(-)-Methyl 3-Hydroxybutyrate (12). (*R*,*S*)-BNP-12: $[\alpha]^{23}_D$ -25° (*c* = 1.1); UV, λ_{max} (log ϵ) 216 (4.98), 302 (4.13) nm; NMR, δ 1.48 (*S*, d, *J* = 6.38 Hz, 3-Me), 1.59 (*R*, d, *J* = 6.39 Hz, 3-Me), 2.57 (*R*, br dd, *J* = 15.80, 6.39 Hz, 2-H), 2.64 (*S*, br dd, *J* = 15.80, 5.71 Hz, 2-H), 2.79 (*R*, dd, *J* = 15.80, 7.06 Hz, 2-H), 2.83 (*S*, dd, *J* = 15.80, 7.73 Hz, 2-H), 3.59 (*R*, 0.523 H_3, s, OCH_3), 3.78 (*S*, 0.477 H_3, s, OCH_3), 5.26 (*R* and *S*, m, 3-H), 7.25-8.10 (12 H, m, arom). Anal. Calcd for $C_{25}H_{21}O_6P$: C, 66.96; H, 4.72. Found: C, 66.88; H, 4.72.

(*R*)-BNP-12: $[\alpha]^{23}_D$ -201° (*c* = 0.3); UV, λ_{max} (log ϵ) 216 (4.94), 302 (4.07) nm; NMR, δ 1.60 (d, *J* = 6.35 Hz, 3-Me), 2.58 (ddd, *J* = 15.80, 6.39, 2.02 Hz, 2-H), 2.79 (dd, *J* = 15.80, 7.06 Hz, 2-H), 3.59 (s, OCH_3), 5.25 (m, 3-H), 7.25-8.10 (12 H, m, arom). Anal. Calcd for $C_{25}H_{21}O_6P$: C, 66.96; H, 4.72. Found: C, 67.00; H, 4.79.

(*S*)-BNP-12: $[\alpha]^{23}_D$ +369° (*c* = 0.3); UV, λ_{max} (log ϵ) 216 (4.95), 302 (4.13) nm; NMR, δ 1.48 (d, *J* = 6.39 Hz, 3-Me), 2.64 (br dd, *J* = 15.80, 5.71 Hz, 2-H), 2.83 (dd, *J* = 15.80, 7.73 Hz, 2-H), 3.79 (s, OCH_3), 5.30 (m, 3-H), 7.25-8.10 (12 H, m, arom). Anal. Calcd for $C_{25}H_{21}O_6P$: C, 66.96; H, 4.72. Found: C, 66.92; H, 4.73.

(2*R*,3*R*)-(-)-Dimethyl 2-*O*-Acetyltartrate (13). (*R*,*S*)-BNP-13: $[\alpha]^{23}_D$ -63° (*c* = 1.3); UV, λ_{max} (log ϵ) 216 (4.97), 302 (4.12) nm; NMR, δ 2.08 (*S*, s, OAc), 2.12 (*R*, s, OAc), 3.82 (*R*, s, OMe), 3.92 (*S*, 0.401 H_3, s, OMe), 3.99 (*R*, 0.599 H_3, s, OMe), 5.79 (*R*, d, *J* = 2.69 Hz, 3-H), 5.82 (*S*, d, *J* = 2.69 Hz, 3-H), 5.83 (*S*, d, *J* = 2.69 Hz, 3-H), 5.86 (*S*, d, *J* = 2.69 Hz, 3-H), 5.73 (*S*, d, *J* 2.69 Hz, 2-H), 5.74 (*R*, d, *J* = 2.69 Hz, 2-H), 5.78 (*S*, d, *J* = 2.69 Hz, 2-H), 5.79 (*S*, d, *J* = 2.69 Hz, 2-H), 7.25-8.10 (12 H, m, arom). The many signals of the C2 and C3 protons may be caused by a blocking effect of the BNP group for the rotation around a C2-C3 bond. Anal. Calcd for $C_{28}H_{23}O_{10}P$: C, 61.10; H, 4.21. Found: C, 60.93; H, 4.30.

