matography (18 g silica gel, 5% ethyl acetate/hexane) to afford 0.379 g (oil, 80%) of the bicyclic ketone **20a**.

In separate experiments, the major diastereomer of the **18a**/**19a** mixture was found to rearrange to ketone **20a** in 87% yield, and the minor diastereomer also rearranged to produce ketone **20a** in 80% yield.

Bicyclic ketone **20a** gave the following spectral data which is identical with that previously published for this compound:[25] NMR (CCl_4) δ 5.10 (1 H, br s), 1.0–3.0 (15 H, m); IR (CCl_4) 2940 (s), 1700 (s), 1450 (m), 1080 (m), 900 cm^{-1} (m); MS (15 eV) *m/e* 164 (M^+), 146, 136, 107 (base), 94, 79, 57, 43.

5-Methylbicyclo[5.3.1]undec-1(11)-en-4-one (20b). Rearrangement of the diastereomeric mixture of **18b**/**19b** (0.360 g, 1.72 mmol) was accomplished by the procedure described for preparation of **20a** to afford **20b** (0.222 g oil, 72% yield) as a single diastereomer which gave the following spectral data: NMR (CCl_4) δ 5.10 (1 H, br s), 1.0–3.0 (14 H, m), 0.87 (3 H, d, J = 7 Hz); IR (CCl_4) 2940 (s), 1705 (s), 1450 (m), 1140 (m), 1075 (m), 920 (m), 890 cm^{-1} (m); MS (70 eV) *m/e* 178 (M^+), 136, 110, 94, 79 (base), 67, 55.

Acknowledgment. This research was supported in part by a grant from the Northwestern University Research Grants Committee. We also thank Mr. Mark Rubino for his assistance in the preparation of starting materials. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. **1**, 41597-03-9; **2a**, 81388-59-2; **2b**, 81388-60-5; **2c**, 81388-61-6; **3a**, 81388-62-7; **3b**, 81388-63-8; **3c**, 81388-64-9; **4a**, 81388-65-0; **4c**, 81388-66-1; **8**, 81338-67-2; **9c**, 81388-68-3; **11a**, 81388-69-4; **11b**, 81388-70-7; **11c**, 81388-71-8; **12a**, 81388-72-9; **12b**, 81388-73-0; **12c**, 81388-74-1; **13**, 23153-80-2; **13** mesylate, 81388-75-2; **14**, 81388-76-3; **14** ethylene ketal, 81388-77-4; **15** (isomer 1), 81388-78-5; **15** (isomer 2), 81388-79-6; **16**, 81388-80-9; **17**, 41597-04-0; **18a**, 81388-81-0; **18b**, 81388-82-1; **18c**, 81388-83-2; **19a**, 81388-84-3; **19b**, 81388-85-4; **19c**, 81388-86-5; **20a**, 77080-07-0; **20b**, 81388-87-6; isobutylene, 75-28-5; 1,2-dibromo-2-methylpropane, 594-34-3; 1-bromo-2-methylpropene, 3017-69-4; acrolein, 107-02-8; vinyllithium, 917-57-7; propen-2-yllithium, 3052-45-7; 2-methylpropen-1-yllithium, 29917-94-0; bis(4-chlorophenyl) diselenide, 20541-49-5; cyclopropyl phenyl sulfide, 14633-54-6; 2-[[(*p*-chlorophenyl)selenyl]methyl]-1-[1-(phenylthio)cycloprop-1-yl]cyclohexan-1-ol, 81408-02-8; vinyl bromide, 593-60-2; isopropenyl bromide, 557-93-7; isobutenyl bromide, 3017-69-4.

