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Hydrocarbonylation of prop-2-en-1-ol to butane-1,4-diol and 2-methylpropan-1-ol catalysed by rhodium triethylphosphine complexes†

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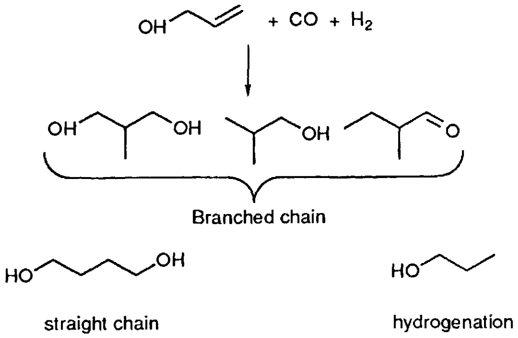
The hydrocarbonylation of prop-2-ene-1-ol catalysed by $[Rh_2(O_2CMe)_4]$–PEt_3, which gives $[RhH(CO)(PEt_3)_2]$ as the active species, has been found to produce predominantly butane-1,4-diol and 2-methylpropan-l-ol with small amounts of 2-methylpropane-1,3-diol and propan-1-ol. Neither 2-methylprop-2-enal nor 2-methylprop-2-en-1-ol are intermediates in the production of 2-methylpropan-1-ol. By carrying out the reaction under a variety of reaction conditions and by using deuterium-labelling studies it was possible to formulate a mechanism for the production of 2-methylpropan-1-ol which involves formation of the vinyl alcohol, 2-methylprop-1-en-1-ol, as the primary product followed by tautomerism and hydrogenation, provided that at least two PEt_3 groups are co-ordinated to the rhodium. A dehydration is proposed to occur during the catalytic cycle from a cationic hydroxycarbene intermediate. Using propenyl ethers as substrates similar products are obtained presumably *via* loss of alcohol rather than dehydration. If less than two PEt_3 groups are co-ordinated to rhodium the major branched-chain product from prop-2-en-1-ol is 2-methylpropane-1,3-diol. This is interpreted as indicating that protonation of the acyl intermediate and dehydration of the hydroxycarbene do not occur because of the lower electron density on the acyl O atom.

Butane-1,4-diol is a medium-volume chemical which is used as an intermediate in the formation of tetrahydrofuran and of polyester resins.[1] It is produced by a variety of different processes, the most recent of which involves hydroformylation of prop-2-en-1-ol to 4-hydroxybutanal followed by hydrogenation.[1] By using $[RhH(CO)(PPh_3)_3]$ as the catalyst for the hydroformylation step, it is possible to minimise the amount of the side-product 3-hydroxy-2-methylpropanal, but there are potential problems for this process, partly because the boiling points of butane-1,4-diol and 2-methylpropane-1,3-diol are very similar, making their separation difficult, and partly because the intermediate hydroxyaldehydes have the potential for inter- or intra-molecular acetal formation or for aldol condensation reactions. A process that produced butane-1,4-diol directly from prop-2-en-1-ol without the intermediacy of hydroxyaldehydes would be particularly attractive.

Some reports of this type of reaction have appeared. For example, using $[Rh_6(CO)_{16}]$ in the presence of PBu_3 as catalyst precursor, in benzene, the major product (41%) is butane-1,4-diol, but competing hydrogenation gives propanol (39%). Minor side products are 2-methylpropane-1,3-diol (9%) and 2-methylpropan-1-ol (6%).[2] Less hydrogenation was observed using preformed $[RhH(CO)(PR_3)_3]$, R = Bu or C_6H_{11}, but hydroxyaldehydes rather than diols were the major products.[3] These reactions were all carried out in aromatic solvents, but better selectivities (up to 69% to butane-1,4-diol) were obtained using $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) and trialkylphosphines in carbonitrile solvents.[4]

In the presence of amines, $[Rh_6(CO)_{16}]$ catalyses the direct production of butane-1,4-diol from prop-2-en-1-ol using CO–water in place of CO–H_2 and conditions under which the water gas shift reaction is promoted. Hydrogenation to propan-1-ol and the production of γ-butyrolactone compete, but aldehydes are not detected in the final product mixture.[5]

We have recently reported that, in alcoholic solvents, rhodium trialkylphosphine complexes are precursors for the direct production of alcohols from alkenes under hydroformylation conditions and that aldehydes are *not* intermediates in these reactions.[6–8] We now report the use of the same catalyst system for the hydrocarbonylation of prop-2-en-1-ol and find that not only is the straight-chain product butane-1,4-diol, but also the main branched-chain product under most conditions is 2-methylpropan-1-ol. This is a particularly interesting finding as the boiling points of butane-1,4-diol and 2-methylpropan-1-ol are separated by 120 °C making their fractional distillation trivial. A preliminary account of some of these findings has appeared.[9]



Scheme 1 Products obtained from the hydrocarbonylation of prop-2-en-1-ol in ethanol catalysed by $[Rh_2(O_2CMe)_4]\cdot 2MeOH$ in the presence of PEt_3

Results

Reaction of prop-2-en-1-ol with CO–H_2 (40 atm, 1 : 1) in ethanol containing $[Rh_2(O_2CMe)_4]\cdot 2MeOH$ and PEt_3 (10 mol per mol of Rh) at 120 °C for 4 h leads to complete conversion of the starting material into a mixture of butane-1,4-diol (57%), 2-methylpropan-l-ol (34%), propan-1-ol (5%) and 2-methylpropane-1,3-diol (5%), see Scheme 1.

Analysis of the products by GLC proved to be satisfactory for all except butane-1,4-diol, which gave broad somewhat irreproducible peaks. Better results were obtained using ^{13}C

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† *Non-SI unit employed:* atm = 101 325 Pa.

