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OPTICALLY ACTIVE CYCLIC ALLYLSILANES
PREPARATION BY ASYMMETRIC HYDROSILYLATION AND ANTI STEREOCHEMISTRY IN S_E' REACTIONS[1]

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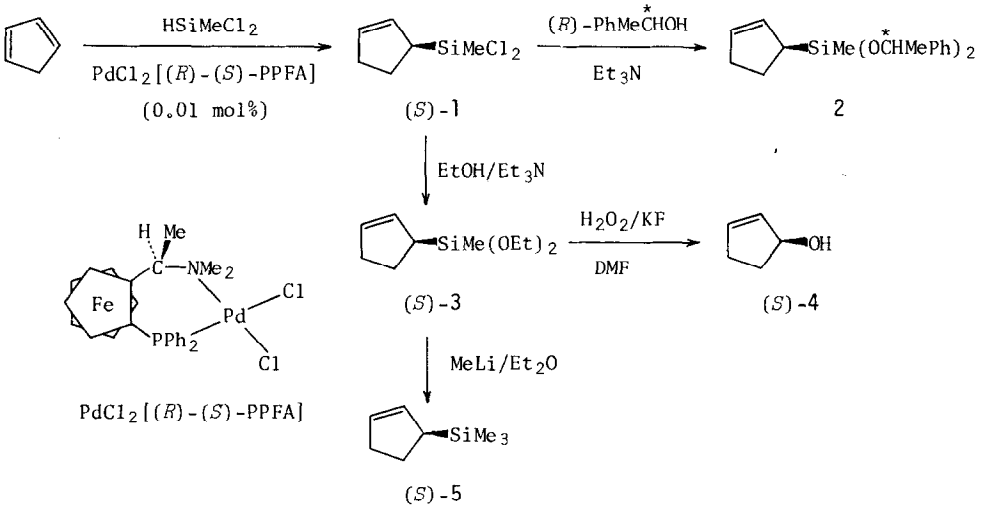
Summary: Reaction of optically active cyclic allylsilanes, (*S*)-3-(trimethylsilyl)cyclopentene and -cyclohexene, which were prepared by palladium-catalyzed asymmetric hydrosilylation of cyclic dienes, with ethylene oxide in the presence of titanium chloride proceeded with anti stereochemistry to give (*R*)-3-(2-hydroxyethyl)cyclopentene and -cyclohexene, respectively.

Allylsilanes are useful intermediates in organic synthesis, reacting with a wide range of electrophiles in a regiospecific manner.[2,3] We have previously demonstrated that the electrophilic substitution (S_E') reaction proceeds with anti stereochemistry by using optically active acyclic linear allylsilanes.[4,5] For cyclic allylsilanes, on the other hand, the reactions of both syn and anti stereochemistry have been reported,[6] where the stereochemistry is considered to be controlled not by the inherent nature of allylsilanes but by the stereochemical bias in the diastereomeric cyclic systems used. We have prepared optically active cyclic allylsilanes which are free from the stereochemical bias and established that the S_E' reaction of cyclic allylsilanes also proceeds with anti stereochemistry.

Hydrosilylation of cyclopentadiene with dichloromethylsilane in the presence of 0.01 mol% of dichloro[(*R*)-*N*,*N*-dimethyl-1-{(*S*)-2-(diphenylphosphino)ferrocenyl}ethylamine]palladium(II)[7] ($PdCl_2$[(*R*)-(*S*)-PPFA]) at 30°C for 20 h gave 3-(dichloromethylsilyl)cyclopentene (**1**)[8,9] in 87% yield (Scheme I). Enantiomeric purity of **1** was determined to be 22~25% by ^{1}H NMR of diastereomeric dialkoxysilane **2**[10] obtained by treatment of **1** with an excess of (*R*)-1-phenylethanol and triethylamine in ether. Dichlorosilane **1** was converted with ethanol and triethylamine into 3-(diethoxymethylsilyl)cyclopentene (**3**)[11] quantitatively which showed $[\alpha]_D^{20}$ -31.9° (*c* 0.5, benzene). Oxidative cleavage of the carbon-silicon bond in (-)-**3** with 30% hydrogen peroxide and potassium fluoride in DMF[12] gave 2-cyclopentenol (**4**) with $[\alpha]_D^{21}$ -30.9° (*c* 1.2, CCl_4), which corresponds to 16% optical purity of *S* isomer.[13] Since the oxidation is established to proceed with retention of configuration at carbon,[12] the diethoxysilane (-)-**3** should have the *S* configuration with 22~25% ee.[14] Methylation of (*S*)-**3** with methyllithium in ether gave (*S*)-3-(trimethyl-

