University of Louisville

ThinkIR: The University of Louisville's Institutional Repository

Electronic Theses and Dissertations

1934

Butyl and ethanol ethers of the ortho, meta and para xenols.

Mary Agatha O'Neill
University of Louisville

Follow this and additional works at: <https://ir.library.louisville.edu/etd>

Part of the [Chemistry Commons](#)

Recommended Citation

O'Neill, Mary Agatha, "Butyl and ethanol ethers of the ortho, meta and para xenols." (1934). *Electronic Theses and Dissertations*. Paper 1851.
<https://doi.org/10.18297/etd/1851>

This Master's Thesis is brought to you for free and open access by ThinkIR: The University of Louisville's Institutional Repository. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of ThinkIR: The University of Louisville's Institutional Repository. This title appears here courtesy of the author, who has retained all other copyrights. For more information, please contact thinkir@louisville.edu.

UNIVERSITY OF LOUISVILLE

BUTYL AND ETHANOL ETHERS OF THE ORTHO, META AND
PARA XENOLS.

A Dissertation

Submitted to the Faculty of the Graduate
School of the University of Louisville
In Partial Fulfillment of the
Requirements for the Degree
of Master of Science

Department of Chemistry

by

Mary Agatha O'Neill

1 9 3 4

CONTENTS.

	Page
Part I.	
Introduction	1
Objective	3
Part II. Phenyl Ethers.	
Purpose	7
Preparations of Ethers in General	9
Preparation of Alkyl Phenyl Ethers	10
Williamson Reaction	11
Purification of Cresyl Ethers	12
Rearrangement of Phenyl Ethers	12
Summary	18
Part III. Xenyl Ethers.	
Preparation	20
Xenyl Ethers (Not Substituted) Found in Literature:	
Table of Their Physical Properties	21
Identification	23
Summary (Historical)	24
Part IV. Preparation of the Butyl and Ethanol Ethers of Ortho, Meta and Para Xenol.	
Reaction to be Used.....	26
Materials	26
Properties of the Ortho, Meta and Para Xenols:	
Table	28
Experimental	
Preparation I of Para Butyl Xenyl Ether	29
(Includes Preparation of Dry Sodium Salt of Para Xenol).	

Preparation II of Para Butyl Xenyl Ether	31
Preparation of Para Ethanol Xenyl Ether	33
Preparation I of Ortho Butyl Xenyl Ether	35
Preparation II of Ortho Butyl Xenyl Ether	37
Preparation I of Ortho Ethanol Xenyl Ether	38
Preparation II of Ortho Ethanol Xenyl Ether ...	39
Preparation III of Ortho Ethanol Xenyl Ether ..	40
Preparation I of Meta Butyl Xenyl Ether	42
Preparation II of Meta Butyl Xenyl Ether	42
Preparation of Meta Ethanol Xenyl Ether	44
Summary	45
Table of Experimental Data	49
Part V. SUMMARY	50
Bibliography	51

Part 1.

INTRODUCTION

The field of organic chemistry has for some years offered rich opportunities to the research chemist. Especially in the last few years has industry found in this branch of science many new fields for developing compounds of great commercial significance. In looking over the advertisements in recent copies of many popular periodicals, the names of duprene, cellophane and hexylresorcinol suggest only partly the important part the organic research man has played in industry today. The very fact that a manufacture puts out an antiseptic, brazenly bidding for popularity, under the burden of the highly technical name of "hexylresorcinol solution" shows that at least he thinks that the average man is aware of the scientific achievements forming the basis for much of our modern life and is acquiring an active interest in scientific things which in the present time due to the approaching perfection of mechanical apparatus is branching out to the broader phases of chemical and physical science. Duprene suggests the romantic lure that the search for a satisfactory substitute for rubber held for the organic chemist for a number of years, culminating last year in the successful product

of Hleuwlend (1) of Notre Dame University which was perfected later in a commercial laboratory. This is the first of the synthetic rubbers (2) that has given the same type of X-ray diagram as the natural product and both equalled and surpassed it in physical properties, its vulcanization being simpler and its latex more penetrating. Turning to magazines of a technical nature, we find greater evidence of the importance of organic research. Morris (3) of the Massachusetts Institute of Technology, while preparing an article on research and industrial chemistry in the latter part of 1931 when the financial condition of the country was at a low point, found in the pages of a copy of Industrial and Engineering Chemistry forty-two compounds advertised that were available for large scale use. Many of these were new substances, the rest have been used but now are at a lower price and in a purer condition as a result of the application of new synthetic methods. "A study of the methods by which these results have been reached shows clearly that chemical research of a high order is the foundation upon which the achievements rest." (3).

There are three driving forces for research in industry.(3)

The first is to reduce the cost of materials used in some preparation in order to lower the cost of the product. Acetic acid is a good example of this. Two new methods have lowered its cost considerably; calcium carbide (from coal), and, catalytic oxidation of alcohol by air. The second motive, the use of waste materials and by-products to prepare valuable substances has always been a

fascinating field of endeavor to the chemists. It is only recently that outstanding results have been obtained: the wastes from oats, cottonseed and corn stalks are now valuable chemical compounds. The third is found when the need arises to prepare substances that possess the particular physical properties required for a specific use. The change from paint to lacquer in the auto industry created a need for solvents. These three commercial needs: reduction of cost of raw materials, use of waste materials, and the lack of a material with specific properties for a certain use constitute the basis for the industrial research.

The three driving forces of industrial research, together with a fourth commonly called pure research, or work on those problems primarily of academic interest but as they involve fundamentally the theories of science often greatly effect the industrial laboratory, constitute also the basis of academic research or that carried out in the laboratories of universities or endowed research centers.

The OBJECTIVE of this particular research problem, the preparation of the butyl and ethanol ethers of the ortho, meta and para xenols,* and, the study of the physical properties of

* The group was first known as "diphenyl". When confusion arose with compounds containing two phenyl groups that were non-adjacent, it was then termed "biphenyl". The most recent name applied to the configuration is "xenyl"; the hydroxy derivatives, previously called "hydroxydiphenyls" or "hydroxybiphenyls" under this new system will be called "xenols".

these ethers, followed from the second commercial motive for research, the use of waste materials and by-products to prepare new substances. The waste material in this instance is the para and ortho xenols now obtained as a by-product in the manufacture of phenol. (4)

(By the addition of diphenyl oxide to a sodium carbonate chlorobenzene reaction mixture, a yield practically one hundred per cent of phenol was obtained with the complete hydrolysis of chlorobenzene. Diphenyl oxide and the benzene halides are mutually miscible and together emulsify with aqueous caustic. The diphenyl oxide restrains the reaction from going too far. The nascent hydrogen found in the reaction in contact with certain metals, and, free phenol which is always found in the presence of sodium phenolate liquors, form xenol, ortho and para. Two explanations are given for this result. First, hot chlorobenzene brought suddenly in contact with caustic soda forms para and ortho chloroxenyl which is the hydrolyzed to the corresponding xenol. Second, Glanz proposes the tautomeric or keto form of phenol. That is in aqueous solutions

Under such conditions we can see the greater tendency for reaction of the hydrogen atoms on the reduced nuclear carbon atoms, and hence condensation with chlorobenzene

might easily produce under the influence of alkali

Para xenol is one of the main products left in the waste tar after the phenol and diphenyl oxide (remaining from the reaction compounds) have been removed from the reaction mass: twenty to twenty-five per cent of waste tar is monoxenol, three-fourths of which is para-xenol, the remainder ortho xenol. It is well established that copper possesses a particular aptitude to speed up its formation and the preparation of these two xenols on a large scale by the use of extensive surfaces of metallic copper in a reaction mixture of benzene halides and caustic alkali, or alkaline-earth hydroxides in aqueous solution, is a simple matter from the manufacturing standpoint and only awaits the creation of an industrial demand for ortho and para xenol. The ortho and para xenol thus obtained as a waste by-product in the manufacture of phenol were to be the starting points for the preparation of the butyl and ethanol ethers of the ortho and para xenols, and, as an additional form, the meta xenol (5), was known to exist, the meta compounds were added to complete the series.