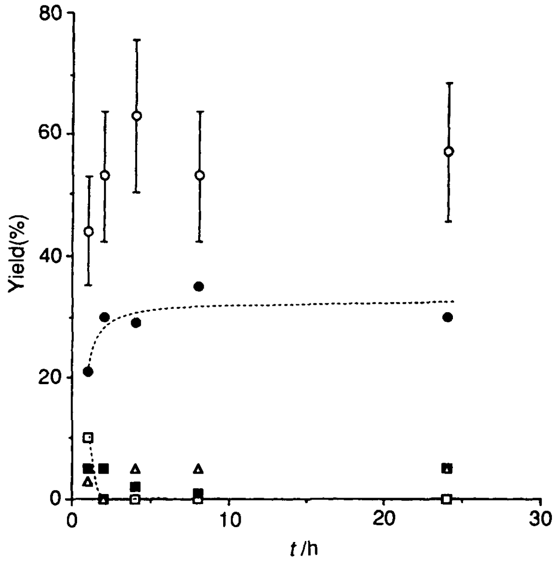


Fig. 1 Effect of time on the yields of products obtained from hydrocarbonylation at 120 °C and CO–H_2 (1 : 1, 40 atm) of prop-2-en-1-ol (1 cm^3) in ethanol (4 cm^3) catalysed by $[Rh_2(O_2CMe)_4]\cdot 2MeOH$ (2.3×10^{-5} mol) and PEt_3 (5×10^{-4} mol). ○, Butane-1,4-diol; ●, 2-methylpropan-1-ol; □, 2-methylpropanal; ■, 2-methylpropane-1,3-diol; △, propan-1-ol. Data from GLC analysis. The interdependence of the yields of 2-methylpropan-1-ol and of 2-methylpropanal is highlighted by the curves

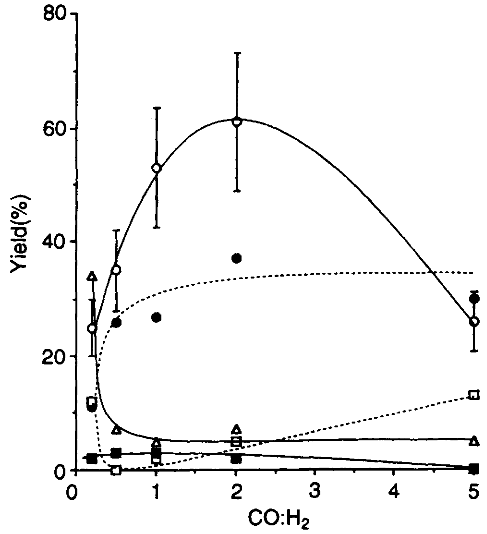


Fig. 2 Effect of CO : H_2 ratio on the yields of products obtained from hydrocarbonylation of prop-2-en-1-ol. Conditions as for Fig. 1 except $t = 4$ h. Symbols as in Fig. 1. Data from GLC analysis. At CO : H_2 = 0.2 : 1 20% of prop-2-en-1-ol is unreacted and there is a significant amount of other unidentified higher-boiling products

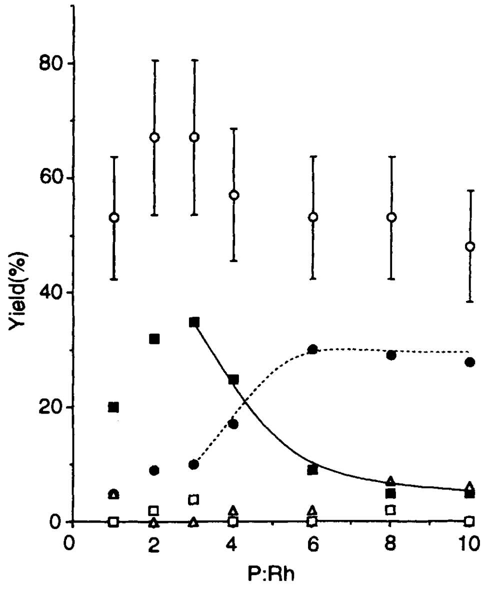


Fig. 3 Effect of PEt_3 : Rh ratio on the yield of products obtained from hydrocarbonylation of prop-2-en-1-ol. Conditions as Fig. 1 except $t = 4$ h. Symbols as in Fig. 1. Data from GLC analysis. The interdependence of the yields of 2-methylpropan-1-ol and 2-methylpropane-1,3-diol is highlighted by the curves

NMR spectroscopy calibrated for the different relaxation times of the nuclei concerned. In toluene, alcohols [butane-1,4-diol (35%) and 2-methylpropan-1-ol (15%)] are again produced but in this case, the aldehydes 4-hydroxybutanal (20%) and 2-methylpropanal (15%) are also products.

Dependence upon reaction conditions

Analysis of the reaction of prop-2-en-1-ol with CO–H_2 in the presence of ethanol suggests that the reaction is essentially complete within 1 h (all substrate exhausted) giving a minimum initial rate of 200 turnovers h^{-1} but that the initial products include 2-methylpropanal. This is converted into 2-methylpropan-1-ol over the next hour (see Fig. 1).

The CO : H_2 ratio does not greatly affect the selectivity of the reaction for values between 1 and 2 : 1 but at much lower CO concentrations (CO : H_2 = 0.2 : 1) propanol and 2-methylpropanal become significant products at the expense of butane-1,4-diol and 2-methylpropan-1-ol respectively (Fig. 2). The reaction under these conditions is much slower with ≈20% prop-2-en-1-ol being recovered unreacted. At higher CO concentrations (CO : H_2 = 5 : 1) 2-methylpropanal is again formed in significant amounts.

Varying the concentration of PEt_3 (Fig. 3) also has a significant effect upon the products of the reaction, the main difference being that at low [PEt_3] the major branched-chain product is 2-methylpropane-1,3-diol but that at higher [PEt_3] this is replaced by 2-methylpropan-1-ol. In addition, hydrogenation to give propan-1-ol becomes more important at higher [PEt_3].

The reaction is essentially independent of temperature between 100 and 170 °C but at 80 °C it is incomplete and 2-methylpropanal rather than 2-methylpropan-1-ol is the major branched product (Fig. 4).

