Mechanism of Oxidative Polymerization of 2,6-Disubstituted Phenols. Structure of Polymers from Mixed Dimers of 2,6-Dimethylphenol and 2,6-Diphenylphenol

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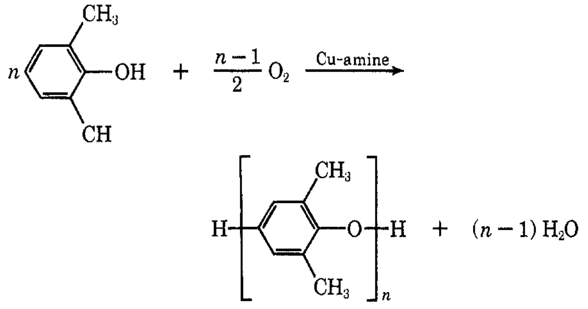
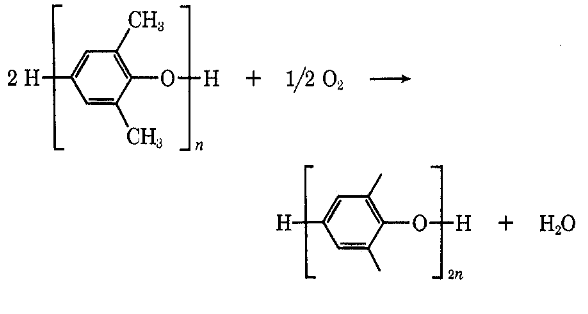
Mixed dimers of 2,6-dimethylphenol and 2,6-diphenylphenol have been prepared and polymerized by oxidative coupling to poly(arylene oxides). Both 2,6-diphenyl-4-(2,6-dimethylphenoxy)phenol (IV) and 2,6-dimethyl-4-(2,6-diphenylphenoxy)phenol (V) reacted with oxygen at 25° in the presence of a cuprous chloride–pyridine catalyst to produce polymers with a random arrangement of methyl- and phenyl-substituted rings, identical with the polymer obtained by oxidation of a mixture of the two monomers. The nmr spectra show four methyl proton signals with chemical shifts corresponding to those calculated for each of the four possible three-ring sequences, including sequences of three or more similar units, which can arise only as a result of redistribution. Oxidation of V at −25° in pyridine yielded low-molecular-weight polymer (DP $\simeq$25) in which the strongest proton nmr signals were those corresponding to sequences of similar units, showing that even under conditions favoring coupling by rearrangement of an intermediate quinone ketal the redistribution process determines the polymer structure.

The oxidative coupling of 2,6-disubstituted phenols to produce poly(1,4-arylene oxides), first reported by Hay in 1959,[1] differs in many ways from the usual addition or condensation polymerization reaction and has been the subject of extensive investigation, summarized in several recent review articles.[2–5] The reaction is a free-radical chain process, with aryloxy radicals as the intermediates, but has the characteristics of a polycondensation; that is, growth occurs by the coupling of polymer molecules.



(1)

I



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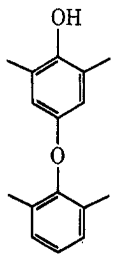
The details of this polymer–polymer coupling reaction have been difficult to resolve; three different explanations have been advanced for the coupling of polymeric aryloxy radicals to poly(1,4-aryleneoxy)phenols. Much of the evidence for these mechanisms rests on the identification of the initial products of oxidation of "dimers", such as II and III, which may be regarded as the simplest representatives of structure I, with $n = 2$.



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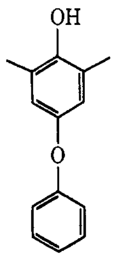
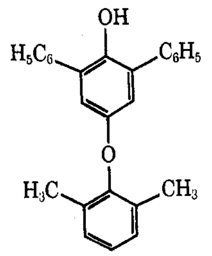
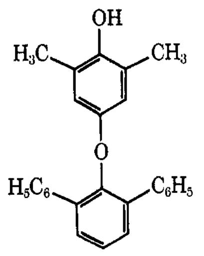


III

The dimers previously examined either have the same substitution pattern in both rings, as in II, so that the rings cannot be distinguished in the product, or have an open ortho position in one or both rings, as in III, which prevents the formation of linear high polymers. We here report the preparation and oxidative polymerization of two "mixed dimers," IV and V. In these compounds both rings correspond to phenols capable of being oxidized to linear high polymers, allowing the mechanism of coupling to be inferred from the structure of the polymeric product.



IV



V

Proposed Coupling Mechanisms.—Three mechanism by which coupling of two polymeric aryloxy radicals may lead to a polymeric phenol were first outlined by Finkbeiner[6] and each has since received some experi-

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

[2] A. S. Hay, *Advan. Polym. Sci.*, **4**, 496 (1967).

[3] G. D. Cooper, *Ann. N. Y. Acad. Sci.*, **159**, 278 (1969).

[4] G. D. Cooper and A. Katchman, *Advan. Chem. Ser.*, No. 91, 660 (1969).

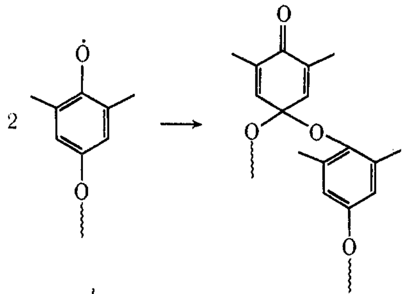
[5] H. L. Finkbeiner and A. S. Hay, "Newer Polymerization Reactions," J. Heller, Ed., Interscience, New York, N. Y., in press.

[6] H. L. Finkbeiner, G. F. Endres, H. S. Blanchard, and J. W. Eustance, *Trans. Soc. Plastics Eng.*, **2**, 112 (1962).

mental support.[7–11] These mechanisms and their structural consequences are outlined below.