In the selection of the particular ethers of the ortho, meta and para xenols to be prepared, the butyl ether was chosen as a simple type of an alkyl xenyl ether (as some of the first

6.
members of the series, the methyl and ethyl (5) (6) (7), were prepared some years ago, it would also serve as a check on the earlier methods of preparation); the ethanol ether furnishes an entirely different type of ether, as it has an alcoholic hydroxyl (OH) group (an interesting result in the rearrangement of this ether might be found). Therefore, these two series of xenyl ethers, the ethanol and the butyl seemed to be a good starting point for further work on the xenyl ethers.

The two probable industrial outcomes seen at the beginning of the problem were the possibilities of the use of the butyl and the ethanol ethers of the ortho, meta and para xenols as starting points for two problems that might have commercial significance; the rearrangement of some to substituted phenols and the establishment of a satisfactory method for the preparation of a stable xenyl-xenyl ether having a higher boiling point than diphenyl oxide and having a similar use as a boiler fluid.(8)

The purely scientific significance of the possible rearrangement of these xenyl ethers is of great interest. Much work has been accomplished in the study of the rearrangement of the more highly substituted xenyl ethers in the study of the stereochemistry of xenyls by Roger and Yuan at the University of Illinois. This is leading to a more complete understanding of the configuration of the xenyl group which has long been a subject of intense interest to organic chemists.

Part II.

PHENYL ETHERS.

In order to facilitate, if possible, the preparation of the ortho, meta and para butyl and ethanol xenyl ethers, ethers in general and phenyl ethers in particular were studied together with their respective methods of preparation. The ethers that are the objective of this particular problem, that is

ortho butyl xenyl ether

meta butyl xenyl ether

para butyl xenyl ether

ortho ethanol xenyl ether

meta ethanol xenyl ether

para ethanol xenyl ether

are related more closely to the alkyl phenyl ether, that is those of the form $\text{O} - \text{R}^*$, than to the simple alkyl ethers of the type $\text{R}^* - \text{O} - \text{R}^*$. A series of the alkyl phenyl ethers, the cresyl ethers, that is an ether with a methyl group directly attached to the benzene ring have ortho, meta and para forms in an isomeric group similar to that of the xenyl ethers. In consideration of these last two facts, this study in the preparation of ethers was limited chiefly to the alkyl phenyl ethers and the alkyl

ALKYL CRESYL ETHERS.

cresyl ethers, because of their close relationship to the desired xenyl ethers.

From the compounds discussed above, it is readily seen that ethers are organic oxides in which the two hydrogen atoms of water have been replaced by alkyl or aryl groups. Williamson definitely proved this explanation of the structure of an ether in the report on his research on etherification first read at the meeting of the British Association at Edinburgh in 1850. This proof followed a procedure analogous to the following (10): methyl ethyl ether is first prepared by heating ethyl iodide with sodium methylate; if the oxide theory was to hold true, methyl ethyl ether should also

*
R an alkyl group, a straight chain of carbon atoms.

be prepared as the result of the interaction of sodium ethylate and methyl iodide; the reaction turned out as expected, there-

fore as methyl ethyl ether can be prepared in both ways, the view that it and other ethers are oxides of radicals in which the two alkyl or aryl groups, or, an alkyl and aryl group are joined directly to oxygen appears to have a satisfactory experimental basis.

There are four general methods for preparing ethers: first, treating alcohols with sulphuric acid (11), an example of which is the preparation of methyl ethyl ether from the respective alcohols, ethyl alcohol and methyl alcohol, by gently heating ethyl alcohol with sulphuric acid to form ethyl sulphuric acid which in turn reacts with methyl alcohol to form methyl ethyl

ether; second, the Williamson reaction (10), examples of which are given in the preceding paragraph on the structure of an ether, that is the action of alkyl halides on sodium or potassium, alkylate or phenylate; third, from alkyl halides and dry silver oxide (11), or mercuric oxide, an example of which is the preparation of ethyl ether from ethyl iodide and silver oxide; and,

fourth,

the dehydration of alcohols or phenols (12), an example of which is the preparation of the ethyl ether from ethyl alcohol when heated to 400° Centigrade in the presence of finely divided

aluminum oxide.

There are two methods which can be used for the preparation of alkyl phenyl ethers. It is possible to prepare them from the second method above, that is by the Williamson reaction (13). Heating phenol with zinc chloride or aluminum chloride will give diphenyl oxide (13) or diphenyl ether in a method analogous to the first method above but sulphuric acid cannot be used. This reaction yields only simple ethers or those that have two similar groups attached to the oxygen atom so it will not give alkyl phenyl ethers whose groups are different. The diazonium salts react with the organic substitution products of water, such as alcohols and phenols. By this method anisole or phenyl ether (14) can be prepared from benzene diazonium chloride and methyl alcohol.

Of the two methods used for the preparation of the alkyl phenyl ethers, the Williamson reaction and the diazonium reaction, the former that is the combination of a sodium salt of a phenol and an alkyl halide seemed to be the simpler so it was investigated

further. It was found (19) that the reaction would have a possibility of taking place in a water medium, or, methyl or ethyl alcohol (also acetone as a rule), or, with perfectly dry materials, but not in a non-dissociating media, e.g. benzene or toluene (in this type of medium, the product would be an alkyl derivative, the alkyl group directly connected to the phenyl group). Vincent (16) prepared phenyl methyl ether or anisole by passing the methyl chloride vapors through dry sodium phenolate heated to 190° - 200° Centigrade. One hour was sufficient to decompose one kilogram phenolate. Vincent prepared this alkyl phenyl ether in a dry medium.

PHENYL METHYL ETHER

Recently, Sowa, Hinton and Nieuwland (22) successfully prepared alkyl phenyl ethers and alkyl cresyl ethers in a water medium. Isopropyl meta cresyl ether was prepared by first weighing one mole of meta cresol into a liter flask fitted with a reflux condensor and a dropping funnel. A sufficient amount of water was added to fifty-nine grams (excess) of potassium hydroxide to make a thick mixture and this was added to the phenol. The whole mass was heated until the solution became complete; then, 125 grams (excess) of isopropyl bromide was added, the contents were refluxed for one and one-half hours, then poured into 400 cubic centimeters of water to dissolve the sodium bromide formed. The oil separating on the top was the ether. The yield in the method

ISOPHOPYL META CRESYL ETHER

was high being about 88 per cent of the theoretical. From the data given above, it is easily seen that the Williamson reaction is very satisfactory for the preparation of alkyl phenyl ethers.

Cresyl ethers prepared according to the Williamson reaction can be purified by first washing with an alkaline solution, then removing the ether in a separatory funnel or in some cases, it was more convenient to extract with ether and evaporate the ether on a water bath. Oil was then washed twice with a fifty cubic centimeter portion of saturated salt solution and then with twenty cubic centimeters of distilled water. Liquid was then dried over potassium carbonate and let stand over night. It was then distilled over sodium and fractionated several times. (15)(17)(22)(8)

REARRANGEMENT OF PHENYL ETHERS.

Since the possibility of the rearrangement of the ortho, meta and para butyl and ethanol xenyl ethers into the corresponding substituted phenols formed one of the probable uses of these ethers, the rearrangements of phenol ethers were investigated.

