

Preparation and Physical Constants  
of Higher Straight Chain Ethers:  
Butyl Hexyl Ether

A Thesis  
by  
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## Introduction

Many of the simpler organic compounds, whose formulas can be so easily written, have never actually been prepared. The literature is as yet incomplete regarding their physical constants and exact methods of preparation. It was the purpose of this thesis to attempt to fill in some of these gaps in chemical knowledge, choosing as a class of compounds the higher, straight-chained, mixed ethers.

The preliminary step was, quite naturally, a literature search to determine what work had already been done in this field, which ethers had already been synthesized and studied, and which others remained as a problem for research. Our survey revealed that the hexyl series of mixed ethers, from propyl hexyl ether and up, was a complete blank and, accordingly, we decided upon this series as the subject of our work.

Besides the recorded physical constants, the literature search also revealed a number of preparations of ethers. A high percentage of these were definitely not feasible with the limited apparatus of the laboratory, particularly in respect to pressure equipment. The classical method of preparing ethers, the Williamson Synthesis, was known by Dr. Reid to give low yields, so he advised us to try other preparations which might give better results.

It was only after repeated failures in these other experiments that the Williamson Synthesis was used. The predicted low results were obtained, but at least they were of a positive nature, and made possible the determination of some of the physical constants of butyl hexyl ether.

The value of research of this type lies not so much in determining the individual constants of the substances prepared, as in viewing a whole series of compounds. Their properties have a systematic variance with the chain length which enables one to predict constants of compounds in advance of their preparation. The checking of these predictions is of great scientific interest in the same way that it is of interest to find the reason for discrepancies, if and where they exist.

The accompanying graph of boiling points shows such a regularity that it seems legitimate to expect the untested ethers to boil very close to their interpolated values. The supposed butyl hexyl ether prepared by the Williamson synthesis is assumed to be that compound largely on the basis of its boiling point which falls within the range predicted from the graph.

A thesis subject such as this has the advantage of offering a variety of types of training, with the avoidance of monotony. Work in the library, organic synthesis, and physical measurements are all involved. It is unfortunate that the greater part of the experimental work produced negative results but we feel that they are not entirely

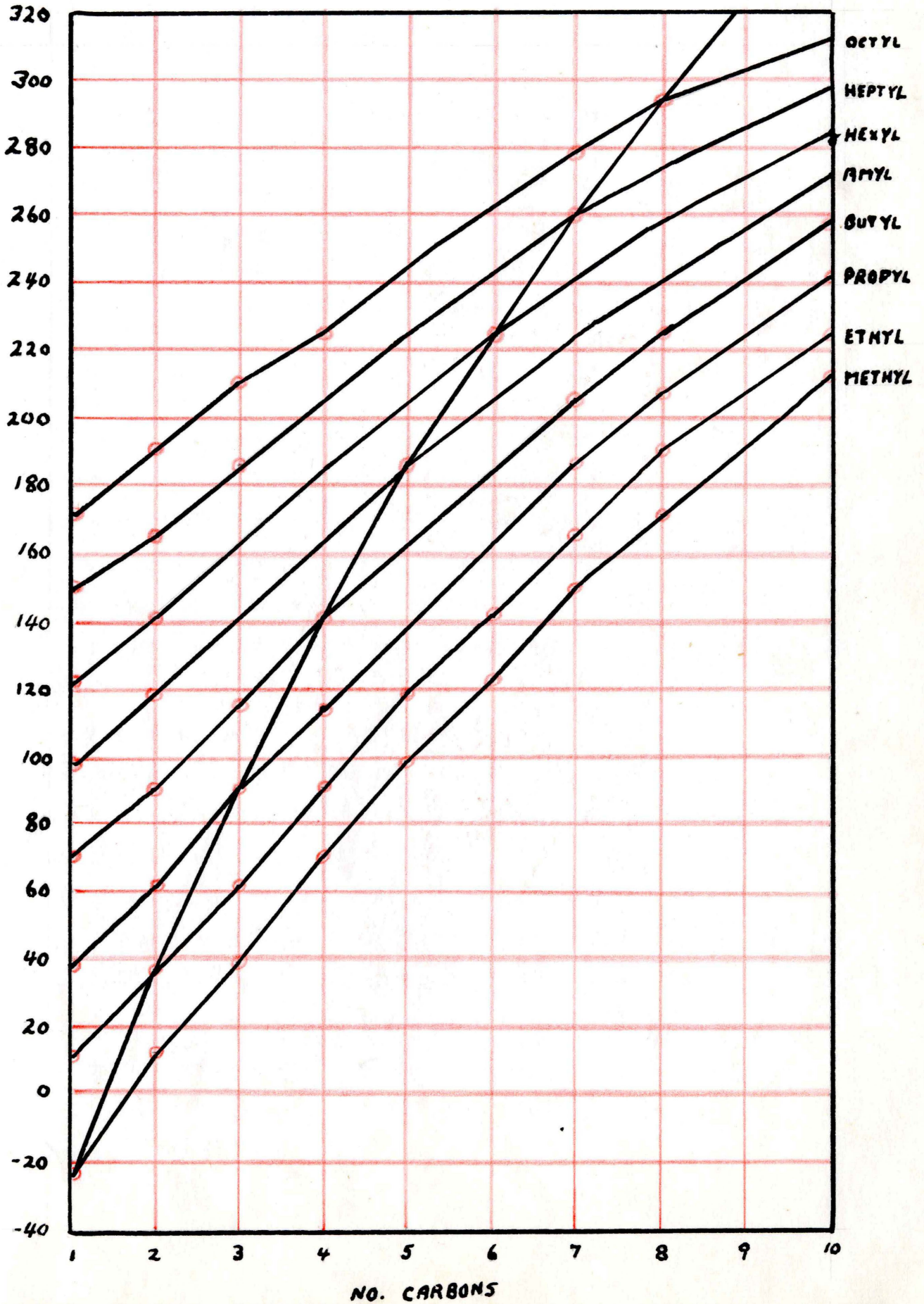
without value and that a great deal of experience was gained in the practical application of the techniques of chemistry.

