immons — Synthesis of cyclic ethers 1919

SYNTHESIS OF CYCLIC ETHERS

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1919

UNIVERSITY OF ILLINOIS

June 7 1919

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Paul Meade Ginnings

ENTITLED Synthesis of cyclic ethers

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry

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SYNTHESIS OF CYCLIC ETHERS

INTRODUCTION

Cyclic ethers, although only recently investigated to any great extent, have promised an interesting field for research and at the same time have shown the possibility of discovering new laws and syntheses in the field of organic chemistry. It was with the object of extending our knowledge of this class of compounds and also to find better synthetical methods, if possible, that this investigation was undertaken.

HISTORICAL

It has been shown that an easy method of preparing cyclic ethers is by using the ortho-allyl phenols as the starting point in the synthesis. Claisen[1] demonstrated that the ortho-allyl phenols can be prepared easily by the rearrangement of the corresponding allyl ethers. The general reaction is given as follows:

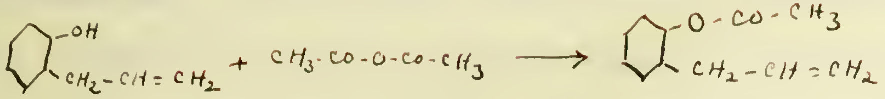
Claisen[2] also used pyridine hydrochloride to convert the ortho-allyl phenols into the methyl coumaranes. Reactions as follows:

R. Adams and R.E. Rindfusz[3] synthesized the methylene coumaranes readily from the ortho-allyl phenols by the following series of reactions:

(1) The acetylation of the ortho-allyl phenol.

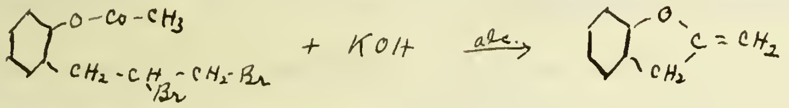
(Reactions given on the next page.)

(1) continued:



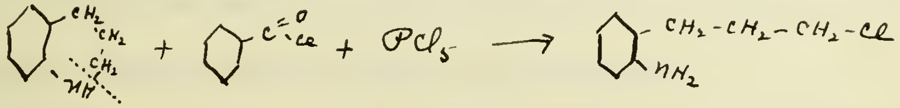
(2) Addition of bromine to the double bond.

(3) Treatment with alcoholic potash.

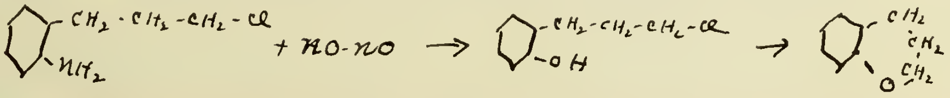


The reaction in the last case has been proved to be general with the ortho-allyl-phenols. In this work[3], they started out with the intention of preparing the six-membered unsaturated cyclic ether or chromene by a similar method to that used by Kostanecki[4] in the preparation of the flavones. But instead of obtaining the chromene as they expected, the last reaction failed to go according to the flavone synthesis and they obtained the methylene coumarane.

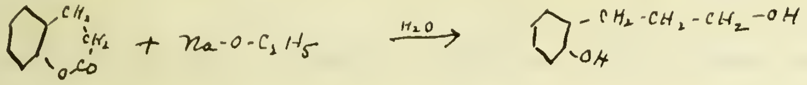
Other methods of attack on the problem of synthesizing these have been used. Von Braun and Steindorff[5] prepared the six-membered saturated cyclic ether or chromane in their work on the splitting of nitrogen ring compounds. They treated tetrahydro-quinoline with benzoyl chloride and phosphorus pentachloride and obtained gamma-chloro-ortho propyl aniline.



Then this last compound was diazotized to replace the amino group by an hydroxyl group and then the ring was closed by means of alkali, the final product being chromane.



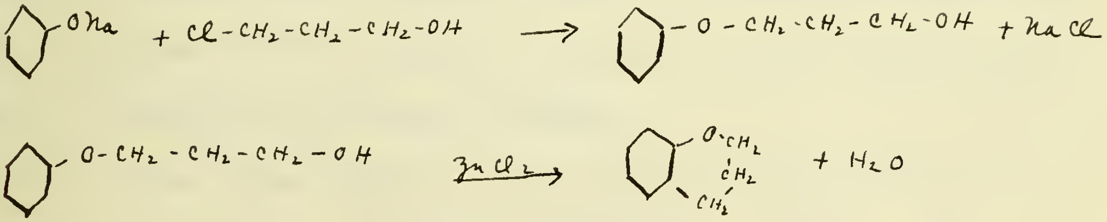
Even at its best, it is a very long and poor synthetical method. In 1906, Semmler[6], using his general method of converting lactones to glycols, reduced coumarin with sodium and alcohol to the ortho-gamma-hydroxy-propyl phenol as follows:



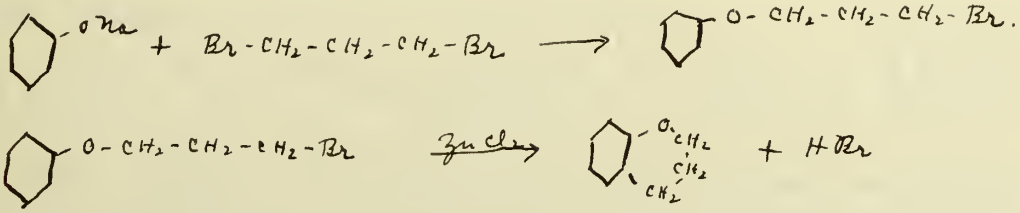
Then from this, he obtained the chromane by dehydration with sulphuric acid or alcoholic hydrogen chloride in a bomb.

