Pergamon

Tetrahedron Letters, Vol. 35, No. 27, pp. 4813-4816, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)00966-X

Asymmetric Synthesis of Allylsilanes by Palladium-Catalyzed Asymmetric Reduction of Allylic Carbonates with Formic Acid[1]

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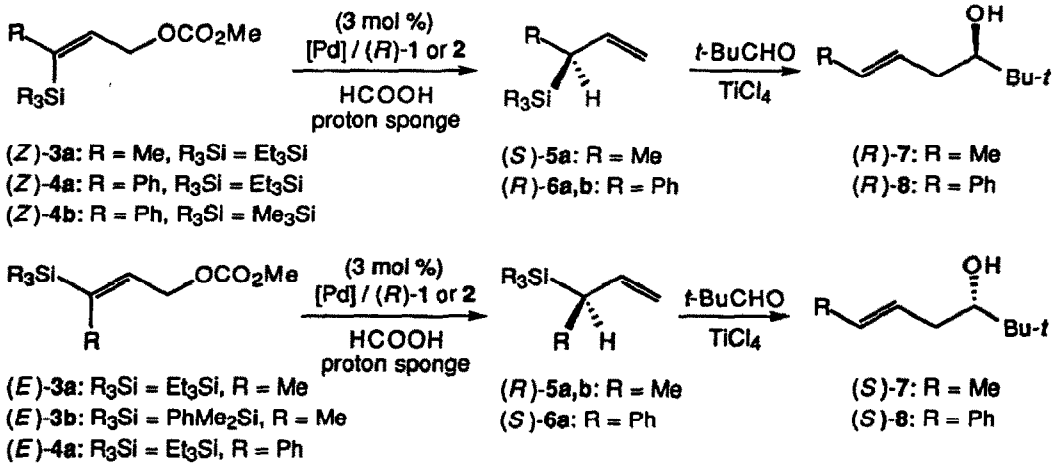
Abstract: Reduction of 3-alkyl-3-trialkylsilyl-2-propenyl methyl carbonates with formic acid and 1,8-bis(dimethylamino)naphthalene in the presence of a palladium catalyst (3 mol %) coordinated with (*R*)-3-diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (MOP-phen) gave optically active allylsilanes (3-alkyl-3-trialkylsilyl-1-propenes) of up to 91% ee.

Optically active allylsilanes are useful chiral reagents in organic synthesis, reacting with electrophiles in an S_E' fashion to give a wide variety of optically active compounds.[2,3,4] Of the various ways to obtain the optically active allylsilanes, the most efficient is asymmetric synthesis by means of a chiral catalyst, as it is the case for any kinds of chiral molecules.[5] We have so far developed several synthetic methods for their preparation by use of palladium-catalyzed asymmetric reactions, *i. e.*, asymmetric cross-coupling of 1-silylalkyl Grignard reagents with alkenyl halides,[6] asymmetric hydrosilylation of 1,3-dienes,[7] and asymmetric silylation of allylic chlorides with a disilane.[8] Here we wish to report an alternative method for their preparation which is achieved by asymmetric reduction of silyl-substituted allylic carbonates with formic acid in the presence of a chiral monodentate phosphine-palladium catalyst (Scheme 1).

We have previously found that the asymmetric reduction of 2-propenyl carbonates bearing two different alkyl groups at 3-position is efficiently catalyzed by a palladium catalyst coordinated with axially chiral monodentate phosphine ligand, (*R*)-2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl ((*R*)-MOP (1)),[9] or its biphenanthryl analog, (*R*)-MOP-phen (2),[10] to give optically active olefins of up to 85% ee.[11] Under similar reaction conditions, the catalytic reduction of (*E*)- and (*Z*)-3-alkyl-3-trialkylsilyl-2-propenyl methyl carbonates **3** and **4**[12] was carried out. The results are summarized in Table 1.

