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A New Monomeric Saturated N-Heterocyclic Silylene as a Racemic Mixture

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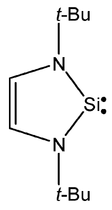
Summary: A new stable silylene, rac-N,N′-di-tert-butylethylene-4,5-dimethyl-1,3-diaza-2-silacyclopentan-2-ylide, has been made by reaction of the corresponding dibromide with KC_8. Unlike the analogous silylene lacking the two methyl groups, which tetramerizes in concentrated solution or as a solid, the new silylene shows no tendency to oligomerize; instead, it persists as a stable colorless liquid.

Silylenes, which can be broadly defined as molecules containing neutral divalent silicon atoms, are key intermediates in numerous thermal and photochemical reactions. As such, they are extremely important in the field of silicon chemistry.[1] Following the first synthesis in 1994 of the thermally stable silylene **1**,[2] an unsaturated N-heterocyclic silylene, a few other stable silylenes have been reported, including **2**,[3] **3**,[4] and **4**.[5] The availability of stable silylenes has allowed the discovery of new compounds and novel reaction chemistry.[6,7]



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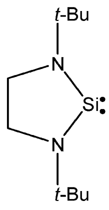

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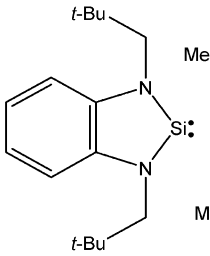

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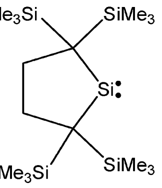

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Of these four stable silylenes, **2**, a saturated N-heterocyclic silylene, has interesting and unusual properties. It is only stable in dilute solution. In the pure solid state or in concentrated solution, a silicon atom of one molecule of **2** inserts into a Si−N bond of another molecule to form an (aminosilyl)silylene, which then dimerizes to generate a disilene (a dark red solid) (Scheme 1). This equilibrium is reversible; in dilute solution **2** is almost exclusively present, while in concentrated solutions or in the solid state the equilibrium favors the disilene.

Here we report the synthesis of a new saturated N-heterocyclic silylene, **5**, obtained as a racemic mixture of **5a** and **5b** (Figure 1). The structure is identical with that of **2**, except that a methyl group is present on each of the ring carbon atoms. Surprisingly, the behavior of **5a**,**b** is quite different from that of **2**. **5a**,**b** persists as a colorless liquid, showing no tendency to oligomerize like silylene **2**. The silylene mixture **5a**,**b** was characterized by ^1H, ^{13}C, and ^{29}Si NMR, high-resolution MS, and elemental analysis. Its ^{29}Si NMR resonance in C_6D_6 falls at +123.4 ppm, quite close to that for monomeric **2** (+119 ppm).[3] The UV−vis spectrum of **5a**,**b** in hexane (ca. 5×10^{-5} M) shows a band maximum at 270 nm (molar extinction 1.2×10^5) and a shoulder at ∼295 nm (Figure 2). Silylene **2** has similar band maxima at 268 and 292 nm. The reason **5a**,**b**, unlike **2**, remains as a monomer in the pure state is not clear. From inspection of molecular models, the two methyl groups on the backbone of the silylene do not appear to be bulky enough to interfere with the insertion of one molecule of **5a**,**b** into a Si−N bond of another molecule to form an (aminosilyl)silylene. Possibly, the slight electron-donating ability of the two methyl groups subtly changes the electronic structure of the silylene, inhibiting the Si−N bond insertion.

