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# PREPARATION OF OPTICALLY ACTIVE ALLYLSILANES BY CATALYTIC ASYMMETRIC HYDROSILYLATION OF 1-ARYLBUTADIENES[1]

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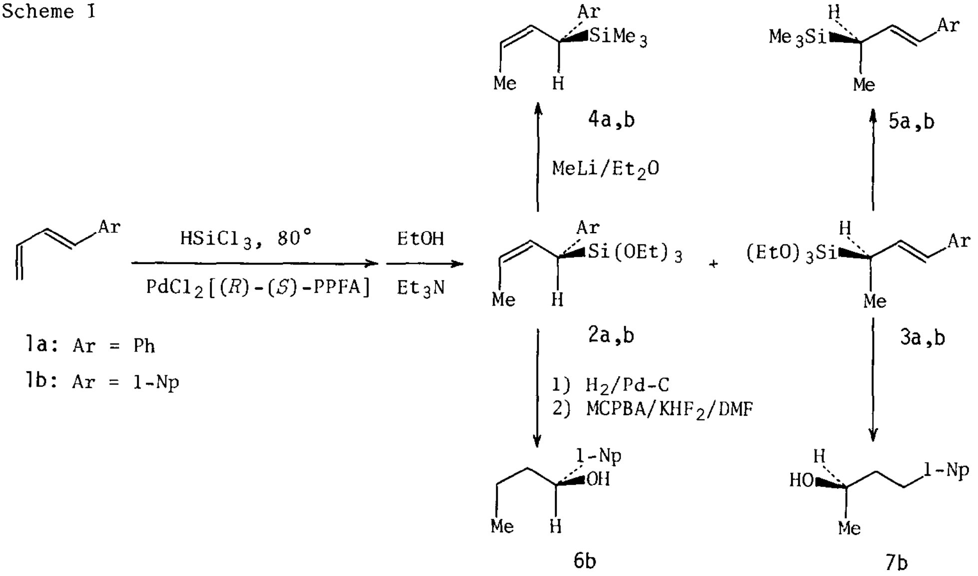
Summary: Asymmetric hydrosilylation of 1-arylbutadienes with trichlorosilane in the presence of a chiral ferrocenylphosphine-palladium catalyst gave optically active allylsilanes, (Z)-1-aryl-1-silyl-2-butenes and their regioisomers.

Here we report asymmetric hydrosilylation of 1-arylbutadienes catalyzed by a chiral phosphine-palladium complex,[2] which produces optically active allylsilanes containing a chiral carbon center directly bonded to the silicon atom and provides significant information regarding the mechanism of the hydrosilylation. Some optically active allylsilanes of this type have been previously prepared by the asymmetric Grignard cross-coupling[3] and shown to be useful for the elucidation of anti stereochemistry of $S_E$' reaction of allylsilanes and for the preparation of various kinds of optically active compounds by an asymmetric induction.[4]

A mixture of trichlorosilane (12 mmol), (E)-1-phenylbutadiene (**1a**) (10 mmol), and dichloro[(R)-N,N-dimethyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine]palladium(II)[5] ($PdCl_2$[(R)-(S)-PPFA]) (0.001 mmol, 0.01 mol%) was heated in a sealed glass tube at 80°C for

