Asymmetric Synthesis

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Asymmetric Hydroxylative Phenol Dearomatization through In Situ Generation of Iodanes from Chiral Iodoarenes and *m*-CPBA**

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The quest for chiral hypervalent iodine (iodane) reagents capable of promoting asymmetric induction in oxygenating reactions, such as the oxidation of sulfides into sulfoxides, the α-oxygenation of ketones, the dioxygenation of olefins, and the oxygenative dearomatization of phenols into cyclohexadienone derivatives, continues to challenge the organic chemistry community.[1] The best results reported so far are: a) the oxidation of methyl *tert*-butylsulfide (56% *ee*) using a (+)-menthylated variant of the λ^3-iodane (i.e., iodine(III)) Koser reagent (**A**, Figure 1),[1a,c] and b) that of methyl *p*-tolylsulfide (29% *ee*) using a chiral λ^5-iodane (i.e., iodine(V)) *N*-(2-iodylphenyl)acylamide (NIPA) reagent developed by Zhdankin and co-workers (**B**, Figure 1);[1d] c) the α-oxytosylation of propiophenone (40% *ee*), and d) the dioxytosylation of styrene (65% *ee*) using a chiral Koser-type reagent developed by Wirth and co-workers (**C**, Figure 1);[1f] and e) an intramolecular dearomatizing spirolactonization of a series of naphthol derivatives (78–86% *ee*) using a chiral bis(λ^3-iodane) spirobiindane-based reagent recently developed by Kita and co-workers (**D**, Figure 1).[1h,15]

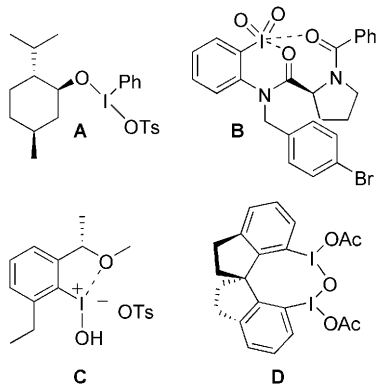

Figure 1. Select examples of chiral λ^3- and λ^5-iodane reagents. Ts = *p*-toluenesulfonyl.

Our own efforts toward the development of asymmetric phenol dearomatization reactions[2] and the efficacy of the λ^5-iodane 2-iodoxybenzoic acid (IBX) or its stabilized non-explosive version (SIBX)[3] in mediating hydroxylative phenol dearomatization (HPD) in a strictly *ortho*-selective manner led us to envisage the use of a chiral oxygenating iodane in this reaction. The HPD reaction is a powerful means for preparing, in one step, chiral 6-alkyl-6-hydroxycyclohexa-2,4-dienones from simple (achiral) 2-alkylphenols or related arenol variants.[4] These systems, trivially referred to as *ortho*-quinols, either constitute the structural core of some natural products or can serve as advanced intermediates in the synthesis of several others.[4,5] Thus, having access to a chiral iodane reagent capable of enantioselectively installing a hydroxy group at an alkylated *ortho* position of a phenol would enable the reagent controlled preparation of *ortho*-quinols in a nonracemic form.

Our first approach toward this objective was to generate IBX analogues having either a center or an axis of chirality as close as possible to the iodine center. The iodoarenes **1a–e** and **2a–c** were thus considered as chiral precursors of either six-membered-ring homologues of IBX or biaryl variants (Figure 2). Extensive efforts were spent on converting these iodoarenes (using either racemates or enantiomerically pure forms) into their corresponding λ^5-iodane iodoxy derivatives using various reagent systems known to achieve this type of

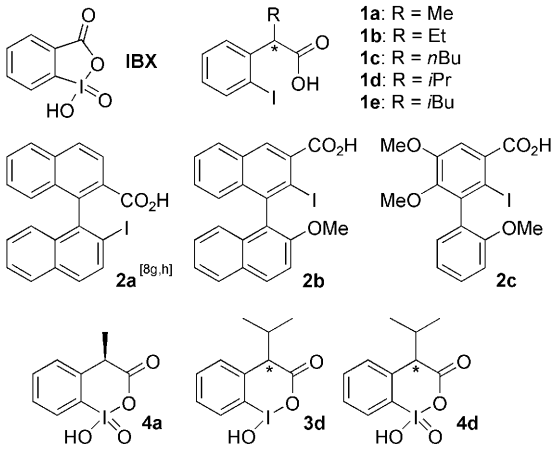

Figure 2. Starting chiral iodoarenes and isolated iodanes.