At this time we wish to express our sincere appreciation to Dr. E. Emmet Reid for his generous expenditure of time and knowledge in the direction of this thesis.

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# BOILING POINTS OF ETHERS

SYMMETRICAL



Experimentation:

Sulfuric Acid Synthesis

The first attempts to prepare the ethers were through the action of a dehydrating agent on a mixture of alcohols. It is known that various alcohols are converted into their ethers by boiling with sulfuric acid, a different strength of acid being best for different alcohols. Hence, the preparation of di-hexyl ether was attempted by the sulfuric acid synthesis.

0.65 moles of hexyl alcohol and sulfuric acid were mixed in a round bottom flask which was attached to a water condenser for refluxing. As soon as the concentrated  $H_2SO_4$  was mixed with the alcohol, tar began to form. Although refluxing increased the amount of tar, it was continued for two hours, during which time large amounts of tar were formed. The solution was then fractionally distilled to recover any di-hexyl ether that may have been formed. Boiling commenced at  $57^\circ$  and moved steadily up to  $87^\circ$  where the temperature stopped climbing. All of this first portion was a colorless liquid. At  $87^\circ$  several milliliters of a distinctly yellow oil distilled off leaving nothing but a tarry mass in the flask. From the amount of tar formed, it was assumed that the concentration of sulfuric acid was too great, and further attempts by this synthesis would require that the ratio of the acid be reduced.

In test tube portions, mixtures were made up of the following ratios:

(1) One mole hexyl alcohol to one-half mole 50%  $H_2SO_4$ .

This mixture turned brown at room temperature and very dark green when heated over a flame.

(2) One mole of hexyl alcohol to one-fourth mole 25%

$H_2SO_4$ . There was no change in color at room temperature, but two layers were formed. On heating, the top (organic) layer turned slightly brown.

This latter ratio appeared the best possibility, for the formation of large amounts of tars would be avoided. Therefore, one-half mole of hexyl alcohol and one-eighth mole of 25%  $H_2SO_4$  were refluxed together for  $6\frac{1}{2}$  hours. At the end of this time there were still two layers, the organic one having turned brown. It was then washed several times with water to remove the acid before fractionation, after which it was dried over calcium chloride.

Distillation Results:

1st Portion	Below $110^\circ$	Colorless Liquid
2nd Portion	$110^\circ$ - $170^\circ$	Colorless Liquid
3rd Portion	$170^\circ$ - $215^\circ$	Colorless Liquid

There was possible loss of ether due to escape of vapor around the charred cork. The third portion was acid to litmus and had a very irritating odor. When neutralized with 1 N. NaOH, the odor almost disappeared. After separation by separatory funnel, the organic layer was washed with calcium chloride solution, after which it was dried over anhydrous calcium chloride.





NaOH were again added in the manner just described with 4 more hours of stirring at low temperature. No oily layer appeared so the mixture was heated to 40° for 15 minutes. The oily layer then showed up and the mixture was filtered through glass wool to take out the crystals which had formed; then the aqueous layer was removed by a separatory funnel. The remaining oil was washed with NaOH and dried over anhydrous K<sub>2</sub>CO<sub>3</sub>. Distillation at reduced pressure was carried out up to 85° at which time decomposition with charring occurred.

