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Asymmetric Hydrosilylation of Symmetrical Diketones Catalyzed by a Rhodium Complex with Trans-Chelating Chiral Diphosphine EtTRAP

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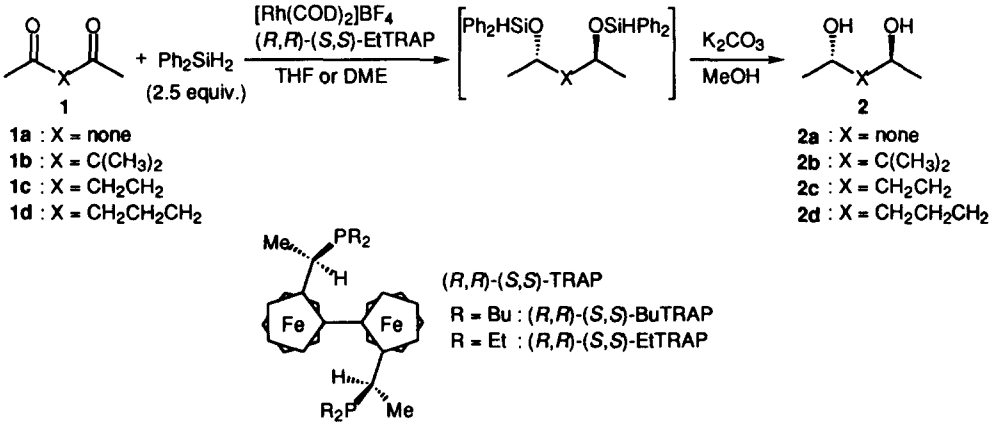
Abstract: Asymmetric hydrosilylation of symmetrical diketones with diphenylsilane in the presence of catalytic amount ([substrate]/[catalyst] = 100) of rhodium complex coordinated with trans-chelating chiral phosphine ligand EtTRAP gave corresponding optically active symmetrical diols with high enantiomeric excesses.

Optically active symmetrical diols are useful as chiral synthetic intermediates. Catalytic asymmetric reduction of diketones provides convenient access to optically active diols, because the introduction of two chiral centers may be feasible in one flask with catalytic amount of chiral source[1,2]. However, only 1,3-diketones have afforded the corresponding 1,3-diols with high enantio- and diastereoselectivities in the asymmetric reduction of diketones by using chiral catalyst[3].

We previously reported that trans-chelating chiral phosphine TRAPs[4,5] bearing linear alkyl chain on phosphorus atoms (Et- and BuTRAP) were effective for the hydrosilylation of simple ketones catalyzed by rhodium complexes[6,7]. Keto esters, which have a secondary coordination site (alkoxycarbonyl group) to rhodium atom, were also hydrosilylated with high enantioselectivities by EtTRAP-rhodium catalyst[8]. Herein, we wish to describe an asymmetric hydrosilylation of various symmetrical diketones catalyzed by EtTRAP-rhodium complex[9] (Scheme 1).

Scheme 1



General procedure for the asymmetric hydrosilylation of symmetrical diketones is presented as follows. To a solution of the catalyst prepared in situ by mixing $[Rh(COD)_2]BF_4$ (0.010 mmol) and (*R*,*R*)-(*S*,*S*)-EtTRAP (0.011 mmol) in THF or DME (1.0 ml) at room temperature, was added diketone (1.0 mmol), diphenylsilane (2.5 mmol) and tridecane as internal standard. The mixture was stirred at the indicated temperature until the reaction was completed, and then the resulting silyl ether was solvolyzed with 50 mg of K_2CO_3 and 2 ml of MeOH. Evapolation of the solvent followed by MPLC or column chromatography on silica gel gave the corresponding diol as a mixture of *dl* and *meso* isomers.

Results are summarized in Table 1. The EtTRAP-rhodium catalyzed asymmetric hydrosilylation of 1,2-diketone **1a**[10] and 1,3-diketone **1b** afforded the corresponding optically active diols not only in high enantioselectivity but also in high diastereoselectivity (ratio of *dl* to *meso* isomer). It may be remarked that the very high stereoselectivity (99% ee, *dl*/*meso* = 96/4) was attained in the reaction of **1b**, which has two methyl substituents at the carbon between the two carbonyl groups. The asymmetric hydrosilylation of 1,4-diketone **1c** and 1,5-diketone **1d** also proceeded with high enantioselectivities, although their diastereoselectivities were moderate. However, acetylacetone, which is a 1,3-diketone bearing active hydrogens, gave 2,5-pentanediol in low enantio- and diastereoselectivity ((*R*,*R*)-(*S*,*S*)-BuTRAP, THF, -30 °C, *dl*/*meso* = 42/58, 35% ee (2*R*,4*R*)). Also, 3,4-hexandione, which has ethyl groups as both substituents of 1,2-diketone moiety, resulted in moderate stereoselectivity ((*R*,*R*)-(*S*,*S*)-EtTRAP, THF, 0 °C, *dl*/*meso* = 77/23, 70% ee).

