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CATALYTIC ASYMMETRIC INTRAMOLECULAR HYDROSILATION[1]

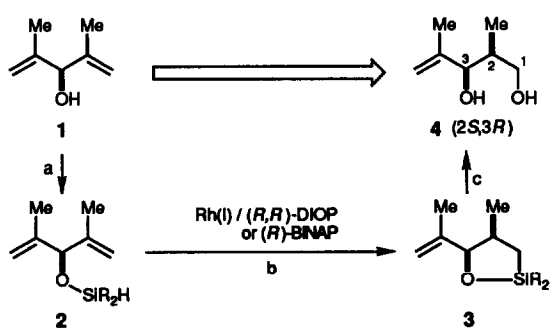
Kohei Tamao,* Toshihiko Tohma, Naoki Inui, Osamu Nakayama, and Yoshihiko Ito*
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Summary: Catalytic asymmetic intramolecular hydrosilation of di(2-propenyl)methanol in the presence of a Rh(I) complex containing (*R,R*)-DIOP or (*R*)-BINAP as ligand, followed by hydrogen peroxide oxidation, afforded optically active (2*S*,3*R*)-2,4-dimethyl-4-pentene-1,3-diol of up to 93% ee.

Asymmetric "hydration" of olefins provides an efficient route to optically active alcohols. This has been accomplished in the past by an asymmetric hydroboration by using a stoichiometric amount of an optically active borane such as isopinocampheylborane, followed by oxidation.[2] Quite recently, a catalytic asymmetric hydroboration has also been shown to be a new method for the synthesis of optically active alcohols from olefins.[3]

We now report preliminary results that the catalytic, asymmetric, intramolecular hydrosilation of allylic alcohols, followed by hydrogen peroxide oxidation[4] affords optically active 1,3-diols. As shown in Scheme I, di(2-propenyl)methanol (**1**) was used as a model compound, because the silyloxy derivative **2** was expected to undergo an enantiotopic group selective (*pro-R* or *pro-S*) and diastereotopic face selective (*syn* or *anti*) hydrosilation[5,6] to give an optically active 1,3-diol which is a useful synthetic intermediate for the synthesis of natural products such as polypropionate derivatives.[7] The reaction was indeed achieved in the presence of a catalytic amount of a rhodium(I) complex with an optically active phosphine ligand such as (*R,R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, (*R,R*)-DIOP[8] or (*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, (*R*)-BINAP.[9] Under appropriate conditions, the reaction proceeded with essentially complete diastereoselectivity (*syn* : *anti* > 99 : 1) and with high enantioselectivity (*pro-R* up to 93% ee) to give (2*S*,3*R*)-2,4-dimethyl-4-pentene-1,3-diol (**4**).[7,10,11] The present results afford the highest enantioselectivity ever reported for catalytic asymmetric hydrosilation of olefins.[13]

Scheme I[a]



[a] a: $(HMe_2Si)_2NH$ or HAr_2SiCl, NH_3, Et_2O. b: $[RhCl(CH_2{=}CH_2)_2]_2$/2(*R,R*)-DIOP or (*R*)-BINAP (2 mol%), $ClCH_2CH_2Cl$. c: 30%H_2O_2, KF, $KHCO_3$, MeOH, THF.

Table 1. Asymmetric synthesis of optically active **4** by intramolecular hydrosilation of **2** catalyzed by Rh(I)/(*R*,*R*)-DIOP, followed by the hydrogen peroxide oxidation[a]

Entry	R in **2** (No.)	temp., time (°C) (days)	yield[b] (%)	**4** (*syn*) / *anti*[c]	% ee of **4**[d]
1	Me (**2a**)	30, 1.2	60	86 / 14	18
2	Me (**2a**)[e]	30, 6.5	96	95 / 5	80
3	Ph (**2b**)	30, 9	94	98 / 2	84
4	Ph (**2b**)[e]	30, 20	51	95 / 5	71
5	Ph (**2b**)	50, 0.6	83	98 / 2	77
6	Ph (**2b**)[f]	30, 30	92	95 / 5	83
7	Ph (**2b**)[g]	30, 1.2	97	99 / 1	83
8	2-MeC_6H_4 (**2c**)	30, 41	45[h]	63 / 37	4[i]
9	3-MeC_6H_4 (**2d**)	30, 7	80	>99 / 1	87
10	4-MeC_6H_4 (**2e**)	30, 21	66	>99 / 1	86
11	3,5-$Me_2C_6H_3$ (**2f**)	30, 11	66	>99 / 1	93

