ORGANIC LETTERS

2000
Vol. 2, No. 21
3373−3376

Stille-Type Cross-Coupling—An Efficient Way to Various Symmetrically and Unsymmetrically Substituted Methyl-Bipyridines: Toward New ATRP Catalysts†

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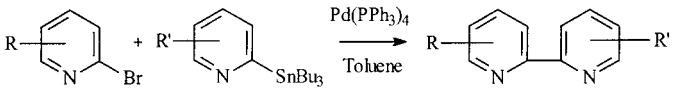
Received August 16, 2000

ABSTRACT



Various mono- and disubstituted 2,2′-bipyridines were synthesized in high yields and multigram scales utilizing Stille-type coupling procedures. The corresponding bromo-picoline and tributyltin-picoline building blocks were prepared from commercially available amino-picoline compounds. As first examples of metal complexes, 4,5′-dimethyl-2,2′-bipyridine was reacted with copper(II) and iron(II) ions and investigated as catalyst in ATRP.

Bipyridines have been well-known as highly interesting organic ligands for transition metals for more than a century.[1] In particular, the 2,2′-bipyridines were used in investigations in analytical chemistry,[2] medical chemistry,[3] and energy conversion.[4] The past decade revealed another area of interest concerning this type of ligands, based on the developments in polymer[5] and dendrimer science;[6] materials with novel photo-,[7] electrochemical,[8] or catalytic[9] features; and novel architectures in supramolecular chemistry.[10] In addition to these fascinating potential applications research still needs to develop directed synthetic routes to suitable bipyridine units, as well as effective functionalization strategies.

There is a great variety of methods described in the literature to synthesize substituted 2,2′-bipyridines.[11] However, many of the methods mainly result in a restriction of

† This paper is dedicated to Professor Dr. H. Kessler of the Technische Universität München on the occasion of his 60th birthday.

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10.1021/ol006473s CCC: $19.00
Published on Web 09/28/2000

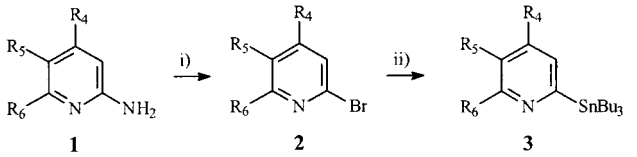
possible functionalization positions, such as with the well-known Kröhnke procedure,[12] or in isomeric mixtures when using Raney nickel catalysts.[13] Other interesting ways to build bipyridines are the extrusion of organophosphorus compounds[14] or ligand coupling with organosulfur compounds.[15] In addition, there are some modern strategies to synthesize monoalkyl-2,2′-bipyridines, e.g., the Suzuki coupling[16] or especially the Negishi-type cross-coupling reaction between pyridyl triflates and pyridyl zinc reagents,[17] which result in excellent yields of the desired products.

In contrast to such monosubstituted methyl-bipyridines and symmetrically disubstitued methyl-2,2′-bipyridines, the unsymmetrically disubstituted methyl-bipyridines are not as common. 5,6′-Dimethyl-2,2′-bipyridine has not yet been synthesized and 4,6′- and the 4,5′-dimethyl-2,2′-bipyridines are reported only as byproducts of the reaction of pyridine-*N*-oxides with pyridine derivatives.[18a] However, such methyl-bipyridines can be used very efficiently as precursors for halomethyl-bipyridines, which can be synthesized via classical NBS halogenation[19] and in very high yields via a new "TMS route".[20] Furthermore, these bipyridines play an important role as ligands for catalysts, e.g., in the recently developed atom transfer radical polymerization (ATRP) methodology.[9c−f]

We describe here a large scale synthetic strategy toward various methyl-substituted 2,2′-bipyridines based on Stille-type cross-coupling reactions utilizing palladium catalysts. This approach was developed during our research on the development of ATRP catalysts and metallo-supramolecular initiators for living and controlled polymerizations.[21]

As basic starting materials we used cheap and commercially available 4-, 5-, and 6-methyl-2-aminopyridines. Following a modified literature procedure[22a] the corresponding 2-bromo-picolines could be synthesized in a 150-g scale in a special 4-L glass reactor (Scheme 1 and Table 1).[23]

Scheme 1[a]



1 **2** **3**

[a] **1a**, **2a**, **3a**: $R_4 = CH_3$; **1b**, **2b**, **3b**: $R_5 = CH_3$; **1c**, **2c**, **3c**: $R_6 = CH_3$. (i) (a) 48% HBr, Br_2 (b) $NaNO_2$, −20 °C (c) NaOH, −15 °C; (ii) (a) *n*-BuLi, THF, −78 °C (b) Bu_3SnCl.

