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Synthesis and chemistry of 2,2′-bis-silyl-substituted 1,1′-binaphthyl derivatives

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Abstract

A number of hitherto unknown 1,1′-binaphthyl derivatives bearing silyl substituents at the 2,2′ positions have been prepared. The 2,2′-bis(dimethylsilyl)-1,1′-binaphthalene **2a** is stable in the pure state, but it converts smoothly into the cyclic disiloxane **4a** with water and acids or bases. The latter siloxane **4a** can be converted back into the starting bishydrosilane **2a** with lithium aluminium hydride.

Keywords: Silicon; Silane; Siloxane; Silazane; Disilane; 1,1-Binaphthalene

1. Introduction

In recent years, the binaphthyl group has become quite popular in organic synthesis [1], largely due to its efficiency in transferring its chiral information, which in turn is mostly due to its geometry and associated C_2 symmetry. Indeed, quite a large number of disubstituted binaphthyl derivatives bearing two identical heteroatomic functionalities at the 2,2′ positions have been prepared and are reported in the literature. A few of them are represented below [2–8]

Though nowadays the list is relatively complete, the bis-silyl derivatives are still missing, despite the fact that they should enjoy practical applications as the chiral versions of 1,2-bis-silyl benzenes. For example, 2,2′-bis(dimethylsilyl)-1,1′-binaphthalene **2a** (Scheme 2) should function like 1,2-bis(dimethylsilyl)benzene (benzostabase) as a protective group for amines [9] and amino acids [10] or for other applications [11], but with the added feature of being chiral and with C_2 symmetry [12]. Here we report the synthesis and characterization of a number of compounds which have as a common feature the presence of two silicon atoms bonded to the binaphthyl ring at the 2,2′ positions. In particular, we will discuss their stability and preliminary reactivity towards representative reagents.

Treatment of 2,2′-dibromo-1,1′-binaphthalene **1e** with buthyllithium affords, as is well known, the 2,2′-dilithium-1,1′-binaphthalene [13], which is reacted in situ with *sym*-dichlorotetramethyldisilane [$(Me_2SiCl)_2$] [14] to obtain disilane **3** in 72% isolated yield. The disilane **3** is the starting material for most of the other binaphthyl derivatives of silicon because the reaction of the dilithium reagent with other silanes gave disubstituted silicon compounds very inefficiently. For example, 2,2′-dilithium-1,1′-binaphthalene gave, with chlorodimethylsilane (Me_2SiClH), very poor yields of the corresponding binaphthyl product **2a**. Also, using the magnesium compound instead of the lithium one did not change the reaction composition except for a minor improvement in yields of **2a**. From a synthetic point of view, however, the reaction is impractical.

Reaction of disilane **3** with halogens produced the chloro or the bromo derivatives **2b** and **2c** in high yields as detected in the ^1H NMR spectrum. Unfortunately, both the chloro and the bromo compounds **2b** and **2c** could not be fully characterized, owing to their tendency to react with adventitious water or atmospheric moisture to give siloxane **4a**. All attempts to purify **2b** and **2c** by crystallization, distillation or chromatography gave the disiloxane **4a** as the only isolable product.

However, the halogeno derivatives can be used without purification for the preparation of the dihydro derivative **2a** by nucleophilic substitution with hydrides. Thus, treatment of either **2b** or **2c** in ether or THF with

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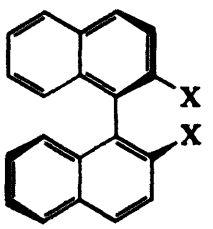
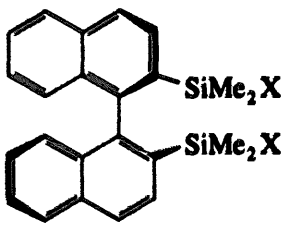
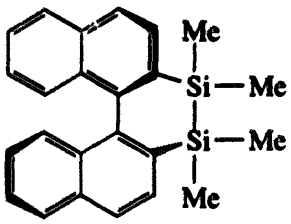


1a X = NH_2 [2]
1b X = OH [3]
1c X = PPh_2 [4]
1d X = SH [5]
1e X = Br [6]
1f X = SnR_3 [7]

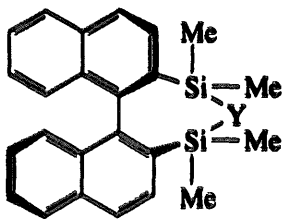
Scheme 1.