Reaction of 2-(Methylseleno)- and 2-(Phenylseleno)benzoic Acids and Their Derivatives with *tert*-Butyl Hydroperoxide. Neighboring Selenium Participation and Facile Formation of Cyclic Selenuranes and a Selenurane Oxide

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The reaction of 2-(methylseleno)benzoic acid with 1,1′-carbonyldiimidazole followed by addition of *tert*-butyl hydroperoxide gave 1,1-dihydro-1-*tert*-butoxy- and 1-hydroxy-1-methyl-3*H*-2,1-benzoxaselenol-3-ones (**3a** and **4a**), suggesting the intramolecular insertion of the neighboring selenium atom into the O–O bond of *tert*-butyl 2-(methylseleno)peroxybenzoate (**1a**). In the reaction of 2-(phenylseleno)benzoyl chloride with *tert*-butyl hydroperoxide, 1,1-dihydro-1-*tert*-butoxy-1-phenyl-3*H*-2,1-benzoxaselenol-3-one (**3b**) and its 1-oxide (**9**) were produced. The latter gave 2-carboxyphenyl phenyl selenone upon aqueous alkaline hydrolysis.

Much progress has recently been made in organo group 4B element chemistry. In addition to and closely related to the versatile reactivities,[1] chemical bonding in high-valent states of these classes of compounds is the subject of interest. Martin and co-workers,[2] for example, found a striking effect of the neighboring sulfur atom on the rate enhancement of the homolytic O–O bond cleavages of *tert*-butyl 2-thioperoxybenzoates. Intermediacy of the sulfuranyl radicals was advocated,[2,3] and stable dialkoxy- and bis(acyloxy)sulfuranes were obtained as an extension of this concept.[4,5] Since the selenium atom can expand its valence shell more readily,[6] and the carboxyl group in the neighborhood of the Se–O bond can act as a ligand to form more stable selenuranes,[7,8] it seemed to us of interest to investigate the anchimeric assistance of the neighboring selenium atom in the decomposition of *tert*-butyl 2-selenoperoxybenzoates. We report here the attempted synthesis of *tert*-butyl 2-(methylseleno)peroxybenzoate (**1a**) and the related reactions of 2-selenobenzoic acids and their derivatives with *tert*-butyl hydroperoxide.[9]

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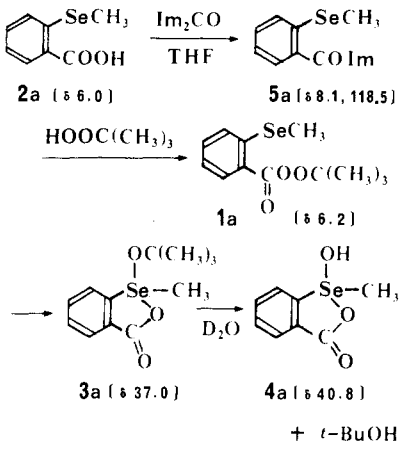
(5) (a) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5519. (b) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *Ibid.* **1974**, *96*, 6735. (c) Martin, J. C.; Perozzi, E. F. *Ibid.* **1974**, 96, 3155. (d) Lau, P. H. W.; Martin, J. C. *Ibid.* **1977**, *99*, 5490. (e) Michalak, R. S.; Martin, J. C. *Ibid.* **1981**, *103*, 214. (f) Adzima, L. J.; Chiang, C. C.; Paul, I. C.; Martin, J. C. *Ibid.* **1978**, *100*, 953. (g) Lam, W. Y.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 4462, 4468. See also: Okuma, K.; Tanaka, Y.; Ohta, H. *J. Am. Chem. Soc.* **1981**, *103*, 5976.

