OXIDATION OF ALCOHOLS BY TRANSITION METAL COMPLEXES—IV

THE RHODIUM CATALYSED SYNTHESIS OF ESTERS FROM ALDEHYDES AND ALCOHOLS

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(Received in UK 18 May 1981)

Abstract—Both RhH(CO)PPh₃)₃ and a catalyst made *in situ* from RhCl₃·3H₂O, PPh₃ and Na₂CO₃ catalyse the reaction of a range of aldehydes with simple primary alcohols to give esters together with alcohols formed by reduction of the aldehydes. The proportion of ester can be increased by adding an efficient hydrogen acceptor. The reaction can also be used to produce 5- and 7-membered lactones from aromatic dialdehydes. Propan-2-ol and the *in situ* catalyst reduce some aromatic aldehydes to the corresponding alcohols without concomitant ester formation.

There are few reports of the reaction of an aldehyde with an alcohol to give an ester. It is known that a number of aliphatic and aromatic aldehydes react with a range of alcohols to give esters in a reaction catalysed by palladium chloride.² This system involves reduction of the nalladium chloride to Pd metal and is therefore operated in the presence of cupric and lithium acetates and molecular oxygen to effect reoxidation of Pd(O) to Pd(II). Other workers³ have described the use of various ruthenium, rhodium and iridium complexes for the reaction of acrolein with ethanol to give ethyl acrylate, acrolein diethyl acetal, propionaldehyde diethyl acetal and other products. The yields of ester were not high but could be slightly increased by the presence of oxygen. Propionaldehyde gave much lower yields of ester than acrolein. Recently RuH₂(PPh₃)₄ and other ruthenium complexes have been reported to be efficient catalysts for the conversion of aldehydes to esters $(1 \rightarrow 2)$ in a Tishchenko type ester formation.⁴ A range of C₃ to C₆ aliphatic aldehydes worked satisfactorily but benzaldehyde gave a low conversion to benzyl benzoate.

We wish to report the rhodium catalysed reaction of a range of aliphatic and aromatic aldehydes with alcohols to give ester together with alcohol formed by reduction of the aldehyde. When a mixture of benzaldehyde and ethanol was of benzyl alcohol (Table 1). Thus the overall function of the catalysts is to effect hydrogen transfer with part of the benzaldehyde acting as the hydrogen acceptor and part undergoing oxidation.

Alcohols other than ethanol showed interesting differences (Table 1). Methanol gave similar results for both catalysts A and B with benzaldehyde, but reaction was slower, as expected, in the lower boiling alcohol. Propan-2-ol, which is a better hydrogen donor than either methanol or ethanol, reduced benzaldehvde to benzvl alcohol but only in the presence of catalyst B. Under similar conditions p-methoxy-, p-methyl- and p-chlorobenzaldehyde and thiophene-2-carboxaldehyde also gave only the corresponding alcohols (Table 2). In contrast catalyst A in propan-2-ol converted benzaldehyde to 4 via transfer hydrogenation of the aldol product (3). Support for this sequence was provided by heating a mixture of benzaldehyde, acetone and ethanol in the presence of catalyst A when both 3 and 4 were produced. The different products arising from benzaldehyde and propan-2-ol in the presence of catalysts A and B thus reflects the fast hydrogen transfer reduction of benzaldehyde by catalyst B compared to a slow aldol condensation between benzaldehyde and acetone (Table 1). Reaction of n-butanol with benzaldehyde in the presence of catalyst A gave butyl benzoate, benzyl alcohol, some



boiled under reflux with a catalytic amount (5 mole%) of $HRh(CO)(PPh_3)_3$ (catalyst A) under nitrogen, good yields of ethyl benzoate and benzyl alcohol were obtained (Table 1). Much faster reaction occurred when catalyst B, made *in situ* from RhCl₃·3H₂O, PPh₃ and Na₂CO₃ was employed, but this reaction gave a higher proportion

butyl butyrate and traces of two, as yet unidentified, products (Table 1). The butyl butyrate must arise by reaction of butyraldehyde with butanol. Ethanol could react similarly, but ethyl acetate has not been detected presumably due to acetaldehyde being lost during the reaction consequent on its greater volatility. t-Butanol

