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Asymmetric reduction of prochiral ketones with borane using chiral squaric amino alcohols derived from camphor as catalysts

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Abstract

A series of new chiral squaric amino alcohols derived from (*R*)-(+)-camphor and squaric acid were synthesized, and applied to the enantioselective reduction of prochiral ketones with borane to give secondary alcohols with excellent enantiomeric excesses (up to 99%).

Keywords: Camphor; Squaric acid; Borane; Ketone; Asymmetric reduction

1. Introduction

Asymmetric reduction of prochiral ketones using oxazaborolidines has become one of the standard tools for the synthetic chemist, allowing access to enantiomerically enriched secondary alcohols with excellent enantiomeric excesses that may serve as the chiral ligands for enantioselective synthesis and highly useful intermediates in the synthesis of bioactive compounds and natural products [1–5]. Since the introduction of this catalyst by Itsuno [6,7] and subsequent developments by Corey et al. [8,9], the studies on mechanistic investigations, substrate applicability, and catalyst optimization have never stopped and many interesting results have been obtained. However, it is difficult to synthesize both enantiomers of a product because both antipodes of a ligand are not always readily available. Therefore, if the products could be prepared in both optical forms without troublesome resolution and the configuration of the products could be predicted, this method would be very attractive and desirable from a synthetic viewpoint. As a cheap and commercially available chiral source, camphor is structurally rigid and can be easily modified to form two chiral centres at atoms C-2, C-3. However, to the best of our knowledge, the derivatives from (*R*)-(+)-camphor were rarely used as chiral ligands in asymmetric reduction of prochiral ketones [10–17].

Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione), as an aromatic four-membered cyclic compound with unique characteristics, has been applied widely in many different fields [18–22]. Based on the cyclobutenedione structure, the acidic hydroxyl groups can be replaced by various functional groups so that many chiral ligands can be conveniently prepared. The advantages of the structures are that the rigid ring of squaric acid can be attacked to either one or two chiral amino alcohols and that, at the same time, the rigid ring moiety provides an efficient chiral environment for coordination of the substrates as well as the reagents in reactions. The monoaminoalcohols of squaric acid can serve as prototypical examples of bifunctional catalysts, since their substitutents at C-3 of the squaric acid ring can be conveniently modified by introducing a second function group, which can preferentially coordinate with the borane, thus leading to intramolecular delivery of hydride to the carbonyl group in a highly selective manner. In our laboratory, chiral squaric acid derivatives

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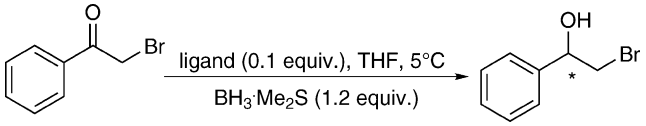
were first used as efficient ligands for asymmetric reduction of prochiral ketones [23–27]. It seemed of interest to further examine their use as chiral ligands for these reactions. In this paper, we synthesized a series of new chiral squaric amino alcohols derived from (*R*)-(+)-camphor and squaric acid and subsequently utilized them in the catalytic asymmetric reduction of prochiral ketones to achieve high enantioselectivity.

2. Results and discussion

The synthesis of chiral squaric amino alcohols derived from (*R*)-(+)-camphor and squaric acid is shown in Scheme 1. The 1,2-amino alcohols **3**, **4** from (*R*)-(+)-camphor were prepared according to the literature procedure [28–30]. The squaric acid diesters **2** were formed by refluxing of squaric acid in corresponding alcohols. Subsequent treatment of **2** with the *cis-endo-endo* amino alcohol **3** and the *cis-exo-exo* amino alcohol **4** in the presence of Et_3N gives corresponding squaramidoalcohols **5**, **6**. In order to study the effect of C-3 substituents of the squaric acid ring, we prepared a series of ligands with different alkoxy groups on C-3 position. All the ligands are new compounds and their structures were confirmed by elemental and spectral analyses.

