The Synthesis of 4-Hydroxyarylene Ethers by the Equilibration of Phenols with Poly(2,6-dimethyl-1,4-phenylene ether)[1]

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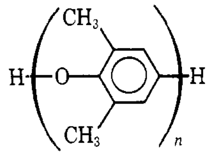
Hydroxyarylene ethers, **6**, have been synthesized by equilibrating phenols with poly(2,6-dimethyl-1,4-phenylene ether). The mixtures of phenolic products were converted into thermally stable derivatives (acetates, methyl ethers, trimethylsilyl ethers) and separated by fractional distillation. The purified derivatives were cleaved to the free hydroxyarylene ethers. With the trimethylsilyl ethers, the cleavage proceeded quantitatively at room temperature. The equilibration reactions were initiated with either benzoyl peroxide or 3,3',5,5'-tetramethyl-4,4'-diphenoquinone. Phenol, resorcinol, halophenols, alkylphenols, alkoxyphenols, and aryloxyphenols equilibrated extensively with the polymer. Phenols with strong electron-withdrawing groups generally were unreactive. The molecular weight distribution of the low molecular weight products depended on the initial ratio of starting phenol to polymer.

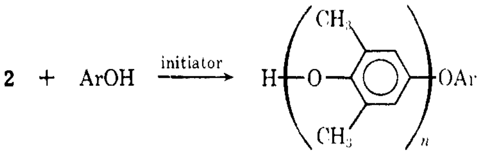
Many 4-aryloxyphenols redistribute in the presence of an initiator to form a mixture of phenols.[2,3] For example, 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol (**2**) is converted into an equilibrium mixture of 2,6-dimethylphenol (**1**) and higher molecular weight hydroxyphenylene ethers (reaction 1), and the quantities



1, $n = 1$
2, $n = 2$
3, $n = 3$
4, $n = 4$

$$\mathbf{2} \xrightarrow{\text{initiator}} \mathbf{1} + \mathbf{2} + \mathbf{3} + \mathbf{4} + \cdots \qquad (1)$$

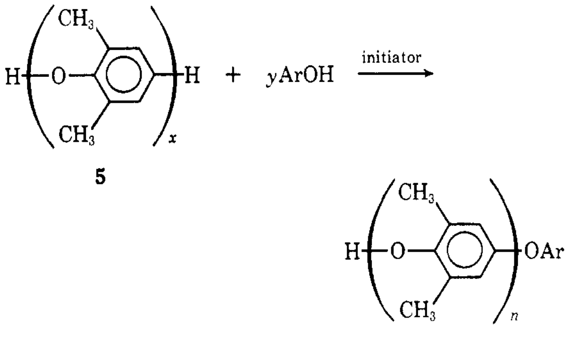
of the products at equilibrium occur in the order **1** > **2** > **3** > **4** >.... When a second phenol is present during the redistribution of **2**, a coequilibration may occur in addition to reaction 1 and a second series of products can result (reaction 2). This report describes



(2)

$n = 0, 1, 2, 3 \cdots$

a synthetic method for the preparation of 4-hydroxyarylene ethers which utilizes reactions which are similar to 1 and 2. Instead of using a "dimer" as **2**, an equilibration mixture is attained from the coredistribution of a high molecular weight hydroxyarylene ether, poly(2,6-dimethyl-1,4-phenylene ether) (**5**), with a phenol. Reaction 3 describes the conversion. When ArOH is compound **1**, the products are the same as those from reaction 1. When ArOH is a phenol other than **1**, the products are the same as those from reaction 2, and only trace quantities of the products from reaction 1 are present. Since the polymer, **5**, is readily available,[4,5] the equilibration of **5** with phenols often provides a convenient synthetic method for the preparation of entire series of 4-hydroxyarylene ethers. In many instances (*e.g.*, halogenated products or compounds with two or more ether linkages), syntheses by conventional organic procedures often require many more steps and result in very low yields.[6]



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6, $n = 0, 1, 2, 3 \cdots$

The equilibration mixture, **6**, which contained the starting phenol and hydroxyarylene ethers ranging from $n = 1$ up to methanol-insoluble polymer ($n >$ *ca.* 10), in most cases was highly reactive[2,3] and would redistribute during isolation. To avoid redistribution, the phenols were converted into esters or ethers which did not redistribute.[7] The separation procedure varied with the specific conditions but involved some or all of the following operations: (a) precipitation of the methanol-insoluble polymer if much was present; (b) extraction of the phenol, ArOH, and certain other impurities with aqueous base; (c) conversion of the hydroxyarylene ethers into thermally stable derivatives, *e.g.*, the trimethylsilyl ether (eq 4);[8] (d) fractional distillation of the derivatives; and (e) hydrolysis of the purified derivative. The trimethyl-

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[1] A portion of this work was described at the Phoenix Meeting of the American Chemical Society, Division of Polymer Chemistry, Preprints, 1966, p 178.

[2] G. D. Cooper, A. R. Gilbert, and H. Finkbeiner, ref 1, 1966, p 166.

[3] D. A. Bolon, *J. Org. Chem.*, **32**, 1584 (1967).

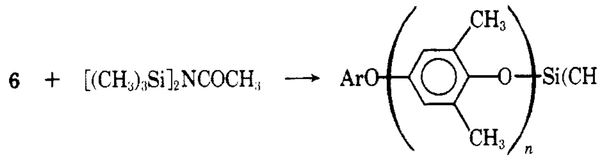
[4] A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Amer. Chem. Soc.*, **81**, 6335 (1959); A. S. Hay, *J. Polym. Sci.*, **58**, 585 (1962).

[5] G. F. Endres and J. Kwiatek, *ibid.*, **58**, 593 (1962).

[6] Alternate procedures would require methods such as the Ullmann ether synthesis [H. E. Unganade, *Chem. Rev.*, **38**, 405 (1946)] or involve aryl iodonium intermediates [H. Ziegler and C. Marr, *J. Org. Chem.*, **27**, 3335 (1962), and references therein].

[7] G. D. Cooper, H. S. Blanchard, G. F. Endres, and H. L. Finkbeiner, *J. Amer. Chem. Soc.*, **87**, 3996 (1965).

[8] J. F. Klebe, H. Finkbeiner, and D. M. White, *ibid.*, **88**, 3390 (1966).