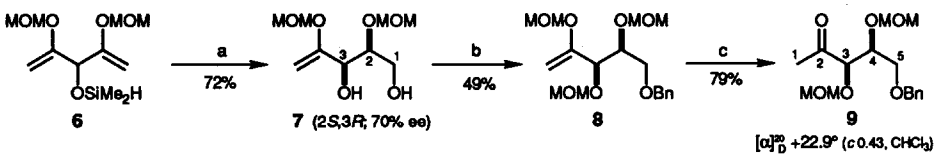
[a] Intramolecular hydrosilation was carried out by heating a mixture of **2** (1 mmol scale), $[RhCl(CH_2{=}CH_2)_2]_2$ (2 ~ 2.5 mol%), (*R*,*R*)-DIOP (L*/Rh = 1.3 ~ 1.5), and dry $ClCH_2CH_2Cl$ (2 mL/mmol) under nitrogen at 30 or 50 °C for a given period of time, unless otherwise noted. The completion of the reaction was monitored by GLC. After removal of Rh species by treating the mixture with EDTA•2Na followed by filtration, the product was oxidized by mixing with 30% H_2O_2 (1.2 equiv/Si-C), KF (2 equiv), $KHCO_3$ (1 equiv) in MeOH/THF (1 : 1) at room temperature for 15 h. [b] Isolated yield of a mixture of **4** and the *anti* isomer. [c] Determined by ^1H NMR and/or HPLC. Enantiomeric excess and the absolute configuration of the minor anti isomer were not determined. [d] The (2*S*,3*R*)-(+) isomer predominated, unless otherwise noted. The enantiomeric excess was determined by HPLC analysis of the 1-TBS ether and 3-(3,5-dinitrophenyl carbamate) derivative **5**.[10] [e] (*R*)-BINAP was used as ligand. [f] L*/Rh ratio = 4.5. [g] $[RhCl(COD)]_2$ was used as the catalyst precursor; a mixture of $[RhCl(COD)]_2$, (*R*,*R*)-DIOP and solvent was treated with hydrogen (1 atom) at room temperature for 1 h, followed by slight evaporation of the solvent (not to dryness), prior to the addition of the substrate. [h] Conversion ca. 80%. [i] The major isomer was the (2*R*,3*S*) isomer.

Some representative results are listed in Table 1. The reaction generally proceeded cleanly but rather slowly in $ClCH_2CH_2Cl$[14] at 30 °C under nitrogen in the presence of a neutral Rh(I)-phosphine complex (Rh = 2 ~ 2.5 mol%, ligand/Rh = ca. 1.5)[15] prepared *in situ* from $[RhCl(CH_2{=}CH_2)_2]_2$ or $[RhCl(COD)]_2$ and optically active phosphine. For the HMe_2Si derivative (**2a**) the use of (*R*)-BINAP as ligand afforded **4** with much higher diastereoselectivity and enantiomeric purity than (*R*,*R*)-DIOP (entries 1 and 2). In contrast, for the HPh_2Si derivative (**2b**) (*R*,*R*)-DIOP seemed to be better ligand than (*R*)-BINAP (entries 3 and 4). Higher reaction temperatures greatly accelerated the reaction, however a decrease in enantioselectivity was observed (entries 3 and 5). Use of excess amounts of phosphine ligand partly inhibited the reaction without notable improvement of the stereoselectivity (entry 6). The choice of catalyst precursors had little effect on stereoselectivity (entries 3 and 7). Variation of the aryl groups on silicon (HAr_2Si) exhibited the largest effect. With sterically hindered *ortho*-tolyl derivative **2c**, the reaction proceeded sluggishly and with poor selectivity (entry 8), while the *meta*- and *para*-tolyl

derivatives, **2d** and **2e**, and 3,5-xylyl derivative **2f** afforded compound **4** with the complete diastereoselectivity and in the highest enantiomeric purities (86 ~ 93% ee; entries 9, 10, and 11). The moderate reaction rate and the highest stereoselectivity observed in the meta-substituted phenyl derivatives may particularly be noted.[16]

Catalytic asymmetric intramolecular hydrosilation of methoxymethoxyvinyl derivative **6**[17] was also achieved under similar conditions, but the best results (70-78% ee) were obtained with (*R*)-BINAP as a ligand, as shown in Scheme II. The *syn* : *anti* ratio observed for compound **7** was 98 : 2. The product **7**[12] was transformed into optically active (3*R*,4*S*)-3,4,5-trihydroxypentan-2-one derivative **9**,[18a] which is a useful synthetic intermediate in optically active natural products.[18,19]

Scheme II[a]



[a] a: (1) [RhCl(CH2=CH2)2]2 / 2(*R*)-BINAP (2.8 mol%), ClCH2CH2Cl, 30 °C, 6.5 days. (2) 30%H2O2, KF, KHCO3, MeOH, THF, room temperature, 15 h. b: (1) *t*-BuMe2SiCl, Et3N, CH2Cl2. (2) NaH, ClCH2OMe, THF. (3) *n*-Bu4NF, THF. (4) NaH, PhCH2Br, *n*-Bu4NI, THF. c: 0.02N HCl, THF, room temperature, 7 days.

