Journal of Organometallic Chemistry 693 (2008) 3131–3134

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Enantioselective reductions of [m] ferrocenophanones

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ARTICLE INFO

Article history:
Received 3 June 2008
Received in revised form 26 June 2008
Accepted 1 July 2008
Available online 10 July 2008

Keywords:
Ferrocenophane
Enantioselective reduction
Oxazaborolidine

ABSTRACT

Enantioselective reductions of prochiral ferrocenophane ketones were investigated. Oxazaborolidine mediated reduction led to corresponding chiral alcohols generally in good yields and enantioselectivities up to 97% ee. Ruthenium-catalyzed transfer hydrogenation was rather unsuccessful in reducing cyclic ferrocene ketones. Proline-derived activator together with trichlorosilane also proved to be an effective method for some substrates (up to 99% ee). Pronounced tendency of α-ferrocenyl ketones toward reductive deoxygenation was studied by DFT computational methods.

1. Introduction

Enantioselective reduction of unsymmetrical ketones is one of the key strategies for preparation of chiral alcohols. During past decades large number of stoichiometric [1] as well as catalytic methods has been developed. Among catalytic methods, various boron-mediated transformations [2–4] attracted much attention, because of their reliability and generally high enantioselectivities. From transition metal mediated reductions, chiral rhodium, iridium and especially ruthenium complexes catalyzed reductions and hydrogen transfer reactions proved effective for a wide range of substrates [5,6]. Although many protocols for enantioselective ketone reductions have been developed, reductions of specialized substrates are not always simple.

Ferrocenophanes, bridged ferrocene derivatives, were utilized as a scaffold for preparation of chiral ligands for asymmetric catalysis [7–9]. During our studies of ferrocenophane-based ligands [10,11] we repeatedly come across a problem of generation of stereogenic center in the carbon-bridge of these molecules. Introduction of oxo functionality into ferrocenophane derivatives is rather straightforward, thus enantioselective reduction of corresponding ketones appears as a sensible way for incorporation of chiral information. The resulting enantiomerically enriched alcohols are precursors for synthesis of chiral ligands. Therefore, we decided to investigate possibilities of enantioselective reduction of ferrocenophane ketones in more detail. Easy access to ferrocenophane alcohols with high enantiomeric purity would streamline synthesis of new chiral derivatives based on this scaffold.

In this paper, we present studies of enantioselective reductions of several ferrocenophane ketones.

2. Results and discussion

At the beginning we chose oxazaborolidine-mediated Corey–Bakshi–Shibata (CBS) reduction [12,13], because it is an efficient protocol for reduction of various acylferrocenes. Reeves and co-workers showed that simple acylferrocenes were reduced with high enantioselectivities by CBS-method [14]. Later Knochel and co-workers extended use of this reaction also to diketones and functionalized ketones [15–19]. Schmalz used CBS-reduction successfully on bisferrocenyl diketones [20].

Under standard conditions (20–50% of CBS, 0 °C), oxazaborolidine-mediated reduction of ketones **1**–**3** and **7** (Scheme 1) proceeded quickly, with good to excellent enantioselectivities (Table 1). Yields of corresponding alcohols were often lowered because of competitive reductive deoxygenation, therefore, the progress of reactions must be carefully monitored.

Under optimized conditions, reduction of ketone **1** proceeded in high yields but the best enantioselectivity was only 80% ee. Decrease of enantioselectivity was observed at temperatures bellow 0 °C, what could be explained by formation of less active catalyst dimer [21]. Small decrease of enantioselectivity was observed also at 50 °C and alcohol **4** was accompanied also by product of deoxygenative reduction (ferrocene-1,1′-propandiyl, 10% yield). Catalyst prepared from $PhB(OH)_2$ or $B(MeO)_3$, instead of $MeB(OH)_2$, afforded alcohol **4** in high yields (98% and 99%) yield but only with

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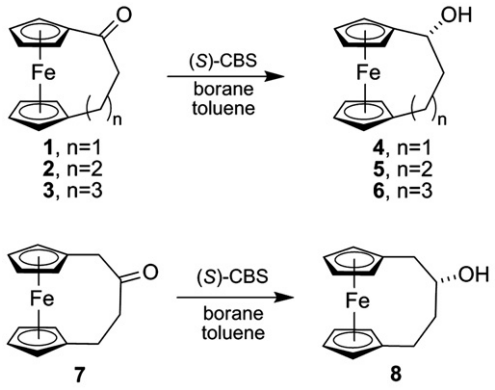
doi:10.1016/j.jorganchem.2008.07.004



Scheme 1.

