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HOMOGENEOUS CATALYTIC HYDROGENATION OF FREE CARBOXYLIC ACIDS IN THE PRESENCE OF CLUSTER RUTHENIUM CARBONYL HYDRIDES *

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Summary

Saturated monocarboxylic acids up to C_6, several bicarboxylic acids and some of the corresponding anhydrides are hydrogenated in the homogeneous phase with $H_4Ru_4(CO)_8(PBu_3)_4$ as catalyst to give the corresponding alcohols (present among the reaction products as esters) or lactones at 100—200°C under a pressure of 100—200 atm of hydrogen. Anhydrides react at temperatures lower than those needed for acids. Esters are not reduced. Only δ-valerolactone is hydrogenated to 1,5-pentanediol. Ruthenium carbonyl carboxylates have been recovered at the end of the reaction and appear to be catalytically active intermediates.

Introduction

The hydrogenation of α,β-unsaturated bicarboxylic acids in the presence of a soluble cluster ruthenium carbonyl hydride, $H_4Ru_4(CO)_8((-)\text{-DIOP})_2$, leading to the formation of unsaturated and saturated lactones, provided the first example of catalytic reduction of a free COOH group in the homogeneous phase [2,3]. Carboxylic acids can be reduced in homogeneous phase, but only

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TABLE 1

HYDROGENATION OF VARIOUS FUNCTIONAL GROUPS IN THE PRESENCE OF $H_4Ru_4(CO)_{12-x}L_x$ COMPLEXES

Catalyst	Conversion (%)		
	Cyclohexene [a]	Cyclohexanone [b]	Acetic acid [c]
$H_4Ru_4(CO)_{12}$	17.5	75.0 [d]	—[e]
$H_4Ru_4(CO)_{10}(PPh_3)_2$	n.d.[f]	8.6	trace
$H_4Ru_4(CO)_9(PPh_3)_3$	n.d.[f]	13.5	1.0
$H_4Ru_4(CO)_8(PPh_3)_4$	3.0	54.3	2.0
$H_4Ru_4(CO)_9(PBu_3)_3$	n.d.[f]	4.5	13.1
$H_4Ru_4(CO)_8(PBu_3)_4$	12.0	16.0	16.7

[a] Catalyst 6.7×10^{-5} mol; olefin 10 ml; decalin 30 ml; $p(H_2)$ 80 atm at 20°C; reaction time 30 min; T 100°C; reaction product cyclohexane. [b] See ref. [10]; catalyst 6.7×10^{-5} mol; ketone 10.3 ml; tetrahydrofuran 30 ml; $p(H_2)$ 100 atm at 20°C; reaction time 6 h; T 100°C; reaction product cyclohexanol. [c] Catalyst 3.5×10^{-5} mol; acid 25 ml; $p(H_2)$ 130 atm at 20°C; T 180°C; reaction time 14 h; reaction product ethyl acetate. [d] Reaction time 90 min. [e] No reduction before catalyst decomposition (150°C). [f] n.d. = not determined.

using stoichiometric amounts of $LiAlH_4$ [4] or boranes [5—8]. In the present investigation we examine the possibility of reducing carboxylic groups of substrates not containing other functional groups.

We therefore examined in explanatory runs, the catalytic activity of $H_4Ru_4(CO)_{12}$ and some of its substitution derivatives [9], namely $H_4Ru_4(CO)_8(PBu_3)_4$, $H_4Ru_4(CO)_8(PPh_3)_4$, $H_4Ru_4(CO)_9(PBu_3)_3$, $H_4Ru_4(CO)_9(PPh_3)_3$, and $H_4Ru_4(CO)_{10}(PPh_3)_2$, in the hydrogenation of acetic acid. The results obtained (Table 1) show that the various cluster ruthenium carbonyl hydrides display quite different activities. $H_4Ru_4(CO)_{12}$, which is most active in the hydrogenation of cyclohexane and cyclohexanone [10] at 100°C, cannot be used for the reduction of acetic acid; below 135°C a yellow insoluble material is formed, $[Ru(CO)_2(CH_3COO)]_n$ [11], and no catalytic activity is noticed, while at 150°C the carbonyl decomposes with formation of a black solid, probably ruthenium metal, which, however, is still catalytically inactive.

