5
8:00	6	61.8	107.5	3.5	-	1.4923	-	11.5
9:00	7	63.0	120.0	3.5	-	1.4926	-	6.2

Stopped distilling - Still temp. was too high

Final product of *cis*-3-methyl-2-penten-4-yne-1-ol

M.P.	-
Purity	100.0%
N_D20	1.4913
%HOH	0.035
Sp.Gr.	0.897
B.P.	61.5°C(3.5 mm.)

(Karl Fischer percentage of water is found by titrating the K. F. solution with ten mls. of sample that is poured into neutralized methanol. An electric eye is used to indicate the end point.)

$$\frac{100 \times \text{K.F.Factor} \times \text{mls. of titrant}}{\text{Mls. of sample} \times \text{Sp. Gr.}} = \%\text{HOH}$$

FIGURE I

% PURITY VS. M.P. AND N_D^{20}

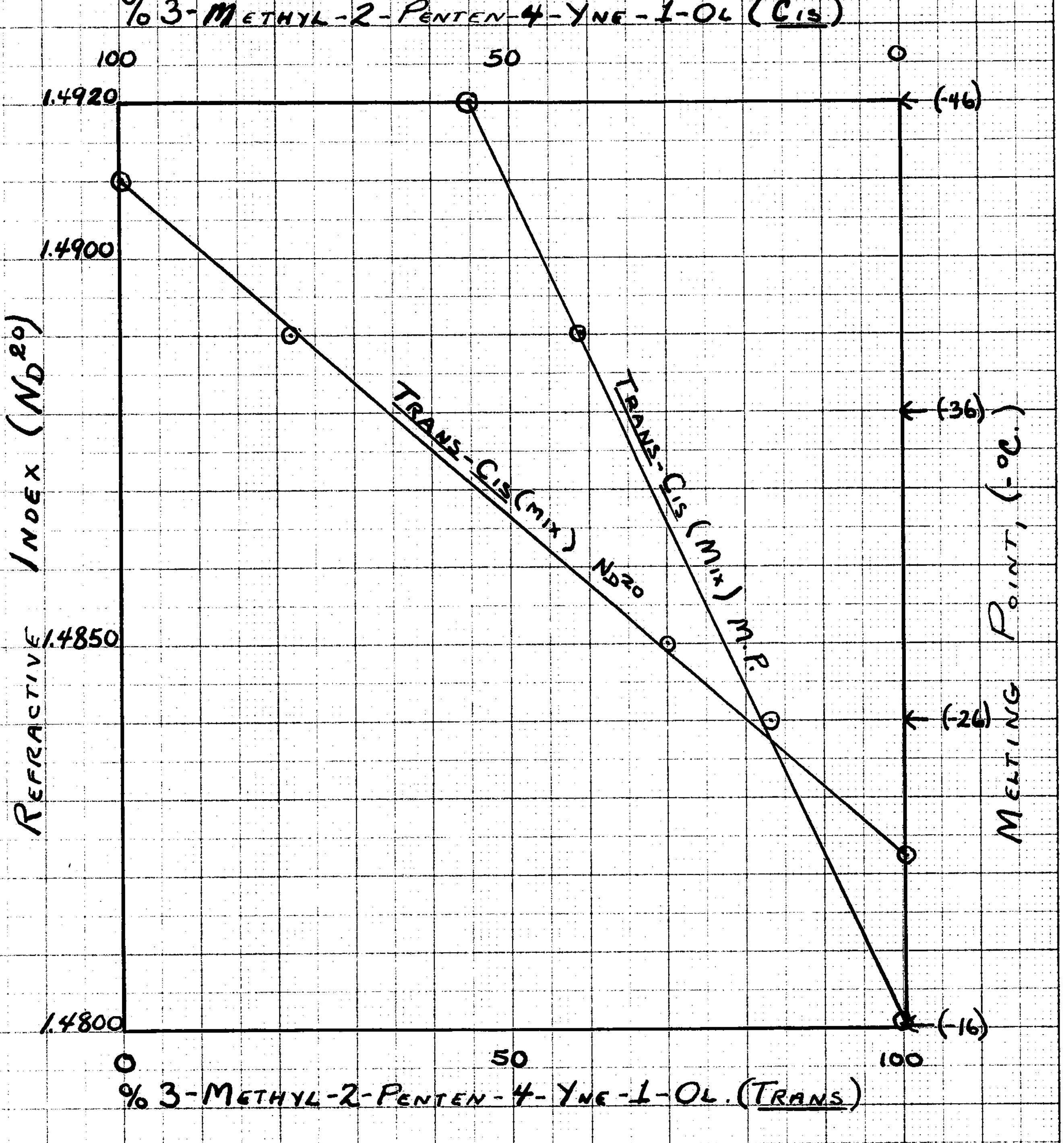
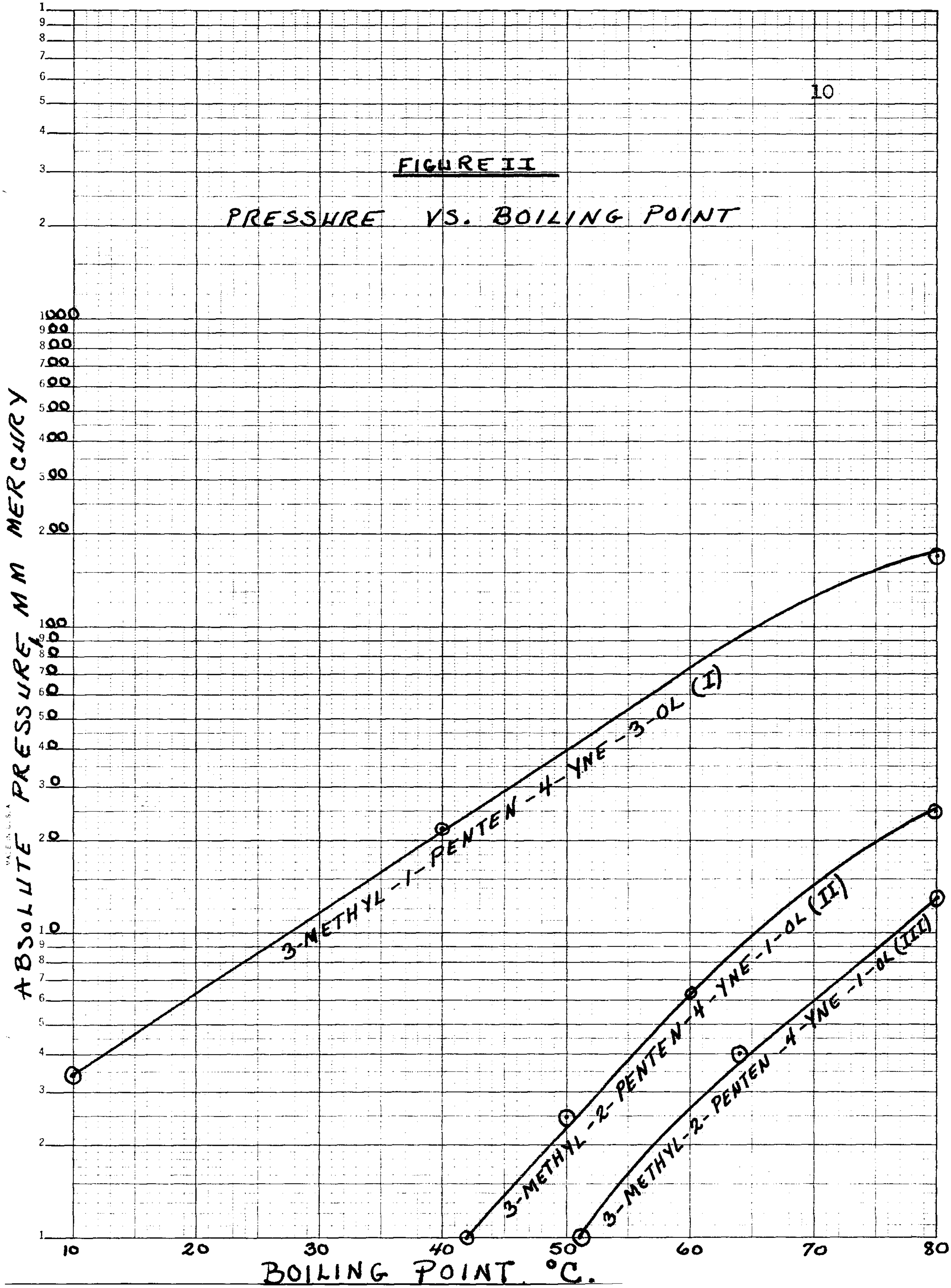
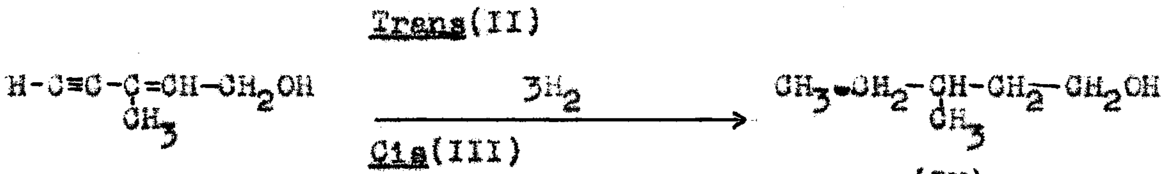


