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Synthesis of Regulated Structure

Polyphenylether - Siloxane Elastomers

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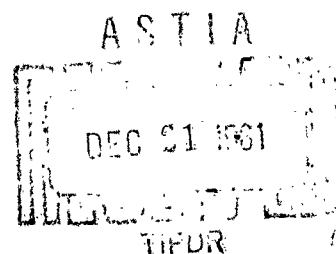


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ABSTRACT

Synthesis of polyphenylether-siloxane elastomers involves three separate phases:

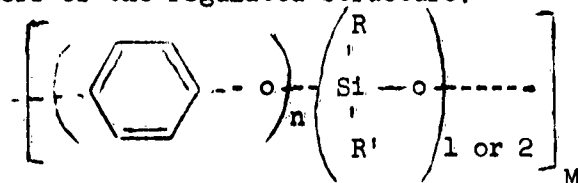
- A. Synthesis of p,p'-dihydroxypolyphenylether blocks.
- B. Condensation of the above blocks with silane groups to yield high molecular weight block copolymers.
- C. Development of suitable vulcanizing systems for these block copolymers.

This report deals with phase A.

Guided by the findings of our literature survey, two methods of preparing the first member of the dihydroxypolyphenylether series have been investigated. The first method, the alkaline fusion of the alkali salts of the commercially available oxy-bis-(p-benzene sulfonate) was unsuccessful and has been abandoned. The second method, the synthesis and subsequent hydrolysis of 4,4'-dibromodiphenylether has thus far, given only low yields of the desired 4,4'-dihydroxydiphenylether. It is believed, however, that this hydrolysis reaction can be developed into a practical synthesis.

INTRODUCTION

This contract involves the synthesis of polyphenylether-siloxane block copolymers of the regulated structure:



where: $n = 2, 3 \text{ --- } 8 \text{ --- } 10 \text{ ---}$

$R = \text{CH}_3, \text{C}_6\text{H}_5, \text{t-C}_4\text{H}_9, \text{etc.}$

$R' = R, \text{CH=CH}_2, \text{etc.}$

$M = 100 \text{ --- } 200 \text{ --- } 1,000 \text{ ---}$

In view of the known thermostability of polyphenylethers and of the mono- and disiloxane blocks these block copolymers should possess superior thermostability. In addition the flexible, non-polar nature of both the polyphenylether and the siloxane blocks, should result in an appreciable amount of high elasticity, - providing sufficiently high degrees of polymerization are obtained.

Retention of physical properties at elevated temperatures is much more difficult to achieve than mere "survival" at elevated temperatures. Retention of physical properties is dependent upon retention of the intermolecular forces responsible for microcrystallization, whereas "survival" merely requires the absence of any significant decomposition (i.e. bond breaking or redistribution). Elevation of this crystalline melting point is a requisite for good high temperature physicals. It is hoped that by adjusting the size and uniformity of the polyphenylether blocks and the size and nature of the siloxane framing groups (R & R'), the resulting structurally regular macromolecules would be capable of retaining the necessary intermolecular attraction and chain alignment over a greater temperature range than conventional high temperature rubbers (such as silicones). In order to retain the advantages of these structurally regulated block copolymers, a vulcanization reaction should be achieved which will produce intermolecular strong cross links free of any intramolecular side reactions. It is hoped to achieve this quality of cross linking either through the silane groups (via vinyl framing groups) or the aryether blocks (via methylene bridges).

Production of polyphenylether-siloxane high temperature elastomers involves three separate and distinct problems.

- A. Synthesis of the desired p,p' - dihydroxypolyphenylether monomer blocks.
- B. Condensation of the dihydroxypolyphenylether blocks with the siloxane blocks to form high molecular weight block copolymers.
- C. Develop vulcanizing systems appropriate for these high temperature block copolymers.

This first quarterly report deals with problem #A, the synthesis of the p,p' - dihydroxypolyphenylether monomers. These monomers are not commercially available.