Scheme 1



(*Z*)-**3a**: R = Me, R_3Si = Et_3Si
(*Z*)-**4a**: R = Ph, R_3Si = Et_3Si
(*Z*)-**4b**: R = Ph, R_3Si = Me_3Si

(*S*)-**5a**: R = Me
(*R*)-**6a,b**: R = Ph

(*R*)-**7**: R = Me
(*R*)-**8**: R = Ph

(*E*)-**3a**: R_3Si = Et_3Si, R = Me
(*E*)-**3b**: R_3Si = $PhMe_2Si$, R = Me
(*E*)-**4a**: R_3Si = Et_3Si, R = Ph

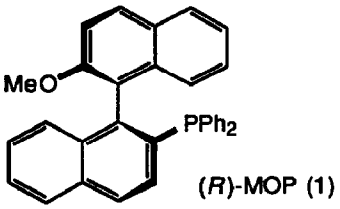
(*R*)-**5a,b**: R = Me
(*S*)-**6a**: R = Ph

(*S*)-**7**: R = Me
(*S*)-**8**: R = Ph

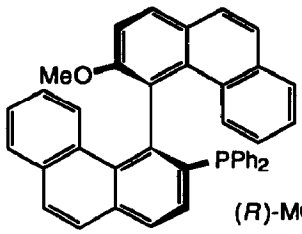
Table 1. Asymmetric Synthesis of Allylsilanes by Catalytic Asymmetric Reduction of Allylic Carbonates 3 and 4 with Palladium-MOP (1) or Palladium-MOP-phen (2) Catalyst[a]

entry	allylic carbonate	ligand	reaction time (h)	product	yield[b] (%)	$[\alpha]_D^{20}$ (benzene)[c]	abs config[d]	% ee[e] of 7 or 8
1	(*Z*)-**3a**	(*R*)-MOP-phen (**2**)	23	**5a**	90	−38.1	*S*	72 (**7**)
2	(*Z*)-**3a**	(*R*)-MOP (**1**)	15	**5a**	89		*S*	60 (**7**)
3	(*Z*)-**4a**	(*R*)-MOP-phen (**2**)	36	**6a**	98	−55.2	*R*	88 (**8**)
4	(*Z*)-**4a**	(*R*)-MOP (**1**)	31	**6a**	95		*R*	69 (**8**)
5	(*Z*)-**4b**	(*R*)-MOP-phen (**2**)	26	**6b**	93	−57.1	*R*	91 (**8**)
6	(*Z*)-**4b**	(*R*)-MOP (**1**)	24	**6b**	87		*R*	80 (**8**)
7	(*E*)-**3a**	(*R*)-MOP (**1**)	15	**5a**	98		*R*	45 (**7**)
8	(*E*)-**3b**	(*R*)-MOP-phen (**2**)	14	**5b**	91	+23.9	*R*	44 (**7**)
9	(*E*)-**3b**	(*R*)-MOP (**1**)	6	**5b**	91		*R*	37 (**7**)
10	(*E*)-**4a**	(*R*)-MOP (**1**)	23	**6a**	87		*S*	33 (**8**)

[a] The reduction was carried out at 20 °C with 2.2 equiv of formic acid in dioxane in the presence of 1.2 equiv of 1,8-bis(dimethylamino)naphthalene and 3.0 mol % of catalyst prepared in situ by mixing $Pd_2(dba)_3$•$CHCl_3$ and a chiral ligand (2 equiv to Pd). [b] Isolated yield by silica-gel column chromatography. [c] *c* = 0.5-1.0. [d] The configurations of **5a**, **5b** and **6b** were determined by comparison of their optical rotation values with those reported (ref 6). For **6a**, its configuration was deduced from the absolute configuration of the homoallyl alcohol **8** (ref 3c). The optical rotation of (*R*)-**8** obtained in entry 8 is $[\alpha]_D^{20}$ +39.5 (*c* 0.6, CCl_4). [e] Determined by HPLC analysis of 3,5-dinitrophenyl carbamate esters of **7** and **8** with chiral stationary phase column (Sumichiral OA-4500 and OA-4900 cascade connection for **7** and OA-4500 for **8**) (*n*-hexane/dichloroethane/ethanol = 68/17/1).



(*R*)-MOP (**1**)

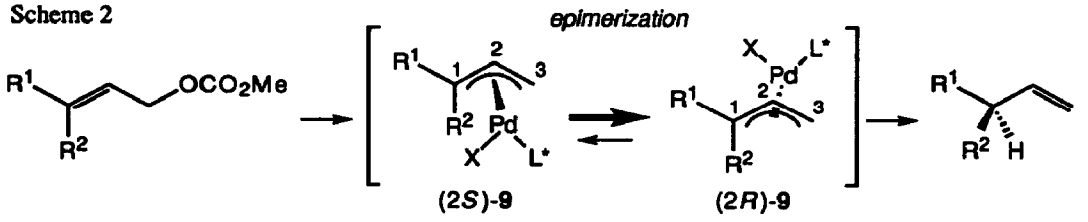


(*R*)-MOP-phen (**2**)