These are the only methods of preparing chromane that have been published up to 1919. In this year, R.E.Rindfusz[7] prepared chromane by three new methods.

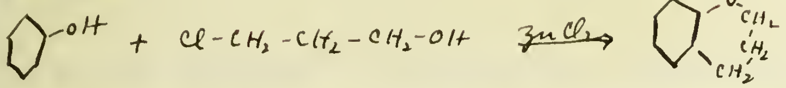
(1) "Trimethylene-glycol-monophenyl ether or ethylene-glycol-mono-phenyl ether, which are easily prepared from the corresponding chlorhydrine and sodium phenolate, is heated with zinc chloride. The reaction going as follows:



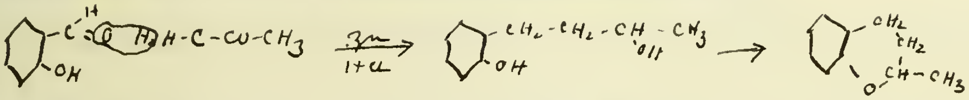
(2) Beta-bromo-ethyl-phenyl ether and gamma-bromo-propyl-phenyl ether are converted into cyclic ethers by the action of zinc chloride. The reaction being as follows:



(3) Free phenol when heated with ethylene or trimethylene chlorohydrine and zinc chloride gives coumarane or chromane as the case may be".

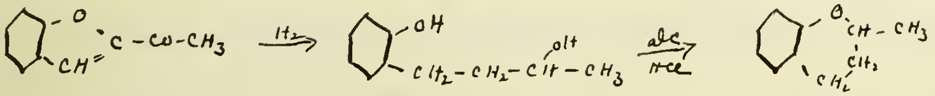


Other cyclic ethers, however, have been worked upon. Alpha-methyl chromane has been twice synthesized, by the path of ortho-gamma-hydroxy-butyl phenol. Harries and Busse[8] condensed salicylic aldehyde with acetone and reduced the product with sodium amalgam to give the saturated ketonic phenol:

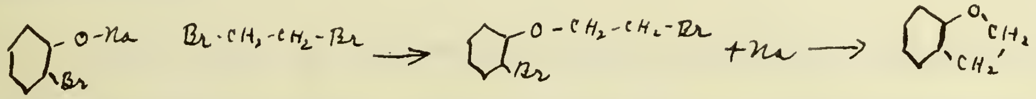


Then he reduced this still further with zinc and hydrochloric acid and this changed the group to an alcohol which reacted at once to form methyl chromane.

Stoermer[9] prepared and isolated this intermediate alcohol by reducing alpha-acetyl coumarone and then closed the ring by means of alcoholic hydrogen chloride.

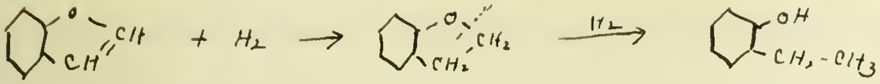


As concerning the work on coumaranes, Stoermer and Gohl[10] synthesized the parent substance by treating ortho-bromo-sodium phenolate with one molecule of ethylene bromide and then adding sodium.

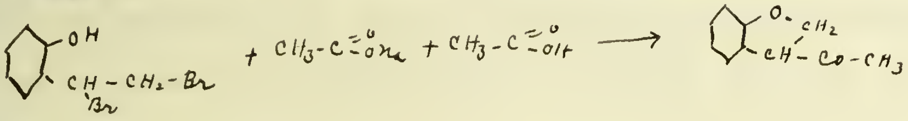


They also prepared the derivatives with one and two methyl groups in the benzene ring.

Alexander[11] had already obtained the same substance together with ortho-ethyl phenol by the reduction of coumarone.



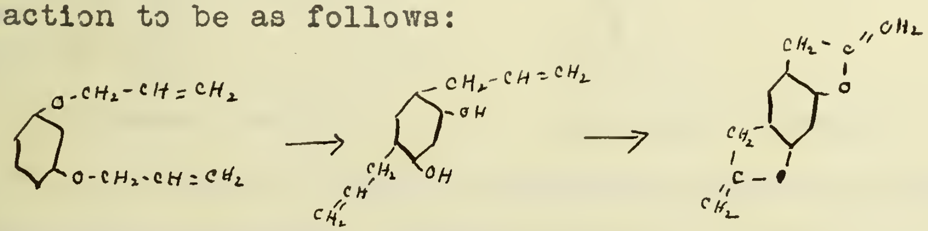
Fries and Moskopp[12] prepared the beta-acetyl derivative by treating ortho-1,2-dibromo-ethyl phenol with sodium acetate and acetic acid.



THEORETICAL PART.

An attempt at rearrangement of resorcinol di-allyl ether.

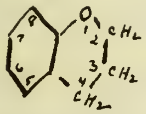
The first part of this investigation consisted in an attempt at the double rearrangement of the di-allyl ether of resorcinol. As Claisen[1] had been able to rearrange the allyl ethers of the phenols to the corresponding ortho-allyl phenols and R.Adams and R.E.Rindfusz[3] had taken the ortho-allyl phenols and prepared the corresponding methylene coumaranes, it was thought that it might be possible to get the double rearrangement of the di-allyl ether of resorcinol. Then by the method of Adams and Rindfusz, make the double methylene coumarane derivative. The probable reaction to be as follows:



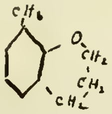
The di-allyl ether of resorcinol was accordingly made and the rearrangement attempted. Various ranges of temperatures and also catalysts were tried to induce the rearrangement but to no avail. The ether boiled at a high temperature and all attempts at rear-

rangement resulted in a mass of tars and carbon. Neither one or two allyl ether groups rearranged as was shown by the fact that none of it dissolved in strong alkali. Evidently then, the di-hydroxy phenols did not have the same property as the mono-hydroxy phenols, that of the rearrangement of the allyl ethers as was shown by Claisen[1], or the necessary temperature can not be reached without decomposition. Since the di-allyl ether would not rearrange then of course it was impossible to carry through the rest of the proposed synthesis.

