

THE ADDITION OF  
A HALOGEN HYDRIDE  
TO 3-HEPTENE.

Thesis

by

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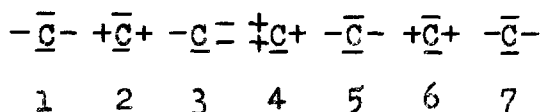
INTRODUCTION.

The purpose of this study is to determine the relative affinity for electrons of the ethyl and propyl groups and thereby to check the indications of the ionization constants of certain acids and amines. The ionization constants of methyl, ethyl and propyl amines and acetic, propionic and butyric acids, indicate that the ethyl group has a smaller affinity for electrons than either the methyl or the propyl group. Lucas and Moyses<sup>(1)</sup> have shown this to be true with respect to the methyl group and it is the intent of this work to investigate the evidence with respect to the propyl group.

Two theories regarding the electronic character of carbon union have been proposed. The first is the alternate polarity theory which has been supported and worked on by Cuy<sup>(2)(3)</sup>. The second is the displacement theory which has been proposed by Lewis<sup>(4)</sup> and has been used by Latimer and Rodebush<sup>(5)</sup> in accounting for the ionization constants of some acids of phosphorus. The latter theory has also been worked on in this laboratory by Lucas and Jameson<sup>(6)</sup>, Lucas, Simpson and Carter<sup>(7)</sup> and Lucas and Moyses<sup>(8)</sup>.

According to the alternate polarity theory the carbon

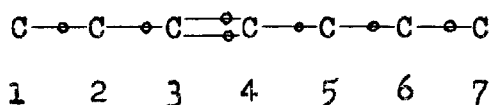
atoms in aliphatic chain tend to become arranged alternately positive and negative. Therefore, 3-heptene (minus the hydrogen atoms) would appear to be :



As may be seen C-3 is preponderantly negative while C-4 is positive. Therefore, when a strong polar compound such as hydrogen bromide is added to this unsaturated hydrocarbon, the positive hydrogen will go to C-3, while the bromine will go to C-4. The theory consequently predicts the formation of 4-bromo-heptane on the addition of hydrogen bromide to 3-heptene.

The ionization constant,  $K_a$  of propionic acid<sup>(9)</sup> is  $1.35 \times 10^{-5}$  and of butyric acid is  $1.65 \times 10^{-5}$ , while  $K_b$  of ethyl amine is  $5.6 \times 10^{-4}$  and of propyl amine is  $4.7 \times 10^{-4}$ . These values indicate that the propyl group has a greater affinity for electrons than the ethyl group. The validity of this apparent difference in affinity for electrons forms the basic assumption on which the displacement theory is based. This difference results in the displacement of the electronic orbits in the chain, which may be represented by a displacement of the average position of the electron pair. Therefore, 3-heptene (minus the hydrogen atoms) would

appear to be  $(10)$ ;



Consideration of the preceding diagram indicates that C-3 is essentially positive in comparison to C-4 . When hydrogen bromide is added to this hydrocarbon the theory predicts the formation of 3-bromo-heptane. This is opposite to that predicted by the first theory.

A factor which must be considered in dealing with this problem is that of symmetry of the molecule. Reference to innumerable organic compounds shows that the tendency towards this symmetrical formation is exceedingly great. In the addition of hydrogen bromide to 2-pentene as well as to 3-heptene, as mentioned above, the two theories predict different products. In the case of 2-pentene, the symmetrical form is predicted by the displacement theory, and this isomer in the work of Lucas and Moyses was found to be formed in excess. However, in the case of 3-heptene the unsymmetrical form is predicted. Therefore if the unsymmetrical form is produced in excess the evidence shows unquestionably the agreement of the electron affinities of the ethyl and propyl groups with the indications of the ionization constants. It also shows the factor of symmetry to be of minor importance compared to that of

electron affinity. On the other hand, if the symmetrical form is produced in excess the evidence shows that the factor of symmetry is not of minor importance.

OUTLINE OF WORK.