The highest activity among the substituted hydrides is shown by the tetrakis(tributylphosphine)-substituted derivative at 180°C and 130 atm of hydrogen: this behaviour is analogous to that found in the hydrogenation of cyclohexene, but differs from that observed in the hydrogenation of cyclohexanone.

Results

Formic acid decomposes extensively before reduction and only traces of methyl alcohol were recovered as methyl formate. Carbon dioxide is present in a high percentage among the reaction products together with carbon monoxide; this is due to the activity of the complex as catalyst for the water gas shift reaction [12,13]. The thermal decomposition of formic acid leads exclusively to carbon monoxide and water.

Acetic acid is reduced (Table 2) at 180°C with formation of ethyl acetate. After 48 h at this temperature a conversion of 37.4% is obtained, while at 200°C in the same time the conversion is 69.5%. At 200°C a considerable

TABLE 2

HYDROGENATION OF ALIPHATIC MONOCARBOXYLIC ACIDS IN THE PRESENCE OF $H_4Ru_4(CO)_8(PBu_3)_4$

(Substrate 220 mmol; catalyst 25 mg; $p(H_2)$ 130 atm at 20°C; reaction time 48 h)

Substrate RCOOH	T (°C)	Conversion (%)	Reaction products composition (mol %)		X [b] (%)
			$RCOOCH_2R$	RCH_2OH	
CH_3COOH	180	37.4	100	—	18.7
	200	69.5	72.0	28.0	44.5
	200 [a]	21.5	61.4	38.6	15.0
CH_3CH_2COOH	180	26.2	97.4	2.6	13.3
	200	46.7	90.5	9.5	24.5
$CH_3(CH_2)_2COOH$	180	54.1	96.0	4.0	27.6
	200	73.9	90.0	10.0	38.9
$(CH_3)_2CHCOOH$	180	19.0	100	—	9.5
	200	38.6	94.0	6.0	20.4
$CH_3(CH_2)_3COOH$	180	10.4	100	—	5.2
	200	26.0	100	—	13.0
$CH_3CH_2CH(CH_3)COOH$	200	21.2	100	—	10.6
$CH_3CH(CH_3)CH_2COOH$	200	18.2	100	—	9.1
$CH_3(CH_2)_4COOH$	200	2.0	100	—	1.0

[a] Test carried out on a CH_3COOH/H_2O mixture (1/1 by volume). [b] X: equivalents carboxylic groups reduced/equivalents carboxylic groups charged.

amount of free ethyl alcohol is also formed. The ratio between ethyl acetate and ethyl alcohol formed is decreased only slightly in the presence of water.

The reduction rate of the carboxylic group of alkanoic acids decreases rapidly as the molecular weight increases, butanoic acid being the only exception to the trend. The only reaction product is the corresponding alcohol which, however, is almost completely (90%) taken up to form the ester with the starting acid.

Branching on the chain of the acid causes a decrease in rate, as shown by the lower conversions obtained for reduction of 2- and 3-methylbutanoic and 2-methylpropanoic acids compared with those for the linear pentanoic and butanoic acids.

The formation of small amounts of the free alcohol could arise, in principle, not only by reduction of the substrate, but also by reduction of the ester which is the main reaction product. This latter possibility is ruled out by the fact that ethyl acetate and propyl propanoate were recovered unchanged after attempted hydrogenation at 200°C. Carboxylic acid anhydrides, on the contrary, show higher reactivities than the corresponding acids: in Table 3 we list the results obtained in the hydrogenation of acetic and butyric anhydrides. Acetic anhydride is reduced at 100°C with formation of ethyl acetate and acetic acid (eq. 1, 2). At relatively high degree of conversion the reduction clearly involves the free acid.