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oxidation (e.g., $KBrO_3/H_2SO_4$, NaOCl/H_2O-TBABr, $NaIO_4/H_2O$, $MeCO_3H/H_2O$, H_2O_2/H_2O-Ac_2O, Oxone/H_2O, TBA-OX/$MeSO_3H$-CH_2Cl_2, DMDO/acetone or CH_2Cl_2; TBA = tetra-*n*-butylammonium, TBA-OX = tetra-*n*-butylammonium oxone, DMDO = dimethyldioxirane),[6] but in most cases satisfactory conversions were not observed.

The only bits of encouragement were the oxone-mediated oxidation of **1a** into the λ^5-iodane **4a** in 62% yield and the DMDO-mediated oxidation of **1d** into the λ^3-iodane **3d** in yields ranging from approximately 50 to 90%, together with the isolation of a white solid whose structure could be attributed to the λ^5-iodane **4d** (little structural evidence was obtained to confirm this attribution). To test the oxygenating and asymmetry-induction capabilities of these materials, (−)-**4a** was engaged in a HPD reaction using 2,6-dimethylphenol (**5a**) in THF at −78°C. The expected *ortho*-quinol dimer **6a** (vide infra)[4b,d] was obtained in quantitative yield, but in only 20% *ee*. Under the same reaction conditions, the λ^3-iodane **3d** was totally inefficient, but each of its optical antipodes could oxidize methyl *p*-tolylsulfide into the corresponding sulfoxides in good yields (ca. 50 to 70%), albeit in poor enantiomeric excesses (7–8% *ee*).[7] Finally, each optical antipode of the presumed λ^5-iodane **4d** successfully mediated the HPD of **5a** into **6a** in yields of 70–75% with opposite but less than 10% *ee* (see the Supporting Information).

The overall difficulty in oxidizing our starting iodoarenes into iodanes led us to look for another approach. We turned our attention toward methodologies based on the in situ generation of iodanes from iodoarenes in the presence of a co-oxidant, a process having the possibility of proceeding with only catalytic amounts of iodoarenes.[8] We therefore verified the potential of this process in an HPD reaction, again using 2,6-dimethylphenol (**5a**) as a test substrate in various combinations with 2-iodophenyl acetic acid (**1f**) and *m*-CPBA, which was recently introduced by Kita and co-workers[8e] and Ochiai and co-workers[8d] as a terminal co-oxidant of choice in related iodoarene-catalyzed reactions. By using 0.1 equivalent of **1f** and 1.0 equivalent of *m*-CPBA in CH_2Cl_2 at room temperature for 2 hours (Table 1, entry 1), **5a** was partially converted into the expected racemic dimer **6a**, which was isolated in a 55% yield. Some starting **5a** was also recovered (16% yield), together with the isolation of a small amount of the epoxidized *ortho*-quinol *rac*-**7a** (8% yield), and the observation of another minor product (vide infra).

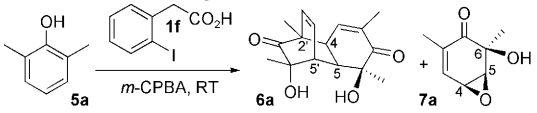
Although the outcome of this reaction confirmed the catalytic action of **1f**, which is oxidized in situ by *m*-CPBA into some oxygenating iodane species (vide infra), *m*-CPBA was also capable of trapping the initially formed *ortho*-quinol intermediate through epoxidation of its Δ-4,5 bond. The use of equimolar amounts of **1f** and *m*-CPBA did not improve the reaction outcome, but a twofold excess of **1f** increased the yield of **6a** to the detriment of the epoxidation event (Table 1, entries 2 and 3). On the contrary, only the epoxide **7a** was isolated in 47% yield when a large excess of *m*-CPBA (10 equiv) and a catalytic amount of **1f** (0.1 equiv) were added to a less concentrated solution of **5a** in acetone, a better solvent than CH_2Cl_2 for dissolving *m*-CPBA; the higher dilution was applied with the aim of limiting the dimerization process (Table 1, entry 4). The exclusive regio- and diastereoselectivity observed for **7a** (and other related epoxides described below) in favor of a *cis* epoxidation of the Δ-4,5 bond, relative to the orientation of the OH group at C6 of the orthoquinol intermediate, is a directivity gift offered by this allylic hydroxy group.[9]