It is evident that the addition of hydrogen chloride or hydrogen bromide to 3-heptene will serve the purpose of determining the relative affinity for electrons of the ethyl and propyl groups. The position taken by the two groups of such a polar compound will be a measure of this relation. In order to study this problem the following steps must be taken :

- a) the preparation of 4-heptanol.
- b) the preparation of 3-heptanol.
- c) the preparation and identification of the  
4-halogen heptanes.
- d) the preparation and identification of the  
3-halogen heptanes.
- e) the preparation of 3-heptene.
- f) the addition of a halogen hydride to 3-heptene.
- g) the analysis of the mixture of halogen heptanes.

Due to the lack of time the problem has not been completed. The work has been carried out only through the first four steps.

The 4-heptanol was prepared by the Grignard reaction<sup>(11)</sup> of propyl magnesium bromide on ethyl formate. This method was chosen because of the ease with which it may be pre-

pared in a high degree of purity. The propyl magnesium bromide was made in the usual manner by adding an ethereal solution of propyl bromide to magnesium shavings. The addition compound resulting from the reaction of the magnesium bromide with ethyl formate was changed into the alcohol with ammonium chloride solution.<sup>(12)</sup> The use of this latter reagent however was found to be unsatisfactory because of the formation of a precipitate of magnesium carbonate, which was found to occlude a great amount of the ethereal solution. Refractive index and density readings on the sample were made in order to check the values of previous preparations and to compare with the values of 3-heptanol.

The attempt was made to make the 3-heptanol by a similar Grignard reaction of ethyl magnesium bromide and butyl magnesium bromide on ethyl formate. It was thought that the reaction would take place in steps, that is, that the one oxygen bond would be affected completely before the second one was touched. However, the attempt was unsuccessful, for a mixture of di-ethyl and di-butyl carbinols resulted. This indicates that the reaction of an alkyl magnesium halide with the formate, affects both of the oxygen bonds of a particular molecule at the same time. This indication is substantiated by the evidence found in



regard to the preparation of aldehydes by this method.<sup>(13)</sup>

The results of this experiment might have been anticipated because it was noted that only carbinols having the two substituted groups the same, had been made by this method. However, as no statement to the contrary was found it was thought feasible.

After the failure of the above method the 3-heptanol was conveniently prepared by the action of butyl magnesium bromide on propionic aldehyde and the subsequent changing of the resulting addition compound into the alcohol by means of dilute sulphuric acid. The results of the refractive index, density, and boiling point values, showed the alcohol to have properties exceedingly similar to those of 4-heptanol. These results may be indicative of those that may be expected to be found between the two forms of chlorides and bromides. They are therefore indicative of difficulty in analyzing a mixture of the two isomers. The heavier atoms associated with the carbon atom may however have a greater affect on these values than does the light hydroxyl group. Also the factor of symmetry of the two forms may affect the freezing point to a much greater degree than any other property, in which case this last method may have to be relied upon for the analysis.

The bromo-heptanes were produced by heating constant boiling aqueous hydrogen bromide with the alcohols for a period of four hours.<sup>(14)</sup> The bromides were purified in the usual manner but the physical constants were not determined because of the lack of time.

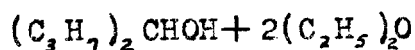
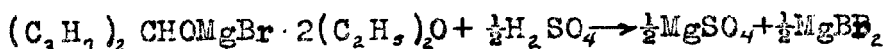
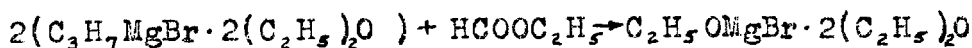
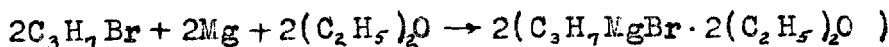
The chloro-heptanes were produced by heating concentrated hydrogen chloride with the alcohols in the presence of anhydrous zinc chloride.<sup>(15)</sup> These were left in the same state as the bromides.

