by Markovski, Romanenko, and Kirsanov.[6] Such homogeneous reactions of (dialkylamino)dichlorophosphines with $(Me_3Si)_2Hg$ in hydrocarbon solvents such as pentane and benzene could form tetrakis(dialkylamino)cyclotetraphosphines according to the following equation:

$$4R_2NPCl_2 + 4(Me_3Si)_2Hg \rightarrow (R_2N)_4P_4 + 4Hg + 8Me_3SiCl \quad (3)$$

These reactions proceed under mild conditions and therefore can be followed readily by phosphorus-31 NMR spectroscopy with the results indicated in Table I. The use of this milder reagent suppressed diethylamino redistribution in the dehalogenation of Et_2NPCl_2 so that the major product was the cyclotetraphosphine $(Et_2N)_4P_4$ as indicated by the ion $(Et_2N)_4P_4^+$ as the highest m/e ion in the mass spectrum of the crude product. However, pure $(Et_2N)_4P_4$ could not be crystallized or sublimed from this crude product. Reaction of Me_2NPCl_2 with $(Me_3Si)_2Hg$, however, still resulted only in redistribution of the dimethylamino groups, but the major product was $(Me_2N)_2PCl$ rather than the $(Me_2N)_3P$ formed as the major product from Me_2NPCl_2 and magnesium. These observations support the greater extent of dialkylamino redistribution on phosphorus with smaller dialkylamino groups but also indicate a lesser extent of dialkylamino redistribution with the homogeneous reagent $(Me_3Si)_2Hg$ than the heterogeneous reagent magnesium.

The availability of relatively large quantities of $(i\text{-}Pr_2N)_4P_4$ from the reaction of $i\text{-}Pr_2NPCl_2$ with magnesium prompted a study of its chemical reactivity. In most cases the steric hindrance of the diisopropylamino groups in $(i\text{-}Pr_2N)_4P_4$ reduced its chemical reactivity relative to that of the relatively well-known cyclotetraphosphines having alkyl or aryl substituents. Thus $(i\text{-}Pr_2N)_4P_4$ is apparently complete stable toward atmospheric oxygen under ambient conditions. It appears to be unreactive toward metal carbonyls under conditions where Et_4P_4 and Ph_4P_4 give metal carbonyl complexes.[12-15] Furthermore, $(i\text{-}Pr_2N)_4P_4$ does not form any soluble anionic derivatives upon treatment with excess metallic potassium in boiling tetrahydrofuran for several days in contrast to cyclotetraphosphines such as Et_4P_4 and Ph_4P_4 which form interesting and preparatively useful anionic derivatives.[16-19] The dialkylamino groups in $(i\text{-}Pr_2N)_4P_4$ are not solvolyzed by water or by alcohols under conditions where $(i\text{-}Pr_2N)_2PH$ reacts with alcohols to form the corresponding $(i\text{-}Pr_2N)$-(RO)PH derivatives.[20]

The major exception to the low reactivity of $(i\text{-}Pr_2N)_4P_4$ occurs upon treatment with halogens and hydrogen halides. We hoped that hydrogen chloride under mild conditions would cleave the exocyclic phosphorus–nitrogen bonds in $(i\text{-}Pr_2N)_4P_4$ to form the interesting tetrachlorocyclotetraphosphine, P_4Cl_4. However, the major products from the treatment of $(i\text{-}Pr_2N)_4P_4$ with hydrogen chloride at 0 °C are $i\text{-}Pr_2NPCl_2$ and $(i\text{-}Pr_2N)_2P_2Cl_2$ indicating that the P_4 ring in $(i\text{-}Pr_2N)_4P_4$ is more readily cleaved than the exocyclic phosphorus–nitrogen bonds. Halogens (e.g., bromine and iodine) also readily cleave the P_4 ring in $(i\text{-}Pr_2N)_4P_4$ forming the corresponding $i\text{-}Pr_2NPX_2$ derivative as the major product.