FIGURE II

PRESSURE VS. BOILING POINT





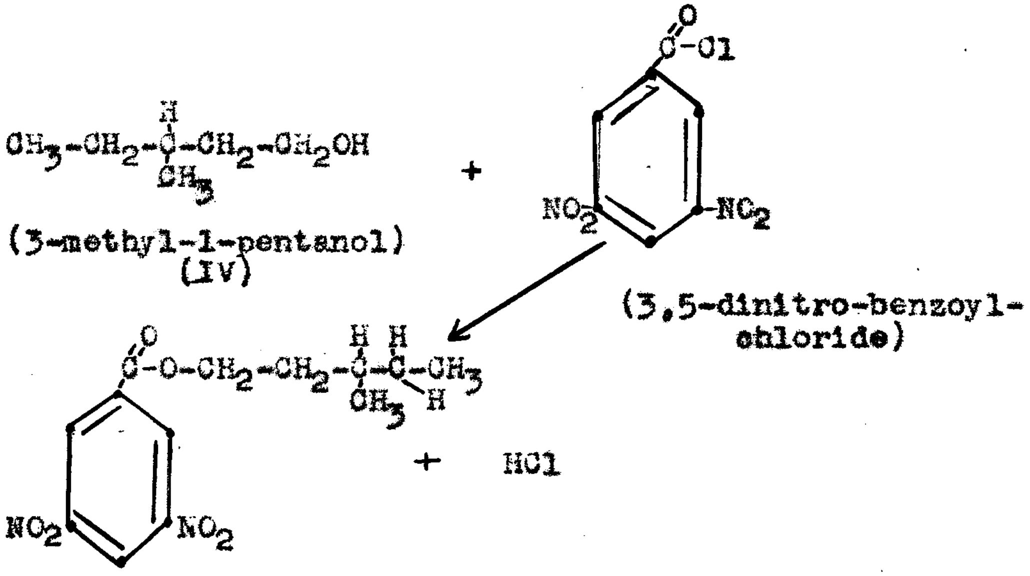
$$H-C\equiv C-\underset{CH_3}{C}=CH-CH_2OH \xrightarrow[\text{\underline{Cis}(III)}]{\text{\underline{Trans}(II)}\quad 3H_2} CH_3-CH_2-\underset{CH_3}{CH}-CH_2-CH_2OH$$

(IV)

The *trans* and *cis* isomers were hydrogenated under high pressure and at a temperature of thirty degrees centigrade. The isomers, 19.2 grams in each case, were charged in separate runs to a high pressure still which contained 100 mls. of 2BA alcohol. Platinum oxide, 0.2 gm., was used as the catalyst. The *trans* form absorbed 84.5% of the required three moles of hydrogen. The *cis* form absorbed 88.3% of the required three moles of hydrogen. A sintered glass funnel was used to filter off the catalyst. A water aspirator was used in the filtration. The resulting solutions were clear and yellowish green in color. The appearance of both samples were very similar. The odor was like that of amyl alcohol: heavy, sweet, and choking. The alcohol was stripped from both samples under vacuum and at 20° centigrade temperature. A literature search was made (3,4) on 3-methyl-1-pentanol. The physical properties and those of the distillates were as follows:

	B.P.	N_D^{20}
3-methyl-1-pentanol	152.3-153.0°C	1.4177(Lit.)
Trans isomer Totally (Hydrogenated)	152.0-154.0°C	1.4182
Cis isomer Totally (Hydrogenated)	152.0-154.0°C	1.4195

The agreement was very close. In order to confirm the findings, the 3,5-dinitro benzoate was made from the products of each distillate. The reaction went as follows:



(3-methyl-1-pentanol)
(IV)

(3,5-dinitro-benzoyl-chloride)

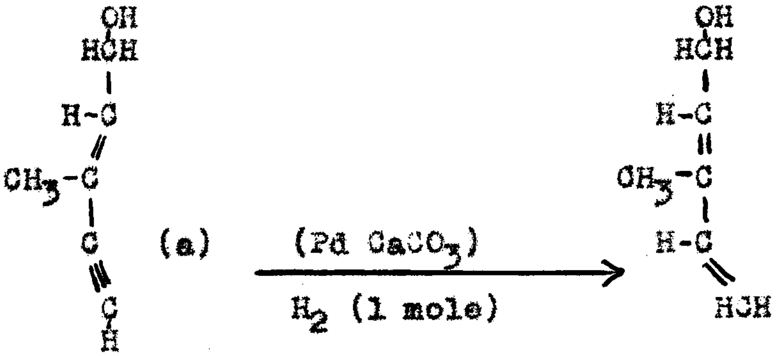
(3-methyl pentyl-3,5-dinitro benzoate)
(VII)

The procedure followed was that of Shriner and Fuson (5). A half gram of 3,5-dinitro benzoyl chloride was mixed with 2 mls. of the unknown alcohol in a test tube and the mixture was boiled for five minutes. Ten mls. of water were then added and the tube was cooled in an ice bath. The precipitate was collected on a filter and washed with 2 per cent sodium carbonate and then recrystallized until a pure product was obtained. The procedure was followed but the reaction did not take place because the alcohol was not soluble in the water solution.

