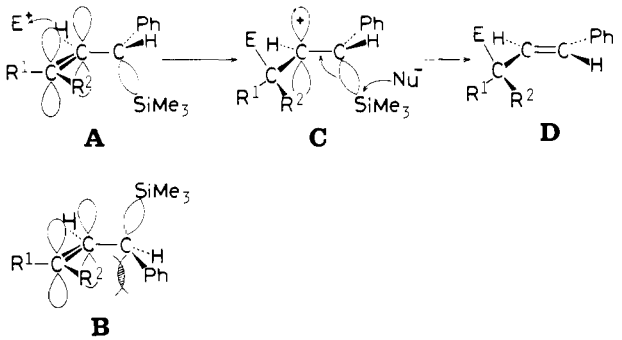
Scheme III



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.

0002-7863/82/1504-4963$01.25/0

Table I. Reaction of Allylsilanes 1a and 1b with Aldehydes 2 in the Presence of $TiCl_4$ in CH_2Cl_2[a]

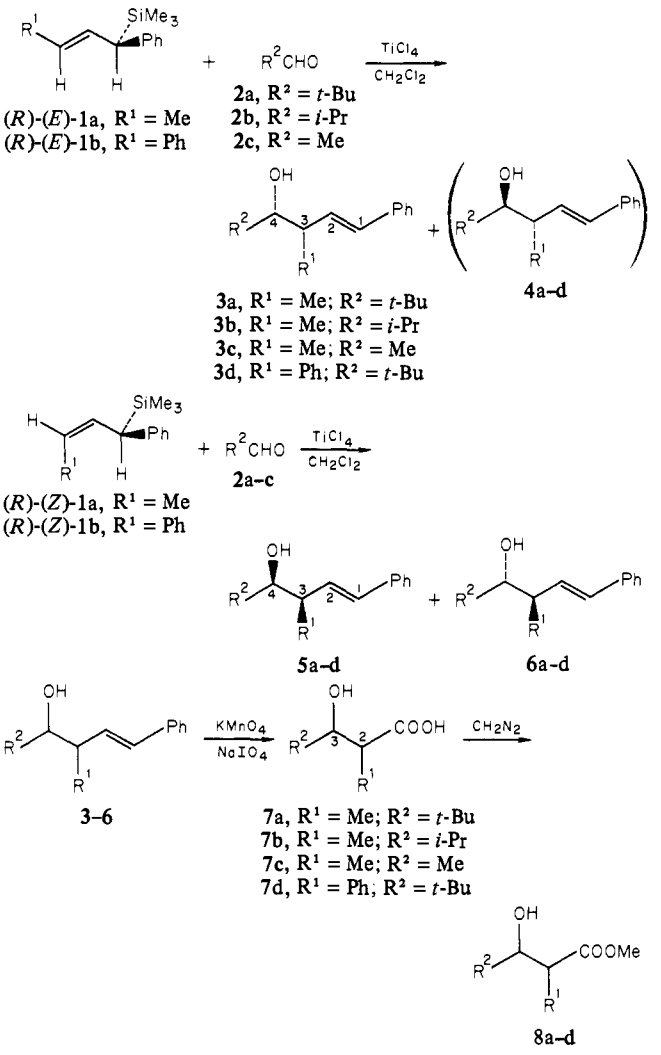
entry	allylsilane 1 (% ee)	aldehyde 2	yield,[b] %	3/4 or 5/6[c]	$[\alpha]^{20}_D$ (3 or 5) (c in CCl_4), deg	% ee[d] (3 or 5) (confign)[e]	$[\alpha]^{20}_D$ (4 or 6) (c in CCl_4), deg	% ee[d] (4 or 6) (confign)[e]
1	(R)-(E)-1a (85)	t-BuCHO (2a)	47	>99/<1 (3a/4a)	−36.3 (1.1)	88 (3S,4R)		
2	(R)-(Z)-1a (24)	t-BuCHO (2a)	27	>99/<1 (5a/6a)	+9.9 (1.1)	24 (3R,4S)		
3	(R)-(E)-1a (85)	i-PrCHO (2b)	67	95/5 (3b/4b)	−28.0 (0.9)	87 (3S,4S)	−8 (0.4)[f]	(3S,4R)
4	(R)-(Z)-1a (24)	i-PrCHO (2b)	61	65/35 (5b/6b)	+9.9 (0.7)	28 (3R,4R)	+6.1 (0.7)	29 (3R,4S)
5	(R)-(E)-1a (85)	MeCHO (2c)	76	92/8 (3c/4c)	−43.5 (2.1)[g]	86 (3S,4S)		
6	(R)-(Z)-1a (24)	MeCHO (2c)	82	50/50 (5c/6c)	+9.6 (0.7)	24 (3R,4R)	+13.9 (1.1)	22 (3R,4S)
7	(R)-(E)-1b (95)	t-BuCHO (2a)	44[h]	>99/<1 (3d/4d)	+4.85 (1.3)	92 (3R,4R)		
8	(R)-(Z)-1b (13)	t-BuCHO (2a)	10[i]	>99/<1 (5d/6d)		14 (3S,4S)		

