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Selective Hydrogenation of Cyclic Ester to α, ω-Diol Catalyzed by Cationic Ruthenium Complexes with Trialkylphosphine Ligands

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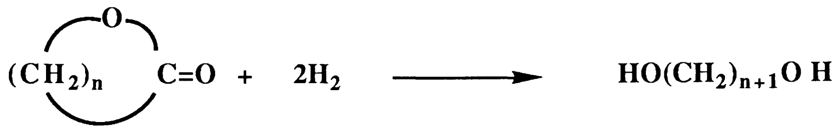
Cyclic esters like γ-butyrolactone were smoothly hydrogenated in the presence of a series of ruthenium complexes with trialkylphosphine ligands under mild conditions to afford the correspondig α,ω– diols with high selectivity. The ruthenium complexes prepared in the presence of additional NH_4PF_6 or H_3PO_4 turned out to have the superior catalytic activity .

Hydrogenation reaction of carbon-carbon bond has been readily achieved under mild conditions by a variety of homogeneous noble metal catalysts,1) whereas the reaction of ester group remains still a challenging target. The catalytic transformation of esters into the alcohols by the heterogenous hydrogenation catalysts like copper-chromium mixed oxide requires rigorous reaction conditions and gives relatively low selectivity for the product. The hydrogenation of cyclic ester on the heterogeneous catalyst, for an example, is usually accompanied by the formation of considerable amount of ether.2) On the other hand, only limited number of reports have appeared in the literature on the homogeneous metal catalysis. The catalyst employed by Matterol et al. requires also high pressure of hydrogen and long reaction period.3)

We reported previously that Ru(acac)$_3$, coupled with tri-n-octylphosphine and p-toluenesulfonic acid, catalyzed the hydrogenation of succinic anhydride to produce γ-butyrolactone with unexpectedly high



selectivity.[4)] Now we describe the first example of the catalytic transformation of cyclic esters into the corresponding α,ω-diols by a series of homogeneous ruthenium complex catalysts under mild conditions.[5)]

In a typical experiment, a solution of a cyclic ester in tetraglyme containing $Ru(acac)_3$, tri-n-octylphosphine, and NH_4PF_6 was stirred in an autoclave. The reaction was continued under hydrogen pressure of 5 MPa at 200 °C for 3 h to yield a yellow solution. It was soon found that the catalytic activity depended strongly on the nature of phosphine used. In Table 1 was summarized the effect of phosphine ligand where the reactions were carried out in the absence of NH_4PF_6. The catalyst systems shown in Table 1 gave exclusively 1,4-butanediol and only a small amount of tetrahydrofuran was detected as a by-product. Only tri-(linear alkyl) phosphines were effective, wheras triarylphosphines and tri-(branched alkyl) phosphines, like triphenyl phosphine and tri-iso-propyl phosphine, respectively, were inadequate for the reaction. The similar phenomena were reported for the ketone hydrogenation catalyzed by rhodium complexes.[6)]

Table 1. Effect of Phosphine in Catalytic Hydrogenation of γ-Butyrolactone by Ruthenium Complexes[a)]

Catalyst	Reaction rate b)	1,4-Butanediol selectivity / %
$Ru(acac)_3/P(n\text{-}Bu)_3$	78	99
$Ru(acac)_3/P(n\text{-}C_8H_{17})_3$	80	99
$Ru(acac)_3/PPh_3$	5	99
$Ru(acac)_3/P(i\text{-}Pr)_3$	2	99
$Ru(acac)_3/P(c\text{-}C_6H_{11})_3$	2	99

a) $Ru(acac)_3$ 0.05 mmol, phosphine 0.5 mmol, γ-butyrolactone 78 mmol, tetraglyme 16 ml, 5 MPa, 200 °C, 3 h. b) Mol 1,4-butanediol/g-atom Ru.h.

Results of the hydrogenation of kinds of esters were illustrated in Table 2. The catalyst exhibited high catalytic activity toward cyclic esters, but was far less active to linear esters like ethyl acetate. It was also found that the hydrogenation reaction of γ-butyrolactone was suppressed by the presence of a small amount of succinic anhydride. In order to explain this observation, the hydrogenation reaction of succinic anhydride was examined briefly.[4)] A typical time-course curve in the hydrogenation process was depicted in Fig. 1. The overall reaction was consistent with the successive process in which γ-butyrolactone was an intermediate in the hydrogenation of succinic anhydride. The reaction of γ-butyrolactone started only after a large part of succinic anhydride had been consumed. The large difference in accessibility to the ruthenium center between succinic anhydride and γ-butyrolactone seems to be responsible to the reason why the reaction of succinic anhydride affords γ-butyrolactone with exceptionally high selectivity.[4)]

Table 2. Hydrogenation of Esters Catalyzed by a Series of Ruthenium Complexes[a)]

Ester	(mmol)	Promoter	Reaction rate b)	Ester conv./%	Diol select./% c)
γ-Butyrolactone	(78)	——	80	15	99
γ-Butyrolactone	(78)	NH_4PF_6	151	29	97
γ-Butyrolactone	(78)	H_3PO_4	141	27	95
γ-Butyrolactone	(78)	$(2\text{-Et-hexyl-O})_2PO_2H$[e)]	92	17	100
γ-Butyrolactone[d)]	(78)	NH_4PF_6	101	20	97
δ-Valerolactone	(65)	NH_4PF_6	112	26	94
ε-Caprolactone	(65)	NH_4PF_6	87	20	92
EtOAc	(50)	NH_4PF_6	10	3	—

a) $Ru(acac)_3$ 0.05 mmol, tri-n-octylphosphine 0.5 mmol, promoter 0.25 mmol, tetraglyme 16 ml, hydrogen 5 MPa, 200 °C, 3 h . b) Mol diol or alcohol /g-atom Ru.h. c) Selectivity for product in mol %. d) in the presence of succinic anhydride 10.0 mmol. e) phosphoric acid di (2-ethyl-hexyl) ester

