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REGIO-SELECTIVE REACTION OF CYCLIC ANHYDRIDE WITH $RuH_2(PPh_3)_4$

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$RuCl_2(PPh_3)_3$ is known to catalyze the homogeneous hydrogenation of succinic and phthalic anhydride to corresponding lactones.[1)] In this reaction the unsymmetrical cyclic anhydrides could be converted into γ-lactones with high regio-selectivity.[2)] However, little has been reported about the mechanism of this reaction in detail. We wish now to report the stoichiometric reaction of cyclic anhydrides with ruthenium complex, $RuH_2(PPh_3)_4$(A), to afford a new type of ruthenium aldehydic carboxylate complexes, RuH-(O_2CCHR'CHR"CHO)$(PPh_3)_3$, and show the reaction of these complexes with carbon monoxide affording the lactones and carbon dioxide.

A typical reaction is shown as follows. Equimolar reaction of phthalic anhydride with (A) in toluene under argon or in vacuo at 50° gave an orange crystalline complex(I) (mp 176-8°). Complex(I) is soluble in almost all organic solvent and recrystallized from CH_2Cl_2-Et_2O to give orange crystals. Table 1 summarizes the IR and NMR data for the obtained complexes.[3)]

TABLE 1 IR[a)] and NMR[b)] data for I-IV

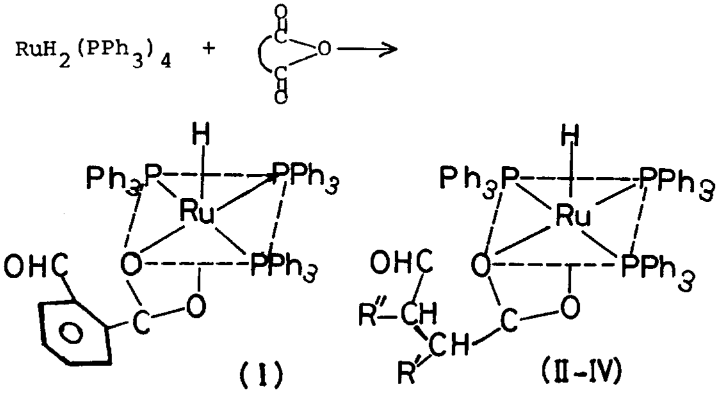
	ν(Ru-H)	ν(C=O)	ν_{as}(COO)	ν_s(COO)	(CHO)	(Ru-H)	others δ(ppm)
I	1980	1700	1520	1435	10.7(s)	-17.8(q)	7.2($C_6\underline{H}_5$-)
II	1980	1720	1530	1430	9.2(s)	-18.0(q)	1.8(-$C\underline{H}_2C\underline{H}_2$-)
IIIa	1960	1720	1520	1430	9.4(s)	-18.2(q)	0.75(-$C\underline{H}_3$)
IIIb	1960	1720	1520	1430	9.3(s)	-18.2(q)	0.65(-$C\underline{H}_3$)
IVa	1970	1720	1520	1430	9.4(s)	-18.2(q)	0.43(-$CH_2C\underline{H}_3$)
IVb	1970	1720	1520	1430	9.23(s)	-18.3(q)	0.56(-$CH_2C\underline{H}_3$)

a) KBr discs, b) in d_6-benzene, (s): singlet, (q): quartet

IR spectrum of (I) shows that carboxyl group coordinated to ruthenium as a bidentate ligand.[4] ^{1}H-NMR spectrum shows a symmetrical quartet due to the hydrogen bound to ruthenium and mutually cis to three phosphorous atoms.[5] (J_{P-H}=26Hz). Aldehyde group, which is formed during the reaction, is identified by IR and NMR spectra of (I). From these results and ^{13}C and ^{31}P-NMR spectra we assumed the complex (I) has a structure as shown in Fig. 1.

Complex(I) can also be prepared by the treatment of (A) with o-phthalaldehydic acid, and the complex thus obtained was proved to be identical with that from IR and NMR spectra.