Finally, varying the total pressure of CO–H_2 has little effect on the yields of propan-1-ol and of butane-1,4-diol, but the relative amounts of 2-methylpropane-1,3-diol and 2-methylpropan-1-ol alter, with the latter being favoured at lower pressures. This effect is most noticeable if the reaction is carried out with a relatively small excess of PEt_3 (Fig. 5). Using a 10-fold excess the products are essentially independent of total pressure up to 70 atm with 2-methylpropan-1-ol being the predominant branched-chain product.

Other substrates

The production of 2-methylpropan-1-ol from hydrocarbonylation of prop-2-en-1-ol, which formally arises from addition of methane across the C=C, probably involves a dehydration at some stage on the mechanistic pathway. We have, therefore, investigated the reactivity of 2-methylprop-2-enal and of 2-methylprop-2-en-1-ol towards CO–H_2 using the same catalytic system. Neither of these substrates gave large amounts of 2-methylpropan-1-ol, although small amounts (< 5%) were detected in the product mix. For 2-methylprop-2-en-1-ol the major products were diols (40% linear, 5% branched) and aldehydes (15% linear, < 5% branched and the conversion

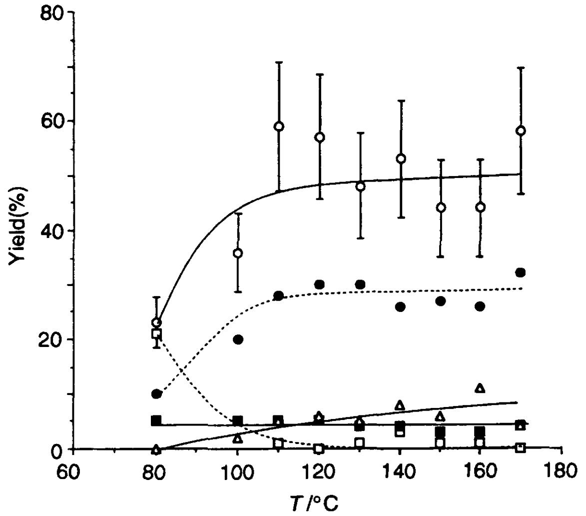


Fig. 4 Effect of temperature on the yields of products obtained from the hydrocarbonylation of prop-2-en-1-ol. Conditions as Fig. 1 except t = 4 h. Symbols as in Fig. 1. Data from GLC analysis. At 80 °C prop-2-en-1-ol (4%) is unreacted and small amounts of other (unidentified) products are observed

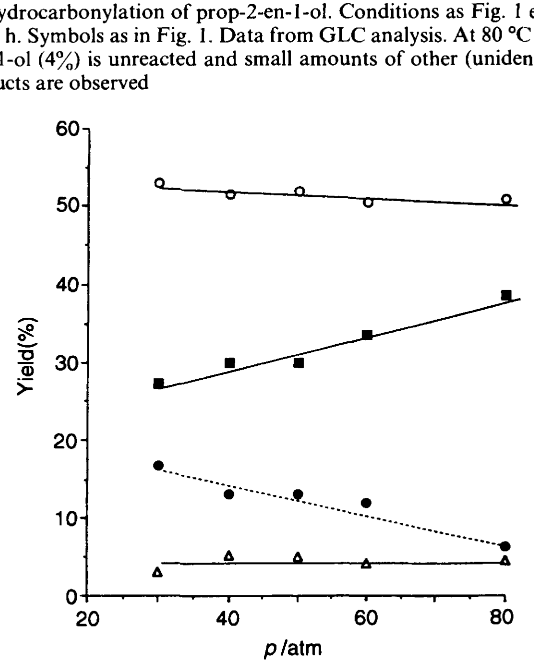


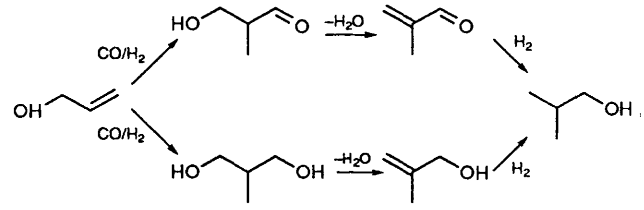
Fig. 5 Effect of total pressure on the yields of products obtained from the hydrocarbonylation of prop-2-en-1-ol. Conditions as Fig. 1 except t = 4 h, $[Rh_2(O_2CMe)_4]\cdot 2MeOH$ (7 × 10^{-5} mmol) and PEt_3 (4.2 × 10^{-4} mmol). Symbols as in Fig. 1. Data from ^{13}C NMR analysis

was only *ca.* 60%). But-3-en-1-ol gives mainly pentane-1,5-diol and 2-methylbutane-1,4-diol together with traces of butan-1-ol, whilst propenyl ethers ($CH_2{=}CHCH_2OR$, R = Ph, Et or propenyl) give mixtures of 4-hydroxybutyl ethers $[RO(CH_2)_4OH]$, 2-methylpropanol and ROH, although for R = propenyl further reaction to give butane-1,4-diol also occurs.

Labelling studies

In order to obtain further information on the mechanism of formation of 2-methylpropan-1-ol in the hydrocarbonylation of prop-2-en-1-ol, reactions were carried out in the presence of D_2 and/or EtOD. The 2-methylpropan-1-ol produced was separated by fractional distillation and analysed by ^1H, $^{13}C\text{-}\{^1H\}$ and $^{13}C\text{-}\{^1H, ^2H\}$ NMR spectroscopy. Details of the interpretation of the spectra obtained have been published previously[10] and they allow the quantification of up to 18 different isotopomers of the product 2-methylpropan-1-ol. The results are collected in Table 1.

Similar reactions were also carried out using 2-methylpropanal as the substrate. As expected on the basis of the results obtained for the hydrogenation of heptanal under similar conditions,[8] reactions in D_2–EtOH largely give products with H on C^2 but have a mixture CHD and CH_2 on C^1; reactions in H_2–EtOD give the same range of products but with significantly increased amounts of the product with CH_2 on C^1 and in D_2–EtOD, C^1 has almost entirely CH_2D, but there is a small amount (15%) of incorporation of D onto C^2. These results are also collected in Table 1.



