Stereoselective Synthesis of Silyl Enol Ethers via the Iridium-Catalyzed Isomerization of Allyl Silyl Ethers

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Received September 22, 1998

The stereoselective isomerization of allyl silyl ethers to (*E*)- or (*Z*)-silyl enol ethers was carried out in the presence of a cationic iridium(I) catalyst. The complex, prepared in situ by treating $[Ir(cod)_2]PF_6/2PPr_3$ with hydrogen, was found to be an excellent catalyst for the isomerization of primary and secondary allyl ethers in high yields. The primary allyl silyl ethers produced *(E)*-enol ethers and the secondary allyl ethers afforded (*Z*)-enol ethers with high stereoselectivity, often exceeding 99%.

Introduction

Considerable attention has recently been focused on the synthesis of silyl enol ethers due to their usefulness in various synthetic transformations.[1] One of the early and still one of the most frequently used routes to (*E*)- or (*Z*)-silyl enol ethers is the trapping of ketone or aldehyde enolates generated under conditions of either kinetic- or equilibrium-controlled conditions.[2] The catalytic isomerization of allyl ethers is another convenient and straightforward method that allows the large-scale preparation of silyl enol ethers.[3] Many metal complexes have been reported to be effective catalysts for the isomerization of allylic ethers,[4] but the stereoselectivity of such transformations has not received much attention. The enol ethers thus obtained are either (*Z*)- or (*E*)-isomers or, in most cases, a mixture of the two. For example, the ruthenium complex gives an equilibrium mixture with the (*Z*)-enol ether predominating (*Z* > 55−68%).[5] In contrast, the cationic iridium(I) complex stereospecifically produces (*E*)-enol ethers (*E* > 97%).[6] We have recently demonstrated the efficiency of the cationic iridium catalyst for the stereoselective preparation of (*E*)-γ-alkoxyallylboronates from (3-alkoxy-1-alkenyl)boronates.[7] However, difficulty in reproducing the high stereoselectivities with various substrates prompted us to reinvestigate the reaction in detail using allyl silyl ethers. The iridium(I) complex was prepared in situ by treating $[Ir(cod)_2]PF_6/2PPr_3$ with hydrogen and was found to be an excellent catalyst for achieving high yields and high stereoselectivity in the isomerization of various allyl silyl ethers under mild conditions (eqs 1 and 2).[8]

Results and Discussion

Reaction Conditions. The iridium(I) catalyst active for the isomerization of primary allyl ethers was prepared in situ by treatment of $[Ir(cod)(PPh_2Me)_2]PF_6$ (cod = 1,5-cyclooctadiene)[6] with hydrogen or metal hydrides, as shown in Table 1.

Hydrogen, catecholborane, and diisobuthylaluminum hydride (DIBAL-H) were found to be very effective in removing the cod ligand in $[Ir(cod)(PPh_2Me)_2]PF_6$ via hydrogenation[9] or hydrometalation (entries 1, 2, and 4), but the use of catecholborane is recommended because of the operational simplicity in its use to achieve reproducible results. The isomerization was readily initiated by the addition of catecholborane (1 equiv to the Ir complex) to a mixture of $[Ir(cod)(PPh_2Me)_2]PF_6$ and an allyl silyl ether. Various metal hydrides hydro-

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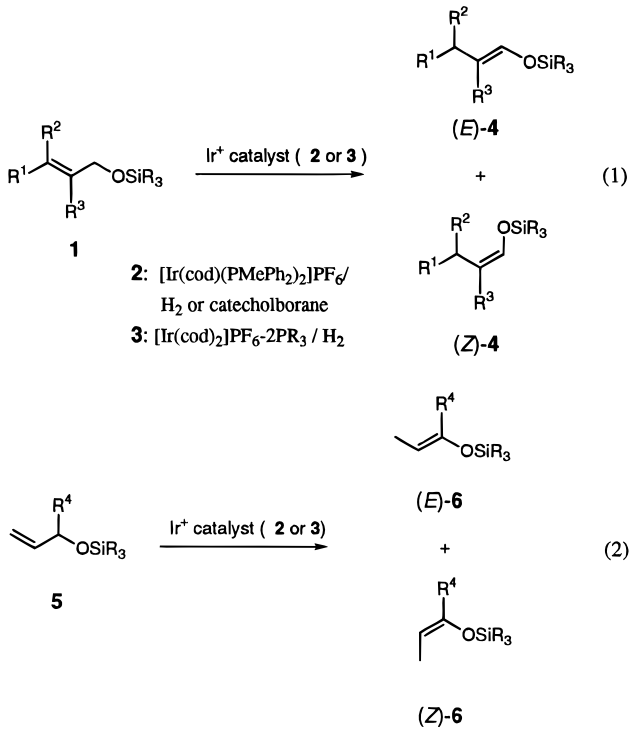
10.1021/om980794e CCC: $18.00
Publication on Web 12/31/1998

