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Regio- and Enantioselective Hydrosilylation of 1-Arylalkenes by Use of Palladium–MOP Catalyst

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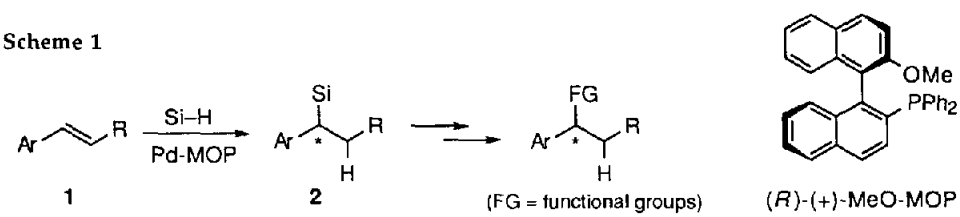
Abstract: Hydrosilylation of styrenes bearing β-substituents with trichlorosilane was catalyzed by a palladium complex (0.1 mol %) coordinated with (*R*)-2-methoxy-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-MeO-MOP) to give high yields of optically active 1-aryl-1-silylalkanes (80~85% ee) as single regioisomers. The resulting silanes were readily converted into the corresponding optically active alcohols (80~99% yield).

Catalytic asymmetric functionalization of olefins constitutes one of the most powerful methods for the preparation of optically active compounds.[1] Recently, we have developed optically active monodentate phosphine ligands, 2-(diphenylphosphino)-1,1'-binaphthyls (MOP's),[2] which are highly effective for the palladium-catalyzed asymmetric hydrosilylation of terminal olefins[3] and cyclic meso olefins.[4] Our continuing interest in asymmetric hydrosilylation led us to examine the hydrosilylation of acyclic internal olefins[5] by use of the palladium-MOP catalyst (Scheme 1). We wish to report herein the asymmetric hydrosilylation of β-substituted styrenes catalyzed by the palladium-MOP which achieves both high enantioselectivity and high regioselectivity giving optically active benzylic silanes of up to 85% ee. Although several reports have appeared on the catalytic asymmetric functionalization of styrene derivatives[6] including hydrometallation reactions[7] such as hydrosilylation and hydroboration, the high enantioselectivity has been achieved only for the styrenes which do not have substituents at the β-position.

