Co(salen)-Catalyzed *tert*-Butyl Hydroperoxide Oxidation of *tert*-Butylphenols Bearing an Unsaturated Side Chain

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Co(salen)-catalyzed oxidation of 2,4- and 2,6-di-*tert*-butylphenols bearing an unsaturated side chain, with *tert*-butyl hydroperoxide (TBHP) in CH_2Cl_2 at rt, results predominantly in the formation of *tert*-butylperoxylated products. The position of *tert*-butylperoxylation depends on the nature of the unsaturated side chain: predominantly the ortho position for 4-alkynyl-2,6-di-*tert*-butylphenols, the side chain for 4-alkenyl-2,6-di-*tert*-butylphenols, and the para position for 4-cyano- or 4-(1-methoxyimino)alkyl-2,6-di-*tert*-butylphenols as well as 2-alkynyl-, 2-alkenyl-, and 2-cyano-4,6-di-*tert*-butylphenols. The ortho *tert*-butylperoxylated products arise mainly from initially formed para *tert*-butylperoxylated products, by migration of the *tert*-butylperoxy group.

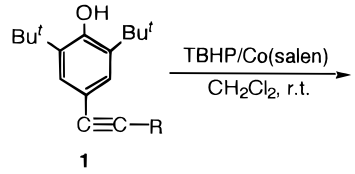
Introduction

Mechanistic studies of metal-catalyzed oxidations are of value not only from the standpoint of understanding enzymatic oxidations, but also for the development of new synthetic methods.[1] Cobalt Schiff base complexes catalyze highly selective oxidation reactions using molecular oxygen which lead to dioxygenations,[2] monooxygenations,[3] and dehydrogenations[4] that mimic biological oxidations. Among the cobalt Schiff base complexes, Co^{II}(salen) [H_2 salen = 1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene] has been found to also catalyze the *tert*-butyl hydroperoxide (TBHP) oxidation of 4-alkyl- and 4-aryl-2,6-di-*tert*-butylphenols,[5] aromatic ketoximes,[6] 2,6-di-*tert*-butylanilines,[7] benzyl alcohols,[8] and benzylamines.[9] The TBHP oxidations of phenolic substrates normally give *tert*-butylperoxylated products in which the *tert*-butylperoxy group is incorporated exclusively at the para position.[5] However, little is known about such TBHP oxidations of phenols that bear an unsaturated group.

The present paper deals with the Co(salen)-catalyzed TBHP oxidation of 2,6- or 2,4-di-*tert*-butylphenols bearing an unsaturated side chain at the 4- or 6-position. We find that mainly *tert*-butylperoxylated products are obtained, but the position for incorporation of the *tert*-butylperoxy group depends on the nature of the unsaturated substituent. The *tert*-butylperoxylation takes place predominantly at the para position for 6-alkenyl-, 6-alkynyl-, and 6-cyano-2,4-di-*tert*-butylphenols, and also for 2,6-di-*tert*-butylphenols bearing a sterically less hindered alkenyl or α-(methoxyimino)alkyl group at the 4-position. Interestingly, however, ortho *tert*-butylperoxylated products are obtained exclusively with 4-alkynyl-2,6-di-*tert*-butylphenols, 2,6-di-*tert*-butyl-4-(1-isopropyl-2-methyl-1-propenyl)phenol, and 2,6-di-*tert*-butyl-4-[2,2-dimethyl-1-(methoxyimino)propyl]phenol. The formation of the ortho *tert*-butylperoxylated products are shown to result from migration of the *tert*-butylperoxy group of the first formed 4-*tert*-butylperoxylated products.

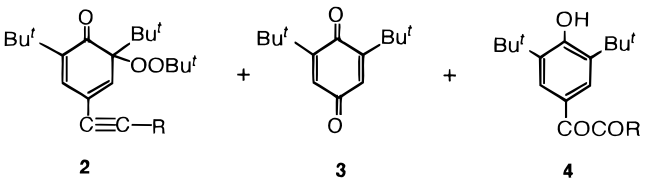
Results

Oxidation of 4-Alkynyl-2,6-di-*tert*-butylphenols (1) with TBHP. A mixture of 4-alkynylphenol (**1**) (1 mmol) and TBHP (10 mmol) in CH_2Cl_2 in the presence of Co(salen) (0.1 mmol) was stirred at rt under N_2. The oxidation of **1** was completed in 20 min. Separation of products from the mixture gave 4-alkynyl-6-*tert*-butylperoxy-2,6-di-*tert*-butyl-2,4-cyclohexadienone (**2**), 2,6-di-*tert*-butyl-*p*-benzoquinone (**3**), and 4-(acylcarbonyl)-2,6-di-*tert*-butylphenol (**4**) (Table 1).

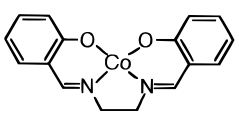


1

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



2 **3** **4**



Co(salen)

Analytical and NMR data of the compounds **2** are in good agreement with their structures. ^{1}H NMR signals

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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Table 1. Co(salen)-Catalyzed Oxidation of Phenols 1 with TBHP

1	reaction time (min)	conversion (%)	yield (%)[a] 2	3	4
1a	20	100	91.7	—[b]	3.3
1b	20	100	47.6	23.8	17.3
1c	20	100	58.7	18.9	14.5

[a] Isolated yield. [b] Not determined.

Table 2. ^{1}H NMR ($CDCl_3$) Data (δ, ppm) for Analogs of 2

2	2-Bu^t	6-Bu^t	−OOBu^t	3-CH	5-CH	R
2a	1.21	0.96	1.21	6.48	6.48	1.29
2b	1.24	0.93	1.24	6.54	6.54	—[a]
2c	1.24	1.02	1.27	6.75b	6.64b	—[c]

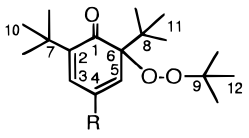
[a] 0.18−1.8 (m, 7H), 2.1−2.5 (m, 2H). [b] d, 1H, J = 2.0 Hz. [c] 7.2−7.7 (m, 5H).

for the 3- and 5-positions of the 2,4-cyclohexadienone system normally appear as a set of doublets around δ 6−7 ppm.[10] However, the corresponding signals of **2a** and **2b** appear as singles (Table 2), although the signals for the 2-*t*-Bu and 6-*t*-Bu groups appear at the expected chenical shifts.[10] Therefore, there is no way to determine the structure of **2** by means of the ^{1}H NMR data alone. The characteristic ^{13}C NMR data for **2** are consistent with the cyclohexa-2,4-dienone system (Table 3).

The similar chemical shifts observed for the protons at the 3- and 5-positions in **2a** and **2b** are probably due to the electronic effect of the alkynyl group at the 4-position. The spectral data of the analogs of **4** were identical to those of known products.[11] The characteristic ^{13}C NMR data of **2** may be utilized conveniently for the specification of the cyclohexa-2,4-dienone system (Table 3).

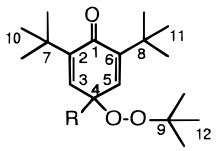
Chemical Shifts in ^{13}C NMR spectra as Structural Probes for Cyclohexadienone Systems. Carbon NMR spectroscopy is useful for distinguishing structures of the 2,5- and 2,4-cyclohexadienone systems.[12] Thus, we examined ^{13}C NMR spectra of 6-*(tert*-butylperoxy)-2,6-di-*tert*-butyl-2,4-cyclohexadienones (**5**), 4-*(tert*-butylperoxy)-2,6-di-*tert*-butyl-2,5-cyclohexadienones (**6**),[5] the analogs of **2**, and related systems. Characteristic data for 2,4-cyclohexadienones and 2,5-cyclohexadienones are given in Tables 3 and 4, respectively.

As seen from Tables 3 and 4, the chemical shifts for C-1, C-4, and C-6 (a *tert*-butylperoxy group is attached), and C-7 (2-*t*-Bu group) (Table 5) conveniently distinguish between **5** and **6**. These data can also be applied to the structural determination of other cyclohexadienone systems described in this work. Thus, the 2,4-cyclodienone structures of compounds **2** are readily apparent from their ^{13}C NMR data.



