The Formation of p-Benzoquinones in the Oxidation of Polyphenylene Ethers

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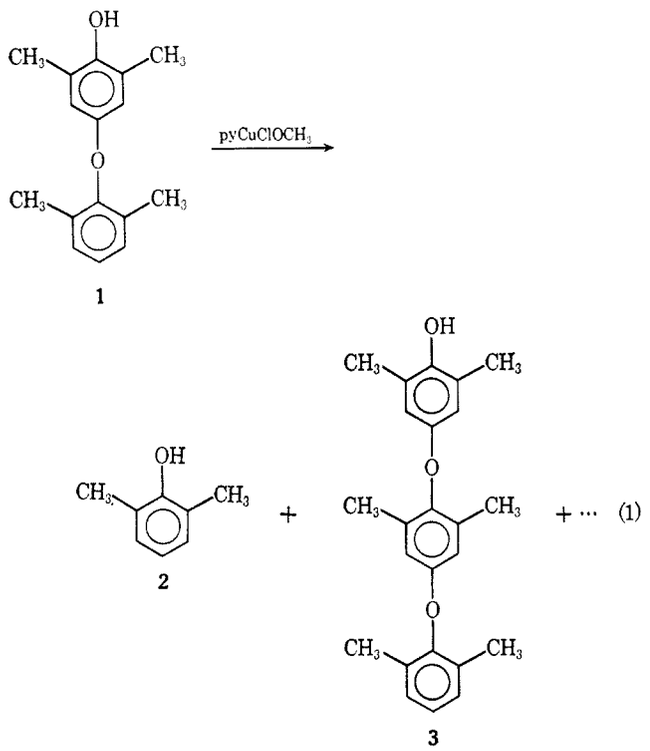
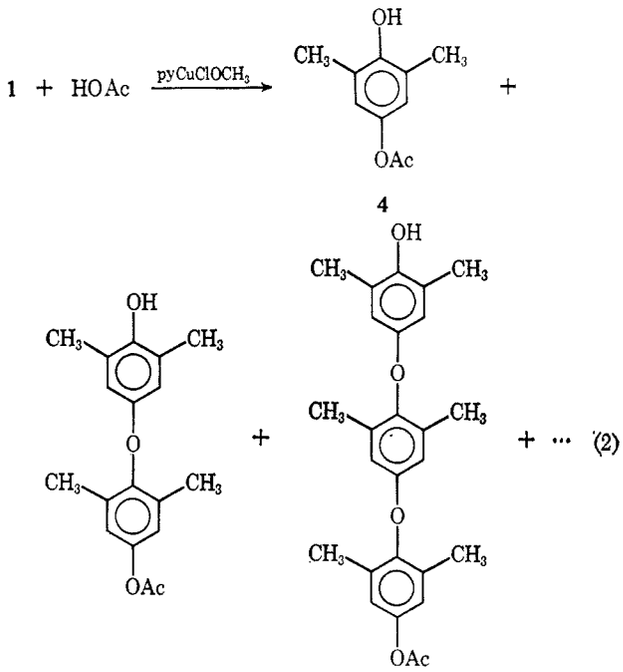
A number of oxidizing agents attack polyphenylene ethers in acetic acid solution to produce either 4-acetoxyphenols or p-benzoquinones. The nature of the final product depends on the ratio of oxidizing agent to polymer, since 4-acetoxyphenols are initially formed and subsequently oxidized to the benzoquinone. A mechanism is proposed for the reaction.

During the course of work on the stability of diphenyl ether group in 2,6-dimethylpolyphenylene ether,[1] an attempt was made to carry out a redistribution of the xylenol dimer, 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol (**1**), in refluxing acetic acid using chloromethoxy(pyridine)copper[2] as the initiator. The expected products were 2,6-xylenol (**2**), xylenol trimer (**3**), xylenol tetramer, and higher oligomers as shown in eq 1.



Although the expected reaction did occur, vapor phase chromatography showed a second set of products which was identified by mass spectrometry and nmr spectroscopy as an analogous oligomeric series having an acetoxy group in the ultimate *para* position as shown in eq 2.

Although the formation of this series of products can be explained as the coredistribution of 4-acetoxy-2,6-dimethylphenol (**4**) with the xylenol dimer **1**, a type of reaction that had been previously demonstrated for a number of other phenols,[1,3] the origin of **4** remained to be determined. This paper reports the formation of acetoxyphenols from a number of polyphenylene ethers and their subsequent oxidation to p-benzoquinones.