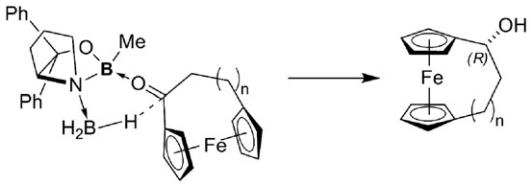
low enantioselectivities (8% and 20% ee, respectively). Use of catecholborane as a source of hydrogen resulted in rapid and entire reductive deoxygenation to alkane. Ketone **2** was reduced using 30 mol% of CBS-catalyst with 77% ee and optical purity of alcohol **5** degraded after recrystallization. Increasing catalyst loading to 50 mol% led to considerable improvement of enantioselectivity (96% ee). Highly enantioselective reaction was also observed with ketone **3**. The corresponding alcohol **6** was isolated in 70% yield and 97% ee (almost enantiomerically pure product (99% ee) can be obtained after one recrystallization from Et_2O). Reduction of ketone **7** afforded alcohol **8** again with medium enantioselectivity (78% ee). It is, however, interesting result because ketone **7** could be considered as aliphatic, which are generally more difficult substrates.

Alcohols **4** and **6,** obtained by CBS-reduction, have (*R*)-absolute configuration. For alcohol **4**, optical rotatory data were compared with the literature [22]. X-ray structures of compounds derivatived from alcohol **6** established (*R*)-configuration of stereogenic center [10,11]. These observations can be explained by Corey's model for prediction of stereochemical outcome of oxazaborolidine reductions, applied to ferrocenophane ketones (Scheme 2). Configuration of alcohols **5** and **8** was assigned also as (*R*) by analogy with compounds **4** and **6**, assuming same stereochemical course of CBS-reduction of corresponding ketones.

Ruthenium-catalyzed hydrogen transfer reduction of ketones is, for its operational simplicity, often a useful alternative to hydrogenations that use hydrogen. Recently, several ferrocenyl alcohols were produced by this method in good yields and with enantioselectivities up to 98% ee [23]. Patti showed that in 1-ferrocenyl-1,3-diketones only more distant oxo group from ferrocene moiety was reduced by transfer hydrogenation [24]. Our investigation shows that cyclic ferrocene ketones are difficult substrates for hydrogen transfer reaction. Using Ru/TsDPEN catalyst (**9**) (Fig. 1) and sodium formiate as hydrogen source, only ketones **1** and **7** were reduced

Table 1
CBS-reduction of ketones **1**–**3** and **7**

Substrate	CBS (mol %)	Borane	Temperature	Yield (%)	ee (%)
1	20	$BH_3 \cdot SMe_2$	0	99	78 (*R*)
1	30	$BH_3 \cdot SMe_2$	0	99	80 (*R*)
1	30	$BH_3 \cdot SMe_2$	−5	98	52 (*R*)
1	30	$BH_3 \cdot SMe_2$	−20	99	17 (*R*)
1	30	$BH_3 \cdot SMe_2$	50	83	70 (*R*)
1	30	Catecholborane	−78	0	–
2	30	$BH_3 \cdot SMe_2$	−5	73	77 (*R*)
2	50	$BH_3 \cdot SMe_2$	−5	67	96 (*R*)
3	30	$BH_3 \cdot SMe_2$	−5	70	97 (*R*)
7	50	$BH_3 \cdot SMe_2$	−5	78	80 (*R*)



Scheme 2.

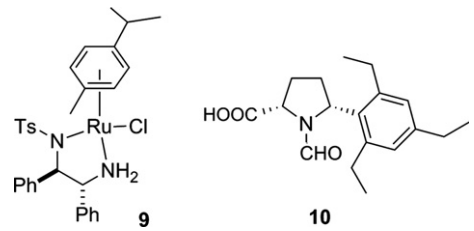


Fig. 1. Structure of Ru/TsDPEN complex (**9**) and proline-based activator (**10**).

with mediocre enantioselectivities (56% yield, 50% ee and 49% yield, 6% ee, respectively). In water, alcohol **4** was obtained only in 25% yield. Insolubility of starting material in water was considered as a possible reason for low yield. Using ionic liquid [emim]$EtOSO_3$ as reaction medium led to increase of yields alcohols **4** and **8**. Interestingly, no reaction was observed with ketones **2** and **3** and only starting materials were isolated (see Table 2).

