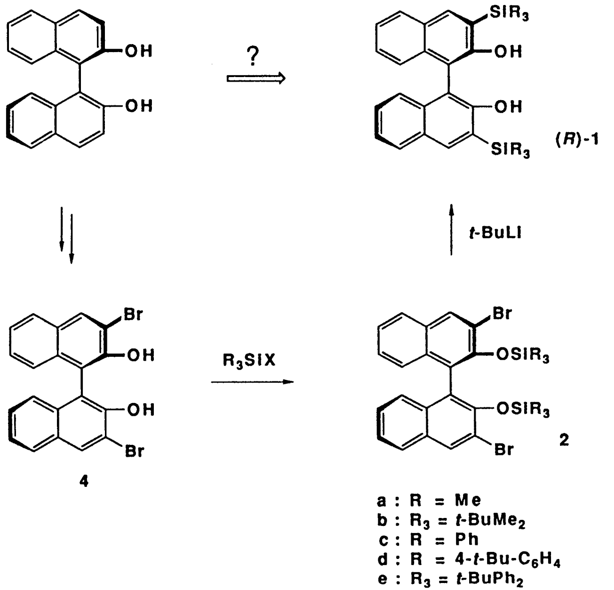
Efficient Synthesis of Sterically Hindered Chiral Binaphthol Derivatives

Keiji Maruoka, Takayuki Itoh, Yoshitaka Araki, Tadashi Shirasaka, and Hisashi Yamamoto*
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464-01

(Received March 28, 1988)

Synopsis. A highly effective method for preparation of a variety of sterically hindered chiral binaphthol derivatives has been described which involves the intramolecular 1,3-rearrangement of bis(trialkylsilyl ether) of chiral 3,3′-dibromo-1,1′-bi-2-naphthol with *t*-BuLi.

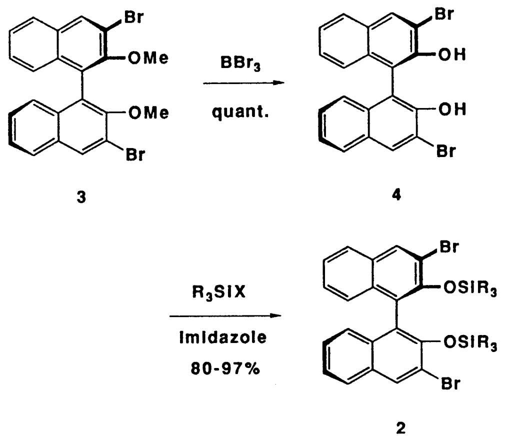
In connection with our recent study on the enantioselective activation of carbonyl moiety by complexing with the exceptionally bulky, chiral organoaluminum reagents,[1,2] it was required to synthesize certain sterically hindered, chiral phenol derivatives. An attractive possibility for the synthesis appeared to be the effective introduction of bulky trialkylsilyl substituents adjacent to hydroxyl groups of chiral binaphthols in view of the readily availability of a wide variety of trialkylsilyl derivatives. Here we report a new and highly effective approach to the synthesis of such sterically hindered, chiral 3,3′-bis(trialkylsilyl)-1,1′-bi-2-naphthol (*R*)-**1** and (*S*)-**1** based on the remarkably facile 1,3-rearrangement of bis(trialkylsilyl ether) of chiral 3,3′-dibromo-1,1′-bi-2-naphthol with *t*-BuLi as illustrated in Scheme 1.[3]

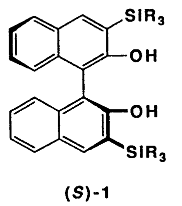


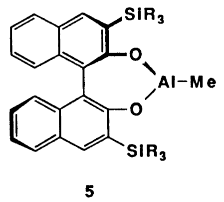
a : R = Me
b : R$_3$ = *t*-BuMe$_2$
c : R = Ph
d : R = 4-*t*-Bu-C$_6$H$_4$
e : R$_3$ = *t*-BuPh$_2$
f : R = 3,5-Xylyl

Scheme 1.