ROH	Catalyst	Time	<u>PhC0₂R(%)</u>	<u>PhCH₂OH(%)</u> ^e	PhCH0(%) ^e	Other products(%) ^e
Me0H	۸ ^c	3.5 dy.	35(20)	50(20)		
	Bd	9.2 h	28(19)	50(35)		
EtOH	A	3 dy.	42(35)	42(24)	14(14)	
	B	3 h	34	48		
i-PrOH	A	43 h	14	10		Ph(CH ₂) ₂ COMe 66
	в	3 h		99(68)		
n-BuOH	A	6 d	43	22	14	n-PrCO ₂ Bu 17 + 2 unidentified products (total 5%)
t-BuOH	A	31 d	trace	trace		
EtOH/Me ₂ C	A 0	27 h				PhCH=CHCOMe 35(24) Ph(CH ₂) ₂ COMe 38(28)

Table 1. Rhodium catalysed reaction of benzaldehyde^a with various alcohols^b

a. 1-5g with A, 0.5-2.1g with B

b. 10-60mml with A, 20-50mml with B; reaction carried out in boiling alcohol

c. RhH(CO)(PPh3)3 5 mole % relative to PhCHO

d. RhCl₃. $3H_20$ (10 mole %), PPh₃ (50 mole %), Na_2CO_3 (36 mole %) relative to PhCHO

e. Figures in brackets are isolated yields, others are calculated from glc charts

Table 2. Reduction of aldehydes by catalytic" hydrogen transfer from propan-2-ol

RCHO	Time (h)	RCH_OH (%) ^b		
		<u> </u>		
PhCHO	3	68(99)		
<u>р</u> -меос _б н ₄ сно	5.5	79		
<u>р</u> -мес ₆ н ₄ сно	4	79		
p-CIC ₆ H ₄ CHO	24	(20) ^c		
thiophene-2-carboxaldehyde	5	92		
n-с ₅ н ₁₁ сно	24	trace		
n-C ₃ H ₇ CH0	24	trace		

a. RhCl₃. $3H_2O$ (10 mole %), PPh₃ (50 mole %), Na₂CO₃ (36 mole %) relative to aldehyde

b. isolated yields, figures in brackets refer to glc estimates

c. 80% starting material present

did not react to any great extent with benzaldehyde using catalyst A, possibly because it cannot undergo a metal catalysed dehydrogenation (but see later).

The effect of varying the catalyst was investigated (Table 3). The reaction of benzaldehyde with ethanol was much slower with a modified catalyst B in which triphenyl phosphine was replaced by triphenylphosphite, and the reaction did not proceed at all when dimethyl-sulphoxide replaced triphenylphosphine. Using RhCl₃·3H₂O as catalyst in the absence of both phosphine and base led to the formation of benzyl alcohol and benzaldehyde diethyl acetal but no ester was produced. A similar lack of catalytic activity was noted in the CuOBu¹ catalysed Tishchenko reaction,⁵ where in the absence of added ligand (phosphine or amine) no reac-

tion occurred and added triphenylphosphine gave a more efficient catalyst than trimethylphosphite. Acetal formation occurred using RhCl(PPh₃)₃ as catalyst in the absence of base and this rhodium complex has been observed to promote acetal formation when used as a homogeneous hydrogenation catalyst in methanol.⁶ In the presence of base, RhCl(PPh₃)₃ was as good as catalyst B for the conversion of benzaldehyde and ethanol to ethyl benzoate and benzyl alcohol. Rhodium (I) hydrides RhH(PPh₃)_n (n = 3 or 4) are likely intermediates in the latter catalyst system.¹ Therefore HRh(PPh₃)₄ was tested as a catalyst in the absence of base, and found to work efficiently (Table 3). 5% Rh/C led to very slow production of ester and acetal. These results are summarised in Table 3, which also lists various Ru, Pd and Ir species

