A NEW OXIDATIVE CLEAVAGE OF $\alpha\text{-DIKETONES}$ AND $\circ\text{-OUINONES}$ BY AN OXYGEN ADDUCT OF COBALTOCENE

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 α -Diketones or o-quinones can be oxidized by several reagents such as hydrogen peroxide¹, benzoic peracid², and chromium trioxide³ 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 isonitriles⁴. In the course of our investigation^{5,6} on the oxygen adduct(I) of cobaltocene formed by the reaction of cobaltocene with oxygen, we

$$2 (\pi - c_5 H_5)_2 co + 0_2 \longrightarrow [(c_5 H_5)_2 co]_2 0_2$$
(1)

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

 α -Diketones are oxidized easily with an equimolar amount of complex(I) under a nitrogen atmosphere at -50°. 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 recrystalization from CH₂Cl₂-THF gave the greenish yellow

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solid(${\rm III}a$). The compound(${\rm III}a$) was confirmed to be cobalticinium benzoate based on the IR spectrum and the chemical reactions since the analysis was difficult

RCOCOR +
$$[(C_5H_5)_2Co]_2O_2$$
 \longrightarrow 2 $[(\pi-C_5H_5)_2Co]^+[RCOO]^-$
(IIa,b) (II) (IIIa,b)
IIa, R=Ph.
IIb, R=CH₃. 2 RCOOH + 2 $[(\pi-C_5H_5)_2Co]^+C1^-$
(IVa,b) (V)

for its highly hygroscopic property. The IR spectrum exhibited the presence of the COO $^-$ group at 1380 and 1550 cm $^{-1}$, and of the $(\pi-C_5H_5)_2Co^+$ group at 865, 1010, 1110, and 1420 cm $^{-1}$. By the treatment of the compound(IIIa) with a solution of hydrogen chloride in ether, benzoic acid(IVa) and cobalticinium chloride(V) were isolated in quantitative yields. The same reaction of diacetyl(IIb) gave acetic acid(IVb) in 50% yield, after the acidification of cobalticinium acetate(IIIb).

By the reaction of the cobalticinium carboxylate with appropriate reagents

$$[(\pi-c_5H_5)_2co]^+[Phc00]^- \xrightarrow{(CH_3)_2so_4} Phc00CH_3 + [(\pi-c_5H_5)_2co]^+[CH_3so_4]^-$$

$$(VI)$$

such as acid halides or dialkyl sulfates, the carboxylate moiety can be led to acid derivatives in almost quantitative yields. For examples, the compound(IIIa) reacted with benzoyl chloride to give benzoyl anhydride(97% yield) along with cobalticinium chloride(100% yield). From the reaction with dimethyl sulfate, methyl benzoate(98% yield) and cobalticinium methylsulfate(VI, 96% yield) were formed.

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 (VIIIa), in 95% yield. By the treatment of the compound(VIIIa) 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.

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