Reaction of (*Z*)-3-triethylsilyl-2-butenyl methyl carbonate ((*Z*)-**3a**) with formic acid (2.2 equiv) and 1,8-bis(dimethylamino)naphthalene (proton sponge) (1.2 equiv) in the presence of 3 mol % of a palladium catalyst generated in situ from $Pd_2(dba)_3$•$CHCl_3$ and (*R*)-MOP-phen (**2**) (P/Pd = 2/1) in dioxane at 20 °C for 23 h proceeded regioselectively to give 90% yield of (*S*)-3-triethylsilyl-1-butene[6] (**5a**) ($[\alpha]_D^{20}$ −38.1 (*c* 0.7, benzene)) (entry 1). Treatment of the allylsilane (*S*)-**5a** with trimethylacetaldehyde and titanium tetrachloride in dichloromethane at −78 °C gave optically active homoallyl alcohol, (*R*)-2,2-dimethyl-5-hepten-3-ol[6,13] (**7**), by the chirality transfer from the allylsilane at the S_E' reaction.[3c,6] Its enantiomeric purity was determined to be 72% ee by HPLC analysis of its 3,5-dinitrophenyl carbamate ester with a chiral stationary phase column (OA-4500 and OA-4900), indicating that the enantiomeric purity of allylsilane (*S*)-**5a** produced by the catalytic asymmetric reduction is at least 72% ee. The asymmetric reduction of (*Z*)-3-phenyl-3-silylpropenyl carbonates (*Z*)-**4a** and (*Z*)-**4b** proceeded with higher enantioselectivity to give allylsilanes (*R*)-**6a** and **6b** that contain phenyl group at the chiral carbon center (entries 3 and 5). Their enantiomeric purities were determined to be

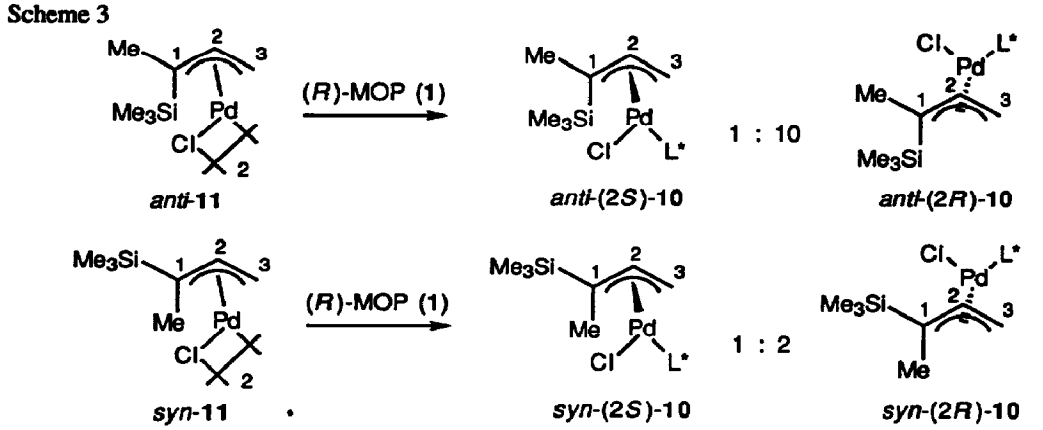
higher than 88% and 91% ee, respectively, by converting the allylsilanes into homoallyl alcohol (*R*)-(*E*)-**8**[14] in a similar manner. The binaphthyl ligand MOP (**1**) was not so effective as the biphenanthryl analog **2** for the present asymmetric reduction (entries 2, 4, and 6), as it has been usually observed for the reduction of other allylic carbonates.[10,11] The asymmetric reduction of the allyl carbonates bearing (*E*) double bond under the same reaction conditions gave the corresponding allylsilanes with opposite configuration to those from (*Z*) carbonates (entries 7-10). The reaction pathway in the catalytic asymmetric reduction where (*E*) and (*Z*) carbonates produce the olefins with opposite absolute configuration has been discussed in the reaction of 3,3-dialkyl-2-propenyl carbonates in our previous paper (Scheme 2).[10,11] It has been proposed by NMR studies of model π-allylpalladium complexes that π-allylpalladium intermediates **9** undergo the epimerization but do not undergo the *syn-anti* isomerization and the enantiomeric purity of the product is determined mainly by the thermodynamic stability of the epimeric π-allylpalladium intermediates **9**.[10,11]

