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Rhodium versus ruthenium: contrasting behaviour in the asymmetric transfer hydrogenation of α-substituted acetophenones

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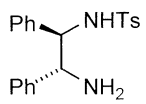
Abstract—The reduction of a number of α-substituted acetophenones has been achieved using both ruthenium(II)- and rhodium(III)-based asymmetric transfer hydrogenation catalysts employing formic acid as the hydrogen donor.

1. Introduction

The asymmetric transfer hydrogenation of ketones, which offers a convenient route to enantiomerically pure secondary alcohols, has been the subject of a number of investigations in our group.[1] The use of formic acid as the hydrogen donor offers the possibility of performing the reaction under essentially irreversible conditions. In order to utilise formic acid as the hydrogen donor, monotosylated diamines offer the best option for use as ligands.[2] In particular Noyori's *N*-(*para*-toluenesulfonyl)-1,2-diphenylethylene diamine (TsDPEN) is possibly the optimal ligand of this type for the ruthenium(II)-catalysed asymmetric transfer hydrogenation of ketones and imines and the rhodium(III)-catalysed asymmetric transfer hydrogenation of imines.[3] As yet there has been no reported rhodium-catalysed asymmetric transfer hydrogenation of ketones using formic acid as the hydrogen donor. Herein we report the results of our studies on the asymmetric transfer hydrogenations of α-tosyl ketones using both rhodium and ruthenium systems.



(*R,R*)-TsDPEN

2. Results and discussion

α-Tosyloxyacetophenone **1** was synthesised from acetophenone in two steps in an overall yield of 69% using the hypervalent iodine compound hydroxytosyliodobenzene (HTIB).[4] It was anticipated that, following reduction of the carbonyl group, the alcohol would either spontaneously cyclise to eliminate the tosyloxy group or could be isolated so that such a transformation could be performed in a separate step. Upon reduction using formic acid as the hydrogen donor and the pentamethylcyclopentadienyl rhodium-based catalyst, 2-tosyloxy-1-phenylethanol **2** was obtained in 65% yield (Scheme 1). Upon reduction using $LiAlH_4$ the tosyloxy group was removed to yield (*R*)-1-phenylethanol **3** which was shown to be of 93% e.e. by using chiral HPLC.[1b]

However, when the same substrate **1** was exposed to the reduction conditions using the ruthenium(II)-based catalyst, a cyclic carbonate was isolated with no evidence of either the expected alcohol or epoxide. The carbonate was converted to (*S*)-1-phenylethan-1,2-diol **5** by reaction with base. Chiral HPLC analysis of the diol showed it to be of >94% e.e. These two results seem remarkable because the only difference between the sets of reaction conditions are the metal complex and the temperature (the Rh-catalysed reaction was performed at room temperature, ca. 20°C, and the Ru-catalysed reaction at ca. 30°C). To prove that the temperature was not the decisive factor in the formation of the