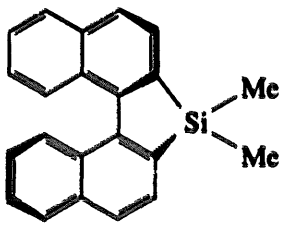




2a X = H
2b X = Cl
2c X = Br
2d X = Me

3





4a Y = O
4b Y = N–CH_2Ph
4c Y = N–H

5

Scheme 2.

lithium aluminium hydride cleanly delivers the bishydrosilane **2a**. In preparative runs, the use of the dibromo compound **2b** is preferable because bromine is more practical to use and to add in the equimolar quantity. The dihydrosilane **2a** is rather stable in the pure state, even in the presence of oxygen or water, but it converts rapidly into **4a** with acids and bases as well as with fluoride ions and Pt(II) catalysts. The latter **4a** (which is formed as a by-product in many other reactions) can be readily transformed in high yield into the starting dihydrosilane **2a** with lithium aluminium hydride in dry THF.

The addition of methyllithium to **2b** gives the bis(trimethylsilyl)derivative **2d**, which is, however, more readily available through direct reaction of the dilithium derivative of binaphthyl with trimethylchlorosilane. The latter 2,2'-bis(trimethylsilyl)-1,1'-binaphthalene **2d** does not react with dimethylchlorosilane in the presence of $AlCl_3$ in chloroform to give the dichloro compound **2c** [14], precluding an alternative entry into the silane **2a**.

The dihydrosilane **2a** is the precursor of the silazane **4b** via reaction of benzylamine and palladium catalyst (Pd on C, 10%). The reaction takes several hours to reach completion, as verified by ^{1}H NMR monitoring. Unfortunately, the silazane is very sensitive to water and could not be isolated. The parent silazane **4c**, derived from ammonia, appears to be similarly reactive. The only product obtained was the disiloxane **4a**. Attempts to isolate **4b** by flash chromatography led to the formation of the five-membered ring compound **5**.

In conclusion, we have synthesized a few representative silicon derivatives of binaphthyl and determined their stability and reactivity. The present study is preliminary to the use of binaphthyl silicon reagents in asymmetric syntheses.

2. Experimental section

Flash chromatography was performed with 230–400 mesh silica gel (Merck 60). Melting points were determined with an Electrothermal M.P.A. and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were performed with a Bruker AC 200 instrument operating at 200 and 50 MHz respectively (TMS as internal standard). IR data were recorded with a Bio-Rad FTS-40 instrument.

2.1. 3,4-Disila-3,3,4,4-tetramethyl-3,4-dihydrodibenzo[c,g]phenanthrene 3

A solution 1.7 M of *t*-butyllithium in pentane (7.5 ml, 12.75 mmol) was added at −100°C (pentane/N_2 slurry) to a solution of 2,2'-dibromo-1,1'-binaphthalene (**1e**) (2.50 g, 6.78 mmol) in 30 ml of dry THF/*n*-pentane (1:1) under nitrogen. The solution was stirred at this temperature for 10 min, then warmed to −78°C (acetone/N_2 slurry) and stirred for an additional 15 min. *Syn*-dichlorotetramethyldisilane (1.1 ml, 5.9 mmol) (obtained from hexamethyldisilane, acetyl chloride and aluminium trichloride [14]) was added at −78°C and the temperature was allowed to slowly reach room temperature. After 12 h, aqueous ammonium chloride was added and the organic compounds were extracted with diethylether. After drying over Na_2SO_4 and concentration, the crude was purified by flash chromatography (eluent, 9:1 hexanes/dichloromethane). Recrystallization from *n*-hexane gave 1.6 g of colorless crystals, m.p. 199–203°C (72% yield). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.89 (2H, d, 1/2 AB system, J = 7.8 Hz), 7.87 (2H, d, J = 7.3 Hz), 7.72 (2H, d, 1/2 AB system, J = 7.8 Hz), 7.49–7.39 (2H, m), 7.21–710 (2H, m), 7.01 (2H, d, J = 7.0 Hz), 0.50 (6H, s), −0.33 (6H, s). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 143.86, 134.59, 134.24,

132.70, 129.97, 128.05, 127.07, 126.91, 125.73, 125.42, −5.26, −5.71. IR (KBr): 3049, 2956, 813, 800, 783, 761, 745 cm^{-1}. Anal. Found: C, 78.41; H, 6.57. $C_{24}H_{24}Si_2$. Calc.: C, 78.20; H, 6.56%.

