HYDROFORMYLATION OF LESS REACTIVE OLEFINS WITH MODIFIED RHODIUM CATALYSTS

P.W.N.M. VAN LEEUWEN and C.F. ROOBEEK

Koninklijke/Shell-Laboratorium, Amsterdam, (Shell Research B.V.), P.O. Box 3003, 1003 AA Amsterdam (The Netherlands)
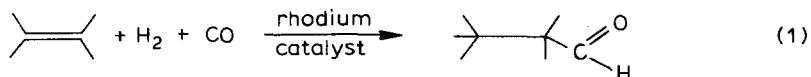
Summary

The otherwise unreactive olefins (2-methyl-1-hexene, limonene, cyclohexene, methylene cyclohexane) are hydroformylated under mild conditions (90°C, 10 bar) in the presence of phosphite-modified rhodium catalysts. The high rates observed are attributed to the steric and electronic properties of these phosphite ligands and their ability to stabilize unsaturated rhodium species. Examples of these ligands are tris(*o*-t-butylphenyl) phosphite and tris(hexafluoroisopropyl) phosphite, which are, respectively, sterically demanding and strongly electron-withdrawing.

Introduction

Even in the initial work of Wilkinson et al. [1] on the use of $HRh(PPh_3)_3CO$ as a hydroformylation catalyst it was noted that 1,2- and 2,2-dialkylethenes are much less reactive than terminal olefins in the rhodium catalysed hydroformylation reaction (eq. 1).

$$\diagdown \!\!=\!\! \diagup + H_2 + CO \xrightarrow[\text{catalyst}]{\text{rhodium}} \diagdown \!\!\diagup \diagdown C\overset{\displaystyle O}{\underset{\displaystyle H}{\diagup\!\!\!\diagdown}} \qquad (1)$$

Cyclic olefins and internal olefins react more slowly than terminal olefins, although the rate differences, depend a great deal on the conditions and the ligand modification of the catalyst. For example, 1-heptene is hydroformylated 30 times faster than 2-heptene (25°C, 1 bar, $HRh(PPh_3)_3CO$ as the catalyst) [1], and 60 times faster than 2-methyl-1-pentene. At 70°C and 130 bar without phosphine [2] the rates of terminal and internal olefins differ less than a factor of two, but at 100°C and 140 bar (with PPh_3) the differences are large, as was found in studies with n-dodecenes [3]. As a result, the hydroformylation of the less reactive olefins are carried out at higher pressures [4,5] (terpenes at 600 bar) or higher temperatures (e.g. the hydroformylation of methyl oleate > 120°C [6]).

Hydroformylation is a promising method for both the industrial and the laboratory preparation of intermediates [5], in particular in the synthesis of terpenes and

344

derivatives thereof [5,7]. Many of the molecules of interest, however, are unreactive since they contain disubstituted olefinic moieties. In this communication we describe [8] rhodium-modified catalysts which are effective catalysts for reactions of these otherwise unreactive olefins, and an explanation is offered for their high activities on the basis of ligand properties.

Results

2-Methyl-1-hexene

As a simple substrate for modelling the terpene molecules of interest we chose 2-methyl-1-hexene, which contains the characteristic isopropenyl group. We have hydroformylated 2-methyl-1-hexene with rhodium catalysts * under mild conditions (10–20 bar, 70–90°C, $H_2/CO = 1$ or 2) using a variety of ligands. Representative examples are listed in Table 1. Hydroformylation yields almost exclusively 3-methyl-heptaldehyde, and the aldehyde containing a quaternary carbon is not formed, as is also the case for cobalt catalysts [9]:
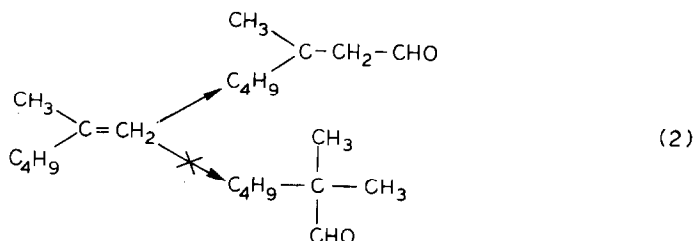

(2)

TABLE 1

HYDROFORMYLATION OF 2-METHYL-1-HEXENE [a]