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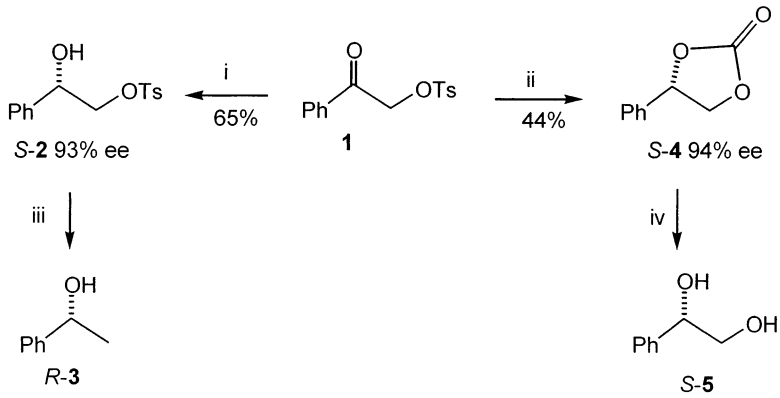
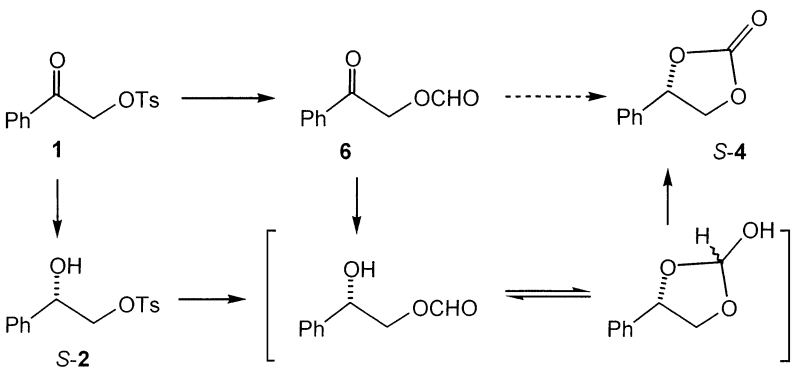


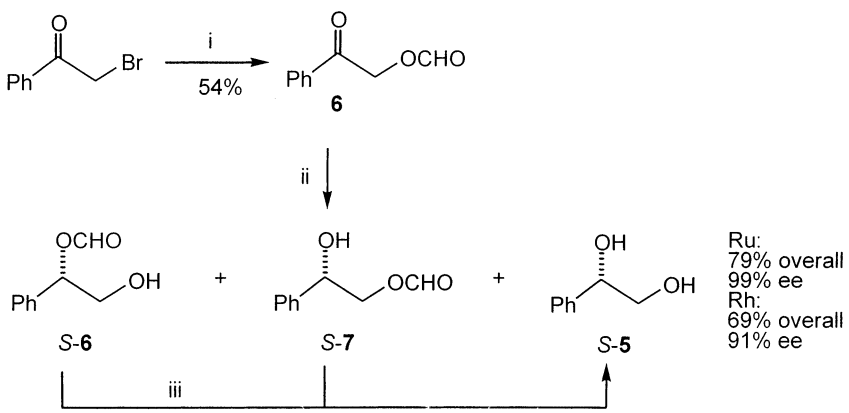
Scheme 1. *Reagents and conditions*: (i) 0.25 mol% $[Rh(C_5Me_5)Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), rt; (ii) 0.25 mol% $[Ru(p\text{-cymene})Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), rt; (iii) $LiAlH_4$, THF, 0°C to rt; (iv) Et_2O, NaOH, 0°C to rt.

carbonate the rhodium-catalysed transfer hydrogenation was repeated at 30°C. This again resulted in formation of **2** in the lower yield of 35% but with identical e.e.

We wished to investigate the mechanism for the formation of the carbonate. The first step may be either displacement of the tosyloxy group by formic acid or reduction of the ketone. As the displacement of the tosyloxy group is much more likely to have taken place in the ketone rather than the alcohol we drew up a possible mechanism for this pathway (Scheme 2). In an attempt to prove this mechanism, phenacyl formate **6** was synthesised and reduced under the standard conditions for the ruthenium-based catalyst (Scheme 3).



Scheme 2. Possible routes to carbonate **4**.



Scheme 3. *Reagents and conditions*: (i) NaOCHO, DMF, rt; (ii) 0.25 mol% $[Ru(p\text{-cymene})Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), 28°C or 0.25 mol% $[Rh(C_5Me_5)Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), rt; (iii) Et_2O, NaOH, 0°C to rt.

However, no carbonate could be identified in the crude ^{1}H NMR of the reduction and there appeared to be only a mixture of the three products **5**, **7** and **8**. Stirring this crude mixture with base afforded 1-phenylethan-1,2-diol **5** as the only product in 79% yield and 99% e.e. (Scheme 3). Phenacyl formate **6** was also reduced using the rhodium-based asymmetric transfer hydrogenation catalyst and the crude mixture converted to 1-phenylethan-1,2-diol **5** by stirring with base to afford the diol in 69% yield and 91% e.e. (Scheme 3).

