superior in some respects to those, commonly used,[15] of Schaad and Hess,[4] given that a physical significance can be ascribed to them: they can be regarded as being approximately twice the orbital energy values of the π-localized molecular orbitals centered upon the corresponding double bonds. In accordance to that, their values are completely determined by the least-squares fit and do not contain any arbitrarily assigned parameter.

An even more promising application of these new parameters relies on the fact that, due to their close relationship to LMOs, they allow the decomposition of the RE of a conjugated molecule into local contributions, i.e., they can be used to evaluate "local" or "bond" aromaticities. The results of our studies on this subject will be reported in a forthcoming paper. It must be also kept in mind that the treatment presented in this article can be effected at any level of approximation higher than that of the presently used HMO method, although we have refrained from doing so because the resonance energy values are only semiquantitative and do not justify the huge amount of computational time required for a more precise evaluation.

Acknowledgment. Computational facilities given to us by the Centre de Càlcul de la Universitat de Barcelona are gratefully acknowledged.

Appendix: Derivation of a Two-Parameter Expression for the Total π-Energy of an Acyclic Conjugated Polyene

If the small energy effect associated to branching in adjacent carbon atoms is neglected, the eight bond types of Table I reduce to five; if we simplify accordingly the notation by dropping the subscripts in the bond-type notation, we obtain the following expression for the total π-energy of an acyclic conjugated polyene P_N, in terms of the π-LMO energies e_i:

$$E_\pi(P_N)/2 = n_1e_1 + n_2e_2 + n_{2'}e_{2'} + n_3e_3 + n_4e_4$$

Introducing the set of eq 12 in the π-LMO energies we obtain

$$E_\pi(P_N)/2 = n_1(1 + c) + n_2(1 + 2c) + n_{2'}(1 + 2c - b) + n_3(1 + 3c - b) + n_4(1 + 4c - 2b) = (n_1 + n_2 + n_{2'} + n_3 + n_4) + c(n_1 + 2n_2 + 2n_{2'} + 3n_3 + 4n_4) - b(n_{2'} + n_3 + n_4)$$

Expressing the total number of carbon atoms (N), the total number of branching sites (T) and the total number of end-chain carbons (S) of the polyene in terms of the n_i's,

$$N = 2(n_1 + n_2 + n_{2'} + n_3 + n_4)$$

$$T = n_{2'} + n_3 + 2n_4$$

$$S = n_1 + n_{2'}$$

and using the trivial relationship

$$S = T + 2$$

one obtains the desired two-parameter expression:

$$E_\pi(P_N) = N + c(2N - 4) - 2bT \quad (14)$$

For the particular case of a linear conjugated polyene of N atoms (L_N), $T = 0$ and the total π-energy reduces to

$$E_\pi(L_N) = N + c(2N - 4) = N(1 + 2c) - 4c$$

so that expression (14) can be written in the same form as eq 3

$$E_\pi(P_N) = E_\pi(L_N) - 2bT$$

A direct least-squares fit of this equation to the π-energies of the set of acyclic polyenes considered in this paper gives a b value of 0.05 β unit. This is somewhat greater than that (0.04 β unit) derived from the π-LMOs energies (Table I) and eq 12 due to the effect of branching on carbons adjacent to the double bonds (see text).

Registry No. **23**, 71-43-2; **24**, 91-20-3; **25**, 120-12-7; **26**, 92-24-0; **27**, 135-48-8; **28**, 85-01-8; **29**, 218-01-9; **30**, 56-55-3; **31**, 65777-08-4; **32**, 217-59-4; **33**, 129-00-0; **34**, 198-55-0; **35**, 208-96-8; **36**, 187-78-0; **37**, 194-32-1; **38** (n = 1), 1120-53-2; **38** (n = 3), 629-20-9; **38** (n = 4), 3227-76-7; **38** (n = 5), 3227-77-8; **38** (n = 6), 2873-14-5; **38** (n = 7), 3332-38-5; **38** (n = 8), 2040-73-5; **38** (n = 9), 3227-78-9; **38** (n = 10), 3227-79-0; **39**, 1552-98-3; **40**, 3227-90-5; **41**, 3227-91-6; **42**, 3227-92-7; **43**, 3227-93-8; **44**, 3332-43-2; **45**, 497-20-1; **46**, 539-79-7; **47**, 53477-08-0; **48**, 4026-23-7; **49**, 277-98-5; **50**, 249-99-0; **51**, 259-79-0; **52**, 588-59-0; **53**, 1608-08-8; **54**, 6249-23-6; **55**, 91-12-3; **56**, 1961-84-8; **57**, 531-45-3; **58**, 250-25-9; **59**, 275-51-4; **60**, 257-24-9; **61**, 257-55-6; **62**, 267-21-0; **63**, 92-52-4; **64**, 5291-90-7.

Oxygenation of *tert*-Butylphenols with an Unsaturated Side Chain

Akira Nishinaga,* Hitoshi Iwasaki, Tadashi Shimizu, Yasushi Toyoda, and Teru Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan

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Base- and Co(Salpr)-promoted oxygenations of title compounds have been investigated with a view to obtaining further details concerning controlling factors in regioselective O_2 incorporation into phenols. In the oxygenation of 4-alkenyl-2,6-di-*tert*-butyl- and 2-alkenyl-4,6-di-*tert*-butylphenols (**1** and **12**), the reactivity of the substrates and regioselectivity in the O_2 incorporation may be interpreted in terms of electronic and steric effects of the alkenyl group as well as association effect of the countercation K^+ on the transition-state **26** involving a charge transfer from the substrate anion to O_2. With 4-alkynyl-2,6-di-*tert*-butylphenols (**21**), dioxygen was incorporated exclusively into the ortho position only when the phenolate anion was associated with K^+. On the contrary, in the oxygenation of **1** and **12** with Co(Salpr), O_2 was incorporated exclusively into the alkenyl side chain, regardless of the nature of the substituent, whereas with **21**, O_2 incorporation was distributed to both the ortho and the alkynyl side chain. The substituent-dependent regioselectivity in the oxygenation of phenols with Co(Salpr) is because the reactive phenolate–Co^{III} species undergo homolysis to form phenoxy radical–Co^{II} species reversibly, whose oxygenations compete with each other. When the oxygenation of the anionic species predominates, O_2 is incorporated into the ortho position, whereas with the radical species the para and side chain oxidations predominate.

4-Substituted 2,6-di-*tert*-butylphenols are normally oxygenated by promotion of Co(Salpr), a five-coordinate cobalt(II) Schiff base complex, resulting in regioselective dioxygen incorporation into the phenol substrates. The regioselectivity depends on the nature of substituent in the 4-position of the phenols. With 4-alkyl-2,6-di-*tert*-bu-

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Table I. Oxygenation of Phenols 1[a]

1	method[b]	reacn time, h	conversion, %	product yield, %[c] 2	3	8	4	9	11
1a	B	2.5	100		93				
1a	C	0.5	100		43	39			
1b	A	1.2	100	65[d]	35[d]				
1b	B	6.0	40		50	30			
1b	B	24.0	100		50				
1b	C	0.5	100		57	20			
1c	A	1.0	100		88				
1c	B	2.0	100		91				
1c	C	0.5	100		80[d]	20[d]			
1d	B	1.5	100		34	12		22	
1d	C	1.5	100		40	18			
1e	A	4.0	90	66[d]			34[d]		
1e	B	19.0	90		34[d]			54[d]	
1e	C	1.5	100		34		15	8	
1f	A	4.0	100	72[d]	28[d]				
1f	B	20.0	100		40[d]			60[d]	
1f	C	0.5	100		62			12	
1g	A	4.0	80	80[d]	20[d]				
1g	B	20.0	100					95	
1g	C	1.0	100						98

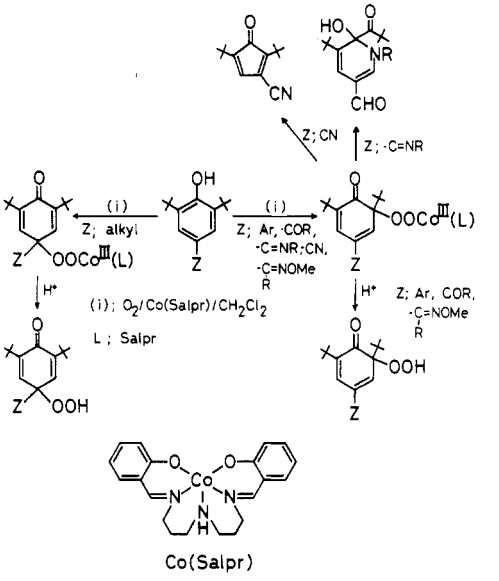
[a] Oxygenation of **1a** and **1d** with Co(Salpr) gave a complex mixture which was not further investigated. [b] Method A, 1 (1 mmol)/Co(Salpr) (1.2 mmol)/CH_2Cl_2 (30 mL)/0 °C; B, 1 (1 mmol)/*t*-BuOK (4 mmol)/DMF (30 mL)/room temperature; C, 1 (1 mmol)/*t*-BuOK (4 mmol)/*t*-BuOH (20 mL)/*n*-C_6H_{14} (10 mL)/0 °C. [c] Isolation yield. [d] Determined by ^1H NMR of the reaction mixture.

tylphenols, the oxygenation takes place in the para position of the phenolic ring to give peroxy-*p*-quinolato Co^{III}(Salpr) complexes, and with 4-aryl-2,6-di-*tert*-butylphenols, dioxygen is incorporated exclusively into the ortho position to give rise to peroxy-*o*-quinolato Co^{III}(Salpr) complexes. The peroxy complexes give corresponding *p*- and *o*-hydroperoxides quantitatively upon treatment with silica gel (Scheme I).[1]

The same regioselective dioxygen incorporation has been observed in base-promoted oxygenation of these phenols although the nature of the products depends on reaction conditions. With 4-alkyl-2,6-di-*tert*-butylphenols, the oxygenation in alkaline ethanol gives peroxy-*p*-quinols, whereas in *N*,*N*-dimethylformamide (DMF) containing *t*-BuOK, epoxy-*p*-quinols resulting from an intramolecular decomposition of the peroxy-*p*-quinols are exclusively obtained. 4-Aryl-2,6-di-*tert*-butylphenols are oxygenated only when reaction conditions are selected so that phenolate anions are able to be associated with the countercation of the base used, and dioxygen is incorporated exclusively into the ortho position to give peroxy-*o*-quinols at low temperature, epoxy-*o*-quinols at 40 °C, and cyclopentadienones at 70 °C (Scheme II).[2]

2,6-Di-*tert*-butylphenols with an electron-withdrawing group in the 4-position are normally unsusceptible to the base-promoted oxygenation, but they are readily oxygenated in the presence of Co(Salpr), leading to the dioxygen incorporation into the ortho position, where the nature of the products depends on that of the substituent. With an acyl group and its oxime *O*-methyl ether, the peroxy-*o*-quinols are obtained quantitatively, whereas imines and nitriles give characteristic products resulting from intramolecular decomposition of peroxy-*o*-quinolato Co^{III}(Salpr) intermediates (Scheme I).[3] These observations provide useful suggestions for mechanistic consideration on the dioxygen incorporation into phenolic substances and decomposition path of the primary peroxidic intermediates, which are of interest in both biological and synthetic systems. As a part of a series of our investigations to search the regioselectivity in the oxygenation of phenolic substrates, we have examined the oxygenation of *tert*-butylated phenols bearing an unsaturated C–C bond in the ortho or para position being conjugated to the phenolic ring. We now find that Co(Salpr)-promoted oxygenation of these phenolic substrates leads to the dioxygen incorporation into the unsaturated side chain, whereas the regioselectivity in the base-promoted oxygenation of these phenols was not always compatible with that in the Co(Salpr)-promoted oxygenation. These results are different from those observed in the cases with other 2,6-di-*tert*-butylphenols and provide significant suggestion on the mechanistic consideration in detail for the dioxygen incorporation into the phenolic substrates.