Scheme 2 Possible routes to 2-methylpropan-1-ol from hydrocarbonylation of prop-2-en-1-ol

Discussion

We have shown that the active catalytic species obtained from $[Rh_2(O_2CMe)_4]$ and PEt_3 under CO–H_2 in ethanol is the same as that produced from $[RhH(PEt_3)_3]$, *i.e.* predominantly $[RhH(CO)(PEt_3)_3]$ under hydrogen-rich conditions.[8] This system produces C_7 alcohols as the primary products from hex-1-ene, CO and H_2 by a mechanism involving an hydroxycarbene intermediate if the reaction is carried out in alcoholic solvents.[8] The products expected from prop-2-en-1-ol are, therefore, butane-1,4-diol and 2-methylpropane-1,3-diol. Propanol presumably arises from isomerisation of the substrate to give propanal followed by hydrogenation, since this system shows good activity for the hydrogenation of aldehydes but not of C=C. The surprising product is 2-methylpropan-1-ol, since this formally arises from addition of methane across the C=C.

The production of butane-1,4-diol and 2-methylpropan-1-ol as the major straight and branched products is of considerable interest since their boiling points differ by 120 °C, making their separation by fractional distillation straightforward. The direct formation of alcohols also removes complications arising from aldol condensation and intra- or inter-molecular acetal formation.

In principle, 2-methylpropan-1-ol could be formed *via* a number of pathways but they must involve dehydration at some point followed by hydrogenation. Two possible pathways are shown in Scheme 2. One involves initial formation then dehydration of 3-hydroxy-2-methylpropanal whilst the other involves dehydration of 2-methylpropane-1,3-diol. Since neither of the dehydration products, 2-methylprop-2-enal and 2-methylprop-2-en-1-ol, are significantly hydrogenated to 2-methylpropan-1-ol under the normal reaction conditions the processes of Scheme 2 can be discounted.

Analysis of the products as a function of time shows that 2-methylpropan-l-ol is not a primary reaction product, but rather that it is formed *via* 2-methylpropanal as an intermediate. Separate experiments have shown that the same catalytic system smoothly hydrogenates 2-methylpropanal to 2-methylpropan-1-ol. Furthermore, analysis of the H atom on C^2 from the various labelling reactions (Table 2) strongly suggests that this H atom is derived from the solvent and not from the gas phase. We note at this point that reactions in EtOD are not isotopically pure because the substrate contains OH and H_2O is liberated during the reaction. We return to a detailed analysis of the labelling later. The most likely mechanism by which the H/D atom on C^2 can be incorporated from the solvent OH/D involves the formation of 2-methylpropanal from 2-methylprop-1-en-1-ol *via* enol–keto tautomerism. The relatively small amount of deuterium incorporation onto C^2 in reactions

Table 1 Percentages of labelled 2-methylpropan-1-ol obtained from reaction of prop-2-en-1-ol or 2-methylpropanal with CO–H(D)$_2$ in EtOH(D)[a]

	2-Methylpropanal			Prop-2-en-1-ol		
Isotopomer	D$_2$–EtOD[b]	D$_2$–EtOH	H$_2$–EtOD[b]	D$_2$–EtOD	D$_2$–EtOH[c]	H$_2$–EtOD[6]
$(CH_3)_2CHCH_2OH/D$	4.2 (9)	38.1 (4)	76.0 (11)		1.3	49.0 (15)
$(CH_3)_2CDCH_2OH/D$	0.8 (9)	4.1 (4)	6.5 (11)		0.3	28.8 (15)
$(CH_3)_2CHCHDOH/D$	80.0 (9)	49.8 (4)	16.2 (11)		3.5	14.0 (15)
$(CH_3)_2CDCHDOH/D$	15.1 (9)	8.0 (4)	1.4 (11)		0.8	8.2 (15)
$(CH_3)_2CHCD_2OH/D$					1.5	
$(CH_3)_2CDCD_2OH/D$					0.4	
$CH_3(CH_2D)CHCH_2OH/D$					2.5	
$CH_3(CH_2D)CDCH_2OH/D$					0.6	
$CH_3(CH_2D)CHCHDOH/D$				2.1 (3)	19.1	
$CH_3(CH_2D)CDCHDOH/D$				3.4 (6)	4.3	
$CH_3(CH_2D)CHCD_2OH/D$				4.7 (3)	13.1	
$CH_3(CH_2D)CDCD_2OH/D$				7.1 (4)	2.9	
$(CH_2D)_2CHCH_2OH/D$					0	
$(CH_2D)_2CDCH_2OH/D$					0	
$(CH_2D)_2CHCHDOH/D$				9.7 (3)	22.5	
$(CH_2D)_2CDCHDOH/D$				10.9 (7)	4.9	
$(CH_2D)_2CHCD_2OH/D$				26.8 (5)	18.2	
$(CH_2D)_2CDCD_2OH/D$				35.1 (7)	4.0	

[a] Estimated using the methods of ref. 10 using $^{13}C-\{^1H, ^2H\}$ NMR spectra at 151 MHz. Numbers in parentheses are estimated errors arising from the measurement of peak areas. [b] From $^{13}C-\{^1H\}$ NMR spectra at 75.5 MHz. [c] Values quoted as 0 are < 0.5%.

Table 2 Isotopic labelling pattern for C atoms of 2-methylpropan-1-ol derived from prop-2-en-1-ol or 2-methylpropanal based on ^{13}C analysis[a]

		Prop-2-en-1-ol			2-Methylpropanal[b]	
Atom	System	CH_2	CHD	CD_2	CH_2	CHD
C^1	EtOD–H_2	78	22	—	77	23
	EtOH–D_2	5	55	40	40	60
	EtOD–D_2	—	26	74	2	98
		CH	CD		CH	CD
C^2	EtOD–H_2	63 (52)[b]	37 (48)[b]		95	5
	EtOH–D_2	82 (78)[b]	18 (22)[b]		93	7
	EtOD–D_2	43 (46)[b]	57 (54)[b]		90	10
		$(CH_3)_2$	$CH_3(CH_2D)$	$(CH_2D)_2$		
C^3	EtOD–H_2	100				
	EtOH–D_2	8	42	50		
	EtOD–D_2	0	17	83		

[a] The C atoms are numbered as: $(C^3H_3)_2C^2HC^1H_2OH$. [b] Data from ^1H NMR spectra.