Another literature search was made and a successful procedure was found using petroleum ether (6,7). The mixture of alcohol and the 3,5-dinitro-benzoyl chloride were mixed with five parts of petroleum ether and one part of ethyl ether, a mixture in which the acid chloride is slightly soluble. The precipitate which came down was filtered off and dried under vacuum. Each sample was recrystallized eight times and a melting point of each compound was taken each time. The literature stated that the ester consisted of yellowish leaflets and had a melting point of 38°C.. The melting point of the trans isomer's derivative was 35-36°C.; the cis isomer's derivative had a melting point of 35.5-36.5°C..

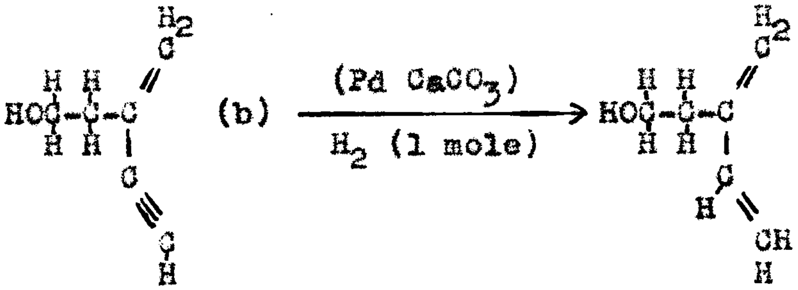
An infra red spectrum in the solid state was run on both samples. A Baird infra red machine was used which plotted a series of absorptions on a chart. (The wave length band is from 2 to 15 microns and certain functional groups are characteristic for each micron).The solid unknown was put into mineral oil and this mixture was placed into the machine. The readings were plotted on a graph. The peaks at the different wave lengths showed which groups were in the unknown compound. The spectrum showed an ester band at 5.80 microns, nitro bands at 6.62 and 7.4 microns, and a characteristic phenyl absorption.

These findings,which were essentially the same on both samples, made it clear that the isomer must be either (a) or (b) as listed on page 4. In order to decide between these two possibilities, the Diels-Alder reaction was used. The isomer in question was partially hydrogenated and reacted with maleic anhydride to form an adduct. This adduct was identified by reference to the literature. The reactions are as follows;



(3-methyl-2,4-pentadien-1-ol) (VIII)

(cis isomer)



(3-methylene-4-penten-1-ol) (IX)

The reactions above show the two compounds that can be formed when (a) and (b) have one mole of hydrogen added to the molecule. 3-methyl-2,4-pentadien-1-ol(VIII) is formed when the cis isomer is partially reduced, and 3-methylene-4-penten-1-ol (IX) is formed when the other possibility is partially reduced.

Cis-3-methyl-2-penten-4-yne-1-ol, 20 grams, was poured into a flask containing 50 mls. of methyl acetate. This mixture was shaken in hydrogen in the presence of palladium-calcium carbonate catalyst (two grams of six per cent palladium chloride) until 5018 mls. of gas was absorbed at 20°C. and 760 mms. pressure (table 3). The reaction was stopped and the catalyst was filtered off. (The reaction was carried out in a small laboratory hydrogenator which used water displacement to measure the hydrogen that went into the reaction). The filtrate was distilled from a small round bottom flask with a vacuum take off and the residue was placed in a small semi micro fractionating unit that had a cow arrangement for the collection of the product cuts which were to follow (Fig. 3). The literature stated that compound (VIII) had a boiling point of 68-71°C. at 15 mm. vacuum and a refractive index of 1.4840-1.4920. The product was collected in several fractions and this was the reason for the range in the refractive index. The compound formed had a boiling range of 35-40°C. at 0.6 mm. vacuum and had a refractive index of 1.4825-1.4920. This result looked very good and therefore a reaction with maleic anhydride would be expected to yield an adduct that would have a lactone structure (8):