Exp. no.		L/Rh ratio	Temp. (°C)	Pressure (bar)	H_2/CO ratio	Rate [b] (mol mol^{-1} h^{-1})	Cone angle, θ (deg.)	χ-value
1	PPh$_3$	10	72	18	2	50	145	13
2	P(OPh-o-Bu^t)$_3$	10	70	18	2	1600	175	28
3	P(OC$_3$F$_6$H)$_3$ [c]	10	70	18	2	1000	135	51
4	P(OPh-o-Me)$_3$ [e]	10	80	14	1	30	141	28
5	P(OPh-o-Pr^i)$_3$	10	80	14	1	300	150	28
6	P(OPh-o-Bu^t)$_3$	10	80	14	1	1000	175	28
7	P(OPh-m-Bu^t)	10	80	14	1	150	141	28
8	P(OC(Ph)HCF$_3$)$_3$ [d]	10	80	20	1	540	150	37
9	P(menthol)$_3$	4	80	20	1	375		23
10	P(OCH(CH$_3$)C$_2$F$_5$)$_3$ [d]	4	80	20	1	1000	130	40
11	P(OPr^i)$_3$	4	80	20	1	< 40	130	23
12	P(C$_6$H$_{11}$)$_3$	10	90	20	1	50	170	0

[a] Conditions, 0.01–0.02 mmol Rh(COD)OAc, 10 mmol 2-methyl-1-hexene, 20 ml benzene, 100-ml autoclave, reaction time 30–60 min. [b] Average rate over first 50% conversion calculated from recorded pressure drop. [c] Linearity 90% (3-methylheptanal), 55% selectivity to isomerization. [d] 15% isomerization to internal 2-methylhexenes. [e] Rate of 1-hexene, 3000 mol mol^{-1} h^{-1}.

* The precursor, [Rh(acetate)(1,5-cyclooctadiene)]$_2$, is instantly reduced under the reaction conditions to the hydride complex catalyst.

It is seen that use of triphenylphosphine as ligand leads to only modest rates, but several other ligands induce rates more than thirty times higher, approaching those achieved with 1-alkene and rhodium-triphenylphosphine catalysts. The best ligands turn out to possess large cone angles θ (examples 4, 5, 6) and a moderately high χ-value [10] (cf. examples 6 and 12), such as tris(o-t-butylphenyl) phosphite. A very high χ-value coupled with a medium cone angle viz. $P(O\text{-}i\text{-}C_3HF_6)_3$ (entry 3) also leads to a high activity. The latter ligand gives substantial isomerization as well, which is unusual for 2-methyl-1-alkenes.

Methylenecyclohexane

When methylenecyclohexane is subjected to hydroformylation conditions with rhodium as the catalyst and triphenylphosphine as the ligand, no reaction takes place. However, when tris(o-t-butylphenyl)phosphite is used (substrate/metal = 500/1, 20 bar, $H_2/CO = 2$, 75°C, 10 mmol olefin in benzene) a fast hydroformylation takes place (initial rate 3000 mol mol^{-1} h^{-1}).

Limonene

In our experiments we used natural limonene I, and a synthetic mixture containing I and isomer II in a ratio 1/1 synthesized from isoprene [11]. Experiments 13 and 14 (Table 2) show that the rate of hydroformylation increases 35 fold when PPh$_3$ is replaced by the bulky phosphite, tris(o-t-butylphenyl)phosphite. The turnover per hour is somewhat lower in experiment 15, but in this instance the temperature is 10°C lower and the rhodium concentration is higher, which often leads to a lower rate per mole of metal. Even at a pressure as low as 3 bar the rate with bulky
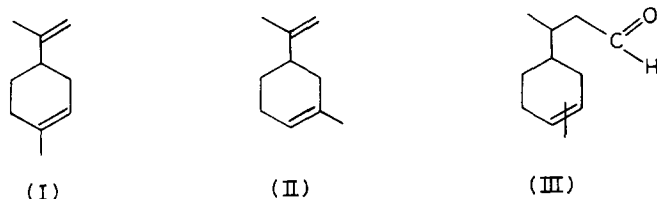

(I)   (II)   (III)

TABLE 2

HYDROFORMYLATION OF LIMONENE [a]