Scheme I

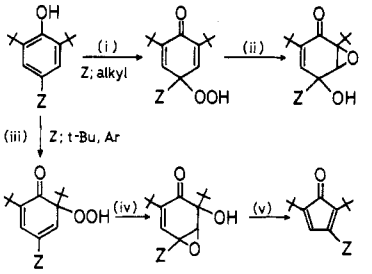


Results

Co(Salpr)-Promoted Oxygenation of 4-Alkenyl-2,6-di-*tert*-butylphenols 1. The oxygenation of **1** with an equimolar amount of Co(Salpr) in dichloromethane at 0

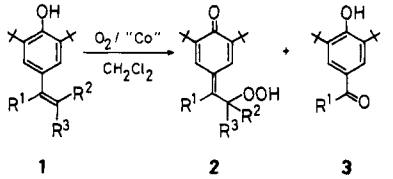
(1) Nishinaga, A.; Tomita, H.; Nishizawa, K.; Matsuura, T.; Ooi, S.; Hirtsu, K. *J. Chem. Soc., Dalton Trans.* **1981**, 1504.
(2) (a) Nishinaga, A.; Itahara, T.; Shimizu, T.; Matsuura, T. *J. Am. Chem. Soc.* **1978**, *100*, 1820. (b) Nishinaga, A.; Itahara, T.; Matsuura, T.; Rieker, A.; Koch, D.; Albert, K.; Hitchcock, K. B. *Ibid.* **1978**, *100*, 1826. (c) Nishinaga, A.; Shimizu, T.; Matsuura, T. *J. Org. Chem.* **1979**, *44*, 2893. (d) Nishinaga, A.; Shimizu, T.; Fujii, T.; Matsuura, T. *Ibid.* **1980**, *45*, 4997.
(3) Nishinaga, A.; Shimizu, T.; Toyoda, Y.; Matsuura, T.; Hirotsu, K. *J. Org. Chem.* **1982**, *47*, 2278.

Scheme II[a]



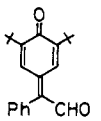
[a] (i) O_2/KOH/EtOH/0 °C or O_2/*t*-BuOK/*t*-BuOH; (ii) O_2/*t*-BuOK/DMF; (iii) O_2/*t*-BuOK/*t*-BuOH–hexane/0 °C; (iv) O_2/*t*-BuOK/*t*-BuOH/40 °C; (v) O_2/*t*-BuOK/*t*-BuOH/70 °C.

°C followed by filtration of the reaction mixture through a short silica gel column to remove the metal complex gave hydroperoxyquinonemethides **2** and *p*-acylphenols **3** as main products which were isolated as crystals. The yields



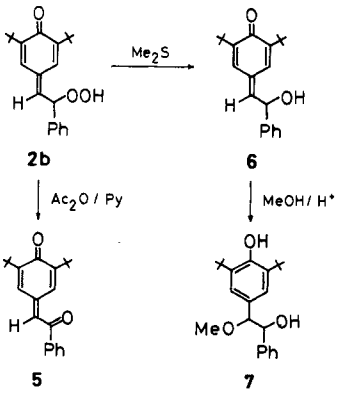
1 **2** **3**

a; $R^1 = R^2 = H$, $R^3 = Me$
b; $R^1 = R^2 = H$, $R^3 = Ph$
c; $R^1 = H$, $R^2 = R^3 = Me$
d; $R^1 = Me$, $R^2 = R^3 = H$
e; $R^1 = Ph$, $R^2 = R^3 = H$
f; $R^1 = Ph$, $R^2 = R^3 = Me$
g; $R^1 = i\text{-}Pr$, $R^2 = R^3 = Me$



4

of the products depended on the nature of the alkenyl group in **1** (Table I). In the case of **1e**, formylquinonemethide **4** was obtained instead of **3**. The oxygenation of **1a** and **1d** with Co(Salpr) gave a complex mixture, which was not further investigated. Compounds **3** were identified with authentic samples.[3] Compounds **2** show characteristic spectra: their IR bands (ν_{OH}, 3420–3480 cm^{-1}; ν_{CO}, around 1600 cm^{-1}) and ^1H NMR olefinic proton signals (δ 6.42–7.44 and 7.48–8.17, a pair of doublets, J = 3 Hz) are in good agreement with the structure.[4,5] Although hydroperoxide **2b** was not isolated in pure form, its chemical reactions confirm the structure. The reaction of **2b** with acetic anhydride in the presence of pyridine gave compound **5** quantitatively. The reduction of **2b** with dimethyl sulfide resulted in the quantitative formation of alcohol **6**, which gave a 1:1 mixture of diastereoisomers of compound **7** in acidic methanol.



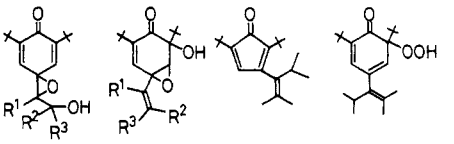
2b **6**

5 **7**

(4) Nishinaga, A.; Tomita, H.; Tarumi, Y.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 4849.
(5) Becker, H. D.; Gustafson, K. *J. Org. Chem.* **1976**, *41*, 214.

These results indicate that the Co(Salpr)-promoted oxygenation of phenols **1** leads to the dioxygen incorporation exclusively into the side chain. Compounds **3** and **4** resulted undoubtedly from the decomposition of the Co^{III}(Salpr) complex of the peroxy anion of **2** formed as the primary perioxidic product.[1]

Base-Promoted Oxygenation of 1. (a) With *t*-BuOK in DMF. The oxygenation of **1** in *N*,*N*-dimethylformamide (DMF) containing an excess of *t*-BuOK at room temperature gave compounds **3**, **8**, and **9**. The ratio of these products and the reactivity of **1** depended on the nature of the substituent in the para position of **1** (Table I). Spectral and analytical data of **8** and **9** are in good agreement with their structures. When compound **9g** was



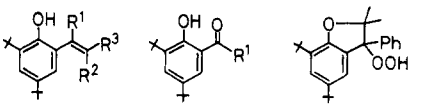
8 **9** **10** **11**

heated with *t*-BuOK in *t*-BuOH, cyclopentadienone **10** was obtained. This result also supports the epoxy-*o*-quinol structure of **9**.[2b] In a short time oxygenation of **1b**, the formation of **8b** was recognized, but after a prolonged reaction **8b** disappeared, indicating that compounds **8** are not stable under the reaction conditions. Unsatisfactory material balance observed in some cases should be due to the instability of **8**.

In general, with phenols **1** whose alkenyl side chain can be freely rotated, the oxygenation proceeds smoothly, resulting in the dioxygen incorporation exclusively into the side chain to give **3** and **8**. As the rotation of the alkenyl group in **1** is hindered, the oxygenation becomes slow and tendency of the dioxygen incorporation into the ortho position increases. Thus, the exclusive ortho dioxygen incorporation is remarkable with **1g**.

(b) With *t*-BuOK in *t*-BuOH. When *t*-BuOH was employed as solvent instead of DMF, the oxygenation took place faster than that in DMF to give the products **3**, **8**, **9**, and **11**. In contrast with the reaction in DMF, the reaction rate in the *t*-BuOK/*t*-BuOH system was not much affected by the nature of the alkenyl substituent, and the dioxygen incorporation into the side chain dominated, although the material balance was not good in some cases (Table I).

Co(Salpr)-Promoted Oxygenation of 2-Alkenyl-4,6-di-*tert*-butylphenols 12. Phenols **12** were synthesized from 2-acyl-4,6-di-*tert*-butylphenols **13** by addition of the appropriate Grignard reagent followed by dehydration (see Experimental Section). In the oxygenation of **12** with an



12 **13** **14**

a; $R^1 = R^2 = H$, $R^3 = Me$
b; $R^1 = R^2 = H$, $R^3 = Ph$
c; $R^1 = H$, $R^2 = R^3 = Me$
d; $R^1 = Me$, $R^2 = R^3 = H$
e; $R^1 = Ph$, $R^2 = R^3 = H$
f; $R^1 = Ph$, $R^2 = R^3 = Me$
g; $R^1 = i\text{-}Pr$, $R^2 = R^3 = Me$

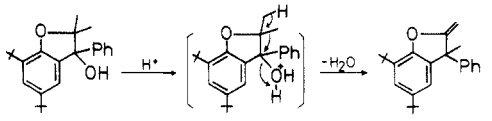
equimolar amount of Co(Salpr) in dichloromethane at 0 °C, **12a–c** gave the corresponding 2-acyl-4,6-di-*tert*-butylphenols **13** exclusively, whereas the reactions of **12d**,**12e**, and **12g** were quite slow even at room temperature to give a complex mixture. Interestingly, the oxygenation of **12f**

Table II. Oxygenation of Phenols 12

12	method[a]	reacn time, h[b]	product yield, %[c] 13	18	19	20	14
12a	A	7.5	96				
12a	B	7.5[d]		64			
12a	C	25.0[d]	10	42			
12b	A	2.5	73				
12b	B	5.5		45			
12b	C	25.0		63			
12c	A	3.5	100				
12c	B	2.5[d]		91			
12c	C	9.0	9	39		22	
12d	B	6.0[d]		95			
12d	C	8.0		50		28	
12e	B	3.5		100			
12e	C	5.0		65		12	
12f	A	30.0[e]	5				78
12f	B	3.0		94			
12f	C	9.0		15		18	52
12g	B	5.5		15[f]	73[f]		
12g	C	8.0		4[f]	18[f]	61	

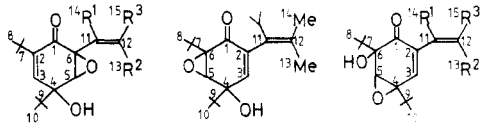
[a] Method A, 12 (1 mmol)/Co(Salpr) (1.2 mmol)/CH_2Cl_2 (30 mL)/0 °C; B, 12 (0.5 mmol)/*t*-BuOK (2 mmol)/DMF (15 mL)/room temperature; C, 12 (0.5 mmol)/*t*-BuOK (2.5 mmol)/*t*-BuOK (10 mL)/*n*-C_6H_{14} (5 mL)/room temperature. [b] Time required for completion of the reaction. [c] Isolation yield. [d] At 0 °C. [e] At room temperature. [f] Determined by ^1H NMR of the isolated mixture of **18g** and **19g**, which could not be separated.

was slow but gave an unusual product **14** in good yield (Table II). The reduction of **14** with PPh_3 gave the corresponding alcohol **15** quantitatively, and heating of the resulting alcohol **15** with *p*-toluenesulfonic acid in benzene gave compound **16**, of which the formation can be rationalized by assuming a cationic intermediate **17**, in which the methyl group is migrated to the cationic carbon. These results support the structure **14**.



