Free-Radical Redistribution of Phenol Dimers

DONALD A. BOLON

General Electric Research and Development Center, Schenectady, New York

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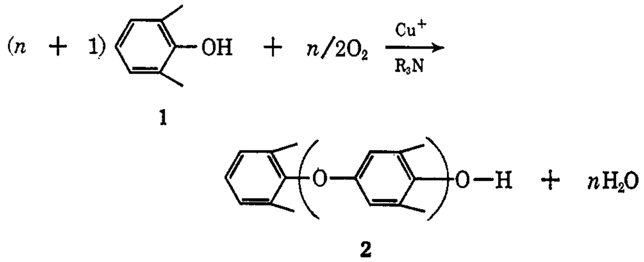
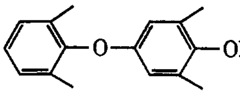
A novel free-radical redistribution is reported. In a general reaction phenoxy phenols (phenol dimers) under the influence of free-radical initiators redistribute to give monomers, trimers, and tetramers. Substituents upon the phenol rings sterically influence the reaction. Groups upon the phenol ring have more effect upon the redistribution reaction than those upon the phenoxy ring. A radical-chain sequence which rapidly attains equilibrium is postulated for the mechanism.

The discovery by Hay, Blanchard, Endres, and Eustance[1] that phenols could be oxidatively coupled to yield polyaryl ethers directed our attention to the chemistry of these ether linkages. In later papers the scope of the reaction and the catalyst, a copper–amine system,[2] was discussed.

The oxidative coupling reaction of xylenol (**1**) can be written



Endres and Kwiatek[2b] have demonstrated that polymer **2** is a linear polyphenylene oxide and that the polymerization characteristics are those of a bifunctional polycondensation. These workers demonstrated that the postulated intermediates such as xylenol dimer **3** and **4** could also be oxidized to the identical polymer



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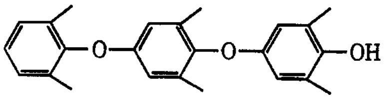

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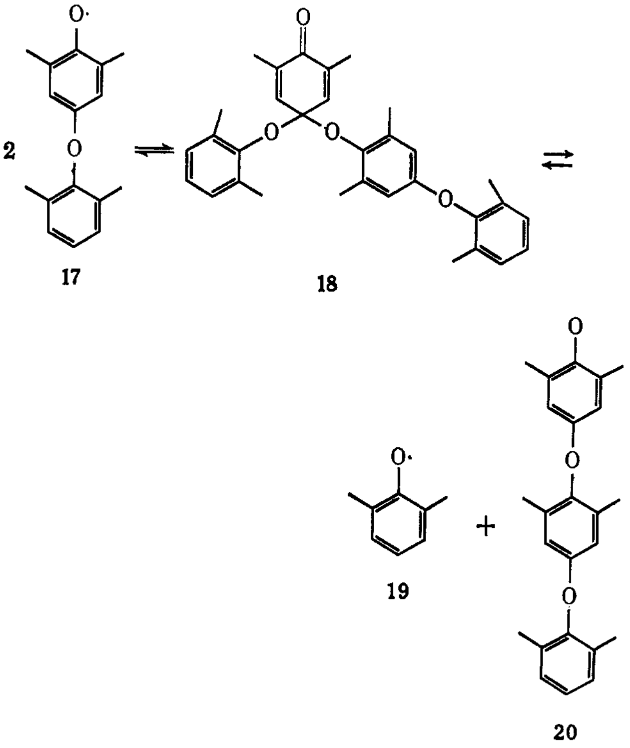
(**2**). Two general mechanisms have been proposed to account for the conversion of **3** and **4** to **2**. One is a radical coupling process[3,4] where the essential step is the transmittal of an odd electron along an aryl ether chain. The other is the "quinone ketal" mechanism[3] where one xylenol unit at a time is transferred from polymer chain to polymer chain. This mechanism can be illustrated by the combination of two dimer phenol radicals **17** to give quinone ketal **18** which can reverse or break down into a xylenol radical **19** and a trimer radical **20**.



The existence of the latter reaction was demonstrated by Cooper[5] who oxidized dimer **3** and found that xylenol **1** was an intermediate oxidation product. Xylenol could only have arisen from a quinone ketal like **18** under these relatively mild conditions.

It is important to note that in this sequence of reactions no change in the oxidation state of the intermediate occurs. Cooper, Finkbeiner, and Gilbert[6] discovered that preoxidized copper catalyst or stable free radicals, such as tri-*t*-butylphenoxyl, would cause dimer xylenol to redistribute to monomer, trimer, tetramer, and higher polymers in the absence of oxygen.

The ease with which dimer xylenol redistributed led us to examine other dimers under similar conditions of radical initiation. It was hoped that we could learn the steric and electronic effects of various substituents. In particular, we wished to learn the generality of the redistribution reaction and apply the found substituent effects to understanding the mechanism.

Results

In order to examine the scope of the redistribution reaction, it was necessary to synthesize a number of phenol dimers and trimers. The Ullman coupling, as described by Bruice, Kharasch, and Wingler,[7] of the potassium phenolate and the corresponding *p*-bromo-

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[1] A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959).