Exp. no.	Limonene	Ligand	Rh(COD)OAc, (mmol)	P/Rh, ratio	Temp. (°C)	Pressure (bar)	H$_2$/CO ratio	Rate (mol mol^{-1} h^{-1})
13	12 mmol of synthetic mixture	PPh$_3$	0.01	20	90	14	2	100
14	,,	P(OPh-o-Bu^t)$_3$	0.01	15	90	14	2	3500
15	60 mmol of natural product in 10 ml benzene	P(OPh-o-Bu^t)$_3$	0.03	7	80	14	1	1700
16	,,	,,	0.03	7	80	3	1	240
17	,,	P(OPh-o-Ph)$_3$	0.02	10	80	10	2	1500

[a] Conditions: 100-ml autoclave, 30 min–3 h, 20 ml benzene.

TABLE 3

HYDROFORMYLATION OF CYCLOHEXENE [a]

Exp. no.	Amount of olefin (mmol)	Ligand	Rh(COD)OAc (mmol)	L/Rh ratio	Temp. (°C)	Pressure (bar)	H_2/CO ratio	Rate (mol mol^{-1} h^{-1})	Cone angle, θ (deg.)	χ-value
18	20	PPh_3	0.01	20	90	15	1	20	145	13
19	20	PBu_3t	0.01	20	90	15	1	20	182	0
20	20	PPh_2Bu^t	0.01	20	90	15	1	150	157	9
21	15	PPh_3	0.02	4	70	18	2	<25	145	13
22	10	$P(Ph\text{-}o\text{-}Me)_3$	0.01	10	90	20	1	150	194	10
23	10	$P(C_6H_{11})_3$	0.01	10	90	20	1	<50	180	0
24	15	$P(OPh\text{-}o\text{-}Bu^t)_3$	0.02	5	70	18	2	660	175	28
25	15	$P(OPh\text{-}o\text{-}Bu^t)_3$	0.02	10	90	18	2	4000	175	28
26	15	$P(OC_3HF_6)_3$	0.02	5	70	18	2	1900	135	51

[a] Conditions, 20 ml benzene, 100 ml autoclave, 0.5–2 h.

phosphite (exp. 16) is higher than the rate with triphenylphosphine at 14 bar. o-Phenylphenylphosphite, too, gives a fast reaction. The only product formed in all these experiments is III, and hydroformylation of the trialkyl-substituted ring olefin is not observed.

Cyclohexene

Cyclohexene showed no hydroformylation at all under the mild conditions used by Wilkinson [1]. At 130 bar, with no ligand added, it reacted ten times as slowly as terminal olefins [2]. Table 3 shows that for cyclohexene both steric bulk and higher χ-values promote the hydroformylation reaction. This is already evident at low χ-values, when the χ-value increases from 0 to only 13 (exp. 22 vs. 23, and 18, 19 vs. 20). The highest rates are obtained with the most bulky aryl phosphite (o-t-butylphenyl phosphite).

Tris-hexafluoroisopropyl phosphite, which usually shows substantial isomerization, is an interesting ligand in this instance, because isomerization leaves the substrate unchanged, and hence a high selectivity to the hydroformylation product is observed.

Discussion

The first general conclusion that emerges from the results is that sterically more demanding olefins such as 2-alkyl-1-alkenes and cyclohexene can be efficiently hydroformylated with a rhodium catalyst carrying bulky phosphite ligands. This is surprising in that the low reactivity of the olefins might at first sight be ascribed to steric factors [1]. The second conclusion is that ligands with higher χ-values give more active catalysts for the dialkyl olefins. In both cases phosphites are involved, and we will first consider the effect of phosphites on the reaction in general.

The effect of aryl phosphites on the rhodium-catalysed hydroformylation has been studied by Pruett and Smith [12]. They found that in the case of terminal olefins these ligands lead to higher linearities in the aldehyde product, with two notable exceptions, viz. o,o-dimethylphenyl phosphite and o-phenyl-phenyl phosphite, which give linearities as low as 50%. They explained this in terms of the steric bulk of the ligands which prohibit the formation of bisligand or trisligand species necessary for a high preference for terminal hydroformylation. This explanation is similar to that offered by Wilkinson for the triphenylphosphine system [13].

