Table IV. Summary of Crystallographic Data

molecular formula	$C_{18}H_{20}O_2$
mol wt	268.4
linear absorption coeff	0.88 cm^{-1} (Mo K$\bar{\alpha}$)
ρ(calcd)	1.274 g/cm^3
ρ(exptl)	1.273 g/cm^3
space group	$P2_1/c$
cell dimensions	a = 12.029 (5) Å
	b = 6.6447 (2) Å
	c = 17.49 (1) Å
	β = 90.23 (7)°
	Z = 4
	V = 1399 Å^3
no. of reflections measd	3500
no. of reflections obsd	759
final R	0.027
final R_w	0.023

dec); ^{13}C NMR ($CDCl_3$ with Me_4Si reference) 19.8, 23.8, 30.0, 30.1, 47.7, 54.3, 134.0, 134.4, 207.9 ppm.

The tetrahydro derivative III was prepared by hydrogenation in ethanol over 10% Pd/C, as described by Alder and Stein.[4] Recrystallization from ethyl acetate gave glistening flakes, mp 248–252 °C (lit.[4] mp 245 °C).

Diol IV. A suspension of 0.5 g of III in 25 mL of dry methanol was treated with 0.2 g of $NaBH_4$, refluxed 2 h, and stirred overnight at 25 °C. IR analysis showed that reduction was incomplete, so the product was heated at reflux with 0.3 g of $NaBH_4$ in 25 mL of methanol for 48 h. The cooled reaction mixture was diluted with water and extracted with ether (3 × 50 mL). The extracts were dried over $MgSO_4$ and concentrated, and the solid residue (still showing some carbonyl absorption in the IR spectrum) was recrystallized from $CHCl_3$. Colorless crystals (0.15 g, 30%) of a pure diol separated: mp 233–235 °C; IR (Nujol) 3250 (br, OH), no absorption between 1500 and 1800 cm^{-1}; ^{13}C NMR (Me_2SO-d_6 with Me_4Si reference) 19.8, 22.8, 22.9, 24.3, 26.6, 28.3, 40.7, 41.1, 65.5 ppm.

Crystal Structure Determination. The adduct was recrystallized from ethyl acetate and the sample used in the structure determination was cut from a longer needle crystal. All diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using Mo K$\bar{\alpha}$ radiation and a graphite monochromator. The orientation matrix and cell dimensions were determined from 15 accurately centered reflections. Pertinent crystallographic information is summarized in Table IV.

Intensity data were corrected for Lorentz-polarization effects but not for absorption. In all, 759 unique nonzero reflections were used in the structural analysis. The structure was solved by the direct methods program MULTAN[13] (E's ≥ 1.4). The E map produced from phases with the highest ABSFOM value (3.38) revealed starting positions for the 20 nonhydrogen atoms. Refinement of these atomic positions and generation of a difference map gave starting positions for the 20 hydrogen atoms. Full-matrix least-squares refinement with anisotropic temperature factors for the carbon and oxygen atoms, isotropic temperature factors for hydrogen atoms, and weights of $1/\sigma_{F_o}$ gave a final R of 0.027 (R_w = 0.023).

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation in the purchase of the JEOL PFT-100 NMR spectrometer on which the ^{13}C spectra were obtained.

Registry No. I, isomer E, 73035-87-7; II, isomer C, 73035-88-8; IIIB, 72952-87-5; IV, 72952-88-6; 1,3-cyclohexadiene, 592-57-4; *p*-benzoquinone, 106-51-4.

Supplementary Material Available: Table of positional coordinates and temperature factors (3 pages). Ordering information is given on any current masthead page.

(13) Program MULTAN written by P. Main and M. U. Woolfson, University of York, York, England, and G. Germain, Universite de Louvain, Louvain, Belgium.

Quinone Dehydrogenation. Oxidation of Benzylic Alcohols with 2,3-Dichloro-5,6-dicyanobenzoquinone

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2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) reacts with primary and secondary aryl-substituted alcohols under mild conditions in dioxane solution to give the corresponding carbonyl compounds in high yields. In contrast to other oxidants, DDQ can be applied advantageously for the oxidation of hydroxyaryl-substituted alcohols. A mechanism involving participation of the phenolic hydroxyl group in the dehydrogenation reaction is discussed. Oxidations of hydroxyaryl-substituted alcohols by DDQ in methanol solution resulting in the formation of benzoquinones by loss of the hydroxyalkyl side chain are interpreted in terms of phenol oxidation. An example of a pyridine-catalyzed Smiles rearrangement of an *o*-hydroxy-substituted diphenyl ether is reported.