2.2. [1,1'-Binaphthyl]-2,2'-diylbis[dimethylchlorosilane] 2b

Chlorine was bubbled for a few seconds at 0°C into a solution of 3,4-disila-3,3,4,4-tetramethyl-3,4-dihydro-dibenzo[c,g]phenanthrene (3) in carbon tetrachloride. Yields (NMR) are virtually quantitative. ^1H NMR (CCl_4, 200 MHz): δ 7.91 (s), 7.79 (d, $J = 8.0$ Hz), 7.45–7.33 (m), 7.23–7.11 (m), 7.05 (d, $J = 8.5$ Hz), −0.15 (s), −0.22 (s).

2.3. [1,1'-Binaphthyl]-2,2'-diylbis[dimethylbromosilane] 2c

Bromine was added at 0°C to a carbon tetrachloride solution of 3. Yields (NMR) are virtually quantitative. ^1H NMR (CCl_4, 200 MHz): δ 7.91 (s), 7.90 (s), 7.78 (d, $J = 7.8$ Hz), 7.45–7.30 (m), 7.25–7.10 (m), 7.05 (d, $J = 8.4$ Hz), 0.01 (s), −0.04 (s).

2.4. 3,5-Disila-3,3,5,5-tetramethyl-3,5-dihydro-dinaphtho[2,1-c:1',2'-e]oxepin 4a

Sodium hydroxide (0.5 ml, 1 M solution) was added at room temperature to 2,2'-bis(dimethylsilyl)-1,1'-binaphthalene (2a) (100 mg, 0.27 mmol) dissolved in 5 ml of ethanol. After 48 h, the reaction mixture was concentrated, neutralized with aqueous ammonium chloride and extracted with diethylether. Combined extracts were dried (Na_2SO_4), concentrated and purified by flash chromatography (eluent, 7:3 hexanes/dichloromethane). Recrystallization from methanol gave 98 mg of colorless crystals, m.p. 182–188°C (95% yield). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.87 (2H, d, 1/2 AB system, $J = 8.1$ Hz), 7.92 (2H, d, $J = 8.2$ Hz), 7.80 (2H, d, 1/2 AB system, $J = 8.1$ Hz), 7.51–7.40 (2H, m), 7.24–7.11 (2H, m), 7.06 (2H, d, $J = 8.0$ Hz), 0.57 (6H, s), −0.62 (6H, s). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 144.98, 137.14, 133.86, 133.43, 129.36, 127.97, 127.46, 127.40, 126.26, 125.92, −0.27, −0.45. IR (KBr): 3051, 2941, 969, 819, 797 cm^{-1}. Anal. Found: C, 74.72; H, 6.18. $C_{24}H_{24}Si_2O$. Calc.: C, 74.95; H, 6.29%.

2.5. [1,1'-Binaphthyl]-2,2'-diylbis[dimethylsilane] 2a

Method A. Bromine (16 ml, 0.31 mmol) was added at 0°C to a solution of 3 (100 mg, 0.27 mmol) in 2 ml of THF under nitrogen. After 10 min at 0°C, $LiAlH_4$ (20 mg, 0.53 mmol) was added, stirred for 15 min at 0°C and refluxed for 24 h. The crude was poured into ice-water and extracted with diethylether. Combined extracts were dried (Na_2SO_4), concentrated and purified by flash chromatography (eluent, 9:1 hexanes/dichloromethane) to afford 90 mg of a colorless oil (90% yield). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.96 (2H, d, 1/2 AB system, $J = 8.3$ Hz), 7.91 (2H, d, $J = 7.3$ Hz), 7.75 (2H, d, 1/2 AB system, $J = 8.3$ Hz), 7.51–7.41 (2H, m), 7.29–7.18 (2H, m), 7.15 (2H, d, $J = 7.8$ Hz), 3.79 (2H, m), 0.02 (6H, d, $J = 3.7$ Hz), −0.29 (6H, d, $J = 3.7$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 145.47, 135.54, 133.62, 133.25, 130.32, 127.78, 127.07, 126.89, 126.26, 125.87, −3.16, −3.41. IR (film): 3050, 2956, 2150, 1246 cm^{-1}. Anal. Found: C, 77.62; H, 7.41. Calc.: $C_{24}H_{26}Si_2$. C, 77.77; H, 7.07%.

