then from methanol-benzene gave the hydrochloride of XXV, m.p. 243–244° dec.

The brown ether solution was evaporated to dryness and the residue was recrystallized from benzene–petroleum ether and then from ether–petroleum ether (b.p. 40–60°) to give 25% of 5-bromo-2-chloro-4-(*p*-fluoroanilino)-6-methylpyrimidine as white needles (XXX), m.p. 143°.

5-Bromo-2,4-dianilino-6-methylpyrimidine (XXIV). The procedure was substantially the same as that for XXVI except that the reaction mixture was warmed in benzene for 24 hr. at 40–60°. The insoluble product was washed with ether, taken up in methanol, and precipitated by addition of benzene to give crystalline material, m.p. 247–249° dec. This was probably the hydrochloride of XXIV. The free base (50% yield) was obtained by recrystallization of the salt from dilute acetic acid. Further recrystallization from ether–petroleum ether (b.p. 40–60°) gave micro-needles, m.p. 111–112°.

5-Bromo-2,4-dimethoxy-6-methylpyrimidine (XXVIII). To a solution of 5.06 g. of sodium in 200 ml. of absolute methanol at 10–15° was added with stirring a solution of 13.3 g. of XV in 100 ml. of absolute methanol over 25 min. The mixture was refluxed for an hour and stirred at room temperature for 15 hr. The solid was filtered and washed with methanol. Carbon dioxide was passed into the filtrate until the *p*H was about 8. The separated solids (5.2 g.) were collected and the filtrate was taken to dryness. The residue was triturated with water leaving 10.0 g. (78%) of white insoluble material. Distillation gave 7.2 g. of material, b.p. 96–99° (0.5 mm.), m.p. 76–77°.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

Preparation and Infrared Absorption Spectra of Some Phenyl Ethers[1]

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The preparation and infrared absorption spectra of a number of aryl and alkyl–aryl ethers are recorded. In general, the assignments in the infrared regions of the spectra agree with those reported in the literature for benzene derivatives and aryl ethers. The *m*-disubstituted materials have their benzene-oxygen stretch band at a lower frequency than those previously reported.

A number of phenyl and alkyl-phenyl ethers were recently prepared for evaluation as radiation-resistant, high temperature lubricants.[2] Many of the products have not previously been reported. At the same time the infrared absorption spectra of both known and new compounds were recorded and the results compared with those of previous workers.[3–10]

Phenyl ethers and certain of their derivatives were prepared because, unlike alkyl ethers, they are very resistant to oxidation. Their thermal decomposition temperatures far exceed those of present synthetic lubricants and their resistance to radiolysis is excellent.

The high melting points of many of the products exclude them from consideration as lubricants for ordinary applications.[2] The literature shows that the better known *para*-linked polyphenyl ethers show a rise in melting point with increasing chain length. In the *meta*-linked series the melting point of certain compounds is surprisingly low. Thus, while *m*-diphenoxybenzene melts at 47° or 60° depending on crystal form, bis(*m*-phenoxyphenyl) ether (III) melts at 41°. The *meta*-linked ethers have a strong tendency to supercool; so far the higher members of the series (XI and XII) have not been obtained in crystalline form.

Most of the ethers were prepared by the Ullmann[11] ether synthesis. The exceptions (XXIX and XXX) were prepared from bis(chloromethyl)-durene and potassium *o*- or *p*-*tert*-butylphenate under milder conditions.

Synthetic problems arose only in the preparation of the *meta*-linked ethers. *m*-Dibromobenzene was prepared from *m*-bromoaniline *via* the Sandmeyer reaction. *m*-Bromophenyl phenyl ether was prepared either from *m*-phenoxyaniline by the same reaction or from phenol and *m*-dibromobenzene by the Ullmann procedure. *m*-Phenoxyphenol[12,13] was prepared by three different routes (Fig. 1), as stability problems connected with certain starting materials required clarification.

The most obvious method (A. R = H), reaction

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[1] The greater part of this work was sponsored by Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] C. L. Mahoney, E. R. Barnum, W. W. Kerlin, K. J. Sax, and W. A. Saari, "Polyphenyl Ethers as High-Temperature Radiation Resistant Lubricants," *J. Chem. Eng. Data Series*, Vol. 5, No. 2, 172.

[3] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London, 1954, p. 102.

[4] L. H. Briggs, L. D. Colebrook, H. M. Fales, and W. C. Wildman, *Anal. Chem.*, **29**, 904 (1957).

[5] R. R. Randle and D. H. Whiffen, *Molecular Spectroscopy*, G. Sell, ed., Inst. of Petroleum, London, 1955, p. 111.

