

**THE PREPARATION, CHARACTERIZATION  
AND  
DEHYDRATION  
OF  
2,2-DIMETHYL-1-PENTANOL**

**A Thesis  
Presented to  
the Faculty of the Department of Chemistry  
College of Arts and Sciences  
University of Houston**

**In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science**

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**by  
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**159206**

## ABSTRACT

It was the purpose of this investigation to synthesize 2,2-di-methyl-1-pentanol, an alcohol which had not been previously prepared or characterized, to determine its physical constants, characterize it by the preparation of several common derivatives, and to determine quantitatively and qualitatively the rearranged products obtained upon dehydration.

The synthesis was accomplished by the following series of reactions: n-propyl magnesium bromide was prepared and treated with acetone, giving, on hydrolysis, 2-methyl-2-pentanol. This compound, after purification, was converted to 2-chloro-2-methyl pentane, by the action of cold concentrated hydrochloric acid. The Grignard reagent of 2-chloro-2-methyl pentane was prepared, and treated with carbon dioxide, giving, on hydrolysis, 2,2-di-methyl pentanoic acid, which was identified by boiling point, and preparation of the amide. The acid was converted to 2,2-dimethyl-1-pentanol by reduction with lithium aluminum hydride. The alcohol thus obtained was shown to have better than 99 mole % purity by gas-liquid partition chromatography.

Eight derivatives were prepared.

The rearrangement and dehydration of 2,2-dimethyl-1-pentanol was accomplished by heating the alcohol with 8% by weight of concentrated sulfuric acid at its boiling point. The determination of the unsaturated rearranged products was accomplished by ozonization of the double bond, and reductive cleavage of the ozonides with lithium aluminum hydride to give a mixture of alcohols. These alcohols were identified and determined quantitatively by gas-liquid partition chromatography.

All five of the theoretically possible rearranged products were identified.

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**PART I**  
**INTRODUCTION**  
**AND**  
**STATEMENT OF THE PROBLEM**

It was the purpose of this investigation to synthesize and characterize by the preparation of several common derivatives, 2,2-dimethyl-1-pentanol, an alcohol which had not previously been prepared. Its synthesis in this laboratory, by the treatment of the Grignard reagent of 2-chloro-2-methyl pentane with formaldehyde, had previously given an impure product, hence, a different method of synthesis appeared desirable. It seemed that carbonation of the Grignard reagent, to give 2,2-dimethyl-1-pentanoic acid, followed by reduction of the acid to the alcohol, would give a product of greater purity.

Examination of the structure of 2,2-dimethyl-1-pentanol reveals that there are no hydrogens on the carbon adjacent to the  $\text{CH}_2\text{OH}$  group, hence, if this alcohol is dehydrated, it must first rearrange. Considerable work on the dehydration and rearrangement of alcohols has been done by Whitmore (1), who proposed the following mechanisms for such dehydrations. The first step in the process is the loss of the OH with its electrons, leaving a primary carbonium ion. The second step is the migration of a group on an adjacent carbon to the position of the primary carbonium ion, forming a tertiary carbonium ion on the adjacent carbon.

This tertiary carbonium ion may now lose a proton from a carbon adjacent to the carbonium ion to form an olefin. This type of proton elimination is said to follow an E1 mechanism, that is, a unimolecular elimination.

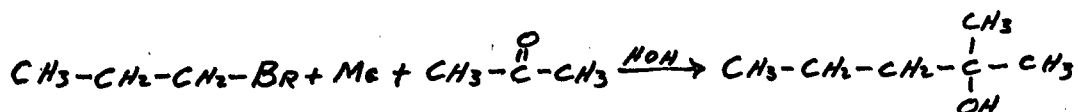
Whitmore (2) studied the dehydration of 2,2-dimethyl-1-hexanol, and found four of the five possible rearranged olefins to be formed. The technique of dehydration used by him appeared to be adequate, but the method of analysis of the unsaturated products left much to be desired. Briefly, after dehydration the unsaturated components were isolated by fractional distillation, this was followed by ozonization, and acid cleavage of the ozonides to give a mixture of aldehydes and ketones. These were separated by fractional distillation and identified by derivatives. A better approach, not available to Whitmore, appeared to be the use of gas-liquid chromatography to identify the unsaturated products. Since neither authentic samples of each of the anticipated olefins, nor chromatographic columns which would resolve such a mixture were available, it was decided to ozonize the olefins, and cleave the ozonides



with lithium aluminum hydride to give a mixture of alcohols (3). Authentic samples of all the possible alcohols were commercially available, and all could be easily separated and identified by gas-liquid chromatography. Further, since only a few milligrams of sample are necessary for analysis by gas-liquid partition, the entire procedure should require only a few grams of the original alcohol. This approach avoids the losses and uncertainties which would accompany fractional distillation of a mixture of aldehydes and ketones, and provided that the products were chromatographed on different columns at different temperatures, would identify the products, as well as giving the mole % composition of the mixture (4).

**PART II**  
**EXPERIMENTAL**

# PREPARATION OF 2-METHYL-2-PENTANOL

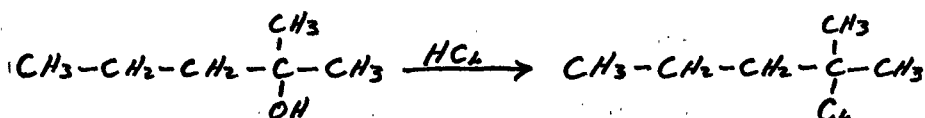


In a 3 liter 3 neck flask fitted with a reflux condenser, a separatory funnel, and a mercury seal stirrer, was placed 75 grams (3.1 moles) of magnesium turnings. Sufficient dry ether was added to cover the magnesium turnings and 1 ml. of 1-bromopropane was added, without stirring. The flask was warmed to initiate the reaction.

After the reaction had commenced 1 liter of dry ether was added and the solution was stirred vigorously. Three hundred sixty nine grams ( 3 moles) of 1-bromopropane in 500 ml. of dry ether was added drop-wise during a period of 3 hours. The mixture was refluxed 24 hours to assure completion of the reaction. The reaction mixture was cooled to  $-10^{\circ}$ , and 200 grams (3.5 moles) of dry acetone in 300 ml. of dry ether was added drop-wise with stirring over a period of 2 hours. The reaction mixture was allowed to warm to room temperature and finally refluxed for 30 minutes. The mixture was then cooled to  $0^{\circ}$  and 450 ml. of saturated ammonium chloride solution was added drop-wise with vigorous stirring.

Upon completion of the addition the ether layer was decanted and the residue washed twice with 200 ml. portions of ether. The combined ether extracts were filtered and evaporated to 500 ml. and transferred to a 1 liter round-bottom flask and distilled through a 60 plate column. The material boiling from  $119^{\circ}$  -  $122^{\circ}$  amounted to 240 grams (2.35 moles) or 78% of theoretical based on 1-bromopropane.