[a] Titanium chloride (1.1 equiv) was added at −78 °C to a mixture of an allylsilane (1.0 equiv) and an aldehyde (1.1 equiv) in dichloromethane. The mixture was stirred at −78 °C for 4–5 min, unless otherwise noted, and quenched with water. [b] Isolated by preparative TLC (silica gel/chloroform or benzene). Yields are based on 1 and not optimized. [c] The ratio 3/4 or 5/6 was determined by HPLC and ^{1}H NMR. Stereochemistry (erythro or threo) of the products 3–6 was determined by comparing ^{1}H NMR spectra of the β-hydroxy acids 7 with those reported in ref 1e, 5a, 5b. [d] Determined by ^{1}H NMR spectra of the alcohols or the β-hydroxy esters 8 using chiral shift reagent tris(d,d-dicampholylmethanato)europium(III) [Eu(dcm)$_3$]. [e] The alcohols 3a (5a) and 3d (5d) were converted into diastereomeric esters of (R)-O-methylmandelic acid, and the absolute configuration of the alcohols was assigned by ^{1}H NMR spectra of the esters: Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* 1973, *95*, 512. The absolute configuration of 3b (5b), 3c (5c), 6b (4b), and 6c was determined by the optical rotation data of erythro and threo β-hydroxy acids 7 and esters 8: ref 1a, 1b, 1d, and 5c. [f] Contaminated with ca. 50% of unidentified impurities. [g] The rotation includes 4c. [h] Reaction at 20 °C for 1 h. [i] Reaction at 0 °C for 1 h.

with ~70% stereoselectivity.[2] In both cases, the stereochemistry is considered to be determined in the six-membered diastereomeric transition states, though the mechanism of the enantioselection has not always been well understood. We report here a new type of highly effective stereocontrol observed in the reaction of optically active allylsilanes with aldehydes, where the reaction proceeds via acyclic linear diastereomeric transition states and both enantio- and diastereoselectivities can be clearly interpreted by simple steric interactions in the transition states.