High-potential quinones such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or *o*-chloranil are well-established reagents for the conversion of allylic alcohols into the corresponding α,β-unsaturated carbonyl compounds.[1-4] By contrast, quinones have found only sporadic use, mainly in mechanistic studies, as oxidants for benzylic alcohols.[5,6] Long reaction times and low yields reported previously for the dehydrogenation of benzyl alcohol and diphenylcarbinol by *o*-chloranil may have discouraged preparative applications.[7]

In some analytical experiments, we had noted several years ago that DDQ smoothly oxidized, selectively, certain

(1) Jackman, L. M. In "Advances in Organic Chemistry: Methods and Results"; Raphael, R. A., Taylor, E. C., Wynberg, H., Eds.; Interscience: New York, 1960; Vol. II, 329.
(2) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153.
(3) Becker, H.-D. In "The Chemistry of the Quinonoid Compounds"; Patai, S., Ed.; Wiley-Interscience: New York, 1974; pp 335–423.
(4) Turner, A. B. In "Synthetic Reagents"; Pizey, J. R., Ed.; Halsted Press (Wiley): New York, 1977; Vol. 3, pp 194–225.
(5) Brown, D. R.; Turner, A. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1307.
(6) Ohki, A.; Nishiguchi, T.; Fukuzimi, K. *Tetrahedron* **1979**, *35*, 1737.
(7) Braude, E. A.; Linstead, R. P.; Wooldridge, K. R. *J. Chem. Soc.* **1956**, 3070.

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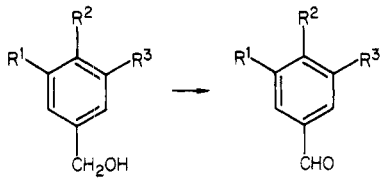
Table I. Oxidation of Substituted Benzyl Alcohols 1[a]



1 2

compd	R^1	R^2	R^3	% yield of 2
a	H	H	H	80[b]
b	H	CH_3	H	93[c]
c	H	$SO_2C_6H_5$	H	14[d]
d	H	H	OH	83
e	H	OCH_3	OH	97
f	H	OH	H	74
g	H	OH	OCH_3	85
h	OCH_3	OH	OCH_3	86
i	Cl	OH	Cl	92
j	t-C_4H_9	OH	t-C_4H_9	91

[a] General reaction conditions were as follows: Addition of DDQ (4 mmol) to a solution of the benzyl alcohol (4 mmol) in dioxane (24 mL) at room temperature. Workup (see Experimental Section) after 16 h. For exceptions, see footnotes *b–d*. [b] Isolated as 2,4-dinitrophenylhydrazone after 90 h. [c] Isolated as 2,4-dinitrophenylhydrazone. [d] After 5 weeks at room temperature.

substituted benzylic alcohols related to lignin chemistry.[8,9] Because of the absence of oxidative coupling products, DDQ was found to have considerable advantages over other oxidants (e.g., active manganese dioxide[10]) when applied to phenolic benzyl alcohols. In order to evaluate the general applicability of DDQ, we have investigated the oxidation of a series of substituted arylcarbinols described in this paper.

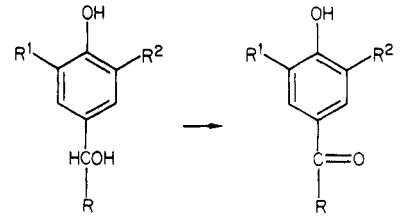
Results and Discussion

The dehydrogenation of aryl-substituted carbinols was found to proceed smoothly in dioxane solution under mild conditions. In a typical experiment, equimolar amounts of DDQ and the carbinol are dissolved at room temperature. As the deep color of an initially formed charge-transfer complex fades, 2,3-dichloro-5,6-dicyanohydroquinone ($DDQH_2$) starts precipitating. After the reaction is complete (checked by TLC), the workup procedure comprises vacuum evaporation of solvent, treatment of the residue with methylene chloride, and removal of insoluble $DDQH_2$ by filtration. Vacuum evaporation of solvent from the filtrate generally affords the pure carbonyl compound. The results of the dehydrogenation of primary arylcarbinols **1**, secondary carbinols **3**, salicylic alcohols **5**, and diarylcarbinols **7** are summarized in Tables I–IV.

The following features of the dehydrogenation of benzylic alcohols by DDQ in dioxane are apparent. Electron-donating substituents, particularly a hydroxyl group in the para position, facilitate the oxidation of the carbinol group. By contrast, electron-withdrawing substituents render the oxidation more difficult. For example, the oxidation of 4-hydroxybenzyl alcohol (**1f**) is complete within minutes at room temperature, while oxidation of 4-(phenylsulfonyl)benzyl alcohol (**1c**) is exceedingly slow under these conditions. Likewise, the conversion of 2-hydroxy-3-methyl-5-*tert*-butylbenzyl alcohol (**5b**) into the salicylaldehyde **6b** proceeds at room temperature, but the oxidation of 2-hydroxy-3-methyl-5-(methylsulfonyl)benzyl

(8) Becker, H.-D.; Adler, E. *Acta Chem. Scand.* **1961**, *15*, 218.
(9) Adler, E.; Becker, H.-D.; Ishihara, T.; Stamvik, A. *Holzforschung* **1966**, *20*, 3.
(10) Adler, E.; Becker, H.-D. *Acta Chem. Scand.* **1961**, *15*, 849.