The silylene mixture **5a**,**b** was prepared by the reduction of the dibromosilane compounds **6a**,**b** with potassium graphite (KC_8) in THF and triethylamine at room temperature, as shown in Scheme 2. First, *N*,*N*′-di-*tert*-butylethylenediimine, obtained from the reaction of glyoxal with *tert*-butylamine, was treated with methyllithium to produce a pair of enantiomeric diamine compounds in 90% yield.[8,9] No *meso* diamine compound was

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(9) Synthesis of *rac-N*,*N*′-di-*tert*-butyl-2,3-dimethylethylenediamine: a solution of LiMe (160 mmol, 100 mL of a 1.6 M solution in Et_2O) was stirred at 0 °C and solid *N*,*N*′-di-*tert*-butylethylenediimine (13.32 g, 79.4 mmol) added portionwise over 20 min. The resulting pale yellow solution was warmed to room temperature, stirred for 1 h, and rechilled to 0 °C, and ice−water (60 mL) was added dropwise. After the mixture was warmed to room temperature, the organic layer was extracted with hexane (3 × 30 mL), stirred over $MgSO_4$, and filtered. The resulting solution was put on a vacuum line to remove solvent to yield a pale yellow liquid, which was distilled in vacuo to give a colorless oil. Yield: 14.27 g, 90%. ^1H NMR (C_6D_6): δ 0.57 (b, 2H), 1.01 (s, 6H), 1.03 (s, 18H), 2.44 (m, 2H). ^{13}C NMR (C_6D_6): δ 20.50, 30.94, 50.78, 53.67. High-resolution mass spectrometry: calcd for $[C_{12}H_{26}N_2 + H^+]$ 201.2330, found 201.2325.

10.1021/om060544v CCC: $33.50

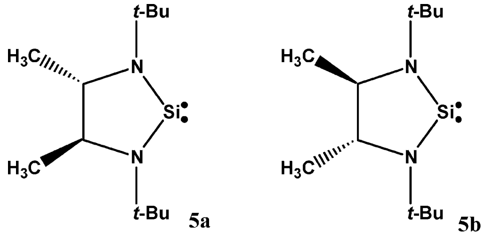


Figure 1. The new stable silylenes **5a**,**b**.

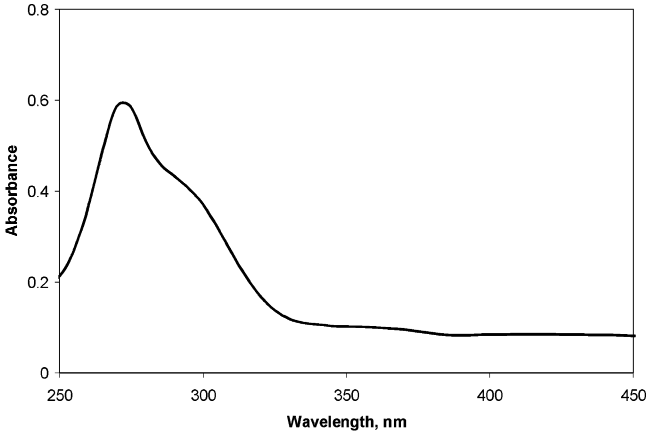


Figure 2. UV−vis spectrum of silylenes **5a**,**b**.

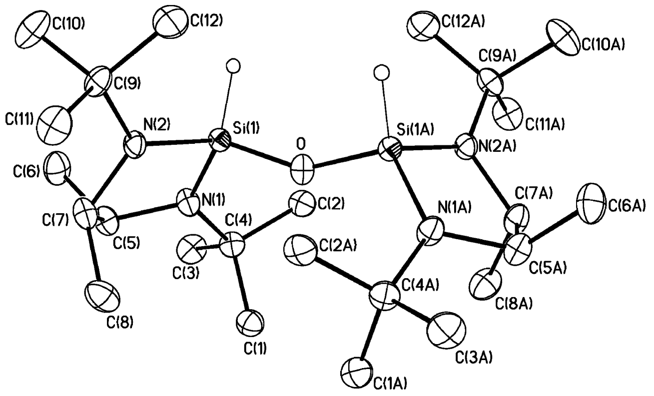
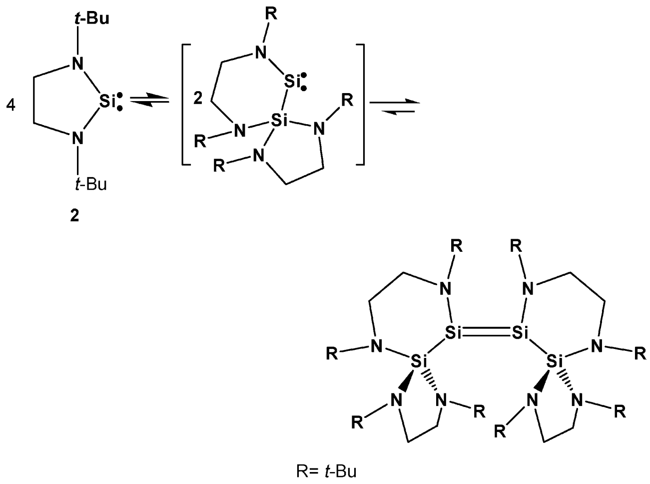