Table 1. Preparation of Catalysts[a]

entry	reducing agent	yield/%[b]	*E*/*Z*
1	H_2	92	92/8
2	catecholborane	93	81/19
3	9-BBN	0	
4	DIBAL-H	84	91/9
5	$HSiCl_3$	0	
6	$HSiEt_3$	22	100/0
7	$HSnBu_3$	25	100/0

[a] All reactions were carried out in THF at 20 °C for 30 min using **1** ($R^1 = C_3H_7$, R^2, $R^3 = H$, $SiR_3 = Si^tBuMe_2$) (0.5 mmol) and an iridium catalyst obtained in situ from $[Ir(cod)(PPh_2Me)_2]PF_6$ (3 mol %) and a reducing reagent (3 mol %). [b] Isolated yields.



metalate alkenes either in the presence of or in the absence of a catalyst, but the addition of 9-borabicyclo-[3.3.1]nonane (9-BBN), silanes, or stannanes resulted in lower yields (entries 3, 5, 6, and 7).

The effects of solvent and reaction time on yields and stereoselectivity in the isomerization of a primary allyl ether **1** ($R^1 = C_3H_7$; R^2, $R^3 = H$; $SiR_3 = Si^tBuMe_2$) are shown in Table 2.

The order of donor strength of solvents to the iridium metal center is $H_2O \cong$ THF < ^{t}BuOH < ^{i}PrOH < acetone < EtOH < MeCN.[10] No reaction was observed in a solvent that strongly coordinates to the metal such as DMF and MeCN (entries 1 and 2). In contrast, the reaction was very fast in methylene chloride, but an equilibrium mixture of both stereoisomers resulted in a nondonor solvent (entry 7). Promising results were obtained in acetone and THF (entries 3−5). Although the reactions in both solvents achieved complete conversion within 30 min with high (*E*)-stereoselectivities (entries 3 and 5), the product of the reaction in THF tended to isomerize slowly to an (*E*)- and (*Z*)-**4** mixture

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Table 2. Effects of Solvent and Reaction Time on the Isomerization of 1 ($R^1 = C_3H_7$, R^2, $R^3 = H$, $SiR_3 = Si^tBuMe_2$)[a]

entry	solvent	time (min)	conversion/%[b]	*E*/*Z*
1	DMF	30	0	
2	CH_3CN	30	0	
3	acetone	30	99	*E*>99
4		900	99	96/4
5	THF	30	99	97/3
6		1440	99	51/49
7	CH_2Cl_2	30	99	32/68
8	CH_2Cl_2/acetone (50/1)	5[c]	61	98/2
9		20[c]	95	95/5
10		60[c]	>99	85/15
11		180[c]	>99	57/43
12		360[c]	>99	38/62

[a] A mixture of **1** ($R^1 = C_3H_7$, R^2, $R^3 = H$, $SiR_3 = Si^tBuMe_2$), $[Ir(cod)(PPh_2Me)_2]PF_6$ (3 mol %), and catecholborane (3 mol %) was stirred at 20 °C. [b] The ratio of product/substrate. [c] The reactions were carried out at 0 °C in a NMR tube.

because of its lower donor ability compared to that of acetone (entry 6). Thus, acetone was recognized as the best solvent, to achieve both quantitative conversion and high (*E*)-selectivity, since the undesirable *cis*−*trans* isomerization was very much slower than the positional isomerization of the double bond.