Catalyst ^{a,b,c}	Time(h)	PhCO ₂ Et(%)	PhCH ₂ OH(%)	PhCHO(%)	PhCH(OEt) ₂ (%)
RhCl ₃ . 3H ₂ 0/P(OPh) ₃ /Na ₂ CO ₃ ^d	21	10	12	78	
RhC1, 3H20/DMS0/Na2C03	21			100	
RhC1 3. 3H20	96		13	26	31
RhCl (PPh ₃) ₃ ^e	71			50	28
RhCl(PPh3)3/Na2CO3	3	39	51		
RhH(PPh ₃) ₄	3	39	57	4	
5% Rh/C ^d	288	5		90	5
RuCl ₃ .H ₂ 0/KOH/PPh ₃	2		77		
RuCl ₂ (PPh ₃) ₃ /Na ₂ CO ₃	5.3		98		
$Ru(CO)_{3}(PPh_{3})_{2}^{e}$	96		46	_	

Table 3. Reaction of benzaldehyde with ethanol using various catalysts

a. 10 mole % of metal complex relative to aldehyde

b. ligand, where used, 50 mole % and base, where used, 36 mole % relative to aldehyde

c. PdCl₂/PPh₃/Na₂CO₃; IrCl₃.3H₂0/PPh₃/Na₂CO₃ and IrH(CO)(PPh₃)₃ were inactive

d. results estimated by glc.

e. 5 mole % of metal complex relative to aldehyde.

which were not effective catalysts for ester formation although the Ru compounds promoted hydrogen transfer to benzaldehyde, a process known to be catalysed by Ru complexes.⁷

Having established that Rh complexes were the most effective out of the range of complexes surveyed further work was confined largely to catalyst systems A and B. A range of aryl and heteroaromatic aldehydes was reacted with ethanol in the presence of catalysts A and B (Table 4). In all cases reaction was very much faster with catalyst B, but this catalyst gave a lower proportion of ester than the less active catalyst A. The heterocyclic aldehydes were substantially less reactive than the aryl aldehydes possibly due to relatively stable chelation of these aldehydes to Rh producing less reactive intermediates. No obvious relationship could be discerned, for the small number of p-substituted benzaldehydes studied, between the substituent and the ester/benzyl alcohol ratio. However the slower reaction of p-MeOCsHaCHO with catalyst B results in the lowest ester: alcohol ratio (0.285) due to more effective competition from aldehyde reduction by hydridorhodium species with ethanol acting as the hydride source. The overall rate of reaction for p-RCsHaCHO with catalyst B is p-H > Me, Cl > OMe. The anomalous position of p-ClCsHaCHO may reflect a slow hydrogenation step, a necessary process for the regeneration of the active catalyst (Table 2). p-Nitro benzaldehyde under the influence of catalyst B, gave quite different products, i.e. 5 and 6, from the other aldehydes. These arise from



reduction of the nitro group to amine followed by condensation of the amine with a nitro group to give 5 or an aldehyde to give 6.

o-Phthalaldehyde (7a) gave lactone 8 with both catalysts A and B in ethanol. No diester (7b) or dialcohol (7c) were detected in this reaction, but there were other minor unidentified products when catalyst A was used. The dialcohol (7c) slowly reacted in bromobenzene at 110° in the presence of catalyst B to give a low yield ($\sim 6\%$) of 8. Diphenyl - 2,2' - dicarboxaldehyde (9a) also gave good yields of the 7-membered lactone (10) with both catalysts ((Table 4), although the less active catalyst A produced a small amount of 9b as well.

Some aliphatic and α , β -unsaturated aldehydes were reacted with ethanol using catalysts A and B (Table 5). Butanal was converted to both ethyl butanoate and butanol together with unidentified products which were particularly prominent when the less active catalyst A was used. Citronellal also gave good yields of the corresponding alcohol and ethyl ester. The α , β -unsaturated aldehydes showed a distinct tendency to undergo transfer hydrogenation of the C=C bond especially with catalyst A. Thus with catalyst B, cinnamaldehyde gave normal products, albeit slowly, whilst with catalyst A the major product was the ethyl ester of dihydrocinnamic acid. Differences were also noted with crotonaldehyde where both catalysts gave ethyl butanoate but catalyst A gave butanal but no butanol, and catalyst B gave butanol but no butanal.

An attempt was made to increase the proportion of ester formed relative to benzyl alcohol when benzaldehyde was treated with catalyst B in ethanol, by the addition of various hydrogen acceptors (Table 6). Ethyl acrylate proved to be the most efficient hydrogen acceptor of those studied. Thus, in the presence of ethyl acrylate the ester/benzyl alcohol ratio could be increased from 1.02 to 6.50. Addition of azobenzene had only a small effect whilst acrylonitrile actually decreased the ester/benzyl alcohol ratio to 0.67.

