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Asymmetric Synthesis of 1-Aryl-1,2-ethanediols from Arylacetylenes by Palladium-Catalyzed Asymmetric Hydrosilylation as a Key Step

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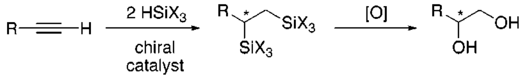
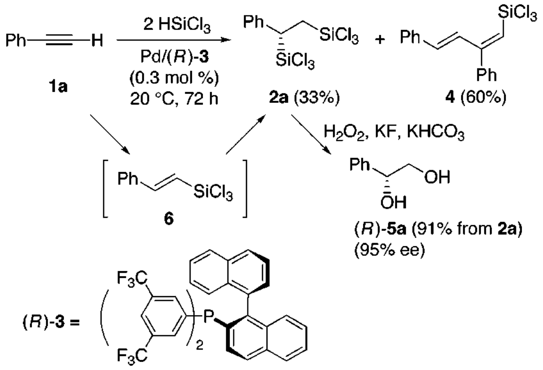
Methods of transforming alkynes into 1,2-diols have not been well developed so far due to the difficulty in the addition of water or its synthetic equivalent twice in a regioselective manner.[1] Especially, asymmetric synthesis of 1,2-diols from alkynes by this transformation is a formidable challenge in organic synthesis. Recently, Weissensteiner has reported the first example of this type of asymmetric transformation using rhodium-catalyzed asymmetric hydroboration of an alkenylboronic ester which is accessible by hydroboration of phenylacetylene,[2] but the selectivity in giving diol or the enantioselectivity is not high enough despite his extensive studies on the reaction conditions. Our plan is to use the catalytic asymmetric hydrosilylation[3] as a key step (Scheme 1). If the double hydrosilylation took place with high regioselectivity and with high enantioselectivity[4] and the oxidation of the resulting 1,2-disilylalkanes into 1,2-diols[5] proceeded in a high yield without loss of their enantiomeric purity, the asymmetric synthesis of 1,2-diols from alkynes would be successful.

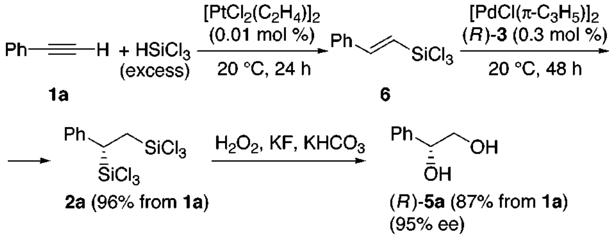
Scheme 1



Scheme 2



Scheme 3



Our initial studies were focused on the screening of chiral transition metal catalysts which are capable of promoting double hydrosilylation of phenylacetylene (**1a**) giving 1,2-bis(silyl)phenylethane. It was found that the double hydrosilylation takes place with trichlorosilane in the presence of a palladium complex coordinated with axially chiral monodentate phosphine ligands (MOP),[6,7] though the selectivity in giving 1,2-bis(trichlorosilyl)phenylethane (**2a**) was not high enough. Thus, as one of the best examples, the reaction of **1a** with 4.5 equiv of trichlorosilane in the presence of 0.3 mol % (Pd) of a palladium catalyst generated from $[PdCl(\pi\text{-}C_3H_5)]_2$ and (*R*)-2-bis[3,5-bis(trifluoromethyl)phenyl]phosphino-1,1′-binaphthyl (**3**)[8] (two equivalents to Pd) at 20 °C for 72 h (Scheme 2) gave 33% yield of 1,2-bis(trichlorosilyl)phenylethane (**2a**) together with 60% yield of 1-trichlorosilyl-2,4-diphenyl-1,3-butadiene (**4**).[9] The oxidation of **2a** with hydrogen peroxide in the presence of potassium fluoride[10] gave (*R*)-phenyl-1,2-ethanediol (**5a**)[11,12] of 95% ee in 91% yield (based on **2a**). The high enantiomeric purity of **5a** may demonstrate that the oxidation of 1,2-bis(trichlorosilyl)alkane **2a** proceeded without loss of stereochemistry as has been observed for the oxidation of mono(silyl)alkanes.[3,10] Monitoring the palladium-catalyzed hydrosilylation of **1a** by GLC analysis revealed that most of the phenylacetylene (**1a**) is consumed in 24 h to give (*E*)-1-phenyl-2-trichlorosilylethene (**6**) and **4** in a ratio of about 1 to 2 and the mono-hydrosilylation product **6** is slowly converted into the double hydrosilylation product **2a** at the later stage. In a separate experiment, the reaction of monohydrosilylation product **6** with trichlorosilane catalyzed by 0.3 mol % of the palladium/(*R*)-**3** complex at 20 °C for 42 h gave 96% yield of 1,2-bis(trichlorosilyl)alkane **2a** which is the (*R*) isomer of 96% ee. It follows that the palladium/(*R*)-**3** complex catalyzes the second hydrosilylation with perfect regioselectivity and with high enantioselectivity[13] though the first hydrosilylation is accompanied by the dimerization−hydrosilylation of alkyne forming **4**.