Scheme I

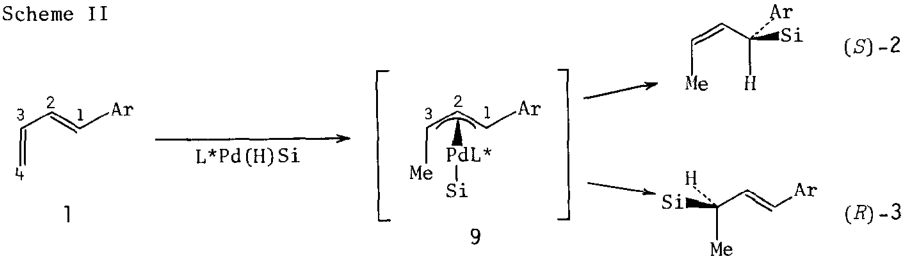


16 h. Treatment of the reaction mixture with ethanol and triethylamine afforded 62% yield of allyltriethoxysilanes consisting of (*Z*)-1-phenyl-1-triethoxysilyl-2-butene (**2a**) ($[\alpha]_D^{20}$ +54.5° (*c* 4.5, benzene)) and its regioisomer (*E*)-1-phenyl-3-triethoxysilyl-1-butene (**3a**) in a ratio of 94 : 6. Methylation of the triethoxysilanes **2a** and **3a** with methyllithium in ether gave known optically active allyltrimethylsilanes (*S*)-(*Z*)-**4a** ($[\alpha]_D^{20}$ +56.2° (*c* 5.15, benzene), 64% ee)[3] and (*R*)-(*E*)-**5a** ($[\alpha]_D^{20}$ +6.7° (*c* 0.22, benzene), 30% ee),[6] respectively.

Asymmetric hydrosilylation of (*E*)-1-(1-naphthyl)butadiene (**1b**) carried out in a similar manner gave (*S*)-(*Z*)-allylsilane **4b** ($[\alpha]_D^{20}$ +19.3° (*c* 0.8, benzene), 29% ee) and its regioisomeric allylsilane (*R*)-(*E*)-**5b** ($[\alpha]_D^{20}$ +13.7° (*c* 1.8, benzene), 55% ee) in a ratio of 49 : 51. The configuration and enantiomeric purity of these allylsilanes were determined by converting allyltriethoxysilanes **2b** and **3b** into optically active secondary alkyl alcohols **6b** and **7b**, respectively, by catalytic hydrogenation followed by oxidation of the carbon-silicon bond with MCPBA and $KHF_2$ in DMF (Scheme I). The oxidation has been known to proceed with retention of configuration at carbon.[7]

The stereo- and regiochemical results may be illustrated by the mechanism[8] shown in Scheme II which involves π-allyl(silyl)palladium complex **9** as a key intermediate. Coordination of the diene **1** in a *cisoid* conformation with a hydrido(silyl)palladium species followed by migration of the hydride to the terminal carbon C-4 produces the π-allylpalladium **9**, where the aryl group is located in the *syn* position and the methyl group coming from the terminal carbon is located in the *anti* position. Transfer of the silicon from palladium to the π-allyl carbons C-1 and C-3 leads to **2** and **3**, respectively. The silicon-carbon bond formation must be fast compared with the *syn*-*anti* rearrangement of the π-allyl.[6,9] Preferential attack of the palladium on the *si* face (designated with respect to position 1) of the diene **1** will produce the allylsilanes with the observed absolute configuration. It is likely that the ratio of regioisomers **2** : **3** is determined by the steric factors of the substituents on carbon atoms C-1 and C-3 in the intermediate **9**. The π-allyl carbon with an *anti* substituent seems less liable to undergo the carbon-silicon bond formation than that with a *syn* substituent.

Scheme II



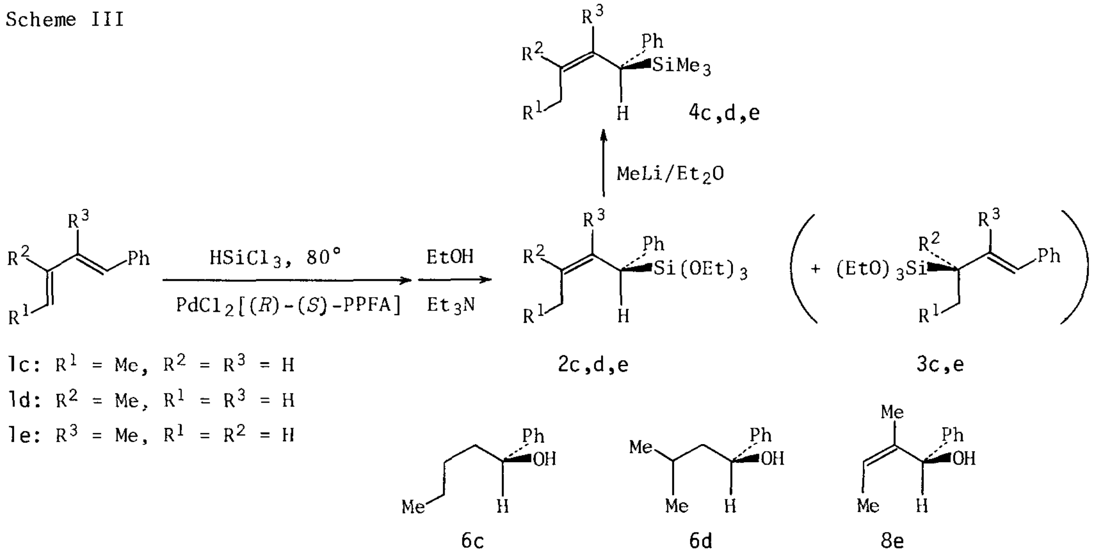
Hydrosilylation of methyl-substituted 1-phenylbutadienes **1c,d,e** was also carried out in the presence of the palladium-PPFA catalyst (Scheme III). Allylsilanes 2 containing the silyl group at the chiral carbon substituted with a phenyl group were formed preferentially over their regioisomers **3**. They had a (*Z*) double bond and their configuration was always (*S*). These results, summarized in Table 1, can be also accommodated within the mechanism in Scheme II.