15 17 16

Base-Promoted Oxygenation of 12. (a) With *t*-BuOK in DMF. Dioxygen was incorporated selectively into the para position of **12**, contrary to the case with **1**, where dioxygen was incorporated into the side chain (vide supra), to give epoxy-*p*-quinols **18** from **12a–f** and a mixture of **18g** and **19** from **12g** (Table II). The ^1H NMR

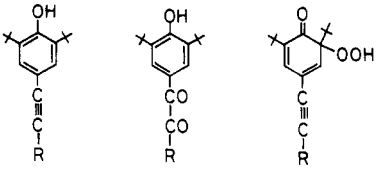


18 19 20

spectra of the products showed a doublet of doublets at δ 3.5–3.8 and 6.0–6.2 with J = 3 Hz, which are typical signals for epoxy-*p*-quinols[2a] but are not useful to distinguish which structure is the case, **18** or **19**. The chemical shifts of the *tert*-butyl groups in the ^{13}C NMR spectra of the products are characteristic to distinguish these structure (Table 3, supplementary material). As seen from Table 3 (supplementary material), the quaternary carbon and the methyl group in the *tert*-butyl group attached to the sp^2 carbon appear at δ 34.6–34.8 and 29.0–29.2, respectively, and those attached to the epoxy ring at δ 32.0–32.2 and 25.8-25.9, respectively.

(b) With *t*-BuOK in *t*-BuOH. The oxygenation of **12** with *t*-BuOK in *t*-BuOH was slower than that in DMF and gave a complex mixture including compounds **13**, **14**, **18**, **19**, and epoxy-*o*-quinol **20** (Table II). The structure of **20** was determined by the elemental analysis, ^1H NMR [δ 3.7–3.9 (d, 1 H, J = 1.4 Hz), 6.8–6.9 (d, 1 H, J = 1.4 Hz)],[2b] and ^{13}C NMR (δ 37.2–37.4, 24.9–25.3 (the quaternary carbon and the methyl carbon in the *t*-BuCOH moiety)]. The results obtained in this system are in contrast to those in the oxygenation of 4-substituted 2,6-di-*tert*-butylphenols in the same system where high regioselective dioxygen incorporation has been observed[2] (vide supra).

Co(Salpr)-Promoted Oxygenation of 4-Alkynyl-2,6-di-*tert*-butylphenols (21). Phenols **21** were conveniently prepared by the reaction of 2,6-*tert*-butyl-*p*-benzoquinone with the appropriate Grignard reagent RC≡CMgBr prepared simply from the exchange between acetylenes and C_2H_5MgBr, followed by the reduction of the resulting quinol with Zn–HCl in ethanol (see Experimental Section). The oxygenation of **21** with Co(Salpr) gave a mixture of compounds **22** and **23** (Table IV). Although

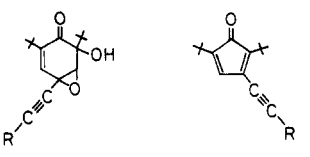


21 22 23

a; R = Ph b; R = n-Bu c; R = t-Bu

23 could not be isolated in pure form, the ^1H NMR showed the caracteristic signals for the peroxy-*o*-quinol structure. Compound **22** resulted evidently from dioxygen incorporation into the side chain triple bond followed by rapid decomposition of the primary peroxidic intermediate.

Base-Promoted Oxygenation of 21. Interestingly, phenols **21** were not susceptible to the oxygenation in the *t*-BuOK/DMF system, similarly to the case of 4-aryl- and 4-acyl-2,6-di-*tert*-butylphenols in the same system. The oxygenation of **21** in the *t*-BuOK/*t*-BuOH system, on the other hand, took place readily to give epoxy-*o*-quinols **24** and cyclopentadienones **25** resulting from the dioxygen incorporation into the ortho position (Table IV). The



24 25

Table IV. Oxygenation of Phenols 21

21	method[a]	reacn time, h[b]	product yield, %[c] 22	23	24	25
21a	A	1.0	63 (68)[e]	(32)[d]		
21a	B	6.0			64	16
21b	A	1.0	70			
21b	B	2.0			77	
21c	A	1.0	56 (58)[d]	40 (42)[d]		
21c	B	2.0			76	14

[a] Method A, **21** (0.5 mmol)/Co(Salpr) (0.6 mmol)/CH_2Cl_2/0 °C. B, **21** (0.5 mmol)/*t*-BuOK (2.5 mmol)/*t*-BuOH (10 mL)/*n*-C_6H_{14} (5 mL)/room temperature. [b] Time required for completion of the reaction. [c] Isolation yield. [d] Values in parentheses are determined by ^1H NMR of the reaction mixture, in which no other products were detected (TLC).

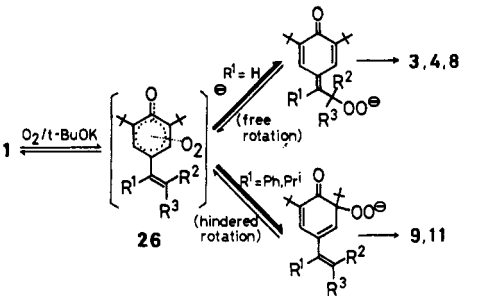
results are quite similar to those observed in the oxygenation of 4-aryl-2,6-di-*tert*-butylphenols.[2b] Although 3-aryl-2,5-di-*tert*-butyl-2,4-cyclopentadienones are normally obtained by the base-catalyzed decomposotion of epoxy-*o*-quinols of type **24**, the treatment of **24** with *t*-BuOK in *t*-BuOH at high temperatures did not give **25**. The behavior of **21** against the base-promoted oxygenation resembles that of 4-acyl-2,6-di-*tert*-butylphenols.[3]

Discussion

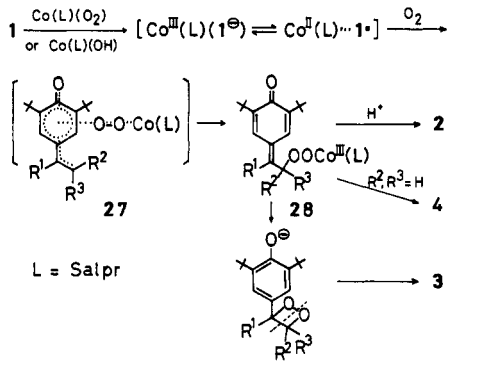
Oxygenation of 1. The base-promoted oxygenation of **1** may be understood to be a bimolecular reversible reaction between O_2 and phenolate anion 1^-.[2,3] Such a bimolecular reaction is rationalized by assuming the rate-determining formation of a charge-transfer complex **26** (π-complex) as the transition state similarly to the cases with other 2,6-di-*tert*-butylphenols.[2,3,6] Since the electronic configuration of the ground state of oxygen is in the triplet state, the transition state **26** (CT) is required to undergo spin inversion $^3(CT) \rightarrow {}^1(CT)$ in order to reach the singlet state of peroxidic product, although this process has normally been forbidden by the spin conservation rule.[7] Similar bimolecular interaction between O_2 and organic substrates has been shown also in oxygenations of organic compounds having low oxidation potential.[8]

In general, phenolate anions exist in free state in the *t*-BuOK/DMF system because of the solvation of the countercation K^+, whereas in the *t*-BuOK/*t*-BuOH system they are associated with the cation.[2,3] Therefore, in the oxygenation of **1** with *t*-BuOK, the solvent-dependent reaction rate is slower in DMF than in *t*-BuOH (Table I) as observed similarly in the base-promoted oxygenation of other 2,6-di-*tert*-butylphenols[2,3] because **26** in a free state (in DMF) has high potential in the reaction coordinate due to an electronic repulsion between the π-system of the substrate anion and the oxygen species, whereas in *t*-BuOH the potential may be lowered by the association with K^+. The difference in the reaction rates, **1b**, **1e**, **1f**, **1g** ≪ **1a**, **1c**, **1d** (Table I), indicates that the potential of **26** is also affected by the 4-substituent in **1**. The steric repulsion due to the R^1 group (**1e–g**) and high delocalization of the π-electron system (**1b**) in the transition state may be responsible for the slow reactions. However, as seen from the results in *t*-BuOH, these substituent effects are diminished by the association with K^+. The association of *t*-BuOK also results in the stabilization of product anions: in DMF the anions of **8** and **11** undergo rapid decomposition.

Scheme III



Scheme IV



The conversion of **26** to product system in the reaction coordinate is dependent upon both bulkiness of R^1 in **1** and presence of K^+. With phenols **1** (R^1 = H, *i*-Pr) the position of the dioxygen incorporation is governed by the 4-substituent in **1**, regardless of the participation of K^+ (Scheme III). On the other hand, with **1** (R^1 = Me, Ph) the presence of K^+ affects conversion route of **26**: in the case of free state of **26**, the dioxygen incorporation into the ortho position increases simply with increase in the bulkiness of the 4-substituent in **1**, probably because of steric inhibition of resonance due to hindered rotation of the 4-substituent. The predominant side chain oxidation in *t*-BuOH suggests that peroxidic product anion association with K^+ formed in the side chain is thermodynamically stable compared to that in the ortho position.

Interestingly, the oxygenation of **1** with Co(Salpr) leads to the selective dioxygen incorporation into the alkenyl side chain, regardless of the nature of the side chain. The same results were obtained with Co(Salpr)(OH) used in place of Co(Salpr).