[2] (a) A. S. Hay, *J. Polymer Sci.*, **58**, 581 (1962); (b) G. F. Endres and J. Kwiatek, *ibid.*, **58**, 593 (1962); (c) H. S. Blanchard, H. L. Finkbeiner, and G. A. Russell, *ibid.*, **58**, 469 (1962); (d) G. F. Endres, A. S. Hay, and J. W. Eustance, *J. Org. Chem.*, **28**, 1300 (1963).

[3] H. L. Finkbeiner, G. F. Endres, H. S. Blanchard, and J. W. Eustance, American Chemical Society Division of Polymer Chemistry Preprint Booklet No. 2, Washington, D. C., Sept 1961, p 340.

[4] W. A. Butte, Jr., and C. C. Price, *J. Am. Chem. Soc.*, **84**, 3567 (1962).

[5] G. D. Cooper, H. S. Blanchard, G. F. Endres, and H. Finkbeiner, *ibid.*, **87**, 3998 (1965).

[6] G. D. Cooper, H. Finkbeiner, and A. R. Gilbert, Polymer Preprints of Phoenix Meeting of American Chemical Society, Washington, D. C., 1966, p 166.

[7] T. C. Bruice, N. Kharasch, and R. J. Wingler, *J. Org. Chem.*, **18**, 83 (1953).

anisole was used. Hydriodic acid cleavage of the resulting methyl ether gave the phenol.

The general method of accomplishing the redistribution is to treat the phenol dimer in solution with a stable free radical such as tri-*t*-butylphenoxyl or a one-electron oxidizing agent such as basic potassium ferricyanide. When the reaction mixture was to be analyzed, the redistribution was stopped by converting the phenols to their corresponding trimethylsilyl ethers.[8,9]

Some of the phenol trimethylsilyl ethers were prepared and characterized and are listed in Table I.

TABLE I

TRIMETHYLSILYL ETHERS OF PHENOLS[a]

Phenol	Mp or bp (mm), °C
3	60
4	66–68
7	180 (4.7)
12	132 (1.7)
13	117 (2.5)

[a] All compounds analyzed within ±0.3% of theoretical.

In most of the examples, however, the pure phenols were converted to their trimethylsilyl ethers and chromatographed without isolation and characterization. If a question as to identity arose, the trimethylsilyl ether was collected and hydrolized to the pure dimer by acid catalysis.

Two representative dimers were examined in detail. In the cases of **3** and **12**, the monomer, dimer, trimer, and their corresponding trimethylsilyl ethers were prepared and characterized. All of the other monomers and dimers were available as pure phenols and the silyl ethers were made and characterized by vapor phase chromatography. The respective trimers were not known and their structure was assigned by analogy.

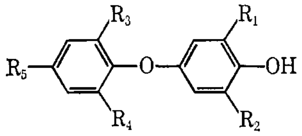
In Table II are listed the phenols that were redistributed. They redistributed with varying degrees of ease. We established 5% redistribution (5% of the dimer disappearing) as the standard and the number in the last column is the ratio of the phenol dimer to stable radical needed to achieve this level. Redistribution stopped after a few minutes in the case of **3–9** while 15–30 min was required for compounds **10–16**. The reactions were generally run for several hours to ensure no further changes.

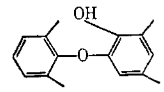
The chain length of the redistribution was determined by decomposing azobisisobutyronitrile (AIBN) in the presence of dimer **3**. By counting the monomers or trimers formed per cyanoisopropyl radical liberated, the chain length was calculated to be at least 45. Even though cyanoisopropyl radicals were continually being produced, the chain length rapidly decreased, indicating the presence of an equilibrium. The equilibrium is not static as evidenced by the slow appearance of tetramethyldiphenoquinone resulting from reaction of the liberated 2,6-dimethylphenol with the initiator radicals.

If Table II is examined, there are several striking observations. First, in the group of dimers **3–9** which redistributes at room temperature, all have one or more substituents in the top or phenol ring. With the exception of **15** and **16**, this is a general requirement. Conversely, those dimers with no substituents in the top ring (**10–14**) require elevated temperatures for redistribution.

TABLE II

PHENOLS **3–9** AT 25° AND **10–16** AT 80°[a]



Phenol	R_1	R_2	R_3	R_4	R_5	Mp, °C	Red[b]
3	Me	Me	Me	Me	H	111	10^3
4	Me	Me	Me	Me	*c*	112–113	10^3
5	Me	Me	Me	Me	Me	133–135	10^4
6	Me	Me	Me	H	H	54–55	10^2
7	Me	Me	H	H	Me	60–61	10^3
8	Me	Me	H	H	H	Oil[d]	10
9	Me	H	Me	Me	H	154–155	10^2
10	H	H	Me	Me	H	84	10^3
11	H	H	H	H	MeO	89–90	10^3
12	H	H	H	H	H	84[e]	10
13	H	H	H	H	C_6H_5O	103–104	10^3
14	H	H	Me	*i*-Pr	H	82–83	10^3
15	MeO	MeO	H	H	Me	96	10^3
16						89	10^3

[a] All compounds analyzed within ±0.3% of theoretical. [b] Ratio of phenol dimer to TTBP for 5% redistribution. [c] 2,5-Dimethylphenoxy. [d] Bp 130° (1 mm). [e] Commercially available.

Secondly, substituents in the bottom ring are important. The completely unsubstituted dimer **12** is the hardest to redistribute. Substituents in the bottom ring make the dimers easier to redistribute. A striking example is trimer **13**. The bottom phenoxy group serves as a substituent and this material redistributes to a tetramer and a dimer. The dimer formed is **12** and hence does not easily redistribute further. Bulky substituents aid the redistribution to a small degree.