Results and Discussion

Xylenol dimer **1** readily undergoes redistribution reactions with itself to produce an oligomeric series[1,3] which severely complicated the study of the formation of **4** and its subsequent redistribution with **1**. White[4] has shown that, while poly-2,6-dimethylphenylene ether does not redistribute with itself to produce any low-molecular weight products, it readily coredistributes with a variety of phenols. These products form an oligomeric series whose ultimate group is derived from the added phenol and the remainder of each molecule from the polymer. This suggested to us that high polymer would be ideally suited for determining if acetoxyxylenol **4** is produced by a direct copper-catalyzed oxidative coupling of acetic acid and hydroxy-terminated phenylene ethers rather than from one of the redistribution products of **1**.

Poly-2,6-dimethylphenylene ether (prepared by the method of Endres[5]) was dissolved in toluene; acetic acid was added followed by chloromethoxy(pyridine)copper.[2] This mixture was refluxed until the green color of the copper complex was discharged. Vpc showed only the expected set of products (eq 2), suggesting that the acetoxyxylenol had been directly formed from acetic acid and the polymer.

Previous work[1,4] had shown that a variety of oxidizing agents such as tetramethyldiphenoquinone and benzoyl peroxide would initiate the redistribution of xylenol

(1) G. C. Cooper, A. R. Gilbert, and H. Finkbeiner, *Polymer Preprints*, **7**, 166 (1966).

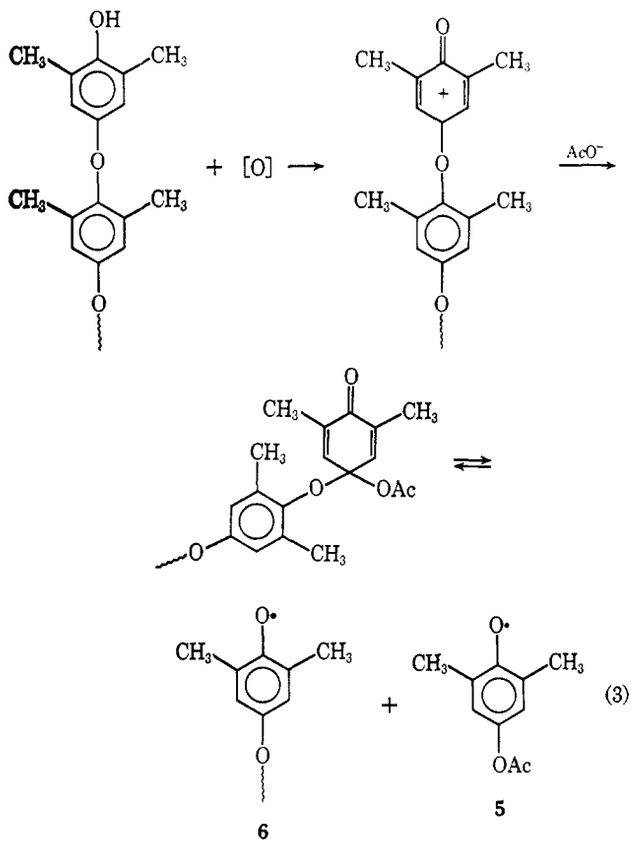
(2) H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).

(3) D. A. Bolon, *ibid.*, **32**, 1584 (1967).

(4) D. M. White, *Polymer Preprints*, **7**, 178 (1966).

(5) G. F. Endres and J. Kwiatek, *J. Polym. Sci., Part A*, **58**, 593 (1962).

polymer. When experiments similar to the one described above were carried out with these two oxidizing agents, essentially identical results were obtained. The formation of 4-acetoxyxylenol can be explained in each of these cases as the attack of acetate ion on a phenonium ion formed by the oxidation of the phenolic end group of the polymer chain, as shown in eq 3. Since