5

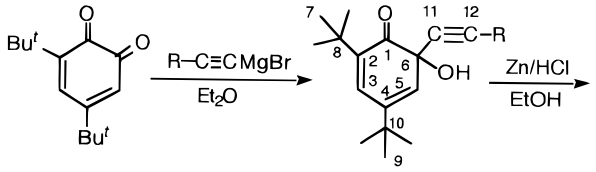
a; R = *t*-Bu
b; R = Ph
c; R = 2,4,6-$Me_3C_6H_2$



6

a; R = *t*-Bu
b; R = Me
c; R = Ph
d; R = 4-$MeOC_6H_4$

Oxidation of 2-Alkynyl-4,6-di-*tert*-butylphenols (8) with TBHP. Analogs of phenol **8** were prepared by the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with an appropriate alkynylmagnesium bromide[13] to give the corresponding 6-alkynyl-2,4-di-*tert*-butyl-6-hydroxy-2,4-cyclohexadienones (**7**), followed by the reduction with Zn/HCl in EtOH.



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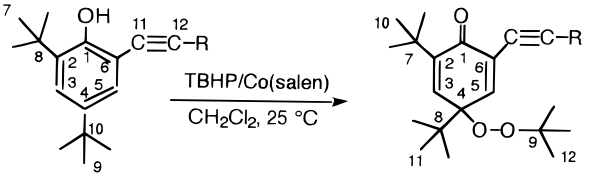
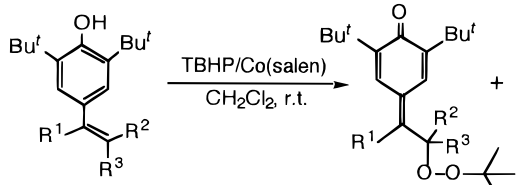


8 **9**

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

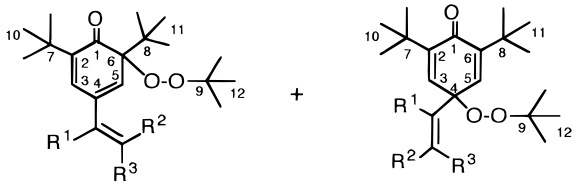
The oxidation of **8** with TBHP under the same conditions described for **1** gave 2-alkynyl-4,6-di-*tert*-butyl-4-(*tert*-butylperoxy)-2,5-cyclohexadienones (**9**) in approximately quantitative isolated yields: **9a**, 95%; **9b**, 95%; **9c**, 95%. These structures are clearly supported by their ^{13}C NMR (Table 4) and analytical data.

Oxidation of 4-Alkenyl-2,6-di-*tert*-butylphenols (10) with TBHP. The oxidation of **10** has been briefly reported,[5] but not in detail. Thus, we reinvestigated more thoroughly the oxidation of 4-alkenylphenols **10**. The reaction was usually completed in 20 min. Silica gel TLC separation of the reaction mixture gave quinone methide **11** in which the *tert*-butylperoxy group is incorporated into the side chain, peroxy-*o*-quinol ether **12**, and peroxy-*p*-quinol ether **13**. Analytical and spectral data



10 **11**

	a	b	c	d	e
R^1	H	H	H	Ph	*i*-Pr
R^2	H	H	Me	Me	Me
R^3	Me	Ph	Me	Me	Me



12 **13**

were in good agreement with the structures of these

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Table 3. Characteristic ^{13}C NMR ($CDCl_3$, δ) Data for *o*-Quinoid Compounds

compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
2a	199.7	145.6	143.5	119.9	136.2	88.6	42.0	34.6	80.0	29.3	25.2	26.8
2c	199.5	146.1	145.3	119.6	135.2	88.8	42.1	34.8	80.2	29.3	25.1	26.5
2b	199.3	145.5	143.4	119.8	135.7	88.4	41.7	34.4	79.7	29.2	24.9	26.5
5a	201.2	145.1	134.1	143.0	132.1	88.1	41.1	34.7	79.4	29.4	25.0	26.6
5b	200.5	146.1	137.3	140.0	135.2	88.6	41.8	34.8	79.8	29.4	25.1	26.6
5c	201.3	146.0	139.3	137.8	137.1	88.0	41.4	34.7	79.7	29.5	25.1	26.6
12d	201.3	145.0	138.9	140.8	137.1	88.2	41.4	34.5	79.7	29.3	25.2	26.6
12e	201.5	144.5	139.1	139.7	135.5	88.0	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]
25a	199.8	146.7	143.2	130.0	129.7	88.6	41.8	34.9	80.1	29.3	25.0	26.6
25b	200.0	145.5	139.0	132.0	131.9	88.5	41.8	34.9	80.0	29.3	25.2	26.6
25e	200.7	144.9	137.7	130.4	135.5	88.6	41.2	34.5	79.7	29.4	24.9	26.6

[a] Not determined.

Table 4. Characteristic ^{13}C NMR ($CDCl_3$, δ) Data for *p*-Quinoid Compounds

compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
6a[a]	186.8	148.0	141.5	82.5	141.5	148.0	35.0	35.0	79.2	29.6	29.6	26.5
6b	186.6	146.7	141.7	76.1	141.7	146.7	34.7	34.7	79.3	29.5	29.5	26.5
6c	187.1	146.7	140.9	79.9	140.9	146.7	34.9	34.9	79.7	29.5	29.5	26.6
6d	187.0	146.4	141.1	79.6	141.1	146.4	34.8	34.8	79.3	29.5	29.5	26.6
26a	186.4	148.5	134.9	76.4	134.9	148.5	35.1	35.1	80.3	29.3	29.3	26.5
26b	186.7	147.8	136.1	79.0	136.1	147.8	35.1	35.1	80.0	29.4	29.4	26.5
26c	186.6	147.4	136.8	79.9	136.8	147.4	35.0	35.0	79.3	29.3	29.3	26.5
26d	186.5	147.4	136.8	79.9	136.8	147.4	35.1	35.1	79.7	29.4	29.4	26.5
26f	186.5	147.4	137.2	80.2	137.1	147.4	35.1	35.1	78.9	29.3	29.3	26.5
9a[b]	182.0	146.7	143.0	82.2	149.5	127.1	34.8	—	79.6	29.2	—	26.4
9b[c]	182.6	146.8	143.5	82.4	150.2	127.2	34.9	—	79.8	29.3	—	26.4
9c[d]	182.0	147.0	143.6	82.5	151.4	147.0	35.0	—	79.9	29.3	—	26.4
15a[e]	185.9	138.2	144.4	82.5	143.4	147.1	34.9	—	79.4	—	29.4	26.1
15b[f]	185.2	142.1	143.6	82.5	142.7	147.5	34.9	—	79.6	—	29.5	26.1
15c[g]	184.8	143.0	142.9	82.6	146.4	147.6	34.9	—	79.6	—	29.3	26.5
15d[g]	185.3	143.7	142.7	82.6	145.8	147.5	34.9	—	79.5	—	29.3	26.5

[a] 4-*t*-Bu: 40.5, 26.1 (Me). [b] 4-*t*-Bu: 40.5, 25.9 (Me). [c] 4-*t*-Bu: 40.7, 26.1 (Me). [d] 4-*t*-Bu: 40.8, 26.1 (Me). [e] 4-*t*-Bu: 40.4, 26.1 (Me). [f] 4-*t*-Bu: 40.6, 26.1 (Me). [g] 4-*t*-Bu: 40.2, 26.1 (Me).

Table 5. Chemical Shifts in ^{13}C NMR as Structural Probe for 5 and 6[a]

compd	C-1	C-4	C-6	2-*t*-Bu
5	200.7	—	88.4	41.5
6	186.7	79.1	—	35.0

[a] Average values are given.