[6] F. S. Mortimer, unpublished work.

[7] J. E. Stewart and M. Hellman, *J. Res. Nat. Bur. Std.*, **60**, 125 (1958).

[8] N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).

[9] A. Stojilkovic and D. H. Whiffen, *Spectrochim. Acta*, **12**, 47 (1958).

[10] Y. Mikawa, *J. Chem. Soc. Jap.*, **29**, 110 (1956).

[11] F. Ullmann and P. Sponagel, *Ber.* **38**, 2211 (1905); *Ann.* **350**, 83 (1906).

[12] (a) G. Lock, *Monatsh.*, **55**, 183 (1930); (b) H. Ungnade and K. T. Zilch, *J. Org. Chem.*, **15**, 1108 (1950); (c) A. Luttringhaus, *Ann.*, **528**, 181, 211, 233 (1937).

[13] G. Lock, *Monatsh.*, **55**, 180 (1930).

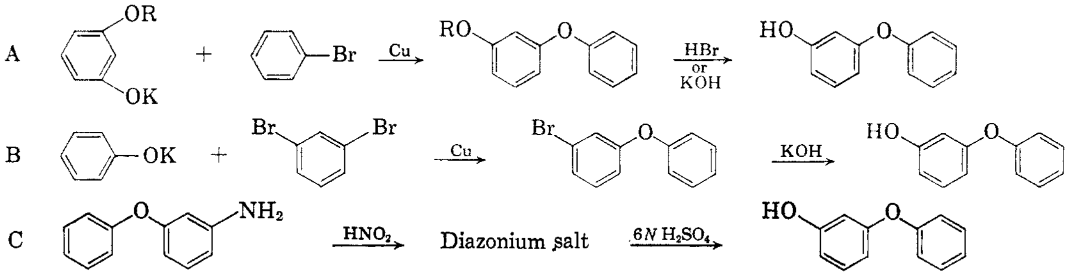

Fig. 1. Preparation of *m*-phenoxyphenol

of the monopotassium salt of resorcinol with bromobenzene, gives only tars. Method A (R = alkyl) gives pure *m*-phenoxyphenol after either acid[12a] or base[12b] hydrolysis unless the starting material contains ring-alkylated impurities. These impurities were demonstrated in a commercial sample of *m*-methoxyphenol by NMR spectroscopy,[14] although they could not be found by either gas-liquid chromatography or infrared absorption spectroscopy. The ring-substituted methyl absorption is easily distinguished from the methoxyl or any other methyl absorption and may be used for semi-quantitative work. No such absorption was found with materials of known purity. Thus no ring alkylation occurs during hydrolysis.

Ring alkylation of resorcinol during the preparation of its ethers has long been known.[15] It is usually connected with methyl iodide or dimethyl sulfate alkylations. However, *m*-ethoxyphenol and *m*-*n*-butoxyphenol, prepared from resorcinol, potassium hydroxide, and the appropriate alkyl bromide in aqueous ethanol, were free from ring-alkylated contaminants.

Base hydrolysis of *m*-ethoxyphenyl phenyl ether required a higher temperature than that needed for the methoxy compound. The *n*-butyl derivative could not be hydrolyzed by base without extensive decomposition.

Methods B and C were also investigated. Method B gave a 45% yield of *m*-phenoxyphenol. A 60% yield was obtained by method C. Both methods provided a route to the *meta*-linked ethers before the impurity problem connected with Method A was finally solved.

In preparations involving the Ullmann ether synthesis we have found that products prepared at 180–220° are generally purer than those prepared at higher temperatures. Although the usual copper catalyst was used during most of this work, cuprous oxide was used in some instances and was quite as satisfactory. The long reaction times used by some earlier workers and, in part, ourselves are usually unnecessary. However, presence of impurities in starting materials or low reactivity of certain compounds may require more vigorous conditions. The reaction is quite rapid; even two hours at reaction temperature is possibly excessive in many cases.

A number of new compounds were prepared from *p*-α-cumylphenol. Although these products and those prepared from *p*-*tert*-butylphenol lack the outstanding thermal and oxidation stability of the unsubstituted polyphenyl ethers, they are much more stable than present synthetic lubricants.[2]

The properties of the ethers prepared during this work are summarized in Table I.

As there is very little in the literature about these types of molecules, it was thought that a spectrum-structure correlation would be interesting. The spectra are a composite of the spectra of ethers and polyphenyl structures, with the exception that most of the ethers in this study exhibit their benzene-oxygen stretch band near 1215 cm.$^{-1}$ rather than near 1250 cm.$^{-1}$ as in vinyl and simple phenyl ethers. The absorption peaks that can be used to characterize the aryl ethers are given in the correlation chart in Table II.