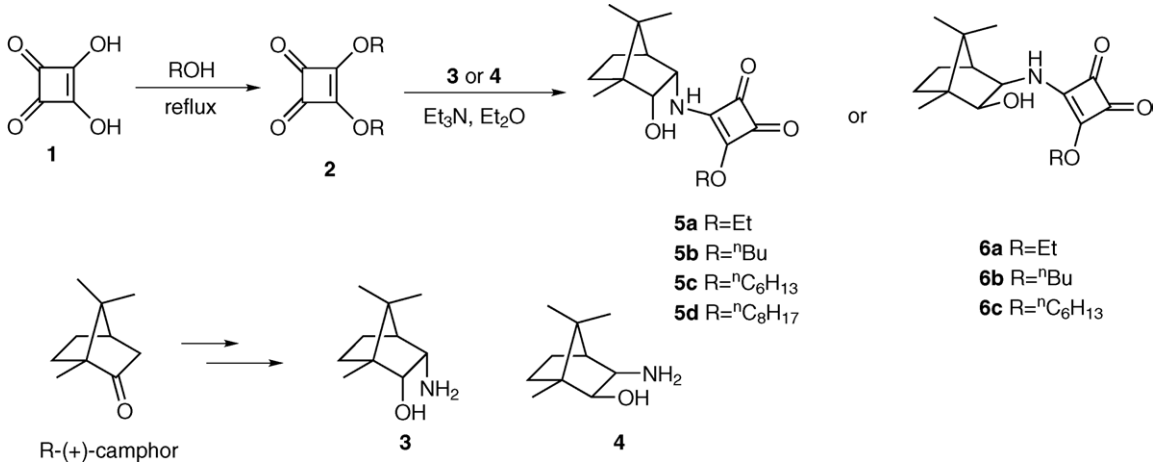
These squaramidoalcohol ligands were applied to the asymmetric reduction of prochiral aromatic ketones. According to our previous investigation [31,32], the reaction conditions were optimized, and the effects of solvents, temperature and catalyst loading were scrutinized in the reduction of *ω*-bromoacetophenone. THF was found to be far superior to other solvents, such as toluene and dichloromethane. The enantioselectivity were obviously affected by temperature and the best temperature was 50 °C. When the reactions were carried out at room temperature, low chemical yield was obtained and no asymmetric induction was observed. The catalyst loading was also an important factor the optimum catalyst loading was about 10%. Further increasing the amount of ligands led to the decrease in the e.e. value. The reason for this phenomenon is that the excess ligands maybe form the multinuclear aggregates, which limit asymmetric catalysis in the reaction system. Therefore, the optimum reaction conditions are that the catalysts were formed in situ by mixing the ligands (0.1 equivalent) and $BH{\cdot}Me_2S$ (1.2 equivalent) at 0 °C, and that the subsequent reduction of prochiral ketones was performed at 50 °C in THF. We applied the ligands in the asymmetric reduction of *ω*-bromoacetophenone, the secondary alcohol products were obtained with e.e. value of up to 99% (Table 1). All the ligands gave good to excellent enantioselectivity. In the asymmetric reduction catalyzed by the *cis-endo-endo* amino alcohol ligands **5,** the higher e.e. values were obtained than in the reactions catalyzed by *cis-exo-exo* ligands **6**. The effect of C-3 substituents on the e.e. values was inconspicuous (entries 1–4). Interestingly, when we used the *cis-endo-endo* amino alcohols **5** derived oxazaborolidines as catalysts, the configuration of the products was found to be *S* and *R*-alcohol was obtained by using the *cis-exo-exo* amino alcohols **6**.

Table 1
Asymmetric reduction of *ω*-bromoacetophenone using chiral squaric amino alcohols[a]



Entry	Ligand	E.e. (%)[b]	Configuration[c]
1	**5a**	95	S
2	**5b**	99	S
3	**5c**	94	S
4	**5d**	96	S
5	**6a**	77	R
6	**6b**	84	R
7	**6c**	82	R

[a] All of the chemical yield were >80% (isolated yield).
[b] Determined by capillary GC analysis with a CP-cyclodex 236 M (0.25 mm × 25 m) column.
[c] Determined by optical rotations comparing with the literature.



Scheme 1.

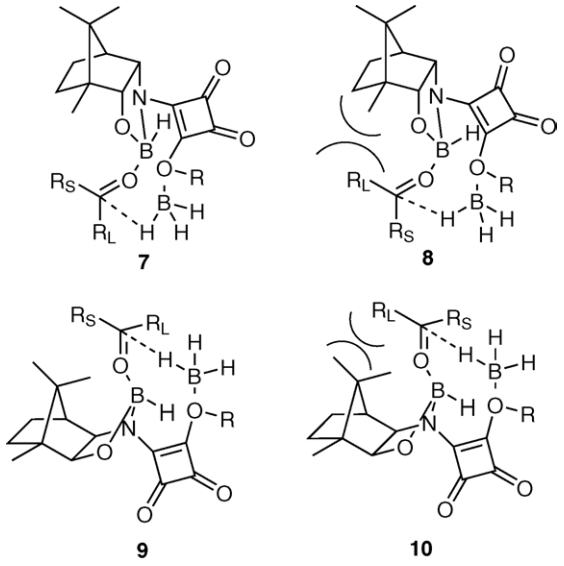


Fig. 1. Postulated reactive complexes.

