Reductive Carbonylation of Alkenes using Zwitterionic Rhodium Complexes as Catalysts

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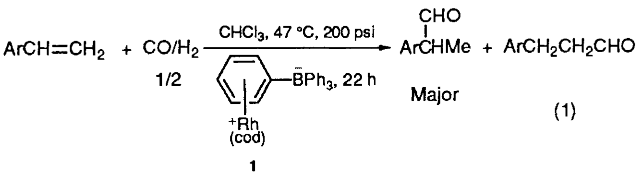
Alkenes react with carbon monoxide, sodium borohydride, propan-2-ol and a catalytic amount of Rh(cod)(η^6-PhBPh$_3$) (cod = cyclooctadiene) to give alcohols in fine yields; high regioselectivity for the branched or linear alcohol is usually observed, depending on the organic substrate.

One of us has recently demonstrated the use of zwitterionic rhodium complexes as catalysts for the hydroformylation of alkenes. Branched-chain aldehydes can be obtained in a very selective manner by reaction of a monosubstituted vinyl arene or vinyl ether with carbon monoxide and hydrogen in the presence of the zwitterionic rhodium η^6-tetraphenylborate complex **1** [eqn. (1)]. Appropriate aliphatic or aromatic 1,1-disubstituted alkenes gave linear aldehydes in a regiospecific manner.[1] Another important process is the conversion of alkenes to alcohols by reductive carbonylation.[2] This communication describes the use of **1** for achieving the regioselective synthesis of branched or linear alcohols, subject to the nature of the reactant. These constitute the first examples, to our knowledge, of a borohydride based hydroformylation reaction, as well as the first direct regioselective route to branched chain alcohols from styrene derivatives.

Treatment of styrene **2** (R = Ph) with an equivalent amount of sodium borohydride, propan-2-ol, and the rhodium catalyst **1** in chloroform, for 22 h at 100 °C and 500 psi of carbon monoxide, gave isomeric alcohols in 83% yield, the ratio of branched **3** to linear **4** products being 95:5. The ratio of reactant to metal catalyst was 100:1. No reaction occurs in the absence of either sodium borohydride or propan-2-ol. The



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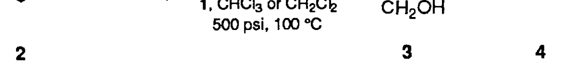

2 **3** **4**

Table 1 Reductive carbonylation of alkenes[a]

Alkene	Rhodium catalyst	Yield of alcohols[b] (%)	**3**:**4**[c]
2; R = Ph	**1**	83	95:5
	5	90	64:36
	6	92	80:20
2; R = *p*-MeC_6H_4	**1**	77	93:7
	5	95	77:23
	6	90	75:25
2; R = *p*-ClC_6H_4	**1**	93	75:25
	5[d]		
2; R = *p*-FC_6H_4	**1**	70	91:9
2; R = *p*-Me_2CHCH_2	**1**	73	89:11
2; R = *p*-$MeOC_6H_4$	**1**	91	95:5
2; R = n-C_8H_{17}	**1**	90	47:53
2; R = $C_3H_7CMe_2$	**1**	88	1:99
2; R = cyclohexyl	**1**	87	10:90
2; R = cyclohex-3-en-1-yl	**1**	54	15:85
2-methyl-undec-1-ene	**1**	75	1:99
R(+)-limonene	**1**	74	0:100

[a] General procedure: A mixture of 4.0 mmol of substrate, 0.150 g (4.0 mmol) of $NaBH_4$, 0.5 ml of propan-2-ol and 0.04 mmol of **1**,**5** or **6** in 4 ml of CH_2Cl_2 ($CHCl_3$ was used for **2**, R = Ph or *p*-$MeOC_6H_4$) was stirred at 100 °C, under 500 psi of carbon monoxide, for 22 h when an aryl alkene was used, and for 30 h if the reactant was non-aromatic. Water (10 ml) was added to the cooled mixture, and the layers were separated. The aqueous layer was extracted with ethyl acetate (20 ml) and the organic solutions were combined. Concentration of the organic phase followed by alumina column chromatography using hexane–ethyl acetate afforded pure branched and linear alcohols. [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. [d] 10% *p*-chloroethylbenzene was isolated using **5** as the catalyst.

products were identified by comparison of spectral data with those for authentic materials and/or literature results.

It was instructive to compare the results using **1** as the catalyst with representative cationic and neutral rhodium complexes. Substitution of (cycloocta-1,5-diene)bis(triphenylphosphine)rhodium(I) tetraphenylborate, $[(Ph_3P)_2Rh(cod)]^+BPh_4^-$ **5**,[3] for **1** in the reaction of styrene resulted in a 90% yield of alcohols. Unfortunately, the regioslectivity observed (branched = linear, 64:36) when **5** was the catalyst is clearly inferior to that found using **1**. The neutral complex, hydridocarbonyltris(triphenylphosphine) rhodium **6**[4–8] is also an effective catalyst for the reductive carbonylation of styrene (92% yield), but again the regioselectivity (80:20, **3**:**4**) for production of **3**, R = Ph, is considerably lower than that observed using **1** as the catalyst. The superiority of the zwitterionic rhodium catalyst in terms of product selectivity was again found when *p*-methylstyrene was used as the alkene (see Table 1 for results). Furthermore, while *p*-chlorostyrene gave the least favourable branched to linear ratio (3:1) of any styrene derivative when **1** was employed as the catalyst, use of the cationic rhodium hydride **5** resulted in alkene polymerization while the neutral hydride **6** converted **2**, R = *p*-ClC_6H_4, to *p*-chloroethylbenzene in 10% yield with the remainder being recovered starting material. In contrast to *p*-chlorostyrene, the *p*-fluoro analogue reacted in the presence of **1** to form **3** and **4** in a 91:9 ratio. Good regioselectivity for **3** was also observed in the case of *p*-isobutylstyrene and *p*-methoxystyrene.

A simple aliphatic monoalkene such as dec-1-ene displays little regiochemical control in the reductive carbonylation reaction using **1**, **5** or **6** as catalysts, although product yields are good. However, if the R group of **2** is quite bulky [*e.g.* *tert*-butyl, cyclohexyl, cyclohex-3-en-1-yl], then good to excellent selectivity for the linear alcohol results using **1** as the catalyst. When limonene and 2-methyl-undec-1-ene, which are 1,1-disubstituted alkenes were used as reactants, then the linear alcohols were isolated in good yield, the reaction having proceeded with excellent regiochemical control.

Finally, it should be noted that sodium triacetoxyborohydride can be used instead of $NaBH_4$ in these reactions, but the chemo- and regio-selectivity is unsatisfactory. For instance, styrene reacts with carbon monoxide and $NaBH(OAc)_3$, in the presence of **1**, to give a mixture of alcohols [16% yield, 59:41, **3**:**4**] and aldehydes [39% yield, 60:40, **3**:**4**].

In summary, the zwitterionic rhodium complex-catalysed carbonylation of alkenes to alcohols usually occurs in high regioselectivity and yield. This research also demonstrates the usefulness of a borohydride for such an organic transformation.

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