Table 1

compound	R_4	R_5	R_6	yield (%)	lit. yield[a] (%)
2a	CH_3	H	H	85	80 ref 22b
2b	H	CH_3	H	89	93 ref 22a
2c	H	H	CH_3	90	68 ref 24
3a	CH_3	H	H	50	
3b	H	CH_3	H	99	84 ref 25a,b
3c	H	H	CH_3	99	

[a] Described in the cited paper (different approaches).

Reaction with *n*-butyllithium at −78 °C gave the corresponding lithio compounds, which were immediately treated

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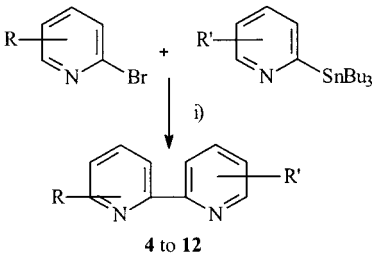
with tributyltin chloride to yield the desired 2-tributylstannyl-picolines using Kugelrohr distillation for purification (Scheme 1 and Table 1).[26] The compounds **2b** and **2c** reacted nearly quantitatively, whereas the 4-position (**2a**) gave only 50% yield. This is probably due to a partial decomposition of that material.

All of the different methyl-substituted 2,2′-bipyridines (monomethyl-substituted, dimethyl-substituted; symmetrically and unsymmetrically substituted) were then synthesized utilizing Stille-type palladium-catalyzed cross-couplings of the 2-bromo-picolines **2a**−**c** with the corresponding 2-tributylstannyl-picolines **3a**−**c**, using tetrakis(triphenylphosphine)-palladium as catalyst and toluene as solvent (Scheme 2 and Table 2).[27]

Scheme 2[a]



[a] (i) $Pd(PPh_3)_4$, toluene, reflux 48 h.

The yields were found to be between 50% and 87% and show no clear dependency on the substitution pattern. Most prepared bipyridines were white solids with melting points between 39 and 174 °C. As expected, the symmetrically disubstituted bipyridines revealed the highest melting points (89−174 °C), whereas the crystalline monomethyl-substituted bipyridines and the unsymmetrically dimethyl-substituted bipyridines showed melting points in the same rather low-temperature range (41−51 °C).

Table 2

bpy	no.	R_4	R_5	R_6	$R_{4'}$	$R_{5'}$	$R_{6'}$	yield (%)	lit. yield[a] (%)
4-	**4**	CH_3	H	H	H	H	H	56	92 ref 17
5-	**5**	H	CH_3	H	H	H	H	64	85 ref 17
6-	**6**	H	H	CH_3	H	H	H	75	88 ref 17
6,6′-	**7**	H	H	CH_3	H	H	CH_3	50	51 ref 25a
5,5′-	**8**	H	CH_3	H	H	CH_3	H	87	36 ref 19a
4,4′-	**9**	CH_3	H	H	CH_3	H	H	67	40 ref 18b
4,6′-	**10**	CH_3	H	H	H	H	CH_3	72	13 ref 18a
5,6′-	**11**	H	CH_3	H	H	H	CH_3	67	
4,5′-	**12**	CH_3	H	H	H	CH_3	H	80	13 ref 18a

[a] Described in the cited paper (different approaches).