Table 1. Asymmetric Hydrosilylation of Diketones Catalyzed by (*R*,*R*)-(*S*,*S*)-EtTRAP-Rhodium Complex[a].

entry	diketone	solvent	temp, °C	time, h	product	yield[b], % (*dl* : *meso*)[c]	% ee (config.)[d]
1	**1a**	DME	0	30	**2a**	69 (90 : 10)	95[e] (2*S*,3*S*)
2	**1b**	THF	-30	58	**2b**	58 (96 : 4)	99[e] (2*S*,4*S*)[f]
3	**1c**	DME	-30	30	**2c**	97 (75 : 25)	97[g] (2*S*,5*S*)
4	**1d**	THF	-30	30	**2d**	75 (69 : 31)	89[g] (2*S*,6*S*)

[a] The ratio of $[Rh(COD)_2]BF_4$/(*R*,*R*)-(*S*,*S*)-EtTRAP/diketone/Ph_2SiH_2 was 1/1.1/100/250. [b] Isolated yield. [c] Determined by capillary GLC analysis of crude product. [d] Absolute configuration was determined by optical rotation unless otherwise noted. [e] Determined by HPLC analysis of bis[*N*-(3,5-dinitorophenyl)carbamate] derivative with SUMICHIRAL OA-4000. [f] Assigned by comparison between the retention time of the major isomer in HPLC analysis and that of authentic bis[*N*-(3,5-dinitorophenyl)carbamate] of (2*S*,4*S*)-**2b** (ref 11). [g] Determined by HPLC analysis of bis[*N*-(3,5-dinitorophenyl)carbamate] derivative with SUMICHIRAL OA-4100.

Of mechanistic interest is whether the chirality of the catalyst and/or substrate (initially produced silyloxyketone) controls the course of stereoselection at the second hydrosilylation. Both of the diastereo- and enantioselectivity in the present asymmetric hydrosilylation of diketones are calculated according to scheme 2, if the chirality of the initially produced silyloxyketone has no influence on the stereoselection at the second hydrosilylation. In the calculation, the respective enantioselectivties X and Y for the first and second hydrosilylation may be approximated by those observed in the reactions of the keto esters (eq. 1)[8] and the simple ketones (eq. 2)[6], respectively. The approximation is based on the assumption that in the first hydrosilylation of diketone the another carbonyl group may be coordinated to rhodium complex like the alkoxycarbonyl group in the hydrosilylation of keto ester, while the silyloxy group initially formed has little ability to coordinate onto rhodium in the second hydrosilylation. The stereoselectivities with **1a**-**1d** thus

calculated (Table 2) are in good agreement with the observed enantio- and diastereoselectivities. Then, it is concluded that the stereoselectivity at second hydrosilylation is not determined by the chirality of substrate but by that of catalyst.

Scheme 2

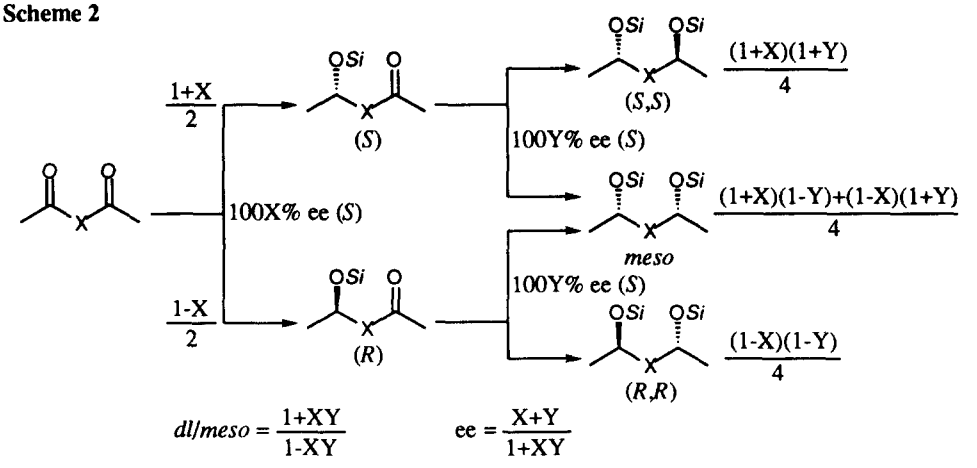
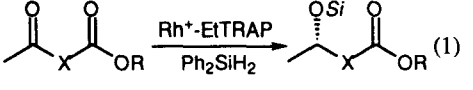


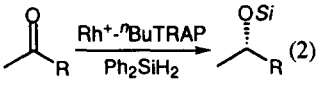
Table 2. Calculated Stereoselectivity of EtTRAP-Rhodium Catalyzed Asymmetric Hydrosilylation of Diketones based on Figure 1.

entry	diketone	X[a]	Y[b]	*dl:meso*	% ee
1	**1a**	0.80	0.80	82 : 18	97.6
2	**1b**	0.98	0.91	95 : 5	99.9
3	**1c**	0.88	0.59	76 : 24	96.8
4	**1d**	0.69	0.59	70 : 30	91.0

[a] Each enantioselectivity X for the first step hydrosilylation was determined according to the selectivity in the corresponding reaction in eq. 1 (ref 8). [b] Each enantioselectivity Y for the second step hydrosilylation was determined according to the selectivity in the corresponding reaction in eq. 2 (ref 6).



