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Synthesis of bi(cyclohexasilanyl) derivatives ☆

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Abstract

Starting from 1,3- or 1,4-diphenyldecamethylcyclohexasilane, one phenyl group can be split off selectively by action of trifluoromethanesulfonic acid. The syntheses of some new mixed substituted cyclohexasilanes 1,3- and 1,4-Ph–Si_6Me_{10}–X (X = CF_3SO_3, H, Cl or Br) are reported. By reaction of 1,3- and 1,4-Ph–Si_6Me_{10}–Cl with undecamethylcyclohexasilanyl potassium, novel monophenylated bi(cyclohexasilanyl) derivatives are obtained. The preparation of the corresponding monochlorinated derivatives is also reported.

Keywords: Disubstituted permethylcyclohexasilanes; Monosubstituted bi(cyclohexasilanyl) derivatives; Cyclosilanes; Phenyl; Triflate

1. Introduction

Some years ago we synthesized new bicyclosilanes such as bi(undecamethylcyclohexasilanyl) [1]. We have been interested in derivatives with functional groups for the use of these polycyclic silanes for other syntheses.

One of the ways to obtain these functional polysilanes is partial demethylation with chlorinating agents such as antimony pentachloride. Recently we investigated this reaction with the bi(undecamethylcyclohexasilanyl) and we found exclusive monochlorination [2]. In this first investigation we were not able to determine the position of the chlorine on the cyclosilane. Therefore we were interested in special syntheses to form such functional bi(cyclohexasilanyl) derivatives in order to compare these compounds with the product of the direct chlorination of the permethylated bicyclus.

The synthesis of functional bi(cyclohexasilanyl) derivatives required novel mixed substituted cyclohexasilanes as starting materials. Recently we published a new method to separate 1,3- and 1,4-disubstituted methylcyclohexasilanes by use of oxygen-bridged and dihydroxy derivatives [3]. Before we found this method, the separation of the mixture of dichlorinated decamethylcyclohexasilane isomers, which were formed in the reaction of antimony pentachloride with dodecamethylcyclohexasilane, was difficult and troublesome. This new result allows us to initiate new syntheses with the pure isomers.

2. Syntheses

By the reaction of 1,4- or 1,3-dichlorodecamethylcyclohexasilane, now easily available by a simple route for the separation of these isomers via the hydroxy derivatives [3], with phenyllithium the corresponding diphenyl derivatives 1,4- and 1,3-diphenyldecamethylcyclohexasilane (**1a** and **1b**) were formed quantitatively. Treatment of **1a** or **1b** with one equivalent of trifluoromethanesulfonic acid (TfOH) [4,5] at low temperature and under high dilution conditions afforded the novel disubstituted cyclohexasilanes **2a** or **2b** (greater than 90%), which were easily transformed into the hydro derivatives (**3a** and **3b**) by action of $LiAlH_4$ in a one pot procedure. Alternatively the reaction with LiX (X = Cl or Br) yielded the halogenated derivatives (**4a**, **5a**, **4b** and **5b**)(Fig. 1).

However, starting from 1,4- and 1,3-dichlorodecamethylcyclohexasilane the reaction with only one equivalent of phenyllithium also resulted in the formation of **4a** and **4b** in suitable yields (gas chromatography (GC) analyses, greater than 80%). So the synthesis of **4a** and **4b** could also be achieved directly from the chloro derivatives without using trifluoromethanesulfonic acid.

☆ Dedicated to Professor H. Schmidbaur on the occasion of his 60th birthday.

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Because 1-hydro-4-phenyldecamethylcyclohexasilane (**3a**) and 1-hydro-3-phenyldecamethylcyclohexasilane (**3b**) can be purified by distillation very easily, the most efficient way for the syntheses of the halogenated cyclohexasilanes (**4a**, **5a**, **4b** and **5b**) was the reaction of **3a** and **3b** with CHX_3 (X = Cl or Br) (Fig. 1).

Further reaction of **4a** and **4b** with undecamethylcyclohexasilanyl potassium, a novel synthesis which has recently been reported [6], afforded the monosubstituted permethylated bicycles (**6a**) and (**6b**) (Fig. 2).