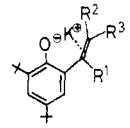
Co(Salpr)(OH) has been shown to act as a base toward 2,6-di-*tert*-butylphenols to form phenolato Co^{III} complexes by an acid–base reaction.[1] The difference in the regioselectivity observed in the dioxygen incorporation between the base- and the Co(Salpr)-promoted oxygenations of **1** is remarkable in contrast to the oxygenation of other 4-

(6) Nishinaga, A.; Shimizu, T.; Matsuura, T. *Chem. Lett.* **1977**, 547.
(7) Doering, W. v. E.; Haines, R. M. *J. Am. Chem. Soc.* **1954**, *76*, 482.
(8) Winberg, H. E.; Dowing, J. R.; Coffman, D. D. *J. Am. Chem. Soc.* **1965**, *87*, 2054. Hoffmann, R. W.; Schneider, J. *Chem. Ber.* **1967**, *100*, 3698. Vorsanger, J. J. *Bull. Soc. Chim. Fr.* **1964**, 119. Wanzlich, H. W.; Kleiner, H. J.; Lasch, I.; Füldner, H. U. Steinmaus, H. *Justus Liebigs Ann. Chem.* **1967**, *708*, 155. Wanzlich, H. W.; Schikora, E. *Chem. Ber.* **1961**, *94*, 2389. Malhotra, S. K.; Hostynek, J. J.; Lundin, A. F. *J. Am. Chem. Soc.* **1968**, *90*, 6565.

substituted 2,6-di-*tert*-butylphenols where the same regioselectivity was observed in both systems.[1-3] This discrepancy is because the Co(Salpr)-promoted oxygenation of **1** involves substrate radical in the dioxygen-incorporation step resulting from homolysis of the phenolatocobalt(III) complex Co^{III}(Salpr) (1^-) produced in an early stage of the reaction (Scheme IV). Actually, the rapid formation of the phenoxy radical **1g**· was detected by the ESR measurement of a mixture of **1g** and Co^{III}(Salpr)(OH) in dichloromethane at room temperature.[9]

On the other hand, the oxidation of **1a–b** with *t*-BuOOH in the presence of a catalytic amount of Co(Salen)(OO-*t*-Bu)[10] leads exclusively to the *tert*-butylperoxylation at the alkenyl group to give *tert*-butylperoxyquinonemethides of type **2**, whereas that of **1g** gave only 6-*tert*-butylperoxy-2,4-cyclohexadienone derivative of type **11**.[11] Since this oxidation with *t*-BuOOH involves free phenoxy radical,[11] it is concluded that the incorporation of dioxygen species into **1g** in both anionic and free radical processes always takes place at the ortho position. Therefore, the exclusive dioxygen incorporation into the alkenyl group in the Co(Salpr)-promoted oxygenation of **1** cannot be interpreted merely in terms of a free phenoxy radical process but rationalized by assuming that the dioxygen incorporation takes place under a strong interaction of phenoxy radical **1** with Co(Salpr) probably to form a transient π-complex **27**, which is then converted to the peroxidic product **28**, so that the unfavorable steric repulsion between the substrate and Co(Salpr) moieties is minimized. The mechanism for the formation of **3** from **28** may involve a dioxetane intermediate (Scheme IV), because the anionic nature of the peroxy group and the weak Lewis acidic nature of Co^{III}(Salpr) in **28** are quite unfavorable for the proper polarization of the peroxy bond required for the Baeyer–Villiger-type decomposition, which is normally accepted for the decomposition of hydroperoxidic compounds.[12]

Oxygenation of 12. The formation of epoxy-*p*-quinols in the *t*-BuOK/DMF system is of normal.[2] The predominant formation of **19** from **12g** may be attributable to larger steric hindrance of the alkenyl group than the *t*-Bu group. The unusual slower oxygenation in the *t*-BuOK/*t*-BuOH system than that in the *t*-BuOK/DMF system is probably due to stabilization of the phenoxide structure by the aggregation of the phenolate anion 12^- with the countercation implicating the alkenyl group (**29**), which



29

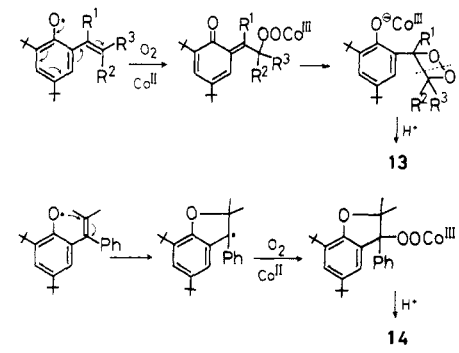
may also be responsible for the complexity of the oxygenation products including the unusual formation of epoxy-*p*-quinols **18** resulting from the dioxygen incorporation into the para position of the phenols. The conversion of the CT complex of type **26** derived from the dioxygenation of **29** to the para peroxidic product may be energetically favorable. The formation of **14** in the oxygenation of **12f** in the *t*-BuOK/*t*-BuOH system may involve phenoxy radical **12f**·, taking into account the results obtained in the Co(Salpr)-promoted oxygenation (vide infra).

The exclusive oxidation of the alkenyl side chain in the Co(Salpr)-promoted oxygenation may be understood similar to the formation of **2** from **1** with Co(Salpr). The predominant formation of **14** in the oxygenation of **12f** with Co(Salpr) should be the result of the radical process where the alkenyl group and the phenoxy radical close to each other resulting in the cyclization (Scheme V).

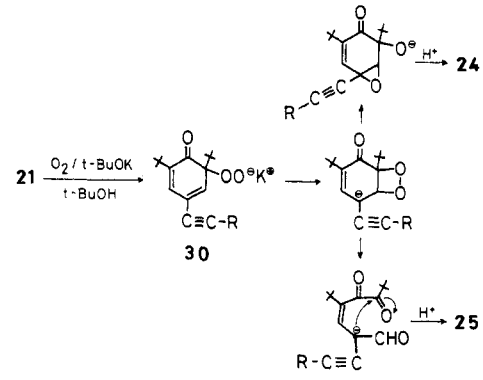
Oxygenation of 21. The nonreactivity of **24** against the *t*-BuOK/*t*-BuOH system at high temperature indicates that compound **24** cannot be the intermediate of **25** contrary to the case with 4-aryl derivatives.[2] The resuls are rationalized by assuming a dioxetane intermediate **30**, from which compounds **24** and **25** are formed separately (Scheme VI).

It is noted that the oxygenation of **21** with Co(Salpr) gives a mixture of **22** and **23**. Similar results were also obtained when Co(Salpr)(OH) was used in place of Co(Salpr). On the other hand, when **21c** was treated with an equimolar amount of Co(Salpr)(OH) in dichloromethane under nitrogen at room temperature for 6.5 h, the radical dimer **31**[13] was obtained quantitatively, indicating that the phenolato Co(Salpr) complex intermediate undergoes homolysis. Further, the oxygenation of **21c** with Co(Salen) or Co(Salen)(OH), by which phenolato complexes formed undergo homolysis efficiently to give phenoxy radicals, did not give **23c** at all but a mixture of **22c** and **31** isolated in 43% and 30% yield, respectively.

Scheme V



Scheme VI



(9) The ESR spectrum showed 0.84 G spaced 12 lines with intensities 1:7.4:23:46:76:97:97:76:46:23:7.4:1, which can be analyzed as hfs resulting from two protons (a_H = 1.68 G) and seven protons (a_H = 0.84 G) coupling system (theoretical signal intensities, 1:7:23:49:78:98:98:78:49:23:7:1). The small discrepancy between the observed and theoretical values may be due to a little nonequivalency of seven protons in the side chain. As the former hfs constant is assigned for the phenolic ring protons of the phenoxy radical and exhibits a normal value for the meta proton,[23] the spin density of **1g**· is retained mainly in the phenolic ring but not in the side chain due to steric inhibition of resonance caused by hidered rotation of the alkenyl group. Similarly, when phenols **32** (Z = alkyl, Ar, COR, CR=NOMe) were mixed with Co(Salpr)(OH) in dichloromethane at room temperature under nitrogen, the characteristic signals due to **32**·[23] were observed. The intensities of the signals depended on the nature of the substituent Z: weak signals for **32** with an electron-withdrawing group.

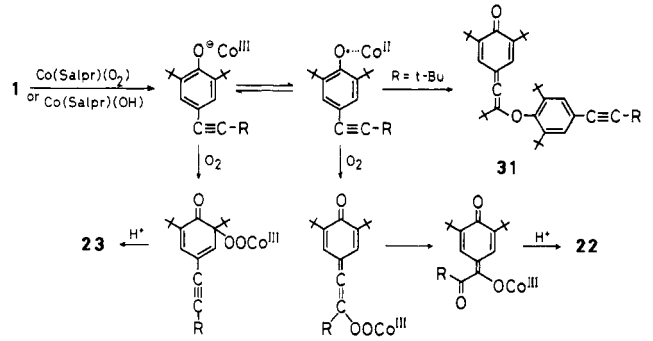
(10) Nishinaga, A.; Tomita, H.; Ohara, H. *Chem. Lett.* **1983**, 1751.

(11) Nishinaga, A.; Yamazaki, S.; Nogusa, H.; Shimoyama, T.; Matsuura, T. *Nippon Kagaku Kaishi* **1985**, 378.

(12) Hamilaton, G. A. In *Molecular Mechanism of Oxygen Activation*; Hayaishi, O., Ed.; Academic: New York, 1974; p 405.

(13) Hauff, S.; Krauss, P.; Rieker, A. *Chem. Ber.* **1972**, *105*, 1446.

Scheme VII

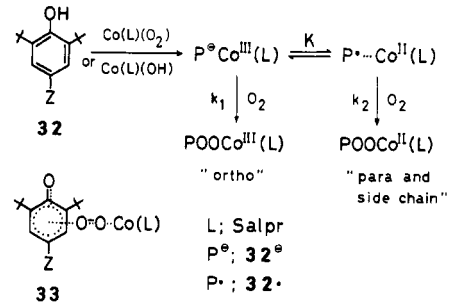


These results suggest that the formation of **22** results from the reaction between the phenoxy radical **21**· and O_2 while compounds **23** are formed by dioxygen incorporation into the phenolate species Co^{III}(Salpr) (21^-). Taking into account the findings of 4-aryl-2,6-di-*tert*-butylphenoxy radicals are reduced by Co(Salpr) to phenolate species[1] and the reaction of 4-aryl-, 4-(alkoxycarbonyl)-, 4-acyl-, and 4-cyano-2,6-di-*tert*-butylphenoxy radicals with superoxo Co^{III} complexes gave exclusively peroxy-*p*-quinols,[14] whereas the oxygenation of the parent phenols of these radicals with Co(Salpr) gave only peroxy-*o*-quinols,[1,3] the mechanism of the oxygenation of **21** with Co(Salpr) is reasonably understood by the diagram shown in Scheme VII).

