reduced pressure to leave 1.037 g of a liquid, which was chromatographed on Woelm neutral alumina, activity II. Elution with 125 ml of petroleum ether gave 0.240 g of liquid; solvents of increasing polarity through ether gave 0.721 g of liquid. The infrared spectrum of the first fraction showed it to be mainly K, but the presence of a few additional bands suggested the presence of an impurity. The larger fraction was evaporatively distilled at 0.5 mm (bath temperature 60°) to provide analytically pure K. The spectral and analytical properties of K are described above.

2-(2-Oxopropyl)cyclohexanone Ethylene Ketal (R).—To 17.5 ml of dry, ice-cold, stirred pyridine, 1.55 g (1.55×10^{-2} mole) of chromium trioxide was added in small portions during 20 min. To the resultant yellow suspension, 1.00 g (5.0×10^{-3} mole) of the ketal alcohol O in 2.5 ml of pyridine was added; the mixture was stirred for 0.5 hr in an ice bath, and then at room temperature for 5.5 hr. The brown mixture was taken up in 125 ml of water and extracted four times with ether; the combined extracts were washed four times with ice-cold 3.7% hydrochloric acid, followed immediately by 30 ml of 10% sodium carbonate in two portions, and finally with water and saturated brine. The ether was dried and was removed at reduced pressure. The total residue was chromatographed on Woelm neutral alumina, activity I. Elution with 425 ml of ether gave 0.546 g of product, which was evaporatively distilled at 0.2 mm (bath temperature 75°) to give 0.477 g of R (48% yield). Vpc on a 5-ft 20% Ucon Polar column showed purity of about 99%. Analytically pure material was obtained by preparative vpc.

The infrared spectrum showed strong bands at 1717 (ketone), 1088 (ketal), 948, and 924 cm^{-1}. The nmr spectrum showed a singlet at δ 2.02 (CH_3—C=O) and a singlet at δ 3.83 (protons of dioxolane ring).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.40; H, 9.28.

The **semicarbazone**, after two recrystallizations from ethanol-water and sublimation at 0.08 mm (bath temperature 140°), melted at 154.5–155.5°.

Anal. Calcd for $C_{12}H_{21}N_3O_3$: C, 56.45; H, 8.29. Found: C, 56.64; H, 8.28.

α-(2-Oxocyclohexyl)acetone (M).—A solution of 0.451 g (2.28×10^{-3} mole) of R in a mixture of 2 ml of 95% ethanol and 1 ml of water containing 2 drops of 37% hydrochloric acid was refluxed for 1.1 hr. The reaction mixture was then diluted with water and extracted three times with ether. The combined ether extracts were washed with saturated bicarbonate, water, and finally with saturated brine. After the ether was dried, it was evaporated to give 0.172 g of an oil.

Vpc on a 5 ft × 0.25 in. 20% Ucon Polar on Chromosorb P column (column temperature 153°, flow rate 75 cc of He/min) showed the product at 11.0 min, preceded by several small peaks. The total crude product was injected in 25–30-μl portions, and the peak at 11.0 min was collected to give 0.078 g of the diketone M of 99+% purity (n^{25}_{D} 1.4615, lit.[12] n^{25}_{D} 1.4655).

The infrared spectrum showed a band at 1710 cm^{-1}, with a shoulder at 1725 cm^{-1}, strong bands at 1165 and 1130 cm^{-1}, and a weak, sharp band at 3400 cm^{-1}. The nmr spectrum showed a singlet at δ 2.08 (CH_3—C=O) and complex absorption at δ 1.5–3.0.

The bis-2,4-dinitrophenylhydrazone was prepared as above and had the same properties as the derivative obtained from the oxidation product of the hydroxy ketone K.

The Oxidative Coupling Reactions of 2,6-Xylenol with Activated Manganese Dioxide[1]

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Dimeric and polymeric products are obtained by the reaction of 2,6-xylenol and activated manganese dioxide. The tail-to-tail dimer, 2,2′,6,6′-tetramethyl-*p,p*′-biphenol, is formed when a molar excess of 2,6-xylenol is treated with the activated oxide, whereas the head-to-tail polymer is the principal product with excess oxide. The head-to-tail dimer, 4-(2′,6′-xylenoxy)-2,6-xylenol, reacts with the oxide to afford polymer and small amounts of 2,6-xylenol and the tail-to-tail dimer. Low molecular weight oligomer is converted by means of the oxide to higher molecular weight oligomer, 2,6-xylenol, the tail-to-tail dimer, and 3,3′,5,5′-tetramethyldiphenoquinone. Similar findings were obtained with silver oxide, lead dioxide, copper–pyridine, and basic ferricyanide. These observations and other considerations support a quinol–ether mechanism for this type of reaction rather than a nonclassical electron-transfer mechanism.