$$(CH_3CO)_2O + 2\ H_2 \rightarrow CH_3COOCH_2CH_3 + H_2O \quad (1)$$

$$(CH_3CO)_2O + H_2O \rightarrow 2\ CH_3COOH \quad (2)$$

TABLE 3

HYDROGENATION OF ALIPHATIC ANHYDRIDES IN THE PRESENCE OF $H_4Ru_4(CO)_8(PBu_3)_4$

(Substrate 260 mmol; catalyst 50 mg; $p(H_2)$ 130 atm at 20°C)

Substrate $(RCO)_2O$	T (°C)	Reaction time (h)	Conversion (%)	Reaction products composition (mol %)		X [c] (%)
				RCOOH	$RCOOCH_2R$	
$(CH_3CO)_2O$	100	48	22.6	67.0	33.0	5.6
	120	22	52.2	66.0	34.0	13.0
	120	48	73.5	65.0	35.0	19.0
	150	62	100	62.0	38.0	27.5
	180	3	100	62.0	38.0	27.5
	180	48	100	56.0	44.0	30.5
	200	22	100	52.5	47.5	32.0
	200	48	100	44.0	51.0 [a]	37.0
$(C_3H_7CO)_2O$ [b]	180	22	100	69.0	31.0	23.7
	200	22	100	67.0	33.0	24.8

[a] 5% ethyl alcohol also present. [b] Substrate 220 mmol; catalyst 25 mg. [c] X: equivalents carboxylic groups reduced/equivalents carboxylic groups charged.

The reduction of aromatic carboxylic acids such as benzoic and phenylacetic acids does not take place below 200°C. At this temperature benzoic acid gives exclusively benzyl alcohol (9% conversion in 48 h); phenylacetic acid was converted (18.2%) exclusively to 2-phenylethanol (17.1%) and 2-phenylethyl phenylacetate (1.1%).

The reduction of some bicarboxylic acids and their anhydrides with the same catalytic system was also investigated. Oxalic acid is almost exclusively decomposed to carbon dioxide and formic acid in runs at 120°C; only 3% glycolic acid is detected in the reaction solution. At the same temperature malonic acid undergoes decarboxylation to acetic acid. Succinic acid is slowly converted at 150°C into γ-butyrolactone with 100% selectivity (Table 4). By increasing the

TABLE 4

HYDROGENATION OF SUCCINIC ACID, ITS ANHYDRIDE AND METHYLSUCCINIC ACID IN THE PRESENCE OF $H_4Ru_4(CO)_8(PBu_3)_4$

(Substrate 22 mmol; solvent dioxane (30 ml); catalyst 100 mg; $p(H_2)$ 130 atm at 20°C)

Substrate	T (°C)	Reaction time (h)	Conversion (%)	Reaction products composition (mol %)	X [a] (%)
Succinic acid	150	20	11.2	γ-Butyrolactone (100)	5.6
	180	22	83.0	γ-Butyrolactone (100)	41.5
	180	48	100	γ-Butyrolactone (100)	50.0
Succinic anhydride	100	22	40.0	γ-Butyrolactone (40.0) Succinic acid (60.0)	8.0
	100	48	78.0	γ-Butyrolactone (47.0) Succinic acid (53.0)	18.3
	170	40	100	γ-Butyrolactone (100)	50.0
Methylsuccinic acid	180	22	97.3	α-Methyl-γ-butyrolactone (46.0) β-Methyl-γ-butyrolactone (54.0)	48.6

[a] X: equivalents carboxylic groups reduced/equivalents carboxylic groups charged.

TABLE 5

HYDROGENATION OF GLUTARIC ACID AND ITS ANHYDRIDE IN THE PRESENCE OF $H_4Ru_4(CO)_8(PBu_3)_4$

(Substrate 22 mmol; solvent toluene (15 ml)/diethylether (15 ml); catalyst 100 mg; $p(H_2)$ 130 atm at 20°C)