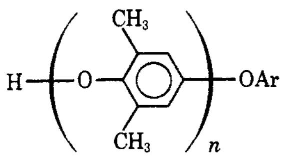

(4)

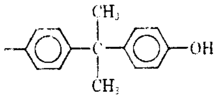
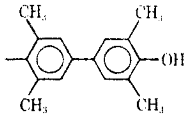
silyl ethers were convenient derivatives since they were stable during distillation and the protective group could be hydrolyzed after distillation under conditions which were sufficiently mild to prevent redistribution of the free 4-hydroxyarylene ether.

The major products which were isolated from preparative-scale equilibrations with 2,6-dimethylphenol, phenol, *p*-bromophenol, 3,3′-5,5′-tetramethyl-4,4′-dihydroxybiphenyl (**20**), and 4,4′-isopropylidenediphenol are listed in Table I.[9] In some cases, the intermediate trimethylsilyl ethers were crystalline solids (*e.g.*, the trimethylsilyl ether of **11**, mp 68–70°) and could be purified by recrystallization. The products in Table I which are new compounds have been characterized by infrared (ir) and nuclear magnetic resonance (nmr) spectroscopy, elemental analysis, and thin layer and gas chromatographic behavior. The preparation of these compounds illustrates the use of halo- and alkylphenols and unsubstituted and difunctional phenols in equilibrations for synthetic purposes. The scope of the reaction is discussed in more detail, below, after several other features of the reaction have been presented.

TABLE I

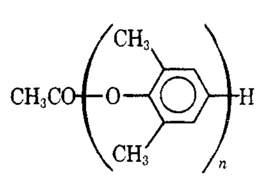
PRODUCTS FROM THE EQUILIBRATION OF PHENOLS (ArOH) WITH POLY(2,6-DIMETHYL-1,4-PHENYLENE ETHER)



Compd no.	*n*	Ar	Mp, °C
2	1	2,6-Dimethylphenyl	108.5–109[a]
3	2	2,6-Dimethylphenyl	112.5–112.7[b]
4	3	2,6-Dimethylphenyl	165–167 (acetate)
7	1	Phenyl	Amorphous
8	2	Phenyl	Amorphous
9	3	Phenyl	Amorphous
10	1	4-Bromophenyl	62.5–63.5
11	2	4-Bromophenyl	100–102
12	1		201.5–202.5
13	1		118–119

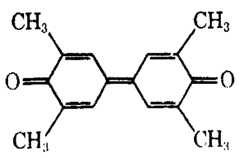
[a] Lit.[3] mp 111°. [b] Lit.[3] mp 112–113°.

The quantities of products from a large-scale equilibration of 2,6-dimethylphenol with polymer **5** illustrate yields for a reaction where the acetates of the dimer, trimer, and tetramer were isolated. From 1000 g of 2,6-dimethylphenol and 1000 g of polymer, the isolated derivatives were **14** (293 g), **15** (220 g), and **16** (35 g). Only a portion of **16** was isolated. Gas chromatographic analysis indicated that approximately 100 g was in the reaction mixture.



14, $n = 2$
15, $n = 3$
16, $n = 4$

A variety of oxidizing agents can serve as initiators for the equilibrations. The two materials used in this study were benzoyl peroxide and 3,3′,5,5′-tetramethyl-1,4-diphenoquinone (**17**). *o*-Chloranil (**18**) and 2,4,6-tri-*t*-butylphenoxyl (**19**) were moderately effective initiators but were not used in preparative reactions. *p*-Benzoquinone and *p*-chloranil did not produce extensive equilibration. Side reactions, principally with the phenol, rapidly decreased the concentrations of the latter two initiators.



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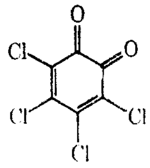

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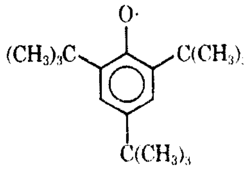

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The quantities of benzoyl peroxide and **17** varied from 3 to 10% of the weight of the polymer. The latter quantity was used only when smaller quantities did not produce extensive equilibration. Low initiator concentrations were preferred since the quantities of side products were less.

Several side products from reactions of the initiators were isolated. With **17** as the initiator, phenols with low oxidation potentials were oxidized usually to carbon–carbon coupled dimers.[10] In the case of 2,6-dimethylphenol, the product was 3,3′,5,5′-tetramethyl-4,4′-dihydroxybiphenyl (**20**). Compound **20** equilibrated with the polymer to produce compound **12** (eq 5) and higher oligomeric products. (This side reaction was used preparatively; see Table I.) With benzoyl peroxide as an initiator, the sequence of reactions shown in eq 6 occurred. The formation of

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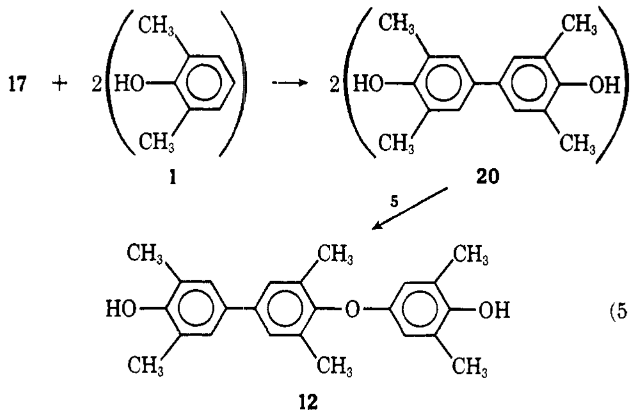
[9] A preparative-scale equilibration using 2,4,6-trimethylphenol is described in ref 8.

[10] A. S. Hay, *Tetrahedron Lett.*, 4241 (1965); R. G. R. Bacon and O. J. Stewart, *Chem. Commun.*, 977 (1967).