Table II. Oxidation of Secondary 4-Hydroxybenzyl Alcohols 3[a]

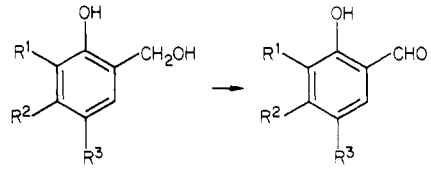


3 4

compd	R	R^1	R^2	% yield of 4
a	$C_6H_5CH_2$	H	H	92
b	$C_6H_5CH_2$	H	OCH_3	89
c	$C_6H_5CH_2$	OCH_3	OCH_3	92
d	$C_6H_5CH_2$	CH_3	CH_3	83
e	$C_6H_5CH_2$	allyl	OCH_3	88
f	$C_6H_5CH_2$	t-C_4H_9	t-C_4H_9	90[b]
g	$C_6H_5CH_2$	Cl	Cl	82
h	$C_6H_5CH_2$	C_6H_5	C_6H_5	89[c]
i	C_2H_5	CH_3	CH_3	80
j	C_2H_5	OCH_3	OCH_3	70
k	C_2H_5	t-C_4H_9	t-C_4H_9	94

[a] For general reaction conditions, see Table I, footnote *a*. [b] Formation of 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone detectable by TLC. [c] Reaction time 76 h.

Table III. Oxidation of 2-Hydroxy-Substituted Arylcarbinols 5

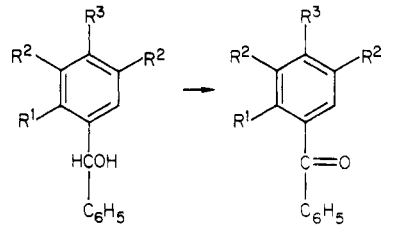


5 6

compd	R^1	R^2	R^3	reaction time	% yield of 6
a	H	H	H	16 h	57[a]
b	CH_3	H	t-C_4H_9	20 h	85
c	t-C_4H_9	H	t-C_4H_9	68 h	85
d	H	CH_3	CH_3	5 min	89
e	CH_3	H	CH_3SO_2	16 h reflux	64[b]

[a] Isolated as 2,3-dinitrophenylhydrazone. [b] See Experimental Section.

Table IV. Oxidation of Diarylcarbinols 7[a]



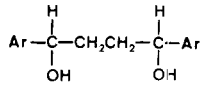
7 8

compd	R^1	R^2	R^3	% yield of 8
a	H	H	H	80
b	H	H	OH	82
c	H	t-C_4H_9	OH	95
d	OH	t-C_4H_9	H	71

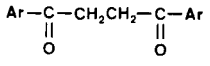
[a] For general reaction conditions, see Table I, footnote *a*. In the case of carbinols **7a–7c**, reactions were completed within 15 min.

alcohol (**5e**) to give salicylaldehyde **6e** requires reflux temperature. The dehydrogenation of 2-hydroxy-substituted benzylic carbinols also appears to be subject to steric effects. Thus, the oxidation of 3-*tert*-butyl-substituted 2-hydroxyarylcarbinols **5c** and **7d** is slow at room temperature (2–3 days), but 4,5-dimethyl-2-hydroxybenzyl alcohol (**5d**) reacts with DDQ instantaneously to give the corresponding salicylaldehyde **6d** in excellent yield (cf. Tables III and IV).

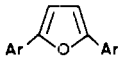
Unexpected results were obtained in the DDQ oxidation of aryl-substituted diols. Thus, oxidation of 1,4-diphenylbutane-1,4-diol (**9a**) gave 1,2-dibenzoylethane (**10a**) in only 19% yield, the major product being 2,5-diphenylfuran (**11a**, 66% yield). In the oxidation of the *p*-tolyl derivative **9b**, the yield of 1,2-di-*p*-toluoylethane (**10b**) was 68%, while 2,5-di-*p*-tolylfuran (**11b**) was formed in only 11% yield. The formation of the furans probably involves the cyclization of the primary oxidation product **12** to give the hemiketal **13** whose dehydration would lead to the readily oxidizable 2,3-dihydrofuran **14**. The higher yield of **10b**, compared to the yield of **10a**, is suggestive of an enhanced rate of oxidation due to the *p*-methyl substitution of the intermediate carbinol **12b**. An analogous substituent effect is observed in the oxidation of aromatic glycols. Thus, hydrobenzoin (**15a**) upon oxidation with DDQ did not give benzil (**17a**), but yielded benzoin (**16a**). Hydrovanilloin (**15b**), by contrast, reacted rapidly with DDQ to give the corresponding dicarbonyl compound **17b** in excellent yield.