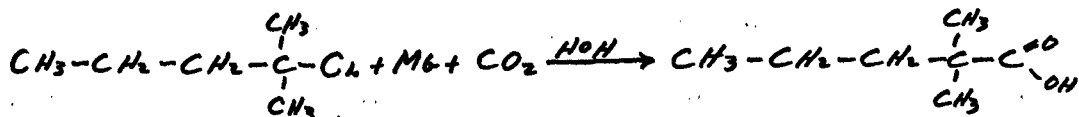
# PREPARATION OF 2-CHLORO-2-METHYL PENTANE



Eighty grams (.79 moles) of 2-methyl-2-pentanol was placed in a 500 ml. separatory funnel. One hundred ninety four ml. (2.35 moles) of concentrated hydrochloric acid was added and the mixture agitated occasionally over a period of 30 minutes. Sufficient technical grade calcium chloride was added to nearly saturate the aqueous layer, which was then discarded. The organic layer was washed with 5% sodium bicarbonate solution and with saturated sodium chloride solution.

This procedure was repeated twice, and the three halide fractions were combined and dried over anhydrous calcium chloride for 24 hours. The halide was filtered into a 250 ml. round-bottom flask, and treated with 50 grams of phosphorous pentoxide and distilled through a short Vigreux column. The fraction boiling between 110-112° was collected. It amounted to 183 grams (1.53 moles) or 64.8% of theoretical.

# PREPARATION OF 2,2-DIMETHYL PENTANOIC ACID



Forty grams (1.65 moles) of magnesium turnings was placed in a 2 liter 3 neck flask fitted with a reflux condenser, separatory funnel and mercury-seal stirrer. Sufficient dry ether was added to cover the magnesium, followed by 1 ml. of dry ethyl bromide. The flask was warmed without stirring, to initiate the reaction. Five hundred ml. of dry ether was added and vigorous stirring was started.

One hundred eighty grams (1.5 moles) of 2-chloro-2-methyl pentane in 500 ml. of dry ether was added over a period of 5 hours. The mixture was refluxed for an additional 16 hours and the flask cooled to  $-10^\circ$  with ice and salt.

An excess of carbon dioxide, obtained from dry ice and dried by passage through a calcium chloride drying tower, was passed into the flask with vigorous stirring. The reaction mixture was allowed to stand 16 hours at which time it was heated to reflux for 30 minutes. After cooling with ice, the reaction mixture was hydrolysed with an excess of 10% sulfuric acid.

The products were washed into a 3 liter separatory funnel and the ether layer removed. The aqueous layer was extracted twice with ether and finally discarded. The combined ether extracts were washed with saturated sodium chloride solution and extracted with 1 liter of 3 molar potassium hydroxide divided into 4 portions. The combined alkaline extracts were filtered, acidified with excess sulfuric acid and extracted 3 times with 200 ml. portions of ether. The alkaline extraction procedure, acidification, and extraction with ether was repeated in order to isolate positively only acidic material.

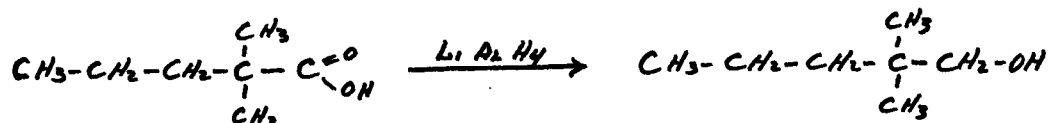
A greater portion of the ether was removed by evaporation and the residue dried overnight with anhydrous calcium sulfate. The dried material was filtered into a 250 ml. round-bottom flask and distilled through a 60 plate column. Material boiling between 202-204° was collected, it amounted to 52 grams (.4 moles) or 26.7% of the theoretical.

The amide was prepared, and gave the following:

Melting Point: 98.5-99° (corr.)

The literature gives melting point: 100°

# PREPARATION OF 2,2-DIMETHYL-1-PENTANOL



Seventeen grams (.45 moles) of lithium aluminum hydride was weighed into a 2 liter round-bottom flask and covered with 500 ml. of dry ether. A magnetic stirring bar was introduced and a Claisen head, fitted with a reflux condenser and separatory funnel, was attached to the flask. The mixture was stirred until a smooth slurry was formed.

Fifty two grams (.4 moles) of 2,2-dimethyl pentanoic acid dissolved in 500 ml. of dry ether was placed in the separatory funnel. The ethereal solution of acid was added drop-wise with stirring to the slurry of lithium aluminum hydride. The rate of addition was regulated to maintain continuous reflux of ether. Upon completion of the addition the reaction mixture was refluxed for 3 hours, and the excess lithium aluminum hydride was destroyed by the addition of water saturated ether.

The flask was cooled, and 500 ml. of 10% sulfuric acid was added and the mixture transferred to a 3 liter separatory funnel. After shaking, the aqueous layer was drawn off and discarded and the ether layer was filtered.



The ether layer was then washed twice with 5% sodium hydroxide, twice with saturated sodium chloride solution and filtered through anhydrous sodium sulfate. A majority of the ether was removed by evaporation, and the residue dried over anhydrous calcium sulfate. The ethereal solution was filtered into a 100 ml. round-bottom flask and fractionated through a 60 plate column with a reflux ratio of 10:1.

After the ether had distilled, the boiling point rose to  $153^{\circ}$  with the distillation of only 1-2 ml. of liquid. Two ml. boiling from  $153.5$  to  $154^{\circ}$  was collected. The remainder of the material distilled over at  $154^{\circ}$  with no observable boiling range.

This material amounted to 28 grams (.24 moles), or 60% of theoretical.

#### Analysis for Carbon:

Calculated:	72.35%
Found:	72.44%

#### Analysis for Hydrogen:

Calculated:	13.88%
Found:	14.14%

## PHYSICAL CONSTANTS OF 2,2-DIMETHYL-1-PENTANOL

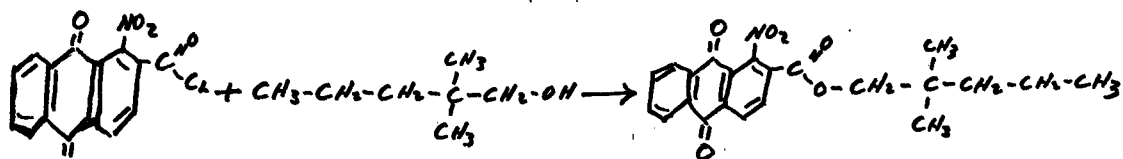
Boiling Point: 154° (760 mm.)

Refractive Index:  $n_d^{24}$  1.4223

Specific Gravity:  $D_{20}^{20}$  .8244

$D_4^{20}$  .8229

PREPARATION OF THE 1-NITRO-ANTHROQUINONE-  
2-CARBOXYLATE OF 2,2-DIMETHYL-1-PENTANOL



Seven hundred mg. (2 mm. plus 10% excess) of 1-nitroanthroquinone-2-carbonyl chloride was placed in a 15 ml. centrifuge tube. Three tenths ml. (2 mm.) of 2,2-dimethyl-1-pentanol was added followed by 10 ml. of dry pyridine (freshly distilled from sodium hydroxide pellets). The tube was heated on the steam bath for 4 hours and poured into 100 ml. of ether. The ether layer was extracted 4 times with 25 ml. portions of 10% hydrochloric acid, 3 times with 10% sodium carbonate, and twice with saturated sodium chloride solution. The ether layer was filtered through anhydrous sodium sulfate and evaporated to dryness. A dark residual oil, smelling of the original alcohol remained. This was cooled to  $-20^{\circ}$  and the walls of the flask scratched. No crystals were formed on standing for 3 days.