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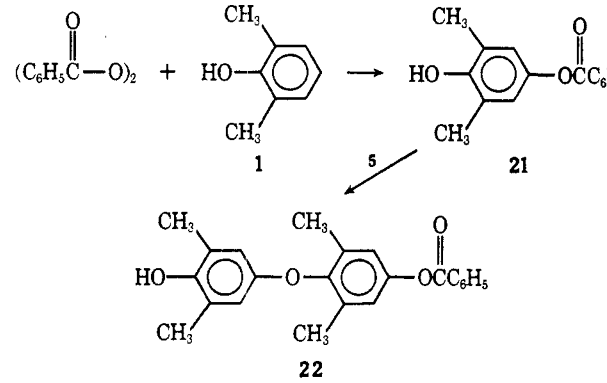

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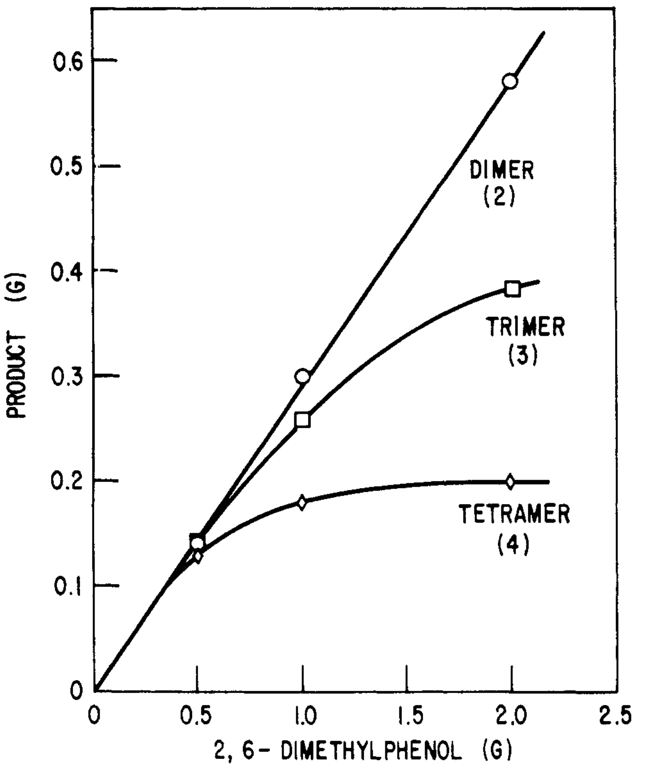

Figure 1.—Change in product composition with initial 2,6-dimethylphenol concentration for the equilibration with 1.00 g of polymer **5** at 80° for 2 hr. The quantity of initiator **17** was 3 wt % of the 2,6-dimethylphenol.

4-benzoyloxy-2,6-xylenol (**21**) from the reaction of benzoyl peroxide with 2,6-xylenol has been reported.[11,12] An extensive equilibration of **21** with polymer **5** to form **22** and higher oligomers occurred and is described in a later section. Another source of **21** is the reaction of benzoyl peroxide with the polymer. This is indicated by the isolation of **21** in small amounts from equilibrations which did not have **1** as the starting phenol. The yields of the side products were low; typical values based on the equilibration of 100 g of polymer with 100 g of 2,6-dimethylphenol were 2 g of **20** and 0.5 g of **12** from 3 g of initiator **17** and 2 g of **21** and 0.5 g of **22** from 10 g of benzoyl peroxide.

The relative quantity of each component in the equilibrated reaction mixture depends on the number average degree of polymerization, $\overline{\mathrm{DP}}_n$, of the mixture. When polymer was equilibrated completely with an equal weight of 2,6-dimethylphenol, the distribution of the products was the same as that for the equilibration of the dimer **2** alone. In this case, the molar concentration of 2,6-dimethylphenol was almost equal to the molar concentration of monomeric units in the polymer, *i.e.*, $x = y$ in reaction 3, and the $\overline{\mathrm{DP}}_n$ was almost 2. Similarly, a monomer-polymer solution with a $\overline{\mathrm{DP}}_n$ of 3 was converted into the same distribution which was attained from equilibration of the trimer **3**. The effect of changes of the $\overline{\mathrm{DP}}$ is illustrated in Figure 1 for three 2,6-dimethylphenol concentrations. For a $\overline{\mathrm{DP}}$ of 3 (0.50 g of **1**/g of **5**), the weight ratio of 2:3:4 was approximately 1:1:1. For a $\overline{\mathrm{DP}}$ of 1.5 (2.0 g of **1**/g of **5**) the ratio was approximately 3:2:1. The changes in product distribution can be interpreted as mass law effects on the many equilibration reactions which are occurring. Two equilibrium reactions are represented by eq 7 and 8. Compound **6′** is an oligomer with one less monomeric unit than in **6**. An increase in the phenol **1** drives the equilibrium to the right and

$$\mathbf{1} + \mathbf{6} \rightleftharpoons \mathbf{2} + \mathbf{6'} \tag{7}$$

$$\mathbf{2} + \mathbf{6} \rightleftharpoons \mathbf{3} + \mathbf{6'} \tag{8}$$

the dimer **2** is increased. The increase in **2** causes a corresponding shift in equilibrium 8 to the right and the concentration of **3** is increased. The increase of **3** is not so pronounced as the increase in **2**, however, since the equilibrium concentration of **2** is less than that of **1**. The effect of the concentration of **1** on higher oligomer concentrations is progressively less as the size of the oligomer increases.

From the data in Figure 1, an equilibrium constant can be calculated for the equilibrium between compounds **1**, **2** and **3** (eq 9). The value, $K_2 = 2.3 \pm$

$$2(\mathbf{2}) \rightleftharpoons \mathbf{1} + \mathbf{3} \tag{9}$$

0.2, is in agreement with the value of 2.44 for the redistribution of **2**.[2] For equilibrium 10, $K_3 = 0.91 \pm$

$$2(\mathbf{3}) \rightleftharpoons \mathbf{2} + \mathbf{4} \tag{10}$$

0.1. Equilibrium constants for analogous redistribution of higher oligomers also appear to be near unity. Only the equilibrium constant which involves an equilibrium with component **1**, a phenol which cannot redistribute (reaction 1), has the high value.

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(11) S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.* (London), 3189 (1949); 388 (1951).

(12) C. Walling and R. B. Hodgdon, *J. Amer. Chem. Soc.*, **80**, 228 (1958).

The reactivity of the polymer, **5**, in the equilibration is dependent on its molecular weight and on the nature of the phenolic end group. The phenolic end group is the site of initial reaction in the polymer chain. This was demonstrated by the inability of completely acetylated polymer to coredistribute under equilibration conditions. Since the concentrations of phenolic end groups are inversely proportional to the molecular weight, low polymer has a higher molar concentration of end groups than an equal weight of high polymer. For low polymer faster equilibration results and fewer side reactions, as reactions 5 and 6, occur. The other factor is the nature of the phenolic end group. The concentration of irregularities in the structures of the phenolic end groups appears to increase with higher molecular weight owing to side reactions during polymerization which reduce the reactivity of some of the polymer molecules. For these reasons, equilibration is more extensive and side products are less with low molecular weight polymer. The use of very low molecular weight polymer for equilibrations with phenols other than 2,6-dimethylphenol is avoided, however, since the molar concentration of polymer will be sufficiently high to allow the buildup of an appreciable amount of equilibration products from a redistribution reaction similar to reaction 1. Thus, polymers with molecular weights between *ca.* 2000 and 10,000 (intrinsic viscosity in chloroform at 30° from *ca.* 0.1 to 0.3 dl/g) have been used most successfully in these preparations.