The regioselective dioxygen incorporation observed in the oxygenation of 2,6-di-*tert*-butylphenols **32** (Z = Ar, COR, CR=NOMe) promoted by Co(salpr) has been understood so far to result simply from nonradical one-step dioxygen insertion to the reactive phenolatocobalt(III) species on the basis of the results obtained in the *t*-BuOK-promoted oxygenation of **32**.[1-3,15] However, the present findings tell us that further elaborate discussion is necessary for general understanding of the regioselectivity in the Co(Salpr)-promoted oxygenation of phenols **32**. Similarly to the case with **1g**,[9] it has been found that phenolato Co^{III}(Salpr) complexes derived from the phenols **32** and Co(Salpr)(OH) produce the corresponding phenoxy radicals in almost cases as observed by ESR.[9] Furthermore, when oxygen was bubbled through the resulting solutions containing the phenoxy radicals, peroxy-*p*-quinols and peroxy-*o*-quinols were specifically formed from **32** (Z = alkyl) and **32** (Z = Ar, COR, CR=NOMe), respectively, as observed so far.[1-3]

From all the findings we have obtained in the Co(Salpr)-promoted oxygenation of *tert*-butylated phenols as well as the oxygenation of phenoxy radicals,[1-4,14,17] the regioselectivity in the dioxygen incorporation is rationalized by the diagram depicted in Scheme VIII. Phenolatocobalt(III) complex (P^-Co^{III}) undergoes electron transfer in an equilibrium to give phenoxy radical coordinated to Co(Salpr) [P·–Co^{II}]. The oxygenation path is governed by the magnitude of K, k_1, and k_2. In the cases of phenols **1** and **21**, since K values must be large as judged by the ESR, path b predominates. With phenols **32** (Z = alkyl), as k_2 is much larger than k_1,[1,17] path b also predominates to give peroxy-*p*-quinolato Co^{III}(Salpr). For phenols **32** (Z = Ar), on the contrary, k_1 is much larger than k_2,[2] and the K value for **32** (Z = COR, CR=NOMe, CN) should be extremely small as judged by ESR (nearly no signal was detected), path a being predominant. In any case, transition-state **33** involving charge- or electron-transfer nature is reasonably considered. The possibility may not be ruled out that the direction to the final products is controlled in such a way that the steric interaction between the phenoxy and Co(Salpr) moieties is minimized, regardless of the nature of the activated substrate intermediate, anionic or radical.

Scheme VIII



Experimental Section

All melting points are uncorrected. Elemental analyses were performed at the Analytical Center of Pharmaceutical Department, Kyoto University. Infrared spectra were recorded on a JASCO IR-1 spectrophotometer. Ultraviolet spectra were recorded on a Shimazu UV-240 spectrophotometer. Proton magnetic resonance spectra were determined with a Varian T-60 spectrometer. Carbon-13 NMR spectra were obtained with a Varian FT-80A spectrometer. Mass spectra were taken with a JEOL-JMS-DX300 spectrometer. ESR spectra were taken with a Varian E3 spectrometer.

Preparation of 4-Alkenyl-2,6-di-*tert*-butylphenols 1. General Procedure. To a stirred solution of the appropriate Grignard reagent (90 mmol) in ether (150 mL) was added dropwise a solution of 4-acyl-2,6-di-*tert*-butylphenol[3] (30 mmol) in ether (250 mL) at room temperature in 1 h. After completion of the addition, the mixture was refluxed for 2.5 h and allowed to stand at room temperature over night. The resulting mixture was poured into an aqueous NH_4Cl solution and extracted with ether. The organic layer was removed, dried (Na_2SO_4), and evaporated to give an oily residue, which was dissolved in acetic acid (100 mL) and was refluxed under a nitrogen atmosphere for 10 min. The resulting mixture was poured onto ice–water and extracted with hexane. The extract was washed with water and then aqueous $NaHCO_3$ solution to remove acetic acid. The organic solution was dried (Na_2SO_4) and evaporated to give an oily residue, which was chromatographed on a silica gel column by eluting with hexane to give phenol **1**. The following results were obtained. The yields were based on the 4-acylphenols.

1a: yield 58%; mp 68.5–69.0 °C; ^1H NMR ($CDCl_3$) δ 1.44 (s, 18 H), 1.85 (d, 3 H, J = 5.4 Hz), 5.13 (s, 1 H, OH), 6.1–6.4 (m, 2 H), 7.17 (s, 2 H).

1b: yield 60%; mp 94–95 °C (lit.[18] 91–93 °C); ^1H NMR ($CDCl_3$) δ 1.46 (s, 18 H), 5.16 (s, 1 H, OH), 6.87 (br s, 1 H), 6.90 (br s, 1 H), 7.0–7.5 (m, 7 H).

1c: yield 31%; mp 45.0–48.0 °C; ^1H NMR ($CDCl_3$) δ 1.46 (s, 18 H), 1.84 (br s, 3 H), 1.87 (br s, 3 H), 5.07 (s, 1 H, OH), 6.17 (m, 1 H), 7.03 (s, 2 H); IR (Nujol) 3435 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O$: M^+ 260.2141. Found: 260.2134.

1d: yield 42%; mp 74.5 °C dec; ^1H NMR ($CDCl_3$) δ 1.46 (s, 18 H), 2.14 (br s, 3 H), 4.98 (m, 1 H), 5.20 (s, 1 H, OH), 5.20 (m, 1 H), 7.33 (s, 2 H); IR (Nujol) 3735 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O$:

(14) Nishinaga, A.; Tomita, H.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 3407.

(15) Sheldon and Kochi[16] have proposed a chain mechanism involving phenoxy radical for the formation of peroxyquinolatocobalt(III) complexes, but their radical mechanism cannot explain the ortho regioselectivity in the dioxygen incorporation into **32**, because the combination of the phenoxy radicals with O_2 takes place normally at the para position and no interconversion between peroxy-*p*-quinolato- and peroxy-*o*-quinolatocobalt(III) complexes has been observed.

(16) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1982; p 95.

(17) Nishianga, A.; Itahara, T.; Shimizu, T.; Tomita, H.; Nishizawa, K.; Matsuura, T. *Photochem. Photobiol.* **1979**, *28*, 687.

(18) Becker, H. D. *J. Org. Chem.* **1969**, *34*, 1211.

M^+ 246.1985. Found: 246.2000.

1e: yield 91%; mp 68.5–69.0 °C; ^1H NMR ($CDCl_3$) δ 1.43 (s, 18 H), 5.20 (s, 1 H, OH), 5.29 (d, 1 H, J = 1.4 Hz), 5.34 (d, 1 H, J = 1.4 Hz), 7.12 (s, 2 H), 7.28 (br s, 5 H); IR (Nujol) 3760 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.67; H, 9.29.

1f: yield 57%; mp 83.0–85.0 °C; ^1H NMR ($CDCl_3$) δ 1.36 (s, 18 H), 1.72 (s, 3 H), 1.79 (s, 3 H), 4.99 (s, 1 H, OH), 6.82 (s, 2 H), 7.11 (br s, 5 H); IR (Nujol) 3665 cm^{-1}. Anal. Calcd for $C_{24}H_{32}O$: M^+ 336.2455. Found: 336.2410.

1g: yield 80%, mp 66.2–67.0 °C; ^1H NMR ($CDCl_3$) δ 0.84 (d, 6 H), 1.40 (s, 3 H), 1.42 (s, 18 H), 1.81 (s, 3 H), 3.0 (sept, 1 H, J = 7 Hz), 6.67 (s, 2 H), 4.96 (s, 1 H); IR (Nujol) 3738 cm^{-1}. Anal. Calcd for $C_{21}H_{34}O$: C, 83.38; H, 11.44. Found: C, 83.09; H, 11.44.

Preparation of 2-Alkenyl-4,6-di-*tert*-butylphenols 12. General Procedure. Phenols **12** were synthesized from 2-acyl-4,6-di-*tert*-butylphenols (2-acetyl- and 2-methylpropanoyl derivatives) (see below) by addition of the appropriate Grignard reagent followed by dehydration. The procedure was essentially the same as that described for the preparation of **1**. The following results were obtained.

12a: this phenol was prepared by the reported method;[19] ^1H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 1.45 (s, 9 H), 5.03 (s, 1 H, OH), 5.80–6.22 (m, 1 H), 6.87–7.21 (m, 2 H).

12b: yield 53%; mp 66.5–68.5 °C; ^1H NMR ($CDCl_3$) δ 1.33 (s, 9 H), 1.44 (s, 9 H), 5.15 (s, 1 H, OH), 7.0–7.6 (m, 9 H); IR (Nujol) 3633, 3570 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.58; H, 9.31.

12c: yield 76%; oil; ^1H NMR ($CDCl_3$) δ 1.37 (s, 9 H), 1.40 (s, 9 H), 1.62 (s, 3 H), 1.92 (s, 3 H), 5.10 (s, 1 H, OH), 6.05 (s, 1 H), 6.80 (d, 1 H, J = 3 Hz), 7.10 (d, 1 H, J = 3 Hz); IR (neat film) 3600 cm^{-1}.

12d: yield 95%; bp 110–114 °C (2 mmHg); ^1H NMR ($CDCl_3$) δ 1.34 (s, 9 H), 1.47 (s, 9 H), 2.14 (m, 3 H), 5.15 (m, 1 H), 5.45 (m, 1 H), 5.89 (s, 1 H, OH), 6.98 (d, 1 H, J = 2 Hz), 7.24 (d, 1 H, J = 2 Hz); IR (neat film) 3600 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.62; H, 10.64.

12e: yield 69%; mp 55.5–56.5 °C; ^1H NMR ($CDCl_3$) δ 1.30 (s, 9 H), 1.42 (s, 9 H), 5.21 (s, 1 H, OH), 5.34 (d, 1 H, J = 2 Hz), 5.84 (d, 1 H, J = 2 Hz), 6.87 (d, 1 H, J = 3 Hz), 7.2–7.3 (m, 6 H); IR (Nujol) 3600 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.55; H, 9.28.

12f: yield 55%; mp 79.0–80.5 °C; ^1H NMR ($CDCl_3$) δ 1.24 (s, 9 H), 1.42 (s, 9 H), 1.72 (s, 3 H), 1.90 (s, 3 H), 5.47 (s, 1 H, OH), 6.80 (d, 1 H, J = 3 Hz), 7.1–7.2 (m, 6 H); IR (Nujol) 4545, 3525 cm^{-1}. Anal. Calcd for $C_{24}H_{32}O$: C, 85.66; H, 9.59. Found: C, 85.44; H, 8.84.

12g: yield 45%; oil; ^1H NMR ($CDCl_3$) δ 0.75 (d, 3 H, J = 7 Hz), 1.00 (d, 3 H, J = 7 Hz), 1.27 (s, 9 H), 1.38 (s, 9 H), 1.45 (s, 3 H), 1.87 (s, 3 H), 2.94 (sept, 1 H, J = 7 Hz), 5.20 (s, 1 H, OH), 6.65 (d, 1 H, J = 2 Hz), 7.09 (d, 1 H, J = 2 Hz); IR (neat film) 3500 cm^{-1}. Anal. Calcd for $C_{21}H_{34}O$: C, 83.38; H, 11.33. Found: C, 83.20; H, 11.44.

2-Acetyl-4,6-di-*tert*-butylphenol. To a solution of methylmagnesium iodide (1.5 M) in ether (100 mL) was added dropwise a solution of 2,4-di-*tert*-butyl-6-cyanophenol[20] (0.5 M) in ether, prepared from 2,4-di-*tert*-butyl-6-formylphenol,[21] at 0 °C in 30 min. The mixture was then allowed to stand at room temperature overnight and worked up as usual. Recrystallization of the product from methanol gave 2-acetyl-4,6-di-*tert*-butylphenol in pure form: yield 58%; mp 43.0–44.5 °C; ^1H NMR ($CDCl_3$) β 1.33 (s, 9 H), 1.43 (s, 9 H), 2.63 (s, 3 H), 7.53 (m, 2 H), 12.95 (s, 1 H, OH); IR (Nujol) 3000, 1640 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_2$: C, 77.34; H, 9.74. Found: C, 77.07; H, 9.96.