The results may be rationalized by the proposed mechanism in Fig. 1. Owing to the steric effect of two rigid rings of squaric acid and camphor, the borane molecule as hydride donor is difficult to coordinate with the nitrogen atom on the oxazaborolidine ring to form the transition state proposed by Corey et al. [8]. Besides, according to MOPAC simulation, the hydride transfer is easy to occur when the second borane molecule as hydride donor was coordinated with the oxygen atom on C-3 of the squaric acid ring. Thus, we proposed that the first borane molecule could combine to the nitrogen atom to form Corey's oxazaborolidine and that then the secondary borane molecule can only combine to the oxygen atom at C-3 of squaric acid ring. As a result the facial attack of hydride to ketone substrates occurs through a macroheterocycle. In the transition state **7** and **8**, **7** is more favored than **8** because of the steric interactions between the rigid ring of camphor and ketones, and hence the attack of hydride occurs on the *Si*-face of the electronically deficient carbonyl carbon atom to form chiral secondary alcohols. For the same reason, in the transition state **9** and **10**, **9** is more favored than **10** and the hydride attacked on the *Re*-face of the carbonyl group to form chiral secondary alcohols with the opposite configuration.

We then applied the best ligand **5b** to the asymmetric reduction of several ketones (Table 2). In all cases, α-halogenated substrates, which are versatile intermediates for further synthetic manipulations were reduced with good to excellent enantioselectivity (entries 5 and 6).

3. Experimental

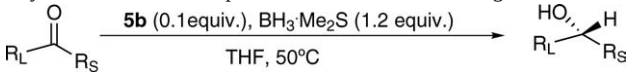
3.1. Instruments and materials

Melting points were determined on a YRT-3 melting apparatus and have not been corrected. Optical rotations were measured at room temperature on a WZZ-1S automatic polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker UltraShield^{TM} 300 MHz spectrometer with chemical shift in ppm and tetramethylsilicon as internal standard. Mass spectra data were obtained on a Finnigan-LCQ^{DECA} spectrometer. Flash chromatography was carried out using SiO_2 (230–400 mesh). Elemental analyses were performed with a Carlo Erba 1106 elemental analyzer. $BH_3{\cdot}Me_2S$ (5 M) was purchased from Alfa Aesar. The solvent (THF) and all prochiral ketones were purified before use. Other chemicals were obtained and used without any further purification.

3.2. Preparation of squaramidoalcohols *5*, *6*

To a solution of squaric acid diesters [31,32] (1.1 mmol) in 20 ml of ether was added triethylamine (1.0 mmol) and 1,2-amino alcohol (**3** or **4**) (1.0 mmol). The mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and residue was purified through column chromatography on silica gel with petroleum:ethyl acetate, 3:2 (v/v) to give product as oil and then a white solid on standing.

Table 2
Asymmetric reduction of prochiral aromatic ketones using **5b**



Entry	Ketone	Yield (%)[a]	E.e. (%)[b]	Configuration[c]
1	Tetralone	87	54	R
2	*β*-Acetonaphthalone	91	35	R
3	*p*-Chloroacetophenone	68	65	R
4	*p*-Trifluoromethylacetophenone	80	75	R
5	*ω*-Bromoacetophenone	90	99	S
6	*ω*-Chloroacetophenone	81	93	S
7	Propiophenone	85	51	R
8	Acetophenone	82	56	R

[a] Isolated yield.
[b] Determined by capillary GC analysis with a CP-cyclodex 236 M (0.25 mm × 25 m) column.
[c] Determined by optical rotations comparing with the literature.

3.2.1. 3-Ethoxy-4-{(1R,2R,3S,4S)-2-hydroxy-1,7,7-trimethylbicyclo[2,2,1]heptan-3-ylamino}cyclobut-3-ene-1,2-dione ***5a***

65% Yield; Mp 141–143 °C. $[\alpha]_D^{25}$ +60.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz $CDCl_3$) *δ*: 0.91 (s, 3H), 0.94 (s, 6H), 1.22 (m, 2H), 1.46–1.48 (m, 5H), 1.83–1.88 (m, 1H), 2.05 (s, 1H), 4.13 (m, 2H), 4.77 (dd, 2H), 7.19 (brs, 1H); ^{13}C NMR (300 MHz $CDCl_3$) *δ*: 191.11, 181.73, 178.61, 170.97, 73.09, 69.88, 53.58, 51.34, 50.14, 45.45, 25.53, 19.98, 19.20, 18.17, 15.83, 13.58; MS (*m*/*z*): 292 (M^+ −1, 100), 263 (M^+ −29, 61); Anal. Calcd for $C_{16}H_{23}NO_4$: C, 65.62; H, 7.95; N, 4.76; Found: C, 65.53; H, 7.85; N, 4.78.