The problem of the synthesis of the cyclic ethers can be approached from another angle, that is, the formation of the cyclic ether from the plain ether instead of from the ortho-allyl-phenol. Rindfusz[3] had prepared the chromane or coumarane by three different methods as was described under "Historical" on page three. As it was desirable to get the corresponding toluene chromane or 8-methyl chromane from ortho-cresol, the following procedure was performed: (The nomenclature used here in naming the chromanes will be the same as used by R.Stoermer.[14]) (In other words, the positions are numbered as shown in the following nucleus):



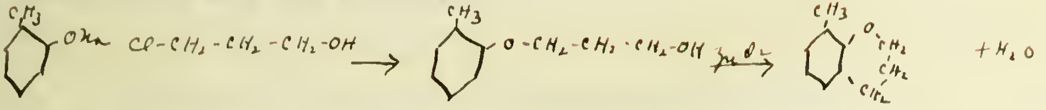
chromane nucleus



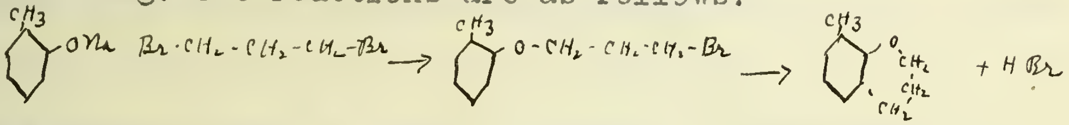
8-methyl chromane

In the synthesis, trimethylene hydrine ether of ortho-cresol or gamma-hydroxy-propyl toluene ether was prepared by the intera ation of sodium-cresolate and trimethylene chlorhydrine. The resulting ether was then heated with zinc chloride to close the ring. (See next page.)

The reactions are as follows:



The 8-methyl chromane was also prepared by first, the interaction of sodium cresolate and trimethylene bromide to form the gamma-bromo-propyl-toluene ether and then second, the action of heat on this ether in the presence of zinc chloride as a catalyst to close up the ring. The reactions are as follows:



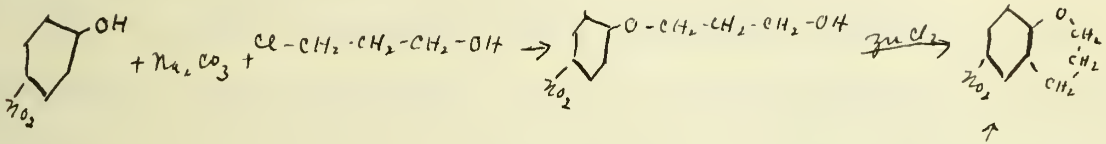
The 8-methyl chromane was prepared by a third method which consisted of the heating of a mixture of the free ortho-cresol, the trimethylene chlorhydrine and zinc chloride. However, the yields were too poor to make the method practical.

In the course of this investigation, the author thoughtof the possibility of the use of phosphoric pentoxide as the dehydrating agent for the closing up of the ring to form the chromane or the coumarane as the case may be. On first trial, the phosphorus pentoxide alone proved to be too strong and violent in its action so the next problem was to discover some means of slowing down the reaction and controlling it. This object was accomplished by diluting the ether with some non-reactive solvent such as benzene or toluene and then adding the phosphoric pentoxide, or still better, the phosphoric pentoxide is covered with the non-reactive solvent and then the ether is added to the solvent in small portions The mixture is then refluxed for a few hours, the excess of phosphorus pentoxide destroyed, diluted with water, the cyclic ether extracted with ethyl ether and distilled. The last method seemed to

give the greatest yields of any. In one case of the 8-methyl chromane, 76 % were obtained.

Attempt to prepare the 6-nitro-chromane.

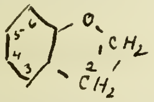
In this attempt, the trimethylene hydrine ether of the para-nitro phenol was prepared by refluxing the phenol with sodium carbonate and the trimethylene chlorhydrine for several hours. No trouble was experienced in obtaining the straight ether but attempts to close the ring were not rewarder with any success. Both the zinc chloride method and the phosphoric pentoxide method were tried but all went to tars and carbon. If the reaction had gone as was expected, it would probably been as follows:



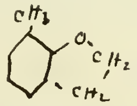
6-nitro-phenol.

Synthesis of the toluene coumarane or 6-methyl coumarane.

†In the naming of the coumarane derivatives, the nomenclature of R.Stoerner[15] will be used. The positions in the coumarane nucleus are numbered as follows according to the above nomenclature:

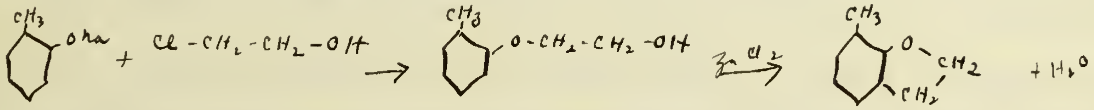


coumarane nucleus.

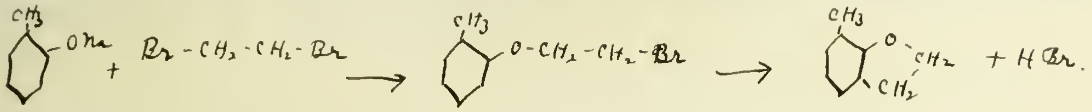


6-methyl-coumarane.