Activated manganese dioxide is a reagent used widely in organic syntheses for the specific oxidation of benzylic or allylic alcohols to aldehydes or ketones. This and other reactions of this material have been reviewed by Evans.[2a] Factors influencing the rate and specificity of the allylic oxidation have been well examined by Gritter,[2b,c] and modes of activity have been investigated by Pratt[3] and Henbest.[4] Recently, activated manganese dioxide has been applied as an agent for oxidative coupling in several enzyme-miming syntheses of phenolic natural products such as diploicin,[5] dehydrogriseofulvin,[6,7] and picrolichenic acid.[8] In the present investigation, an examination of the oxidative coupling reactions of activated manganese dioxide and a less elegant phenol, 2,6-xylenol, has been made in order to expand the scope of this reaction and to clarify the general mode of oxidative polymerization of phenols.

The oxidative polymerization of 2,6-xylenol has been accomplished heretofore by silver oxide[9] and a copper-pyridine complex.[10] The studies of the latter system have shown that the reaction involves free-radical intermediates and a stepwise polycondensation wherein the polymerization of dimer, trimer, or oligomer may be obtained without monomer. These observations prompted an unusual mechanistic proposal.[11]

Results

Activated manganese dioxide reacts with 2,6-xylenol (I) to form a polyphenylene ether (II), 2,2′,6,6′-tetra-

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(1) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; Abstracts, p 15S.

(2) (a) R. M. Evans, *Quart. Rev.* (London), **13**, 61 (1959); (b) R. J. Gritter and T. J. Wallace, *J. Org. Chem.*, **24**, 1051 (1959); (c) R. J. Gritter, G. D. Dupre, and T. J. Wallace, *Nature*, **202**, 179 (1964).

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(4) N. B. Henbest and M. J. Stratford, *Chem. Ind.* (London), 1170 (1961).

(5) C. J. Brown, D. E. Clark, W. D. Ollis, and P. L. Veal, *Proc. Chem. Soc.*, 393 (1960).

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(7) J. R. Lewis and J. A. Vickers, *Chem. Ind.* (London), 779 (1963).

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(9) B. O. Lindgren, *Acta Chem. Scand.*, **14**, 1203 (1960).

(10) (a) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959); (b) A. S. Hay, *J. Polymer Sci.*, **58**, 581 (1962); (c) G. F. Endres and J. Kwiatek, *ibid.*, **58**, 593 (1962); (d) G. F. Endres, A. S. Hay, and J. W. Eustance, *J. Org. Chem.*, **28**, 1300 (1963).

(11) (a) H. L. Finkbeiner, G. F. Endres, H. S. Blanchard, and J. W. Eustance, *SPE Trans.*, **2**, 112 (1961); (b) W. A. Butte, Jr., and C. C. Price, *J. Am. Chem. Soc.*, **84**, 3567 (1962).

TABLE I

OXIDATION OF 2,6-XYLENOL WITH MANGANESE DIOXIDE AND OXIDES[a]

	Yield, %[b]							
	Oxidant							
Products (mol wt)	MnO_2[c]	MnO_2[d]	MnO_2[e]	MnO_2[f]	MnO_2[g]	MnO_2[h]	PbO_2	Ag_2O
Oligomer, (242–1100)	15	24	52	84	9		68	28
Oligomer (1100–4000)	38	32	22				8	26
Oligomer (4000–9000)	42	36	10				4	33
3,3′,5,5′-Tetramethyldiphenoquinone			13	8	4		12	6
Surface area of oxidant, m^2/g	66	55	51	66	6.4	0.4		

[a] Reaction conditions: 20 mmoles of 2,6-xylenol, 100 mmoles of oxidant, 50 ml of petroleum ether (bp 60–110°), nitrogen atmosphere, room temperature, 30 min. [b] Yields based on 20 mmoles of 2,6-xylenol. [c] Prepared by method of Pratt and Van DeCastle.[8] [d] Purchased from Beacon Chemical Industries, Inc. [e] Prepared by method of S. Ball, T. W. Goodwin, and R. A. Morton, *Biochem. J.*, **42**, 516 (1948). [f] Electrolytic grade MnO_2 purchased from the American Potash and Chemical Corp. [g] Naturally occurring MnO_2 (85%). [h] Crystalline MnO_2 (99%).