The 2,6-dimethoxy substituents in **15** slow the redistribution down while compound **16** demonstrates that *o*-phenoxy groups will redistribute.

The coredistribution of phenols with dimer phenols to form a new sequence of dimer, trimer, and higher homologs has been examined. In Table III are listed the phenols that were coredistributed with dimer **3** and the results obtained at 25°. Many of the dimers formed are new compounds and were not further characterized. Those phenols in Table III with superscript *a* have dimers which were available. In all cases, these dimers were shown to be identical with the corresponding dimers in Table II.

The phenols are rather arbitrarily grouped according to their substitution. These substituents have a marked effect upon the ability of a phenol to undergo coredistribution. Groups *ortho* to the hydroxyl have no steric effect until they achieve the size of a *t*-butyl group. Other positions are free of steric effects.

Electronic effects are more pronounced. Electronegative groups, such as halogen, prevent a phenol from coredistributing unless the phenol is sufficiently substituted with positive groups to override the effect.

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[8] G. D. Cooper, H. S. Blanchard, G. F. Endries, and H. L. Finkbeiner, *J. Am. Chem. Soc.*, **87**, 3996 (1965).

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

TABLE III

COREDISTRIBUTION AT 25°

ortho-Substituted phenol	Coredistribute
Unsubstituted	No
2-Methyl	No
2,6-Dimethyl[a]	Yes
2-Methyl-6-ethyl	Yes
2,6-Diethyl	Yes
2-Methyl-6-*i*-propyl	Yes
2,6-Diisopropyl	Yes
2-Methyl-6-*t*-butyl	No
2-Methyl-6-chloro	No
2,6-Dichloro	No
2,6-Dimethoxy	No
2,6-Dihydroxy (pyrogallol)	No[b]
para-Substituted phenol	Coredistribute
4-Methyl[a]	Yes
4-Ethyl	Yes
4-Isopropyl	Yes
4-*t*-Butyl	Yes
4-Methoxy	Yes
4-Bromo	No
4-Chloro	No
4-Phenoxy	No
4-Phenyl	No
4-Hydroxy (hydroquinone)	No[b]
4-Nitro	No
para-Substituted 2,6-dimethylphenols	Coredistribute
4-Methyl[a]	Yes
4-*t*-Butyl	Yes
4-Methoxy	Yes
4-Benzamido	No
4-Nitro	No
4-Bromo	No[b]
4-Chloro	Yes
4-Phenyl	No
meta-Substituted phenols	Coredistribute
3,5-Dimethyl	No
3-Hydroxy	No
2,3,4,5,6-Pentachloro	No
2,3,5,6-Tetramethyl	Yes
1-Naphthol	No
2-Naphthol	No
Thiophenol	No[b]
4-Methylthiophenol	No[b]

[a] These dimer trimethylsilyl ethers were identical in every respect with the compounds prepared and listed in Table IV. [b] Inhibits redistribution.

Almost any electropositive substituent aids the reaction provided it is in the *ortho* or *para* position; *meta* substituents have no effect.

Many of the phenols will not coredistribute at 25°. However, they do not appear to otherwise affect the reaction. Dimer **3** will redistribute in the presence of phenol, for example, although no dimers or trimers with a phenol ring are obtained. Certain other phenols, such as hydroquinone, can easily furnish hydrogens by going to an oxidized form and quench a free-radical reaction.

Many of the phenols which will not coredistribute at room temperature will give some indication of coredistribution when the reaction is run at elevated temperatures. At 80°, for example, a measurable amount of phenol coredistributed with dimer **1**. However, when the temperature was raised, observable amounts formed of the dimeric products of phenol itself, 2-phenoxyphenol, and 2,2′-dihydroxydiphenyl.

The unusual inhibitor is 4-bromo-2,6-dimethylphenol. An explanation for this is offered in the Discussion.

Since many of the new dimers that were obtained in the sequence had sufficiently different retention times for their trimethylsilyl ethers upon the vapor phase chromatographic columns to allow easy separation, it was thought that a series of competitive coredistributions could be run and relative values could be obtained for substituent effects upon the coredistributive ability of various phenols. This was accomplished by mixing equimolar amounts of each of two phenols and of dimer **3**. The sample was then redistributed with TTBP, silylated, and analyzed by vapor phase chromatography. The ratio of the areas of the new dimers was determined.

In Table IV are listed the phenols compared with 4-methoxy-2,6-dimethylphenol. It was necessary to use a single phenol as a reference compound because the stability of the radical formed from a phenol affects the life of a less stable radical. For example, 4-methoxy-2,6-dimethylphenol coredistributes 33 times as fast as 4-methylphenol with **3**. However, in this example more 4-methylphenol coredistributes than would be the case when it is in competition with 4-*t*-butylphenol.

TABLE IV

Phenol	Relative Coredistribution
4-Methoxy-2,6-dimethyl	100
2,4,6-Trimethyl	29
4-Methoxy	23
4-Chloro-2,6-dimethyl	10
4-*t*-Butyl	10
2,6-Diisopropyl	7.5
4-Ethyl	3.5
4-Methyl	3.0
Phenol	0

The important observations in Table IV are the order and magnitude of the coredistributive ability of the phenols, not their absolute values. The trend clearly follows the electronic nature of the substituents.