The NMR spectra of the $(R_2N)_4P_4$ derivatives (I, R = isopropyl and cyclohexyl) are relatively simple indicating the expected equivalence on the NMR time scale of all four phosphorus atoms and all eight alkyl groups. The NMR spectra of solutions of the $(i\text{-}Pr_2N)_2P_2X_2$ derivatives (II, X = Cl and Br) indicate only one type of phosphorus atom but several types of isopropyl groups. Since $(i\text{-}Pr_2N)_2P_2X_2$ derivatives have two asymmetric phosphorus atoms, meso and *dl* diastereomers (IIa and IIb, respectively) are possible as has been reported for $(Me_3C)_2P_2Cl_2$.[21] The complexity of the carbon-13 NMR spectra of both $(i\text{-}Pr_2N)_2P_2X_2$ derivatives (X = Cl and Br) may be an indication of different isopropyl groups in the meso and *dl* isomers with the possibility on the NMR time scale of one type of isopropyl group in the meso isomer but two types of isopropyl groups in the less symmetrical *dl* isomer. However, it is interesting that the two diastereomers of $(Me_3C)_2P_2Cl_2$ have phosphorus-31 resonances differing by ~7 ppm,[21] whereas only a single phosphorus NMR resonance is found in each $(i\text{-}Pr_2N)_2P_2X_2$ derivative. Possibly phosphorus-31 NMR is less sensitive than carbon-13 NMR to the subtle changes of environment in the meso and *dl* diastereomers of the $(i\text{-}Pr_2N)_2P_2X_2$ derivatives.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grants AFOSR-81-0051 and AFOSR-84-0050.

(12) Ang, H. G.; Shannon, J. S.; West, B. O. *Chem. Commun.* **1965**, 10.
(13) Ang, H. G.; West, B. O. *Aust. J. Chem.* **1967**, *20*, 1133.
(14) Forster, A.; Cundy, C. S.; Green, M.; Stone, F. G. A. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 233.
(15) Cundy, C. S.; Green, M.; Stone, F. G. A.; Taunton-Rigby, A. *J. Chem. Soc. A* **1968**, 1776.
(16) Issleib, K.; Krech, K. *Chem. Ber.* **1965**, *98*, 2545.
(17) Issleib, K.; Fluck, E. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 587.
(18) Baudler, M.; Koch, D.; Tolls, E.; Diedrich, K. M.; Kloth, B. *Z. Anorg. Allg. Chem.* **1976**, *420*, 146.
(19) Baudler, M.; Gruner, Ch.; Fürstenberg, G.; Kloth, B.; Saykowski, F.; Özer, U. *Z. Anorg. Allg. Chem.* **1978**, *446*, 169.
(20) King, R. B.; Sundaram, P. M. *J. Org. Chem.* **1984**, *49*, 1784.
(21) Baudler, M.; Hellmann, J.; Hahn, J. *Z. Anorg. Allg. Chem.* **1982**, *489*, 11.

Selective Indirect Oxidation of Phenol to Hydroquinone and Catechol

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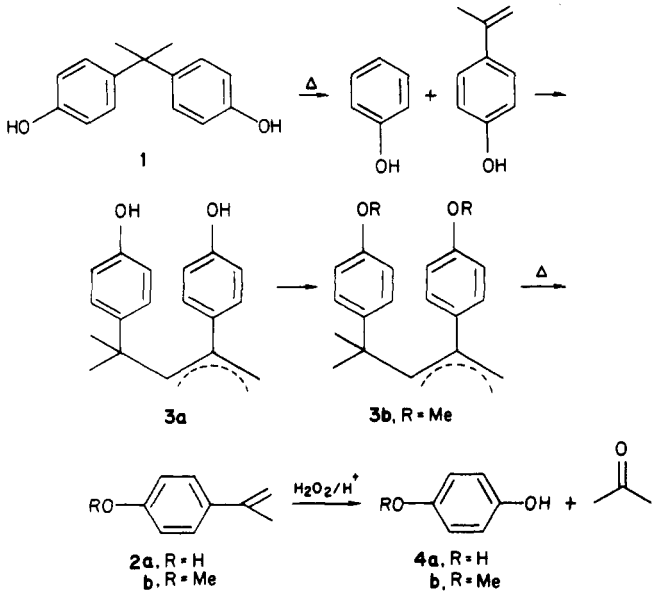
Received December 4, 1984

The introduction of a hydroxyl function into phenol to give hydroquinone and catechol can be achieved in high yields by the reaction of hydrogen peroxide with alkenylphenols. These alkenylphenols are obtained by thermolysis of bisphenol A, alkylation of phenol with cyclopentadiene followed by isomerization, and alkylation of phenol with mesityl oxide followed by thermolysis to give 4-isopropenylphenol, 2- and 4-(cyclopenten-1-yl)phenol, and 2,2,4-trimethyl-1,2-chromene, respectively.