TABLE II

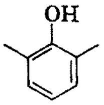
SIDE PRODUCTS OF 2,6-XYLENOL DIMER (II, n = 0) AND OLIGOMER (II) POLYMERIZATION[a]

	Oxidant						
	MnO_2[b]	PbO_2[b]	Ag_2O[b]	MnO_2[c]	Cu-pyridine[c]	Cu-pyridine[b]	$K_3Fe(CN)_6$[b]
Yield I, wt %	2.5	2.6	3.0	5.7	2.0		0.3
Yield III, wt %	0.5			1.4	2.2	1.2	1.0
Yield IV, wt %	2.7						

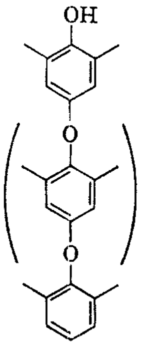
[a] For conditions, see Experimental Section. [b] Starting material was compound II. [c] Starting material was compound II, n = 0.

methyl-p,p'-biphenol (III), and 3,3′,5,5′-tetramethyldiphenoquinone (IV).

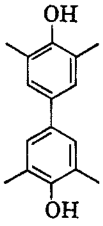
The polymer formed in this reaction is identical with the polymer formed by the action of silver oxide[9] or the copper–pyridine system[10a] on I, according to analyses by nuclear magnetic resonance and infrared. The molecular weight of the polymer can be varied from 2000 to 20,000 by a selection of reactant ratios, methods of oxide preparation, solvents, and other variables. The polymer is the principal product of the reaction when the oxide–xylenol ratio is 3:1 or greater. Yields based on 2,6-xylenol range from 60 to 95%. The remaining products are either III or IV or a mixture of both. Whenever the 2,6-xylenol is in molar excess of the oxide, the principal products are III and low molecular weight oligomer. Yields based on oxide are about 60% for III and 30% for II at a xylenol–oxide mole ratio of 20:1. Biphenol III is converted to IV by reaction with activated manganese dioxide. Examples of the effect of methods of oxide preparation on product distribution are listed in Table I.



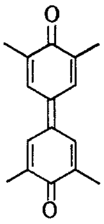
I



II



III



IV

Low molecular weight oligomer was distilled to afford the head-to-tail dimer II (n = 0). The dimer, in turn, can be polymerized to higher molecular weight oligomer without the addition of monomer. Similarly, low molecular weight oligomer can be polymerized without monomer to higher polymer. In both cases, the polymerization can be run in such a fashion as to isolate I, III, and/or IV in low yield as well as the principal product, the polymer. Suitable steps were taken to ensure that the starting material contained neither monomer nor dimer III. These results with oligomer behavior were extended to silver oxide, lead dioxide, the copper–pyridine system, and basic ferricyanide (Table II).

An examination of the activated manganese dioxide–xylenol reaction was made in an esr spectrometer. A basic pattern of seven triplets was observed. The principal splitting was 5.0 ± 0.2 oersteds with a subsplitting of 1.0 ± 0.2 oersteds. This spectrum is in keeping with radicals derived from II wherein the larger splittings are attributed to six methyl hydrogens and the minor splittings to two ring hydrogens. Spectra identical with this spectrum were obtained when low molecular weight polymer was treated with activated manganese dioxide or silver oxide or the copper–pyridine system. The esr spectra of III with either activated manganese dioxide or the copper–pyridine system contained seven unresolvable broad lines separated by 5.0 ± 0.2 oersteds. Since a flow system was not used, the spectrum from the radical derived from I[12] was not observed.

Although the fate of the MnO_2 is not related directly to the purpose of this work, it is noteworthy that X-ray diffraction data indicate that the amorphous activated manganese dioxides are converted to a mixture whose only crystalline component is Mn_3O_4 (hausmannite structure). This finding is in keeping with the cathodic reduction[13] of MnO_2 to Mn_3O_4 and the thermal hydrogenation[14] of the MnO_2 to Mn_3O_4. The latter oxide does not react with 2,6-xylenol.