Table 6. Product Distribution in Oxidation of 10 with TBHP

	product yield[a]		
10	**11**	**12**	**13**
10a	89.8%	—[b]	6.1
10b	94.5	—[b]	—[b]
10c	81.5	—[b]	9.5
10d	41.0	13.7	39.9
10e	—[b]	73.0	—[b]

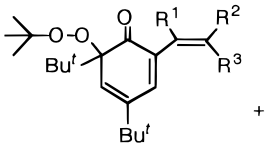
[a] Isolated yield. [b] Not detected.

products. The ^{13}C NMR data of **12d** and **12e** are given in Table 3. Although the ^{13}C NMR data of **13a**, **13c**, and **13d** were not available, ^1H NMR data support their the structures. Product distribution seems to be affected by the substituent in the side chain (Table 6). That is, in the case of **10a**−**10c** which have a relatively unhindered side chain (R^1 = H), the reaction takes place at the side chain leading to the predominant formation of **11**. As the steric hindrance presented by the alkene side chain increases, the reaction center shifts to the aromatic ring. Interestingly, **10e** gives only (*tert*-butylperoxy)-*o*-quinol ether **12e**, probably resulting from direct *tert*-butylperoxylation at the ortho position. These results are rationalized in terms of the phenoxy radical intermediates of these phenols.[5]

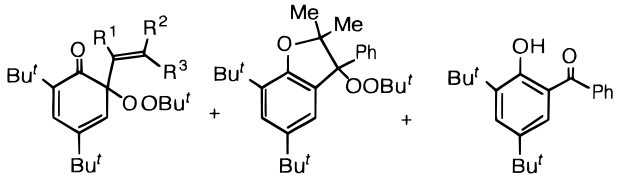
Oxidation of 2-Alkenyl-4,6-di-*tert*-butylphenols (14) with TBHP. The Co(salen)-catalyzed oxidation of 2-alkenyl-4,6-di-*tert*-butylphenols (**14**) with TBHP gave different types of products (**15**−**19**), depending on the

14 **15**

	a	b	c	d
R^1	H	Me	Ph	Ph
R^2	Me	H	H	Me
R^3	Me	H	H	Me



16



17 **18** **19**

nature of the alkenyl side chain, although the main product was 2-alkenyl-4,6-di-*tert*-butyl-4-(*tert*-butylperoxy)-2,5-cyclohexadienones (**15**), for which ^{13}C NMR data are listed in Table 4. The product distribution is given in Table 7. Analytical and spectral data of the products were in good agreement with structures **15**−**19** (see the Experimental Section).

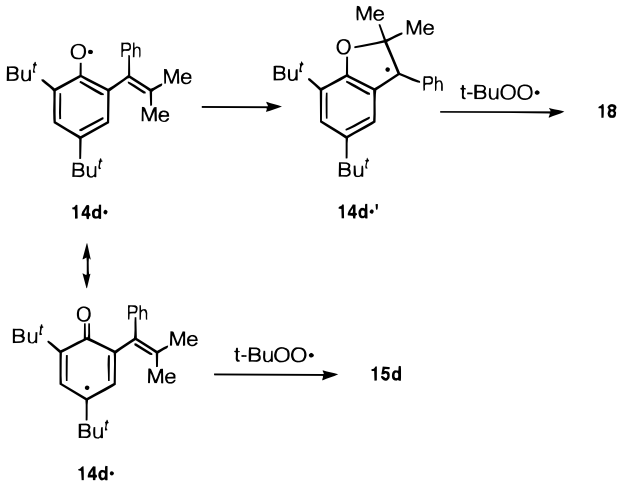
The ^{13}C NMR spectrum of **16a** shows methyl signals at 25.0 (4-*t*-Bu), 26.7 (*t*-BuOO), and 29.0 (6-*t*-Bu) ppm. On the other hand, the *tert*-butyl carbon signals of **17b**

Table 7. Product Distribution in Oxidation of 14 with TBHP

	product yield (%)[a]				
14	**15**	**16**	**17**	**18**	**19**
14a	58.6	7.8	—[b]	—[b]	—[b]
14b	41.9	—[b]	43.2	—[b]	—[b]
14c	51.2	—[b]	22.1	—[b]	—[b]
14d	41.0	—[b]	—[b]	42.6	2.5

[a] Isolated yield. [b] Not determined.

Scheme 1



appear at 26.6 (*t*-BuOO), 28.8 (4-*t*-Bu), and 29.2 (6-*t*-Bu), and for **17c** at 26.6 (*t*-BuOO), 28.5 (4-*t*-Bu), and 29.3 (6-*t*-Bu) ppm, respectively. These data as well as ^{1}H NMR data are in good agreement with these structures. Interestingly, **14d** gave compound **18** as one of the main products, which strongly suggests an intramolecular addition of a phenoxy radical intermediate[5] to the alkene side chain followed by the *tert*-butylperoxylation. The comparable formation of **18** and **15d** from **14d** suggests that the *tert*-butylperoxylation on the aromatic ring competes with the intramolecular addition of phenoxy radical **14d**• to the double bond in the side chain leading to **14d**•' (Scheme 1).

Oxidation of Di-*tert*-butylcyanophenols with TBHP. In the oxidation of 2,6-di-*tert*-butyl-4-cyanophenol (**20**) and 2,4-di-*tert*-butyl-6-cyanophenol (**22**) with TBHP, the *tert*-butylperoxylation took place predominantly at the 4-position to give 2,6-di-*tert*-butyl-4-*tert*-butylperoxy-4-cyano-2,5-cyclohexadienone (**21**) (53%) and 2,4-di-*tert*-butyl-4-*tert*-butylperoxy-6-cyano-2,5-cyclohexadienone (**23**) (99%), respectively, although the reaction of **20** did not go to completion and gave two other unknown products. The products **21** and **23** gave satisfactory analytical and spectral data.

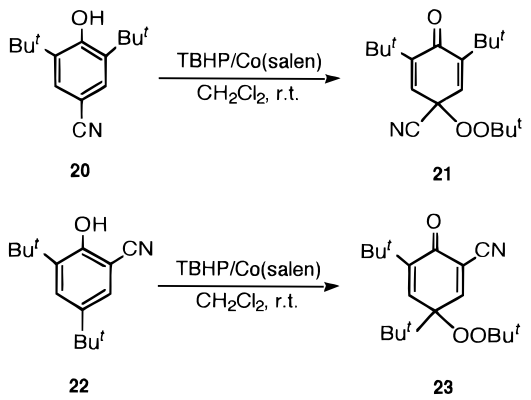
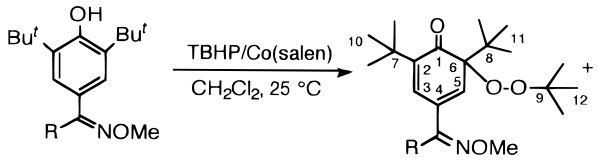


Table 8. Product Distribution in Oxidation of 24 with TBHP

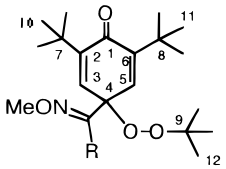
	product yield(%)[a]	
24	**25**	**26**
24a	51.8	47.8
24b	8.1	87.8
24c	6.9	92.2
24d	16.1	79.9
24e	91.1	6.8
24f	29.6	69.9

[a] Isolated yield.

Oxidation of 2,6-Di-*tert*-butyl-4-acylphenol Oxime *O*-Methyl Ethers (24) with TBHP. The Co(salen)-catalyzed oxidation of 2,6-di-*tert*-butyl-4-acylphenol oxime *O*-methyl ethers (**24**) with TBHP gave *o*-(*tert*-butylperoxy)quinol ether **25** and *p*-(*tert*-butylperoxy)quinol ether **26** as main products. No oxidation at the nitrogen atom in the side chain was observed. The structures of **25** and **26** are supported by their ^{13}C NMR data (Table 3 and Table 4). The distribution of the products depended on the substituent R on **24** (Table 8).



a; R = H **b**; R = Me **c**; R = Et
d; R = i-Pr **e**; R = t-Bu **f**; R = Ph



As seen in Table 8, the *tert*-butylperoxy group was incorporated predominantly into the 4-position, except in the case of **24e**. Compounds **25d**, **26c**, and **26d** are composed of syn and anti stereoisomers, which were not separated, but the ratio of the isomers could be determined by ^{1}H NMR spectroscopy: (syn/anti) **25d** (67/33), **26c** (90/10), and **26d** (86/14). The predominant formation of **25e** should be attributed to the steric nature of the side chain.

