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Preliminary communication

Biphasic reduction of unsaturated aldehydes to unsaturated alcohols by ruthenium complex-catalyzed hydrogen transfer

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Abstract

Unsaturated aldehydes can be reduced under very mild conditions (30–80 °C) with good yields and excellent selectivities to the corresponding unsaturated alcohols by hydrogen transfer from $HCOONa/H_2O$ catalyzed by a complex of Ru^{II} with sulphonated triphenylphosphine in aqueous/organic biphasic systems.

Owing to the interest in the selective hydrogenation of a carbonyl function in the presence of C=C double bonds, a number of methods have been developed for this reduction including a few homogeneously catalyzed reactions [1–7]. While cinnamaldehyde can be reduced with good yield and selectivity [2–5], in the case of aliphatic aldehydes side reactions may occur [6]. The complex $RuCl_2(PPh_3)_3$ has proved particularly active as catalyst for hydrogen transfer from formate to aldehydes both in homogeneous [5] and in biphasic systems [8]. In the latter case, however, a phase transfer agent must be added to facilitate the transfer of (hydrated) formate ions from the aqueous phase to the aldehyde- and catalyst-containing organic phase.

The study of water soluble phosphine complexes has led to a number of important applications [9–11]. The main advantage of using an aqueous/organic biphasic reaction mixture lies in the easy and practically complete recovery of the precious metal-based catalysts. During our investigations of these hydrophilic catalysts we have found that unsaturated aldehydes, neat or dissolved in an organic solvent, can be easily and selectively reduced to the corresponding unsaturated alcohols by use of an aqueous solution of HCOONa as hydrogen donor and the water soluble complex of Ru^{II} with *m*-sulphophenyldiphenylphosphine, $RuCl_2(m\text{-}SPPh_2)_2$ [12], as catalyst:

$$RCH{=}CHCHO \xrightarrow[HCOONa_{aq},\ 30\text{–}80\,^{\circ}C,\ N_2]{RuCl_2(m\text{-}SPPh_2)_2\ +\ m\text{-}SPPh_2} RCH{=}CHCH_2OH$$

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Table 1

Selective reduction of unsaturated aldehydes by hydrogen transfer from $HCOONa/H_2O$, catalyzed by $RuCl_2(m\text{-}SPPh_2)_2$ [a]

No.	Substrate	T (°C)	Reaction time (h)	Yield [b] (%)
1	Cinnamaldehyde	80	5	98 (92)
2	Crotonaldehyde	30 [c]	2.5	78
3	1-Citronellal	80	4	93 (90)
4	Citral [d]	80	7	98 (95)

[a] 0.015 mmol Ru, 1 mmol substrate, 11 mmol HCOONa. All substrates and products showed correct NMR spectra. Conditions are not optimized. [b] GLC yields. Isolated yields are in parentheses. [c] Side reactions at 80 °C. [d] Mixture of geranial and neral 2/1. No isomerization was observed.

As can be seen from Table 1, isolated yields are > 90%. Neither hydrogenation of nor isomerization around the olefinic bond was observed, in keeping with the complete lack of reactivity of simple olefins (e.g. 1-decene). Acetophenone and benzylideneacetophenone were recovered unchanged after 3 h at 80 °C. No phase transfer agent is needed for a reasonably fast reaction of aldehydes. A unique advantage of this method over those mentioned above is that the product is easily separated into the organic phase and the catalyst is recovered in the aqueous phase. The system is also useful for the reduction of other aliphatic and aromatic aldehydes, and details will be published elsewhere, together with a discussion of the reaction mechanism, which is currently being investigated.

The following procedure is representative. A catalyst solution was prepared by heating under nitrogen 1 ml of 1 *M* HCOONa solution containing 15 mg (0.015 mmol) of $RuCl_2(m\text{-}SPPh_2)_2$ and 6 mg (0.015 mmol) of m-$SPPh_2$ at 80 °C until a bright yellow solution was formed (2–3 min). A mixture of 1 mmol of the substrate (neat), 2 ml of 5 *M* HCOONa solution, and 1 ml of the former catalyst solution was stirred in a thermostatted ($T \pm 0.2$ °C) flask while nitrogen was passed slowly through the system and the extent of conversion monitored by GLC. When the reaction was complete the mixture was extracted with $CHCl_3$ and the organic phase was washed with water, dried ($MgSO_4$) and evaporated to dryness, to leave the expected alcohol.

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