Discussion

Consonant with these results is a quinol–ether mechanism (Scheme I), whose outlines were sketched by

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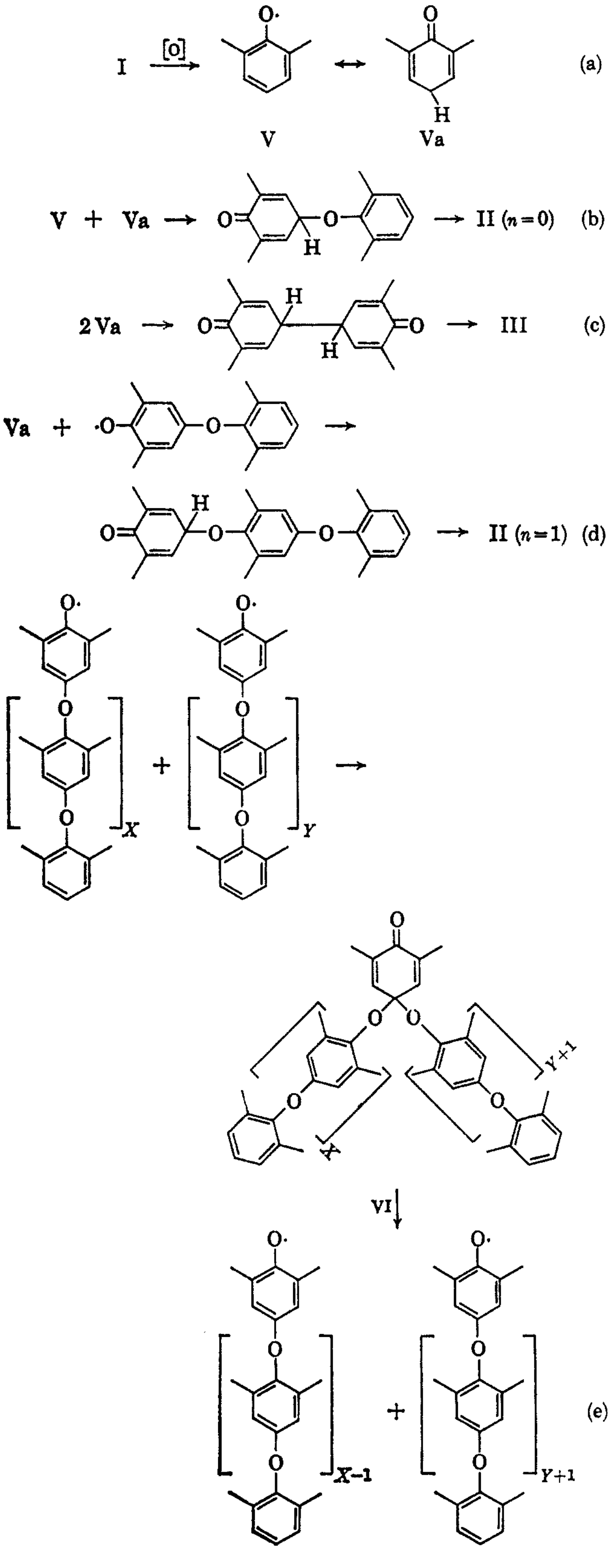
(12) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 213 (1964).

(13) S. Ghosh and J. P. Brenet, *Electrochem. Acta*, **1**, 449 (1962).

(14) A. K. Askin and S. T. Rostovtsev, *Izv. Vysshikh Uchebn. Zavedenii, Chern. Met.*, **1**, 5 (1964).