We have found that in the case of sterically-demanding phosphites the situation is slightly more complicated than outlined previously [12]. The preference of these catalysts for terminal carbon atoms in α-olefins is not all that low [18], but there is excessive isomerization to internal olefins. Unlike other phosphite and phosphine ligand systems the present catalysts have a relatively high activity for hydroformylation of internal olefins. Together with the isomerization, this results in a low linearity. The substrates used in this study, however, are not prone to isomerization (2,2-dialkylethenes), since that would require the intermediacy of an energetically unfavourable tertiary-alkyl-rhodium species. Cyclohexene is a different case because it is unchanged by isomerization. The absence of isomerization explains why a single product is obtained, and only the high rate needs explanation, and this is given in terms of the steric and electronic properties of the ligands and their ability to stabilize unsaturated species.

Bulky ligands such as P(Cy)$_3$, cone angle 180°, form complexes with rhodium containing at most two of these ligands [14]. We expect the same for o-t-butylphenyl-phosphite: bulky phosphite ligands induce low coordination numbers and the resulting unsaturated rhodium species will be very reactive towards olefins. We suggest that the high degree of unsaturation also finds its expression in the activity for isomerization of the olefin, since this is brought about via a vacant site present on the intermediate alkyl-rhodium complex. The initial complex formation between rhodium and olefin is faster with bulky phosphite ligands since these presumably form mainly mono-ligand complexes. This will result in higher overall reaction rates if this step is to some extent rate-determining, either as the rate-determining step itself or as pre-equilibrium. The present conditions resemble those of Cavalieri d'Oro [15], who found that the reaction orders in H$_2$ and CO were almost zero, and that indeed the initial complex (be it olefin or alkyl complex) formation may be rate determining.

Hexafluoroisopropyl phosphite is not as bulky as o-t-butylphenyl phosphite, but it also gives rise to high rates with 2,2-dialkylethene substrates, whereas P(Cy)$_3$, which has a large cone angle of 170°, does not produce fast reactions. Hence there is an electronic effect as well. The behaviour of hexafluoroisopropyl phosphite has been studied in somewhat more detail. It has a very high χ-value [11] of 51, and is comparable in electronic terms with carbon monoxide. In view of the instability of HRh(CO)$_4$, it is therefore not surprising that we did not succeed in synthesizing HRhL$_4$ and HRhL$_3$(CO) with L = hexafluoroisopropyl phosphite by the common borohydride reduction method [16,17]. For lower χ-values, c.f. trifluoroethyl phosphite (χ = 39), both complexes have been prepared [18]. Likewise, HRhL$_3$(CO) with L = isopropyl phosphite can be easily prepared (δ(^{1}H) = −11.1 ppm, J(Rh–H) = J(P–H) = 5.5 Hz). Replacement of triphenylphosphine in HRh(PPh$_3$)$_3$CO by phosphites yields in all cases the fully substituted complex HRhL$_3$(CO) (or HRhL$_4$ with excess L), although with the exception already noted of L^F = hexafluoroisopropyl phosphite. The complex isolated even with large excess of the phosphite (in tetrahydrofuran and toluene) is HRh(PPh$_3$)$_2$(L^F)(CO) (δ(^{1}H) 10.1 ppm, double quartet 13 and 2 Hz). It is concluded that the strong electron-withdrawing properties of hexafluoroisopropyl phosphite inhibit the complexation of more than one of this ligand to rhodium. When under hydroformylation conditions only L^F and CO are present, we assume that coordinatively unsaturated species are formed which are less prone to condensation to clusters than ligand-free rhodium carbonyls due to the steric requirements of L^F. Hence there is a drastic difference between L^F (χ = 51) and the other phosphites (χ = 25–39) which form stable saturated rhodium complexes. The behaviour for L^F under hydroformylation conditions is thus similar to that of bulky phosphites as described above.

Ligands with less extreme χ-values were also shown to induce higher activities on rhodium for dialkylolefins than electron-donating ligands such as P(Cy)$_3$. In the former complexes rhodium is more electrophilic, and since dialkylethenes are more electron-rich than terminal alkenes, this effect may also contribute to the higher rates observed.

The regioselectivity of the rhodium catalyst with ligands of high χ-value is not so high as for the bulky phosphite. For instance, hexafluoroisopropyl phosphite gives as much as 55% isomerization of 2-methyl-1-hexene. At χ-values of 37 and 40 a selectivity to isomerization of 15% was noted. Whether this involves the formation of

tertiary-alkyl-rhodium compounds remains uncertain, since no hydroformylation products (2,2-dimethylhexaldehyde) with a quaternary carbon atom have been detected. The higher preference of more positively charged rhodium species to attack at carbon-2 is not expected, since the two donating alkyl groups should favour attack at carbon-1.