Method B. $LiAlH_4$ (20 mg, 0.53 mmol) was added under nitrogen to a solution of 4a (50 mg, 0.13 mmol) in 2 ml of THF at 0°C. After 15 min at 0°C and 48 h at reflux, the reaction mixture was poured into ice-water and extracted with diethylether. Combined extracts were dried (Na_2SO_4), concentrated and purified by flash chromatography (eluent, 9:1 hexanes/dichloromethane) to give 43 mg of colorless oil (90% yield), identical (NMR, TLC) to the sample obtained as above.

2.6. N-Benzyl-3,5-disila-3,3,5,5-tetramethyl-3,5-dihydro-dinaphtho[2,1-c:1',2':e]azepine 4b

The bis-silane 2a (200 mg, 0.54 mmol) and dry benzylamine (0.07 ml, 0.6 mmol) were dissolved under nitrogen in 3 ml of anhydrous benzene, and 10% Pd on charcoal (15 mg) was added. The mixture was stirred at 120°C for 48 h in a sealed tube, cooled to room temperature, filtered through a glass-wool plug and rotoevaporated. The residual oil (230 mg, 90% yield) readily decomposes in air but gave satisfactory spectroscopic analysis. ^1H NMR ($CDCl_3$, 200 MHz): δ 8.02 (2H, d, 1/2 AB system, $J = 7.6$ Hz), 7.94 (2H, d, $J = 8.7$ Hz), 7.83 (2H, d, 1/2 AB system, $J = 7.6$ Hz), 7.53–7.40 (2H, m), 7.31–7.12 (9H, m), 4.15 (2H, d, $J = 1.5$ Hz), 0.42 (6H, s), −0.89 (6H, s). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 145.12, 143.54, 137.05, 133.25, 132.80, 129.20, 127.76, 127.65, 127.39, 127.36, 126.27, 126.00, 125.85, 125.62, 48.17, −0.43, −2.48. IR (film): 3050, 2956, 2927, 2857, 1256, 1097, 815 cm^{-1}.

2.7. 7-Sila-7,7-dimethyl-7H-dibenzo[a,h]fluorene 5

In an attempt to purify 4c by flash chromatography (eluent, 9:1 hexanes/dichloromethane), 90 mg of a colorless oil (48% yield) was obtained. ^1H NMR ($CDCl_3$, 200 MHz): δ 8.50–7.77 (8H, m), 7.58–7.46 (2H, m), 7.45–7.32 (2H, m), 0.47 (6H, s). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 144.0, 139.59, 135.45, 129.44, 128.22, 127.99, 127.62, 127.55, 125.47, 123.99, −3.60.

IR (film): 3043, 2953, 2924, 1321, 883, 814, 780, 768 cm^{-1}. Anal. Found: C, 85.32; H, 5.71. $C_{22}H_{18}Si$. Calc.: C, 85.11; H, 5.84%.

2.8. [1,1'-Binaphthyl]-2,2'-diylbis[trimethylsilane] 2d

A solution of *t*-butyllithium in pentane (1.7 M, 0.5 ml, 0.85 mmol) was added to a solution of 2,2'-dibromo-1,1'-binaphthalene (1e) (150 mg, 0.36 mmol) in 4 ml of THF/*n*-pentane (1:1) under nitrogen, at −100°C (pentane/N_2 slurry). The solution was stirred for 10 min at this temperature and 15 min at −78°C (acetone/N_2 slurry). Trimethylchlorosilane (0.07 ml, 0.9 mmol) was added and the solution was allowed to reach room temperature over 1 h. After 12 h the reaction mixture was poured into aqueous ammonium chloride and extracted with diethylether. Combined extracts were dried (Na_2SO_4), concentrated and purified by flash chromatography (eluent, 7% dichloromethane in hexanes). A colorless oil (72 mg, 50% yield) was obtained. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.94 (2H, d, 1/2 AB system, $J = 8.3$ Hz), 7.88 (2H, d, $J = 8.2$ Hz), 7.76 (2H, d, 1/2 AB system, $J = 8.3$ Hz), 7.50–7.38 (2H, m), 7.27–7.15 (2H, m), 7.14 (2H, d, $J = 7.7$ Hz), −0.27 (12H, d, $J = 3.7$ Hz). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 145.12, 137.96, 133.66, 133.40, 130.56, 127.60, 127.30, 126.67, 126.12, 125.66, −0.13. IR (film): 3047, 2954, 2926, 1247, 840, 830, 759 cm^{-1}. Anal. Found: C, 78.48; H, 7.50. $C_{26}H_{30}Si_2$. Calc.: C, 78.33; H, 7.58%.

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