It was then decided to attack the problem from the other direction, preparing the butyl ester for reaction with the sodium derivative of hexyl alcohol. The directions for ester formation previously followed dealt specifically with the butyl ester instead of the hexyl, so this time the ester, dissolved in benzene, was successfully prepared. The majority of the benzene was distilled off over a steam bath and we then tried to purify the ester by distillation at reduced pressure (15 M.M., 170°). The solution started boiling at the temperature expected with a few drops distilling over. Then the fumes of the vaporized ester caused the pressure to rise which in turn meant a rise in the boiling point. The extra heat which had to be applied to continue the distillation soon caused decomposition of the ester.

The same preparation was tried again, this time using the unpurified ester. A small sample of this ester was reacted with the sodium derivative of hexyl alcohol until

the whole contents of the test tube were a spongy yellow solid. It seemed unlikely that any ether could be present here so the product was discarded. Later conversations with Dr. Reid, however, brought out the fact that before assuming a completely negative result, we should have let the reaction continue over a steam bath for a considerable time and then tried steam distillation. The remainder of the ester was mixed with an excess of hexyl alcohol and heated on the steam bath for approximately 10 hours, during which time a light brownish color developed due to charring. Distillation was then started but excessive charring occurred and at 132° SO<sub>2</sub> fumes came over. The distillation was stopped and the mixture washed with water. Separate layers did not form in the separatory funnel so the mixture was discarded. Evidently it was the unreacted ester which charred and gave off free sulfur. Reasoning, backwards, it would have been wise to have removed this ester before distillation by saponification with NaOH, then washing with water. This would have eliminated the sulfur and left only butyl alcohol along with the excess hexyl alcohol and possible butyl hexyl ether; all of which could be separated by fractional distillation. The ether formation was unlikely though, because of the above mentioned lack of separate organic and aqueous layers when the belated washing was administered. Due to the time element, no further experimentation with these esters was carried out because we realized that even if the process were perfected, it would still be a long operation involving a lengthy preparation of an intermediate.

### Use of Catalysts

The next possible preparation of ether experimented with was the catalytic action of p-toluene sulfonyl chloride upon two alcohols to cause the formation of ethers and water. With two alcohols, there should be three ethers formed, statistical yields giving two moles of the mixed ether per one mole each of the two symmetrical ethers.

Butyl and hexyl alcohols were used, one mole of each, with 0.1 moles of p-toluene sulfonyl chloride. After refluxing for three hours, the mixture was distilled, giving off fractions whose boiling points made them appear to be di-butyl ether (140°) and unreacted butyl alcohol (117°) and hexyl alcohol (157°). At this point, very little liquid was left. The temperature climbed steadily as the distillation continued and at 187° all the liquid had come over. An odor of sulfur oxides was detected towards the last of the distillation. Because of the sulfur odor, it was decided that it would be more expedient to remove the unreacted p-toluene sulfonyl chloride from the mixture before distillation. Accordingly, the experiment was repeated, washing after the refluxing process with sodium hydroxide. After further washing with water and drying over  $K_2CO_3$ , the mixture was distilled. This distillation was similar to the previous one with the exception that this time there was no odor of sulfur. The volume remaining after hexyl alcohol had distilled off was so small as to indicate that little or no reaction had taken place in the formation of ethers.

A similar experiment was tried, using p-toluene sulfonic acid instead of the chloride derivative as the catalyst. This time there was a slight tarring on first mixing the ingredients which gave promise of a faster, more positive reaction of some sort. But failure once more resulted as there seemed to be little in the distillate besides unreacted alcohols.

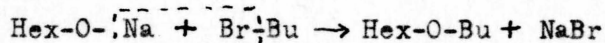
Perhaps we could have successfully prepared the ethers by this method with longer refluxing. We felt, however, that if refluxing for a day or two would give good yields, surely the first 3 or 4 hours of refluxing [during which time the rate of reaction is fastest] would give some detectable amounts of ether.

Copper Sulfate Synthesis

The catalytic synthesis had proved to be too mild for effectiveness. Sulfuric acid, on the other hand, which depended upon its dehydrating action (pulling out a molecule of water from between two alcohol molecules), was perhaps too vigorous. Among Dr. Reid's notes was a suggestion for using  $\text{CuSO}_4$  which would serve as a mild dehydrating agent. We hoped to find the happy medium here but after refluxing for 15 hours, a mixture of hexyl and butyl alcohols over anhydrous  $\text{CuSO}_4$ , there was no sign of reaction. If the white, anhydrous  $\text{CuSO}_4$  had acted as a dehydrating agent it would have been converted into the blue hydrated form. Such was not the case.