The NMR study of the reaction mixture of **1** ($R^1 = C_3H_7$; R^2, $R^3 = H$; $SiR_3 = Si^tBuMe_2$) and **2** (3 mol %) in CD_2Cl_2/acetone-d_6 (50/1) at 0 °C revealed that the reaction involves two isomerization processes; the positional isomerization of the double bond to give (*E*)-**4** was followed by its stereochemical isomerization leading to a mixture of (*E*)- and (*Z*)-**4** (entries 8−12). The initial reaction to give the (*E*)-**4** was very fast and highly stereoselective (entries 8 and 9), but the enol ether thus obtained was slowly converted into an equilibrium mixture (*E*/*Z* = 38/62) upon prolongation of the reaction time over 6 h (entry 12). In another experiment, an equilibrium mixture of **4** (*E*/*Z* = 33/67) also resulted when a pure (*E*)- or (*Z*)-enol ether **4** ($R^1 = C_3H_7$, R^2, $R^3 = H$, and $SiR_3 = Si^tBuMe_2$) was independently treated with **2** (3 mol %) at 20 °C for 30 min in CH_2Cl_2/acetone (80/1). Although the (*Z*)-selectivity often exceeded 70%, all attempts at obtaining 100% (*Z*)-silyl enol ethers were unsuccessful for primary allyl silyl ethers.

The effect of catalysts on the isomerization of **5** ($R^4 =$ Ph, $SiR_3 = Si^tBuMe_2$) is shown in Table 3.

The catalyst developed by Felkin[6] efficiently catalyzes the isomerization of various primary allyl ethers, but unfortunately it was not effective for secondary allyl ethers (entry 1). The treatment of $[Ir(cod)(PPh_2Me)_2]PF_6$ with catecholborane generated a more active catalyst solution than that with hydrogen, but arylphosphine derivatives did not give good results due to their large steric hindrance (entries 2 and 3). Finally, Ir-trialkylphosphine complexes (**3**) obtained by hydrogenation of a mixture of $[Ir(cod)_2]PF_6$ and PR_3 (R = Et, Pr, Bu) (2 equiv) were found to be excellent catalysts for the isomerization of secondary allyl ethers with the (*Z*)-**6** predominating (*Z*, 88−92%) (entries 5−7). The reaction was very slow in pure acetone, but fast in a mixed solvent of CH_2Cl_2/acetone. Trimethylphosphine, tricyclohexylphosphine (PCy_3), and bidentate phosphine ligands such as dppe (1,2-bis(diphenylphosphino)ethane) were not effective (entries 4, 8, and 9).

Table 3. Effect of Catalyst on the Isomerization of 5 (R^4 = Ph, SiR_3 = Si^tBuMe_2)

entry	catalyst	yield/%	*E*/*Z*
1	$[Ir(cod)(PPh_2Me)_2]PF_6/H_2$[a]	trace	
2	$[Ir(cod)(PPh_2Me)_2]PF_6$/catecholborane[b]	12	36/64
3	$[Ir(cod)(PPh_3)_2]PF_6$/catecholborane[b]	10	42/58
4	$[Ir(cod)_2]PF_6-2PMe_3/H_2$[a]	0	
5	$[Ir(cod)_2]PF_6-2PEt_3/H_2$[a]	76	8/92
6	$[Ir(cod)_2]PF_6-2PPr_3/H_2$[a]	92	12/88
7	$[Ir(cod)_2]PF_6-2PBu_3/H_2$[a]	96	10/90
8	$[Ir(cod)_2]PF_6-2PCy_3/H_2$[a]	0	
9	$[Ir(cod)_2]PF_6$-dppe/H_2[a]	0	

[a] To a solution of $[Ir(cod)(PR_3)_2]PF_6$ (0.015 mmol) (entry 1) or a mixture of $[Ir(cod)_2]PF_6$ (0.015 mmol) and R_3P (0.03 mmol) (entries 1 and 4−9) in CH_2Cl_2 (3 mL)/acetone (0.037 mL, 0.5 mmol) treated with H_2 was added **5** (R^4 = Ph, SiR_3 = Si^tBuMe_2) (0.5 mmol), and the resulting solution was then stirred for 30 min at room temperatuture. [b] To a solution of $[Ir(cod)(PR_3)_2]PF_6$ (0.015 mmol) and **5** (R^4 = Ph, SiR_3 = Si^tBuMe_2) (0.5 mmol) was added catecholborane (0.015 mmol) at room temperature.