The scope of the equilibration between phenols and poly(2,6-xylylene oxide) is indicated by the results of equilibrations with 28 phenols which are summarized in Table II. Extensive equilibration (as indicated by low yields of recovered polymer) occurred with phenol, many alkylated and halogenated phenols, and certain phenols with an oxygen atom in the *meta* or *para* position. In general, compounds that equilibrate poorly are the phenols which have lowest oxidation potentials and undergo side reactions with the initiator or phenols that have the highest oxidation potentials and are inert (*e.g.*, *p*-nitrophenol). Steric effects may account for the lower reactivity with *o*-bromophenol than with *p*-bromophenol. Two of the phenols in Table II, **20** and **21**, are side products from the initiators. Their ability to react with polymer is demonstrated here.

The polymer for the series of reactions in Table II had a relatively high intrinsic viscosity (0.34 dl/g, $\bar{M}_n$ *ca.* 15,000) to provide a less reactive system than would result with lower molecular weight polymers. Thus, the reactivity scale of the more active phenols was, in effect, expanded. As a result, some of the active phenols had intermediate reactivity in this case, and did equilibrate more extensively with polymers that were more reactive.

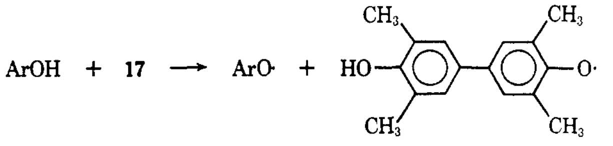
Benzoyl peroxide and 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone were compared for equilibrations with several phenols (Table II). In these cases, benzoyl peroxide was either equally effective or more effective than the diphenoquinone. In certain cases, however, the diphenoquinone was preferred since the 4-aryloxy-2,6-xylenol (**6**, $n = 1$) could be separated more easily from side product **20** than from side product **21**.

TABLE II

EQUILIBRATION OF POLY-(2,6-DIMETHYL-1,4-PHENYLENE ETHER) WITH VARIOUS PHENOLS

Phenol	Yield of recovered polymers for two initiators: Benzoyl peroxide, %	Yield of recovered polymers for two initiators: 3,3′,5,5′-Tetramethyl-4,4′-diphenoquinone, %
Phenol	6	
o-Bromophenol	31	48
m-Bromophenol	28	
p-Bromophenol	11	
p-Iodophenol	16	35
p-Chlorophenol	5	
2,6-Dichlorophenol	64	
Pentachlorophenol		86
o-Cresol	3	4
m-Cresol	5	17
p-Cresol	4	
2,6-Xylenol (**1**)	4	6
Mesitol	47	
2,6-Dimethyl-4-(benzoyloxy)phenol (**21**)	10	
p-Methoxyphenol	46	
p-Phenoxyphenol	4	
Hydroquinone monobenzoate		13
Hydroquinone		98
Resorcinol		33
4,4′-Dihydroxydiphenyl ether		95
4,4′-Isopropylidenediphenol		4
3,3′,5,5′-Tetramethyl-4,4′-biphenyl (**20**)		60
p-Hydroxybenzonitrile	88	
2,6-Diphenylphenol	64	
p-Nitrophenol	90	
β-Naphthol		64
Methyl *p*-hydroxybenzoate		88
Methyl salicylate		96

The mechanism of the equilibration of poly(2,6-dimethyl-1,4-phenylene ether) with phenols appears to be very similar to the mechanism described for the redistribution of compound **2**[2] and the coredistribution of phenols with compound **2**.[3] The initiation step is the oxidation of the phenolic group. With the diphenoquinone **17** as an initiator, the monomer and the polymer are converted into the corresponding phenoxy radicals (eq 11 and 12). The reduced diphenoquinone, **23**, can either abstract another hydrogen and form **20** or can transfer a hydrogen to reduce an aryloxy radical. The radicals ArO· and **24** couple to form a quinone ketal, **25** (eq 13), one of the types of intermediates in the propagation step. With benzoyl peroxide as an initiator, the initial step may be the formation of a quinolbenzoate, **26** (eq 14), in analogy with the formation of 4-benzoyloxy-2,4,6-trimethyl-2,5-cyclohexadienone from benzoyl peroxide and mes-



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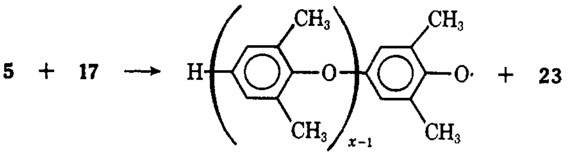

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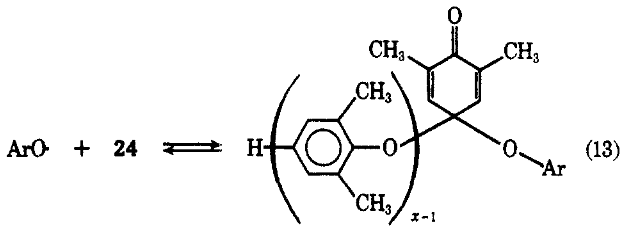

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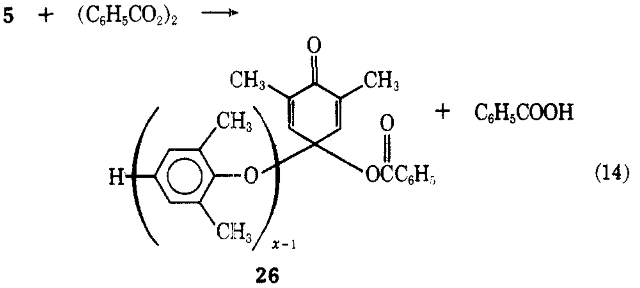

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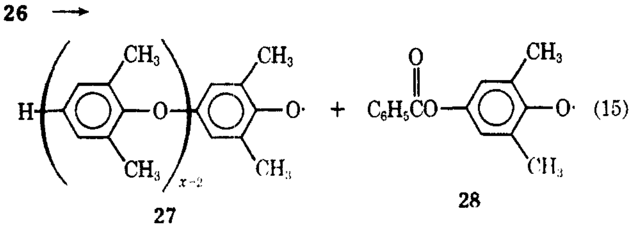
itol.[11] Compounds **25** and **26** can dissociate to form a polymer radical **27** (which reacts similarly to **24**) and the radical **28** (eq 15) which can be reduced to form the side product **21** or can equilibrate further.