Optically active (R)-allylsilanes (E)- and (Z)-**1a** and -**1b**[3] were allowed to react with aldehydes **2** in the presence of titanium chloride in dichloromethane[4] to give optically active homoallylic alcohols **3–6** with the carbon–carbon double bond of E configuration. Their stereochemistry was determined by converting the alcohols into known β-hydroxy acids **7** or esters **8**[1,5] by oxidative cleavage of the olefinic double bond (Scheme I). Results summarized in Table I contain the following significant features: (1) The present asymmetric reaction is stereospecific, the enantiomeric excess of all the products being essentially identical, within an experimental error, to that of the starting allylsilanes, and hence the alcohols of very high percent enantiomeric excess (>85%) could be obtained in the reaction of (E)-**1a** or (E)-**1b** (entries 1, 3, 5, and 7). (2) The allylsilanes with an E olefinic double bond, (R)-(E)-**1a** and -**1b**, afforded alcohols **3** with high selectivity, their diastereomeric isomers **4** being formed in at most 8% (entries 1, 3, 5, and 7). All the alcohols **3** obtained are those related to erythro β-hydroxy acids and have the absolute configuration shown in Scheme I. (3) In the reaction of (Z)-allylsilanes, the ratio of diastereoisomeric products depends upon the structure of aldehydes **2**. Thus, **2a** (R^2 = t-Bu) gave selectively the alcohol **5a** or **5d**, which are enantiomeric isomers of **3a** or **3d**, respectively (entries 2 and 8), while **2b** (R^2 = i-Pr) and **2c** (R^2 = Me) gave not only the erythro alcohols **5** but also the threo alcohols **6** in comparable amounts (entries 4 and 6). The diastereomeric isomers **5** and **6** have the same configuration R at the 3-position and the opposite configuration at the 4-position (the numbering of the position is shown in Scheme I). (4) The configurations at the 3-position of the homoallylic alcohols **3–6** are all consistent with those expected from the stereochemistry of S_E' reaction where the electrophile

Scheme I



attacks the carbon–carbon double bond anti with respect to the leaving silyl group.[3]

All the stereochemical results obtained above can be illustrated by the mechanism shown in Scheme II.[6] The acyclic linear

(2) (a) Hoffmann, R. W.; Ladner, W. *Tetrahedron Lett.* **1979**, 4653. (b) Hoffmann, R. W.; Zeiss, H.-J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 218. See also: (c) Herold, T.; Schrott, U.; Hoffmann, R. W. *Chem. Ber.* **1981**, *114*, 359. (d) Hoffmann, R. W.; Herold, T. *Ibid.* **1981**, *114*, 375.

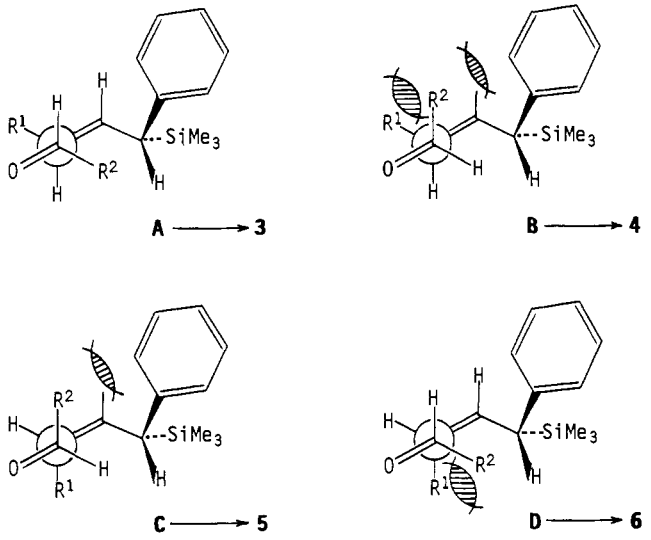
(3) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(4) (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (b) Fleming, I.; Paterson, I. *Synthesis* **1979**, 446.

(5) (a) Mulzer, J.; Zippel, M.; Bruntrup, G.; Segner, J.; Finke, J.; *Liebigs Ann. Chem.* **1980**, 1108. (b) Maskens, K.; Polgar, N. *J. Chem. Soc., Perkin Trans. 1* **1973**, 109. (c) Tai, A.; Imaida, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1114.

(6) Titanium chloride is omitted for simplicity, which may activate aldehydes by coordinating to the carbonyl oxygen. Concerning the conformation of allylsilanes at the reaction, see ref 3.

Scheme II



transition state[7] is proposed on the basis of the anti stereochemistry established for the S_E' reaction of allylsilanes.[3,8] In the reaction of the (*E*)-allylsilanes, the transition state A where the aldehyde is attacked on its *re* face leading to the alcohol **3** is sterically much favored over the diastereomeric transition state B, which suffers steric repulsion between the alkyl group R^2 on the aldehyde and R^1 on the allylsilane (gauche interaction) and also steric repulsion between R^2 and the phenyl group on the allylsilane.[9] In case of the (*Z*)-allylsilanes, the steric repulsions between R^1 and R^2 and between R^2 and the phenyl make both the diastereomeric transition states C and D less favorable. When R^2 is *t*-Bu, the gauche interaction is more decisive, and the alcohols **5** are produced via C. On the other hand, when R^2 is smaller (*i*-Pr or Me), the two kinds of steric repulsions have competitive effects on the stereoselection, leading to both **5** and **6** in comparable amounts.