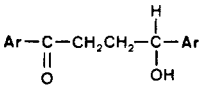
9a,b



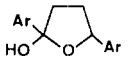
10a,b



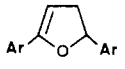
11a,b



12a,b

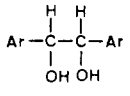


13a,b

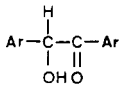


14a,b

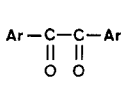
9—14a, Ar = phenyl
b, Ar = p-tolyl



15a,b



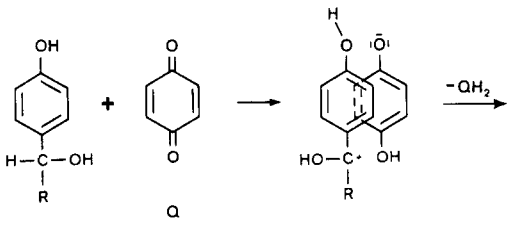
16a,b



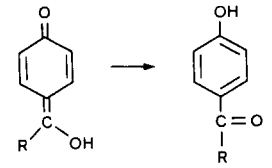
17a,b

15—17a, Ar = phenyl
b, Ar = 4-hydroxy-3-methoxyphenyl

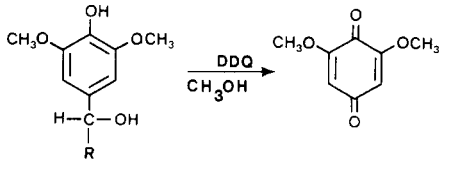
As far as the mechanism of the dehydrogenation of alcohols by DDQ is concerned, the results of a recent kinetic investigation[6] are in agreement with a reaction sequence in which hydride ion transfer from the α carbon of the alcohol is the rate-determining step. It is conceivable that in the dehydrogenation of 4-hydroxyarylcarbinols described above the hydroxyl group participates by functioning as proton donor for the intermediate hydroquinone anion.



Q



The choice of solvent for the dehydrogenation of 4-hydroxyaryl-substituted carbinols to the corresponding carbonyl compounds was found to be of some importance. Thus, evidence for a phenol oxidation pathway in methanol solution was obtained in the reaction of DDQ with carbinols **3**, which afforded mixtures of the expected ketones and the correspondingly substituted 1,4-benzoquinones. In particular, oxidation of (3,5-dimethoxy-4-hydroxyaryl)carbinols **18** by DDQ in methanol gave 2,6-dimethoxybenzoquinone (**19**) in high yield (about 75%). The other fragment, believed to be the aldehyde derived from the carbinol side chain, was not analyzed, but was detectable by the odor of phenylacetaldehyde in the oxidation of **3c**. Remarkably, even 3,5-dimethoxybenzaldehyde upon oxidation with DDQ in methanol gave **19**.

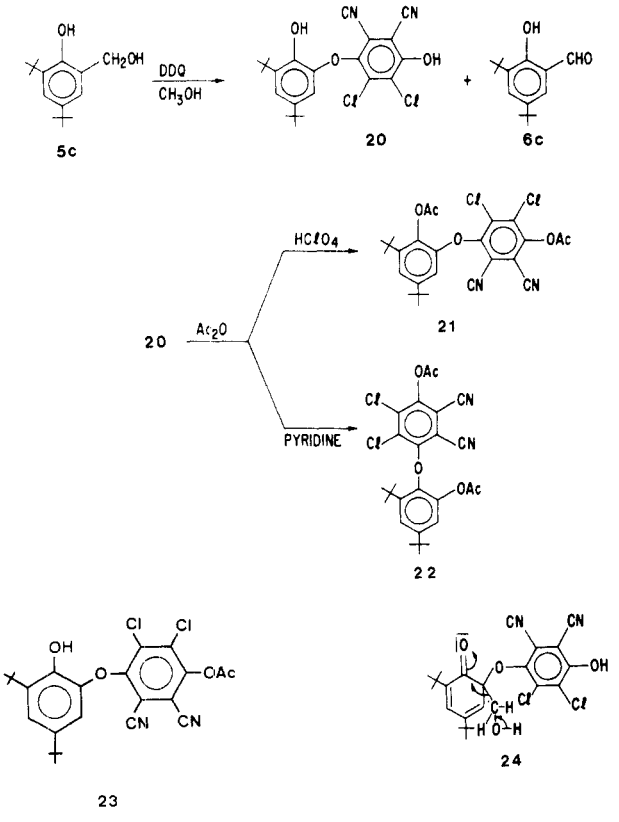


18 19

An example of oxidative coupling in methanol solution involving loss of hydroxyalkyl side chain was found in the reaction of DDQ with 3,5-di-*tert*-butylsalicyl alcohol (**5c**), which gave the diphenyl ether **20** in 54% yield (salicylaldehyde **6c** being formed in 35% yield). The structure of **20** is supported by ^{1}H NMR spectral data of its diacetate **21**, which was obtained by acid-catalyzed acetylation with acetic anhydride. Remarkably, acetylation of **20** with acetic anhydride in the presence of pyridine was found to give an isomeric diacetate to which we ascribe structure **22**. It seems reasonable to assume that the formation of **22** involves a pyridine-catalyzed Smiles rearrangement of the monoacetate **23**.