A. End Linking.—The polymeric aryloxy radicals couple head to tail, with the oxygen of the first attacking the para position of the terminal ring of the second. This process, applied to a dimer AB, yields a perfectly alternating copolymer (ABABABAB...). The phenolic ring in every polymer molecule must be an A unit, that is, the same as the phenolic ring of the dimer.

B. Quinone Ketal Rearrangement.—Coupling of the two radicals yields a quinone ketal; that is, the oxygen of one radical attacks the para position of the phenolic ring of the second. Rearrangement of the dienone yields a new ketal, in which the second ring has become the "head", or dienone ring. When by successive rearrangements of this type one of the terminal rings becomes the dienone ring, tautomerization yields the coupled phenol. This process can lead to many different sequences of rings in the polymer from dimer AB, but cannot yield any species having more than two similar rings in succession; the sequences ABA, AAB, BBA, etc., are possible, but not BBB or AAA.[12] The phenolic ring of every polymer molecule must be a B ring.



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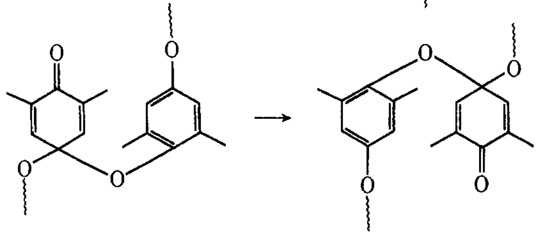

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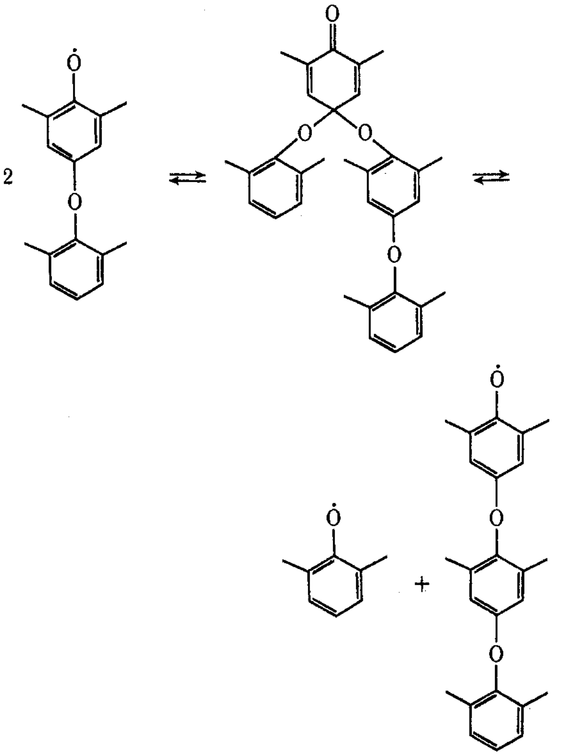
C. Quinone Ketal Redistribution.—This mechanism also postulates that the initial product of reaction of aryloxy radicals is the quinone ketal, but assumes that the ketal rapidly dissociates either to regenerate the radicals from which it was formed or to produce two new radicals, one containing one more and the other one fewer aryloxy units than the original. The coupling of polymer radicals to polymeric phenols is the result of rapid redistribution of polymeric phenols to produce monomer, which couples with another phenolic species. The combination of redistribution and coupling reactions allows the formation of polymer molecules having any sequence of rings, with either ring of the dimer appearing as the phenolic ring of the polymer.[13]



(5)

Experimental Section

Nmr spectra were taken in $CDCl_3$ solution with a Varian HA-100 spectrometer, using tetramethylsilane as an internal standard. Melting points were determined with a Perkin-Elmer DSC IB differential scanning calorimeter. Gas chromatographic analyses of reaction mixtures were carried out after conversion of the phenols to trimethylsilyl ethers by reaction with bis(trimethylsilyl)acetamide in pyridine. Near-infrared spectra were measured in carbon disulfide solution with a Beckman DK 2A spectrophotometer.

2,6-Diphenyl-4-bromoanisole.—The dry sodium salt of 2,6-diphenyl-4-bromophenol (86 g, 0.25 mol) was dissolved in 100 ml of a 2 *M* solution of sodium methoxide in methanol, 30 g of dimethyl sulfate was added, and the solution was stirred for 16 hr. The precipitate was filtered off, washed with water, dried, and recrystallized from 95% ethanol, yielding 62 g (73%) of 2,6-diphenyl-4-bromoanisole, mp 91.5–92°.

Anal. Calcd for $C_{19}H_{15}OBr$: C, 59.4; H, 4.2; Br, 30.3. Found: C, 59.5; H, 4.4; Br, 30.7.

2,6-Diphenyl-4-(2,6-dimethylphenoxy)anisole.—A solution of 23 g of potassium *tert*-butoxide in 40 ml of dimethylformamide was added to a three-neck round-bottom flask equipped with a stirrer, a nitrogen by-pass, and a Dean–Stark trap. A solution of 25 g (0.205 mol) of 2,6-xylenol in 36 g of hexamethylphosphoramide was added and the mixture was refluxed under nitrogen with vigorous stirring for 3 hr, during which time 20 ml of distillate was withdrawn from the Dean–Stark trap. The mixture was allowed to cool and 4.0 g of cuprous bromide was added, followed by 100 ml of dimethylformamide and 60 g (0.177 mol) of 2,6-diphenyl-4-bromoanisole. The mixture was again refluxed and the first 30 ml of distillate was removed from the

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(7) W. A. Butte, Jr., and C. C. Price, *J. Amer. Chem. Soc.*, **84**, 3567 (1962).