The spectra were recorded on a Beckman IR-4 spectrophotometer equipped with sodium chloride optics. The samples were run in carbon disulfide solutions between 7.5 and 15 μ and in carbon tetrachloride solutions between 2 and 7.5 μ. A variable thickness cell was used to compensate for solvent absorption.

The compounds with an O—C (aliphatic) group have a strong band at 1040 ± 2 cm.$^{-1}$ which is not present in any of the other spectra. This supports the contention of Briggs, *et al.*[4] that the band near 1040 cm.$^{-1}$ rather than the 1120 cm.$^{-1}$ band is due to the O—CH_3 stretch vibration. The addition of bromine in the *para*-substituted compounds gives rise to a strong, sharp band at 822 ± 3 cm.$^{-1}$ and 1006 cm.$^{-1}$. Stojilkovic and Whiffen[9] mention that these bands are difficult to assign, but that the bands do indicate the presence of *para*-halogen substitution in aryl ethers. Characteristic absorption for mono-, *meta*- and *para*-substitution is found in the 860 cm.$^{-1}$ region. Two unique strong bands at 1132 ± 8 cm.$^{-1}$ and 977 ± 2 cm.$^{-1}$ are present only in 1,3-diaryloxybenzenes.

One of the strongest bands is due to the benzene-oxygen stretching mode. The majority of the samples have the band within the limits 1218 ±

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(14) Spectra were obtained with a Varian Associates Model V-4300 High Resolution NMR Spectrometer at 40 megacycles per second.

(15) J. Herzig and S. Zeisel, *Monatsh.*, **10**, 144 (1889).

TABLE I

PHENYL ETHERS

	Compound	M.W.	KOH, Moles	Starting Materials		
				Phenol	Bromo cpd.	Moles
I	*m*-Diphenoxybenzene	262.3	1.6	Phenol	*m*-DBB[b]	0.64
II	Bis(*p*-phenoxyphenyl) ether	354.4	See general method in experimental			—
III	Bis(*m*-phenoxyphenyl) ether[d]	354.4	1.0	*m*-Phenoxy-	*m*-BPPE	0.933
IV	Bis(*o*-phenoxyphenyl) ether	354.4	0.1	*o*-Phenoxy-	*o*-BPPE	0.093
V	*o*-Phenoxyphenyl *p*-phenoxyphenyl ether	354.4	0.33	*o*-Phenoxy-	*p*-BPPE	0.33
VI	*m*-Phenoxyphenyl *p*-phenoxyphenyl ether	354.4	0.32	*p*-Phenoxy-	*m*-BPPE	0.31
VII	*m*-Phenoxyphenyl *o*-phenoxyphenyl ether	354.4	0.33	*o*-Phenoxy-	*m*-BPPE	0.33
VIII	*m*-Bis(*m*-phenoxyphenoxy)benzene[e]	446.5	0.4	*m*-Phenoxy-	*m*-DBB	0.19
IX	*p*-Bis(*m*-phenoxyphenoxy)benzene	446.5	1.08	*m*-Phenoxy-	*p*-DBB	0.64
X	*m*-Bis(*p*-phenoxyphenoxy)benzene	446.5	0.5	*m*(*p*-Phenoxy-phenoxy)-	*p*-BPPE	0.5
XI	Bis[*m*-(*m*-phenoxyphenoxy)phenyl] ether	538.6	0.27	*m*-(*m*-Phenoxy-phenoxy)-	1-*m*-BP-3-PB	0.27
XII	*m*-Bis[*m*-(*m*-phenoxyphenoxy)phenoxy]benzene[f]	630.7	0.35	*m*-(*m*-Phenoxy-phenoxy)-	*m*-DBB	0.17
XIII	*m*-Bis[*m*-(*p*-phenoxyphenoxy)phenoxy]benzene[g]	630.7	0.36	*m*-(*p*-Phenoxy-phenoxy)-	*m*-DBB	0.17
XIV	1-(*o*-Phenylphenoxy)-4-phenoxybenzene	338.4	See experimental			
XV	1-(*m*-Methoxyphenoxy)-4-phenoxybenzene	292.3	3.5	*m*-Methoxy-	*p*-BPPE	3.0
XVI	1-(*p*-*tert*-Butylphenoxy)-4-phenoxybenzene	318.4	0.8	*p*-*tert*-Butyl-	*p*-BPPE	0.7
XVII	Bis[*p*-(*m*-methylphenoxy)phenyl] ether	382.4	2.0	*m*-Cresol	Bis(*p*-BP)E	0.75
XVIII	Bis[*p*-(*p*-*tert*-butylphenoxy)phenyl] ether	466.6	1.0	*p*-*tert*-Butyl-	Bis(*p*-BP)E	0.35
XIX	Bis[*p*-(*p*-*tert*-amylphenoxy)phenyl] ether	494.6	1.0	*p*-*tert*-Amyl-	Bis(*p*-BP)E	0.35
XX	1-(*p*-α-Cumylphenoxy)-4-methoxybenzene	318.4	1.0	*p*-α-Cumyl-	*p*-Bromoanisole	0.85
XXI	1-(*p*-α-Cumylphenoxy)-4-ethoxybenzene	332.4	1.1	*p*-α-Cumyl-	*p*-Bromophenetole	1.0
XXII	*p*-(*p*-α-Cumylphenoxy)phenyl pivalate	388.5	See experimental			
XXIII	1-(*p*-α-Cumylphenoxy)-4-phenoxybenzene	380.5	1.0	*p*-α-Cumyl-	*p*-BPPE	0.84
XXIV	*m*-Bis(*p*-α-cumylphenoxy)benzene	498.6	0.67	*p*-α-Cumyl-	*m*-DBB	0.27
XXV	Bis[*p*-(*p*-α-cumylphenoxy)phenyl] ether	590.7	0.65	*p*-α-Cumyl-	Bis(*p*-BP)E Bis(*p*-BP)E	0.25 0.4
XXVI	Bis[*p*-(2-phenyl-4-*tert*-butylphenoxy)phenyl] ether	618.8	0.94	2-Phenyl-4-*tert*-butyl-		
XXVII	*p*-(*m*-Phenoxyphenoxy)bromobenzene	341.2	Obtained as a byproduct of IX			
XXVIII	*m*-(*m*-Phenoxyphenoxy)bromobenzene	341.2	See experimental			
XXIX	Bis(*p*-*tert*-butylphenoxymethyl)durene	458.7	See experimental			
XXX	Bis(*o*-*tert*-butylphenoxymethyl)durene	458.7	See experimental			