The metal catalysed formation of ester from aldehyde and alcohol is closely related to the reaction of two molecules of aldehyde to form ester $(1 \rightarrow 2)$ under the influence of various catalysts such as metal alkoxide and boric acid.⁸ This reaction, the Tishchenko reaction, is also catalysed by Cu(I)⁵ and Ru(II)⁴ complexes. Disodium tetracarbonylferrate is an efficient catalyst for the Tishchenko reaction involving aryl aldehydes but promotes aldol condensation with aliphatic aldehydes.⁵ The catalysts that effect the Tishchenko reaction can be divided into two broad groups, those promoting direct carbon \rightarrow carbon hydride transfer [e.g. B(OH)₃, Al(OR)₃, $Fe(CO)_{4}^{2}$ and those involving metal hydride intermediates. The advantage of the metal hydride systems is that they are applicable to aldehydes with α -H atoms. Conventional Tishchenko catalysts promote aldol condensation of such aldehydes. The Rh catalysts reported in this paper are members of the metal hydride group and thus function with aliphatic aldehydes (Table 5). Furthermore, our substrate systems are at a lower oxidation level (aldehyde + alcohol) than the conventional Tishchenko system (aldehyde + aldehyde), and therefore require a hydride "sink" to regenerate the catalyst. Hence the reduction of aldehyde to alcohol.

The greater reactivity of catalyst B using triphenyl phosphine (Table 1) as opposed to triphenylphosphite (Table 3) supports a process involving nucleophilic attack of the catalyst on the aldehyde as does the greater reactivity of RhH(PPh_3)_4 (Table 3) compared to HRh(CO)(PPh_3)_3 (Catalyst A; Table 1). However a number of mechanistic schemes can be written for the overall process, particularly the key ester forming step. The following mechanistic scheme is proposed for catalyst B.

The ester generating step is portrayed in the scheme as

RCHO	Catalyst	Time(h)	RCO ₂ Et(%)	RCH2OH(%)	RCH0(%)	Other Produc
PhCHO	A B	72 3	42(35) 34	42(24) 49		
p-MeOC ₆ H ₄ CHO	A B	72 10	45(30) 18(9)	32(32) 63(43)	14(14)	
<u>р</u> -мес ₆ н ₄ сно	A B	168 5	52(41) 37(22)	26(1 ⁻ 9) 42(39)	11(6)	
<u>р-сіс₆н₄сно</u>	A B	72 5	42(30) 25(17)	37(27) 32(27)		
<u>р</u> -No ₂ c ₆ H ₄ сно	В	6				$\begin{pmatrix} 5, 11\% \\ 6, 14\% \end{pmatrix}$
Pyridine-2-carboxaldehyde	A B	264 48	11 44	3 47	36	
Thiophene-2-carboxaldehyde	A B	504 8	34 (25) (23)	10(7) (19)		
Furan-2-carboxaldehyde	A B	120 24	41(20) 21	25(18) 53	5(3)	
7a	A B	360 2.3				(<u>8</u> , 49%) (<u>8</u> , 74%)
9a	A	360				$(\frac{10}{9b}, 72\%)$ $(\frac{9}{2b}, 14\%)$
	B	2				(<u>10</u> , 93%)

Table 4. Rhodium catalysed* reaction of aldehydes with boiling ethanol^b

a. Catalysts A and B as in Table 1

b. Yields estimated by nmr. Yields in brackets refer to isolated material

RCO2Et RCHO Catalyst Time(h) RCH, OH RCHO $\widehat{\mathbf{A}^{\mathbf{C}}}$ 22 4 n-C3H7CHO 23 7 Bd 5 49 34 72 citronellal A 71 23 B 8.3 54 45 ۸^e PhCH=CH-CHO 72 -.... R 72 18 20 62 MeCH=CHCH0 23 A вg 5 8

Table 5. Rhodium catalysed^a reactions of aliphatic aldehydes with boiling ethanol^b

a. Catalysts A and B as in Table 1

- b. Products estimated by glc
- c. Two unidentified products (16 and 51%)
- d. Unidentified product (7%)
- e. Product was Ph(CH₂)₂CO₂Et (42%)
- f. Major products were $C_3H_7CO_2Et$ (34%), C_3H_7CHO (34%) plus an unidentified product (32%).
- g. C3H7C02Et (61%), C4H90H (31%)