Scheme 2



L* = (*R*)-MOP (**1**) or (*R*)-MOP-phen (**2**): X = OCO_2Me, OCHO, H

Scheme 3



It is interesting that the enantioselectivity observed in the asymmetric reduction of (*Z*) carbonates is always higher than that of (*E*) carbonates in the present system. ^1H and ^{31}P NMR studies of *syn* and *anti* isomers of a model π-allylpalladium complex, PdCl(η^3-1-methyl-1-(trimethylsilyl)allyl)((*R*)-MOP) (**10**), indicated that the higher enantioselectivity in the reaction of (*Z*) carbonates can be accounted for by the larger difference in thermodynamic stability between the epimeric pairs of *anti*-π-allylpalladium complex than those of the *syn* isomer (Scheme 3). Thus, the *anti* isomer of π-allyl(MOP)palladium complex **10**, generated by mixing [PdCl(η^3-*anti*-1-methyl-1-(trimethylsilyl)allyl)]$_2$[15] (*anti*-**11**) with 1 equiv (to palladium atom) of (*R*)-MOP (**1**) in $CDCl_3$ at 0 °C, was found to exist as a mixture of epimers in a ratio of 10 to 1,[16] while the ratio of the epimers of the *syn* isomer (*syn*-**10**) generated in a similar manner from *syn*-**11**[15] was 2 to 1.[17] The unusually high field shift of the proton (2.95 ppm)[16] on C-2 carbon on the π-allyl group of the major epimer of *anti*-**10** suggests that

the major isomer has (2*R*) absolute configuration,[11] which is consistent with the absolute configuration of the allylsilanes formed by the catalytic asymmetric reduction of (*Z*)-carbonates.

Acknowledgment. We thank the Ministry of Education, Japan, for a Grant-in-Aid for Scientific Research, Uehara Memorial Foundation for partial financial support of this work.

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13 The *E*/*Z* ratio of homoallylalcohol **7** is 18/1.

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16 NMR (δ, $CDCl_3$, 0 °C) for *anti*-**10**. Major isomer: ^1H NMR: –0.20 (s, 9 H), 1.24 (d, J = 8.6 Hz, 3 H), 1.33 (d, J = 11.9 Hz, 1 H), 2.81 (d, J = 6.9 Hz, 1 H), 2.95 (dd, J = 6.9, 11.9 Hz, 1 H), 3.20 (s, 3 H), 6.8-8.0 (m, 22 H), $^{31}P\{^1H\}$ NMR: 18.1 (s). Minor isomer: ^1H NMR: 0.22 (s, 9 H), 1.65 (d, J = 8.6 Hz, 3 H), 2.62 (d, J = 12.0 Hz, 1 H), 2.77 (d, J = 7.0 Hz, 1 H), 3.51 (s, 3 H), 5.18 (dd, J = 7.0, 12.0 Hz, 1 H), 6.8-8.0 (m, 22 H), $^{31}P\{^1H\}$ NMR: 26.6 (s).

17 NMR (δ, $CDCl_3$, 0 °C) for *syn*-**10**. Major isomer: ^1H NMR: 0.19 (s, 9 H), 1.02 (d, J = 5.9 Hz, 3 H), 1.92 (d, J = 12.5 Hz, 1 H), 2.51 (d, J = 6.6 Hz, 1 H), 3.49 (s, 3 H), 4.04 (dd, J = 6.6, 12.5 Hz, 1 H), 6.8-8.0 (m, 22 H), $^{31}P\{^1H\}$ NMR: 22.6 (s). Minor isomer: ^1H NMR: 0.24 (s, 9 H), 1.24 (d, J = 5.6 Hz, 3 H), 2.73 (d, J = 6.5 Hz, 1 H), 2.80 (d, J = 12.0 Hz, 1 H), 3.61 (s, 3 H), 5.20 (dd, J = 6.5, 12.0 Hz, 1 H), 6.8-8.0 (m, 22 H), $^{31}P\{^1H\}$ NMR: 29.9 (s).

(*Received in Japan* 11 *April* 1994; *accepted* 11 *May* 1994)