The work necessary to be carried out in the future consists in the last three steps outlined above, as well as the determination of the physical constants of the chlorides and bromides that have been made. These latter results will determine the method by which a mixture of the two isomeric forms will be analyzed.

EXPERIMENTAL WORK

## 1) The Preparation of 4-heptanol.

The reactions involved in this preparation were:



The materials used were;

<u>Substance</u>	<u>Mole used</u>	<u>Weight</u>	<u>Vol.</u>
C <sub>3</sub> H <sub>7</sub> Br	3.14	386	283
Mg	3.21	78	
HCOOC <sub>2</sub> H <sub>5</sub>	1.53	113.5	123.5
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	9.18	680	945
H <sub>2</sub> O	1.53	27.6	27.6
NH <sub>4</sub> Cl	1.53	81.9	

The propyl bromide was prepared from Eastman's propyl alcohol, sodium bromide and concentrated sulphuric acid.<sup>(16)</sup>

The crude product was washed with water, concentrated sulphuric acid, water, sodium carbonate solution and water.

After drying with calcium chloride it was distilled. It was dried again, this time with potassium carbonate, and then redistilled, after which the product boiled at 68.2°-69.2°(uncorr). The ethyl formate, previously prepared,

was redistilled after drying with phosphoric anhydride.

Its boiling point was 52.0° - 53.4°(uncorr). The ether was

absolute and was dried with a small amount of sodium just previous to its use. Eastman's magnesium shavings were used for the Grignard reaction, after being dried at 100° for an hour.

The dry magnesium shavings were placed in a 3-liter 3-neck flask. (See diagram #1.) surrounded by a water bath. The shavings were agitated by means of a mechanical stirrer inserted in the center neck. A reflux condenser provided with a large calcium chloride drying tube was attached to the one side neck and a 250 c.c. dropping funnel to the other. A small portion of the propyl bromide was added directly to the magnesium shavings to start the reaction, after which some ether was added. The remainder of the bromide was mixed with an equal volume of ether and dropped slowly into the reaction flask through the funnel. At convenient intervals the remainder of the ether was added. (Note.- An excess of ether over the two mols required for the production of the addition compound is always necessary in order to keep the products in solution.) The mixture after the completion of the addition was stirred for a short time and then allowed to stand. The ethyl formate mixed with an equal volume of ether was next added drop by drop accompanied vigorous stirring. The water bath at this point was replaced by a salt and ice mixture.

After standing over night the ammonium chloride dissolved in 500 c.c. of water was added. This was done slowly at first due to the violence of the reaction. The solution separated into a clear ethereal layer and an opaque water layer containing a considerable amount of flocculent magnesium carbonate precipitate. The two layers were separated and the precipitate in the water layer dissolved with sulphuric acid. The ethereal solution which was occluded by the precipitate was added to the previous solution. This was washed with water, dried with calcium chloride and distilled to a three degree boiling range. (150° - 153°). The fractions obtained in this distillation were ;

1.	34° - 40°	Ether to be recovered.
2.	40° - 70°	3 c.c.
3.	70° - 105°	5 c.c.
4.	105° - 150°	8 c.c.
5.	150° - 153°	160 c.c.
6.	153° -	8 c.c.

The crude product of fraction 5 was redistilled after a thorough drying with anhydrous potassium carbonate with the following results ;