The monophenylated bicycles **6a** and **6b** were converted into the corresponding chlorinated derivatives **7a** and **7b** by treatment with trifluoromethanesulfonic acid and subsequent reaction with LiCl in a one-pot procedure (Fig. 3).

Starting from the permethylated bicycle (**7**), the reaction with 0.6 equivalent of antimony pentachloride also resulted in the formation of a monochlorinated bicycle (GC analysis, 60%), but it was not possible to determine the position of the chlorine substituent exactly [2]. Now, by comparison with **7a** and **7b**, the result of the chlorination of **7** with $SbCl_5$ was assigned to be the 4-substituted bicyclus **7a** (Fig. 4).

3. Experimental section

3.1. General data

All manipulations involving air-sensitive materials were performed under nitrogen or argon with use of

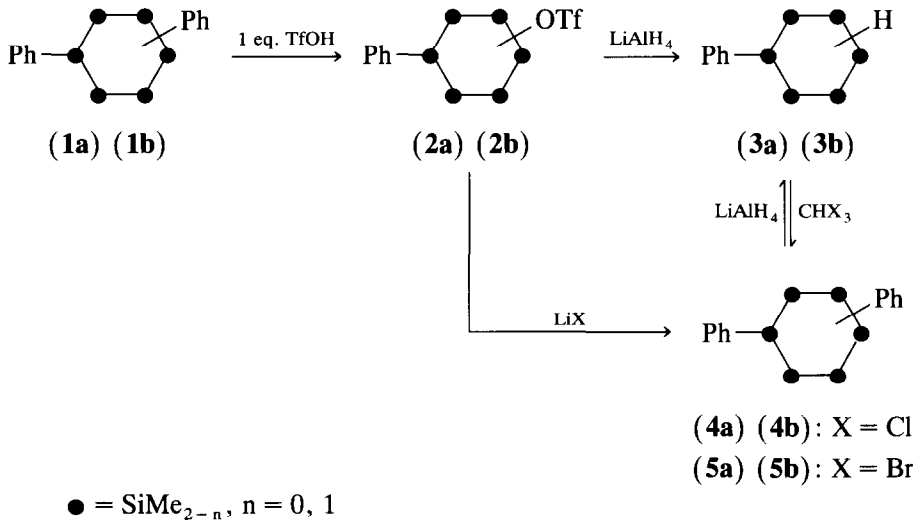


Fig. 1. Syntheses of 1,4- (**1a–5a**) and 1,3- (**1b–5b**) disubstituted permethylated cyclohexasilanes.

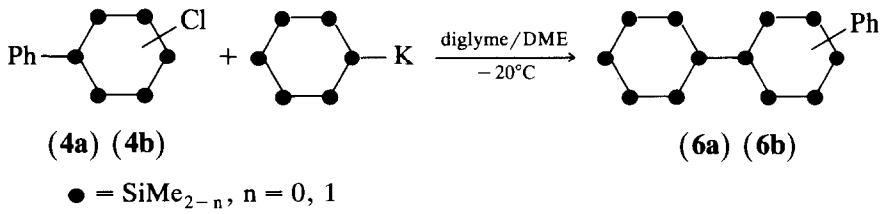


Fig. 2. Synthesis of 1-phenyl-4-(undecamethylcyclohexasilanyl)decamethylcylclohexasilane (**6a**) and 1-phenyl-3-(undecamethylcyclohexasilanyl) decamethylcyclohexasilane (**6b**): DME = Dimethoxyethane (glyme).

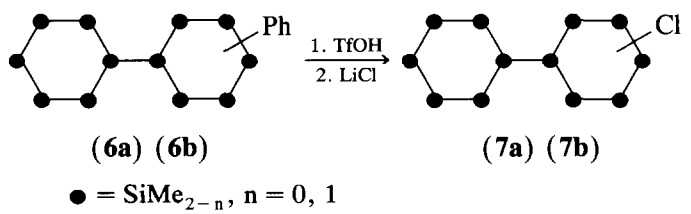
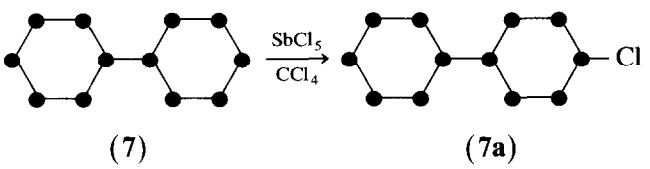


Fig. 3. Synthesis of 1-chloro-4-(undecamethylcyclohexasilanyl)decamethylcyclohexasilane (**7a**) and 1-chloro-3-(undecamethylcyclohexasilanyl) decamethylcyclohexasilane (**7b**).