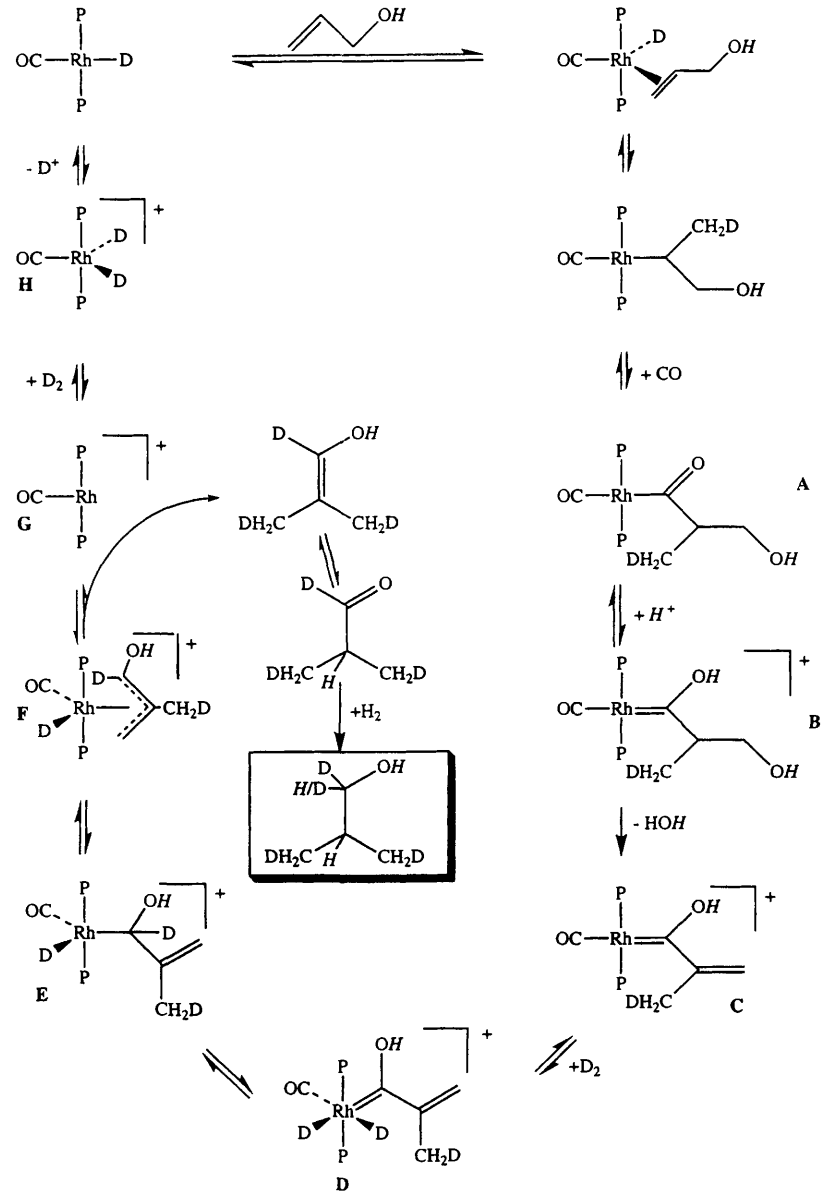
starting from 2-methylpropanal shows that simple exchange with the solvent cannot explain the H/D incorporation for the reactions starting from prop-2-en-1-ol.

Our work on the hydrocarbonylation of hex-1-ene using the same catalytic system, together with related studies of model compounds,[8] has provided evidence that the first steps of the reaction are identical to those proposed for hydroformylation reactions catalysed by *e.g.* $[RhH(CO)(PPh_3)_3]$ but that the electron-donating phosphines build up sufficient negative charge density on the acyl oxygen atom in $[Rh(RCO)(CO)(PEt_3)_2]$, **A** in Scheme 3, for it to be protonated by alcoholic solvents. Assuming that this sequence of reactions occurs for prop-2-en-1-ol and considering Markownikoff addition of the Rh–H bond across the C=C, we can begin to construct a mechanism for the formation of 2-methylpropan-1-ol (Scheme 3). In order to obtain the required product it is necessary to propose that dehydration of the hydroxycarbene ligand in intermediate **B** occurs. This is likely because it then places a C=C in conjugation with the Rh=C. An alternative possibility is that dehydration occurs from the acyl group in intermediate **A** since this would also lead to conjugated double bonds (C=C and C=O) and that protonation of the O atom of the unsaturated acyl group occurs to give **C**.

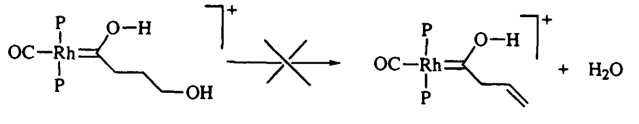
Oxidative addition of H_2 to the rhodium centre in the unsaturated hydroxycarbene intermediate **C** followed by transfer of H will give the 16e η^1-allyl complex **E**. It is expected that this will rapidly transform to the 18e η^3-allyl **F**. A further hydrogen transfer specifically to the end of the alkyl group that does not bear the OH group will give the desired vinyl alcohol which, after tautomerism and hydrogenation, will give the observed 2-methylpropan-1-ol.

Various observations support a mechanism of this kind. First, the fact that anti-Markownikoff insertion of the C=C into the Rh–H bond leads selectively to butane-1,4-diol supports the suggestion that conjugation is the driving force for the dehydration (as indeed it is for 3-hydroxyaldehydes in *e.g.* aldol condensation reactions) since dehydration of the hydroxycarbene derived from the anti-Markownikoff insertion would not give conjugated double bonds (Scheme 4). Furthermore, using but-3-en-1-ol, both the straight- and branched-chain products are diols since neither hydroxycarbene can dehydrate to give conjugated double bonds.