Scope and Limitations. The two catalysts (**2** and **3** (R = Pr)) are compared for the isomerization of the representative primary allyl silyl ethers (Table 4).

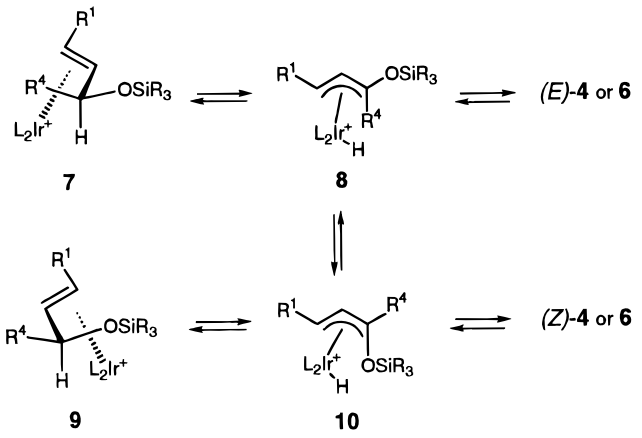
Both catalysts readily achieved complete conversion within 20 min at room temperature, providing (*E*)-**4** in high yields and with high selectivity (entries 1−4). The concentration of the catalyst often affects the selectivity. Thus, the isomerization of the crotyl ether in the presence of 3 mol % of **3** resulted in *E*/*Z* = 97/3, but a similar reaction with 1 mol % of **3** gave 99% (*E*)-selectivity (entry 2). The use of a low concentration of **3** was also advantageous to achieve 99% (*E*)-selectivity in the reaction of the 2-hexenyl ether (entry 4). The (*E*)-selectivity was not significantly affected either by the bulkiness of the silyl ligands (entries 4−7) or by the stereochemistry of the starting allyl ether (entry 9), but the MOM (CH_3OCH_2) ether, which has potential ligating ability to the iridium metal center, gave a mixture of two stereoisomers (entry 8). The reaction of the prenyl ether was very slow, presumably due to its steric hindrance during the coordination to the iridium metal, but the tripropylphosphine complex **3** was active enough to induce the isomerization (entry 11). The reaction was very slow in acetone, but an 85% yield was readily achieved in a mixed solvent of CH_2Cl_2/acetone.

The results of the isomerization of various secondary allyl ethers are summarized in Table 5.

The Ir-arylphosphine complex **2** exceptionally catalyzed the isomerization of **5** (R = Me) with the predominating (*E*)-isomer when the reaction was carried out in CH_2Cl_2/acetone (80/1) (entries 2 and 3). A bulky tri(isopropyl)silyloxy ether gave 96% (*E*)-selectivity as the result of its large steric difference between the methyl and silyloxy groups (entry 3). The catalyst **2** was not effective for other secondary allyl ethers (entries 5, 8, and 12), but **3** apparently demonstrated a higher catalytic efficiency for secondary allyl ethers. Thus, a complete conversion within 30 min at 20 °C was readily achieved with the Ir-tripropylphosphine complex **3** (entries 1−12). The reaction predominantly produced the (*Z*)-isomer, the yield of which exceeded 99% when R^4 was the secondary alkyls (entries 5−8).

Mechanism. The isomerization mechanism involves the oxidative addition of an allylic C−H bond to the Ir(I) complex to give π-allyliridium species (**8** and **10**),

Scheme 1. Mechanism of Isomerization



followed by reductive elimination to afford enol ether **4** or **6** (Scheme 1).[6,11]

The isomerization involves two processes: the first and selective formation of (*E*)-**4** (kinetically controlled process) is followed by the equilibration to a mixture of (*E*)- and (*Z*)-**4** through the anti-π-allyl intermediate (thermodynamically controlled process). Both the oxidative addition and equilibration processes can be retarded in a solvent that strongly coordinates to the iridium metal, but they are very fast in CH_2Cl_2. Acetone, having a medium donor strength, allows the smooth oxidative addition of a primary allyl ether to **2** or **3** with retarding the *cis*, *trans*-isomerization process. The Ir-trialkylphosphine complexes **3**, having a relatively small cone angle, was highly effective for secondary allyl ethers because of the steric hindrance around the allylic hydrogen.