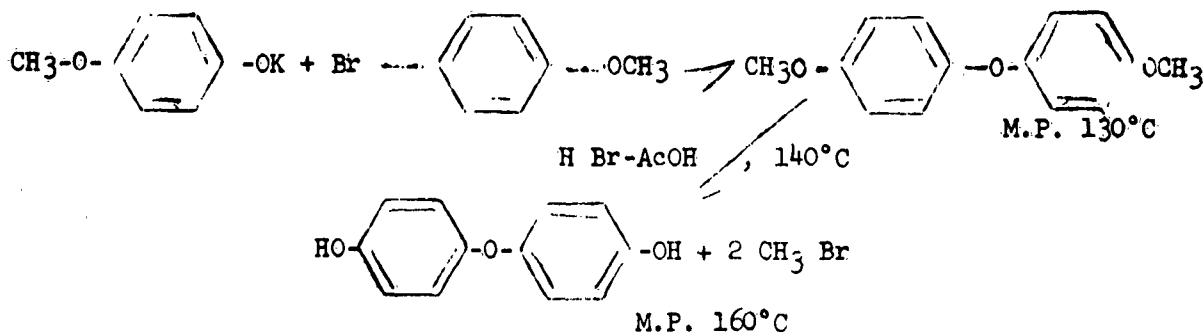
LITERATURE SURVEY

Since p,p' - dihydroxypolyphenylethers are the required monomer units, the greater part of this search was directed at their synthesis, with particular reference to the lowest member of the series; 4, 4' - dihydroxydiphenylether. In addition the literature was scanned for all polyphenylethers which might be convertible to the required dihydroxy-derivatives.

a) 4, 4' - Dihydroxydiphenylether

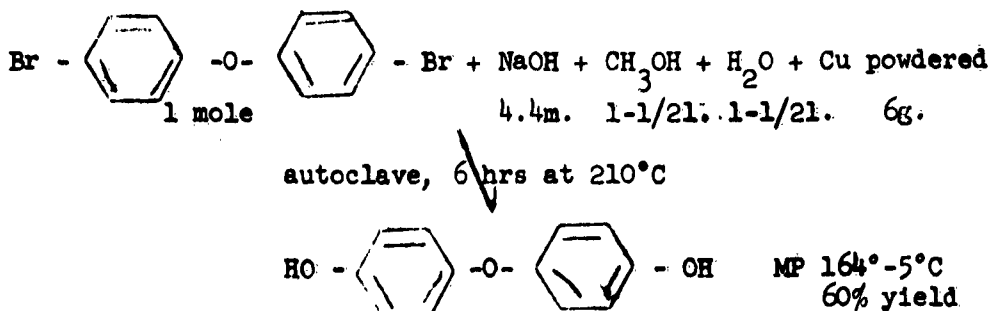
This first member of the p,p' - dihydroxypolyphenylether series was prepared 64 years ago by Hausermann and Bauer (Ber. 30 738 (1897)) via diazotization of 4, 4' - diaminodiphenylether followed by hydrolysis. Yield of the desired dihydroxy compound was extremely poor.

Some 30 years later Oesterlin (Monatsch 57 36(1930)) obtained the same product by condensing two moles of p-bromoanisole in the presence of alkali and copper to form 4, 4' - dimethoxydiphenylether. The latter was then cleaved with aluminum chloride to the desired dihydroxy compound. M. Tomita (J. Pharm. Soc. Japan 53 775 (1933)) improved this yield by application of the Williamson synthesis to the appropriate phenylether, thus:

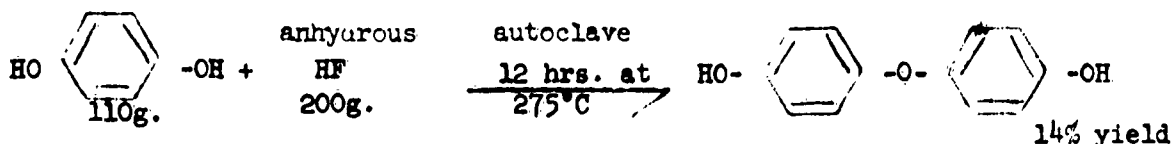


Preparation of hydroxydiphenylethers by the more practical, one step fusion of sodium sulfonates with sodium hydroxide was attempted by Sutor (J. Am. Chem. Soc. 53 1112 (1931)). Alkali fusion, however, resulted in complete destruction of the diphenylether link with zero yield of the desired hydroxycompound.

A more successful one step synthesis was described by K. W. Rittler in German Patent 609,080 (1/17/35). Rittler's process involves the high temperature aqueous hydrolysis of halo diphenylethers and is claimed to give high yields of the desired dihydroxydiphenylether, thus;



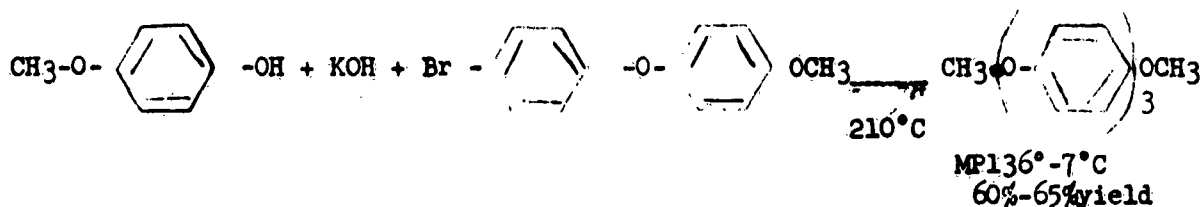
A more recent competitive process is claimed by Universal Oil Products Company (CB Linn; U.S. Pat. 2,739,171 (5/2/51) which involves the condensation of dihydroxyaromatic compounds in the presence of dehydrating agents, such as anhydrous hydrogen fluoride. For example;