The oil was dissolved in hot petroleum ether and cooled to  $-20^{\circ}$ . Only amorphous material was obtained.

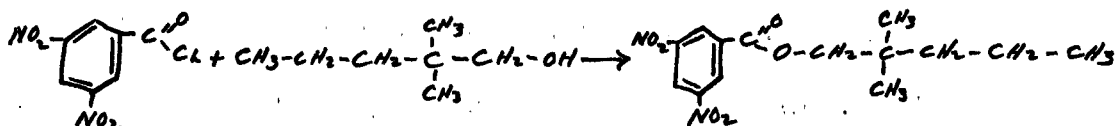
The above procedure was repeated, except that the acid chloride and alcohol were dissolved in 40 ml. of dry ether

and 5 ml. of pyridine. After standing at room temperature for 48 hours the products were worked up in the above manner.

Again, a residual oil was obtained. This oil was put under high vacuum (10 microns) for 24 hours. At the end of this time only a small quantity of amorphous brown material remained, which could not be recrystallized.

Three variations of the above procedures were attempted, varying both time and temperature of reaction, but no crystalline product was isolated at any time.

**PREPARATION OF 3-5-DINITRO BENZOATE OF  
2,2-DIMETHYL-1-PENTANOL**



Five hundred mg. ( 2 mm plus 10% excess) of 3-5-dinitro benzoyl chloride and 0.3 ml. ( 2 mm.) of 2,2-dimethyl-1-pentanol were placed in a centrifuge tube and 5 ml. of dry pyridine added.

The tube was heated on the steam bath 16 hours and poured into 50 ml. of ether. The ether layer was washed 4 times with 10% hydrochloric acid, 3 times with 5% sodium hydroxide, twice with saturated sodium chloride solution, filtered through anhydrous sodium sulfate and evaporated to dryness.

The residual oil thus obtained was dissolved in 3 ml. of ethanol, heated on the steam bath, and water added dropwise until the solution was cloudy. The solution was cleared with a few drops of ethanol and allowed to cool.

The product crystallized in the form of light tan needles. After 4 recrystallizations from ethanol and water, white crystals were obtained, and after drying in vacuo over phosphorous pentoxide the crystals gave the following:

Melting Point: 49-50° (corr.)

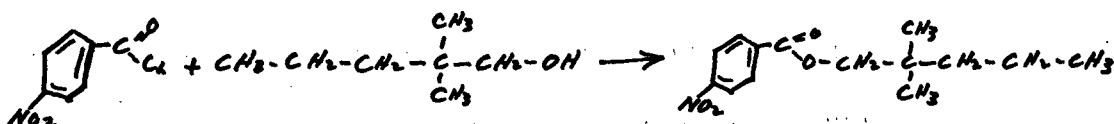
**Analysis for Carbon:**

Calculated: 54.19%  
Found: 53.94%

**Analysis for Hydrogen:**

Calculated: 5.85%  
Found: 6.48%

**PREPARATION OF PARA-NITRO BENZOATE  
OF 2,2-DIMETHYL-1-PENTANOL**



Four hundred ten mg. ( 2 mm. plus 10% excess) of para-nitro benzoyl chloride and 0.3 ml. ( 2 mm.) of 2, 2-dimethyl-1-pentanol were placed in a centrifuge tube and 5 ml. of dry pyridine added.

The tube was heated on a steam bath for 4 hours and poured into 50 ml. of ether. The ether layer was washed 4 times with 10% hydrochloric acid, 3 times with 5% sodium hydroxide, twice with saturated sodium chloride solution, filtered through anhydrous sodium sulfate and evaporated to dryness.

The residual oil thus obtained was dissolved in 3 ml. of ethanol, heated on the steam bath, and water added dropwise until the solution was cloudy. The solution was cleared with a few drops of ethanol and allowed to cool.

The product crystallized in the form of white needles. After four recrystallizations from ethanol and water the crystals were dried in vacuo over phosphorous pentoxide and gave the following:

Melting Point: 65-65.5° (corr.)

Analysis for Carbon:

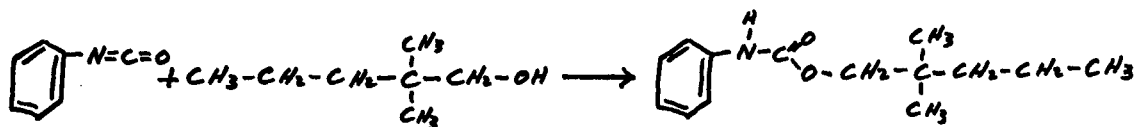
Calculated:	63.38%
Found:	62.97%

Analysis for Hydrogen:

Calculated:	7.22%
Found:	7.36%



PREPARATION OF PHENYL URETHANE OF  
2,2-DIMETHYL-1-PENTANOL



Two hundred sixty-five mg. ( 2 mm. plus 10% excess) of phenyl isocyanate and 0.3 ml. ( 2 mm.) of 2,2-dimethyl-1-pentanol were placed in a 15 ml. centrifuge tube and heated on the steam bath for 4 hours. The reaction mixture was extracted with 5 ml. of hot petroleum ether, filtered, and cooled. Only a residual oil which would not crystallize was formed.

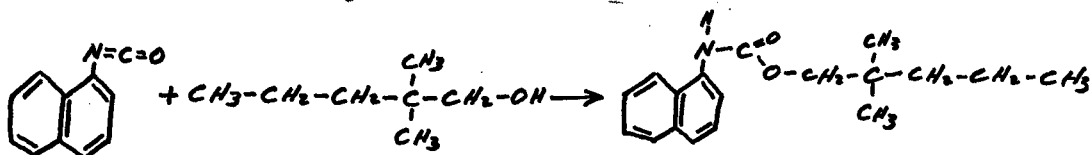
The above procedure was repeated using 5 ml. of petroleum ether as a solvent for the reaction. Again, no crystalline material was obtained.

The procedure was repeated a third time, using 5 ml. of petroleum ether as a solvent and 0.1 grams of fused sodium acetate as a catalyst. Again, only a residual oil was obtained.

The residual oils from the above procedures were combined and chromatographed on 15 grams of silicic acid, previously activated by acetone-ether pre-wash. The fraction elutable with petroleum ether was dissolved in 5 ml. of

isopentane and allowed to stand at  $-20^{\circ}$ . A crystalline product was obtained which melted before it could be filtered by suction.

PREPARATION OF ALPHA-NAPTHYL URETHANE OF  
2,2-DIMETHYL-1-PENTANOL



Three hundred seventy-six mg. ( 2 mm. plus 10% excess) of alpha-naphthyl isocyanate and 0.3 ml. ( 2 mm.) of 2,2-dimethyl-1-pentanol were placed in a 15 ml. centrifuge tube. After heating on the steam bath for 4 hours the reaction mixture was extracted with 5 ml. of hot petroleum ether. Upon evaporation of the petroleum ether, only a residual oil was obtained.

The above procedure was repeated using 5 ml. of dry petroleum ether as a solvent. Again, only a residual oil was obtained.