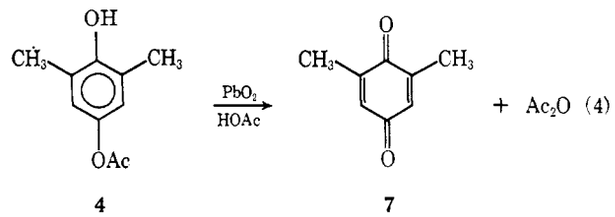
(3)

each of the products, **5** and **6**, formed in such a sequence should be capable of oxidizing phenolic end groups and the net oxidation state of the products was unchanged from that of the starting materials, it was expected that the redistribution reaction would be catalytic as in previously studied cases.[1,4] Quantitative examination of the product showed, however, that the amount of 4-acetoxyxylenol formed was only slightly greater than the number of moles of oxidizing agent used. Indeed, as the amount of oxidizing agent was increased, the yield of 4-acetoxyxylenol quickly reached a steady-state concentration suggesting that it was being formed and consumed at about equal rates. Table I shows the results obtained when lead dioxide was used to oxidize 1.0 g of polymer. Further examination of the reaction mixture showed that 2,6-dimethylbenzoquinone was being produced from the acetoxyxylenol. Since benzoquinone is in a higher oxidation state than the starting material, its formation also explains why the acetoxyxylenol formation is not catalytic.

TABLE I

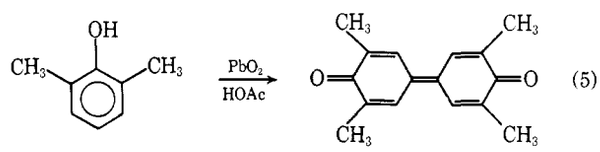
Total PbO_2, mg	4-Acetoxyxylenol, mg
200	167
400	415
600	410
800	420
1000	405

When the above reaction was repeated, except that a total of 3 g of lead dioxide were used, only 2,6-dimethylbenzoquinone was detected. In a separate experiment, acetoxyxylenol was oxidized to dimethylbenzoquinone (**7**) (eq 4).



The discovery that poly-2,6-dimethylphenylene oxide could be oxidized to 2,6-dimethyl-*p*-benzoquinone prompted an examination of other 2,6-disubstituted polyphenylene ethers. The oxidation of six different polymers using a stoichiometric amount of lead dioxide gave the *p*-benzoquinones described in Table II.

All of the polymers used in Table II were prepared by the method of Endres and Kwiatek[5] from the appropriate phenol. McNelis[6] has reported the polymerization of 2,6-dimethylphenol with lead dioxide as the oxidizing agent. If the polymer prepared in this fashion also undergoes further oxidation to benzoquinone, then it should be possible to go directly from the phenol to the benzoquinone without isolating the polymer. On attempting a reaction of 2,6-dimethylphenol with lead dioxide in acetic acid, only 3,3′,5,5′-tetramethyldiphenoquinone was produced (see eq 5).



However, when the lead dioxide oxidation of 2,6-dimethylphenol was carried out in toluene, polymerization took place readily. Acetic acid was then added and, after further oxidation, a 45% yield of 2,6-dimethylbenzoquinone was obtained.

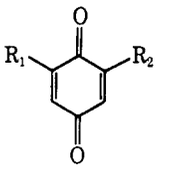
Several other solvents have been examined for the oxidation of high polymer with lead dioxide. Under identical conditions, the lead dioxide oxidation of poly-2,6-dimethylphenylene ether gave a 54% yield of dimethylbenzoquinone in acetic acid, a 41% yield in chloroacetic acid, and a 12% yield in propionic acid. A mixture of refluxing chlorobenzene and benzoic acid gave an 18% yield of 2,6-diphenylbenzoquinone from the polymer, almost identical (19%) with that obtained in acetic acid. The oxidation in the chlorobenzene–benzoic acid mixture was much faster, but this was probably largely due to the higher temperature used.

As might have been expected, phenol ethers such as 4-phenoxyphenol did not give identifiable products, no doubt because of the reactive *ortho* positions of the phenolic group. It was also shown that neither 1,4-diacetoxy-2,6-dimethylbenzene nor acetate-capped polymer react.