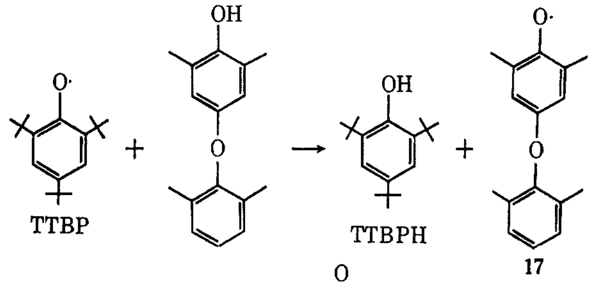
One experiment confirmed the equilibrium character of the coredistribution. When 4-(2,4,6-trimethylphenoxy)-2,6-dimethylphenol (**5**) is coredistributed with 2,6-dimethylphenol the identical sequence of monomers, dimers, and trimers is obtained as from the coredistribution of 2,4,6-trimethylphenol and 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol (**3**).

Discussion

The evidence presented here supports the idea that redistribution is an important reaction that occurs during the oxidative polymerization of 2,6-xylenol. The extreme ease with which the phenol groups migrate is a new and unique reaction with broad usefulness in phenol chemistry.

The radical tri-*t*-butylphenoxy (TTBP) was chosen as the means of generating the dimer phenoxy radicals because it is easily measured and it was thought to furnish a total source of radicals rather than a continuous source over a period of time. The blue color of the TTBP was always discharged instantly upon contact with phenols. It is apparent, however, that the use of TTBP introduces the possibility of another step into the sequence of reactions that occur. Muller[10] and Becker[11a] have demonstrated that the first reaction of TTBP with a phenol produced a phenoxy radical. The second step is believed to be the reaction of the new phenoxy radical with another TTBP to form a quinol ether like **21**. In view of the low concentration of TTBP present, this is rather surprising but it is the only explanation that will account for the facts.[11b] With the addition of this intermediate, a radical "sink," we can now postulate a sequence of reactions which account for the results (eq 1–8).

The equations as written constitute a radical-chain reaction with initiation, propagation, and termination steps. The equations are written using dimer **3** as an example but identical sequences can be written for the other dimers.



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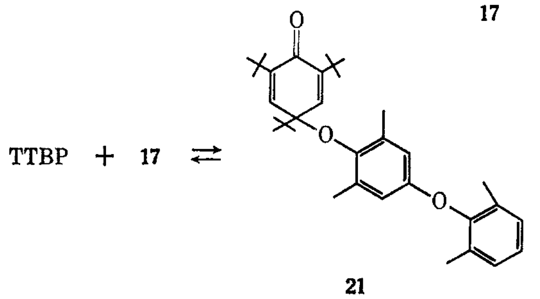

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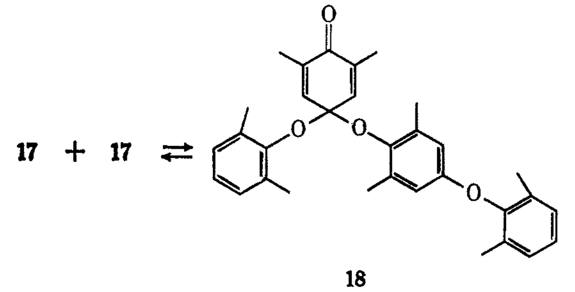

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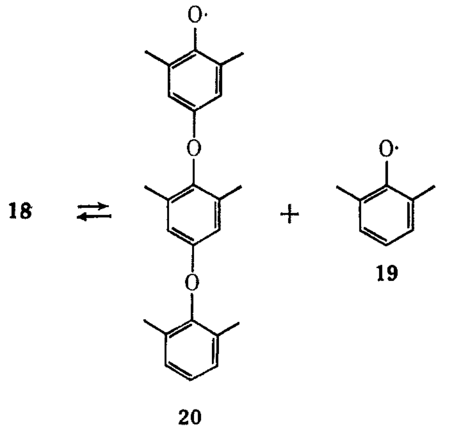

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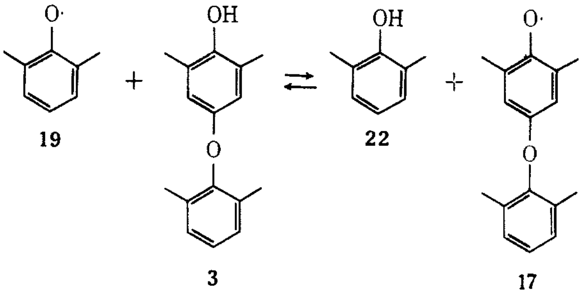

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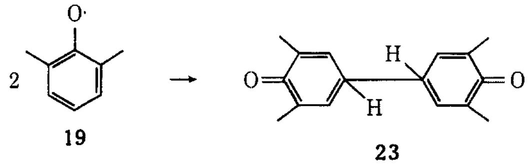

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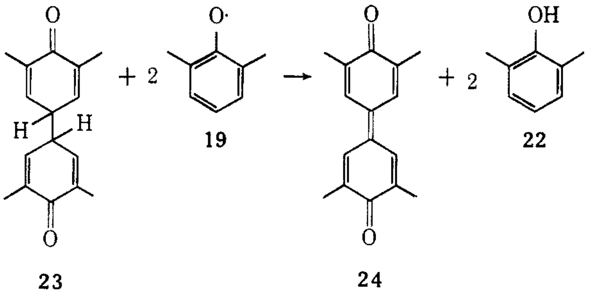