Ethers are very stable compounds but some phenol ethers have been found under certain conditions to rearrange within the molecule into the isomeric phenol. The processes were simple and form easy methods for preparing the respective substituted alkyl phenols, which would be difficult to prepare otherwise (24). In this manner a new method has been found for the preparation of thymol (1-methyl-4 isopropyl-3-hydroxy-benzene) (18), a germicide that is less active and less poisonous than phenol, from the intramolecular rearrangement of isopropyl meta cresyl ether, a meta methyl para isopropyl phenol being formed at the same time. Therefore it was hoped that some of the butyl and ethanol xenyl ethers would rearrange into the isomeric phenols; this was true especially of the ethanol ethers, as from the data given in the following paragraph, it was scarcely probable that the normal butyl xenyl ethers would give their isomeric phenolic compounds.

In the course of research on the cresyl ethers, it has been found that normal, propyl, butyl and amyl para cresyl ethers would not rearrange (24) but gave the original phenol and the corresponding alkyl acetate. All of the secondary alkyl phenyl ethers studied, rearranged, while tertiary alkyl phenyl ethers gave the best yield of substituted phenol on rearrangement. This rearrangement of phenyl and cresyl ethers has been accomplished by four different methods: first, heating the ether to a high temperature (20) (21); second, using a reaction mixture of zinc chloride and hydrochloric acid (23); third, using a reaction mixture of glacial acetic and sulphuric acids (24); and, fourth, by treatment with

boron fluoride gas.

By the first method alkyl phenyl ethers have been rearranged. Alkylated phenols and their derivatives are prepared by heating alkyl ethers (20) of the phenols or their derivatives to a high temperature under pressure, optionally in the presence of surface catalyzers. Thus phenyl ethyl ether was heated to 280° - 320° Centigrade in an autoclave to give para ethyl phenol and a small quantity of diethylphenol. Claisen (21) by heating certain allyl aryl ethers to a high temperature, transformed them into the isomeric nuclear substituted phenols, i.e. the allyl phenols. If the alkyl group (22) is substituted for the allyl group, isomerisation does not take place under the influence of heat alone, the presence of inorganic substances being necessary in most cases.

The second method for the rearrangement of phenyl ether, that is treating the ether with zinc chloride was used in the transforming (23) of ortho tolyl triphenyl methyl ether into 4-2 hydroxyphenyl- β, β, β -triphenylethane. The ether was treated with half its weight of dry zinc chloride for one hour at 180° Centigrade. It was isolated by a method originated by Van Alphen. The migration of the triphenyl methyl group to the methyl group wasn't entirely anticipated but this formation has been confirmed by two separate and distinct pieces of work on this subject (23) (22). But, in the case of triphenyl methyl phenyl ether, when rearranged according to this method, i.e. when treated with hydrochloric acid or zinc chloride, the triphenyl group migrated to the para position

in the ring as would be expected forming para triphenyl phenol.

The third method, that is using a reaction mixture of glacial acetic acid and concentrated sulphuric acid, was the one most commonly used, most likely as it gave good results while at the same time making use of common laboratory reagents and apparatus. Following this method Niederl and Matelson (25), used a reaction mixture of 200 cubic centimeters of concentrated sulphuric acid in sufficient glacial acetic acid to make up a liter. One molecular weight of the prepared ether was placed in a round bottom flask and 250 cubic centimeters of the above mixture added. The mixture was then refluxed for five hours. Two layers separated at first which redissolved. On long standing, about five hours, a heavy oil separated at the top. This was separated. After extraction with ten per cent potassium hydroxide, a small amount of ether remained which was reclaimed. When the alkaline residue was neutralized, an oil separated on standing which was in turn extracted with ether, the ether then distilled off, and the residue fractionated. The intramolecular rearrangement of isopropyl meta cresyl ether, under the influence of this mixture, gave thymol and meta methyl para isopropyl phenol (preparations mentioned in first paragraph under the REARRANGEMENT OF PHENOL ETHERS page 12), the products thus obtained furnishing a new synthesis of thymol.

The fourth method, treatment with boron fluoride gas (22), a result of the search for uses for this new compound, is the most recent. It was carried out by weighing one mole of the alkyl phenyl or alkyl cresyl ether into a 500 cubic centimeter flask

fitted with a three hole stopper through which a thermometer and an inlet tube were inserted to reach below the surface of the liquid. Boron fluoride gas was passed into the ether through the inlet tube. Temperature ranged from 27° to 43° Centigrade when three grams were added. The reaction took place immediately and gave a high yield of the isomeric phenol which was then purified.

The study of the rearrangements of these ethers leads to an interesting field in theoretical chemistry, that is the explanation of the reaction that takes place when a phenyl ether changes into a substituted phenol.

That the chemical nature of the catalyzer does not play any integral part in these molecular migrations has been shown (26) and has been further verified recently by Sowa, Hinton and Nieuwland (22) who checked the synthesis of thymol. The following conclusions were drawn: first, the reaction appears to be unimolecular in nature; second, the reaction is not reversible; third, rearrangement is possible by the mere application of heat, or by the use of a rearranging agent which seems to play the part of a catalyst (zinc chloride or hydrochloric acid; glacial acetic acid and sulphuric acid; boron fluoride).

Claisen and his co-workers state that the allyl radical (24) does not attach itself to the cyclic nucleus through the same carbon atom which was bound to the oxygen, in the rearrangement of allyl phenyl ethers, and so started chemists thinking towards

the formation of a reasonable theory that would be supported by the experimental data on the rearrangement of phenol ethers already in literature. Van Alphen advanced a theory of oxonium compound formation which cannot be applied without reservation, because rearrangement of unsaturated and also of long chain saturated alkyl phenyl ethers is possible by mere application of heat. Considering this discrepancy, Niederl and Storch (18) advanced a reaction mechanism for the rearrangement of ethers as well as the addition reaction of the corresponding phenols to allyl alcohols involving the postulations of Van Alphen, Lapworth, Latimer and others. In the case of the sulphuric acid rearrangement mixture, the ether forms a transitory phenyl isopropenyl oxonium sulphate (II) with a higher energy potential, then goes to the more stable quinoid configuration (III). Then to a still more stable one of a hemi-acetal structure (IV). Hydrolysis with the elimination of sulphuric is brought about resulting in the phenol (V).

The reaction from (I) to (II) is a gain of repulsion energy. All the succeeding intramolecular rearrangements are accompanied by

losses of repulsion energy until the more stable phenol with the least intramolecular energy content is obtained. This mechanism is not specific for a rearranging mixture of sulphuric acid and glacial acetic acid. Where boron trifluoride or other substances have been used, the reaction mechanism may be postulated as being quite similar except that as addition of boron trifluoride takes place instead of sulphuric acid in (II). In cases where heat alone has been applied, assuming the formation of oxonium compounds between identical molecules, then the succeeding transitory bimolecular addition compounds of the quinhydrone type may be formed and finally the substituted phenol is obtained.

SUMMARY.

I. Because of the similarity of structure between the ortho, meta, and para, butyl and ethanol xenyl ethers, and, the alkyl phenyl and alkyl cresyl ethers, the preparations of the latter were studied in order to facilitate the preparation of the former, the OBJECTIVE of this thesis.

II. One of the general methods for preparing ethers, the Williamson reaction, that is the reaction between the sodium salt of an alcohol or of a phenol, and an alkyl halide, (which reaction Williamson used to definitely prove the structure of an ether as an organic oxide in which the two hydrogen atoms of water have been replaced by alkyl or aryl groups) has been successfully used

in a dry medium, a water medium, and methyl or ethyl alcohol, to prepare alkyl phenyl ethers and alkyl cresyl ethers. Another reaction was found in which diazonium salts react with the organic substitution products of water, such as alcohols and phenols to form alkyl phenyl ethers. The Williamson reaction was the simpler of the two and the one more widely used.