In the synthesis of the beta-hydroxy-ethyl toluene ether, it was first prepared by the interaction of ethylene chlorhydrine and sodium cresolate and then the ring closed by the action of heat and zinc chloride as the catalyst. The reaction is as follows:



The 6-methyl coumarane was also prepared by first, the synthesis of beta-bromo-ethyl toluene ether by the interaction of sodium cresolate and ethylene bromide and then closing the ring by heating with zinc chloride as a catalyst. Reaction as follows:



6-methyl coumarane.

The 6-methyl coumarane was prepared thirdly by the heating of a mixture of free ortho-cresol, ethylene chlorhydrine, and zinc chloride but the yields were very poor, too small to make the method practical.

The 6-methyl coumarane was synthesized fourthly by the phosphoric pentoxide method. First, the beta-hydroxy-propyl-toluene ether was prepared by the interaction of ethylene chlorhydrine and sodium cresolate. Then this was dehydrated in exactly the same manner as is given under the preparation of the toluene chromane or 8-methyl chromane on page seven.

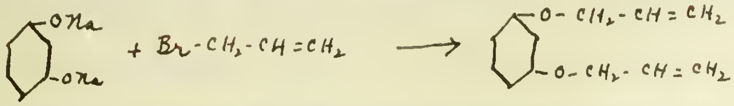
In comparing the above four methods, the phosphoric pentoxide in general gave the greatest yields, the chlorhydrine and zinc chloride method second, the bromo ether and zinc chloride third in order, and the lowest yields by the heating of the mixture of the free phenol, the chlorhydrine, and the zinc chloride. Other catalysts might possibly be used but none were found that worked so well as the anhydrous zinc chloride.

The action of anhydrous zinc chloride is not as a selective catalytic agent because, as is seen above, it will either split out the HOH or the HBr as the case may be. On the other hand, the

phosphoric pentoxide is selective in that it splits out HOH from the hydroxy ether and does not split out the HBr from the bromo ether. This fact will probably play an important part in the synthesis of cyclic ethers.

EXPERIMENTAL PART

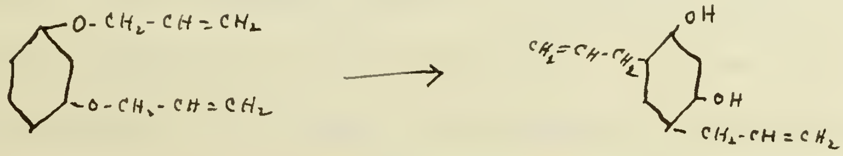
SYNTHESIS OF THE DI-ALLYL-RESORCINOL ETHER



10 grams of sodium were dissolved in 300 cc. of absolute alcohol. Then 22 grams of resorcinol were added with shaking and the mixture heated on the steam bath for 30 minutes. 44 grams of allyl bromide were then added in small portions through the top of the reflux condenser to the sodium cresolate and this refluxed on the steam bath for about two hours. The reaction being completed, the flask was changed to a distilling apparatus and most of the alcohol in the mixture distilled off. The residual solution was then diluted several times with water, extracted with ether, the ether extract washed with water several times, and then dried with anhydrous sodium carbonate. The ether extract was then distilled under reduced pressure and the fraction of 210-215 degrees taken. This upon redistillation gave a practically colorless viscous liquid boiling at 212-213 degrees under 60 mm. pressure. It boils also at 158 degrees at 7 mm. pressure. Yield= 30 % of the theoretical. Refractive index= 1.5470 at 27 degrees C. Specific gravity = 1.0830 at 29 degrees.

Analysis gave:-- 859.6 cc. of CO_2 at 741.4 mm. pressure, and 31 deg.
% of C found in the above compound = 74.1. Theoretical = 75.78.

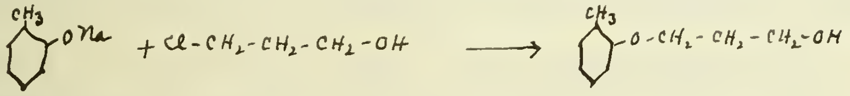
ATTEMPTS TO REARRANGE THE DI-ALLYL-RESORCINOL ETHER



The first attempt to rearrange the ether was by simply heating di-allyl resorcinol ether for various lengths of time. However, the ether gradually went to tars and carbon upon long periods of heating. None of the product would dissolve in strong alkali, showing that none, not even one of the allyl groups had rearranged.

The next attempt was by the use of a catalyst, the one tried being anhydrous zinc chloride. This presence of the catalyst seemed to speed up the decomposition but none of the ether would rearrange, not even on long continued periods of heating of the ether in a ground glass round bottomed reflux air condenser. Considerable carbonization and tarry products were obtained in all cases and no rearrangement could be produced.

SYNTHESIS OF THE GAMMA-HYDROXY-PROPYL-ORTHO-TOLUOL ETHER



In this synthesis, practically molecular proportions can be taken. - 58 grams of sodium were dissolved in 500 cc. of absolute alcohol in a five liter flask which was connected up to a water reflux condenser. Then 270 grams of ortho-cresol were added to this in small portions and with shaking. 235 grams of trimethylene chlorhydrine were added and the mixture refluxed several hours on the steam bath until the reaction was complete. The flask was then transferred to a distilling apparatus and most of the alcohol distilled off. The residual portion was diluted with water, dried over night with anhydrous sodium carbonate, and then distilled under reduced pressure. A viscous, colorless oil came over at 174-176

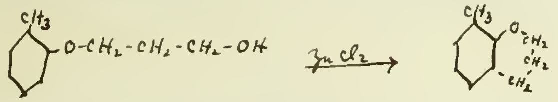
degrees at 42 mm. pressure. The yield was 65 % of the theoretical. Refractive index = 1.5219 at 27 degrees C. Specific gravity was 1.0530 at 29 degrees C.