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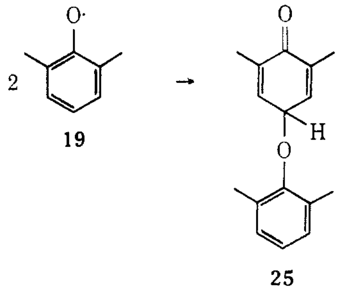

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Initiation.—The initial reaction occurred rapidly as evidenced by the immediate discharge of the blue color of the TTBP upon contact with the phenol. This hydrogen transfer was undoubtedly fast. Kreilick and Weissman have found that the second-order rate constant is 300 at 30° for the transfer of a hydrogen between TTBP and its corresponding phenol.[12] The transfer in the case of less hindered phenols would be even faster.

At this point the solution had no visible or esr spectrum and any free radicals must have been present only in small amounts. However, the solution was still reacting at this point as evidenced by periodic sampling and examination of the ratio of monomer or trimer to dimer. This ratio increased for about 15 min in the case of **3**. Therefore, the reverse of eq 2 to give TTBP and phenoxy radicals must still have been occurring after the initial TTBP is gone.

It was in this reverse disassociation (eq 2) that the difference in reactivities between **8** and **10** was manifested. Dimer **8** formed quinol ether **26** which was more sterically hindered and hence more unstable than the quinol ether **27** formed from dimer **10**. Thusly the

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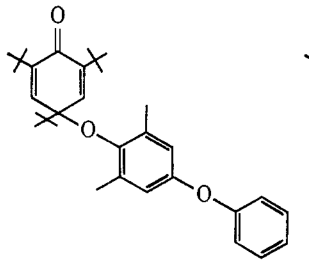
[10] E. Muller, K. Ley, and G. Schlechte, *Chem. Ber.*, **90**, 3660 (1957), and earlier papers.

[11] (a) H.-D. Becker, *J. Org. Chem.*, **29**, 3068 (1964). (b) Since this paper was submitted, M. A. DaRooge and L. R. Mahoney [*ibid.*, **32**, 1 (1967)] have demonstrated that the reaction of a 100-fold excess of *p-t*-butyl or *p*-methoxyphenol with tri-*t*-butylphenoxy stable free radical forms only 1 mole of tri-*t*-butylphenol and 1 mole of the quinol ether which corresponds to **21**.

[12] R. W. Kreilick and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 306 (1962).



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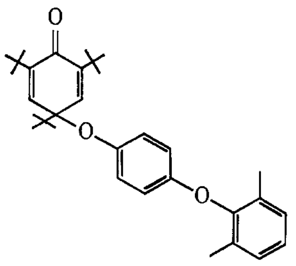

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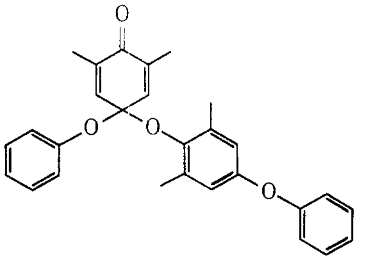
higher temperature was needed to allow the redistribution of **10**.

Propagation.—The propagation portion of the redistribution scheme is the novel part of this reaction. This includes reactions 3–5. A postulated intermediate is the quinone ketal **18** which has not yet been isolated but whose existence is demanded by the nature of the observed products. The rate constants of the various steps have not been determined. The fastest reaction should be that of **3**, the hydrogen transfer, since when a redistribution is carried out to low conversion the only products found other than recovered dimer are monomer **22** and trimer **4**. If H transfer were slower than radical combination, we should expect tetramer resulting from trimer reacting with dimer to show up at these low conversions.

The hydrogen transfer (eq 3) allows another reaction to occur. If another phenol is present and exchanges its hydrogen with **19**, it becomes a new monomer phenoxy radical. It then can enter into reaction with other radicals, undergoing the reverse of eq 4 and 3 and emerge as a new dimer corresponding to **17**. This does occur and will subsequently be discussed under Coredistribution.

The quinone ketal **18** is another place where steric and electronic effects will be observed. However, the steric effects should not be as great between the two quinone ketals **28** and **29** (from **8** and **10**, respectively) as it is between **26** and **27** since the crowing around the tetrahedral carbon is approximately the same.



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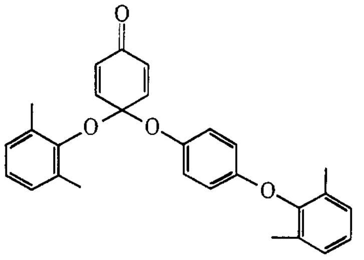

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The assumption is made in this scheme that the length of the phenyl ether chain, after one unit, does not affect the reactivity. Two trimer phenoxy units (**20**) should combine at the same rate as two dimer units (**17**) as should tetramers and higher polymers. All of these reactions should have the same rate as eq 3 and 4.

This reaction sequence has been written as a radical-chain reaction with one important difference. All of the propagation steps are reversible. Consequently, an equilibrium is rapidly set up among the various phenol groups and is only affected by removal of one of the products. Of course, in the reactions described in this paper, an attempt was made to minimize secondary reactions by keeping conversion low. Hence, a true equilibrium was not attained. The equilibrium constants have been determined for some oxidations of dimer **3**.[6]

Termination.—The termination steps of the reaction describe some ways in which the equilibrium can be affected by removal of products. The three reactions (6–8) are ways in which radicals are destroyed. In addition, eq 6 and 8 describe ways in which monomer **22** can be removed, thus driving reaction 4 toward higher polymers.