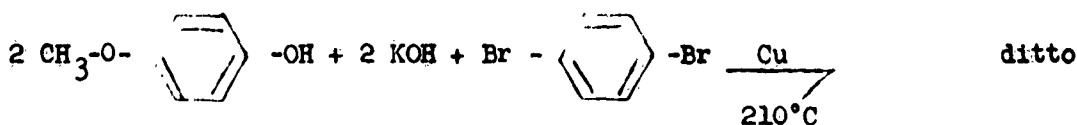
Superficially, the German Rittler hydrolysis process with a 60% yield is by far the best synthesis. In fact, in view of this patent, it is surprising that Universal Oil Products Co. bothered to patent a manifestly more expensive, less efficient (14% yield) process 16 years later.

b) p,p' - Dihydroxypolyphenylethers

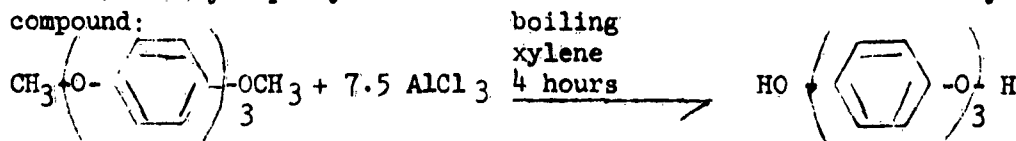
The only specific reference uncovered concerning a higher member of this series was that of Oesterlin (Monatsch 57 36 (1930)). Oesterlin produced the dimethoxy intermediate for pp-dihydroxytriphenylether in two ways:



and by



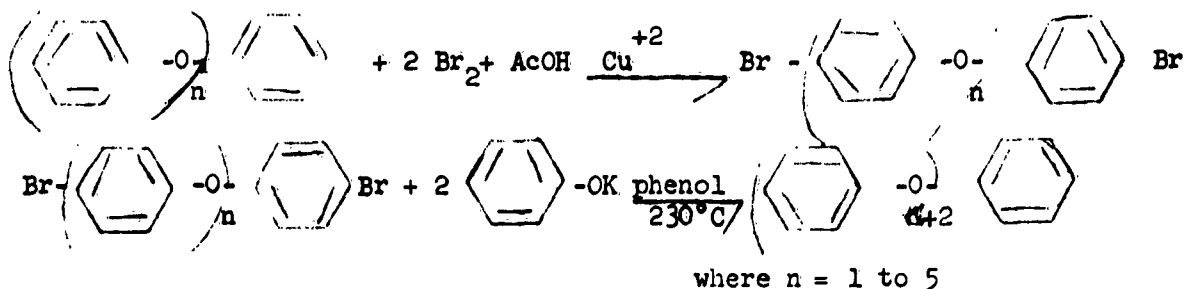
This dimethoxytriphenylether was then cleaved to the desired dihydroxy compound:



This reaction sequence, unfortunately, is not applicable to the higher hydroxypolyphenylethers.

c. Polyphenylethers

The one good reference uncovered, concerning specific lower members of the polyphenylether series was an abstract (C.A. 40 557³ (1946)) of a Russian article by Z.S. Akchurin (Uchenye Zapiski Kazan. Gosudarst. Univ. im. V.I. Ul'yanova-Lenina No. 3, Sbornik Studenscheskikh Robot No. 2, 61-3 (1941)). Akchurin describes the preparation of a homologous series of lower polyphenylethers, as high as the octaphenylether, by successive brominations followed by the Williamson ether synthesis;

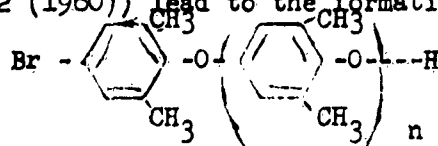


Unfortunately the original Russian article is no longer available, even from the U. S. Dept. of Agriculture Library (Washington, D.C.) which was the original abstractor of this article. Nevertheless, this sequence of Akchurin in combination with the hydrolysis procedure of Rittler offers the most convenient route to these lower p,p' - dihydroxypolyphenylethers.

