Ruthenium(II)–BINAP† Catalysed Stereoselective Homogeneous Hydrogenation of 1,3-Diketones

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Ruthenium–BINAP† catalysed hydrogenation of 1,3-diketones gives 1,3-diols with extremely high diastereo- and enantio-selectivity.

Catalytic asymmetric hydrogenation of prochiral alkenes has been extensively investigated and various homogeneous catalysts, most of which are rhodium based, have been developed.[1] However, far fewer transition metal complexes have been found which effect practical enantioselectivity [>90% enantiomeric excess (e.e.)] in the asymmetric hydrogenation of ketones.[2] Here we report that the chiral ruthenium complex, $Ru_2Cl_4[(R)\text{–BINAP}]_2(NEt_3)$[3] (**1**),† has been used as an efficient catalyst for the asymmetric hydrogenation of 1,3-diketones.

When pentane-2,4-dione (**2a**) was hydrogenated in the presence of 0.2 mol% of (**1**) for 20 h under a pressure of 50 kgw/cm^2 (1 kgw/cm^2 = 9.81 × 10^4 Pa) of H_2 at 50 °C in methanol, pentane-2,4-diol (**3a**) was isolated in 98% yield after simple bulb-to-bulb distillation. The optical rotation and ^{1}H n.m.r. analysis of its (*R*)-MTPA[5] ester† showed the product to be substantially pure *R*,*R*-isomer (**3a**), contaminated with a trace amount of the *syn*-isomer (**4a**). The results obtained using several 1,3-diketones are summarised in Table 1.

Most of the 1,3-diketones (**2a**—**e**) were smoothly hydrogenated to give the corresponding *anti*-1,3-diols (**3a**—**e**) with excellent diastereoisomeric and enantiomeric excesses. Under the same reaction conditions, the hydrogenation of 1-phenylbutane-1,3-dione (**2f**) yielded predominantly 3-hydroxy-1-phenylbutan-3-one (**5f**), the β-hydroxyketone produced by selective reduction of the acetyl carbonyl of (**2f**). This diketone needed harsh conditions to be fully hydrogenated to the 1,3-diol (**3f**). The isolation of (**5f**) indicates the stepwise formation of 1,3-diols from 1,3-diketones *via* β-hydroxyketones as intermediates.

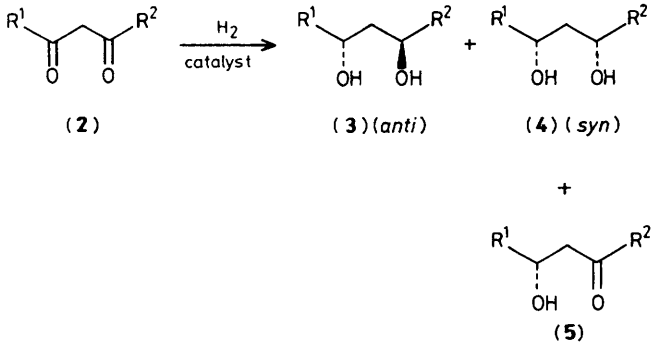
A simple monoketone (pentan-2-one) was hardly hydrogenated under the reaction condition stated above. Chelating interaction between the 1,3-dicarbonyl group of the substrate and the ruthenium catalyst is thought to play a crucial role in the catalytic cycle. Hydrogenation of butane-2,3-dione (a 1,2-diketone) and hexane-2,5-dione (a 1,4-diketone) gave complex mixtures of high boiling point by-products, which have not been identified.

Table 1. Catalytic hydrogenation of 1,3-diketones.[a]

Diketone	Yield of alcohols/%	Ratio of product (**3**) : (**4**) : (**5**)	E.e. of major product[b]/%
(**2a**)	98	99 : 1 : —	>99
(**2b**)	89	94 : 6 : —	94
(**2c**)	92	97 : 3 : —	98
(**2d**)	84	91 : 9 : —	98
(**2e**)	92	98 : 2 : —	96
(**2f**)	89	2 : — : 98	98
(**2f**)	58[c]	89 : 9 : 2	99

[a] Typical reaction conditions: diketone (10 mmol), catalyst (**1**) (0.02 mmol), methanol solvent, hydrogen pressure 50 kgw/cm^2, 50 °C, 20 h. [b] Absolute configuration of each dominant enantiomer is shown in Scheme 1. [c] Hydrogen pressure 100 kgw/cm^2, 100 °C. Low boiling point by-product was produced in 32% yield.

† BINAP = 2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl;[4] MTPA = methoxy(trifluoromethyl)phenylacetyl.



(**a**); R^1 = Me, R^2 = Me
(**b**); R^1 = Me, R^2 = Et
(**c**); R^1 = Me, R^2 = Pr^i
(**d**); R^1 = Me, R^2 = Bu^i
(**e**); R^1 = Et, R^2 = Et
(**f**); R^1 = Me, R^2 = Ph

Scheme 1

The present reaction has some characteristic features in that it is the first example of the hydrogenation of 1,3-diketones using homogeneous catalysis, two asymmetric centres are catalytically introduced into a prochiral substrate with excellent diastereo- and enantio-selectivity, and *anti*-1,3-diols are selectively obtained. Only a limited number of selective hydride reduction methods which give *anti*-1,3-diols have been developed previously[6] and it should be noted that the chiral β-hydroxyketone obtained from the diketone having a phenyl substituent should also be a promising intermediate for *anti*- and *syn*-1,3-diols, because efficient procedures for diastereoselective reduction of β-hydroxyketones have been developed.[6,7] Thus the present reaction not only introduces a novel class of stereoselective reaction using a transition metal complex as catalyst, but should also provide a powerful tool for organic synthesis.

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