of ligands, as will be reported elsewhere. B is a thiolate–Co(II)TPP complex, although the possibility of a dithiolate–Co(II)TPP coordination is not thoroughly ruled out yet. C was not detected by usual EPR spectroscopy, suggesting that this complex is very unstable and has a short half-life.

Since superoxide is very reactive,[1,2] it is interesting that it can be detected during formation of a simple complex. The value of $g_{\parallel}$ in the EPR spectrum of superoxide is known to depend on the nature of the solvent or environment of the superoxide.[5] Recently Bray et al. reported that $g_{\parallel}$ value of superoxide shifts markedly toward $g_{\perp}$ in the presence of cations such as Ca(II), Ba(II), and Na(I), indicating solvent-shared ion-pair formation.[19] Judging from the $g_{\parallel}$ value in the spectrum of superoxide observed in our system, there may be little interaction between superoxide and cobalt ion or solvent.

This work provides the direct evidence for the generation of superoxide in a chemical model, a cobalt–porphyrin complex. We believe that this system provides not only a simple method for generation of superoxide but also an insight into the mechanism for oxygen activation depending on heme proteins in many biological processes.

Acknowledgment. This research was partially supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, and a Grant-in-Aid of new drug development from the Ministry of Health and Welfare of Japan.

Registry No. A, 82555-90-6; B, 82555-91-7; C, 82571-32-2; $Co^{II}TPP$, 14172-90-8; TGE, 623-51-8; Me_4NOH, 75-59-2; O_2^-, 11062-77-4; O_2, 7782-44-7; cytochrome P450, 9035-51-2; oxidase, 9035-73-8; monooxygenase, 9038-14-6.

(19) Bray, R. C.; Mautner, G. N.; Fielden, E. M.; Carle, C. I. In "Superoxide and Superoxide Dismutases"; Michelson, A. M.; McCord, J. M.; Fridovich, I., Eds.; Academic Press: New York, 1977; pp 61–75.

Optically Active Allylsilanes. 1. Preparation by Palladium-Catalyzed Asymmetric Grignard Cross-Coupling and Anti Stereochemistry in Electrophilic Substitution Reactions

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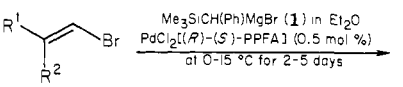
Received March 2, 1982

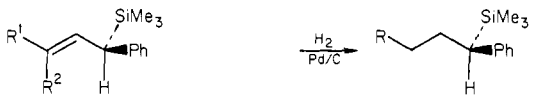
We have succeeded, for the first time, in a simple and efficient synthesis of optically active allylsilanes with high optical purity, by the aid of the catalytic asymmetric Grignard cross-coupling.[1] The allylsilanes contain an asymmetric carbon atom directly bonded to the silicon atom and could hardly be obtained by other methods. We report here the first general procedure for preparation of the optically active allylsilanes and the first unambiguous stereochemistry (anti attack) of S_E' reaction[2] of the allylsilanes with various electrophiles.

Dichloro[(*R*)-*N*,*N*-dimethyl-1-{(*S*)-2-(diphenylphosphino)-ferrocenyl}ethylamine]palladium(II) ($PdCl_2$[(*R*)-(*S*)-PPFA])[1,3] was found to be an effective catalyst for the cross-coupling of α-(trimethylsilyl)benzylmagnesium bromide[4] (**1**) with vinyl bromide (**2a**), (*E*)- and (*Z*)-1-bromopropene (**2b**), and (*E*)- and (*Z*)-β-bromostyrene (**2c**) to give, in good yields, the corresponding allylsilanes (**3**)[5] in an optically active form without *E*–*Z* isomerization of the olefinic double bond. The results summarized in Scheme I[6] show that the allylsilanes with high optical purity were obtained in the reaction of **2a**, (*E*)-**2b**, and (*E*)-**2c** and that the *R* isomer was formed preferentially in every case. The se-

Scheme I

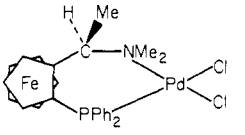


2a, $R^1 = R^2 = H$
(*E*)-2b, R^1 = Me; R^2 = H
(*Z*)-2b, R^1 = H; R^2 = Me
(*E*)-2c, R^1 = Ph; R^2 = H
(*Z*)-2c, R^1 = H; R^2 = Ph



	yield, %	$[\alpha]^{20}_D$, deg[a]	ee, %
(*R*)-3a:	42	−61.8	95
(*R*)-(*E*)-3b:	77	−36.3	85
(*R*)-(*Z*)-3b:	38	−21.3	24
(*R*)-(*E*)-3c:	93	−43.9	95
(*R*)-(*Z*)-3c:	95	−44.3	13

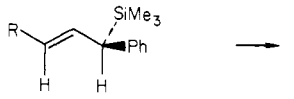
4a, R = H
4b, R = Me
4c, R = Ph



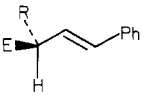
$PdCl_2$[(*R*)-(*S*)-PPFA]

[a] Benzene.