TABLE III

Partial reduction of 3-methyl-2-penten-4-yne-1-ol

Temp.	(Min.) Time	Read.	Diff.	(mls.) Volume
		0		
7.0	15	300	300	300
7.0	25	500	200	500
7.0	55	900	400	900
7.0	85	1350	450	1350
7.0	105	1630	280	1630
-	-	0	-	-
6.5	135	380	380	2010
5.0	165	800	420	2430
7.0	195	1200	400	2830
8.0	225	1600	400	3230
-	-	0	-	-
7.0	255	400	400	3630
7.0	285	720	320	3950
9.0	315	1100	380	4330
7.0	345	1420	320	4650
-	-	0	-	-
7.0	375	300	300	4950
7.0	395	400	100	5050

(Theoretical hydrogen take up)

(Reaction was stopped and proceeded as per write up)

Fractionation date of the residue

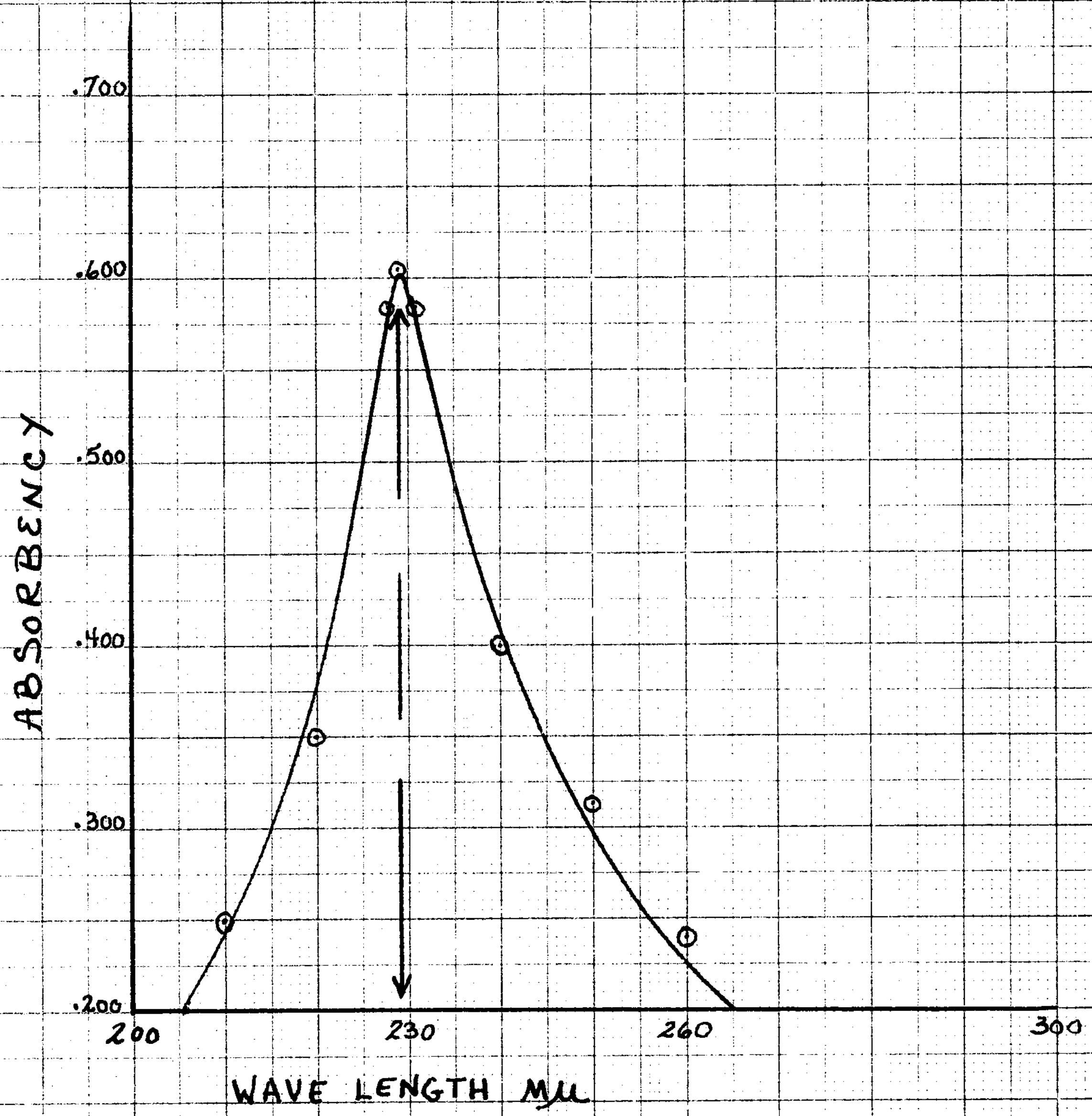
Cuts	(mm.) Vacuum	(°C.) Temp.	N_D20	(Gms.) Wgt.
1	0.2	35.0	1.4790	0.5
2	0.2	36.0	1.4825	1.5
3	0.9	37.0	1.4872	6.0
4	0.9	39.0	1.4920	6.0