2,4-Di-*tert*-butyl-6-(2-methylpropanoyl)phenol. This phenol was prepared from 2,4-di-*tert*-butyl-6-cyanophenol and isopropylmagnesium chloride by the same procedure described above: yield 83%; mp 33.5–34.5 °C; ^1H NMR ($CDCl_3$) δ 1.20 (d, 6 H, J = 6.8 Hz), 1.23 (s, 9 H), 1.43 (s, 9 H), 3.59 (sept, 1 H, J = 6.8 Hz), 7.43 (d, 1 H, J = 2.4 Hz), 7.52 (d, 1 H, J = 2.4 Hz), 13.13 (s, 1 H, OH); IR (Nujol) 3020, 1636 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.32; H, 10.23. Found: C, 78.21; H, 10.21.

Preparation of 4-Alkynyl-2,6-di-*tert*-butylphenols (21). The phenols **21** have been synthesized by Rieker et al.[13] from the reaction of 2,6-di-*tert*-butyl-*p*-benzoquinone with the corresponding alkynyllithium in liquid ammonia followed by the reduction of the resulting quinols with lithium aluminum hydride. However, the method is somewhat troublesome and the yields are not good. Simplified modification has now been found to improve the yields.

General Procedure. A solution of 2,6-di-*tert*-butyl-*p*-benzoquinone (2 equiv) in ether was added at −70 °C to a solution of the alkynyl Grignard reagent prepared from the reaction of the alkyne with ethylmagnesium bromide. The mixture was warmed up to room temperature, poured into an aqueous NH_4Cl solution, and extracted with ether. Evaporation of the solvent and crystallization of the resulting crude product gave 4-alkynyl-2,6-di-*tert*-butyl-2,5-cyclohexadienone (*p*-quinol): yield (based on the Grignard reagent used), 70%, 77%, and 64% for PhC≡C, *n*-BuC≡C, and *t*-BuC≡C derivatives, respectively. The *p*-quinol obtained above was reduced by Zn–HCl in ethanol according to the procedure reported[22] to give **21**: yield (based on the quinol used), **21a** (77%), **21b** (70%), and **21c** (94%).

Oxygenation of 1 with Co(Salpr). The oxygenation was carried out by the same method previously reported.[2] The products were separated by silica gel chromatography (1:1 CH_2Cl_2/hexane) and crystallized from hexane. The results are listed in Table I. Spectral data of the products are given below.

2b: only ^1H NMR data was available because of its instability; ^1H NMR ($CDCl_3$) δ 1.27 (s, 9 H), 1.30 (s, 9 H), 6.05 (d, 1 H, J = 8.5 Hz), 6.37 (d, 1 H, J = 8.5 Hz), 6.80 (d, 1 H, J = 3 Hz), 7.52 (d, 1 H, J = 3 Hz), 7.33 (s, 5 H), 8.75 (s, 1 H, OOH).

2e: mp 105 °C dec; ^1H NMR ($CDCl_3$) δ 1.15 (s, 9 H) 1.30 (s, 9 H), 5.15 (s, 2 H), 7.32 (d, 1 H, J = 3 Hz), 7.32 (s, 5 H), 7.48 (d, 1 H, J = 3 Hz), 8.26 (s, 1 H, OOH); IR (Nujol) 3420 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.04; H, 8.21.

2f: mp 130 °C dec; ^1H NMR ($CDCl_3$) δ 1.10 (s, 9 H), 1.32 (s, 9 H), 1.41 (br s, 6 H), 6.42 (d, 1 H, J = 3 Hz), 8.17 (d, 1 H, J = 3 Hz), 6.9–7.4 (m, 5 H), 7.69 (s, 1 H, OOH); IR (Nujol) 3460, 1600 cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_3$: C, 78.22; H, 8.75. Found: C, 77.81; H, 8.88.

2g: mp 94 °C dec; ^1H NMR ($CDCl_3$) δ 1.30 (s, 18 H), 1.42 (d, 6 H, J = 7 Hz), 1.42 (br s, 6 H), 2.73 (sept, 1 H, J = 7 Hz), 7.44 (d, 1 H, J = 3 Hz), 8.00 (d, 1 H, J = 3 Hz), 7.45 (s, 1 H, OOH); IR (Nujol) 3480, 1605 cm^{-1}. Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.35; H, 10.42.

4: mp 95–96 °C; ^1H NMR ($CDCl_3$) δ 1.16 (s, 9 H), 1.33 (s, 9 H), 6.94 (d, 1 H, J = 3 Hz), 8.00 (d, 1 H, J = 3 Hz), 7.0–7.5 (m, 5 H), 10.55 (s, 1 H); IR (Nujol) 1680, 1625 cm^{-1}. Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.74; H, 8.05.

Reduction of 2b with Me_2S. To a slution of **2b** in CH_2Cl_2, prepared from the oxygenation of **1b** (2 mmol) with Co(Salpr) in CH_2Cl_2 (20 mL) followed by removal of the complex by filtration of the reaction mixture through a silica gel layer as described (vide supra), was added dimethyl sulfide (5 mL). The mixture was allowed to stand at room temperature for 30 min, the solvent and dimethyl sulfide were evaporated, and the mixture was chromatographed on a silica gel plate developed with a mixture of dichloromethane and hexane (1:1) to give **6** as yellow crystals (62% yield), which were recrystallized from hexane to give yellow prisms: mp 123–125 °C (crystallized from hexane); ^1H NMR ($CDCl_3$) δ 1.27 (s, 9 H), 1.30 (s, 9 H), 2.33 (d, 1 H, J = 3 Hz, OH), 5.88 (dd, 1 H, J = 9, 3 Hz), 6.30 (d, 1 H, J = 9 Hz), 6.80 (d, 1 H, J = 3 Hz), 7.35 (br s, 6 H); IR (Nujol) 3460, 1610 cm^{-1}; UV (cyclohexane) λ_{max} 306 nm (log ϵ 4.48). Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.22; H, 8.58.

The similar reduction of **2e** gave the corresponding alcohol as yellow crystals in 59% yield: mp 100–102 °C; ^1H NMR ($CDCl_3$) δ 1.17 (s, 9 H), 1.34 (s, 9 H), 1.80 (s, 1 H, OH), 4.85 (s, 2 H), 7.40 (br s, 5 H), 6.93 (d, 1 H, J = 3 Hz), 7.55 (d, 1 H, J = 3 Hz); IR (Nujol) 3440, 1615 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H,

(19) Oki, M. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1319.

(20) This phenol was prepared by reflux of a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde oxime in acetic anhydride in 70% yield: mp 114–114.5 °C; ^1H NMR ($CDCl_3$) δ 1.24 (s, 9 H), 1.38 (s, 9 H), 7.07 (d, 1 H, J = 3 Hz), 7.17 (d, 1 H, J = 3 Hz); IR (Nujol) 2240 cm^{-1}.

(21) Naik, R. M.; Thakov, N. M. *J. Org. Chem.* **1957**, *22*, 1626.

(22) Rieker, A.; Scheffler, K. *Justus Liebigs Ann. Chem.* **1965**, *689*, 78.

(23) Buchachenko, A. L. *Stable Radical*; Consultants Bureau: New York, 1965; p 58.

8.70. Found: C, 81.57; H, 8.79.

Acid Treatment of 6 in Methanol. To a solution of **6** (0.4 mmol) in methanol (8 mL) was added one drop of trifluoroacetic acid. The original yellow color of the solution disappeared immediately. Evaporation and silica gel layer chromatography (CH_2Cl_2) of the mixture gave the addition product **7** and its diastereomer in 50% and 50% yields, respectively.

7: colorless needles (from hexane); mp 90–92 °C; ^1H NMR ($CDCl_3$) δ 1.37 (s, 18 H), 2.43 (br s, 1 H, OH), 3.22 (s, 3 H), 4.23 (d, 1 H, J = 5 Hz), 4.77 (br signal, with addition of D_2; with addition of D_2O, d, 1 H, J = 5 Hz), 5.10 (s, 1 H, OH), 6.77 (s, 2 H), 7.13 (br s, 5 H); IR (Nujol) 3650, 3430 cm^{-1}. Anal. Calcd for $C_{23}H_{32}O_3$: C, 77.49; H, 9.05. Found: C, 77.36; H, 8.86.

Stereoisomer of 7: colorless needles (hexane); mp 119–120 °C; ^1H NMR ($CDCl_3$) δ 1.33 (s, 18 H), 3.33 (s, 3 H), 3.47 (br s, 1 H, OH), 4.02 (d, 1 H, 8.5 Hz), 4.52 (d, 1 H, J = 8.5 Hz), 5.07 (s, 1 H, OH), 6.65 (s, 2 H), 6.8–7.3 (m, 5 H); IR (Nujol) 3640, 3520 cm^{-1}. Anal. Calcd for $C_{23}H_{32}O_3$: C, 77.49; H, 9.05. Found: C, 77.54; H, 9.31. From the NMR data, **7** and its isomer are reasonably assigned as *RR* (*SS*) and *RS* (*SR*) forms, respectively.

Reaction of 2b with Acetic Anhydride. Acetic anhydride (2 mL) and pyridine (4 mL) were added to a solution of **2b** in CH_2Cl_2, prepared similarly to the case for the reduction described above in which **2b** was contained in 52% as determined by the NMR of the mixture. The resulting mixture was allowed to stand at room temperature for several hours, evaporated, and chromatographed on a silica gel plate (1:1 CH_2Cl_2/hexane) to give **5** in 50% yield (based on **1b** employed): orange prisms (from hexane); mp 109–110 °C; ^1H NMR ($CDCl_3$) δ 1.28 (s, 9 H), 1.31 (s, 9 H), 6.83 (d, 1 H, J = 2 Hz), 7.05 (s, 1 H), 7.93 (d, 1 H, J = 2 Hz), 7.2–8.0 (m, 5 H); IR (Nujol) 1635, 1615 cm^{-1}; UV (cyclohexane) λ_{max} 331 nm (log ϵ 4.52). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.99; H, 8.13.

Base-Promoted Oxygenation of 1. General Procedure. To a solution of *t*-BuOK (4 mmol) in the appropriate solvent (DMF or 2:1 *t*-BuOH/hexane) under bubbling of oxygen was added **1** (1 mmol) at room temperature in DMF and at 0 °C in *t*-BuOH/hexane. Oxygen was bubbled until the completion of the reaction as monitored by TLC. The mixture was poured into an aqueous NH_4Cl solution and extracted with hexane. The extract was washed with water, dried (Na_2SO_4), and evaporated. The resulting residue was chromatographed on a silica gel plate (1:1 CH_2Cl_2/hexane) to give the products **3**, **4**, **8**, **9**, and **11** as listed in Table I. Compounds **3** were identified with authentic samples.[10] The physical data for other products are given below.