[a] Two crystal forms. [b] Abbreviations: DBB = dibromobenzene; BPPE = bromophenyl phenyl ether; Bis(*p*-BP)E = bis(*p*-bromophenyl) ether; 1-*m*-BP-3-BP = 1-(*m*-bromophenoxy)-3-phenoxybenzene. [c] These melting points were obtained from precision melting point curves. Calculated to be over 99.5% pure. [d] Density 1.18 g./ml. [e] Cuprous oxide catalyst. [f] Density 1.20 g./ml. [g] Purified by partial oxidation in a Dornte[17] apparatus followed by chromatography.

10 cm.$^{-1}$ which is lower than the values reported by Bellamy[3] and by Briggs, *et al.* but higher than those reported for vinyl ethers by Mikawa.[9] Thus the range quoted by Bellamy for the benzene-oxygen stretch frequency should be extended from 1230–1270 to 1210–1270 cm^{-1}.

Monosubstituted aryl ethers have their strong band near 1240 cm.$^{-1}$ but the addition of an oxygen to the *ortho* position moves the band to 1250 cm^{-1}. However, *meta*- or *para*-substitution shifts the band to near 1215 cm^{-1}.

Other bands, some almost as intense as those above, can be used for characterization. *Ortho*- and *para*-disubstitution results in a band at 1190 ± 10 cm.$^{-1}$ which is not present in the spectra of *meta* compounds. A strong, broad *meta* band appears near 1270 cm.$^{-1}$ and is very characteristic of this type of substitution.

The strong *meta* band near 1214 cm.$^{-1}$ is interesting. Even when the number of *m*-substituted rings increases from sample to sample (III, VIII, XI) the frequency does not change by more than one wave number. Thus for 1,3-disubstitution in aryl ethers, the frequency is depressed considerably below the limits for *m*-substitution set by Colthup.[8]

EXPERIMENTAL

Details of several experimental conditions used in the preparation of the ethers are reported. With the exception of XXII, XXIX, and XXX, the preparations reported in Table I were carried out essentially by the detailed procedure reported for bis(*p*-phenoxyphenyl) ether (II). An

TABLE I (*Contd.*)

