WADC TECHNICAL REPORT 54-532
PART III.
ASTIA DOCUMENT No. AD 118179

HIGH-TEMPERATURE HYDRAULIC FLUIDS

PART III. DEVELOPMENT OF AROMATIC ETHERS AS BASE STOCK

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APRIL 1957

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2623
PROJECT No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
300 - May 1957

FOREWORD

This report was prepared by Monsanto Chemical Company, Research and Engineering Division, Chemical Research Department, Dayton, Ohio, under USAF Contract No. AF 33(616)-2623, Supplemental Agreement No. S3(56-262). This contract was initiated under Project No. 7340 "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers". It was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Dr. Christ Tamborski as Project Engineer.

This report covers the period of work of July, 1955, through July, 1956.

ABSTRACT

Over fifty alkyl-substituted and unsubstituted aromatic ethers have been synthesized, many of which are new compounds. The melting point, pour point, vapor pressure, viscosity, and thermal stability of most of these ethers have been measured from which correlations have been made by which the boiling point, 210°F viscosity and 210-400°F ASTM slope, and thermal stability of a new ether can be predicted. From the data at hand it should be possible to synthesize aromatic ethers stable to 700°F, liquid at 0°F, viscosity $<$550 cs at 32°F and with a vapor pressure $<$600 mm/700°F.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. Whitmore

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Technical Director
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Directorate of Research

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I. INTRODUCTION

Unsubstituted aromatic ethers are known to have excellent thermal stability but relatively high melting points. As a class they have not received much attention as base stock for high temperature hydraulic fluids and/or lubricants. However, with suitable improvement in the liquid range the possibility for such use appears extremely good.

The study reported below was directed toward the molecular design of an alkyl aromatic ether to obtain the optimum rheological properties for this class with a minimum sacrifice in thermal stability. The correlations that are made on the effect of type and position of alkyl substitution in aromatic ethers on the pour point, viscosity, and thermal stability are the result of an extensive synthesis and testing program.

This report on the development of aromatic ethers as base stock for high temperature hydraulic fluids and/or lubricants was preceded by two reports (WADC TR 54-532 March 1955 and WADC TR 54-532, Part 2, January 1956). The first covered a broad literature search and parallel screening program with recommendations for a research program for the development of a high temperature (700°F) hydraulic fluid base stock. The second reported on the thermal stability screening of an additional fifty compounds, among which tert-alkylcarbinyl sebacates were shown to be remarkedly more thermally stable (104-122°F) than n-alkyl sebacates. This should raise the temperature barrier for ester base fluids to 622°F, from the present 522°F (ca).

II. PROGRESS

Progress under this contract, from a thermal stability standpoint, can best be appreciated by inspection of Fig. 1 which shows the decomposition rates of five compounds as a function of temperature. The decomposition point is defined as the temperature at which the isothermal rates of pressure rise attain a rate of 0.014 mm Hg/sec. which corresponds to a rate of 500 mm Hg pressure rise for 10 hrs. Curve A is bis(2-ethylhexyl) sebacate, a widely used synthetic lubricant. Curve B is bis(1-methylcyclohexylmethyl) sebacate, prepared under this program, which shows an improvement in decomposition point of 100°F. Curve C is a hydrocarbon, n-octacosane, included for comparison. Curve D is o-tolyl p-phenoxyphenyl ether, which approaches the optimum properties to be expected of an alkyl-substituted aromatic ether. Its decomposition point is 200°F higher than bis(2-ethylhexyl) sebacate. Curve E is bis(p-phenoxyphenyl) ether, which has a decomposition point 300°F higher than bis(2-ethylhexyl) sebacate. Compounds of this type may become of interest when high thermal stability is essential and a significant relaxation in pour point specifications can be tolerated.

While we do not have a single aromatic ether which will satisfy the hydraulic fluid liquid temperature range (0-700°F), low temperature viscosity ($<$2500 cs), and maximum vapor pressure (600 mm/700°F) speci-

Manuscript released by authors December 21, 1956 for publication as a WADC Technical Report

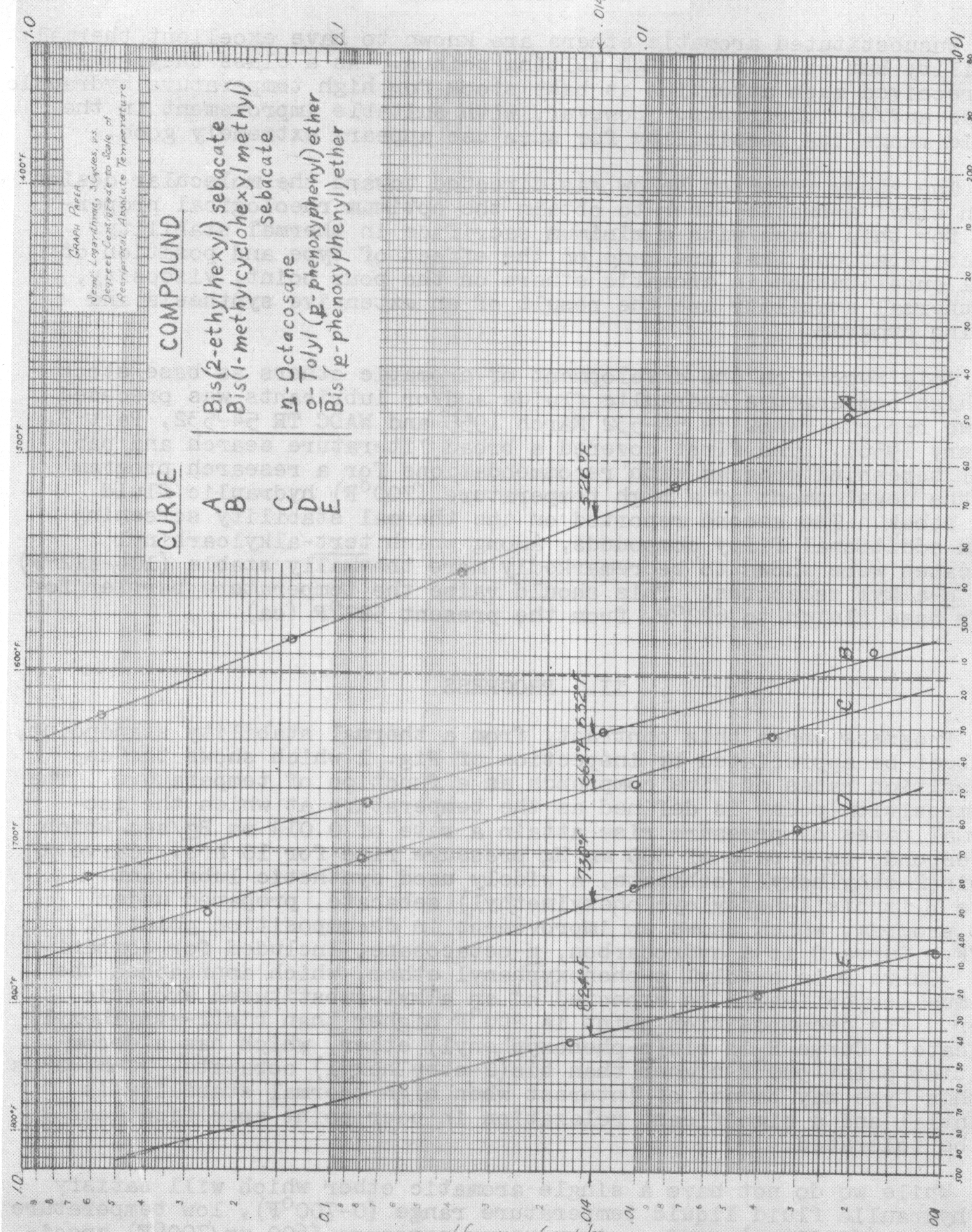


Figure 1 Decomposition Rates of Selected Compounds

fications, we have evidence that either blends of isomeric ethers or individual compounds by molecular design from data at hand will admirably satisfy the above specification requirements except for <2500 cs at 0°F. Such aromatic ethers will possess a viscosity of approximately 550 cs at 32°F and a pour point of $<$ 0°F. For example, blends of ethers such as o-tolyl p-phenoxyphenyl ether, m-tolyl p-phenoxyphenyl ether and 2,4-bisphenoxy toluene which essentially satisfy the above specifications have been subjected to temperature cycling for an extended period without undergoing crystallization.

We are not hopeful of meeting the 1 cs viscosity at 700°F specification. Numerous structure correlations have been developed which will be a material aid in the future synthesis of aromatic ethers with optimum properties.

Constant effort toward the improvement of physical testing methods throughout this study was rewarded with several worthwhile techniques.

III. APPROACH TO THE PROBLEM

One of the important problems in this program was to design low melting aromatic ethers. Diphenyl ether, for example, is a solid at room temperature. It seemed logical that the introduction into aromatic ether nucleii of a non-polar substituent, such as alkyl, halo or alkoxy groups, might lower the melting point of the substituted parent compound per se or lower the melting point by decreasing the symmetry of the molecule.

The literature was therefore surveyed with the object of finding correlations between type and position of substitution, and melting point. The number of ethers from which conclusions might be drawn was, unfortunately, limited. While over 400 aromatic ethers have been reported, almost two-thirds of them have highly polar substituents such as the nitro group and any correlations derived would probably not apply to ethers substituted with non-polar substituents. Therefore, only a few nitrated ethers were considered.

Since diphenyl sulfide is lower melting than diphenyl ether, aromatic sulfides and ethers were compared (Table 1) to determine if this behavior was general. The data in Table 1 show that in general the sulfide is likely to melt higher than the ether. The sulfides appeared to offer no decided advantage with respect to melting point, and, since sulfides would be more susceptible to oxidation than the ethers, and more difficult to synthesize, no extensive work on sulfides was planned.

In Table 2, the effect of different types of substituents on the melting and boiling points of diphenyl ether is compared. When the symmetry of the molecule is maintained (the 4,4'-disubstituted ethers), all substituents except the fluoro group raise the melting point. (4,4'-Diethylphenyl ether was not obtained crystalline, but it has a lower degree of symmetry than most of the other disubstituted compounds.)

TABLE 1

COMPARISON OF THE MELTING POINTS OF ANALOGOUS AROMATIC ETHERS AND SULFIDES

Ether	M.P., °C	M.P., °C of sulfur analog
Diphenyl ether	27	-22
o-Tolyl phenyl ether	22	oil
Bis(o-tolyl) ether	oil	64
Bis(p-tolyl) ether	50	57
Bis(4-methyl-2-nitrophenyl) ether	126	176
Bis(p-chlorophenyl) ether	30	89
p-Bromophenyl phenyl ether	18	25
Bis(p-bromophenyl) ether	61	110
p-Iodophenyl phenyl ether	47	35
p-Nitrophenyl phenyl ether	61	55
Bis(p-nitrophenyl) ether	143	154
p-Methoxyphenyl p-methylphenyl ether	48	46
p-Bisphenoxybenzene	77	82
p-Bis(p-toloxy)benzene	103	99
p-Bis(2,4-dinitrophenoxy)benzene	68	168
Average M.P., °C	63	81

TABLE 2

THE EFFECT OF TYPE OF SUBSTITUENT ON THE MELTING AND BOILING POINTS OF DIPHENYL ETHER

Substituents	M.P., °C	B.P., °C	Liquid Range, °C
None	27	259	232
4-Methyl	oil	274	-
4-Methoxy	oil	296	-
4-Phenoxy	77	389	312
4-Fluoro	-	254	-
4-Chloro	-	285	-
4-Bromo	18	305	287
4-Iodo	47	(3-Iodo) 338	291
4,4'-Dimethyl	50	285	235
4,4'-Diethyl	-	336	-
4,4'-Dimethoxy	102	338	236
4,4'-Diphenoxy	110	465	355
4,4'-Difluoro	-	240	-
4,4'-Dichloro	30	314	284
4,4'-Dibromo	60.5	340	280
4,4'-Dinitro	143	-	-

The chloro group is of interest because it causes a large increase in boiling point with little change of melting point. The phenoxy group while causing the greatest increase in melting point gives the greatest overall increase in liquid range: over 100°C greater than the methoxy group which gives almost the same melting point. The data in Table 2 point up the importance of symmetry in the melting point of aromatic ethers; it shows that methoxy, phenoxy and nitro groups cause the greatest increase in the melting point and that chloro and phenoxy groups cause the greatest increase in liquid range.

The effect of positions of substitution on the melting point of diphenyl ethers is compared in Table 3. With but one exception, the meta isomer melts lower than the para, while with but three exceptions, the meta melts lower than the ortho. On the other hand, four of the ortho isomers melt lower than the para and five melt higher. Substituents in the meta position, therefore, seem to be low melting compounds more often than the ortho- and para-substituted isomers. In addition, since m—bisphenoxybenzene melts lower than the other two isomers, derivatives of this structure would probably be the lowest melting.

TABLE 3

THE EFFECT OF POSITION OF SUBSTITUTION ON THE MELTING POINT OF DIPHENYL ETHER

Ether	M.P., °C when x is o-	m-	p-
x-Methoxyphenyl phenyl ether	78	oil	18
x-Phenoxyphenyl phenyl ether	93	62	77
x-Iodophenyl phenyl ether	56	oil	47
x-Nitrophenyl phenyl ether	<-20	oil	61
x-Methylphenyl 4-nitrophenyl ether	20	63	68
x-Methylphenyl 2,4-dinitrophenyl ether	142	138	120
x-Chlorophenyl 2,4-dinitrophenyl ether	99	75	126
x-Nitrophenyl 4-chlorophenyl ether	46	60	76
1,4,Bis(x-methylphenoxy)benzene	51	57	103

The trifluoromethyl group has the advantage over the methyl group of being relatively inert to oxidation. In addition there are reports that the stability of a whole molecule toward heat and oxygen has been improved by the introduction of a trifluoromethyl group. If this group also improved the liquid range of an aromatic ether, it would be very promising indeed. The data in Table 4, however, show that the trifluoromethyl group is unpromising as a means of increasing the liquid range of aromatic ethers. The boiling point is not raised by the substitution of even four trifluoromethyl groups while with only two trifluoromethyl groups the pour point is -25°C.

TABLE 4

COMPARISON OF TRIFLUOROMETHYL- AND METHYL-SUBSTITUTED DIPHENYL ETHERS

Position of Substituents	Trifluoromethyl Derivative		Methyl Derivative	
	M.P., °C	B.P., °C	M.P., °C	B.P., °C
None	27	259	27	259
m	oil	255	oil	275
m, m'	oil	252	oil	291
3,3',5	oil	247	-	-
3,3',5,5'	96	245	61	325
2,4	glass -25	244	oil	295

The melting points of alkyl-substituted diphenyl ethers were not compared because relatively few have been reported, and of these many are reported as oils. These are probably low melting solids, difficult to crystallize.

The conclusions from the literature survey were summarized as follows:

1. As a class aromatic sulfides are higher melting than aromatic ethers.

2. Symmetrical aromatic ethers are usually higher melting than less symmetrical ones.

3. Of alkyl-, halo-, methoxy-, and phenoxy-substituted diphenyl ethers, the phenoxy group gives the greatest overall increase in liquid range while the chloro group gives the greatest increase in liquid range with the smallest increase in melting point.

4. Meta-substituted diphenyl ethers melt lower than the para isomers and usually lower than the ortho isomers. Derivatives of m-bisphenoxybenzene should melt lower than derivatives of o- or p-bisphenoxybenzene.

5. The trifluoromethyl group is not promising as a substituent to increase the liquid range of an aromatic ether.

With the literature background and without losing sight of the ultimate goal, namely the development of a practical functional fluid in the class of aromatic ethers, we chose to pursue a systematic approach in the synthesis program. By so doing, we expected to obtain a body of data from which useful correlations could be made on the effect of structure on the thermal stability and viscosity properties of aromatic ethers.

This systematic approach was adopted because, except for melting and boiling points, the literature is devoid of data from which such correlations can be made. If such correlations could be made from the data to be gathered in this work, then an ether could be designed which would have not only a good but the best combination of properties for present fluid requirements obtainable with this class of compounds. Further, if specifications should be changed in the future, then an ether having the optimum combination of properties for the new requirements could be readily designed.

Alkyl derivatives of bisphenoxybenzenes and bis(phenoxyphenyl) ethers were selected for the most intensive investigation. These ethers were chosen as the basic structures because of the low volatility specifications for a high temperature fluid. The alkyl group was chosen because substitutions by a long aliphatic chain should be the most effective way to improve the viscosity-temperature characteristics and lubricity of an aromatic ether. In addition, because of ease of synthesis and availability of starting materials, a variety of alkyl-substituted ethers could be obtained. Again for synthetic reasons, a larger proportion of the ethers synthesized were para-substituted para-linked ethers. It was believed that relations observed in this series would be general for other types of aromatic ethers.

In addition to the work on alkyl-substituted aromatic ethers of known structure, several were prepared by direct alkylation which generally leads to mixed isomers. Since the cost of manufacturing a given ether might be high, it was desirable to gather data on ethers which could be made at relatively low cost.

A few ethers outside the class of alkylated aromatic ethers were prepared as the work progressed.

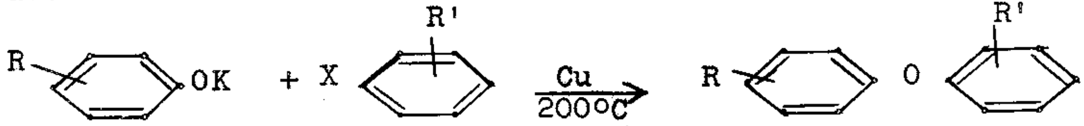
IV. SYNTHESIS

Discussion

Ullmann Reaction

Syntheses for aromatic ethers are decidedly limited, both in number and in scope. The Williamson synthesis has been used for preparing ethers from a phenol and an aromatic halide activated by one or more nitro groups. The Ullmann reaction, involving a copper catalyst, is used for more refractory halides. Reaction of a phenol and an aromatic halide at high temperatures is used industrially, chiefly for the preparation of diphenyl ether. Most of the aromatic ethers in the literature have been prepared by direct substitution or transformation of substituents on diphenyl ethers.

The Ullmann reaction (1) is the most general method for the preparation of aromatic ethers.



It has been used successfully where R = alkyl (1), alkoxy (3,5), and R' = alkyl, nitro or amino (1), hydroxy or alkoxy (3), or phenoxy (4). The copper catalyst is essential to the reaction.

Polyphenyl ethers are readily obtained by the Ullmann reaction by reacting phenols with dihalides, dibromobenzene or dibromopolyphenyl ethers (4). The reverse reaction using dihydroxybenzene fails (1). The yields vary from above 85% for unsubstituted ethers to less than 20% for ethers having substituents such as nitro or halo that are sensitive to the reaction conditions. Aromatic bromides give the best yields followed by the chlorides and iodides (1).

In this work 39 aromatic ethers, of which many are new, were prepared by the Ullmann reaction. Table 5 gives the reactants, reaction conditions, and yields for these syntheses. The chief limitation of the Ullmann reaction for our program was the limited availability of m-dibromobenzene which made access to the m-bisphenoxybenzene series difficult. Though m-dichlorobenzene (or 2,4-dichloro toluene) is more readily available, yields from it are low in the Ullmann reaction. (No reactions were carried out on the dichlorides in an autoclave to prove if this failure was related to the low boiling point of the aromatic chlorides.) Other routes to the meta series, via m-bromoanisole or m-methoxyphenol involve expensive intermediates and a multistep synthesis. Several ideas on improved synthesis for m-phenoxybenzene are under consideration.

An attempt to carry out an Ullmann reaction with potassium p-chlorophenoxide and dibromobenzene failed when the chlorophenoxide reacted upon addition of the copper catalyst and before addition of the aromatic halide. Reaction between a phenoxide and bromophenol is known (2,3), although the yields are poor. An attempt to couple p-bromophenyl phenyl ether with KOH in the presence of copper gave only starting material and tarry products.

Williamson reactions between p-chloronitrobenzene and resorcinol and hydroquinone in ethanol gave, respectively, as the only products isolated p,p'-dichloroazobenzene and p,p'-dichloroazoxybenzene. The analogous reaction with 2,4-dinitrochlorobenzene is reported to give good yields of the aromatic ether (6).

Two thio ethers were prepared by the Ullmann reaction, namely bis(2,4-phenylmercapto)toluene and bis(p-phenylmercaptophenyl) ether. The Ullmann reaction with a thiophenate is more difficult than with phenates, due probably to the more solid state of the thiophenate which makes good mixing and cooling more difficult.

Although we had predicted that trifluoromethyl alkylation of aromatic ethers was unpromising for increasing the liquid range, nevertheless, two unsuccessful attempts were made to couple p-chloro-α,α,α-trifluorotoluene with resorcinol by the Ullmann reaction. In the first experiment dipotassium resorcinate was reacted with 2 moles of the halide in butanol (solubilizing and suspending agent). The reaction was carried out in an autoclave to contain the p-chloro-α,α,α-trifluorotoluene (b.p. 138°C) at a reaction temperature of 260°C. If any of the desired ether was produced here, it was in insufficient amount to warrant the identification effort.

On the assumption that excess resorcinol (2 moles) might function to dissolve monopotassium resorcinate (1 mole) and thus improve the reaction with p-chloro-α,α,α-trifluorotoluene (1 mole), an attempt was made to prepare a mono ether of resorcinol for subsequent reaction. This reaction was conducted at atmospheric pressure. Essentially, all of the halide was recovered unchanged.

It seemed desirable to know the effect of the naphthyl group in poly aromatic ethers on the melting point. Attempts to react 1,5-naphthalenediol with bromobenzene and of α-naphthol with p-bromodiphenyl ether by the Ullmann reaction resulted in the first instance in a charred black mass and in the second reaction not enough material of possible uniform composition was obtained to warrant identification. However, the reaction between dibromonaphthalene and m-cresol yielded a small amount of crystalline product, m.p. 56-58°C, which, pending analyses, is regarded as the desired ether. From these three reactions it appears that the Ullmann reaction will be much less useful in the preparation of mixed aromatic ethers from naphthols and naphthalene bromides than from phenol and bromobenzenes.

Intermediates

Several brominated aromatics were prepared in anticipation of subsequent use as intermediates in the Ullmann reaction. All brominations were conducted in the absence of light using both iron powder and either ferrous or ferric bromide as a catalyst.

Infrared spectra of the dibrominated products from the dibromination of ethyl benzene and of toluene indicated essentially all 1,2,4-substitution, contaminated with trace amounts of the 1,2,3 isomers.

Cyclohexylbenzene was brominated in the absence of light using ferrous bromide and iron powder as a catalyst. Mixed isomers were obtained and even the most careful fractionation did not yield the 1-cyclohexyl-4-bromobenzene free of the ortho and meta isomers. However, subsequent reaction of this bromide with p-cyclohexylphenol in the Ullmann reaction yielded a product which, after purification was exclusively para-substituted as indicated by infrared analyses.

Similarly, but using iron and iodine as a catalyst, the product contained an even higher ratio of ortho and meta isomers. This contrasts with a literature report (7) that bromination of cyclohexylbenzene, in which iodine was used as a catalyst and a modification of this procedure in which iron was also added, yields the pure para isomer.

Since the tert-butyl group appears to be reasonably thermally stable, a tert-butyldibromobenzene was prepared for subsequent reaction to observe the effect on the liquid properties of o-tert-butyl- as compared to methyl-substituted aromatic ethers. This is unfinished work.

As previously stated it appeared desirable to know more about the effect of the naphthyl group on the melting point and thermal stability when incorporated into an aromatic ether. Accordingly, dibromonaphthalene, methyldibromonaphthalene and tetrahydronaphthalene bromide were prepared. These products are all assumed to be a mixture of isomers. The dibromonaphthalene was reacted with meta cresol to produce a very low yield of what is thought to be the diether.

4-Cyclohexylcyclohexyl bromide was prepared by the usual procedure of treating an alcohol with 48% hydrogen bromide in the presence of conc. sulfuric acid.

Also prepared by standard methods for use in the Ullmann reaction were: p-propylphenol, p-octylphenol, p-cyclopentylphenol, m-phenoxyphenol, p-phenoxyphenol, m-bromophenyl phenyl ether, and 2-methyl-5-phenoxyaniline.