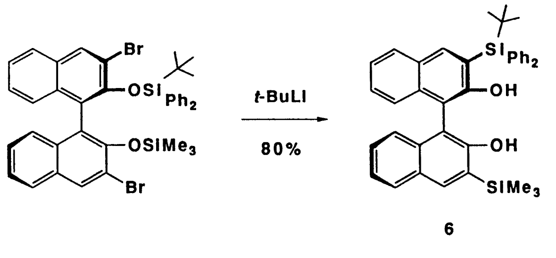
The requisite bis(silyl ether) **2** was readily obtainable from the known (*R*)-(+)-3,3′-dibromo-1,1′-bi-2-naphthol dimethyl ether (**3**)[4] in two steps. Thus, demethylation of **3** with BBr$_3$ (5.5 equiv) in CH$_2$Cl$_2$ at room temperature for 3 h afforded (*R*)-(+)-3,3′-dibromo-1,1′-bi-2-naphthol (**4**) quantitatively, which without purification was treated with trialkylsilyl halide (2.5—3 equiv) and imidazole (3—4 equiv) in DMF at 20—70 °C for several hours, producing the bis(silyl ether) **2** in 80—97% yield. Treatment of the bis(silyl ether) **2** with *t*-BuLi (3—3.5 equiv) under mild conditions furnished the corresponding (*R*)-(+)-3,3′-bis(trialkylsilyl)-1,1′-bi-2-naphthol (*R*)-**1** in 85—96% yield. The enantiomeric (*S*)-**1** can be prepared from (*S*)-(−)-1,1′-bi-2-naphthol in a same manner as described above. The readily obtainable, optically pure 3,3′-bis(silylated) binaphthol of type **1** should have vast synthetic potential as chiral bidentate ligands for designing of chiral metal catalyst or reagent as recently shown in our laboratory to be quite effective as a modified organoaluminum catalyst **5** (R=Ph or 3,5-Xylyl) for asymmetric hetero-Diels-Alder and ene reactions.[1]




(*S*)-**1**


5

Since the present 1,3-rearrangement proceeds rigorously in an intramolecular fashion, introduction of different trialkylsilyl groups at the 3,3′-positions of chiral binaphthols appeared feasible, thereby further enhancing the synthetic utility of the present method as exemplified by the facile synthesis of (*R*)-(+)-3-(*t*-butyldiphenylsilyl)-3′-(trimethylsilyl)-1,1′-bi-2-naphthol (**6**) in 80% yield.



6

Experimental

The IR spectra were measured on a Hitachi 260-10 spectrometer. The ^{1}H NMR spectra were recorded on a JNM-PMX 60 spectrometer, using TMS (tetramethylsilane) as an internal standard. Splitting patterns are indicated as s, singlet; m, multiplet. Melting points are not corrected. The microanalysis was performed at the Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University. Tetrahydrofuran (THF) was distilled from benzophenone ketyl. Dichloromethane (CH_2Cl_2) and *N,N*-dimethylformamide (DMF) were stored over 4-A Molecular Sieves. All experiments were carried out under an argon atmosphere. Purification of the product was carried out by column chromatography on silica gel Fuji-Davison BW-300.