Substrate	T (°C)	Reaction time (h)	Conversion (%)	Reaction products composition (mol %) [a]					X [b] (%)
				A	B	C	D	E	
Glutaric acid	180	22	32.5	—	4.8	85.6	2.6	7.0	17.4
	180	48	76.2	—	4.8	63.5	13.0	18.7	43.8
	200	22	57.5	—	4.3	71.6	8.7	15.4	32.0
	200	48	96.8	—	2.9	28.7	47.7	20.7	68.7
Glutaric anhydride	180	22	100	20.0	3.7	55.8	14.7	5.8	49.2
	180	48	100	4.0	4.0	38.1	38.9	15.0	66.9
	200	22	100	5.0	5.6	44.3	33.1	12.0	65.0
	200	48	100	~0	2.6	19.7	67.0	10.7	81.4

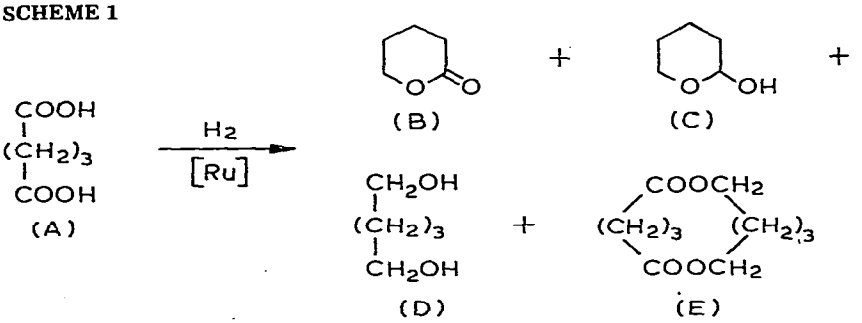
[a] A: glutaric acid; B: 2-hydroxytetrahydrophan; C: δ-valerolactone; D: 1,5-pentanediol; E: 1,7-dioxacyclododecane-2,6-dione. [b] X: equivalents carboxylic groups reduced/equivalents carboxylic groups charged.

reaction temperature it is possible to achieve quantitative transformation of this bicarboxylic acid into the corresponding lactone.

As previously observed for aliphatic monocarboxylic acids, succinic anhydride has a higher reactivity than the acid, and even at 100°C the reaction takes place smoothly (Table 4). Also in this case succinic anhydride is converted into the corresponding acid by the water formed in the reduction process, and so after the rapid reduction of the starting anhydride we observed a slower reaction corresponding to the hydrogenation of succinic acid to lactone. The reduction of methylsuccinic acid proceeds smoothly with formation of α-methyl- and β-methyl-γ-butyrolactones in equivalent amounts (Table 4) [2,3].

The results obtained from the hydrogenation of glutaric acid (Scheme 1) are listed in Table 5.

SCHEME 1



The selectivity of the catalytic process is markedly lower in this case than with the other substrates and depends upon the temperature and the degree of conversion: four products are formed (Scheme 1), namely δ-valerolactone (B), 2-hydroxytetrahydropyran (C), 1,5-pentanediol (D), and the cyclic diester 1,7-dioxacyclododecane-2,6-dione (E) derived from the starting acid and the glycol.

TABLE 6

HYDROGENATION OF ADIPIC ACID IN THE PRESENCE OF $H_4Ru_4(CO)_8(PBu_3)_4$

(Substrate 22 mmol; solvent 30 ml; catalyst 100 mg; $p(H_2)$ 130 atm at 20°C)

Solvent	T (°C)	Reaction time (h)	Conversion [a] (%)
Toluene/diethyl ether (1/1)	150	36	8.8
	180	48	25.2
Dioxane	180	48	6.2
	220	26	27.0
Tetrahydrofuran	180	38	6.6

[a] ϵ-Caprolactone is the only reaction product.

The lactone predominates at low temperatures and low conversions, whereas the glycol reaches at 46.2% yield at 200° C in 48 h (Table 5). Glutaric anhydride gives the same reduction products in higher yields under the same conditions: 1,5-pentanediol, up to 67% yield is obtained at 200° C (Table 5).

Adipic acid on hydrogenation gives exclusively ϵ-caprolactone. The conversion does not exceed 27% whatever the solvent and the conditions used (Table 6).