III. Since the possibility of the rearrangement of the ortho, meta and para butyl and ethanoxenyl ethers into the corresponding substituted phenols formed one of the probable uses of these ethers, the rearrangement of phenyl and cresyl ethers were likewise investigated. This was found to take place usually in the presence of a catalyst, such as zinc chloride, hydrochloric acid, glacial acetic acid and concentrated sulphuric acid, or, boron fluoride gas. As normal butyl para cresyl ether did not rearrange into the corresponding cresol, it was not probable that the butyl para xenyl ether would rearrange. The explanation of the migration that takes place within the molecule forms an interesting study in theoretical chemistry, the latest theory advanced being an oxonium quinoid - hemi - acetal postulation involving the earlier theories of Van Alphen, Lapworth, Latimer and others.

Part III.

XENYL ETHERS.

Several of the simple xenyl ethers have been prepared although most of the work of the research chemist has been on the substituted ethers of the xenyl series, as the dinitromethoxyxenyl (26). The ortho methyl xenyl ether (7), the ortho ethyl xenyl ether (7) and the meta ethyl xenyl ether* (5) (6) have been prepared according to the two methods discussed in the preceding chapter for the preparation of alkyl phenyl and alkyl cresyl ethers, that is the Williamson reaction, and, the reaction between diazonium salts and the organic substitution-products of water, such as alcohols and phenols. Para methyl xenyl ether (28) has been recently prepared as a dehydrogenation product (27) of 1-para anisyl-cyclohexanol which was in turn obtained from para anisyl-magnesium bromide and cyclohexane in an attempt to discover a better process for the preparation of the unsymmetrical derivatives of xenyl. The preparation of the xenyl ethers from the Williamson reaction and the diazonium reaction will be discussed in the following paragraphs.

Two of the xenyl ethers mentioned above, the ortho methyl xenyl ether and the ortho ethyl xenyl ether were prepared in a perfectly dry media under the pressure of a column of mercury. Honigschmidt (7) heated ortho xenol with ethyl iodide and sodium

* An early dissertation of Teichmann gives the first data on these ethers (6).

XENYL ETHERS (NOT SUBSTITUTED) FOUND IN LITERATURE

XENYL ETHER	FORMULA	MELTING POINT	BOILING POINT	SOLUBILITY	METHODS OF PREPARATION
meta ethyl (6)	OCH	34 C	305 C 310 C 227-230 C 25 mm	Soluble in organic solvents insoluble in water	I Desaminized product of ortho ethoxy benzidine (5) II Williamson reaction (5) in dry medium
ortho ethyl (32)	OCH	34 C	276 C	readily soluble in ethyl alcohol benzene ethyl ether	I Williamson reaction (7) in dry medium
ortho methyl (32)	OCH	29 C	274 C		I Williamson reaction (7) in dry medium
para methyl (28)		90 C 89 C (27)	174 C (18 mm)		Dehydrogenation of 1-para anisylcyclohexanol (28)
	OCH				

phenolate on a water bath under a pressure of an eight centimeter long mercury column. He obtained lustrous prisms of ortho ethyl xenyl ether that after recrystallization from petroleum ether had a melting point of 34° Centigrade and a boiling point of 276° Centigrade. The compound was readily soluble in alcohol, ether, benzene, chloroform, logroin, and insoluble in water. In an analogous way ortho methyl xenyl ether was prepared. Itcrystallized in lustrous prisms from petroleum ether with a melting point of 29° Centigrade and a boiling point of 274° Centigrade. The molten substance crystallized in long flat tablets.

For the preparation of meta ethyl xenyl ether, Jacobson and Loeb (5) used a medium of absolute alcohol. They refluxed meta xenol in absolute alcohol with an equivalent of metallic sodium in absolute alcohol, and ethyl iodide for four hours. The alcohol and water were then distilled over. The alkali residue under vacuum distillation, 2 millimeters pressure at 160° - 161° Centigrade gave about two grams of oil, crystals immediately forming. Recrystallization from dilute ethyl alcohol of the meta ethyl xenyl ether prepared in the above manner gave crystals melting at 34° - 35° Centigrade.

Two of the xenyl ethers prepared according to the Williamson reaction were also prepared by the second method for the preparation of alkyl phenyl ethers, that is by the diazotation of an oxybenzidine. To prepare ortho methyl xenyl ether, Honigschmidt (6) dissolved methoxybenzidine in concentrated hydrochloric acid and diazotized it. The ice cold diazonium product was then mixed with cold stannous chloride. After standing for two hours, the chlorohydrate was mixed with soda lye precipitating the free hydrazin with ether. Then the ether extract was heated to boiling under

good agitation with a ten per cent solution of copper sulphate. The methyl xenyl ether was formed while passing into this solution a stream of water vapor. It was left in the form of a brown oil which was identified by mixing the known crystals with the oil obtained. The mixture solidified and the surplus oil was pressed out on clay. The new crystals melted at 29° Centigrade, the melting point of the ether prepared according to the Williamson reaction. The deaminized product of ortho ethoxybenzidine gave a melting point of 34° Centigrade, the same as that of the meta ethyl xenyl ether prepared by Jacobson and Loeb.

In establishing the formula for these compounds, carbon (6) hydrogen analysis gave a fairly good check, for example in the identification of meta ethyl xenyl ether the following was obtained:

	carbon	hydrogen
calculated	84.81%	7.12%
found	84.24%	7.13%

(from a 0.2331 gram sample, taken of the substance, was

obtained 0.1484 grams water, and 0.7220 gram carbon dioxide).

but Teichman originated a hydrogen-iodide red phosphorus method of proving the structure of an alkyl phenyl ether which was used to further substantiate the identification of these ortho methyl, ortho ethyl and meta ethyl xenyl ethers. An example is the identification of ortho methyl xenyl ether by converting it into xenol. The ortho methyl xenyl ether was refluxed with five parts

of hydrogen iodide for eight hours. The product was then treated with red phosphorus and the comparison extended to the xenol. The impurities were removed through extraction with ether. The ether solution was then passed through dilute alkali and then precipitated with carbonic acid. After recrystallization from petroleum ether, the melting point was 68° Centigrade. There was no lower melting point obtained when a mixed melting point was taken with Honigschmidt's ortho xenol and the product obtained. By using the carbon hydrogen analysis and the hydrogen-iodide-red phosphorus methods, a double check was used in the identification of these ethers.

SUMMARY.

Several of the more simple xenyl ethers have been prepared although most of the work of the research chemist has been on the substituted ethers of the xenyl series as the dinitromethoxyxenyls. In 1901, Honigschmidt prepared the ortho methyl and ethyl xenyl ethers with a modification of the Williamson reaction. Later he prepared the ortho methyl and the meta ethyl ethers as reduction products of ortho methoxy and ethoxybenzidine. The accounts of the preparations of the preceding ethers mention a dissertation of Teichmann as giving the first data on these compounds. The para methyl xenyl ether has been prepared by the dehydrogenation of 1-para-anisylcyclohexanol obtained through the use of a Grignard reagent, para-anisyl magnesium bromide, and cyclohexane in an

attempt to discover a better process for the preparation of unsymmetrical derivatives of xenyl than the methods now in use. In addition to the carbon hydrogen Liebig combustion analysis method for organic compounds, a hydrogen iodide - red phosphorus method originated by Teichmann may be used for the identification of ethers by converting them to the original phenol.

Part IV.

PREPARATION OF THE BUTYL AND ETHANOL ETHERS OF ORTHO, META AND PARA XENOL.