Scheme I
Quinol–Ether Mechanism



Finkbeiner and co-workers,[11a] wherein a phenoxyl radical may couple with another phenoxyl either at the oxygen atom (V) or at the *para* position (Va). The coupling may be largely head-to-tail as in the polymerization with excess manganese dioxide. It may be exclusively *para* coupling if steric hindrance limits reaction at the oxygen atom, such as in 2,6-di-*t*-butylphenol. Step e in Scheme I presents an explanation for the polymerization of dimer II ($n = 0$) and oligomer without monomer. Intermediate quinone ketals similar to VI have been shown by Becker[15] to be isolable but reactive. By this path, one oligomer chain polymerizes at the expense of other chains by removing a 2,6-xylenol unit. This "unzipping" reaction generates two more radicals, and the process is eventually stopped by hydrogen abstraction or reaction with a monomer radical leading to tautomerization. If the monomer radical to oligomer radical concentration ratio remains high, as in the case of excess 2,6-xylenol with activated manganese dioxide, a buildup of III by step c relative to growth steps d and e would be predicted. The formation III, which is subject to further oxidation to IV, is irreversible. A corollary of the unzipping concept is that, under conditions designed to ensure short contact time, some 2,6-xylenol, the dimer III, and/or IV should be detected in reactions involving oligomer. These products have been isolated in certain polymerization reactions of dimer II ($n = 0$) and low molecular weight oligomer. Since this important finding was observed for silver oxide, lead dioxide, the copper–pyridine system, and basic ferricyanide, as well as for activated manganese dioxide, the quinol–ether mechanism may be general for oxidative polymerization of phenols by all one-electron oxidizing agents.[16]

In considering the arguments for a nonclassical electron mechanism,[11a] Butte and Price[11b] proposed that such interaction of chains in the quinol–ether mechanism would give extensive opportunity for equilibration of large and small radicals. No such equilibration was noted by them when 2,6-xylenol was partially polymerized in the presence of high molecular weight polymer with the copper–pyridine system. The interpretation of this experiment, however, failed to take into consideration the stoichiometry of such an oxidative coupling reaction wherein the monomer radicals were greatly in excess of polymer radicals and only moderate reduction of molecular weight would be predicted by a quinol–ether mechanism. Such was the case; the intrinsic viscosity of the polymer decreased from 0.93 to 0.75 dl/g.

In this same work, 2,6-xylenol-4-^{3}H was reported to incorporate 23.1% of the tritium in the polymer whereas the polymer from 2,6-xylenol-3-^{3}H contained 92% of the label. This was considered as support for the nonclassical mechanism (Scheme II), which invokes intermediate VII, which would be capable of losing tritium in the 3 position or retaining tritium originally in the 4 position by a hydride shift followed by loss of proton in addition to the more prevalent direct loss of proton at the 4 position. Here again these results are in accord with the quinol–ether mechanism since, in the reaction of monomer phenoxyl with growing polymer phenoxyl or other monomer phenoxyl, intermediate VIII tautomerizes to a phenol by a protonation step which places a positive charge on the 3 position and sets in movement the aforementioned chain of exchange events, as shown in Scheme III.

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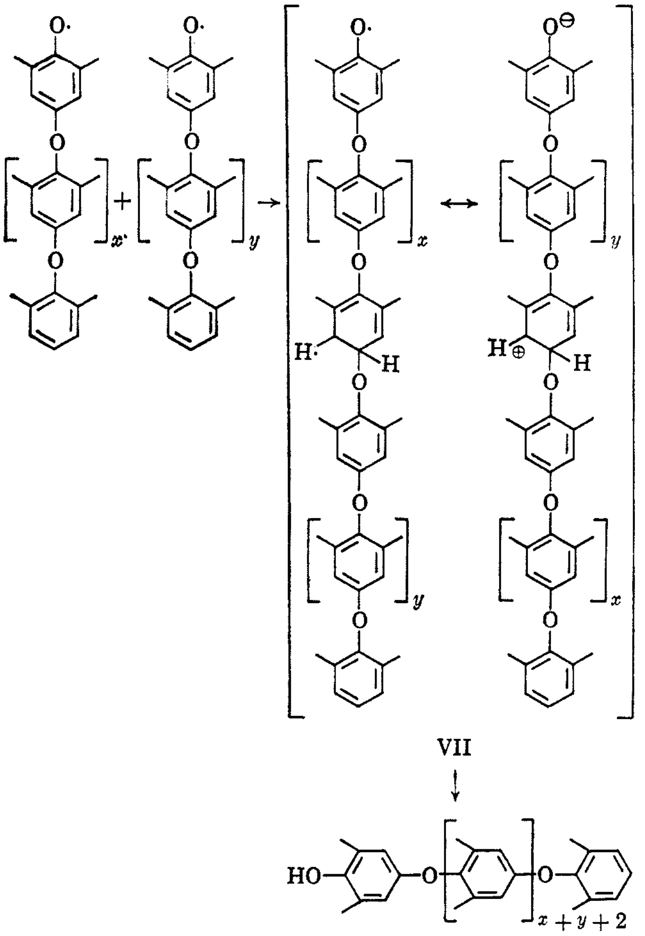
[15] H. D. Becker, *J. Org. Chem.*, **29**, 3068 (1964).