X = none	80% ee
X = $C(CH_3)_2$	98% ee (ref 12)
X = CH_2CH_2	88% ee
X = $CH_2CH_2CH_2$	69% ee

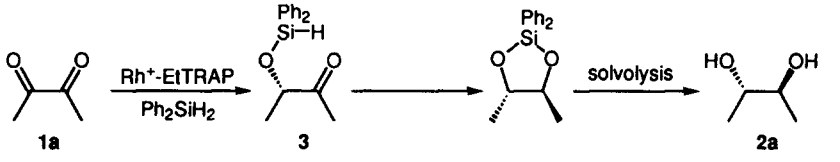


R = *cyclo*-Hexyl	80% ee
R = α-Adamantyl	91% ee
R = *n*-Hexyl	59% ee

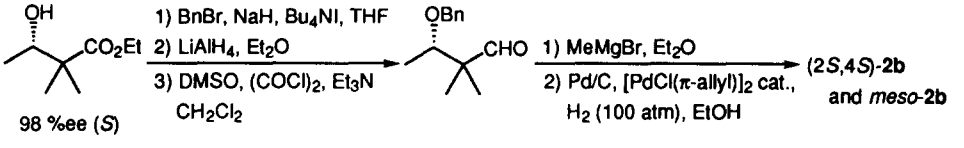
References and Notes

1. Asymmetric hydrogenation of diketones catalyzed by ruthenium BINAP complex: (a) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. *J. Am. Chem. Soc.*, **1988**, *110*, 629. (b) Kawano, H.; Ishi, Y.; Saburi, M.; Uchida, Y. *J. Chem. Soc. Chem. Commun.*, **1988**, 87.

2. Asymmetric hydrogenation of diketones catalyzed by asymmetrically modefied Raney nickel: (a) Ito, K.; Harada, T.; Tai, A.; Izumi, Y. *Chem. Lett.*, **1979**, 1049. (b) Ito, K.; Harada, T.; Tai, A. *Bull. Chem. Soc. Jpn.*, **1980**, *53*, 3367.
3. The asymmetric hydrogenation of 2,3-butanedione catalyzed by ruthenium-BINAP gave 2,3-butandiol in 100 %ee, but this reaction gave mainly *meso*-2,3-butandiol (*dl*/*meso* = 26/74)[1a].
4. (*S*,*S*)-2,2"-Bis[(*R*)-1-(dialkylphosphino)ethyl]-1,1"-biferrocene.
5. (a) Sawamura, M.; Hamashima, H.; Ito, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 593. (b) Sawamura, M.; Hamashima, H.; Sugawara, M.; Kuwano, R.; Ito, Y. *Organometallics* submitted for publication.
6. Sawamura, M.; Kuwano, R.; Ito, Y. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 111.
7. For reviews of asymmetric hydrosilylation, see: (a) Ojima, I; Hirai, K. in *Asymmetric Synthesis, Vol. 5* (Eds.: Morrison, J. D.), Academic Press, New York, **1985**, Chapter 4. (b) Brunner, H.; Nishiyama, H.; Itoh, K. in *Catalytic Asymmetric Synthesis* (Eds.: Ojima, I.), VCH Publishers, Inc., New York, **1993**, Chapter 6.
8. Sawamura, M.; Kuwano, R.; Shirai, J.; Ito, Y. *Synlett* in press.
9. Preliminary experiments using EtTRAP and BuTRAP showed that the former was superior to the later in all cases in Table 1.
10. The reaction of **1a** was completed by using 1.5 equiv diphenylsilane at the same condition. However, the enantio- and diastereoselectivity in this reaction was low (84% yield, *dl*/*meso* = 72/28, 83% ee (2*S*,3*S*)). In this reaction using 1.5 equiv diphenylsilane, a part of the silyloxy ether **3** resulting from the first hydrosilylation turned to **2a** through intramolecular hydrosilylation as below. This intramolecular hydrosilylation seemed to be prevented by using 2.5 equiv diphenylsilane.



11. The authentic sample of (2*S*,4*S*)-**2b** was prepared from (*S*)-ethyl 3-hydroxy-2,2-dimethylbutanoate[8] as follows:



12. We have already reported that the hydrosilylation of ethyl 3-oxo-2,2-dimethylbutanoate (**4**) proceeded with 93% ee (*S*) by EtTRAP-rhodium catalyst in 1.0 M solution[9]. However, we recently found that **4** was hydrosilylated with 98% ee (*S*) by 0.5 mol% catalyst in 2.0 M solution.

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