To additionally evaluate the scope and limitations of the in situ generation of HPD-mediating iodanes, two additional phenols (i.e., **5b** and **5c**) and 2-methylnaphthol (**5d**) were utilized as starting materials (Table 2). Under catalytic conditions, 2,4,6-trimethylphenol (**5b**) led to a complex mixture from which the racemic dimer **6b**[4b] and epoxide **7b** could each be isolated in low yields. Traces of the *ortho*-quinol *m*-chlorobenzoate **7b′** were also detected (Table 2, entry 1). The latter compound, resulting from a surprising (only observed when using **5b**) participation of *m*-chlorobenzoic acid in the dearomatization process, could be isolated in 11% yield from a reaction in which a twofold excess of **1f** was used (Table 2, entry 2). Again, the use of such an excess of the iodoarene prevented the epoxidation event, but the expected formation of **6b** in high yield did not occur.

Under catalytic conditions, carvacrol (**5c**) was converted into biscarvacrol (**6c**)[2a,4b] and epoxide **7c**, together with significant amounts of the *para*-quinone **7c′** (Table 2, entries 3 and 4). We presume that **7c′** resulted from a 1,2-hydride shift (also known as an NIH shift)[10] of the epoxide **7c** in the acidic medium used (see arrows in Table 2). In fact, the same transformation also occurred with the disubstituted epoxide **7a**, but only traces (up to less than 10% as estimated by NMR analysis) of the corresponding quinone were observed (vide supra). This epoxide chemistry was again of no concern when using a twofold excess of **1f**, which led to the isolation of exclusively **6c** in 41% yield (Table 2, entry 5).

The reaction outcome was much simpler when using 2-methylnaphthol (**5d**), the hydroxylative dearomatization of which led to a nondimerizing *ortho*-quinol *rac*-**6d** and/or to its epoxide derivative *rac*-**7d** (Table 2, entries 6–9). Most remarkably, the *ortho*-quinol **6d** was obtained in 82% yield when using a twofold excess of the iodoarene **1f** with an equimolar amount of *m*-CPBA (Table 2, entry 8), whereas only the epoxide **7d** was generated in high yield when using a larger excess of *m*-CPBA (here limited to 2.5 equiv) and a catalytic amount of **1f** (Table 2, entry 9).

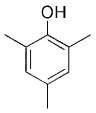
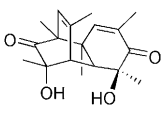
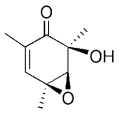
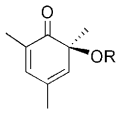
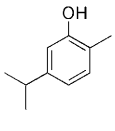
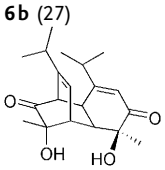
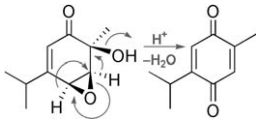
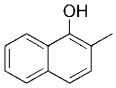
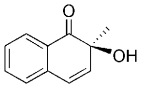
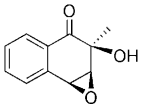
Table 1: Preliminary evaluation of reaction conditions for in situ generation of HPD-mediating iodanes from iodoarenes.[a]



Entry	**1f** [equiv]	*m*-CPBA [equiv]	Recovered **5a** [%]	**6a** [%]	**7a** [%][b]
1	0.1	1	16	55	8
2	1	1	18	58	3
3	2	1	13	64	n.d.
4[c]	0.1	10	n.d.	n.d.	47

[a] The reactions were conducted in CH_2Cl_2 for 2 h, [**5a**] = 0.33 M, unless otherwise noted. [b] Relative stereochemistry determined by NOESY experiments. [c] [**5a**] = 0.05 M in acetone. n.d. = not detected.