0022-3263/82/1947-2275$01.25/0

Scheme I



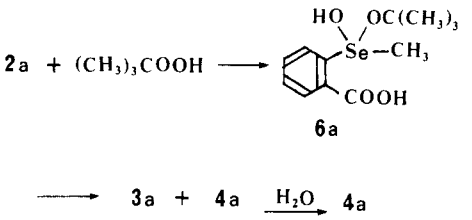
Results and Discussion

2-(Methylseleno)benzoic acid (**2a**) was allowed to react with 1,1′-carbonyldiimidazole in THF, followed by addition of excess *tert*-butyl hydroperoxide at low temperature. The product obtained was not the expected *tert*-butyl 2-(methylseleno)peroxybenzoate (**1a**) but selenurane **3a** together with a small amount of the 2-carboxyphenyl methyl selenoxide **4a** after evaporation of THF at low temperature. A sample of **4a** was independently prepared for comparison and was shown to have the ring-closed selenurane structure.[8] During attempted purification, most of **3a** was converted into **4a**.

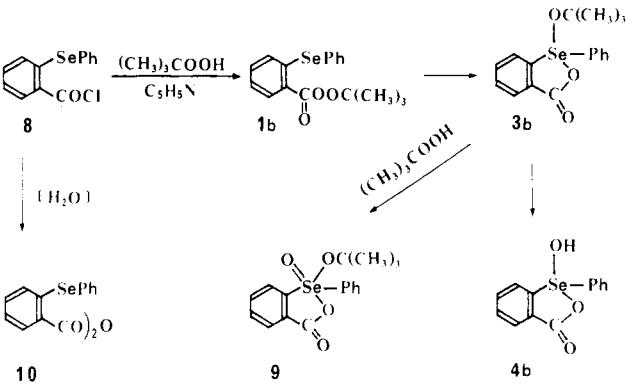
The above reaction was monitored by ^{13}C NMR spectroscopy. When 1,1′-carbonyldiimidazole was added, evolution of carbon dioxide took place, and the methyl carbon of **2a** at δ 6.0 was replaced by a new signal at δ 8.1. The spectral change indicated the formation of imidazolide **5a** of **2a**. In the aromatic region, a signal at δ 118.5 was characteristic of **5a**. When excess *tert*-butyl hydroperoxide was added to the solution, a new signal developed at δ 6.2 in place of the peak at δ 8.1 in about 1 h. A few hours later, an additional signal at δ 37.0 due to **3a** started to grow at the expense of the signal at δ 6.2. Addition of 1 drop of D_2O quenched the signal at δ 37.0, and the signals due to **4a** (δ 40.8) and *tert*-butyl alcohol were obtained (Scheme I). Aromatic and carbonyl ^{13}C signals also changed as did those of the methyl carbons.

The interpretation is consistent with the known reaction pattern of an organic imidazolide with *tert*-butyl hydroperoxide[10] and with the typical ^{13}C chemical shift values of ^{13}C-labeled substituted selenoanisoles[11] where the methyl carbons fall in the range δ 5.9–8.7. The intermediate having the methyl carbon at δ 6.2 is thus concluded to be **1a**. The observed efficient conversion of **1a** to **3a** would be the O–O bond cleavage assisted by the neighboring selenium atom. The half-life of **1a** at the ambient NMR probe temperature of 29 °C was ca. 2.5 h. When this value is compared with the half-life of ca. 40 h deduced for *tert*-butyl 2-methylthioperoxybenzoate under similar conditions,[2a,b] the rate enhancement factor for the 2-methylseleno group is estimated to be 15–16 times larger than that for the 2-methylthio group in the decomposition of *tert*-butyl peroxybenzoates.

Scheme II

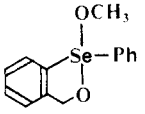


Scheme III



It might be argued that *tert*-butyl hydroperoxide could have attacked the selenium atom of **5a** directly. The contribution of such a reaction seems to be smaller since the reaction of *tert*-butyl hydroperoxide with **2a** is slower than that with **5a** by a factor of 20 in THF. The reaction of **2a** with *tert*-butyl hydroperoxide did occur in chloroform and was completed in 1 h to give predominantly **3a**. In the presence of imidazole, the reaction produced **3a** and **4a** in a ratio of ca. 1:9 (based on ^{13}C NMR intensities). Adduct **6a** is considered to be an intermediate from which may be obtained **3a** by dehydration and **4a** by base-catalyzed elimination of *tert*-butyl alcohol. After removal of chloroform under reduced pressure, only **4a** was isolated (Scheme II).