Reduction using Cl_3SiH with proline-based activator **10** (Fig. 1) was recently showed to be an efficient protocol for various aromatic ketones. Also acetylferrocene was reduced in 99% yield and with more than 99% ee by this method [25]. Therefore, we were interested whether it will be also suitable for cyclic ferrocene ketones. Ketone **1** was at room temperature reduced with 72% ee, but at −10 °C enantioselectivity increased up to 99% ee. With substrate **2**, no alcohol **5** was isolated, instead complete reduction to alkane 1,1′-(1,4-butanediyl)ferrocene was observed. Interestingly, ketone **3** was entirely unreactive under these conditions. Reduction of ketone **7** was partially successful, affording alcohol **8** with medium enantioselectivity (51% ee) (see Table 3).

Over-reduction to alkane often complicates reductions, particularly CBS-method. Reductive deoxygenation of ferrocenyl ketones and alcohols proceeds rapidly even by simple $BH_3 \cdot SMe_2$ [26,27]. Interestingly, it does not occur with ketone **7**. Possible explanation could be orbital stabilization of carbocation in the α-position to ferrocene, which should be formed as an intermediate in this process. Such stabilization is not possible with cation in the β-position. The α-carbocation stabilization in ferrocene derivatives was well documented [28]. Erker suggested iron-stabilized α-carbenium ion also in [3] ferrocenophane derivative [29]. Our DFT calculations of tentative carbenium ions in α and β-position derived from [4] ferrocenophane also support this notion. The stabilization of α-carbocation is evident from bending of Cp–Cα bond toward iron.

Table 2
Ru-catalyzed hydrogen transfer reduction of ketones **1**–**3** and **7**

Substrate	Solvent	Yield (%)	ee (%)
1	[emim]$EtOSO_3$	56	50 (*R*)
1	H_2O	25	60 (*R*)
2	[emim]$EtOSO_3$	0	–
3	[emim]$EtOSO_3$	0	–
3	H_2O	0	–
7	[emim]$EtOSO_3$	49	6

Table 3
Reduction of ketones **1**–**3** and **7** with Cl_3SiH/activator **10** method

Substrate	Time (h)	Temperature (°C)	Yield (%)	ee (%)
1	1	r.t.	54	72 (*R*)
1	6	−10	55	99 (*R*)
2	24	r.t.	0	–
3	72	r.t.	0	–
7	6	r.t.	84	51 (*S*)
7	6	−10	90	48 (*S*)

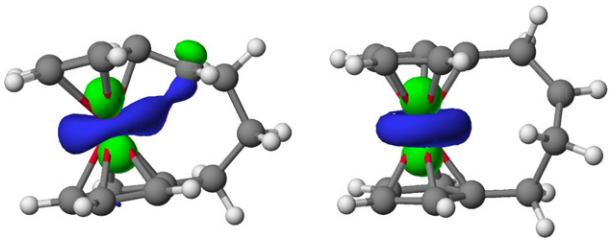


Fig. 2. Isosurface plots of HOMO−2 of carbocations derived from alcohols **5** and **8**, calculated by DFT, using B88-LYP functional and DZVP basis set.

Distance between iron and Cα is 2.40 Å and the interaction is also visible from isosurface plot of HOMO−2 molecular orbital (Fig. 2).

3. Conclusion

Our investigation of enantioselective reductions of cyclic ferrocene ketones showed that highly enantiomerically enriched ferrocenophane alcohols can be prepared, but none of the used methods can be generally applied for this kind of substrates. However, each of ferrocenophane ketones can be efficiently reduced by at least one method. Most satisfactory results were obtained with CBS-reduction. Ketones **2** and **3** were reduced with high enantioselectivities (96% and 97%, respectively) by this method. Ruthenium-catalyzed hydrogen transfer reaction was rather unsuccessful, reducing only ketones **1** and **7** with moderate enantioselectivities. Similarly, also Cl_3SiH method worked only partially. On the other hand it is complementary to oxazaborolidine reduction of ketone **1**, which was problematic with CBS-method, was reduced with excellent enantioselectivity (99% ee).