Thus, the stereochemistry of **4** was highly dependent on the catalyst, the solvent, reaction time, and the substrate. When primary allyl ethers were reacted in acetone, the kinetic products ((*E*)-**4**) were obtained through the *syn*-π-allyl intermediate (**7** → **8** → (*E*)-**4**). On the other hand, high (*Z*)-selectivity was achieved for secondary allyl ethers under the conditions leading to the equilibration because the steric difference between the R^4 and R_3Si groups controls the stereochemistry of the products (**7** → **8** → **10** or **9** → **10** → (*Z*)-**4**).

Experimental Section

$[Ir(cod)(PPh_2Me)_2]PF_6$,[12] $[Ir(cod)(PPh_3)_2]PF_6$,[13] $[Ir(cod)(PCy_3)(Py)]PF_6$,[14] and $[Ir(cod)_2]PF_6$[15] were prepared by the reported procedures.

Isomerization with $[Ir(cod)(PPh_2Me)_2]PF_6$/Catecholborane. A dry 25 mL flask equipped with a septum inlet and a magnetic stirring bar was charged with $[Ir(cod)(PPh_2Me)_2]$-

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Table 4. Isomerization of Primary Allyl Silyl Ethers (1)

						[Ir(cod)(PPh$_2$Me)$_2$]PF$_6$[a]		[Ir(cod)$_2$]PF$_6$/2PPr$_3$[b]	
entry	R^1	R^2	R^3	SiR$_3$	time (min)	yield/%	*E*/*Z*	yield/%	*E*/*Z*
1	H	H	H	Si^{t}BuMe$_2$	10	78	99/1	74	99/1
2	CH$_3$	H	H	Si^{t}BuMe$_2$	20	84	97/3	92[c]	99/1
3	H	H	CH$_3$	Si^{t}BuMe$_2$	20	91			
4	C$_3$H$_7$	H	H	Si^{t}BuMe$_2$	20	93	88/12	97[c]	99/1
5				SiPh$_2$Me	20	87	94/6		
6				SiPhMe$_2$	20	81	93/7		
7				SiMe$_3$	20	64	95/5		
8				CH$_2$OCH$_3$	20	84	68/32		
9	H	C$_3$H$_7$	H	Si^{t}BuMe$_2$	10	74	95/5		
10	Ph	H	H	Si^{t}BuMe$_2$	30	76	98/2	77	96/4
11	CH$_3$	CH$_3$	H	Si^{t}BuMe$_2$	240	<10		85[d]	88/12

[a] A mixture of [Ir(cod)(PPh$_2$Me)$_2$]PF$_6$ (3 mol %) and **1** (0.5 mmol) in THF was treated with catecholborane (3 mol %) at 20 °C. [b] A solution of [Ir(cod)$_2$]PF$_6$ (3 mol %) and PPr$_3$ (6 mol %) in acetone was treated with hydrogen to prepare the catalyst, which was then stirred with **1** at 20 °C. [c] The reaction was carried out for 10 min in the presence of 1 mol % of the catalyst. [d] The reaction was carried out in CH$_2$Cl$_2$/acetone (80/1). An 8% yield of **1** (R^1, R^2 = Me, R^3 = H) was recovered with an accompanying 2% of 2-methyl-4-(*tert*-butyldimethylsilyloxy)-1-butene.

Table 5. Isomerization of Secondary Allyl Silyl Ethers (5)

				[Ir(cod)(PPh$_2$Me)$_2$]PF$_6$[a]		[Ir(cod)$_2$]PF$_6$/2PPr$_3$[b]	
entry	R^4	SiR$_3$	time (min)	yield/%	*E*/*Z*	yield/%	*E*/*Z*
1	CH$_3$	SiMe$_3$	30			71[c]	26/74
2	CH$_3$	Si^{t}BuMe$_2$	30	82	72/28	89[c]	28/72
3	CH$_3$	Si^{i}Pr$_3$	30	96	96/4	95[c]	63/37
4	C$_2$H$_5$	SiMe$_3$	30			83	12/88
5	2-C$_3$H$_7$	SiMe$_3$	30	trace		89	*Z* > 99
6	CH(CH$_3$)C$_3$H$_7$	SiMe$_3$	30			93	*Z* > 99
7	CH(C$_2$H$_5$)C$_2$H$_5$	SiMe$_3$	30			92	*Z* > 99
8	*cyclo*-C$_6$H$_{11}$	SiMe$_3$	30	trace		96	*Z* > 99
9	^{t}C$_4$H$_9$	SiMe$_3$	30			3	
10	C$_5$H$_{11}$	SiMe$_3$	30			82[d]	21/79
11	Ph	SiMe$_3$	30			96	18/82
12	Ph	Si^{t}BuMe$_2$	30	trace		92	12/88

