Direct Chirality Determination of Secondary Carbinol by Chirality Recognition Ability of C_2 Symmetry 1,1′-Binaphthyl-2,2′-diyl Phosphoryl Chloride

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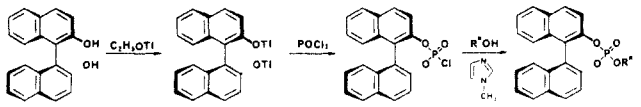
Abstract: The chirality of the secondary carbinol carbon atom can, directly and highly sensitively, be decided by derivation into a C_2 symmetry 1,1′-binaphthyl-2,2′-diyl phosphate. The secondary carbinols and 1,1′-binaphthyl-2,2′-diyl phosphoryl chloride ((BNP)Cl) with the same chirality react preferentially over that with different chirality. The result is characteristically confirmed by the CD spectrum, since the intramolecular bonded naphthol–naphthol moiety causes a Davydov splitting with a very strong intensity. The chirality recognition ability of the BNP reagent is not affected by ring size, neighboring functional groups, or the configuration of the hydroxyl group in the alcohol compounds. And, the ability is exhibited with acyclic alcohols, as well as the cyclic compounds. The diastereomeric excess of the preferential pair can be calculated easily by the integrated area of the signals on the NMR spectrum.

In CD spectra, the ketone-Cotton effect[1] and exciton chirality method[2] are general and useful methods for the determination of the absolute stereochemistry of organic compounds. There are, however, some limitations for the case undergoing conformational changes[3] and for applications to acyclic or monohydroxy compounds. We have sought a novel method for determination of an asymmetric carbinol by direct chirality recognition rather than the indirect methods of Horeu[4] and others.[5]

We find that the chirality of the secondary carbinol carbon atom can, directly and highly sensitively, be determined by derivation into a C_2 symmetry 1,1′-binaphthyl-2,2′-diyl phosphate (**1**). When racemic 1,1′-binaphthyl-2,2′-diyl phosphoryl chloride (abbreviated to [(*R*,*S*)-(BNP)Cl, **2**]) derived from 1,1′-bi-2-naphthol (**3**)[6] reacts with a chiral alcohol, an excess diastereomer with the same chiralities is formed in the BNP derivatives obtained. The preferential result is shown by the strong Cotton effects with Davydov splitting[7] caused by the intramolecularly bonded naphthol–naphthol exciton coupling.[2] The clear discrimination is principally produced from extremely intense split Cotton effects at 225 ($\Delta\epsilon > 700$) and 213 nm ($\Delta\epsilon > 500$) of (*R*)-(−)- and (*S*)-(+)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate [(*R*)- and (*S*)-(BNP)OH, **4** and **5**] (Table I).[8]

Scheme I. Preparation of (*R*)-(−)-BNP Chiral Alcohol Derivatives [(*S*)-(+)- and (*R*,*S*)-BNP Derivatives Obtained by the Same Procedure]



(*R*)-(−)- and (*S*)-(+)-1,1′-binaphthyl-2,2′-diyl phosphoryl chlorides [(*R*)- and (*S*)-(BNP)Cl, **6** and **7**] are derived from dithallous (*R*)- and (*S*)-1,1′-bi-2-naphthoxides,[9] respectively, and $POCl_3$ in situ. On treatment with 1-methylimidazole[10] and each chloride, dihydrocholesterol (**8**) gives (*R*)- and (*S*)-BNP-dihydrocholesterols (Scheme I).[11] Latter two show opposite intense splitting Cotton effects at 223 and 212 nm (Figure 1).[12] In the same manner, (*R*,*S*)-(BNP)Cl and **8** provide (*R*,*S*)-BNP-dihydrocholesterol,[12] which show +1 and −2 Cotton effects corresponding to the differential CD spectrum of the (*S*)- and (*R*)-BNP phosphates (Figure 1; Table I). The fact is that (*S*)-(BNP)Cl discriminates preferentially the (*S*)-carbinol. The elucidation is also corroborated by comparing their specific rotations (Table I).