The steps in the propagation reaction involve the same reversible dissociations of quinone ketals which were described by Bolon,[3] *e.g.*, eq 16–18, etc. Intermediates such as **29** and **31** can react further with other phenoxy radicals such as **24** and **27** or can abstract hydrogen atoms from other phenols to form **6** and new phenoxy radicals.



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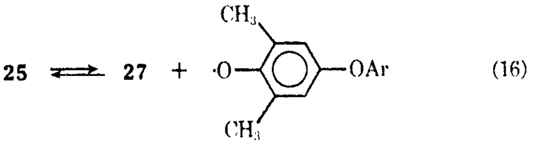

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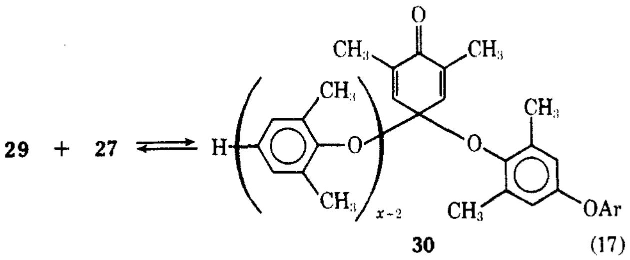

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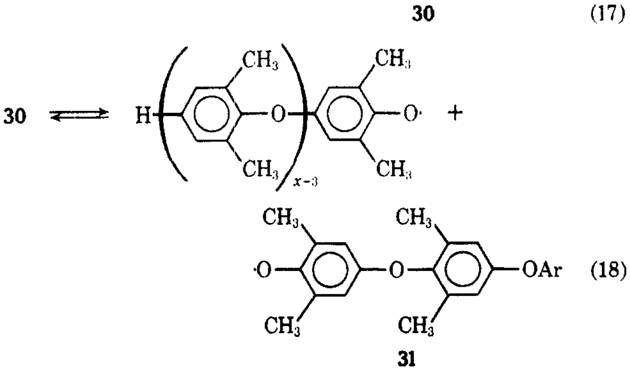

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Strong support for the quinone ketal dissociation mechanism[2,3] is given by the structures of the products which were isolated in this study. This mechanism predicts that only the terminal aryloxy rings of the hydroxyarylene ethers are derived from the phenol, ArOH. All of the remaining rings are derived from the polymer. The nmr studies of the composition of the hydroxyarylene ethers indicated that they do have structure **6**.

Experimental Section[13]

Poly(2,6-dimethyl-1,4-phenylene ether) (5).—The polymers were prepared by a modification of the method of Endres and Kwiatek.[5] 2,6-Dimethylphenol (10.0 g, 0.082 mol; three times recrystallized) was added to an oxygenated, stirred solution of cuprous chloride (0.50 g, 0.005 mol; reprecipitated from hydrochloric acid with methanol and dried) and pyridine (100 ml; reagent grade) in a flask in a stirred water bath at 20°. Oxygen (0.15 ft^3/hr) was bubbled into the solution. The temperature of the reaction mixture rose to 23° after 7 min. After 17 min, the temperature began to drop and the reaction mixture was transferred to a beaker and stirred vigorously. Methanol (500 ml; containing 5 ml of concentrated hydrochloric acid) was added to precipitate the polymer. The polymer was collected on a filter, washed two times by trituration with 500 ml of hot methanol, and dried at 50° for 20 hr at reduced pressure. The polymer weighed 8.6 g; its intrinsic viscosity in chloroform at 30° was 0.37 dl/g. Small decreases in reaction times produced polymers with lower viscosities. For example, a 15-min reaction produced a polymer with an intrinsic viscosity of 0.11 dl/g.

Small-Scale Equilibration Reactions.—Poly(2,6-dimethyl-1,4-phenylene ether) (0.500 g; intrinsic viscosity in chloroform at 30°, 0.34 dl/g), the substituted phenol[14] (0.0042 mol), and either 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (**17**, 15.0 mg, 0.063 mmol) or benzoyl peroxide (50 mg, 0.21 mmol) in benzene (25 ml) were heated at reflux for 2 hr and then the solution was cooled to 25°. Methanol (250 ml) was added dropwise and the precipitated polymer was transferred quantitatively to a filter, washed thoroughly with methanol, dried at 50° (10 mm) for 24 hr, and weighed. The yields of recovered polymers are listed in Table II. A 5-ml aliquot of the filtrate was concentrated on a rotary evaporator, converted into the trimethylsilyl ether derivative by adding 2 drops of bis(trimethylsilyl)acetamide, and analyzed by gas chromatography on a 2-ft silicone rubber column with a program from 100 to 300° at 10°/min. The composition of the methanol-soluble fractions was similar to that of the equilibration of the dimer **2** and was proportional to the quantities of isolated products from large-scale preparative equilibrations.

Preparation of Low Molecular Weight Hydroxyarylene Ethers, "Dimers," "Trimers," and "Tetramers."—The details of the procedures varied according to the reactivity of the particular equilibration mixture. If the yield of methanol-insoluble polymer was relatively high, a precipitation step was used. If a large quantity of initiator **17** was required, a base extraction step was used to remove the 3,3′,5,5′-tetramethyl-4,4′-dihydroxybiphenyl (**20**). In many cases a small-scale reaction (described above) was used to determine the preferred procedure.

Equilibration with 2,6-Xylenol. Preparation of 4-(2,6-Dimethylphenoxy)-2,6-dimethylphenol (2), 4-[4-[2,6-Dimethylphenoxy)-2,6-dimethylphenoxy]-2,6-dimethylphenol (3), and 4-{4-[4-(2,6-Dimethylphenoxy)-2,6-dimethylphenoxy]-2,6-dimethylphenoxy}-2,6-dimethylphenol (4).—Low molecular

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[13] Melting points were determined on a Leitz hot-stage microscope and are corrected. Boiling points and distillation pressures are approximate. Nmr spectra were measured on a Varian A-60 spectrometer unless stated otherwise.