(8) G. D. Cooper, H. S. Blanchard, G. F. Endres, and H. L. Finkbeiner, *ibid.*, **87**, 3996 (1965).

(9) E. McNelis, *J. Org. Chem.*, **31**, 1255 (1966).

(10) D. M. White, *Poly. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **9**, 663 (1968).

(11) These mechanisms are critically discussed in the review articles of ref 2–5, which include experimental results not published elsewhere.

(12) When two polymeric radicals couple in this fashion one of the terminal rings becomes the phenolic ring of the product. The sequence of rings is obtained by counting backwards from the tail to the head of one radical, then from head to tail of the other (ref 2, 5). Thus trimers ABC and DEF can form two hexamers, CBADEF and FEDABC. The sequences possible from the coupling of dimer AB to high polymer may be established by following the reaction for a few steps. Coupling of dimer produces tetramer BAAB, reaction of tetramer with dimer forms hexamers BABAAB and BAABAB, coupling of hexamers with dimer can yield three octamers (BABABAAB, BAABABAB, BABAABAB); coupling of tetramer yields BAABBAAB. None of the oligomers has two similar units in sequence either at the head or tail of the chain and no further coupling of these species with each other or with dimer can form any three-ring sequence not present in the octamers.

(13) The only restriction on polymer structure in this case is that every polymer molecule must have as its terminal ring a unit which was a terminal ring of the dimer. This restriction is common to all three mechanisms.

Dean–Stark trap. Refluxing and stirring was continued for 3 hr. After cooling, 125 ml of methanol was added, followed by 50 ml of concentrated hydrochloric acid, and the mixture was poured over cracked ice. The red, tarry mixture was extracted with benzene and the extract was washed thoroughly with water, then twice with 15% sodium hydroxide solution, and finally with water. The solution was dried over sodium sulfate and the benzene was removed on a rotary evaporator. The residue, after recrystallization from ethanol, yielded 25 g (37%) of 2,6-diphenyl-4-(2,6-dimethylphenoxy)anisole as a light tan powder, mp 134–135°.

Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.2; H, 6.3. Found: C, 84.9; H, 6.3.

2,6-Diphenyl-4-(2,6-dimethylphenoxy)phenol (IV).—2,6-Diphenyl-4-(2,6-dimethylphenoxy)anisole (20 g, 0.053 mol) was refluxed for 16 hr, under nitrogen, with 50 ml of glacial acetic acid and 20 ml of 57% hydriodic acid. The mixture was poured over crushed ice and extracted with benzene. The extract was washed thoroughly with water, dried over sodium sulfate, and evaporated to dryness. Gas chromatographic analysis of the residue showed that uncleaved ether was still present; so the hydriodic acid treatment was repeated and the product was isolated as before. Recrystallization from *n*-hexane yielded 9.2 g (48%) of 2,6-diphenyl-4-(2,6-dimethylphenoxy)phenol, mp 140–141.5°.

Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.3; H, 6.0. Found: C, 84.7; H, 6.1.

2,6-Dimethyl-4-(2,6-diphenylphenoxy)anisole.—A solution of 123 g (0.5 mol) of 2,6-diphenylphenol, 56 g (0.57 mol) of potassium *tert*-butoxide, 90 g of hexamethylphosphoramide, and 100 ml of dimethylformamide was refluxed for 3 hr, under nitrogen, as in the preparation of the methyl ether of IV described previously. At the end of this time 60 ml of distillate was collected and discarded. After cooling the solution, 10 g of cuprous bromide, 110 g (0.49 mol) of 2,6-dimethyl-4-bromoanisole, and 175 ml of dimethylformamide were added. The mixture was refluxed for 3 hr and methanol and hydrochloric acid were added as in the previous case. The mixture was poured over ice and extracted with benzene, and the extract was washed with water. Extraction with 15% sodium hydroxide solution produced a large amount of gelatinous precipitate which was removed by filtration through glass wool. The dark blue extract was then washed repeatedly with water until the blue color disappeared. The solution was dried over sodium sulfate and concentrated on a rotary evaporator. Some diphenylphenol separated at this point; this was filtered off and washed with *n*-hexane; and the filtrate and washings were combined. Gas chromatographic analysis showed that in addition to the desired product the solution contained large amounts of unreacted diphenylphenol and 2,6-dimethyl-4-bromoanisole. Attempts to remove the diphenylphenol by extraction with Claisen's potash were unsuccessful and the solvent was again removed. Addition of *n*-hexane to the residue caused the separation of 2.2 g of light tan plates melting at 87–89°. The filtrate was again stripped and the residue was distilled under vacuum. One fraction of 16 g, boiling at 210–245° (2.5 mm), crystallized on seeding with the crystals previously isolated. The total yield of crude product was 28.2 g (15%). Recrystallization from hexane yielded pure 2,6-dimethyl-4-(2,6-diphenylphenoxy)anisole as colorless plates, mp 92–93°.

Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.2; H, 6.3. Found: C, 85.2; H, 6.4.