Figure 3. Molecular structure of **8**. Thermal ellipsoids are given at the 40% probability level, and the hydrogen atoms at the carbon atom are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)−N(1), 1.7030(15); Si(1)−N(2), 1.7044(14); Si(1)−H, 1.37(2); Si(1)−O, 1.6242(7); Si(1)−O−Si(2), 150.17(13); O−Si(1)−N(1), 112.80(8); O−Si(1)−N(2), 115.11(6); N(1)−Si(1)−N(2), 95.57(7); O−Si(1)−H(1), 106.4(8).

Scheme 1. Equilibrium of Silylene 2 and the Tetrameric Disilene



observed in this reaction, as the second nucleophilic addition of CH_3^- to a C=N bond is evidently highly stereoselective, guided by the first methyl group. The diamine compound was then converted to the corresponding dihydrosilane after reaction with dichlorosilane in the presence of 1,8-diazabicyclooctane (DABCO).[10] The dibromosilane compounds **6a**,**b** were produced by bromination of the dihydrosilane.[11] When the dibromosilane compounds were reduced by KC_8 in THF in the presence of triethylamine at room temperature, the silylene mixture **5a**,**b** was produced in 70% yield.[12] Silylenes **5a**,**b** can be purified by distillation at 150 °C (0.1 Torr). The triethylamine is essential in this reaction. Without triethylamine, the silylenes easily became overreduced (most likely to silyl anions), resulting in a low yield.

5a,**b** show reactivity similar to that of silylenes **1** and **2**. Silylenes **5a**,**b** react with methanol in hexane at −78 °C via an expected insertion into the O−H bond to afford the corresponding methoxyhydrosilanes **7a**,**b**. Silylene **5a** reacts similarly with phenols to afford the corresponding alkoxyhydrosilanes. With water, silylenes **5a**,**b** insert into the O−H bond to yield the corresponding silanol, which self-condenses to give a disiloxane compound, as shown in Scheme 3. Both *rac* and *meso* isomers