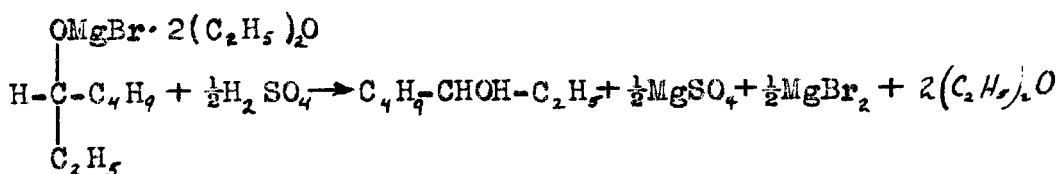
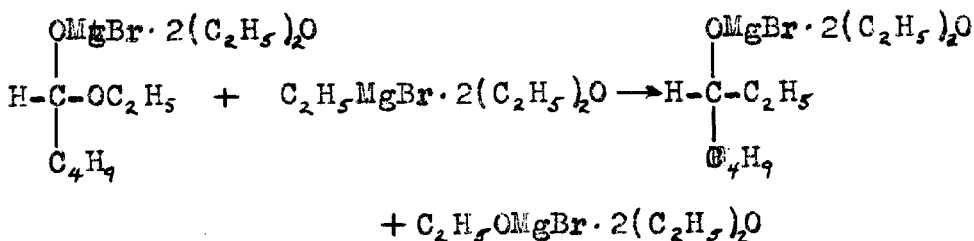
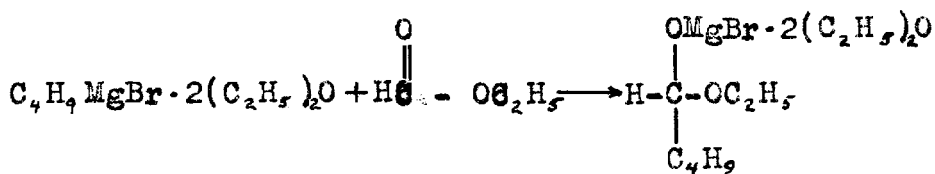
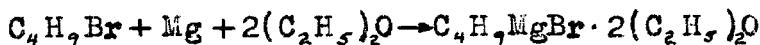
1.	150.6° - 153.4°	8 c.c.	} 1st. thermometer
2.	153.4° - 153.6°	84 gm.	
	153.9° - 154.3°	29 gm.	} 2nd. thermometer
3.	154.3° -	3 c.c.	

The gap in the boiling point range of the second fraction is probably due to a discrepancy in one of the two thermometers that were used in the distillation. The yield

of 4-heptanol was 113 gms. ( 84 gms. 29 gms.) or 63.5% with a boiling point of 153.4° - 153.6° and 153.9° - 154.3° (corr) at 745 mm. ;  $D_4^{25}$  - .8175 :  $n_D^{20}$  - 1.4195 , 1.4190 :  $n_D^{25}$  - 1.4173 , 1.4170

## 2) The Preparation of 3-heptanol.

The attempt to prepare this alcohol by a method similar to that used in the preparation of the 4-heptanol was unsuccessful. It was thought that the Grignard method illustrated by the following reactions would take place :



However from the results of the experiment it was found



same as in the previous experiment.

The apparatus used is shown in diagram #2. The butyl magnesium bromide was made in the small flask and then slowly siphoned into the ethyl formate contained in the large flask. After standing for some time the ethyl magnesium bromide was made in the small flask and it likewise added to the large flask and allowed to stand. As in the previous experiment all of these additions were accompanied by stirring. A cooling bath was also used. The mixture on treatment with the dilute sulphuric acid yielded the two layers. The ethereal layer was separated, washed with water, dilute sodium carbonate solution and dilute sodium thiosulphate solution. The latter was done in order to remove the iodine which was produced by side reactions and was dissolved in the layer. The solution was again washed with water and dried with potassium carbonate. The first distillation yielded the following results :

1. 34° - 40° Ether to be recovered.
2. 40° - 100° 2 c.c.
3. 100° - 114° 15 c.c.
4. 114° - 120° 12 c.c.
5. 120° - 145° 10 c.c.
6. 145° - started to decompose.