2,6-Dimethyl-4-(2,6-diphenylphenoxy)phenol (V).—2,6-Dimethyl-4-(2,6-diphenylphenoxy)anisole (25 g, 0.066 mol) was refluxed for 16 hr, under nitrogen, with 75 ml of glacial acetic acid and 25 ml of 57% hydriodic acid. The mixture was poured over ice and extracted with benzene. The extract was washed with water, then with 1% ammonium carbonate solution, and again with water. The solution was dried over sodium sulfate and the benzene was stripped off under vacuum, leaving a colorless and extremely viscous glass. Gas chromatographic analysis of this product indicated that it contained, in addition to the major component, a small amount of uncleaved ether, a large amount, possibly one-third the total, of diphenylphenol, and at least one higher boiling compound. Some of these products arose from decomposition in the injection port, as the apparent concentration of diphenylphenol was substantially reduced upon conversion to the trimethylsilyl ethers by reaction with bis(trimethylsilyl)acetamide in pyridine. Solution chromatography on an alumina column did not yield any fraction which could be induced to crystallize or was significantly purer than the starting material. The fractions were therefore combined, dissolved in pyridine, and refluxed with 10 ml of bis(trimethylsilyl)acetamide. After evaporation of the solvent the residue was distilled under vacuum. A fraction of 9.5 g, boiling at 210–220° (0.33 mm), was shown to be essentially pure by gas chromatographic analysis. It was dissolved in 25 ml of methanol, one drop of concentrated hydrochloric acid was added, and the solution was allowed to stand for 1 hr at room temperature. The methanol was stripped off under vacuum, leaving 7.8 g (37%) of colorless solid, which appeared to melt at 45–50° when heated in a capillary tube in the usual manner, but was shown by differential scanning calorimetry to be amorphous. Gas chromatographic analysis showed this material to be more than 95% pure, with the principal impurities being diphenylphenol and the methyl ether of V. Repeated efforts to crystallize this material were unsuccessful, and it was used without further purification.

Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.3; H, 6.0. Found: C, 85.3; H, 6.1.

Redistribution of Dimers.—Catalytic redistribution of the dimers was carried out by refluxing a solution of 0.5 g of the dimer and 0.015 g of tetramethyldiphenoquinone in 10 ml of benzene.[14] After 2 hr, 2 ml of pyridine and 0.5 ml of bis(trimethylsilyl)acetamide were added. Refluxing was continued for 10 min and the mixture was analyzed by gas chromatography. Thermal redistributions were carried out by refluxing a solution of 0.25 g of dimer in 3 ml of chlorobenzene for 1 hr, followed by trimethylsilylation and gas chromatographic analysis.

Polymerization.—In most cases oxidation of the dimers was carried out at 25° in a 50 ml flask stirred by a Vibro-Mixer stirrer and connected to a gas buret filled with oxygen. In a typical example 5 mg of cuprous chloride was stirred in the reaction flask under oxygen for 10 min in 8 ml of benzene and 2 ml of pyridine. A solution of 0.732 g (0.002 mol) of dimer V in 3 ml of benzene was added and oxygen absorption was measured at intervals of approximately 1 min. Absorption ceased after approximately 30 min, at which time 19.4 ml (87% of theory) had been absorbed. After 2 hr, the mixture was washed several times with 10% hydrochloric acid, and the benzene layer was separated, dried over sodium sulfate, and evaporated to dryness. The residue was dissolved in 2 ml of chloroform and filtered, and the polymer was precipitated with methanol, yield 0.605 g (83%).

Low-temperature polymerizations were carried out following the procedures described for low-temperature oxidation of the dimer of 2,6-xylenol.[10] A solution of 1.0 g of "methanol green," copper complex having the empirical formula $[\text{py CuCl(OCH}_3)]_x$,[15] in 10 ml of pyridine was cooled to −25° and 366 mg of V was added. The solution was stirred for 2 hr at −25°, after which the temperature was lowered to −50° and the reaction was terminated by the addition of 5 ml of 36% hydrochloric acid. The solution was allowed to warm to room temperature and 75 ml of water and 50 ml of benzene were added. The organic layer was separated, washed repeatedly with 5% hydrochloric acid and with water, and concentrated to a volume of 2–3 ml. Addition of methanol yielded 288 mg (78%) of colorless polymer; the molecular weight (determined by vapor osmometry) was 4250 and the composition (by comparison of intensity of methyl and aromatic protons in the nmr spectrum) 45 mol % diphenyl and 55% dimethyl units. Gas chromatographic analysis of the methanol filtrate showed the presence of diphenylphenol, a little unreacted V, and a high-boiling material, probably a trimer.

Results

Synthesis of Dimers.—Both dimers were prepared by the Ullmann coupling of a potassium phenoxide with a 4-bromoanisole, followed by hydriodic acid cleavage of the methyl ether. The general procedure has been previously described,[16] but was modified in this case by the use of a mixture of dimethylformamide and hexamethylphosphoramide as the solvent, and cuprous

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(14) G. D. Cooper, A. R. Gilbert and H. Finkbeiner, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **7**, 166 (1966).

(15) H. S. Blanchard, H. L. Finkbeiner, and G. A. Russell, *J. Polym. Sci.*, **58**, 469 (1962).

(16) G. F. Endres and J. Kwiatek, *ibid.*, **58**, 593 (1962).