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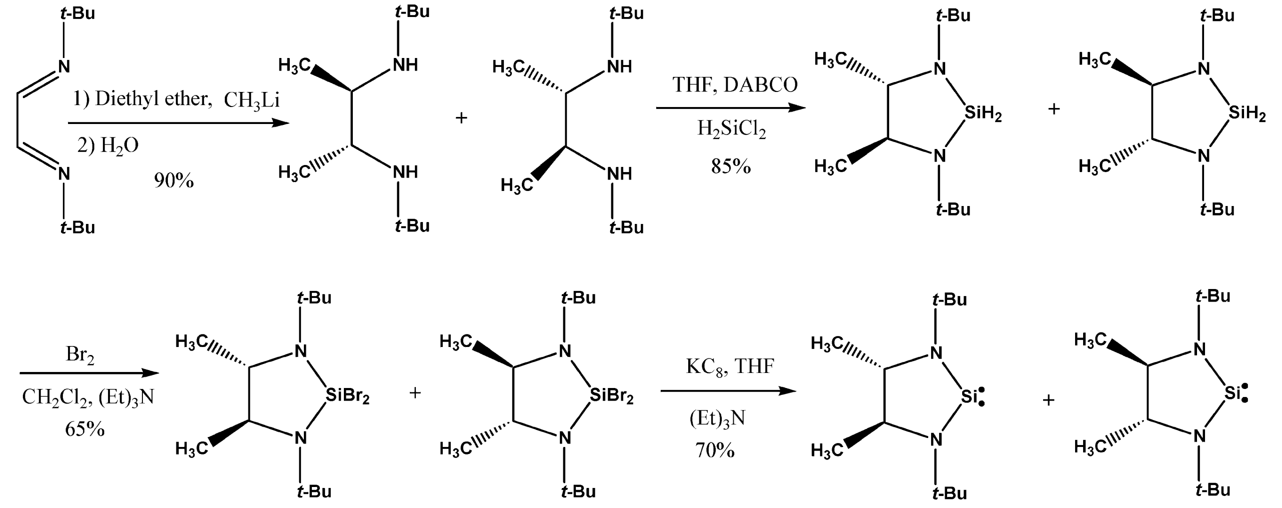
(10) Synthesis of *rac-N,N′*-di-*tert*-butyl-4,5-dimethyl-1,3-diaza-2,2-dihydro-2-silacyclopentane: to a solution of DABCO (7.54 g, 67.2 mmol) in 25 mL of THF was added *rac-N,N′*-di-*tert*-butyl-2,3-dimethylethylenediamine (6.34 g, 32 mmol) in THF (85 mL). H_2SiCl_2 in xylene (20 mL, 49.5 mmol) was added dropwise, immediately producing a voluminous white solid. The mixture was stirred for a further 2 h and then filtered, and the resulting solution was put on a vacuum line to remove solvents, giving a pale yellow oil. The oil was distilled in vacuo to give a colorless liquid. Yield: 6.14 g, 85%. ^1H NMR (C_6D_6): δ 1.09 (d, 6H, J = 3 Hz), 1.16 (s, 18H), 2.69 (q, 2H, J = 3 Hz), 5.31 (s, 2H). ^{13}C NMR (C_6D_6): δ 24.81, 31.23, 51.22, 58.06. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −41.06. High-resolution mass spectrometry: calcd for $C_{12}H_{28}N_2Si$ 228.2022, found 228.2019.