4. Experimental

Reactions were carried out in N_2 atmosphere and reactions using organometallic reagents were performed using standard Schlenk techniques. NMR spectra were recorded on Varian Mercury plus instrument, operating at 300 MHz for ^1H and 75 MHz for ^{13}C. Chemical shifts (δ) are given as ppm relative to tetramethylsilane as internal standard, for ^1H NMR; relative to residual solvent peak, for ^{13}C NMR. Optical rotations were measured on a Perkin–Elmer polarimeter. Melting points are uncorrected. Column chromatography was performed on Merck silica gel 60. Thin-layer chromatography was performed on Merck TLC-plates silica gel 60, F-254. Enantiomeric excesses were determined by HPLC using Chiralcel OD-H and Chiralpak AD-H (Daicel Chemical Industries) column with hexane/*i*-propanol as a mobile phase and detection by UV-detector at 254 nm. Solvents were distilled prior use; Et_2O and toluene were dried with sodium/benzophenone and distilled. CBS toluene solution was purchased from Aldrich. Ferrocenophane ketones **1**–**3** and **7** were prepared according to literature procedures [10,30,31]. Activator **10** was obtained by procedure described by Matsumura [25].

*General procedure for CBS-reduction of ketones **1–3** and **7**.* CBS (2 mL, 2.0 mmol, 1 M in tol.) and $BH_3 \cdot SMe_2$ (1 mL, 2.0 mmol, 2 M in THF) were mixed and cooled to −5 °C. After 15 min stirring, ketone (6.0 mmol) in toluene (13 mL) and the remaining portion of $BH_3 \cdot SMe_2$ (4 mL, 8.0 mmol) were added simultaneously over 15 min. After additional 5 min no starting material was detected by TLC and MeOH (5 mL) was added slowly at 0 °C. Then sat. NH_4Cl was added carefully (gas evolution) and the solution was extracted with Et_2O (3 × 25 mL). The combined organic extracts were washed with sat. NH_4Cl solution and brine, dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 1:1).

*General procedure for hydrogen transfer reduction of ketones **1–3** and **7**.* $[RuCl_2$p-cymene$]_2$ (3.4 mg, 0.005 mmol) and (*R,R*)-TsDPEN (5.6 mg, 0.012 mmol) were dissolved in H_2O (2 mL) or ionic liquid (1 mL). The resulting solution was degassed and stirred for 1 h at 40 °C. Into this solution HCOONa (380 mg, 5 mmol) and ketone (1 mmol) were added. The reaction mixture was degassed again and stirred for 24 h at 50 °C. Then the mixture was extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 4:1).

*General procedure for Cl_3SiH/10 reduction of ketones **1–3** and **7**.* Ketone (0.3 mmol) and activator **10** (9.1 mmol; 0.03 mg) were dissolved in $CHCl_3$ (1.5 mL). The solution was cooled in an ice water bath, and a solution of Cl_3SiH (0.091 mL; 0.9 mmol) in $CHCl_3$ (0.5 mL) was added to the solution. The reaction mixture was stirred at 0 °C for 30 min and then at r.t. for 6 h. The reaction was quenched by an aqueous conc. $NaHCO_3$ solution (10 mL), and the organic portion was extracted by CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), and after filtration, the solvent was evaporated. The residue was purified column chromatography (SiO_2, AcOEt/hexane = 1:5). The activator was recovered by acidifying the aqueous layer followed by extraction with CH_2Cl_2.

4.1. Characterisation and spectroscopic data for alcohols **4–6**, and **8**

*(R)-1,3-(1,1′-Ferrocendiyl)propan-1-ol (**4**).* M.p. 125–127 °C (literature [22] 122–124 °C). ^1H NMR (300 MHz, $CDCl_3$) δ: 4.44 (dd, J = 5.5, 2.5 Hz, 1H, H-C^{Fc}), 4.42 (m, 1H, H-C), 4.15 (m, 1H, H-C^{Fc}), 4.11–4.08 (m, 1H, H-C^{Fc}), 4.06 (m, 3H, H-C^{Fc}), 3.98 (m, 1H, H-C^{Fc}), 2.42–2.28 (m, 2H, CH_2), 2.15–2.00 (m, 2H, CH_2), 1.75 (s, 1H). $[\alpha]_D$ = +23.5 (c 1.0, $CHCl_3$). HPLC (Chiralpak AD-H, hexane/*i*-PrOH 90:10, 0.5 mL/min) t_R(major) = 23.92 min; t_R(minor) = 31.77 min.