Benzylic oxidation of 4-alkyl-substituted phenols by DDQ in methanol solution is known to proceed smoothly and has been explained in terms of phenol oxidation.[11] Likewise, the conversion of (4-hydroxyaryl)carbinols into benzoquinones as well as the formation of diphenyl ether **20** may be explicable by the intermediacy of phenol oxidation products of cyclohexadienone structure (e.g., **24**). Similar or analogous cyclohexadienones have been invoked previously to account for the oxidative demethylation of *p*-methoxyphenols,[11] the oxidative coupling of mesitol by manganese dioxide,[12,13] and the formation of formaldehyde in the oxidation of hydroxybenzyl alcohols by potassium ferricyanide[14] or periodate.[15]

(11) Becker, H.-D. *J. Org. Chem.* **1965**, *30*, 982.
(12) McNelis, E. *J. Am. Chem. Soc.* **1966**, *88*, 1074.
(13) McNelis, E. *J. Org. Chem.* **1966**, *31*, 1255.



Experimental Section

DDQ was recrystallized from methylene chloride. Dioxane was purified by distillation. Melting points were taken on a hot-stage microscope and are not corrected. ^1H NMR spectra were obtained on a Varian A-60 instrument, and chemical shift data are given in parts per million (δ) with Me_4Si as internal standard.

DDQ Oxidations in Dioxane Solution. Standard Procedure. DDQ (908 mg, 4 mmol) was added to a solution of 4-hydroxybenzyl alcohol (496 mg, 4 mmol) in dioxane (24 mL). The reaction mixture immediately turned deep green (exothermic reaction), and $DDQH_2$ started precipitating within 1 min. TLC analysis indicated consumption of starting material after 15 min. The solvent was removed from the yellow reaction mixture by vacuum evaporation. Treatment of the residue with methylene chloride left $DDQH_2$ undissolved (quantitatively). Filtration followed by evaporation of methylene chloride gave 4-hydroxybenzaldehyde (74%) which was recrystallized from water; mp 115–116 °C.

DDQ Oxidations in Methanol Solution. Standard Procedure. DDQ (908 mg, 4 mmol) was added to a solution of **3c** (1.097 g, 4 mmol) in methanol (24 mL). The reaction mixture immediately turned brown (exothermic reaction), and 2,6-dimethoxybenzoquinone (**19**) started precipitating within 1 h. Filtration after 16 h gave 240 mg (36%). Further addition of DDQ (908 mg, 4 mmol) to the filtrate gave an additional 269 mg of **19**; total yield, 76%.

The oxidation of syringyl alcohol and ethylsyringylcarbinol with 2 molar equiv of DDQ gave 2,6-dimethoxybenzoquinone in 72% and 76% yield, respectively.

The oxidation of 3,5-dimethoxy-4-hydroxybenzaldehyde (1 mmol) with DDQ (2 mmol) in methanol (6 mL) gave 2,6-dimethoxybenzoquinone in 42% yield.

4-(Phenylsulfonyl)benzyl alcohol (1c) was prepared by reduction of 4-(phenylsulfonyl)benzaldehyde with $NaBH_4$ in methanol and recrystallized from benzene (yield 53%): mp 135–137 °C; NMR ($CDCl_3$) δ 2.43 (1 H, OH), 4.73 (s, 2 H, CH_2), 7.65 (m, 9 H, aromatic). Anal. Calcd for $C_{13}H_{12}O_3S$ (mol wt, 248.30): C, 62.88; H, 4.87. Found: C, 63.24; H, 4.93.

1-(3,5-Dichloro-4-hydroxyphenyl)-2-phenylethanol (3g) was prepared from benzylmagnesium chloride and 3,5-dichloro-4-hydroxybenzaldehyde and recrystallized from methanol–water (yield 79%): mp 154–155 °C; NMR (acetone-d_6): δ 2.98 (d, J = 7 Hz, 2 H, CH_2), 4.88 (t, J = 7 Hz, 1 H, CH), 5.22 (1 H, OH), 7.23 (m, 7 H, aromatic). Anal. Calcd for $C_{14}H_{12}Cl_2O_2$ (mol wt, 283.16): C, 59.39; H, 4.27. Found: C, 59.30; H, 4.28.