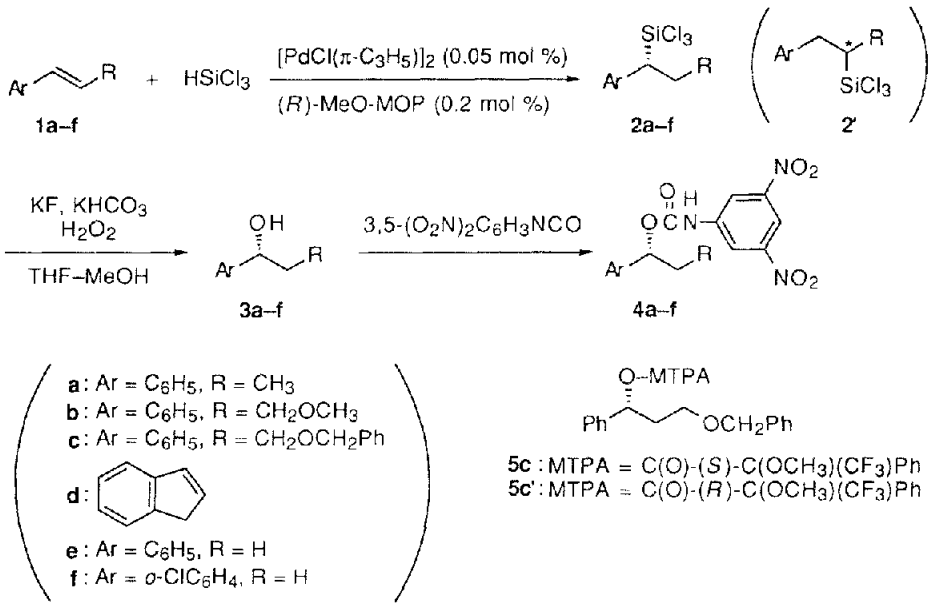
Scheme 1



Treatment of (*E*)-1-phenyl-1-propene (**1a**) with trichlorosilane in the presence of 0.1 mol % of palladium-MOP complex, generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and (*R*)-2-methoxy-2'-diphenylphosphino-1,1'-binaphthyl ((*R*)-MeO-MOP), in toluene at 40 °C for 48 h gave an 89% yield of 1-phenyl-1-trichlorosilylpropane (**2a**) as a single regioisomer. The carbon-silicon bond of **2a** was cleaved oxidatively by a modified Tamao's method (KF, $KHCO_3$, 30% H_2O_2, THF-MeOH, rt, 10 h)[4a,8] to give 1-phenylpropanol (**3a**) in 88% yield. The absolute configuration was determined to be *R* by measurement of the optical rotation of **3a** ($[\alpha]_D^{20}$ +35.2 (*c*

1.34, chloroform). lit.[9] for (*S*)-**3a**: $[\alpha]_D$ –45.45 (*c* 5.15, chloroform)), and the enantiomeric excess was determined to be 82% ee by HPLC analysis of the (3,5-dinitrophenyl)carbamate ester **4a** with a chiral stationary phase column (SUMICHIRAL OA-4100, *n*-hexane/dichloroethane/ethanol = 50/15/1) (Scheme 2).

Scheme 2



The asymmetric hydrosilylation of (*E*)-1-phenyl-3-alkoxy-1-propenes **1b** and **1c** took place under similar conditions to give high yields of the corresponding benzylic silanes **2b** and **2c**. Both of these were found to have an 80% ee by the HPLC analysis of carbamates **4b** and **4c**. The high regio- and enantioselectivity was also demonstrated in the asymmetric hydrosilylation of a cyclic substrate containing an arylalkene moiety. Thus, indene (**1d**) underwent the hydrosilylation reaction under similar conditions to give 88% yield of 1-silylindane **2d** as a single regioisomer. Oxidative cleavage of the carbon-silicon bond gave optically active (*R*)-1-hydroxyindane (**3d**) in 94% yield (**3d**: $[\alpha]_D^{22}$ –29.2 (*c* 1.02, chloroform), lit[10] for (*S*)-**3d** of 97% ee: $[\alpha]_D^{22}$ +32.98 (*c* 3, chloroform)). The enantiomeric excess of **3d** was determined to be 85% ee by the HPLC analysis of **4d**. These results are summarized in Table 1, which also includes the results obtained for the reaction of β-unsubstituted styrenes **1e** and **1f** for comparison. The regioselectivity in the formation of the benzylic silanes **2** was perfect (>99/1) for all the arylalkenes, regioisomers **2'** being not detected (entries 1–4). High regioselectivity in forming benzylic silanes has been reported for palladium-catalyzed hydrosilylation of β-unsubstituted styrenes.[11] The enantioselectivity observed for the reaction of β-substituted styrenes **1a–d** was higher than that for styrene (**1e**) (entry 5), indicating that the substituents at β-position of styrenes raise the enantioselectivity. It is noteworthy that the present asymmetric hydrosilylation is in striking contrast to the rhodium-catalyzed asymmetric hydroboration[7d] where β-substituted styrenes suffer from significant loss of enantioselectivity. Thus the enantioselectivity observed for the hydroboration of **1a** and **1d** catalyzed by

rhodium-BINAP is lower than 50% ee while that for styrene is 96% ee.[7d] Accordingly, the asymmetric hydrosilylation reaction plays a complementary role to the hydroboration in the preparation of optically active alcohols from a variety of arylalkenes. It is also interesting that *o*-chlorostyrene (**1f**) gave a higher enantiomeric excess than styrene (**1e**) in the hydrosilylation reaction (entries 5 and 6). In the rhodium-catalyzed hydroboration, the introduction of an *ortho*-substituent resulted in lower enantioselectivity.[7d]