The differential CD spectra show that (*R*)- and (*S*)-carbinols of (−)- and (+)-menthol (**9** and **10**) are preferentially recognized by (*R*)- and (*S*)-(BNP)Cl, respectively. The chirality recognition ability of the BNP reagent is shown in the reaction with a steric crowding terpene alcohol **11**. It is noteworthy and conclusively distinct from the other methods[1,2] that this ability works not only with cyclic compounds but also with chiral carbinol groups of acyclic compounds **12–14**. The chirality recognition is not affected by ring size, neighboring functional groups, or the configuration of the chiral hydroxyl groups **15–17**. α,β-Unsaturated and saturated ketones **18** and **19** do not disturb the process by which the chiralities are established, since the Cotton effect intensities of the (*R*,*S*)-BNP derivatives are superior to those of the ketones.[13]

(1) Legrand, M.; Rougier, M. J. *Stereochemistry*; Georg Thieme Publishers: Stuttgart, 1977; Vol. 2, pp 33–183. Moscowitz, A. *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry*; Heyden & Son Ltd.: London, 1967. Crabbe, P. *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry*; Holden-Day: San Francisco, 1965.

(2) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*; University Science Book and Oxford University Press: California and Oxford, 1983.

(3) Morita, M.; Kojima, Y.; Kato, N.; Niwa, K.; Tanaka, I.; Yamane, T.; Ashida, T. *Tetrahedron Lett.* **1983**, *24*, 5631–5634. Kubo, I.; Kido, M.; Fukuyama, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 897–898. Trivedi, G.; Komura, H.; Kubo, I.; Nakanishi, K. *J. Chem. Soc., Chem. Commun.* **1979**, 885–886. Rogers, D.; Uhnal, G. G.; Williams, D. J.; Ley, S. V.; Sim, G. A.; Joshi, B. S.; Ravindranath, K. R. *J. Chem. Soc., Chem. Commun.* **1979**, 97–99. Hosozawa, S.; Kato, N.; Munakata, K. *Tetrahedron Lett.* **1974**, 3753–3756.

(4) Horeu, A. *Stereochemistry*; Georg Thieme Publishers: Stuttgart, 1977; Vol. 3, pp 51–94.

(5) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549. Raban, M.; Mislow, K. *Topics in Stereochemistry*; Interscience Publishers: New York, 1967; Vol. 2, pp 199–230.

(6) Cyclic phosphoric acid (i) and chelate metal hydride and metal catalysts (ii) that were derived from C_2 symmetry 1,1′-bi-2-naphthol produced superior chirality recognition and induction abilities, respectively: (i) Jacques, J.; Fouquey, C.; Viterbo, R. *Tetrahedron Lett.* **1971**, 4617–4620. (ii) Noyori, R. *Pure Appl. Chem.* **1981**, *53*, 2315–2322. Noyori, R.; Takaya, H. *Chem. Scr.* **1985**, *25*, 83–89.

(7) Davydov, A. S. *Theory of Molecular Excitons*; McGraw-Hill: New York, 1982.

(8) (*R*)- and (*S*)-(BNP)OH (**4**, **5**) exhibit an identical intramolecular charge-transfer absorption at 218 nm (ϵ 102 000).

(9) Taylor, E. C.; McKillop, A. *Acc. Chem. Res.* **1970**, *3*, 338–346.

(10) When triethylamine was used as a base, (BNP)Cl did not react with the alcohols under any condition. It has been reported, however, that a chiral cyclic phosphoryl chloride reacted with alcohols by using it: Anderson, R. C.; Shapiro, M. J. *J. Org. Chem.* **1984**, *49*, 1304–1305.

(11) (*R*)- and (*S*)-BNP derivatives for several alcohols were prepared to confirm that their CD spectra and specific rotations were dependent on (*R*)- and (*S*)-BNP groups, respectively, and (*R*,*S*)-BNP derivatives were constructed from their mixtures only.