Table 2: Iodoarene-mediated oxygenating dearomatization of select arenols in the presence of *m*-CPBA.[a]

Entry	Arenol	**1f**/*m*-CPBA	Product(s) (% yield)[b,c]		
					
1	**5b**	0.1:1.0	**6b** (16)	**7b** (7)	**7b′** (trace)[d]
2	**5b**	2.0:1.0	**6b** (27)	n.d.	**7b′** (11)
					
3	**5c**	0.1:1.0	**6c** (19)	**7c** (6)	**7c′** (23)
4	**5c**	0.1:1.5	**6c** (32)	**7c** (10)	**7c′** (37)
5	**5c**	2.0:1.0	**6c** (41)	n.d.	n.d.
					
6	**5d**	0.1:1.0	**6d** (13)	**7d** (37)	
7	**5d**	1.0:1.0	**6d** (67)	n.d.	
8	**5d**	2.0:1.0	**6d** (82)	n.d.	
9	**5d**	0.1:2.5	n.d.	**7d** (91)	

[a] The reactions were conducted in CH_2Cl_2 at room temperature for 2–3 h, [**5**] = 0.33 M. [b] 15–35% of **5** were recovered, except for entries 4, 8, and 9. [c] Relative stereochemistry of epoxides determined by NOESY experiments. [d] In **7b′**, R = *m*-chlorobenzoyl. n.d. = not detected.

The naphthol **5d** was thus selected as a most convenient susbtrate to evaluate the capacity of the chiral iodoarenes **1a–e** and **2a–c** (Figure 2) to induce asymmetry during the reaction. The most significant results are given in Table 3. Iodoarenes having a chiral benzylic center, such as **1d** and **1e**, afforded maximum *ee* values of 21–23% for the *ortho*-quinol **6d** and 14-17% for its epoxide **7d** (Table 3, entries 1–4). Iodoarenes featuring axial chirality were much better inducers of asymmetry (Table 3, entries 5–10).

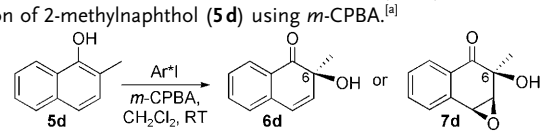
The best performances were achieved with the binaphthyl iodoarene **2b**. For example, using only a catalytic amount of (−)-**2b** and a 2.5-fold excess of *m*-CPBA, the expected epoxide **7d** was obtained in high yield and 29% *ee* (Table 3, entry 5). Most significantly, the use of equimolar amounts of either (−)-**2b** or (+)-**2b** and *m*-CPBA enabled the exclusive formation of the *ortho*-quinol **6d** in good yields and with *ee* values of 45–47%, with the major isomer being (−)-**6d** or (+)-**6d**, respectively (Table 3, entries 6 and 7). As previously observed (Table 2, entries 7 and 8), the use of a twofold excess of the iodoarene (+)-**2b** led to a better yield of **6d**, in this case up to 83%, and resulted in a slight increase of the *ee* value up to 50% in favor of (+)-**6d** (Table 3, entry 8).

Even though the resulting *ee* values are still moderate, these are the first examples of asymmetric iodoarene-mediated phenol dearomatization reactions, using an external oxygenating species, to be reported. To ascertain the stereochemical filiation between the iodoarene reagent **2b** and the *ortho*-quinol product **6d**, we determined the absolute stereochemistry of their stereoisomers by using vibrational circular dichroism (VCD).[11] The VCD spectra of each atropisomer of **2b** and of each enantiomer of **6d** were recorded, using $CDCl_3$ as the solvent, and then compared with the predicted VCD spectra of (*S*)-**2b** and (*R*)-**6d**; the predicted VCD spectra were calculated by using density functional theory (DFT) calculations using the B3LYP functional and 6-311 + G* basis set, except for the iodine atom for which the LANL2DZ basis set was used (see the Supporting Information). These comparisons unambiguously established that the axial chirality of (−)-**2b** is *S* and the configuration at C6 of (−)-**6d** is *R*. Thus, the sense of asymmetric induction is that (*S*)-(−)-**2b** gives rise to (*R*)-(−)-**6d** as the major product, and (*R*)-(+)-**2b** leads to (*S*)-(+)-**6d** (Table 3).