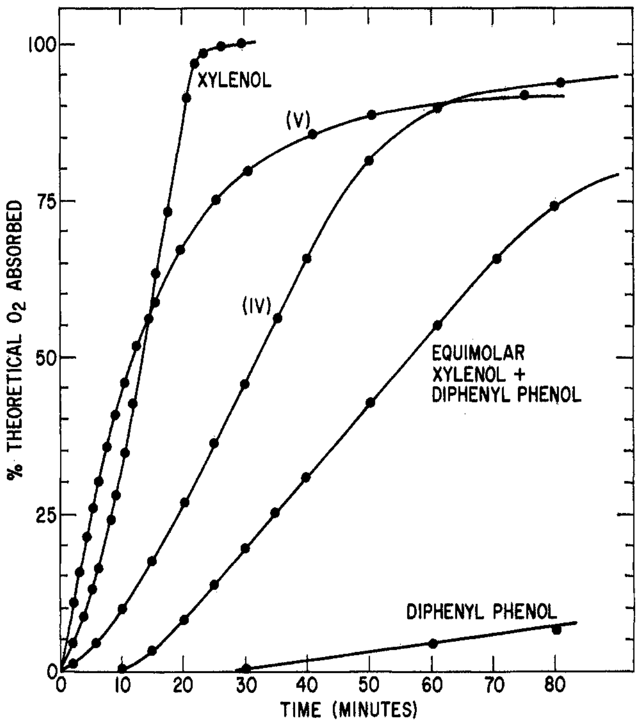
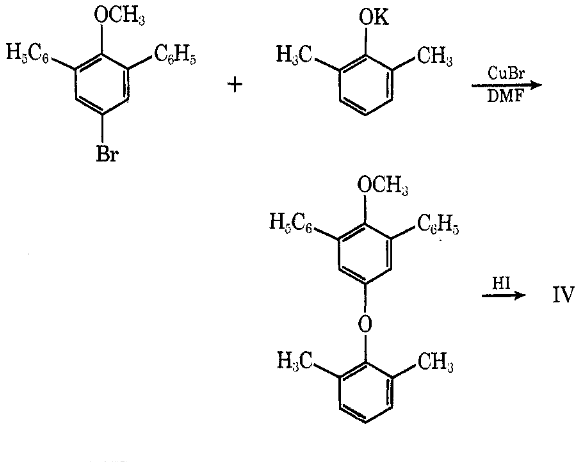


Figure 1.—Rate of oxygen absorption of phenols in benzene at 25°; CuCl–pyridine catalyst.

bromide rather than copper powder as the coupling agent.[17]



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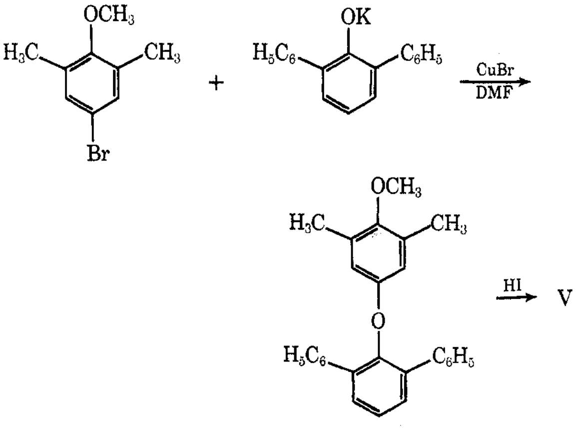


(7)

Preparation of IV in this way presented no difficulties and it was obtained in 16% overall yield. The yield in the Ullmann coupling reaction leading to V was much lower and the methyl ether could not easily be separated from the large amount of unreacted diphenylphenol. The final product V, furthermore, could not be induced to crystallize and could not be distilled because of thermal redistribution to diphenylphenol, trimers, tetramers, etc. It was obtained in a satisfactorily pure state (>95%) by conversion to the trimethylsilyl ether, distillation, and cleavage with dilute hydrochloric acid in methanol, but the overall yield was only 5%.

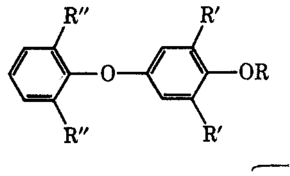
Oxidation of Dimers.—Both IV and V were readily oxidized to poly(arylene oxides) by means of a pyridine–cuprous chloride catalyst at 25°. Dimer V, with the methyl substituents in the phenolic ring, absorbed oxygen at approximately twice the rate of IV, which has phenyl substituents in the phenolic ring; the difference is in the direction expected on the basis of the reactivity of the corresponding monomers, xylenol being oxidized much more rapidly than diphenylphenol. It is somewhat surprising that IV oxidizes as fast as it does, as the oxidation of diphenylphenol is extremely slow under these conditions.[18] An equimolar mixture of dimethylphenol and diphenylphenol, however, can be oxidized quite readily (Figure 1), both monomers being consumed completely. Methanol-insoluble copolymers were obtained in 80–90% yield from IV, V, and from the mixture of dimethylphenol and diphenylphenol.

Determination of Polymer Structure.—Distinguishing among the proposed coupling mechanisms requires the identification of specific sequences of units in the copolymers, a problem which was attacked by analysis of the methyl region of the proton nmr spectra. If only the effects of the nearest neighboring unit are considered, there are four possible magnetic environments for the methyl protons of a dimethylphenoxy unit. The dimethylphenoxy unit may be situated between two other methyl substituted units (M*M*M), between two phenyl-substituted units (P*M*P), or between one of each type; in this case there are two different arrangements, depending on whether the phenyl substituted ring is directed toward the head of the chain (M*M*P) or toward the tail (P*M*M).

In Table I are listed the chemical shifts of the methyl protons in the phenolic dimers II, IV, V, and their

TABLE I

CHEMICAL SHIFTS OF METHYL PROTONS IN DIMERS



R	R′	R″	δ, ppm "Head" ring	δ, ppm Terminal ring
H	CH_3	CH_3	2.12	2.10
H	C_6H_5	CH_3		2.19
H	CH_3	C_6H_5	1.89	
CH_3	CH_3	CH_3	2.20	2.12
CH_3	C_6H_5	CH_3		2.19
CH_3	CH_3	C_6H_5	1.95	

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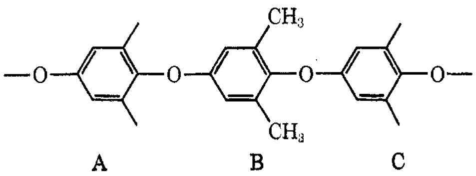
[17] H. L. Finkbeiner and D. M. White, private communication.