The procedure was repeated a third time using 5 ml. of petroleum ether as a solvent and 0.1 gram of fused sodium acetate as a catalyst. Again, only a residual oil was obtained.

This residual oil was dissolved in isopentane and allowed to stand at  $-20^{\circ}$ . After 3 days, a few large crystals were obtained which were removed by filtration. The crystals presented a brownish appearance which proved

to be an oily coating. When the crystals were crushed, the interior appeared much lighter in color. These crystals, after drying, gave the following:

Melting Point:  $45.5-46.5^{\circ}$  (corr.)

A sample of these crystals was set aside for seed and the residual oils from the previous reactions were combined and chromatographed on 15 grams of silicic acid, previously activated by acetone-ether pre-wash. The fraction elutable with petroleum ether was colorless, giving, upon evaporation, a clear residual oil.

This oil crystallized readily from isopentane at  $-20^{\circ}$  when seeded, giving clear white crystals.

These crystals were filtered off with suction and after drying overnight in vacuo over phosphorous pentoxide, gave the following:

Melting Point:  $47.-47.5^{\circ}$  (corr.)

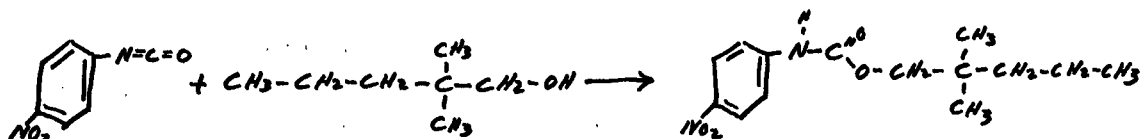
Analysis for Carbon:

Calculated:	74.60%
Found:	74.67%

Analysis for Hydrogen:

Calculated:	8.84%
Found:	8.63%

**PREPARATION OF PARA-NITRO PHENYL URETHANE  
OF 2,2-DIMETHYL-1-PENTANOL**



Three hundred sixty-five mg. ( 2 mm. plus 10% excess) of para-nitro phenyl isocyanate and 0.3 ml. ( 2 mm.) of 2,2-dimethyl-1-pentanol were placed in a 15 ml. centrifuge tube and heated on the steam bath for 4 hours. The reaction mixture was extracted with 5 ml. of hot petroleum ether, after filtering and evaporation of the solvent, gave a heavy yellow oil which could not be crystallized.

The above procedure was repeated using 5 ml. of petroleum ether as a solvent for the reaction. The insoluble material was removed by filtration and the petroleum ether solution allowed to stand at  $-20^{\circ}$ . After 2 days, crystalline material, faintly yellow in color, was obtained.

After four recrystallizations from ethanol and water and drying in vacuo over phosphorous pentoxide, white crystalline material was obtained, which gave the following:

Melting Point:  $53^{\circ}$  (corr., no range observable).

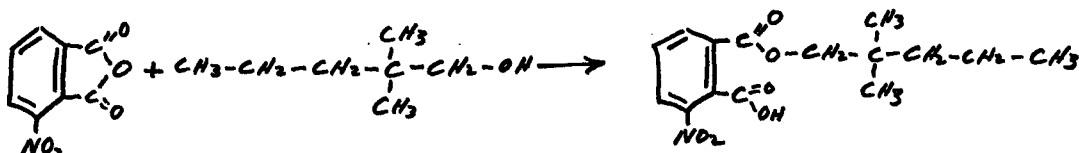
Analysis for Carbon:

Calculated:	59.98%
Found:	59.64%

**Analysis for Hydrogen:**

**Calculated: 7.58%**  
**Found: 7.19%**

**PREPARATION OF HYDROGEN-3-NITRO PHTHALATE  
OF 2,2-DIMETHYL-1-PENTANOL**



Four hundred thirty mg. ( 2 mm. plus 10% excess) of 3-nitro phthalic anhydride and 0.3 ml. ( 2 mm.) of 2,2-dimethyl-1-pentanol were placed in a 15 ml. centrifuge tube and heated on the steam bath for 4 hours.

The mixture was poured into 25 ml. of boiling water. After filtering and cooling no crystalline product was obtained.

The water was extracted three times with ether and the ether layer evaporated to dryness. A residual oil was obtained, which was chromatographed on 15 grams of silicic acid activated by acetone-ether pre-wash. The benzene elutable material was evaporated to dryness, giving a clear oil which could not be crystallized.

The above procedure was repeated using 2 ml. of anhydrous pyridine as a solvent for the reaction. After the heating period, the reaction mixture was poured into ether and the ether layer was extracted 3 times with 10% hydrochloric acid, washed with saturated sodium chloride

solution, filtered through anhydrous sodium sulfate, and evaporated to dryness.

A residual oil was obtained which crystallized from 1 ml. of pentane.

The crystalline material was recrystallized 4 times by dissolving in 2 ml. of ethanol at room temperature and adding water to turbidity. Upon cooling to  $-20^{\circ}$ , and scratching the sides of the vessel, white crystals appeared. After filtration the crystals were dried in vacuo over phosphorous pentoxide and gave the following:

Melting Point:  $128-132^{\circ}$

In view of the melting point range, it was decided that additional purification was necessary.

Half of the product was chromatographed on 15 grams of silicic acid, previously activated by acetone-ether pre-wash.

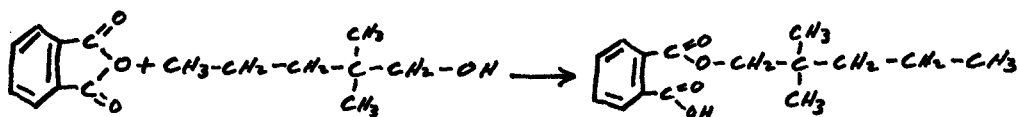
The benzene elutable fraction crystallized when seeded. It was twice recrystallized from ethanol and water and after drying in vacuo over phosphorous pentoxide it gave the following:

Melting Point:  $147-148^{\circ}$  (corr.)



**Analysis for Carbon:****Calculated: 58.24%****Found: 58.47%****Analysis for Hydrogen:****Calculated: 6.19%****Found: 6.52%**

**PREPARATION OF HYDROGEN PHTHALATE  
OF 2,2-DIMETHYL-1-PENTANOL**



Three hundred thirty mg. ( 2 mm. plus 10% excess) of phthalic anhydride and 0.3 ml. ( 2 mm.) of 2,2-dimethyl-1-pentanol were placed in a 15 ml. centrifuge tube and heated on the steam bath for 4 hours.

After cooling, the product was extracted with ether, which upon evaporation, gave an oil which could not be crystallized.

The above procedure was repeated except that 2 ml. of anhydrous pyridine were used as a solvent for the reaction.

After heating on the steam bath the product was washed into 50 ml. of ether. The ether layer was extracted 3 times with 10% hydrochloric acid, washed with saturated sodium chloride solution, and filtered through anhydrous sodium sulfate.

Upon evaporation of the ether a residual oil was obtained which crystallized when 1 ml. of pentane was added and the sides of the flask scratched.

The crystalline material thus obtained was recrystallized 4 times from ethanol and water. After drying in vacuo over phosphorous pentoxide the crystals gave the following:

Melting Point: 54.5-55° (corr.)