Having established that the mechanism for the formation of the carbonate does not involve the intermediate phenacyl formate we subjected alcohol **2** to reduction using the ruthenium-based catalyst. Carbonate **4** was formed in 70% yield together with 1-phenylethan-1,2-diol **5** in 15% yield (Scheme 4). This result suggests that the mechanism for the carbonate formation must proceed via the alcohol with reduction being the first step of the process.

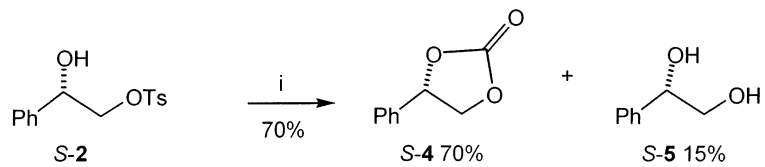
We considered the possibility that the carbonate may have been the result of epoxide formation followed by carbon dioxide insertion. Such processes have recently been reported to be catalysed by certain metal complexes.[5] We subjected racemic styrene oxide to the reduction conditions; however, no carbonate was formed, suggesting that the epoxide is not an intermediate in its formation. A further possibility is that the carbon dioxide originates from ruthenium-catalysed decomposition of the formic acid, a process which we are currently investigating.

The results so far have given us two separate pathways to synthesise 1-phenylethan-1,2-diol in high e.e. The final and most obvious way to achieve this is via the reduction of α-hydroxyacetophenone **9**. Remarkably this can be achieved directly using both the ruthenium and rhodium systems (Scheme 5). The successful reduction of this substrate was surprising as the hydroxy group was expected to bind to the metal centre of the catalyst leading to deactivation of the catalyst.[1d]

α-Haloacetophenones can also be reduced using asymmetric transfer hydrogenation to furnish 2-halo-1-phenylethanols. Commercially available α-chloroacetophenone **10** is reduced by both the ruthenium- and rhodium-based catalysts to give (*S*)-2-chloro-1-phenylethanol **11** in good yield and e.e. (Scheme 6). The ruthenium-based catalyst is the more enantioselective giving the product with e.e. of 85%.

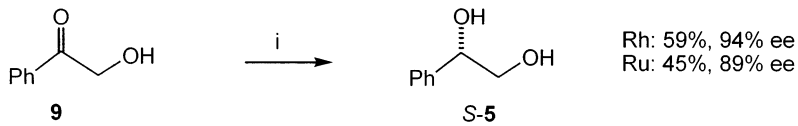
The reduction product for the asymmetric transfer hydrogenation of α-bromoacetophenone **12** is dependent upon the metal catalyst. The rhodium-based catalyst, at room temperature, will reduce the carbonyl group to give (*S*)-2-bromo-1-phenylethanol in only 15% yield and 5% e.e. (not illustrated). The low yield can be attributed to the fact that a bromide ion is a better leaving group than a chloride ion and the formate displacement reaction operates in competition with the reduction. Phenacyl formate was isolated in 44% yield.

Although no products from the reduction of phenacyl formate were isolated during this reaction, when it was repeated at the higher temperature of 30°C the reaction afforded a mixture of compounds. This mixture was too complicated to isolate each compound individually. After stirring with excess NaOH only (*R*)-1-phenylethan-1,2-diol **5** was isolated in any significant amount (23% yield and 5% e.e.). This enantiomer is the opposite of what we would have expected, as only the (*S*)-enantiomer of each compound had been isolated previously.