[18] The production of high-molecular-weight homopolymer from 2,6-diphenylphenol requires a high temperature and a very active polymerization catalyst, such as tetramethylethylenediamine–cuprous bromide: A. S. Hay, *Macromolecules* **2**, 107 (1969).

methyl ethers. Substitution of phenyl groups for methyl in the head (phenolic) ring of II resulted in a downfield shift of 0.09 ppm for the methyl protons of the terminal ring, while replacement of methyl by phenyl in the terminal ring caused an upfield shift of 0.23 ppm for the methyl protons of the head ring; the same pattern is observed for the methyl ethers. Apparently the orientation of the methyl groups to the plane of the pendant phenyl groups in structures of this type depends on whether the adjacent unit is directed toward the head or the tail of the chain, a fortunate circumstance which makes it possible to distinguish between the M*M*P and P*M*M sequences.

Consider a three-ring segment (VI) of a polymer chain with the rings labeled as shown below.



VI

The methyl groups of poly(2,6-dimethyl-1-4-phenylene oxide) absorb at 2.08 ppm, establishing the position of the M*M*M sequence. Substitution of phenyl groups into ring A should shift the methyl protons of B upfield by 0.23 ppm from this value; substitution in ring C should produce a downfield shift of 0.09 ppm. If additivity is assumed, then introduction of phenyl groups in both A and C should result in an upfield shift of 0.14 ppm.

Polymer Nmr Spectra.—The nmr spectra of the polymers prepared from IV, V, and from an equimolar mixture of 2,6-dimethylphenol and 2,6-diphenylphenol are shown in Figure 2. All have four peaks in the methyl region, with chemical shifts corresponding closely to the values predicted above for the four sequences possible in a random copolymer of dimethylphenol and diphenylphenol (Table II). Further evidence of the random nature of the polymers is shown in the region of the aromatic backbone hydrogens. Each polymer shows at least six of these peaks,[19] two of which, at 6.25 and 6.46 ppm, correspond to the homopolymers of diphenylphenol and dimethylphenol, respectively, and thus are presumably due to P*P*P and M*M*M sequences.[20]

TABLE II

CHEMICAL SHIFTS OF METHYL PROTONS IN POLYMERS

	δ, ppm			
Polymer source	P*M*M	P*M*P	M*M*M	M*M*P
Calculated[a]	1.85	1.94	2.08	2.17
IV	1.87	1.94	2.08	2.14
V	1.84	1.93	2.08	2.14
Mixture of monomers	1.86	1.93	2.08	2.13

[a] Calculated from chemical shifts in phenolic dimers.

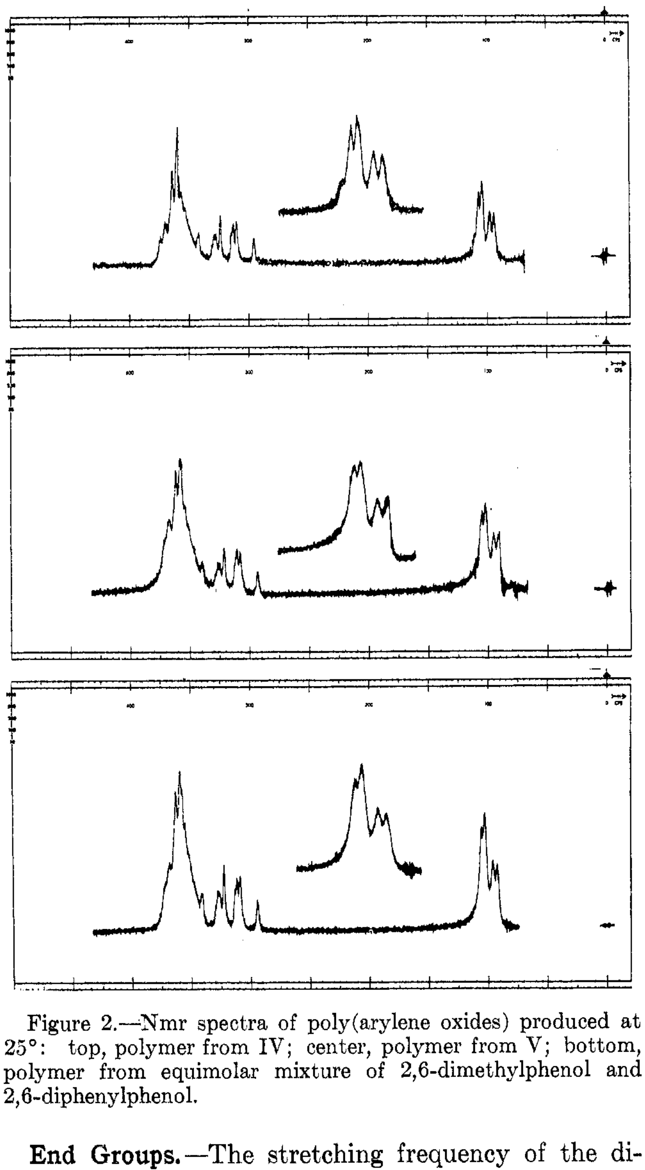


Figure 2.—Nmr spectra of poly(arylene oxides) produced at 25°: top, polymer from IV; center, polymer from V; bottom, polymer from equimolar mixture of 2,6-dimethylphenol and 2,6-diphenylphenol.

End Groups.—The stretching frequency of the diphenylphenol hydroxyl in IV is 3540 cm^{-1}; that of the dimethylphenol group in V is 3610 cm^{-1}. The near-infrared spectra of the three copolymers shows a single peak at 3545 cm^{-1}, Clearly all, or nearly all, of the polymer molecules have a diphenylphenol unit at the head of the chain. The absorption coefficient of the hydroxyl in IV is approximately three times that of V, but it is estimated that, if as much as 5% of the total hydroxyl in these low molecular weight copolymers were of the dimethylphenol type, its presence would be easily detectable.