Preparation of (*R*)-(+)-3,3′-Bis(triphenylsilyl)-1,1′-bi-2-naphthol ((*R*)-1c): To a solution of (*R*)-(+)-3,3′-dibromo-1,1′-bi-2-naphthol dimethyl ether (**3**)[4] (2.78 g, 5.9 mmol) in CH_2Cl_2 (180 mL) was added BBr_3 (3.13 mL, 33 mmol) at 0 °C. The mixture was stirred at room temperature for 5 h. Then excess BBr_3 was decomposed by adding water carefully at 0 °C. The mixture was washed with water, extracted with CH_2Cl_2, dried over Na_2SO_4, and evaporated. The crude (*R*)-(+)-3,3′-dibromo-1,1′-bi-2-naphthol (**4**), thus obtained, was dissolved in DMF (36 mL), and imidazole (1.22 g, 18 mmol) followed by triphenylsilyl chloride (4.42 g, 15 mmol) was added at room temperature. The resulting mixture was stirred at room temperature for 5 h, poured into saturated $NaHCO_3$, and extracted with CH_2Cl_2. The organic layers were washed again with saturated $NaHCO_3$, dried over Na_2SO_4, and concentrated. The crude solid was applied to short-path column chromatography on silica gel (CH_2Cl_2/hexane=1 : 2 as eluent) to furnish bis(triphenylsilyl ether) **2** (5.48 g, 5.7 mmol) in 97% yield. To a solution of **2** in dry THF (80 mL) was added dropwise a 2.67 M pentane solution (1M=1 mol dm^{-3}) of *t*-BuLi (6.4 mL, 17.1 mmol) over a period of 10 min at 0 °C. The mixture was stirred at room temperature for 30 min, poured into saturated NH_4Cl, and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (benzene/hexane=1 : 2 to 1 : 1 as eluent) to give (*R*)-(+)-3,3′-bis(triphenylsilyl)-1,1′-bi-2-naphthol ((*R*)-**1c**) (3.89 g, 85% yield) as white solids: $[\alpha]_D$ +125° (*c* 1.11, THF); mp 165—167 °C; IR ($CHCl_3$) 3540, 3065, 3015, 1590, 1428, 1359, 1305, 1105, 988, 910 cm^{-1}; ^{1}H NMR (CCl_4) δ=7.87 (s, 2H, Ar-H), 6.93—7.85 (m, 38H, Ar-H), 5.24 (s, 2H, OH); Anal. ($C_{56}H_{42}O_2Si_2$) C, H. If necessary, this material was further recrystallized from CH_2Cl_2/hexane at low temperature to furnish white crystals.

Other chiral 3,3′-bis(trialkylsilyl)-1,1′-bi-2-naphthols were prepared in a similar manner as described above. Their analytical and physical data are listed below.

(*R*)-(+)-3,3′-Bis(trimethylsilyl)-1,1′-bi-2-naphthol ((*R*)-1a): Yield: 86%; mp 68—71 °C; $[\alpha]_D$ +143° (*c* 0.985, THF); IR (CCl_4) 3540, 1584, 1356, 1305, 1248, 1181, 1149, 840 cm^{-1}; ^{1}H NMR (CCl_4) δ=7.97 (s, 2H, Ar-H), 7.63—7.96 (m, 2H, Ar-H), 6.84—7.43 (m, 6H, Ar-H), 5.15 (s, 2H, OH), 0.40 (s, 18H, CH_3); Anal. ($C_{26}H_{30}O_2Si_2$) C, H.

(*R*)-(+)-3,3′-Bis(*t*-butyldimethylsilyl)-1,1′-bi-2-naphthol ((*R*)-1b): Yield: 87%; mp 63—66 °C; $[\alpha]_D$ +136° (*c* 1.02, THF); IR (CCl_4) 3535, 1584, 1355, 1250, 1194, 830 cm^{-1}; ^{1}H NMR (CCl_4) δ=7.93 (s, 2H, Ar-H), 7.56—7.84 (m, 2H, Ar-H), 6.78—7.37 (m, 6H, Ar-H), 5.10 (s, 2H, OH), 0.97 (s, 18H, *t*-Bu), 0.41 (s, 12H, CH_3); Anal. ($C_{32}H_{42}O_2Si_2$) C, H.

(*R*)-(+)-3,3′-Bis[tris(4-*t*-butylphenyl)silyl]-1,1′-bi-2-naphthol ((*R*)-1d): Yield: 96% (amorphous solid); $[\alpha]_D$ +91.4° (*c* 1.22, THF); IR (CCl_4) 3550, 2980, 1395, 1270, 1095 cm^{-1}; ^{1}H NMR (CCl_4) δ=7.90 (s, 2H, Ar-H), 7.10—7.70 (m, 32H, Ar-H), 5.23 (s, 2H, OH), 1.31 (s, 54H, *t*-Bu); Anal. ($C_{80}H_{90}O_2Si_2$) C, H.