Compunds **8** were obtained as crystals which were recrystallized from hexane to give colorless prisms except for **8d**.

8a: mp 114.0–114.7 °C; ^1H NMR ($CDCl_3$) δ 1.27 (s, 18 H), 1.27 (m, 3 H), 3.2–4.1 (m, 2 H), 2.47 (br s, 1 H, OH), 6.13 (d, 1 H, J = 3 Hz), 6.38 (d, 1 H, J = 3 Hz); IR (Nujol) 3500, 1655, 1635 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.06; H, 9.62.

8b: mp 144.0–145.0 °C; ^1H NMR ($CDCl_3$) δ 1.18 (s, 9 H), 1.25 (s, 9 H), 2.60 (br s, 1 H, OH), 3.58 (d, 1 H, J = 8 Hz), 4.80 (d, 1 H, J = 8 Hz), 6.02 (d, 1 H, J = 3 Hz), 6.52 (d, 1 H, J = 3 Hz), 7.25 (s, 5 H); IR (Nujol) 3300, 1645, 1630 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.89; H, 8.56.

8c: mp 112–113 °C; ^1H NMR ($CDCl_3$) δ 1.11 (s, 18 H), 1.39 (s, 6 H), 3.23 (s, 1 H), 6.00 (d, 1 H, J = 3 Hz), 7.04 (d, 1 H, J = 3 Hz); IR (Nujol) 3600, 1645, 1630 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.90; H, 9.91.

8d: ^1H NMR ($CDCl_3$) δ 1.24 (s, 18 H), 1.54 (s, 3 H), 3.84 (s, 2 H), 6.42 (d, 1 H, J = 3 Hz), 6.56 (d, 1 H, J = 3 Hz). This compound could not be obtained in pure form, but the NMR data of the crude material is in good agreement with the structure.

9d: liquid, which was not further purified; ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.27 (s, 9 H), 1.84 (m, 3 H), 3.68 (d, 1 H, J = 1 Hz), 4.05 (s, 1 H, OH), 5.13 (m, 2 H), 6.88 (d, 1 H, J = 1 Hz); IR (neat film) 3590, 1700 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.58; H, 9.60.

9e: mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 1.01 (s, 9 H), 1.15 (s, 9 H), 3.89 (d, 1 H, J = 1 Hz), 4.03 (s, 1 H, OH), 5.60 (s, 2 H), 6.73 (d, 1 H, J = 1 Hz), 7.43 (s, 5 H); IR (Nujol) 3580, 1715 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.51; H, 8.38.

9f: mp 110 °C dec; ^1H NMR ($CDCl_3$) δ 0.56 (s, 9 H), 1.20 (s, 9 H), 1.53 (s, 3 H), 1.98 (s, 3 H), 3.62 (d, 1 H, J = 1 Hz), 3.86 (s, 1 H, OH), 6.84 (d, 1 H, J = 1 Hz), 7.0–7.4 (m, 5 H); IR (Nujol) 3580, 1695 cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_3$: C, 78.22; H, 8.75. Found: C, 77.73; H, 8.93.

9g: liquid, which was not further purified; ^1H NMR ($CDCl_3$) δ 1.01 (s, 9 H), 1.21 (s, 9 H), 1.20 (d, 6 H, J = 7 Hz), 2.83 (sept, 1 H, J = 1 Hz), 1.78 (br s, 3 H), 1.83 (br s, 3 H), 3.76 (d, 1 H, J = 1 Hz), 3.94 (s, 1 H, OH), 6.64 (d, 1 H, J = 1 Hz); IR (neat film) 3590, 1685 cm^{-1}. Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.41; H, 10.37. Found: C, 74.72; H, 10.37.

11: pale yellow needles (from hexane); mp 95 °C dec; ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.00 (d, 6 H, J = 7.5 Hz), 1.22 (s, 9 H), 1.64 (s, 3 H), 1.74 (s, 3 H), 2.97 (sept, 1 H, J = 7.5 Hz), 6.01 (d, 1 H, J = 2 Hz), 6.43 (d, 1 H, J = 2 Hz), 8.50 (s, 1 H, OOH); IR (Nujol) 3500, 3416, 1650 cm^{-1}. Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.45; H, 10.46.

Conversion of 9g to Cyclopentadienone 10. A solution of **9g** (0.48 mmol) and *t*-BuOK (215 mg, 4 equiv) in *t*-BuOH (20 mL) was heated at 70 °C under nitrogen for 40 h. The mixture was poured into an aqueous NH_4Cl solution and extracted with hexane. Chromatographic separation using a silica gel plate (hexane) gave **10** as liquid, which was crystallized on standing: bp 75 °C (1 mmHg); mp 41.5–42.4 °C; ^1H NMR ($CDCl_3$) δ 1.15 (br s, 18 H), 1.15 (m, 6 H), 1.66 (s, 3 H), 1.72 (s, 3 H), 6.04 (s, 1 H); UV (cyclohexane) λ_{max} 412 nm (ϵ 465); IR (neat film) 1710 cm^{-1}. Anal. Calcd for $C_{20}H_{30}O$: C, 83.27; H, 11.18. Found: C, 83.00; H, 10.95.

Oxygenation of 12 with Co(Salpr). The oxygenation was carried out by the same way as described for **1**. The usual workup gave **13** and **14**. The results are listed in Table II. The oxygenations of **12d**, **12e**, and **12g** were extremely slow and gave complex mixtures which were not further investigated. Compound **13** (R^1 = H) was identified with an authentic sample.[14] The structure of **13f** was determined by its ^1H NMR spectrum: δ 1.24 (s, 9 H), 1.47 (s, 9 H), 7.3–7.8 (m, 7 H), 12.72 (s, 1 H, OH).

14: mp 170 °C dec; ^1H NMR ($CDCl_3$) δ 1.33 (s, 9 H), 1.44 (s, 9 H), 0.88 (s, 3 H), 1.57 (s, 3 H), 7.30 (s, 1 H, OOH), 7.2–7.6 (m, 7 H); IR (Nujol) 3521 cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_3$: C, 78.22; H, 8.75. Found: C, 78.28; H, 8.65.

Reduction of 14. To a solution of **14** (0.11 mmol) in CH_2Cl_2 (5 mL) was added triphenylphosphine (0.22 mmol). The mixture was allowed to stand at room temperature for 1 h. Chromatographic separation of the products on a silica gel plate (1:1 CH_2Cl_2/hexane) gave **15** (98% yield), which was recrystallized from hexane to give colorless needles: mp 100–101 °C; ^1H NMR ($CDCl_3$) δ 1.33 (s, 9 H), 1.43 (s, 9 H), 0.85 (s, 3 H), 1.57 (s, 3 H), 2.00 (br s, 1 H, OH), 7.0–7.6 (m, 7 H); IR (Nujol) 3510 cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 81.59; H, 9.41.

Acid Treatment of 15. A solution of **15** (0.62 mmol) and *p*-toluenesulfonic acid (190 mg) in benzene (20 mL) was refluxed for 2 h. The mixture was poured into ice-cooled water and separated the organic layer, which was washed with an aqueous $NaHCO_3$ solution and evaporated. Chromatographic separation of the product on a silica gel plate (1:1 CH_2Cl_2/hexane) gave **16** (27% yield). Recrystallization from hexane gave colorless prisms: mp 108–109 °C; ^1H NMR ($CDCl_3$) δ 1.34 (s, 9 H), 1.44 (s, 9 H), 1.85 (s, 3 H), 4.77 (s, 1 H), 5.36 (s, 1 H), 7.2–7.6 (m, 7 H). Anal. Calcd for $C_{24}H_{30}O$: C, 86.18; H, 9.04. Found: C, 86.03; H, 9.14.

Base-Promoted Oxygenation of 12. The oxygenation was carried out by the same way as described for **1**. The usual workup of the oxygenation mixture gave **13**, **14** and **18–20**. The results are listed in Table II. The physical data of the products are given below.

18a: liquid; bp 135–138 °C (3 mmHg); ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.18 (s, 9 H), 1.78 (d, 3 H, J = 5.5 Hz), 3.57 (d, 1 H, J = 3 Hz), 6.06 (d, 1 H, J = 3 Hz), 5.4–6.2 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 195.36 (C_1), 143.29 (C_2), 138.78 (C_3), 74.71 (C_4), 61.28 (C_5), 64.14 (C_6), 34.61 (C_7), 29.04 (C_8), 37.66 (C_9), 24.58 (C_{10}), 129.28 (C_{11}), 121.28 (C_{12}), 17.70 (R^3); IR (neat film) 3570, 1680 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.09; H, 9.46.

18b: liquid; ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.21 (s, 9 H), 2.67 (s, 1 H, OH), 3.67 (d, 1 H, J = 3 Hz), 6.19 (d, 1 H, J = 3 Hz), 6.67 (d, 1 H, J = 16 Hz), 6.93 (d, 1 H, J = 16 Hz), 7.1–7.6 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 194.86 (C_1), 143.59 (C_2), 138.83 (C_3), 74.99 (C_4), 61.80 (C_5), 65.46 (C_6), 34.83 (C_7), 29.15 (C_8), 37.76 (C_9), 24.64 (C_{10}), 119.79 (C_{11}), 131.92 (C_{12}), 135.84 (C_1'), 126.68 (C_2', C_6'), 128.50 (C_3', C_5'), 128.09 (C_4'); IR (neat film) 3505, 1663 cm^{-1}; UV (cyclohexane) λ_{max} 208, 253 nm (log ϵ 4.24, 4.29). Anal. Calcd for

$C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.64; H, 8.46.

18c: colorless prisms (from hexane), mp 83–85 °C; ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H), 1.15 (s, 9 H), 1.67 (s, 3 H), 1.76 (s, 3 H), 2.33 (s, 1 H, OH), 3.55 (d, 1 H, J = 3 Hz), 6.00 (d, 1 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$) δ 195.24 (C_1), 143.54 (C_2), 138.04 (C_3), 74.89 (C_4), 61.70 (C_5), 62.00 (C_6), 34.78 (C_7), 29.06 (C_8), 37.53 (C_9), 24.72 (C_{10}), 114.80 (C_{11}), 142.51 (C_{12}), 19.65 (R^3), 25.89 (R^2); IR (Nujol) 3470, 1680 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.65; H, 9.65.

18d: colorless prisms (from hexane); mp 100–102 °C; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.18 (s, 9 H), 1.90 (br s, 3 H), 2.26 (s, 1 H, OH), 3.59 (d, 1 H, J = 3 Hz), 5.11 (br s, 2 H), 6.13 (d, 1 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$) δ 194.23 (C_1), 143.55 (C_2), 138.79 (C_3), 74.57 (C_4), 62.50 (C_5), 64.96 (C_6), 34.79 (C_7), 29.10 (C_8), 37.39 (C_9), 24.81 (C_{10}), 138.76 (C_{11}), 114.93 (C_{12}), 19.86 (R^1); IR (Nujol) 3522, 1679 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.42; H, 9.41.