Introduction of hydroxyl functions into aromatic hydrocarbons by known oxidation methods is often burdened by low conversion, byproduct formation, and difficult separation of reaction products. For instance, in the in-

0022-3263/85/1950-1722$01.50/0

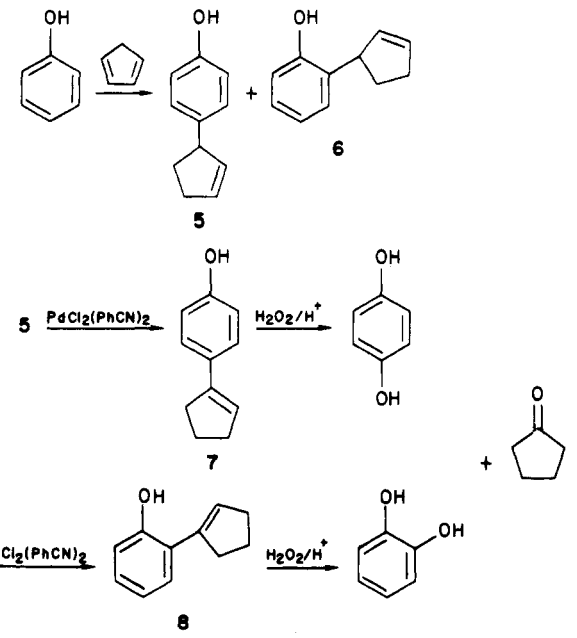
Scheme I



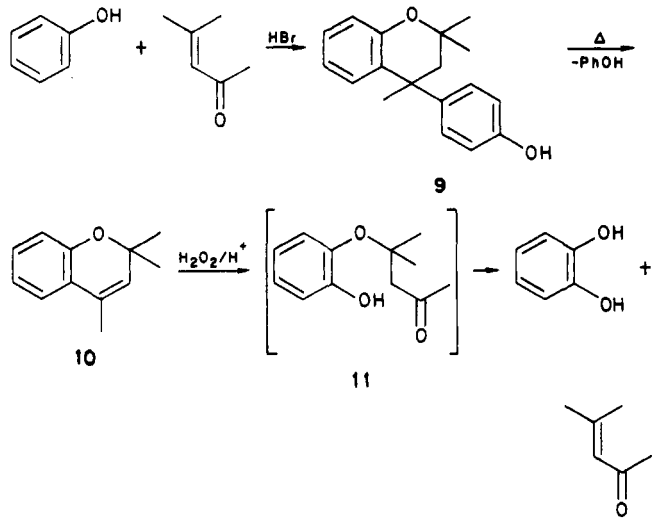
dustrial production of phenol,[1] the air oxidation of cumene to cumyl hydroperoxide is generally maintained below 40% conversion to minimize the decomposition of the hydroperoxide. In addition, acetone is formed as a coproduct with phenol in the acid rearrangement of the hydroperoxide. Similar autoxidation processes of diisopropylbenzenes[2] to prepare hydroquinone, resorcinol, and catechol are even more troublesome due to more byproduct formation and difficult separation of pure product from the reaction mixtures. Direct hydroxylation of phenol or anisole with hydrogen peroxide by either a cationic[3] or a free radical[4] process is not satisfactory since mixtures of hydroquinone and catechol are produced.