Analysis gave:- Sample used = .2864 grams.

458.9 cc. CO_2 were generated at 741.3 mm. pressure and 30.7 deg.C.

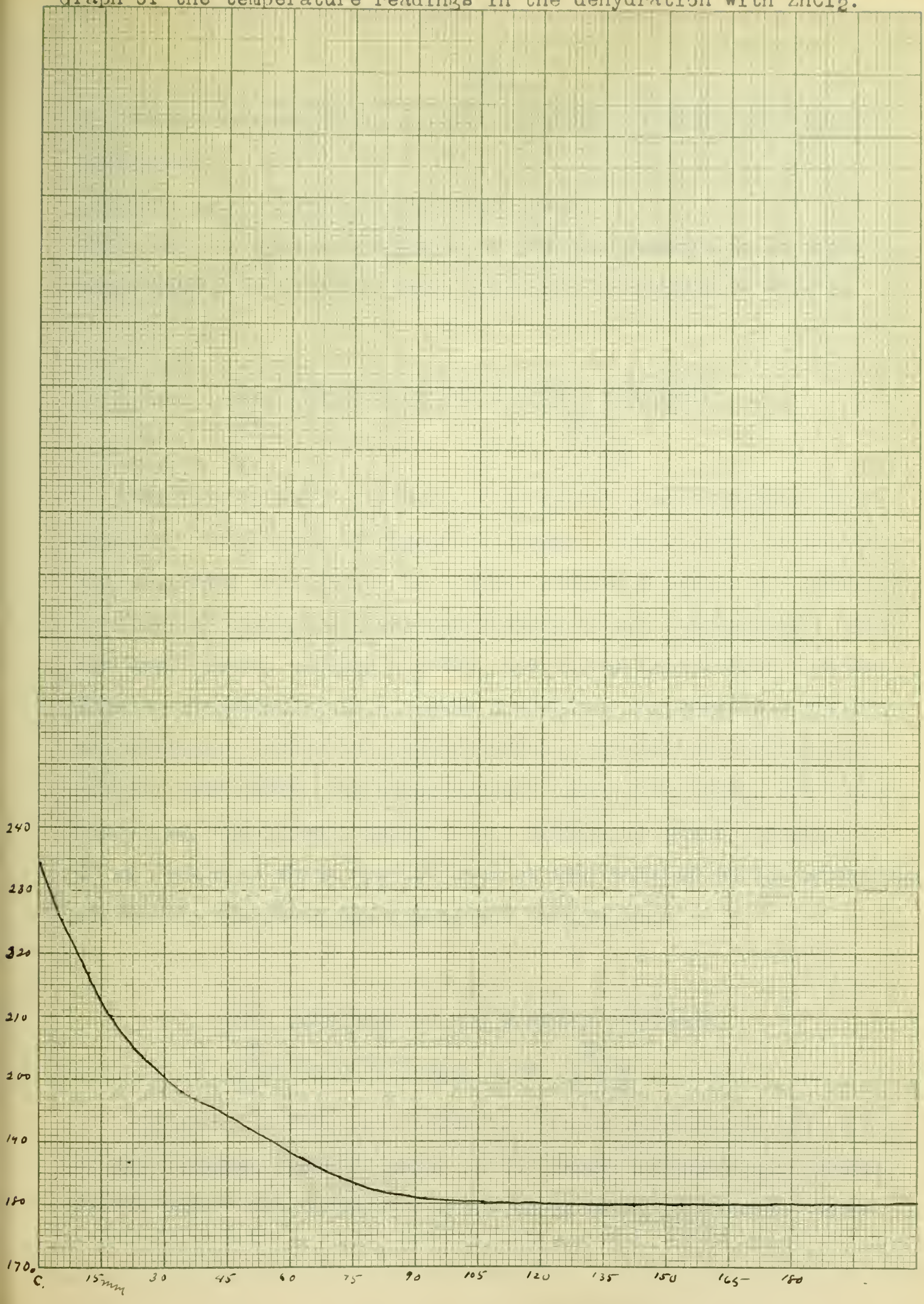
Found 71.85 % of C in the above compound. Theoretical = 72.3 %.

I- SYNTHESIS OF THE 8-METHYL CHROMANE.



70 grams of the gamma-hydroxy-propyl-ortho-toluol ether were heated in a ground glass air reflux condenser for three hours at a temperature of from 180 to 230 degrees Cent., with 10 grams of anhydrous zinc chloride. The zinc chloride dissolved rapidly and after a few minutes of heating, water began to condense on the upper portions of the reflux tube. The temperature drop was considerable as can be seen by the graph on the next page. As soon as the temperature of the thermometer , which had been lowered through the top of the reflux tube, was constant, the bulb was cooled and the contents of the flask transferred to a distilling flask. The mixture was distilled under reduced pressure and the fraction from 90-120 degrees C. collected. This was refractionated and the fraction 98-105 degrees saved. This was refractionated still another time, the final product boiling at 101-103 degrees at 16 mm. pressure (or 114-5 degrees at 20 mm. pressure). It is a colorless oil the odor of which is like that of cresol but none of it dissolves in alkali,showing that none of the free cresol is present. The yield obtained was 5 % of the theoretical. Refractive index = 1.5416

Graph of the temperature readings in the dehydration with $ZnCl_2$.