Discussion

Reaction Path for the Formation of 2 from 1. The course of the oxidation of **1a** was tracked by ^{1}H NMR spectroscopy by looking at the change in chemical shift of the CH proton of the cyclohexa-2,4-dienone system (Figure 1). As seen from Figure 1, the signal that appeared at δ 6.6 ppm in the initial stage, assignable to a cyclohexa-2,5-dienone system,[13] shifted gradually to δ 6.5 ppm. This time-dependent change is rationalized by assuming that *tert*-butylperoxylation takes place first at the para position leading to 2,5-cyclohexadienone **27,** followed by the migration of the *tert*-butylperoxy group to the ortho position to give **2a** (Scheme 2). A similar migration reaction has been reported in the conversion of 4-bromo-2,4,6-tri-*tert*-butyl-2,5-cyclohexadienone to

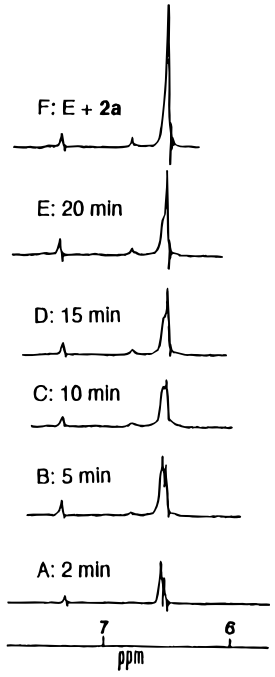
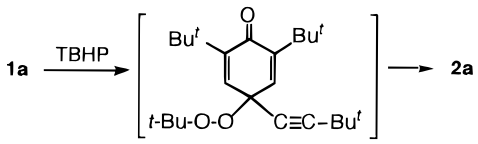


Figure 1. Time-dependent chemical shift of ring CH signal of the product in the oxidation of **1a**.

Scheme 2



27

6-bromo-2,4,6-tri-*tert*-butyl-2,4-cyclohexadienone.[14] The migration of a *tert*-butylperoxy group was actually demonstrated by the thermal reaction of **26b**. Heating a solution of **26b** in $CHCl_3$ at 50 °C for 7 h gave **24b** (12%), **25b** (18%), and *o*-benzoquinone **29** (45%), whereas at 40 °C for 5 h, **25b** (26%) and **29** (5%) were obtained with 37% conversion. The formation of **24b** at 50 °C suggests that the reaction proceeds via a π-complex intermediate **28**. Since compound **29** apparently arises from the thermal decomposition of the resulting **25b**, the migration reaction takes place almost quantitatively at lower temperature. In fact, the time course of the thermal reaction of **26b** as monitored by ^{1}H NMR spectroscopy (38.8 °C) (Figure 2) showed that the conversion of **26b** to **25b** proceeds quantitatively within 12 h, following first-order kinetics with respect to the substrate. A plot of log *y* vs time gives a straight line up to 55% conversion (Figure 3; $k_{obs} = 1.7 \times 10^{-5}$ s^{-1}), followed by the formation of **26b**. The results also support the mechanism involving intermediate **28** (Scheme 3). On the other hand, a similar experiment with **25b** in an NMR tube at 38.8 °C showed only the formation of **29** but not **26b**. Therefore, the conversion of **26b** to **25b** must be irreversible. The involvement of an intermediate of type **28** was also supported by the thermal decomposition of **6d**, from which products **30**−**32** were obtained. In the presence of a radical scavenger such as ascorbic acid, the formation of **32** predominates (Table 9), suggesting radical nature of the intermediates of type **28**.

(14) Rieker, A.; Zeller, N.; Kessler, H. *J. Am. Chem. Soc.* **1968**, *90*, 6566.

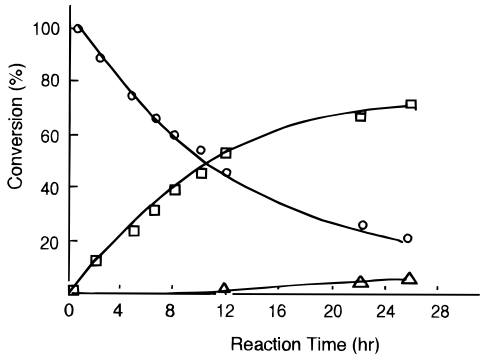


Figure 2. Time course of thermal rearrangement of **26b** to **25b** at 38.8 °C determined by ^{1}H NMR following change in strength of signals for ring CH protons: **26b** (○), **25b** (□), and **29** (△).

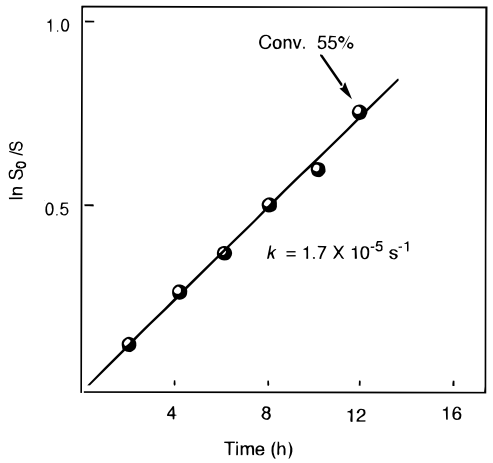
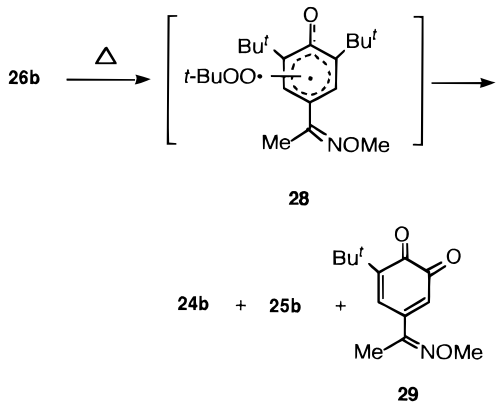


Figure 3. Plot of the initial rate in the rearrangement of **26b** to **25b**.

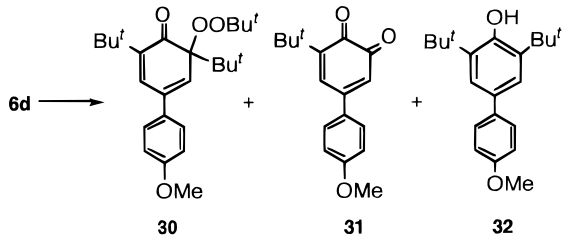
Scheme 3



Mechanism for Oxidation of 1. The involvement of phenoxy radical intermediates has been well documented for the Co(salen)-catalyzed TBHP oxidation of 4-alkyl- and 4-aryl-2,6-di-*tert*-butylphenols.[5] Thus, the mechanism for the oxidation of **1** may be similarly rationalized as depicted in Scheme 4. The reaction is initiated by the hydrogen abstraction of **1** with *t*-BuOO•, resulting from the decomposition of Co^{III}(salen)(OOBu^t) formed in situ.[5,15] The coupling between *t*-BuOO• and a mesomeric species **33′** must be kinetically preferable to give **27**, which undergoes migration via a radical pair transition state **28′** to thermodynamically preferable

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

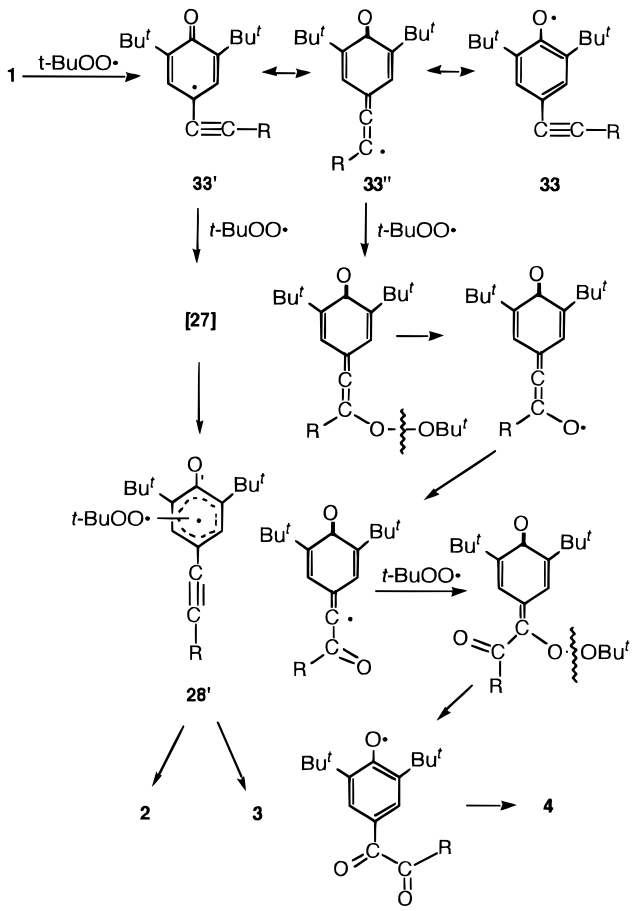
Table 9. Thermal Rearrangement of 6d[a]



				product yield(%)[b]		
solvent	T (°C)	t (h)	conv (%)	**30**	**31**	**32**
MeOH	60	2	100	26.4	11.7	25.3
i-PrOH	60	2	100	41.5	5.9	30.3
$(CH_2)_2Cl_2$	60	2.5	86	51.8	10.9	–
MeOH	40	12	54	42.3	5.1	1.9
MeOHc	60	1	100	1.3	1.1	91.0

[a] **6d** (1 mmol), solvent (40 mL) under nitrogen. [b] Isolated yield. [c] Ascorbic acid (10 mmol) was added.