Chlorinations

Two experiments were carried out on the chlorination of p-bisphenoxybenzene prepared by the Ullmann reaction. In the first, a mixture of predominantly heptachlorobisphenoxybenzenes was obtained which was separated into a crystalline solid and a glass. The second experiment was more promising in that the product was a mixture of predominantly dichlorobisphenoxybenzenes. The product was separated into a solid, m.p. 99-100°C, and an oil, pour point -12°C, b.p. 195°C/0.7 mm. Further work along this line will depend on the thermal stability tests and viscosity measurements.

Alkylation

p-(4-Cyclohexylcyclohexyl)phenyl phenyl ether was prepared at room temperature by the Friedel-Crafts reaction from 4-cyclohexylcyclohexyl bromide in carbon disulfide, using a mole excess of diphenyl ether. Despite this excess of diphenyl ether, a low yield of the monosubstituted product was obtained, along with a large quantity of an undistillable tar. This product was of interest for comparison with cyclohexylphenyl phenyl ether. The cyclohexyl group had previously been shown to possess high thermal stability.

In this contract period only one additional alkylated aromatic ether, 4-(4-chlorobenzyl)phenyl phenyl ether was prepared by the one step Friedel-Crafts alkylation although three other alkylated aromatic ethers (Table 6, Cpds. 9, 10, 13) prepared earlier are reported for viscosity comparisons.

Because of the dearth of viscosity and liquid range data on alkylated diphenyl ethers, bis(p-ethylphenyl) ether and bis(p-butylphenyl) ether were prepared and these properties were determined (Table 6, Cpds. 4, 5). These two ethers were prepared via acylation of diphenyl ether followed by reduction of the bisketone.

Diacylation and diaroylation of diphenyl ether by the Friedel-Crafts reaction using the respective acid chlorides proved to be a good laboratory method for the production of p,p'-disubstituted diphenyl ethers.

4,4'-Bis(acetylphenyl) ether was reduced to the 4,4'-bis(ethylphenyl) ether in 40% yield by the Clemmensen reduction. The Wolff-Kishner reduction method afforded this dialkyl ether in a 64% yield. Presumably this difference may be due to the higher solubility of the carbonyl compound in the Wolff-Kishner reagents. Reduction by the Wolff-Kishner method of the 4,4'-bis(butyrylphenyl) ether, 4,4'-bis(benzoylphenyl) ether and of p-benzoyl-m-methylphenyl p-benzoylphenyl ether proceeded in yields of 45, 55 and 49% respectively.

In view of the fact that the melting points of diphenyl ether and diphenyl methane are the same (27°C) bis(p-benzyl phenyl) ether was prepared for comparison with bis(p-phenoxyphenyl) ether.

It was found that bis(p-benzylphenyl) ether (m.p. 55-56°C) has a relatively high thermal stability (721°F). Liquefaction of this low-melting solid was therefore attempted by alkyl substitution. Previous work had shown that alkyl substitution in bis(p-phenoxyphenyl) ether (m.p. 107-109°C to produce bis/ p-(m-toloxy)phenyl / ether (m.p. 61-62°C) lowered the melting point by 46°C and in p-diphenoxybenzene (m.p. 75-76°C) to produce m-tolyl p-phenoxyphenyl ether (m.p. 22-23°C) lowered the melting point by 53°C. However, alkyl substitution of bis-(p-benzylphenyl) ether to produce p-benzyl-m-methylphenyl p-benzylphenyl ether (m.p. 64.5-66°C) actually raised the melting point by 9°C. Although the oxidative stability of the methylene link in this type of molecule is questionable, it remains of interest to synthesize a few additional compounds with methyl substitution for melting point characterization. This would be of even greater interest if oxidative stability were favorable.

Experimental

Thirty-nine ethers prepared by the Ullmann reaction are listed with pertinent experimental details in Table 5. The following are typical examples of the procedures used. As the objective in each synthesis was to obtain as pure a product as possible, the yields in Table 5 are for analytically pure material. It is to be expected that yields could be increased substantially if necessary.

1,4-Bis(p-Isopropylphenoxy)benzene

A mixture of 177 gm. (1.3 moles) of p-isopropylphenol, 61.6 gm. (1.1 moles) of potassium hydroxide and 50 ml. of xylene was heated at reflux until 25 ml. (theory 19.8 ml.) of water had collected in a Dean and Stark trap. The xylene was removed by distillation, the temperature raised to 200°C and 5 gm. of copper powder was added. Then 118 gm. (0.5 mole) of p-dibromobenzene was added in portions so that the reaction mixture was refluxed for four hours at 250°C and then poured hot into 1 liter of 5% potassium hydroxide solution. The organic material was taken up by extraction with three 500-ml. portions of benzene. The combined benzene extract was washed with two 300-ml. portions of 10% potassium hydroxide, two 300-ml. portions of 10% sodium sulfate solution, dried over anhydrous sodium sulfate, filtered and stripped of solvent. The residue was distilled through an 11-in. Vigreux column and the fraction boiling at 165-208°C/0.9 mm was collected. This fraction was dissolved in 250 ml. of benzene, percolated through a 3 x 15 cm. column of alumina, and eluted with 200 ml. of benzene. The benzene was stripped off and the residue distilled through an 8-in. column packed with 4-mm glass helices. The fraction boiling at 211-213°C/0.9 mm was collected. It weighed 106 gm. (86% yield) and melted at 64.5-66°C.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.57. Found: C, 83.25; H, 7.32.

1,4-Bis(p-cyclopentylphenoxy)benzene

A mixture of 73 gm. (0.45 mole) of p-cyclopentylphenol, 24 gm. (0.43 mole) of potassium hydroxide and 30 ml. of xylene was heated at reflux until 11 ml. (theory 10 ml.) of water had collected. The xylene was distilled, temperature was raised to 160°C and 47 gm.

(0.2 mole) of p-dibromobenzene was added. The temperature was raised to 190°C and 0.6 gm. of copper powder was added. The reaction proceeded exothermically, raising the temperature to 215°C. After the initial reaction had subsided, the mixture was stirred at 200°C for four hours and then poured hot into 700 ml. of 5% sodium hydroxide solution. The organic material was taken up by extraction with four 400-ml. portions of benzene. The combined benzene extract was washed with two 300-ml. portions of 10% sodium hydroxide, two 400-ml. portions of water, dried over sodium sulfate, filtered and stripped of solvent up to 160°C/15 mm. The residue was distilled through an 11-in. Vigreux column and the fraction boiling at 240-244°C/0.3 mm, weight 61 gm., was collected. The product, a solid, m.p. 108-110°C, was recrystallized from a mixture of 1400 ml. of ethanol and 100 ml. of benzene. Colorless plates, m.p. 110-111°C, were formed; they weighed 50 gm. (63% yield).

Anal. Calcd. for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59. Found: C, 84.62; H, 7.84.

4,4'-Bis(cyclohexylphenyl) ether

A mixture of 132 gm. (0.75 mole) of p-cyclohexylphenol, 42 gm. (0.75 mole) of potassium hydroxide and approximately 350 ml. of xylene was heated at reflux with stirring under a Dean and Stark trap until the theoretical quantity of water had collected. The xylene was then removed by distillation and the temperature was raised to 230°C at which point 15 gm. of copper powder was added followed by the portion-wise addition of 150 gm. (0.627 mole) of p-bromocyclohexylbenzene. A temperature surge was evidenced with each addition. After all was added, the temperature was held at 260°C for five hours. The reaction product was taken up in ether, washed free of caustic, dried over anhydrous sodium sulfate, filtered and vacuum-topped to remove the ether. The residue was vacuum-distilled through a 10-in. heated Vigreux column. The product was collected at 201-203°C/0.25-0.3 mm. Further purification by recrystallization out of ethanol yielded a white, crystalline product, melting 69-71°C. Infrared indicated all substitution was para.

Anal. Calcd. for $C_{24}H_{30}O$: C, 86.16; H, 9.04; Found: C, 85.88; H, 9.16.

1,3-Bis(p-trifluoromethylphenoxy)benzene (unsuccessful)

The water was azeotroped from a mixture of resorcinol (110 gm., 1 mole) and potassium hydroxide (112 gm., 2 moles) using xylene (300 ml.). The xylene was removed by distillation and butanol (400 ml.) was added to the solid salt and refluxed to break up the lumps. The butanol suspension was charged into a 1-liter stirred autoclave along with p-chloro-α,α,α-trifluorotoluene (443 gm., 2.45 moles) and copper powder (20 gm.). This mixture was heated with stirring for six hours at 260°C. During the heating up period no temperature surge was noticeable. The reaction product was taken up in ether, washed free of caustic and topped under water pump vacuum (approx. 15 mm) to 150°C. This should have removed any unreacted p-chloro-α,α,α-trifluorotoluene (b.p. 138-139°C). The residue was subjected to vacuum distillation and a broad fraction was collected, b.p. 75-160°C/3 mm. This material was redistilled through a 10-in. heated Vigreux column, to obtain the following fractions.

Fraction	B.P., °C/mm	Gms.	N_D^{25}
1	-106/0.3	10	1.4555
2	106-116/0.3	2.5	1.4830
3	116-125/0.3	3.5	1.4923
4	125-132/0.3	5.0	1.4985
5	132-139/0.3	4.5	1.5040
6	139-146/0.3	7.5	1.5080
7	146-151/0.3	6.5	1.5093
8	151-156/C.3	7.5	1.5101

An infrared analysis of a mixture of fractions 5, 6, and 7 did not characterize the product. This experiment was not sufficiently encouraging to pursue it further.

1,5-Bis(phenoxynaphthalene) (unsuccessful)

A mixture of 1,5-naphthalenediol (160 gm., 1 mole), potassium hydroxide (112 gm., 2 moles) and xylene was heated with stirring under a Dean and Stark trap until the theoretical quantity of water had collected. The xylene was then essentially all removed under a water-pump vacuum. The potassium salt was transferred to a rocking autoclave with 10 gm. of copper powder. Bromobenzene (314 gm., 2 moles) was added in three portions to the autoclave at approximately 220°C. Heating was continued for five hours. The autoclave product was a charred black mass, considered unworthy of further effort to identify.

p-(α-Naphthyloxy)diphenyl ether (unsuccessful)

The potassium-α-naphthenate was prepared as usual using α-naphthol (115.7 gm.) and potassium hydroxide (45 gm.) The xylene was removed, 5 gm. of copper powder was added and the temperature was raised to 230°C at which point p-bromodiphenyl ether (200 gm.) was added portion wise. Heating was continued for five hours at 250-260°C. The product was taken up in ether and washed free of caustic. Solvent was removed and the residue was distilled in a quick take over,

Fraction 1, up to 130°C/0.1 mm, 73 gm.
Fraction 2, 183-250°C/0.12 mm, 50 gm.
Residue 54 gm.

Fractionation of Fraction 1 yielded nothing definite as shown by refractive index and all the material distilled below the desired range.

Redistillation of Fraction 2 yielded fractions as follows:

Fraction	B.P., °C/mm	n_D^{25}	Weight, gm.
1	up to 190/0.15		5
2	190-197/0.15	1.6488	1
3	197-198/0.15	1.6560	7
4	198-199/0.15	1.6597	7
Residue			25

An attempted recrystallization of the residue from alcohol yielded a product which shrinks at 145° C and melts at 165°C. The alcohol-insoluble product was taken up in benzene and precipitated with hexane, m.p. > 310°C.

No product appeared sufficiently definite to warrant identification efforts.

Reaction of p-bromophenyl phenyl ether and potassium hydroxide (unsuccessful)

A mixture of 25 gm. (0.1 mole) of p-bromophenyl phenyl ether, 11.2 gm. (0.2 mole) of potassium hydroxide and 1 gm. of copper powder was heated at 260°C for six hours. The reaction mixture was taken up by extraction with 25-ml. portions of alternate benzene and water. All extracts were combined and the benzene and water layers separated. The benzene layer was washed successively with dilute sodium hydroxide solution and water, and dried over sodium sulfate. The aqueous layer and basic extracts were acidified and extracted with ether. The ether extract yielded only 100 mg. of a black resin showing that little or no phenols were formed.

From the benzene extract after removal of solvent and drying agent and distillation of the residue was obtained 18 gm. (72% recovery) of p-bromophenyl phenyl ether, b.p. 150-155°C/13 mm, n_D^{25} 1.6053, and 2 gm. of tar.

Reaction of p-chlorophenol and dibromobenzene (unsuccessful)

A mixture of 246 gm. (2.3 moles) of p-chlorophenol, 1.18 gm. (2.1 moles) of potassium hydroxide, and 50 ml. of xylene was heated at reflux until 42 ml. of water (theory 37.8 ml.) had collected in a Dean and Stark trap. The xylene was distilled and the temperature raised to 185°C. Upon addition of 5 gm. of copper powder the temperature rose rapidly to 350°C and the reaction went out of control. The product was an intractable black solid.

Reaction of resorcinol and p-chloronitrobenzene

A solution of 23 gm. (1 mole) of sodium, 50 gm. (0.45 mole) of resorcinol, 158 gm. (1 mole) of p-chloronitrobenzene in 1 liter of ethanol was heated at reflux for 3 days. It was diluted with 3 liters of water and extracted with six 1-liter portions of chloroform. After the chloroform extract was washed with three 1-liter portions of water, dried over sodium sulfate and concentrated, it yielded 26 gm. of dark crystals, which after successive recrystallizations from ethanol and acetic acid, melted at 184-185°C. The analysis agreed with that for *p,p'*-dichloroazobenzene (m.p. 183-184°C).

Anal. Calcd. for $C_{12}H_{10}N_2Cl_2$: C, 56.94; H, 3.98; N, 11.07. Found: C, 57.44; H, 3.76; N, 11.51.

p-Phenoxyphenol

p-Methoxyphenyl phenyl ether. This ether was prepared by the Ullmann procedure from 1.6 moles of *p*-bromoanisole, 1.8 moles of phenol, 1.6 moles of potassium hydroxide and 1 gm. of copper powder at 190°C for three hours. The product weighed 241 gm. (75% yield) and boiled at 160-167°C/15 mm, n_D^{25} 1.5750.

p-Phenoxyphenol. *p*-Methoxyphenyl phenyl ether was cleaved by acetic acid - 48% hydrobromic acid in the same manner as *m*-methoxyphenyl phenyl ether. The product, m.p. 77-81°C; b.p. 179-184°C/13 mm, weighed 186 gm. (89% yield). The overall yield based on *m*-bromoanisole was 66%.

m-Phenoxyphenol

m-Methoxyphenyl phenyl ether. This ether was prepared in 75% yield by the Ullmann reaction from *m*-methoxyphenol, potassium hydroxide, and bromobenzene (1.6 moles each) and 4 gm. of copper powder at 215°C for six hours. The product, 239 gm., boiled at 155-167°C/13 mm, n_D^{25} 1.5758.

m-Phenoxyphenol. A mixture of 800 ml. acetic acid, 700 ml. 48% hydrobromic acid and 225 gm. (1.13 moles) of *m*-methoxyphenyl phenyl ether was heated at reflux for 48 hours. The reaction mixture was diluted with 2.5 liters of water and the organic layer taken up with four 500-ml. portions of benzene. The combined benzene solution was washed with two 500-ml. portions of water, one 500-ml. portion of 5% sodium carbonate solution and four 500-ml. portions of water and dried over sodium sulfate. The red oil remaining after the drying agent and solvent were removed was distilled through an 11-in. Vigreux column to give 192 gm. of a red oil, b.p. 172-186°C/15 mm, n_D^{25} 1.5973. Fractionation through an 8-in. column packed with 4-mm glass helices yielded 179 gm. (96% yield) of a light yellow oil, b.p. 113-115°C/0.3 mm, n_D^{25} 1.5980.

The overall yield based on *m*-methoxyphenol was 72%.

2,4-Dibromoethylbenzene

Bromine (959 gm., 6 moles) was added dropwise to a stirred and cooled (<10°C) mixture of ethylbenzene (218 gm., 3 moles), iron powder (15 gm.) and ferric bromide (15 gm.) from which light was excluded. After all the bromine had been added, the reaction was allowed to stir for four hours and then stand for two days. The reaction was washed free of hydrogen bromide and vacuum distilled through a 20-in. Vigreux column. Nine fractions were collected.

Fraction	B.P., °C/mm.	Weight, gm.	n_D^{25}
1	-104/16	43	1.5450
2	104-110/16	25	1.5541
3	110-124/16	23	1.5625
4	124-127/16	39	1.5775
5	127-128/16	137	1.5885
6	128/14	87	1.5885
7	128-129/14	128	1.5885
8	129-130/14	104	1.5884
9	130-132/14	45	1.5884

Fractions 5 through 9 were combined.

Anal. Calcd. for $C_8H_8Br_2$: Br, 60.5. Found: Br, 59.93. Infrared analysis indicated essentially all 1,2,4-substitution with some 1,2,3.

2,4-Dibromotoluene

Bromine (640 gm., 4 moles) was added dropwise with stirring to a cooled (<15°) mixture of o-bromotoluene (794 gm., 4.65 moles), iron powder (10 gm.) and ferric bromide (5 gm.). Light was excluded from the reaction flask. The reaction was stirred for four hours and then washed free of hydrobromic acid. One fractionation through a 20-in. Vigreux column yielded 693 gm. of liquid product, b.p. 110-112°C/13 mm, n_D^{25} 1.5999.

Anal. Calcd. for $C_7H_6Br_2$: Br, 63.96. Found: Br, 61.47. Infrared indicated the substitution to be essentially 1,2,4.

1-Cyclohexyl-4-bromobenzene

Bromine (3 moles, 480 gm.) was added dropwise to a stirred mixture of cyclohexyl benzene (2.92 moles, 466 gm.), ferrous bromide (30 gm.) and iron powder (20 gm.). During the addition the reaction flask was cooled in an ice bath and light was excluded. The brominated product was washed free of acid and distilled through a 90 cm. x 25 mm column packed with 6-mm glass helices. Ten fractions were collected.

Fraction	Weight, gm.	B.P., °C/mm	n_D^{25}
1	50.5	up to 103/1	--
2	6.5	102/1	1.5550
3	7.0	102/1	1.5585
4	11.0	101-104/1-1.2	1.5582
5	15.0	104-106/1.2	1.5580
6	52.0	106-108/1.2	1.5575
7	54.0	108-110/1.4	1.5573
8	129.0	110/1.5	1.5573
9	121.0	113-114/1.6	1.5573
10	93.0	113-118/3.2	1.5573

Infrared indicated that in Fraction 8 the para isomer predominated, but ortho and meta isomers were present. Fraction 6 through 10 were combined for further reaction.

A previous reaction as described by Marvel and Himel (7), in which both iodine and iron were used as a catalyst yielded a product containing a higher ratio of ortho and meta isomers, as indicated by infrared. The product in this instance was distilled through a 10-in. Vigreux column, b.p. 122-123°C/2.5 mm, n_D^{25}, 1.5582. The above reference reports, b.p. 106-108°C/1.5 mm, n_D^{20}, 1.5588.

tert-Butyldibromobenzene

With the temperature held below 15°C, bromine (518 gm., 3.24 moles) was added dropwise with stirring to a mixture of tert-butylbenzene (217 gm., 1.61 moles), ferrous bromide (5 gm.) and iron powder (5 gm.). Light was excluded from the bromination flask. After all the bromine had been added, the reaction was allowed to stir for several hours and then stand overnight. The reaction product was taken up in ether, washed free of acid, and finally free of bromine with sodium bisulfite solution. The ether was removed and the residue was distilled thru a 10-in. Vigreux column.

Fraction	B.P., °C/mm	n_D^{25}	Weight, gm.
1	77-78/0.2	1.5538	9
2	78/0.2	1.5567	24
3	72-73/0.08	1.5583	19
4	72/0.08	1.55628	279
5	72-104/0.04	1.55685	53

Anal. of Fraction 4. Calcd. for $C_{10}H_{12}Br_2$: C, 41.1; H, 4.14. Found: C, 42.61; H, 4.34.

Dibromonaphthalene

Bromine (959 gm., 6 moles) was added dropwise with stirring and cooling ($< 0^\circ C$) to a mixture of naphthalene (384 gm., 3 moles), carbon disulfide (800 ml.), iron powder (10 gm.), and ferric bromide (10 gm.). The brominated product was dissolved in ether and washed free of acid. The ether was removed by distillation and the residue was recrystallized out of ethanol after treating with decolorizing charcoal; m.p. 65-70°C.

Anal. Calcd. for $C_{10}H_6Br_2$: C, 41.97; H, 2.11. Found: C, 42.02; H, 2.26.

α-Methyldibromonaphthalene

Bromine (959 gm., 3 moles) was added dropwise to a stirred mixture of α-methylnaphthalene (426 gm., 3 moles), ferric bromide (10 gm.), and iron powder (10 gm.). Light was excluded from the flask and the temperature was held below 0°C during the addition. During the bromination considerable tar was produced. The brominated product was taken up in ether and washed free of acid with sodium carbonate solution. The solvent was distilled off and the residue was vacuum-distilled; b.p. 167-200°C/11-13 mm. This distilled product was twice fractionated through a 10-in. column packed with glass helices. The second fractionation yielded the following fractions.

Fraction	B.P., °C/mm	n_D^{25}	Weight, gm.
1	97-98/0.08	1.6577	28
2	98-102/0.08	1.6620	50
3	102-104/0.05	1.6675	73
4	104-105/0.05	1.6727	68
5	105/0.04	1.6772	73
6	105-107/0.04	1.6807	55
7	107-108/0.05	1.6813	32
8	108-117/0.05	1.6818	78

Tetrahydronaphthalene bromide

Bromine (800 gm., 5 moles) was added dropwise to a cooled (-10°C) stirred mixture of tetralin (754 gm., 5.7 moles), iron powder (30 gm.), and ferric bromide (20 gm.) from which light was excluded. After all the bromine had been added, the reaction stood for two days and was then taken up in ether and washed free of hydrogen bromide. The ether was removed by distillation and the residue was distilled thru a 20-in. heated Vigreux column. Seven fractions were collected.

Fraction	B.P., °C/mm	Weight, gm.	n_D^{25}
1	-78/0.6	145	1.5475
2	78-82/0.6	82	1.5683
3	82-85/0.7	81	1.5770
4	85-87/0.7	232	1.5823
5	86-91/0.7	114	1.5850
6	91-110/0.7	53	1.5878
7	110/0.7	18	1.5916

Fractions 4, 5 and 6 were combined.

Anal. Calcd. for $C_{10}H_{11}Br$: Br, 37.87. Found: Br, 37.11.

4-Cyclohexylcyclohexylbromide

A mixture of 4-cyclohexylcyclohexanol (500 gm., 2.74 moles), 48% hydrogen bromide (552 gm., 3.28 moles) and conc. sulfuric acid (95 ml.) was refluxed with stirring for seven hours. The bottom layer was separated, taken up in ether and washed free of acid. The ether solution was dried over sodium sulfate, filtered, and the ether was removed by distillation. The residue was vacuum distilled through a 20-in. jacketed and heated Vigreux column. The following seven fractions were collected.

Fraction	B.P., °C/mm	Weight, gm.	n_D^{25}
1	-81/1.3	5	--
2	81-87/1.3	20	1.4984
3	76-86/0.5	15	1.4990
4	86-105/0.3	113	1.5080
5	105/0.3	154	1.5193
6	103/0.7	98	1.5215
7	103-105/0.6	106	1.5245

Fractions 5, 6, and 7 were combined for analysis (8) and subsequent reaction; reported distillation range 150-155°C/14 mm (8).

Anal. Calcd. for $C_{12}H_{21}Br$, 32.59. Found: Br, 31.33.

p-Propylphenol

This phenol was prepared by reduction of anethole (640 gm., 4.3

moles) over 25 gm. of W-4 Raney nickel at 2200 psi. and 60°C followed by dealkylation by heating the reduction product for 18 hours in 2 liters of glacial acetic acid and 1.5 liters of 48% hydrobromic acid (9, 10). The product weighed 507 gm. (87%) yield); b.p. 66-67°C/0.7 mm; n_D^{25} 1.5212.

Reaction of hydroquinone and p-chloronitrobenzene

An attempt was made to prepare 1,4-bis(p-nitrophenoxy)benzene by the procedure of Nietzki and Schundelen (6) for 1,3-bis(2,4-dinitrophenoxy)benzene.