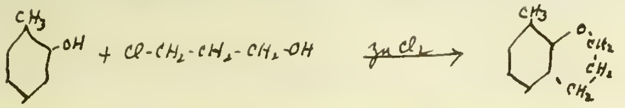
at 27 degrees Centigrade. Specific gravity = 1.0390 at 29 degrees Centigrade.

Analysis gave:- Sample taken .3716 grams.

623.1 cc. of CO_2 were generated at 747 mm. pressure at 24 degs. C.

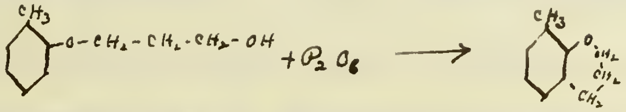
Found 81.4 % of C in the above compound. Theoretical = 81.1 %.

II- SYNTHESIS OF THE 8-METHYL CHROMANE.



In this method, a mixture of 64 grams of trimethylene chlorhydrine , 73.5 grams of the ortho-cresol , and 5 grams of anhydrous zinc chloride were heated in a glass stoppered reflux air condenser for several hours until the temperature of the thermometer , which had been lowered through the top, had become practically constant. This was transferred to a vacuum distilling apparatus and the liquid distilled. After two fractionations, the oil was washed with alkali, with water, the ether extract dried with $CaCl_2$, and again distilled, the product being an oil boiling at 114-115 degrees at 20 mm. pressure which was the same as was obtained in the preceding synthesis. The yield was 1 % of the theoretical.

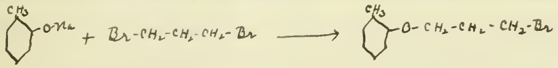
III- SYNTHESIS OF THE 8-METHYL CHROMANE.



40 grams of P_2O_5 were taken in a flask and covered with 200 cc. of dry benzene. Then 100 grams of the gamma-hydroxy-propyl-ortho-toluol ether were added, the flask being cooled meanwhile. Ether

was added (the gamma-hydroxy-propyl-ortho-toluol ether) in small portions with shaking to mix thoroughly and , after using all ofthe 100 grams , the benzene portion was transferred to a vacuum distilling apparatus and the liquids fractionated out. The fraction 114-16 degrees amounted to about all, other than the benzene. This was washed with alkali, with water , dried , and redistilled with practically no loss in weight , showing that there was very little splitting of the ether. It gave the same colorless oil with the cresol odor that was obtained in the above two syntheses. The yield was 76 % of the theoretical. This method gave by far the best product, the boiling point being constant at 114-5 degrees at 20 mm. pressure.

SYNTHESIS OF GAMMA-BROMO-PROPYL-ORTHO-TOLUOL ETHER.



23 grams of sodium were dissolved in 200 cc. of absolute alcoholand to this, 108 grams of the ortho-cresol were added with shaking until the completion of the reaction. Then to this mixture of the sodium cresolate, twice the molecular amount of the trimethylene bromide or 405 grams was added in one portion so that there was an immediate excess of the trimethylene bromide[13]. The mixture was refluxed on the steam bath for two hours, the contents transferred to a distilling apparatus , most of the alcohol distilled off, the residual liquid diluted with water, extracted with ether, the ether extract washed with alkali, with water, dried with $CaCl_2$ and distilled in a fractionating column. The product or gamma-bromo-propyl-ortho-toluol ether is a clear oil,has a fragrant odor and boils at

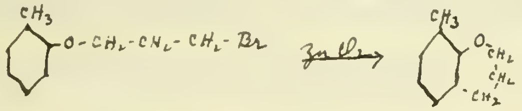
154-6 degrees Centigrade at 20 mm. pressure. Index refraction = 1.5354 at 27 degrees Centigrade. Specific gravity = 1.2990 at 29 degrees Centigrade. Yield = 25 % of the theoretical.

Analysis:- Sample taken =.2816 grams.

Obtained .2280 grams of silver bromide.

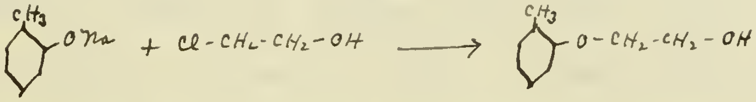
Found 34.5 % of Br in the above compound. Theoretical = 34.9 %.

IV- SYNTHESIS OF 8-METHYL CHROMANE.



50 grams of the gamma-bromo-propyl-ortho-toluol ether were placed in a glass stoppered , reflux air condenser and 5 grams of anhydrous zinc chloride added. The mixture was heated to about the boiling point whereupon clouds of HBr were emitted from the top of the tube of the condenser. The heating was continued for one-half hour, the mixture transferred to a distilling apparatus, and the 8-methyl chromane distilled over at 114 to 116 degrees at 20 mm. pressure. This was washed with alkali, water, dried with $CaCl_2$, and distilled, giving the final product or the 8-methyl chromane. The physical properties coincide with those of the products obtained by the other three methods.

SYNTHESIS OF BETA-HYDROXY-ETHYL-ORTHO-TOLUOL ETHER.



46 grams of sodium were dissolved in about 200 cc. of absolute alcohol and, after the sodium ethylate was completely formed, 216 grams of ortho-cresol were added, and the mixture was then heated

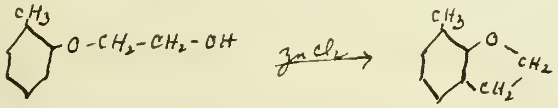
for a short time on the steam bath. 160 grams of ethylene chlorhydrine were added in small portions with shaking, and the resulting mixture refluxed on the steam bath for three hours. The contents were transferred to a distilling apparatus, most of the alcohol distilled over, water added, extracted with ether (ethyl) , the ether extract distilled under reduced pressure after drying and an oily product obtained. The clear viscous oil boiled at 143-5 degrees under 20 mm. pressure. The yield was 72 % theoretical. Index refraction= 1.5284 at 27 degrees Centigrade. Specific gravity was 1.0785 at 29 degrees Centigrade.