In addition to lead dioxide, nickel peroxide, active manganese dioxide, and manganic acetate were used in the oxidation of 4′-(2,6-dimethylphenoxy)-2′,3,5,6′-

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

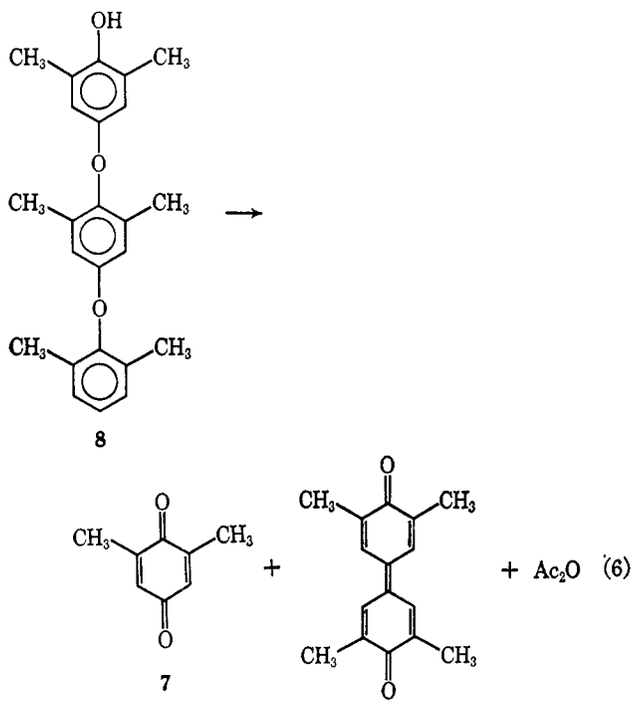
TABLE II

PREPARATION[a] OF 

R_1	R_2	Registry no.	Yield, %	Mp, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Mol wt Calcd	Mol wt Found
C_6H_5	C_6H_{11}	17603-87-1	47	100–105	81.17	6.81	81.1	7.0	266	293
i-C_3H_7	CH_3	17603-88-2	16	120–121	73.14	7.37	72.1	8.5	164	171
C_6H_5	C_6H_5	2887-97-0	19	133–135	83.06	4.64	83.0	4.7	260	265
C_6H_5	CH_3	17603-89-3	76	51–54	78.77	5.09	78.8	5.2	198	204
$C_6H_5CH_2$	CH_3	17603-81-5		*b*	79.22	5.70	79.0	5.6	212	230
CH_3	CH_3	527-61-7	62	70–72						

[a] In each case, the nmr and mass spectrum was in agreement with the assigned structure. [b] This benzoquinone is apparently a liquid and was isolated by thin layer chromatography.

tetramethyl-4-hydroxydiphenyl ether (**8**) (2,6-dimethylphenol trimer). The reaction with nickel peroxide and active manganese dioxide proceeds smoothly at acetic acid reflux temperature to produce 2 mol of 2,6-dimethylbenzoquinone, 0.5 mol of 3,3′,5,5′-tetramethyldiphenoquinone, and acetic anhydride. When xylenol trimer **8** redistributes, the terminal group appears as free xylenol (eq 6). In these experiments, the xylenol

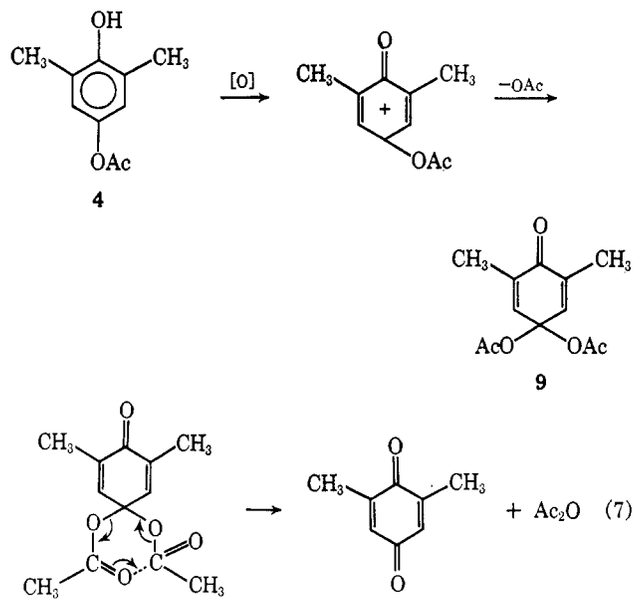


is oxidatively coupled to diphenoquinone by the manganese dioxide or nickel peroxide. Acetic anhydride formation was established by vpc and conversion into *o*-bromoacetanilide.

Manganic acetate was examined as an oxidizing agent for 2,6-xylenol trimer since it is soluble in acetic acid. The reaction of 1 g of trimer with a stoichiometric amount of manganic acetate was complete in less than 2 hr at room temperature. A 93% yield of benzoquinone was obtained.