The last fraction was subjected to a vacuum fractional distillation. (See diagram #3) The results of this distillation were :



1.	30° - 58°	15 mm.	2 c.c.
2.	58° - 80°	12 mm.	3 c.c.
3.	80° - 84°	10 mm.	60 c.c.
4.	84° -	4 mm.	3 c.c. Would not

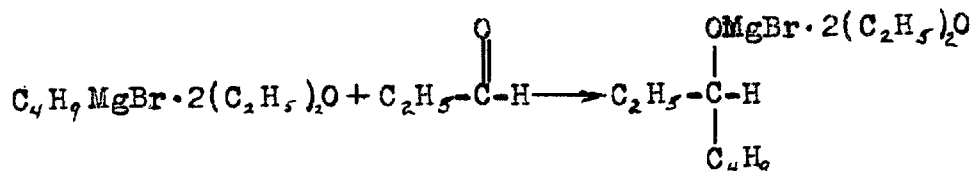
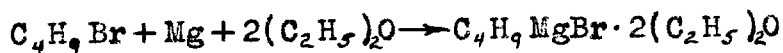
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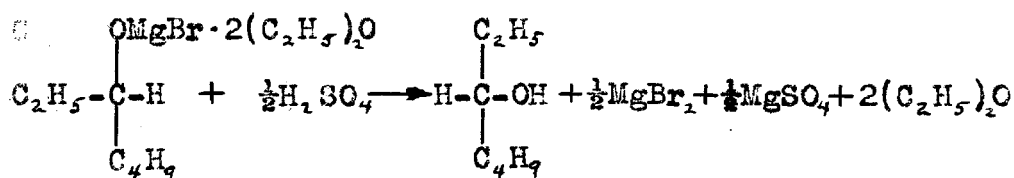
A second fractional distillation of all of the fractions gave the following results ;

1.	35° - 105°	749 mm.	1 c.c.
2.	105° - 110°	749 mm.	20 c.c.
3.	110° - 120°	749 mm.	13 c.c.
4.	25° - 76°	10 mm.	6 c.c.
5.	76° - 80.8°	10 mm.	60 c.c.

The last results indicated that the desired alcohol, namely, 3-heptanol, was not present as its boiling point is 157° at 750 mm.<sup>(17)</sup> The substance of lower boiling point appeared to be 3-pentanol <sup>(18)</sup> which boils at 116°. The higher boiling substance appeared to be 5-nonanol; which was found in an accompanying experiment to have a boiling point of 77° - 79.5° (uncorr) at 10 mm. (193° at 766 mm.) <sup>(19)</sup>. The 5-nonanol was prepared in the same manner as the 4-heptanol.

The reactions involved in the second and successful attempt to prepare 3-heptanol were :





The materials used were :

Substance	Mole used	Weight	Volume
$\text{C}_4\text{H}_9\text{Br}$	1.13	155.0	121
Mg	1.15	27.5	-
$\text{C}_2\text{H}_5\text{CHO}$	1.13	65.6	81.3
$(\text{C}_2\text{H}_5)_2\text{O}$	6.79	503.0	698.0
$\text{H}_2\text{SO}_4$ (6n.)	.57	-	190.0

The butyl bromide supply was purified in the usual manner, the product used boiling at  $99.1^\circ - 100.0^\circ$  (uncorr). The propionic aldehyde was prepared by the oxidation of propyl alcohol with sodium dichromate and concentrated sulphuric acid. The crude product was dried carefully with potassium carbonate and fractionated three times in order to obtain the final product boiling at  $45.5^\circ - 50.5^\circ$  (uncorr). The ether, magnesium and sulphuric acid were the same as in previous experiments.

The butyl magnesium bromide was made as in the other work, by dropping the bromide onto the magnesium contained in the three neck flask. (See diagram #1) After standing the aldehyde mixed with an equal volume of ether was added. The product was decomposed with sulphuric acid and the alcohol purified as before. The first distillation yielded the following results :

1.  $34^\circ - 40^\circ$  Ether to be recovered.

2.	40° - 100°	5 c.c.
3.	100° - 130°	5 gm.
4.	130° - 140°	5.5 gm.
5.	140° - 150°	8.9 gm.
6.	150° - 154°	52.7 gm.
7.	154° - 161°	17.3 gm.
8.	161° -	4.0 gm.

Using fractions 4, 5, and 6, a second and third distillation gave :

Second.

1.	140° - 151°	3.0 gm.
2.	151° - 155°	51.5 gm.
3.	155° - 157.5°	11.7 gm.
4.	157.5° -	3.0 gm.