The products of the reaction carried out in toluene are also of interest. Since the substrate, prop-2-en-1-ol, is an alcohol, a proton source is present so that protonation of the acyl can still occur. Hence, the same products as are obtained in ethanol as a solvent are observed. Interestingly, much less of the 2-methylpropanal is hydrogenated than under similar conditions where the solvent is ethanol. We have previously shown that aldehyde hydrogenation using this catalyst system occurs *via* two pathways, one of which involves protonation of the metal.[8] With the reduced concentration of the protic solvent present in the reaction carried out in toluene, this pathway is likely to be slowed so that the overall rate of aldehyde hydrogenation will be reduced and hence 2-methylpropanal is observed as a product. The observation of 4-hydroxybutanal as a product in the hydrocarbonylation of prop-2-en-1-ol carried out in toluene suggests that oxidative addition of H_2 to the straight-chain acyl compound, followed by reductive elimination, competes with protonation of the acyl under conditions where the concentration of proton donors is low. If this is the case, it is surprising that neither 3-hydroxy-2-methylpropanal nor 2-methylprop-2-enal is a product, since these would be expected from oxidative addition of H_2 to intermediate **A** or its dehydrated form followed by reductive elimination of aldehyde.

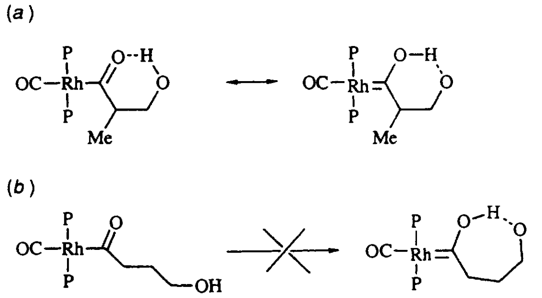


Scheme 3 Proposed mechanism for the formation of 2-methylpropan-1-ol from hydrocarbonylation of prop-2-en-1-ol catalysed by Rh/PEt$_3$ complexes. Atoms incorporated from the gas phase are labelled D, those from solution O*H* are labelled *H*. P ≡ PEt$_3$



Scheme 4 The intermediate that would be formed from dehydration of the hydroxycarbene intermediate proposed to be formed from the anti-Markownikoff insertion product during hydrocarbonylation of prop-2-en-1-ol catalysed by Rh/PEt$_3$ complexes. P ≡ PEt$_3$

One possible explanation for this apparent anomaly is that the hydroxy group of intermediate **A** can protonate the acyl group intramolecularly *via* the six-membered ring intermediate shown in Scheme 5(*a*). The probability of this occurring is further enhanced by the steric requirements of the methyl group so that the cycle of Scheme 3 will occur, rather than the formation of aldehyde. For the anti-Markownikoff addition of the Rh–H bond across C=C, the acyl intermediate has the hydroxy group on the γ-carbon atom so that the internal self-protonation would involve a much less favoured seven-membered cyclic intermediate [Scheme 5(*b*)]. If this explanation is correct it seems probable that protonation of the acyl to give the hydroxycarbene precedes loss of water on the pathway to 2-methylpropan-1-ol, as shown in Scheme 3.



Scheme 5 (*a*) Proposed cyclic intermediate formed by intramolecular protonation in intermediate **A** of Scheme 3. (*b*) Formation of a seven-membered cyclic intermediate if a similar intermediate to that in (*a*) were formed from the straight-chain acyl complex. P ≡ PEt$_3$

One other interesting observation is that 2-methylpropane-1,3-diol does become an important product (at the expense of 2-methylpropan-1-ol) under conditions of low [PEt$_3$] or high p_{CO}.

Under these conditions it is possible that PEt_3 is replaced by CO to give $[RhH(CO)_2(PEt_3)]$ as the active catalytic species. If so the electron density on Rh and hence on the acyl O atom may not be sufficient for protonation of the acyl species to occur, dehydration would not occur and oxidative addition of H_2 to intermediate **A** followed by reductive elimination would give 3-hydroxy-2-methylpropanal *via* the 'normal' hydroformylation mechanism. Subsequent hydrogenation would give the observed diol. Low partial pressure of H_2 presumably accounts for the relatively large amount of 2-methylpropanal observed under these conditions. 2-Methylpropanal also becomes a significant product under conditions of low partial pressure of CO, perhaps because a major species present is $[RhH(PEt_3)_3]$ and this is too sterically crowded to allow hydrogenation of the branched aldehyde. In partial support of this suggestion is the observation that the major product under these conditions is propanol probably formed *via* isomerisation of the prop-2-en-1-ol rather than hydrocarbonylation, suggesting that less CO is present on the catalyst. This time the linear aldehyde, which is less sterically demanding, does hydrogenate.

Interestingly, the products obtained from reactions of propenyl ethers are analogous to those obtained from prop-2-en-1-ol, namely 4-hydroxyethers and 2-methylpropan-1-ol. This suggests that the relevant alcohol can be lost instead of water to form the conjugated unsaturated hydroxycarbene intermediate **C**.

Labelling studies on 2-methylpropan-1-ol

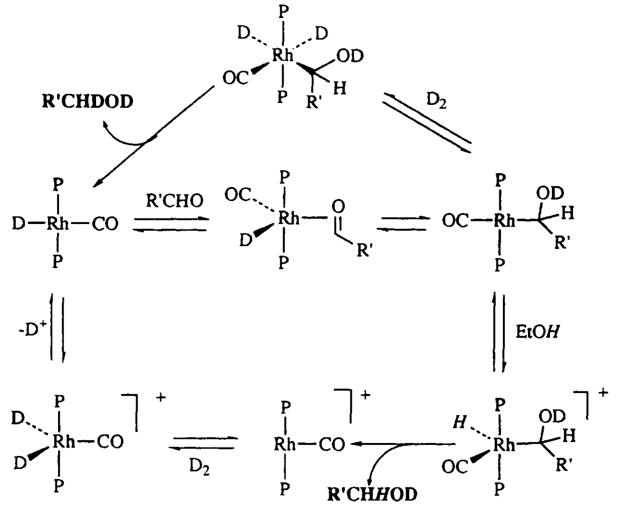
(*a*) Hydrogenation of 2-methylpropanal. We have previously shown that two mechanisms operate during the hydrogenation of heptanal catalysed by $[RhH(PEt_3)_3]$[8] (see Scheme 6). The labelling patterns for 2-methylpropan-1-ol obtained from hydrogenation of 2-methylpropanal carried out under similar conditions to those used in the hydrocarbonylation reactions are shown in Tables 1 and 2.