It was decided to prepare the ethers that form the objective of this problem, that is ortho butyl xenyl ether, meta butyl xenyl ether, para butyl xenyl ether, ortho ethanol xenyl ether, meta ethanol xenyl ether, and para ethanol xenyl ether (formulas given on page 7) according to the Williamson reaction as (a) the reaction substances were readily available, (b) it was the simpler of the two reactions found for preparing alkyl phenyl ethers and alkyl cresyl ethers, and, (c) it had already been used successfully in the preparation of other members of the simple alkyl xenyl ether series, that in the ortho methyl and ethyl, and, meta ethyl xenyl ethers.

The raw materials necessary for the Williamson reaction for the preparation of ethers were the potassium or sodium salt of an alcohol or phenol, and an alkyl halide. For the preparations of these ethers, the potassium and sodium salts of the ortho, meta and para xenols were used together with butyl bromide for the butyl ethers, and ethylene chlorohydrin for the ethanol ethers. The xenols were obtained from a manufacture of phenol,* the ortho and para being waste by-products in the manufacture of phenol but the meta was a synthetic compound. To convert the xenols into the

* Dow Chemical Company, Dow, Michigan.

PHYSICAL PROPERTIES OF THE XENOLS

XENOL	FORMULA	MELTING POINT	BOILING POINT	SOLUBILITY
ortho		53°C.(32) 56°C.	145°C.(35) 14 mm. 275°C. 760 mm.	*soluble in ethyl alcohol ethyl ether insoluble in cold water
meta		76°C.(5)		soluble in (5) benzene ethyl alcohol ethyl ether chloroform glacial acetic acid *difficultly soluble in hot water insoluble in cold water cold toluene
para		160- 162°C.(33) 164- 165°C.	305- 308°C.(33)	*soluble in ethyl ether hot toluene hot benzene hot butyl bromide insoluble in water cold toluene cold benzene cold butyl bromide

*Tested in laboratory.

The dry reaction between sodium salt of a phenol and an alkyl halide was first tried as it was successfully used in the preparation of ortho methyl and ethyl xenyl ethers.

EXPERIMENTAL.

PREPARATION I OF PARA BUTYL XENYL ETHER.

The sodium salt of para xenol was prepared from sodium hydroxide and para xenol. One half mol (85.5 grams) para xenol was refluxed for one hour with a 15 per cent excess of 0.5 mol (25 grams) sodium hydroxide in 206 cubic centimeters of water so that the sodium salt could crystallize from a hot 30 percent solution of the same. The white flaky precipitate

was filtered hot with small loss. The product was a white monoclinic crystalline substance which was then washed with concentrated sodium hydroxide and dried under suction (in vacuum) for one-half hour at room temperature, put on oil bath which was kept at 100° Centigrade for two hours, raised to 200° - 210° Centigrade for four hours and then cooled gradually still connected with the suction pump. The sodium salt of para xenol prepared in this manner was thought to be perfectly dry and

free from the original xenol.

One-tenth mol of the sodium salt was refluxed with 0.4 mol (61.1 grams) butyl bromide which was first redistilled and the middle portion (boiling point 100° Centigrade) used, for eight and one-half hours with a calcium chloride tube on end of the condensor. The cold substance contained a white pre-

cipitate which was filtered off and extracted with ether. The ether extract when evaporated yielded a small amount of para xenol (melting point 163° Centigrade). When the butyl bromide liquid residue* was evaporated, it yielded a very small portion of a white flaky substance with a melting point of 69°-70° Centigrade which was thought to be the para butyl xenyl ether.

A second run was made using identical amounts of material but refluxing for seventeen and one-half hours. 16.5 grams of solid remained after extracting the product with ether. The ether extract yielded, after evaporation, a solid of about one gram.

A second attempt was made to prepare a purer portion of the sodium salt of para xenol. Forty-five percent excess of

*One gram of para xenol was completely dissolved by boiling for three minutes in ten grams of butyl bromide; on cooling it re-crystallized out in a yield of 100% of para xenol.

sodium hydroxide in 350 cubic centimeters of water, with 0.5 mol of para xenol was heated until all the lumps of the phenol dissolved; on cooling a good yield of the white flaky sodium salt was obtained which was then dried in a vacuum on an oil bath at 100° to 140° Centigrade for two hours. Then a small stream of air, first dried by passing through calcium chloride, was passed through it and the bath gradually heated to 190°-200° Centigrade during twenty five minutes. Three layers formed. The top was a white substance consisting of needles of para xenol, melting point 165° Centigrade; the middle was burned to a dark brown; and, on the bottom was a very fine white crystalline substance thought to be the sodium salt. The bottom layer gave no melting point, a characteristic of sodium salts. The sodium salt evidently when heated in air was converted back into the original para xenol. Therefore to obtain a pure sodium salt, the substance must be in a vacuum and should be used immediately to give the best results, as it will then have the smallest probability of containing the impurity of the original phenol.

PREPARATION II OF PARA BUTYL XENYL ETHER.

The next preparation of para butyl xenyl ether was made according to the preparation of alkyl phenyl ethers directly from the phenol, potassium hydroxide and the alkyl halide, all carried out in a water medium. (22)

One-tenth mol (17 grams) of para xenol was weighed into a 500 cubic centimeter flask fitted with a reflux condensor and a dropping funnel. Twenty cubic centimeters of water were added

to 7.3 grams potassium hydroxide (30 percent excess of 0.1 mol) and added to the phenol. It was then heated for five minutes until solution became complete, a brown liquid forming. Then 30 percent excess of 0.1 mole (17.8 grams) of butyl bromide was added slowly while shaking and warming. Reaction took place immediately. After all the butyl bromide was added, the mixture was refluxed for one hour. 150 cubic centimeters of water when added to the hot mixture precipitated a white solid which was filtered off and washed with 50 cubic centimeters of water dilute potassium hydroxide and then with water. The precipitate weighed 18 grams, melting point 73° Centigrade. On standing, the liquid filtered off formed white flat, flaky, shining, opaque crystals with the same melting point, raising the total yield to 21 grams. Washed with hot water, the product had a melting point of 71.5° Centigrade; recrystallized from hot ethyl alcohol, it gave a melting point of 73° Centigrade which was not changed by further recrystallization from alcohol.

A second run was made using two times the quantity of phenol and potassium hydroxide as used above with 0.2 mole (28 grams) of butyl bromide. The yield was forty grams. Purified as above, the product gave a melting point of 73° Centigrade. Mixed melting point of the two products did not lower this figure. From this run, it is seen that the excess amount of butyl bromide, other than the molecular combining weight needed for the reaction, is not necessary.

Analysis for carbon and hydrogen content according to the Liebig combustion method gave

	I.	II.
grams sample	0.1427	0.1506
grams water obtained	0.1028	0.1070
grams carbon dioxide obtained	0.4448	0.4681
carbon content	84.97%	84.80%
hydrogen content	8.08%	7.95%
percentage carbon content (found)	84.89%	
percentage hydrogen content (found)	8.00%	
percentage carbon content (calculated)	84.90%	
percentage hydrogen content (calculated)	8.02%	

PREPARATION OF PARA ETHANOL XENYL ETHER.

Para ethanol xenyl ether was prepared in an analogous manner to PREPARATION OF PARA BUTYL XENYL ETHER II. The reacting substances used were; 30% excess of 0.1 mole (26.3 grams of 40 per cent water solution) ethylene chlorohydrin; 0.1 mole (17 grams) para-xenol; and, 30 per cent excess of 0.1 mole (7.3 grams) potassium hydroxide in 20 cubic centimeters of water. The mixture was continuously stirred by a glass stirring rod extending through the condenser down to the reaction flask from an electric motor. The ethylene chlorohydrin was dropped slowly into the hot mixture of potassium hydroxide, para-xenol and water during two hours of refluxing, the mixture being constantly stirred. The refluxing was then continued for an additional hour.