NMR data are identical to the literature [22].

*1,4-(1,1′-Ferrocendiyl)butan-1-ol (**5**).* M.p. 103–105 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.43(dd, J = 8.3, 2.3 Hz, 1H, CH^{Fc}), 4.35 (td, J = 2.3, 1.1 Hz, 1H, CH), 4.01–4.14 (m, 6H), 2.44–2.52 (m, 1H), 2.02–2.24 (m, 3H), 1.83–1.94 (m, 1H), 1.58–1.72 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 88.5 (C^{Fc}), 88.3 (C^{Fc}), 73.0 (CH^{Fc}), 69.8 (CH^{Fc}), 69.4 (CH^{Fc}), 68.9 (CH^{Fc}), 68.5 (CH^{Fc}), 68.1 (CH^{Fc}), 67.8 (CH^{Fc}), 66.6 (CH^{Fc}), 65.4 (CHOH), 36.5 (CH_2), 28.6 (CH_2), 24.9 (CH_2). Elemental Anal. Calc. for $C_{14}H_{16}FeO$ (256.1): C, 65.65, H, 6.30. Found C, 65.46, H, 6.31%. $[\alpha]_D$ = +121.6 (c 0.7, $CHCl_3$) 96% ee. HPLC (Chiralpak AD-H, hexane/*i*-PrOH 85:15, 0.75 mL/min) t_R(major) = 15.71 min; t_R(minor) = 13.36 min.

*(R)-1,5-(1,1′-Ferrocendiyl)pentan-1-ol (**6**).* ^1H NMR (300 MHz, $CDCl_3$): δ 4.67 (ddd, J = 7.3, 7.3, 4.9 Hz, 1H), 4.20 (ddd, J = 2.4, 1.4, 1.4 Hz, 1H), 4.14–4.18 (m, 2H), 4.12 (ddd, J = 2.4, 2.4, 1.3 Hz, 1H), 4.08 (ddd, J = 2.4, 2.4, 1.3 Hz, 1H), 4.01–4.04 (m, 1H), 3.95–3.98 (m, 1H), 2.40–2.58 (m, 1H), 2.32–2.39 (m, 2H), 1.96–2.05 (m, 2H), 1.68–1.95 (m, 3H), 1.41 (d, J = 4.9 Hz, 1H). HPLC (Chiralcel OD-H, hexane/*i*-PrOH 85:15, 0.5 mL/min) t_R(major) = 23.9 min; t_R(minor) = 29.3 min.

NMR data are identical to the literature [10].

*1,4-(1,1′-Ferrocendiyl)butan-2-ol (**8**).* M.p. 120–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.01–4.19 (m, 9H, CH^{Fc}, CH), 2.78 (dd, J = 14.3, 3.0 Hz, 1H, CH_2), 2.60–2.69 (m, 1H, CH_2), 2.52 (dd, J = 10.1, 14.3 Hz, 1H, CH_2), 2.31–2.40 Hz (m, 1H, CH_2), 2.03–2.20 (m, 1H, CH_2), 1.57 (d, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 87.3 (C^{Fc}), 82.8 (C^{Fc}), 72.2 (CH), 69.8 (CH), 69.1 (CH), 68.1 (CH), 68.0 (CH), 67.4 (CH), 67.3 (CH), 67.2 (CH), 67.1 (CH), 38.0 (CH_2), 37.2 (CH_2), 25.4 (CH_2). Elemental Anal. Calc. for $C_{14}H_{16}FeO$ (256.1): C, 65.65, H, 6.30. Found C, 65.50, H, 6.19%. $[\alpha]_D$ = +75.3 (c 0.6, $CHCl_3$) 80% ee. HPLC (Chiralcel OD-H, hexane/*i*-PrOH 85:15, 0.75 mL/min) t_R(major) = 12.53 min; t_R(minor) = 11.03 min.

4.2. Details of the quantum chemical calculations

Calculations were performed with DGAUSS 4.1 module from CACHE 7.5 software package by Fujitsu. Structures were fully optimized at the density functional level employing the B88-LYP [32] functional and DZVP basis set [33] for all atoms.

Acknowledgements

Financial support from Ministry of education of Slovak republic, grant no. MVTS-COST/UK/07 and Slovak grant agency VEGA, grant no. VEGA 1/3569/06. We thank Mr. Pavol Tisovský for performing some experiments.

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