No reduction is observed with azelaic acid at 180° C. Unsaturated bicarboxylic acids, maleic and glutaconic acids, are hydrogenated at 120° C and 130 atm almost exclusively to saturated acids. Fumaric and maleic acids and maleic anhydride at 170—180° C give γ-butyrolactone in quantitative yields.

It is noteworthy that *o*-phthalic acid is reduced with our catalytic system under the same conditions to give much higher yields than those from benzoic acid: the aromatic bicarboxylic acid is quantitatively converted into phthalide at 150° C and 130 atm of hydrogen in 22 h. At 200° C, even after 48 h no products of further reduction are observed (Table 7). The same product is obtained at a higher rate from phthalic anhydride.

TABLE 7

HYDROGENATION OF *o*-PHTHALIC ACID AND ITS ANHYDRIDE IN THE PRESENCE OF $H_4Ru_4(CO)_8(PBu_3)_4$

(Substrate 22 mmol; solvent toluene (15 ml)/diethyl ether (15 ml); catalyst 100 mg; $p(H_2)$ 130 atm at 20°C)

Substrate	T (°C)	Reaction time (h)	Conversion [a] (%)
o-Phthalic acid	100	22	0.0
	120	22	5.4
	150	22	100
	200	48	100
Phthalic anhydride	100	22	0.0
	120	22	100 [b]
	150	22	100

[a] Phthalide is the only reaction product. [b] *o*-Phthalic acid is also present: 18% total reaction products.

Discussion

The use of $H_4Ru_4(CO)_8(PBu_3)_4$, which has a higher thermal stability than its unsubstituted precursor $H_4Ru_4(CO)_{12}$ *, allows the hydrogenation in homogeneous phase of the acyl group present in carboxylic acids or their anhydrides.

Aliphatic C_2—C_4 carboxylic acids undergo reaction even at 150° C, but temperatures above 180° C are necessary in order to achieve reasonable rates. The initial product is the ester of the corresponding alcohol, which is accompanied at high conversion degrees by the free alcohol. The reactivity of linear acids rapidly decreases as the number of carbon atoms increases from C_2 to C_6, except for butanoic acid, which has given high rate.

A remarkable decrease in reactivity also occurs on going to branched chain acids from the corresponding linear isomers. The order of decreasing reactivity is: acetic > butanoic > propanoic > 2-methylpropanoic > pentanoic > 2-methylbutanoic > 3-methylbutanoic > hexanoic.

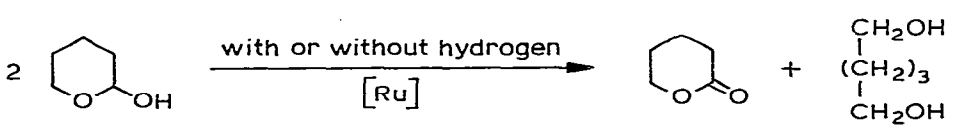
Anhydrides react at temperatures lower than those needed for the corresponding acids, and give the same products: the reaction rate remains high until they are completely hydrolyzed by the water formed in the reduction.

Aliphatic esters are not reduced with this catalytic system even under more drastic conditions (220° C) than those used for the reduction of the free carboxylic acids.

Aromatic acids are reduced, with preferential formation of the alcohol, much less rapidly than the aliphatic acids. Bicarboxylic acids with more than three carbon atoms, with the notable exception of glutaric acid, yield lactones almost exclusively as the hydrogenation products. In the case of glutaric acid, products of further reduction are also present (Scheme 1). δ-Valerolactone can be regarded as an intermediate in the formation of 1,5-pentanediol: in fact, hydrogenation of preformed δ-valerolactone leads mainly to 1,5-pentanediol and to minor amounts of 2-hydroxytetrahydropyran. This last compound under the conditions used quickly gives a mixture of δ-valerolactone and 1,5-pentanediol (Scheme 2). Since these last two products are also formed in the absence of hydrogen, a bimolecular transfer process appears to operate in the hydrogenation of 2-hydroxytetrahydropyran [14].

δ-Valerolactone is the only ester we were able to reduce to alcohol: the other lactones and esters we examined were unchanged under the conditions used.