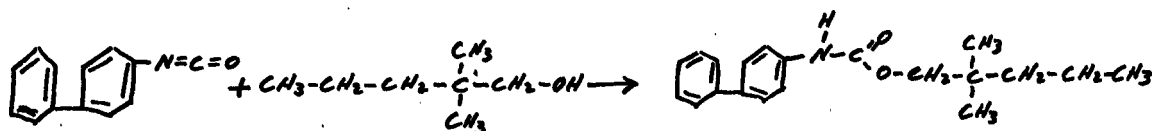
**Analysis for Carbon:**

Calculated:	68.16%
Found:	68.37%

**Analysis for Hydrogen:**

Calculated:	7.63%
Found:	7.38%

PREPARATION OF PARA-DIPHENYL URETHANE OF  
2,2-DIMETHYL-1-PENTANOL



Four hundred thirty mg. ( 2 mm. plus 10% excess) of para-diphenyl isocyanate were dissolved in 5 ml. of hot petroleum ether. Three tenths ml. ( 2 mm.) of 2,2-dimethyl-1-pentanol was added and the mixture heated on the steam bath for 4 hours. The hot solution was filtered and allowed to cool, giving a slightly discolored crystalline material.

After 4 recrystallizations from petroleum ether, and drying in vacuo over phosphorous pentoxide white crystals were obtained which gave the following:

Melting Point: 88.5° ( corr. no range observable).

Analysis for Carbon:

Calculated:	77.13%
Found:	77.21%

Analysis for Hydrogen:

Calculated:	8.09%
Found:	8.11%

PREPARATION OF ALPHA-NAPHTHYLAMINE COMPLEX OF  
3,5-DINITROBENZOATE OF 2,2-DIMETHYL-1-PENTANOL

Ten mg. of the 3,5-dinitrobenzoate ester of 2,2-dimethyl-1-pentanol was dissolved in 0.1 ml. of ether. Ten mg. of alphanaphthylamine in 0.1 ml. of 80% ethanol was added.

There was an immediate color change and on standing, orange crystals were obtained.

The crystals were filtered by centrifugation and recrystallized 3 times from 80% ethanol. After drying in vacuo over phosphorous pentoxide the crystals gave the following:

Melting Point: 72-73° (corr.)

DEHYDRATION OF 2,2-DIMETHYL-1-PENTANOL  
(First Trial)

Five ml. ( 4.1 grams, 36.0 mm.) of 2,2-dimethyl-1-pentanol and 0.328 grams of concentrated sulfuric acid were placed in an addition funnel. The addition funnel was attached to a pear-shaped flask with a Claisen head, and immersed in an oil bath at 177-180°.

The mixture of alcohol and acid was added drop-wise to the hot flask. The products distilled over almost immediately.

The distillate was washed with 5% sodium carbonate and saturated sodium chloride solution and dried over anhydrous potassium carbonate. It amounted to 3.5 ml. and was assayed by gas-liquid chromatography, and found to consist of 60% olefin, and 40% 2,2-dimethyl-1-pentanol.

DEHYDRATION OF 2,2-DIMETHYL-1-PENTANOL  
(Second Trial)

One hundred eighty-nine mg. (16.0 mm.) of 2,2-dimethyl-1-pentanol and 180 mg. of concentrated sulfuric acid were placed in a 10 ml. flask, capped with an indented side arm Claisen head, and heated by boiling xylene vapor at 137° for 24 hours.

At the end of this period, no dehydration had occurred, as evidenced by lack of any distillate.

The mixture was then heated for an additional 24 hours at 155° by boiling bromo benzene vapors. At the end of this period only a residual tar remained in the flask.

The distillate was washed with sodium carbonate solution and saturated sodium chloride solution. It was then treated with phosphorous pentoxide to remove any residual alcohol, and lyophilized into a test tube with a ground glass top. It amounted to 1.5 ml., and when assayed by gas-liquid chromatography, showed only a mixture of olefins.

OZONIZATION OF HEPTYLENES AND THE REDUCTIVE  
CLEAVAGE OF THE RESULTING OZONIDES

The mixture of heptylenes obtained in the preceding dehydration was dissolved in 50 ml. of methylene chloride and placed in a small gas-washing cylinder. The solution was cooled to  $-45^{\circ}$  and treated with an excess of ozone. The solution was then flushed for 1 hour with dry nitrogen to remove all unreacted ozone and dissolved oxygen. The solution of the resulting ozonides in methylene chloride was then washed into a 100 ml. round-bottom flask with 50 ml. of dry ether. The flask was fitted with a Claisen head having a reflux condenser and separatory funnel attached, cooled to  $-45^{\circ}$  and stirred with a magnetic stirring bar.

A solution of 0.33 grams ( 7.9 mm. plus 10% excess) of lithium aluminum hydride in 10 ml. of dry ether was placed in the separatory funnel and added drop-wise to the solution of the ozonides.

The mixture was allowed to warm to room temperature and finally heated to reflux for 15 minutes. The flask was then cooled to  $-15^{\circ}$  and 12 ml. of 20% sulfuric acid was added drop-wise. The flask was allowed to warm to room



temperature, an excess of anhydrous potassium carbonate was added and the mixture was allowed to stir overnight. The solution was filtered into a 100 ml. round-bottom flask and attached to a 60 plate fractionating column.

The solvents were removed by distillation, with a reflux ratio of 5:1, until the temperature of the still pot rose to 65°. Five ml. of carbon disulfide was added and 4 ml. distilled off. Two more 2 ml. portions of carbon disulfide were added and distilled off.

At this point the distillation was terminated and the column allowed to drain back into the still pot. The still pot was then connected to a lyophilization apparatus and the volatile products lyophilized into a small tube.

## GAS-LIQUID PARTITION CHROMATOGRAPHY OF THE ALCOHOL MIXTURE

The mixture of alcohols in carbon disulfide from the preceding ozonization and reductive cleavage were chromatographed as follows: Two columns of dinonyl phthalate on celite were connected in series, and the column temperature adjusted to 90°. The columns were flushed with helium for a 45 minute period, at the end of which time the base line had stabilized, and no temperature changes were noted. A trial run was made, using 10 microliters of solution; to determine the sensitivity of range, and the peak heights. Finally, 20 microliters of solution was injected, and a recording was made of the components. Ten microliters of a synthetic mixture of the anticipated alcohols was injected, and a recording made of its components. Two microliter samples of each of the authentic alcohols were then chromatographed in order to positively identify each peak. This procedure was repeated using a column of silicone on celite in series with a column of dinonyl phthalate on celite at 100°.

It was found in each case that the emergence times of

of the known alcohols in the synthetic mixture were precisely superimposable upon the emergence times of the peaks in the unknown mixture.

