

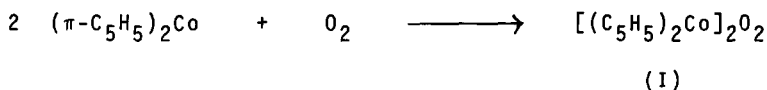
A NEW OXIDATIVE CLEAVAGE OF  $\alpha$ -DIKETONES AND  
o-QUINONES BY AN OXYGEN ADDUCT OF COBALTOCENE

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$\alpha$ -Diketones or o-quinones can be oxidized by several reagents such as hydrogen peroxide<sup>1</sup>, benzoic peracid<sup>2</sup>, and chromium trioxide<sup>3</sup> yielding acids and/or acid anhydrides. So far no oxidative cleavage of diketones and quinones with the aid of organometallic complexes is reported, although some of those complexes are known to catalyze an oxygenation of organic compounds such as phosphines and isonitriles<sup>4</sup>. In the course of our investigation<sup>5,6</sup> on the oxygen adduct(I) of cobaltocene formed by the reaction of cobaltocene with oxygen, we

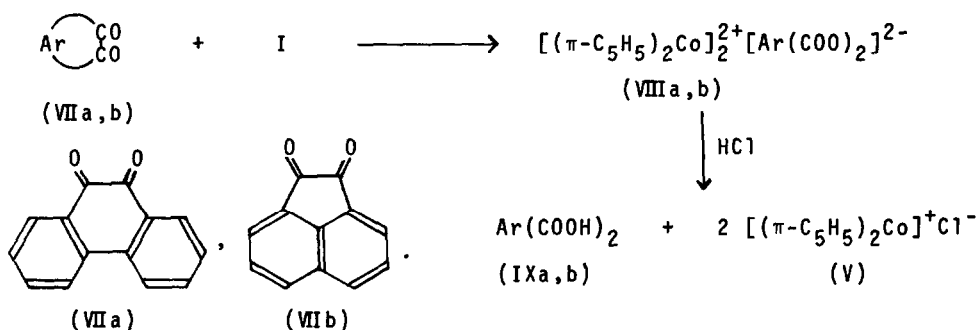


found the complex(I) was a very active reagent for an oxidative cleavage of a carbon-carbon bond in  $\alpha$ -diketones and o-quinones to give cobalticinium carboxylates. This oxidation reaction also takes place when a mixture of cobaltocene and  $\alpha$ -diketone(or o-quinone) is reacted with molecular oxygen at low temperature.

$\alpha$ -Diketones are oxidized easily with an equimolar amount of complex(I) under a nitrogen atmosphere at  $-50^\circ$ . Thus, on adding 2 mmoles of benzil(IIa) to the deep red solution of the complex(I)(2 mmoles) in 50 ml of methylene chloride, the reaction mixture turned immediately to greenish yellow in color. After removal of the solvent, the recrystallization from  $\text{CH}_2\text{Cl}_2$ -THF gave the greenish yellow



In the case of the oxidation of *o*-quinones by the complex(I) the corresponding dibasic acids were obtained.



The reaction between 2 mmoles of phenanthrene quinone(VIIa) and 2 mmoles of the complex(I) at 15° gave a greenish yellow compound, bis-cobalticinium diphenate (VIII a), in 95% yield. By the treatment of the compound(VIII a) with hydrogen chloride, diphenic acid(IXa) was obtained in 91% yield.

Acenaphthene quinone(VIIb) was also oxidized to naphthalene-1,8-dicarboxylic acid(IXb) in 80% yield.

These oxidations are of interest in terms of easy cleavage of carbon-carbon bond under extremely mild conditions.

## REFERENCES

1. E.B. Reid, and R.B. Fortenbaugh, *J. Org. Chem.*, 16, 33(1951).
2. P. Karrer, and L. Schneider, *Helv. Chim. Acta.*, 30, 859(1947).
3. Y.S. Zal'kind, E.D. Venus-Danilova, and V.I. Ryabtseva, *Zh. Obshch. Kim.*, 20, 2222(1950).
4. S. Takahashi, K. Sonogashira, and N. Hagihara, *Nippon Kagaku Zasshi*, 87, 610(1966).
5. H. Kojima, S. Takahashi, H. Yamazaki, and N. Hagihara, *Bull. Chem. Soc. Japan*, 43, 2272(1970).
6. H. Kojima, S. Takahashi, and N. Hagihara, *J.C.S. Chem. Comm.*, 1973, in press.