(7) (7a)

● = $SiMe_{2-n}$, n = 0, 1

Fig. 4. Chlorination of bi(undecamethylcyclohexasilanyl) (7) with $SbCl_5$.

standard Schlenk techniques. All solvents were dried with Na–K alloy under nitrogen and distilled prior to use. Trichloromethane and tribromomethane were dried with phosphorus pentaoxide and destilled.

1,4- and 1,3-dichlorodecamethylcyclohexasilane [3] and undecamethylcyclohexasilanyl potassium [5] were prepared according to published procedures.

All NMR spectra were recorded with a Bruker MSL 300 spectrometer (^1H, 300.13 MHz; ^{29}Si, 59.627 MHz; ^{13}C, 75.47 MHz). Samples were dissolved in $CDCl_3$ (**1b**, **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, **7a** and **7b**), C_6D_6 (**3a** and **3b**) or toluene with a capillary filled with D_2O (**2a** and **2b**).

UV spectra (*n*-hexane) were recorded with a Philips PU-8740 spectrometer and IR spectra (CsBr and paraffin) with a Perkin–Elmer 883 IR spectrometer. C and H analyses were performed on Heraeus–Mikro-K1 apparatus. GC analyses were carried out on a HP 5890 series II (capillary column DB-1HT;15 m × 0.251 mm; 0.10 μm; flame ionization detector). Mass spectra were obtained with a HP 5971 (**1–5**) and a Varian CH-7 spectrometer (**6** and **7**).

3.2. Synthesis of *1a* and *1b*

Lithium chippings (0.25 g, 36 mmol) were dispersed in 10 ml of dry diethyl ether and a solution of 2.42 g (15.4 mmol) of bromobenzene in 10 ml of diethyl ether was added slowly. After stirring the mixture for 1 h under reflux, the phenyllithium solution was added dropwise to a solution of 3.0 g (7.70 mmol) of 1,4- or 1,3-dichlorodecamethylcyclohexasilane in 30 ml of diethyl ether under reflux. When no more starting material and no more **4a** and **4b** could be detected by GC analysis, HCl (10 ml, 1 M) was added slowly. After extraction with three portions of 30 ml of diethyl ether the combined extracts were dried over Na_2SO_4 and the solvent was evaporated to leave a white solid residue. Recrystallization from 1-propanol gave white crystals of **1a** or **1b** (yield, 90%).

3.3. 1,3-Diphenyldecamethylcyclohexasilane (*1b*)

^{29}Si NMR tetramethylsilane (TMS); δ −39.88/−40.33, −40.88/−40.99, −41.06/−41.26, −41.44 (2Si), −41.90/−41.67, −42.32/−42.06 ppm, ^1H NMR (TMS): δ 7.40 (m, 10H), 0.33 (m, 30H) ppm. ^{13}C NMR (TMS): δ 137.75 (*i*), 134.95 (*o*), 128.07 (*m* + *p*), −3.72–−6.84 ppm. UV: λ (ε) 245.1 (13 600) nm. MS: *m/z* 430 (M^+, 19.00%), 337 (Si_5Me_8Ph, 6.59%), 264 (Si_4Me_5Ph, 16.34%), 135 ($SiMe_2Ph$, 62.17%), 73 ($SiMe_3$, 100%). Anal. Found: C, 44.62; H, 8.36. Calc.: C, 44.54; H, 8.18%.

3.4. Synthesis of the silyltriflates *2a* and *2b*

To a solution of 2.0 g (4.2 mmol) of **1a** or **1b** in 50 ml of dry toluene, 0.37 ml (4.2 mmol) of trifluoromethanesulfonic acid was added very slowly at −20°C. After addition the mixture was stirred at room temperature until no more starting material could be detected by GC analysis (30 min). The resulting solution was used without further purification for the synthesis of **3a** and **3b**.