Considerably more information exists on the preparation of less clearly defined (but obviously polymeric) polyphenylene ether mixtures. Most of these preparations involve the coupling of substituted phenols by means of diazodecomposition oxidative coupling, etc. For example, Sus (Ann. 598 123 (1956)) and Demar (J 1958 917) studied the photochemical decomposition of various diazo-oxides. Although polymeric phenylethers (molec. wt. 1,000-3,000) are produced, these polymers do not appear to have the regular ether structure, $\left[\text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 \right]_n$, but rather include a high proportion of poly-

phenol groups, $\left[\text{C}_6\text{H}_3(\text{OH}) - \text{O} - \text{C}_6\text{H}_4 \right]_n$ formed via nuclear coupling, displacement

reactions. By contrast Hunter, et. al. (J. Am. Chem. Soc. 54 2456 (1932)) reported the formation of poly (halo-phenyl) ethers from the decomposition of phenol silver salts. Recent modifications of this reaction by Stiffin and Price (J. Am. Chem. Soc. 82 3632 (1960)) lead to the formation of linear poly - 2, 6 - dimethylphenylethers,



Oxidative coupling of substituted phenols has been extensively studied during the past decade. Depending on phenol structure and reaction conditions, either nuclear oxidative coupling (Bacon et al, J. 1954 2275; 1960 1339) or ether oxidative coupling (Plummerer, Chem. Ber. 85 535 (1951); C. D. Cook, J. Am. Chem. Soc. 75 6242 (1953); etc. can occur. Recently the oxidative coupling reaction has been developed by Hay et. al. (J. Am. Chem. Soc. 81 6335 (1959)) into an effective method for preparing high molecular weight

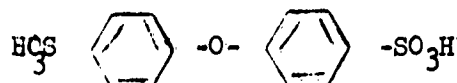
2, 6 - disubstituted - 1,4 - phenylenether polymers.

It is probable that several of the above cited reactions could be modified (possibly by utilizing chain terminating phenols) to produce the lower molecular weight polyphenylether blocks required for this elastomer research.

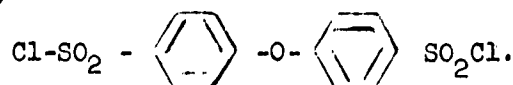
III. EXPERIMENTAL

a) Alkaline Fusion of p,p'-Oxy-bis- (P-sodium benzenesulfonate)

The only commercially available reactive, di-para-substituted derivatives of diphenylether are the disulfonic acid,

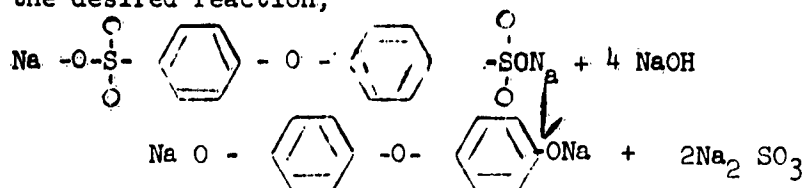


and the corresponding disulfonyl chloride,



If these sulfonyl groups can be replaced directly by hydroxyl groups, an extremely cheap route to the desired 4,4'- dihydroxydiphenylether would be available.

Our literature survey, however, had disclosed that the phenylether link (of compounds such as sodium p-phenoxy-benzene sulfonate) does not survive the conventional alkali-fusion so applicable to the manufacture of phenol (Sutor, J. Am. Chem. Soc. 53 1112 (1931)). It is apparent, therefore, that the conventional alkaline-fusion procedure must be significantly modified before the desired reaction;



will be achieved. The most obvious modification is that of operating under more carefully controllable conditions, including the complete exclusion of oxygen (Boswell, J. Am. Chem. Soc. 40 1786 (1918)), than are attainable in a conventional alkali fusion. Accordingly, a series of reactions were performed in a stainless steel, high pressure, stirred autoclave under nitrogen at temperatures ranging from 150° to 280°C. Since the disulfonic acid of diphenylether is a poorly defined, hygroscopic material which cannot be satisfactorily recrystallized even in the form of its salts (Fittig, Ann. 125 329 (1863)), the disulfonyl chloride was utilized as the starting material.

Plant grade oxy-bis-(p-benzene sulfonyl chloride) is a stable white powder; mp 134°-6°C, with the characteristic absorption curve designated as #1 on attached Plate. The aromatic bands at 3.25 μ, 6.3 μ and 6.7 μ together with the ether absorption at 8.50 μ are characteristic of the basic diphenylether structure. The 8.6 μ and 7.67 μ bands and the 8.43 μ and 7.25 μ bands are indicative of the SO₂ and SO₂Cl groups respectively.

The only indication of impurity was the moderately strong hydroxyl absorption at 2.9μ . This was shown (by pH measurements, fractional crystallization and isolation) to be due to the presence of a small proportion of free disulfonic acid.