The high water sensitivity of compound **3a** which has a *tert*-butoxy group (^{13}C NMR at δ 26.0 and 82.1) and gives **4a** and *tert*-butyl alcohol is reminiscent of the extremely water-sensitive cyclic dialkoxyselenurane **7** reported by Reich.[12]



7

2-(Phenylseleno)benzoyl chloride (8) was allowed to react with *tert*-butyl hydroperoxide in ether in the presence of pyridine at low temperature for 5 days. A mixture of the two compounds **3b** and **9** was obtained by chromatography of the reaction products on basic alumina. One of them, **9**, was isolated by crystallization from ether as a microcrystalline solid. Since purification of **3b** was difficult, owing to its sensitivity to moisture, it was identified as the cyclic 2-carboxyphenyl phenyl selenoxide **4b** after hydrolysis. As **4b** is known to be a cyclic selenurane,[13] the structure of **3b** may be assumed to be a cyclic *tert*-butoxyselenurane similar to **3a** and formed as shown in

(6) Klayman, D. L.; Günther, W. H. H. "Organic Selenium Compounds: Their Chemistry and Biology"; Wiley: New York, 1973. For recent reviews on organic syntheses, see: Sonoda, N.; Kondo, K. *Yuki Gosei Kagaku* **1977**, *35*, 775. Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049.
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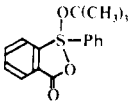
Table I. Carbonyl Stretchings of Organosulfur and Organoselenium Compounds

compd	ν, cm^{-1}	compd	ν, cm^{-1}
2a	1678	**13**	1645, 1692
2b	1678	2-$PhSC_6H_4COOH$	1685
2-$MeSeC_6H_4COOMe$	1714	2-$PhSC_6H_4COCl$[a]	1724, 1760
2-$PhSeC_6H_4COOMe$	1710	2-$PhSC_6H_4COOOBu\text{-}t$[b]	1748
8	1725, 1760		1640
2-$MeSe(O)C_6H_4COOMe$	1700	2-$PhSO_2C_6H_4COOH$	1740, 1750
4a	1622		
4b	1630		
9	1665		

[a] Reference 14. [b] Reference 2a.

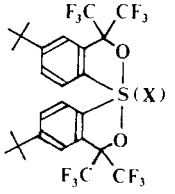
Table II. ^{13}C NMR Chemical Shifts of Organoselenium Compounds

		chemical shift,[d] δ										
compd	solvent	C=O	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′
2b	$CDCl_3$	171.8	141.5	126.4	132.3	124.8	133.3	129.2	128.9	137.5	129.7	129.2
	CD_3OD	170.0	141.3	128.7	132.5	125.7	133.4	130.1[c]	130.4	138.4	130.7	129.8[c]
2-$PhSeC_6H_4COOMe$[a]	CD_3OD	168.4	140.8	128.4	132.1	125.9	133.5	130.1[c]	130.3	138.2	130.7	130.2[c]
8	$CDCl_3$	167.4	143.0	127.9	134.2	125.2	135.4	129.3[c]	130.2	137.3	129.9	129.5[c]
10	$CDCl_3$	162.0	143.6	125.4	132.2	124.8	133.8	129.3	128.2	137.5	129.8	129.3
4b	CD_3OD	171.5	142.0	135.1	134.0[c]	131.2	134.6[c]	128.4	137.3	128.9	130.7	133.0[c]
9[b]	$CDCl_3$	169.0	139.2	134.2	132.9	130.3	133.4	128.5	135.6	127.7	129.8	131.9
13	$CDCl_3$	168.4	143.9	132.0	134.0	130.7	134.9	129.7	134.7	127.0	130.1	131.9

[a] δ 52.6 (OMe). [b] δ 26.4 and 82.7 ($OC(C^*H_3)_3$ and $OC^*(CH_3)_3$, respectively). [c] Assignments are tentative. [d] From internal Me_4Si.

