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HOMOMOLECULAR ESTERIFICATION OF ALDEHYDES CATALYZED BY HYDRIDOTETRAKIS(TRIPHENYLPHOSPHINE)RHODIUM(I)

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Summary

Homomolecular esterification of benzaldehyde has been carried out under mild conditions using $RhH(PPh_3)_4$ as catalyst. A kinetic study of the reaction has revealed a law rate of the form $r = k$ [benzaldehyde]^2[catalyst]. The rate-limiting step in the mechanism is the complexation of the second aldehyde molecule with the catalyst. As expected from this result, the lactonisation of *ortho*-phthalaldehyde is instantaneous at 19°C.

In this homomolecular esterification $RhH(PPh_3)_3$ is the catalytic species and slowly transfers its hydrogen ligand to benzaldehyde to form benzyl alcohol in concentration less than half of that of the catalyst. The complex $Rh(PPh_3)_3$ which is formed also catalyses the homomolecular esterification, but 1.6 times less readily than $RhH(PPh_3)_3$.

Introduction

In the presence of hydridocarbonyltris(triphenylphosphine)rhodium a mixture of benzaldehyde and ethanol gives ethyl-benzoate in 42% yield after 3 days reflux [1]. With cluster ruthenium complexes $Ru_3(CO)_{12}$, esterification of an aliphatic or aromatic aldehyde requires both the participation of alcohol-tolane couple and a temperature as high as 147°C [2]. Horino et al. have shown that only aliphatic aldehydes are readily self-esterified in good yields using $RuH_2(PPh_3)_4$ as a catalyst, and vacuum sealed tubes are needed [3]. This technique is unsatisfactory, however, for aromatic aldehydes. Thus the mechanism of the reaction is usually obscured by the severe experimental conditions necessary [4].

We have studied, under mild conditions, the homomolecular esterification (HME) of benzaldehyde in the presence of $RhH(PPh_3)_4$. Various kinetic and spectroscopic approaches have been used which allow a complete reaction pathway for this process to be outlined. To our knowledge, this is the first report of the esterifying ability of this catalyst.

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Results

Kinetic study of HME of benzaldehyde

The reaction was studied using GPC analysis along with authentic samples of benzyl benzoate and benzyl alcohol. The first approach was made by IR spectroscopy. The spectrum of a mixture of 8×10^{-2} *M* benzaldehyde and 2×10^{-2} *M* $RhH(PPh_3)_4$ in benzene, shows the concomitant disappearance of the carbonyl vibration of benzaldehyde at 1706 cm^{-1} and the growth of a band at 1725 cm^{-1} characteristic of the C=O group of benzyl benzoate and a band at 3592 cm^{-1} characteristic of benzyl alcohol. The results in Table 1 represent the outcome of frequent sampling of the reaction mixture followed by GPC analysis. The overall process is:

$$2\ PhCHO \xrightarrow{RhH(PPh_3)_4} PhCH_2OCOPh$$

It gives good yields at 30°C, but formation of a small quantity of benzyl alcohol is always observed (less than 10^{-2} *M*). Table 1 shows the ester yields for several concentrations of catalysts, and benzaldehyde and two different temperatures. The ester build up is rapid during the first 5 min and then slows down. After 240 min the reaction can be considered as complete, with a conversion into ester of nearly 90%. Only traces of biphenyl were observed, indicating that only a very small amount of decarbonylation takes place.

Increase in temperature raises the rate, as can be seen from columns I and IV in Table 1. The Arrhenius law applies accurately in the range 20–80°C. A three fold increase in the concentration of benzaldehyde leads to a nine fold increase in the reaction rate, which is also directly proportional to the concentration of catalyst. The overall rate law is thus of the form:

$$r = k[\text{benzaldehyde}]^2[\text{catalyst}].$$

Substituent effects

A quantitative study was attempted of the electronic influence of the X sub-

TABLE 1

YIELDS FOR CONVERSION OF BENZALDEHYDE INTO BENZYL BENZOATE

Time (min)	$PhCO_2CH_2Ph$ (%)			
	50°C [a]	50°C [b]	50°C [c]	30°C [a]
0.5	5	14	27	1.2
1	10	21.9	43	3
3	25	40.2	57.5	7.7
5	32.5	54	69	11.5
7	40	63	76	15.5
10	47.5	67	81	18
15	57.5	71	83	28
30	67.5	76.5	85	43.7
60	77.5	81.5	88.5	57.5
240	89	90	–	82

[a] [PhCHO] 8×10^{-2} *M*; [$RhH(PPh_3)_4$] 2×10^{-2} *M* in benzene. [b] [PhCHO] 25×10^{-2} *M*; [$RhH(PPh_3)_4$] 2×10^{-2} *M* in benzene. [c] [PhCHO] 25×10^{-2} *M*; [$RhH(PPh_3)_4$] 4×10^{-2} *M* in benzene.