One of the unusual aspects of these reactions is their apparently selective nature. When dimers with free *ortho* positions are redistributed, there is no evidence of any *ortho* coupling, either carbon–carbon or carbon–oxygen. The identical series of monomer, dimer, trimer, and tetramer are obtained (individual ratios may vary) from the redistribution of **12** or **13**. The retention time of the trimethylsilyl derivatives of the *ortho*-coupled carbon–oxygen product of phenol, *o*-phenoxyphenol, is 6.8 min which is sharply different from the dimer **12** trimethylsilyl ether time of 7.8 min. Carbon–carbon and carbon–oxygen coupled products began to appear only after long heating of TTBP and a phenol. In addition, the reactions of various phenols which are unsubstituted in the *ortho* position with TTBP at 25° yield none of the *ortho*-coupled dimers.

In the termination sequence, all of the monomers have been written as coming from the phenoxy portion of the phenoxyphenols. The presence of a monomer arising from the phenol or top ring of the dimer has never been observed. The only monomers found always come from the bottom ring of the dimer. This is further support for a quinone ketal type of intermediate.

A key experiment was run by Blanchard[13] and repeated in this work which convincingly demonstrates that reactions 6–8 do occur simultaneously when xylenol radicals **19** are in solution. Blanchard treated 2,6-xylenol with an equimolar amount of 2,4,6-tri-*t*-butylphenoxyl (TTBP). When the reaction mixture was warmed, silylated, and examined by vpc, 2,4,6-tri-*t*-butylphenol, tetramethyldiphenoquinone (**24**), and xylenol dimer **3** were found among the products.

All of the evidence is consistent with the illustrated sequence. When the *para* position of the dimer is blocked as in **5**, the ejected monomer, mesitol, cannot undergo termination reactions 6 and 8. This should lead to an increase in the rate of attainment of the equilibrium and an increase in the extent of the redistribution. This was exactly what was observed. At a radical to dimer concentration of 1:10,000, **5** reached equilibrium (about 20% redistributed) in less than 20 sec. Dimer **3** only achieved 5% redistribution at

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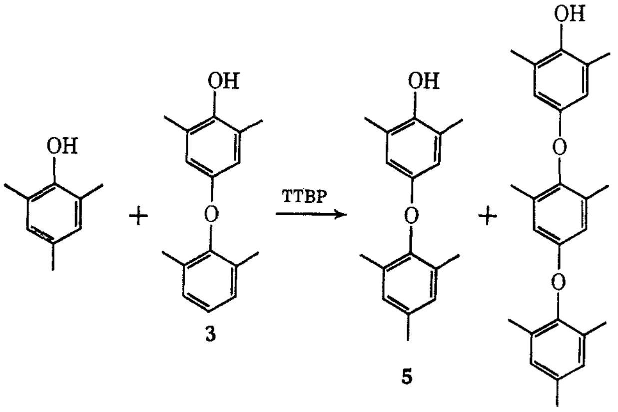
(13) H. S. Blanchard, private communication.

equilibrium and required about 15 min to reach this point.

Two other pieces of evidence support this concept of an equilibrium superimposed upon a radical chain. First, when dimer **3** was treated with increasing amounts of TTBP, the total amount of low molecular weight materials decreased and the higher molecular weight material increased. This is ascribed to removal of larger amounts of xylenol by reaction 6, thus shifting equilibrium 4 to favor the higher molecular weight materials.

The second piece of evidence involves removal of another monomer, *p*-cresol. When dimer **7** was redistributed, *p*-cresol was the monomer released by reaction 4. Advantage of the difference in base solubility between the hindered dimer or higher polymers and the *p*-cresol was taken by running the redistribution in benzene slurried with 10% sodium hydroxide solution. At the termination of the reaction, the basic solution contained appreciable amounts of *p*-cresol and the benzene contained polymeric materials 10–12 units long, much longer than the 3–4-unit materials usually found in the reaction. The removal of monomer had shifted the equilibrium.

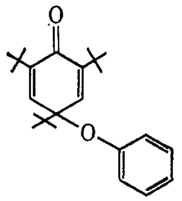
Coredistribution.—It has been mentioned that phenols placed in a redistributing mixture become incorporated into the sequence and form new dimers, trimers, and higher oligomers. For example, when 2,4,6-trimethylphenol was present in a redistributing mixture of xylenol dimer **3** and TTBP, a new dimer **5** and trimer are formed in addition to the xylenol oligomers.



A large number of phenols were coredistributed with xylenol dimer **3**. A list of these is provided in Table III. It is evident that both steric and electronic effects are important. An *ortho* *t*-butyl group is sufficiently large to prevent the phenol from becoming incorporated into the redistribution. Electron-withdrawing groups also prevent phenols from coredistributing.

Certain phenols as seen in Table II did not coredistribute at the temperature of the usual reaction. Several of these, such as phenol and *o*-cresol, could be made to coredistribute but they require higher temperatures and do so to a much smaller extent.

In view of the stability of the quinol ether from 2,4,6-tri-*t*-butylphenol and phenol **30**[11] it is conceivable that the phenols that do not coredistribute are actually converted to the phenoxy radicals and form stable quinol ethers like **30** rather than react with dimer **3**. This could be further supported by the observation that when **30** was heated with dimer **3**, phenol entered into coredistribution in the same manner as when TTBP was added to a hot mixture of phenol and dimer **3**.