Although the asymmetric double hydrosilylation catalyzed by the palladium/(*R*)-**3** complex gave the diol **5a** with high enantioselectivity, the yield is not high enough. On the basis of the report that the platinum-catalyzed hydrosilylation of 1-alkynes gives a high yield of (*E*)-1-(silyl)-1-alkenes,[14] $[PtCl_2(C_2H_4)]_2$[15] was used for the hydrosilylation of phenylacetylene (**1a**) with trichlorosilane. At 20 °C for 16 h, the reaction with 0.01 mol % of the platinum catalyst gave 97% yield of **6** together with a small amount of its regioisomer, 1-phenyl-1-trichlorosilylethene (1%), and 1-phenyl-2-trichlorosilylethane (2%). It is important that the selectivity in forming **6** is high and the platinum does not catalyze the second hydrosilylation under the reaction conditions. These results indicate that the high-yield asymmetric double hydrosilylation of acetylene **1a** in one pot should be realized by use of the platinum catalyst for the first-step hydrosilylation and the palladium/(*R*)-**3** catalyst for the second-step[16] (Scheme 3). Thus, to a mixture of phenylacetylene (**1a**) (1.02 g, 10.0 mmol) and $[PtCl_2(C_2H_4)]_2$ (0.3 mg, 1 μmol Pt) was added trichlorosilane (4.5 mL, 45 mmol), and the mixture was stirred at 20 °C. After consumption of **1a** (24 h), a solution of $[PdCl(\pi\text{-}C_3H_5)]_2$ (5.5 mg, 30 μmol Pd) and (*R*)-**3** (43 mg, 60 μmol) in toluene

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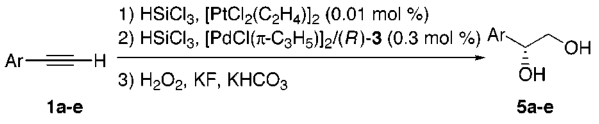
Scheme 4



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-$CF_3C_6H_4$ (**d**), 3-$NO_2C_6H_4$ (**e**)

Table 1. Catalytic Asymmetric Synthesis of 1,2-Diols **5** Starting from Arylacetylenes **1** by Successive Platinum- and Palladium-Catalyzed Hydrosilylation[a]

	acetylene	time (h)		yield[b] (%)	% ee[c] of	[α]$^{20}_{D}$ of
entry	**1**	Pt[d]	Pd[e]	of **5**	**5** (config)	**5** (*c* 1.0)
1[f]	**1a**	24	48	87 (**5a**)	95 (*R*)	
2	**1a**	24	48	75 (**5a**)	95 (*R*)	−36.4 (EtOH)
3	**1b**	18	24	83 (**5b**)	95 (*R*)	−64.9 ($CHCl_3$)
4	**1c**	24	72	75 (**5c**)	94 (*R*)	−57.0 ($CHCl_3$)
5[g]	**1d**	24	168	50 (**5d**)	96 (*R*)	−46.0 ($CHCl_3$)
6[g]	**1e**	20	72	67 (**5e**)	98 (*R*)	−26.8 (MeOH)