1-(3,5-Diphenyl-4-hydroxyphenyl)-2-phenylethanol (3h). A solution of 3,5-diphenyl-4-hydroxybenzaldehyde (10 g) in ether (1450 mL) was added to benzylmagnesium chloride (prepared from 7 g of magnesium and 30 g of benzyl chloride in ether). The reaction mixture was refluxed overnight and worked up in the usual manner. Vacuum evaporation of the solvent gave a colorless crystalline residue that was triturated with petroleum ether and removed by filtration. The yield from two identical experiments was 22 g (82%) after recrystallization from hot 2-propanol; mp 118–119 °C. Anal. Calcd for $C_{22}H_{22}O_2$ (mol wt, 366.44): C, 85.21; H, 6.05. Found: C, 85.20; H, 5.99.

(3,5-Dimethyl-4-hydroxyphenyl)ethylcarbinol (3i) was prepared by reduction of 3,5-dimethyl-4-hydroxypropiophenone (8.9 g) with $NaBH_4$ (5.8 g) in methanol (75 mL) and recrystallized from ethyl acetate–hexane (yield 76%); mp 97–98 °C. Anal. Calcd for $C_{11}H_{16}O_2$ (mol wt, 180.25): C, 73.30; H, 8.95. Found: C, 73.03; H, 8.85.

Benzyl 4-hydroxy-3-methoxyphenyl ketone (4b) was recrystallized from methanol–water: mp 108–110 °C; NMR ($CDCl_3$) δ 3.87 (s, 3 H, OCH_3), 4.20 (s, 2 H, CH_2), 6.27 (s, 1 H, OH), 7.27 (m, 8 H, aromatic). Anal. Calcd for $C_{15}H_{14}O_3$ (mol wt, 242.28): C, 74.36; H, 5.82. Found: C, 74.61; H, 5.91.

Benzyl 3,5-dimethoxy-4-hydroxyphenyl ketone (4c) was recrystallized from acetic acid–water: mp 117–118 °C; NMR ($CDCl_3$) δ 3.90 (s, 6 H, OCH_3), 4.23 (s, 2 H, CH_2), 6.00 (1 H, OH), 7.27 and 7.29 (7 H, aromatic). Anal. Calcd for $C_{16}H_{16}O_4$ (mol wt, 272.30): C, 70.57; H, 5.92. Found: C, 70.52; H, 5.92.

Benzyl 3,5-dimethyl-4-hydroxyphenyl ketone (4d) was recrystallized from methanol–water: mp 117–118 °C; NMR ($CDCl_3$) δ 2.23 (s, 6 H, CH_3), 4.20 (s, 2 H, CH_2), 5.80 (s, 1 H, OH), 7.25 and 7.67 (5 + 2 H, aromatic). Anal. Calcd for $C_{16}H_{16}O_2$ (mol wt, 240.31): C, 79.97; H, 6.71. Found: C, 80.09; H, 6.78.

Benzyl 3-allyl-4-hydroxy-5-methoxyphenyl ketone (4e) was recrystallized from methanol: mp 140–142 °C; NMR ($CDCl_3$) δ 3.44 (d, 2 H, CCH_2), 3.90 (s, 3 H, OCH_3), 4.22 (s, 2 H, $COCH_2$), 4.95 and 5.02 (m, 1 + 1 H, $C{=}CH_2$), 5.77 (m, 1 H, CH), 7.27 and 7.48 (5 + 2 H, aromatic). Anal. Calcd for $C_{18}H_{18}O_3$ (mol wt, 282.34): C, 76.57; H, 6.43. Found: C, 76.80; H, 6.40.

Benzyl 3,5-di-*tert*-butyl-4-hydroxyphenyl ketone (4f) was recrystallized from methanol–water: mp 129–130 °C; NMR ($CDCl_3$) δ 1.45 (s, 18 H, *t*-Bu), 4.22 (s, 2 H, CH_2), 5.73 (s, 1 H, OH), 7.28 and 7.90 (5 + 2 H, aromatic). Anal. Calcd for $C_{22}H_{28}O_2$ (mol wt, 324.47): C, 81.44; H, 8.70. Found: C, 81.84; H, 8.73.

Benzyl 3,5-dichloro-4-hydroxyphenyl ketone (4g) was recrystallized from methanol–water: mp 132–135 °C; NMR (acetone-d_6) δ 4.55 (s, 2 H, CH_2), 7.33 and 8.07 (5 + 2 H, aromatic). Anal. Calcd for $C_{14}H_{10}Cl_2O_2$ (mol wt, 281.40): C, 59.81; H, 3.39. Found: C, 59.80; H, 3.64.

Benzyl 3,5-diphenyl-4-hydroxyphenyl ketone (4h) was recrystallized from methanol: mp 155–156 °C; NMR ($CDCl_3$) δ 4.23 (s, 2 H, CH_2), 5.87 (s, 1 H, OH), 7.58 (m, 17 H, aromatic). Anal. Calcd for $C_{26}H_{20}O_2$ (mol wt, 364.45): C, 85.69; H, 5.53. Found: C, 85.96; H, 5.63.

