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AN OPTICALLY ACTIVE PROPARGYLSILANE: PREPARATION BY ASYMMETRIC GRIGNARD CROSS-COUPLING AND STEREOCHEMISTRY IN AN ELECTROPHILIC SUBSTITUTION[1]

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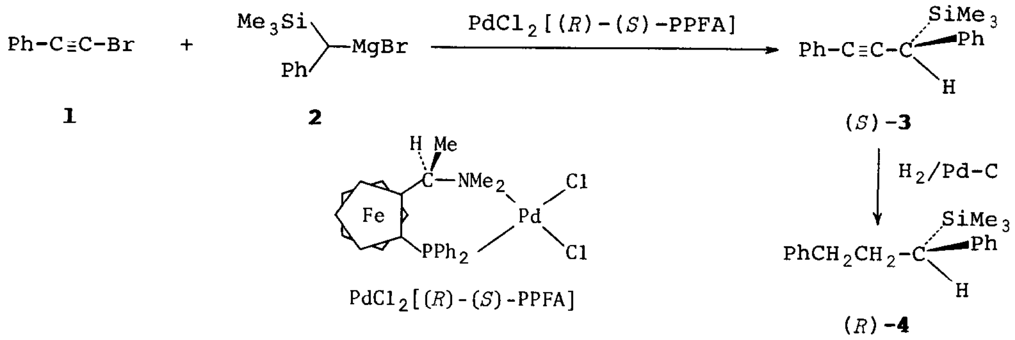
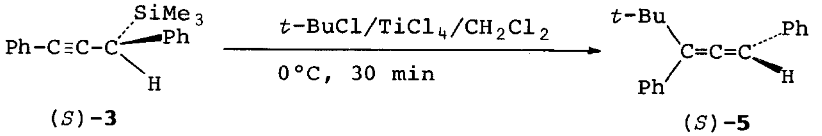
Summary: An optically active propargylsilane, (*S*)-1,3-diphenyl-3-trimethylsilylpropyne, prepared by palladium-catalyzed asymmetric Grignard cross-coupling, was found to react with *t*-butyl chloride in the presence of titanium chloride with *anti* stereochemistry to give (*S*)-1,3-diphenyl-4,4-dimethyl-1,2-pentadiene.

Previously we have reported the preparation of optically active allylsilanes by palladium-catalyzed asymmetric Grignard cross-coupling and *anti* stereochemistry in S_E' reaction of the allylsilanes with various electrophiles.[2] Here we describe the application of the asymmetric cross-coupling to the preparation of an optically active propargylsilane and the first stereochemical result of S_E' reaction of propargylsilane.[3]

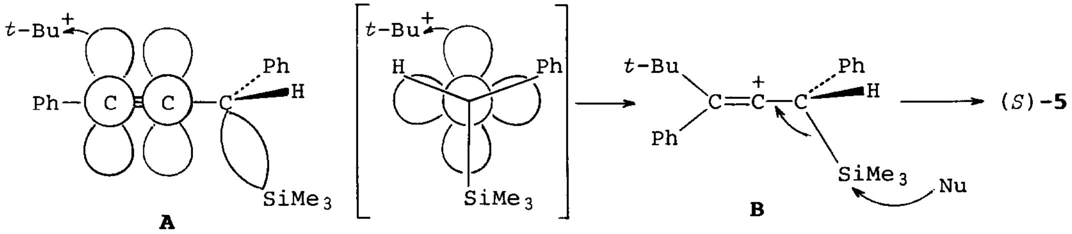
In the presence of dichloro[(*R*)-*N*,*N*-dimethyl-1-{(*S*)-2-(diphenylphosphino)ferrocenyl}ethylamine]palladium(II) ($PdCl_2$[(*R*)-(*S*)-PPFA]) as a catalyst (0.5 mol%), phenylbromoacetylene (**1**) was allowed to react with α-trimethylsilylbenzylmagnesium bromide (**2**) (2 eq) at ambient temperature for 1 day. Hydrolysis with dil HCl, extraction with ether, and silica gel column chromatography (hexane) gave 62% yield of 1,3-diphenyl-3-trimethylsilylpropyne (**3**)[4] which had $[\alpha]_D^{20}$ +9.84° (*c* 6.0, benzene). Hydrogenation of (+)-**3** provided known (*R*)-1,3-diphenyl-3-trimethylsilylpropane (**4**) with $[\alpha]_D^{20}$ -0.42° (*c* 2.9, benzene), indicating that the propargylsilane **3** is an *S* isomer of 18% ee.[2]