(-)-2-Octanol (14). (*R*,*S*)-BNP-14: $[\alpha]^{23}_D$ -31° (*c* = 0.6); UV, λ_{max} (log ϵ) 216 (4.99), 302 (4.14) nm; NMR, δ 0.82 (*R*, 0.541 H_3, br t, *J* = 7.06 Hz, 7-Me), 0.92 (*S*, 0.459 H_3, br t, *J* = 7.06 Hz, 7-Me), 1.38 (*S*, d, *J* = 6.39 Hz, 2-Me), 1.50 (*R*, d, *J* = 6.39 Hz, 2-Me), 4.86 (*R* and *S*, m, 2-H), 7.25-8.10 (12 H, m, arom). Anal. Calcd for $C_{28}H_{29}O_4P$: C, 73.03; H, 6.35. Found: C, 72.98; H, 6.37.

Teststerone (15). (*R*,*S*)-BNP-15: $[\alpha]^{23}_D$ +115° (*c* = 1.0); UV, λ_{max} (log ϵ) 216 (4.97), 302 (4.12) nm; NMR, δ 0.74 (*S*, 0.559 H_3, s, 13-Me), 0.81 (*R*, 0.441 H_3, s, 13-Me), 1.15 (*S*, s, 10-Me), 1.20 (*R*, s, 10-Me), 4.58 (*R* and *S*, m, 17-H), 5.73 (*R* and *S*, s, 4-H), 7.25-8.10 (12 H, m, arom). anal. Calcd for $C_{39}H_{39}O_5P$: C, 75.71; H, 6.35. Found: C, 75.63; H, 6.32.

Diacetone D-Glucose (16). (*R*,*S*)-BNP-16: $[\alpha]^{23}_D$ +81° (*c* = 1.6); UV, λ_{max} (log ϵ) 216 (5.01), 302 (4.12) nm; NMR, δ 0.99 (*R*, 0.291 H_3, s, Me), 1.29 (*S*, 0.709 H_3, s, Me), 1.33 (*R*, s, Me), 1.36 (*R*, s, Me), 1.51 (*R* and *S*, s, Me_2), 1.52 (*R* and *S*, s, Me_2), 5.09 (*R*, dd, *J* = 7.06, 2.35 Hz, 3-H), 5.20 (*S*, dd, *J* = 7.20, 1.80 Hz, 3-H), 4.83 (*R*, d, *J* = 3.70 Hz, 2-H), 4.98 (*S*, d, *J* = 3.69 Hz, 2-H), 5.82 (*S*, d, *J* = 3.69 Hz, 1-H), 5.97 (*R*, d, *J* = 3.70 Hz, 1-H), 7.25-8.10 (12 H, m, arom). Anal. Calcd for $C_{32}H_{31}O_9P$: C, 65.08; H, 5.29. Found: C, 65.15; H, 5.33.

3-*O*-Acetyl-6-hydroxydihydrocholesterol (17). (*R*,*S*)-BNP-17: $[\alpha]^{23}_D$ -148° (*c* = 1.6); UV, λ_{max} (log ϵ) 216 (5.01), 302 (4.15) nm; NMR, δ 0.46 (*S*, 0.167 H_3, s, 13-Me), 0.66 (*R*, 0.833 H_3, s, 13-Me), 0.85 (*S*, d, *J* = 6.72 Hz, 25-Me), 0.86 (*S*, d, overlapping, 25-Me), 0.88 (*R*, d, *J* = 6.72 Hz, 25-Me), 0.89 (*R*, d, *J* = 6.72 Hz, 25-Me), 0.80 (*R*, s, 10-Me), 0.86 (*S*, s, 10-Me), 1.95 (*R*, s, OAc), 2.07 (*S*, s, OAc), 4.70 (*S*, br s, 6-H), 4.87 (*R*, br d, *J* = 5.38 Hz, 6-H), 4.67 (*R* and *S*, m, 3-H), 7.25-8.10 (12 H, m, arom). Anal. Calcd for $C_{49}H_{61}O_6P$: C, 80.73; H, 8.43. Found: C, 80.55; H, 8.39.