Ethylene chlorohydrin reacts with the potassium (30) hydroxide to form ethylene oxide, which in turn reacts with the phenol to form an ether.

ETHYLENE
CHLORO- POTASSIUM ETHYLENE POTASSIUM
HYDRIN plus HYDROXIDE yields OXIDE plus WATER plus CHLORIDE

PARA ETHYLENE
XENOL plus OXIDE yields PARA ETHANOL XENYL ETHER.

The product was diluted with 200 cubic centimeters distilled water and filtered. The filtrate was washed with hot water. Crystals in the cold resultant filtrate melted at 138° to 144° Centigrade, evidently some unchanged para-xenol. The precipitate was again washed with hot water and then extracted with ether. The ether extract when evaporated yielded a white substance, melting point of 107° Centigrade which did not change on repeated recrystallization from hot anhydrous toluene. A yield of 16 grams, (77 per cent) was obtained.

A second run was made with double the amount of the reacting substances that was used in the first preparation. Ten grams additional potassium hydroxide were added and the refluxing continued one half hour longer. A yield of thirty eight grams of 88 per cent was obtained. The two products had identical melting point 107 Centigrade of small white crystals, the entire product

being powdery in appearance as a whole.

grams sample	0.1713
grams water obtained from analysis	0.1010
grams carbon dioxide obtained from analysis	0.4922
percentage carbon content (found)	78.37%
percentage hydrogen content (found)	6.59%
percentage carbon content (calculated)	78.47%
percentage hydrogen content (calculated)	6.59%

PREPARATION I OF ORTHO BUTYL XENYL ETHER.

The ortho butyl xenyl ether was prepared by dropping 30 per cent excess of 0.3 mol of butyl bromide (53.4 grams) into a hot refluxing mixture of 0.3 mol (51 grams) ortho xenol and 30 percent excess of 0.3 mol potassium hydroxide (21.9 grams) in 200 cubic centimeters of water, during two hours and then refluxing for one hour. The reaction mixture was stirred constantly with an electrically driven glass stirring rod extending through the reflux condenser. On cooling two layers separated. The top

dark orange layer was treated with 50 percent potassium hydroxide solution, and the alkaline layer drawn off. The other layer, still dark orange, was acidified with dilute hydrochloric acid and the acid layer separated. The liquid thought to be ortho butyl xenyl ether still retained the orange color. Yield was 54.5 grams. Vacuum distillation gave three fractions as follows:

	temperature	pressure
I. colorless	70°C.-100°C	200mm
II. yellow orange liquid.....	268°C.-270°C.	200mm
III. pale yellow liquid.....	135°C.-160°C.	24mm

Fractions II and III were redistilled;

IIA. pale yellow liquid.....	132°C.-138°C.	18mm.
IIIA. pale yellow liquid.....	134°C.-138°C.	16mm.

The heavy dark residue in both cases was thrown away. Fractions IIA and IIIA were redistilled over an oil bath. The middle fraction with a constant boiling point of 134.3°Centigrade at a pressure of 10 millimeters was used for analysis. Yield was 15 grams.

Analysis for carbon and hydrogen content according to the Liebig combustion method:

	sample I.	sample II.
grams sample	0.1500	0.1612
grams water obtained on analysis	0.1063	0.1118
grams carbon dioxide obtained on analysis	0.4634	0.4953.
percentage carbon (found)	84.26%	83.80%
percentage hydrogen (found)	7.97%	7.76%

average percentage carbon (found)	84.03%
average percentage hydrogen (found)	7.87%
calculated carbon content	84.90%
calculated hydrogen content	8.02%

PREPARATION II OF ORTHO BUTYL XENYL ETHER

The ortho butyl xenyl ether was prepared a second time in a manner analogous to the first preparation, the same quantities of the same materials treated in the same manner. The purification was carried out in a different way. After the reaction was completed, the solution was allowed to cool and then the water insoluble layer was separated. This was then neutralized, water layer separated; insoluble layer treated with 50 per cent solution of potassium hydroxide, water layer discarded, neutralized, water layer again discarded, and dried over night over calcium chloride. Sixty-three grams of a clear liquid was obtained. This liquid was then distilled under pressure giving the following fractions:

	temperature	pressure
I. clear liquid.....	under 100°C	22 mm.
II. clear yellow liquid.	136.5°C to 142°C	20 mm to 22 mm.

Fraction II weighed 20 grams. This fraction was redistilled, the middle fraction saved which had a constant boiling point of 137° Centigrade at 18 millimeters. This was then dissolved in anhydrous ethyl ether, put over freshly cut sodium and let stand

over night. The ethyl ether was distilled off over an oil bath, the remaining liquid vacuum distilled giving the following fractions:

	temperature	pressure
I. white solid.....	90°C-96°C	8 mm.
II. clear yellow liquid.....	135°C-140°C	8 mm.

Fraction I had a melting point of 60° Centigrade. When mixed with ortho xenol (melting point 52° Centigrade), the mixed melting point was 50° - 51° Centigrade. Evidently the impurity was the ortho xenol. The second fraction after standing for three days over sodium gave white crystals when extracted with anhydrous ethyl ether, melting point of 60° Centigrade which raised to 67° Centigrade on standing in air for two hours. A mixed melting point with Fraction I gave 68° Centigrade; with para butyl xenyl ether (melting point 73° Centigrade) a melting point of 49° Centigrade; with ortho xenol, a melting point of 52° Centigrade. It was concluded that the purification of the ortho butyl xenyl ether was made difficult by the presence of the unchanged ortho xenol.

The purification of ortho butyl xenyl ether under the PREPARATION I OF ORTHO XENYL ETHER was more efficient and gave a purer product than the above method, so it was used in the preparation of the ether for analysis.

PREPARATION I OF ORTHO ETHANOL XENYL ETHER.

The ortho ethanol xenyl ether was prepared by dropping 30 percent excess of 0.1 mol ethylene chlorohydrin (12.5 grams of a 30 per cent water solution) into a hot refluxing solution

of 0.1 mol (17 grams) ortho xenol and 75 percent excess of 0.1 mol (10 grams) potassium hydroxide in 100 cubic centimeters of water during one hour with constant stirring. It was cooled, then diluted with 200 cubic centimeters water, filtered by suction on a Buchner funnel. A brown gelatinous mass formed, a small portion of which when washed with 20 cubic centimeters water and pressed on a porous plate gave a white crystalline substance was dried under suction and recrystallized from toluene and water in white crystals melting at 69° - 70° Centigrade. The 200 cubic centimeters of filtrate that remained when the gelatinous substance was filtered formed, on setting over night, a small amount of white crystals melting at 69° Centigrade. The crystals melting at 69° - 70° Centigrade were dissolved in toluene and fractionally distilled at atmospheric pressure:

	temperature
I. clear white liquid.....	85° - 120° Centigrade
II. " " " (small).....	155° - 160° Centigrade
III. heavy white liquid.....	295° Centigrade
(turned cloudy in ice bath)	

The white crystals melting at 68° Centigrade were soluble in ethyl alcohol, toluene (anhydrous), chloroform, acetone, but insoluble in cold water.

PREPARATION II OF ORTHO ETHANOL XENYL ETHER.