Scheme 4



compound **2**. The coupling of *t*-BuOO• with another resonance species **33″** should give diketone **4**. The involvement of **33″** in the formation of **4** from **1** has also been demonstrated in the Co(salen)-catalyzed oxygenation of **1**.[11] A detailed mechanism for the formation of *p*-benzoquinone **3** is not yet known, but a succeeding reaction of diketone **4** with TBHP may be responsible.[5]

Experimental Section

All melting points are uncorrected. Elemental analyses were performed by the Analytical Center of our department. The assignments for the ^{13}C NMR data are based on the literature.[12] Co(salen),[16] Co(salpr),[17] alkynylphenols,[11] alkenylphenols,[11] cyanophenols,[18] and 2,6-di-*tert*-butyl-4-acylphenol oxime *O*-methyl ether[18] were prepared following the reported methods.

2-Alkynyl-4,6-di-*tert*-butyl-2-hydroxy-3,5-cyclohexadienones (7). The procedure for para isomers reported in the literature[19] was modified. To a solution of an appropriate alkynylmagnesium bromide (22.7 mmol) in THF (20 mL), prepared from the reaction of ethylmagnesium bromide with the corresponding alkyne, was added dropwise a solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (5.0 g, 22.7 mmol) in THF (15 mL) with stirring at −78 °C. The resulting mixture was warmed to room temperature over a period of 0.5 h. A saturated NH_4Cl aqueous solution was then added. Extraction with ether followed by silica gel column chromatographic separation gave 2-alkynyl-4,6-di-*tert*-butyl-2-hydroxy-3,5-cyclohexadienones. Analytical and spectral data for **7** thus obtained are given below.

7a: Yield 57%; pale yellow prisms; mp 40.0−41.0 °C; IR (KBr) 3496, 2234, 1653, 1688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (s, 18 H), 1.26 (s, 9 H), 3.66 (br s, 1 H), 6.01 (d, 1 H, J = 2.4 Hz), 6.75 (d, 1H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 199.9 (1), 143.3 (2), 140.9 (4), 134.9 (3), 128.6 (5), 91.4 (12), 76.1 (11), 72.1(6), 34.3 (8 or 10), 34.2 (8 or 10), 30.6 (R), 29.2 (7), 28.3 (9), 27.3 (R). Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.35; H, 9.92. Found: C, 79.13; H, 9.96.

7b: Yield 52%; pale yellow oil; IR (neat) 3497, 2218, 1688, 1653 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7−1.7 (m, 5 H), 1.15 (s, 9 H), 1.29 (s, 9 H), 2.0−2.4 (m, 2 H), 3.77 (br s, 1 H), 6.04 (d, 1 H, J = 2.4 Hz), 6.79 (d, 1 H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 199.6 (1), 143.2 (2), 140.9 (4), 135.2 (3), 128.3 (5), 83.6 (12), 77.5 (11), 71.9 (6), 34.2 (8 or 10), 34.1 (8 or 10), 30.2 (R), 29.0 (7), 28.3 (9), 21.6 (R), 18.2 (R), 13.4 (R). Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.35; H, 9.92. Found: C, 79.30; H, 9.91.

7c: Yield 53%; pale yellow prisms; mp 103.3−104.3 °C; IR (KBr) 3468, 2218, 1684, 1651 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 9 H), 1.31 (s, 9 H), 3.99 (br s, 1 H), 6.12 (d, 1H, J = 2.2 Hz), 6.82 (d, 1H, J = 2.2 Hz), 7.1−7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 199.2 (1), 143.5 (2), 141.7 (4), 135.5 (3), 131.9 (R), 128.7 (5), 128.2 (R), 127.7 (R), 122.1 (R), 86.3 (12), 82.5 (11), 72.4 (6), 34.5 (8 or 10), 34.3 (8 or 10), 29.2 (7), 28.4 (9). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.87; H, 8.06. Found: C, 81.90; H, 7.98.

2-Alkynyl-4,6-di-*tert*-butylphenols (8). The phenols were obtained by reduction of **7** with Zn powder and concentrated HCl in EtOH according to the known procedure,[20] and the products were recrystallized from EtOH. Analytical and spectral data for these phenols are given below.

8a: Yield 59%; colorless plate; mp 130.8−131.2 °C; IR (KBr) 3492 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 9 H), 1.36 (s, 9 H), 1.41 (s, 9 H), 6.01 (s, 1 H), 7.18 (d, 1 H, J = 2.2 Hz), 7.24 (d, 1 H, J = 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 152.6 (1), 141.8 (4), 134.4 (2), 125.5 (5), 124.3 (3), 109.8 (6), 105.5 (12), 74.1 (11), 34.9 (8 or 10), 34.3 (8 or 10), 31.5 (9), 31.2 (R), 29.5 (7), 28.4 (R). Anal. Calcd for $C_{20}H_{30}O$: C, 83.78; H, 10.47. Found: C, 83.81; H, 10.47.

8b: Yield 77%; colorless oil; IR (KBr) 3496 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7−1.1 (m, 3 H), 1.2−1.8 (m, 4 H), 1.26 (s, 9 H), 1.41 (s, 9 H), 2.3−2.6 (m, 2 H), 6.03 (s, 1 H), 7.14 (d, 1 H, J = 2.2 Hz), 7.23 (d, 1 H, J = 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 152.9 (1), 134.5 (2), 141.9 (4), 124.3 (3), 125.5 (5), 110.0 (6), 97.1 (12), 75.6 (11), 34.9 (8 or 10), 34.2 (8 or 10), 31.5 (9), 30.9 (R), 29.5 (7), 22.1 (R), 19.3 (R), 13.5 (R). Anal. Calcd for $C_{20}H_{30}O$: C, 83.78; H, 10.47. Found: C, 83.85; H, 10.42.

8c: Yield 53%; colorless needles; mp 81.8−82.6 °C; IR (KBr) 3506 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 (s, 9 H), 1.42 (s, 9 H), 6.05 (s, 1 H), 7.2−7.7 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 152.9 (1), 142.3 (4), 134.9 (2), 131.6 (R), 128.6 (R), 128.5 (R), 125.8 (5), 125.3

(16) Calvin, M.; Barklew, C. H. *J. Am. Chem. Soc.* **1946**, *68*, 2267.
(17) Sacconi, L.; Bertini, I. *J. Am. Chem. Soc.* **1966**, *88*, 5180. Nishinaga, A.; Tomita, H.; Nishizawa, K.; Matsuura, T. *J. Chem. Soc., Dalton Trans.* **1981**, 1504.
(18) Nishinaga, A.; Shimizu, T.; Toyoda, Y.; Matsuura, T. *J. Org. Chem.* **1982**, *47*, 2278.
(19) Hauff, V.; Krauss, P.; Rieker, A. *Chem. Ber.* **1972**, *105*, 1446.
(20) Rieker, A.; Scheffler, K. *Justus Liebigs Ann. Chem.* **1965**, *78*, 689.

(3), 122.7 (R), 109.4 (6), 95.9 (12), 84.2 (11), 35.1 (8 or 10), 34.3 (8 or 10), 31.5 (9), 29.5 (7). Anal. Calcd for $C_{22}H_{26}O$: C, 86.15; H, 8.48. Found: C, 85.97; H, 8.44.

