

Reduction of Carbonyl Compounds by Catalytic Hydrogen Transfer from 1,4-Butanediol

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Z. Naturforsch. **39b**, 1823–1824 (1984);
received April 3, 1984

Hydrogen Transfer, Carbonyl Compounds,
1,4-Butanediol Ruthenium(II) Complexes

Hydrogen transfer from appropriate hydrogen donors to unsaturated substrates catalysed by transition metal complexes offers some advantages over hydrogenation with molecular hydrogen [1]. These reactions have been carried out mainly with stoichiometric or excess amounts of primary or secondary alcohols [2–7], hydroaromatic compounds [8] and formic acid [9] as hydrogen donors.

Although bis primary diols exhibit relatively high propensity for hydrogen donation [10, 11], little attention has been paid to the employment of these compounds as the source of hydrogen in hydrogenation reactions. The aim of the present investigation was to examine the potential use of 1,4-butanediol as the source of hydrogen in the catalytic reduction of carbonyl compounds, using ruthenium(II) complexes as homogeneous catalysts.

Experimental

Carbonyl compounds and 1,4-butanediol were commercial products, and were distilled before use.

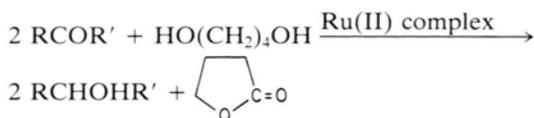
Ruthenium(II) complexes, RuHClCO(PPh₃)₃ [12], RuCl₂(PPh₃)₃ [13] and RuH₂(PPh₃)₄ [14] were prepared by published methods.

In a typical hydrogen transfer experiment, carbonyl compound (10 mmol), 1,4-butanediol (5 mmol) and ruthenium(II) complex (0.03 mmol) were placed in a glass ampoule, and the air was replaced with nitrogen. The sealed ampoule was placed in a thermostated oil bath and heated at 140 °C for 20 h. Reaction products were analysed by GLC. The analysis was carried out with a HP 5790 apparatus connected to a HP 3390 A calculating integrator. Separation of reaction products was accomplished using Carbowax 20 M on a Chromosorb WHP 80/110 mesh column.

Results and Discussion

In the reaction between equimolar quantities of carbonyl compounds and 1,4-butanediol in the presence of catalytic amounts of ruthenium(II) com-

plexes, carbonyl compounds were reduced to corresponding alcohols, while 1,4-butanediol was converted to γ -butyrolactone:



The reactions were carried out in bulk without solvent, and some representative results are presented in Table I. Among ketones an excellent yield was observed for the reduction of cyclohexanone to cyclohexanol. By increasing the ring size of the cyclic ketone, the yield on the cyclic alcohol dropped considerably. This is probably caused by steric hindrance of the more bulky groups. Aryl alkyl ketones were reduced to secondary alcohols in good yields. In contrast, 4-methyl-2-pentanone is relatively resistant to reduction. When ketones were reduced with secondary alcohols as hydrogen donors, the maximum yield of the reduced product was determined by the equilibrium existing in such systems [2]. This is not the case in the system presented here, where the yield of the reduced product was determined kinetically.

In the reduction of α,β -unsaturated ketones, the C=C bond undergoes reduction before the carbonyl group. However, addition of the second equivalent of 1,4-butanediol caused reduction of a saturated

Table I. Reduction of carbonyl compounds by hydrogen transfer from 1,4-butanediol catalysed by RuHClCO(PPh₃)₃.

Carbonyl compound	Product	Yield [%] ^a
Cyclohexanone	Cyclohexanol	95
Cycloheptanone	Cycloheptanol	58
Cyclooctanone	Cyclooctanol	24
Acetophenone	1-Phenylethanol	65
Propiophenone	1-Phenylpropanol	70
Benzophenone	Diphenylcarbinol	70
4-Methyl-2-pentanone ^b	4-Methyl-2-pentanol	37
Benzylidenacetone	4-Phenyl-2-butanone	91
	4-Phenyl-2-butanol	4
Mesityl oxide	4-Methyl-2-pentanone	93
Benzaldehyde	Benzylalcohol	87
1-Hexanal	1-Hexanol	88
Cinnamic aldehyde	3-Phenylpropanal	8
	Cinnamic alcohol	16
Crotonaldehyde ^c	Butanal	28
	2-Buten-1-ol	6

Conditions: carbonyl compound (10 mmol), 1,4-butanediol (5 mmol) RuHClCO(PPh₃)₃ (0.03 mmol), T = 140 °C, Time = 20 h; ^a determined by GLC analysis and based on the amount of carbonyl compound used; ^b dibutyl ether (2 ml) as solvent; ^c T = 90 °C.

ketone to the corresponding alcohol in 60% yield. Similar observations were reported for hydrogen transfer from 2-propanol to α,β -unsaturated ketones catalysed by iridium(I) complexes [15].

Among aldehydes, benzaldehyde and hexanal were efficiently reduced to primary alcohols. This is not the case with cinnamic aldehyde and crotonaldehyde. Besides low yields of saturated aldehydes and unsaturated alcohols, condensation side products were observed. This may be due to the stabilisation by resonance between C=C and C=O bonds and coordination to the metal center as bidentate ligand, blocking the coordination of hydrogen donor.

In separate experiments, the catalytic activities of ruthenium(II) complexes in the reaction between cyclohexanone and 1,4-butanediol have been examined. Thus after 1 h of the reaction, the extent of reduction decreased in the sequence, $\text{RuHClCO}(\text{PPh}_3)_3$ (78%), $\text{RuCl}_2(\text{PPh}_3)_3$ (68%) and $\text{RuH}_2(\text{PPh}_3)_4$ (46%).

The results obtained here demonstrate, that stoichiometric amounts of 1,4-butanediol can be successfully explored as hydrogen donors in the catalytic reduction of aldehydes and ketones in bulk without solvent, producing primary and secondary alcohols in satisfactory yields.

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