Initiation



Ester formation



Catalyst regeneration



Table 6. Effect of hydrogen acceptors on the rhodium catalysed reaction of benzaldehyde with boiling ethanoi^a

Hydrogen acceptor	PhCO ₂ Et(%)	РhCH ₂ 0H(%)	PhCO2Et/PhCH2OH
	51	49	1.02
acrylonitrile	40	60	0.67
azobenzene ^b	49	32	1.53
ethyl acrylate ^C	80	14	5.71
ethyl acrylate ^d	65	10	6.50

- a. a mixture of benzaldehyde (4.8 x 10^{-5} mole), RhCl₃.3H₂O (5 x 10^{-4} mole), PPh₃ (2.5 x 10^{-3} mole) and Na₂CO₃ (1.8 x 10^{-5} mole) in EtOH (15 ml), containing the hydrogen acceptor (10^{-2} mole) was boiled under reflux for 1.5 h. Product ratios obtained by glc.
- b. two unidentified products (4.8% and 13.6%) also produced
- c. unidentified product (6%) also present
- d. 2 x 10^{-2} mole of acrylate. PhCHO (9.6%) and an unidentified product (15.5%) also present

an intramolecular 1,2-ethoxide shift $(11 \rightarrow 12)$ but could equally well involve attack of external alcohol on an intermediate acylrhodium complex. Solvolytic cleavage of metal acyls to carbocyclic acid derivatives is well known.¹⁰ Other schemes can be written for the ester forming step (e.g. $13 \rightarrow 15$), but although the β -hydride elimination step $(14 \rightarrow 15)$ is attractive and intuitively expected to be facile it does not accord with the ligand effects which suggest a nucleophilic metal centre is important [i.e. insertion into the aldehyde C-H bond giving an acylrhodium hydride(11)].



Recently Maitlis et al.¹¹ have observed the homogeneously catalysed conversion of an acetaldehydewater system into ethanol and acetic acid using 16 and related Ru and Ir complexes. Kinetic studies establish the active catalyst is a monometallic complex derived from 16. In this case solvolysis of the intermediate acyl complex involves attack by water generating acetic acid.

The proposed mechanistic scheme for catalyst B is reasonably consistent with the observation that when benzaldehyde is boiled with CH_3CH_2OD and CH_3CD_2OH in turn, in the presence of catalyst B, the benzyl alcohol produced was found to contain 9%d, and 31%d, respectively (glc-ms).

EXPERIMENTAL

RuCl₂(PPh₃)₃ and Ru(CO)₃(PPh₃)₂ were supplied by Engelhard and RhCl₃·3H₂O and Na₂IrCl₆ by Johnson Matthey. HIr(CO) (PPh₃)₃,¹² HRh(PPh₃)₄¹³ and HRh(CO)(PPh₃)₃¹⁴ were prepared by the published procedures. Aldehydes were distilled before use except o-phthalaldehyde which was used as supplied (Aldrich). 1,2-Benzenedimethanol (Aldrich) was also used without purification. 2,2'-Biphenyldicarboxaldehyde was prepared by the ozonolysis of phenanthrene.¹⁵ M.p.'s were determined on a Kofler hot stage and are uncorrected.

Catalyst A. A mixture of aldehyde (1-5 g), HRh(CO)(PPh₃)₃ (5 mole% based on aldehyde used), and alcohol (10-60 ml) was gently boiled under reflux and magnetically stirred under N₂. The progress of the reaction was monitored by glc. After completion, the mixture was allowed to cool to room temp, the catalyst removed by filtration through a sintered glass funnel and the filtrate concentrated. The remaining soluble catalyst was removed by passing the concentrated filtrate through a neutral alumina column and eluting with 40-60° petroleum ether and/or ether. The crude product mixture obtained after removal of the solvent was purified by distillation or column chromatography.

Catalyst B. A mixture of RhCl₃·3H₂O (5.0×10^{-4} mole), PPh₃ (2.5×10^{-3} mole), and Na₂CO₃ (1.8×10^{-3} mole) in alcohol (20 ml) was boiled under reflux, and magnetically stirred under N₂ for 15 min, when an orange yellow ppt had formed. The aldehyde (5.0×10^{-3} mole) was then added and the progression of the reaction monitored by glc. The method of isolation of the products was similar to that described above.