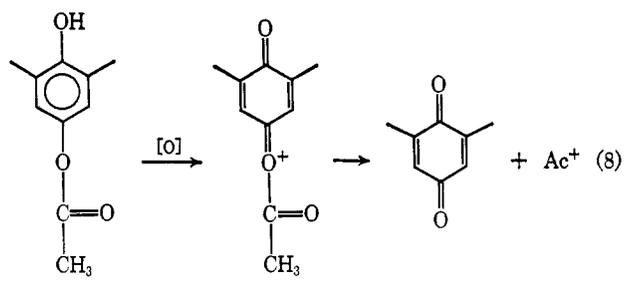
The displacement of a phenoxy group from a hydroxypolyphenylene ether either by a phenol[1-3] or by acetate almost certainly proceeds by prior formation of a cyclohexadienone derivative as in eq 3, followed by homolytic cleavage to form two phenoxy radicals.

The oxidation of hydroquinone monoacetates to the corresponding benzoquinones can be viewed as proceeding through a similar mechanism forming first the 4,4-diacetoxycyclohexadienone as shown in eq 7 for



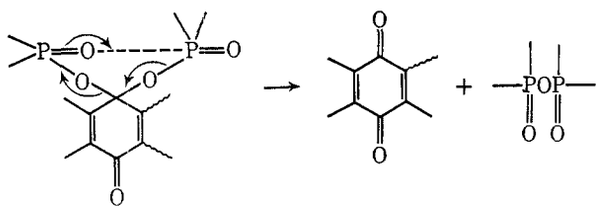
2,6-dimethyl-4-acetoxyphenol. The diacetate would then rearrange to benzoquinone and acetic anhydride.

The recent work of Thanassi and Cohen[7] has shown that 4-acetoxyphenols can be oxidized by N-bromosuccinimide in acetic acid to produce the benzoquinone and acetic anhydride. Thanassi and Cohen feel that the acetic anhydride is formed by oxidation of the phenol to a phenonium ion followed by ejection of an acylium ion which combines with acetate (eq 8). In support of this view, they cite the work of Snyder and



(7) J. W. Thanassi and L. A. Cohen, *J. Amer. Chem. Soc.*, **89**, 5733 (1967).

Rapoport[8] on quinones in cell-free oxidative phosphorylation wherein it was established that neither of the oxygens of the original quinone are exchanged during the oxidation–reduction cycle. This argument has the difficulty that conditions are certainly conceivable that would require the decomposition of a diphosphate always to proceed by a route that would



leave the original oxygen intact. At present, we feel that the formation of a cyclohexadiene such as **9** followed by immediate decomposition to benzoquinone takes into account the observations made in the present study and, in addition, the fact that, while 2,2-diacetoxy-3,5-cyclohexadienones are well known,[9] the 4,4-diacetates have never been prepared.

Experimental Section

Unless listed below, all starting materials were commercially available and used as received. The nmr spectra were determined using a Varian A-60 and the mass spectra were obtained using a General Electric MS600 monopole mass spectrometer.

2,6-Dialkylpolyphenylene Ethers.—All of the polymers used were prepared by the method of Endres and Kwiatek using the appropriate phenol. The phenols in turn were prepared by conventional synthetic methods.

Oxidation of 2,6-Dimethylpolyphenylene Ether with Lead Dioxide. A.—To a refluxing suspension of 1 g of 2,6-dimethylpolyphenylene ether (μ = 0.52) in 20 ml of acetic acid was added 300 mg of lead dioxide. After 30 min, the brown color of the lead dioxide had disappeared, and an additional 700 mg of lead dioxide was added. The mixture was refluxed for 1 hr and cooled to room temperature, and 50 ml of benzene was added. The benzene solution was washed several times with water, dried over magnesium sulfate, and distilled. A total of 300 mg of 4-acetoxy-2,6-dimethylphenol, mp 93–95° (lit.[10] mp 94–95°), was obtained. The nmr spectrum showed the expected peaks, and the mass spectrum had prominent peaks at 180 (M) and 138 (M − 42) with the base peak at 43.

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; mol wt, 180. Found: C, 66.4; H, 6.7; mol wt, 184.