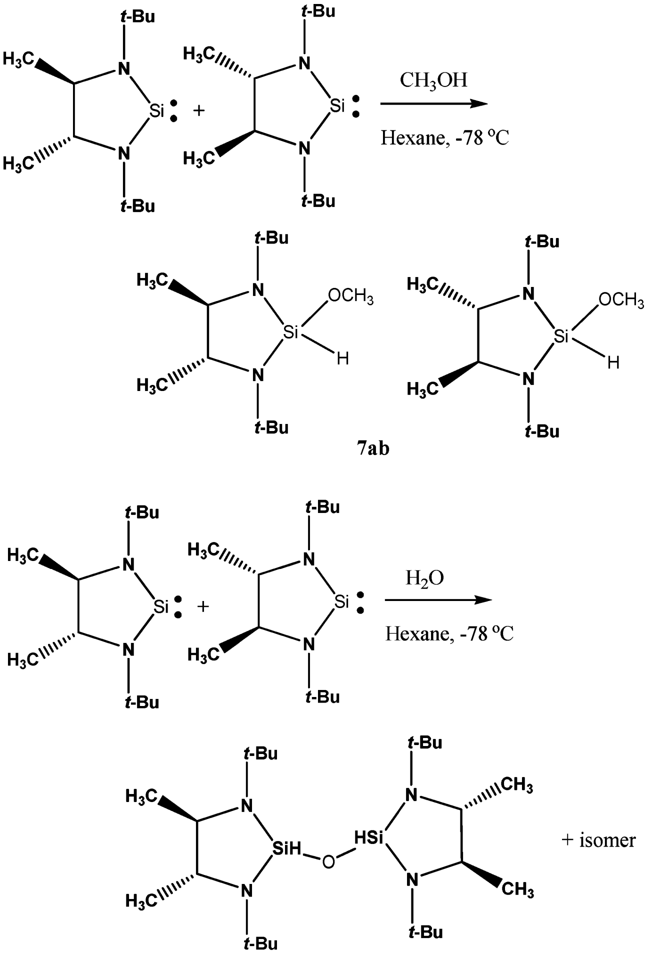
(11) Synthesis of **6a**,**b**: to a solution of *rac-N,N′*-di-*tert*-butylethylene-4,5-dimethyl-1,3-diaza-2,2-dihydro-2-silacyclopentane (6.84 g, 30.0 mmol) in 75 mL of CH_2Cl_2 was added triethylamine (7.08 g, 70 mmol). Bromine (9.92 g, 62 mmol) in CH_2Cl_2 (10 mL) was added dropwise. The mixture was refluxed for 12 h. The solvents were removed under vacuum, yielding a brown gel solid. The solid was extracted with 50 mL of hexane, and the solution was evaporated under vacuum, giving a pale yellow solid. Yield: 7.53 g, 65%. ^1H NMR (C_6D_6): δ 1.11 (d, 2H, J = 4.2 Hz), 1.26 (s, 16H), 2.69 (q, 2H, J = 4.2). ^{13}C NMR (C_6D_6): δ 24.18, 30.99, 52.97, 57.97. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −51.51. High-resolution mass spectrometry: calcd for $[C_{12}H_{26}N_2SiBr_2 - CH_3]$ 368.9997, found 368.9997. A white crystal was produced by slow evaporation of hexane solution of this compound. Anal. Calcd for $C_{12}H_{26}N_2SiBr_2$: C, 37.53; H, 6.82; N, 7.29. Found: C, 37.28; H, 7.04; N, 7.10. Synthesis of **5a**,**b**: In a 250 mL Schlenk flask was placed 4.50 g of potassium graphite (62 mmol). To this flask were added 100 mL of THF and 20 mL of triethylamine. This solution was stirred overnight. Then, **6a**,**b** (6.78 g, 30 mmol) dissolved in 20 mL of THF was added. The reaction was monitored by ^1H NMR until all the starting material disappeared (∼6 h). The reaction mixture was filtered, and the resulting solution was put under vacuum to remove solvents, giving a pale yellow liquid. The yellow oil was distilled at 0.1 Torr to give a colorless liquid. Yield: 2.78 g, 70%. ^1H NMR (C_6D_6): δ 1.08 (d, 6H, J = 3 Hz), 1.27 (s, 18H), 2.81 (q, 2H, J = 3 Hz). ^{13}C NMR (C_6D_6): δ 26.76, 33.62, 53.19, 61.23. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ +123.44. High-resolution mass spectrometry: calcd for $C_{12}H_{26}N_2Si$ 226.1865, found 226.1862. Anal. Calcd for $C_{12}H_{26}N_2Si$: C, 63.72; H, 11.58; N, 12.34. Found: C, 63.86; H, 11.55; N, 11.93.

(12) Synthesis of **7**: at −78 °C, to a 15 mL THF solution of **5a**,**b** (0.46 g, 2 mmol) was slowly added methanol (0.16 g, 5 mmol) in 10 mL of hexane. The reaction mixture was warmed and stirred for 5 h. The solvent was evaporated, yielding a colorless oil, which was distilled under vacuum. Yield: 0.38 g, 60%. ^1H NMR (C_6D_6): 1.12 (d, 3H, J = 10 Hz), 1.16 (d, 3H, J = 10 Hz), 1.16 (s, 9H), 1.21 (s, 9H), 2.55−2.76 (m, 2H), 3.42 (5, 3H), 5.12 (s, 1H). ^{13}C NMR (C_6D_6): 27.52, 27.59, 33.55, 33.65, 51.06, 52.95, 53.13, 57.68, 60.49. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −39.53, J_{Si-H} = 132 Hz. High-resolution mass spectrometry: calcd for $[C_{13}H_{30}N_2SiO - CH_3]$ 243.45, found 243.20. Anal. Calcd for $C_{13}H_{30}N_2SiO$: C, 60.41; H, 11.70; N, 10.84. Found: C, 60.31; H, 11.90; N, 10.71.