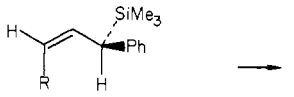
Scheme II[a]



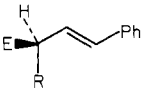
(*R*)-(*E*)-3b, R = Me (85% ee)
(*R*)-(*E*)-3c, R = Ph (95% ee)



(a) (*S*)-5b (87% ee), R = Me; E = *t*-Bu
(b) (*S*)-5c (93% ee), R = Ph; E = *t*-Bu
(c) (*S*)-6 (53% ee), R = Me; E = MeCO
(d) (*S*)-7 (86% ee), R = Me; E = $HOCH_2$



(*R*)-(*Z*)-3b, R = Me (24% ee)
(*R*)-(*Z*)-3c, R = Ph (13% ee)



(a) (*R*)-5b (27% ee), R = Me; E = *t*-Bu
(b) (*R*)-5c (15% ee), R = Ph; E = *t*-Bu
(c) (*R*)-6 (19% ee), R = Me; E = MeCO

[a] (a) 3b, *t*-BuCl/$TiCl_4$, CH_2Cl_2, −78 °C, 1 min; (b) 3c, *t*-BuCl/$TiCl_4$, CH_2Cl_2, 0 °C, 1 h; (c) 3b, MeCOCl/$AlCl_3$, CH_2Cl_2, −78 °C, 5 min; (d) 3b, HCHO or trioxane/$TiCl_4$, CH_2Cl_2, −78 °C, 5 min.

(1) Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180 and references cited therein.
(2) Reviews: (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1.
(3) Hayashi, T.; Tamao, K.; Katsuro, Y.; Nakae, I.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 1871.
(4) Hauser, C. R.; Hance, C. R. *J. Am. Chem. Soc.* **1952**, *74*, 5091.
(5) The reaction was carried out in a similar procedure to that described in ref 1. The physical data of the allylsilanes **3** are available as supplementary material.
(6) The configuration *R* and enantiomeric purity of the allylsilanes **3** were determined by comparing the optical rotation data of alkyltrimethylsilanes **4** obtained by hydrogenation of **3** with those of **4** obtained by palladium-catalyzed asymmetric hydrosilylation of styrene derivatives.[3] The maximum rotations of the alkylsilanes (*S*)-**4a**, **-4b**, and **-4c** are $[\alpha]_D^{20}$ +1.42, −9.55, and +2.36° (*c* 3–6, benzene), respectively. The asymmetric hydrosilylation will be fully described elsewhere.

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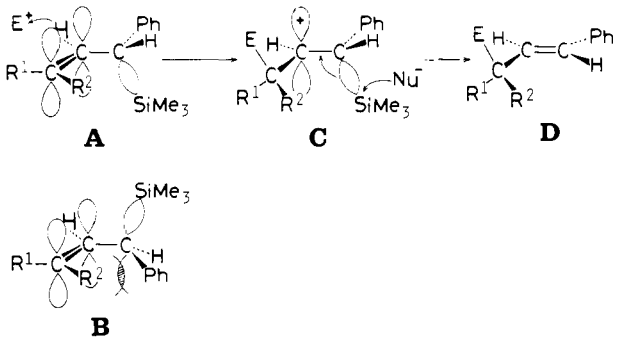
Scheme III



lectivity attained here with **2a** and (*E*)-**2c**, >97% *R* selective, is among the highest of asymmetric reactions by means of chiral catalysts,[7] especially for carbon–carbon bond-forming reactions.