PHENYL ETHERS

Catalyst, g.	Time, hr.	Temp.	Yield, %	M.P.°	B.P.°/mm.	n_D^{20}	Analyses, %			
							Calcd.		Found	
							C	H	C	H
2	4	180–210	—	46.5–47.5 59.5–60 [a]	145–151/0.3	—	82.4	5.4	82.4	5.4
—	—	—	—	110.3[c]	245/2	—	—	—	—	—
5	20	230–250	74	41.1[c]	217–221/0.07	1.6234	81.3	5.1	81.4	5.1
3	10	250	22	122.0	185–215/0.4	—	81.3	5.1	81.5	5.2
3[e]	2	180–220	81	83.7[c]	209–219/0.8	—	—	—	—	—
3[e]	2	180–220	74	48.0[c]	230–235/0.15	—	—	—	—	—
3[e]	2	180–220	73	73.9[c]	207–213/0.15	—	—	—	—	—
3	6	210–240	54	oil	295–305/1.0	1.6322	80.7	5.0	80.8	5.0
7	6.5	210–230	39	77–79	290–307/1.0	—	80.7	5.0	81.0	5.0
5	4	250	39	88–89	287–293/0.3	—	80.7	5.0	80.8	5.0
4	5	240–245	42	oil	255–272/0.07	1.6380	80.3	4.9	80.5	4.9
5	8	205–208	35	oil	335–362/0.25–0.35	1.6420	80.0	4.8	79.9	4.8
	3	240–255								
6	2.5	250	22	87.5–88.5	337–375/0.2–0.6	—	80.0	4.8	80.0	4.8
				87–88	195–228/0.5	—	—	—	—	—
10	6	205–225	50	oil	190–200/0.7	—	78.1	5.5	78.2	5.5
10	2	240–260	61	53–55	182–186/0.5	—	83.0	7.0	83.0	6.9
10	2	250–300	56	58–60	250/1—	—	—	—	—	—
0.5	3.5	200–290	66	79.5–81	292–300/1	—	82.4	7.3	82.3	7.4
0.5	5	180–300	53	58–59	285–295/0.3	1.5823	82.6	7.7	82.6	7.8
20	3	200–250	66	oil	176–182/0.2 185–189/1—	1.5973 1.5971	83.0	7.0	83.1	7.0
5	4	220–280	76	oil	183–200/0.2	1.5888	83.1	7.3	83.0	7.3
				oil	204/0.25—	1.5633	—	—	—	—
15	3	200–250	59	55–56	230–234/0.5	—	85.2	6.4	85.2	6.4
1	2	210–290	73	oil	230–234/0.5	—	86.7	6.9	86.8	6.9
10	1	250	70	oil	300/0.5	—	85.4	6.5	85.4	6.6
5	2	270–340	40	oil	360/1 μ	—	85.4	6.8	85.5	6.9
			19	oil	170–177/0.15	1.6165	63.4	3.8	63.3	3.9
				oil	204–207/0.5	1.6257	—	—	—	—
				242–243.5	—	—	—	—	—	—
				217–218.5	—	—	—	—	—	—

[a] Two crystal forms. [b] Abbreviations: DBB = dibromobenzene; BPPE = bromophenyl phenyl ether; Bis(*p*-BP)E = bis(*p*-bromophenyl) ether; 1-*m*-BP-3-PB = 1-(*m*-bromophenoxy)-3-phenoxybenzene. [c] These melting points were obtained from precision melting point curves. Calculated to be over 99.5% pure. [d] Density 1.18 g./ml. [e] Cuprous oxide catalyst. [f] Density 1.20 g./ml. [g] Purified by partial oxidation in a Dornte[17] apparatus followed by chromatography.

excess of the reported phenol was used as solvent in these cases. No particular effort was made to obtain the best possible yield. Melting and boiling points are uncorrected except as indicated. Some boiling point ranges may have a wide spread from superheating near the end of the distillation.

Bis(p-phenoxyphenyl) ether[11] (II). A mixture of phenol (103 g., 1.1 moles) and 86% potassium hydroxide (65 g., 1.0 mole) was heated until potassium phenate formed. Water and phenol were removed under vacuum at 130–145°. When potassium phenate began to separate from the mixture, distillation was stopped. Two grams of copper powder[16] and 148 g. (0.45 mole) of bis(*p*-bromophenyl) ether were added. On further heating a very vigorous reaction raised the temperature to 220°. After 2 hr. at this temperature with occasional shaking, the reaction mixture was poured into xylene and the hot suspension was filtered. Excess phenol was extracted with 20% potassium hydroxide solution. After washing with water and drying over magnesium sulfate, the xylene was evaporated and the product distilled, b.p. 220–240°/1 mm. Recrystallization from acetone gave 115 g. (72%), m.p. 109.5–110°.