(12) (*R*)-, (*S*)-, and (*R*,*S*)-BNP-dihydrocholesterols exhibit a identical intramolecular charge-transfer absorption at 216 nm with a similar strength (ϵ ca. 110 000).

(13) Velluz, L.; Legrand, M.; Vienner, R. *C. R. Hebd. Seances Acad. Sci.* **1965**, *261*, 1687–1692. Ziffer, H.; Robinson, C. H. *Tetrahedron* **1968**, *24*, 5803–5816.

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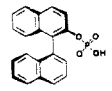
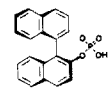
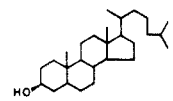
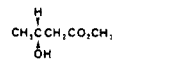
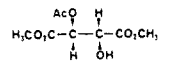
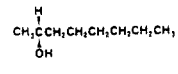
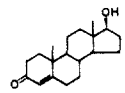
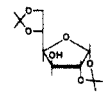
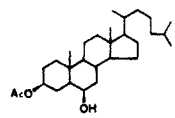
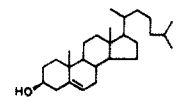
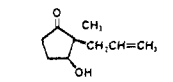
Table I. CD Spectral Data and Specific Rotations of 1,1′-Binaphthyl-2,2′-diyl Phosphates

compound[a]				BNP derivative: $\Delta\epsilon$ (λ,[b] nm)			
structure	no.	$[\alpha]_D$, deg	chirality of carbinol	*R,S*	*R*	*S*	$[\alpha_D$,[c] deg] de,[d] %
	**4**	−605			−746 (225) +562 (213)		
	**5**	+605				+720 (225) −538 (213)	
	**8**	+23.8	*S*	+77 (223) −62 (212) [+29]	−521 (223) +428 (212) [−176]	+633 (223) −543 (212) [+207]	10 (*S–S*)
	**9**	−50	*R*	−85 (223) +68 (212) [−56]	−595 (223) +467 (212) [−318]	+691 (223) −572 (212) [+319]	19 (*R–R*)
	**10**	+48	*S*	+58 (223) −60 (212) [+32]	−565 (223) +451 (212) [−310]	+478 (223) −395 (212) [+337]	9 (*S–S*)
	**11**	−35	*S*	+31 (223) −28 (212) [+8]	−631 (223) +450 (212) [−335]	+478 (223) −398 (212) [+382]	21 (*S–S*)
	**12**	−19.5	*R*	−21 (223) +23 (212) [−25]	−584 (223) +446 (212) [−201]	+611 (223) −465 (212) [+369]	9 (*R–R*)[e]
	**13**[f]	−2.2	*R*	−102 (223) +73 (212) [−63]			33 (*R–R*)
	**14**	−9	*R*	−34 (223) +17 (212) [+31]			15 (*R–R*)
	**15**	+109	*S*	+30 (237)[g] +86 (223) −61 (212) [+115]			21 (*S–S*)
	**16**	−18.5	*S*	+246 (223) −209 (212) [+81]			59 (*S–S*)
	**17**	−6.1	*R*	−415 (223) +330 (212) [−148]			80 (*R–R*)
	**18**	−39.5	*S*	+68 (223) −43 (212) [+12]			11 (*S–S*)
	**19**	+79.2	*S*	+51 (223) −35 (212) [+135]			26 (*S–S*)

[a] Chiral compounds were supplied by Aldrich and Tokyo Kasei Chemical Co., Ltd. [b] CD measurement was performed with a Jasco J-20 spectropolarimeter in EtOH. Cotton effects showed intense peaks only separated by Davydov splitting. [c] Specific rotation was measured with a Jasco DIP-181 polarimeter in $CHCl_3$. [d] Diastereomeric excess. [e] When the diastereomeric excess is lower than 10%, maximum values of the Cotton effects may not satisfy quantitativeness because of noisy CD spectra due to the effects of absorption chromophore. [f] Dimethyl-(*R,R*)-2-acetyl-3-hydroxy tartrate. [g] The maximum is the Cotton effect attributed to α,β-unsaturated ketone. The exciton Cotton effect by the BNP group is overlapped with the effect of the ketone.

