Homogeneous Catalytic Hydrogenolysis of the C–O Bond: the Selective Reduction of Cyclic Carboxylic Acid Anhydrides to γ-Lactones Catalysed by [$RuCl_2(Ph_3P)_3$]

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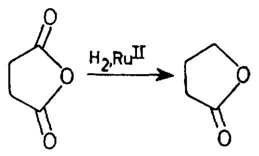
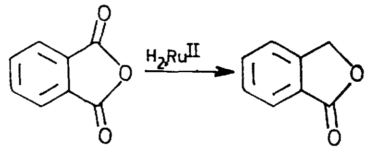
Summary [$RuCl_2(Ph_3P)_3$] is an efficient catalyst for the selective partial hydrogenation of carboxylic acid anhydrides; γ-lactones are formed from succinic and phthalic anhydrides.

Although C–O bond hydrogenolysis can be carried out over heterogeneous catalysts, few reports of the homogeneous transition-metal catalysed hydrogenolysis of the carbon–oxygen bond have appeared in the literature[1]. It has now been shown that 0·025 M solutions of [$RuCl_2(Ph_3P)_3$][2] efficiently catalyse the selective homogeneous hydrogenolysis of carboxylic acid anhydrides at 100°C under 150 lb in.$^{-2}$ hydrogen (Table). Succinic anhydride (**1**) was converted to γ-butyrolactone (**2**) and phthalic anhydride (**3**) was reduced to the phthalide (**4**). The corresponding carboxylic acid was also formed in high yield, presumably from hydrolysis of unreacted anhydride by water formed during the reduction. The ruthenium complex was a uniquely active homogeneous catalyst for the hydrogenolysis of anhydrides; several other typical homogeneous



(1) (2)



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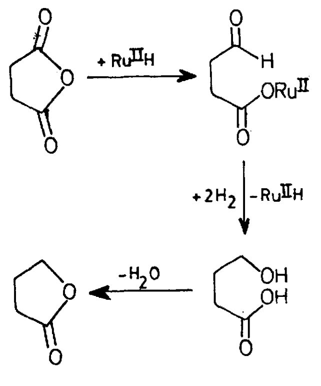

Scheme

hydrogenation catalysts, $[\mathrm{IrCl(CO)(Ph_3P)_2}]$, $[\mathrm{RhCl(CO)(Ph_3P)_2}]$, $[\mathrm{RhCl(Ph_3P)_3}]$, and $[\mathrm{Co_2(CO)_8}]$ were ineffective under the reaction conditions. When CO–H_2 mixtures are used, cobalt octacarbonyl catalyses the reduction of both succinic anhydride[1c] and phthalic anhydride,[1d] but in neither case were γ-lactones obtained.

A suggested reaction pathway for the catalytic reduction of cyclic anhydrides (Scheme) could involve the cleavage of the C–O bond by a ruthenium hydride intermediate such as $[\mathrm{RuHCl(Ph_3P)_3}]$, a catalytically active species formed in olefin hydrogenation.[1d] Precedent for such a reaction has recently been established by Komiya and Yamamoto[3] who have shown that the C–O bond in vinyl acetate is stoicheiometrically cleaved by a ruthenium hydride complex. Once the C–O bond of the anhydride is cleaved, hydrogenation of the carbonyl group[4] followed by elimination of water, could yield the lactone. Carboxylic acids could form by hydrolysis of unreacted anhydride with water liberated in the condensation step.

TABLE Hydrogenolysis of carboxylic acid anhydrides catalysed by $[\mathrm{RuCl_2(Ph_3P)_3}]$[a]

Reactant/mmoles	Reaction time/h	Conversion/%[b]	H_2-Uptake /mmoles	Products/mmoles
Succinic anhydride (20) ..	21	100	10	γ-butyrolactone (10·0) succinic acid (9·9)
Succinic anhydride (20) ..	8	58	7	γ-butyrolactone (6·7) succinic acid (5·1)
Phthalic anhydride (15) ..	23	100	9	phthalide (8·9) phthalic acid (6·1)
Acetic anhydride (20) ..	3	60	7	ethyl acetate (7·2) acetic acid (10·0)

[a] The anhydride was stirred in 4·0 ml toluene containing $1\cdot0 \times 10^{-4}$ mole $[\mathrm{RuCl_2(Ph_3P)_3}]$ at 100 °C under 150 lb in.$^{-2}$ H_2 for the designated time. [b] Mole % anhydride reacted.

In a typical experiment 20 mmoles of succinic anhydride in 4·0 ml of toluene containing 0·10 mmole of $[\mathrm{RuCl_2(Ph_3P)_3}]$ was stirred in a glass aerosol tube at 100 °C under 150 lb in.$^{-2}$ H_2 delivered from a calibrated reservoir. After 3 h the initially red reaction mixture had become a clear, orange solution which persisted throughout the course of the reaction. Hydrogen uptake (10 mmole) ceased after 20 h, and the pressure was released after 21 h. Succinic acid, 9·4 mmoles, m.p. 181—182° (confirmed by i.r. and n.m.r. spectroscopy), crystallized on cooling to room temperature. Gas chromatographic analysis of the toluene solution showed 0·50 mmole succinic acid and 10·0 mmole of γ-butyrolactone in the liquid phase. The lactone was isolated by preparative g.l.p.c. and identified by comparison of i.r. and n.m.r. spectra with an authentic sample. The ruthenium(II) complex was incapable of catalysing further reduction of the γ-lactone so that tetrahydrofuran, butyric acid, and other by-products of further reduction which are unavoidable in many heterogeneous hydrogenolyses of succinic anhydride,[5] were not detected.

The author thanks Martha Hibberd for technical assistance.

(*Received, 25th February* 1975; *Com.* 242.)

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