[16] Since the first announcement[1] of this work, Finkbeiner and co-workers [G. D. Cooper, H. S. Blanchard, G. F. Endres, and H. Finkbeiner, *J. Am. Chem. Soc.*, **87**, 3996 (1965)] have published preliminary results reporting the isolation of a derivative of I and IV from dimer II ($n = 0$).

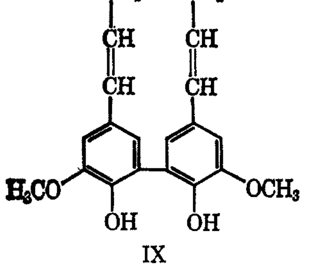
Scheme II

Nonclassical Electron Mechanism



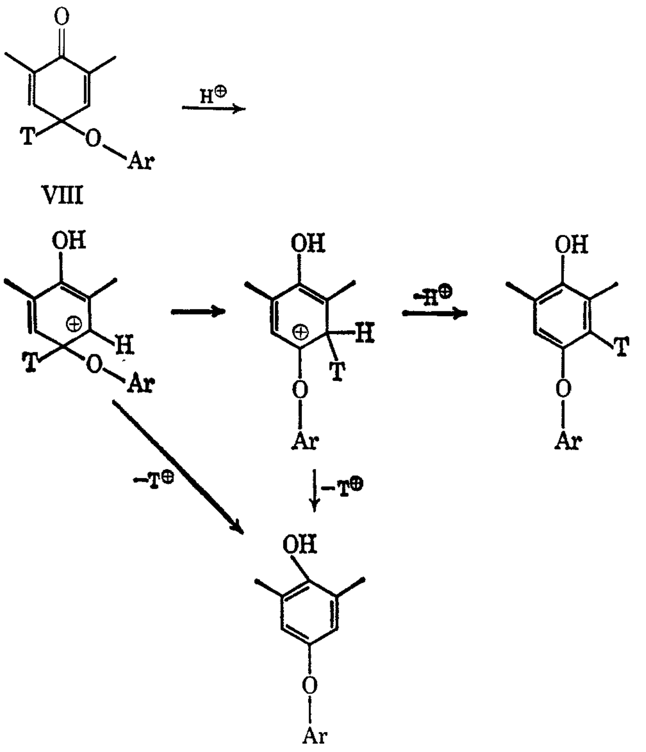
Other objections to the nonclassical electron mechanism are as follows. (a) The finding of tail-to-tail products III and IV as well as I in the polymerization of dimer and oligomer cannot be explained by this mechanism. (b) The charge separation in the "resonance" structure VII may be enormous.

In addition to resolving a mechanistic dilemma in the oxidative polymerization of 2,6-xylenol, the finding of "unzipping" ought to provide a useful implement for probing the structure of other aromatic polyethers such as lignin. In addition, it affords a possible explanation for certain structural features of lignin models.[17] Prominent among the latter is the lack of a rationale for the absence of products resulting from O-coupling at the 5 position of coniferyl alcohol in preference to C-coupled products such as dehydrobisconiferyl alcohol (IX).



IX

Scheme III



Experimental Section[18]

Materials.—Eastman White Label 2,6-xylenol was used without purification. Other phenols were purchased from Aldrich Chemical Co. and purified further by crystallization or distillation.

2,6-Xylenol and Activated Manganese Dioxide. a. Excess Oxide.—Activated manganese dioxide (8.70 g) was added to a solution of 2,6-xylenol (4.10 g) in 50 ml of benzene. The mixture was refluxed under nitrogen for 2 hr with magnetic stirring. After cooling to room temperature, the mixture was filtered and the residual oxide was washed with 150 ml of benzene. The combined benzene solutions were washed with a 5% solution of sodium hydroxide. The benzene solution was stripped to give 3.82 g of crude polymer. The yield based on starting material was 93%. The crude polymer dissolved in 25 ml of chloroform was coagulated by pouring into excess methanol. The solid polymer weighed 2.00 g and melted between 176 and 182°.