Co(salen)-Catalyzed Oxidation of 4-Alkynylphenols (1) with TBHP. To a solution of **1** (1 mmol) and TBHP (70%, d = 0.91, 1400 μL, 10 mmol) in CH_2Cl_2 (15 mL) was added dropwise a solution of Co(salen) (32.5 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) under N_2 with stirring at rt. After completion of the reaction (20 min), monitored by TLC, the complex was removed by filtration of the mixture through a short silica gel column eluted with CH_2Cl_2, and the filtrate was evaporated. The resulting residue was dissolved in pentane and the solution was washed with water to remove unreacted TBHP. The pentane layer was dried (Na_2SO_4) and evaporated to give a mixture of **2, 3**, and **4**, which were separated by silica gel TLC. The results are listed in Table 1. ^{1}H NMR and characteristic ^{13}C NMR data of **2** are listed in Tables 2 and 3, respectively. Analytical and other spectral data for **2** are given below. Spectral data of **3** and **4** were identical with those of authentic samples.[12]

2a: Yellow prisms; mp 89.7−90.3 °C; IR (KBr) 2220, 1686, 1642 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 97.3, 78.6, 31.1, 27.9. Anal. Calcd for $C_{24}H_{38}O_3$: C, 76.89; H, 10.15. Found: C, 76.88; H, 10.13.

2b: Yellow oil; IR (neat) 2226, 1684, 1640 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 89.1, 79.9, 30.7, 21.9, 18.9, 13.5. Anal. Calcd for $C_{24}H_{38}O_3$: C, 76.89; H, 10.15. Found: C, 76.41; H, 10.13.

2c: Yellow needles; mp 82.8−73.5 °C; IR (KBr) 2212, 1684, 1636 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 131.7, 128.5, 128.4, 122.9, 88.7, 88.4. Anal. Calcd for $C_{26}H_{34}O_3$: C, 79.08; H, 8.62. Found: C, 79.14; H, 8.87.

4a: ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 1.45 (s, 18 H), 5.87 (s, 1 H), 7.69 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 212.1, 204.7, 159.8, 136.4, 127.5, 124.9, 42.6, 34.4, 30.0, 26.6.

4b: ^{1}H NMR ($CDCl_3$) δ 0.9−1.4 (m, 7 H), 1.46 (s, 18 H), 2.6−3.0 (t, 2 H, J = 7 Hz), 5.89 (s, 1 H), 7.85 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 204.7, 192.4, 160.0, 136.4, 128.0, 123.84 38.7, 34.3, 30.0, 25.0, 23.0, 13.7.

4c: ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 1.45 (18 H), 5.87 (s, 1 H), 7.69 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 195.3, 193.9, 160.2, 136.6, 134.5, 133.6, 129.9, 128.8, 128.0, 125.0, 30.0, 34.4.

Co(salen)-Catalyzed Oxidation of 2-Alkynylphenols (8) with TBHP. The oxidation of **8** was carried out similar to that of **1**. Cyclohexa-2,5-dienones **9** were obtained in approximately quantitative yield as described in the text. Characteristic ^{13}C NMR data are listed in Table 4. Analytical and other spectral data of **9** are given below.

9a: Colorless needles; mp 93.8−94.8 °C; IR (KBr) 2224, 1669, 1651, 1618 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9 H), 1.24 (s, 9 H), 1.29 (s, 9 H), 1.35 (s, 9 H), 6.77 (d, 1 H, J = 2.8 Hz), 7.05 (d, 1 H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ 101.4 (R), 73.6 (R), 30.8 (R), 26.9(R). Anal. Calcd for $C_{24}H_{38}O_3$: C, 76.89; H, 10.15. Found: C, 76.81; H, 10.16.

9b: Colorless oil; IR (neat) 2234, 1669, 1647, 1613 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7−1.8 (m, 7 H), 0.98 (s, 9 H), 1.19 (s, 9 H), 1.24 (s, 9 H), 2.2−2.6 (m, 2 H), 6.77 (d, 1 H, J = 2.8 Hz), 7.09 (d, 1 H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ 94.0 (R), 75.2 (R), 30.7 (R), 22.1 (R), 19.3(R), 13.5 (R). Anal. Calcd for $C_{24}H_{38}O_3$: C, 76.89; H, 10.15. Found: C, 76.88; H, 10.21.

9c: Colorless needles; mp 107.3−108.8 °C; IR (KBr) 2254, 1669, 1647, 1613 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9 H), 1.21 (s, 9 H), 1.27 (s, 9 H), 6.78 (d, 1 H, J = 2.8 Hz), 7.1−7.6 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 131.8 (R), 128.4 (R),128.1 (R), 122.9-(R), 92.7 (R), 84.2 (R). Anal. Calcd for $C_{26}H_{34}O_3$: C, 79.08; H, 8.62. Found: C, 78.87; H, 8.50.

Co(salen)-Catalyzed Oxidation of 4-Alkenylphenols (10) with TBHP. The oxidation of **10** was carried out similar to that of **1** described above. Compounds **11**−**13** were isolated by silica gel TLC. The results are given in Table 6. Characteristic ^{13}C NMR data for **12d** and **12e** are listed in Table 3. Analytical and other spectral data for **11**, **12**, and **13** are given below.

11a: Yellow prisms; mp 57.2−58.1 °C [lit.[5] mp 57.2−58.1 °C]; IR (KBr) 1618 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 9 H), 1.30 (s, 18 H), 1.37 (d, 3 H, J = 7.5 Hz), 5.09 (m, 1 H), 6.12 (d, 1 H, J = 9.0 Hz), 6.80 (d, 1 H, J = 2.0 Hz), 7.23 (d, 1 H, J = 2.0); ^{13}C NMR ($CDCl_3$) δ 186.7, 148.9, 148.0, 144.6, 134.6, 132.5, 126.3, 80.5, 75.1, 35.3, 34.9, 29.5, 26.4, 18.9.

11b: Yellow needles; mp 73.8−84.3 °C; IR (KBr) 1632, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 18 H), 1.32 (s, 9 H), 5.96 (d, 1 H, J = 8.4 Hz), 6.39 (d, 1 H, J = 8.4 Hz), 6.84 (d, 1 H, J = 2.4 Hz), 7.34 (br s, 6 H); ^{13}C NMR ($CDCl_3$) δ 186.5, 149.2, 148.1, 142.0, 138.5, 134.6, 132.7, 128.8, 128.6, 127.5, 126.4, 81.6, 80.9, 31.6, 30.2, 29.6, 29.5, 26.5. Anal. Calcd for $C_{26}H_{36}O_3$: C, 78.75; H, 9.15. Found: C, 78.79; H, 9.12.

11c: Yellow prisms; mp 68.9−69.5 °C; IR (KBr) 1618 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 9 H), 1.24 (s, 9 H), 1.27 (s, 9 H), 1.51 (s, 6 H), 6.26 (br, 1 H), 6.76 (d, 1 H, J = 2.4 Hz), 7.96 (d, 1 H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 186.4, 149.3, 148.0, 147.1, 135.8, 131.7, 127.8, 80.8, 79.1, 35.4, 34.8, 29.6, 29.5, 29.3 26.7. Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.82; H, 10.41. Found: C, 75.09; H, 10.65.

11d: Yellow needles; mp 101.5−102.1 °C; IR (KBr) 1613 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 9 H), 1.26 (s, 9 H), 1.35 (s, 9 H), 1.41 (s, 6 H), 6.46 (d,1 H, J = 2.4 Hz), 6.9−7.5 (m, 5 H), 8.34 (d, 1 H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 186.8, 158.4, 146.6, 146.2, 140.6, 132.9, 130.7, 130.0, 128.4, 127.7, 127.2, 83.2, 79.2, 31.1, 30.6, 29.8, 29.3, 28.6, 26.8. Anal. Calcd for $C_{28}H_{40}O_3$: C, 79.20; H, 9.49. Found: C, 79.10; H, 9.46.

12d: Yellow prisms; mp 74.2−75.4 °C; IR (KBr) 1684, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H), 1.12 (s, 9 H), 1.18 (s, 9 H), 1.76 (s, 3H), 1.94 (s, 3H), 6.19 (d, 1 H, J = 2.0 Hz), 6.29(d, 1 H, J = 2.0 Hz) 7.23 (br s, 5H); ^{13}C NMR ($CDCl_3$) δ 137.0, 136.3, 131.6, 129.8, 128.0, 126.5, 22.7, 22.1. Anal. Calcd for $C_{28}H_{40}O_3$: C, 79.20; H, 9.49. Found: C, 79.22; H, 9.45.