SCHEME 2



The higher reactivity of anhydrides compared with that of carboxylic acids, may be ascribed to the more facile cleavage of the acyl—oxygen bond of anhy-

* $H_4Ru_4(CO)_8(PBu_3)_4$ has been recovered unchanged after heating at 200°C in cyclohexane solution under 130 atm of hydrogen.

drides in the oxidative addition to the metal [15,16] (eq. 3)

$$(RCO)_2O + Ru \rightarrow \underset{[\ ]}{RCO}—\underset{[\ ]}{Ru}—O—COR \qquad (3)$$

In order to gain insight into the novel catalytic behavior shown by the ruthenium cluster complexes used in the reduction of free carboxylic groups we tried to determine the fate of the catalyst during the reaction. While $H_4Ru_4(CO)_8(PBu_3)_4$ can be recovered unchanged at the end of the reduction of cyclohexene and cyclohexanone at 100°C, this complex undergoes modifications during the hydrogenation of acetic acid. At the end of this reaction, after evaporation of all the liquid a yellow residue is recovered which, on the basis of its IR spectrum (bands at 2035vs, 2019s, 1970vs, 1938s, 1620s, 1590s, 1460m, 1450m, 1430m, 1420m, 1370s), seems to be a mixture of mono- and bidentate carboxylate complexes [11,17—21]. These complexes may also be formulated as carbonyl carboxylates on the basis of the absence of signals due to hydridic hydrogens and the presence of those associated with isolated methyl groups in the NMR spectrum. Upon crystallization, a compound of the yellow residue is recovered which shows an IR spectrum identical to that reported by Crooks et al. [11] for $[Ru(CO)_2(CH_3COO)(PBu_3)]_2$. This complex shows also a 232 cm^{-1} absorption band in the Raman spectrum which may be attributed to a Ru—Ru stretching mode [22]. This compound catalyses the reduction of acetic acid and, when heated in the presence of hydrogen under pressure, gives rise to ethyl acetate and ethyl alcohol. The bridging carboxylate ligand seems therefore to be an activated form of the carboxylic group.

Experimental

GLC analyses were performed on a Perkin—Elmer F30 instrument; preparative GLC separations were performed on a Perkin—Elmer F21 apparatus; NMR spectra were recorded with a Perkin—Elmer R32 spectrometer; Mass spectra were recorded with a Perkin—Elmer 270B spectrometer; IR spectra were recorded with a Perkin—Elmer 580 instrument; Raman spectra were measured with the aid of a double monochromator Jobin Yvon model HG-2S, and a photon counting system equipped with a photomultiplier type IP 28. The 5145 Å exciting line, working at a power of 300 mW, of a Coherent Radiation Model 52 Ar^+ laser, was used as radiation source.

Materials

All substrates used were commercial products. Liquids were distilled and solids were crystallized before use.

Solvents were purified following standard methods. Hydrogen was 99.99% pure. Methyl adipate, methyl glutarate, propyl propanoate, butyl butanoate, 2-methylpropyl 2-methylpropanoate, pentyl pentanoate, 2-methylbutyl 2-methylbutanoate, and hexyl hexanoate were obtained from the corresponding acids following standard procedures. 1,5-Pentanediol was prepared in 76% yield through $LiAlH_4$ reduction of glutaric anhydride in diethyl ether/tetrahydrofuran solution followed by alkaline hydrolysis [23].

Catalysts

$H_4Ru_4(CO)_{12}$, $H_4Ru_4(CO)_9(PBu_3)_3$, $H_4Ru_4(CO)_8(PBu_3)_4$, $H_4Ru_4(CO)_{10}(PPh_3)_2$, $H_4Ru_4(CO)_9(PPh_3)_3$, and $H_4Ru_4(CO)_8(PPh_3)_4$ were prepared by published methods [9].

$[Ru(CO)_2(CH_3COO)(PBu_3)]_2$ was prepared from $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ as described in the literature [11].

