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Oxidative Fission of the Carbon–Carbon Bond in α-Hydroxy Ketones by Cuprous Chloride in Pyridine

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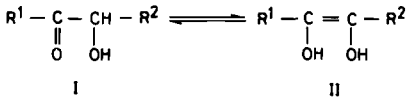
Acyloins – especially the aliphatic ones – are easily oxidized to the corresponding 1,2-diketones by molecular oxygen.[1] Cupric ions catalyse this oxidation which is widely used in the preparation of aromatic 1,2-diketones.[2] Kinoshita[3] has found that benzoin and benzil could be oxygenated to benzoic acid by cuprous chloride in pyridine.

α-Hydroxy ketones have two tautomeric forms I and II



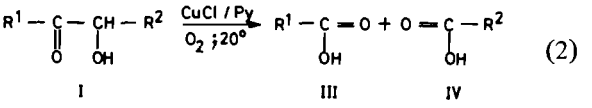
(1)

I II

the equilibrium being usually largely shifted to the left side. However, in the case of pyridoin where intramolecular hydrogen bonding is possible the endiol form was proposed to be more stable.[4]

The structure of endiols II resembles closely that of pyrocatechin which is oxidized to muconic acid by the dioxygenase-type enzyme pyrocatechase as demonstrated earlier.[5] The oxidative splitting of the carbon–carbon double bond of II with incorporation of both oxygen atoms catalysed by metal complexes may be therefore a good model for this enzymatic reaction. For this reason we examined more systematically the oxygenation of α-hydroxy ketones in the presence of dioxygen-carrying systems as models for dioxygenase metallo-enzymes.

When the oxygenation of several different α-hydroxy ketones (Ia - g) was carried out in the presence of cuprous chloride in pyridine as solvent at 20 °C one mol of dioxygen was consumed by one mol of α-hydroxy ketone and the corresponding acids (IIIa - g and IVa - g) were formed in rather good (80 - 96%) yields (Eqn. 2 and Table 1). The corresponding 1,2-diketones could also be oxygenated with the same catalyst system to the carboxylic acids III and IV. Pyrocatechin was oxygenated in similar manner but no products could be isolated until now.



(2)

I III IV

a: $R^1 = R^2 = Me$
b: $R^1 = Ph$; $R^2 = Me$
c: $R^1 = R^2 = Ph$
d: $R^1 = R^2 = MeOC_6H_4$
e: $R^1 = R^2 = MeC_6H_4$
f: $R^1 = R^2 = 2$-furyl
g: $R^1 = R^2 = 2$-pyridyl

TABLE 1. The CuCl-catalysed Oxygenation of α-Hydroxy Ketones (I) in Pyridine at Room Temperature.[a]

	Products III and IV		
	Time (h)	Yield[b] (%)	M.p. (°C)
(Ia)	1.5	92	–
(Ib)	1.8	80	122
(Ic)	2.0	96	122
(Id)	2.0	90	182
(Ie)	2.0	85	181
(If)	2.5	92	131
(Ig)	1.5	88	136

[a] 1.0 mol. equiv. of CuCl was used. [b] Yield after complete oxygenation based on isolated products and glc (at Ia and Ib).

Some information about the mechanism of the reaction is gained from the observation that two mol of the CuCl–pyridine complex take up one mol of dioxygen suggesting a bridged cupric dioxygen complex in accord with some copper containing enzymes such as hemocyanine[6] and quercetinase.[7] This complex may interact with the α-hydroxy ketones probably in the endiol tautomeric form II giving first 1,2-diketones which are rapidly oxygenated further ending up with the oxygen inserted products III and IV.

Oxygenation of I is also catalysed by $CuCl_2$ in pyridine but without cleavage of the carbon–carbon bond thus leading to 1,2-diketones. Bis(salicylidene)-ethylenediaminatocobalt(II), [Co(salen)], and the 1:1 pyridine adduct of bisdimethylglyoximatocobalt (II), ["cobaloxime"], showed no catalytic activity for the oxygenation of benzoin according to reaction (2).

Acknowledgement

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