3.5. (*4-Phenylundecamethylcyclohexasilanyl*)*trifluoromethanesulfonate* (*2a*)

^{29}Si NMR (TMS): δ 49.85/49.37 (Si–OTf), −39.42/−40.74, −41.78/−42.07, −43.05/−43.33 ppm.

3.6. (*3-Phenylundecamethylcyclohexasilanyl*)*trifluoromethanesulfonate* (*2b*)

^{29}Si NMR (TMS): δ 50.42/49.53 (Si–OTf), −39.47/−39.57, −41.08/−41.19, −42.22/−42.44, −42.90/−43.02, −43.36/−43.77 ppm.

3.7. Synthesis of the hydro derivatives *3a* and *3b*

After the addition of 30 ml of diethyl ether to the solution of the silyl triflates **2a** or **2b**, described above, a 2.1 mmol portion of $LiAlH_4$ in 2 ml of diethyl ether was added dropwise at 0°C. The reaction mixture was allowed to warm to room temperature and subsequently was stirred for 1 h. The solution then was poured into 30 ml of ice-cooled 1 N H_2SO_4. The aqueous layer was extracted with three portions of 10 ml of *n*-pentane. The combined organic layers were dried with Na_2SO_4 and the solvents evaporated to leave a colorless oily residue. Purification by Kugelrohr distillation (80°C; 10^{-2} Torr) gave **3a** or **3b** (yield, 90–93%).

3.8. 1-Hydro-4-phenyldecamethylcyclohexasilane (*3a*)

^{29}Si NMR (TMS): δ −40.44/−40.53, −40.77/−41.15, −41.31/−41.46, −66.52/−68.88 ppm, ^1H

NMR (TMS): 7.34 (m, 5H), 3.66 (Si–H), 0.49 (s, 3H), 0.32 (s, 6H), 0.31 (s, 6H), 0.27 (s, 9H), 0.18 (s, 6H) ppm. ^{13}C NMR (TMS): δ 138.05, 135.45, 129.05, 127.91, −7.98 m ppm. UV: λ (ε): 243.0 (28 000) nm. IR: ν 2065 w (Si–H), 1246 s, 871 w, 842 w, 803 vs, 782 vs, 732 s, 698 w, 684 vw, 639 w, 474 vw cm^{-1}. MS: *m/z* 396 (M^+, 28.99%), 322 (Si_5Me_7Ph, 20.33%), 263 (Si_4Me_5Ph, 26.99%), 135 ($SiMe_2Ph$, 79.06%), 73 ($SiMe_3$, 100%). Anal. Found: C, 48.46; H, 9.25. Calc.: C, 48.41; H, 9.14%.

3.9. 1-Hydro-3-phenyldecamethylcyclohexasilane (3b)

^{29}Si NMR (TMS): δ −40.03/−40.27, −40.44/−40.57, −41.15/−41.21, −41.28/−41.33, −41.40/−41.66, −65.34/−68.60 ppm. ^{1}H NMR (TMS): δ 7.37 (m, 5H), 3.42 (Si–H), 0.56–0.18 (m, 30H) ppm. ^{13}C NMR (TMS): δ 137.90, 135.49, 128.90, 128.10, −7.23 m ppm. UV: λ (ε) 245.3 (22 200) nm. IR: ν 2067 w (Si–H), 1246 s, 870 w, 837 w, 803 vs, 784 vs, 731 s, 698 w, 686 vw, 638 w, 473 vw cm^{-1}. MS: *m/z* 396 (M^+, 68.13%), 322 (Si_5Me_7Ph, 27.68%), 263 (Si_4Me_5Ph, 34.59%), 135 ($SiMe_2Ph$, 68.70%), 73 ($SiMe_3$, 100%). Anal. Found: C, 48.52; H, 9.32. Calc.: C, 48.41; H, 9.14%.

3.10. Synthesis of the halogenated derivatives 4a, 4b, 5a and 5b

3a or **3b** (2.0 g, 5 mmol) and CHX_3 (X = Cl or Br) (10 mmol) were refluxed in 30 ml of toluene for about 6 h. Removal of the solvents under reduced pressure left a solid residue, which was purified by vacuum sublimation (80°C; 10^{-2} Torr), to give white **4a**, **4b**, **5a** and **5b** (yield 90–94%).