TABLE 2

ELECTRONIC POPULATION ON THE OXYGEN ATOM CALCULATED BY THE CNDO/2 METHOD, AND THE HME INITIAL RATE FOR VARIOUS BENZALDEHYDES

X (X-PhCHO)[a]	q_π^O	Initial rate ($M\ min^{-1} \times 10^4$)
4-OMe	1.2118	1.3
4-Me	1.2045	6
H	1.1981	39
4-Cl	1.1892	320
3-Cl	1.1915	816
4-NO_2	1.1737	0

[a] [X-PhCHO] 8×10^{-2} M; [$RhH(PPh_3)_4$] 2×10^{-2} M. In benzene at 50°C under argon.

stituents in the benzene ring of benzaldehyde. Their presence modifies the electronic density on the aldehydic oxygen atom. CNDO/2 calculations [5,6] have been used to obtain the π electron density on this oxygen atom q_π^O for all the compounds used in this work, and the results are listed in Table 2. The same table also shows the HME initial rate for each compound. On going from benzaldehyde itself to *para*-methoxybenzaldehyde, as q_π^O increases, the HME initial rate falls by a factor of 30, i.e. the rate is lowered as the π charge density is increased. Conversely, electron withdrawing substituents such as chlorine decrease the electron density on the oxygen atom and the HME initial rate increases. A linear relationship is obtained between q_π^O and the logarithms of initial HME rates, as shown in Fig. 1. The

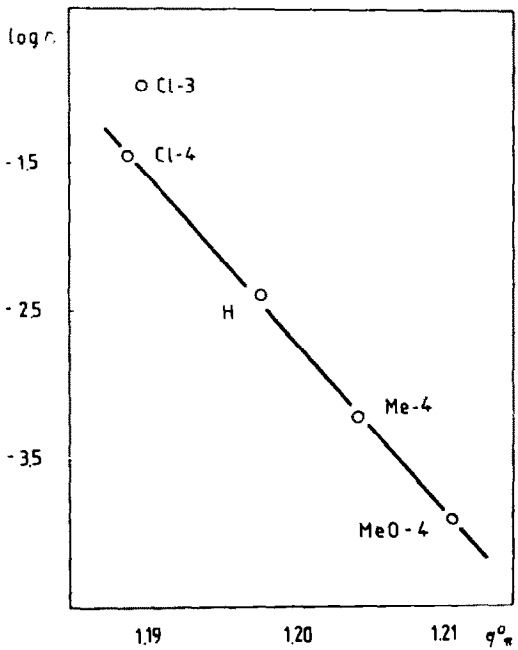


Fig. 1. HME of substituted benzaldehydes: Relationship between logarithm of initial rate and calculated π electronic population on the oxygen atom.

TABLE 3

STERIC EFFECTS ON THE INITIAL RATE OF HME OF BENZALDEHYDE DERIVATIVES

Aldehydes [a]	Initial rate ($M\ min^{-1} \times 10^4$)
PhCHO	524
2-MePhCHO	120
2,4,6-Me_3PhCHO	31

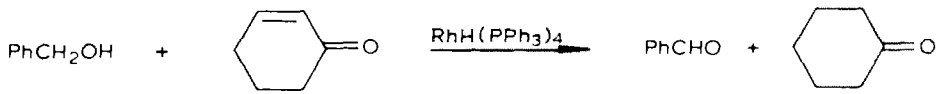
[a] [Aldehyde] 8×10^{-2} *M*; [$RhH(PPh_3)_4$] 2×10^{-2} *M*. Solvent: benzene. Temperature 50°C.

exceedingly low reaction rate for *para*-nitrobenzaldehyde, evident from Table 2, cannot, however, be attributed to electronic effects.

Table 3 shows results for benzaldehyde alongside those for two very hindered derivatives. The effect is large, a rate decrease of almost 20 being observed.