Discussion

Although there are minor differences in the relative intensities of some of the signals, the nmr spectra of copolymers from IV and V are essentially the same as that of the copolymer obtained by oxidation of the mixture of monomers. They show all of the four possible methyl group signals, including that due to the M*M*M sequence, and the same group of peaks due to aromatic backbone protons. Of the three coupling mechanisms discussed above, only C, in which growth takes place by redistribution to form monomer and removal of monomer by coupling, is consistent with the observed structure. Neither mechanism A nor B allows

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[19] The type of analysis applied to the methyl protons was not attempted because of the complexity of this region of the spectrum. Assuming only nearest neighbor interactions there are eight possible types of backbone protons (four from each type of unit). Some of these probably do not differ enough in their chemical shifts to be resolved; others may be obscured by interference from the protons of the pendant phenyl rings.

[20] J. G. Bennett, Jr. and G. D. Cooper, *Macromolecules*, **3**, 101 (1970).

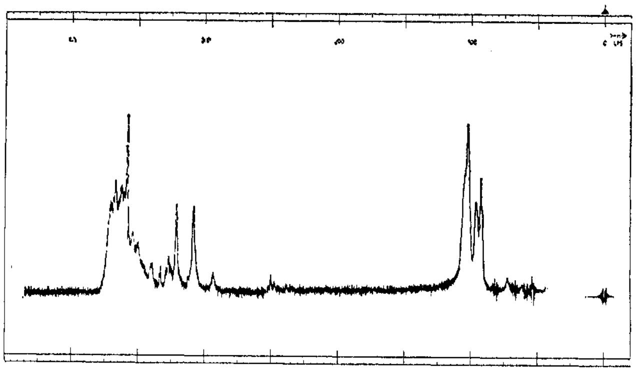
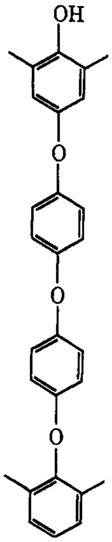


Figure 3.—Nmr spectrum of polymer obtained by oxidation of V at −25° in pyridine.

the formation of *MMM* or *PPP* sequences from the dimers; these groups can occur only as the result of the redistribution reaction. Furthermore, the formation of polymer molecules with diphenylphenol head groups from V is not consistent with mechanism A, nor is their formation from IV permitted by mechanism B. The preponderance of this type of phenolic group is to be expected from the redistribution mechanism. Molecules with a diphenylphenol group at the head of the chain are less readily oxidized than those with the dimethylphenol group and consequently accumulate in the polymer as the more reactive molecules are removed.

The fact that redistribution occurs does not rule out polymerization by other processes, as long as it is accompanied by redistribution, although the largely randomized structure of the polymer[21] shows that the redistribution is extensive and mechanism C is sufficient alone to explain the coupling reaction.

Low-Temperature Polymerization.—The products of oxidation of dimers at low temperature are, in many cases, different from those obtained at higher temperatures. The initial products of oxidation at 25° of II are a mixture of monomer, dimer, trimer, etc., that is, redistribution products.[8] At −25° with a limited amount of a preformed copper complex, $[\text{py CuCl(OCH}_3)]_x$, as the oxidizing agent only compounds with an even number of rings are obtained,[10] principally tetramer, with smaller amounts of hexamer and higher products. Similarly, III, the mixed dimer of phenol and xylenol, forms redistribution products at 25°,[3,22] but at −25° yields tetramer VII, which has the structure expected of coupling by formation and rearrangement of the ketal, mechanism B.[23] Other lightly substituted dimers behave in the same way.[22]



VII

These observations suggest that the activation energy for rearrangement of the intermediate ketal, eq 4, is lower than for dissociation according to eq 5, so that at a sufficiently low temperature redistribution becomes unimportant and polymer coupling occurs by mechanism B,[8] but this could not be tested by examination of polymer structure; dimer III, which has distinguishable rings, could not be oxidized past the tetramer stage, even with a large excess of the oxidizing agent.

Oxidation of IV at −25° in pyridine with an excess of the copper complex, conditions favoring coupling by rearrangement, yielded no isolable polymer. The only products detected, other than the unreacted started material, of which more than 90% was recovered, were small amounts of compounds having gas chromatographic retention times identical with those obtained by thermal or catalytic redistribution of IV.

Oxidation of V under the same conditions yielded 78% of methanol-insoluble polymer having a molecular weight of 4250 and a composition of 55 mol % M and 45% P units; the average molecule thus consists of 13 M and 11 P units. More than 98% of the hydroxyl groups were of the diphenylphenol type. The nmr spectrum of this polymer is shown in Figure 3. Methyl proton signals appear at δ 1.87, 1.93, and 2.07 ppm, with a shoulder at 2.12 ppm possibly representing the *MMP* sequence. The strongest signal in the methyl region is that for the *MMM* sequence, while in the aromatic backbone region the strong signals are those corresponding to *MMM* and *PPP* groups. The presence of the "forbidden" *MMM* and *PPP* sequences and the loss of approximately 15% of the P units provide conclusive evidence of redistribution.

Redistribution and rearrangement involve the same intermediate and are complementary reactions. Dissociation of the ketal into aryloxy radicals may occur at any stage of the progress of the dienone from the head to the tail of the chain, so that redistribution may proceed by transfer of more than one unit from one molecule to another. It has been suggested that the polymer coupling reaction involves both processes, with their relative importance determined by reaction conditions. The results with V show that, even under conditions favoring coupling by rearrangement, redistribution occurs with sufficient frequency to determine the polymer structure.[24]

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[21] None of the copolymers are completely random. All possible arrangements appear to be present, but sequences of similar units occur somewhat more often than is statistically to be expected.

[22] W. J. Mijs, O. E. Von Lohuisen, J. Bussink, and L. Vollbracht, *Tetrahedron*, **23**, 2253 (1967).