The same reacting substances were used in this preparation as in the first, but more potassium hydroxide was put in in order

to dissolve the ortho-xenol below 50° Centigrade. The solution turned yellow, then a dark brown. The entire reaction was carried out over a water bath to avoid excessive heating. While dropping in the ethylene chlorohydrin slowly, the ether began to form with water bath at 70° Centigrade. A greater portion formed with it between 87° and 90° Centigrade. The reaction was completed in one half hour. It was cooled by dropping cold water through the dropping funnel continuing the stirring. An amorphous brown substance formed on the bottom, a yellow water layer on top. When filtered on a Buchner, funnel, the amorphous substance came through. The water was decanted off and a solid came out when the residue was washed with more water. Yield was 13 grams. A portion when pressed on porous plate, formed white powder melting at 63° - 64° Centigrade. When washed with potassium hydromide solution and then with water, the melting point was raised to 68° - 70° Centigrade. The entire yeild was dissolved in ethyl alcohol and crystallized out with water. White powder formed which melted at 68°-69° Centigrade. When recrystallized from ethyl alcohol and water, white needles formed melting at 68° Centigrade.

PREPARATION III OF ORTHO ETHANOL XENYL ETHER.

The third preparation of ortho ethanol xenyl ether followed the procedure in the second preparation taking double the material and using a large excess of ethylene chlorohydrin (about 10 grams).

After the reaction was completed, the product was diluted with water and allowed to stand over night. A few crystals formed when the amorphous substance was washed with dilute potassium hydroxide and then with water. Melting point was 69° - 70° Centigrade. The crystals were thrown out of the remaining portion with 100 cubic centimeters of forty per cent potassium hydroxide. The cream colored precipitate was washed twice with forty per cent potassium hydroxide solution and then with water. The crystals formed melted at 70° - 72° Centigrade. Recrystallized from alcohol and water, white needles were formed that melted at 68° Centigrade. The same melting point was obtained on recrystallization.

Analysis for carbon and hydrogen content according to the Liebig combustion method yielded

	sample I	sample II
grams sample	0.2261	0.2170
grams water obtained on analysis	0.1326	0.1256
grams carbon dioxide obtained on analysis	0.6464	0.6203
carbon content (found)	77.97%	77.98%
hydrogen content (found)	-----6.55%-----	6.52%
average carbon content (found)	77.97%	
average hydrogen content (found)	6.54%	
calculated carbon content	78.47%	
calculated hydrogen content	6.59%	

PREPARATION I OF META BUTYL XENYL ETHER.

The meta butyl xenyl ether was prepared by dropping 30 per cent excess of 0.5 mol (8.9 grmas) butyl bromide into a mixture of 0.05 mol (8.5 grams) meta xenol and 30 per cent

excess of 0.05 mol (8.9 grams) potassium hydroxide in 200 cubic centimeters of water, on a water bath during one hour, refluxing with constant stirring. When cooled the mixture formed two layers. The water layer was separated and the ether layer dried with calcium chloride over night. Vacuum distillation gave three fractions;

	temperature	pressure
I. clear liquid.....	vaporized below 100°C.	5mm.
II. clear white liquid.....	157° - 160°C. (mostly 159.5° - 160)	5mm.
III. dark residue.		

The oil bath was kept between 195° - 210° Centigrade.

PREPARATION II OF META BUTYL XENYL ETHER.

The same materials and the same procedure was used for this as in PREPARATION I OF META BUTYL XENYL ETHER except in place of water bath and oil bath was substituted. The ether began to form

when the bath was at 95° Centigrade. The bath was kept between 95° - 100° Centigrade. After one hour, 7 grams of butyl bromide were added. Refluxing was continued for one half hour longer, with the oil bath at 100° Centigrade. Then 17 grams of potassium hydroxide in concentrated solution was added and the mixture allowed to stand for one hour. It was then heated and bottom potassium hydroxide layer separated from the top yellowish butyl bromide layer while the mixture was still hot. About five cubic centimeters of butyl bromide was distilled off the top layer. It was then treated with 150° cubic centimeters water and ten grams potassium hydroxide. The water layer was then discarded and the residue treated again with water and potassium hydroxide. After the ether layer was separated, it was dried over calcium chloride over night. The yield was a yellowish liquid weighing 11.6 grams. When this was vacuum distilled, the major portion came over in the middle fraction, at 155°-156° Centigrade at a pressure of 5 millimeters.

Carbon combustion gave:

grams sample	0.2432
grams water obtained on analysis	0.1581
grams water obtained on analysis	0.6701
carbon content (found)	75.15%
hydrogen content (found)	6.81%
carbon content (calculated)	84.90%
hydrogen content (calculated)	8.02%

The boiling point of the middle fraction of preparation I and that of preparation II varies four degrees although distilled

at the same pressure. This discrepancy and the low carbon and hydrogen content make it doubtful if the desired ether was obtained even in a very impure state.

PREPARATION OF META ETHANOL XENYL ETHER.

0.1 mol (17 grams) of meta xenol and 30 per cent excess of 0.1 mol (7.3 grams) of potassium hydroxide in 200 cubic centimeters of water were heated in a round bottom flask connected with a reflux condensor, a dropping funnel and an electrically driven stirring rod, on an oil bath. When the bath was at 95 Centigrade pure ethylene chlorohydrin was started dropping through the funnel slowly, 30 per cent excess of 0.1 mol being used during one half hour. The oil bath was kept between 100°-110° Centigrade. A white foamy reaction took place. A yellowish brown layer formed on the bottom. When 15 grams of potassium hydroxide in concentrated solution was added through the dropping funnel and the mixture heated for an additional half hour, the bottom layer disappeared. When more ethylene chlorohydrin was added, about five grams, reaction evidently took place. The top greenish yellow layer was separated in a separatory funnel while still hot. Yield was 22.6 grams. Vacuum distillation on oil bath gave

	temperature	pressure
I. clear colorless liquid.....	165°-168° C.	17mm
II. " " "	186°-186.5 C.	17mm
III. brownish residue.....		

Carbon analysis by Liebig method gave:

grams sample	0.1351
grams water obtained on analysis	0.0825
grams carbon dioxide obtained on analysis	0.3801
carbon content (found).....	76.73%
carbon content (calculated).....	78.47%
hydrogen content (found).....	6.82%
hydrogen content (calculated).....	6.59%

If desired ether was obtained, it was somewhat impure.

SUMMARY.

The butyl and ethanol ethers of ortho, meta and para xenols were prepared according to the Williamson reaction for the preparation of ethers, as this reaction had been used in the preparation of the ortho and meta methyl and ethyl xenyl ethers and the materials were readily available.

The dry reaction between a phenol and an alkyl halide was first attempted in the preparation of the para butyl xenyl ether. In the preparation of the sodium salt of para xenol it was found that it was difficult to prepare as it was easily converted into the original xenol on heating in air. Also on refluxing this salt with butyl bromide for seventeen and one-half hours, the

yield of the para butyl xenyl ether obtained was very low, 4 per cent of the theoretical.

The same reaction carried out in a water solution was then used as it had been successfully used in the preparation of cresyl ethers. The following method with slight modifications, which will be noted, for the different ethers was used. One-tenth mol of the xenol was weighed into a 500 cubic centimeter round bottom flask fitted with a reflux condensor and a dropping funnel, 30 per cent excess of one-tenth mol of potassium hydroxide was dissolved in from 20 to 50 cubic centimeters of water and added to the phenol. The mixture was heated until solution was complete, then 30 per cent excess of 0.1 mol of the alkyl halide was slowly dropped into the hot mixture which was continuously stirred by an electrically driven glass stirring rod extending through the reflux condensor. After all of the alkyl halide was added, the mixture was refluxed for different periods of time for the different ethers. The para butyl ether was refluxed for one hour giving a yield of 97 per cent, the highest yield obtained; the meta butyl ether gave a yield of 51 per cent (see next paragraphs); the ortho butyl ether a yield of 22 per cent after refluxing one hour. In the ethanol ethers, additional potassium hydroxide was used to insure the alkalinity of the solution. The para ethanol ether gave a yield of 88 per cent with one and one half hours refluxing, the meta a very small yield with one-half hour refluxing, and the ortho a 60 per cent yield with one-half hour refluxing. The para ethers were formed readily, heating the flask with a bunsen burner; in

the ortho ethers, the butyl was heated in the same way but the ethanol gave the best results when heated on a water bath. Both meta reactions were carried out on a water bath or on an oil bath which was kept below 100° Centigrade.