Cholesterol (18). (*R*,*S*)-BNP-18: $[\alpha]^{23}_D$ +12° (*c* = 1); UV, λ_{max} (log ϵ) 216 (5.00), 302 (4.08) nm; NMR, δ 0.67 (*R* and *S*, s, 13-Me), 0.86 (*R* and *S*, d, *J* = 6.72 Hz, 25-Me), 0.87 (*R* and *S*, d, *J* = 6.72 Hz, 25-Me), 1.00 (*R* and *S*, s, 10-Me), 4.57 (*R* and *S*, m, 3-H), 5.38 (*S*, 0.529 H, d, *J* = 5.04 Hz, 6-H), 5.47 (*R*, 0.471 H, d, *J* = 5.12 Hz, 6-H), 7.25-8.10 (12 H, m, arom). Anal. Calcd for $C_{47}H_{57}O_4P$: C, 98.41; H, 8.01. Found: C, 98.39; H, 8.01.

(+)-2-Allyl-3-hydroxy-2-methylcyclopentanone (19). (*R*,*S*)-BNP-19: $[\alpha]^{23}_D$ +135° (*c* = 0.8); UV, λ_{max} (log ϵ) 216 (4.96), 302 (4.11) nm; NMR, δ 1.00 (*S*, 0.575 H_3, s, 2-Me), 1.06 (*R*, 0.425 H_3, s, 2-Me), 5.09 (*S*, br d, *J* = 5.37 Hz, 3-H), 5.13 (*R*, br d, *J* = 5.04 Hz, 3-H), 4.87 (*S*, d, *J* = 5.04 Hz, =CH(H)), 5.24 (*R*, d, *J* = 4.03 Hz, =CH(H)), 4.92 (*S*, s, =CH(H)), 5.20 (*R*, s, =CH(H)), 5.60 (*S*, m, -CH=), 5.94 (*R*, m, -CH=), 7.25-8.10 (12 H, m, arom). Anal. Calcd for $C_{29}H_{25}O_5P$: C, 71.89; H, 5.20. Found: C, 71.77; H, 5.18.

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Highly Stereoselective Allylation of Aldehydes with Pentacoordinate Allylsilicates in Hydroxylic Media. Discrimination between Linear and α-Branched Alkanals[1]

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Abstract: Allylation of aldehydes with allyltrifluorosilanes in the presence of a wide variety of hydroxy compounds and triethylamine gave the corresponding homoallyl alcohols in regio- and stereospecific manner. Pentacoordinate allylsilicates are suggested as intermediates. The present reagent system can discriminate linear from α-branched alkanals. The structure and reactivity relationship in pentacoordinate allylsilicates is discussed in terms of Lewis acidity of the central silicon.

The majority of organometallic reactions useful for organic syntheses requires strictly anhydrous reaction conditions. Allylation reactions with allylsilanes, one of the most versatile organic transformations,[2] are not exceptions. In this paper, however, we report the allylation of aldehydes with allyltrifluorosilanes in the presence of a wide variety of hydroxy compounds and triethylamine under mild conditions. The reaction involving pentacoordinate silicate intermediates is not only operationally convenient but also the stereochemical outcome suggests useful future applications in stereocontrolled organic synthesis. The highly regio- and stereocontrolled reaction with allylic metals are of current interest.[3]

(1) Chemistry of Organosilicon Compounds. 259.

(2) Allyltrialkylsilanes have been used as excellent allylation reagents of carbonyl compounds in the presence of a Lewis acid or fluoride ion. (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (b) Hosomi, A.; Shirahata, A.; Sakurai, H. *Ibid.* **1978**, 3043. (c) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (d) Sakurai, H. *Ibid.* **1985**, *57*, 1759. (e) Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 83. (f) Hosomi, A.; Sakurai, H. *J. Synth. Org. Chem. Jpn.* **1985**, *43*, 406.