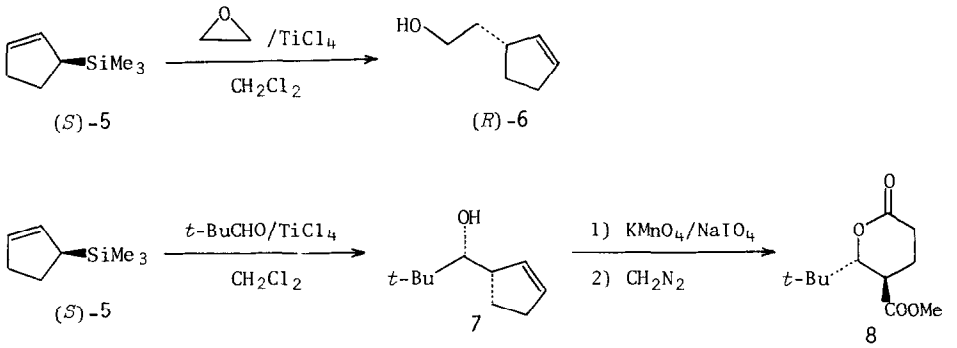
Scheme I



silyl)cyclopentene (**5**)[8,9] with $[\alpha]_D^{20}$ -49.1° (*c* 0.5, benzene).

Trimethylsilane (*S*)-5 was allowed to react with ethylene oxide (1.6 eq) in the presence of titanium chloride (1.2 eq) in dichloromethane at -78°C for 1 min to afford 93% yield of 3-(2-hydroxyethyl)cyclopentene (**6**), which has the rotation of $[\alpha]_D^{26}$ -30.3° (*c* 5.6, $CHCl_3$) indicating that **6** is an *R* isomer of 24% ee.[15] Thus, the S_E' reaction of 3-silylcyclopentene **5** was demonstrated to proceed with anti stereochemistry, the electrophile entering the double bond anti with respect to the leaving trimethylsilyl group (Scheme II).[16]

Scheme II

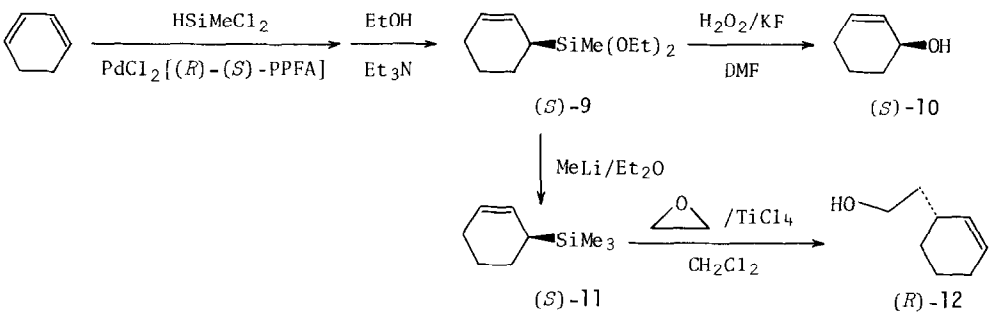


Reaction of (*S*)-5 with pivalaldehyde (1.2 eq) in the presence of titanium chloride (1.2 eq) at -10∿-20°C for 1 h gave 3-(1-hydroxy-2,2-dimethylpropyl)cyclopentene (**7**) in 52% yield. ^1H NMR studies using $Eu(fod)_3$ and $Eu(dcm)_3$[17] showed that **7** consists of two diastereoisomers in a ratio of 83 : 17 and both of the isomers have 24∿26% enantiomeric purity.[18] The major isomer was determined to be erythro by converting it into lactone **8** which has *t*-butyl and methoxycarbonyl

groups in trans positions.[19] The ratio erythro/threo is in good agreement with that observed in the reaction of *cis*-crotyl- and cinnamylsilanes.[20]