Hydrogenation experiments and analytical methods

Hydrogenations of cyclohexene were carried out as described elsewhere [10].

Hydrogenation of acids and acid derivatives were carried out in a 180 ml stainless "Hastelloy C" steel rocking autoclave heated in a thermostated oil bath; the temperature could be maintained constant within ±1°C. The catalyst and solid substrates were placed in the autoclave, the vessel was closed and evacuated from air (0.1 mmHg). Liquid substrates and/or solvents were introduced by suction. Hydrogen up to the desired pressure was introduced and the reaction vessel was rocked in the oil bath. After the reaction had stopped, the autoclave was rapidly cooled with water, gases were collected in a gasometer, and the reaction solution immediately analyzed.

The product distribution of residual acid (RCOOH), the corresponding ester ($RCOOCH_2R$) and/or the alcohol (RCH_2OH) in the crude was determined by GLC (2 m column packed with FFAP 5% on Chromosorb G AW-DMCS or Carbowax 20M 15% on Chromosorb W) using calibration curves obtained from mixtures of standards of known composition. The residual acidity was also determined by volumetric analysis. In the case of bicarboxylic acids, conversion and composition in the crude product mixture were determined by volumetric analysis and by GLC analysis after treatment with CH_2N_2 (2 m column packed with DEGS 20% on Chromosorb W HMDS or Carbowax 20M 15% on Chromosorb W). Gases from experiments with formic, oxalic, and malonic acids were analysed by IR spectroscopy.

Separation and identification of the reaction products

Esters and/or alcohols were separated by distillation or preparative GLC (3 m column packed with BDS 20% on Chromosorb A) from the crude product after neutralization with KOH solution, and identified by comparison of their IR and NMR spectra with those of authentic materials.

Phthalide, the hydrogenation product of *o*-phthalic acid and its anhydride, was purified by crystallization from hexane.

2-Hydroxytetrahydropyran was identified by comparison of its GLC-mass spectrum with that of an authentic sample prepared from 3,4-dihydro-2*H*-pyran as reported by Woods and Sanders [24].

1.7-Dioxacyclododecane-2,6-dione did show: a 1740 cm^{-1} absorption band in the IR spectrum; a multiplet at δ(TMS, $CDCl_3$) 4.1 ($OC\underline{H}_2CH_2$), 2.4 ($C\underline{H}_2CH_2CO$), and 2.1—0.9 ($CH_2C\underline{H}_2CH_2$), with areas in the ratio 1/1/2 in the NMR spectrum. After saponification of the product and the usual work up only 1,5-pentanediol and glutaric acid were recovered.

Hydrogenation of δ-valerolactone

δ-Valerolactone (0.022 mol) in 30 ml toluene/diethyl ether (1/1) was hydro-

genated at 180° C under 130 atm of H_2 in the presence of $H_4Ru_4(CO)_8(PBu_3)_4$ (0.069 mmol) with the procedure previously described. After 48 h the conversion was 22%: 1,5-pentanediol (21.7% yield) and a very small amount of 2-hydroxytetrahydropyran were found in the reaction solution by GLC analysis.

Hydrogenation of 2-hydroxytetrahydropyran

2-Hydroxytetrahydropyran (0.022 mol) was hydrogenated as previously described for δ-valerolactone. After 22 h the composition of the reaction solution (GLC analysis) was: starting material 12.5%, δ-valerolactone 21.0%, and 1,5-pentanediol 66.5%.

Disproportionation reaction of 2-hydroxytetrahydropyran

2-Hydroxytetrahydropyran (0.022 mol) in 30 ml of toluene/diethyl ether (1/1) was heated at 180° C in an autoclave under nitrogen in the presence of $H_4Ru_4(CO)_8(PBu_3)_4$ (0.069 mmol) for 22 h. Almost quantitative conversion of the substrate was obtained (>99%). The composition of the reaction solution (GLC analysis) was: δ-valerolactone 69.5%, 1,5-pentanediol 29.5%, and 2-hydroxytetrahydropyran 1.0%.