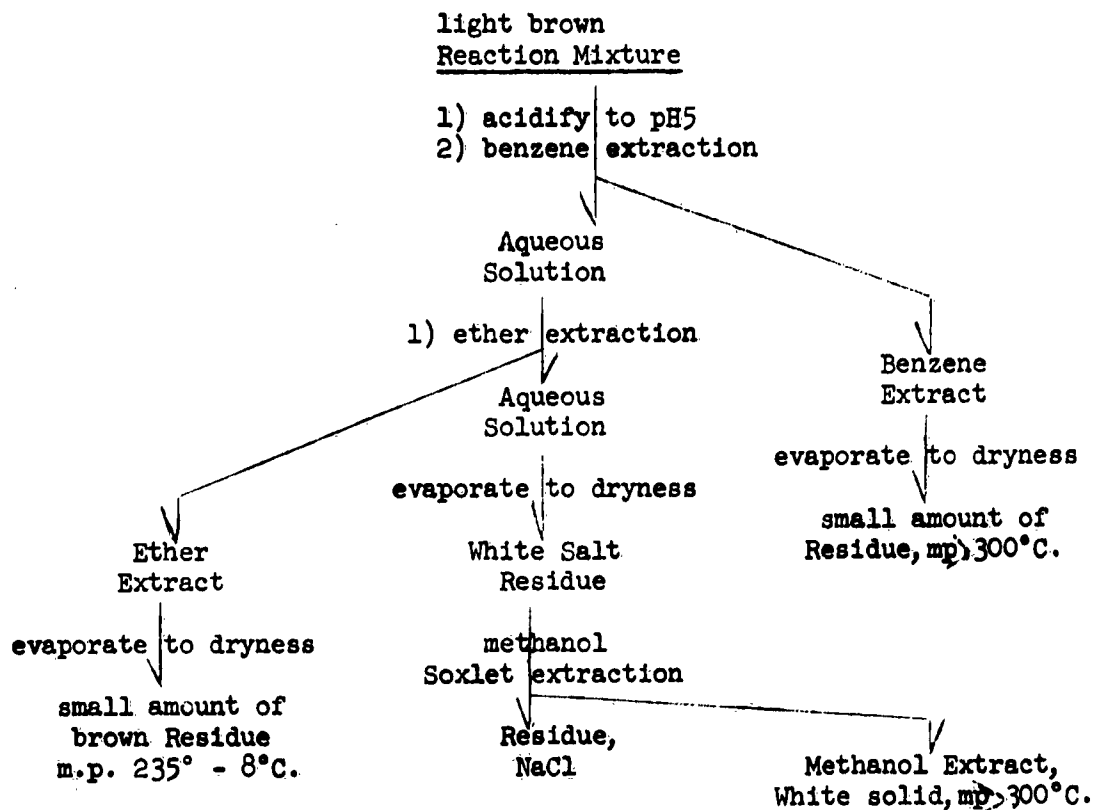
Oxy-bis-(p-benzene sulfonyl chloride) was hydrolyzed to the disodium and dipotassium sulfonates by treatment with a 10% excess of the designated alkali. Due to the limited solubility (ca 10g/100g water) of the disodium oxy-bis-(p-benzene sulfonate) hydrolysis of the disulfonyl chloride proceed slowly unless a large volume of dilute aqueous alkali is employed at elevated temperatures. Due to the greater solubility ($\geq 27\text{g}/100\text{cc}$ water) of the dipotassium oxy-bis-(p-benzene sulfonate) a much more rapid hydrolysis with KOH is obtained even at room temperature.

The alkali sulfonates prepared in this way are isolated by evaporation to dryness under vacuum followed by drying over P_2O_5 . The resulting crude salts, contaminated with NaCl or KCl and residual free alkali, can be partially purified by washing with several small portions of water and finally extracting with alcohol. The infrared absorption spectra of a sample of "purified" disodium oxy-bis-(p-benzene sulfonate) is reproduced in spectra #II of the attached Plate. In addition to displaying the typical aromatic and ether absorption of a 4,4'-disubstituted diphenylether molecule, a strong absorption band at 9.55μ indicates the presence of SO_3^- ion while a strong band at 8.85μ may indicate the presence of SO_4^- ion. Several bands in the 7.5 to 9μ region defy assignment, however, there is considerable confusion in the literature regarding assignments in this region.

Three attempted experiments (numbers CO-3(1), CO-3(3) and CO-3(4)) were performed at 150° , 200° and 250°C for 5 hours in a stirred, 1 liter, stainless steel autoclave. The same charge;

0.1 mole disodium oxy-bis-(p-benzene sulfonate)
0.5 " sodium hydroxide
500cc deionized water

was used in all cases. The reaction mixtures were worked up according to the scheme outlined below (actual data taken from experiment number CO-3(3)).



Since the desired product (4,4'-dihydroxydiphenylether) has a m.p. 160°-5°C., it is apparent that none of the isolated fractions contained significant amounts of the desired material. Infrared spectra indicated that all fractions were largely unchanged starting material. Even the ether extracted fraction, m.p. 235°-8°C., which contained the largest amount of organic impurities, contained nothing which absorbed strongly in the 3.4 μ (hydroxyl) region.

