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OXYGENATION OF 2,6-DI-t-BUTYLPHENOLS WITH SUPEROXO Co(III) COMPLEXES

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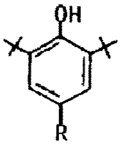
Superoxo Co(III) complexes, $[Co(CN)_5O_2][X]_3$ where X = Et_3N^+ and $(Ph_3P)_2N^+$, mediate the dioxygen incorporation into 2,6-di-t-butylphenols (1) with the same regioselectivity as that in the base-catalyzed oxygenation of 1. The superoxo species acts as a base but is not incorporated into the substrate.

The oxygenation of 4-substituted 2,6-di-t-butylphenols with pentacoordinate Co(II)-Schiff base complexes has been found to lead to the regioselective formation of peroxyquinolato Co(III) complexes, where superoxo Co(III) complexes reversibly formed were suggested to initiate the reaction by hydrogen abstraction from the phenols.[1,2] With a view to obtaining further informations on the reactivity of superoxo complexes, we have investigated the reaction of 2,6-di-t-butylphenols (1) with superoxo Co(III) complexes, $[Co(CN)_5O_2]^{3-}$ (2) irreversibly formed.[3]



1

a; R = t-Bu   b; R = Me   c; R = 4-MeOPh

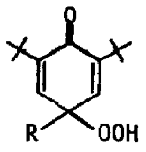
$[Co^{III}(CN)_5O_2][X]_3$

2

a; X = Et_4N^+

b; X = $(Ph_3P)_2N^+$

Interestingly, no oxidation of 1 takes place when the superoxo complexes 2 are mixed with 1 in solutions under nitrogen atmosphere, whereas dioxygen bubbling through the mixture in DMF led to the regioselective dioxygen incorporation into 1 to give the products 3 - 7 same as those in the base-catalyzed oxygenation of 1[6] (Table 1). This indicates that the coordinated dioxygen species, contrary to the superoxo Co(III)-Schiff base complexes, does not abstract hydrogen from



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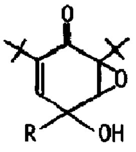

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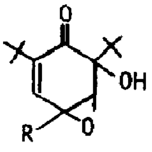

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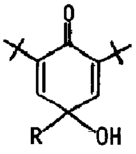

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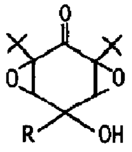

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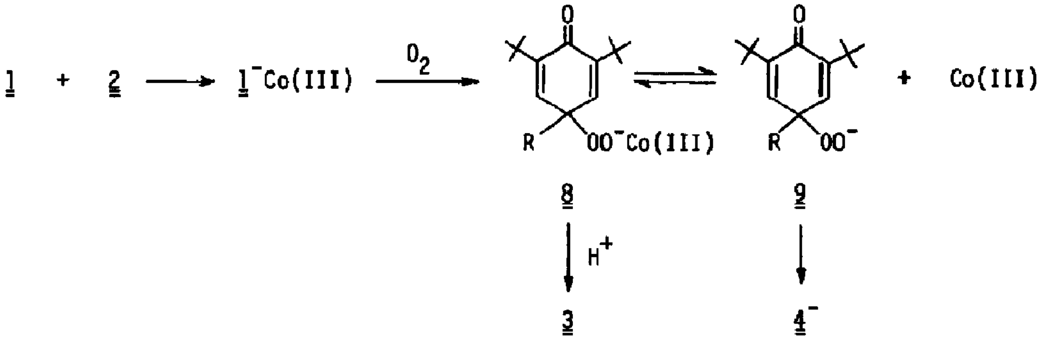
Table 1. Oxygenation of 1 mediated by 2.[a]

1	2	Reaction Temperature (°C)	Reaction Time (h)	Conversion (%)	Product, yield (%)				
					3	4	5	6	7
1a	2a	0	1.5	20	100	-	-	-	-
		0	14	100	88[b]	8	-	-	-
		25	3	100	-	88	10	2	-
	2b	0	5	60	100[b]	-	-	-	-
		25	5	100	trace	trace	-	90	-
1b	2a	0	2	88	91	9	-	-	-
		25	1.5	100	-	35	-	37[c]	28
1c	2a	0	2	0					
		25	96	60	-	-	100	-	-

[a] Oxygen was bubbled through a solution of 1 (0.5 mmol) and 2 (1 mmol) in DMF (100 ml). The products were isolated after acidifying the mixture and identical with authentic samples.[6] [b] Trace amounts of an isomeric o-hydroperoxide are contained. [c] A small amount of 3b is contained.