Anal. Calcd. for $C_{24}H_{18}O_3$ (354.4): C, 81.3; H, 5.1. Found: C, 81.2; H, 5.1.

1-(o-Phenylphenoxy)-4-phenoxybenzene (XIII). From 272 g. (1 mole) of 97% sodium *o*-phenylphenate tetrahydrate, 189 g. (0.8 mole) *p*-bromophenyl phenyl ether, and 10 g. of copper at 275–300° for 5 hr., 196 g. of product, b.p. 195–228°/0.5 mm. was obtained. Crystallization from acetone-methanol gave a 58% yield, m.p. 87–88°.

Anal. Calcd. for $C_{24}H_{18}O_2$ (338.4): C, 85.2; H, 5.4. Found: C, 85.2; H, 5.4.

p-(p-α-Cumylphenoxyl)phenyl pivalate (XXII). A mixture of 160 g. (0.53 mole) of *p*-(*p*-α-cumylphenoxy)phenol, 160 ml. of pyridine, and 150 ml. of toluene was treated with

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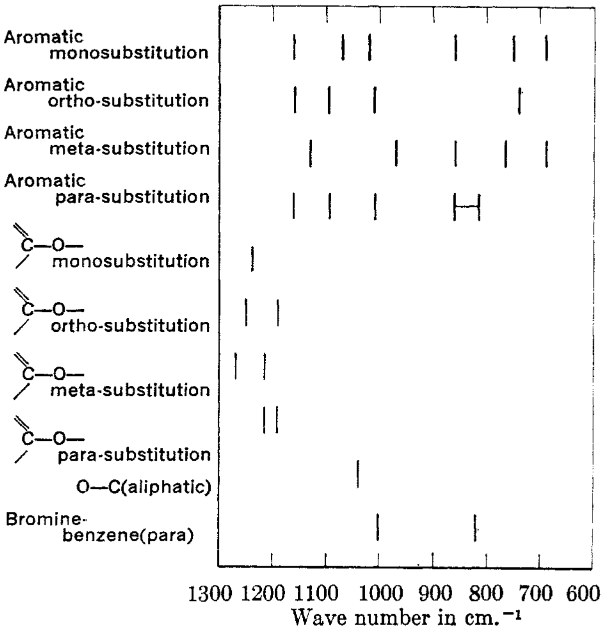
[16] R. Brewster and T. Groening, *Org. Syntheses*, **Coll. Vol. II,** 445 (1943).

TABLE II

CORRELATION CHART, ARYL ETHERS



68 g. (0.57 mole) of pivalyl chloride and refluxed 6 hr. The mixture was poured into an ice–hydrochloric acid slurry and the organic layer was separated, washed with water, dilute sodium hydroxide solution, and water. It was dried over magnesium sulfate, filtered, and distilled. The fraction boiling at 204°/0.25 mm., 171 g. (83%) was collected.

Anal. Calcd. for $C_{26}H_{28}O_3$ (388.5): C, 80.4; H, 7.3. Found: C, 80.8; H, 7.3.

m-(m-Phenoxyphenoxy)bromobenzene (XXVIII). *m*-Phenoxyphenol (500 g., 2.67 moles) was heated to 130° and treated with 140 g. (2.12 moles) of 85% potassium hydroxide. Bis[2-(2-methoxyethoxy)ethyl] ether (200 ml.) was added as a solvent and water was removed under vacuum. The hot solution was added dropwise during 2 hr. to a rapidly stirred mixture of 1 kg. (4.24 moles) of *m*-dibromobenzene and 17 g. of copper catalyst at 180–200°. The mixture was stirred at 230–240° for 4 hr. and was cooled, filtered, diluted with toluene, and extracted with 10% aqueous potassium hydroxide solution. The product layer was washed with water and the solvent was evaporated. The oily residue was distilled through a 1″ × 30″ column packed with protruded stainless steel packing. A forecut of 485 g. of *m*-dibromobenzene was recovered. The product, 503 g., b.p. 204–207°/0.5 mm., n_D^{20} 1.6257, was obtained in 70% yield.

Anal. Calcd. for $C_{18}H_{13}O_2Br$ (341.2): C, 63.4; H, 3.8. Found: C, 63.5; H, 3.9.