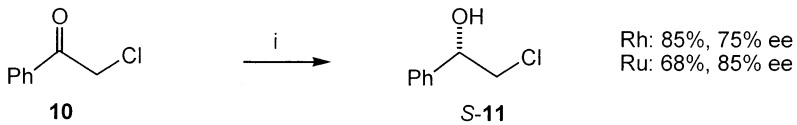
S-**2** *S*-**4** 70% *S*-**5** 15%

Scheme 4. *Reagents and conditions*: (i) 0.25 mol% $[Ru(p\text{-cymene})Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), 28°C.



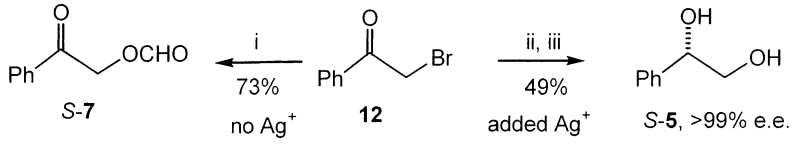
9 *S*-**5**

Scheme 5. *Reagents and conditions*: (i) 0.25 mol% $[Rh(C_5Me_5)Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), rt or 0.25 mol% $[Ru(p\text{-cymene})Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), 28°C.



10 *S*-**11**

Scheme 6. *Reagents and conditions*: (i) 0.25 mol% $[Rh(C_5Me_5)Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), rt or 0.25 mol% $[Ru(p\text{-cymene})Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), 28°C.



Scheme 7. *Reagents and conditions*: (i) 0.25 mol% $[Ru(p\text{-cymene})Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), 28°C; (ii) 0.25 mol% $[Ru(p\text{-cymene})Cl_2]_2$, 0.5 mol% (*R*,*R*)-TsDPEN, HCO_2H, Et_3N (5:2 molar ratio), 28°C, AgOTs; (iii) Et_2O, NaOH.

When the ruthenium-based catalyst was employed in the reduction of α-bromoacetophenone only phenacyl formate was isolated in 73% yield with no sign of any reduction of the product or substrate (Scheme 7). As we already knew that phenacyl formate was a viable substrate for reduction it was hypothesised that the bromide ions released by the displacement reaction may be inhibiting the catalyst from performing any reduction. To test this theory the reaction was repeated with the addition of silver tosylate to remove any bromide ions formed by displacement and the crude reaction mixture was stirred with sodium hydroxide to give (*S*)-1-phenylethan-1,2-diol **5** as the only product in>99% e.e. (Scheme 7).

3. Conclusions

In conclusion, we have demonstrated that the ruthenium(II)- and rhodium(III)-TsDPEN systems for transfer hydrogenation of ketones can give sharply contrasting results for certain substrates. A convenient synthetic approach has been developed for the preparation of enantiomerically enriched α-hydroxy and α-tosyl alcohols.

4. Experimental

4.1. Synthesis of hydroxytosyloxyiodobenzene (HTIB)

Toluene sulfonic acid monohydrate (5.7 g) was added to a solution of iodobenzene diacetate (9.66 g) in acetonitrile (150 mL) and stirred overnight at rt. Following this time the reaction mixture was concentrated in vacuo and the crude product recrystallised (methanol/ethylacetate) to give HTIB (10.59 g, 94%). ^{1}H NMR (300 MHz, DMSO): δ 9.5 (1H, br s, OH), 8.2 (2H, m, *J* 8.0 Hz, ArH), 7.9–7.2 (5H, m, Ph), 7.1 (2H, m, *J* 8.0 Hz, ArH), 2.3 (3H, s, CH_3).[6]

4.2. Synthesis of α-tosyloxyacetophenone 2

Hydroxytosyloxyiodobenzene (3 g) was added to a stirred solution of acetophenone (0.9 g) in acetonitrile (60 mL). The reaction mixture was stirred under reflux for 2 h, cooled to rt and then concentrated in vacuo. Ethanol (2 mL) was added and the mixture was left overnight in a fridge. The suspension was then filtered and the solid washed with cold ethanol to give white crystals. Ethanol (1 mL) was added to the filtrate and the solution was left in the fridge overnight. The suspension was filtered, washed with cold ethanol and the crystals combined with the first batch to afford α-tosyloxyacetophenone (1.6 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.9–7.7 (4H, m, Ar/Ph), 7.6–7.3 (5H, m, Ar/Ph), 5.3 (2H, s, CH_2), 2.4 (3H, s, CH_3).[4,7]