Catalytic reduction of acetic acid in the presence of $[Ru(CO)_2(CH_3COO)(PBu_3)]_2$

Acetic acid (0.433 mol) and hydrogen (130 atm) were heated at 180° C in the presence of $[Ru(CO)_2(CH_3COO)(PBu_3)]_2$ (0.12 mmol). After 24 h the conversion was 26.1%; the composition of the reaction medium was: ethyl acetate 15.0%, ethanol (traces), acetic acid 85.0%.

Reaction of $[Ru(CO)_2(CH_3COO)(PBu_3)]_2$ with hydrogen under pressure

The above ruthenium carboxylate complex (1.8 mmol) dissolved in 7.5 ml of decalin (purified by preparative GLC) was heated at 180° C in an autoclave under 130 atm of hydrogen for 22 h. In the resulting deep red solution ethanol and ethyl acetate were present in a 87.3 to 12.7 ratio.

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References

1 1st Intern. Symp. Homogeneous Catalysis, Amer. Chem. Soc. 34th Annual Southwest Regional Meeting, Corpus Christi, Texas, November 29—December 1, 1978, Paper 69.
2 M. Bianchi, F. Piacenti, P. Frediani, U. Matteoli, C. Botteghi, S. Gladiali and E. Benedetti, J. Organometal. Chem., 141 (1977) 107.
3 M. Bianchi, F. Piacenti, G. Menchi, P. Frediani, U. Matteoli, C. Botteghi, S. Gladiali and E. Benedetti, Chim. Ind. (Milan), 60 (1978) 588.
4 H.O. House, Modern Synthetic Reactions, II, W.A. Benjamin, Inc., Menlo Park, 1972, p. 45.
5 N.M. Yoon, C.S. Pak, H.C. Brown, S. Krishnamurthy and T.P. Stocky, J. Org. Chem., 38 (1973) 2786.
6 C.F. Lane, Chem. Rev., 76 (1976) 773.
7 H.C. Brown and T.P. Stocky, J. Amer. Chem. Soc., 99 (1977) 8218.
8 G.W. Kabalka, J.D. Baker, Jr., and G.W. Neal, J. Org. Chem., 42 (1977) 512.

9 F. Piacenti, M. Bianchi, P. Frediani and E. Benedetti, Inorg. Chem., 10 (1971) 2759.
10 P. Frediani, U. Matteoli, M. Bianchi, F. Piacenti and G. Menchi, J. Organometal. Chem., 150 (1978) 273.
11 G.R. Crooks, B.F.G. Johnson, J. Lewis, I.G. Williams and G. Gamlen, J. Chem. Soc., A, (1969) 2761.
12 R.M. Laine, R.G. Rinker and P.C. Ford, J. Amer. Chem. Soc., 99 (1977) 252.
13 P.C. Ford, R.G. Rinker, C. Ungermann, R.M. Laine, V. Landis and S.A. Moya, J. Amer. Chem. Soc., 100 (1978) 4595.
14 G. Descotes, J. Sabadie and D. Sinou, Tetrahedron Lett., (1978) 3351.
15 D.M. Blake, S. Shields and L. Wyman, Inorg. Chem., 13 (1974) 1595.
16 J.A. van Doorn, C. Masters and C. van der Woude, J. Organometal. Chem., 141 (1977) 231.
17 M. Mukaida, T. Nomura and T. Ishimori, Bull. Chem. Soc. Japan, 45 (1972) 2143.
18 R.W. Mitchell, A. Spencer and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1973) 846.
19 A. Spencer and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1972) 1570.
20 D.F. Gill, B.E. Mann and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1973) 311.
21 F.A. Cotton and J.G. Norman, Jr., Inorg. Chim. Acta, 6 (1972) 411.
22 M.P. Marzocchi, L. Angeloni, E. Benedetti, M. Bianchi and P. Frediani, Indian J. Pure Appl. Phys., 16 (1978) 304.
23 V.M. Micovic and M.LJ. Mihailovic, J. Org. Chem., 18 (1953) 1190.
24 G.F. Woods and H. Sanders, J. Amer. Chem. Soc., 68 (1946) 2111.