Scheme III. The results are also consistent with the Reich's results.[12] From the ether-insoluble fraction of the products was obtained 2-(phenylseleno)benzoic anhydride (**10**) after washing with water followed by crystallization from benzene. The anhydride **10** was prepared independently from the reaction of 2-(phenylseleno)benzoic acid (**2b**) with its chloride (**8**) in ether in the presence of a base. The yields of **4b** and **9** were below 10%, but that of **10** amounted to 37%.

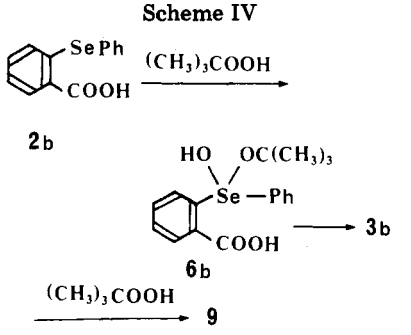
The molecular formular of **9** is $C_{17}H_{18}O_4Se$ from elemental analyses. The carbonyl stretching and ^{13}C NMR chemical shift data of **9** and the related compounds are shown in Tables I and II, respectively. Monocyclic carboxysulfuranes are known to have low C=O frequencies.[14] These requirements are satisfied in **4a** and **4b**, which have their IR absorptions at 1622 and 1630 cm^{-1}, respectively. On the contrary, **9** absorbs at 1665 cm^{-1}, which is substantially higher than the wavenumbers for **4a** and **4b** but lower than 1710 cm^{-1} for methyl 2-(phenylseleno)benzoate. The apical bonds of sulfuranes are highly ionic[4] and the carbonyl group in the carboxysulfuranes behaves as if it were a carboxylate ion in IR spectra.[14] The low IR frequencies for **4a** and **4b** are explained also by the highly polar character of the apical bonds. On the other hand, the bond order of the apical bonds of sulfurane oxide **12**



11; X = null
12; X = O

(14) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5761.

Scheme IV



is reported to be larger than that of parent sulfurane **11**.[5b] The S–O bond lengths of apical positions of **11** and **12** are ca. 1.82 and 1.78 Å, and the bond orders are estimated at 0.62 and 0.74 Å, respectively. The S–O bond at the equatorial position is ca. 1.44 Å, which is close to those of aryl sulfones.[5b] Thus the C=O stretching of **9** is consistent with the selenurane oxide structure. ^{13}C NMR chemical shifts of **9** are very similar to those of **4b** and 2-carboxyphenyl phenyl selenone (**13**), which is also consistent with the selenurane oxide structure of **9** as shown in Scheme III. The ^{77}Se NMR chemical shift of **9** is δ 785 on the dimethyl selenide scale and corroborates the assigned structure.

Cyclic selenurane oxide **9** was also obtained almost quantitatively from the reaction of 2-(phenylseleno)benzoic acid (**2b**) with 2 equiv of *tert*-butyl hydroperoxide in chloroform (Scheme IV). No ^1H and ^{13}C NMR signal due either to **6b** or **3b** was found during the reaction. Instead, the signals due to **9** and *tert*-butyl alcohol appeared from the beginning. The formation of **6b** is thus suggested to be slow while cyclization to **3b** and further oxidation to **9** may be relatively fast in chloroform-*d* at an ambient temperature of 29 °C. The oxidation of selenurane **3b** with *tert*-butyl hydroperoxide should be compared with that of sulfurane **11** with ruthenium tetraoxide and the related reactions.[5] In the reaction of **2b** with *tert*-butyl hydro-

peroxide, **4b** was also produced in some quantity if the reaction was not moisture free. The formation of **4b** in this reaction suggests the intermediacy of **3b**.