12e: Yellow prisms; mp 95.0−96.5 °C; IR (KBr) 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9 H), 1.04 (d, 6 H, J = 7.5), 1.22 (s, 9 H), 1.26 (s, 9H), 1.65 (s, 3H), 1.78 (s, 3 H), 2.95 (m, 1 H), 5.90 (d, 1 H, J = 2.0 Hz), 6.34 (d, 1 H, J = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 138.3, 126.5, 30.0, 22.4, 21.6, 21.4, 19.3. Anal. Calcd for $C_{28}H_{40}O_3$: C, 79.20; H, 9.49. Found: C, 79.22; H, 9.45.

13a: Colorless oil; IR (neat) 1667, 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9 H), 1.23 (s, 18 H), 1.64 (br d, J = 4.8 Hz, 3 H), 5.3−5.6 (m, 2 H), 6.54 (s, 2 H).

13c: Colorless oil; IR (neat) 1669, 1647 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H), 1.24 (s, 18 H), 1.64 (br, 3 H), 1.73 (br, 3 H), 5.14 (br, 1 H), 6.50 (s, 2 H).

13d: Colorless oil; IR (neat) 1667, 1644 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 18 H), 1.19 (s, 9 H), 1.46 (s, 3 H), 2.12 (s, 3H), 6.56 (s, 2 H), 6.7−7.3 (m, 5 H).

Co(salen)-Catalyzed Oxidation of 2-Alkenylphenols (14) with TBHP. The procedure was the same as that for **1**. Compounds **15**−**19** were obtained. The results are listed in Table 7. Analytical and spectral data for these products are given below. Characteristic ^{13}C NMR data for **15** are listed in Table 4.

15a: Colorless oil; IR (neat) 1665, 1644 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 9 H), 1.22 (s, 9 H), 1.26 (s, 9 H), 1.80 (br s, 3 H), 1.87 (br s, 3 H), 6.06 (br s, 1 H), 6.77 (d, 1 H, J = 2.8 Hz), 6.79 (d, 1 H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ 137.1, 119.8, 40.4, 26.6, 26.5, 19.6. Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.75; H, 10.33. Found: C, 75.52; H, 10.12.

15b: Colorless prisms, mp 31.5−31.8 °C; IR (KBr) 1667, 1647 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.21 (s, 9 H), 1.26 (s, 9 H), 1.97 (br s, 3H), 5−5.2 (m, 2 H), 6.79 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 143.4, 115.6, 40.6, 26.5, 22.5. Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.34; H, 10.16. Found: C, 75.27; H, 10.37.

15c: Colorless prisms; mp 103.5−104.3 °C; IR (KBr) 1669, 1649, 1615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 9 H), 1.22 (s, 9 H), 1.25 (s, 9 H), 5.27 (d, 1 H, J = 2.0 Hz), 5 58 (d, 1 H, J = 2.0 Hz), 6.79 (d, 1 H, J = 2.6 Hz), 6.93 (d, 1 H, J = 2.6 Hz) 7.1−7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 146.2, 139.9, 128.2, 127.5, 126.1, 115.1, 40.2, 26.1. Anal. Calcd for $C_{26}H_{36}O_3$: C, 78.67; H, 9.08. Found: C, 78.66; H, 8.97.

15d: Colorless prisms; mp 81.0−82.0 °C; IR (KBr) 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.20 (s, 18 H), 1.74 (s, H), 1.79 (s, 3 H), 6.75 (s, 2 H), 7.22 (br s, 5 H); ^{13}C NMR ($CDCl_3$) δ 141.9, 132.5, 129.2, 127.5, 125.9, 40.2, 26.2, 21.6, 22.6. Anal. Calcd for $C_{28}H_{40}O_3$: C, 79.13; H, 9.42. Found: C, 79.11; H, 9.52.

16a: Yellow oil; IR (neat) 1686, 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 9 H), 1.13 (s, 9 H), 1.17 (s, 9 H), 1.74 (s, H), 1.78 (br

s, 3 H), 1.84 (br s, 3 H), 6.06 (d, 1 H, $J = 2.4$ Hz), 6.16 (d, 1 H, $J = 2.4$ Hz), 6.75 (br s, 1 H); ^{13}C NMR ($CDCl_3$) for *t*-Bu groups δ 24.98, 26.70, 28.97.

17b: Yellow prisms; mp 37.8−39.0 °C; IR (KBr) 1684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9 H), 1.24 (s, 18 H), 1.64 (br s, 3 H), 4.88 (br s, 3 H), 5.06 (br s, 1 H), 5.98 (d, 1 H, $J = 2.4$ Hz), 6.81 (d, 1 H, $J = 2.4$ Hz); ^{13}C NMR ($CDCl_3$) for *t*-Bu groups δ 26.6, 28.8, 29.2. Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.34; H, 10.16. Found: C, 74.92; H, 10.69.

17c: Yellow oil; IR (neat) 1684, 1657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9 H), 1.17 (s, 9 H), 1.20 (s, 9 H), 5.21 (d, 1 H, $J = 1.2$ Hz), 5.46 (d, 1 H, $J = 1.2$ Hz), 5.95 (d, 1 H, $J = 2.4$ Hz), 6.93 (d, 1 H, $J = 2.4$ Hz), 7.0−7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) for *t*-Bu groups δ 26.6, 28.5, 29.3. Anal. Calcd for $C_{26}H_{36}O_3$: C, 78.72; H, 9.15. Found: C, 78.66; H, 9.23.

18: Colorless prisms; mp 122.3−123.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 3 H), 0.83 (s, 9 H), 1.28 (s, 9 H), 1.36 (s, 9 H), 1.54 (s, 3 H), 7.1−7.7 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 156.6, 141.3, 138.6, 132.4, 128.3, 127.8, 127.5, 124.2, 123.4, 93.5, 91.5 79.7, 34.6, 34.3, 32.0, 29.5, 26.4, 26.0, 19.4. Anal. Calcd for $C_{28}H_{40}O_3$: C, 79.13; H, 9.42. Found: C, 78.88; H, 9.32.

19: ^{1}H NMR data [($CDCl_3$) δ 1.24 (s, 9 H), 1.47 (s, 9 H), 7.3−7.8 (m, 7 H), 12.72 (s, 1 H)] were identical with that of an authentic sample.[11]

Co(salen)-Catalyzed Oxidation of Cyanophenols (20 and 22) with TBHP. The procedure was the same as that for **1**. Only cyclohexa-2,5-dienones **21** and **23** were isolated.

21: Colorless needles; mp 86.5−87.2 °C; IR (KBr) 1673, 1653, 1624 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 18 H), 1.34 (s, 9 H), 6.61 (s, 2 H). Anal. Calcd for $C_{19}H_{29}NO_3$: C, 71.39; H, 9.08; N, 4.38. Found: C, 71.46; H, 9.06; N, 4.43.

23: Colorless prisms; mp 90.2−91.8 °C; IR (KBr) 2240, 1671, 1647, 1615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 9 H), 1.21 (s, 9 H), 1.28 (s, 9 H), 6.86 (d, 1 H, $J = 2.8$ Hz), 7.66 (d, 1 H, $J = 2.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 178.6, 160.3, 146.9, 144.5, 119.4, 114.0, 92.6, 80.6, 41.1, 35.1, 29.0, 26.3, 25.9. Anal. Calcd for $C_{19}H_{29}NO_3$: C, 71.39; H, 9.08; N, 4.38. Found: C, 71.40; H, 9.10; N, 4.35.

Co(salen)-Catalyzed Oxidation of 4-Acylphenol Oxime *O*-Methyl Ethers (24) with TBHP. The procedure was the same as that for **1**. Cyclohexadienones **25** and **26** were obtained. Analytical and spectral data for these products are given below. Characteristic ^{13}C NMR data for **25a, 25b**, and **25e** are listed in Table 3, and for **26a**−**26d**, and **26f** in Table 4, respectively.