18e: colorless prisms (from hexane); mp 170–172 °C; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9 H), 1.19 (s, 9 H), 2.31 (s, 1 H, OH), 3.86 (d, 1 H, J = 3 Hz), 5.34 (s, 1 H), 5.73 (s, 1 H), 6.09 (d, 1 H, J = 3 Hz), 7.1–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 195.30 (C_1), 143.73 (C_2), 138.17 (C_3), 75.07 (C_4), 61.76 (C_5), 65.49 (C_6), 34.78 (C_7), 29.04 (C_8), 37.54 (C_9), 24.89 (C_{10}), 141.90 (C_{11}), 117.30 (C_{12}), 137.56 (C_1'), 126.28 (C_2', C_6'), 128.14 (C_3', C_5'), 127.86 (C_4'); IR (Nujol) 3522, 1685 cm^{-1}; UV (cyclohexane) λ_{max} 207, 230 nm (log ϵ 4.14, 4.10). Anal. Calcd for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.79; H, 8.31.

18f: colorless prisms (from hexane); mp 153–154 °C; ^{1}H NMR ($CDCl_3$) δ 0.62 (s, 9 H), 1.22 (s, 9 H), 1.60 (s, 3 H), 1.82 (s, 3 H), 2.19 (s, 1 H, OH), 3.61 (d, 1 H, J = 3 Hz), 6.03 (d, 1 H, J = 3 Hz), 7.0–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 195.48 (C_1), 143.71 (C_2), 137.66 (C_3), 75.06 (C_4), 61.73 (C_5), 65.05 (C_6), 34.77 (C_7), 29.04 (C_8), 36.96 (C_9), 24.73 (C_{10}), 134.76 (C_{11}), 129.26 (C_{12}), 139.10 (C_1'), 128.15 (C_2', C_6'), 128.89 (C_3', C_5'), 126.68 (C_4'); IR (Nujol) 3527, 1683 cm^{-1}; UV (cyclohexane) λ_{max} 207, 230 nm (log ϵ 4.12, 3.87). Anal. Calcd for $C_{24}H_{32}O_3$: C, 78.22; H, 8.75. Found: C, 78.12; H, 8.82.

19. This compound was obtained as a mixture with **18g**, which could not be separated by the TLC, but the elemental analysis shows a mixture of materials with same composition. The olefinic proton signals of the minor component [δ 3.71 (d, 1 H, J = 3 Hz) and 6.02 (d, 1 H, J = 3 Hz)] could be assigned for **18g**.

19: ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 9 H), 1.14 (s, 9 H), 0.90 (d, 6 H, J = 8 Hz), 2.17 (s, 1 H, OH), 2.5–3.0 (m, 1 H), 2.76 (br s, 6 H), 3.71 (d, 1 H, J = 3 Hz), 6.02 (d, 1 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$) δ 195.18 (C_1), 137.41 (C_2), 140.60 (C_3), 74.95 (C_4), 59.73 (C_5), 66.11 (C_6), 32.23 (C_7), 25.82 (C_8), 37.24 (C_9), 24.95 (C_{10}), 134.76 (C_{11}), 128.89 (C_{12}), 19.24 (R^3), 20.49 (R^2) [δ 21.08, 22.36, and 22.71 may be tentatively assigned to R^1]. Anal. Calcd for $C_{21}H_{34}O_3$ as the mixture of **19** and **18g**: C, 75.40; H, 10.25. Found: C, 75.64; H, 10.38.

20c: liquid; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9 H), 1.09 (s, 9 H), 1.82 (m, 6 H), 3.81 (d, 1 H, J = 1.4 Hz), 5.87 (m, 1 H), 6.81 (d, 1 H, J = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 199.96 (C_1), 139.84 (C_2), 140.58 (C_3), 63.49 (C_4), 57.82 (C_5), 80.58 (C_6), 37.06 (C_7), 25.35 (C_8), 32.24 (C_9), 25.78 (C_{10}), 117.32 (C_{11}), 138.56 (C_{12}), 19.54 (R^3), 24.80 (R^2); IR (neat film) 3533, 1681 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.29; H, 9.79.

20d: liquid; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.10 (s, 9 H), 1.92 (br s, 3 H), 3.77 (d, 1 H, J = 1.4 Hz), 3.96 (s, U H, OH), 5.17 (m, 1 H), 5.32 (m, 1 H), 6.88 (d, 1 H, J = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ (C_1 missed) 141.89 (C_2), 138.53 (C_3), 63.52 (C_4), 57.91 (C_5), 81.65 (C_6), 37.28 (C_7), 25.50 (C_8), 32.46 (C_9), 25.93 (C_{10}), 136.82 (C_{11}), 118.39 (C_{12}), 21.23 (R^1); IR (neat film) 3525, 1681 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.22; H, 9.61.

20e: liquid; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.04 (s, 9 H), 3.79 (d, 1 H, J = 1.4 Hz), 3.88 (s, 1 H, OH), 5.41 (br s, 1 H), 5.49 (br s, 1 H), 6.80 (d, 1 H, J = 1.4 Hz), 7.24 (br s, 5 H); ^{13}C NMR ($CDCl_3$) δ 199.64 (C_1), 143.19 (C_2), 143.38 (C_3), 63.48 (C_4), 58.06 (C_5), 81.46 (C_6), 37.42 (C_7), 25.34 (C_8), 32.35 (C_9), 25.94 (C_{10}), 141.29 (C_{11}), 118.75 (C_{12}), 140.07 (C_1'), 127.81 (C_2', C_6'), 128.17 (C_3', C_5'), 127.51 (C_4'); IR (Nujol) 3524, 1680 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.62; H, 8.23.

20g: colorless prisms (from hexane); mp 113–114 °C; ^{1}H NMr ($CDCl_3$) δ 0.86 (d, 3 H, J = 7 Hz), 0.96 (d, 3 H, J = 7 Hz), 1.08 (br s, 18 H), 1.77 (s, 3 H), 1.46 (s, 3 H), 2.9 (sept, 1 H, J = 7 Hz), 3.69 (s, 1 H, OH), 3.90 (d, 1 H, J = 1.4 Hz), 6.88 (d, 1 H, J = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 198.29 (C_1), 142.44 (C_2), 147.68 (C_3), 63.14 (C_4), 58.28 (C_5), 80.07 (C_6), 37.28 (C_7), 25.42 (C_8), 32.09 (C_9), 25.80 (C_{10}), 133.46 (C_{11}), 130.71 (C_{12}), 19.70 (R^3), 20.86 (R^2), [R^1 not identified]; IR (Nujol) 3501, 1655 cm^{-1}. Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.14; H, 10.42.

Oxygenation of 21. The oxygenation of **21** was carried out in the same way described for **12**. Compounds **22** and **23** were obtained in the Co(Salpr)-promoted reaction whereas **24** and **25** in the *t*-BuOK/*t*-BuOH system. The results are listed in Table III. The physical data of these products are given below.

22a: colorless prisms (from hexane); mp 105–106 °C; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 18 H), 5.94 (s, 1 H, OH), 7.2 (m, 5 H), 7.85 (s, 2 H); IR (Nujol) 3638, 1675, 1655 cm^{-1}; UV (cyclohexane) λ_{max} 210, 253, 292 nm (log ϵ 4.28, 4.12, 4.10). Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 78.20; H, 7.72.

22b: colorless prisms; mp 187–188 °C; ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 18 H), 0.9–1.4 (m, 7 H), 2.6–3.0 (t, 2 H, J = 7 Hz), 5.89 (s, 1 H, OH), 7.85 (s, 2 H); IR (nujol) 3631, 1745, 1655 cm^{-1}; UV (cyclohexane) λ_{max} 203, 228, 295 nm (log ϵ 4.14, 3.90, 3.99). Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.16; H, 9.72.

22c: colorless prisms (from hexane); mp 136–137 °C; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 18 H), 1.31 (s, 9 H), 5.87 (s, 1 H, OH), 7.69 (s, 2 H); IR (Nujol) 3617, 1696, 1659 cm^{-1}; UV (cyclohexane) λ_{max} 205, 225, 282 nm (log ϵ 4.15, 4.04, 4.08). Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.32; H, 9.58.

Compounds **23** could not be purified because of their instability. Data of ^{1}H NMR are given below.

23a: ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.26 (s, 9 H), 6.63 (d, 1 H, J = 1.4 Hz), 6.75 (d, 1 H, J = 1.4 Hz).

23c: ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 9 H), 1.25 (s, 9 H), 1.31 (s, 9 H), 6.56 (d, 1 H, J = 1.4 Hz), 6.60 (d, 1 H, J = 1.4 Hz), 8.60 (s, 1 H, OOH).

24a: liquid; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9 H), 1.23 (s, 9 H), 4.02 (s, 1 H, OH), 4.02 (d, 1 H, J = 1.4 Hz), 6.80 (d, 1 H, J = 1.4 Hz), 7.2–7.6 (m, 5 H); IR (neat film) 3520, 2225, 1678 cm^{-1}; UV (cyclohexane) λ_{max} 246, 205 nm (log ϵ 4.31, 4.26). Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 78.25; H, 7.95.

24b: liquid; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9 H), 1.22 (s, 9 H), 1.0–1.5 (m, 7 H), 2.0–2.3 (m, 2 H), 3.86 (d, 1 H, J = 1.4 Hz), 4.02 (s, 1 H, OH), 6.68 (d, 1 H, J = 1.4 Hz); IR (neat film) 3542, 2233, 1676 cm^{-1} UV (cyclohexane) λ_{max} 205, 253 nm (log ϵ 3.72, 3.64). Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.46; H, 9.75.

24c: liquid; ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.23 (s, 9 H), 1.29 (s, 9 H), 3.84 (d, 1 H, J = 1.4 Hz), 3.97 (s, 1 H, OH), 6.67 (d, 1 H, J = 1.4 Hz); IR (neat film) 3519, 2225, 1678 cm^{-1}; UV (cyclohexane) λ_{max} 205, 252 nm (log ϵ 3.74, 3.66). Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.15; H, 9.66.

25a: orange needles (from methanol); mp 81–82 °C; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H), 1.36 (s, 9 H), 6.38 (s, 1 H), 7.2–7.5 (br s, 5 H); IR (Nujol) 1708 cm^{-1}. Anal. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 85.95; H, 8.34.

25c: orange oil; ^{1}H NMR ($CDCl_3$) 1.10 (s, 9 H), 1.25 (s, 18 H), 6.12 (s, 1 H). Anal. Calcd for $C_{19}H_{28}O$: M^+ 272.4296. Found: 272.2144.

Supplementary Material Available: ^{13}C NMR data for compounds **18–20** (Table 3) (1 page). Ordering information is given on any current masthead page.