Table 1. Asymmetric Hydrosilylation of Aryl-Substituted Olefins Catalyzed by Palladium-MOP[a]

entry	styrene **1**	conditions	yield of **2**[b] (**2**/**2'**)[e]	yield of **3**[b,c]	% ee[d] (config)[f]
1[g]	**1a**	40 °C, 48 h	89 (>99/1)	88	82 (*R*)[h]
2[i]	**1b**	40 °C, 72 h	94 (>99/1)	99	80 (*R*)[j]
3[g]	**1c**	40 °C, 7 d	91 (>99/1)	80	80 (*R*)[k]
4[l]	**1d**	5 °C, 72 h	88 (>99/1)	94	85 (*R*)[m]
5[i]	**1e**	5 °C, 44 h	100 (>99/1)	97	71 (*R*)[n]
6[l]	**1f**	5 °C, 13 h	99 (>99/1)	95	81 (*R*)[o]

[a] All reactions were run in the presence of palladium-MOP catalyst prepared in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and ligand (*R*)-MeO-MOP. The ratio of **1**/$HSiCl_3$/Pd/P is 1/1.2/0.001/0.002. [b] Isolated yield. [c] Derived from **2** by the oxidation (see text). [d] Determined by HPLC analysis of **4** with a chiral stationary phase column (SUMICHIRAL OA-4000 or 4100). [e] Determined by GLC or ^1H NMR analysis. [f] Determined by measurement of optical rotation unless otherwise noted. [g] Solvent = toluene (1 M soln). [h] $[\alpha]_D^{20}$ +35.2 (*c* 1.34, chloroform) (ref 9). [i] Solvent = benzene (1 M soln). [j] $[\alpha]_D^{20}$ +30.1 (*c* 0.74, cyclopentane) (lit[12] for (*R*)-**3b** of 34% ee: $[\alpha]_D^{20}$ +11.1 (*c* 3.78, cyclopentane)). [k] $[\alpha]_D^{20}$ +20.0 (*c* 0.47, chloroform). Absolute configuration was determined by NMR studies on MTPA esters **5c** and **5c'** (ref 12, 13, 14). [l] Without solvent. [m] $[\alpha]_D^{22}$ −29.2 (*c* 1.02, chloroform) (lit[10] for (*S*)-**3d** of 97% ee: $[\alpha]_D^{22}$ +32.98 (*c* 3, chloroform)). [n] $[\alpha]_D^{22}$ +35.8 (*c* 0.96, dichloromethane) (lit[15] for (*S*)-**3e**: $[\alpha]_D^{22}$ −52.5 (*c* 1.3, dichloromethane)). [o] $[\alpha]_D^{20}$ +48.4 (*c* 0.27, chloroform) (lit[7d] for (*R*)-**3f** of 72.1% ee: $[\alpha]_D^{20}$ +22.4 (*c* 1.1, chloroform). See also ref 16).

On account of the synthetic utility of the optically active benzylic silanes, where the carbon-silicon bond is readily convertible into a corresponding carbon-carbon bond as well as a carbon-oxygen bond in a stereo-retention manner,[17] this asymmetric hydrosilylation process is of importance for the preparation of a variety of chiral compounds in optically active form.

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14 Selected NMR data (ppm) are as follows: **5c**: ^{19}F NMR ($CDCl_3$, reference = CF_3COOH) δ 6.31. ^{1}H NMR ($CDCl_3$) δ 2.08 (-CH_2CH_2O-), 2.28 (-CH_2CH_2O-), 4.47 (-OCH_2Ph). **5c'**: ^{19}F NMR ($CDCl_3$, reference = CF_3COOH) δ 6.49. ^{1}H NMR ($CDCl_3$) δ 2.05 (-CH_2CH_2O-), 2.25 (-CH_2CH_2O-), 4.41 (-OCH_2Ph).

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