The chirality recognition of the (BNP)Cl reagents for the chiral carbinol removed from the different ligands as shown in **8** and **18** is regarded as significant, because the facts assure not only formal but real conformity with Cahn–Ingold–Prelog's sequence rule.[14]

The ^{1}H NMR spectrum of the (*R,S*)-BNP derivative shows a superimposed spectrum of those of (*R*)- and (*S*)-BNP derivatives. Anisotropic effects of each naphthol ring in the (*R*)- or (*S*)-BNP derivatives largely affect the protons localized far from the chiral carbinol group. Therefore, an excess of (*R*)-BNP–(*R*)-alcohol or (*S*)-BNP–(*S*)-alcohol [*R–R* or *S–S* diastereomeric excess (de)] as compared with *R–S* or *S–R* diastereomers can be easily calculated from an integrated area of each shifted signal.[15] The compounds **13**, **16**, **17**, and **19** probably have a different

(14) Cahn, R. S.; Ingold, Sir, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–415.

(15) Differences between chemical shifts were observed between the alcohols and the BNP derivatives and between the (*R*)- and (*S*)-BNP derivatives. For example, data for **17** follow. $\Delta\delta$((*R*)-alcohol): 0.08 (AcO), 0.25 (10-Me), 0.03 (13-Me), −0.02 (25-Me_2) ppm. $\Delta\delta$((*S*)-alcohol): −0.04 (AcO), 0.19 (10-Me), 0.23 (13-Me), 0.01 (25-Me_2) ppm.

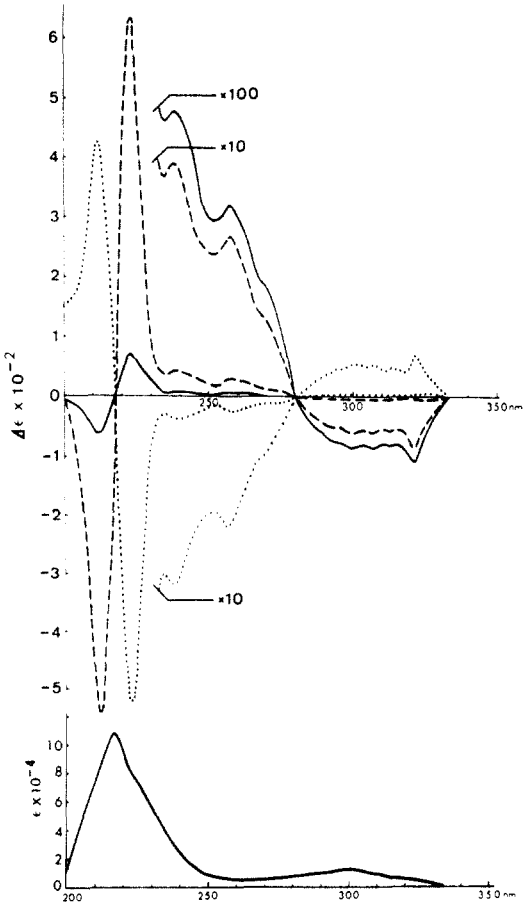


Figure 1. CD spectra of (*R*)-, (*S*)-, and (*R,S*)-BNP-dihydrocholesterols represented by dotted, broken, and solid lines, respectively. UV spectra of the derivatives are shown with very similar maxima and shapes.

distribution of rotatory conformers around the BNP–alcohol bond in the *R* and *S* systems, because the methine proton on their carbinol carbon appears to have different chemical shifts on the spectra.

Further investigations of chiral carbinol compounds with other different configurations and substituents will be performed and reported elsewhere.