[14] All phenols and initiators were purified by recrystallization or redistillation.

weight poly(2,6-dimethyl-1,4-phenylene ether) (**5**) (100 g; intrinsic viscosity in chloroform at 30°, 0.14 dl/g), 2,6-dimethylphenol (100 g, 0.82 mol), 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (**17**, 3.0 g, 0.013 mol), and benzene (2 l.) were heated at reflux with stirring for 2 hr. The solution was concentrated to 700 ml with a rotary evaporator and extracted with aqueous 10% sodium hydroxide to remove 2,6-xylenol and **20**. The organic layer was washed with 5% hydrochloric acid and then with water. Methanol (2 l.) was added over a 30-min period to the benzene solution. The precipitated polymer was removed by filtration and the filtrate was concentrated to a viscous oil (59 g). A solution of the oil in benzene (500 ml) and bis(trimethylsilyl)-acetamide (100 g, 90% pure, 0.45 mol) in benzene was heated for 2 hr, then concentrated to an oil which was fractionally distilled at reduced pressure. The cuts given in Table III were obtained.

Table III

Fraction	Bp (mm), °C	Wt, g	Principal components, trimethylsilyl ether derivatives
A	76 (2.5)	20	**1**
B	142 (0.8)	25	**2**
C	190 (0.6)	21	**3**
D	220 (0.005)	13	**4**

The trimethylsilyl groups were removed by dissolving the fractionated trimethylsilyl ether (10 g) in methanol (200 ml) at room temperature and adding 1 drop of hydrochloric acid and sufficient water (*ca.* 100 ml) to reach the cloud point. On cooling (0°), the product crystallized out of the solution and was collected on a filter, washed with cold aqueous methanol, and dried at room temperature under reduced pressure. A second crop of crystals was obtained by the addition of more water to the filtrate. The over-all yields of the dimer and trimer from fractions B and C were 20.2 g of **2**, and 13.8 g of **3**. Compounds **2** and **3** were identical with authentic samples.[3,5]

Redistillation of the highest boiling cut, D, produced a light amber, glassy solid which was 90% trimethylsilyl ether of **4** according to gas chromatography and nmr. The sample did not crystallize either as the silyl ether or when converted into the free phenol. The bands in the nmr spectrum (in carbon tetrachloride, TMS reference) due to the trimethylsilyl ether of **4** occurred at 0.21, 2.05, 2.09, 2.13, 6.24, 6.37, and 6.96 ppm with the relative intensity ratio 9:3:6:3:2:4:2. Compound **4** was converted into the acetate derivative, mp 165–167°, which was identical with compound **16** which is described below.

Equilibration with Phenol. Preparation of 4-Phenoxy-2,6-dimethylphenol (7), 4-(4-Phenoxy-2,6-dimethylphenoxy)-2,6-dimethylphenol (8), and 4-[4-(4-Phenoxy-2,6-dimethylphenoxy)-2,6-dimethylphenoxy]-2,6-dimethylphenol (9).—Phenol (100 g, 1.06 mol), poly(2,6-dimethyl-1,4-phenylene ether) (45 g; intrinsic viscosity, 0.62 dl/g), and 3,3′,5,5′-tetramethyldiphenoquinone (**17**, 4.5 g, 0.02 mol) in benzene (500 ml) were heated at reflux for 15 min. The solution was concentrated at atmosphere pressure to 250 ml over a 20-min period. Hexane (1500 ml) was added to precipitate the remaining polymer. After filtration (which removed 10 g of polymer), the filtrate was concentrated, trimethylsilylated, and fractionally distilled. The product yields after hydrolysis to the free phenols are listed in Table IV. Compound **7** was identical (nmr and ir spectra) with an authentic sample.[3] The ir spectrum of the pure liquid showed characteristic absorption at 3500, 1240, 1210, 890, 760, and 700 cm^{-1}. The nmr spectrum (in deuteriochloroform, TMS reference) showed singlet bands at 2.15, 4.85, and 6.75 ppm and a complex grouping at 6.8–7.3 ppm in the relative intensity ratio 6:1:2:5.

Table IV

Product	Wt, g	Bp (mm), °C, of trimethylsilyl ether
7	21	112 (0.05)
8	6.5	185 (0.02)
9	1.0	215 (0.02)

The ir spectrum of the pure liquid trimethylsilyl ether of **8** showed bands at 1230, 1210, 860, 760, and 700 cm^{-1} which were characteristic of the aryl ether links, the isolated aryl hydrogens, and the monosubstituted benzene ring. The nmr spectrum (in carbon tetrachloride, TMS reference) showed singlet bands at 0.23, 2.10, 2.15, 6.42, and 6.76 ppm and a complex grouping at 6.8–7.3 ppm in the relative intensity ratio 9:6:6:2:2:5.

The ir spectrum of the pure liquid sample of the trimethylsilyl ether of **9** showed bands at 1230, 1210, 860, 760, and 700 cm^{-1} which are characteristic of the ether links, the isolated aryl hydrogens, and the monosubstituted benzene ring. The nmr spectrum (in deuteriochloroform, TMS reference) showed bands at 0.23, 2.08, 2.14, 6.50, and 6.75 ppm and a series of bands from 7.0 to 7.5 ppm in the relative intensity ratio 9:6:12:2:4:5.

Equilibration with *p*-Bromophenol. Preparation of 4-(4-Bromophenoxy)-2,6-dimethylphenol (10) and 4-[4-(4-bromophenoxy)-2,6-dimethylphenoxy]-2,6-dimethylphenol (11).—A solution of poly(2,6-dimethyl-1,4-phenylene ether) (100 g; intrinsic viscosity, 0.34 dl/g), *p*-bromophenol (144 g, 0.83 mol), and benzoyl peroxide in benzene (2000 ml) was heated to reflux. After 2 hr, bis(trimethylsilyl)acetamide (223 g, 90% pure, 1.0 mol) was added. After 1 hr, the reaction mixture was cooled, concentrated, and distilled rapidly. The distillate boiling higher than the trimethylsilyl ether of *p*-bromophenol was redistilled carefully. The yields and boiling points of the trimethylsilyl ethers follow: trimethylsilyl ether of **10**, 37 g, bp 120° (0.03 mm); trimethylsilyl ether of **11**, 17 g, bp 150° (0.03 mm). The nmr spectrum (in deuteriochloroform, TMS reference) of the trimethylsilyl ether of **10** showed singlet bands at 0.25, 2.16, and 6.64 ppm and a quartet at 6.70, 6.75, 7.27, and 7.32 ppm in the relative intensity ratio 9:6:2:4. The trimethylsilyl ether was hydrolyzed in nearly quantitative yield by dissolving it in methanol–water and adding 1 drop of hydrochloric acid. Compound **10** was recrystallized from hexane: mp 62.5–63.5°. The ir spectrum of the sample in a KBr pellet showed bands at 3440, 1193, 875, and 820 cm^{-1} which are characteristic of the hydroxyl group, the ether link, and the isolated and two adjacent aryl hydrogens. The nmr spectrum (in carbon tetrachloride, TMS reference) showed singlet bands at 2.20, 4.58, and 6.64 ppm and a quartet at 6.70, 6.75, 7.26, and 7.41 ppm in the relative intensity ratio 6:1:2:4.