Charged: (20 grams) 3-methyl-2-penten-
4-yne-1-ol
(50 mls.) Methyl acetate
(2.0 grams) Catalyst Pd-$CaCO_3$

FIGURE III

ABSORBENCY VS. WAVE LENGTH

% 3-METHYL-2,4-PENTADIEN-1-OL



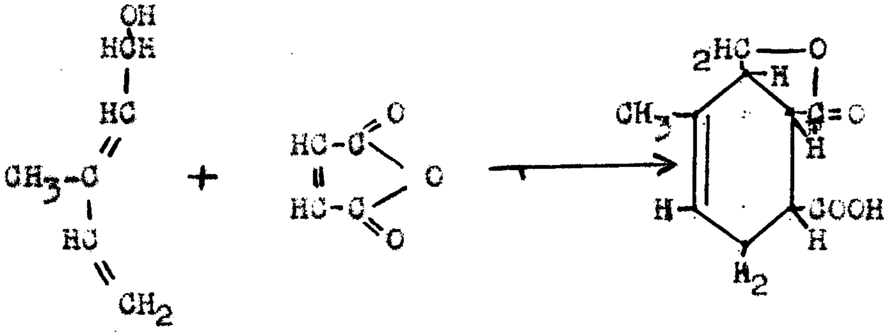
WgT. of SAmplE = .0537 gms.

ε % THEO. = 2500

DILUTIONS = $\frac{WgT}{100} \times \frac{10}{100} \times \frac{5}{200}$

$$\% = \frac{ABS. \times DIL. \times 100}{\frac{WgT}{100\,ML} \times \varepsilon\%}$$

$$\% = \frac{.605 \times 200 \times 100}{.0537 \times 2500} = 90.4$$



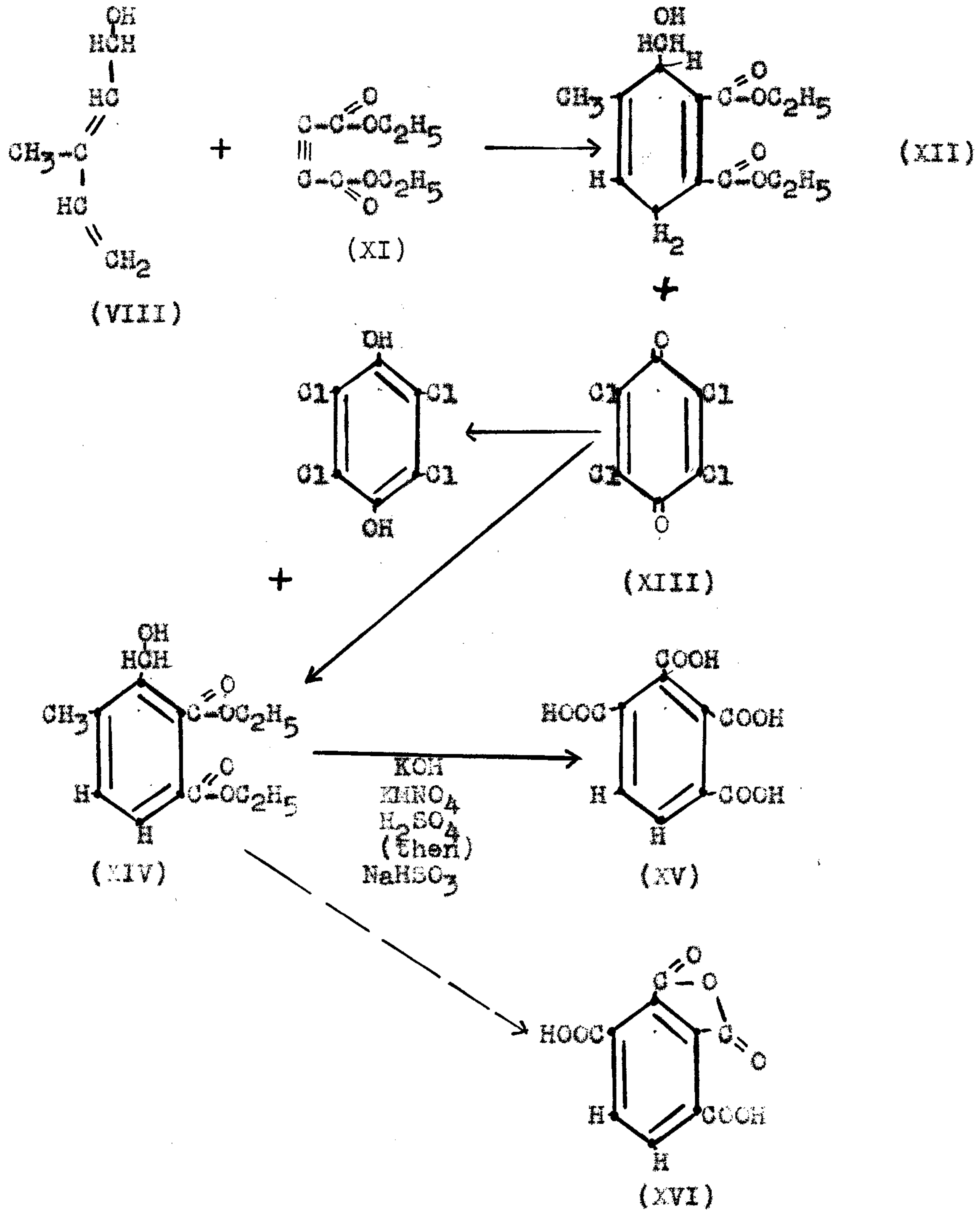
(VIII)