Experimental Section

Preparation of Dithallous (*R*)-1,1′-Bi-2-naphthoxide. Dithallous (*R*)-1,1′-bi-2-naphthoxide was obtained by addition of (*R*)-(+)-1,1′-bi-2-naphthol (1.14 g, 4 mmol) in EtOH (100 mL) to a EtOH solution (100 mL) of C_2H_5OTl (2.4 g, 9.5 mmol). After the solution was stirred for 12 h at ambient temperature, water (200 mL) was added to the yellow colloidal solution followed by filtration and washing with water and EtOH and the filtrate was dried in vacuo. The dithallous (*R*)-1,1′-bi-2-naphthoxide was obtained as a pale yellow powder, 2.74 g (99% yield). Dithallous (*S*)- and (*R,S*)-1,1′-bi-2-naphthoxides were obtained in good yield with the same procedure.

Typical Procedure of (*R*)-1,1′-Binaphthyl-2,2′-diyl Phosphate. The dispersed dithallous (*R*)-1,1′-bi-2-naphthoxide (104 mg, 0.15 mmol) in dry CH_2Cl_2 (3 mL) was added to $POCl_3$ (28 mg, 0.18 mmol) followed by stirring for 2 h in the dark. The (*R*)-(−)-1,1′-binaphthyl-2,2′-diyl phosphoryl chloride solution was poured into a mixture of dihydrocholesterol (38.8 mg, 0.1 mmol), 1-methylimidazole (82 mg, 1 mmol), and (dimethylamino)pyridine (catalyst). When TlCl of the byproduct was added to the flask, the precipitate did not interfere with phosphate formation. After the solution was stirred for 4 h at ambient temperature in the dark, it was worked up in the usual manner followed by purification on TLC. After recrystallization from EtOAc–*n*-hexane, (*R*)-BNP-dihydrocholesterol was obtained as a crystal: 58 mg (83% yield); mp 177–178 °C. The (*S*)- and (*R,S*)-BNP derivatives were prepared with the same procedure, while the latter was derived by using a 2 mol equiv solution of the (*R,S*)-(BNP)Cl.

In general, crystalline (*R*)- and (*S*)-BNP derivatives were purified by recrystallization from EtOAc–*n*-hexane, whereas the noncrystalline and (*R,S*)-BNP derivatives were purified by repeated TLC. Satisfactory spectroscopic data (NMR, UV) and elemental analyses were obtained for the BNP derivatives of alcohols **8–19**.

Spectral Data. Specific rotations were measured by a Jasco DIP-181 polarimeter in $CHCl_3$. UV spectra were measured by a Jasco UVI-DEC-610C spectrophotometer in EtOH. NMR spectra were measured by a Jeol JNM-GX 270 spectrometer (270 mHz) in $CDCl_3$ with TMS as a reference. In NMR spectral data of (*R,S*)-BNP derivatives, *R* and *S* in parentheses indicated the signals assigned to the (*R*)- and (*S*)-BNP derivatives, respectively, and the ratio of each diastereomer was shown by the area ratio of the isolated signals. Aromatic protons on the binaphthol ring appeared at δ 7.25–8.10 (12 H, m) with the same splitting pattern.

Dihydrocholesterol (8). (*R,S*)-BNP-8: $[\alpha]^{23}_D$ +29° (*c* = 1.0); UV, λ_{max} (log ε) 216 (5.04), 302 (4.11) nm; NMR, δ 0.64 (s, 13-Me), 0.79 (s, 10-Me), 0.86 (d, *J* = 6.72 Hz, 25-Me), 0.87 (d, *J* = 6.72 Hz, 25-Me), 0.90 (d, *J* = 6.39 Hz, 20-Me), 2.00 (*R*, 0.524 H, br d, *J* = 12.4 Hz, 2-H), 2.12 (*S*, 0.476 H, br d, *J* = 12.4 Hz, 2-H), 4.65 (*R* and *S*, m, 3-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{47}H_{59}O_4P$: C, 78.52; H, 8.27. Found: C, 78.41; H, 8.36.