The prepared bipyridine derivatives represent very interesting building blocks for further functionalization or use for metal complexation. This could lead to novel supramolecular assemblies, metallo-supramolecular architectures, and new catalysts, as well as metal-containing polymers. As first examples in the direction of new catalysts we reacted the interesting unsymmetrical 4,5′-dimethyl-2,2′-bipyridine with copper(II) acetate and iron(II) acetate.[28] The corresponding octahedral metal complexes **13** and **14** were formed by self-assembly processes in methanol and could be isolated after anion exchange utilizing a large excess of ammonium hexafluorophosphate in 40% and 34% yield, respectively (Figure 1). Depending on the metal ion used, blue or red

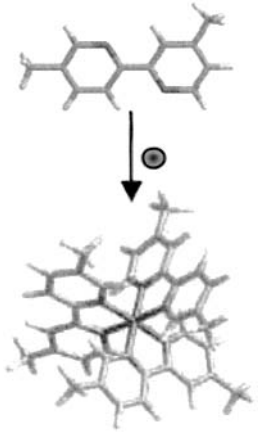


Figure 1. Copper(II)-*tris*(4,5′-dimethyl-2,2′-bipyridine)-hexafluorophosphate **13**. HyperChem modeling; MM^+ force field calculation (● = Cu(II) ion).

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(23) **2-Bromo-picolines. General Synthetic Strategy.** Powdered 2-amino-picoline (100 g, 0.92 mol) was added under vigorous stirring in portions to 48% hydrobromic acid (500 mL) at 20 to 30 °C in a 4-L glass reactor. After all of the compound was dissolved, the mixture was cooled at −20 °C. To this suspension was added cooled bromine (133 mL, 2.59 mol) dropwise over 30 min, maintaining the temperature at −20 °C. The resulting paste was stirred for 90 min at this temperature. Then sodium nitrite (170 g, 2.46 mol) in water (250 mL) was added dropwise. After that the reaction mixture was allowed to warm to 15 °C over 1 h and was stirred for an additional 45 min. The mixture was cooled to −20 °C and treated with cooled aqueous NaOH (667 g, 1000 mL H_2O). During the addition the temperature was kept at −10 °C maximum. The mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was extracted with ethyl acetate, the organic phase was dried with Na_2SO_4, and the solvent was removed in vacuo. The residue was subjected to distillation in vacuo to yield the desired 2-bromo-picoline. Selected analytical data follows. **2a**: white solid, mp 39.5 °C (lit.[24] 39−40 °C); ^{1}H NMR ($CDCl_3$) δ (ppm) 2.23 (s, 3 H, H-7), 6.94 (d, 1 H, J = 4.96 Hz, H-5), 7.20 (s, 1 H, H-3), 8.10 (d, 1 H, J = 4.95 Hz, H-6). Anal. C_6H_6NBr (172.02): calcd C, 41.86; H, 3.49; N, 8.14; found C, 41.48; H, 3.54; N 8.08. **2b**: white solid, mp 39−40 °C (lit.[22a] 41 °C); ^{1}H NMR ($CDCl_3$) δ (ppm) 2.28 (s, 3 H, H-7), 7.35 (d, 2 H, J = 1.5 Hz, H-3, 4), 8.19 (1 H, s, H-6). Anal. C_6H_6BrN (172.02): calcd C, 41.86; H, 3.49; N, 8.14; found C, 41.76; H, 3.50; N, 8.19. **2c**: colorless liquid, bp 129−132 °C (2.6 mbar) (lit.[22b] 87 °C, 13 mbar); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 2.49 (s, 3 H, H-7), 7.08 (d, 1 H, J = 7.6 Hz, H-5), 7.24 (d, 1 H, J = 7.6 Hz, H-3), 7.41 (t, 1 H, H-4). Anal. C_6H_6BrN (172.02): calcd C, 41.86; H, 3.49; N, 8.14; found C, 41.68; H, 3.40; N, 7.97.

crystals could be isolated and characterized utilizing elemental analysis, UV−vis spectroscopy, NMR spectroscopy, and MALDI-TOF mass spectrometry.

The metal complexes **13** and **14** can be directly used as catalysts in ATRP, opening a novel entrance to tailor-made catalysts for this academically and industrially important polymerization process. First results revealed an enormous influence on the polymerization behavior, which should lead to an intelligent catalyst design[29] (see also ref 9d,f).