3.11. 1-Chloro-4-phenyldecamethylcyclohexasilane (4a)

^{29}Si NMR (TMS): δ 18.10/16.73, −38.74/−39.47, −40.98/−41.05, −41.70/−42.18 ppm. ^{1}H NMR (TMS): δ 7.36 (m, 5H), 0.65–0.16 (m, 30H) ppm. ^{13}C NMR (TMS): δ 137.8, 134.87, 128.25, 127.95, −3.32 m ppm. UV: λ (ε) 245.1 (13 600) nm. MS; *m/z* 430 (M^+, 19.00%), 337 ($Si_5Me\ ^8Ph$, 6.59%), 264 (Si_4Me_5Ph, 16.34%), 135 ($SiMe_2Ph$, 62.17%), 73 ($SiMe_3$, 100%). Anal. Found: C, 44.62; H, 8.36 Calc.: C, 44.54; H, 8.18%.

3.12. 1-Chloro-3-phenyldecamethylcyclohexasilane (4b)

^{29}Si NMR (TMS): δ 18.71/16.89, −38.73/−38.82, −39.81/−39.87, −40.46/−41.45, −41.72/−41.92, −42.19/−42.47 ppm. ^{1}H NMR (TMS): δ 7.36 (m, 5H), 0.66–0.15 (m, 30H) ppm. ^{13}C NMR (TMS): δ 136.92, 134.85, 128.35, 128.01, −3.21 m ppm. UV: λ (ε) 246.5 (14 700) nm. MS: *m/z* 430 (M^+, 21.33%), 337 (Si_5Me_8Ph, 6.63%), 263 (Si_4Me_5Ph, 45.53%), 135 ($SiMe_2Ph$, 67.21%), 73 ($SiMe_3$, 100%). Anal. Found: C, 44.64; H, 8.31. Calc.: C, 44.54; H, 8.18%.

3.13. 1-Bromo-4-phenyldecamethylcyclohexasilane (5a)

^{29}Si NMR (TMS): δ 11.12/8.74, −38.78/−39.47, −40.65/−41.02, −41.57/−41.82 ppm. ^{1}H NMR (TMS): δ 7.32 (m, 5H), 0.83–0.00 (m, 30H) ppm. ^{13}C NMR (TMS): δ 137.39, 135.43, 129.00, 127.81, −3.35 m ppm. UV: λ (ε) 243.0 (28 000) nm. MS: *m/z* 476 (M^+, 18.10%), 263 (Si_4Me_5Ph, 54.93%), 135 ($SiMe_2Ph$, 85.92%), 73 ($SiMe_3$, 100%). Anal. Found: C, 40.46; H, 7.52. Calc.: C, 40.38; H, 7.41%.

3.14. 1-Bromo-3-phenyldecamethylcyclohexasilane (5b)

^{29}Si NMR (TMS): δ 12.04/9.08, −38.72/−38.88, −39.81/−40.00, −41.11/−41.26, −41.54/−41.83, −41.94/−42.10 ppm. ^{1}H NMR (TMS): δ 7.29 (m, 5H), 0.79–0.06 (m, 30H) ppm. ^{13}C NMR (TMS): δ 137.20, 135.45, 129.34, 127.98, −3.27 m ppm. UV: λ (ε) 247.3 (7700) nm. MS: *m/z* 476 (M^+, 20.08%), 263 (Si_4Me_5Ph, 46.74%), 135 ($SiMe_2Ph$, 70.34%), 73 ($SiMe_3$, 100%). Anal. Found: C, 40.52; H, 7.56. Calc.: C, 40.38; H, 7.41%.

3.15. Synthesis of the monophenylated bicycles 6a and 6b

1.0 g (2.3 mmol) of **4a** or **5a** was dissolved in 10 ml of dimethoxyethane and a solution of undecamethylcyclohexasilanyl potassium (2.3 mmol) in diglyme was added dropwise at −20°C. The reaction mixture was allowed to warm to room temperature and subsequently was stirred for 12 h. After the addition of some drops of concentrated HCl, the removal of the solvent left a solid residue, which was dispersed in toluene. Subsequent filtration and evaporation of toluene yielded a white solid. Recrystallization from ethyl acetate–methanol gave white crystals of **6a** or **6b** (yield, 65–70%).