The synthetic mixture, prepared from 1.0 ml. of each alcohol, gave the following results for the high boiling alcohols:

<u>ALCOHOL</u>	<u>CALCULATED</u>	<u>FOUND</u>
Butanol 2	27.9%	26.5%
Butanol 1	28.0%	26.5%
Pentanol 2	23.6%	23.8%
Hexanol 3	20.5%	23.2%

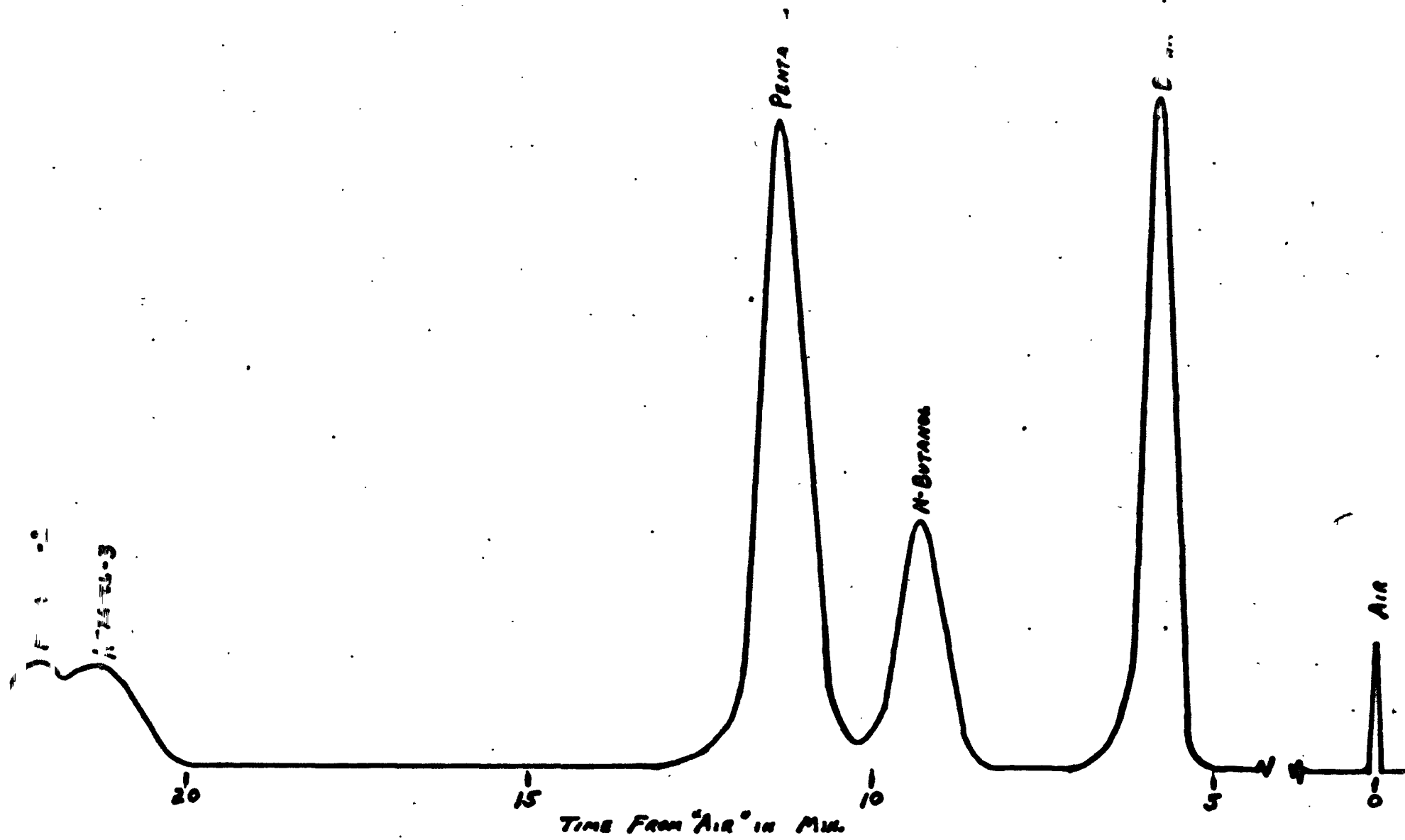
The two unknown mixtures from the two dehydrations gave the following results:

<u>ALCOHOL</u>	<u>#1</u>	<u>#2</u>	<u>AVERAGE</u>
Butanol 2	10.8%	7.9%	9.4%
Butanol 1	21.2%	29.6%	25.4%
Pentanol 2	54.1%	59.4%	56.8%
Hexanol 3	3.1%	0.9%	2.0%
Hexanol 2	10.8%	2.3%	6.5%

An Authentic sample of Hexanol 2 was not available at the time the synthetic mixture was chromatographed, and its

time of emergence was determined at a later date.

A blank run of ozonization, reduction with lithium aluminum hydride, distillation and lyophilization was made upon the solvents in order to be certain that no unexpected products were formed. Only, ether, carbon disulfide, and methylene chloride peaks were found when the residue was chromatographed.

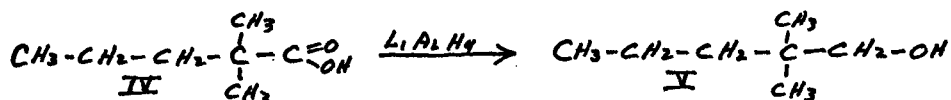


**PART III**

**RESULTS**

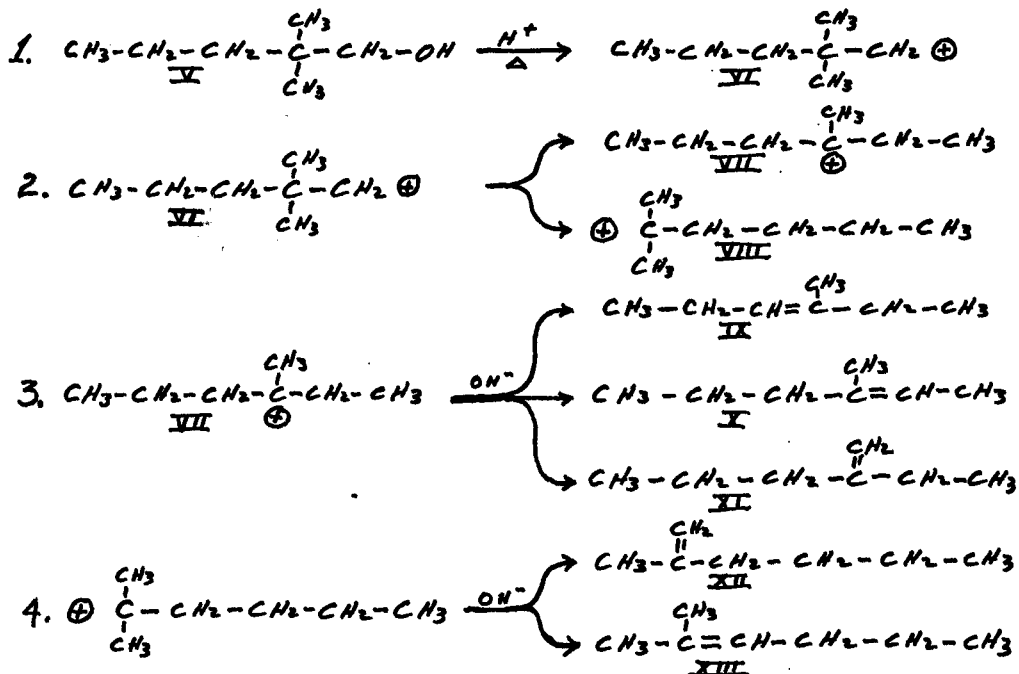


yields, and lack of side reactions (5).