The described synthetic procedures yield a variety of different methyl-substituted 2,2′-bipyridines in multigram quantities, utilizing bromination of amino-picolines and Stille-coupling procedures. As a first application the 4,5′-dimethyl-2,2′-bipyridine ligand was utilized for the preparation of the corresponding copper(II) and iron(II) complexes. Further studies concerning the behavior as catalysts in ATRP, as intercalation agents, and for the construction of extended metallo-supramolecular architectures or metal-containing polymers are currently in progress.

Acknowledgment. This study was supported by the Bayerisches Staatsministerium für Unterricht, Kultus, Wissenschaft und Kunst, the Fonds der Chemischen Industrie, and the Deutsche Forschungsgemeinschaft (SFB 266, Teilprojekt B 15 and Schu-1229/5-1). We thank Reilly Tar and Chemical Corp., Indianapolis, IN for contributing some of the amino-picoline starting material.

OL006473S

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(26) **2-Tributylstannyl-picolines.** To 2-bromo-picoline (28.4 g, 165 mmol) in absolute THF (250 mL) at −78 °C was added dropwise *n*-butyllithium (110 mL, 178 mmol, 1.6 M in hexane). After the solution was stirred at −78 °C for 90 min, tributyltinchloride (53.6 mL, 198 mmol) was added, and the mixture was allowed to warm to room temperature. Water (90 mL) was poured into the reaction mixture, and the phases were separated. The aqueous layer was extracted with diethyl ether (4 × 200 mL). The combined organic phases were dried over Na_2SO_4, and the solvent was removed in vacuo. The resulting oil was purified by fractionated Kugelrohr distillation. Selected analytical data follows. **3a**: colorless liquid, bp 120 °C (2.5×10^{-5} mbar); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.81 (t, 9 H J = 7.25 Hz, H-4′), 1.04 (t, 6 H, J = 8.21 Hz, H-1′), 1.26 (m, 6 H, H-3′), 1.49 (m, 6 H, H-2′), 2.21 (s, 3 H, H-7), 6.85 (d, 1 H, J = 4.96 Hz, H-4), 7.14 (s, 1 H, H-3), 8.51 (d, 1 H, J = 4.96 Hz, H-6). Anal. $C_{18}H_{33}NSn$ (382.2): calcd C, 56.56; H, 8.64; N, 3.67; found C, 56.22; H, 8.70; N, 3.21. **3b**: colorless liquid, bp 130 °C (5×10^{-6} mbar) (lit.[25a] 130−135 °C, 0.7 mbar); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.88 (t, 9 H, J = 7.25 Hz, H-4′), 1.11 (t, 6 H, J = 8.01 Hz, H-1′), 1.32 (m, 6 H, H-3′), 1.56 (m, 6 H, H-2′), 2.28 (s, 3 H, H-7), 7.30 (m, 2 H, H-3, 4), 8.59 (s, 1 H, H-6). Anal. $C_{18}H_{33}NSn$ (382.2): calcd C, 56.56; H, 8.64; N, 3.67; found C, 56.29; H, 8.84; N, 3.78. **3c**: colorless liquid, bp 140 °C (5×10^{-5} mbar); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 0.88 (t, 9 H, J = 7.25 Hz, H-4′), 1.02 (t, 6 H, J = 8.02 Hz, H-1′), 1.26 (m, 6 H, H-3′), 1.49 (m, 6 H, H-2′), 2.46 (s, 3 H, H-7), 6.87 (d, 1 H, J = 8.01 Hz, H-3), 7.10 (d, 1 H, J = 7.63 Hz, H-5), 7.28 (t, 1 H, J = 7.63 Hz, H-4). Anal. $C_{18}H_{33}NSn$ (382.2): calcd C, 56.56; H, 8.64; N, 3.67; found C, 56.35; H, 8.66; N, 3.41.