3.16. 1-Phenyl-4-(undecamethylcyclohexasilanyl)decamethylcyclohexasilane (6a)

152–54°C. ^{29}Si NMR (TMS): δ −35.90, −36.58, −38.93, −39.90, −42.03, −42.91, −68.82, −68.88 ppm. ^{1}H NMR (TMS): δ 7.37 (m, 5H), 0.47–0.10 (m, 66H) ppm. ^{13}C NMR (TMS): δ 138.03, 134.90, 129.14, 127.94, −5.07 m ppm. UV: λ (ε): 244.7 (36 200), 276.7 (25 200) nm. MS: *m/z* 730 (M^+, 54.91%), 396 ($Si_6Me_{10}Ph$, 26.47%), 318 (Si_6Me_{10}, 85.40%). Anal. Found: C, 44.56; H, 9.25. Calc.: C, 44.43; H, 9.39%.

3.17. 1-Phenyl-3-(undecamethylcyclohexasilanyl)decamethylcyclohexasilane (6b)

m.p., 149–51°C. ^{29}Si NMR (TMS): δ −36.52, −36.59, −36.65, −37.24, −39.36, −39.88 (2Si), −39.97, −41.85, −42.97, −68.36, −68.74 ppm. ^{1}H NMR (TMS): δ 7.35 (m, 5H), 0.49–0.12 (m, 66H) ppm. UV: λ (ε) 242.4 (32200), 277.6 (25900) nm. MS: m/z 730 (M^+, 69.27%), 396 ($Si_6Me_{10}Ph$, 19.11%), 318 (Si_6Me_{10}, 98.97%). Anal. Found: C, 44.64; H, 9.52. Calc.: C, 44.43; H, 9.39%.

3.18. Synthesis of the monochlorinated bicycles 7a and 7b

0.2 g (0.27 mmol) of **6a** or **6b** were dissolved in 5 ml of dry toluene, and 25 μl of trifluoromethanesulfonic acid was added at 0°C. After stirring the solution at room temperature for 1 h, 5 ml of diethyl ether and 0.05 g of LiCl (1.2 mmol) were added. The reaction mixture was subsequently stirred for 3 h. The solvents were removed under reduced pressure and the solid residue was dispersed in petrolether. Filtration and evaporation of the solvent left a white solid residue of **7a** or **7b** (yield, 92–94%).

3.19. 1-Chloro-4-(undecamethylcyclohexasilanyl)decamethylcyclohexasilane (7b)

^{29}Si NMR (TMS): δ 17.83/15.94, −28.57/−30.24, −36.46/−36.50, −36.57/−36.88, −38.74/−39.90, −42.82/−42.92, −68.74/−68.90, −69.27/−69.47 ppm. ^{1}H NMR (TMS): δ 1.27–0.16 (m, 63H) ppm. UV: λ (ϵ): 238.0 (22800), 274.1 (17000) nm. MS: m/z 688 (M^+, 46%), 353 ($Si_6Me_{10}Cl$, 88%), 333 (Si_6Me_{11}, 37%), 318 (Si_6Me_{10}, 100%). Anal Found: C, 36.78; H, 9.38. Calc.: C, 36.65; H, 9.23%.

3.20. 1-Chloro-3-(undecamethylcyclohexasilanyl)decamethylcyclohexasilane (7 b)

^{29}Si NMR (TMS): δ 32.08/31.77, −27.46/−28.64, −30.27/−31.58, −35.02//−35.83, −36.33/−36.57, −36.69/−36.89, −37.06/−37.40, −39.87/−39.92, −40.41/−40.73, −42.78/−42.92, −71.30/−71.97, −77.59/−78.83 ppm. ^{1}H NMR (TMS): δ 1.27–0.17 (m, 63H) ppm. UV: λ (ϵ) 247.4 (29500) nm. MS: m/z 688 (M^+, 49%), 353 ($Si_6Me_{10}Cl$ 100%), 333 (Si_6Me_{11}, 32%), 318 (Si_6Me_{10}, 98%). Anal. calc. Found: C, 36.83; H, 9.42. Found: C, 36.65; H, 9.23%.

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