B.—The above experiment was repeated using 3.0 g of lead dioxide. After drying the benzene extract, the solvent was removed and the residue was sublimed at 20 mm. The 2,6-dimethylbenzoquinone was recrystallized from benzene, mp 70–72° (lit.[11] mp 71–72°). The nmr and infrared spectrum were in agreement with those of authentic 2,6-dimethylbenzoquinone. The parent ion in the mass spectrum was 136, and the fragmentation agreed with the cracking pattern of 1,4-benzoquinones.

General Method of Oxidizing Polymers with Lead Dioxide.—A solution of 24 g of the polymer in 200 ml of toluene was prepared by refluxing the toluene. To the hot solution, 100 ml of glacial acetic acid was slowly added. A total of 40 g of lead dioxide was added in small portions over about a 3-hr period. The reaction mixture was cooled and poured into 600 ml of water, the toluene phase was separated, and the aqueous phase was extracted with two additional 200-ml portions of toluene. After approximately 400 ml of the toluene was distilled, the remainder was poured into 500 ml of methanol to precipitate any unreacted polymer. After filtering, the product was isolated by distillation and purified by recrystallization from *n*-hexane. Table II gives the analytical data for the 1,4-benzoquinones prepared.

Direct Polymer Preparation and Oxidation.—After preparing a solution of 10 g of 2-methyl-6-phenylphenol in 50 ml of toluene, a total of 32 g of lead dioxide was slowly added. An exothermic reaction took place and, after the mixture had cooled to room temperature, 50 ml of glacial acetic acid was added. The reaction mixture was refluxed for 12 hr and poured into 200 ml of water, and the toluene layer was removed. After extracting the aqueous phase with two 50-ml portions of toluene, the extracts were combined, dried over magnesium sulfate, and distilled to yield 5.1 g (45%) of 2-methyl-6-phenylbenzoquinone, bp 103° (0.1 mm), mp 51–54°.

Preparation of Manganese(III) Acetate, $Mn(OAc)_3 \cdot 2H_2O$.—Manganic acetate was prepared by adding 98 g of $Mn(OAc)_2 \cdot 4H_2O$ (0.4 mol) to 500 ml of glacial acetic acid. The mixture was heated to reflux and $KMnO_4$ addition was started. A total of 16 g of permanganate was added to the refluxing mixture in *ca.* 1-g portions. When the addition of the permanganate was complete (20–30 min), the solution was refluxed for an additional 25 min and cooled to 15° with an ice bath, and 85 ml of water was added. On stirring overnight, the $Mn(OAc)_3 \cdot 2H_2O$ crystallized. After filtering, the solid was washed with 100 ml of cold glacial acetic acid and air dried. The product was obtained as a red-brown powder in 90–95% yield (120–125 g). The manganese(III) content was determined by iodine or ferrous sulfate titration as 19.5–20.2% (theory 20.5%).

Oxidation of 4′-(2,6-Dimethylphenoxy)-2′,6′,3,5-tetramethyl-4-hydroxydiphenyl Ether (2,6-Xylenol Trimer) with Manganic Acetate.—A solution of 1.0 g of 2,6-xylenol trimer and 4.5 g of $Mn(OAc)_3 \cdot 2H_2O$ in 25 ml of glacial acetic acid was stirred at 30°. After 2 hr the dark color of the manganic acetate had been replaced by the pale yellow of 2,6-dimethylbenzoquinone. The reaction mixture was filtered to remove the precipitated manganous acetate and poured into 50 ml of benzene. After extracting the acetic acid by washing the solution four times with 20-ml portions of water, it was dried and the benzene was removed on a rotary evaporator. The 2,6-dimethylbenzoquinone was dissolved in 50 ml of *n*-hexane and filtered to remove the 3,3′,5,5′-tetramethyldiphenoquinone. The yield of crude 2,6-dimethylbenzoquinone was 700 mg (93%) and of diphenoquinone 188 mg (57%).

2′,3,5,6′-Tetramethyl-4-hydroxydiphenyl ether (1) and 4′-(2,6-dimethylphenoxy)-2′,3,5,6-tetramethyl-4-hydroxydiphenyl ether (8) were prepared by the redistibution of 2,6-xylenol with 2,6-xylenol polymer according to the method of White.[4]

Oxidation of 8 with Nickel Peroxide.—Nickel peroxide was prepared according to Nakagawa, *et al.*,[12] and an oxidation of xylenol trimer **8** was carried out by adding 2.78 g of nickel peroxide to a solution of 1.0 g of trimer in 25 ml of glacial acetic acid. After the mixture was refluxed for 2 hr, black nickel peroxide was replaced by a pale green solid. After filtering off the solid, it was washed with 100 ml of benzene; the benzene was added to the acetic acid solution; and the mixture was extracted three times with 25-ml portions of water. After drying over magnesium sulfate, the benzene was removed on a rotary evaporator, and the product was sublimed at 20 mm. The yield of crude 2,6-dimethylbenzoquinone was 186 mg (25%).