4.3. General procedure for asymmetric transfer hydrogenation using rhodium

Pentamethylcyclopentadiene rhodium chloride dimer (6.2 mg, 0.01 mmol) and (1*R*,2*R*)-TsDPEN (7.3 mg, 0.02 mmol) were stirred in a formic acid–triethylamine mixture (2 mL, 5:2 molar ratio) in a flame dried Schlenk under a nitrogen atmosphere for 20 min. Ketone (4 mmol) was added and the reaction was stirred at rt until the substrate had been consumed by TLC (typically 12–48 h). The reaction mixture was then filtered through a plug of silica and washed with ethyl acetate (2×50 mL). The organic fractions were collected, combined and concentrated in vacuo to give the crude product. This was purified by flash column chromatography (5–20% v/v ethyl acetate/hexane) to give the product.

4.4. General procedure for asymmetric transfer hydrogenation using ruthenium

(*p*-Cymene)ruthenium chloride dimer (6.2 mg) and (*R*,*R*)-TsDPEN (7.3 mg) were stirred in a formic acid–triethylamine mixture (2 mL, 5:2 molar ratio) in a flame dried Schlenk under a nitrogen atmosphere at 28°C for 20 min. Ketone (4 mmol) was added and the reaction was stirred at 28°C until the substrate had disappeared by TLC (typically 48 h). The reaction mixture was then filtered through a plug of silica and washed with ethyl acetate (2×50 mL). The organic fractions were collected, combined and concentrated in vacuo to give the crude product which was purified by flash column chromatography (5–20% ethyl acetate in hexane) to give the product.

4.5. Reduction of 2-tosyloxy-1-phenylethanol 2 to 1-phenylethanol 3

2-Tosyloxy-l-phenylethanol (0.25 g) was carefully added to a stirred suspension of lithium aluminium hydride (0.15 g) in freshly distilled THF (5 mL) at 0°C in a flame dried round bottom flask under nitrogen. The reaction mixture was allowed to warm to rt and stirred overnight. Sodium sulfate decahydrate (0.3 g) was added carefully and the reaction was stirred for 1 h. The suspension was then filtered through Celite and concentrated in vacuo to give the crude product which was purified by flash column chromatography (5–10%

ethyl acetate in hexane) to afford 1-phenylethanol (27 mg, 26%).

4.6. Carbonate hydrolysis to prepare diol 5

Sodium hydroxide (10 mL, 2 M) was added to the crude reaction mixture (approx. 4 mmol) dissolved in diethyl ether (10 mL) at 0°C. The reaction mixture was allowed to warm to rt and stirred for 2 h. The reaction mixture was extracted with ethyl acetate (3×25 mL) and the organic fractions were collected, combined, washed with brine (10 mL), dried (Na_2SO_4) and concentrated in vacuo to give 1-phenylethan-1,2-diol **5**.

4.7. Synthesis of phenacyl formate 6 from α-bromoacetophenone 12

α-Bromoacetophenone (4 g) and sodium formate (0.77 g) were stirred in DMF (40 mL) at rt for 12 h. Water (50 mL) was added and the reaction mixture was extracted into ether (3×100 mL). The ethereal layers were collected, combined, dried ($MgSO_4$) and concentrated in vacuo to give the crude product which was purified by Kugelrohr distillation to give phenacyl formate (1.75 g, 54%).[8]

4.8. 2-Tosyloxy-l-phenylethanol 2

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7 (2H, d, J 8.3 Hz, ArH), 7.32–7.28 (7H, m, Ar/Ph), 4.9 (1H, m, C*H*OH), 4.1 (1H, dd, J 10.3, 3.3 Hz, C*H*HOTs), 4.0 (1H, dd, J 10.3, 8.4 Hz,, CH*H*OTs), 2.9 (1H, br s, CHO*H*), 2.4 (3H, s, CH_3),[9] $[\alpha]_{18}^{D}$ = +48.9 (c 1.15, $CHCl_3$) corresponding to 93% e.e. as demonstrated by reduction to 1-phenylethanol.