2-(Hydroxymethyl)-6-methyl-4-(methylsulfonyl)phenol (5e). A solution of 2-(hydroxymethyl)-6-methyl-4-(methylthio)phenol (10 g) in a mixture of acetic acid (100 mL) and hydrogen peroxide (30%, 20 mL) was kept at 45 °C for 6 h. Evaporation of solvents at room temperature left a solid colorless residue which was washed with ether to give 7.4 g of crude **5e**. Recrystallization from acetone by precipitation with petroleum ether (bp 40–60 °C) gave 6.5 g (55%) of colorless crystals: mp 142–145 °C; NMR (acetone-d_6) δ 2.35 (br s, 3 H, CH_3), 3.08 (s, 3 H, SO_2CH_3), 4.97 (br s, 2 H, OH), 7.63 ("s", 2 H, aromatic). Anal. Calcd for $C_9H_{12}O_4S$ (mol wt, 216.26): C, 49.99; H, 5.59. Found: C, 50.13; H, 5.64.

2-Hydroxy-3-methyl-5-(methylsulfonyl)benzaldehyde (6e). A solution of 2-(hydroxymethyl)-6-methyl-4-(methylsulfonyl)-phenol (2.38 g, 11 mmol) and DDQ (2.5 g, 11 mmol) in dioxane (40 mL) was refluxed for 16 h. When the solution was cooled to

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room temperature, $DDQH_2$ (2.5 g) precipitated from the dark brown reaction mixture. Vacuum evaporation of solvent from the filtrate left a brown crystalline residue which was recrystallized by dissolving in methylene chloride and adding hexane to yield 1.45 g (64%) of tan colored crystals: mp 160–161 °C; NMR ($CDCl_3$) δ 2.33 (br s, 3 H, CH_3), 3.08 (s, 3 H, SO_2CH_3), 7.90 (m, 1 H), 8.07 (d, J = 2.5 Hz, 1 H), 9.93 (s, 1 H, CHO), 11.73 (s, 1 H, OH). Anal. Calcd for $C_9H_{10}O_4S$ (mol wt, 214.24): C, 50.46; H, 4.70. Found: C, 50.41; H, 4.62.

3,5-Di-*tert*-butyl-2-hydroxydiphenylcarbinol (7d). A solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) in ether (50 mL) was treated with phenyllithium solution (2 molar equiv). Vacuum evaporation of solvent after addition of methanol left a residue which was dissolved in aqueous acetic acid. Extraction of the aqueous solution with petroleum ether (bp 40–60 °C) gave an oily product which crystallized when treated with pentane to yield 2.2 g (70%), mp 95–97 °C. Anal. Calcd for $C_{21}H_{28}O_2$ (mol wt, 312.46): C, 80.73; H, 9.03. Found: C, 80.77; H, 9.07.

3,5-Di-*tert*-butyl-2-hydroxybenzophenone (8d) was recrystallized from aqueous ethanol to give yellow crystals, mp 60–62 °C. Anal. Calcd for $C_{21}H_{26}O_2$ (mol wt, 310.44): C, 81.25; H, 8.44. Found: C, 81.30; H, 8.40.

Oxidation of 4,6-Di-*tert*-butyl-2-(hydroxymethyl)phenol by DDQ in Methanol (20). DDQ (9.08 g, 40 mmol) was added to a solution of **5c** (9.44 g, 40 mmol) in methanol (55 mL). After about 15 min a pale yellow crystalline material started to precipitate. Filtration after 72 h gave 9.38 g (54%) of pale yellow crystalline product, mp 234–236 °C. Recrystallization by dissolving in acetone and adding methanol did not raise the melting point. Anal. Calcd for $C_{22}H_{22}Cl_2N_2O_3$ (mol wt, 433.34): C, 60.98; H, 5.12. Found: C, 61.25; H, 5.10.

Vacuum evaporation of solvent from the filtrate obtained after isolation of **20** gave a solid residue which was treated with methylene chloride. Filtration gave 3.4 g (37%) of $DDQH_2$. The solid residue obtained from the filtrate after vacuum evaporation of solvent was subjected to vacuum sublimation (5×10^{-2} torr, bath temperature 60 °C). The yield of sublimed 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was 3.3 g (35%); mp 58–60 °C.

Diacetate 21. A solution of **20** (1 g) in 2 M acetic anhydride in ethyl acetate/perchloric acid (20 mL) was kept at room temperature for 2 h and then diluted with methanol (20 mL). Vacuum evaporation of solvents gave a crystalline colorless residue which was recrystallized from boiling aqueous methanol to yield 820 mg: mp 168–169 °C; NMR ($CDCl_3$) δ 1.25 (s, 9 H, *t*-Bu), 1.38 (s, 9 H, *t*-Bu), 2.27 (s, 3 H, Ac), 2.48 (s, 3 H, Ac), 6.57 (d, J = 2.5 Hz, 1 H), 7.27 (d, J = 2.5 Hz, 1 H). Anal. Calcd for $C_{26}H_{26}Cl_2N_2O_5$ (mol wt, 517.41): C, 60.36; H, 5.07. Found: C, 60.55; H, 5.07.