A sample of (V) obtained by this sequence, when assayed by gas-liquid partition chromatography, showed better than 99 mole % purity, the contaminant being an unidentified low boiling impurity.

The dehydration of (V) presents an interesting problem, since dehydration cannot occur without rearrangement; a primary carbonium ion which rearranges to a tertiary carbonium ion, is believed to be the intermediate. Five possible unsaturated products are theoretically possible, by the following mechanism.





The dehydration was accomplished by heating (V) with 8% by weight of concentrated sulfuric acid. Two sets of conditions were used. In the first procedure, the mixture of (V) and sulfuric acid was added slowly drop by drop to a flask immersed in an oil bath at  $177^{\circ}$ . The products distilled off almost immediately. This procedure is identical to that used by Whitmore (2).

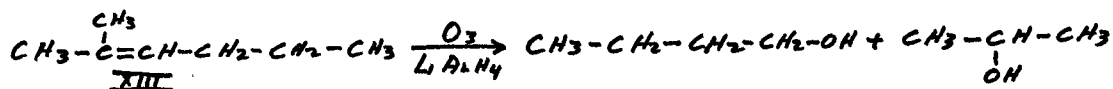
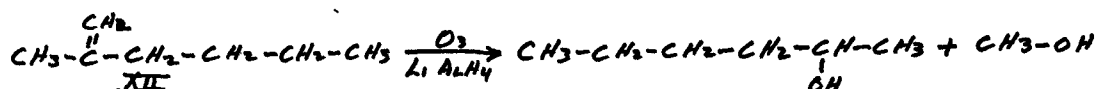
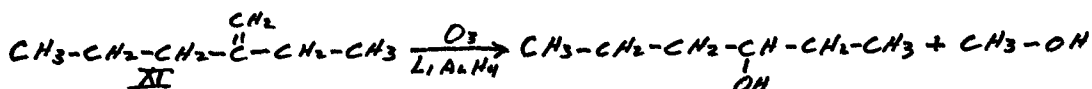
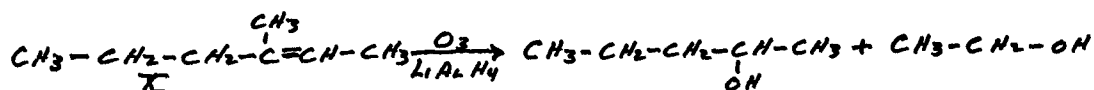
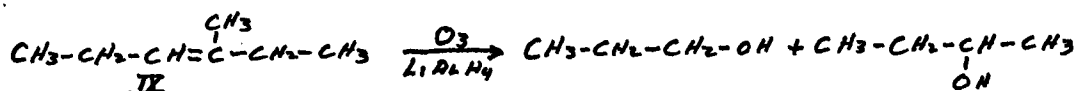
In the second procedure, the mixture of (V) and sulfuric acid were heated at  $155^{\circ}$  for twenty-four hours, the products distilling off as they were formed.

The results from the two methods were nearly identical, in regard to yield, and unsaturated components. However, the products from the first procedure were contaminated by approximately 40% of (V), while in the second case the amount of (V) was reduced to less than 10%.

Samples of the unsaturated material were subjected to gas-liquid partition chromatography (\*) on columns of dinonyl phthalate on celite and silicone on celite, but a satisfactory separation of the components was impossible with the liquid phases used. The presence of five components was noted however, two major components, two minor components, and a fifth component which appeared intermediate in quantity, and emerged from the column immediately preceding the two major components.

\*Perkin Elmer Vapor Fractometer, Model 154

Only the time of emergence, and approximate peak height were determinable. These components could have been identified, quantitatively and qualitatively, if better liquid phases were available, and authentic samples of the postulated reaction products could have been obtained. However, a sample of the unsaturated material was dissolved in methylene chloride, and treated with an excess of ozone. The excess ozone was removed by flushing with nitrogen, and the ozonides were cleaved with lithium aluminum hydride (3), to give a mixture of alcohols corresponding to the portions of the molecule on either side of the double bond, as follows:



The solvents, consisting of methylene chloride, from the ozonolysis, and ethyl ether, from the lithium aluminum hydride cleavage, were removed by distillation through a 60 plate column. When the still pot temperature rose to 65°, a small portion of carbon disulfide was added, and distilled off, two more portions of carbon disulfide were added and distilled off in the same manner to insure removal of the two solvents. The residue was then lyophilized, to remove non-volatile material, without loss of the volatile alcohols.

The products thus obtained were subjected to gas-liquid partition on two dinonyl phthalate on celite columns in series, and excellent separation of all components was obtained. These components were identified by their time of emergence, obtained from authentic samples of the alcohols, and the mole percents of the five high boiling alcohols were determined from the areas under the curves, using a planimeter. A synthetic mixture of known composition was also chromatographed, to determine the degree of accuracy obtainable by this method.

The mixture of alcohols from the two dehydrations gave the following:

<u>ALCOHOL</u>	<u>#1</u>	<u>#2</u>	<u>AVERAGE</u>
Butanol 2, from (IX)	10.8%	7.9%	9.4%
Butanol 1, from (XIII)	21.2%	29.6%	25.4%
Pentanol 2, from (X)	54.1%	59.4%	56.8%
Hexanol 3, from (XI)	3.1%	0.9%	2.0%
Hexanol 2, from (XII)	10.8%	2.3%	6.5%

The synthetic mixture gave the following:

<u>ALCOHOL</u>	<u>CALCULATED</u>	<u>FOUND</u>
Butanol 2	27.9%	26.5%
Butanol 1	28.0%	26.5%
Pentanol 2	23.6%	23.8%
Hexanol 3	20.5%	23.2%

No attempt was made to correct the values obtained from the unknown mixtures for the differences found in the synthetic mixture.

In an attempt to further verify the identities of the alcohols, the unknown and synthetic mixtures were rechromatographed, using a column of silicone on celite in series with a column of dinonyl phthalate on celite. The order of emergence of the peaks were unchanged from that of the synthetic

mixture. The only difference observed, was the shift of the carbon disulfide peak to the center of the area between the the isopropyl and the n-propyl alcohol peaks. This method of qualitative analysis is essentially the same as used by Lewis (4).

**PART IV**  
**DISCUSSION**

The preparation of 2,2-dimethyl-1-pentanol, by the sequence of reactions previously indicated, gave a product of high purity. This degree of purity is directly attributable to the fact that it was prepared by the reduction of 2,2-dimethyl pentanoic acid which could be purified easily.

No unusual difficulties were encountered, except in the distillation of 2-chloro-2-methyl pentane. This compound, after exhaustive drying, could not be distilled without excessive decomposition.

In view of the fact that the 2-chloro-2-methyl pentane, before distillation, was contaminated by 2-methyl-2-pentanol, it is probable that some elimination of hydrogen chloride from the halide occurred, followed by the acid catalysed dehydration of the alcohol, producing water which could hydrolyse the chloride to produce more acid and free alcohol.

In addition to this cyclic decomposition, the water being produced, as well as the low boiling hexenes, resulted in an extremely impure distillate. This difficulty was overcome by distilling the halide from phosphorus pentoxide, which removed the alcohol and water as they were formed, effectively breaking the cycle. The product obtained was undoubtedly contaminated by hexenes and hydrogen chloride,

but after standing over anhydrous potassium carbonate the hydrogen chloride was removed, and it was felt that the presence of the hexenes would not interfere with the next reaction.