Bis(o-tert-butylphenoxymethyl)durene (XXX). Bis(chloromethyl)durene (46 g., 0.2 mole) was refluxed with a mixture of 60 g. (0.4 mole) of *o-tert*-butylphenol and 26 g. (0.4 mole) of 86% potassium hydroxide in 500 ml. of acetone and 250 ml. of toluene for 8 hr. The product, which crystallized from the hot reaction mixture, was filtered and washed with acetone. It was boiled with 500 ml. of water for 0.5 hr. filtered, and washed with water and acetone. The product was dissolved in boiling toluene; the solution was filtered hot and concentrated to 300 ml. Cooling gave 61 g. (67%), m.p. 217–218.5°.

Anal. Calcd. for $C_{32}H_{42}O_2$ (458.7): C, 83.8; H, 9.2. Found: C, 83.8; H, 9.2.

Bis(p-tert-butylphenoxymethyl)durene (XXIX) was prepared as above without toluene in the reaction step, from bis(chloromethyl)durene and *p-tert*-butylphenol in 28% yield, m.p. 242–243.5°.

Anal. Calcd. for $C_{32}H_{42}O_2$ (458.7): C, 83.8; H, 9.2. Found: C, 83.8; H, 9.3.

o-Bromophenyl phenyl ether. o-Aminophenyl phenyl ether[18] (51 g., 0.275 mole) was converted to the diazonium bromide and added to a boiling mixture of 43.3 g. (0.3 mole) of cuprous bromide and 39 ml. of 48% hydrobromic acid during 45 min. The reaction mixture was refluxed an additional half hour. After cooling, the product was extracted with ether and the extract was washed with 5% hydrochloric acid, 10% potassium hydroxide, and water. The product was dried and distilled from a Vigreux-Claisen flask. The product was dried and distilled from a Vigreux-Claisen flask. The fraction boiling at 97–100°/0.1 mm. was recrystallized from methanol to give 47.4 g. (69%), m.p. 43.5–44.5°.

Anal. Calcd. for $C_{12}H_9OBr$ (249.1): C, 57.9; H, 3.6; Br, 32.1. Found: C, 57.9; H, 3.7; Br, 32.4.

m-Bromophenyl phenyl ether. This product was prepared from *m*-aminophenyl phenyl ether[13] by a procedure identical with that used for the preparation of *o*-bromophenyl phenyl ether. Distillation in a packed column gave a 58% yield, b.p. 156–158°/10 mm., n_D^{20} 1.6076.

Anal. Calcd. for $C_{12}H_9OBr$ (249.1): C, 57.9; H, 3.6; Br, 32.1. Found: C, 57.9; H, 3.7; Br, 32.4.

m-Phenoxyphenol.[12,13] (1) A mixture of 50 g. (0.25 mole) of 3-phenoxyanisole, 82 g. (0.5 mole) of 48% hydrobromic acid, and 200 ml. of glacial acetic acid was treated with 60 ml. of acetic anhydride and refluxed 5 hr. Most of the solvent was distilled. The residue was treated with water, extracted with xylene, and the xylene solution was extracted with aqueous potassium hydroxide solution. The aqueous layer was washed with xylene and the product was liberated with carbon dioxide. The ether extract of the product was dried and distilled to yield 35.5 g. (76%), b.p. 143–146°/2 mm., n_D^{20} 1.6005.

Anal. Calcd. for $C_{12}H_{10}O_2$ (186.2): C, 77.4; H, 5.4. Found: C, 77.4; H, 5.5.

(2) *m*-Phenoxyaniline (185 g., 1 mole) was diazotized with 700 ml. of 6*N* sulfuric acid and 71 g. (1 mole) of sodium nitrite. The solution was filtered to remove a small amount of unchanged amine sulfate. Excess nitrous acid was destroyed with urea and the diazonium salt was slowly poured into boiling 6*N* sulfuric acid. After an additional 5 min. the mixture was cooled, extracted with ether, and the product extracted from the ether with potassium hydroxide solution. The basic layer was washed with ether, acidified with acetic acid, and the product extracted with ether. On distillation, 112 g. (60%) of *m*-phenoxyphenol, b.p. 165–167°/7 mm., was obtained.