Diacetate 22. Acetylation of **20** (2 g) with acetic anhydride (20 mL) in the presence of pyridine (0.5 mL) at room temperature (24 h) gave an isomeric diacetate (1.5 g): mp 138–141 °C; NMR ($CDCl_3$) δ 1.32 (s, 9 H, *t*-Bu), 1.45 (s, 9 H, *t*-Bu), 1.85 (s, 3 H, Ac), 2.45 (s, 3 H, Ac), 6.98 (d, J = 2.5 Hz, 1 H), 7.33 (d, J = 2.5 Hz, 1 H). Anal. Calcd for $C_{26}H_{26}Cl_2N_2O_5$ (mol wt, 517.41): C, 60.36; H, 5.07. Found: C, 60.56; H, 5.08.

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Registry No. 1a, 100-51-6; **1b**, 589-18-4; **1c**, 7705-64-8; **1d**, 620-24-6; **1e**, 4383-06-6; **1f**, 623-05-2; **1g**, 498-00-0; **1h**, 530-56-3; **1i**, 22002-17-1; **1j**, 88-26-6; **2a** DNP, 1157-84-2; **2b** DNP, 2571-00-8; **2c**, 66-39-7; **2d**, 100-83-4; **2e**, 621-59-0; **2f**, 123-08-0; **2g**, 121-33-5; **2h**, 7311-34-4; **2i**, 2314-36-5; **2j**, 1620-98-0; **3a**, 73049-07-7; **3b**, 73049-08-8; **3c**, 19566-78-0; **3d**, 19566-76-8; **3e**, 19566-77-9; **3f**, 19566-75-7; **3g**, 73049-09-9; **3h**, 73049-10-2; **3i**, 73049-11-3; **3j**, 10061-52-6; **3k**, 20017-35-0; **4a**, 2491-32-9; **4b**, 66476-02-6; **4c**, 73049-12-4; **4d**, 73049-13-5; **4e**, 73049-14-6; **4f**, 14035-39-3; **4g**, 73048-86-9; **4h**, 73048-87-0; **4i**, 5384-09-8; **4j**, 5650-43-1; **4k**, 14035-34-8; **5a**, 90-01-7; **5b**, 13464-23-8; **5c**, 16373-02-7; **5d**, 10496-92-1; **5e**, 73048-88-1; **6a** DNP, 1160-76-5; **6b**, 1666-01-9; **6c**, 37942-07-7; **6d**, 1666-03-1; **6e**, 73048-89-2; **7a**, 91-01-0; **7b**, 833-39-6; **7c**, 20017-39-4; **7d**, 40473-49-2; **8a**, 119-61-9; **8b**, 1137-42-4; **8c**, 7175-89-5; **8d**, 24242-58-8; **9a**, 2085-90-7; **9b**, 15982-67-9; **10a**, 495-71-6; **10b**, 13145-56-7; **11a**, 955-83-9; **11b**, 57196-75-5; **19**, 530-55-2; **20**, 73048-90-5; **21**, 73048-91-6; **22**, 73048-92-7; DDQ, 84-58-2; benzyl chloride, 100-44-7; 3,5-diphenyl-4-hydroxybenzaldehyde, 3437-80-7; 2-(hydroxymethyl)-6-methyl-4-(methylthio)phenol, 32867-65-5.

Structure and Reactivity of α,β-Unsaturated Ethers. 17. Oxidations by Permanganate and Osmium Tetraoxide

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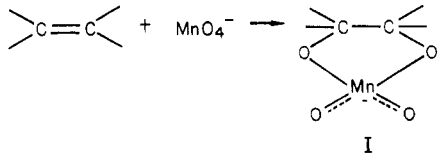
Rates of the reactions of various enol ethers with potassium permanganate and osmium tetraoxide in aqueous solution and carbon tetrachloride, respectively, have been measured at 30 °C. The reactions of some alkenes and acrylates were also examined for the sake of comparison. The osmium reaction was found to be electrophilic, while the permanganate reaction was accelerated by both electron-donating and -attracting groups. β-Alkyl substitution enhanced the reactivity of vinyl ether while an α-methyl group exerted little effect in both reactions. The trans isomers were found to be more reactive than the cis counterparts. The results can be rationalized by assuming a transition state resembling intermediate cyclic esters.

Permanganate and osmium tetraoxide are well-known as useful oxidants which convert an olefin to a cis diol.[1,2] The primary step of these oxidations has been established to be the formation of cyclic ester, I or II.[1-5] The cyclic



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osmate II was actually isolated,[4] and the manganate I has recently been detected spectrophotometrically.[5] The rates

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