We describe here a method to introduce selectively a hydroxyl function into phenols to form hydroquinones and catechols. In the two-step process an alkenyl group is first introduced at a specific position in phenol or anisole, and then the vinylic function is oxidized with hydrogen peroxide. This method of oxidation has been previously indicated by Kharash.[5] In both steps the presence of the initial hydroxyl or ether function presented the advantage of directing the site of alkylation and enhancing the rates of the alkylation and the oxidation reactions. For example, bisphenol A, [4,4'-(1-methylethylidene)bisphenol], the reaction product of acetone with phenol, acts as a precursor for 4-isopropenylphenol (Scheme I). Dissociation of bisphenol A occurs by heating at 240 °C under reduced pressure and in the presence of a catalytic amount of sodium hydroxide.[6] In this process 4-isopropenylphenol is formed, which subsequently dimerizes on standing to form the stable dimers **3a**,[7] upon removal of the phenol by vacuum distillation. The dimers **3a** can be methylated

Scheme II



Scheme III



with dimethyl sulfate[8] to give high yields of the phenol ethers **3b**.[9] Pyrolysis of the dimers **3a** and **3b** produces the monomeric olefins **2a** and **2b**. The acid-catalyzed oxidation of these olefins with 30% hydrogen peroxide at room temperature readily yields hydroquinone and the hydroquinone monomethyl ether in high yield (91–95%), whereas the oxidation of alkenylbenzenes is much less efficient.[5] In contrast to autoxidation processes, complete and rapid conversion of the starting material is achieved by using this method. In addition, hydroquinone monoalkyl ether is prepared selectively, whereas alkylation of hydroquinone leads to a mixture of mono and dialkyl ether.[10] Recycling of acetone, the coproduct in the oxidation reaction, and phenol, the coproduct in the dissociation reaction, to synthesize the starting material, bisphenol A, eliminates any waste or disposal problems.

The introduction of a hydroxyl group in the phenol can also be accomplished from 4-(cyclopenten-1-yl)phenol (**7**). The alkylation of phenol with cyclopentadiene in the

(1) (a) Yen, Y. C. "Phenol", Chemical Economics Programme, Stanford Research Institute, 1967. (b) M. Sittig, "Alcohols, Polyols and Phenols Manufacture and Derivatives" (Noyes, 1968), p 96.
(2) (a) Brit. Pat. 1 423 378, 1976 (to Sumitomo Chem. Co.). (b) A. H. Olzinger, Chem. *Eng.* **1975**, 50.
(3) (a) Brit. Pat. 1 521 400, 1978 (to Rhône-Poulenc). (b) U.S. Pat. 4 045 496, 1977 (to Bayer). (c) U.S. Pat. 4 078 006, 1978 (to Ube Industries).
(4) Sosnovsky, G.; Rawlingson, D. J. "Organic Peroxides", Swern, D., Ed.; Wiley-Interscience: New York, 1970; Vol. 2, p 269.
(5) (a) Kharasch, M.; Fono, A.; Nudenberg, W. *J. Org. Chem.* **1950**, *15*, 748. (b) Kharasch, M.; Fono, A.; Nudenberg, W.; Poshkus, A. C. *ibid.* **1950**, *15*, 775.
(6) Schnell, H.; Krimm, H. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 373.
(7) U.S. Pat. 4 054 611, 1977 (to Mitsui-Toatsu Chemicals).
(8) McKillop, A.; Fiaud, J. C.; Hug, R. P. *Tetrahedron* **1974**, *30*, 1379.
(9) Ger. Pat. 25 08 512, 1976 (to Bayer).
(10) (a) Brit. Pat. 1 277 186, 1972 (to Rhône-Poulenc). (b) U.S. Pat. 3 274 260, 1966 (to Universal Oil Products).

presence of phosphoric acid[11] (Scheme II) yields 4-(cyclopenten-2-yl)phenol (**5**) and 2-(cyclopenten-2-yl)phenol (**6**) in a 88 to 12 ratio and an overall yield of 83.2%. The two isomers can be separated by distillation. The isomerization of **5** to **7** was reported[11] to take place in poor yield but was achieved in the present work in almost quantitative yield by using dichlorobis(benzonitrile)palladium-(II)[12] as catalyst in refluxing benzene. Oxidation of **7** with 30% hydrogen peroxide in the presence of a trace of hydrochloric acid afforded hydroquinone in 91.6% yield. The results for alkylated hydroquinones have been previously published.[13] In the process cyclopentanone is formed as a coproduct.