(*R*)-BNP-8: mp 177–178 °C; $[\alpha]^{23}_D$ −176° (*c* = 0.2); UV, λ_{max} (log ε) 216 (5.00), 302 (4.08) nm; NMR, δ 0.64 (s, 13-Me), 0.79 (s, 10-Me), 0.86 (d, *J* = 6.72 Hz, 25-Me_2), 0.89 (d, overlapping, 20-Me), 2.00 (br d, *J* = 12.4 Hz, 2-H), 4.65 (m, 3-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{47}H_{59}O_4P$: C, 78.52; H, 8.27. Found: C, 78.31; H, 8.39.

(*S*)-BNP-8: mp 187 °C; $[\alpha]^{23}_D$ +207° (*c* = 0.2); UV, λ_{max} (log ε) 216 (5.04), 302 (4.08) nm; NMR, δ 0.64 (s, 13-Me), 0.79 (s, 10-Me), 0.86 (d, *J* = 6.72 Hz, 25-Me), 0.87 (d, *J* = 6.72 Hz, 25-Me), 0.90 (d, *J* = 6.39 Hz, 20-Me), 2.12 (br d, *J* = 12.4 Hz, 2-H), 4.66 (m, 3-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{47}H_{59}O_4P$: C, 78.52; H, 8.27. Found: C, 78.54; H, 8.38.

(−)-Menthol (9). (*R,S*)-BNP-9: $[\alpha]^{23}_D$ −56° (*c* = 0.7); UV, λ_{max} (log ε) 216 (4.96), 302 (4.09) nm; NMR, δ 0.75 (*R*, d, *J* = 7.06 Hz, 7-Me), 0.78 (*R*, d, *J* = 7.06 Hz, 7-Me), 0.90 (*S*, 0.448 H_3, d, *J* = 6.39 Hz, 5-Me), 0.97 (*S*, d, *J* = 7.06 Hz, 7-Me), 0.98 (*S*, d, *J* = 7.06 Hz, 7-Me), 1.01 (*R*, 0.552 H_3, d, *J* = 6.38 Hz, 5-Me), 2.48 (*R*, br d, *J* = 11.43 Hz, 6-H), 2.29 (*S*, m, 6-H), 1.93 (*R*, m, 2-H), 4.58 (*R* and *S*, m, 1-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{30}H_{31}O_4P$: C, 74.06; H, 6.42. Found: C, 73.92; H, 6.50.

(*R*)-BNP-9: $[\alpha]^{23}_D$ −318° (*c* = 0.3); UV, λ_{max} (log ε) 216 (4.96), 302 (4.08) nm; NMR, δ 0.75 (d, *J* = 7.06 Hz, 7-Me), 0.79 (d, 6.73 Hz, 7-Me), 1.01 (d, *J* = 6.39 Hz, 5-Me), 2.48 (br d, *J* = 11.43 Hz, 6-H), 1.93 (m, 2-H), 4.58 (m, 1-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{30}H_{31}O_4P$: C, 74.06; H, 6.42. Found: C, 74.01; H, 6.49.

(*S*)-BNP-9: mp 165–167 °C; $[\alpha]^{23}_D$ +319° (*c* = 0.4); UV, λ_{max} (log ε) 216 (4.98), 302 (4.11) nm; NMR, δ 0.90 (d, *J* = 6.39 Hz, 5-Me), 0.97 (d, *J* = 6.72 Hz, 7-Me_2), 2.29 (m, 6-H and 2-H), 4.57 (m, 1-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{30}H_{31}O_4P$: C, 74.06; H, 6.42. Found: C, 74.00; H, 6.46.