In an effort to catalyze the desired reaction, a series of mixtures consisting of:

- 0.1 mole disodium oxy-bis-(p benzene sulfonate)
- 0.5 " sodium hydroxide
- 250cc deionized water
- 250cc methanol
- 2g. copper powder

was subjected to temperatures ranging from 200°C. to 280°C. (CO-4(1), CO-4(II), CO-4(III)). Two different isolation procedures were employed for this series of reactions; the scheme shown above and the one shown on the next page:

The first step of this sequence, the bromination of diphenylether was found to occur smoothly and in good yields under conventional, ionic catalyzed, bromination conditions.

One mole (170g) of recrystallized, plant grade diphenylether was charged into a 1 liter, 3 neck, round bottom flask equipped with motor-driven stirrer, reflux condenser, H Br trap, addition funnel and thermometer. 500cc of glacial acetic acid containing 1 g. of $\text{Cu CO}_3 - \text{Cu(OH)}_2$ was added. The resulting light green solution was heated to $90^\circ - 95^\circ\text{C}$., and 2 moles (320g) of bromine were added dropwise over 3 hours time. H Br evolution was evolved copiously and continuously throughout the addition. The reaction mixture was held at 90°C for an additional 2 hours during which H Br evolution was completed. After cooling to about 50°C , the reaction solution was gravity filtered through a sintered glass Buchner funnel into a stirred volume (2 liters) of water. Light yellow plates separated immediately. After thoroughly washing with water the volumous filter-cake recrystallized from hot 95% ethanol as fine white plates; mp $58-9^\circ\text{C}$;

yield = 80% of theory
Bromine analysis; found - 48.2%
calculated - 48.5%

I.R. spectra; shown in the attached plate, - spectra #3. This spectra exhibits the absorption (3.3μ , 6.3μ , 6.7μ and 8.0μ) so typical of diphenylether and its derivatives. The C-Br absorption is found at 15.4μ . In general the substitution pattern is distinctly that of 1:4 disubstitution. The small absorption at 2.9μ is undoubtedly due to traces of moisture present in the ground KBr used as the dispersing matrix. All samples, whose spectra are shown in the attached plate, were taken in the form of K Br-pellets.

c) Alkaline Hydrolysis of 4,4' - Dibromodiphenylether

Efforts, thus far, have been limited to attempting to duplicate example #1 of German Patent 609,080 (K.W. Rittler). This example translates quite simply as: "328g. (1 mole) of 4,4'-dibromodiphenylether dissolved in 175g. (4.4m) of sodium hydroxide, 1.5 liters of water and 1.5 liters of methanol, with the addition of 6 g. of copper powder, was heated with stirring for 6 hours at 210°C . The resulting solution was freed of alcohol, filtered, and the 4,4' - dihydroxydiphenylether precipitated out with CO_2 . Recrystallization from toluene yields 120 grams (or 60% of theory) of colorless crystals; mp $164^\circ - 5^\circ\text{C}$."

These reaction conditions were repeated verbatim, twice (experiments Y1,A and Y1,A(1)) in a stainless steel stirred autoclave. Less than a 1% yield of reasonably pure dihydroxydiphenylether, mp $162^\circ - 5^\circ\text{C}$, was isolated either time. An extensive reaction, however, had occurred since neutralization aliquots indicate that more than 50% of the initial charge of alkali had reacted and that no unchanged dibromodiphenylether was recovered. In spite of all this only a small amount of poorly characterized by-product was obtained.

The infrared absorption spectra of a representative sample of 4,4' - dihydroxydiphenylether; mp $162^\circ - 5^\circ\text{C}$, is designated as curve IV on the attached spectra Plate. Salient characteristic of this curve are the extremely strong hydroxyl band at 3μ and the even stronger phenolic absorption at 8.25μ . The overall absorption pattern is that of the 4,4' - disubstituted diphenylether pattern previously observed, except that the C-H bending absorption at 3.32μ is considerably suppressed. The strong ether linkage (normally located at 8.0 to 8.1μ) is discernable only as a shoulder on the stronger 8.25μ phenolic band.