A solution of sodium (11.5 gm., 0.5 mole) hydroquinone (27.5 gm., 0.25 mole), p-nitrochlorobenzene (78.5 gm., 0.5 mole), and 500 ml. of absolute ethanol was warmed at 50°C for one hour and then allowed to stand at room temperature for three weeks. The black reaction mixture was diluted with 1 liter of water and extracted with six 300-ml. portions of benzene. The combined benzene extracts were washed with three 500-ml. portions of water and dried over sodium sulfate. After the drying agent was removed by filtration and the solution was concentrated to 150 ml. and allowed to cool, 40 gm. of dark red needles crystallized. After two recrystallizations from ethanol the product melted at 152-153°C. The analysis agrees with that of p,p'-dichloroazoxybenzene (m.p. 154°C).

Anal. Calcd. for $C_{12}H_{10}OCl_2N_2$: C, 53.55; H, 3.75; N, 10.41. Found: C, 52.90; H, 3.78; N, 10.82.

p-(n-Octyl)phenol

p-(1-Octenyl)anisole. A mixture of 78 gm. (3.2 moles) of magnesium, 500 ml. of dry ether, 50 gm. of n-heptyl chloride and 1 ml. of methyl iodide was warmed with stirring until reaction began. Then a solution of 365 gm. (total, 415 gm. or 3.1 moles) of n-heptyl chloride in 1 liter of ether was added in one hour, and the mixture was heated at reflux for one additional hour. To the solution of heptylmagnesium chloride was added in one hour a solution of 408 gm. (3 moles) of anisaldehyde (Eastman) in 700 ml. of ether and the mixture was stirred at reflux for one hour. The mixture was hydrolyzed by the addition of 200 ml. of water followed by 1 liter of 10% sulfuric acid. The ether layer was separated and the aqueous layer extracted with two 500-ml. portions of ether. The ether solutions were combined with 500 ml. of benzene and solvents were stripped off up to 100°C/20 mm. The product was distilled through an 11-in. Vigreux column in the presence of 2 gm. of hydroquinone and 535 gm., b.p. 120-165°C/1.0 mm was collected. Refractionation through the 11-in. Vigreux column yielded 503 gm. (77% yield) of p-(1-octenyl)anisole, b.p. 115-120°C/0.5 mm, n_D^{25} 1.5260.

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.14; H, 10.15

p-Octylanisole. A 1-liter stainless steel rocking autoclave was charged with 500 gm. (2.29 moles) of p-(1-octenyl)anisole, and

50 gm. of copper chromite catalyst and flushed with hydrogen. The autoclave was pressured with hydrogen to 1100 psi. and heated to 170°C. Hydrogen was added as needed to maintain a pressure of 2000 psi. until no more hydrogen was consumed; one hour was required for the reduction. The catalyst was removed by filtration leaving 490 gm. of a colorless liquid, n_D^{25} 1.4894.

p-Octylphenol. The crude p-octylanisole was refluxed for six hours with a solution of 2 liters of glacial acetic acid and 750 ml. of 48% hydrobromic acid solution. Then an additional 500 ml. of 48% hydrobromic acid was added and heating was continued for 18 hours. The cooled reaction mixture was diluted with 2 liters of water, the organic layer was separated and the aqueous layer extracted with 1 liter of benzene. The combined organic layers were washed with four 300-ml. portions of water, two 200-ml. portions of saturated sodium bicarbonate solution and two 100-ml. portions of saturated sodium chloride solution and dried over sodium sulfate. The solution was filtered and stripped of solvent at atmospheric pressure. The residue, 465 gm. of dark oil, was distilled in vacuo through an 8-in. column packed with 4-mm glass helices. The product collected at 132°C/1.0 mm - 122°C/0.7 mm, weighed 414 gm. [88% yield based on p-(1-octenyl)anisole]. It solidified on cooling; m.p. 42-43.5°C. The overall yield was 68% based on anisaldehyde.

p-Cyclopentylphenol

p-(1-Cyclopentenyl)anisole. To a mixture of 57 gm. (2.35 moles) of magnesium (activated by being heated with 0.5 gm. iodine) and 300 ml. of dry ether was added 50 gm. of p-bromoanisole. When the initial vigorous reaction subsided, 500 ml. of ether was added and then a solution of 362 gm. (total of 412 gm. or 2.25 moles) of p-bromoanisole in 700 ml. ether was added in one hour. The mixture was heated at reflux for one-half hour and then a solution of 202 gm. (2.4 moles) of cyclopentanone in 500 ml. of ether was added in one hour. After the mixture was heated at reflux for one hour, it was hydrolyzed by the addition of 200 ml. of water followed by 1200 ml. of ice cold 20% sulfuric acid. The ether layer was separated and the aqueous layer was extracted with three 500-ml. portions of ether. All the ether solutions were combined with 500 ml. of benzene and the solvents distilled at atmospheric pressure. The residue was distilled through a 10-in. Vigreux column and 246 gm. (59% yield) of p-(1-cyclopentenyl) phenol was collected at 125°C/1.0 - 132°C/0.8 mm. It melted at 84-86°C.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 81.72; H, 8.15.

p-Cyclopentylanisole. A 1-liter stainless steel rocking autoclave was charged with 246 gm. (1.42 moles) of p-(1-cyclopentenyl)-anisole and 25 gm. of copper chromite catalyst, purged with hydrogen and pressured to 1500 psig. The temperature was raised to 230°C and hydrogen was added as needed to maintain a pressure of 1800 psig. After one hour no more hydrogen was absorbed and the bomb was emptied and rinsed with benzene. The product and benzene were combined, the catalyst was removed by filtration and the solvent stripped off. A yellow oil weighing 193 gm., n_D^{25} 1.5276 was obtained.

p-Cyclopentylphenol. A mixture of 193 gm. of crude *p*-cyclopentylanisole, 800 ml. of glacial acetic acid and 250 ml. of 48% hydrobromic acid was heated at reflux for four hours. An additional 100 ml. of 48% hydrobromic acid was added at the end of the first hour and another 100 ml. at the end of the second hour. The cooled reaction mixture was diluted with 1500 ml. of water, the organic layer separated and the aqueous layer extracted with two 500-ml. portions of benzene which were added to the organic layer. The benzene solution was washed with four 200-ml. portions of 5% sodium bicarbonate solution and two 200-ml. portions of saturated sodium chloride solution and dried over sodium sulfate. The residue which remained after the solvent and drying agent were removed was distilled through an 11-in. Vigreux column and 157 gm. of crude cyclopentylphenol collected at 100-108°C/0.7 mm. This cut was fractionated through an 8-in. column packed with 4-mm glass helices and 140 gm. [61% yield based on *p*-(1-cyclopentyl)anisole] collected at 106-109°C/0.7 mm. It melted at 63-66°C. The overall yield was 36% based on cyclopentanone.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.86; H, 8.87.

m-Nitrophenyl phenyl ether. This ether was prepared in 17% yield by the Ullmann procedure from 1.2 moles of phenol, 0.31 mole of potassium hydroxide, 0.3 mole of 3-chloronitrobenzene and 1 gm. of copper powder at 160°C for four hours followed by one hour at 180°C. The product, b.p. 175-190°C/15 mm, n_D^{25} 1.6010, weighed 11 gm. From 3-bromonitrobenzene, a 90% yield has been reported (1). In view of the poor yield it was decided to prepare *m*-aminophenyl phenyl ether directly from *m*-bromoaniline.

m-Bromophenyl phenyl ether.

m-Aminophenyl phenyl ether. This ether was prepared by the Ullmann procedure from 1.9 moles of phenol, 1.8 moles of potassium hydroxide, 1.73 moles of *m*-bromoaniline and 1 gm. of copper powder at 190°C for three hours. The product weighed 222 gm. (70% yield) and boiled at 183-187°C/13 mm, n_D^{25} 1.6205.

m-Bromophenyl phenyl ether. A diazonium solution was prepared by adding in one-half hour at -5° to 0°C a solution of 203 gm. (1.1 mole) of *m*-aminophenyl phenyl ether, 370 ml. of 48% hydrobromic acid and 250 ml. of water to a solution of 76 gm. (1.1 mole) of sodium nitrite in 200 ml. of water. A suspension of cuprous bromide was prepared by adding a solution of 47.5 gm. (0.25 mole) of $Na_2S_2O_5$, 32 gm. (0.8 mole) of sodium hydroxide and 250 ml. of water to a hot (70°C) solution of 200 gm. (0.8 mole) of $CuSO_4 \cdot 5H_2O$, 103 gm. (1 mole) of sodium bromide and 500 ml. of water. The cuprous bromide suspension was cooled to 30°C, 180 ml. of 48% hydrobromic acid added and then the diazonium solution was added as rapidly as possible (30 min.). The reaction mixture was heated at 95°C for one hour and then steam distilled. From a distillate of 20 liters, chloroform extraction yielded 78 gm. of a dark red oil which was distilled through an 11-in. Vigreux column. The fraction boiling at 160-165°C/0.5 mm., n_D^{25} 1.6051, was collected. It weighed 55 gm. (20% yield).

Anal. Calcd. for $C_{12}H_{11}OBr$: C, 57.34; H, 4.42; Br, 31.82. Found: C, 57.89; H, 3.84; Br, 31.70.

2-Methyl-5-phenoxyaniline

4-Methyl-5-nitroaniline. This compound was prepared in 79% yield (596 gm.) by the nitration of p-toluidine according to the procedure of Nolting and Collins, (11).

4-Bromo-2-nitrotoluene. This compound was prepared from 4-methyl-2-nitroaniline by the Sandmeyer reaction according to the procedure of Gibson and Johnson, (12). From 590 gm. (3.88 moles) was obtained 707 gm. (84% yield) of product, m.p. 44-45°C.

4-Methyl-3-nitrophenyl phenyl ether. This ether was prepared by the Ullmann procedure (1) using 7.5 moles of phenol, 1.5 moles of potassium hydroxide, 1.5 moles of 4-bromo-2-nitrotoluene and 10 gm. of copper powder at 150°C for four hours followed by one hour at 180°C. The product weighed 240 gm. (70% yield) and boiled at 128-130°C/0.5 mm, n_D^{25} 1.5930.

Anal. Calcd. for $C_{13}H_{11}O_3N$: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.47; H, 5.19; N, 6.11.

2-Methyl-5-phenoxyaniline. A 1 liter stainless steel rocking autoclave was charged with a solution of 240 gm. (1.05 moles) of 4-methyl-3-nitrophenyl phenyl ether in 300 ml. of 95% ethanol and 8 gm. of Raney nickel. Hydrogen at 700 psig. was added and the bomb heated to 115°C. Hydrogen was added as needed to maintain a pressure of 700 psig. When no more hydrogen was absorbed, the bomb was cooled, emptied and washed out with ethanol. The catalyst was removed by filtration, ethanol was stripped off and the residue was distilled through an 11-in. Vigreux column. The fraction boiling at 125-133°C/2 mm was collected. It weighed 174 gm. (83% yield) and melted at 80-81.5°C.

Anal. Calcd. for $C_{13}H_{13}ON$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.12; H, 6.73; N, 7.38

Chlorination of 1,4-bisphenoxybenzene

Heptachloro 1,4-bisphenoxybenzene. Chlorine was bubbled at 45°C through a solution of 131 gm. (0.5 mole) of 1,4-bisphenoxybenzene in 350 ml. of chloroform containing 4 gm. of anhydrous ferric chloride until 106 gm.(1.5 mole) had been absorbed. The solution was filtered, washed with three 200-ml. portions of 10% sodium hydroxide solution and two 200-ml. portions of water and dried over sodium sulfate. The residue remaining after removal of drying agent and solvent was distilled through an 11-in. Vigreux column. The fraction boiling at 245°C/0.6 - 263°C/0.8 mm was collected; it melted from 120-145°C and weighed 197 gm. After one recrystallization from acetic acid followed by recrystallization from an ethanol-benzene mixture 64 gm. of white crystals, m.p. 147-152°C, were obtained which corresponded by analysis to a heptachloro bisphenoxybenzene.

Anal. Calcd. for $C_{18}H_7O_2Cl_7$: C, 42.94; H, 1.40; Cl, 49.30. Found: C, 43.70; H, 1.90; Cl, 47.92.

The mother liquor from the first recrystallization was stripped of solvent and the residue, 52 gm., was distilled through an 11-in. Vigreux column. The fraction boiling at 250-255°C/0.7 mm, 47 gm., was collected. It was a glass and corresponded by analysis to heptachloro bisphenoxybenzene, an isomer of the solid of m.p. 147-152°C.

Found: C, 43.39; H, 1.85; Cl, 48.52.

Dichloro-1,4-bisphenoxybenzene

Chlorine was bubbled at 20°C through a solution of 131 gm. (0.5 mole) of 1,4-bisphenoxybenzene and 4 gm. anhydrous ferric chloride in 350 ml. of carbon tetrachloride until 34 gm. (0.96 mole) had been absorbed. The solution was filtered, washed with 300 ml. of 5% sodium carbonate and two 300-ml. portions of water and dried over sodium sulfate. The residue remaining after removal of drying agent and solvent was distilled through an 11-in. Vigreux column. The distillate, 156 gm., b.p. 195-215°C/0.7 mm, partially solidified on standing and was crystallized from 1 liter of ethanol. There was obtained 62 gm. of colorless plates, m.p. 99-100°C, presumed to be 1,4-bis(*p*-chlorophenoxy)-benzene.

Anal. Calcd. for $C_{18}H_{12}O_2Cl_2$: C, 65.27; H, 3.65; Cl, 21.41. Found: C, 64.90; H, 3.74; Cl, 20.38.

The ethanol was stripped off leaving 90 gm. of a viscous oil which was distilled through an 11-in. Vigreux column. The distillate, 74 gm., b.p. 165-175°C/0.1 mm was fractionated through an 8-in. helices-packed column. Two fractions were collected: *A*, 31 gm., b.p. 191-195°C/0.7 mm n_D^{25} 1.6183, pour point -12°C, and *B*, 12 gm., b.p. 195-198°C/0.7 mm, n_D^{25} 1.6203, pour point -3°C. Fraction *A* is predominantly dichloro-1,4-bisphenoxybenzene while *B* is predominantly trichloro-1,4-bisphenoxybenzene.

Anal. Calcd. for $C_{18}H_{12}O_2Cl_2$: C, 65.27; H, 3.65; Cl, 21.41. Found: Fraction *A*: C, 63.68; H, 3.45; Cl, 23.22. Calcd. for $C_{18}H_{11}O_2Cl_3$: C, 59.13; H, 3.03; Cl, 29.09. Found, Fraction *B*: C, 60.63; H, 3.50; Cl, 26.62.

Chlorination of diphenyl ether

Chlorine was bubbled through a stirred mixture of 170 gm. (1 mole) of diphenyl ether and 3 gm. of ferric chloride at 80°C until 145 gm. (4.1 mole) of chlorine had been absorbed (5 hr.). The reaction mixture was taken up in 1 liter of benzene and washed with four 200-ml. portions of 10% sodium carbonate solution, two 300-ml. portions of water, dried over sodium sulfate, filtered, and stripped of solvent up to 170°C/15 mm. The residue was distilled through an 11-in. Vigreux column and the fraction boiling at 170-171°C/2 mm, n_D^{25} 1.6161, was collected; weight 204 gm. This fraction was treated with 30 gm. of attapulgus earth and distilled through an 8-in. helices-packed column. The fraction boiling at 144-145°C/0.6 mm, n_D^{25} 1.6139, weight 82 gm., had an analysis corresponding to the tetrachlorinated derivative.

Anal. Calcd. for $C_{12}H_6OCl_4$: C, 46.79; H, 1.96; Cl, 46.05. Found: C, 45.84; H, 2.09; Cl, 46.64.

p-(4-Cyclohexylcyclohexyl)phenyl ether

4-Cyclohexylcyclohexylbromide (245 gm., 1 mole) was added dropwise over a period of five hours to a stirred mixture of aluminum chloride (272 gm., 2.04 moles), diphenyl ether (340 gm., 2 moles), and carbon disulfide (1000 ml.). After standing for three days the reaction was poured onto ice to decompose the complex and the liquid was taken up in ether and washed free of hydrogen bromide. The carbon disulfide and ether were removed by distillation and the residue was subjected to vacuum distillation through a 10-in. Vigreux column. A crude fraction was collected, b.p. 121-230°C/0.3 to 0.8 mm. After two fractionations, 43 gm. of product was collected, b.p. 178-192°C/0.25 mm, n_D^{25} 1.5699.

Anal. Calcd. for $C_{24}H_{30}O$: C, 86.1; H, 9.04: Found: C, 86.8, H, 8.94.

An approximate pour point is -4°C. This compound was assumed to be the para isomer.

4-(4-Chlorobenzyl)phenyl phenyl ether

p-Chlorobenzyl chloride (241.5 gm., 1.5 moles) was added dropwise during six hours to a stirred mixture of diphenyl ether (1000 gm.) and aluminum chloride (26.6 gm., 0.2 mole) at 150°C. The reaction was stirred for one-half hour and sufficient diethyl ether was added to effect a top layer on washing with water. The organic layer was separated, the diethyl ether and excess diphenyl ether were removed under waterpump vacuum and the residue was fractionated three times through a 10-in. heated Vigreux column. A greenish liquid fraction (74 gm.) boiling at 165-171°C/0.1 to 0.12 mm, n_D^{25} 1.6092 was collected as the desired compound.

Anal. Calcd. for $C_{19}H_{15}OCl$: Cl, 12.0. Found: Cl, 11.53

Bis(p-acetylphenyl) ether

Acetyl chloride (157 gm., 2 moles) was added dropwise with stirring and cooling ($<$20°C) to a mixture of carbon disulfide (500 ml.), diphenyl ether (170 gm., 1 mole) and aluminum chloride (427 gm., 3.2 moles).

After all of the acetyl chloride had been added, stirring was continued for four hours. The reaction was poured into water, separated by filtration and washed on the filter. The partially dried product appeared to undergo considerable resinification on vacuum distillation, b.p. 220-230°C/2-4.5 mm, yield 117 gm. (46%); m.p. 98-102°C, reported 100-101°C (13).

A second preparation of this compound following the procedure described for Bis(p-butyrylphenyl) ether below gave an 86.5% yield (m.p. 100-101°C). The essential difference from the above preparation was recrystallization instead of distillation of the partially dried product.

Bis(p-ethylphenyl) ether

To a solution of bis(p-acetylphenyl) ether (116 gm., 0.45 mole) in 800 ml. of acetic acid was added amalgamated zinc (300 gm.), conc. hydrochloric acid (300 ml.) and water (225 ml.) and the mixture was brought to reflux. At this time 300 ml. more conc. hydrochloric acid was added and refluxing was continued for 12 hours with stirring. A specimen from the top layer on treatment with dinitrophenylhydrazine showed no precipitate, indicating the reduction was complete. Filtration of the reaction yielded 200 gm. of amalgamated zinc, which is abnormally high. The liquid product was taken up in ethyl ether and washed free of mineral acid. The ether was removed by distillation and the product was vacuum distilled through a 10-in. heated Vigreux column, b.p. 138-140°C/1.5-1.8 mm (56 gm.). Redistillation yielded 45 gm; (40%) of a water clear liquid; b.p., 153-154°C/3.4-3.8 mm, n_D^{25}, 1.5530.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.9; H, 8.02. Found: 85.35; H, 7.73.

Infrared indicated that a trace of monoethyldiphenyl ether may be present.

The amalgamated zinc was prepared in the usual manner by stirring mossy zinc (300 gm.) for five minutes with mercuric chloride (30 gm.), conc. hydrochloric acid (15 ml.) and water 300 ml. The liquid was decanted and the zinc used directly.

Bis(p-ethylphenyl) ether

This compound (b.p. 139-142°C/2 mm, n_D^{25} 1.5520) was also prepared in a 64% yield by the Wolff-Kishner reduction (14) as described below for the bis(p-n-butylphenyl) ether.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.8; H, 8.02. Found: C, 84.36; H, 8.29.

Bis(p-butyrylphenyl) ether

Butyryl chloride (213 gm., 2 moles) was added dropwise with stirring to a mixture of diphenyl ether (170 gm., 1 mole), aluminum chloride

(427 gm., 3.2 moles) and carbon disulfide (1000 ml.). Stirring was continued for five hours, then the reaction mass was cautiously poured onto ice with vigorous stirring. The solid product was filtered off, washed, air-dried (216 gm., 70%) and recrystallized out of ethanol. The white glistening compound melted 103.5-104.5°C.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.37; H, 7.14. Found: C, 77.93; H, 7.98.

Bis(*p*-*n*-butylphenyl) ether

A stirred mixture of bis(p-butyrylphenyl) ether (211 gm., 0.68 mole), potassium hydroxide (145 gm., 2.59 moles), 85% hydrazine hydrate (185 ml.), and triethylene glycol (920 ml.) was heated at reflux for 1 hour. The water was then removed by distillation and the temperature was raised to 195°C, where it was held for four hours. The reaction mass was poured into 12 liters of water and extracted repeatedly with diethyl ether. The diethyl ether was removed by distillation and the residue was purified by vacuum distillation through a 10-in. heated Vigreux column. On the second fractionation a water-white liquid (86 gm., 45%) was collected as the product at 190-192°C/2.8 mm; n_D^{25} 1.5293.

Anal. Calcd. for $C_{20}H_{26}O$: C, 85.0; H, 9.27. Found: C, 82.86; H, 9.23.

Bis(*p*-benzoylphenyl) ether

Benzoyl chloride (281 gm., 2 moles) was added dropwise at room temperature to a stirred mixture of diphenyl ether (175 gm., 1.03 moles), aluminum chloride (451 gm., 3.38 moles) and carbon disulfide (1500 ml.). The reaction was stirred for five hours, allowed to stand over night and then poured onto ice and conc. hydrochloric acid. The presence of a small amount of ether appeared to aid in decomposing the aluminum chloride complex. The solid product was washed free of acid by slurrying in dilute sodium carbonate solution. Recrystallization out of glacial acetic yielded 310 gm., (82%) of white crystalline product, m.p. 162-163°C.

Anal. Calcd. for $C_{26}H_{18}O_3$: C, 82.5; H, 5.04. Found: C, 82.79; H, 4.79.

Bis(*p*-benzylphenyl) ether

This ether was prepared using the Wolff-Kishner [reduction of the bis(*p*-benzoyl phenyl) ether] following the procedure described above for the bis(*p*-*n*-butyl phenyl) ether.

Charge:

Bis(*p*-benzoylphenyl) ether	283.8 gm.(0.75 mole)
Triethylene glycol	1500 ml.
Potassium hydroxide	160.4 gm. (2.865 moles)
Hydrazine hydrate, 85%	204 ml.

The solid product was filtered from the 12 liters of water, dissolved in ether and filtered to remove some insoluble residue. The ether was evaporated and the residue was recrystallized from ethanol. Yield 105 gm. (55%); m.p. 55-56°C.

Anal. Calcd. for $C_{26}H_{24}O$: C, 88.5, H, 6.86. Found: C, 89.46; H, 6.61.

p-Benzoyl-m-methylphenyl p-benzoylphenyl ether

This preparation was carried out using the same procedure and molecular ratios as described for bis(p-benzoylphenyl) ether. The pasty product was taken up in ether and washed free of acid. The residue after removal of the ether was recrystallized from ethanol, yielding 263 gm. (63%) of a white crystalline product, m.p. 84-85°C.

Anal. Calcd. for $C_{27}H_{20}O$: C, 82.61; H, 5.14. Found: C, 82.87; H, 5.26.

p-Benzyl-m-methylphenyl phenyl ether

The Wolff-Kishner reduction was carried out as previously described. The charge was:

p-Benzoyl-m-methyl phenyl p-benzoylphenyl ether -	196 gm.(0.5 mole)
Triethylene glycol	1000 ml.
Hydrazine hydrate, 85%	136 ml.
Potassium hydroxide	107 gm.(1.91 moles)

The product was taken up in ether and washed until neutral. The ether was removed by distillation and the solid residue was vacuum distilled. A solid fraction (89 gm., 49%) distilling 242-259°C/0.45 mm was collected and recrystallized out of ethanol; m.p. 64.5-66°C.

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.93; H, 6.64. Found: C, 88.73; H, 6.77.

V. PHYSICAL TESTING

Physical measurements made on the compounds listed include relative thermal stability, viscosity and vapor pressure by the isoteniscope method, melting or pour points, boiling points, and crystallizability.