Table 1. Asymmetric Hydrosilylation of 1-Arylbutadienes **1a–e**.

| butadiene **1** | yield (%) of **2** + **3** | ratio of **2** / **3** | $[\alpha]_D^{20}$ (c, benzene) of **2** and **4** | % ee | $[\alpha]_D^{20}$ (c, benzene) of **3** and **5** | % ee |
|---|---|---|---|---|---|---|
| **1a** | 62 | 94/6 | **2a** +54.5°(4.5) | | | |
| | | | **4a** +56.2°(5.2) | 64(S)[a] | **5a** +6.7°(1.0) | 30(R)[a] |
| **1b** | 66 | 49/51 | **2b** +17° (0.4) | 29(S)[b,c] | **3b** +9.2°(0.7) | 55(R)[b,c] |
| | | | **4b** +19.3°(0.8) | | **5b** +13.7°(1.8) | |
| **1c** | 56 | 93/7 | **2c** +26.9°(4.8) | 31(S)[b,d] | | |
| | | | **4c** +22.9°(5.2) | | | |
| **1d** | 66 | 100/0 | **2d** +42.4°(3.9) | 50(S)[b,d] | | |
| | | | **4d** +33.9°(5.1) | | | |
| **1e** | 74 | 99/1 | **2e** +35.3°(5.1) | 39(S)[b,c] | | |
| | | | **4e** +37.2°(4.6) | | | |

[a] The maximun rotations of (S)-(Z)-1-phenyl-1-trimethylsilyl-2-butene (**4a**) and (R)-(E)-1-phenyl-3-trimethylsilyl-1-butene (**5a**) are $[\alpha]_D^{20}$ +88.4° (benzene) and $[\alpha]_D^{20}$ +22.5° (benzene), respectively (ref. 3 and 5). [b] The enantiomeric purity was determined by $^1H$ NMR spectra of the alcohols, **6b,c,d**, **7b**, and **8e** using chiral shift reagent tris[d,d-dicampholylmethanato]europium(III) [Eu(dcm)$_3$] (ref. 10). **6b**: $[\alpha]_D^{20}$ -20.4° (c 2.0, chloroform). **7b**: $[\alpha]_D^{20}$ -11.4° (c 4.4, chloroform). **6c**: $[\alpha]_D^{20}$ -12.9° (c 1.5, benzene). **6d**: $[\alpha]_D^{25}$ -24.6° (c 1.6, benzene). **8e**: $[\alpha]_D^{20}$ +65.4° (c 1.9, chloroform). [c] The absolute configuration was assigned by $^1H$ NMR of (R)-O-methylmandelic acid esters of **6b**, **7b**, and **8e** (ref. 11). [d] The absolute configuration was determined by comparison of optical rotations of alcohols **6c** and **6d** with those of the pure enantiomers reported in the literature (ref. 12).

Scheme III



1c: $R^1$ = Me, $R^2$ = $R^3$ = H
1d: $R^2$ = Me, $R^1$ = $R^3$ = H
1e: $R^3$ = Me, $R^1$ = $R^2$ = H

Optically active (E)-allylsilanes have been prepared with high enantiomeric purity by the asymmetric Grignard cross-coupling,[3] but the cross-coupling has revealed low stereoselectivity in the preparatin of (Z)-allylsilanes.[3] The present asymmetric hydrosilylation is practically useful in giving the optically active (Z)-allylsilanes (up to 64% ee), though the stereoselectivity still remains to be improved.

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