Since C^2 is not involved in the hydrogenation reaction it should remain with 100% H throughout. This turns out not to be the case with small but significant amounts of D being introduced in all reactions. This presumably arises from a small amount of keto–enol tautomerism. For the reactions involving D_2–EtOH the deuterium used for this tautomerism must arise from product $Me_2CHCH(H/D)OD$.

As with heptanal, the labelling of C^1 for the 2-methylpropan-1-ol formed in D_2–EtOH or H_2–EtOD suggests that H can be incorporated from the solvent OH/D or from the gas phase. The two mechanisms by which this is proposed to occur are shown in Scheme 6. Significant isotope effects evidently operate with the top cycle proceeding faster in H_2–EtOD and the bottom cycle faster in D_2–EtOH. In D_2–EtOD it would be expected that neither cycle should introduce H onto C^1 but a small amount of such incorporation (2%) is observed. This presumably arises *via* the bottom cycle with protonation by OH introduced into the solvent *via* the keto–enol tautomerism that introduces D onto C^2.

(*b*) Hydrocarbonylation of prop-2-en-1-ol. *Solvent composition.* Before considering whether the results obtained from the deuterium-labelling experiments are compatible with the mechanism for 2-methylpropan-1-ol production proposed in Scheme 3 it is necessary to discuss the OH/D composition of the solvent.

Since the prop-2-en-1-ol used in all the reactions did not contain deuterium in any position, reactions carried out using EtOD as solvent contained a mixture of OH : OD in the molar ratio 0.22:0.78. However, there is a further complication because the OH/D composition changes during the course of the reaction. This change arises because: (*a*) for each molecule of alcohol (butane-1,4-diol or 2-methylpropan-1-ol) produced a proton is lost from intermediate **H** in the last step of recycling the catalyst (if the mechanism of Scheme 3 is correct this proton originates from the gas phase); (*b*) in the dehydration of intermediate **B** in Scheme 3 an extra proton is added to the solution for each molecule of 2-methylpropan-1-ol produced [this proton arises from a C–H bond of the 2-methylpropan-1-ol, so is always H^+ (not D^+)] and (*c*) during the final hydrogenation of 2-methylpropanal the OH group is formed from the H_2/D_2 in the gas phase, but also the lower cycle in Scheme 6 leads to the consumption of 1 mol of H^+/D^+ from the solvent OH/D and the release of 1 mol of H^+/D^+, which originated from H_2/D_2 in the gas phase, during the catalyst regeneration.



Scheme 6 Mechanism proposed in ref. 8 for the hydrogenation of aldehydes catalysed by Rh/PEt_3 complexes. Atoms incorporated from the gas phase are labelled D, those from solution are labelled *H*. For 2-methylpropanal, R' = Me_2CH. P ≡ PEt_3

In these reactions, the ratio of butan-1,4-diol : 2-methylpropan-1-ol is *ca.* 2 : 1 so that the final OH/D composition of the solvent can be calculated (see Table 3).

Labelling of C^3. Following the mechanism of Scheme 3, each C^3 atom has one H/D atom added to it during the catalytic cycle. The atoms attached to C^3 would be expected to be exclusively H_2X where X comes from the gas phase. In practice (Table 2), for a gas phase of H_2, all the C^3 atoms are as expected and for reactions under D_2 $>90\%$ are H_2D. Thus, it appears that the labelling patterns of $>90\%$ of the products are consistent with the proposed mechanism, but that ≈ 8–9% are either formed by a different pathway or that exchange of H/D^+ occurs with the solvent OH/D in one of the protonated intermediates **D**–**F** or **H** of Scheme 3. We have previously noted a similar phenomenon during labelling studies of the hydrocarbonylation of hex-1-ene using the same catalyst system.[8]

Labelling of C^2. Since the proton on C^2 is proposed to arise from ketonisation of a vinyl alcohol, it should reflect the solvent composition. Table 3 shows the actual H : D ratios observed as determined by ^1H NMR spectroscopy together with the initial and final composition of the OH/D of the solvent. Using these initial and final solvent compositions it is possible to calculate upper and lower limits for primary kinetic isotope effects that would be required to obtain the observed product ratios. These are also shown in Table 3 and suggest k_H/k_D values of 4. Isotope effects have been measured for the conversion of vinyl alcohol into ethanol as 4.7 for the acid-catalysed reaction and 3.4 for the base-catalysed reaction,[11] whilst the tautomerism of prop-1-en-1-ol to propanal catalysed by a rhodium phosphine complex has an upper limit of 4.[12]

Our estimated value of 4 is, thus, in the region expected for a tautomerism of this kind and the labelling pattern on C^2 is thus consistent with the mechanism of formation of 2-methylpropan-1-ol proposed in Scheme 3.

Table 3 The H : D ratio on C^2 of 2-methylpropan-1-ol obtained from prop-2-en-1-ol and the solvent composition (H : D) at the start and finish of the reaction and isotope effects calculated from these data *

		Solvent composition (H : D)		k_H/k_D	
System	H : D (C^2)	Start	Finish	Start	Finish
EtOD–H_2	1.1	0.21	0.59	5.2	1.9
EtOH–D_2	3.5	100/0	3.8	—	0.9
EtOD–D_2	0.85	0.21	0.21	4.0	4.0

* Data for C^2 were taken from ^1H NMR spectra; the isotope effects were calculated using the solution composition at the start and finish of the reaction. They, therefore, represent upper and lower limits. Conditions: prop-2-en-1-ol (1 cm^3), EtOH/D (4 cm^3), CO–H(D)$_2$ (40 atm, 1 : 1), $[Rh_2(O_2CMe)_4]\cdot 2MeOH$ (2.3×10^{-5} mol), PEt_3 (5×10^{-4} mol), 120 °C, 4 h.