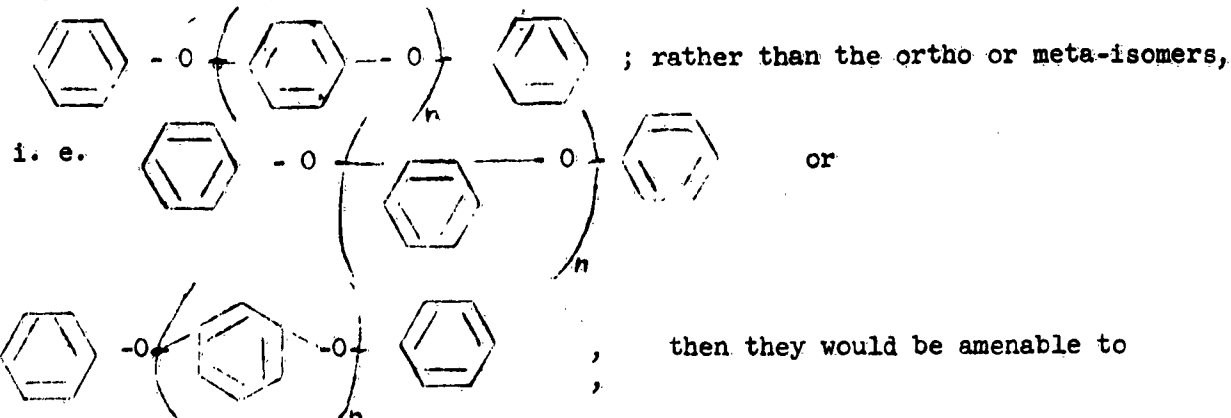
In an effort to obtain larger amounts of by-products, for chemical assay, this first example was repeated using 2 moles of dibromodiphenylether together with 8.8 moles of sodium hydroxide per 3 liters of aqueous methanol (experiment Y1, A(2)). Surprisingly, this increase in concentration changed the course of this hydrolysis. In addition to the usual 1% yield of the desired dihydroxydiphenylether, an appreciable quantity of diphenylether together with an even larger amount of unknown, white, organic solid was isolated. The identity of the diphenylether was proven unequivocally by the infrared spectra and amounted to 7 g./mole of dibromodiphenylether charged (i.e. 3-1/2% of theory). The unknown organic solid amounted to 48 g./mole of dibromodiphenylether charged. Its work up and analysis are still in progress.

In an effort to determine the cause of the discrepancy between our results and the claims of the Rittler patent, some exploratory catalyst work was under taken. In view of the large variation in catalytic activity of copper catalysts, (prepared in different ways), Rittler's catalyst description given simply as "copper powder" is hardly adequate. Since the surface of the copper powder employed as a catalyst in our reactions was appreciably oxidized, one hydrolysis (exp. Y1, A4) was performed under a hydrogen atmosphere instead of the usual nitrogen atmosphere, in hope of obtaining in situ a reductive activation of the catalyst. However, instead of catalyst activation, the hydrogen atmosphere resulted in one 85% reduction of the dibromodiphenylether to free diphenylether. Apparently this same type of reaction (Busch & Stöve, Ber. 49 1063 (1916)) occurred even in the earlier experiments performed under nitrogen and was responsible for reducing 3-1/2% of the dibromodiphenylether to diphenylether.

One further catalytic screening experiment (Y1, A5) involved replacing the usual copper powder by "copper-bronze" powder. The results were identical with those obtained earlier; less than a 1% yield of the desired dihydroxydiphenylether being obtained.

d) Structural Analysis of Commercial Polyphenylethers

In recent years low molecular weight polyphenylethers have been developed for use as lubricating and hydraulic oils designed for service conditions at high temperatures or high ionizing radiation. These polyphenylethers, (commercially available from Dow Chemical, Monsanto or Shell Oil), are claimed to consist of compounds such as bis (phenoxyphenyl) ether and bis (phenoxyphenoxyphenyl) ether. However, the precise structure of these polyethers has not been reported. If they consist of the para-isomers, i. e.



exclusive terminal modifications and would constitute valuable starting materials for the synthesis of the p,p'- dihydroxypolyphenylether blocks of this contract.

In order to determine the positional isomer structure of these oils they were subjected to infrared spectrometry. Infrared spectrographs show none of the absorption bands in the 12.2-.3 μ and 13.6 μ regions, so characteristic of para-substituted benzenes. The complete absence of any para-isomers was confirmed by measuring the absorption spectrum in the 5 μ to 6 μ region on thick films of the polyphenylether oils as recommended by Young, et. al. (Anal. Chem. 23 (15), May 1951). These last measurements disclosed that these polyphenylether oil are predominately meta-isomers.

IV CONCLUSIONS

a) Alkali Fusion of p,p'-Oxy-bis-(p-sodium benzene sulfonate)