Similarly, **6** can be isomerized to **8** and subsequently oxidized to produce catechol. An additional new method (Scheme III) to introduce selectively a hydroxyl function ortho to another hydroxyl group in a benzene ring can be achieved from 2,2,4-trimethyl-1,2-chromene (**10**). The reaction of phenol with mesityl oxide in the presence of hydrogen bromide produces 2,2,4-trimethyl-4-(4-hydroxyphenyl)chroman (**9**) in good yield. This reaction previously reported[14] was catalyzed at a much lower rate by hydrogen chloride. Analysis of the reaction mixture show that bisphenol A is formed as a byproduct. The acid-catalyzed thermal dissociation of **9** yields **10** which, upon oxidation with hydrogen peroxide, leads directly to catechol. This reaction proceeds via the isolable but unstable intermediate **11**. Mesityl oxide is regenerable in the oxidation step and can be recycled.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian T-60 spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 297 spectrophotometer. Vapor-phase chromatography (GC) was carried out on a Hewlett-Packard Model 7620A chromatograph equipped with dual 3% SP-2100 columns and flame ionization detector. Melting points and boiling points are uncorrected. HPLC analyses were obtained on a Water's liquid chromatograph (6000A) equipped with a μ-Porasil column using acetonitrile (14%) and ethylene chloride (86%) as eluting solvents.

Thermal Dissociation of 1. A 100-mL, single-necked, round-bottomed flask fitted with an 8-in. distillation head (Ace Glass, 5133-10) and a thermometer was connected to a 100-mL receiving flask by an adapter (Ace Glass, 5192-12). Pyrolysis flask was charged with **1** (69.0 g, 0.30 mol), sodium hydroxide (0.08 g), and a magnetic stirrer. The pressure inside the system was reduced to 18 mm by a water aspirator. The flask was then heated in a silicone oil bath started at 200 °C. The steady distillation of dissociation products was maintained by slowly increasing the bath temperature from 200 °C to 280 °C. The amount of product collected between 75 °C to 135 °C was 64.7 g (93.8%). An HPLC analysis indicated that the combined yield of phenol and **2a** was 95% in the product mixture.

Dimerization of 2a: Fractionation of Phenol from the Dissociation Product. Fractionation of phenol was performed immediately after pyrolysis simply by replacing the pyrolysis flask with the receiving flask containing the product in the previous experiment. During fractionation, the oil bath temperature was maintained between 135 °C and 160 °C. Fractionation afforded 27.0 g of phenol, bp 80–88 °C (18 mm), which was 96.0% pure by GLC analysis (therefore 94.0% yield). The yellow residue (37.0 g) was found to have the following composition based on HPLC analysis: **3a** (84%), **2a** (12%), and **1** (4%).

4-Isopropenylphenol (2a). The yellow residual oil (37.0 g) from previous experiment was repyrolyzed with 0.08 g of sodium hydroxide as for **1**. Pyrolysis yielded 36.1 g of a waxy solid. GC analysis found that the pyrolysis product contained 92% **2a**, 7% phenol, and traces of **3a**.

Further purification of **2a** was done by an aqueous washing. Pyrolysis product (36.1 g) was dissolved in 100 mL of ether, and the solution was added to 600 mL of deionized water. The mixture was stirred while a rapid stream of nitrogen was bubbled through the solution to evaporate ether at room temperature. After 55 min of stirring, a white precipitate formed and was collected by suction filtration. The precipitate (31.5 g, mp 75–80 °C) was found to consist of 96.5% of **2a**. An analytical sample of **2a** was obtained by recrystallization of the precipitate from ethylene chloride solution: mp 83–85 °C (lit.[6] mp 85 °C); ^{1}H NMR (acetone-d_6) δ 8.48 (s, 1), 7.35 (d, 2), 6.75 (d, 2), 5.10 (m, 1), 4.75 (m, 1), 2.04 (m, 3).