Isotope effect

When the aldehydic hydrogen is replaced by a deuterium atom, the initial reaction rate is increased. The ratio r_H/r_D is roughly 0.5; this reaction was conducted by the standard procedure used throughout this work (Table 4), but it was desirable to check independently that this isotope effect is not due to an artifact. To ensure the absence of benzoic acid from the benzaldehyde sample, the aldehyde was generated directly in the reaction mixture. Fortunately, it was known that the transfer hydrogenation of α,β-ethylenic ketones by alcohols in the presence of $RhH(PPh_3)_4$ occurred rapidly under mild conditions [7,8]. For instance the following reaction:



is complete at 60°C in less than 3 min. Advantage was taken of this process to synthesize benzaldehyde in situ and follow the initial HME rate. The results for $PhCH_2OH$ and $PhCD_2OH$ again indicated an isotope effect of nearly 0.5.

^1H NMR study of the catalyst during the HME

With a benzene solution at 30°C containing 8×10^{-2} *M* PhCDO and 4×10^{-2} *M*

TABLE 4

ISOTOPE EFFECT FOR HME OF BENZALDEHYDE

	Time (min)								
	0.5	1	3	5	7	10	15	30	60
[$PhCO_2CH_2Ph$] [a] ($\times 10^3$)	2.0	4.0	10	13	16	19	23	27	31
[$PhCO_2CD_2Ph$] [a] ($\times 10^3$)	3.9	7.8	14	17	19	22	24	28	31.5

[a] [PhCHO] = [PhCDO] = 8×10^{-2} *M*; [$RhH(PPh_3)_4$] 2×10^{-2} *M*. Solvent: benzene. Temperature 50°C.

$RhH(PPh_3)_4$ the features of the ^1H NMR spectral changes are: (a) no shift of the characteristic doublet of $RhH(PPh_3)_3$ at -8.25 ppm is observed [9], but only a slight decrease in its intensity; (b) during the experiment two weak singlets appear at 9.66 and 5.16 ppm and two other signals at 4.46 and 1.5 ppm. This latter observation shows that there is a little exchange between PhCDO and $RhH(PPh_3)_4$ in solution; after about 6 min reaction the signal at 9.66 ppm represents 10% of the total aldehyde. Because of this exchange, the obtained ester $PhCO-O-CD_2Ph$ contains a small amount of PhCO–O–CDHPh characterized by a signal at 5.16 ppm. Finally, the alcohol PhCDHOH contains only hydrogen from the catalyst itself. However, since the dissociation of the catalyst, of the form,

$$RhH(PPh_3)_4 \rightleftharpoons RhH(PPh_3)_3 + PPh_3$$

has previously been unambiguously established [10–12], we were unsure whether kinetic data could yield information about the nature of the true catalytic intermediate. The in-situ synthesis of $Rh(PPh_3)_3$ was carried out using a mixture of 2×10^{-2} *M* $RhH(PPh_3)_4$ and 10^{-2} *M* 2-cyclohexenone in benzene at 40°C (the removal of the hydrogen from the catalyst is known to be fairly fast under these conditions [13]) then 1.5×10^{-2} *M* benzaldehyde was added. The HME initial rate was $r_i = 68 \times 10^{-4}$ *M* min^{-1}, and no benzyl alcohol was obtained. To complete the study, the effect of the presence of 10^{-2} *M* cyclohexanone was examined in another run with $RhH(PPh_3)_3$ as a catalyst; in a benzene solution of 1.5×10^{-2} *M* PhCHO, 10^{-2} *M* cyclohexanone, and 2×10^{-2} *M* $RhH(PPh_3)_3$, an initial HME rate constant of 109×10^{-4} *M* min^{-1} was obtained. Thus the reaction is 1.6 times faster with $RhH(PPh_3)_4$ than with $Rh(PPh_3)_3$ as catalyst.

Discussion

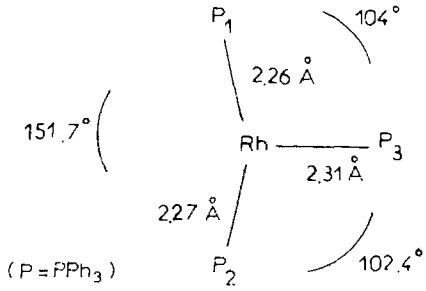
Previous results have revealed the catalytic activity of $RhH(PPh_3)_4$ in transfer hydrogenation [14,15]. This catalyst has now been shown to be very effective in HME of aldehydes. It is noteworthy that results by Horino [3] predict that butyraldehyde undergoes self-esterification only to a stoichiometric extent with this catalyst.