Williamson Synthesis

This well-known synthesis was resorted to, in spite of the fact that we had been warned against low yields, only after all the unsuccessful attempts previously described. A test-tube experiment was first tried, using butyl bromide and a slight excess of the sodium derivative of hexyl alcohol:



A heavy precipitate of sodium bromide was formed very quickly. This inorganic precipitate was washed out with water, the organic layer being dried and distilled. From the boiling point of one of the fractions of the product, we concluded that some ether had been formed. Accordingly, we followed the same procedure on a larger scale, heating the mixture for eight hours over the steam bath. The same precipitate of sodium bromide was formed and removed as before, and the organic layer was fractionally distilled. That fraction collected over the range which was predicted for butyl-hexyl ether was collected and dried over metallic sodium. The sodium reacted on the traces of hexyl alcohol in the ether, forming an alcoholate removable by filtration and distillation.

Physical Properties of the Product

So far as we were able to discover from a search of the Chemical literature, this is the first time that butyl hexyl ether has been prepared and estimates made of its physical properties. As previously stated, the yield from the Williamson Synthesis was very low, but it was the only synthesis that gave detectable quantities of the ether. We started with  $1/2$  mole portions of the alcohols which would have given a 100 % yield of 93 c.c. It was impossible to measure accurately the total ether formed, for much was lost in the attempts to remove the traces of alcohol by reaction with metallic sodium and distillation. A liberal estimate of the volume prepared would be approximately 10 c.c. giving an over-all yield of 11%.

A 0-300° degree thermometer, with divisions in whole degrees and calibrated through the range 122.5°-216° degrees by the melting points of various pure compounds, was used in the boiling point measurements. The ether vapors distilled over from an unpacked distillation flask between the range 181.5°-182.5°. Corrections were applied which gave the true boiling points as 185.5°-186.5° degrees at 740 mm. pressure.

A Fisher Refractometer, calibrated to units of 0.01, and with an accuracy of  $\pm 0.002$  was used in measuring the refractive indices of the two samples of ether prepared. These varied slightly in



the third decimal place, showing that either one or both of the samples had a small amount of impurity, - probably a trace of alcohol. These measurements were taken at 22.<sup>0</sup>

For the specific gravity, a 2 cc. weighing bottle was heated in a thermostat to constant weight. It was then filled with distilled water and weighed, the volume of the bottle being calculated from the specific gravity of water at the temperature used. Densities of the two samples were obtained by weighing in the bottle of known volume. The value of 0.777[8] for sample "B" is the one we think to be nearer correct because this sample was purified more carefully. As the chief impurity should have been a trace of alcohol with a density higher than this, it was only to have been expected that the less pure sample should show a somewhat higher density.

Tabulated Results

Of the two samples, "B" was reacted much longer with metallic sodium and we accordingly favor these results as more nearly representing the pure compound.

Boiling Point: 185.5<sup>o</sup>- 186.5<sup>o</sup> [740 mm]

Index of Refraction:

<u>A</u>	<u>B</u>
1.41[5]	1.41[3]
1.41[6]	1.41[3]
1.41[5]	1.41[4]

Specific Gravity:

<u>A</u>	<u>B</u>
0.780[1]	0.777[8]

Conclusion

Certain minor ideas on improvement of technique became obvious during the course of the experimentation. But the preparation of these higher mixed ethers remains a difficult problem and we are unable to suggest a simple synthesis which we think likely to produce good yields. The chemical literature mentioned, in several instances, catalytic preparations using very high pressures. With the proper equipment and more time to work on the subject, it would have been interesting to follow through on this type of synthesis.

Equipped as we are at present, however, the only method we can recommend as at all practical is the Williamson Synthesis which gave the results herein described. Certain other reactions might have given the desired products if we had had more time to follow through on them. Notable among these was the ester synthesis where our mistake was pointed out in not washing properly. And yet, the reaction as far as we carried it out did not show sufficient promise to warrant our further experimentation.

When an ether is synthesized, alcohol will nearly always be present to some extent as an impurity. The removal of this alcohol presents a perplexing problem and one with which it is difficult to cope. Even though their boiling points are nearly 30 degrees apart, hexyl alcohol and the ether could not be completely separated by a distillation column. Most of the hexyl alcohol came off at 153° and from there the temperature climbed slowly to 182° [uncorrected]. This brings to mind the question of an azeotropic mixture, which means that other means must be sought to remove alcohol from the ether.

Dr. Reid recommended the use of phthalic anhydride to form a mono ester [which is a solid], but this reaction did not go to completion as evidenced by liberation of hydrogen when a chip of metallic sodium was added. Removal by sodium was also slow, even when carried out on a boiling water bath, and the mixture had to be constantly redistilled to remove the sodium alcoholate which further slowed the reaction. Still, there appeared to be less loss of ether with the sodium and this was the method that we employed.

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