Oxide **9** was stable to moisture but, when allowed to react with aqueous sodium hydroxide, gave 2-carboxyphenyl phenyl selenone (**13**) in good yield. The formation of **13** from **9** also provides support for the selenurane oxide structure of **9**.

Experimental Section

^1H and ^{13}C NMR spectra were taken at an ambient temperature of 29 °C on a JEOL FX-60Q spectrometer operating at 60 and 15 MHz, respectively. ^{77}Se NMR spectra were obtained on a Varian FT-80A spectrometer at 15.2 MHz. IR spectra were determined for Nujol mulls with a Hitachi 295 infrared spectrophotometer.

Preparations of **4a,b**, **2a,b**, and **7** are described elsewhere.[8,13]

Reaction of 2a with *tert*-Butyl Hydroperoxide in the Presence of 1,1'-Carbonyldiimidazole. To a stirred solution of 1 g (4.7 mmol) of **2a** in 50 mL of THF was added 5.0 mmol of 1,1'-carbonyldiimidazole. After 30 min at 40 °C, 1.3 g (14 mmol) of *tert*-butyl hydroperoxide in 10 mL of THF was added at −10 °C, and the mixture was stirred for 30 h at −15 °C. The solvent was removed under reduced pressure at temperature below 0 °C. The residue contained **3a** and **4a** in a ratio of ca. 4:1 as judged by ^{13}C NMR: δ 37.0 for **3a** and δ 40.8 for **4a**. After attempted separation by fractional dissolution in ether, only **4a** [0.74 g (69%); mp 161–162 °C (lit.[13] mp 162–163 °C)] was obtained.

^{13}C NMR Monitoring of the Reaction of 2a with *tert*-Butyl Hydroperoxide. A solution of 100 mg of **2a** in 1.5 mL of THF was placed in a 10-mm-o.d. NMR tube fitted with a D_2O capillary for an external lock. The reaction was started by adding 70 mg of 1,1'-carbonyldiimidazole to the solution. ^{13}C NMR spectra were measured by using a 45° pulse of 3 s. A reasonable s/n ratio of higher than 5 of the methyl carbon signals was obtained by accumulating ca. 300 transients. Measurements were repeated every 20–40 min.

The reactions in chloroform were similarly monitored.

Reaction of 8 with *tert*-Butyl Hydroperoxide. To a solution of 5.0 g (55 mmol) of *tert*-butyl hydroperoxide and 5.9 g (75 mmol) of pyridine in 150 mL of ether was added dropwise 9.5 g (32 mmol) of 2-(phenylseleno)benzoyl chloride (**8**) in 200 mL of ether at −10 °C, and the mixture was stirred for 5 days at −15 °C. The reaction mixture was filtered, and the filtrate was concentrated to about 30 mL at a temperature below 0 °C. The residue was chromatographed on basic alumina (Merck, aluminum oxide 60, activity grade I) with ether at −15 °C. Two compounds **3b** and **9** were obtained. After recrystallization from ether, **9** was isolated as microcrystalline colorless solid: 0.96 g (8.2%); mp 153.5–155 °C. Anal. Calcd for $C_{17}H_{18}O_4Se$: C, 55.89; H, 4.96. Found: C, 55.59; H, 4.97. During the attempted purification of **3b** from the mother liquor, the ^1H NMR signal due to **3b** at δ 1.25 disappeared and **4b** [0.73 g (7.8%); mp 198–201 °C] was obtained instead. Anal. Calcd for $C_{13}H_{10}O_3Se$: C, 53.26; H, 3.44. Found: C, 53.04; H, 3.49.

The insoluble fraction from the reaction mixture gave, after washing with water and recrystallization from benzene, 3.2 g (37%) of 2-(phenylseleno)benzoic anhydride (**10**) as colorless needles, mp 162–163 °C. Anal. Calcd for $C_{26}H_{18}O_3Se_2$: C, 58.21; H, 3.36. Found: C, 58.05; H, 3.34.