25a: Yellow prisms; mp 72.8−73.6 °C; IR (KBr) 1686, 1653 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 9 H), 1.20 (s, 9 H), 1.26 (s, 9 H), 3.93 (s, 3 H), 6.43 (d, 1 H, $J = 2.0$), 7.20 (d, 1 H, $J = 2.0$), 7.74 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 147.4, 62.0. Anal. Calcd for $C_{20}H_{33}NO_4$: C, 68.34; H, 9.46; N, 3.98. Found: C, 68.32; H, 9.25; N, 3.95.

25b: Yellow oil; IR (neat) 1684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 9 H), 1.18 (s, 9 H), 1.25 (s, 9 H), 2.06 (s, 3 H), 6.54 (d, 1 H, $J = 2.0$), 7.39 (d, 1 H, $J = 2.0$); ^{13}C NMR ($CDCl_3$) δ 152.4, 62.0, 10.5. Anal. Calcd for $C_{21}H_{35}NO_4$: C, 68.94; H, 9.58; N, 3.83. Found: C, 68.82; H, 9.42; N, 3.63.

25c: Yellow oil; IR (neat) 1684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H), 1.11 (t, 3 H, $J = 7.5$ Hz), 1.20 (s, 9 H), 1.25 (s, 9 H), 2.60 (q, 2 H, $J = 7.5$ Hz), 3.97 (s, 3 H), 6.59 (d, 1 H, $J = 2.2$ Hz), 7.42 (d, 1 H, $J = 2.2$ Hz).

Compound 25d was obtained as a mixture of *syn* and *anti* stereoisomers which could not be separated, but was recognized readily by ^{1}H NMR.

25d (*syn*): ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.24 (d, 6 H, $J = 6.2$ Hz), 1.57 (s, 9 H), 1.59 (s, 9 H), 3.39 (sep, 1 H, $J = 6.2$ Hz), 3.93 (s, 3 H), 6.52 (d, 1 H, $J = 2.2$ Hz), 7.03 (d, 1 H, $J = 2.2$ Hz).

25d (*anti*): ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.09 (d, 6 H, $J = 6.2$ Hz), 1.57 (s, 9 H), 1.59 (s, 9 H), 2.69 (sep, 1 H, $J = 6.2$ Hz), 3.84 (s, 3 H), 6.19 (d, 1 H, $J = 2.0$ Hz), 6.44 (d, 1 H, $J = 2.0$ Hz).

25e: Yellow prisms; mp 52.2−53.3 °C; IR (KBr) 1684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.19 (s, 9 H), 1.23 (s, 18 H), 3.82 (s, 3 H), 6.03 (d, 1 H, $J = 2.0$ Hz), 6.27 (d, 1 H, $J = 2.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 164.8, 61.3, 37.2, 28.1. Anal. Calcd for $C_{24}H_{41}NO_4$: C, 70.77; H, 10.06; N, 3.43. Found: C, 70.69; H, 10.08; N, 3.36.

26a: IR (KBr) 1671, 1653 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 9 H), 1.29 (s, 18 H), 3.82 (s, 3 H), 6.63 (s, 2 H), 7.40 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 130.0, 61.9.

26b: Pale yellow needles; mp 43.6−44.2 °C; IR (KBr) 1667, 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 9 H), 1.26 (s, 18 H), 1.91 (s, 3 H), 3.79 (s, 3 H), 6.64 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 146.8, 61.8, 10.8. Anal. Calcd for $C_{21}H_{35}NO_4$: C, 68.94; H, 9.58; N, 3.83. Found: C, 68.93; H, 9.66; N, 3.77.

Compound 26c was obtained as a mixture of *syn* and *anti* stereo isomers which could not be separated, but recognized readily by ^{1}H NMR. The same is the case for **26d**.

26c (*syn*): Colorless oil; IR (KBr) 1669, 1651 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (t, 3 H, $J = 7.6$ Hz), 1.22 (s, 9 H), 1.26 (s, 18 H), 2.37 (q, 2 H, $J = 7.6$ Hz), 3.77 (s, 3 H), 6.65 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 160.9, 61.8, 19.4, 11.0. Anal. Calcd for $C_{22}H_{37}NO_4$: C, 69.62; H, 9.83; N, 3.65. Found: C, 69.46; H, 9.85; N, 3.66.

26c (*anti*): Colorless oil; IR (KBr) 1669, 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9 H), 1.20 (d, 3 H, $J = 7.5$ Hz), 1.23 (s, 18 H), 2.45 (q, 2 H, $J = 7.5$ Hz), 3.61 (s, 3 H), 6.48 (s, 2 H).

26d (*syn*): Pale yellow prisms; mp 51.2−52.1 °C; IR (KBr) 1669, 1651 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9 H), 1.26 (s, 18 H), 1.26 (d, 6 H, $J = 7.2$ Hz), 2.81 (sep, 1 H, $J = 7.2$ Hz), 3.73 (s, 3 H), 6.66 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 163.1, 61.8, 30.1, 18.5. Anal. Calcd for $C_{23}H_{39}NO_4$: C, 70.13; H, 9.91; N, 3.56. Found: C, 70.13; H, 9.92; N, 3.61.

26d (*anti*): Colorless oil; IR (neat) 1669, 1647 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 (d, 6 H, $J = 6.8$ Hz), 1.19 (s, 9 H), 1.23 (s, 18 H), 2.93 (sep, 1 H, $J = 6.8$ Hz), 3.60 (s, 3 H), 6.47 (s, 2 H).

26e: Colorless oil; IR (neat) 1669, 1647 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H), 1.23 (s, 18 H), 1.34 (s, 9 H), 3.54 (s, 3 H), 6.29 (s, 2 H); ^{13}C NMR ($CDCl_3$) for *t*-Bu group δ 29.4, 26.7, 29.3.

26f (*syn*): Colorless prisms; mp 82.5−83.8 °C; IR (KBr) 1667, 1647 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 27 H), 3.74 (s, 3 H), 6.57 (s, 2 H), 7.0−7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 157.5, 132.2, 128.6, 128.3, 127.4, 62.3. Anal. Calcd for $C_{26}H_{37}NO_4$: C, 73.04; H, 8.72; N, 3.28. Found: C, 73.08; H, 8.76; N, 3.18.

Thermal Decomposition of 26b. A solution of **26b** (366 mg, 1 mmol) in $CHCl_3$ (30 mL) was heated at 50 °C under N_2. The original material disappeared in 7 h. The reaction mixture was concentrated and separated by silica gel TLC (CH_2Cl_2/hexane = 2/1) to give **24b** (40 mg, 12%), **25b** (61 mg, 18%), and **29** (106 mg, 45%). When **26b** (366 mg, 1 mmol) was heated at 40 °C for 5 h, **25b** (97 mg, 27%) and **29** (13 mg, 5%) were obtained with recovery of **26b** (232 mg, 63%).

29: Green needles; mp 111.5−111.9 °C; IR (KBr) 1659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9 H), 2.09 (s, 3 H), 4.06 (s, 3 H), 6.44 (d, 1 H, $J = 2.2$ Hz), 7.64 (d, 1 H, $J = 2.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 181.5, 179.7, 152.3, 149.8, 146.3, 131.9, 123.9, 63.3, 35.6, 29.2, 10.4. Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.31; H, 7.12; N, 5.94.

Time Course of Thermal Rearrangement of 26b. A solution (0.25 mol/L) of **26b** (37 mg, 0.1 mmol) in $CDCl_3$ was kept in an NMR tube set up in an NMR machine at 38.8 °C, and the reaction was followed by ^{1}H NMR spectroscopy. The results are given in Figure 2.

Thermal Rearrangement of 6d in Various Solvents. A solution of **6d** (401 mg, 1 mmol) in an appropriate solvent (40 mL) was heated at 60 °C under N_2. The reaction mixture was separated by silica gel TLC to give compounds **30** [^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H), 1.19 (s, 9 H), 1.23 (s, 9 H), 3.79 (s, 3 H), 6.49 (d, 1 H, $J = 2.3$ Hz), 6.98 (d, 1 H, $J = 2.3$ Hz), 6.7−7.5 (m, 4 H)], **31**, and **32**. Addition of ascorbic acid as a radical scavenger (1.75 g, 10 mmol) in MeOH (40 mL) afforded **32** (284 mg, 91%) along with a minute amount of **30** (5 mg, 1%) and **31** (3 mg, 1%). The results are given in Table 9.

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