Anal. Calcd for $C_{14}H_{13}BrO_2$: C, 57.4; H, 4.5; mol wt, 293. Found: C, 57.7; H, 4.5; mol wt (Mechrolab osmometer in chloroform), 285.

The trimethylsilyl ether of **11** was recrystallized from hexane, mp 68–70°. The nmr spectrum (in deuterochloroform; TMS reference) showed singlet bands at 0.23, 2.09, 2.14, 6.37, and 6.73 ppm and a quartet at 6.81, 6.97, 7.34, and 7.49 ppm in a relative intensity ratio of 9:6:6:2:2:4.

Anal. Calcd for $C_{25}H_{29}BrO_3Si$: C, 62.0; H, 6.0; Br, 16.5; mol wt, 485. Found: C, 61.9; H, 5.9; Br, 16.6; mol wt (Mechrolab osmometer in benzene), 475.

The trimethylsilyl ether of **11** was hydrolyzed in nearly quantitative yield by dissolving it in methanol–water and adding 1 drop of hydrochloric acid. Compound **11** was recrystallized from hexane: mp 100–102°. The ir spectrum in a KBr pellet showed bands at 3400, 1230, 1190, 878, 850, and 820 cm^{-1} which are characteristic of the hydroxyl group, the two aryl ether links, the two types of isolated aryl hydrogens, and two adjacent aryl hydrogens.

Anal. Calcd for $C_{22}H_{21}BrO_3$: C, 63.8; H, 5.1; mol wt, 413. Found: C, 63.7; H, 5.1; mol wt (Michrolab osmometer in benzene), 392.

Equilibration with 20. Preparation of 4-(3,5-Dimethyl-4-hydroxyphenoxy)-4′-hydroxy-3,3′,5,5′-tetramethylbiphenyl (12).—To a stirred mixture of 3,3′,5,5′-tetramethyl-4,4′-dihydroxybiphenyl (**20**, 100 g, 0.41 mol) and 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (**17**, 15 g, 0.063 mol) in benzene (2000 ml) at 80° was added poly(2,6-dimethylphenylene ether) (50 g; intrinsic viscosity, 0.27 dl/g). After 16 hr at reflux, a gas chromatographic analysis indicated the presence of approximately 30 g of **12**. Bis(trimethylsilyl)acetamide (204 g, 0.92 mol, based on 90% purity) was added dropwise. After 2 hr, the mixture was concentrated and then distilled at reduced pressure to yield two high boiling fractions: bis(trimethylsilyl ether) of **20**, 80 g, bp 155° (0.01 mm); bis(trimethylsilyl ether) of **12**, 40 g, bp 190° (0.01 mm). Hydrolysis of these fractions gave nearly quantitative yields of the free diols. The product from the first fraction, mp 224–226°, was identical with an authentic sample of **20**.[11] The hydrolysis product from the second fraction was a solid which was recrystallized from chloroform–hexane and sublimed: **12**, mp 201.5–202.5°. The ir spectrum of this substance (in a KBr pellet) showed strong bands at 3450, 1185, and 860 cm^{-1} which are characteristic absorptions for the hydroxyl group, the ether link, and the isolated aryl hydrogens of the 1,2,3,5-tetrasubstituted aryl groups, respectively. The nmr spectrum (in perdeuteriodimethyl sulfoxide, TMS reference) showed singlet bands at 2.05, 2.20, 6.27, 7.15, 7.25, 7.70, and 8.20 ppm in the relative intensity ratio 12:6:2:2:2:1:1.

Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.6; H, 7.2; mol wt, 362.5. Found: C, 79.3; H, 7.3; mol wt (Mechrolab osmometer in chloroform), 359.

Equilibration with 4,4′-Isopropylidenediphenol. Preparation of 4-[4-(Hydroxyphenylisopropylidene)phenoxy]-2,6-dimethylphenol (13).—A solution of low molecular weight poly(2,6-dimethyl-1,4-phenylene ether) (20.0 g; intrinsic viscosity, 0.11 dl/g), 4,4′-isopropylidenediphenol (40 g, 0.175 mol), 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (0.60 g, 0.0025 mol), and benzene (600 ml) was heated at reflux 2 hr. Bis(trimethylsilyl)-acetamide (64 g, 0.28 mol, 90% pure) was added dropwise and the solution was heated at reflux for 1 hr. The solution was distilled through a 3-ft spinning-band column to yield two high boiling fractions: bis(trimethylsilyl ether) of 4,4′-isopropylidenediphenol, 45 g, bp 130–135° (0.01 mm); bis(trimethylsilyl ether) of **13**, 28 g, bp 195–200° (0.01 mm.)

A small sample of the bis(trimethylsilyl ether) of **13** was redistilled. The ir spectrum of this compound (pure liquid) showed absorptions at 1240, 880, and 840 cm^{-1} which are characteristic of the diaryl ether link and the isolated aryl hydrogens, and two adjacent aryl hydrogens, respectively. The nmr spectrum (in carbon tetrachloride, TMS reference) showed singlet bands at 0.32, 1.68, and 2.22 ppm and a complex of nine bands at 6.6–7.2 ppm in the relative intensity ratios 18:6:6:10.

Anal. Calcd for $C_{29}H_{40}O_3Si_2$: C, 70.7; H, 8.1. Found: C, 70.7; H, 8.2.