Anal. Calcd for C_8H_8O: C, 79.97; H, 6.71; O, 13.32. Found: C, 79.45; H, 6.93; O, 13.38.

The molecular weight of the solid by vapor pressure osmometer was 1816. The coagulate displayed no X-ray diffraction pattern. The nmr spectrum of the coagulate in deuteriochloroform displayed peaks at 2.1 and 6.5 ppm relative to $(CH_3)_4Si$ on a Varian 60-Mc spectrometer. The infrared spectrum of the polymer beyond 8.0 μ had the following bands: 8.4 (s), 9.8 (s), 10.4 (m), 11.6 (s), and 12.0 μ (w).

The base-soluble material from the reaction weighed 0.18 g (4.5%) and was 2,2′,6,6′-tetramethyl-*p*,*p*′-biphenol according to an infrared comparison with authentic material.[9] The molecular weight by mass spectra analysis was 242 (calcd, 242).

b. Excess 2,6-Xylenol.—Activated manganese dioxide (0.970 g) was added to a solution of 2,6-xylenol (24.2 g) in 50 ml of benzene. The mixture was stirred under nitrogen for 2 hr. After filtration, the excess 2,6-xylenol was distilled off. The residual material was dissolved in ether and extracted with 5% NaOH. The nonbase-soluble material was oligomer II (0.375 g) according to an infrared spectrum. The base-soluble material after acidification was dimer III (0.740 g) according to an infrared spectrum. Chloroform washing of the oxide afforded 0.257 g of diphenoquinone IV.

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(17) K. Freudenberg, *Science*, **148**, 595 (1965).

(18) The following members of the Research Services Division of Sun Oil Co. contributed to the analytical work: D. S. Baugher (mass spectrometry), J. A. Huston (X-ray diffraction), and J. T. Stiles (elemental analyses).

c. **Tail-to-Tail Dimer.**—Activated manganese dioxide (8.70 g) was added to a solution of III (2.40 g) in 50 ml of acetone. The mixture was refluxed for 2 hr in a nitrogen atmosphere. After cooling and filtration, the acetone solution was stripped to a red residue; weight 0.075 g. A chloroform washing (500 ml) of the insoluble oxide was stripped to a red residue (2.314 g). The infrared spectra of both residues were superimposable upon that of authentic IV. No III was recovered.

2,6-Di-*t*-butylphenol.—Activated manganese dioxide (8.7 g) was added to a solution of 2,6-di-*t*-butylphenol (6.8 g) in 50 ml of benzene. The mixture was refluxed for 2 hr. The material soluble in benzene was red, weighed 6.72 g (98%), and was identified by infrared spectrum as 3,3'5,5'-tetra-*t*-butyldiphenoquinone. The molecular weight by mass spectral analyses of a sample crystallized from methanol was 408 (calcd, 408). The crystallized yield was 4.12 g. (60%).

Reaction of Oligomer with Oxides.—Oligomeric 2,6-xylenol polymer was dissolved in ether. The ether solution was extracted three times with a 5% NaOH solution, two times with a 10% KOH solution, and once with water. The solution was dried and stripped. The last base wash was acidified and extracted with ether to detect residual 2,6-xylenol. None was detected.

The low molecular weight oligomer (0.460 g) was dissolved in 50 ml of ethyl ether. Lead dioxide (2.00 g) was added. The mixture was stirred for 15 min at room temperature. After filtration, the ether solution was washed with 20 ml of 10% KOH solution. The base was acidified and extracted with ether. The ether was dried and stripped to afford 12 mg of 2,6-xylenol, identified by infrared spectrum and mass spectrum.

The oligomer (1.957 g) was treated similarly with silver oxide (0.429 g). 2,6-Xylenol (9 mg) was isolated.

The oligomer (1.957) was allowed to react with activated manganese dioxide (0.970 g) to give 70 mg of a base-soluble mixture which was composed of 2,6-xylenol (52 mg) and 2,2',6,6'-tetramethyl-*p*,*p*'-biphenol. The limited solubility of the latter in petroleum ether (bp 30–60°) was used to separate the components. A washing of the MnO_2 with chloroform gave a 74-mg mixture of polymer and 3,3',5,5'-tetramethyldiphenoquinone. The quinone (53 mg) was isolated by means of its limited solubility in ethyl ether.