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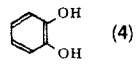
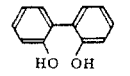
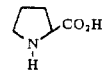
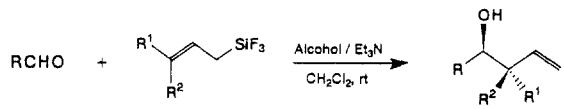
Table I. Allylation of Aldehydes with Prenyltrifluorosilane in the Presence of a Hydroxy Compound and Triethylamine[a]

entry	aldehyde	hydroxy compd	reaction time (h)	yield (%)
1	C_6H_5CHO (1)	 (4)	20	93
2	4-$MeOC_6H_4CHO$	4	20	82
3	4-CNC_6H_4CHO (2)	4	20	84
4	$Ph(CH_2)_2CHO$	4	20	86
5	$CH_3(CH_2)_7CHO$ (3)	4	20	87
6	1	 (5)	48	88
7	2	5	46	84
8	3	5	60	70
9	1	$C_6H_5CH(OH)COOH$	24	83
10	1	$(COOH)_2$	24	90[b]
11	1		15[c]	72
12	1	$NH_2(CH_2)_2OH$	30[c]	45
13[d]	1	MeOH	48	83

[a] Unless otherwise noted, the following molar ratio of the reagents was used. aldehyde/prenyltrifluorosilane/diol/Et_3N = 1:1.5:1.5:3. [b] A regioisomer was detected (10%). [c] Without triethylamine. [d] The following molar ratio of the reagents was used: aldehyde/prenyltrifluorosilane/methanol/Et_3N = 1:2:4:4.

Results and Discussion

The new allylation reaction was carried out as shown in the following typical example. To a CH_2Cl_2 solution of catechol (3 mmol) and triethylamine (6 mmol) was added prenyltrifluorosilane (3 mmol) at 0 °C, and it stirred for 30 min. After addition of benzaldehyde (2 mmol), the solution was stirred for 20 h at ambient temperature in the atmosphere. The mixture was quenched with HCl. Usual workup and distillation gave 2,2-dimethyl-1-phenylbut-3-en-1-ol in 93% yield.

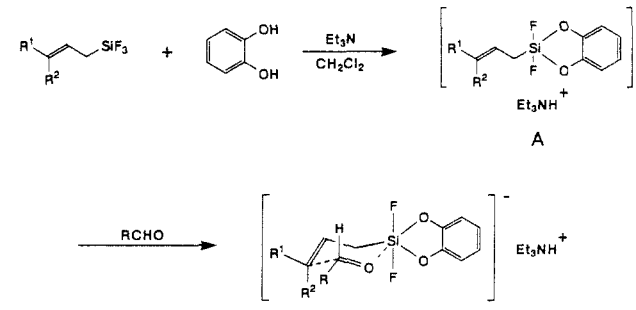


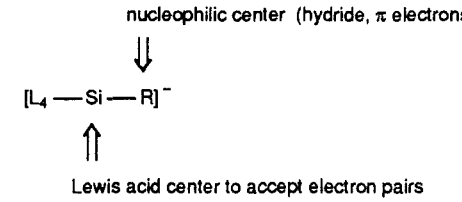
The results of prenylation of various aromatic and linear aliphatic aldehydes are shown in Table I. This one-pot allylation is operationally very simple and can be carried out even in the presence of water. Monohydroxy compounds such as methanol can also be used as auxiliary but are less effective than diols. When an aminoxy compound was utilized instead of a diol, the prenylation occurred in the absence of triethylamine.