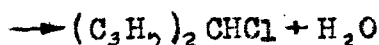
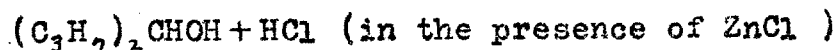
Third.

1.	145° - 153.2°	5.0 gm.
2.	153.2° - 156.0°	53.1 gm.
3.	156.0° -	1.5 gm.

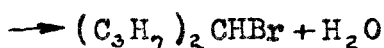
The second fraction of this third distillation was taken as the yield of 3-heptanol. It was 53.1 gms. or 40.6% yield, with a boiling point of 153.2° - 156.0° (corr) at 745 mm.:  $D_4^{25} = .8159$  ;  $n_D^{20} = 1.4197$  ;  $n_D^{25} = 1.4175$  .

### 3) Preparation of the 4-halogen heptanes.

The reactions involved in the preparation of these heptanes were ;



The materials used were :



The materials used were :

Substance	Mole used	Weight	Volume
$(\text{C}_3\text{H}_7)_2\text{CHOH}$	.141	15.0	18.5
HCl (conc)	.282	-	23.5
ZnCl <sub>2</sub>	.282	38.4	-
$(\text{C}_3\text{H}_7)_2\text{CHOH}$	.141	15.0	18.5
HBr	.564	-	58.3

The hydrogen chloride was concentrated and C.P. and the zinc chloride was anhydrous. The hydrogen bromide was constant boiling of sp. gr. 1.49 and contained 52.5% of hydrogen bromide. The alcohol was the 4-heptanol prepared in a previous experiment.

The zinc chloride was dissolved in the cold concentrated hydrogen chloride and put into a 100 c.c. flask provided with a condenser. The alcohol was added and the mixture refluxed for an hour and a half. The chloride layer was distilled from the mixture and the resulting two layers separated in a funnel. The chloride layer was washed twice with water, thrice with cold concentrated sulphuric acid and twice with saturated sodium carbonate solution. This procedure required considerable time because of the formation of an emulsion which was difficult to handle. This formed at the time of the first washing and persisted throughout the remainder of them. The chloride was then dried with potassium carbonate for several days, after which the

several days, after which it showed a considerable decrease in its opaqueness. At this point the cloudiness was probably due to suspended potassium carbonate.

The work will be continued from this point in the future.

In the case of the bromide the aqueous hydrogen bromide was added to the alcohol contained in a flask fitted as in the previous case. The mixture was refluxed for period of five hours and then it was treated as in the preceeding experiment. One deviation was made in that the first washing with water was replaced by a sodium carbonate solution. The emulsion even though slightly heavier was easier to handle because the boundary line between the wash solution and the bromide was more pronounced. The bromide was dried with potassium carbonate and was thus left for future work.

#### 4) The Preparation of the 3-halogen heptanes.

The reactions involved are the same as in the preceeding experiment except that 3-heptanol was used instead of 4-heptanol.

The materials used and the procedure followed were also the same. The crude products were left in the same condition as those above.

RESULTS.

The results of this problem are not complete as the time available has been insufficient for completing the work. The work accomplished consists in :

- 1) preparing 4-heptanol by means of the Grignard reaction of propyl magnesium bromide on ethyl formate,
- 2) showing that both of the oxygen bonds of a molecule of ethyl formate are affected by the Grignard reagent at the same time,
- 3) preparing 3-heptanol by means of the Grignard reaction of butyl magnesium bromide on propionic aldehyde,
- 4) preparing 3- and 4-bromo-heptanes,
- and 5) preparing 3- and 4-chloro-heptanes.

CONCLUSIONS.

No conclusions in regard to the solution of the actual problem being studied can be made at this time. However, some conclusions in regard to particular problems involved in the work may be drawn. They are :

1) that considerable investigation into the applications of and the proper conditions for the use of the Grignard reagent is needed, and

2) that more care should be exercised by authors of articles in order to make them comprehensible and complete and yet concise.