1, but acts as a base.[7] It is therefore noted that the different coordinated state of superox species results in the different reactivity toward 1. The epoxyquinol 4 is obtained only when the peroxyquinolate anion 9 is in a free state. Similarly, 5 arises only from a free form of ortho isomer of 9.[6] The peroxyquinolates are stabilized only when they are solvated or associ with metal ions.[1,2,6] Furthermore, dioxygen can combine with the phenolate anion $1c^-$ only whe it is in an aggregate with metal ions such as K^+ and Co(III) species.[1,6] Therefore, the resu summarized in Table 1 are rationalized by the following scheme involving a temperature depende equilibrium between the peroxyquinolato Co(III) complex and the free peroxyquinolate anion 9. Such an equilibrium has not been observed with peroxyquinolato Co(III)-Schiff base complexes.



The oxygenation of 1a with 2b in DMF resulted in the exclusive formation of a *p*-quinol 6a, although 2b was inactive in CH_2Cl_2. This is due to the reduction of 9a with the countercation of 2b probably *via* nucleophilic attack on a phosphorous atom of the cation by 9a.[9] The products 6b and 7b from 1b are, on the other hand, reasonably considered to result from the Michael addition of 9b to 4b.[6] The inactivity of 2b in CH_2Cl_2 may be due to the formation of an aggregate of this complex in nonpolar solvents, hindering the interaction of the substrate with the superoxo species.

If the equilibrium between 8 and 9 is the case, the oxygenation of 1 should proceed catalytically, because the phenolato complex, 1⁻Co(III) is expected to regenerate by proton transfer from 1 to 4⁻. It has been known that no proton transfer occurs from 1 to the peroxy complex 8.[2] Thus, the oxygenation of 1a in DMF in the presence of a catalytic amount of 2a at room temperature, where five catalytic cycles were achieved in 17 h, gave 4a in 70% yield together with 5a, 6a, and 7a in 9%, 13%, and 8% yield, respectively. A similar catalysis occured with 2b to give 6a in 69% yield accompanying 3a (20%) and 4a (8%). These results provide further chemical evidences for the equilibrium, which is the first observation with peroxy transition metal complexes.

References and Notes

(1) A. Nishinaga, K. Nishizawa, H. Tomita, and T. Matsuura, J. Am. Chem. Soc., 99, 1287 (1977).

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(3) The superoxo complex 2a was obtained as crystals by irreversible oxygenation of $[Co(CN)_5][NEt_4]_3$ in DMF[4] and 2b which is soluble in CH_2Cl_2 was synthesized by the reaction

of 2a with $[Ph_3P{=}\overset{\pm}{N}{=}PPh_3]CN^-$ [5] in aqueous methanol at 0 °C.

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(7) Since the phenoxy radical of 1 has been found to combine with 2 to give the correspondin peroxyquinolato Co(III) complex,[8] if the superoxo complexes 2 abstract hydrogen from 1, oxygenation products from 1 should be obtained even under nitrogen atmosphere. A furthe evidence for the superoxo complexes 2 acting as a base is available from the reaction of 3a with 2a in DMF, where the same products 4a (93%) and 5a (7%) as those in the reaction 3a with bases are formed.[6]

(8) A. Nishinaga, H. Tomita, and T. Matsuura, to be published elsewhere.

(9) The addition of $(Ph_3P)_2N^+Br^-$ to a mixture from the oxygenation of 1a with 2a in DMF resu in the formation of 6a, which is also obtained nearly quantitatively from the reaction o 3a with 2b in DMF at 25 °C.

The coordinated form 8 should not be reactive against the counter cation $(Ph_3P)_2N^+$ becau the peroxy moiety of indissociable peroxyquinolato Co(III)-Schiff base complexes are not reduced by 2b or $(Ph_3P)_2N^+Br^-$.

The nature of oxidation products of the cation has not been clarified yet, and no Ph_3P= is formed.

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