The para butyl, the para ethanol and the ortho ethanol xenyl ethers were solids. They were purified by washing with forty per cent potassium hydroxide solution and recrystallization from a solvent. The para butyl xenyl ether gave white flaky opaque crystals from ethyl alcohol, melting point 73° Centigrade, which gave a satisfactory carbon hydrogen analysis (within 0.1 of one per cent of the theoretical). The para ethanol xenyl ether gave white crystals from anhydrous toluene, melting point 107° Centigrade, which likewise gave a satisfactory analysis (within 0.1 of one per cent of the theoretical)*. The ortho ethanol xenyl ether formed white needles from a mixture of ethyl alcohol and water which melted at 68° Centigrade and gave an analysis within 0.5 of one per cent of the theoretical.

The meta, butyl, ortho butyl and meta ethanol xenyl ethers were liquids and were purified by washing with 40 per cent potassium hydroxide solution and fractionating with vacuum distillation. The meta butyl xenyl ether gave two distinct boiling points on the two preparations, 159.5° - 160° Centigrade and 155° - 156° Centigrade, both at a pressure of 5 millimeters, a discrepancy of four degrees; it also gave a low carbon hydrogen analysis which makes it doubtful if the desired ether was obtained

* One analysis only.

even in a very impure state. The ortho butyl xenyl ether gave a yield of 22 per cent of a liquid that had a boiling point of 134.3° Centigrade at 10 millimeters, and, 137° Centigrade at 18 millimeters pressure, with a carbon hydrogen analysis within 0.87 per cent of the theoretical. The meta ethanol xenyl ether had a boiling point of 186° - 186.5° Centigrade at 17 millimeters and the analysis was within 1.3 per cent of the theoretical. These three liquid xenyl ethers were clear colorless compounds.

RESULTS OF EXPERIMENTAL WORK.

XENYL ETHER	FORMULA	MELTING POINT	BOILING POINT	YIELD	CARBON-HYDROGEN ANALYSIS (FOUND) (THEORETICAL)	
para butyl		73°C.		I. 97% II. 88%	C 84.80% H 8.00%	84.90% 8.02%
meta butyl			I. 159.5°-160°C. (5mm.) II. 155°-156°C. (5mm.)	51%	C 75.15% H 6.81%	84.90% 8.02%
ortho butyl			I. 134.3°C (10mm.) II. 137°C. (10mm.)	I. 22% II. 29%	C 84.03% H 7.87%	84.90% 8.02%
para ethanol		107°C.		I. 77% II. 88%	C 78.37% H 6.59%	78.47% 6.59% **
meta ethanol			136°-136.5°C. (17mm.)	very small	C 76.68% H 6.82%	78.47% 6.59%
ortho ethanol		68°C.		60%	C 77.97% H 6.54%	78.47% 6.59%

* Liebig Combustion Method.

on one analysis only.

Part V.

SUMMARY.

The preparation of the ortho, meta and para butyl and ethanol ethers of the corresponding xenols was undertaken as an additional study in a series of studies in the Xenyl Series made in this laboratory.

The preparation of the ortho and para compounds used as a starting point the respective xenols, which are a waste material in the manufacture of phenol (4) and for which uses are now being sought.

The Williamson reaction in a water medium, a procedure successfully used in the preparation of cresyl ethers (22), was selected as the method of preparation as the dry reaction was made difficult by the easy hydrolysis of the dry sodium xenol salts in air. The preparations were completed in a maximum time of one and one-half hours and were carried out over a bunsen flame, the ortho ethanol, meta butyl and meta ethanol being kept below 100 Centigrade.

The para butyl, the para ethanol, and the ortho ethanol xenyl ethers were solids and were purified by washing with 40 per cent potassium hydroxide solution and recrystallisation.* The others were liquids and after washing with the alkali solution were fractionated in a vacuum.*

* See table on page 49.

The para and ortho ethers* gave satisfactory carbon hydrogen analyses, the meta ethanol an analysis within 1.8% of theoretical.

The yields* were good, 51 to 97 per cent, except in the meta ethanol, and, the ortho butyl.

*See table on page 49.

BIBLIOGRAPHY

- (1) "New Rubber Romance", Literary Digest 111,11 (November 21, 1931)
- (2) McHugh, F.D., "New Commercial Synthetic Rubber" Scientific American 146,42 (January 1932)
- (3) Norris, James F., "Research and Industrial Organic Chemistry" Science 75 5-10 (January 1,1932).
- (4) Hale and Britton, Industrial and Engineering Chemistry 20 : 114-124 (1928)
- (5) Jacobson and Loeb, Berichte 36 : 4085 (1903).
- (6) Jacobson, Franz, Honigsberger, Berichte 36 : 4075-4080 (1903).
- (7) Honigschmeid, Centralblatt 72, 2:769 (1901)
- (8) Smith, Journal American Chemical Society 56 : 717-718 (1934).
- (9) Cohen, Organic Chemistry
Julius B., Edward Arnold, London England (1918), 1 :41
- (10) Norris, James F., Organic Chemistry
McGraw-Hill, New York, N.Y. (1912), 145
- (11) Berthsen, A., Organic Chemistry
revised by J.J. Sudborough;
Van Nostrand Co., New York, N.Y. (1923), 87.
- (12) *ibid*, 750
- (13) *ibid*, 437
- (14) Norris, James F., Organic Chemistry
McGraw-Hill, New York, N.Y. (1912), 433.
- (15) Niederl and Natelson, Journal of the American Chemical Society 53:272-277.(1931)
- (16) Vincent,Camille, Berichte 16 : 2513 (1883).
- (17) Niederl and Natelson, Journal of the American Chemical Society 53:1928-1934 (1931.)
- (18) Niederl and Storch, Journal of the American Chemical Society 55: 284-290 (1933).
- (19) Claisen, Journal Chemical Society 124, 1:1094 (1923)

- (20) Schöeller, Jordan and Clerc, German Patent 520,859
Chemical Abstracts 25 : 3359 (1932)
- (21) Claisen, Berichte 45 : 3157 (1912)
58 : 275 (1925)
59 : 2344 (1926)
- (22) Sowa, Hinton and Nieuwland, Journal American Chemical
Society 54 : 2019-2021 (1932)
- (23) Parsons and Porter, Journal of the American Chemical
Society 54 : 363-365 (1932)
- (24) Niederl and Matelson, Journal of the American Chemical
Society 54 : 1066 (1932)
- (25) *ibid.*, 1068.
- (26) Bell and Kenyon, Journal of the Chemical Society 129:3048 (1926).
- (27) Sherwood, Short, Stansfield, Journal of the Chemical
Society 135: 1832-5 (1932)
- (28) Werner, Centralblatt, 73, 2:283 (1902)
- (29) Chemical Engineering Catalog, Chemical Catalog Co., Inc.,
419 Fourth Avenue., New York, N.Y. (1929) 14, 1062.
- (30) Perkin, W.H. and Kipping, F.S., Organic Chemistry
Lippincott, Philadelphia, Penn., (1908) 228- 29.
- (31) Beilstein, Handbuch der Organischen Chemie, *
Leopold Voss, Leipzig, Germany (1896) 1 :114
- (32) *ibid.*, 2 * :538
- (33) *ibid.*, 2 :895.
- (34) Hale, Journal of the American Chemical Society 54:4458-4459 (1932).