(+)-Menthol (10). (*R,S*)-BNP-10: $[\alpha]^{23}_D$ +32° (*c* = 0.7); UV, λ_{max} (log ε) 216 (4.98), 302 (4.09) nm; NMR, δ 0.75 (*S*, d, *J* = 7.06 Hz, 7-Me), 0.79 (*S*, d, *J* = 7.06 Hz, 7-Me), 0.89 (*R*, 0.476 H_3, d, *J* = 6.38 Hz, 5-Me), 0.97 (*R*, d, *J* = 7.06 Hz, 7-Me), 0.98 (*R*, d, *J* = 7.06 Hz, 7-Me), 1.01 (*S*, 0.524 H_3, d, *J* = 6.39 Hz, 5-Me), 2.48 (*S*, br d, *J* = 11.43 Hz, 6-H), 2.29 (*R*, m, 6-H and 2-H), 1.93 (*S*, m, 2-H), 4.57 (*R* and *S*, m, 1-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{30}H_{31}O_4P$: C, 74.06; H, 6.42. Found: C, 74.01; H, 6.43.

(*R*)-BNP-10: mp 165–167 °C; $[\alpha]^{23}_D$ −310° (*c* = 0.2); UV, λ_{max} (log ε) 216 (4.95), 302 (4.07) nm; NMR, δ 0.90 (d, *J* = 6.38 Hz, 5-Me), 0.97 (d, *J* = 7.06 Hz, 7-Me), 0.98 (d, *J* = 7.06 Hz, 7-Me), 2.29 (m, 6-H and 2-H), 4.57 (m, 1-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{30}H_{31}O_4P$: 74.06; H, 6.42. Found: C, 73.68; H, 6.36.

(*S*)-BNP-10: $[\alpha]^{23}_D$ +337° (*c* = 0.4); UV, λ_{max} (log ε) 216 (4.94), 302 (4.07) nm; NMR, δ 0.75 (d, *J* = 7.06 Hz, 7-Me), 0.79 (d, *J* = 7.06 Hz, 7-Me), 1.01 (d, *J* = 6.39 Hz, 5-Me), 2.48 (br d, *J* = 11.43 Hz, 6-H), 1.93 (m, 2-H), 4.58 (m, 1-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{30}H_{31}O_4P$: C, 74.06; H, 6.42. Found: C, 73.98; H, 6.49.

(−)-Borneol (11). (*R,S*)-BNP-11: $[\alpha]^{23}_D$ +80° (*c* = 0.9); UV, λ_{max} (log ε) 216 (4.96), 302 (4.07) nm; NMR, δ 0.86 (*R*, 0.441 H_3, s, 1-Me), 0.87 (*R*, s, 7-Me_2), 0.88 (*S*, s, 7-Me_2), 1.04 (*S*, 0.559 H_3, s, 1-Me), 2.37 (*S*, m, 3-H), 2.48 (*R*, m, 3-H), 4.95 (*R* and *S*, m, 2-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{30}H_{29}O_4P$: C, 74.37; H, 6.03. Found: C, 74.29; H, 6.10.

(*R*)-BNP-11: mp 173–175 °C; $[\alpha]^{23}_D$ −335° (*c* = 0.4); UV, λ_{max} (log ε) 216 (4.95), 302 (4.07) nm; NMR, δ 0.86 (s, 1-Me), 0.87 (s, 7-Me), 2.48 (m, 3-H), 4.94 (m, 2-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{30}H_{29}O_4P$: C, 74.37; H, 6.03. Found: C, 74.42; H, 6.04.

(*S*)-BNP-11: mp 183–185 °C; $[\alpha]^{23}_D$ +382° (*c* = 0.5); UV, λ_{max} (log ε) 216 (4.96), 302 (4.07) nm; NMR, δ 0.88 (s, 7-Me_2), 1.04 (s, 1-Me), 2.37 (m, 3-H), 4.95 (m, 2-H), 7.25–8.10 (12 H, m, arom). Anal. Calcd for $C_{30}H_{29}O_4P$: C, 74.37; H, 6.03. Found: C, 74.19; H, 6.04.

(-)-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]

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