In spite of frequent use of allylsilanes for organic synthesis,[2] only a few examples,[8,9] all of which seem to be special ones (see footnote 18), have so far been reported concerning the stereochemistry of the S_E' reaction, probably due to the difficulty in obtaining allylsilanes with definite configuration. We could examine the stereochemistry by use of the optically active allylsilanes (*E*)- and (*Z*)-**3b,c** obtained above. The results obtained for *tert*-butylation, acetylation, and hydroxymethylation are summarized in Scheme II. The products (**5b,c**, **6**, and **7**) were all highly pure (>99%) *E* isomers, and the stereochemical assignment of the products[10] was carried out by a straightforward degradation to known compounds.[11–13] The significant features in the present S_E' reactions are as follows: (1) The reactions gave corresponding S_E' products with high stereoselectivity.[14] (2) The (*E*)-allylsilanes led to the products of *S* configuration while the (*Z*)-allylsilanes to *R* isomers. These results indicate that the electrophiles entered the double bond selectively anti to the leaving trimethylsilyl group in the S_E' reactions.

The anti stereochemistry can be visualized by the mechanism shown in Scheme III. The (*R*)-allylsilanes **3** are expected to exist in conformation A with the carbon–silicon bond overlapping with the π lobes of the carbon–carbon double bond, due to a strong σ–π conjugative interaction between the carbon–silicon bond and the olefin π system.[15] Another possible conformation, B, with the similar overlapping may be excluded because of the disadvantageous steric repulsion between the olefin moiety and the phenyl group on the α carbon. The electrophile attacks the allylsilane in conformation A from the side opposite to the trimethylsilyl group (anti attack) to form cationic intermediate C where the carbonium ion is stabilized by σ–π conjugation with the neighboring carbon–silicon σ bond.[16] Displacement of the silyl group from the intermediate C by nucleophilic attack gives rise to (*E*)-olefin D, whose configuration of the carbon chirality is in perfect agreement with that of all the products obtained.

The anti attack of electrophiles observed here is consistent with the stereochemistry expected from the theoretical interpretation of the S_E' reaction,[17] and the anti stereochemistry is considered to be essential to electrophilic reaction of allylsilanes[18] and also to that of some other allylic organometallic reagents unless the reaction is forced to proceed via a cyclic transition state.[19]

Acknowledgment. We thank the Ministry of Education, Japan, for Grant-in-Aid for Scientific Research (No. 00547080), Hokko Chemical Industry Co., Ltd., and Shin-etsu Chemical Industry Co., Ltd., for partial financial support of this work.

Registry No. $Me_3SiCHBrPh$, 57482-85-6; **2a**, 593-60-2; (*E*)-**2b**, 590-15-8; (*Z*)-**2b**, 590-13-6; (*E*)-**2c**, 588-72-7; (*Z*)-**2c**, 588-73-8; (*R*)-**3a**, 82537-19-7; (*R*)-(*E*)-**3b**, 82570-93-2; (*R*)-(*Z*)-**3b**, 82570-94-3; (*R*)-(*E*)-**3c**, 82537-20-0; (*R*)-(*Z*)-**3c**, 82537-21-1; (*S*)-**5b**, 82570-95-4; (*S*)-**5c**, 82537-22-2; (*S*)-**6**, 82537-23-3; (*S*)-**7**, 81802-33-7; (*R*)-**5b**, 82570-96-5; (*R*)-**5c**, 82537-24-4; (*R*)-**6**, 82537-25-5; $PdCl_2$[(*R*)-(*S*)-PPFA], 76374-09-9.

Supplementary Material Available: Physical data of the allylsilanes **3** (1 page). Ordering information is given on any current masthead page.

(7) Reviews: (a) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1978**, *10*, 175. (b) Bosnich, B.; Fryzuk, M. D. *Top. Stereochem.* **1981**, *12*, 119.

(8) (a) Carter, M. J.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1976**, 679. (b) Fleming, I.; Au-Yeung, B.-W. *Tetrahedron Suppl.* **1981**, *37*, 13.

(9) Wetter, H.; Scherer, P.; Schweizer, W. B. *Helv. Chim. Acta* **1979**, *62*, 1985.

(10) (*S*)-**5b**: 61% yield, $[\alpha]_D^{20}$ −56.0° (*c* 1.0, CCl_4). (*R*)-**5b**: 75% yield, $[\alpha]_D^{20}$ +17.6° (*c* 1.0, CCl_4). (*S*)-**5c**: 40% yield, $[\alpha]_D^{20}$ +78.6° (*c* 0.4, C_6H_6). (*R*)-**5c**: 25% yield, $[\alpha]_D^{20}$ −12.3° (*c* 0.4, C_6H_6). (*S*)-**6**: 87% yield, $[\alpha]_D^{20}$ +153.3° (*c* 0.25, CCl_4). (*R*)-**6**: 74% yield, $[\alpha]_D^{20}$ −54.2° (*c* 0.26, CCl_4). (*S*)-**7**: 40% yield, $[\alpha]_D^{20}$ −37.5–39.5° (*c* 1.7, CCl_4).