Thermal Stability

Progress in synthesis of relatively stable compounds brought us to a point where a test more sensitive than our original thermal stability test (15) was needed to resolve differences in thermal stability more precisely. Although it seems that no single, simple test can suitably classify various types of compounds as to thermal stability,

TABLE 5

ETHERS PREPARED BY THE ULLMANN REACTION

Sple. No.	REACTANTS				CONDITIONS					PRODUCTS						
	Phenol	Moles	Arylhalide	Moles	KOH Moles	Cu gm.	Temp °C	Time hrs.	Yield %	Physical Constants			Anal.			
										M.P., °C	B.P., °C/mm.	n_D^{25}	Found C	Found H	Calcd. C	Calcd. H
16	Phenol	3	p-Dibromobenzene	1	2.8	5	250	3	65	75-76	150-152/0.6					
14	Phenol	3	o-Dichlorobenzene	1	2.8	5	235	4	42	91-93	139-144/0.4					
34	Carvacrol(5-Isopropyl-2-methylphenol)	1.5	p-Dibromobenzene	0.5	1.3	5	250	4	23		183-185/0.2	1.5663	83.22	7.95	83.38	8.07
47	p-Ethylphenol	1.5	Bis(p-bromophenyl) ether	0.5	1.3	5	250	4	50	110-111	260-265/0.8		82.13	6.29	81.92	6.39
19	p-Cresol	2.0	p-Bromophenyl phenyl ether	0.5	1.9	5	245	4	81	50-51	160/0.5-166/0.8		83.11	6.19	82.58	5.84
24	p-Cresol	2.0	p-Dibromobenzene	0.5	1.9	5	250	4	57	98-100	155-160/0.5		82.83	6.30	82.73	6.25
28	p-Isopropylphenol	1.3	p-Dibromobenzene	0.5	1.1	5	250	4	61	64.5-66	211-213/0.9		83.25	7.32	83.20	7.57
35	Phenol	1.5	2,4-Dichlorotoluene	0.5	1.3	5	240	6	52		156-159/0.6	1.5993	82.81	6.00	82.58	5.84
15	Phenol	1.5	1,3-Dichlorobenzene	0.5	1.5	5	195	6	17	47-48	151-154/0.6		82.43	5.67	82.42	5.38
27	p-Propylphenol	0.8	p-Dibromobenzene	0.35	0.75	3	230	3	55	49-50 (1)	206-209/0.6		82.93	7.85	83.20	7.57
38	p-Propylphenol	0.8	2,4-Dichlorotoluene	0.35	0.78	3	230	6	8		175-178/0.5	1.5670	83.71	7.92	83.29	7.83
29	p- tert.-Butylphenol	1.2	p-Dibromobenzene	0.5	1.1	5	250	4	53	122-123 (1)	230-233/1.		83.49	8.21	83.38	8.07
18	m-Cresol	0.8	p-Brompphenyl phenyl ether	0.5	0.7	5	250	4	77	22-23	145/0.1-153/0.2	1.6005	84.49	5.94	82.58	5.84
23	m-Cresol	1.2	p-Dibromobenzene	0.5	1.1	5	250	4	43	57-58(1)	160-162/0.07		82.79	6.31	82.73	8.25
17	o-Cresol	0.7	p-Bromophenyl phenyl ether	0.5	0.6	5	250	4	29		139-140/0.08	1.6002	82.46	5.81	82.58	5.84
22	o-Cresol	1.5	p-Dibromobenzene	0.5	1.2	5	245	4	44	50-51	156-157/0.4		82.78	6.56	82.73	6.25
46	p-Cresol	1.5	Bis(p-bromophenyl) ether	0.5	1.3	5	245	5	53	142-144(2)	267-269/2.0		81.62	5.60	81.65	5.80
30	p-Octylphenol	0.6	p-Dibromobenzene	0.25	0.55	5	245	4	52	57-58(1)	280-282/0.7		84.06	9.65	83.90	9.53
44	o-Cresol	1.5	Bis(p-bromophenyl) ether	0.5	1.3	5	240	4	59		256-258/2.5	1.6103	81.92	5.87	81.65	5.80
45	m-Cresol	0.6	Bis(p-bromophenyl) ether	0.25	0.55	0.6	200	3	53	61-62(1)	243-247/1.0		80.74	6.01	81.65	5.80
31	p-Cyclopentylphenol	0.45	p-Dibromobenzene	0.2	0.43	0.6	215	4	63	110-111(2)	255-260/1.0		84.62	7.84	84.38	7.59
51	p-Methoxyphenol	0.6	Bis(p-bromophenyl) ether	0.25	0.6	0.5	210	3	41	168-169(2)	280-290/1.3		74.93	5.46	75.35	5.35
42	m-Phenoxyphenol	0.3	p-Bromophenyl phenyl ether	0.3	0.3	1	200	4	35	48-49(1)	220-221/0.4	1.6200	81.40	5.17	81.34	5.12
20	o-Cyclohexylpehnol	0.927	p-Bromophenyl phenyl ether	0.695	0.84	10	250-260	3.5	64	74-76	217-218/0.08		83.99	7.16	83.6	7.02
8	p-Ethylphenol	1.0	p-Bromobiphenyl	0.75	0.90	10	250	4.5	44	66-68	202-203/1.75		87.82	6.61	87.54	6.61
33	Carvacrol	1.0	p-Bromophenyl phenyl ether	0.90	0.90	15	260	5.0	22	-10 p.p.	167-168/0.2	1.5810	82.79	7.06	82.94	6.96
21	p-Cyclohexylpehnol	1.0	p-Bromophenyl phenyl ether	0.90	0.90	15	250-287	5.0	69	82-84	224-225/0.45		84.28	7.22	83.67	7.02

TABLE 5 (cont'd)

Sple. No.	REACTANTS						CONDITIONS			PRODUCTS						
	Phenol		Arylhalide		KOH Moles	Cu gm.	Temp °C	Time hrs.	Yield %	Physical Constants			Anal.			
													Found		Calcd.	
		Moles		Moles						M.P., °C	B.P., °C/mm.	n_D^{25}	C	H	C	H
6	p-Cyclohexylphenol	0.75	p-Bromophenylcyclohexane	0.627	0.75	15	260	5.0	53	69-71			85.88	9.16	86.18	9.04
32	2,4-Di-sec-amylphenol	1.0	p-Bromophenyl phenyl ether	0.9	0.9	15	260	5.0	40		206-207/0.5	1.5560	83.62	8.69	83.54	8.51
37	m-Cresol	2.0	2,4-Dibromoethylbenzene	0.9	2.0	15	260	5.0	48	-13p.p.	163-166/0.25	1.5840	82.43	6.85	82.98	6.96
55	p-Ethylphenol	1.1	1,2,4-Trichlorobenzene	1.0	1.0		270	4.0			186-190/0.20	1.5895				
2	p-Cresol	1.0	1,2,4-Trichlorobenzene	1.8	KOH.0.5 NaOH 0.5	2.5	200	12.0	13	-30p.p.	103-106/.08	1.5900	27.68 (5)		27.63	
39	3,4-Dimethylphenol	1.5	2,4-Dibromotoluene	0.7	1.5	10	255	5.0	39	69-71.5	179/0.06		82.81	7.41	83.0	7.28
40	5-Ethyl-3-methylphenol	1.5	2,4-Dibromotoluene	0.75	1.5	15	260	5.0	24	-8p.p.	168-171/0.07	1.5748	82.49	7.91	83.28	7.83
56	Thiophenol	1.85	2,4-Dibromotoluene	0.92	1.84	10	260	8.0	40	-16p.p.	175-176/0.07	1.6683	20.62 (6)		20.78	
50	o-Cresol	1.5	4,4'-Dibromobiphenyl	0.75	1.5	10	260	6.0		121-123(1)	200-210/0.10		85.22	6.30	85.24	6.05
	o-Cresol	3	Bromobenzene	3	3	10	215	12	32		131/9-10	1.5700				
	m-Cresol	3	Bromobenzene	3	3	10	235	5	53		138-139/11	1.5706				
57	Thiophenol	1	Bis(p-bromophenyl) ether	0.5	1	10	220	4	35	82-86(3)			73.73	4.93	74.59	4.69
58	m-Cresol	1.5	Dibromonaphthalene	0.75	1.5	5	240	5		58-59(4)	191-196/0.05		85.05	5.86	84.66	5.92

(1) Compounds 27,29,23,30,45,42, and 50 were crystallized out of ethanol.

(2) Compounds 31,46, and 51 were crystallized out of benzene + ethanol.

(3) Compound 57 was recrystallized out of hexane.

(4) Compound 58 was recrystallized out of methanol.

(5) Chlorine analysis.

(6) Sulfur analysis.

the isoteniscope test does provide a basis for comparison of decomposition rates at temperatures at which the rates become measurable. Several laboratories use this type of test; however, results from different sources are not comparable because of differences in apparatus and technique. The measurements have also been too time-consuming for extensive use.

To overcome these difficulties, we have constructed a modified isoteniscope, making improvements in technique, procedure, and apparatus which should make the method more widely applicable. It is hoped that the new procedure will serve as a basis for a standardized test.

Three constants are derived from the data for each compound: (1) an empirical decomposition point, defined as the temperature at which the isothermal rates of pressure rise attain a rate of 0.014 mm Hg/sec. (which corresponds to a rate of 500 mm Hg pressure rise per 10 hours); (2) the activation energy for decomposition; and (3) the frequency factor; the latter two constants are the usual empirical constants defined in connection with the Arrhenius reaction rate equation.

Isoteniscope thermal stability data on 44 compounds are reported in Table 6 along with other physical measurements. Vapor pressure data are also obtained incidental to the thermal stability test with the isoteniscope.

Apparatus for Isoteniscope Tests

Figure 2 shows the layout of components in the isoteniscope test apparatus.

The vacuum and gas-handling system has been previously described. (15) The furnace previously used has been replaced by a nitrate bath (eutectic mixture composed of 27.3% $LiNO_3$, 18.2% $NaNO_3$ and 54.4% KNO_3, m.p. ca 250°F) (16) contained in a round-bottom, cylindrical Pyrex glass vessel 4 in. diameter and 11.5 in. tall. This is heated at the bottom by a 590-watt hemispherical heating mantle (Glas-Col 500-ml. quartz mantle). The side walls are insulated by a 9 in. length of 4 in. ID. preformed glasswool pipe insulation having a 1 in. wall thickness. A 1-1/4 in. wide x 5 in. high window in the lower part of the insulation allows observation of the interior. The insulation is held in place by a 6 in. diameter glass cylinder (made from a 4-liter beaker with bottom cut out) which fits snugly over the insulating material. The liquid is agitated by a stainless steel impeller driven by a small electric motor. Temperature regulation is effected with a resistance bridge type automatic temperature controller (Thermotrol Model 1053, Hallikainen Instruments) using a tungsten-in-Pyrex resistance thermometer as the sensing element and a 200-watt control heater (Nichrome in Pyrex) immersed in the bath. This system affords bath temperature control to ± 0.1°F at temperatures up to 860°F, which is especially needed for determining the smaller isothermal rates of pressure rise encountered at the lower end of the measurable range. A few runs were made without automatic regulation, under which conditions,

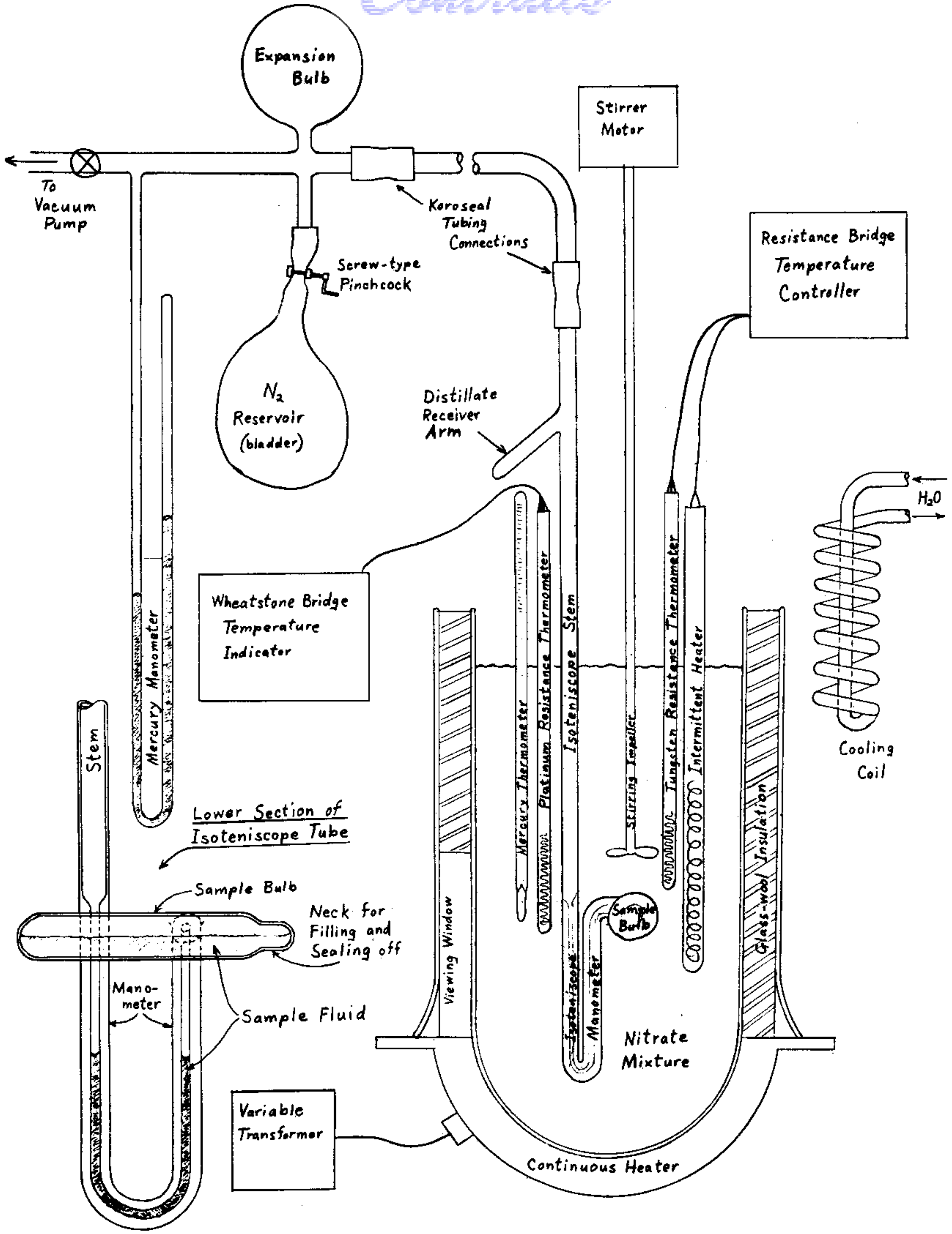


Fig. 2 Apparatus for Isoteniscope Tests

the bath temperature was found to vary by 0.5°F during the time required to establish the lower rates of pressure rise (30 to 45 min.). The automatic controller provides quick attainment of a steady temperature after a change of bath temperature. Bath temperature can be lowered quickly by immersing in the bath a coil of 3/16-in. OD copper tubing through which tap water circulates.

Bath temperatures are determined within ± 0.2°F with a National Bureau of Standards calibrated platinum resistance thermometer using a double slidewire portable precision Wheatstone bridge temperature indicator (No. 8062, Leeds and Northrup). A mercury-in-glass thermometer, calibrated against the platinum resistance thermometer, is used for temperature observations when measuring vapor pressures and when changing the bath temperature.

The isoteniscope tube is similar to the one previously described (15) except that the sample bulb (13 mm OD by 60 mm long) is now mounted with the cylinder axis horizontal instead of vertical. This change provides a larger surface area and smaller depth of sample so that equilibration of decomposition products between liquid and vapor states is much faster.

During some thermal stability tests, sufficient liquid decomposition products are accumulated in the isoteniscope stem to reflux vigorously and mix with the sample fluid in the isoteniscope manometer, causing "bumping" which interferes with the pressure readings. To overcome this, a distillate receiver arm has been added near the top of the isoteniscope stem so that when this condition arises, the more volatile liquid decomposition products can be distilled off and trapped out in the receiver arm. This is done by wrapping the stem with asbestos tape and temporarily reducing pressure in the system.

The isoteniscope tube is connected to the gas handling system by flexible Koroseal surgical tubing connections which permit the movements needed in degassing the isoteniscope tube and the sample under vacuum and positioning it in the bath. Note: The horizontal section of glass tubing between the Koroseal coupling tubes is about 18 in. long, an arrangement that permits manipulation of the isoteniscope bulb into and out of the bath without breaking the vacuum connection.

Procedure for Isoteniscope Measurements

Before use, the sample tubes are cleaned with organic solvents, water, and chromic acid cleaning solution, followed by a water-wash and a drying solvent. The sample is added to half-fill the calibrated sample bulb. (The several bulbs held between 4.0 and 4.4 ml.) The bulb is sealed off, attached to the vacuum-gas handling system, and evacuated. The isoteniscope tube is then heated with a gas flame to out-gas the glass walls, starting at the top of the stem and moving down to the smaller-bore manometer section. After the stem has cooled, the manometer is heated and kept hot while the sample bulb is gradually heated, slowly boiling the sample through the manometer to reflux in the cooler upper part of the stem. When all of the sample liquid has boiled out of the bulb into the stem, the bulb and manometer are further heated for thorough out-gassing. The bulb and manometer are allowed to cool until the sample stops refluxing and begins to re-condense in the sample bulb, then the isoteniscope tube is positioned in the nitrate bath at ca 200°C. Since the samples have low vapor pressures at this temperature (usually less than 1 mm Hg), refluxing stops and most of the sample drains back into the sample bulb. A small amount of nitrogen is let into the system to push all of the sample liquid into the bulb, leaving the manometer tube open. The system is then re-evacuated and the bath temperature gradually increased, distilling sample vapor again through the manometer to sweep out the sample bulb and manometer tube, until a reflux head of about 0.5 ml. of liquid is formed in the isoteniscope stem. At this point the bath temperature corresponds to that for a vapor pressure of about 10 to 12 mm Hg. Nitrogen is then slowly admitted, causing the refluxing liquid to recede and form a pool at the lower end of the stem through which additional vapors are allowed to pass for a brief time to sweep out any nitrogen which may have entered the bulb. Nitrogen pressure is then increased further to force all liquid back into the bulb except enough to serve as manometric fluid in the small isoteniscope manometer. Following this the small manometer is kept in balance as the temperature is raised and the pressure (read on the large mercury manometer) and temperatures are observed periodically, to obtain vapor pressure data.

Better reproducibility of rates of pressure rise is obtained by starting at the high temperature end of the measurable range and determining rates at successively lower temperatures rather than by the earlier method of starting at the low temperature end. By this procedure, relatively volatile or unstable impurities which may be present are largely eliminated at the higher temperatures and their effects minimized before the lower rates of pressure rise are measured.

In the procedure finally adopted as standard, rates are first measured at temperatures which give relatively high rates of pressure rise (about 0.5 mm Hg/sec.). Rates are then measured at three or four successively lower temperatures, at intervals of 15 to 25°C. When the pressure in the system reaches atmospheric pressure, due to accumulation of decomposition products, nitrogen pressure is gradually reduced thus allowing sample vapors and decomposition products to distill through the isoteniscope manometer until the pressure approaches the equilibrium vapor pressure of the sample. Nitrogen pressure is then adjusted to balance the small manometer, whereupon pressure rise measurements can be resumed.

The rates of pressure rise initially observed at any temperature sometimes vary, changing steadily with successive observations, until, in most cases, a constant rate is reached which is reproducible to within the experimental error of the measurements. It has been found, for all compounds tested thus far, that when behavior is such that a constant rate is reached, then the logarithm of the rate gives a straight line when plotted against reciprocal absolute temperature. This serves as a basis for calculating activation energy for the reactions.

For some compounds isothermal rates were found to drift steadily in one direction (either increasing or decreasing) for long periods without reaching a steady value. These data were interpreted to give approximate decomposition points but were not considered adequate for determining the constants for the Arrhenius reaction rate equation.

Treatment of Isoteniscope Data

To aid in recording and interpreting isoteniscope data, convenient recording and computing forms, special graph paper, and some graphical methods have been devised. The recording forms provide for systematic recording of numerical data with adequate space for the sample computations necessary for preparing the data for graphical representation. The special graph paper is three-cycle semi-logarithmic on one axis with degrees centigrade plotted to a scale of reciprocal absolute temperature on the other axis. Vapor pressure and simple reaction rates plotted on such paper give straight lines as illustrated below. Since temperatures are directly obtained in degrees centigrade, pressure and rates can be plotted immediately upon observation so that overall progress of the test can be easily followed as the measurements are being made.

Isoteniscope data for two compounds follow to illustrate processing of observations for obtaining the vapor pressure and stability data listed in Table 6.

In Table 7, the vapor pressure data for 2,4 di-(sec-amyl)-phenyl p-phenoxyphenyl ether (Sample No. 32) are listed for various temperatures during the initial heat-up period. The sequences of isothermal rates of pressure rise for the same compound are listed in Table 8 for observations made at four different temperatures. During the test, pressure and rate data are followed graphically by plotting on graph paper prepared specially for use in the test. A completed graph showing the data of Tables 7 and 8 is given in Fig. 3. The vapor pressure data are seen to follow a straight line to a temperature somewhat above the decomposition point. In this case, the straight line is misleading for actually the data at about 100 mm Hg may be readily shown from the rates of pressure rise given in Table 8 to be in error by about 10% because of the accumulation of decomposition products in the isoteniscope bulb. Vapor pressure data such as these in which a considerable portion of the straight line is above the decomposition point are indicated as approximate (ca) in Table 6. All vapor pressures in Table 6 were similarly obtained by reading from the best straight line drawn through the experimental vapor pressure points. Data not indicated as approximate were obtained by extrapolation from pressures estimated to be in error by less than 2%. Table 9 lists the actual pressure ranges for the 21 compounds for which observations were made within this estimated accuracy. This will indicate to the reader the extent of the extrapolation used to obtain the rounded values in Table 6.