Manganese Dioxide.—The manganese dioxide was prepared by dissolving 20 g of potassium permanganate, 15 g of sodium bicarbonate, and 20 g of potassium carbonate in 400 ml of water. On the addition of 100 ml of 95% ethanol, the temperature rose to 50°. The mixture was vigorously stirred until the temperature had dropped to 25°, at which point the manganese dioxide was filtered off. After slurrying in a solution of 20 g of potassium carbonate in 400 ml of water, the product was again filtered, washed with 400 ml of water, and dried by pulling air through the filter cake for 10 min. The filter cake was then powdered and dried at 110° for 3 hr.

Oxidation of 8 with Manganese Dioxide.—Manganese dioxide (1.5 g) was added to a solution of 1.0 g of xylenol trimer **8** in 25 ml of glacial acetic acid. After 2 hr at reflux, the manganese dioxide had dissolved and the work-up was as described for nickel peroxide. The yield of crude 2,6-dimethylbenzoquinone was 718 mg (96%).

(8) C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, **89**, 1269 (1967).
(9) G. Billek, J. Swoboda, and F. Wessely, *Tetrahedron*, **18**, 909 (1962).
(10) E. Zbiral, F. Wessely, and E. Lahrmann, *Monatsh. Chem.*, **91**, 331 (1960).
(11) G. R. Bacon and D. J. Munro, *J. Chem. Soc.*, 1339 (1960).
(12) K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).

Oxidation of 4-Acetoxy-2,6-dimethylphenol (4) with Lead Dioxide.—A solution of 600 mg of **4** in 10 ml of glacial acetic acid was heated with 700 mg of lead dioxide until a pale yellow homogeneous solution was obtained. Vpc analysis showed essentially quantitative conversion into 2,6-dimethylbenzoquinone.

Acknowledgments.—The authors wish to thank Dr. Hans-Dieter Becker for a gift of nickel peroxide and Dr. John B. Bush, Jr., for a gift of manganese dioxide.

The Synthesis of 2-Methyl-3-vinyl-1,4-naphthoquinones[1]

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Chlorobiumquinone, previously isolated from *Chlorobium thiosulfatophilum* and characterized as a 2-methyl-3-vinylmultiprenyl-1,4-naphthoquinone, is unique among natural multiprenylquinones in being a vinyl- rather than an allylquinone. Various approaches to the synthesis of 2-methyl-3-vinyl-1,4-naphthoquinones have been studied, and two general syntheses have been developed, both constructing the substituted vinyl side chain *via* the Wittig reaction. A primary requirement for both methods was a protecting protocol for the 1,4-oxygen functions which would be inert to the ylide yet would allow generation of the quinone without destruction of the vinyl group. Such functionality was provided by the 1-pivalate ester–4-methyl ether. These groups do not react with the ylide, and removal of the ester with lithium aluminum hydride and oxidation of the 1-hydroxy-4-methoxy compound with ferric chloride gave quinone while leaving the vinyl side chain intact. One synthesis proceeded *via* 3-chloromethyl-4-methoxy-2-methyl-1-naphthol pivalate which was converted into its triphenylphosphonium salt and thence to vinyl derivative by generation of the naphthalenic ylide and reaction with a carbonyl component. The other synthesis utilized the 3-naphthaldehyde, prepared from the chloromethyl compound and potassium 2-propanenitronate, in reaction with the appropriate ylide. To avoid isomers, some secondary ylides were prepared by alkylation of primary ylides. The relative advantages and disadvantages of both methods are considered. The separate, isomeric vinyl compounds were obtained, and *cis* and *trans* stereochemical assignments were made by relating their nmr absorptions to those of unambiguous synthetic models. Various vinyl substitution patterns can be easily distinguished from the ultraviolet absorption of the resulting 2-methyl-3-vinyl-1,4-naphthoquinones.