Addition of NH_4PF_6, phosphoric acid, or its derivatives as promoters to $Ru(acac)_3$/ tri-n-octylphosphine catalyst system enhanced remarkably the reaction rate. We believe that the acceleration resulted from the structural changes in the ruthenium complexes induced by the acidic promoters. The NMR spectra of the catalyst solution, prepared by treating $Ru(acac)_3$ and tri-n-octylphosphine under hydrogen at 200 °C, suggested the formation of dihydride complex $RuH_2[P(n\text{-}C_8H_{17})_3]_4$, 1, together with a small amount of $RuH_2[P(n\text{-}C_8H_{17})_3]_3(\text{solvent})$, 2 . The formation of 1 was supported by a FD-MS spectrum of the same catalyst solution giving

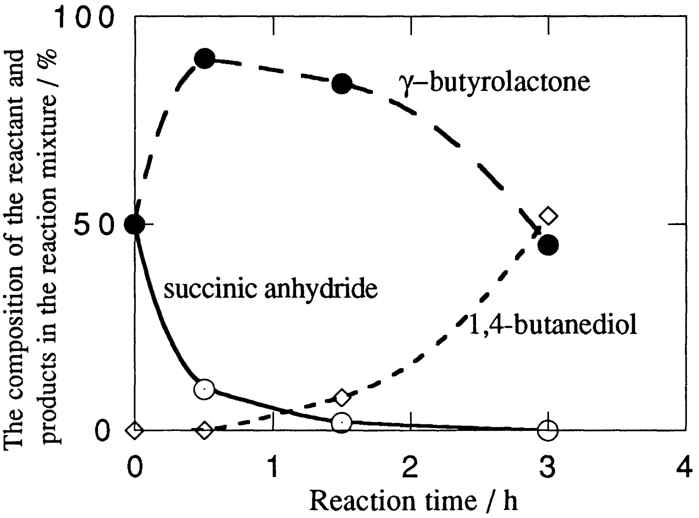


Fig. 1. Time-course plot of the hydrogenation of an equimolar mixture of succinic anhydride and γ-butyrolactone. succinic anhydride 150 mmol, γ-butyrolactone, 150 mmol, phenylcyclohexane 70 ml, $Ru(acac)_3$ 0.5 mmol, tri-n-octylphosphine 5.0 mmol, phosphoric acid di (2-ethyl-hexyl)ester 5.0 mmol, hydrogen 7 MPa, 210 °C.

m/z : 1584 as an abundant ion peak. On the other hand, the addition of acidic promoters to the catalyst solution led to new types of ruthenium species different from the dihydride comlexes. The yellow solution obtained from Ru(acac)$_3$, tri-n-octylphosphine and NH_4PF_6 under hydrogen was supposed to contain the cationic complexes, $\{\eta^2\text{-}H_2(H)Ru[P(n\text{-}C_8H_{17})]_3\}^+ PF_6^-$, 3, and $\{HRu[P(n\text{-}C_8H_{17})_3]_3(\text{solvent})\}^+ PF_6^-$, 4, on the basis of NMR evidence.[7] The essentially same NMR spectra of 3 and 4 were also observed in a sample prepared by ligand exchange reaction between $[HRu(PPh_3)_4]^+ PF_6^-$ [8] and tri-n-octylphosphine under hydrogen of 5 MPa at 100 °C. The more detailed characteristics of these complexes will be reported elsewhere.

References

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5) Lyon described that $RuCl_2(PPh_3)_3$ was unable to catalyze further reduction of γ-butyrolactone formed in the hydrogenation of succinic anhydride ; J. E. Lyon, *J. Chem., Soc., Chem. Commun.*, 1975, 412.

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7) The structure of ruthenium complexes were characterized by ^1H and $^{31}P\{^1H\}$NMR spectra in glyme-d_{10}, TMS and H_3PO_4 being used as internal standards. Selected data: 1; δ-11.8(Ru-H,m), δ 23.9(P_{cis}, t), δ 13.9(P_{trans}, t), $J_{P(cis\text{-}trans)}$ 20 Hz,. 2; δ-8.6(Ru-H_{axial}, dq), δ-10.2(Ru-$H_{equatrial}$, dt), δ 31.5(P_{cis}, d), δ 19.3(P_{trans}, t), $J_{P(cis\text{-}trans)}$ 20 Hz, 3; δ-10.1(Ru-H, br), The lattice relaxation time (T_1) of this signal was 86 ms at 266 K. δ 19(P,s), 4; δ-7.8(Ru-H, dt) , δ 19.8(P_{cis}, d), δ 0.6(P_{trans}, t), $J_{P(cis\text{-}trans)}$ 25 Hz.

8) This compound was synthesized according to the method of Sanders. Anal. Found: C, 66.78; H, 4.80%. Calcd for $C_{72}H_{61}P_5F_6Ru$: C, 66.71; H, 4.74% ; J. R. Sanders, *J. Chem., Soc., Dalton,* 1973, 743.

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