(27) **Bipyridines.** A mixture of 2-tributylstannyl-picoline or 2-tributylstannyl-pyridine (27.0 mmol), 2-bromo-picoline or 2-bromo-pyridine (23.0 mmol), and tetrakis(triphenylphosphine)-palladium(0) (0.95 g, 0.82 mmol) in 65 mL of toluene was refluxed under nitrogen for 48 h. The resulting brown mixture was evaporated in vacuo, and the dark, muddy liquid was dissolved in dichloromethane. The organic phase was washed with aqueous HCl (3 × 20 mL, 6 M). To remove the product from solution the combined aqueous layers were transferred dropwise in aqueous ammonia (10%) under cooling. The resulting oil was extracted with CH_2Cl_2 (3 × 30 mL). The organic phases were washed with ammonia and water, and the solvent was removed. The resulting suspension was purified by column chromatography. Selected analytical data follows. **4**: white solid, mp 61.5 °C (lit.[17] 62−64 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 2.36 (s, 3 H, H-7), 7.06 (d, 1 H, J = 4.96 Hz, H-5), 7.23 (m, 1 H, H-5′), 7.73 (m, 1 H, H-4′), 8.16 (s, 1 H, H-3), 8.32 (d, 1 H, J = 8.01 Hz, H-3′), 8.46 (d, 1 H, J = 4.57 Hz, H-6′), 8.60 (m, 1 H, H-6). Anal. $C_{11}H_{10}N_2$ (170.2): calcd C, 77.65; H, 5.88; N, 16.47; found C, 77.30; H, 5.85; N, 16.35. **5**:[11a,17] colorless liquid; ^{1}H NMR ($CDCl_3$) δ (ppm) 2.27 (s, 3 H, H-7), 7.16 (m, 1 H, H-5′), 7.50 (d, 1 H, J = 7.50 Hz, H-4), 7.67 (m, 1 H, H-4′), 8.19 (d, 1 H, J = 8.01 Hz, H-3), 8.26 (d, 1 H, J = 8.01 Hz, H-3′), 8.40 (s, 1 H, H-6), 8.56 (d, J = 4.58 Hz, H-6′). Anal. $C_{11}H_{10}N_2$ (170.2): calcd C, 77.65; H, 5.88; N, 16.47; found C, 77.79; H, 5.92; N, 16.34. **6**: colorless liquid, bp 118 °C (0.1 mbar) (lit.[11a] bp 73 °C, 2.7×10^{-2} mbar; lit.[17] mp 37−38 °C); ^{1}H NMR ($CDCl_3$) δ (ppm) 2.52 (s, 3 H, H-7), 7.03 (d, 1 H, J = 7.63 Hz, H-5), 7.15 (m, 1 H, H-5′), 7.57 (dd, 1 H, J = 8.01, 7.63 Hz, H-4), 7.66 (m, 1 H, H-4′), 8.07 (d, 1 H, J = 8.01 Hz, H-3), 8.30 (d, 1 H, J = 7.63 Hz, H-3′), 8.56 (m, 1 H, H-6′). Anal. $C_{11}H_{10}N_2$ (170.2): calcd C, 77.65; H, 5.88; N, 16.47; found C, 77.20; H, 5.96; N, 16.21. **7**: white solid, mp 89 °C (lit.[25a] 89−90 °C); ^{1}H NMR ($CDCl_3$) δ (ppm) 2.56 (s, 6 H, H-7, 7′), 7.08 (d, 2 H, J = 7.63 Hz, H-5, 5′), 7.61 (dd, 2 H, J = 7.63, 8.01 Hz, H-4, 4′), 8.11 (d, 2 H, J = 7.63 Hz, H-3, 3′). Anal. $C_{12}H_{12}N_2$ (184.2): calcd C, 78.26; H, 6.52; N, 15.22; found C, 78.11; H, 6.56; N, 15.12. **8**: white solid, mp 114−115 °C (lit.[19a] 114−116 °C); ^{1}H NMR ($CDCl_3$) δ (ppm) 2.37 (s, 6 H, H-7, 7′), 7.60 (dd, 2 H, J = 8.2, 2.1 Hz, H-4, 4′), 8.24 (d, 2 H, J = 8.0 Hz, H-3, 3′), 8.48 (s, 2 H, H-6, 6′). Anal. $C_{12}H_{12}N_2$ (184.2): calcd C, 78.26; H, 6.52; N, 15.22; found C, 78.02; H, 6.54; N, 15.16. **9**: white solid, mp 173.5 °C (lit.[18b] 171−172 °C); ^{1}H NMR ($CDCl_3$) δ (ppm) 2.37 (s, 6 H, H-7, 7′), 7.06 (d, 2 H, J = 4.96 Hz, H-5, 5′), 8.16 (s, 2 H, H-3, 3′), 8.46 (d, 2 H, J = 4.96 Hz, H-6, 6′). Anal. $C_{12}H_{12}N_2$ (184.2): calcd C, 78.26; H, 6.52; N, 15.22; found C, 77.91; H, 6.46; N, 14.88. **10**: white solid, mp 41 °C; ^{1}H NMR ($CDCl_3$) δ (ppm) 2.36 (s, 3 H, H-7), 2.56 (s, 3 H, H-7′), 7.03 (d, 1 H, J = 4.96 Hz, H-5), 7.08 (d, 1 H, J = 7.63 Hz, H-5′), 7.61 (t, 1 H, J = 7.82 Hz, H-4′), 8.08 (d, 1 H, J = 7.63 Hz, H-3′), 8.16 (s, 1 H, H-3), 8.45 (d, J = 4.96 Hz, H-6). Anal. $C_{12}H_{12}N_2$ (184.2): calcd C, 78.26; H, 6.52; N, 15.22; found C, 77.92; H, 6.66; N, 15.05. **11**: white solid, mp 51 °C; ^{1}H NMR ($CDCl_3$) δ (ppm) 2.38 (s, 3 H, H-7), 2.63 (s, 3 H, H-7′), 7.14 (d, 1 H, J = 7.63 Hz, H-5′), 7.60 (m, 1 H, H-4), 7.68 (dd, 1 H, J = 7.63, 8.01 Hz, H-4′), 8.14 (d, 1 H, J = 8.01 Hz, H-3′), 8.28 (m, 1 H, H-3), 8.49 (s, 1 H, H-6). Anal. $C_{12}H_{12}N_2$ (184.2): calcd C, 78.26; H, 6.52; N, 15.22; found C, 78.24; H, 6.92; N, 14.83. **12**: white solid, mp 54 °C (lit.[18a] 58−60 °C); ^{1}H NMR ($CDCl_3$) δ (ppm) 2.37 (s, 3 H, H-7), 2.42 (s, 3 H, H-7′), 7.10 (m, 1 H, H-5), 7.60 (m, 1 H, H-4′), 8.18 (s, 1 H, H-3), 8.25 (m, 1 H, H-3′), 8.43 (m, 1 H, H-6), 8.45 (m, 1 H, H-6′). Anal. $C_{12}H_{12}N_2$ (184.2): calcd C, 78.26; H, 6.52; N, 15.22; found C, 78.24; H, 6.76; N, 15.03.