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5. Platinum-catalyzed intramolecular hydrosilation of **2a** has been shown to proceed in a high syn diastereoselective fashion.[4a]
6. Sharpless asymmetric epoxidation of divinylmethanol derivatives has been reported. (a) Takano, S.; Sakurai, K.; Hatakeyama, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1759. (b) Jager, V.; Schroter, D.; Hafele, B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 87. (c) Schreiber, S. L.; Schreiber, T. S.; Smith, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 1525. (d) Schreiber, S. L.; Goulet, M. T.; Schulte, G. *J. Am. Chem. Soc.* **1987**, *109*, 4718.
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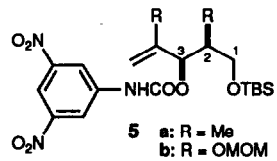
10. The absolute configuration of the major *syn* stereoisomer **4** was determined by comparison with the authentic samples prepared from optically active (*S*)-(+)-methyl 3-hydroxy-2-methylpropionate by a sequencial transformation involving protection of the OH group as the THP ether, reduction with LAH, Swern oxidation, and treatment with 2-propenyl-MgBr. We thank Kanegafuchi Chemical Industry Co., Ltd. for a gift of optically active methyl 3-hydroxy-2-methylpropionate. The enantiomeric excess of **4** was determined by HPLC analysis on a chiral stationary phase column (Sumipax OA-4500, Sumitomo Chemical Co., Ltd.; hexane / 1,2-dichloroethane / ethanol = 100 / 20 / 1) of **5a**, derived from **4** in two steps, (1) TBSCl, Et_3N, DMAP, CH_2Cl_2; (2) 3,5-$(O_2N)_2C_6H_3NCO$, pyridine, toluene, 70 °C, 3 h, according to the Sumitomo direction. Similar derivatives of the minor *anti* isomer showed no separation on the same column. The enantiomeric excess of **7** was also determined on the same chiral column (hexane / 1,2-dichloroethane / ethanol = 50 / 15 / 1) after derivatization to **5b**.



5 **a**: R = Me
b: R = OMOM

11. We have examined in the early stage ferrocenyl-phosphines such as (*R*)-(*S*)-BPPFA[12] as ligand, but obtained rather low asymmetric induction (4 - 27 %ee) with both **2a** (R = Me) and **2b** (R = Ph).
12. Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395.
13. Catalytic, asymmetric, *intermolecular* hydrosilation of olefins and 1,3-dienes has been studied, but the highest optical yield ever reported was 66%. (a) Review: Ojima, I.; Hirai, K. In *Asymmetric Synthesis*, Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 103. (b) Review: Burnner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 897. (c) Hayashi, T.; Kabeta, K. *Tetrahedron Lett.* **1985**, *26*, 3023, and references cited therein.
14. Dichloroethane appeared to be more suitable with respect to the stereoselectivities than other solvents such as CH_2Cl_2, THF, DME, and benzene.
15. In the presence of a cationic complex such as $[Rh(COD)\{(-)\text{-DIOP}\}]^+ClO_4^-$ as catalyst the reaction of **2b** proceeded rather fast (within 1 day at 30 °C) but with poor stereoselectivities (75% yield; **4** *(syn) : anti* = 94 : 6; **4** 26% ee).
16. While stereoselectivity has been shown to be improved by introduction of meta-substituted phenyl-phosphine ligands in certain intermolecular catalytic asymmetric synthesis [Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143], our present results suggest a similar effect on the substrate side in a catalytic intramolecular reaction.
17. Prepared by the reaction of 1-(methoxymethoxy)vinyllithum with ethyl formate followed by quenching with HMe_2SiCl, and isolated by distillation in vacuo. The HPh_2Si counterpart is now under investigation.
18. (a) Optically pure **9**, $[\alpha]_D^{20}$ +33.5° (*c* 4.12, MeOH): Iida, H.; Yamazaki, N.; Kibayashi, C. *J.Org. Chem.* **1986**, *51*, 3769. (b) Yamazaki, N.; Kibayashi, C. *J. Am. Chem. Soc.* **1989**, *111*, 1396.
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