These results raise several questions about the mechanistic aspects of the reaction. Why was it so difficult to independently oxidize carboxylated iodoarenes into iodanes, whereas this oxidation easily occurs in situ in the presence of the phenolic substrate? What kind of iodane (i.e., λ^3 or λ^5) is actually generated in situ? What is the modus operandi of the (enantioselective) oxygen atom transfer at the *ortho*-position of the phenolic substrate? At this stage, we can only offer working hypotheses for future investigations (Scheme 1). The presence of the phenolic substrate in situ must be a determining factor of the advancement of the oxidation of the iodoarene **I**. Thus, an initially formed iodosyl species, shown here as its cyclic tautomer form **III**, could react with the phenolic substrate by ligand exchange, hence driving the oxidation reaction, to furnish a trigonal-bipyramidal aryloxy-λ^3-iodane of type **III′**.

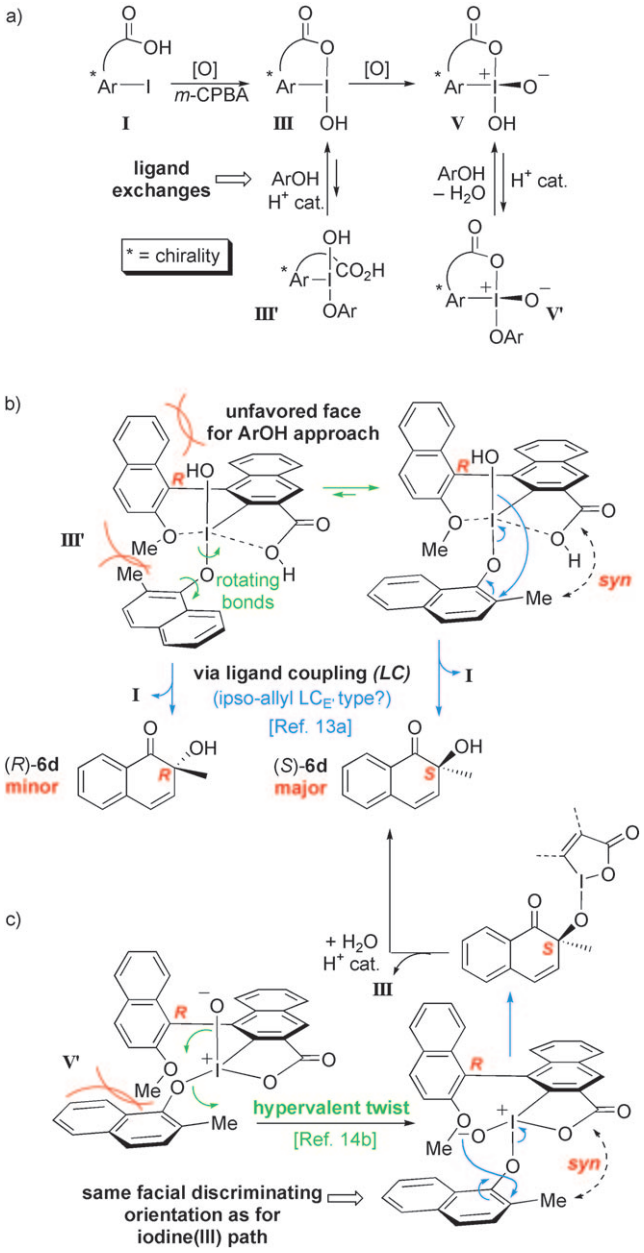
Then, using a chiral iodoarene such as (*R*)-**2b**, the approach of an arenol such as **5d** would occur from the least hindered face of **III** to give **III′**, the configurational

Table 3: Enantioselective iodoarene-mediated hydroxylative dearomatization of 2-methylnaphthol (**5d**) using *m*-CPBA.[a]