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. (*R*)-(*E*)-**1a**, 82570-93-2; (*R*)-(*Z*)-**1a**, 82570-94-3; (*R*)-(*E*)-**1b**, 82537-20-0; (*R*)-(*Z*)-**1b**, 82537-21-1; **2a**, 630-19-3; **2b**, 78-84-2; **2c**, 75-07-0; **3a**, 82545-33-3; **3b**, 82545-34-4; **3c**, 82545-35-5; **3d**, 82545-36-6; **4a**, 82545-37-7; **4b**, 82545-38-8; **4c**, 82545-39-9; **4d**, 82545-40-2; **5a**, 82545-41-3; **5b**, 82545-42-4; **5c**, 82545-43-5; **5d**, 82545-44-6; **6a**, 82545-45-7; **6b**, 82545-46-8; **6c**, 82545-47-9; **6d**, 82545-48-0; **7a**, 82545-49-1; **7b**, 82545-50-4; **7c**, 473-86-9; **7d**, 82545-51-5; **8a**, 82545-52-6; **8b**, 82545-53-7; **8c**, 34293-67-9; **8d**, 82545-54-8.

Supplementary Material Available: ^1H NMR spectra of the homoallylic alcohols (1 page). Ordering information is given on any current masthead page.

(7) (a) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248. (b) Noyori, R.; Nishida, I.; Sakata, J. *Ibid.* **1981**, *103*, 2106. (c) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *Ibid.* **1980**, *102*, 7107. (d) Chêrest, M.; Felkin, H.; Frajerman, C. *Tetrahedron Lett.* **1971**, 379 and their previous papers cited therein.

(8) The erythro selectivity of the (*E*)-allylsilanes may also support the linear transition state and reject the cyclic transition state. See ref 1 and 7. See also: (a) Hoffmann, R. W.; Zeiss, H.-J. *J. Org. Chem.* **1981**, *46*, 1309. (b) Yamaguchi, M.; Mukaiyama, T. *Chem. Lett.* **1980**, 993. (c) Hiyama, T.; Kimura, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1037. (d) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 3229. (e) Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1981**, *22*, 2895 and references cited therein.

(9) The important role of the steric repulsion between R^2 and the phenyl in differentiating the enantiotopic faces of aldehydes has been observed in the enantioselective allylation with (*R*)-3-phenyl-3-(trimethylsilyl)propene where the *re* face of the aldehydes is attacked with high selectivity (~95%). Full details will be reported shortly.

Stereocontrolled Total Synthesis of (±)-Coriamyrtin

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Coriamyrtin (**1**), one member of picrotoxane sesquiterpenes, was first isolated in 1864 from the European *Coriaria* species, *Coriaria myrtifolia*,[1a] and was later found to be the major constituent of Japanese-grown *Coriaria japonica*.[1b] Its characteristic structure of two vicinal oxirane rings on the picrotoxane skeleton was confirmed on the basis of degradative and spectroscopic evidence.[2] The central nervous system stimulant activity of coriamyrtin[3] has been known to be nearly identical with that of picrotoxinin (**2**), which is used as an investigative tool in neuroscience. Despite the unique structures and quite interesting physiological activities of these sesquiterpenes, there was no report on the total synthesis of any member of picrotoxane sesquiterpenes[4] until the elegant total synthesis of picrotoxinin[5] in 1979 and picrotin[6] in 1980 were reported by Corey and Pearce. We describe herein a stereocontrolled total synthesis of (±)-coriamyrtin and a general route for the construction of the picrotoxane skeleton.