(gamma-lactone of 4-methyl-3-methylol-4-hexen-1,2-dicarboxylic acid)

(X)

In the preparation of the gamma-lactone of 4-methyl-3-methylol-4-hexen-1,2-dicarboxylic acid, a 5 gram sample of the carbinol and a 5 gram sample of maleic anhydride were mixed together in a 50 ml. flask with 40 mls. of benzene. The mixture was allowed to stand over night in a cool, dry desiccator. The next morning, the contents of the flask were filtered through a sintered filter and the crystals were washed with cold benzene. The crystals were vacuum dried and then recrystallized from water. The crystals were needle-like in structure and melted at 182-183°C.. A repetition of this procedure with the residue from our distillate gave needle-like crystals with the same melting point as the first run. The literature confirms these findings and therefore these reactions prove definitely that our starting compound can only be the *cis* isomer (III) and that it is the geometric isomer of the *trans* form (II).

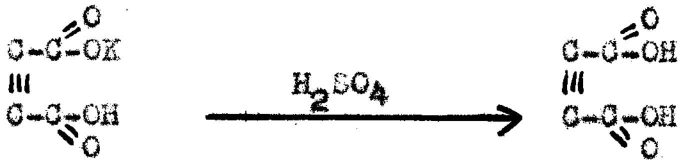
Another proof was tried by way of the following reactions:



A step-by-step description of this synthesis follows.

A. The Preparation of 3-methyl-2,4-pentadien-1-ol (VIII). The partial hydrogenation of the cis-3-methyl-2-penten-4-yne-1-ol isomer to form this compound has been discussed previously.

B. The Preparation of Acetylene Dicarboxylic Acid (XVIII).

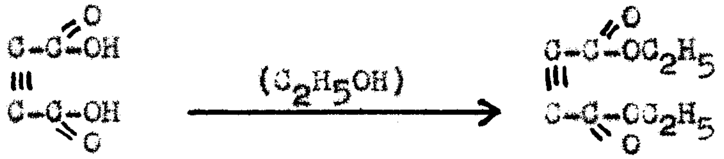


$$KO-\overset{O}{\overset{\|}{C}}-C\equiv C-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{H_2SO_4} HO-\overset{O}{\overset{\|}{C}}-C\equiv C-\overset{O}{\overset{\|}{C}}-OH$$

(XVII) (XVIII)

One hundred grams of acetylene dicarboxylic acid potassium salt (XVII) was dissolved in 240 mls. of concentrated sulfuric acid. The solution was poured into a separatory funnel and extracted with 5 x 100 mls. of ethyl ether. The extracts were evaporated on a steam bath and pure crystals of acetylene dicarboxylic acid hydrate were formed. The hydrated crystals were placed in a vacuum desiccator over concentrated sulfuric acid and dried for two days. The crystals melted with decomposition at 175-176°C.. The literature (9) verifies this melting point.

C. The Preparartion of Diethyl Acetylene Dicarboxylate (XI) (10,11).



$$HO-\overset{O}{\overset{\|}{C}}-C\equiv C-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{(C_2H_5OH)} C_2H_5O-\overset{O}{\overset{\|}{C}}-C\equiv C-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

(XVIII) (XI)

To a one-liter, round flask equipped with a stirrer, thermometer, and reflux condenser were added 20 grams of acetylene dicarboxylic acid. To this acid was added 60 mls. of dry benzene, 23 grams of 2BA alcohol and 4 mls. of sulfuric acid. This reaction mixture was refluxed for twelve hours. After the reflux period, the reaction mixture was poured into a 120 ml. salt solution. The benzene layer separated as the top layer. The benzene layer was distilled under vacuum at 40°C. and the residue was fractionated that yielded a liquid with a refractive index of 1.4420. The literature reports a refractive index of 1.4424.