(*R*)-(+)-3,3′-Bis(*t*-butyldiphenylsilyl)-1,1′-bi-2-naphthol ((*R*)-1e): Yield: 95%; mp 145—147 °C; $[\alpha]_D$ +111° (*c* 1.01, THF); IR (CCl_4) 3530, 1430, 1360, 1150, 1110 cm^{-1}; ^{1}H NMR (CCl_4) δ=7.93 (s, 2H, Ar-H), 7.15—7.80 (m, 28H, Ar-H), 5.32 (s, 2H, OH), 1.23 (s, 18H, *t*-Bu); Anal. ($C_{52}H_{50}O_2Si_2$) C, H.

(*R*)-(+)-3,3′-Bis(tri-3,5-xylylsilyl)-1,1′-bi-2-naphthol ((*R*)-1f): Yield: 90%; mp 285—286 °C; $[\alpha]_D$ +135° (*c* 1.02, THF); IR (CCl_4) 3550, 2930, 1590, 1420, 1400, 1145 cm^{-1}; ^{1}H NMR (CCl_4) δ=7.73 (s, 2H, Ar-H), 6.83—7.33 (m, 26H, Ar-H), 5.13 (s, 2H, OH), 2.22 (s, 36H, Me); Anal. ($C_{68}H_{66}O_2Si_2$) C, H.

(*R*)-(+)-3-(*t*-Butyldiphenylsilyl)-3′-(trimethylsilyl)-1,1′-bi-2-naphthol (6): Yield: 80% (amorphous solid); mp 107—116 °C; $[\alpha]_D$ +128° (*c* 1.16, THF); IR (CCl_4) 3530, 1435, 1365, 1250, 1155 cm^{-1}; ^{1}H NMR (CCl_4) δ=7.03—8.01 (m, 20H, Ar-H), 5.25 (s, 1H, OH), 5.18 (s, 1H, OH), 1.22 (s, 9H, *t*-Bu), 0.41 (s, 9H, SiMe); Anal. ($C_{39}H_{40}O_2Si_2$) C, H.

(*S*)-(−)-3,3′-Bis(triphenylsilyl)-1,1′-bi-2-naphthol ((*S*)-1c): $[\alpha]_D$ −125° (*c* 1.10, THF). The spectral data is in consonance with those of (*R*)-**1c**.

References

1) Enantioselective activation of carbonyl group: K. Maruoka, T. Itoh, T. Shirasaka, and H. Yamamoto, *J. Am. Chem. Soc.*, **110**, 310 (1988); K. Maruoka, Y. Hoshino, T. Shirasaka, and H. Yamamoto, *Tetrahedron Lett.*, in press.

2) For diastereoselective activation of carbonyl group, see: K. Maruoka, T. Itoh, and H. Yamamoto, *J. Am. Chem. Soc.*, **107**, 4573 (1985); K. Maruoka, M. Sakurai, and H. Yamamoto, *Tetrahedron Lett.*, **26**, 3853 (1985); K. Maruoka, T. Itoh, M. Sakurai, K. Nonoshita, and H. Yamamoto, *J. Am. Chem. Soc.*, **110**, 3588 (1988).

3) The anionic 1,3-rearrangements of sterically less hindered trimethylsilyl and triethylsilyl groups in trialkylsiloxybenzenes and trialkylsiloxypyridines have been advanced: G. Simchen and J. Pfletschinger, *Angew. Chem., Int. Ed. Engl.*, **15**, 428 (1976); D. Habich and F. Effenberger, *Synthesis*, 841 (1979); R. J. Billedeau, M. P. Sibi, and V. Snieckus, *Tetrahedron Lett.*, **24**, 4515 (1983).

4) D. S. Lingenfelter, R. S. Helgeson, and D. J. Cram, *J. Org. Chem.*, **46**, 393 (1981).