The reaction of benzaldehyde with a mixture of crotyltrifluorosilanes (E/Z = 95/5) in the presence of catechol and triethylamine gave 2-methyl-1-phenylbut-3-en-1-ol (**6**) in 93% yield with a threo/erythro ratio of 94/6, while another mixture of crotyltrifluorosilanes (E/Z = 5/95) gave **6** in 89% yield with the threo/erythro ratio of 5/95. The reaction was regiospecific and highly diastereoselective like other allylation through pentacoordinate silicates.[4]

Currently, we are developing pentacoordinate silicate chemistry for organic synthesis. Our basic idea is as follows.[4,6] Silicon can expand its coordination number from the normal value of 4 to 5 and 6 to form penta- and hexacoordinate compounds, provided that the silicon atom carries highly electronegative and sterically compact ligands such as fluorine. These pentacoordinate organosilicon species have a unit negative charge so that basically the silyl group in these compounds is electron-releasing. The negative charge is, however, delocalized into electronegative ligands. As a result, the silicon atom becomes rather positively charged with a Lewis acid character of some extent to be able to accept an electron pair. These two apparently conflicting characters of pentacoordinate silicon species render an interesting reactivity which should also be useful for synthetic reactions.

Scheme I





We have already demonstrated such cooperative action of pentacoordinate silicon species in reduction of carbonyl compounds with pentacoordinate hydridosilicates.[7] In these studies, we have demonstrated that pentacoordinate hydridosilicates were a good hydride transfer reagent due to the intrinsic nucleophilicity, while at the same time, the significant Lewis acid character of the silicon center was demonstrated in the activation of the substrate carbonyl compounds.

As we have reported recently, pentacoordinate allylsilicates react with aldehydes to give homoallyl alcohols with exceptionally high regio- and diastereoselectivity.[4] The high reactivity of the allylsilicates is attributed to the significantly high Lewis acidity to give hexacoordinate silicates, which allows a six-membered cyclic transition state as well as the enhanced nucleophilicity of the γ-carbon of the allylsilicates due to σ–π conjugation.

It is very interesting and important to note that the present reagent system can discriminate linear from α-branched alkanals, giving a hitherto unprecedented strategy for organic synthesis by selective allylation among two different aldehydes. Thus prenylation of primary aldehydes proceeds very smoothly, while no reaction takes place with secondary and tertiary aldehydes. Treatment of a 1:1 mixture of a linear and an α-branched alkanal with prenyltrifluorosilane/diol/amine systems resulted in the prenylation of only the linear alkanal in high yields, while the sterically hindered α-branched alkanal was almost quantitatively recovered. The results of the prenylation and crotylation of selected mixtures of alkanals are shown in Table II.

The usual Grignard and alkyllithium compounds are known to add nonselectively to both ketones and aldehydes.[8] In this context, we have examined competitive alkylation of linear and α-branched alkanals by using *sec*-butyl- and *tert*-butyllithium in ether. Thus, when a mixture of nonanal (1 mmol) and 2-ethylhexanal (1 mmol) was treated with 1.56 M pentane solution of *tert*-butyllithium (1 mmol) at −78 °C, *tert*-butylated alcohols were

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(7) (a) Kira, M.; Sato, K.; Sakurai, H. *J. Org. Chem.* **1987**, *52*, 948. (b) Kira et al. *Chem. Lett.* **1987**, 2243.

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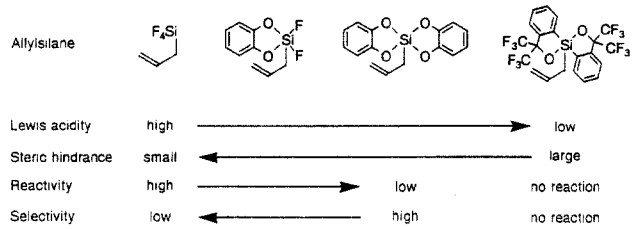
Table II. Selective Allylation of Two Aldehydes with Allyltrifluorosilane/Diol/Triethylamine Systems[a]