Oxidation of 2a with 30% H_2O_2. 2a (4.1 g, 30 mmol) was dissolved in 35 mL of isopropyl alcohol and was stirred in a 100-mL, three-necked flask equipped with a thermometer and a condenser. To the solution was added 3.60 g (35.3 mmol) of 30% hydrogen peroxide in one portion, followed by 0.1 g of concentrated hydrochloric acid. The temperature of the solution was allowed to rise from 20 °C to 40 °C over a 35-min period until no **2a** could be detected by ^{1}H NMR. The solution was hydrogenated with Pd/C (10% on carbon, 0.10 g) in a Parr shaker at 50 psi for an hour. After the catalyst was filtered off, the solution was concentrated on a rotary evaporator to give 3.7 g of solid product. Recrystallization of the product from hot chlorobenzene afforded 3.02 g (91%, mp 168–172 °C) of hydroquinone.

Preparation of 3b from 1. The methylation was essentially that of McKillop's procedure.[8] A solution of 42.0 g of crude dimers (obtained similarly by pyrolyzing 70.0 g of **1** and removal of phenol) in 200 mL of methylene chloride was poured into an aqueous solution (200 mL) containing 50 g (1.25 mol) of NaOH and 0.70 g of benzyltrimethylammonium chloride. To this two-phase solution was added dimethyl sulfate (70.0 g, 0.55 mol) dropwise through an addition funnel over a 30-min period, the reaction mixture was maintained at room temperature by cooling. After addition, the reaction mixture was allowed to stir for an additional 17 h at room temperature. The organic layer was separated and the aqueous layer was extracted twice with 50-mL portions of methylene chloride. The combined extracts after washing with ammonium hydroxide solution were finally washed with brine water (100 mL) and dried ($MgSO_4$). Stripping of solvent yielded 43.2 g of residual oil. HPLC analysis of product showed the following composition: **3b** (80%), **2b** (15%), and the rest was the methylated product of **1**.

Preparation of 2b from 3b. The apparatus assembly and procedure for the acid-catalyzed pyrolysis of **3b** were identical with those used for **1**. Pyrolysis of dimer **3b** (43.2 g) was performed at 180–220 °C (25 mm) with 0.15 g of toluenesulfonic acid as catalyst. The fraction collected between 125 °C and 135 °C (36.3 g, 81% based on **1**) was found to be pure **2b**: mp 34–35 °C (lit.[9] mp 35 °C); ^{1}H NMR δ 7.22 (d, 2) 6.65 (d, 2), 5.13 (m, 1), 4.83 (m, 1), 3.70 (s, 3), 2.08 (m, 3).

Oxidation of 2b with 30% H_2O_2. Hydrochloric acid (38%, 2.0 g) was added dropwise to a solution of **2b** (36.3 g, 0.24 mol) and 30% H_2O_2 (33.1 g, 0.20 mol) in 350 mL of isopropyl alcohol. The temperature of solution was allowed to elevate slowly from room temperature to 60 °C over a 1-h period. The solution was then cooled in an ice bath and the residual H_2O_2 was reduced with a 10% sodium bisulfite solution by dropwise addition with stirring until no sign of active oxygen was detected. The reaction solution was filtered and concentrated on a rotoevaporator. The residue was extracted with ether (200 mL) and separated from inorganic salt. After drying ($MgSO_4$), the solvent was evaporated to give 33.8 g of product. It was vacuum distilled and *p*-methoxyphenol was collected at 80–85 °C (0.15mm) (28.1 g; 76.0% based on **1**): ^{1}H NMR (acetone-d_6) δ 6.72 (s, 4), 3.65 (s, 3).

