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# OXYGENATION OF 2,6-DI-t-BUTYL-4-ALKYLPHENOLS CATALYZED BY COBALT(II) SCHIFF'S BASE COMPLEXES

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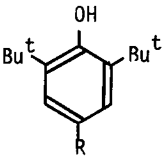
Cobalt(II) Schiff's base complexes such as Co-salen and Co-salpr (where salen = bis(salicylidene)ethylenediamine and salpr = bis(3-salicylideneaminopropyl)amine have been demonstrated to display homogeneous catalysis for the oxidation of phenols with molecular oxygen in organic media.[1-4] These complexes as well as many other Co(II) complexes with nitrogen bases reversibly react with $O_2$ giving rise to the formation of $O_2$ adducts in which 1 : 1 and 1 : 2 ($O_2$ : metal) stoichiometry for Co-salpr and Co-salen, respectively, are known.[5] The binding of $O_2$ to metal ion in the adducts has been the current subject of considerable interest in connection with biological oxygenations.[5,6]

It is expected that the difference between $O_2$ bindings in Co-salpr and Co-salen should be reflected on the catalysis of these complexes for oxidation of organic compounds. From this point of view, we have investigated the catalytic oxygenation of 2,6-di-t-butyl-4-alkylphenols (**1**) with Co-salpr and Co-salen in the present work, and wish to report that there is a difference between the catalyses of these complexes where Co-salpr predominantly gives p-quinols (**2**), of which a part of the results has been previously reported,[4] while Co-salen leads to the preferential formation of peroxides (**3**). The oxygenation was carried out by bubbling of $O_2$ at room temperature through a methanolic solution of **1** and catalytic amounts of Co-salen or Co-salpr. The results are given in Table 1.

When the Co-salpr catalyzed oxygenation of **1** (R = Me) in MeOH was carried out at lowered temperatures (below 10°C), hydroperoxide **8** (R = Me) (yield, ∿80 %) was obtained, and was reduced to **2** (R = Me) with raising temperature of the reaciton mixture. On the other hand, the Co-salpr catalyzed oxygenation of **1** (R = Me) in $CHCl_3$ or $C_6H_6$ gives a complex mixture of oxidation



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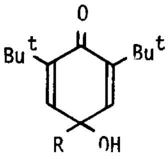

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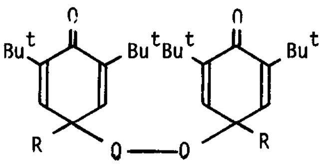

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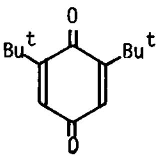

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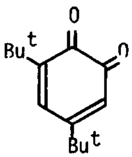

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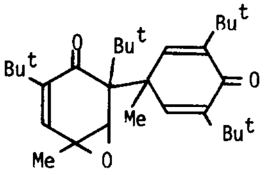

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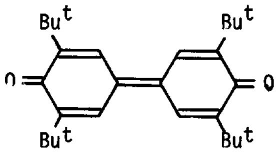

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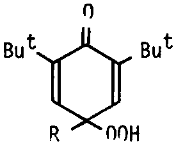

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Table 1. Co-salen and Co-salpr Catalyzed Oxygenation of 1 in MeOH

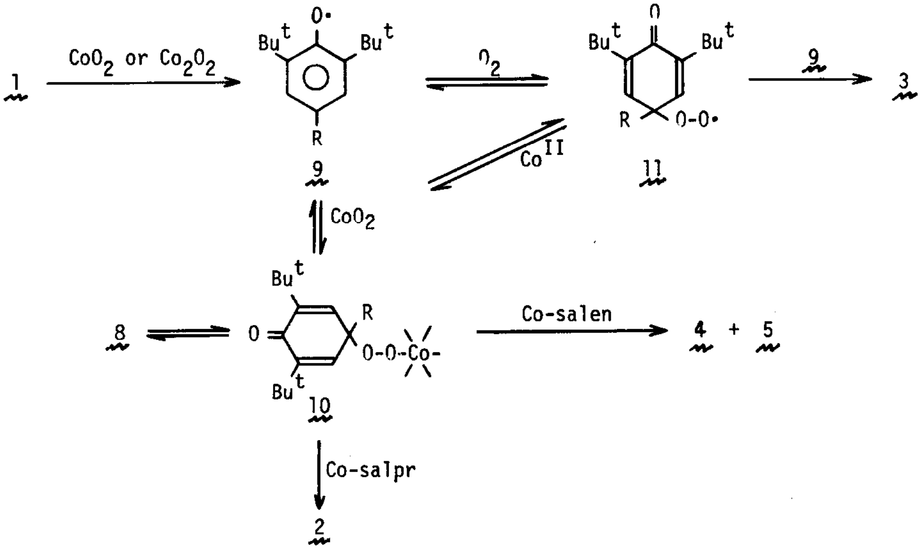
| Phenol | Cat.$^{b)}$ | 1/Cat. | Reaction | Conv. | Product (%)$^{a)}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (1) | | Mol. Ratio | Time | % | 2 | 3 | 4 | 5 | Others |
| R=Bu$^t$ | A | 0.5 | 2.5 | 100 | - | 55 | 32 | 6 | |
| | A | 5 | 20 | 100 | - | 47 | 34 | 12 | |
| | A | 10 | 20 | 100 | - | 47 | 33 | 7 | |
| | A | 50 | 48 | 85 | - | 53 | 24 | 7 | |
| | B | 5 | 39 | 93 | 60 | 10 | 8 | 6 | |
| R=Pr$^i$ | A | 5 | 4 | 99 | 8 | 44 | 45 | | |
| | B | 5 | 64 | 96 | 80 | 12 | 8 | | |
| R=Et | A | 5 | 3 | 96 | 10 | 31 | 19 | | 1(R=$\overset{\mathrm{CH_3}}{\mathrm{CH}}$-$\mathrm{OCH_3}$) 2 |
| | B | 5 | 51 | 96 | 83 | 6 | 3 | | |
| R=Me | A | 5 | 1 | 100 | 8 | - | 14 | | 6 35, 1(R=CHO) 4 |
| | B | 2 | 20 | 100 | 96 | - | - | | |
| R=H | A | 5 | 2 | 100 | | | 80 | | 7 13 |
| | B | 1 | 50 | 90 | | | 73 | | 7 6 |