Importantly, as also noticed before with α,β-ethylenic ketones [7,11] practically no decarbonylation of the aldehyde (such as that encountered with $RhCl(PPh_3)_3$) was observed [11,16]. However, build up of benzyl alcohol to a maximum concentration corresponding to hydrogenation of benzaldehyde by the catalyst alone is unavoidable. This kind of process has been noted before [11,13]:

$$2\ RhH(PPh_3)_3 + PhCHO \rightarrow PhCH_2OH + 2\ Rh(PPh_3)_3$$

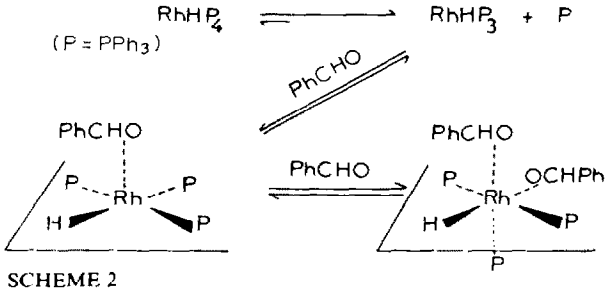
The IR and ^1H NMR studies in the present work prove unambiguously that such a process is favoured. The clear conclusion from this set of results is that the mechanism of the hydrogenation is different from that of the HME. In particular, no hydrogen from the catalyst is found in the ester. Finally, it should be noted that the small amount of benzyl alcohol formed does not participate in the esterification.

A tentative explanation of the fact that $RhH(PPh_3)_3$ gives a faster reaction than $Rh(PPh_3)_3$ can be found in the *trans* effect of the H atom on the rhodium [12,17]. The structure of $RhH(PPh_3)_3$ has been determinated by Strauss, from which it



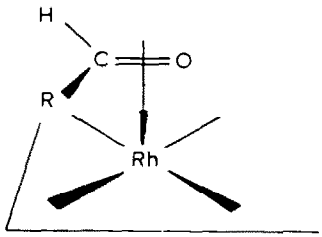
SCHEME 1

appears that the $Rh(PPh_3)_3$ bond is slightly longer than others (Scheme 1). This *trans* effect favours the necessary binding of the second benzaldehyde molecule, as illustrated in Scheme 2. Complexation of this second molecule to the catalyst is slightly more difficult when the H atom is not present.



SCHEME 2

The HME between two benzaldehyde molecules involves the breaking of a C–H bond. The isotope effect measured with PhCDO shows that this step is fast compared to the preceding complexation steps. This reasoning is reinforced by the substituent effects, which are not consistent with the breaking of a C–H bond in the slow step. On the contrary the decrease of the rate of HME with increasing π electron density on aldehydic oxygen atom indicates that at least one complexation step is rate limiting. We suggest the Rh-aldehyde complex to be of the π type [18] indicated below:

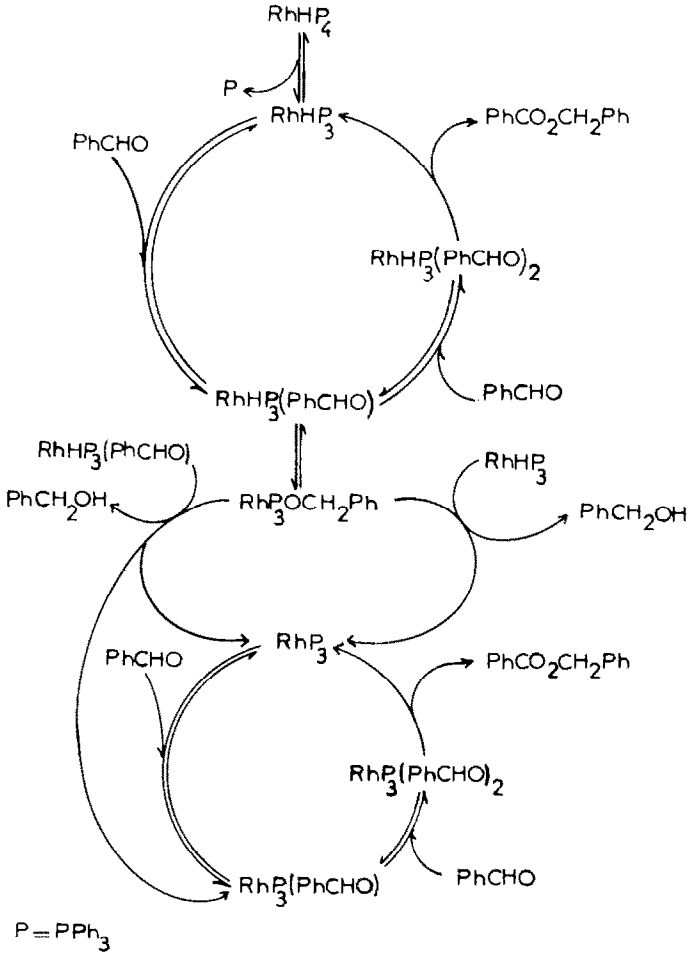


This is supported by the decrease of reaction rate caused by the presence of electron donor substituents. With nitrobenzaldehyde, further complexation of NO_2 with the catalyst probably gives an entity stable enough to be unreactive [19].

A final point concerns the intramolecular esterification of *ortho*-phthalaldehyde,

which is immediate at 19°C. It is known [20] that the proximity of two reactive centers greatly speeds up the rate in spatially favourable cases. In our experiments, the fact that the HME of *ortho*-phthalaldehyde is very fast implies that the geometry of the catalyst is highly favourable to its complexation with the carbonyl groups of the dialdehyde.

On the basis of the kinetic and spectroscopic results reported above, we proposed that the limiting step in the HME of benzaldehydes is the complexation of the second benzaldehyde molecule with the catalyst. The overall mechanistic pathway is represented by Scheme 3. After the dissociation of the catalyst in $RhHP_3$, the first



SCHEME 3

molecule of benzaldehyde gives a complex $RhHP_3(PhCHO)$. This complex can either react with a second molecule of benzaldehyde to produce benzyl benzoate or transfer the hydrogen of the catalyst, complexed or not, can occur to give benzyl alcohol. The intermediary of RhP_3OCH_2Ph is postulated, by analogy with the formation of alkyl intermediates in the transfer hydrogenation of alkenes [21]. This intermediate is

assumed to be formed in a reversible step, in the light of the small amount of exchange between $RhHP_3$ and PhCDO. In the lower part of the scheme, the HME involves the catalyst RhP_3.

Although this study has focussed on benzaldehyde, it should be noted that other aldehydes have been examined and found to behave in the same manner. Even cross esterification processes have been obtained, the catalyst retaining its full activity in such reactions.

Experimental section

Chemicals. Benzene and toluene were kept under argon, and their purity was checked by GPC. The purity of freshly distilled benzaldehyde was checked by GPC and NMR spectroscopy. The catalyst was synthetized as described by Levison and Robinson [22] and stored under vacuum. Deuteriated benzaldehyde was obtained by reduction of $PhCO_2CH_2CH_3$ with $LiAlD_4$ [23], followed by a mild oxidation under argon of the resulting deuteriated alcohol.

Apparatus. GPC analyses were carried out on a VARIAN 1400 chromatograph, with various columns (10 ft DEGS 10% for aldehydes, 10 ft S.E.30 10% for esters). A Perkin–Elmer 281 spectrophotometer was used for IR spectra, and a Bruker 80 WP for NMR spectroscopy.

Typical experimental procedure for the self-esterification

A benzene solution of $RhH(PPh_3)_4$ (2.5 ml of 2×10^{-2} *M*) and 3×10^{-2} *M* of anthracene (used as internal reference) are placed in a glass tube of 5 ml capacity containing a magnetic stirring bar. The tube flushed then filled with argon, and closed by rubber cap fixed with a screw stopper. This tube is placed in a thermostat bath at 50°C and the contents are stirred. The zero time for the experiment is taken to be the time of injection of 8×10^{-2} *M* benzaldehyde. Samples (10 μl) are withdrawn at regular intervals, diluted in 40 μl of acetone and analyzed by GPC. The areas of the chromatogram peaks are measured with a LTT ICAP5 integrator. The reproducibility for separate injections is within 5% error.

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