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# OXYGEN DEPENDENT RING CLEAVAGE IN A COPPER COORDINATED CATECHOL

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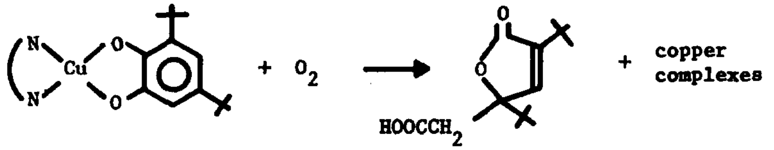
The aromatic dioxygenases are a remarkable class of enzymes capable of oxidatively opening aromatic rings by inserting both atoms of an $O_2$ molecule into the substrate.[1] Very few reactions are known which can be considered analogous to this type of enzymatic reaction. Tsuji has reported a ring cleavage oxygenation catalyzed by copper(I)chloride in pyridine/methanol.[2] Recently, Rogić, et al., have discussed this reaction in some detail.[3] These workers have shown that molecular oxygen is not directly involved in the ring cleavage but serves only to reoxidize the copper in the system. We report here a substantially different copper assisted intradiol ring cleavage which is clearly oxygen dependent.

We have previously reported the preparation of a number of ternary copper(II)catecholato complexes containing nitrogen chelates as counter ligands.[4] Two of these, 3,5-di-*t*-butylcatecholato-1,10-phenanthrolinecopper(II), **1**, and 3,5-di-*t*-butylcatecholato-2,2'-dipyridylcopper(II), **2**, have been found to react with oxygen. Isolation of lactone **3** (eq. 1) indicates that intradiol ring cleavage has occurred.



(eq. 1

**1** when N = 1,10-phenanthroline
**2** when N = 2,2'-dipyridyl

**3**

In a typical experiment 4.0 g of **1** was dissolved in 350 ml of DMSO to afford a dark purple solution. Upon stirring in air the solution gradually turned dark green. This change is clearly oxygen dependent.[5] Upon completion of the reaction, solvent was removed under vacuum followed by ether extraction from aqueous base and then ether extraction from aqueous acid. Analysis of the reaction products revealed the following: a) only traces of the uncoordinated catechol ligand, b) there is no evidence for formation of 3,5-di-*t*-butyl-*o*-quinone, c) lactone **3** is isolated from the acidic ether extract,[6] d) a green insoluble precipitate containing at least two copper complexes is obtained. These complexes have thus far proved to be inseparable.

Compound **3** is known to result from intradiol oxidative cleavage of 3,5-di-*t*-butylcatechol or the corresponding *o*-quinone. For example, **3** can be produced in quantitative yields from the peracid oxidation of 3,5-di-*t*-butylcatechol.[7] Compound **3** has also been found as a major product in the photooxygenation of 3,5-di-t-butylcatechol.[8] The highest yield of **3** thus far obtained in the present study is 25%. Lactone **3** is obtained as well when **2** is used as the starting material. Furthermore, solvents other than DMSO, such as ethanol and benzene, can be employed for the ring cleavage reactions. In benzene the formation of 3,5-di-t-butyl-o-quinone occurs in addition to production of **3**. Yields of **3** are slightly lower in ethanol than in DMSO or benzene. When excess 3,5-di-t-butylcatechol is added to the reaction mixture, there is no evidence of catalytic behavior; however, under these conditions additional quinone is formed.

The ring cleavage reaction is rather slow. Typically, a solution of the initial complex is allowed to stir in the air for one to four days before **3** is isolated. By following the reaction as a function of time it appears the yield of **3** reaches a maximum at four days.

The green insoluble material which is isolated from the reaction has not been fully characterized because it is an inseparable mixture of copper complexes. However, the i.r. spectrum of this mixture indicates the presence of the diimine ligand, coordinated carboxylate (1595 cm$^{-1}$), and the lactone carbonyl (1745 cm$^{-1}$). Thus it appears that additional lactone **3** is present in the form of a copper complex. Additional evidence to support this formulation is the observation that the complex can be treated with a strong ligand such as ethylenediamine and then additional lactone isolated.

The chemistry occurring in this system appears to differ substantially from that reported previously by both Tsuji[2] and Rogić.[3] Molecular oxygen is clearly necessary in order for the reaction to occur. When benzene is employed as solvent, molecular oxygen is certainly the only source of the oxygen atoms incorporated into **3**.[5] Furthermore, it is clear that the properties of the nitrogen counter ligand are crucial in determining the course of the reaction. In a similar compound in which ethylenediamine is the counter ligand, no reaction with oxygen occurs. Additional evidence for the importance of the counter ligands is the fact that Grinstead has found that copper(II) catalyzed oxidation of 3,5-di-t-butylcatechol in basic aqueous methanol gives quantitative yields of the o-quinone.[9] The diimine counter ligand in our system apparently imparts the necessary properties (e.g., redox potential) to the copper to allow ring cleavage.

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3. M. M. Rogić, T. R. Demmin, and W. B. Hammond, J. Amer. Chem. Soc., 98, 7441(1976).
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5. In the absence of oxygen the solutions are stable indefinitely.
6. Characterization of **3** is as follows: m.p., 132-133°C(lit. 133-136°C)[8]; i.r., 2965 cm$^{-1}$, 1745 cm$^{-1}$, 1720 cm$^{-1}$, 1705 cm$^{-1}$(sh); nmr, 0.97 (9H), 1.12 (9H), 2.75 (2H), 6.83 (1H), 10.87 (1H); treatment of **3** with diazomethane gives the methylester; m.p., 66.5-67°C.
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