FiG. 1



II R', R"=H
IIIa R'=CH_3, R"=H
IIIb R'=H, R"=CH_3
IVa R'=C_2H_5, R"=H
IVb R'=H, R"=C_2H_5

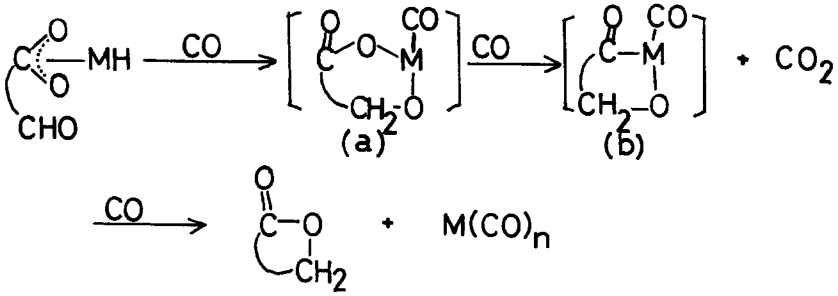
Succinic anhydride reacted with (A) in a similar manner to (I) to give an orange crystalline complex(II)(mp. 188-191°), which is determined by IR and NMR spectra. Complex(II) is unstable in solution and rising the temperature turns the orange color of (II) to pale yellow giving the γ-butyrolactone coordinated complex.

The reactions of methyl and ethyl succinic anhydride with (A) gave the mixtures of two complexes, (IIIa) and (IIIb), and (IVa) and (IVb), respectively, which were determined by IR and NMR spectra. Molar ratio of (IIIa) to (IIIb) and (IVa) to (IVb) is 2.8:1 and 3:1, respectively.

The mechanism of the formation of these complexes probably involves the oxidative addition of one C-O bond of anhydride to produce the ruthenium(IV) complex which undergoes reductive elimination to give the ruthenium aldehydic carboxylate complexes (I-IV). Similar reactions involving cleavage of the C-O bond have been reported in the reactions of vinyl ester,[6)] perfluorocarbocyclic acid anhydride[7)] and several anhydrides[8)] with low valent transition metal complexes. In contrast with the catalytic reaction[2)] of cyclic anhydride such as methyl and ethyl succinic anhydrides, high regioselectivety in this stoichiometric reaction described above seems to the mild reaction conditions and suggests that the reversible interaction between ruthenium metal and the less hindered carbonyl group of anhydride are preceded by oxidative addition of C-O bond.

The isolated complexes (I-IV) in ether suspension reacted with dry HCl to give quantitatively the corresponding lactones which were identified by GC-Mass. Corresponding lactones could be also obtained from the treatment of (I)-(III) with carbon monoxide in ether suspension at atmospheric pressure. Contact of ether suspension of (III) with carbon monoxide gave carbon dioxide as gaseous product and 2-methyl-γ-butyrolactone and 3-methyl-γ-butyrolactone in a 3:1 molar ratio, and afforded ruthenium carbonyl complex with phosphine ligands which was identified by IR spectrum[5)]. On the treatment of (I-III) with carbon monoxide in d_6-benzene γ-lactones obtained had no deuterium atoms, suggesting that hydrogen abstraction from solvent did not occur. From these results we tentatively assume the following scheme for the formation of γ-lactones by action of carbon monoxide,

SCHEME



where M stands for a phosphine coordinated ruthenium complex. In this scheme an attack of CO to ruthenium and the followed migration of hydride to aldehyde group give an alkoxy-carboxylate ruthenium complex(a), which undergoes the deoxygenation of carboxylato ligand with CO to afford acyl-alkoxo ruthenium complex(b) evolving carbon dioxide. On reductive elimination prompted by the attack of carbon monoxide ring closure occurs giving the corresponding γ-lactones. Analogous reduction of transition metal complex with CO has been observed for the reaction of Co(III) complexes in water with CO.9) A similar reductive elimination reaction of acyl-alkoxo complex giving ester has been reported by Yamamoto et al.10)

Further extension of this regioselective reaction to other carbonyl compounds involving acid anhydride is now in progress.

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