[a] A solution of [Ir(cod)(PPh$_2$Me)$_2$]PF$_6$ (3 mmol) and **5** (0.5 mmol) in CH$_2$Cl$_2$ (3 mL)/acetone (0.037 mL, 0.5 mmol) was treated with catecholborane (3 mol %) at 20 °C for 30 min. [b] A solution of [Ir(cod)$_2$]PF$_6$ (3 mol %) and PPr$_3$ (6 mol %) in CH$_2$Cl$_2$(3 mL)/acetone (0.037 mL, 0.5 mmol) was treated with hydrogen to prepeare the catalyst, which was then stirred with **5** (0.5 mmol) at 20 °C for 30 min. [c] The reaction was accompanied with 2-silyloxy-1-butene (5−6%). [d] A mixture of 3-(trimethylsilyloxy)-2-heptene (61%) and 3-(trimethylsilyloxy)-3-heptene (39%) was obtained.

PF$_6$ (0.015 mmol) and flushed with argon. Addition of THF (3 mL) or CH$_2$Cl$_2$ (3 mL) and acetone (0.5 mmol) gave a red suspension in THF or a clear-red solution in CH$_2$Cl$_2$. An allyl silyl ether (0.5 mmol) and catecholborane (0.015 mmol) were successively added. The solution turned to clear red within 3 min and was stirred for 30 min at room temperature. The reaction was quenched with ethylenediamine (0.03 mmol) to deactivate the catalyst. The crude mixture obtained by evaporation of the solvent was analyzed by ^{1}H NMR. The analytically pure product was isolated by column chromatography on silica gel or by bulb-to-bulb distillation.

Isomerization with [Ir(cod)$_2$]PF$_6$/2PR$_3$-H$_2$. A flask was charged with [Ir(cod)$_2$]PF$_6$ (0.015 mmol) and flushed with argon. CH$_2$Cl$_2$ (3 mL), acetone (0.5 mmol), and PR$_3$ (0.015 mmol of bidentate phosphine or 0.03 mmol of monodentate phosphine) were added. Dihydrogen was bubbled into the solution through a needle which reached beneath the surface of the liquid to give a light yellow solution. The excess dihydrogen was thoroughly replaced with argon by passing into the solution. To the catalyst solution thus obtained was added an allyl silyl ether (0.5 mmol), and the mixture was stirred at room temperature for the period shown in Table 5. The reaction was quenched by addition of ethylendiamine (0.03 mmol), and the organic phase was washed with water and dried with MgSO$_4$. The product was purified by chromatography on silica gel or bulb-to-bulb distillation.

^{1}H NMR Study of the Ir-Catalyzed Isomerization (Table 2, Entries 8−12). [Ir(cod)(PPh$_2$Me)$_2$]PF$_6$ (0.002 mmol) was charged in a NMR tube and flushed with argon. CDCl$_3$ (0.7 mL), (CD$_3$)$_2$CO (0.014 mL, 0.2 mmol), and (*E*)-1-(*tert*-butyldimethylsilyloxy)-2-hexene (0.1 mmol) were successively added. The tube was cooled to 0 °C, and catecholborane (0.002 mmol) was then injected to initiate the isomerization. The integration of vinylic protons of (*E*)-enolate at 5.0 and 6.2 ppm and (*Z*)-enolate at 4.4 and 6.1 ppm gave the (*E*/*Z*) ratio shown in Table 2.

Supporting Information Available: Spectral data and copies of ^{1}H NMR spectra of silyl enol ethers (22 pages). See any current masthead page for ordering information.

OM980794E

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