Alkylation of Phenol with Cyclopentadiene. To phenol (94.0 g, 1 mol) in 100 mL of toluene was added 85% H_3PO_4 (115.4 g, 1 mol). To the resulting mixture under stirring at room temperature was added freshly distilled cyclopentadiene (33.0 g, 0.5 mol) in 25 mL of toluene over a period of 2 h. The reaction was monitored by GC analysis and in 2 h the reaction was complete. The reaction mixture was neutralized with 160.0 g of anhydrous Na_2CO_3 and filtered from the precipitate, and the precipitate was further washed with excess toluene. The filtered toluene solutions

(11) Bader, A. *J. Am. Chem. Soc.* **1953**, *75*, 5967.
(12) Golborn, P.; Scheinman, F. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2870.
(13) Rao, D. V.; Stuber, F. A. *Tetrahedron Lett.* **1981**, *22*, 2337.
(14) Baker, W.; Floyd, A. J.; McOmie, J. F. W.; Pope, G.; Weaving, A. S.; Wild, J. H. *J. Chem. Soc.* **1956**, 2010.

were combined and evaporated in vacuo to give a liquid in which the ratio of **5** to **6** was found to be 88/12 with an overall yield of 83.2% (based on cyclopentadiene). It was vacuum distilled and after removal of phenol (49.3 g), two fractions were collected at 90–105 °C (0.1mm) (48.7 g). The first fraction by GC was found to contain **5** and **6** in 75/25 ratio. The second fraction solidified and was found to be pure **5**. It was washed with ligroin and filtered: mp 64–66 °C (lit.[11] mp 64–65 °C); ^{1}H NMR ($CDCl_3$) δ 3.50–4.00 [br m, 1, C(1)-H], 5.58–6.05 [m, 2, C(2)-H-C(3)-H].

Purification of 6. The first fraction from previous experiment was vacuum distilled twice and **6** was collected at 64–66 °C (0.05mm) (94.3% pure by GC): ^{1}H NMR ($CDCl_3$) δ 3.56–4.30 [br m, 1, C(1)-H], 5.60–6.10 [m, 2, C(2)-H-C(3)-H].

Isomerization of 5 to 7. To **5** (30.0 g, 0.1875 mol) in 300 mL of dry benzene was added $PdCl_2(PhCN)_2$ (1.2 g), and the solution was refluxed. In 1 h the isomerization was complete (followed by NMR; disappearance of multiplet at δ 3.50–4.00 corresponding to 1-CH of cyclopentene). After another hour of reaction, the reaction mixture was filtered while hot from the dark precipitate to yield **7** (18.0 g) as a pale yellow crystalline solid. Further concentration of filtrate to $^1/_3$ volume yielded another crop of **7** (9.2 g). Total yield amounted to 90.6%. After one recrystallization from chloroform **7** melted at 148–149 °C (lit.[11] mp 149–150 °C); ^{1}H NMR ($CDCl_3$) δ 5.90–6.10 [1, m, C(2)-H].

Isomerization of 6 to 8. To **6** (10.0 g, 0.062 mol) in 100 mL of dry benzene was added $PdCl_2(PhCN)_2$ (0.4 g), and the solution was refluxed for 2 h. The reaction mixture was filtered and the filtrate was evaporated in vacuo to yield a syrup. It was dissolved in petroleum ether and filtered from insoluble precipitate. Evaporation of the filtrate in vacuo gave **8** (9.7 g) in 97.0% yield: mp 44–46 °C; ^{1}H NMR ($CDCl_3$) δ 5.75–6.13 [1, m, C(2)-H].

Oxidation of 7 to Hydroquinone. To **7** (10.0 g, 0.0624 mol) in 100 mL of isopropyl alchol was added 30% H_2O_2 (9.5 g, 0.084 mol) followed by concentrated HCl (1.0 g). The solution was kept at 50 °C under stirring and in 2 h the reaction was complete (followed by NMR). After another hour the reaction mixture was cooled and neutralized with sodium bicarbonate (2.0 g), and the excess of H_2O_2 was reduced by catalytic hydrogenation in a Parr shaker at 45 psi using 10% Pd–C (0.1 g). The solution was filtered from the catalyst and solids and evaporated to give a crystalline solid (containing cyclopentanone; detected by GC) which after recrystallization from boiling chlorobenzene yielded hydroquinone (6.3 g) in 91.6% yield, mp 168–170 °C.