Labelling of C^1. The mechanism of Scheme 3 suggests that one H on C^1 should be incorporated exclusively from the gas phase whilst the other should be incorporated during the hydrogenation of 2-methylpropanal. Table 2 indicates that for the reactions using EtOD–H_2 or –D_2 at least one H/D comes from the gas phase, whilst for EtOH–D_2 95% of the 2-methylpropan-1-ol have at least one D on C^1 arising from the gas phase. Once again, the other 5% could arise from exchange of D^+ in a protonated intermediate with OH from the solvent. In this case exchange would have to occur in intermediate **D**. Broadly speaking, the H : D ratio for the other proton incorporated should be similar to that for the CH_2 : CHD ratio for the hydrogenation of 2-methylpropanal under the same conditions, except that the products from prop-2-en-1-ol are likely to be enriched in H because of the higher OH concentration in the solution. The similarity would be expected to be best for the reaction in H_2–EtOD where the top cycle of Scheme 6 (not involving the solvent) predominates. Examination of Table 2 shows that these qualitative conclusions are in fact borne out in practice. However, problems associated with changes in solvent composition during the reactions mean that quantitative modelling is not possible.

Conclusion

We conclude that $[Rh_2(O_2CMe)_4]$–PEt_3 shows high activity for the hydrocarbonylation of prop-2-en-1-ol to butane-1,4-diol with 2-methylpropan-1-ol as the major branched product. The two major products can be readily separated by distillation. Butane-1,4-diol is formed as a primary product by a process analogous to that already described for the formation of C_7 alcohols from hex-1-ene using the same catalyst system,[8] whilst 2-methylpropan-l-ol is formed by hydrogenation of the primary product, 2-methylpropanal. The latter comes from tautomerism of 2-methylprop-1-en-1-ol, which in turn is formed by a mechanism that is proposed to involve loss of water from a hydroxycarbene intermediate followed by a sequence of steps involving σ- and π-allyl intermediates and reductive elimination. Labelling studies are consistent with this mechanism.

Experimental

The NMR spectra were recorded on Brüker Associates AM300 (^1H, ^2H, ^{31}P and ^{13}C-{^1H} at 75.5 MHz) and Varian VXr600S (^{13}C-{^1H, ^2H} at 151 MHz) spectrometers in 5 mm glass tubes. The GC mass spectra were obtained on an INCOS 50 system with a Hewlett-Packard 5890 gas chromatograph using either an HP17 (cross-linked 50% phenylmethyl silicone) capillary column programmed to run at 50 °C for 5 min then raised at 10 °C min^{-1} to 200 °C or on a BP1 (dimethylsiloxane) capillary column at 30 °C for 5 min, raised at 34 °C min^{-1} to 200 °C and held for 5 min. Helium (1.6 atm) was the carrier gas and the injector temperature was held at 200 °C. Quantitative GLC analyses were carried out on a Philips PU4500 chromatograph fitted with a fused-silica capillary column with CP-Sil-19CB as stationary phase. The temperature was held at 40 °C for 5 min then raised at 16 °C min^{-1} to 200 °C and held for 5 min. Nitrogen was the carrier gas, the injector temperature was 150 °C and flame ionisation detection was employed. A sample of the reaction solution (1 cm^3) together with toluene (50 μl) as internal standard was prepared and then injected (1 μl).

Standard solutions containing known amounts of the pure standard in ethanol (total volume = 1 cm^3) were prepared. To these were added toluene (50 μl). These were injected (1 μl) onto the column and calibration plots prepared. Each sample and each standard was injected three times and the concentrations of each component were averaged. In all cases good reproducibility was obtained (± 5%). However, this was not always the case for butane-1,4-diol even on injecting the same sample, because the peak was broad with a very poor profile. In cases where this proved especially problematic the crude reaction solution was analysed by ^{13}C-{^1H} NMR spectroscopy. Quantification was carried out using the CH_2 resonances for which the receptivities were checked under identical spectrum accumulation conditions using solutions of known concentration.

Ethanol was dried by distillation from magnesium ethoxide. All reagents and standards were purified by distillation except for 2-methylpropan-1-ol which was distilled from CaO. The compounds $RhCl_3\cdot 3H_2O$ (Johnson Matthey), PEt_3 (Aldrich) and ethyl propenyl ether (Aldrich) were used as supplied; $[Rh_2(O_2CMe)_4]\cdot 2MeOH$ was prepared by a standard literature method.[13]

Catalytic reactions

The apparatus and procedure used were as previously described[8] and the reagents were usually added in the order: $[Rh_2(O_2CMe)_4]\cdot 2MeOH$ (2.3×10^{-5} mol) in ethanol (4 cm^3); alkene (1 cm^3); phosphine (5×10^{-4} mol); gases (40 atm). The autoclaves were heated using heating bands, which allowed the reaction temperature to be reached within 10–15 min, and were stirred magnetically. After the reaction the autoclave was cooled by placing it in cold water, vented and the products carefully removed from inside and outside the glass liner before analysis by GLC, GC-MS and/or ^{13}C NMR spectroscopy.

Labelling studies

Ethanol or EtOD (8 cm^3) containing $[Rh_2(O_2CMe)_4]\cdot 2MeOH$ (4.6×10^{-5} mol) was placed in an autoclave fitted with a glass liner. The autoclave was pressurised with CO (40 atm) and the pressure released. This flushing process was repeated three times. With a steady flow of CO passing through the autoclave, PEt_3 (10^{-3} mol) and the substrate, prop-2-en-1-ol or 2-methylpropanal (2 cm^3), were added. The autoclave was pressurised to 20 atm with D_2, then the pressure was raised to 40 atm using CO. After heating to 120 °C for 4 h with magnetic stirring, the autoclave was cooled and vented. The product was then fractionally distilled and the fraction containing 2-methylpropan-1-ol (b.p. 105–110 °C) collected and analysed by ^1H, ^{13}C-{^1H} and/or ^{13}C-{^1H, ^2H} NMR spectroscopy.[10] For reactions using H_2 the autoclave was flushed and pressurised with CO–H_2 (1 : 1, 40 atm).

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