Reaction between p-nitrobenzaldehyde and ethanol using catalyst ${\bf B}$

The reaction was monitored by glc $(2 \text{ m}, 2.5\% \text{ SGR}, 160^\circ)$. Products 5 and 6 were isolated by column chromatography (SiO₂) eluting with 40-60° petroleum ether-ether (1:1). Compound 5 crystallised from EtOH as orange needles m.p. 124-128° (Found: C, 63.25; H, 5.56; N, 7.96; C₁₈H₁₈N₂O₅ requires C, 63.15; H, 5.30; N, 8.18%). δ (CDCl₃) 1.5 (t, 6H, <u>CH</u>₃CH₂OCO-), 4.5 (q, 4H, CH₃<u>CH</u>₂OCO-), and 8.0-8.4 (m, 8H, Ar-H); ν_{max} (KBr) 1720 0-

(C=O) and 1540 ($-\ddot{N}=N-$) cm '; m/e (%) 342 (M⁺, 10), 327(10),

326(44), 282(2), 281(10), 177(11), 150(12), 144(100), 121(9), 118(4), 104(14), 103(23), 77(4), 76(12), 75(5), 65(13).

Compound 6 was purified by sublimation at 100°/0.05 mm, when it formed yellow needles m.p. 175-179°(Found: C, 63.83; H, 4.78; N, 9.32. C₁₆H₁₄O₄N₂ requires: C, 64.42; H, 4.73; N, 9.39%) δ (CDCl₃) 1.4 (t, 3H, <u>CH₃CH₂OCO-</u>), 4.4 (q, 2H, CH₃<u>CH₂OCO-</u>), 7.1-8.2 (m, 8H, Ar-H), and 8.5 (s, 1H, -CH=N-); ν_{max} (KBr) 1705 (C=O), 1630 (-C=N-), 1600 (aromatic) 1520, and 1350 (NO₂) cm⁻¹;

m/e (%) 298 (M⁺, 4), 253(3), 209(9), 180(9), 178(5), 165(83), 150(16), 137(22), 120(100), 92(34), 76(3), 65(28).

Reaction between o-phthalaldehyde and ethanol

(a) Catalyst A. Monitored by tlc (Al₂O₃, 1:1 ether:CHCl₃). Due to the inaccuracy in the monitoring method the time required for the completion of the reaction may be shorter than reported. Phthalide 8 was obtained from the crude product mixture by column chromatography (neutral alumina, 1:1 ether:CHCl₃) followed by crystallization from water to give colourless needles m.p. 70–72° (lit. 75°, 65.8°).¹⁶ & (CDCl₃) 5.3 (s, 2H, lactone -<u>CH₂</u>-OCO) and 7.7 (m, 4H, Ar-H); ν_{max} (KBr) 1780 (C=O, 5-membered ring lactone) cm⁻¹.

(b) Catalyst B. Monitored by glc (2m, 2½% SGR, 200°). Product (8; 1.48 g; 74%), m.p. 70-71°(colourless needles, from water), was separated by column chromatography.

Reaction between 2,2'-biphenyldicarboxaldehyde and ethanol

(a) Catalyst A. Monitored by tlc (Al₂O₃, 1:1 ether:CHCl₃). Due to the inaccuracy of the monitoring method the time required for the completion of the reaction may be shorter than reported. Products were identified as the lactone 10 and ester 9b and were estimated by NMR spectroscopy.

(b) Catalyst B. Monitored by glc (2m, 2.5% SGR, 210°). The lactone 10 was obtained after column chromatography (neutral alumina, 1:1 ether: CHCl₃) as colourless needles from MeOH, m.p. 134-135.5° (lit. 136-136.5).¹⁷ δ (CDCl₃) 5.0 (s, 2H, lactone -<u>CH</u>₂-OCO) and 7.7 (m, 8H, Ar-H); γ_{max} (KBr) 1710 (C=O) cm⁻¹; m/e (%), 210 (M⁺, 100), 182(75), 166(67), 152(38), 77(40).

Acknowledgement-We thank the SRC and Queen's University for support.

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