[a] The double hydrosilylation was carried out at 20 °C in a one-pot reaction. The platinum catalyst $[PtCl_2(C_2H_4)]_2$ and the palladium catalyst generated from $[PdCl(\pi\text{-}C_3H_5)]_2$ and (*R*)-**3** were used for the first-step and the second-step hydrosilylation, respectively. The hydrogen peroxide oxidation was carried out for the crude hydrosilylation products **2**. The ratio of **1**/$HSiCl_3$/Pt/Pd/(*R*)-**3** is 1/4.5/0.0001/0.003/0.006. [b] Isolated yield. [c] Determined by HPLC analysis with chiral stationary phase columns: Daicel Chiralcel OB-H (**5a**) (eluent, hexane/2-propanol = 90/10), double OB-H (**5b**, **5e**) (eluent, hexane/2-propanol = 90/10), AS (**5c**, **5d**) (eluent, hexane/2-propanol = 90/10). [d] Reaction time for the platinum-catalyzed hydrosilylation. [e] Reaction time for the palladium/**3**-catalyzed hydrosilylation. [f] After the second-step hydrosilylation, the oxidation was carried out for the distilled **2a**. [g] With 0.006 equiv (to arylacetylene) of $[PdCl(\pi\text{-}C_3H_5)]_2$ and 0.012 equiv of (*R*)-**3**.

(1 mL) was added, and the whole mixture was stirred at the same temperature for 48 h. Distillation under reduced pressure gave 3.60 g (96% yield) of 1,2-bis(trichlorosilyl)phenylethane (**2a**), which was subjected to the oxidation with hydrogen peroxide in the presence of potassium fluoride and potassium hydrogen carbonate to give 1.20 g (87% yield from **1a**) of (*R*)-phenyl-1,2-ethanediol (**5a**) whose enantiomeric purity is 95%.[12] Oxidation of the double hydrosilylation product **2a** without isolation is also possible, though the overall yield is somewhat lower, probably due to the decomposition of hydrogen peroxide during the oxidation by the platinum and/or palladium catalysts used for the hydrosilylation (entries 1 and 2 in Table 1).

The catalytic asymmetric synthesis of 1-aryl-1,2-diols **5b**−**e** containing substituents on the phenyl ring was also successful from the corresponding arylacetylenes **1b**−**e**. The results obtained for the successive platinum- and palladium-catalyzed hydrosilylation followed by oxidation of the crude bis(silyl)ethanes are summarized in Table 1. The enantioselectivity is all high (ranging between 94% and 98% ee) irrespective of the electron-donating or -withdrawing characters of the substituents on the phenyl (entries 3−6). It also should be noted that the hydrosilylation was carried out (1) without solvent, (2) in the presence of a very small amount of the catalysts, and (3) at room temperature (20 °C). Unfortunately, alkyl-substituted acetylenes cannot be converted into the corresponding 1,2-diols by the present method because the second palladium-catalyzed hydrosilylation is very slow.

In summary, we have realized the asymmetric synthesis of 1,2-diols from arylacetylenes by use of the palladium-catalyzed asymmetric hydrosilylation as a key step. The present method provides a new efficient and practical route to enantiomerically enriched 1,2-diols, which have been mainly prepared from alkenes by the catalytic asymmetric oxidation reactions.[17,18]

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Supporting Information Available: Experimental procedures and spectroscopic and analytical data for the substrates and products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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