4.9. 1-Phenylethanol 3

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31–7.24 (5H, m, ArH), 4.87 (1H, dq, J 6.4, 3.1 Hz, C*H*OH), 2.2 (1H, brs, OH), 1.50 (3H, d, J 6.4 Hz, CH_3). HPLC analysis (Chiracel OD, 250×4.6 mm), hexane:ethanol: diethylamine = 95:5:0.1 (0.5 mL/min), (*R*) isomer 14.55 min, (*S*) isomer 17.16 min.[1d]

4.10. Cyclic carbonate 4

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 –7.35 (5H, m, ArH), 5.68 (1H, dd, J 8.5, 8.3 Hz, C*H*H), 4.81 (1H, dd, J 8.5, 8.3 Hz, CH*H*), 4.24 (1H, dd, J 8.1 and 8.5 Hz, CH).[10] $[\alpha]_{22}^{D}$ = +51.2 (c 1.0, $CHCl_3$) corresponding to 94% e.e. as demonstrated by hydrolysis to the 1-phenylethan-1,2-diol.

4.11. 1-Phenylethan-1,2-diol 5

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.2–7.1 (5H, m, ArH), 4.6 (1H, dd, J 3.4, 8.3 Hz, C*H*OH), 4.4 (1H, brs, OH), 4.1 (1H, brs, OH), 3.51 (1H, dd J 3.4, 11.7 Hz, C*H*H), 3.43 (1H, dd, J 8.4, 11.7, CH*H*). $[\alpha]_{18}^{D}$ = +65.5 (c 1.25, $CHCl_3$) corresponding to 94% (*S*) e.e. HPLC analysis (Chiracel OD, 250×4.6 mm, hexane:*iso*-propanol: diethylamine = 90:10:0.1, 0.5 mL/min), (*R*) isomer 21.73 min, (*S*) isomer 23.65 min.[11]

4.12. Phenacyl formate 6

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.2 (1H, s, C*H*O), 7.5–7.2 (5H, m, Ph), 5.35 (2H, s, CH_2).[8]

4.13. 2-Chloro-l-phenylethanol 11

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (5H, m, Ph), 4.8 (1H, dd, J 3.5, 3.6 Hz, C*H*OH), 3.7 (1H, dd, J 3.6, 8.7 Hz, C*H*HCl), 3.6 (1H, dd, J 8.7, 3.6 Hz, CH*H*Cl), 2.8 (1H, br s, CHO*H*). HPLC analysis (Chiracel OD, 250× 4.6 mm, hexane:ethanol:diethylamine 95:5:0.1, 0.5 mL/ min), (*S*) isomer 18.45 min, (*R*) isomer 22.79 min.[12,13]

4.14. 2-Bromo-l-phenylethanol 13

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5–7.2 (5H, m, Ph), 4.9 (1H, m, C*H*OH), 3.6 (1H, dd, J 3.6 and 10.5 Hz, C*H*HBr), 3.5 (1H, dd, J 10.5 and 8.9 Hz, CH*H*Br), 2.8 (1H, d, J = 3.2 Hz, CHO*H*). HPLC analysis (Chiracel OD, 250×4.6 mm, hexane:ethanol:diethylamine 95:5:0.1, 0.5 ml/mL), (*S*) isomer 19.24 min, (*R*) isomer 23.37 min.[12]

Acknowledgements

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