TABLE 6

PHYSICAL TEST DATA ON AROMATIC ETHERS

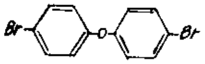
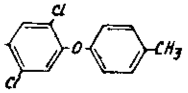
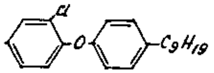
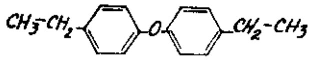
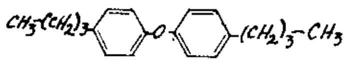
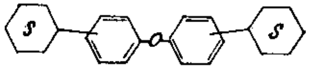
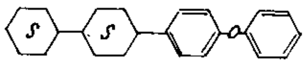
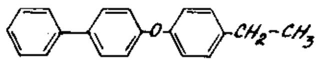
No.	Compound	Melting or Pour Point, °C	Temperature, Deg.C for Vapor Pressure Equal to 10 mmHg	100 mmHg	600 mmHg	760 mmHg	Stability Data Decomp. Point, °F	E' Kcal./mol	A' mmHg/Sec.	Viscosity, cs., at 100°F	210°F	400°F	ASTM Slope 100°-210°F	210°-400°F
1	 Bis(p-bromophenyl) ether	58-60 m	12mm at 201-3°							6.575	1.733	.640	.93	.91
2	 2,5-Dichlorophenyl 4-methylphenyl ether	-15 to +3 m -39 pour								6.512	1.638	.580	.98	.97
3	 o-Chlorophenyl p-nonylphenyl ether													
4	 Bis(p-ethylphenyl) ether	ca.-29 m					>590			3.561	1.373	.572	.81	.86
5	 Bis(p-butylphenyl) ether	ca.-27 m					588			9.046	2.413	.817	.79	.84
6	 Bis(x-cyclohexylphenyl) ether	69-70 m								253.3	11.11	1.879	.89	.79
7	 p-(4-Cyclohexylcyclohexyl)phenyl phenyl ether	-4 pour	ca. 264	ca. 333	ca. 399	ca. 409	659	57.2	2 x 10^{18}	304.0	10.50	1.645	.95	.86
8	 Biphenyl p-ethylphenyl ether	66-68 m									3.561	.987		.86

TABLE 6 (cont'd)

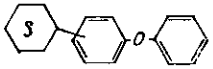
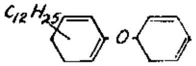
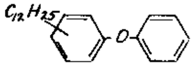
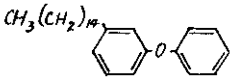
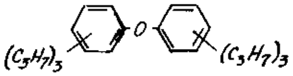
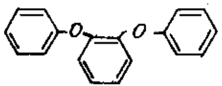
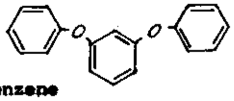
No.	Compound	Melting or Pour Point, °C	Temperature, Deg. C for Vapor Pressure Equal to 10 mmHg	100 mmHg	600 mmHg	760 mmHg	Stability Data Decomp. Point, °F	E' Kcal./mol	A' mmHg/Sec.	Viscosity, cs., at 100°F	210°F	400°F	ASTM Slope 100°-210°F	210°-400°-
9	 Cyclohexylphenyl phenyl ether	-3 m	1.2mm at 154-161							15.58	2.977	.883	.86	.80
10	 Dodecylphenyl phenyl ether	<-39° pour	0.5mm at 191-8							21.26	3.643	.970	.83	.90
11	 Ditto, Isomer	<-39 pour	0.5-0.8 mm at 197-212							29.97	4.63		.80	
12	 3-n-Pentadecylphenyl phenyl ether	30-32m	ca.285			ca.419	650	64.0	$7x10^{20}$	17.21	3.960	1.197	.71	.75
13	 Hexapropyldiphenyl ether	Pasty solid at Rm. T.	0.8mm at 164-7							189.5	16.51	1.656	1.08	.99
14	 o-Diphenoxybenzene	91-93m	203	272	352	364	>756° (1a)				2.910	.809		.96
15	 m-Diphenoxybenzene	47-48m	211	284	361	372	>765 (1b)			12.2	2.632	.816	.86	.89
16	 p-Diphenoxybenzene	75-76m	221	294	371	384	>770 (1c)				2.766	.861		.87

TABLE 6 (cont'd)

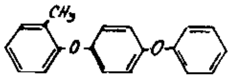
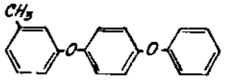
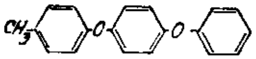
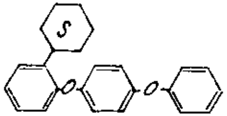
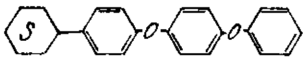
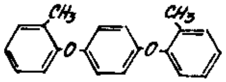
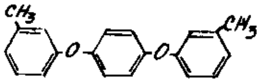
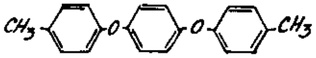
No.	Compound	Melting or Pour Point, °C	Temperature, Deg. C for Vapor Pressure Equal to				Stability Data			Viscosity, cs., at			ASTM Slope	
			10 mmHg	100 mmHg	600 mmHg	760 mmHg	Decomp. Point, °F	E' Kcal./mol	A' mmHg/Sec.	100°F	210°F	400°F	100°-210°F	210°-400°F
17	 o-Tolyl p-phenoxyphenyl ether	+ 9°m - 23p	217	296	376	388	730	ca. 50.3 (2)	6×10^{14}	18.28	3.162	.913	.88	.88
18	 m-Tolyl p-phenoxyphenyl ether	22-23m	225	301	377	389	729	ca. 51.6 (2)	2×10^{15}	15.74	3.006	.905	.86	.86
19	 p-Tolyl p-phenoxyphenyl ether	50-51m	229	304	381	393	732	ca. 50.3 (2)	6×10^{14}	14.36	2.900	.892	.85	.86
20	 o-Cyclohexylphenyl p-phenoxyphenyl ether	81.5-82m	265	343	422	433	669	56.4	6×10^{17}	220.2	8.647	1.484	.97	.88
21	 p-Cyclohexylphenyl p-phenoxyphenyl ether	82-84m	ca.292	ca. 370	ca. 448	ca. 461	706	56.2	1×10^{17}	113.6	8.093	1.639	.86	.78
22	 p-Bis(o-toloxy)benzene	50-51m	224	301	377	388	712			28.90	3.837	0.995	.90	.90
23	 p-Bis(m-toloxy)benzene	57-58m	233	310	387	399	712			20.37	3.319	.958	.88	.86
24	 p-Bis(p-toloxy)benzene	98-100m	244	317	390	402	721				3.084	.932		.85

TABLE 6 (cont'd)

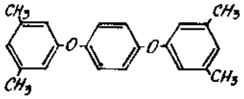
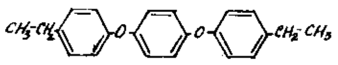
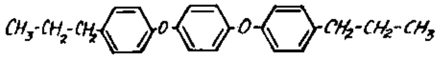
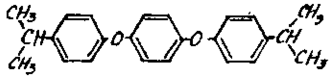
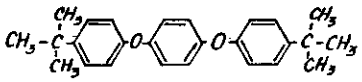
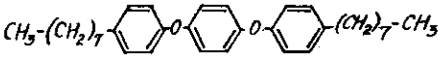
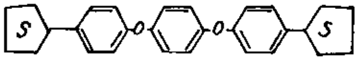
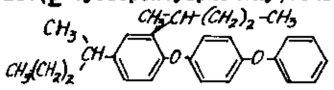
No.	Compound	Melting or Pour Point, °C	Temperature, Deg. C for Vapor Pressure Equal to				Stability Data			Viscosity, cs., at			ASTM Slope	
			10 mmHg	100 mmHg	600 mmHg	760 mmHg	Decomp. Point, °F	E' Kcal./mol	A' mmHg/Sec.	100°F	210°F	400°F	100°-210°F	210°-400°F
25	 p-Bis(3,5-dimethylphenoxy)benzene	95-100 m	251	321	389	400	703	56.4	2×10^{17}		5.281	1.148		.90
26	 p-Bis(p-ethylphenoxy)benzene	52-54 m	259	333	406	417	720				3.464	1.054		.80
27	 p-Bis(p-n-propylphenoxy)benzene	49-50 m	275	350	425	436	670				4.655	1.254		.78
28	 p-Bis(p-isopropylphenoxy)benzene	64.5-66 m	ca. 272			ca. 428	719				5.026	1.285		.78
29	 p-Bis(p-tert-butylphenoxy)benzene	122-123 m	279	358	433	447	700	59.0	2×10^{18}		11.37	1.841		.81
30	 p-Bis(p-n-octylphenoxy)benzene	57-58 m				>425	628	59.5	4×10^{19}		8.549	2.081		.65
31	 p-Bis(p-cyclopentylphenoxy)benzene	110-111 m				ca. 479	678	57.6	1×10^{18}		12.17	2.264		.70
32	 2,4-Di-sec-Amylphenyl p-phenoxyphenyl ether	-18 p	ca. 268			ca. 410	608	54.3	1×10^{18}	121.1	8.273	1.495	.87	.86

TABLE 6 (cont'd)

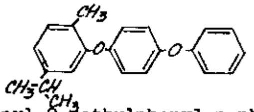
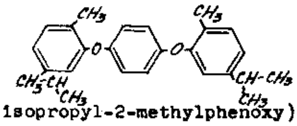
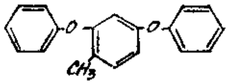
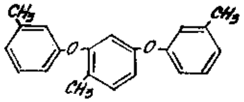
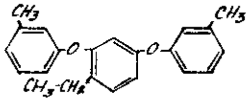
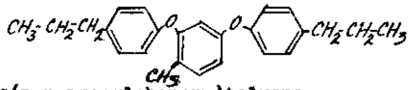
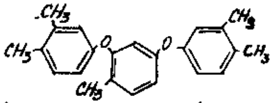
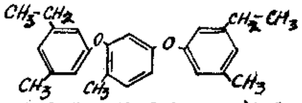
No.	Compound	Melting or Pour Point, °C	Temperature, Deg. C for Vapor Pressure Equal to 10 mmHg	100 mmHg	600 mmHg	760 mmHg	Stability Data Decomp. Point °F	E' Kcal./mol	A' mmHg/Sec.	Viscosity cs., at 100°F	210°F	400°F	ASTM Slope 100°-210°F	210°-400°F
33	 5-Isopropyl-2-methylphenyl p-phenoxyphenyl ether	-18 p	ca. 231			ca. 386	628			48.75	4.912	1.134	.91	.88
34	 p-Bis(5-isopropyl-2-methylphenoxy)benzene	-6° p	0.2mm at 183-4°				621			304.7	10.39	1.613	.98	.97
35	 2,4-Bisphenoxytoluene	7-22.5 m	213	288	363	375	>718 (ld.)			16.60	2.920	.836	.90	.93
36	 2,4-Bis(m-toloxy)toluene	Liquid at Rm. T.	228	302	377	389	635			34.08	3.984	0.990	.93	.92
37	 2,4-Bis(m-toloxy)ethylbenzene	--26 p	233	307	381	391	579	44.0	$6x10^{14}$	32.52	4.097	1.020	.90	.90
38	 p-Bis(p-n-propylphenoxy)toluene	-26 p	263	343	423	435	649	53.9	$2x10^{17}$	40.47	5.240	1.231	.82	.84
39	 2,4-Bis(3,4-dimethylphenoxy)toluene	74-78 m	ca. 259	ca. 331	ca. 401	ca. 411	641			194.1	7.561	1.390	1.01	.88
40	 2,4-Bis(3-ethyl-5-methylphenoxy)toluene	-10 p	ca. 256	ca. 325	ca. 394	ca. 404	630			114.1	7.170	1.353	.92	.88

TABLE 6 (cont'd)

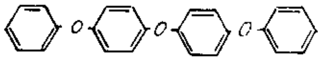
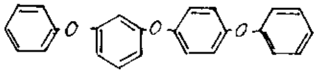
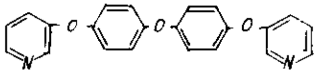
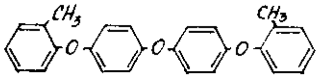
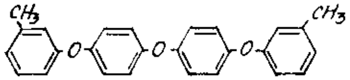
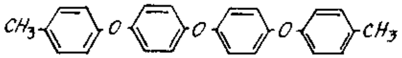
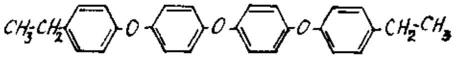
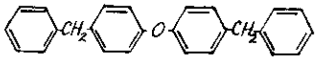
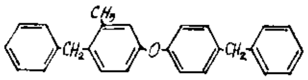
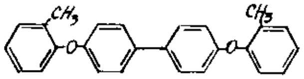
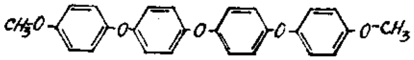
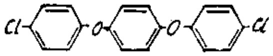
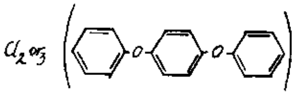
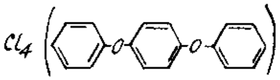
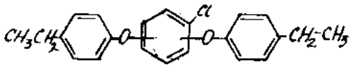
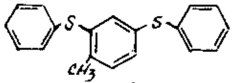
No.	Compound	Melting or Pour Point, °C	Temperature. Deg. C for Vapor Pressure Equal to 10 mmHg	100 mmHg	600 mmHg	760 mmHg	Stability Data Decomp. Point °F	E' Kcal./mol	A' mmHg/Sec.	Viscosity cs., at 100°F	210°F	400°F	ASTM Slope 100°-210°F	210°-400°F
41	 Bis(p-phenoxyphenyl) ether	107-9 m	296	374	450	462	824	68.0	$1x10^{19}$		6.872	1.506		.80
42	 m-Phenoxyphenyl p-phenoxyphenyl ether	48-49 m	288	371	453	466	821	68.4	$1x10^{19}$					
43	 Bis[p-(3-pyridoxy)phenyl] ether	70-71 m	ca. 320	ca. 394	ca. 470	ca. 481	630			339.0	12.41	2.073	.91	.78
44	 Bis[p-(o-toloxy)phenyl] ether	-2 p	ca. 304	ca. 385	ca. 464	ca. 477	585	37.4	$2x10^{12}$	252.0	10.19	1.777	.93	.76
45	 Bis[p-(m-toloxy)phenyl] ether	61-62 m	312	382	450	460	703	52.0	$6x10^{15}$	135.3	8.534	1.698	.88	.78
46	 Bis[p-(p-toloxy)phenyl] ether	142-4 m	ca. 317	ca. 393	ca. 468	ca. 479	698				(300°F) 3.115	1.654		(300°-400°F) 0.766
47	 Bis[p-(p-ethylphenoxy)phenyl] ether	110-1 m	ca. 333	ca. 402		>476	719	52.6	$6x10^{15}$		(300°F) 3.431	1.782		(300°-400°F) .73
48	 Bis(p-benzylphenyl) ether	55-56 m	ca. 291	ca. 357	ca. 420	ca. 430	721	59.4	$9x10^{17}$	46.13	6.137	1.536	.77	.73

TABLE 6 (cont'd)

No.	Compound	Melting or Pour Point, °C	Temperature, Deg. C for Vapor Pressure Equal to 10 mmHg	100 mmHg	600 mmHg	760 mmHg	Stability Data Decomp. Point °F	E' Kcal./mol	A' mmHg/Sec.	Viscosity cs., at 100°F	210°F	400°F	ASTM Slope 100°-210°F	210°-400°F
49	 p-Benzyl-m-methylphenyl p-benzylphenyl ether	64.5-66 m	ca. 304		ca. 448	459	701	57.3	$4x10^{17}$		8.678	1.738		.77
50	 p-p'-Bis(o-toloxy)biphenyl	121-3 m	ca. 306	ca. 380	ca. 453	ca. 464	573				(300°F) 4.779	2.126		(300°-400°F) .83
51	 Bis[p-(p-methoxyphenoxy)phenyl] ether	168-9 m	>330			>390	573	46.6	$8x10^{15}$		(500°F) 1.323	2.173		(400°-500°F) .81
52	 p-Bis(p-chlorophenoxy)benzene	99-100 m	0.4mm at 195-205°											
53	 Chlorinated p-diphenoxybenzene	-12 p	0.7mm at 191-5°											
54	 Tetrachlorinated p-diphenoxybenzene	-17 p	0.6mm at 144-5°											
55	 x,x'-Bis(p-ethylphenoxy)chlorobenzene	-26 p	0.2mm at 186-90°							33.38	4.389	1.094	.86	.87
56	 2,4-Bis(phenylmercapto)toluene	ca + 6 m	ca. 268			ca. 396	599			23.13	3.623	1.014	.86	.85

Notes to Table 6

1. a. For sample 14 decomposition point estimated by extrapolation from dp/dt = .00072mmHg/sec. at 360°C using E' = 60 Kcal.

   b. For sample 15 decomposition point estimated by extrapolation from dp/dt = .00085mmHg/sec. at 367°C using E' = 60 Kcal.

   c. For sample 16 decomposition point estimated by extrapolation from dp/dt = .00050mmHg/sec. at 362°C using E' = 60 Kcal.

   d. For sample 35 decomposition point estimated by extrapolation from dp/dt = .00051mmHg/sec. at 367°C using E' = 60 Kcal.

   e. E' estimated from only two rates.

TABLE 7

VAPOR PRESSURE OF SAMPLE NO. 32, 2,4-Di-(sec.-amyl)phenyl p-phenoxyphenyl ether, During Initial Heat-Up in Isoteniscope

Time, sec.	Temp., °C	Pressure, mm Hg
0	284.0	18.0
111	291.5	23.7
202	297.5	29.4
314	304.0	37.2
418	310.6	46.1
526	317.1	56.9
660	325.3	73.3
747	330.3	86.4
867	337.1	106.4
1068	346.8	146.5
1302	357.5	213.2
1428	362.7	259.9
1524	365.8	300.1

TABLE 8

ISOTHERMAL RATES OF PRESSURE RISE OF SAMPLE NO. 32, 2,4-Di-(sec.-amyl)phenyl p-phenoxyphenyl ether

Time, sec.	Temp., °C	Pressure, mm Hg	Pressure Chg., Δ p, mm Hg	Period Δ t, sec.	Rate, dp/dt mm Hg/sec.
1690	366.5	356.0			
			60.7	171	0.355
1861	"	416.7			
			64.9	181	0.358
2042	"	481.6			
			73.4	204	0.360
2246	"	555.0			
			79.3	212	0.374
2458	"	634.3			
			58.2	152	0.383
2610	"	692.5			
			57.2	149	0.384
2759	"	749.7			
(Pressure reduced to allow decomposition products to bubble out of sample bulb through the isoteniscope manometer. Measurements then resumed)					
0	366.5	307.7			
			88.2	215	0.410
215	"	395.9			
			90.0	225	0.400

TABLE 8 (Cont'd)

Time, sec.	Temp., °C	Pressure, mm Hg	Pressure Chg., Δ p, mm Hg	Period Δ t, sec.	Rate, dp/dt mm Hg/sec.
440	366.5	485.9			
			83.2	202	0.412
642	"	569.1			
			104.3	252	0.414
894	"	673.4			
			75.2	176	0.427
1070	"	748.6			
(Bath cooled to lower temperature; decomposition products pumped out of sample bulb.)					
00	348.1	205.5			
			24.1	173	0.139
173	"	229.6			
			23.1	204	0.113
377	"	252.7			
			25.7	235	0.109
612	"	278.4			
			28.8	260	0.111
872	"	307.2			
			32.2	293	0.110
1165	"	339.4			
			37.9	335	0.113
1500	"	377.3			
			35.5	315	0.113

TABLE 8 (Cont'd)

Time, sec.	Temp., oC	Pressure, mm Hg	Pressure Chg., Δ p, mm Hg	Period Δ t,sec.	Rate, dp/dt mm Hg/sec.
1815	348.1	412.8			
(Bath cooled; decomposition products pumped out of sample bulb.)					
0	329.6	143.9			
			13.2	465	0.0284
465	"	157.1			
			13.8	490	0.0282
955	"	170.9			
			14.3	507	0.0282
1462	"	185.2			
			15.6	556	0.0281
2018	"	200.8			
(Bath cooled; isoteniscope manometer kept balanced; decomposition products not pumped out.)					
0	311.7	181.70			
			11.05	1577	.00701
1577	"	192.75			
			17.50	2398	.00730
3975	"	210.25			

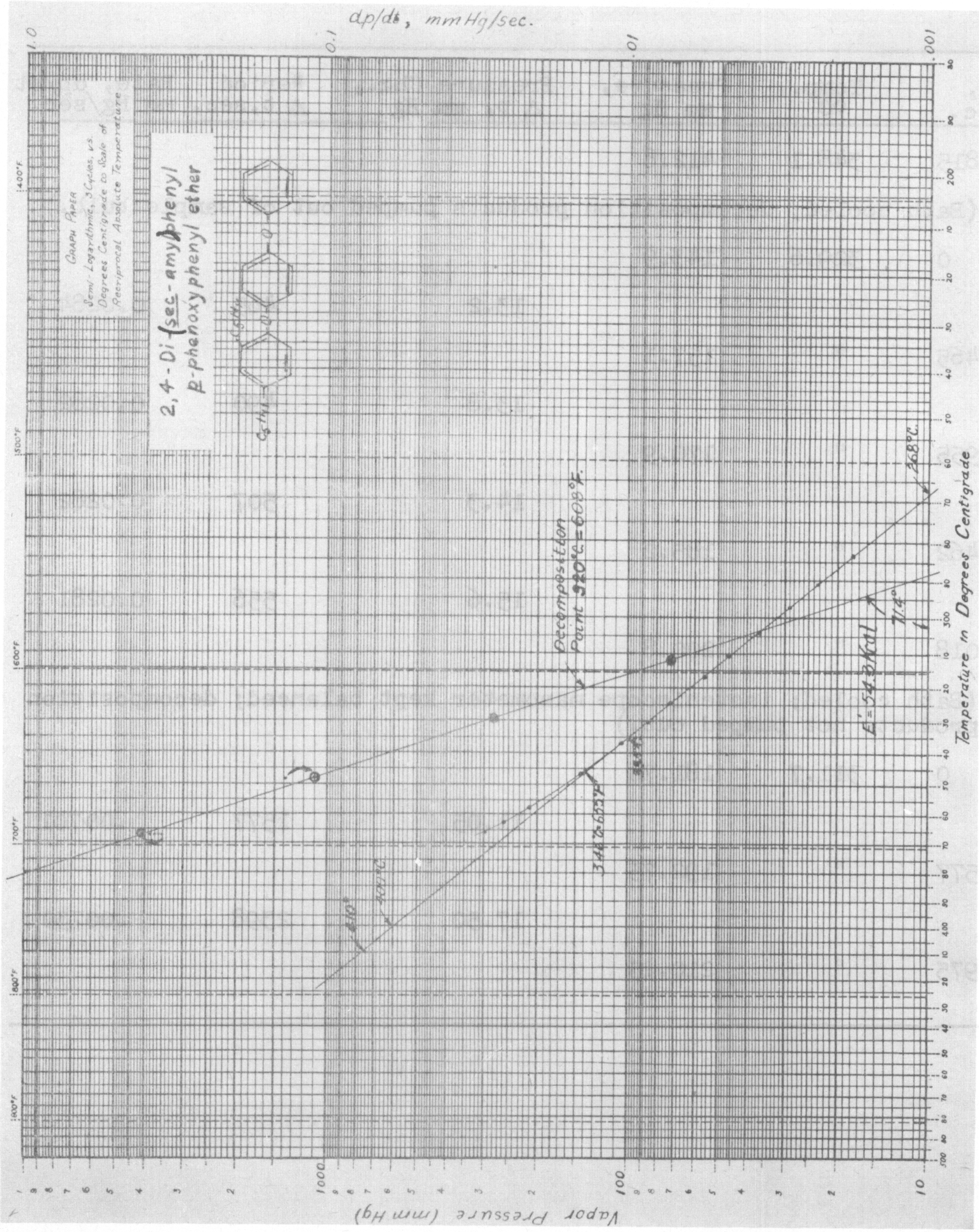


Figure 3 Isoteniscope Data for Sample No. 32.

TABLE 9

RANGES OF ACCURATE VAPOR PRESSURE MEASUREMENTS FOR COMPOUNDS TESTED

Sample Number	Pressure Range, mm Hg	Sample Number	Pressure Range, mm Hg
14	17-705	26	13-210
15	10-680	27	20-80
16	11-600	29	10-105
17	15-600	35	20-630
18	10-450	36	10-105
19	14-450	37	10-70
20	9-75	38	20-80
22	12-600	41	18-290
23	19-300	42	10-350
24	10-35	45	17-50
25	15-250		

Sample numbers correspond to numbering in Table 6

Returning to Fig. 3, the rates, dp/dt mm Hg/sec., have been plotted as points and the limiting rate values as circles. The circles are seen to fall on a straight line. The temperature at which the rate is .014 mm Hg/sec. is read from the graph as the decomposition point.

The rate dp/dt = 0.014 mm Hg/sec. corresponds to a pressure rise of 500 mm Hg in 10 hours in a system half-filled with fluid, and is a new definition of the decomposition point. It was chosen on the practical basis that a hydraulic fluid operating at high temperature should initially have a vapor pressure below 100 mm/Hg at the operating temperature and that during a period of ten hours operation, the pressure should not exceed atmospheric pressure. This definition was chosen to serve as a convenient basis for comparison of relative stability and is not necessarily meant to indicate the limit at which a given compound will be useful in a particular application.

Decomposition points of all the compounds listed in Table 6 and Table 13, were determined as described above.

The rate data have been further treated to yield empirical constants for the Arrhenius reaction rate equation. Data for these calculations were taken from the graphs of log dp/dt vs. 1/T in order to have smoothed or "graphically averaged" data.

Activation energy, E', is given by the equation

$$E' = \frac{2.303\, R \log\left[(dp/dt)_2/(dp/dt)_1\right]}{\frac{1}{T_1} - \frac{1}{T_2}}$$

in which $R = 1.986$ cal. deg^{-1} mole^{-1} and the subscripts 1 and 2 distinguish the two data points read from the straight line plot of log $\frac{dp}{dt}$ vs. $\frac{1}{T}$.

For ease in treating the data, E' is determined graphically by measuring with a protractor the angular slope of the straight line rate plot, then using this angle to determine E' from a graph of E' vs. angular slope. The latter graph is prepared to be consistent with the scale of plotting of the primary rate data.

The frequency factor A' is given by the equation

$$\text{Log } A' = \log \frac{dp}{dt} + \frac{E'}{2.303RT}$$

using for dp/dt and T the numerical values corresponding to the decomposition point. This gives A' in the units mm Hg/sec. whereas it is customary to express the frequency factor for a unimolecular decomposition reaction in reciprocal seconds only. In practice, A' is also determined graphically from E' and the decomposition point using a graph of A' vs. E' for several values of the decomposition point. (see Fig. 5)

Rate measurements for five compounds are shown graphically in Fig. 1. Except for Curve D, these are typical data used for calculating activation energies and frequency factors for the decomposition reactions. From the deviations from the straight line plot the activation energies are estimated to be reproducible to ± 2 Kcal./mole and the frequency factors to within a factor of ten. Activation energies are not reported for data which, for various reasons, were scattered off a straight line, nor were energies calculated on the basis of only two or three observed rates.