The basic synthetic plan came from the retrosynthetic analysis of **1**, which involves the disconnections as illustrated in Scheme I. On the basis of this analysis, our synthesis was undertaken starting from readily available protoanemonin (**5**)[7] and 2-methyl-1,3-cyclopentanedione (**6**). 1,6-Addition of **6** to **5** (Scheme II) gave **4**[8] in 13% yield.[9] The Grignard reaction of **4** with isopropenylmagnesium bromide and the subsequent internal aldol reaction provided two lactones, **7** (mp 148 °C) and **8** (mp 153 °C) in an 8:1 ratio and in 95% yield. The equatorial orientation of the isopropenyl of the two products was indicated by the ^1H NMR ($CDCl_3$) spectra, which revealed coupling of three vicinal protons at C_3, C_4, and C_5 with *J* values of 0–0.5 Hz. These observations indicated the undesired stereostructures of these compounds. The stereostructural assignments of the two compounds will be reported separately.[10] Methanolysis of **4** gave a separable mixture of **9** (mp 66 °C) and **10**[11] (oil) in a 1:1 ratio and in 88% yield. At this stage of investigation, the stereostructures of **9** and **10** could not be specified. The conclusive evidence for the stereostructure of **9** will be given by the stereostructural establishment of **13** and **14** (vide infra, Scheme III). Because of the trans relationship between the acrylic ester side

(1) (a) Riban, M. J. *Bull. Soc. Chim. Fr.* **1864**, *1*, 87; **1867**, *7*, 79. (b) Kariyone, T.; Sato, T. *Yakugaku Zasshi* **1930**, *50*, 106; **1930**, *50*, 659.

(2) Okuda, T.; Yoshida, T. *Tetrahedron Lett.* **1964**, 439; **1965**, 4191.

(3) For a review of the chemistry, biosynthesis, and physiology of picrotexane sesquiterpenes and related substances, see: Porter, L. A. *Chem. Rev.* **1967**, *67*, 441.

(4) For the synthesis of dendrobine, an alkaloid in the same general structural class, see: (a) Yamada, K.; Suzuki, M.; Hayakawa, A.; Nakamura, H.; Nagase, H.; Hirata, Y. *J. Am. Chem. Soc.* **1972**, *94*, 8278. (b) Inubushi, Y.; Kikuchi, T.; Ibuka, T.; Tanaka, K.; Saji, I.; Tokane, K. *J. Chem. Soc., Chem. Commun.* **1972**, 1252; *Chem. Pharm. Bull.* **1974**, *22*, 349. (c) Kende, A.; Bentley, J.; Mader, R.; Ridge, D. *J. Am. Chem. Soc.* **1974**, *96*, 4332. (d) Borch, R. F.; Evans, A. J.; Wade, J. J. *Ibid.* **1975**, *97*, 6282 (epidendrobine). (e) Roush, W. R. *Ibid.* **1978**, *100*, 3599.

(5) Corey, E. J.; Pearce, H. L. *J. Am. Chem. Soc.* **1979**, *101*, 5841.

(6) Corey, E. J.; Pearce, H. L. *Tetrahedron Lett.* **1980**, 1823.

(7) (a) Asahina, Y.; Fujita, A. *Yakugaku Zasshi* **1915**, *396*, 81. (b) Grundmann, C.; Kober, E. *J. Am. Chem. Soc.* **1955**, *77*, 2332.

(8) All new compounds were fully characterized spectroscopically and by combustion and/or high-resolution mass spectral analyses. The complete data will appear in a full paper.

(9) The poor yield was due to the dimerizing nature of **5**, but this was not a serious obstracle to the present synthesis since **5** is readily prepared from levulinic acid on a rather large scale.

(10) Conversion of **7** into the desired **3** was achieved, but this route was abandoned because of the long steps and poor yield. Details of the experiments will be treated when a full account of the work is published.

(11) Equilibration of **10** with 1% HCl in dry methanol provided **9** in 35% yield together with 49% of the recovered **10**, and hydrolysis of **10** with HCl–MeOH–H_2O regenerated **4** in 75% yield. The undesired product **10**, therefore, was recycled along the synthetic route.

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