[23] D. M. White, private communication.

[24] Each step in the rearrangement sequence is reversible. If all units are alike, rearrangement has an equal probability in either direction. The average number of individual rearrangement steps required for producing a polymer molecule by coupling and rearrangment of polymeric radicals is extremely large, so that there is a high probability that dissociation and redistribution will occur at some stage of the process.

Registry No.—IV, 32979-47-8; IV polymer, 33029-40-2; V, 32979-49-0; V polymer, 33029-41-3; 2,6-diphenyl-4-bromoanisole, 20104-39-6; 2,6-diphenyl-4-(2,6-dimethylphenoxy)anisole, 32979-46-7; 2,6-dimethyl-4-(2,6-diphenylphenoxy)anisole, 32979-48-9; copolymer of 2,6-dimethylphenol and 2,6-diphenylphenol, 26006-43-9.

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Nonstereospecific Oxidative Addition of Benzenethiol to Indene[1]

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The oxidative addition of benzenethiol to indene produces a mixture of three isomeric 2-phenylsulfinylindanols that contains 14–18% of the *cis*-hydroxy sulfoxide contrary to previous claims that this reaction leads stereospecifically only to trans addition products. The fourth isomeric 2-phenylsulfinylindanol (cis-syn) was prepared by the oxidation of the sulfide precursor. The examination of the concentration dependence of hydrogen bonding, of the nmr spectra, and of the relative yields permits the assignment of the configurations at the sulfur atom in all four isomers.

Results and Discussion

The four isomeric 2-phenylsulfinylindanols (trans-anti, trans-syn, cis-anti, and cis-syn)[4] have been described in the literature, but unfortunately the reports are inconsistent and incomplete. Thus, Ford and coworkers[5] claimed that direct cooxidation of indene and thiophenol produces only traces (0.25% maximum) of the cis products and described two trans isomers of mp 149.5-150.5 and 99°, respectively. The cis isomers were prepared in a roundabout fashion *via* 2-bromoindanone and were described as solids of mp 158 and 122–123°, respectively. Later Oswald[6] repeated the cooxidation reaction and reported the isolation of *three* isomeric hydroxy sulfoxides of this series of melting points 158–159, 148–150, and 132–135°, respectively. More recently, however, the same investigator[7] stated that only *trans*-2-phenylsulfinylindanols are produced, and the stereospecificity of this reaction has been assumed[8] in the consideration of the bridged nature of the intermediate olefin–thiyl radical adduct.[9] In view of this confusion, and also since "the relationship between the four isomers with respect to the orientation about the sulphur atom is not known,"[5] the cooxidation of indene and thiophenol was reinvestigated with care. The preparation of the cis isomers from 2-bromoindanone was also repeated.

Extensive application of thin layer chromatography (tlc) to the products of the cooxidation of indene and thiophenol showed that the reaction produced three isomers, namely two trans isomers of mp 158 and 101°, respectively, and a high-melting cis isomer (mp 158°). The relative yields of these three isomers were determined by careful column chromatography and by characterization of each fraction by tlc. Regardless of whether the cooxidation was carried out in benzene or hexane, the cis isomer of mp 158° was obtained in 14–18% yield[10] while the yields of the high- and low-melting trans isomers were 24–29 and 56–60%, respectively. In order to obtain information on the relative rates of formation of the three hydroxy sulfoxides during the cooxidation reaction, samples of the reaction mixture were subjected to tlc, and it was found that the cis isomer and the low-melting trans isomer were formed in approximately equal amounts during the early stage of the reaction, while the high-melting trans isomer did not begin to accumulate until later.

The missing cis hydroxy sulfoxide was synthesized in the manner previously described except that sodium borohydride, rather than lithium aluminum hydride, was used in the reduction of 2-phenylmercaptoindanone. It is of interest to note that while the latter reducing agent gave a ratio of hydroxy sulfides 4.6:1 in favor of the trans isomer, the use of the borohydride produced a 15:1 ratio in favor of the cis isomer. The difference in these results is due, in part, to the alkaline conditions of the sodium borohydride reduction, which are known[5] to bring about the decomposition of the *trans*-2-phenylmercaptoindanol. Thus, while the lithium aluminum hydride results are based on essentially quantitative yields of hydroxy sulfides, the total yield of hydroxy sulfides using sodium borohydride was only 33%. However, even if we assume that the loss of the missing hydroxy sulfide is due to the decomposition of the trans hydroxy sulfide, the ratio of trans:cis reduction products is only 2.2:1 in the case of the sodium borohydride. The fate of the *trans*-2-phenylmercaptoindanol during the alkaline decomposition was not ascertained by Ford and coworkers.[5] We have isolated essentially all of the missing phenylmercapto portion of the initial 2-

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[4] The names, in accord with the nomenclature employed by Ghersetti and coworkers, *J. Chem. Soc.*, 3718 (1963), refer, in the first place, to the relative orientation of the hydroxyl and sulfoxide functions, and, secondly, to the orientation of the oxygen of the sulfoxide relative to the benzene ring of indan when the conformation of the sulfoxide group is such that its phenyl group points away from the indan ring.

[5] J. J. Ford, R. C. Pitkethly, and V. O. Young, *Tetrahedron*, **4**, 3251 (1958).

[6] A. Oswald, *J. Org. Chem.*, **26**, 842 (1961).

[7] A. A. Oswald and T. J. Wallace in "Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Myers, Ed., Pergamon Press, Elmsford, N. Y., 1966, p 224.

[8] P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 759 (1966).

[9] P. S. Skell in "Organic Reaction Mechanism," Special Publication No. 19, The Chemical Society, London, 1965, p 143.

[10] H. H. Szmant and J. J. Rigau, *Tetrahedron Lett.*, 3337 (1967).