The propargylsilane (*S*)-**3** was treated with *t*-butyl chloride (1 eq) and titanium chloride (1 eq) in dichloromethane at 0°C for 30 min. Usual work-up and preparative TLC (silica gel, hexane, R_f 0.7) gave 1,3-diphenyl-4,4-dimethyl-1,2-pentadiene (**5**)[5] in 23% yield. The allene **5** showed $[\alpha]_D^{20}$ +13.9° (*c* 7.8, chloroform), $[M]_D^{20}$ +34.5°, and was determined to be an *S* isomer by empirical rules relating the absolute configuration to the sign of the optical rotation.[6,7] The stereochemistry observed here that (*S*)-**3** led to (*S*)-**5** can be visualized by the mechanism shown in Scheme I, which is analogous to that proposed for S_E' reaction of allylsilanes.[2] The propargylsilane **3** is expected to exist in conformation **A** with the carbon-silicon bond overlapping with one of the two π bonds of carbon-carbon triple bond, due to a σ-π conjugation. *t*-Butyl cation attacks the π bond conjugated with the carbon-silicon bond from the side opposite to the silyl group (*anti* attack) to form cationic intermediate **B**. Displacement of the silyl group by nucleophilic attack gives rise to the observed (*S*)-allene **5**.[8,9]

Scheme I



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2. T. Hayashi, M. Konishi, H. Ito, and M. Kumada, *J. Am. Chem. Soc.*, **104**, 4962 (1982).
3. S_E' reaction of propargylsilanes has been reported: (a) P. Bourgeois and G. Mérault, *J. Organomet. Chem.*, **39**, C44 (1972). (b) G. Deleris, J. Dunogues, and R. Calas, *J. Organomet. Chem.*, **93**, 43 (1975). (c) A. D. Despo, S. K. Chin, T. Flood, and P. E. Peterson, *J. Am. Chem. Soc.*, **102**, 5120 (1980). (d) R. Schmid, P. L. Huesmann, W. S. Johnson, *J. Am. Chem. Soc.*, **102**, 5122 (1980). (e) J. Pornet, *Tetrahedron Lett.*, 453 and 455 (1981); J. Pornet and B. Randrianoelina, *Ibid.*, **22**, 1327 (1981); J. Pornet and N. Kolani, *Ibid.*, **22**, 3609 (1981).
4. **3**: ^{1}H NMR (CCl_4/TMS) δ 0.11 (s, 9H), 3.25 (s, 1H), 6.96-7.46 (m, 10H). IR (neat) 2214 cm^{-1} (C≡C). m/e calcd 264.1334, obsd 264.1322. The propargylsilane 3 is slowly decomposed on exposure to air.
5. **5**: ^{1}H NMR (CCl_4/TMS) δ 1.22 (s, 9H), 6.12 (s, 1H), 6.82-7.37 (m, 10H). IR (neat) 1941 cm^{-1} (C=C=C).
6. (a) G. Lowe, *Chem. Commun.*, 411 (1965). (b) J. H. Brewster, *Top. Stereochem.*, **2**, 1 (1967). (c) R. Rossi and P. Diversi, *Synthesis*, 25 (1973). (d) W. Runge and G. Kresze, *J. Am. Chem. Soc.*, **99**, 5597 (1977).
7. According to the semiempirical method (ref. 6d), the enantiomeric purity of the allene **5** is calculated to be 3%.
8. Rotation of the α-trimethylsilylbenzyl group before the displacement would bring about loss of the enantiomeric purity. See note 7.
9. We thank the Ministry of Education for the Grant-in-Aid for Scientific Research (No. 00547080) for partial financial support of this work.

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