A second set of isoteniscope data are presented in Tables 10, 11 and 12, to illustrate estimation of the decomposition point of compounds which decompose only slightly in the vicinity of the boiling point. The data also illustrate the reproducibility of the vapor pressures, showing that observations during initial heat-up for the test are very close to equilibrium vapor pressures. The latter point is of considerable importance since it shows that reliable vapor pressures are obtained incidental to the thermal stability test.

The data are shown graphically in Fig. 4 plotted on the special graph paper (semi-logarithmic, 3 cycles vs. degrees centigrade on a scale of reciprocal absolute temperature). The two sets of vapor pressures are seen to fall almost identically on the same straight line. This behavior was found for several other compounds and is therefore believed to be general, so that the vapor pressures measured in the heat-up period and reported in Table 6 are equivalent to equilibrium vapor pressures over the ranges indicated in Table 9.

The rate data illustrate the behavior observed for several quite stable compounds having boiling points near or below the decomposition point. The isoteniscope apparatus is limited to atmospheric pressure so that fast decomposition rates are not measurable since the pressure would have to exceed one atmosphere. In this case, we have resorted to extrapolation using an assumed activation energy (60 Kcal./mole) to calculate the slope. As seen in the graph, extrapolation was from the lower observed rate. This was done because the rate appeared to be steadily decreasing as though ending toward a limiting value. In the illustrative example, it is doubtful if the limiting rate was attained so the extrapolated decomposition point, using the conservative assumption that E' = 60 Kcal./mole, may quite reasonably be taken as a lower limit.

It is worthwhile to note in the case of several compounds tested early in this program for which the boiling point was well above the decomposition point, that when rates were measured at successively higher temperatures, values obtained at the low (initial) temperatures were unusually high. It was found, however, that if rates were determined at successively lower temperatures, lower rates were subsequently obtained than above and log dp/dt was a linear function of reciprocal absolute temperature as would usually be expected for reliable rate data.

TABLE 10

VAPOR PRESSURE OF SAMPLE NO. 15, m-Diphenoxybenzene During Initial Heat-Up in Isoteniscope

Time, sec.	Temp., °C	Pressure, mm Hg
0	210.0	9.5
140	220.9	14.1
250	229.2	18.6
362	237.6	24.5
455	244.4	30.6
550	251.3	37.8
644	258.1	46.6
723	263.6	55.1
810	269.9	66.0
890	275.4	77.1
995	282.5	94.1
1087	289.7	111.2
1200	295.7	134.2
1311	301.8	158.1
1427	308.0	186.0
1550	314.6	218.2
1665	320.0	249.2
1777	325.2	280.1
1903	330.4	316.9

TABLE 10 (Con't)

Time, sec.	Temp., °C	Pressure, mm Hg
2043	336.2	359.4
2182	341.2	398.9
2313	345.6	438.0
2428	349.3	472.7
2566	352.5	506.4
2756	358.5	569.0
2886	362.4	614.3
3014	366.0	660.0

TABLE 11

ISOTHERMAL RATES OF PRESSURE RISE OF SAMPLE NO. 15, *m*-Diphenoxybenzene

Time, sec.	Temp., °C	Pressure, mm Hg	Pressure Chg. Δ p, mm Hg	Period, Δ t, sec.	Rate, mm Hg/sec.
0	366.8	678.30			
			13.30	6850	.00194
6850	"	691.60			
			7.35	6270	.00117
13120	"	698.95			
			5.55	6380	.00086
19500	"	704.5			

TABLE 12

EQUILIBRIUM VAPOR PRESSURE OF SAMPLE NO. 15, m-Diphenoxybenzene

Temperature, °C	Pressure, mm Hg
366.8	671.0
355.3	536.5
344.8	428.4
334.0	339.8
324.5	274.9
314.0	214.6
303.9	166.8
293.3	128.5
280.6	91.2
263.8	55.3

Note: Pressure measurements were made while temperature was held constant with the automatic controller. Measurements were made in the sequence from top to bottom with the sample being refluxed between temperatures to distill out small amounts of volatile impurities and/or decomposition products.

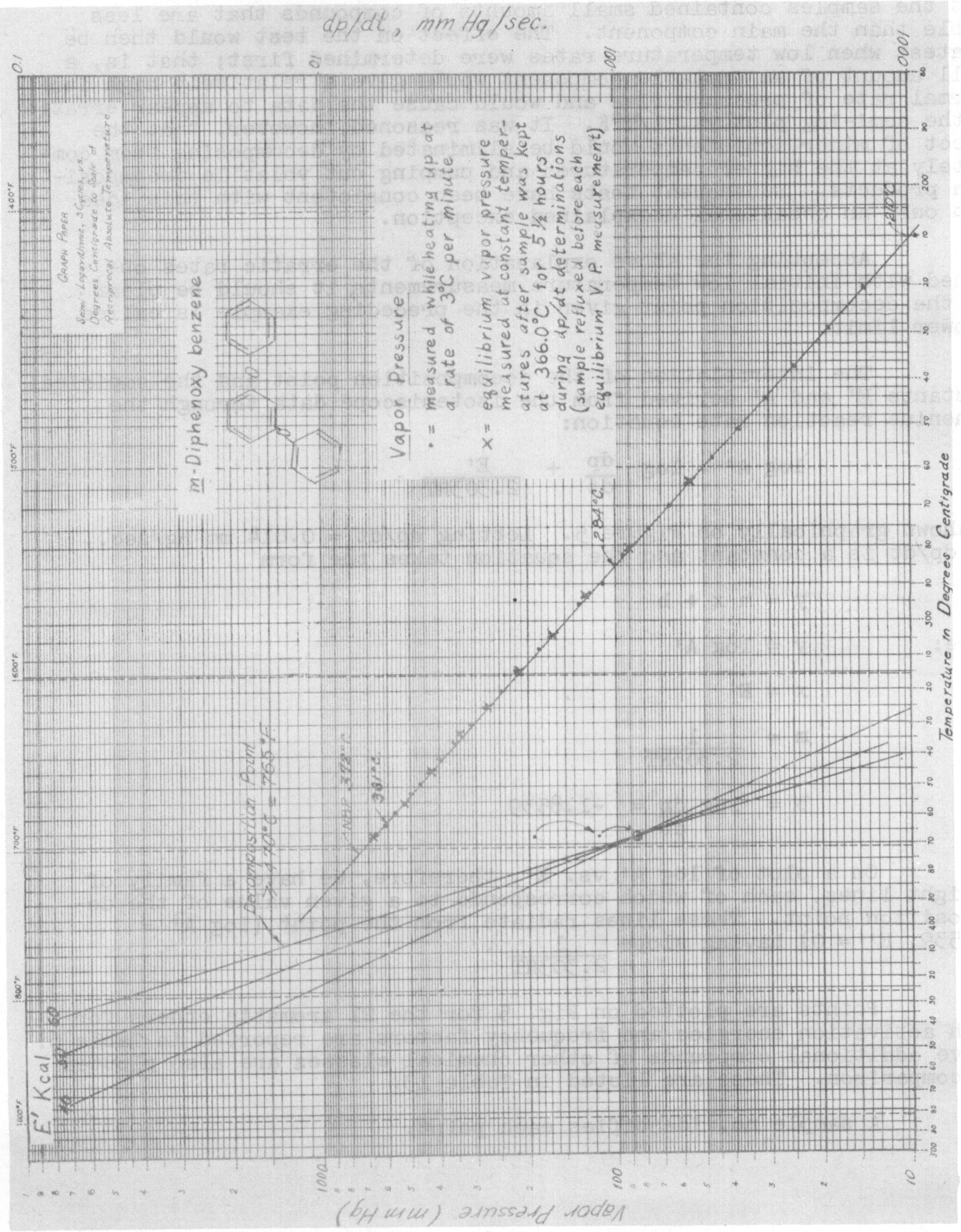


Figure 4. Isoteniscope Data for Sample No. 15.

The most plausible explanation of this behavior seemed to be that the samples contained small amounts of compounds that are less stable than the main component. The effect on the test would then be greatest when low temperature rates were determined first; that is, a small amount of an unstable component would give a relatively high isothermal rate of pressure rise and would cause the data to appear erratic in the semi-log plot vs. $1/T^{o}K$. It was reasoned, however, that the effect of minor components would be eliminated by decomposing them completely at the higher temperatures and pumping out volatile decomposition products. Subsequent tests have been consistent with this idea with only an occasional unexplained exception.

Accepting the above explanation of the erratic rates obtained with initial low temperature measurements, it should be clear why the decomposition point given in the preceding example is called a lower limit.

The interrelation of the decomposition point and the empirical constants E' and A' derived from the isoteniscope data through the Arrhenius reaction rate equation:

$$\log A' = \log \frac{dp}{dt} + \frac{E'}{2.303RT}$$

is shown graphically on Figure 5. Letting dp/dt = 0.014 mm Hg/sec., log dp/dt is a constant and the equation takes the form

$$y = m x + b$$

where:

$$y = \log A'$$

$$x = E'$$

$$m = \frac{1}{2.303RT}$$

$$b = \log \frac{dp}{dt} = -1.8539$$

On a plot of log A' vs. E', therefore, we have a family of straight lines, each of which corresponds to a given value of the decomposition point. These lines radiate from the point (log A' = -1.8539, E' = 0) having slope $\frac{1}{2.303RT}$.

Points are plotted on Fig. 5 for the 21 aromatic ethers for which activation energies and frequency factors are reported in Table 6. Twelve additional compounds of other chemical classes are also plotted for comparison. These are listed in Table 13.

A sample no. identifies each point.

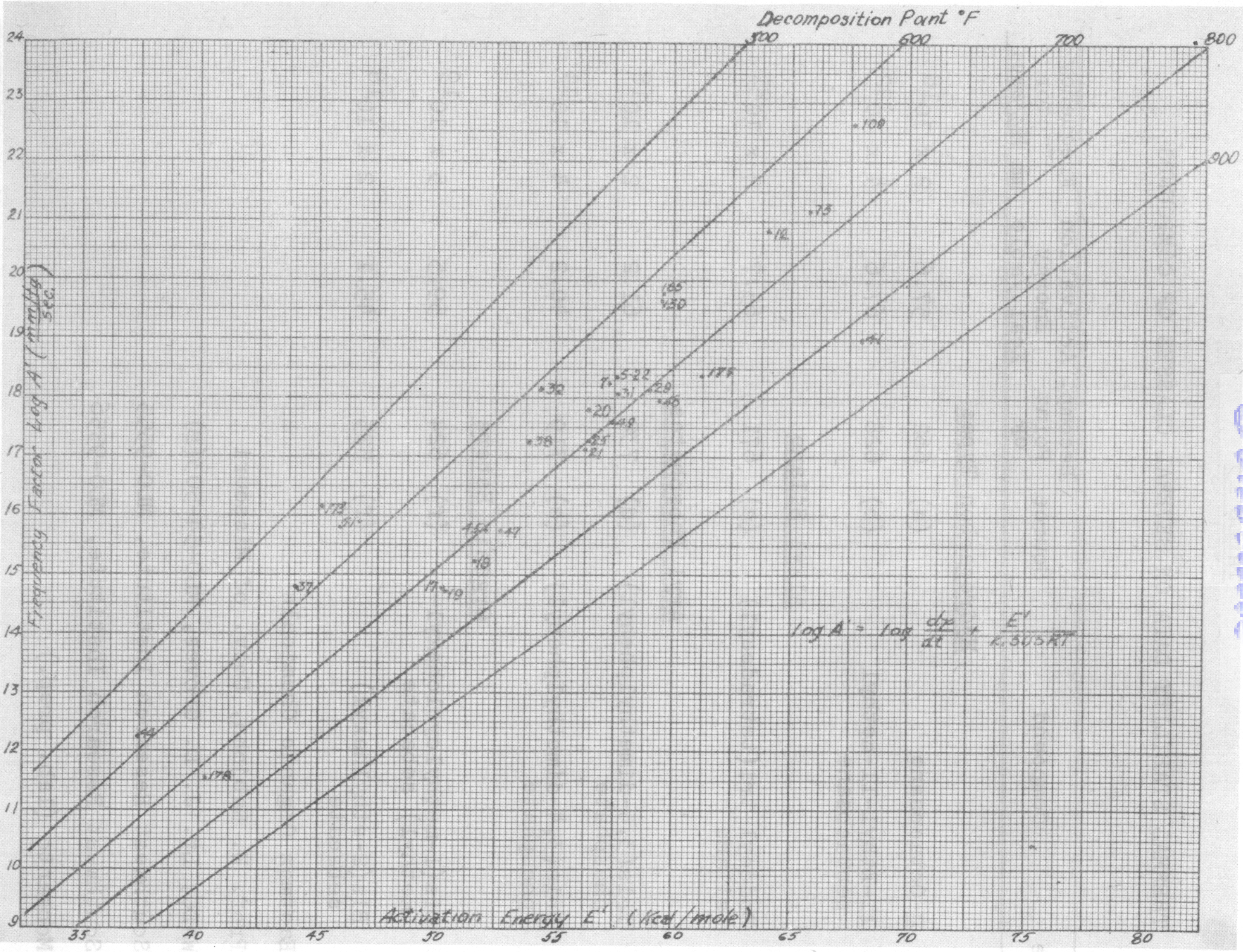


Figure 5. Interrelation of Activation Energy, Frequency Factor and Decomposition Point.

TABLE 13

THERMAL STABILITY DATA ON SEVERAL CLASSES OF COMPOUNDS

Sample No.	Compound	Source	Decomp. Point °F	Activation Energy Kcal./mole	Frequency Factor mm Hg/sec.
	Hydrocarbon Types				
S-22	n-Octacosane	(a)	662	57.6	2×10^{18}
S-109	11-Ethyl-11-methyl pentacosane	(b)	628	67.6	4×10^{22}
	Alkyl Silane				
S-73	Dodecyl-tri(tetradecyl) silane	(c)	671	65.7	2×10^{21}
	Aryl Phosphates				
S-177	Tris(3,5-dimethylphenyl) phosphate	(d)	732	61.2	2×10^{18}
S-178	Tris(3,4-dimethylphenyl) phosphate	(e)	719	40.2	4×10^{11}
	Organic Esters				
S-165	Bis(1-methylcyclohexylmethyl) sebacate	(f)	624	59.5	5×10^{19}
S-173	Bis(2-ethylhexyl) sebacate	(f)	525	45.1	2×10^{16}

(a) Eastman Organic Chemicals

(b) Prof. N. Rabjohn, Univ. of Missouri

(c) WADC, Lt. J. D. Groves, MLO-54-503(B)

(d) Southwest Research Institute, MLO-9555

(e) Southwest Research Institute, MLO-9556

(f) Monsanto (lab. prep.)

Comparison to Other Thermal Stability Tests

Using isothermal rates of pressure rise the onset of thermal decomposition can be detected at temperatures as much as 75°F lower than when using the procedure (17, 18, and 19) of estimating the point of departure of the vapor pressure from a straight line on a log pressure vs. reciprocal absolute temperature graph.

A comparison of results on four compounds tested by both the technique of isothermal rate measurements (A) and the technique of vapor pressure deviation (B) is given in Table 14. These data point up the difference in sensitivity of the two tests.

TABLE 14

COMPARISON OF STABILITY TEST DATA

Compound	Decomposition Point, °F	
	A	B (ref.)
Tris (3,4-dimethylphenyl) phosphate	727	>864 (17)
Tris(3,5-dimethylphenyl) phosphate	741	>846 (17)
Tris(o-bromophenyl) phosphate	671	804 (17)
Di(2-ethylhexyl) sebacate	531	547 (19)
2,4-Di-sec-amylphenyl p-phenoxyphenyl ether	608	655 (Fig.3)

Sommers and Crowell have investigated the thermal decomposition of di-2-ethylhexyl sebacate in detail and obtained 47.0 Kcal./mol. for the activation energy. They also interpreted some early data by Menschutkin (21) for pyrolysis of t-amyl acetate, obtaining an activation energy of 45.8 Kcal./mol. Both of these values are in satisfactory agreement with, and may be compared to, the result obtained with the isoteniscope for di-2-ethylhexyl sebacate, viz. 45.1 Kcal. (Note: In ref. (22) we reported 46.7 Kcal. based on less consistent data than the present results, data for which are shown in Fig. 1.)

Data given in Table 17 for diphenyl ether in comparison to several other unsubstituted aromatic ethers show that the decomposition point of this compound is in the expected range.

These various comparisons show the general agreement with other methods and support the thesis that the present test yields fundamental properties of the test samples rather than completely empirical data which are not simply related to the reaction kinetics involved.

The test method described herein has the advantage over other similar tests that have been described (17, 18, 19) in that for about the same expenditure of time not only is the decomposition point determined but also kinetic data and vapor pressures that closely approximate equilibrium vapor pressure data are obtained.

The complete isoteniscope test can be made by one man and the data processed to obtain the vapor pressure curve, the decomposition point, and the fundamental constants E' and A' in one 8-hour working day.

Viscosity

Viscosities of most of the compounds prepared were measured at 100°, 210°, and 400°F. The viscosity of compounds which are normally solid at any of the bath temperatures was measured below the melting point if the sample could be readily supercooled. The criterion for reporting viscosities of supercooled compounds was reproducibility of successive observations of efflux times as in the usual procedure. In a few cases, where compounds were solid at 210°F, viscosities were measured at 400°F and at either 300° or 500°F to obtain an ASTM slope. Viscosity measurements and ASTM slopes (ASTM chart D341-39) are given in Table 6.

The viscosity determinations at 100° and 210°F followed the detailed procedure given in ASTM Method D445-53T, Appendix A, for compounds that are liquid at room temperature. Small corrections to the viscometer constants are necessary when the pipettes are filled at temperatures other than at room temperature (ca. 25°C or 77°F) as must be done with the higher-melting compounds. The method for calculating this correction and for extrapolating calibration constants to temperatures above 100°F is described below. These corrections are both based on the change in hydrostatic head resulting from thermal expansion of the liquid; since expansion data for compounds of the type concerned were not available, the densities of several typical compounds were measured at 100°, 210°, and 400°F, from which mean coefficients of expansion were obtained. These results indicated that the mean expansion coefficient usually applied for extrapolation of viscometer constants for lube oils is satisfactory for aromatic ethers.

Constant Temperature Baths

A water bath was used for measurements at 100°F and a mineral oil bath at 210°F. Components used in assembling the baths are listed in reference (15). The automatic temperature regulation system for these two baths maintains the control temperature at 100° ± 0.01°F and 210° ± 0.02°F. The 400°F bath, as originally set up and used for several measurements, consisted of a 4-liter Pyrex glass beaker containing DC Silicone Fluid 200 insulated with a one-inch layer of glass wool on the sides (except for a viewing window) and a one-inch layer of Unibestos insulation at the bottom. The beaker and insulation are contained in a heavy-walled, cylindrical Pyrex battery jar 8-1/2 in. diameter by 11-1/4 in. high. A 250-watt knife heater was used for continuous heating and a 125-watt knife heater for intermittent heating. The intermittent heater was controlled via a mercury-in-glass thermoregulator (T-5750 Micro-Set thermoregulator, size B, Kauffman-Lattimer Co.) working through a Fisher 15-445 Electronic Control Unit. A temperature control to ± 0.3°F was obtained at 400°F when the power delivered by the continuous and intermittent heaters was adjusted, by means of variable transformers, to cause the intermittent heater to execute a cycle of 80 seconds on and 220 seconds off. A stirring motor, thermometer, bath cover, and nitrogen inlet tube complete the list of principal parts. Nitrogen was bubbled into the bath to reduce oxidative degradation of the fluid.

This 400°F bath functioned satisfactorily although frequent adjustments of the Micro-Set thermoregulator were necessary because the control point gradually drifted upward due to distillation of mercury to cooler upper regions of the regulator. Also the control point was sometimes suddenly lowered, presumably when a droplet of the distilled mercury fell back into the mercury column. Equivalent errors in the mercury-in-glass thermometer are not expected because the meniscus is outside the bath and is thus practically at room temperature; however, placement of the thermometer for calibration and use must be identical to eliminate the need for stem immersion corrections.

The thermometer used in the 400°F bath was calibrated in place at 300°F, 400°F and 500°F, against a National Bureau of Standards calibrated platinum resistance thermometer placed at the viscometer position in the bath. A Mueller Bridge was employed for the resistance measurements.

The DC Silicone fluid used in the 400°F bath was replaced by a eutectic mixture of lithium, sodium, and potassium nitrates (melting point ca 250°F) which we had used successfully for some time at temperatures up to 860°F with the isoteniscope test apparatus (see below), and is reported to be satisfactory up to 930°F. This bath was further modified by replacing the metal knife heaters, which were attacked by the nitrate mixture, with heaters made in this laboratory using Nichrome wire in Pyrex glass tubing. A 380-watt heater is used for continuous heating and a 230-watt heater for the intermittent control heater. The metal stirring impeller was replaced by a glass one, and a resistance bridge automatic temperature controller (Thermotrol Model 1053, Hallikainen Instruments) using a Tungsten-in-Pyrex resistance thermometer as the sensing element replaced the mercury-in-glass thermoregulator and electronic relay combination, so that temperature control to ± 0.1°F is now obtained. With this arrangement, all bath components in contact with the nitrate mixture are of Pyrex glass. This bath can now be used for viscosity measurements up to 700°F or higher, if desired.

Density and Mean Thermal Expansion Coefficients

The density of three aromatic ethers which are liquid at room temperature was measured at 100°, 210°, and 400°F and three which are solids at room temperature were measured at 210° and 400°F. For results see Table 15.

TABLE 15

DENSITY AND THERMAL EXPANSION OF SEVERAL AROMATIC ETHERS

Compound	Density gm/ml. at			Mean Volume Coefficient of Expansion per Degree Fahrenheit x 10^4		
	100°F	210°F	400°F	100-210°F	210-400°F	100-400°F
Diphenyl ether	1.0601	1.0073	0.9135	4.76	5.41	5.35
2,4-Diphenoxytoluene	1.1096	1.0611	0.9760	4.15	4.59	4.57
1,4-Bis(2-methyl-5-isopropylphenoxy)-benzene	1.0288	0.9840	0.9050	4.14	4.59	4.56
Bis(4-bromophenyl) ether	(solid)	1.6221	1.5012	*3.81	4.24	*4.21
1,4-Bis(4-ethylphenoxy)-benzene	(solid)	1.0201	0.9407	*4.98	4.44	*4.41
Bis(p-phenoxyphenyl) ether	(solid)	1.1210	1.0405	*3.64	4.07	*4.04

* Entries so marked were estimated from experimental values for 210-400°F. See text.

A dilatometer was made for these density measurements by replacing the neck of a 25-milliliter volumetric flask with the graduated part of a 5-milliliter measuring pipette. A filling neck was attached to the side of the flask; this consisted of a 10/30 standard taper ground glass joint (outside member) fitted with a standard taper stopper. All parts were of Pyrex glass.

The volume of the dilatometer up to the lower mark on the pipette was determined by measuring the weight of distilled water contained at 100°F. The absolute density of water at 100°F was taken as 0.99307 gm./milliliter (referred to the density of water at 4°C; from Smithsonian Tables as quoted in 36th Edition of the Chem. Rubber Co. Handbook of Chemistry and Physics). The pipette section was not calibrated; however, an indirect measurement indicated an accuracy of

± 0.01 milliliter at the 27.0 milliliter level. This is equivalent to a total volume error of ± 0.04% or an expansion error of ± 0.6% in the 100-400°F range; ± 1.8% in 100-210°F range.

The steps for measuring density included weighing the empty dilatometer, filling to lower graduation, closing sidearm with stopper to force out excess liquid, wiping off overflow, and weighing. The filled dilatometer was then placed successively in the baths at 100°, 210° and 400°F and the meniscus level was observed after allowing 15 to 20 minutes for establishing temperature equilibrium.