Scheme 2. Synthesis of 5a,b



Scheme 3. Reaction of 5a,b with Methanol and Water



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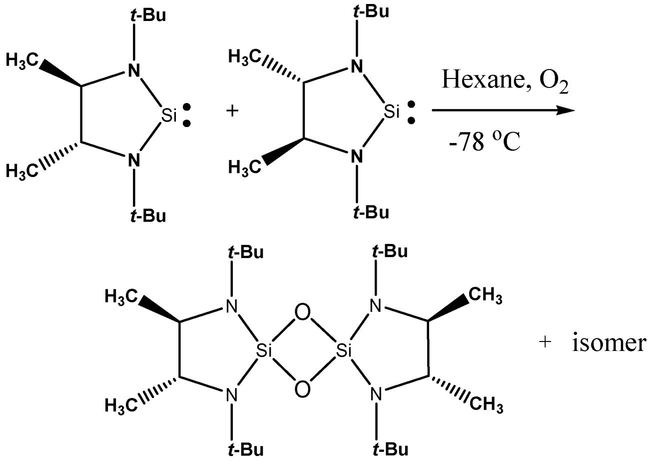
are formed; the *rac* isomer **8** was crystallized, and its structure was determined by X-ray crystallography (Figure 3).

Silylenes **5a**,**b** react with a stoichiometric amount of oxygen in hexane at −78 °C to yield the corresponding 1.3-disiladioxetane (Scheme 4). In this case the *meso* isomer **9** was crystallized and its structure was determined by a single-crystal X-ray study, as shown in Figure 4. Surprisingly, the *rac* isomer was isolated as a colorless liquid. Although silylene **2** reacts with 2,3-dimethylbutadiene to afford a 1-silacyclopent-3-ene compound, the new silylene **5a**,**b** catalyzes the polymerization of 2,3-dimethylbutadiene.

Scheme 4. Reaction of 5a,b with Oxygen



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In conclusion, the new N-heterocyclic saturated silylenes **5a**,**b**, which are monomeric in their pure state, have been synthesized.

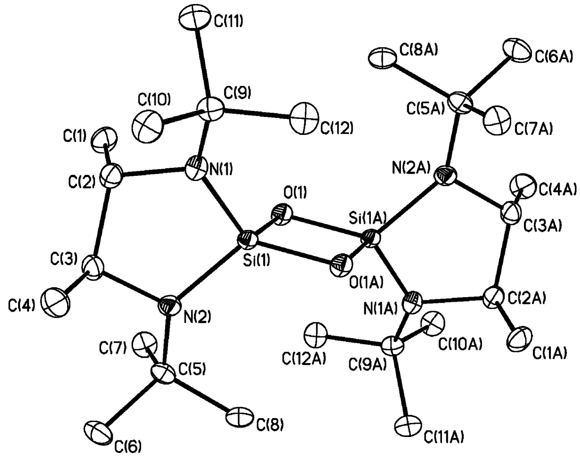

Figure 4. Molecular structure of **9**. Thermal ellipsoids are given at the 40% probability level, and the hydrogen atoms at the carbon atom are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)−N(1), 1.7099(15); Si(1)−N(2), 1.7179(15); Si(1)−O(1), 1.7148(13); Si(1)−O(1)#1, 1.6581(13); O(1)#1−Si(1)−O(1), 87.08(6); Si(1)#1−O(1)−Si(1), 92.92(6); N(1)−Si(1)−N(2), 94.81(7); N(1)−Si(1)−O(1), 118.85(7); O(1)−Si(1)−N(2), 114.51(7).

Future modification of the saturated silylene structure by introduction of different groups as well as theoretical calculations may shed light on the puzzling difference between **2** and **5a**,**b**. Resolution of enantiomers of the new silylene may lead to a chiral silylene chemistry.

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Supporting Information Available: Text giving general experimental procedures, details of the preparation of **8** and **9**, and spectroscopic information and CIF files giving X-ray structural information on **6a**,**b**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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