(11) (*S*)-**5b** and (*S*)-**5c** were oxidized ($KMnO_4/NaIO_4$) into (−)-(*R*)-2,3,3-trimethylbutanoic acid[12a] and (+)-(*S*)-2-phenyl-3,3-dimethylbutanoic acid,[12b] respectively. The enantiomeric purities were determined by ^1H NMR spectra of the methyl esters, obtained by treatment of the acids with diazomethane, in the presence of chiral shift reagent Eu(dcm)$_3$. (*S*)-**6** was converted into (+)-(*S*)-4-phenyl-2-butanol[12c] by hydrogenation (H_2/Pd–C), Baeyer–Villiger oxidation (MCPBA), and treatment with MeMgBr. The key oxidation step has been established to proceed with retention of configuration.[13] (*S*)-**7** was oxidized (O_3/H_2O_2) into (−)-(*R*)-2-methyl-3-hydroxypropanoic acid.[12d]

(12) (a) Folli, U.; Iarossi, D.; Montanari, F.; Torre, G. *J. Chem. Soc. C* **1968**, 1317. (b) Clark, D. R.; Mosher, H. S. *J. Org. Chem.* **1970**, *35*, 1114. (c) Kenyon, J.; Partridge, S. M.; Phillips, H. *J. Chem. Soc.* **1936**, 85. (d) Retey, J.; Lynen, F. *Biochem. Z.* **1965**, *342*, 256.

(13) Mislow, K.; Brenner, J. *J. Am. Chem. Soc.* **1953**, *75*, 2318.

(14) The decrease in the enantiomeric purities during the acylation (85% → 53% for (*E*)-**3b**; 24% → 19% for (*Z*)-**3b**) may be ascribed to acid-catalyzed racemization of the ketone **6** under the reaction conditions. A control experiment showed that (*R*)-**6** of 19% ee racemized into that of 14% ee ($AlCl_3$ in CH_2Cl_2, at −78 °C for 5 min).

(15) (a) Weidner, U.; Schweig, A. *Angew. Chem.* **1972**, *84*, 167. (b) Weidner, U.; Schweig, A. *J. Organomet. Chem.* **1972**, *39*, 261.

(16) (a) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715. (b) Eaborn, C. *J. Chem. Soc., Chem. Commun.* **1972**, 1255.

(17) Anh, N. T. *J. Chem. Soc., Chem. Commun.* **1968**, 1089.

(18) The stereochemistry (both syn and anti) reported[8] for cyclic allylsilanes may be controlled not by the inherent nature of allylsilanes but by the stereochemical bias in the cyclic systems. The apparent syn stereochemistry reported[9] for acylation of an optically active 1-(trimethylsilyl)-1-(dimethylfluorosilyl)-2-alkene may be interpreted consistently with attack of the electrophile anti to the trimethylsilyl group, with the dimethylfluorosilyl group leaving. The mechanism will be fully described in a full article.

(19) The anti stereochemistry has been observed in electrophilic substitution reactions of indenyl–organotin compounds: Kashin, A. N.; Bakunin, V. N.; Khutoryanskii, V. A.; Beletskaya, I. P.; Reutov, O. A. *J. Organomet. Chem.* **1979**, *171*, 309.

Optically Active Allylsilanes. 2. High Stereoselectivity in Asymmetric Reaction with Aldehydes Producing Homoallylic Alcohols

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Of several approaches to obtaining optically active erythro or threo β-hydroxycarbonyl compounds, the enantioselective aldol-type reaction of chiral boron or zirconium enolates has been most successful in giving rise to over 90% stereoselectivity.[1] Reaction using a chiral crotyl boronic ester has been reported also to proceed

(1) (a) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127. (b) Evans, D. A.; McGee, L. R. *Ibid.* **1981**, *103*, 2876. (c) Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *Ibid.* **1981**, *103*, 1566. (d) Meyers, A. I.; Yamamoto, Y. *Ibid.* **1981**, *103*, 4278. See also: (e) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *Ibid.* **1981**, *103*, 3099. (f) Heathcock, C. H.; White, C. T.; Morrison, J. J.; VanDerveer, D. *J. Org. Chem.* **1981**, *46*, 1296 and references cited therein. (g) Masamune, S.; Ali, Sk. A.; Snitman, D. L.; Garvey, D. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 557.

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