30

The evidence against this possibility is that the redistribution of dimer **3** is quantitatively the same whether phenol is present or not. Therefore, the formation of **30** could only be important if it occurred more slowly than redistribution.

There are phenols that do effect the redistribution. In general, these are the polyhydroxybenzenes that have the hydroxy groups *ortho* or *para* to one another. These compounds along with thiophenols give complete inhibition of the redistribution reaction. This is because stable products, quinones, and disulfides, respectively, can be formed and hence kill the "radical character."

The one unusual phenol that inhibits the redistribution is 4-bromo-2,6-dimethylphenol. Evidently the 4-bromo-2,6-dimethylphenoxy radical is less stable than other phenoxy radicals and either undergoes carbon–carbon coupling to give a diphenoquinone or undergoes bromide displacement; either possibility would stop a radical chain. The anomality of this compound is also pointed out in the polymerization of this compound by Staffin and Price.[14] Other halogen compounds and even 4-chloro-2,6-dimethylphenol do not act as inhibitors nor do they polymerize according to the above procedure.

In the case where the added phenols have a free *ortho* position, there exists the possibility that the dimers that are formed result from the dimerization of the added phenol by carbon–oxygen or carbon–carbon coupling. This was eliminated by simple experiments when samples of the pure phenols with no *ortho* substituents were treated with tri-*t*-butylphenoxy stable radical and subsequently treated with the silylating agents there was no indication of appreciable carbon–carbon or carbon–oxygen coupling of the phenol.

It was felt that a relative reactivity order for coredistribution of phenols could be established by competing two phenols for the "radical character" of the TTBP introduced and subsequently coredistributing with xylenol dimer **3**. When the conversions were kept low to minimize succeeding redistributions of the newly formed dimers, it was possible to measure the ratios of the dimers and establish the relative reactivity for the phenols listed in Table IV. It can be seen that the order of radical stability compares with the one determined by McGowan, Powell, and Raw[15] and follows the electron-donating power of the substituents.

All of the reactivities were compared with the most reactive phenol found, 4-methoxy-2,6-dimethylphenol. This was necessary because it was found that the "radical character" life was preserved by more reactive phenols. For example, *p*-cresol coredistributed to a

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(14) G. Staffin and C. C. Price, *J. Am. Chem. Soc.*, **82**, 3632 (1960).

(15) J. C. McGowan, T. Powell, and R. Raw, *J. Chem. Soc.*, 3103 (1959).

greater extent in the presence of 4-methoxy-2,6-dimethylphenol than in the presence of 4-*t*-butylphenol.

Experimental Section

Preparation of 4-(2,6-Dimethylphenoxy)-2,6-dimethylanisole.—The potassium salt of 2,6-xylenol was prepared by heating to reflux a stirred mixture of potassium hydroxide (85% pellets, 65 g, 1 mole), 2,6-xylenol (122 g, 1 mole), and toluene (100 ml). The azeotroped water was collected in a Dean–Stark trap. When the theoretical amount of water was collected, the residual solvent and traces of water were removed by evacuating the system. (The salt must be prepared in an inert atmosphere.)

When the toluene was completely removed, dimethylformamide (100 ml) and 4-bromo-2,6-dimethylanisole (215 g, 1 mole) were added along with active copper powder[16] (0.5 g) and cupric acetate (0.5 g). The reaction mixture was heated to reflux and approximately 20 ml of dimethylformamide was distilled out to remove any remaining water.

Heating of the mixture was continued for 4 hr when the reaction was cooled to room temperature. Methanol (600 ml) was added with vigorous stirring to the reaction mixture followed by concentrated hydrochloric acid (250 ml).

The deep red reaction mixture was poured onto 1000 g of ice and the organic material was extracted with four 250 ml portions of benzene. The benzene was combined and extracted with 100-ml portions of 15% sodium hydroxide and then with water. The benzene was dried ($MgSO_4$) and removed on a film evaporator. The residual oil was distilled giving 74 g (29%) of 4-(2,6-dimethylphenoxy)-2,6-dimethylanisole, bp 130° (0.75 mm), mp 58–60°. A similar method was followed for the other methyl ethers listed in Table I.

Preparation of 4-(2,6-Dimethylphenoxy)-2,6-dimethylphenol (3).—4-(2,6-Dimethylphenoxy)-2,6-dimethylanisole (25.6 g, 0.1 mole) was added to hydriodic acid (57%, 50 ml) and glacial acetic acid (50 ml). This mixture was refluxed 18 hr under nitrogen and then cooled. The mixture was poured onto ice (500 g). The product was extracted from the water with benzene, and the benzene was washed with ammonium carbonate (10%, 50 ml) and water (50 ml) and then dried ($MgSO_4$). The benzene was removed on a film evaporator and the residue was recrystallized from hexane. This gave white crystals of 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol (**3**), mp 110–111° (19 g, 80%). See Table V for data on methyl ethers of phenols.