allylsilane	linear/α-branched aldehydes	total yield of homoallyl alcohols[c] (%)	ratio[b]	recovery of branched aldehyde[c] (%)
PrenylSiF$_3$[d]	$CH_3(CH_2)_7CHO$ (3)/$CH_3(CH_2)_3C(C_2H_5)HCHO$ (7)	88	100/0	91
PrenylSiF$_3$[d]	3/$(CH_3)_3CCHO$	83	100/0	84
PrenylSiF$_3$[d]	$Ph(CH_2)_2CHO$/$PhCH(CH_3)CHO$	85	100/0	89
(*E*)-CrotylSiF$_3$[e]	3/7	83	92/8	81
(*E*)-CrotylSiF$_3$[e]	3/7[f]	66	97/3	70
(*Z*)-CrotylSiF$_3$[e]	3/7[f]	70	100/0	63

[a] Reaction was carried out in CH_2Cl_2 for 20 h at room temperature. Unless otherwise noted, catechol was used as a diol. [b] The ratio of the homoallyl alcohol produced from a linear aldehyde to that from an α-branched aldehyde. [c] Yield determined by GLC. [d] The following molar ratio of reagents was used: linear aldehyde/branched aldehyde/allyltrifluorosilane/diol/Et_3N = 1.0:1.0:2.0:2.0:4.0. [e] The following ratio of reagents was used: linear aldehyde/branched aldehyde/allyltrifluorosilane/diol/Et_3N = 1.0:1.0:1.0:1.0:2.0. [f] Instead of catechol, 2,2′-binaphthol was used as an additive.

Scheme II



obtained in 78% yield. The ratio of the alcohol from nonanal to that from 2-ethylhexanal was 25/75. A similar experiment by using 0.95 M cyclohexane solution of *sec*-butyllithium (1 mmol) gave the corresponding ratio of 32/68, while the total yield of the alkylated alcohols was 75%. The α-branched alkanal was alkylated even more smoothly than the linear alkanals.

Similar highly selective crotylation to linear and α-branched alkanals was observed for crotyltrifluorosilane/diol/amine systems (Table II). It should be noted that tetrafluoroallylsilicates derived from the allyltrifluorosilane/CsF system also exhibited somewhat high selectivity to linear and α-branched alkanals.[9] Therefore, the pentacoordinate allylsilicates may have intrinsically high selectivity toward carbonyl compounds.[10]

The high regio- and stereoselectivity suggests strongly that the reaction proceeds via six-membered cyclic transition states having chair conformation as previously proposed.[11] The efficiency of diols as an additive suggests however that a dialkoxydifluoroallylsilicate like A is involved as a key intermediate as shown in Scheme I.

One of the most interesting points is that the reactivity of the pentacoordinate silicon atom can be modified by substituents. Previously, we have reported that bis(diolato)allylsilicates react with aromatic aldehydes only. No reaction took place with alkanals.[4a] In contrast, both linear and α-branched aldehydes are prenylated smoothly with allyltetrafluorosilicates derived from the allyltrifluorosilane/CsF system.[4b] The reactivity of the present reagent system, which is believed to involve dialkoxydifluoroallylsilicate, is just in between these two systems. It may be interesting to note that allylsilicate with the Martin's ligand did not react at all with aldehydes.[4a] The reactivity of pentacoordinate allylsilicates thus decreases in the following order: allylSiF_4 > allyl$SiF_2(OR)_2$ > allyl$Si(OR)_4$ > allyl$SiR'_2(OR)_2$, while the selectivity increases in the inverse order (Scheme II).

The reactivity–selectivity pattern indicates the importance of the Lewis acidity of pentacoordinate silicon atom in the reactivity, although steric hindrance is also another important factor. The present study demonstrates that pentacoordinate allylsilicate strategy is very promising as a method of finely controlled organic synthesis.