(3) *m*-Bromophenyl phenyl ether (87 g., 0.35 mole) was added to a solution of 65 g. (1 mole) of 86% potassium hydroxide in 600 ml. of diethylene glycol and the mixture was stirred at 200–205°. The reaction was followed by dilution of an aliquot with water and centrifugation. It was complete after 36 hr. The mixture was poured into water, extracted with toluene, and the aqueous layer was acidified with hydrochloric acid. The product was extracted with toluene and distilled to give a 60% yield, b.p. 157–159°/4 mm.

m-(p-Phenoxyphenoxy)phenol. 1-(*m*-Methoxyphenoxy)-4-phenoxybenzene (290 g., 1 mole) was refluxed with 600 ml. of 48% hydrobromic acid in 800 ml. of glacial acetic acid for 72 hr. The reaction mixture was diluted with water and the product was extracted with benzene. Distillation gave 245 g. (88%), b.p. 207–216°/1 mm. In another run the product boiled at 200–206°/0.5 mm.

m-(m-Phenoxyphenoxy)phenol. *m*-(*m*-Phenoxyphenoxy)-bromobenzene (450 g., 1.32 moles) was stirred with 218 g. (3.3 moles) of 85% potassium hydroxide and 1500 ml. of diethylene glycol at 230–240° for 2 hr. The reaction mixture was cooled, diluted with water, and extracted with

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[17] R. W. Dornte, *Ind. Eng. Chem.*, **28**, 26 (1936).

[18] C. M. Suter, *J. Am. Chem. Soc.*, **51**, 2581 (1929).

toluene. The aqueous layer was acidified with hydrochloric acid and the product extracted with toluene. The toluene layer was washed with water; the toluene was evaporated and the product distilled, b.p. 222–230°/1 mm., 180 g., (49.5%), n_D^{20} 1.6188.

Anal. Calcd. for $C_{18}H_{14}O_3$ (278.3): C, 77.7; H, 5.1. Found: C, 77.4; H, 5.1.

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EMERYVILLE, CALIF.

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N-Halogen Compounds. II.[1,2] The N—Cl Stretching Band in Some *N*-Chloroamides. The Structure of Trichloroisocyanuric Acid

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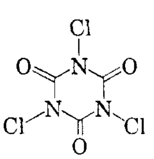
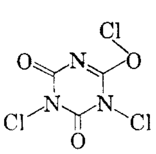
The infrared spectrum of solid trichloroisocyanuric acid is interpreted as confirming the keto structure Ia of Chattaway and Wadmore. The 650–900 cm.$^{-1}$ region of thirteen *N*-chloroamides and of some of their congeners was examined. All the chlorinated cyanuric acids and benzenesulfonamide derivatives studied as well as 1,3-dichloro-5,5-dimethylhydantoin contained a band between 762 and 803 cm.$^{-1}$ which is probably essentially an N-Cl stretching frequency. Compounds containing N-Cl attached to more weakly electronegative groups, such as *N*-chlorosuccinimide and *N*-chloroacetamide, did not have such a band. The preparation of some halogen derivatives of cyanuric acid is described.

As part of a program of examining solid compounds for bleaching activity we have run the infrared spectra of a number of *N*-chloroamides. The main object has been to build a library of reference spectra for identification purposes, but we have studied some of them in detail when structural questions arose, and have sought new spectra-structure correlations.

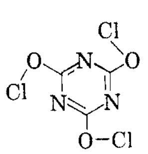
Early in the work it became of practical importance to know whether crystalline trichloroisocyanuric acid (I) was, as Chattaway and Wadmore[4] believed, all in the keto form Ia, or whether it was in some tautomeric form such as Ib or Ic, or was a mixture of two or more such forms.



Ia



Ib



Ic

The available chemical evidence,[1,4] which we confirmed by a molecular weight determination, make it quite certain that I is a trimer, $(CClNO)_3$. Estimates of bond and resonance energies definitely indicate that Ia should be the most stable form, thermodynamically. Nevertheless, in the absence of physical evidence for the location of the chlorine atoms, no definite conclusion could be reached.

No physical evidence for the location of the chlorine in any chloroamide has been found in the literature. However, the infrared spectra of six bromoamides reported by Lacher, Olson, and Park[5] were in accord with a keto-*N*-bromo structure, and a number of amides not containing positive halogen, including cyanuric acid, have been shown[6,7] to be completely in the keto form in the solid state by both x-ray and infrared studies.

The infrared spectrum of crystalline trichloroisocyanuric acid (Fig. 1 and Table I) turned out to be surprisingly simple, as it exhibited only six well-defined bands. In a twelve-atom molecule, this scarcity of bands indicates a symmetrical and probably a planar structure, and favors structure Ia or Ic over forms such as Ib. The strong band near 1740 cm.$^{-1}$ must be due to carbonyl absorption and the shift in its frequency from 1710 cm.$^{-1}$ in cyanuric acid[6] is in the direction expected. The frequency in cyanuric acid may be lowered by hydrogen bonding which is not possible for I, and it seems reasonable for an average of one chlorine substituent *alpha* to the carbonyl, and probably in the same plane, to raise the C═O stretching frequency

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