A sequence of reactions starting with 1,3-cyclohexadiene was carried out in a similar manner (Scheme III). Asymmetric hydrosilylation of 1,3-cyclohexadiene with dichloromethylsilane and the palladium-PPFA catalyst followed by ethanolysis with ethanol and triethylamine gave 95% yield of 3-(diethoxymethylsilyl)cyclohexene (**9**)[21] ($[\alpha]_D^{20}$ -1.8° (*c* 1.4, benzene)). The cyclohexenylsilane proved to be an *S* isomer of over 1% ee by the oxidation of (-)-**9** giving (*S*)-2-cyclohexenol (**10**)[22] with $[\alpha]_D^{20}$ -1.1° (*c* 2.2, $CHCl_3$). Trimethylsilane (*S*)-**11**[8] ($[\alpha]_D^{20}$ -1.7° (*c* 2.4, benzene)) prepared by methylation of (*S*)-**9** was subjected to the S_E' reaction with ethylene oxide and titanium chloride to give (*R*)-3-(2-hydroxyethyl)cyclohexene (**12**)[23] with 1.6% ee ($[\alpha]_D^{25}$ -1.3° (*c* 1.5, $CHCl_3$)) in 70% yield. These results indicate that the S_E' reaction in the six-membered ring system also proceeded with anti stereochemistry, though the enantiomeric purity of the starting allylsilane was low.[16,24]

Scheme III



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10. ^{1}H NMR ($CDCl_3$, 400 MHz): δ -0.03 (s, 3H), 1.39-1.50 (m, 6H), 1.75-2.08, 2.16-2.40 (m, 5H), 4.88-5.00 (m, 2H), 5.525 (dq, J = 5.6, 2.2 Hz), 5.577 (dq, J = 5.6, 2.4 Hz), 5.620 (dq, J = 5.6, 2.4 Hz), 5.679 (dq, J = 5.6, 2.2 Hz), 7.17-7.35 (m, 10H). The resonances of olefinic protons at 5.525, 5.577 (for *S* isomer) and 5.620, 5.679 (for *R* isomer) were used for determination of the diastereomeric excess.
11. **3**: bp 92-96°C/25 mmHg; NMR (CCl_4): δ 0.04 (s, 3H), 1.16 (t, J = 7 Hz, 6H), 1.70-2.50 (m, 5H), 3.69 (q, 4H), 5.40-5.75 (m, 2H).
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18. ^{1}H NMR (CCl_4) of the diastereoisomers **7**: δ 0.93 (s, 9H), 1.45-2.52 (m, 4H), 2.80-3.15 (m, 1.2H), 3.31 (d, J = 2 Hz, 0.8H), 5.38-5.54 (m, 0.8H), 5.60-5.98 (m, 1.2H). In the presence of $Eu(fod)_3$ the *t*-butyl signal of the threo isomer (17%) appeared at lower field than that of the erythro isomer (83%). The NMR spectra in the presence of a chiral shift reagent $Eu(dcm)_3$ showed that the *t*-butyl signal of the major enantiomer of the erythro and threo isomers appeared at lower and higher field, respectively.
19. **8**: NMR (CCl_4): δ 0.97 (s, 9H), 1.85-2.20 (m, 2H), 2.25-2.86 (m, 3H), 3.68 (s, 3H), 4.33 (d, J = 10 Hz, 1H).
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21. **9**: bp 104°C/21 mmHg; NMR (CCl_4): δ -0.07 (s, 3H), 1.16 (t, J = 7 Hz, 6H), 1.3-2.1 (m, 7H), 3.71 (q, 4H), 5.35-5.75 (m, 2H).
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