We have reported the isolation and structure determination of chlorobiumquinone (I), a novel 2-methyl-3-vinylmultiprenylnaphthoquinone isolated from the anaerobic, photosynthetic sulfur bacterium, *Chlorobium thiosulfatophilum*, strain PM.[5,6] Chlorobiumquinone is unique[7] among the menaquinones, ubiquinones, and plastoquinones found in nature in that it has a double bond conjugated with the ring moiety and the side chain contains one carbon less than the multiples of five found in all other natural multiprenylquinones. Hence, chlorobiumquinone may be visualized as menaquinone-7 (II),[8] which also occurs in *C. thiosulfatophilum*, minus the 1′-methylene, rather than as a double-bond isomer.

Our interest in the chemistry of chlorobiumquinone, especially as it relates to a possible role for the quinone in photosynthesis and oxidative phosphorylation in *C. thiosulfatophilum*[9] and the fact that vinylquinones are a little studied class of compounds (except for their use in polymerizations) have led us to develop general methods for the synthesis of vinylnaphthoquinones, which is the subject of this paper.

The syntheses reported in the literature have been designed for the preparation of vinylhydroquinone diesters or diethers with vinyl moieties bearing no substitutents, the object being the preparation of monomers from which a redox polymer might be obtained.[10]

Most of the vinylhydroquinones and vinylhydroquinone derivatives have been prepared by (1) synthesis and decarboxylation of a 2,5-dihydroxy cinnamic acid, (2) reduction of the ketone moiety of an acetylhydroquinone diacetate and dehydration of the resulting alcohol, or (3) metalation or formation of the Grignard reagent of a hydroquinone diether followed by reaction with ethylene oxide or acetaldehyde and dehydration of the resulting alcohol. The reverse of 3, formation of the diether of a 2,5-dihydroxybenzaldehyde followed by reaction with methyllithium or a Grignard reagent, is also known. In only one case did the vinyl group contain a substituent and that was an α-methyl group.[11]

Several 2-hydroxy-3-(1-alkenyl)-1,4-naphthoquinones (IV) have been prepared by heating 2-hydroxy-1,4-naphthoquinone (III) with a variety of straight-chain, aliphatic aldehydes and hydrochloric acid in acetic acid.[12] Under these conditions 1,4-naphthoquinones (V) do not yield (1-alkenyl)-1,4-naphthoquinones (VI) but give instead pigments of the anthocyanidin type,[13] VII. By moderating the conditions, however, 2-methyl-1,4-naphthoquinone (VIII) was successfully condensed with acetaldehyde and hydrogen bromide to afford 2-methyl-3-(1-bromoethyl)-1,4-naphthoquinone

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(2) National Institutes of Health Predoctoral Fellow.

(3) Facultad de Farmacia y Bioquimica, Universidad de Buenos Aires, Buenos Aires, Argentina.

(4) National Science Foundation Undergraduate Research Participant.

(5) B. Frydman and H. Rapoport, *J. Amer. Chem. Soc.*, **85**, 823 (1963); menaquinone-7 also was isolated.

(6) R. Powls and E. R. Redfearn [*Biochem. J.*, **102**, 3c (1967)] also have isolated chlorobiumquinone and menaquinone-7 from *C. thiosulfatophilum*.

(7) A quinone detected spectrophotometrically in *Sarcina lutea* also may be of this type: D. H. L. Bishop, K. P. Pandya, and H. K. King, *ibid.*, **83**, 606 (1962).

(8) IUPAC–IUB Commission on Biochemical Nomenclature Tentative Rules, *Arch. Biochem. Biophys.*, **118**, 505 (1967).

(9) I. Chmielewska [*Biochem. Biophys. Acta*, **39**, 170 (1960)] has postulated the intermediacy of a vinylquinone in the mechanism of the quinone's role in oxidative phosphorylation.

(10) For a review of the synthesis of vinylhydroquinones, see H. C. Cassidy and K. A. Kun, "Polymer Reviews," Vol. 11, Interscience Publishers, New York, N. Y., 1965, Chapter 2.

(11) J. M. Bruce and P. Knowles, *J. Chem. Soc., C*, 1627 (1966).

(12) S. C. Hooker, *J. Amer. Chem. Soc.*, **58**, 1163, 1168 (1936).

(13) M. Fieser and L. F. Fieser, *ibid.*, **63**, 1572 (1941).