Preparation of 4-Hydroxy-4′-methoxydiphenyl Ether (11).—Sodium metal (2.85 g, 0.123 g-atom) was dissolved in methanol under nitrogen. While the solution was stirred, 4,4′-oxydiphenol (25 g, 0.123 mole) was added. When the solution was cool, dimethyl sulfate (11.5 ml, 0.123 mole) was added. After standing for 1 hr, this solution turned into a paste at which time the mixture was heated to reflux for another hour. The methanol was distilled and water (100 ml) was carefully added to the residue. The organics were extracted into ether and the mono- and nonmethylated phenols were extracted with base. After neutralization of the solution with hydrochloric acid, the white solids were collected and extracted with hot water to remove 4,4′-oxydiphenol. The residue was recrystallized from heptane giving white crystals of 4-hydroxy-4′-methoxydiphenyl ether (**11**, 8 g, 30%), mp 87–89°.

TABLE V
METHYL ETHERS OF PHENOLS

Phenol[a]	Mp, °C	Bp (mm), °C
3	60–61	. . .
4	102	. . .
5	92.5–93	. . .
6[b]	. . .	130 (0.1)
7[b]	29–30	. . .
8	. . .	120 (0.8)
9	70–71	. . .
10	42–45	. . .
13	76–77	. . .
14	. . .	117 (1.4)
15	73–75	. . .
16[b]	. . .	109 (0.5)

[a] All compounds analyzed within ±0.4% of theoretical. [b] These ethers were cleaved directly without analytical purification.

2,4,6-Tri-*t*-butylphenoxyl (TTBP).—The radical was prepared in 0.1 *M* solution by oxidizing 2,4,6-tri-*t*-butylphenol with alkaline potassium ferricyanide according to the direction of Cook.[17] The radical concentration was determined each day by means of iodide oxidation and thiosulfate titration of the iodine. The phenols used with the exception of 4-methoxy-2,6-dimethylphenol were commercially available.

4-Methoxy-2,6-dimethylphenol.—This phenol was prepared in 93% yield (mp 76–77°, lit.[18] 76–77°) by the method of Moran, *et al.*[18]

Redistribution of Phenol Dimers.—A standard procedure was utilized for redistribution reactions. A sample of dimer phenol (2×10^{-4} mole) was dissolved in oxygen-free benzene (2 ml) in an inert atmosphere. To this solution was added TTBP (50 μl of 0.1 *N* solution in benzene). The redistribution was allowed to proceed for the allotted time at room temperature (25°) or at reflux (80°). The redistribution was stopped by adding the silylating reagents, pyridine (2 ml), hexamethyldisilazane (1 ml), and trimethylsilylchloride (1 ml). The solution was refluxed for 1.5 hr to complete the silylation and the sample was analyzed by vapor phase chromatography.

The analytical column was a 2-ft silicone gum rubber (20%) on Chromosorb P (60–80 mesh). The conditions were a helium flow of 60 ml/min and linear programming from 100 to 300° at 15°/min. Samples were typically 30–100 μl.

Coredistribution.—Solutions which were 10^{-2} *M* of the dimers and phenols in benzene were prepared. One milliliter of each solution (10^{-5} mole) was pipetted into a flask and redistribution was initiated by the addition of 10 l of 0.1 *M* (10^{-6} mole) TTBP. All reactions were carried out in an atmosphere of nitrogen or argon. The mixture was then silylated and examined by vpc. The ratio of the two new dimers formed by the coredistribution was determined. These were compared with the new dimer from 4-methoxy-2,6-dimethylphenol established as 100. The results are summarized in Table IV.

Trimethylsilylation.—A word about the silylation technique might be in order. Many of the di-, tri-, and tetrameric phenols are unstable at the high temperatures necessary to analyze them by vapor phase chromatography (vpc). In addition, the previously mentioned tailing is a serious problem when the materials have similar retention times. In order to overcome these objections we utilized the technique developed in these laboratories of converting the phenols to their trimethylsilyl ethers.[8] The standard method consists of treating the phenol with trimethylsilylchloride and hexamethyl disilazane in the presence of an amine catalyst. When this work was nearly completed a new silylation technique was established which is considerably less cumbersome than the trimethylsilyl chloride. This involves the use of bis(trimethylsilyl)acetamide.[9] The silylation has been shown to be general for active hydrogen compounds in which the active hydrogen was replaced by trimethylsilyl group. The phenol trimethylsilyl ethers listed in Table IV were prepared by mixing an excess of bis(trimethylsilyl)acetamide with the phenol, warming the mixture at 80° for a few minutes, and distilling at reduced pressure. Unreacted starting material and by-products were removed first and the ether was then distilled.

Registry No.—**3**, 3698-40-6; **4**, 3698-41-7; **5**, 5384-20-3; **6**, 10181-88-1; **7**, 10181-89-2; **8**, 10181-90-5; **9**, 10181-91-6; **10**, 10181-92-7; **11**, 10181-93-8; **12**, 831-82-3; **13**, 10181-94-9; **14**, 10181-95-0; **15**, 10181-96-1; **16**, 10181-97-2; 4-(2,6-dimethylphenoxy)-2,6-dimethylanisole, 10181-98-3.

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[16] Active copper powder was prepared by reducing zinc dust (35 g) with copper sulfate (100 g) and dissolving excess zinc with 10% hydrochloric acid. The copper powder was washed with water and stored while still moist.

[17] C. D. Cook and R. C. Woodworth, *J. Am. Chem. Soc.*, **75**, 6242 (1953).

[18] W. J. Moran, E. C. Schreiber, E. Engel, D. C. Behn, and J. L. Yamins, *ibid.*, **74**, 127 (1952).