3.2.2. 3-n-Butoxy-4-{(1R,2R, 3S,4S)-2-hydroxy-1,7,7-trimethylbicyclo [2.2.1]heptan-3-ylamino) cyclobut-3-ene-1,2-dione ***5b***

45% Yield; Mp 75–77 °C. $[\alpha]_D^{25}$ +43.8 (c 0.8, CHCl3); 1H NMR (300 MHz CDCl3) δ: 0.91–1.00 (m, 12H), 1.18–1.28 (m, 1H), 1.40–1.54 (m, 4H), 1.74–1.83 (m, 4H), 1.88 (s, 1H), 4.16 (m, 2H), 4.74 (t, 2H), 7.14 (brs, 1H); 13C NMR (300 MHz CDCl3) δ: 191.24, 181.75, 178.86, 170.84, 73.56, 73.12, 53.60, 51.39, 50.20, 45.45, 31.89, 25.56, 20.00, 19.19, 18.63, 18.15, 13.60; MS (m/z): 320 (M+ −1, 100), 263 (M+ −57, 26); Anal. Calcd for C18H27NO4: C, 67.34; H, 8.49; N, 4.55; Found: C, 67.29; H, 8.41; N, 4.36.

3.2.3. 3-n-Hexyloxy-4-{(1R,2R,3S,4S)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptan-3-ylamino)cyclobut-3-ene-1,2-dione ***5c***

32% yield; Mp 123–124 °C. $[\alpha]_D^{25}$ +61.6 (*c* 0.23, $CHCl_3$); ^{1}H NMR (300 MHz $CDCl_3$) *δ*: 0.91–1.00 (m, 12H), 1.19–1.55 (m, 10H), 1.76–1.88 (m, 3H), 1.92 (s, 1H), 4.15 (m, 2H), 4.74 (t, 2H), 7.29 (brs, 1H); ^{13}C NMR (300 MHz $CDCl_3$) *δ*: 191.20, 181.83, 178.85, 170.86, 73.83, 73.15, 53.57, 51.37, 50.19, 45.46, 31.27, 29.89, 25.54, 25.08, 22.56, 19.99, 19.18, 18.18, 13.99, 13.59; MS (*m*/*z*): 348 (M^+ −1, 100), 263 (M^+ −85, 9); Anal. Calcd for $C_{20}H_{31}NO_4$: C, 68.66; H, 8.86; N, 4.20; Found: C, 68.76; H, 8.88; N, 4.01.

3.2.4. 3-n-Octyloxy-4-{(1R,2R,3S,4S)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptan-3-ylamino)cyclobut-3-ene-1,2-dione ***5d***

23% Yield; Mp 109–110 °C. $[\alpha]_D^{25}$ +63.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz $CDCl_3$) *δ*: 0.86–0.94 (m, 12H), 1.17–1.57 (m, 14H), 1.74–1.83 (m, 3H), 1.88 (s, 1H), 4.14 (m, 2H), 4.73 (t, 2H), 7.06 (brs, 1H); ^{13}C NMR (300 MHz $CDCl_3$) *δ*: 191.18, 181.87, 178.84, 170.89, 73.81, 73.17, 53.56, 51.37, 50.19, 45.46, 31.74, 29.94, 29.20, 29.09, 25.53, 25.42, 22.63, 19.99, 19.18, 18.18, 14.08, 13.59; MS (*m*/*z*): 376 (M^+ −1, 100), 263 (M^+ −113, 9); Anal. Calcd for $C_{22}H_{35}NO_4$: C, 70.06; H, 9.32; N, 4.05; Found: C, 70.03; H, 9.28; N, 3.71.