Experimental Section

Materials. Catechol and other dioxy and aminoxy compounds were commercially available. (*E*)-Crotyltrifluorosilane (*E*/*Z* = 95/5),[4c] (*Z*)-crotyltrifluorosilane (*E*/*Z* = 5/95),[4c] and prenyltrifluorosilane[4b] were prepared in 80–95% yields by fluorination with antimony trifluoride[14] of the corresponding allyltrichlorosilanes. (*E*)-Crotyltrichlorosilane and prenyltrichlorosilane were prepared by the reactions of the corresponding allyl chlorides with trichlorosilane in the presence of triethylamine and catalytic amounts of Cu^ICl.[15] (*Z*)-Crotyltrichlorosilane was prepared by the hydrosilylation of 1,3-butadiene with trichlorosilane catalyzed by $Pd(PPh_3)_4$.[16] The *E*/*Z* ratios of crotyltrifluorosilanes were determined by GLC (Shimadzu 15A, CBP-1, 50 m).

Prenylation of Aldehydes with Prenyltrifluorosilane/Diol/Triethylamine Systems. To a CH_2Cl_2 (5 mL) solution of catechol (330 mg, 3.0 mmol) and triethylamine (607 mg, 6.0 mmol) was added prenyltrifluorosilane (463 mg, 3.0 mmol) at 0 °C. The mixture was stirred for 30 min before the addition of an aldehyde (2.0 mmol). After stirring for 20 h at ambient temperature, the reaction was quenched by 1 M HCl, and the organic layer was washed with 1 M NaOH. Usual workup and then distillation or preparative TLC gave the corresponding homoallyl alcohol in 82–93% yields. The product was identified by comparing the GLC retention time and ^1H NMR and MS spectra with those of the authentic sample.[4] Analyses by GLC and ^1H NMR spectroscopy revealed the absence of any regioisomers in the product.

Prenylation of Benzaldehyde with Prenyltrifluorosilane/Ethanolamine System. To a CH_2Cl_2 (5 mL) solution of ethanolamine (183 mg, 3.0 mmol) was added prenyltrifluorosilane (463 mg, 3.0 mmol) at 0 °C. The mixture was stirred for 30 min before the addition of benzaldehyde (212 mg, 2.0 mmol). After stirring for 30 h at ambient temperature, the reaction was quenched by 1 M HCl, and the organic layer was washed with 1 M NaOH. 2,2-Dimethyl-1-phenylbut-3-en-1-ol was obtained in 45% yield. The product was identified by comparing the GLC retention time and MS spectrum with the authentic sample.[4] Analysis by GLC revealed the absence of any regioisomers in the product.

Crotylation of Benzaldehyde with (*E*)-Crotyltrifluorosilane (*E*/*Z* = 95/5)/Catechol/Triethylamine System. To a CH_2Cl_2 (5 mL) solution of catechol (330 mg, 3.0 mmol) and triethylamine (607 mg, 6.0 mmol) was added the (*E*)-crotyltrifluorosilane (421 mg, 3.0 mmol) at 0 °C. The mixture was stirred for 30 min before the addition of benzaldehyde (212 mg, 2.0 mmol). After stirring for 10 h at ambient temperature, the reaction was quenched by 1 M HCl, and the organic layer was washed with 1 M NaOH. A mixture of 2-methyl-1-phenylbut-3-en-1-ol was obtained in 93% yield. The products were identified by comparing the GLC retention times and MS spectra with those of the authentic samples.[4] The ratio of threo to erythro alcohols was determined to be 94/6 by GLC (Shimadzu 15A, CBP-20, 25 m). No regioisomers were detected by GLC.

Similarly, when (*Z*)-crotyltrifluorosilane (*E*/*Z* = 5/95) was used, a mixture of 2-methyl-1-phenylbut-3-en-1-ol was obtained in 89% yield with the threo to erythro ratio of 5/95.

(9) For example, when 1:1 mixtures of **3** and **7** were treated with prenyltrifluorosilane, (*E*)- and (*Z*)-crotyltrifluorosilane in the presence of CsF in THF, the **3**/**7** adduct ratios were 95/5, 80/20, and 94/6, respectively.