Hydrolysis of these fractions by dissolving them in methanol–water and adding 1 drop of hydrochloric acid at 25° produced the free diols in nearly quantitative yield. The 4,4′-isopropylidenediphenol was identical with the starting material. Compound **13** was recrystallized from methanol–hexane: mp 118–119°. The ir spectrum of this compound in a KBr pellet showed absorption at 3400, 1210, 882, 830, and 812 cm^{-1} which are characteristic of the hydroxyl group, the ether link, and the isolated and two different sets of two adjacent aryl hydrogens, respectively.

Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.3; H, 6.9; mol wt, 348. Found: C, 79.2; H, 6.8; mol wt (Mechrolab osmometer in benzene), 337.

Preparation of 4-(2,6-Dimethylphenoxy)-2,6-dimethylphenylacetate (14), 4-[4-(2,6-Dimethylphenoxy)-2,6-dimethylphenoxy]-2,6-dimethylphenylacetate (15), and 4-{4-[4-(2,6-Dimethylphenoxy)-2,6-dimethylphenoxy]-2,6-dimethylphenoxy}-2,6-dimethylphenylacetate (16).—A sample of low molecular weight poly(2,6-dimethyl-1,4-phenylene ether) (1000 g; intrinsic viscosity, 0.3 dl/g), 2,6-xylenol (1000 g, 8.2 mol), 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (**17**, 30 g, 0.13 mol), and benzene (5000 ml) were heated at reflux with stirring 4 hr. Pyridine (712 g, 9.0 mol) was added to the reaction mixture, acetic anhydride (919 g, 9.0 mol) was added over a 15-min period, and the solution was heated at reflux. After 2 hr, the benzene, pyridine, and acetic anhydride were removed at reduced pressure in a rotary evaporator. A rapid distillation at 0.1 mm with a Claisen still head produced two fractions: (A) 800 g, bp 50–190°; (B) 295 g, 190–230°. Fraction A was fractionally distilled through a spinning-band column at 0.05 mm. When the still pot contained *ca.* 100 g of material, fraction B was added and the distillation was continued. The products given in Table V were obtained.

TABLE V

Component	Bp (mm), °C	Mp, °C, recrystallized	Yield, g
Acetate of 2,6-xylenol	50	20–21	547
14	130	123–124	293
15	190	121–122	220
16	220	165–167	35

Several side products were obtained: the diacetate of compound **20**, 22 g, which boiled in the range between compounds **14** and **15**; the diacetate of **12**, 10 g; the acetates of the "pentamer" and the "hexamer" which were identified by gas chromatography but not isolated in pure form, *ca.* 3 g and 1 g, respectively.

The diacetates of **12** and **20** and compounds **14** and **15** were identical with the acetate derivatives of authentic samples of the parent compounds (by mixture melting points and ir and nmr spectra). The ir spectrum of compound **16** in a KBr pellet showed bands at 1756, 1225, 1190, 850, and 770 cm^{-1} which are characteristic of the carbonyl group, the ether links, the isolated aryl hydrogen, and the three adjacent aryl hydrogens. The nmr spectrum (in carbon tetrachloride, TMS reference, on a Varian HA-100 spectrometer) showed doublet bands ($J \sim 0.2$ cps) at 2.00, 2.03, 2.05, and 2.12 ppm and singlet bands at 2.15, 6.33, 6.37, and 6.95 ppm in the relative intensity ratios 6:6:6:6:3:2:4:3.

Anal. Calcd for $C_{34}H_{36}O_5$: C, 77.8; H, 6.9; mol wt, 525. Found: C, 77.5; H, 7.2; mol wt (Mechrolab osmometer in chloroform), 534.

Effect of Monomer–Polymer Ratio on Product Distribution.—Three equilibration reactions were carried out on samples of poly(2,6-dimethyl-1,4-phenylene ether) (**5**), 2,6-dimethylphenol (**1**), and 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (**17**) in benzene at 80°. The quantities of reagents are given in Table VII

TABLE VI

1, g	5, g	17, g	Benzene, ml
0.50	1.00	0.015	25
1.00	1.00	0.030	50
2.00	1.00	0.060	100

After 2 hr, excess bis(trimethylsilyl)acetamide was added to each mixture and the trimethylsilylated products were analyzed by gas chromatography. An inert internal standard, 4-methoxyphenyl 3-phenoxyphenyl ether, was present in each mixture to permit quantitative determination of the products (see Figure 1).

Conversion of Poly(2,6-dimethyl-1,4-phenylene ether) into the Acetate and Attempted Equilibration of the Acetate.—Poly-(2,6-dimethyl-1,4-phenylene ether) (10 g; intrinsic viscosity, 0.34 dl/g) was heated at reflux in a mixture of 120 ml of toluene, 120 ml of pyridine, and 8 ml of acetic anhydride for 3 hr under nitrogen and then allowed to cool to 25° overnight. The polymer was isolated by precipitation with methanol and drying at 50° (10 mm) for 24 hr. The ir spectrum of the product (2.5% solution in carbon disulfide in a 1.0-cm cell) indicated that the phenolic hydroxyl absorption at 3610 cm^{-1} was not present. The intrinsic viscosity was 0.34 dl/g.

The acetylated polymer (0.50 g), 2,6-dimethylphenol (0.50 g), initiator **17** (0.015 g), and benzene were heated at 80° for 2 hr. The polymer was precipitated with methanol, washed with methanol, and dried. The polymer weighed 0.50 g and had an intrinsic viscosity of 0.34 dl/g.

Registry No.—**1** (trimethylsilyl ether derivative), 16286-54-7; **2** (trimethylsilyl ether derivative), 15770-98-6; **3** (trimethylsilyl ether derivative), 15770-99-7; **4** (acetate), 15770-86-2; **4** (trimethylsilyl ether derivative), 15875-06-6; **7** (trimethylsilyl ether derivative), 15770-79-3; **8** (trimethylsilyl ether derivative), 15875-05-5; **9** (trimethylsilyl ether derivative), 15770-95-3; **10**, 15770-93-1; **10** (trimethylsilyl ether derivative), 15770-96-4; **11**, 15770-94-2; **11** (trimethylsilyl ether derivative), 15770-97-5; **12**, 15770-87-3; **12** [bis(trimethylsilyl ether derivative)], 15946-65-3; **13**, 16719-51-0; **13** [bis(trimethylsilyl ether derivative)], 16781-29-6; **14**, 15770-84-0; **15**, 15770-85-1; **20** [bis(trimethylsilyl ether derivative)], 16286-53-6; bis(trimethylsilyl ether) of 4,4′-(isopropylidenediphenol), 4387-16-0; acetate of 2,6-xylenol, 876-98-2.

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