3.2.5. 3-Ethoxy-4-{(1R,2S,3R,4S)-2-hydroxy-1,7,7-trimethylbicyclo[2,2,1]heptan-3-ylamino}cyclobut-3-ene-1,2-dione ***6a***

60% Yield; Mp 114-116 °C. $[\alpha]_D^{25}$ +36.7 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz $CDCl_3$) *δ*: 0.91–1.01 (m, 12H), 1.36–1.64 (m, 4H), 1.75–1.92 (m, 1H), 2.05 (s, 1H), 3.75 (t, 1H), 4.10 (d, *J* 7.77, 1H), 4.75 (dd, 2H), 6.97 (brs, 1H); ^{13}C NMR (300 MHz $CDCl_3$) *δ*: 191.08, 181.82, 178.54, 170.62, 78.49, 69.81, 60.77, 52.65, 49.36, 46.54, 32.63, 25.56, 21.62, 20.93, 15.77, 11.13; MS (*m*/*z*): 292 (M^+ −1, 100), 263 (M^+ −29, 61); Anal. Calcd for $C_{16}H_{23}NO_4$: C, 65.60; H, 7.91; N, 4.75; Found: C, 65.53; H, 7.85; N, 4.78.

3.2.6. 3-n-Butoxy-4-{(1R,2S,3R,4S)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptan-3-ylamino)cyclobut-3-ene-1,2-dione ***6b***

46% Yield; Mp 86–88 °C. $[\alpha]_D^{25}$ +37.4 (*c* 0.8, $CHCl_3$); ^{1}H NMR (300 MHz $CDCl_3$) *δ*: 0.87–1.09 (m, 12H), 1.23–1.28 (m, 1H), 1.39–1.56 (m, 4H), 1.68–1.83 (m, 4H), 1.89 (s, 1H), 3.72 (t, 1H), 3.92 (d, J 7.98, 1H), 4.73 (t, 2H), 7.09 (brs, 1H); ^{13}C NMR (300 MHz $CDCl_3$) *δ*: 191.24, 181.78, 178.78, 170.41, 78.45, 73.54, 60.77, 52.68, 49.37, 46.53, 32.63, 31.92, 25.63, 21.63, 20.91, 18.62, 13.62, 11.12; MS (*m*/*z*): 320 (M^+ −1, 100), 263 (M^+ −57, 26); Anal. Calcd for $C_{18}H_{27}NO_4$: C, 67.31; H, 8.45; N, 4.50; Found: C, 67.29; H, 8.41; N, 4.36.

3.2.7. 3-n-Hexyloxy-4-{(1R,2S,3R,4S)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptan-3-ylamino)cyclobut-3-ene-1,2-dione ***6c***

24% Yield; Mp 132–133 °C. $[\alpha]_D^{25}$ +32.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz $CDCl_3$) *δ*: 0.91–1.10 (m, 12H), 1.26–1.42 (m, 8H), 1.46–1.57 (m, 1H), 1.69–1.84 (m, 4H), 1.90 (s, 1H), 3.72 (t, 1H), 3.90 (d, J 7.89, 1H), 4.70 (t, 2H), 7.09 (brs, 1H); ^{13}C NMR (300 MHz d^6-DMSO) *δ*: 194.17, 187.95, 182.79, 177.11, 83.15, 77.70, 65.92, 56.01, 53.79, 51.54, 37.61, 35.95, 34.77, 30.79, 29.75, 27.24, 26.61, 26.01, 19.04, 16.79; MS (*m*/*z*): 348 (M^+ −1, 100), 263 (M^+ −85, 9); Anal. Calcd for $C_{20}H_{31}NO_4$: C, 68.68; H, 8.87; N, 4.18; Found: C, 68.76; H, 8.88; N, 4.01.

3.3. General procedure for the catalytic reduction of prochiral ketones

To a 25 ml round-bottom flask was added 0.05 mmol (0.1 equivalent) of chiral ligand in 3 ml of THF. Under a nitrogen atmosphere and at 0 °C, $BH_3{\cdot}Me_2S$ (5 M) (0.6 mmol, 1.2 equivalent) was added. The mixture was stirred at 0 °C for 0.5 h and subsequent at room temperature for 2 h and warmed to 50 °C for a further hour. The ketone (0.5 mmol) in 2 ml of THF was added slowly over a period of 1.5 h under the same temperature and stirred for a further hour. The reaction mixture was cooled to 0 °C and quenched with a 1N aqueous HCl solution (8 ml), then extracted with ethyl acetate (3 ml × 10 ml). The combined organic layer was washed

twice with brine and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The residue was passed through a short silica gel column to afford the pure product before being subjected to GC analysis.

4. Conclusion

In summary, we have synthesized a series of new chiral squaric amino alcohols derived from (*R*)-(+)-camphor and squaric acid. These squaric amino alcohol ligands were applied to the catalytic asymmetric reduction of prochiral aromatic ketones with good to excellent e.e. values, and the reactions proceeded with predictable absolute stereochemistry. The both enantiomers of the target product were obtained by using two diastereoisomer ligands **5** and **6**.

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