(28) **Copper(II)-*tris*(4,5′-dimethyl-2,2′-bipyridine)-hexafluorophosphate 13.** Blue solid, mp > 250 °C. Anal. $C_{36}H_{36}CuF_{12}N_6P_2 \cdot H_2O$ (924.2): calcd. C, 46.79; H, 4.14; N, 9.09; found C, 46.41; H, 4.05; N, 8.64. UV−vis (CH_3CN) λ_{max} nm (ϵ/(L × mol^{-1} × cm^{-1})) 298 (34500), 249 (35700). **Iron(II)-*tris*(4,5′-dimethyl-2,2′-bipyridine)-hexafluorophosphate 14.** Red crystals, mp > 250 °C.^{1}H NMR (CD_3CN, 300 MHz) δ (ppm) 2.17 (s, 9 H), 2.52 (s, 9 H), 7.13 (m, 9 H), 7.88 (d, 3 H, J = 8.20 Hz), 8.33 (m, 6 H). Anal. $C_{36}H_{36}FeF_{12}N_6P_2 \times 2\ H_2O$ (934.5): calcd C, 46.27; H, 4.31; N, 8.99; found C, 45.79; H, 4.11; N, 9.31. UV−vis (CH_3CN: λ_{max} nm (ϵ/(L × mol^{-1} × cm^{-1})) 520 (7300), 355 (6200), 300 (58000), 253 (29000).

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