Analysis gave:- Sample taken = .4700 grams .

Obtained 750.0 cc. CO_2 at 739.1 mm. pressure and 30.9 degrees Cent.

Found = 71.25 % of C in the above compound. Theoretical = 71.0 %.

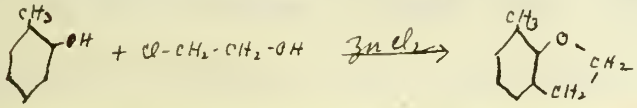
I- SYNTHESIS OF THE 6-METHYL COUMARANE.



75 grams of the beta-hydroxy-ethyl-ortho-toluol ether were put in a ground glass air reflux condener with 7 grams of anhydrous zinc chloride. This was heated about three hours, the procedure being similar to that as described under the preparation of the 8-methyl chromane by the dehydration of the alcohol phenol by means of anhydrous zinc chloride. The product was transferred to a distilling apparatus, distilled, washed with NaOH, water, dried , redistilled giving finally a clear oil with a cresol-like odor , that boiled at 119-20 degrees Centigrade at 65 mm. pressure. Yield = 5.3 % of the theoretical. Index of refraction = 1.5270 at 27 degrees Centigrade Specific gravity = 1.0000 at 29 degrees Centigrade.

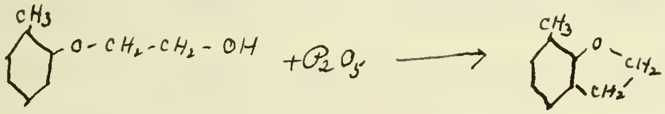
Analysis of the above compound gave :- Sample taken = .2258 grams. 377.2 cc. of CO_2 obtained at 747 mm. pressure and 24 degrees Cent. Found 80.9 % of C in the above compound. Theoretical = 80.6 %.

II- SYNTHESIS OF THE 6-METHYL COUMARANE.



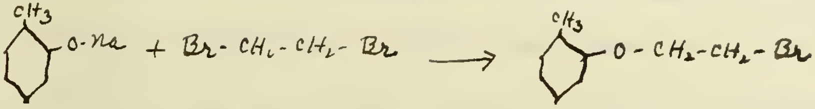
A mixture of 108 grams of ortho-cresol, 80 grams of ethylene chlorhydrine, and 20 grams of anhydrous zinc chloride was refluxed in a ground glass reflux condenser for several hours. The resulting mixture was then distilled , washed with alkali, with water, dried, redistilled twice, and the product taken as that which boiled at 118 to 125 degrees at 65 mm. pressure. It was the same as the product synthesized in the I synthesis above. Yield = 1 % theoretical.

III- SYNTHESIS OF THE 6-METHYL COUMARANE.



The directions for this synthesis are exactly the same as those for the synthesis of the 8-methyl chromane. The product was the same as those obtained in I and II syntheses given above. In this case the yield was about 50 % of the theoretical.

SYNTHESIS OF BETA-BROMO-ETHYL-ORTHO-TOLUOL ETHER.

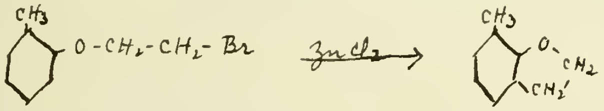


23 grams of sodium were dissolved in 200 cc. of absolute alcohol and then 108 grams of ortho-cresol added to this until the re-

action was completed.[13] 380 grams of ethylene bromide or twice the theoretical amount was added in one portion to this mixture of sodium cresolate. This was refluxed for three hours, the contents transferred to a distilling apparatus, most of the alcohol distilled off, the residual contents diluted with water, extracted with ethyl ether, the ether extract washed with alkali, with water, dried, and redistilled. The product was a clear sweet smelling oil, boiling at 133-4 degrees Centigrade at 20 mm. pressure. Index of refraction = 1.5441 at 27 degrees Centigrade. Specific gravity = 1.3600 at 29 degrees Centigrade. Yield = 39 % theoretical.

Analysis gave :- 37.5 % Br. in compound. Theoretical = 37.2 %.

IV- SYNTHESIS OF THE 6-METHYL COUMARANE.



50 grams of the beta-bromo-ethyl-ortho-toluol-ether were heated in a glass stoppered reflux air condenser with 5 grams of anhydrous zinc chloride for one hour, large volumes of HBr being evolved. The product was transferred to a distilling apparatus, distilled , washed with alkali, with water, dried with $CaCl_2$, redistilled and the product obtained was the same as that in I, II, and III methods of synthesizing the 6-methyl coumarane. Yield = 5 % of the theoretical.