When 2,2-dimethyl-1-pentanol was dehydrated, the resulting olefins were found to be present as follows:

IX	$\text{CH}_3-\text{CH}_2-\text{CH}=\overset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{CH}_2-\text{CH}_3$	9.4% by migration of methyl and loss of proton from propyl
X	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}-\text{CH}_3$	56.8% by migration of methyl and loss of proton from ethyl
XI	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_2}{\underset{  }{\text{C}}}-\text{CH}_2-\text{CH}_3$	2.0% by migration of methyl and loss of proton from methyl
XII	$\text{CH}_3-\overset{\text{CH}_2}{\underset{  }{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	6.5% by migration of propyl and loss of proton from methyl
XIII	$\text{CH}_3-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	25.4% by migration of propyl and loss of proton from butyl



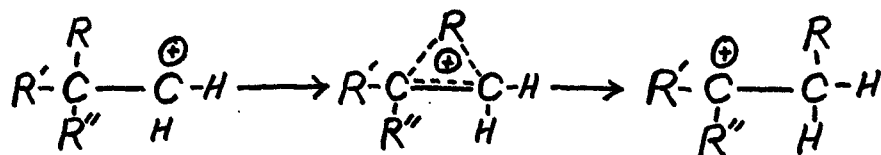
Whitmore and Church (2) studied the dehydration of 2, 2-dimethyl-1-hexanol and found that the compounds analogous to IX, X, XII, and XIII, were formed. No trace of the compound analogous to XI was detected. The percent of each compound isolated was not given in their report. However, it was stated that the compounds analogous to XII and XIII were formed in the ratio of 12:1, loss of the proton from the butyl group being the predominant occurrence. In the <sup>pentyl</sup> case of 2,2-dimethyl-1-pentanol, the ratio is 3.9:1, a rather large difference. They also found that the compounds analogous to IX and X were found in the ratio of 2:1, the loss of the proton from the ethyl group being the preferred event. In the case of 2,2-dimethyl-1-pentanol, it is found that the ratio is 6:1 in favor of the loss of proton from the ethyl group.

Generally, it may be said that agreement is shown between the two studies, in regard to the position of the more labile proton. In addition, compound XI was found in this study to be present to the extent of only 2.0% and could easily have been missed by the methods used by Whitmore. It is indeed unfortunate, for the sake of comparison, that no figures were given to relate the amounts of each product found in their study.

Examination of the amounts of the olefins formed during the dehydration of 2,2-dimethyl-1-pentanol indicates that 68.2% of the rearranged products resulted from methyl group migration, and 31.9% from migration of the propyl group. In view of the fact that two methyl groups are available for migration, it may be assumed that 34.1% of the rearranged products resulted from the migration of a single methyl group, 34.1% from the migration of the second methyl group, and the remaining 31.9% from migration of the propyl group.

These values are in excellent agreement with the theoretical value of 33.3% of each, which would be obtained if all three groups were equally labile.

In view of these results, it seems that dehydration studies of compounds having massive branched groups attached, in place of the propyl group, would clarify the mechanism involved in group migration. Apparently, in the case studied, the difference in size between the methyl and propyl groups is not a factor in determining the extent of migration of the groups, and no steric effect is noted. The mechanism of rearrangement with a carbonium ion, as first proposed by Nevell et al (6), is through an intermediate bridge:



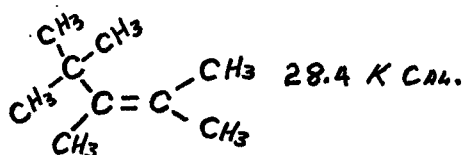
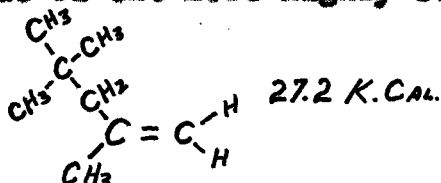
It may then be assumed, if this is the case, that only steric effects would be of importance in determining the extent of migration of the alkyl groups.

Two empirical rules have been advanced to predict the olefin which may be formed by the elimination of a proton from a carbonium ion. The Saytzeff rule (7) states that the most highly branched olefin will be formed. The Hoffman rule (8) states that the least branched olefin will be formed.

These conflicting rules have been discussed by Ingold (9), who proposed that the inductive effects of the attached groups are responsible for the observed orientation. Brown (10) agrees with Ingold that the inductive effect is responsible for orientation in Saytzeff type elimination, but shows that steric effects are responsible for the orientation observed in Hoffman type eliminations.

In the case of 2,2-dimethyl-1-pentanol, Saytzeff type elimination is predominant, and accounts for 91.5% of the olefins formed, only 8.5% resulting from Hoffman type elimination. Examination of the structures indicates that no large steric factor can be anticipated in this case, hence, the predominance of Saytzeff type elimination is in agreement with the proposals of both Brown and Ingold.

It should be pointed out that the interpretations of these two investigators may not be entirely correct. Kistiakowsky (11, 12), has measured the heats of hydrogenation of a number of substituted ethylenes, and found lower heats of hydrogenation for the more highly substituted olefins, indicating that these compounds have the more stable double bond. The notable exception in the series occurred in the case of 2,4,4-trimethyl-1-pentene, and 2,4,4-trimethyl-2-pentene, where the heat of hydrogenation of the least substituted olefin was 1.2 kilo calories lower than that of the more highly substituted olefin.



This case represents an exception to the remainder of the hydrogenation data in the same way Brown has shown that exceptions to the Saytzeff rule can occur when steric factors are present. Examination of the structures of the two molecules indicates that a higher degree of steric strain should be present in the case of the more highly substituted ethylene, which is evidenced by the higher heat of hydrogenation.

Thus, it appears that the Saytzeff rule, and the exceptions due to steric strain, which causes Hoffman type elimination, can be adequately explained in terms of the stability of the olefin which is formed. In the light of these data it seems that the Saytzeff rule should be restated to indicate that in a unimolecular elimination, the olefin formed predominately will be the one having the greatest stability.

Compounds X and IX are found in this study to be formed in the ratio of 6:1. Examination of molecular models of these two compounds indicates a much higher degree of freedom of rotation to be present in X. Thus, it seems possible that the differences in freedom of rotation, may account for the preferred formation of X. On this basis, it appears that the formation of XI would be sterically hindered for a greater part of the existence of the carbonium ion VII than the formation of X, thus, X would have a greater opportunity to be formed. In conclusion, it may be said that the sequence of ozonization, reductive cleavage, and the use of gas-liquid partition chromatography to identify, qualitatively and quantitatively, the unsaturated products formed by the rearrangement of alcohols, should present a real advance in methodology for the study of such reaction.

**PART V**

**SUMMARY**

2,2-dimethyl-1-pentanol has been synthesized, its physical constants have been determined, and it has been characterized by the preparation of eight derivatives.

The alcohol was dehydrated at its boiling point, in the presence of sulfuric acid, and the resulting rearranged olefins have been qualitatively and quantitatively determined.

Orientation in E1 eliminations has been discussed, and it is proposed that the Saytzeff rule should be restated.

**PART VI**  
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