(10) Reetz et al. have successfully demonstrated discrimination between two aldehydes by using a methyltitanium reagent. (a) Reetz, M. T.; Steinbach, R.; Wenderoth, B.; Wetsermann, J. *Chem. Ind.* **1981**, 541. (b) Reetz, M. T.; Westermann, J.; Steinbach, R.; Wenderoth, B.; Peter, R.; Osterk, R.; Sabina, M. *Chem. Ber.* **1985**, *118*, 1421.

(11) The cyclic transition states were proposed first by Zimmerman et al.[12] for reactions involving metal enolates and then extended by Hoffmann et al.[13] to the reaction of allylboronates.

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Selective Allylation of Two Aldehydes with Allyltrifluorosilane/Catechol/Triethylamine Systems. To a CH_2Cl_2 (4 mL) solution of catechol (220 mg, 2.0 mmol) and triethylamine (405 mg, 4.0 mmol) was added an allyltrifluorosilane (2.0 mmol) at 0 °C, and then the mixture was stirred for 30 min. After addition of a mixture of a linear (1.0 mmol) and an α-branched alkanal (1.0 mmol), the solution was stirred for 20 h at ambient temperature. The reaction was quenched by 1 M HCl, and the organic layer was washed with 1 M NaOH. The yields of homoallyl alcohols and recovered aldehydes were determined by GLC.

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Enantiocontrolled Synthesis of Quaternary Carbon Centers via Anionic Oxy-Cope Rearrangement: An Efficient Synthesis of (+)-Dihydromayurone

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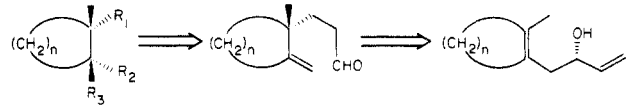
Abstract: (+)-Dihydromayurone (**1**) was enantioselectively synthesized from β-cyclocitral (**7**). The key step in the synthesis involved anionic oxy-Cope rearrangement of allylic alcohol **6** to aldehyde **5**. Efficient transfer of chirality from the secondary allylic alcohol center to the quaternary carbon center was observed via chairlike transition state with the equatorial oxyanionic bond.

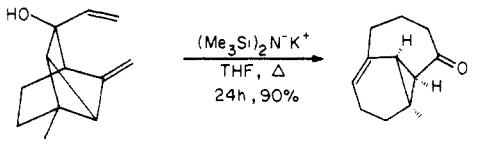
Creation of asymmetric quaternary carbon centers is one of the most important problems for the enantioselective syntheses of natural products such as steroids, terpenoids, and alkaloids. A number of methods have been reported recently[1] for the highly enantioselective construction of quaternary carbon centers in various molecular frames.

Our own interest in the subject led us to consider the possibility of constructing a chiral quaternary carbon center via chirality transfer from a secondary carbinol center using anionic oxy-Cope rearrangement[2] (Scheme I). Optically active allylic alcohols are accessible by a number of standard procedures, for example, asymmetric vinyl or acetylenic addition to aldehydes,[3] asymmetric reduction of corresponding ketones,[4] or allylic transposition of primary allylic alcohols using Sharpless asymmetric epoxidation reaction as the crucial step.[5]

Scheme I



Scheme II



For the transfer of chirality in the types of reactions represented in Scheme I, the relative equatorial/axial preference of the oxyanionic bond ($C-O^-$) is of paramount importance. Inasmuch as the anionic oxy-Cope rearrangement was used frequently in syntheses of complex natural products,[6] we were surprised to realize that this fundamental facet of the reaction had not yet been addressed properly in the literature. The situation is quite different from the case of Claisen rearrangement,[6] which was exhaustively studied in the context of specific chirality transfers in many natural product syntheses.

In many recent cases, anionic oxy-Cope rearrangement is forced to proceed through bridged tricyclic transition states. For example, the crucial step in Paquette's synthesis of cerorubenic acid III ring system involves anionic oxy-Cope rearrangement with a rigid, predetermined transition state[7] (Scheme II).

In more flexible systems, chairlike transition states are generally favored, which then coax the oxyanionic bond to assume either

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