a) Analyzed by isolation (silica gel chromatography)

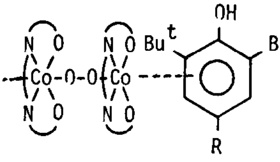
b) A = Co-salen, B = Co-salpr

products, whereas in the presence of $C_6H_5CH_2OH$ the formation of 2 (R = Me) accompanied with $C_6H_5CHO$ (isolated in >30% yield) is seen in the same solvent. These suggest that the solvent acts as reducing agent in the Co-salpr catalyzed oxygenation of 1 in MeOH.

The formation of peroxides 3 is resulted by the coupling of $O_2$ with phenoxy radicals 9, which were detected by ESR in the reaction course. Yield of the peroxides increases with increasing size of R in 1, which is consistent with the stability of phenoxy radicals 9 increasing in order of $Me{\sim}Et<Pr^i<Bu^t$. Thus, it can be seen from Table 1 that products in the catalytic oxygenation vary depending on not only nature of the catalysts but also structure of the phenols, used. For the Co-salen catalyzed oxygenation of 1 (R = $Bu^t$), there is a change only in reaction rate but not in product ratio with changing amounts of the catalyst (Table 1) implicating that the catalytic oxygenation involves path ways wholly governed by the Co-complex catalyst. Moderate change in distribution of oxidation products of 1 (R = $Pr^i$ and Et) in the catalysis of Co-salen and Co-salpr suggests that they are mechanistically correlated with each other. In addition, the stoichiometric oxygenation of 1 (R = $Bu^t$) with Co-salpr gave Co-peroxy complex 10 (R = $Bu^t$), $C_{38}H_{52}N_3O_5Co$, black prism, mp 160-162° (decomp.); $\nu_{max}$, no OH, 1645 $cm^{-1}$ (quinoid carbonyl), which was reduced with iodide giving 2 (R = $Bu^t$) quantitatively, decomposed on standing in MeOH to give a mixture of 2 (R = $Bu^t$), 4, and 5, and liberates 8 (R = $Bu^t$) by silica gel chromatographic separation. According for these observations, the mechanistic path ways of the following scheme, where products are given by the degradation of 10 depending on the ligand, is suggested.



The initial step of the catalytic oxygenation is reasonably considered to be hydrogen abstraction or one electron transfer which takes place via Co-$O_2$ complexes 12 and 13 for Co-salen and Co-salpr, respectively, taking into account the informations about binding and electronic state in the $O_2$ adduct formation of Co-Schiff's base complexes,[5-9] general consideration in catalytic autoxidation,[10,11] and the slower catalysis of Co-salpr than that of Co-salen (Table 1).



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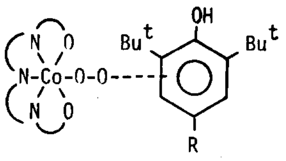

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In the Co-salen catalyzed oxygenation of 1 (R = Me), a compound, $C_{30}H_{46}O_3$, mp 124-126° instead of peroxide 3 (R = Me) was isolated (35%), whose structure can be asigned as 6 from its spectral data and chemical behavior.[12] No compound 6 is obtained by the reaction of 9 (R = Me) with $O_2$ indicating that 6 is not the decomposition product of 3 (R = Me) which was not isolated in the catalytic oxygenation system. It may be formed by the reaction of 10 (R = Me) with 1 or 9.

## References

1. H. M. van Dort and H. J. Geurson, Rec.Trav. Chim., 86, 520 (1967).
2. L. H. Vogt, Jr., J. G. Wirth, and H. L. Finkbeiner, J. Org. Chem., 34, 273 (1969).
3. D. L. Tomaja, L. H. Vogt, Jr., and J. G. Wirth, ibid., 35, 2029 (1970).
4. T. Matsuura, K. Watanabe, and A. Nishinaga, Chem. Commun., 1970, 163.
5. R. G. Wilkins, Advan. Chem. Ser., 100, 111 (1971), and references therein.
6. D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, J. Amer. Chem. Soc., 95, 1796 (1973).
7. G. A. Rodley and W. T. Robinson, Nature, 235, 438 (1972).
8. G. N. Schrauzer and L. P. Lee, J. Am. Chem. Soc., 92, 1551 (1970).
9. R. Nakon and A. E. Martel, Inorg. Chem., 11, 1002 (1972).
10. G. N. Schrauzer, "Transition Metals in Homogeneous Catalysis", Marcel Dekker Inc., New York, p.133 (1971).
    C. F. Wells, Disc. Faraday Soc., 46, 137 (1969).
11. L. Reich and S. S. Stivala, "Autoxidation of Hydrocarbons and Polyolefins Kinetics and Mechanisms", Marcel Dekker Inc., New York, 1969.
12. The results will be published elswhere.