Samples which are solid at room temperature were filled at about 212°F, using the above procedure but omitting the equilibration at 100°F and taking care that the sample did not freeze in the dilatometer prior to making the volume measurements at 210° and 400°F. This precaution is necessary to prevent the entrapping of air on freezing (contracting) and melting. Naturally, samples of the latter types could be weighed only after the volume measurements. Samples which are liquids at room temperature were weighed before and after temperature equilibration. Since no loss occurred with these it seemed safe to assume no loss occurred with samples for which prior weighing was not feasible.

For correcting the volume expansion of the dilatometer the mean coefficient of linear expansion of Pyrex glass was taken as 3.3×10^{-6} per degree centigrade and the coefficient of volume expansion was taken as three times this figure.

The density and thermal expansion values are given in Table 15. The coefficients for the compounds concerned vary between 4.07 and 5.4×10^{-4} per degree Fahrenheit, averaging 4.56×10^{-4}, in the range 210-400°F. The coefficients of expansion which might be expected for the three solid samples were estimated from the values observed in the liquid range, assuming that the coefficients would change with temperature in the same proportion as the average of three liquid compounds. These estimated coefficients are also listed in Table 15 and have been included in computing average coefficients for the set of six compounds. These averages are:

Temperature Range	Mean Coefficient of Volume Expansion
100-210°F	4.08×10^{-4} per degree F
210-400°F	4.56×10^{-4} per degree F
100-400°F	4.52×10^{-4} per degree F

The average value for the range 100-210°F is practically identical to the coefficient suggested by the supplier of the viscometers for petroleum oils (Cannon Instrument Co., "The Magnitude of Various Corrections in Viscometer Calibration", M. R. Cannon, Pennsylvania State College). Cannon states that "one cubic centimeter of oil expands to 1.045 cc in going from 100°F to 210°F....". This gives a mean volume expansion coefficient of $0.045 \div (1 \times 110) = 4.1 \times 10^{-4}$ per degree Fahrenheit. For the viscometers being used the difference between this value and 4.52×10^{-4}, which would be a better average for the present work, represents an error of 0.13% in extrapolating the calibration constant to 400°F. This small error is not significant in our present study of hydraulic fluids and so will be disregarded, the value 4.1×10^{-4} per degree Fahrenheit being adopted for the calculations involving change of viscometer calibration constants with bath and/or filling temperatures.

Viscometer Calibration

The viscometers used in this work were calibrated at 100°F by the Cannon Instrument Company. Extension of the calibration constants to higher temperatures was done according to the method given in the ASTM procedure (ASTM D445-53T, Appendix A) using the following equation:

$$C_2 = C_1 \left[1 - \frac{V_2 - V_1}{0.785\ Hd2} \right]$$

in which

C_2 = viscometer constant at temperature T_2.

C_1 = viscometer constant at temperature T_1, a temperature at which the constant is known.

V_1, V_2 = total volume of liquid in the viscometer at T_1 and T_2, respectively, in cc.

H = fluid head in centimeters.

d = inside diameter of lower reservoir, in cm.

The change in volume, $\Delta V = V_2 - V_1$, was calculated using $\Delta V = \alpha V_1 (T_2 - T_1)$ in which α is the volume coefficient of thermal expansion per degree Fahrenheit for which the value $\alpha = 4.1 \times 10^{-4}$ per degree Fahrenheit was used.

The equation above applies for viscometers calibrated at 100°F but filled at room temperature (ca 25°C or 77°F). Some samples are solid at room temperature and thus require filling at higher temperatures. To standardize, filling temperatures of 212°F and 347°F were chosen for the solids.

The viscometer constant $C^{T_F}_{T_B}$, applicable at various bath temperatures (T_B) when the pipette filling temperature (T_F) is 212°F or 347°F, is calculated by the following more general equation:

$$C^{T_F}_{T_B} = C^{77^\circ F}_{100^\circ F} \left[1 - \frac{\alpha V}{0.785\ Hd^2} (T_B - T_F - 23) \right]$$

where $C_{100^\circ F}^{77^\circ F}$ = viscometer constant which applies at 100°F bath temperature and 77°F filling temperature.

T_B = bath temperature

T_F = filling temperature

and α, V, H, and d have the same meaning as defined above. Like the preceding equation, this expression was derived to correct for changes in fluid head, H, with changes in total volume of fluid with temperature.

The magnitude of the variations with temperature obtained may be seen by evaluating the factor in brackets for the equation using average values for the physical dimensions of the Ostwald-Cannon-Fenske viscometers (sizes 50, 100, 200, 400, and 500) employed in this work;

$V = 7.0$ cc

$H = 9.9$ cm.

$d = 3$ cm.

and taking $\alpha = 4.1 \times 10^{-4}$ per degree Fahrenheit.

TABLE 16

FACTORS FOR COMPUTING VISCOMETER CONSTANTS FOR HIGHER BATH AND FILLING TEMPERATURES

T_B	$T_F = 77^\circ F$ (25°C)	$T_F = 212^\circ F$ (100°C)	$T_F = 347^\circ F$ (175°C)
100°F	1.0000	1.0055	1.0111
210°F	0.9955	1.0010	1.0066
300°F	0.9918	0.9973	1.0029
400°F	0.9877	0.9932	0.9988
500°F	0.9836	0.9891	0.9947

Pour Point and Crystallization

A number of compounds were prepared which appeared to be permanent liquids and which possessed pour points well below 0°C. Included were several of the compounds of considerable promise from the standpoint of thermal stability. These compounds were subjected to temperature cycling tests to determine if they were permanent liquids or if they were cystallizable.

The cycling tests consisted of storing specimens in a deep freeze chest in which temperature was cycled between about 5°C and -20°C with occasional brief excursions to -78°C (effected with dry ice) to promote crystal nucleation.

Prolonged application of this test has brought about crystallization of all compounds that had been found to have decomposition points above 700°F. These more stable compounds have melting points generally in the range above 10°C.

To overcome this low temperature limitation, a number of multicomponent mixtures of these more stable compounds have been made and are currently being subjected to temperature cycling tests. Since the pure crystalline species of each component will be available it will be possible to use direct crystal seeding in these tests. At present, however, temperature cycling with the extreme low temperature thermal shock treatment is the only test applied. Under these conditions, several mixtures have failed to crystallize at test temperatures mainly in the range -10° to -15°C for a period of six weeks.

The composition of several mixtures tested in this way is given in Table 17 in terms of the approximate number of parts by weight of each component. Five of the mixtures have remained liquid under the test, two became completely solid, while two were partly solid. These tests should be continued and augmented with seeding with the individual crystalline components for finally establishing whether the mixtures can be crystallized under any practical conditions.

These results suggest the possibility of preparing relatively low pour point fluids by blending or synthesis so as to produce mixtures of compounds as well as mixtures of isomers of these compounds. If this is borne out, then the fact that a single compound may be crystallizable does not necessarily preclude utility of the class of compounds.

VI. CORRELATIONS

Melting Point

In addition to the correlations as to the effect of structure on melting point made in the literature survey it is possible to make several others based on the data in Table 6.

1. In a series of isomeric methyl-substituted aromatic ethers in which the position of the methyl group is varied with respect to

TABLE 17

COMPOSITION OF MIXTURES OF ETHERS

Compd. No.	Compound	Melting Point °C	Mixtures A	B	C	D	E	F	G	H	I
			Parts by Weight								
12	3-n-Pentadecylphenyl phenyl ether	30-32 m	-	-	-	-	4	-	-	-	-
14	o-Diphenoxybenzene	91-93 m	-	-	-	-	-	-	-	1	-
15	m-Diphenoxybenzene	47-48 m	3	-	3	-	-	-	2	1	-
16	p-Diphenoxybenzene	75-76 m	-	-	-	-	-	-	-	1	-
17	o-Tolyl p-phenoxyphenyl ether	+9°m -23 p	4	3	4	1	-	1	-	-	1
18	m-Tolyl p-phenoxyphenyl ether	22-23 m	-	3	4	1	-	1	-	-	-
23	p-Bis(m-toloxy)benzene	57-58 m	-	-	-	-	-	-	2	-	-
24	p-Bis(m-toloxy)benzene	98-100 m	-	-	-	-	3	-	-	-	-
26	p-Bis(p-ethylphenoxy)benzene	52-54 m	-	-	-	-	5	-	-	-	-
27	p-Bis(p-n-propylphenoxy)benzene	49-50 m	-	-	-	-	4	-	-	-	-
28	p-Bis(p-isopropylphenoxy)benzene	64.5-66 m	-	2	2	-	4	-	-	-	-
35	2,4-Bis(phenoxy)toluene	7-22.5 m	4	-	4	-	-	1	-	-	1
42	m-Phenoxyphenyl p-phenoxyphenyl ether	48-49 m	-	-	-	-	-	-	2	-	-
48	Bis(p-benzylphenyl) ether	55-56 m	-	-	-	-	-	-	1	-	-
Condition of Mixture at -17°C after 37 days on cycling test			Liquid	Slush	Liquid	Liq+Cryst					
Condition of Mixture at -17°C after 34 days on cycling test							Solid	Liquid	Liquid	Solid	
Condition of Mixture at -17°C after 29 days on cycling test											Liquid

the ether link, the melting point decreases in the order para > meta > ortho. The greatest difference occurs between the para and meta isomers (Compare compounds 17, 18, 19 and 35; 22, 23 and 24; 44, 45 and 46).

2. Lengthening the chain of an alkyl substituent on an aromatic ether lowers the melting point until a length of three carbon atoms is attained. At some point beyond three carbons, further increase in length causes an increase in melting point with eight carbons resulting in a higher melting point than three. (Compare compounds 24, 26, 27 and 30).

The observations in the literature survey on the effect of the chloro substituent (compound 52) and the methoxy substituent (compound 51) are supported. The relation between compounds 41 and 42 also supports the observation that meta-linked ethers melt lower than the para isomers.

Thermal Stability

The first problem in studying the effect of the structure of aromatic ethers on their thermal stability was to establish whether there were any differences in the stabilities of unsubstituted aromatic ethers. In Table 18, the thermal stabilities of the isomeric bisphenoxybenzenes and two bis(phenoxyphenyl) ethers are compared with diphenyl ether.

TABLE 18

THE THERMAL STABILITY OF UNSUBSTITUTED AROMATIC ETHERS

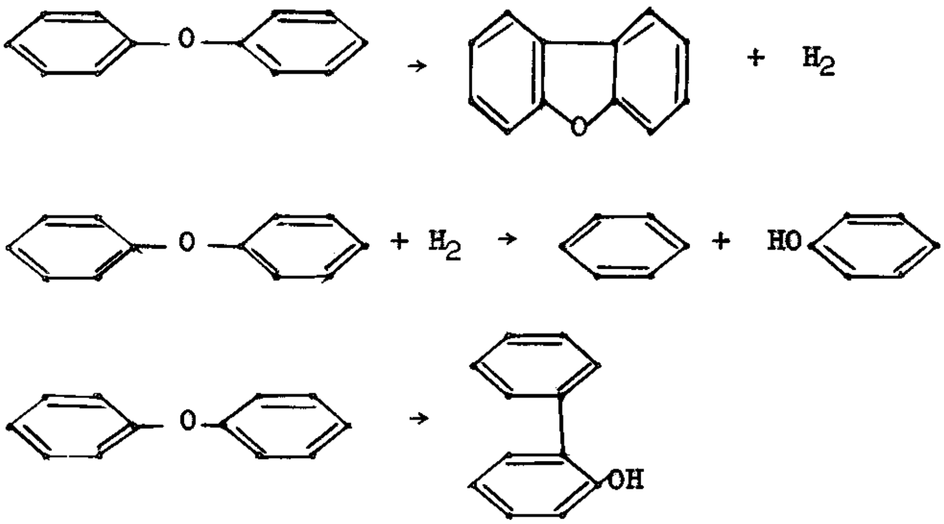
Compound	Decomp. Point, °C
Diphenyl ether*	770
o-Bisphenoxybenzene	>756
m-Bisphenoxybenzene	>765
p-Bisphenoxybenzene	>770
Bis(p-phenoxyphenyl) ether	824
m-Phenoxyphenyl p-phenoxyphenyl ether	821

* Calculated from data in ref. (28).

The data show, within experimental error, there is no decrease in stability over diphenyl ether as diphenyl ether is increased to a polyphenyl ether nor as the relative position of the ether links is changed from para to the meta or ortho positions. Therefore, if synthesis is not a problem, the basic structure for a substituted aromatic ether can be chosen with regard only to obtaining the best pour point and viscosity characteristics.

The decomposition point for diphenyl ether was obtained by converting the rate of decomposition, percent mass fraction/min.of diphenyl ether (25) to the rate of pressure rise, mm Hg/sec., on the assumption that one mole of diphenyl ether gives one mole of gas in decomposition. (Experimentally the formation of 0.85 mole gas/mole decomposition was observed.) The close agreement with the isoteniscope results shows that measurement of pressure rise is a realistic method of studying thermal decomposition of aromatic ethers. It also suggests that the stability of diphenyl ether is not greatly affected by presence of metals; the decomposition was studied in the presence of steel and an alloy (Cerrobend) composed of bismuth, lead, tin, and cadmium.

In addition, the agreement suggests that polyphenyl ethers decompose in the same manner as diphenyl ether. Several of the reactions believed to occur when diphenyl ether decomposes are (25):



Complete breakdown of the molecule also occurs at high temperature since such fragments as ethylene, methane, carbon dioxide and carbon monoxide have been reported (28). It is not to be expected that decompositions of these types can be inhibited by changes in molecular structure nor by additives. The stability of the unsubstituted aromatic ethers, decomposition points from 760-825°F, is, therefore, the ultimate to be obtained with this class of compounds.

That the ultimate stability of the polyphenyl ethers lies in the indicated range may also be concluded by comparison of some bond dissociation energies with the activation energies found in the isoteniscope test. Huggins (26) gives 64-68 Kcal./mole for the carbon-carbon single bond and 68-74 Kcal./mole for the carbon-oxygen single bond. In the isoteniscope test, bis(*p*-phenoxyphenyl) ether was found to have an activation energy of 68 Kcal./mole. From this a reasonable conclusion is that bond dissociation, of either C-C or C-O, is a dominating feature of the thermal decomposition reaction of this unsubstituted ether. If this is true, it seems unlikely that the other unsubstituted ethers could then have any greater stability. Substitutions can be expected to cause only minor variations in the dissociation energy and further it seems unlikely that additives would inhibit the direct thermal dissociation. Substituents on the aromatic ethers can be expected to add their inherent modes of decomposition as well as to add new modes to the routes available to the basic structure and thus to reduce the overall stability of the molecule in all cases.

The second problem was to show if the position of an alkyl substituent relative to an ether link affects thermal stability. In Table 19, the thermal stabilities of several sets of isomers are compared. Except for compounds 44 and 20, there is very little difference between the thermal stabilities of the compounds in Table 19 particularly within sets of isomers. The decomposition point of compound 44 was surprising; the compound has since been found to be contaminated

TABLE 19

THE THERMAL STABILITY OF ISOMERIC ALKYL-SUBSTITUTED AROMATIC ETHERS

No.	Compound	Decomp. Point °C	E'
17	*o*-Toloxy *p*-phenoxyphenyl ether	730	50.3
18	*m*-Toloxy *p*-phenoxyphenyl ether	729	51.6
19	*p*-Toloxy *p*-phenoxyphenyl ether	732	50.3
35	2,4-Bisphenoxy toluene	>718	
22	*p*-Bis(*o*-toloxy)benzene	712	
23	*p*-Bis(*m*-toloxy)benzene	712	
24	*p*-Bis(*p*-toloxy)benzene	721	
44	Bis[*p*-(*o*-toloxy)phenyl] ether	585	37.4
45	Bis[*p*-(*m*-toloxy)phenyl] ether	703	52.0
46	Bis[*p*-(*p*-toloxy)phenyl] ether	698	
20	*o*-Cyclohexylphenyl *p*-phenoxyphenyl ether	669	
21	*p*-Cyclohexylphenyl *p*-phenoxyphenyl ether	706	

with some brominated compound, probably *o*-tolyl *p*-bromophenoxyphenyl ether. The decreased stability of 20 may be real, and, if so, would indicate that a bulky group ortho to the ether link results in lowered thermal stability. From the data in Table 19, the conclusion that substituents meta to an ether link are as stable as the para substituents seems justified; substituents ortho to the ether link, depending on the size, may be slightly less stable than the meta or para. Here again the choice of position for a substituent can be made primarily to obtain the best pour point and viscosity properties.

In contrast to the above correlations is the general lower stability for the series of compounds prepared from dibromotoluene and dibromoethyl benzene represented by compounds 36, 37, 39 and 40 (Table 6). Of course here there is a chance for contamination with some benzyl ether analogs which would lower the stability. These compounds are interesting for their liquid properties and will be subjected to some further purification study prior to rechecking.

The third problem was to determine the effect of the type of alkyl substituent on thermal stability. Here particularly the question of the relations of the length of a normal alkyl substituent to thermal stability was important. In Table 20, the thermal stabilities of a wide variety of alkyl-substituted aromatic ethers are compared.

The first observation made on comparing the stabilities of the 1,4-bis(*p*-alkylphenoxy)benzenes (compounds 16, 19, 24, 26, 27, and 30) is that the stability always decreases as the length of the alkyl chain is increased. This agrees with the fact that the thermal stability of hydrocarbons decreases with increasing chain length. (27). The second and more interesting observation is that there are two large drops in thermal stability. The first occurs on introduction of the first alkyl group (between compounds 16 and 19) and the second between the ethyl- and propyl-substituted ether (between compounds 26 and 27). Since the isopropyl-substituted ether (compound 28) is as stable as the ethyl and the *tert*-butyl (compound 29) is more stable than the propyl, the second drop must occur when the substituent contains not merely three or more carbon atoms but when it has three or more in a straight chain.

These results can be rationalized as follows. The methyl-substituted ether is less stable than the unsubstituted ethers because an additional mode of decomposition involving the formation of a substituted-benzyl radical is now possible. The difference between the ethyl- and propyl-substituted ethers may lie in the difference in stabilities of the methyl and ethyl free radicals which would be

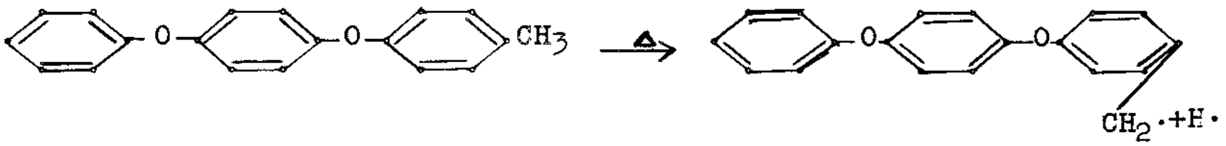
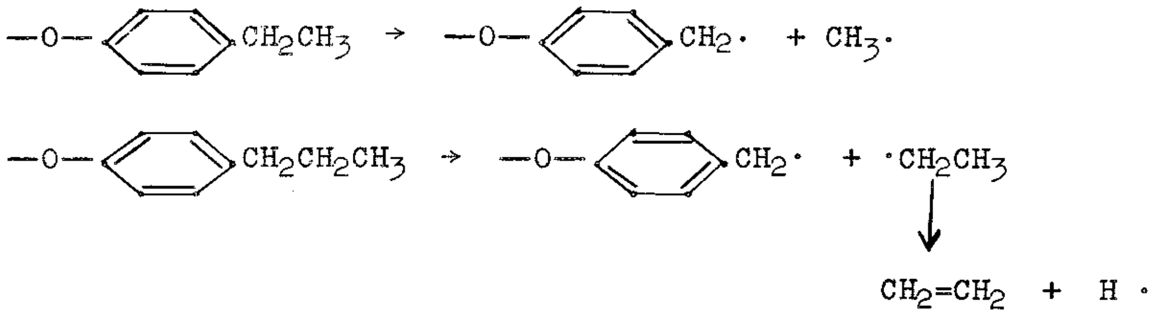


TABLE 20

THE THERMAL STABILITY OF ALKYL-SUBSTITUTED AROMATIC ETHERS

No.	Compound	Decomp. Point °F	E'
16	p-Bisphenoxybenzene	>770	
19	p-Toloxy p-phenoxyphenyl ether	732	ca.50.3
24	p-Bis(p-toloxy)benzene	721	
26	p-Bis(p-ethylphenoxy)benzene	720	
27	p-Bis(p-propylphenoxy)benzene	670	
30	p-Bis(p-octylphenoxy)benzene	628	59.5
28	p-Bis(p-isopropylphenoxy)benzene	719	
29	p-Bis(p-tert-butylphenoxy)benzene	700	59.5
31	p-Bis(p-cyclopentylphenoxy)benzene	678	57.6
25	p-Bis(3,5-dimethylphenoxy)benzene	703	56.4
33	5-Isopropyl-2-methylphenyl p-phenoxyphenyl ether	628	
34	1,4-Bis(5-isopropyl-2-methylphenoxy)benzene	621	
32	2,4-Di(2-pentyl)phenyl p-phenoxyphenyl ether	608	54.3
15	m-Bisphenoxybenzene	>765	
35	2,4-Bisphenoxytoluene	>718	
38	2,4-Bis(p-propylphenoxy)toluene	649	53.9
39	2,4-Bis(3,4-dimethylphenoxy)toluene	641	
40	2,4-Bis(3-ethyl-5-methylphenoxy)toluene	630	
20	o-Cyclohexylphenyl p-phenoxyphenyl ether	669	
21	p-Cyclohexylphenyl p-phenoxy-phenyl ether	706	

formed by this type of decomposition. The ethyl (or larger alkyl



radical) can stabilize itself readily by formation of an olefin, thereby rendering the cleavage permanent. The methyl radical cannot be stabilized in the same way and therefore has a greater opportunity for recombination in the case of liquid phase decomposition.

The cyclopentyl-substituted ether (compound 31) is of some interest because it has a stability higher than the propyl and considerably higher than the sec.amyl-substituted ether (compound 32). Cyclopentyl or cyclohexyl [see compounds 20 and 21 (Table 6)] may then be the only large alkyl substituents having an acceptable thermal stability.

The fourth problem was to determine the effect of the number of alkyl substituents on the thermal stability. A comparison of compounds 16, 19, 24, and 25 in Table 20 shows, as expected, a regular decline in thermal stability with an increasing number of methyl substituents.

In view of the high stability of the methyl- and isopropyl-substituted ethers, the low stability of compounds 33 and 34 was disappointing. Both compounds were prepared from carvacol, a natural product which may have introduced some impurity which was carried along.

The important conclusions to to be drawn from Table 20 are that to obtain an alkyl-substituted aromatic ether having a decomposition point above 700°F, only methyl, ethyl and isopropyl substituents can be used and no more than four and preferably no more than two substituents should be present.

In Table 21 several interesting ethers not falling directly under the classification of alkyl-substituted ethers are compared. The pyridoxy (compound 43) and alkoxy (compound 51) ethers have poor stabilities. The benzyl ethers (compounds 48 and 49) have stabilities like the methyl-substituted ethers (compound 46) rather than the unsubstituted ethers (compound 41). The sulfide (compound 56) had a much lower stability than the analogous ether (compound 35). More examples are needed to establish this fact. No promising leads were uncovered in this group of compounds so that aromatic ethers still seem best for high thermal stability.

TABLE 21

THE THERMAL STABILITY OF MISCELLANEOUS AROMATIC ETHERS

No.	Compound	Decomp. Point °F	E'
43	Bis[p-(3-pyridoxy)phenyl] ether	630	
48	Bis(p-benzylphenyl) ether	721	59.4
49	4-Benzyl-3-methylphenyl p-benzylphenyl ether	701	57.3
41	Bis(p-phenoxyphenyl) ether	824	68.0
46	Bis[p(p-toloxy)phenyl] ether	698	
51	Bis[p-(p-methoxyphenoxy)phenyl] ether	573	46.6
56	2,4-Bisphenylmercaptotoluene	599	
35	2,4-Bisphenoxytoluene	>718	

Pour Point

Comparison of the eighteen compounds in Table 6 (3, 4, 5, 7, 10, 11, 17, 32, 33, 34, 36, 37, 38, 40, 44, 53, 54, 55) which have pour points or melting points below 0°C reveals several structural features which should contribute to a low melting point. Twelve of these compounds (3, 17, 32, 33, 34, 36, 37, 38, 40, 44, 53, 54) have ortho substituents. Eight (10, 11, 36, 37, 40, 53, 54, 55) are possibly mixtures of isomers because of the method of synthesis. All except 7, 34, and 44 are non-symmetrical and seven (34, 36, 37, 38, 40, 54, 55) have more than two substituents.