DIAGRAMS

Diagram #1.

Hg seals.

Diagram #2.

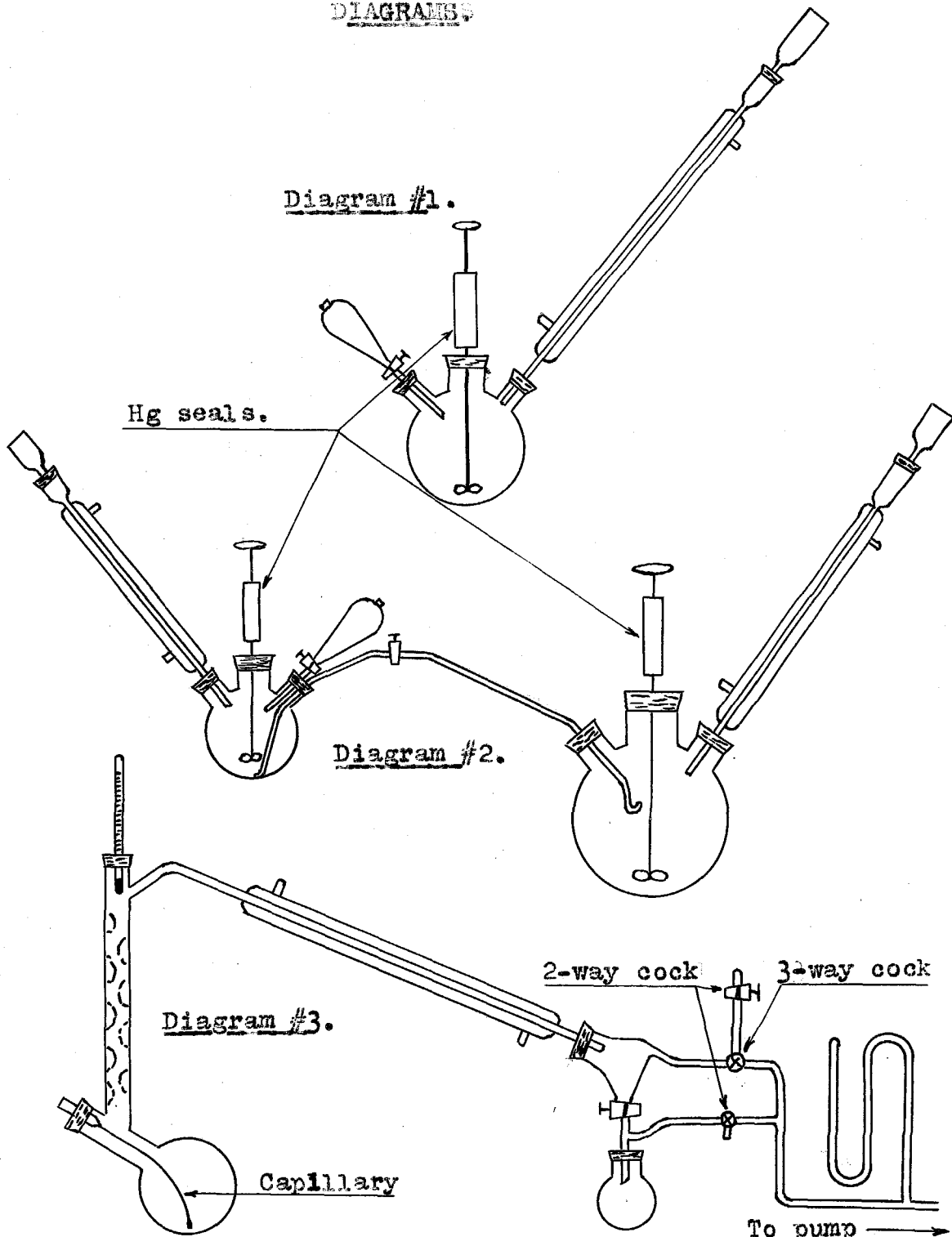
Diagram #3.

Capillary

2-way cock

3-way cock

To pump →





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