Oxidation of 8 to Catechol. The oxidation of **8** was considerably slower than that of **7**. To a solution of **8** (2.5 g, 0.015 mol) and 30% H_2O_2 (2.0 g, 0.017 mol) in 30 mL of isopropyl alcohol was added concentrated HCl (0.2 g), and the mixture was heated at 45–50 °C for 6 h followed by workup similar to that of **7** to yield 2.8 g of a liquid residue containing cyclopentanone (detected by GC). It was chromatographed over 50.0 g of silica gel and elution with cyclohexane gave 0.6 g of 2-cyclopentylphenol (confirmed by NMR). Further elution with cyclohexane–ethyl acetate (8:1) gave catechol (1.0 g) in 58.1% yield, mp 102–103 °C.

Synthesis of Chroman 9. A mixture of phenol (564.0 g, 6 mol) and mesityl oxide (147.0 g, 1.5 mol) was slightly warmed to melt in a 2-L flask. A stream of hydrogen bromide was bubbled through the solution for 2 h at a rate of ca. 300 mL/min. Water cooling was applied to keep the temperature below 35 °C. On standing overnight at room temperature, a red-brown crystalline mass resulted, which was stirred with 800 mL of ether, and the resulting solid precipitate was collected by filtration. It was washed with ether and then water, followed by drying in a vacuum oven (40 °C) to give 237.5 g (first crop) of crystalline chroman–ether complex. The mother liquor was concentrated and let stand overnight. The byproduct, bisphenol A, precipitated as a 1:1 complex with phenol (104.5 g). The filtrate was distilled to remove excess phenol. The residue was crystallized from 150 mL of ether to give 13.5 g (second crop) of chroman–ether complex. The combined yield of chroman as ether complex was 60.0% of theory (based on mesityl oxide). This complex was used for the following pyrolysis.

Synthesis of Chromene 10. The chroman–ether complex (14.0 g, 0.05 mol) was placed in a distilling flask and heated to melt at 170–180 °C, and 0.1 g of concentrated H_2SO_4 was added. With the oil bath at 170–190 °C, the thermal dissociation products were distilled under a reduced pressure (18 mm) into an ice-cooled receiver. The distillate was diluted with 50 mL of carbon tetrachloride and extracted with 10% NaOH (5 × 10 mL) to remove phenol and then washed with brine water. After drying ($MgSO_4$), the organic solution was concentrated and distilled to yield 7.35 g (84.5% of theory) of chromene **10**: bp 58–60 °C (0.2 mm); ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 6), 2.00 (d, 3), 5.35 (m, 1), 6.60–7.30 (m, 4).

Oxidation of Chromene 10. Chromene **10** (2.61 g, 0.015 mol) was dissolved in 10 mL of acetonitrile and cooled in an ice bath. Hydrogen chloride gas was bubbled into the solution for 10 min at a rate of ca. 40 mL/min. A solution of hydrogen peroxide (0.8 g of 70% H_2O_2 in 4 mL of CH_3CN) was added dropwise at such a rate that the temperature was kept below 20 °C. The solution was stirred for additional 30 min at 15–20 °C. The solvent was evaporated under reduced pressure, and to the residue was added 20 mL of water. Unreacted starting material was extracted with carbon tetrachloride. The aqueous layer was then extracted with ether. After drying ($MgSO_4$), the etherate solution was concentrated, giving 1.1 g (67% yield) of catechol, mp 99–102 °C.

Registry No. **1**, 80-05-7; **1** (methylated), 1568-83-8; **2a**, 4286-23-1; **2b**, 1712-69-2; **3a** (isomer 1), 13464-24-9; **3a** (isomer 2), 57244-54-9; **3b** (isomer 1), 61093-30-9; **3b** (isomer 2), 95936-03-1; **4a**, 123-31-9; **4b**, 150-76-5; **5**, 6627-84-5; **6**, 6627-83-4; **7**, 877-46-3; **8**, 72471-05-7; **9**, 472-41-3; **10**, 17937-04-1; C_6H_5OH, 108-95-2; $PdCl_2(PhCN)_2$, 14220-64-5; $CH_3C(CH_3)$=$CHCOCH_3$, 141-79-7; CH_3COCH_3, 67-64-1; 1,3-cyclopentadiene, 542-92-7; cyclopentanone, 120-92-3; catechol, 120-80-9.