Of the seven compounds 4, 5, 10, 11, 37, 38, 55) having pour points below -25°C, only three (37, 38, 55) have more than two substituents. None have branched substituents and all have a relatively linear structure.

If the pour point is considered to be a crude viscosity measurement, then its magnitude for a given compound may be estimated from an ASTM plot of the viscosity of the compound against temperature. If the curve hooks upward at low temperatures (that is, if the slope at low temperature is greater than at high), the pour point will be relatively high. For compounds of low pour point, the curve hooks downward at low temperatures.

The ethers in Table 6 show three types of behavior: Type 1, slope at low temperature (100-210°F ASTM slope) is greater than at high temperature (210-400°F ASTM slope); type 2, the slope at low temperature is equal to (taken to mean ± 0.01 units) the slope at high temperature; type 3, the slope at low temperature is less than the slope at high temperature. The behavior of the type 3 ethers is more desirable, since it leads to a lower pour point.

In Table 22, the ethers are listed according to type.

TABLE 22

COMPARISON OF THE 100-210°F ASTM SLOPE WITH THE 210-400°F ASTM SLOPE OF AROMATIC ETHERS

No.	Compound	m.p. °C	ASTM Slope 100-210°F	ASTM Slope 210-400°F
	Type 1			
1	Bis(*p*-bromophenyl) ether	58-60	.93	.91
7	*p*-(*p*-Cyclohexylcyclohexyl)phenyl phenyl ether	-4 pour	.95	.86
21	*p*-Cyclohexylphenyl *p*-phenoxyphenyl ether	88-90	.86	.78
23	*p*-Bis(*m*-toloxy)benzene	57-58	.88	.86
33	5-Isopropyl-2-methylphenyl *p*-phenoxy phenyl ether	-18 pour	.91	.88
39	2,4-Bis(3,4-dimethylphenoxy)-toluene	74-78	1.01	.88
43	Bis[*p*-(3-pyridoxy)phenyl] ether	70-71	.91	.78
44	Bis[*p*-(*o*-toloxy)phenyl] ether	-2 pour	.93	.76
45	Bis[*p*-(*m*-toloxy)phenyl]	61-62	.88	.78
48	Bis(*p*-benzylphenyl) ether	62.5	.77	.73
	Type 2			
2	2,5-Dichlorophenyl *p*-tolyl ether	+3	.98	.97
18	*m*-Tolyl *p*-phenoxyphenyl ether	22-23	.86	.86

TABLE 22 (Cont'd)

No.	Compound	m.p. °C	100-210°F	210-400°F
19	p-Tolyl p-phenoxyphenyl ether	50-51	.85	.86
22	Bis(o-toloxy)benzene	50-51	.90	.90
34	Bis(5-isopropyl-2-methylphenoxy)-benzene	-6	.98	.97
32	2,4-Di(2-pentyl)phenyl p-phenoxy-phenyl ether	-18 pour	.87	.86
37	2,4-Bis(m-toloxy)ethyl benzene	-26 pour	.90	.90
55	Bis(p-ethylphenoxy)chlorobenzene	-26 pour	.86	.87
56	2,4-Bis(phenylmercapto) toluene	6	.86	.85
	Type 3			
4	Bis(p-ethylphenyl) ether	-29	.81	.86
5	Bis(p-butylphenyl) ether	-27	.79	.84
10	Dodecylphenyl phenyl ether	-39 pour	.83	.90
12	m-Pentadecylphenyl phenyl ether	30-32	.71	.75
15	m-Bisphenoxybenzene	47-48	.86	.89
35	2,4-Bisphenoxytoluene	22	.90	.93
38	2,4-Bis(p-propylphenoxy) toluene	-26 pour	.82	.84

As a group compounds of type 1 melt above 58°C so that the 100°F viscosity was measured on the supercooled liquid. The three non-crystalline compounds may also be supercooled since they have structures which might be expected to crystallize. Compounds of type 2, except for two having a m.p. of 50°C, melt below 37°C (100°F) so that their viscosities were measured wholly in the liquid range. Those of type 3, except for one of m.p. 48°C, also melt below 37°C. As a group, type 3 compounds appear to be lower melting than type 2 compounds. This suggests some correlation between melting point and low temperature viscosity characteristics. In particular, viscosity curves in the supercooled region appear to be different from viscosity curves above the melting point.

The behavior of compounds of type 1 appears to be connected with a phenomenon that has been studied by Dodd and co-workers (28, 29, 32). For several compounds, viscosity and dielectric constants of the normal and supercooled liquids were found to show a discontinuity of slope at the temperature corresponding to the normal melting point. The higher slope in the viscosity-temperature curves occurred below the melting point. This corresponds to the behavior of our compounds of type 1. Similarly, Giller and Drickamer (30), in a study of viscosity of normal hydrocarbons from C_5 to C_{14}, found the free energy of activation for flow and hence viscosity-temperature slope to be substantially independent of temperature except at the freezing point and below, where an increase is noted.

At temperatures below the melting point short-range intermolecular forces are sufficient to bind the molecules into a crystal. A postulate concerning the supercooled liquid state is that the same short-range molecular forces cause association into clusters of molecules with a consequent increase in the activation energy for flow. This accounts qualitatively for the behavior of compounds of type 1. A point of considerable practical significance in this connection is whether mixtures of supercooled liquids display this same phenomenon; hopefully, we might expect that in some cases at least the mixed molecules would not interact as strongly as the pure species and thus would have lower pour points than the properly weighted average of components comprising the mixture.

As a group, the type 3 compounds have generally lower ASTM slopes than types 1 and 2. It will be noted that except for Nos. 15 and 35, type 3 molecules generally have an elongated shape and include a number of single bonds about which rotation may occur; the molecules may be pictured as being rather flexible and thus capable of flow by small segments, the smaller segments requiring relatively low activation energy for flow and hence giving rise to the lower ASTM slope. In contrast, type 1 and 2 compounds have relatively fewer single bonds about which free rotation may occur and thus are stiffer units which must move in larger segments or whole molecules and therefore require greater activation energy for flow and of course give a relatively larger ASTM slope. At higher temperatures, when these stiffer molecules possess more thermal energy, they become more flexible, it is postulated, and can then flow by jumps of smaller segments. This then contributes toward decreasing the rate of rise of activation energy or ASTM slope with temperature. This effect may be operative in type 1 compounds along with the supercooling effect noted above. This effect may also account for the constancy of ASTM slope of type 2 compounds in contrast to the decreasing slope of those of type 3.

Since the ethers inherently possess rather high ASTM slopes, it is fortunate that the change with temperature is in a favorable direction.

That the ASTM slope of compounds 15 and 35 places them in the series with type 3 seems somewhat anomalous. Both have four bonds out of a total molecular length of 12 bonds about which free rotation may occur while the other compounds have a much higher proportion, 6 out of 12, 10 out of 16, 11 out of 16, 17 out of 22 and 10 out of 18. The low proportion of free-to-rotate single bonds would place these two compounds with types 1 and 2. This behavior, along with the relative instability of derivatives of these compounds, suggests that the ether linkage in meta-linked ethers is considerably different from that in para-linked ethers.

If behavior noted here is general, the structure changes which lower the melting point of a compound not only increase the liquid range per se but decrease the pour point of the supercooled liquid. This latter point is important because the additives used to formulate a lubricant or fluid may present a low melting ether from freezing.

It should be established in the future whether the viscosity behavior in the supercooled region of a type 1 ether would be observed with a mixture of type 1 ethers.

Boiling Point

The normal boiling points (as determined by the isoteniscope) of those aromatic ethers in Table 6 which have decomposition points above 660°F were used to compute a boiling point number for the oxygen in aromatic ethers according to the Kinney system (31). The more stable ethers were used since these should have the more accurate boiling points.

The boiling point number (BPN) was found to be + 2.9. The average deviation for the boiling points of ethers calculated using this constant is ± 1.8. units (± 8°C at 700°F). Only three out of the twenty-one ethers used in the calculation had a deviation greater than ± 3 units or ± 13°C. That these deviations are somewhat larger than those encountered for other classes of compounds may be attributed to the fact that variations between the boiling points of positional isomers were not considered in calculating the BPN for aromatic ether oxygen.

The variations between the boiling points of positional isomers are systematic. The boiling point of the bisphenoxybenzenes increases in the order ortho > meta > para (compounds 14, 15, 16) and the boiling points of methyl- and cyclohexyl-substituted ethers increase as the position of the alkyl group with respect to the ether link varies from ortho to meta to para (compare compounds 17, 18 and 19; 20 and 21; 22, 23 and 24; 44, an exception has since been found to be impure, 45 and 46.)

The facts that the boiling points of aromatic ethers fall generally into a system for the prediction of boiling points based on hydrocarbons and the BPN for the oxygen atom is roughly that expected by its atomic weight (consider that the BPN for a methylene group is + 2.8) suggest that there are no unusual association effects in aromatic ethers. This implies that the boiling point is mainly a function of the molecular weight of the molecule.

Viscosity

One of the objectives of the ether program was to obtain sufficient data to be able to predict the properties of a new ether from its structure. From the viscosity data of Table 6 certain generalizations can be made.

Aromatic ethers in which the only substituents are in the para position and in which all the other links are para give the best viscosity behavior. In addition, the longer the alkyl substituent (compare 24, 26, 27, 30) the better the viscosity behavior.

Meta-linked ethers (compare 24 vs. 23, 17 vs. 35, 26 vs. 37) exhibit somewhat poorer behavior than the para, while ortho-linked ethers (compare 24, 23, 22) are much worse than either meta or para. As for the effect of position of substitution, again the para-substituted compounds exhibit better properties than the meta, which in turn are better than the ortho (compounds 17, 18, 19 and 22, 23, 24). In every case, branching in the substituent and increasing the number of short alkyl substituents above two has an adverse effect on the viscosity behavior.

Study of the viscosity data in Table 6 has led to some empirical generalizations by which the 210°F viscosity and the 210-400°F ASTM slope can be approximated, and the derivation of a number by which the viscosity behavior of ethers can be easily compared.

The generalizations were obtained by considering the viscosity behavior of the normal paraffins as standard. The number of carbon atoms in the hydrocarbon having the same viscosity at 210°F as a given ether was considered to be the effective chain length of the ether. With the large amount of data available, it was possible to compute the effective chain lengths of the phenyl group for use in the prediction of viscosity. To take account of the differences in viscosity among isomers, only the para-substituted para-linked ethers were used to calculate the chain length constants for the phenyl group. Deviations from the behavior of the para-ethers shown by ethers with other positions for the ether link and substituents were taken into account and correction factors for specific structural features computed from the data. The viscosity of a new ether can be estimated by computing the chain length and assigning to it the viscosity of the n-paraffin having that number of carbon atoms. A similar method was used for calculating the chain length of phenyl for the purpose of estimating the 210-400°F ASTM slope of an ether. In this case, the number of carbon atoms in the hydrocarbon having a 100-210°F slope equal to the 210-400°F slope of the ether was taken as the effective chain length of the ether.

It is desirable to have a convenient method for discriminating between good and bad properties. The ASTM slope is a fair criterion of the viscosity temperature behavior but it is difficult to compare two compounds of widely different viscosity. An empirical solution to this problem can be found for aromatic ethers by comparing how closely they approach the normal paraffins in viscosity behavior. This can be done by dividing the effective viscosity chain length of the ether by its effective slope chain length. For a paraffin, this value will be 1. For an ether it will be greater than one; the closer the value to one the better the viscosity characteristics of the ether.

The generalizations by which the viscosity and ASTM slope of unsubstituted or alkyl-substituted aromatic ethers can be predicted are as follows.

The 210°F viscosity of an alkyl-substituted aromatic ether is approximated by the 210°F viscosity of the normal hydrocarbon having the same number of carbon atoms as the chain length of the ether. For this purpose the chain length of the ether is obtained as follows:

a) Count the number of carbon and oxygen atoms in the molecule.

b) For each benzene ring in a molecule having three phenyl groups, add 1.3 atoms; add 2.6 atoms for each benzene ring in a molecule having four phenyl groups.

c) Add 9 atoms for each cycloaliphatic group.

d) Add 2 atoms for each alkyl substituent over two.

e) Add 2 atoms for each branch in a side chain.

The 210-400°F ASTM slope of an aromatic ether is approximated by the 100-210°F slope of the normal hydrocarbon having the same number of carbon atoms as the chain length of the ether. For this purpose the chain length is obtained as follows:

a) Count the number of carbon or oxygen atoms in the longest straight chain in the molecule, count each phenyl group in a diphenyl ether or a diphenoxybenzene as three atoms and each phenyl group in a bis(phenoxyphenyl) ether as 3.5 atoms. Do not include ortho or meta methyl groups in counting the longest chain; if a meta substituent longer than methyl is included in the longest chain subtract one atom.

b) Count the cyclopentyl group as 5 and the cyclohexyl group as 3.

c) For an ortho ether linkage subtract 6 atoms; subtract one atom for a meta ether linkage.

d) Subtract 0.5 atom for each substituent over two.

e) Subtract 1 atom for each substituent ortho to an ether link.

In Table 23 are the observed value for 210°F viscosity and the 210-400°F ASTM slope for 35 ethers as compared with the values calculated by the above empirical rules. The values for the normal hydrocarbons were obtained from the API project under R. W. Schiessler and are listed in Table 24.

The average percent deviation for the 210°F viscosity was 7%; only three compounds deviated more than ± 15%. The average deviation for the ASTM slope was 0.016 unit and only four compounds had deviation over 0.03 units. Of the six compounds which show large deviations four (28, 29, 34 and 39) are either highly substituted or have branched chains. This suggests that a high degree of substitution or branching has a more pronounced and less predictable effect on viscosity behavior than the generalizations indicate. The purities of the two compounds (34 and 44) which deviate in both viscosity and slope are suspect.

TABLE 23

CORRELATION OF VISCOSITY BEHAVIOR OF AROMATIC ETHERS WITH STRUCTURE

		210°F Viscosity, cs		210-400°F ASTM Slope		Viscosity Chain Lengths + Slope Chain Lengths	
No.	Compound	Obs	Calcd	Obs	Calcd	Calcd	Obs
4	Bis(p-ethylphenyl) ether	1.373	1.4	.86	.87	1.55	1.33
5	Bis(p-butylphenyl) ether	2.413	2.2	.84	.82	1.40	1.69
7	p-(4-Cyclohexylcyclohexyl)phenyl phenyl ether	10.50	10.	.86	.85	3.31	3.67
8	p-Phenylphenyl p-ethylphenyl ether	3.561	3.1	.86	.86	2.08	2.25
12	m-Pentadecylphenyl phenyl ether	3.960	3.8	.75	.74	1.33	1.40
14	o-Bisphenoxy benzene	2.91	2.8	.96	.95	4.80	4.80
15	m-Bisphenoxy benzene	2.63	2.8	.89	.885	2.4	2.30
16	p-Bisphenoxy benzene	2.766	2.8	.87	.87	2.18	2.18
17	o-Toloxy p-phenoxyphenyl ether	3.162	3.1	.88	.885	2.50	2.50
18	m-Toloxy p-phenoxyphenyl ether	3.006	3.1	.86	.87	2.27	2.08

TABLE 23 (Cont'd)

No.	Compound	210°F Viscosity, cs		210-400°F ASTM Slope		Viscosity Chain Lengths ÷ Slope Chain Lengths	
		Obs	Calcd	Obs	Calcd	Calcd	Obs
19	p-Toloxy p-phenoxyphenyl ether	2.90	3.1	.86	.86	2.08	2.08
21	p-Cyclohexylphenyl p-phenoxyphenyl ether	8.093	7.8	.81	.83	2.79	2.17
22	Bis(o-toloxy)benzene	3.837	3.3	.90	.90	2.89	3.12
23	Bis(m-toloxy)benzene	3.319	3.3	.86	.87	2.36	2.36
24	Bis(p-toloxy)benzene	3.08	3.3	.85	.85	2.00	1.92
25	Bis(3,5-dimethylphenoxy)-benzene	5.29	5.0	.90	.885	3.20	3.67
26	Bis(p-ethylphenoxy)-benzene	3.464	3.8	.80	.82	1.86	1.69
27	Bis(p-propylphenoxy)-benzene	4.655	4.4	.78	.79	1.76	1.72
28	Bis(p-isopropylphenoxy)-benzene	5.026	5.6	.78	.82	2.27	1.78
29	Bis(p-tert-butylphenoxy)-benzene	11.37	8.5	.81	.82	2.66	2.81
30	Bis(p-octylphenoxy)-benzene	8.5	8.5	.65	.66	1.48	1.43
33	5-Isopropyl-2-methylphenyl p-phenoxyphenyl ether	4.912	4.4	.88	.86	2.50	3.20
34	Bis(5-isopropyl-2-methyl-phenoxy)benzene	10.39	8.5	.97	.86	3.33	14.7
31	Bis(p-cyclopentyl-phenoxy)benzene	12.17		.70	.73	2.47	2.08
35	2,4-Bis(phenoxy)toluene	2.92	3.0	.93	.90	2.78	3.57

TABLE 23 (Cont'd)

No.	Compound	210°F Viscosity, cs Obs	210°F Viscosity, cs Calcd	210-400°F ASTM Slope Obs	210-400°F ASTM Slope Calcd	Viscosity Chain Lengths ÷ Slope Chain Lengths Calcd	Viscosity Chain Lengths ÷ Slope Chain Lengths Obs
37	2,4-Bis(*m*-toloxy)-ethylbenzene	4.097	4.4	.90	.90	3.33	3.23
38	2,4-Bis(*p*-propylphenoxy)-toluene	5.24	5.3	.84	.825	2.27	2.46
39	2,4-Bis(3,4-dimethylphenoxy)toluene	7.561	6.0	.88	.885	3.50	3.80
40	2,4-Bis(3-ethyl-5-methylphenoxy)toluene	7.17	6.8	.88	.885	3.70	3.70
41	Bis(*p*-phenoxyphenyl) ether	6.872	6.8	.80	.79	2.17	2.46
44	Bis[*p*-(*o*-toloxy)phenyl] ether	10.19	7.8	.76	.82	2.60	2.15
45	Bis[*p*-(*m*-toloxy)phenyl] ether	8.5	7.8	.78	.79	2.29	2.22
46	Bis[*p*-(*p*-toloxy)phenyl] ether	8.15*	7.8	.77*	.77	2.05	2.05
47	Bis[*p*-(*p*-ethylphenoxy)-phenyl]	8.90*	8.8	.73*	.74	1.95	1.86
48	Bis(*p*-benzylphenyl) ether	6.137	6.8	.73	.79	2.17	1.59

* These values were obtained by extrapolation from viscosity measurement at 300°F and 400°F.

Comparison of the ratio of the viscosity chain length to the slope chain length makes it possible to compare more easily the slope characteristics between different ethers. For a given ether, the closer the value comes to one, the better are the viscosity characteristics or the more nearly like a hydrocarbon. From these data it is possible to predict the viscosity of aromatic ethers of speculative structures and thus aid in the design of optimum molecular structure for a specified requirement.

TABLE 24

THE 210°F and 100-210°F ASTM SLOPE OF THE n-PARAFFINS

Number of Carbon Atoms	210°F viscosity, cs	100-210°F ASTM Slope
12	.7488	.86
13	.8606	.85
14	.9844	.84
15	1.119	.82
16	1.203	.81
17	1.419	.79
18	1.583	.77
20	1.940	.73
24	2.794	.69
26	3.30	.67
28	3.818	.64
32	5.030	.60
36	6.407	.61

VII. CONCLUSIONS

Important and useful correlations on the effect of structure in aromatic ethers on thermal stability, viscosity, freezing point, pour point and boiling point can now be summarized as follows:

Thermal stability

The relative position of the ether links in an unsubstituted aromatic ether does not affect the thermal stability. Unsubstituted aromatic ethers have decomposition points between 770-825°F.

Alkyl-substituted ethers with a substituent ortho to an ether link show a tendency toward lower thermal stability than the meta and para isomers which have equivalent stabilities. Methyl-, ethyl-, and isopropyl-, mono- and disubstituted, para-linked aromatic ethers have decomposition points in the range 700-730°F. Polyalkyl-substituted ethers have a lower stability. Aryl ethers having an alkyl substituent with a straight carbon chain greater than two atoms have decomposition points in the range 630-675°F.

Viscosity

Para-linked aromatic ethers have better viscosity properties than the meta isomers and much better than the ortho. Para alkyl-substituted ethers have better viscosity behavior than the meta isomers, which are in turn better than the ortho. The viscosity behavior of an alkyl-substituted ether improves as the length of the substituent increases but worsens as the number of branches in the chain is increased.

Pour Point

Those non-crystalline (liquid at 25°C) ethers with the best viscosity behavior have the lowest pour point for equivalent 210°F viscosities. Other things being equal (210° F viscosity, ASTM slope) the supercooled pour points of crystalline ethers will be lower the lower the melting point.

Boiling Point

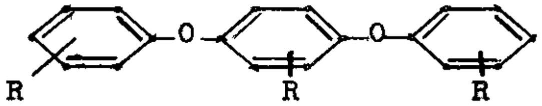
The boiling point of an aromatic ether is roughly proportional to its molecular weight and can be computed by the Kinney system using a BPN of + 2.9 for the ether oxygen.

Melting Point

Symmetrical ethers have higher melting points than unsymmetrical isomers. In the diphenoxybenzene series, the melting point decreases in the order ortho>para>meta. The meta and ortho isomers of alkylated ethers melt lower than the para.

Potential for Aromatic Ether Base Fluids

With relaxation on the pour point to 0°F, within the class of aromatic ethers represented by the structure it appears possible to develop



(R = hydrogen, methyl, ethyl, or possibly, isopropyl)

a functional fluid which will raise the temperature barrier 200°F higher than bis(2-ethylhexyl) sebacate and 100°F higher than tetra(2-ethylhexyl) silicate. It should be possible to do this either via blending aromatic ethers or by molecular design of individual compounds. Such a fluid will satisfy the liquid temperature range (0° to 700°F), will fall well within the maximum vapor pressure specifications of 600 mm/700°F, but will possess a viscosity of approximately 550 cs at 32°F. Aromatic ethers should also possess some plus features, as non-corrosivity and possibly oxidative stability. Nothing is known about lubricity of this class of compounds.

Aromatic ethers such as compounds 35, 37, 36, and 40 (Table 6) have interesting low temperature properties but because of the ease of synthesis of this class of compounds, before they are passed by, it should be firmly established, by more rigorous purification, that what appears to be an inferior thermal stability in this class, is in fact so.

If a decomposition point of over 800°F is essential, then it will be necessary to resort to an unsubstituted ether. So that the ether can be used below its boiling point, a bis(phenoxyphenyl) ether will probably be necessary (p-bisphenoxybenzene boils at 384°C or 723°F).

Although it is doubtful that any of the isomeric bis(phenoxyphenyl) ethers will be non-crystalline, it is probable that a eutectic mixture of bis(m-phenoxyphenyl) ether and m-phenoxyphenyl p-phenoxyphenyl ether would not melt above the pour point. (guestimate: -5°C) No data have been obtained on the oxidation stability nor lubricity of these compounds; such data might alter considerably the picture presented here. Other substituents such as halo or trifluoralkyl may give ethers of somewhat better properties than shown by the alkyl-substituted ethers, particularly in oxidative stability; it is not expected that any great improvement in thermal stability or viscosity behavior will be found.

The thermal stability test by the isoteniscope method has been improved to provide a basis for accurate comparisons of the stability of materials. Using the revised apparatus and procedure, accurate thermal stability and vapor pressure data are obtained. The stability data are shown to be directly related to the kinetics of the decomposition reaction.

VIII. FUTURE WORK ON AROMATIC ETHERS

1. Prepare for simple screening evaluations a maximum of five samples representing what is reasonably optimum in properties for this class of materials.

2. Study the properties of some representative chloro and trifluoromethyl substituted ethers especially as to oxidative and thermal stability.

3. Study further the instability of the poly aromatic ethers prepared from 1 alkyl-2,4-dibromobenzenes.

4. Study the properties of isomeric unsubstituted bisphenoxyphenyl ethers and a few substituted bis(phenoxyphenyl) ethers.

5. Measure oxidative stability of aromatic ethers and substituted aromatic ethers in comparison with selected representatives of other classes.

6. Measure 700° F viscosity of a few representative aromatic ethers unless they are eliminated for some as yet unknown reason.

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