D. The Preparation of the Diethyl Ester of 4-Methyl-3-Methylol-1,4-Cyclohexadien-1,2-Dicarboxylic Acid.(XII) (9) (Diels Alder reaction).

3-methyl-2,4-pentadien-1-ol, 4.9 grams, and 8.5 grams of diethyl acetylene dicarboxylate were poured into a round-bottom flask and the mixture refluxed for twenty four hours. Acetone was used as a solvent for the reaction. After the twenty four hour period, the solvent was distilled from the flask by vacuum and the residue fractionated. The fractional distillate was collected and the refractive index was found to be 1.4998. No test were run on this sample because the next reaction was carried out immediately.

E. The preparation of the Diethyl Ester of 4-Methyl-3-Methylol-1,2-Phthalic Acid (XIV) (12).

Two grams of the diethyl ester of 4-methyl-3-methylol-1,4-cyclohexadien-1,2-dicarboxylic acid and 1.85 grams of chloranil (XIII) were poured into a 100 ml. flask with 20 mls. of xylene. The flask was equipped with a water condenser, drying tube, and a stirrer. The mixture was stirred and refluxed for 5 hours. A heating mantle and a powerstat provided the heat. After the five hours, the reaction mixture was cooled to 0°C., and filtered on a Buchner funnel. The filtrate was diluted with an equal volume of petroleum ether. The solution was placed in a separatory funnel and five washes of five per cent sodium bicarbonate solution were used to make the reaction mixture basic. This was placed over sodium sulfate for a period of twenty-four hours. The solvents were distilled by vacuum from the flask on the next day. The syrup obtained was concentrated to constant weight.

An infra red spectrum was run on the sample. The spectrum of the solid compound showed two carbonyl bands at 5.70 and 5.79 microns and phenyl bands at 6.15 and 6.23 microns. The possible assigment for the observed absorption spectrum could be the diethyl ester groups. The weight of the syrup was 2.0 grams.

F. The Preparation of Prehnitic Acid (XV) (13).

The syrup from reaction (E) was added to 50 mls. of a saturated potassium permanganate water solution, and 5 mls. of a ten per cent potassium hydroxide were added to the solution in a 250 ml. flask equipped with a stirrer and a reflux condenser. The reaction mixture was refluxed over night, and the next morning the mixture was cooled.Five mls. of a concentrated solution of sulfuric acid was then added to the stirred mixture. It was then treated with sodium bisulfite until all the manganese dioxide had disappeared. The solution was filtered through a sintered funnel under vacuum. The filtrate was poured into a separatory funnel and extracted with 5x100 mls. of ethyl ether. The extractions were carried out very slowly due to the solubility of the product in the ether layer. This extracted solution was heated and treated with nuchar for 10 minutes. The charcoal was filtered off. The amber solution was crystallized slowly over a period of two days at zero degree temperature. The crystals were filtered on a cold funnel and dried in a vacuum desiccator. The melting point was 170-171°C.. This did not correspond to the Prehnitic acid melting point (237-238°C.).

An infra red spectrum was run on the sample. The research department of Merck and Co. ran a combustion analysis on the sample and found the carbon content to be 50.65% and the hydrogen content to be 1.92%. The compound that is very close to these findings consisted of a ring compound with an anhydride group and two carboxyl groups (XVI). The theoretical content of this compound is: carbon, 50.8% and hydrogen, 1.69%. This agrees with our analytical data, and the possibility of getting this instead of Prehnitic acid was very possible. This may, therefore, be accepted as the secound proof of the structure, since, as indicated in the equations, Prehnitic acid might very well have been dehydrated to the anhydride (XVI).

Conclusion

The proof of the cis form of 3-methyl-2-penten-4-yne-1-ol has been carried out experimentally. The next step would have to be a conversion of the cis form to the trans form. This procedure has not been carried out successfully because many indications lead one to believe that the arbitrary isomer was just another isomer and it was not stereo in its nature.

There is another possibility that the yield conversion may be such that the efforts of conversion will not practicable. All these questions can only be answered in time when all runs of conversion are tabulated and a conclusion is drawn. Another problem may be in the fractionation of the converted isomer. This step also can cut the yield considerably because a certain quality material can only be used in the process of Vitamin A.

The proof has been presented. If a means of producing this converted isomer, economically, can be found, monetary gains will be achieved. The by product that has been discarded up to now, may well be used in future productions.

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