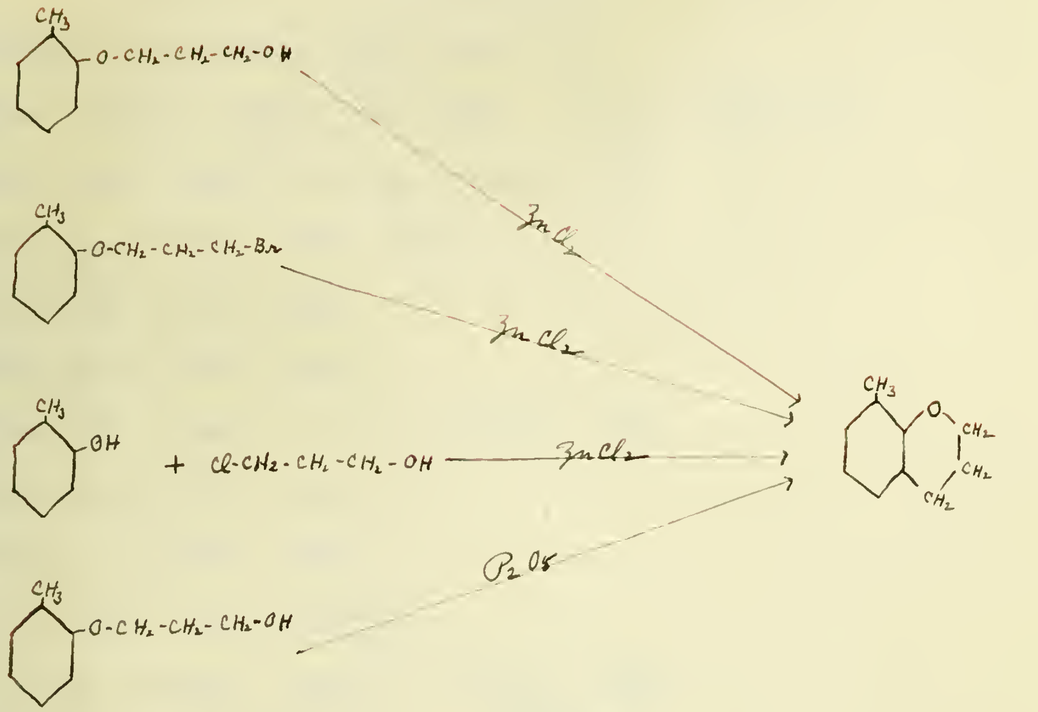
SUMMARY.

I- The di-allyl resorcinol ether has been prepared and it has been shown that it does not rearrange to form the ortho-allyl phenol as is the case with the mono-hydroxy phenols.

II- A new method for the synthesis of cyclic ethers has been

developed, namely, the method using phosphoric pentoxide as the dehydrating agent to close the ring in the chromanes or the coumaranes, as the case may be.

III- Both the chromane and coumarane of ortho-cresol (8-methyl chromane and 6-methyl coumarane) have been prepared by four different methods, the relations being shown diagrammatically on the following page.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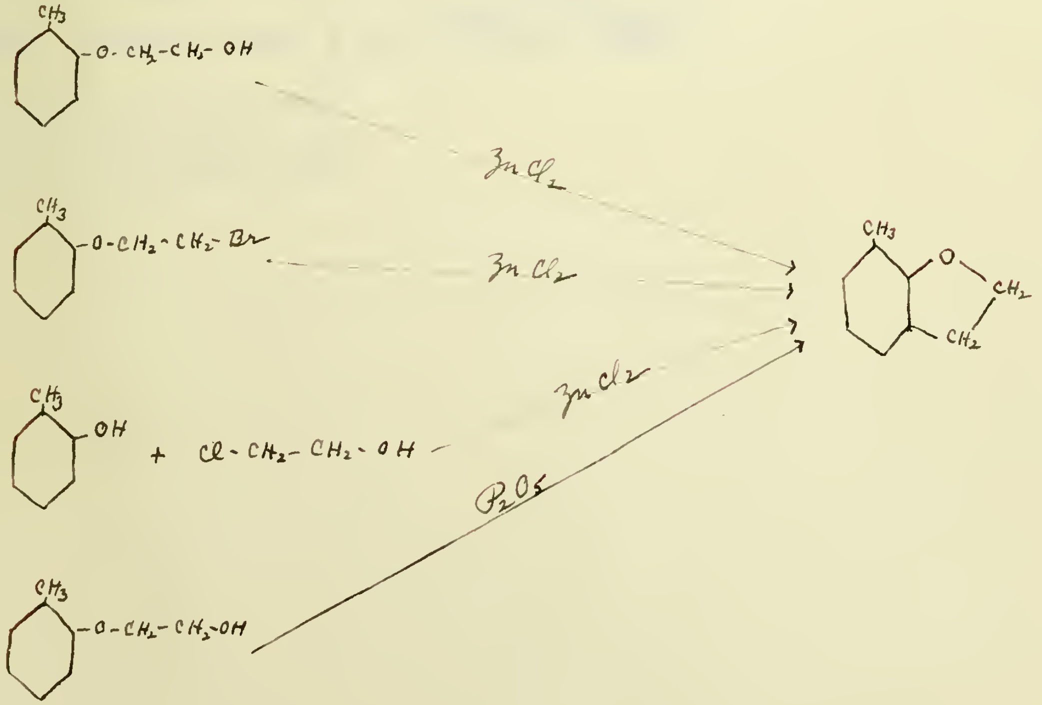
O-CH2-CH2-CH2-OH
CH3
O-CH2-CH2-CH2-Br
CH3
OH
+ Cl-CH2-CH2-CH2-OH
CH3
O-CH2-CH2-CH2-OH
ZnCl2
ZnCl2
ZnCl2
P2O5
CH3
O
CH2
CH2
CH2


CH3
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CH3
O-CH2-CH2-Br
CH3
OH
+ Cl-CH2-CH2-OH
CH3
O-CH2-CH2-OH
ZnCl2
ZnCl2
ZnCl2
P2O5
CH3
O
CH2
CH2

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ACKNOWLEDGMENT

THE WRITER WISHES TO TAKE THIS OPPORTUNITY TO THANK DR. R.E. RINDFUSZ, AT WHOSE SUGGESTION AND UNDER WHOSE KIND DIRECTION THIS WORK HAS BEEN PERFORMED.