Reaction of 2,6-Xylenol Dimer with Manganese Dioxide.—The dimer II ($n = 0$) was prepared by the method of Lindgren.[9] After several crystallizations from petroleum ether (bp 50–110°), the melting point of the dimer was 107–108°. It was treated with base as in the above section. The dimer (0.939 g) was dissolved in 25 ml of acetone and treated with activated manganese (0.261 g) under nitrogen for 30 min. The base-soluble reaction products were shown to be a mixture of 2,6-xylenol (54 mg) and dimer III (13 mg) by infrared spectra and mass spectra.

Reaction of 2,6-Xylenol Dimer and Oligomer with Copper-Pyridine. a.—The head-to-tail dimer (0.895 g), treated as above with base to remove traces of 2,6-xylenol, was dissolved in 5 ml of pyridine and poured into 15 ml of pyridine containing cuprous chloride (35 mg). The latter solution had been stirring in air for 30 min during which time the copper salt had dissolved and a deep green color had formed. The reaction mixture was stirred rapidly for 30 sec and then poured into a 25% HCl solution. The acid solution was extracted with ether, which in turn was washed with 10% KOH. The base was acidified with hydrochloric acid and extracted with ether. The ether layer was washed with water, dried, and stripped to give 18 mg of 2,6-xylenol, identified by infrared spectrum and undepressed melting point upon admixture with authentic material, and 20 mg of III, identified by infrared spectrum.

b.—Oligomer II (0.575 g) was allowed to react in the same fashion as the dimer II ($n = 0$) with the copper system. The base-soluble material weighed 7 mg and displayed an infrared spectrum identical with that of III. It was derivatized by conversion with activated manganese dioxide to IV (5 mg) identified by infrared spectrum and undepressed melting point with authentic material.

Reaction of 2,6-Xylenol Oligomer with Potassium Ferricyanide.—Oligomer II (1.69 g) was dissolved in ethyl ether (50 ml) and shaken for 30 sec with 5% sodium hydroxide solution (25 ml) containing $K_3Fe(CN)_6$ (0.329 g). The layers were separated. The ether layer contained oligomer (1.50 g). The base-soluble reaction products were I (4.7 mg) and dimer III (18.6 mg).

Electron Spin Resonance Spectrum.—The esr spectrum was observed by the use of a Varian V 4500 spectrometer with a 6-in. magnet and 100-kc/sec field modulation. A 10% solution of 2,6-xylenol in benzene was added to a tube (2 mm) containing activated manganese dioxide.[3] The tube was shaken until the color of the liquid above the solids was yellow, and was then placed in the spectrometer in such a way that the solid–liquid interface was in the cavity of the spectrometer.

Acknowledgment.—The author wishes to thank Mr. Wayne Fletcher for the technical assistance, Dr. William C. Neikam for the esr determination, and Dr. Walter A. Butte, Jr., Professor Wayland E. Noland, and Professor Cheves Walling for stimulating discussions.

Fluorination of Perhalobenzenes with Potassium Fluoride in Polar Solvents

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In an effort to prepare highly fluorinated aromatic species an extensive study has been made of the reactions of hexachloro- and hexabromobenzene, pentachlorobenzotrifluoride, and 1,4-bis(trifluoromethyl)tetrachlorobenzene with potassium fluoride in polar solvents. The most desirable solvents were found to be N-methylpyrrolidone or tetramethylene sulfone. The reaction was found to be straightforward until three fluorine atoms had been introduced. Continued reaction gave not only further fluorination but also significant amounts of hydrogen-containing species. This was especially evident with hexabromobenzene and was also noted, although to a lesser degree, with hexachlorobenzene and pentachlorobenzotrifluoride. Completely fluorinated products were obtained only from 1,4-bis(trifluoromethyl)tetrachlorobenzene.

The fluorination of chlorinated aliphatic compounds with potassium fluoride in a polar solvent is a convenient method for the preparation of many highly fluorinated materials.[1,2] The reaction has been shown[3] to proceed by nucleophilic displacement of chlorine by fluoride ion, and with certain substrates perfluoro- or monohydroperfluoro olefins are obtained in high yield.[2,4,5] In contrast, hexachlorobenzene has been

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(2) J. T. Maynard, *J. Org. Chem.*, **28**, 112 (1963).

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(5) G. W. Holbrook and O. R. Pierce, U. S. Patent 3,197,513 (July 27, 1965) (to Dow Corning Corp.).