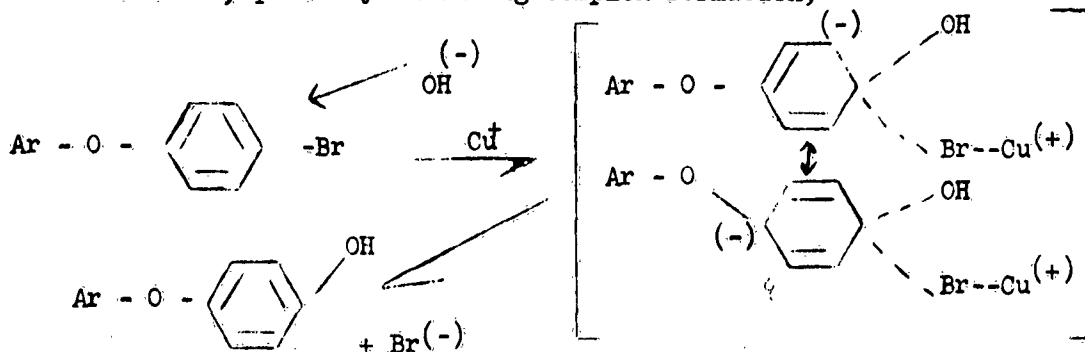
Replacement of sulfonyl group by hydroxyl under strongly alkaline conditions is a complex reaction accompanied by extensive decomposition in the diphenyl-ether series judging from the known effect of electron donor groups, such as the hydroxyl, in facilitating rearrangements and decomposition rather than the desired replacement, (Sutor, "Organic Chemistry of Sulfur," John Wiley, N. Y. 1944, p 420) it is likely that the difficulties encountered in our reactions with the sulfonated diphenylether derivatives arise not from a mere displacement of the phenoxy group but rather from extensive ring cleavage. This concept is supported by the findings of Sutor (J. Am. Chem. Soc. 53 1112 (1931)) who reported that in those cases in which degradation occurred no water insoluble material could be isolated. These findings parallel ours; the only organic material isolated, were diminished amounts of the disodium sulfonate starting material. Attacks on the ether oxygen should produce phenol derivatives. Not the slightest trace of any phenol was ever observed.

Although not impossible, the preparation of dihydroxydiphenylether from the alkali salts of oxy-bis-(p-benzene sulfonate) appears to present too many obstacles to be developed into a practical method within the available time. Therefore no further work will be performed on the alkali fusion of alkali sulfonates.

b) Alkali Hydrolysis of 4,4'-dibromodiphenylether.

It is apparent that the conditions described by Rittler for the hydrolysis of 4,4'-dibromodiphenylether do not work and, therefore, German Patent 609,080 is invalid. This does not say that the alkaline hydrolysis process should be abandoned in favor of some other inherently more expensive method (such as the Universal Oil Products hydroquinone-hydrogen fluoride method). Rather, work should be continued on the alkaline hydrolysis of 4,4'-dibromodiphenylether for the following reasons:

- 1) Alkaline hydrolysis of aryl halides is a technically straight forward reaction, probably involving complex formation;

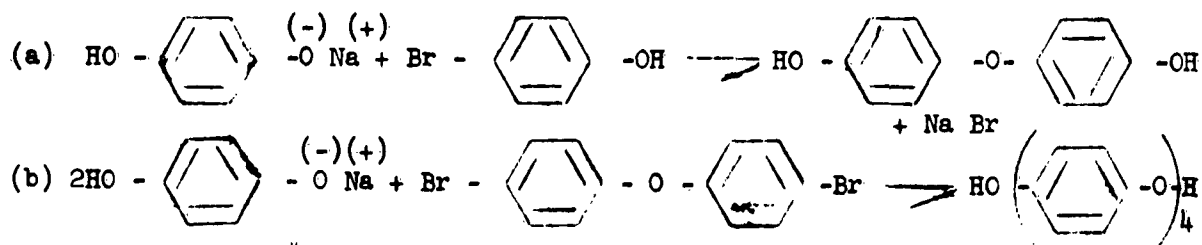


described by Bunnett (Quart. Rev. 12 1 (1958)) rather than a SN_1 or SN_2 reaction. It is believed that suitable reaction conditions can be developed in a reasonably short time.

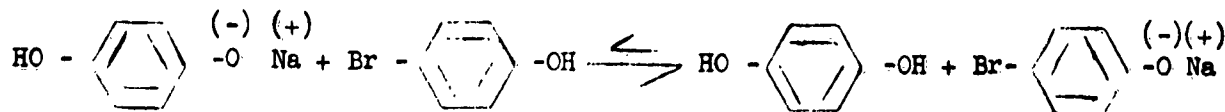
- 2) Coupled with the bromination/Williamson synthesis scheme of Akchurin, the alkaline hydrolysis reaction would permit the preparation of any individual p,p'-dihydroxypolyphenylether which could be required for this program.
- 3) Once satisfactory hydrolysis conditions have been developed for the dibromopolyphenylethers, they should be reasonably easily transferable to the more practical dichloropolyphenylethers.

V PROJECTED WORK

1. Continue investigating the alkaline hydrolysis of 4,4'-dibromodiphenyl ether with special emphasis on reaction temperature, time and concentration. Complete analyzing the high yield organic by-products obtained from the more concentrated reaction mixtures.
2. Utilize the Williamson synthesis as a direct route to the p,p'-dihydroxypolyphenylethers. The following two reactions will be carried out:



Projected reaction [#]a may be complicated by the following exchange reaction:



Fortunately reaction [#]b is free of this complication.

Nearly 2 kg. of dibromodiphenylether has been prepared or procured to carry out the above reactions.