Experimental

Materials. The phosphines were used as purchased from Strem Chemicals. The phosphites were prepared via standard procedures from PCl_3, the alcohol and pyridine (in dry ether) or N,N-dimethylaniline (in xylenes) as reported [11,19]. The product was purified by distillation or recrystallization, as appropriate. The synthetic limone was prepared according to experiment L-12 from Ref. 11 and separated by distillation from the other cyclodimers of isoprene. The olefins used were freed from hydroperoxides by percolation over alumina. The catalyst precursor [Rh(COD)OAc]$_2$ was made according to the literature [20].

Procedure for hydroformylations
The autoclaves (100 ml) were charged with the solutions indicated in the tables under an atmosphere of N_2 and/or Ar. They were heated to the reaction temperature and then pressurized. The pressure drop was recorded via pressure transducers. After 0.1–2 h the autoclaves were cooled, depressurized and the contents analysed. The rates indicated are calculated from the pressure drop curves as the average over the range from 0 to 50% conversion.

Analysis. The products were analysed by GLC on a HP-5840-A instrument, with a column of 10% Carbowax-20 M on HP Chrom. WAW-DMCS 80–100 mesh, 12 ft, 1/8 inch. The compounds were identified by comparison with authentic samples using GLC, ^{13}C and ^{1}H NMR. The NMR spectra were run on a Bruker WH-90 spectrometer.

Synthesis. The attempted synthesis of hydridorhodiumcarbonyl complexes of tris(hexafluoroisopropyl)phosphite and tri(*o*-t-butylphenyl) phosphite was carried out according to ref. 17. A suspension of chlorodicarbonylrhodium (I) dimer in ethanol containing the calculated amount of the phosphite (Rh/P ratio 1/3) was reacted with NaBH$_4$ at -20 to 20°C under CO. No solid complexes were isolated.

References

1 C.K. Brown and G. Wilkinson, J. Chem. Soc. A, (1970) 2753.
2 B. Heil and L. Markò, Chem. Ber., 102 (1969) 2238.
3 W. Cornely and B. Fell, Chem. Z., 105 (1981) 317.
4 W. Aquila, W. Himmele and W. Hoffmann, DOS 2050677 (1970, to BASF) Chem. Abstr., 77 (1972) 19184.
5 H. Siegel and W. Himmele, Angew. Chem., 92 (1980) 182, and references therein.
6 J.P. Friedrich, Ind. Eng. Chem. Prod. Res. Dev., 17 (1978) 205.
7 Europ. Pat. Appl. 0011.272 (1978 to Henkel).
8 G.B. Appl. 80/41,098 (1980 to Shell Research), Chem. Abstr., 97 (1982) 144366.
9 A.J.M. Keulemans, A. Kwantes and T. van Bavel, Rec. Trav. Chim., 67 (1948) 298.
10 For a discussion of the ligand parameters used see: C.A. Tolman, Chem. Rev., 77 (1977) 313.
11 P.W.N.M. van Leeuwen and C.F. Roobeek, Tetrahedron, 37 (1981) 1973.
12 R.L. Pruett and J.A. Smith, J. Org. Chem., 34 (1969) 327.

13 D. Evans, J.A. Osborn and G. Wilkinson, J. Chem. Soc. (A), (1968) 3133.

14 H.L.M. van Gaal, F.G. Moers and J.J. Steggerda, J. Organomet. Chem., 65 (1974) C43.

15 P. Cavalieri d'Oro, G. Gregorio, G. Montrasi, M. Tampieri, G. Pagani and M. Andreeta, Proceedings Symp. Rhodium in Homogeneous Catalysis, Veszprem, 1978, p. 121.

16 P.S. Hallman, D. Evans, J.A. Osborn and G. Wilkinson, Chem. Commun., (1976) 305.

17 K.A. Keblys, U.S.P. 3,907,847 (1975, to Ethyl Corp.).

18 P.W.N.M. van Leeuwen and C.F. Roobeek, manuscript in preparation; G.B. Appl. 2.068.377.

19 A.E. Arbusov, Chem. Abstr. 51 (1957) 5720f.

20 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.