Anhydride **10** was also obtained in good yield from the reaction of **8** with **2b** in ether in the presence of pyridine.

Reaction of 2b with *tert*-Butyl Hydroperoxide. To a solution of 1 g (3.6 mmol) of **2b** in 30 mL of chloroform was added 0.90 g (10 mmol) of *tert*-butyl hydroperoxide in 10 mL of chloroform, and the mixture was stirred for 5 h at an ambient temperature. The residue obtained after evaporation of the solvent in vacuo was washed with ether to give 1.2 g (91%) of **9** as microcrystalline solid.

2-Carboxyphenyl Phenyl Selenone (13). To a solution of 500 mg (1.4 mmol) of **9** in 5 mL of ethanol was added 500 mg of sodium hydroxide in 10 mL of 50% aqueous ethanol, and the mixture was stirred under reflux for 3 h. The solution was concentrated to ca. 5 mL, acidified by dilute hydrochloric acid, and treated with chloroform. Crystallization from hexane–chloroform gave **13**: 270 mg (64%); mp 194–196 °C. Anal. Calcd for $C_{13}H_{10}O_4Se$: C, 50.50; H, 3.26. Found: C, 50.24; H, 2.84.

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Registry No. 1a, 81408-03-9; **2a**, 6547-08-6; **2b**, 25562-42-9; **3a**, 81113-79-3; **3b**, 81113-82-8; **4a**, 40242-21-5; **4b**, 81113-85-1; **5a**, 81113-80-6; **8**, 81113-84-0; **9**, 81113-83-9; **10**, 81389-54-0; **13**, 81389-55-1; 1,1'-carbonyldiimidazole, 530-62-1; *tert*-butyl hydroperoxide, 75-91-2; 2-$MeSeC_6H_4COOMe$, 78377-06-7; 2-$PhSeC_6H_4COOMe$, 80014-45-5; 2-$MeSe(O)C_6H_4COOMe$, 80014-48-8; 2-$PhSC_6H_4COOH$, 1527-12-4; 2-$PhSO_2C_6H_4COOH$, 58844-73-8.

Oxygenation of 2,6-Di-*tert*-butylphenols Bearing an Electron-Withdrawing Group in the 4-Position[1]

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Co(Salpr), a five-coordinate cobalt(II) Schiff base complex, has been found to promote oxygenation of 2,6-di-*tert*-butylphenols bearing an electron-withdrawing group in the 4-position, leading to dioxygen incorporation exclusively into the ortho position of the phenols. 4-Acyl-2,6-di-*tert*-butylphenols (**1**) and their oxime *O*-methyl ethers (**2**) gave the corresponding 6-hydroperoxy-2,4-cyclohexadienone derivatives **3** and **4** quantitatively. Schiff bases **10** derived from 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, on the other hand, gave unexpected products, 1,2-dihydropyridine derivatives **11**, cyclopentadienone **12**, and epoxy-*o*-quinol **13**. The structure of dihydropyridine **11a** was determined by X-ray analysis. 2,6-Di-*tert*-butyl-4-cyanophenol gave 2,5-di-*tert*-butyl-3-cyano-2,4-cyclopentadienone in good yield. The formation of these products can be understood to result from intramolecular decomposition of the corresponding *o*-peroxidic intermediate. Phenols **2** were readily oxygenated in *t*-BuOH containing *t*-BuOK to give epoxy-*o*-quinols **7** in excellent yield, although the other phenols examined were unsusceptible to oxygenation under various basic conditions.

In our previous works,[2] Co(Salpr), a five-coordinate cobalt(II)–Schiff base complex capable of binding dioxygen, has been demonstrated to mediate oxygenation of 4-alkyl- and 4-aryl-2,6-di-*tert*-butylphenols, leading to

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