Entry	Ar*I	Ar*I [equiv]	*m*-CPBA [equiv]	**6d** [%]	**7d** [%]	*ee* [%][b]
1	(+)-**1d**	0.1	2.5	–	89	14 (6*S*)[c]
2	(+)-**1d**	1.0	1.0	70	–	21 (6*S*)
3	(−)-**1e**	0.1	2.5	–	91	17 (6*R*)
4	(−)-**1e**	1.0	1.0	72	–	23 (6*R*)
5	(*S*)-(−)-**2b**	0.1	2.5	–	90	29 (6*R*)
6	(*S*)-(−)-**2b**	1.0	1.0	67	–	45 (6*R*)
7	(*R*)-(+)-**2b**	1.0	1.0	71	–	47 (6*S*)
8	(*R*)-(+)-**2b**	2.0	1.0	83	–	50 (6*S*)
9	(+)-**2c**	0.1	2.5	–	90	23 (6*R*)
10	(+)-**2c**	1.0	1.0	71	–	37 (6*R*)

[a] The reactions were conducted for 2–3 h, [**5d**] = 0.33 M. [b] Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase (Chiralcel AS-H column). [c] Absolute configuration at C6 of the major enantiomer (see below).



Scheme 1. Proposed mechanistic descriptions of iodoarene-mediated hydroxylative phenol dearomatization using *m*-CPBA. a) General mechanism proposal, b) the iodine(III) pathway, and c) the iodine(V) pathway.

stability of its iodine(III) center being maintained by secondary I···O interactions with the OMe and/or the CO_2H group(s).[12] Therefore, having an iodine(III) center loaded with an aryloxy and a hydroxy ligand in such a sterically biased system may lead to a direct and stereoselective ligand-coupling event.[13] Even though coupling of these ligands, both of which are in apical positions, might appear spatially unlikely, topological transformations by, for example, Berry pseudorotation,[13a] will push them toward each other and promote coupling with concomitant reductive elimination of the iodoarene **I**. The sense of asymmetric induction using (*R*)-**2b** to furnish (*S*)-**6d** indicates a preference for an orientation of the sterically demanding aryloxy ligand in **III′** with its methyl group *syn* to the carboxylic acid function of the binaphthyl ligand, as depicted in Scheme 1b. However, since *m*-CPBA could additionally oxidize the iodosyl species **III** up to its iodoxy variant **V**,[14a] the possibility that the arenol could ligate the iodine(V) atom, by ligand exchange, should not be overlooked. Steric repulsion is likely to intervene between the aryloxy ligand and the *ortho*-methoxynaphthyl unit of the resulting 2-iodoxynaphthoic acid **V′**, and could be relieved by a hypervalent twist,[14b] during which the oxygen atom and the aryloxy ligands will move in and out of the plane, respectively, to promote the *ortho*-oxygenation reaction (Scheme 1c). The *ortho*-quinol **6d** would then be obtained after hydrolytic release of the λ^3-iodane **III** in much the same way as in the case of IBX-mediated HPD reactions.[3a,4]

The speculative nature of these descriptions led us to begin a search for evidence of λ^3- and/or λ^5-iodanyl species during the reaction. We monitored the HPD reaction of **5d** to give **6d**, using equimolar amounts of *rac*-**2b** and *m*-CPBA, by using electrospray ionization mass spectrometric (ESI-MS) analysis of aliquots diluted in 0.1% (v/v) AcOH/MeOH. Interestingly, prior to addition of **5d**, the most prominent peak was at *m*/*z* 501, and could correspond to the OH/OMe ligand exchange product of **V**. After addition of **5d**, a peak at *m*/*z* 487, which could be attributed to $[\mathbf{V}+H]^+$, was clearly seen in all spectra. Most importantly, a new peak also appeared at *m*/*z* 627 over the course of the 3 hour reaction. This peak can be assigned to the $[M+H]^+$ ion of **V′** (see the Supporting Information). Although these observations tend to strongly support the iodine(V) path depicted in Scheme 1c, additional investigations are still required before the iodine-(III) path can be completely disregarded.

In summary, we have developed an iodoarene-mediated hydroxylative phenol dearomatization reaction using *m*-CPBA as a co-oxidant. Using iodoarenes as organocatalysts with *m*-CPBA in excess enables subsequent regio- and diastereoselective epoxidation. Using chiral iodobiarenes enables enantioselectivities up to 50% *ee*, unveiling for the first time the potential of chiral iodoarenes for reagent control in asymmetric phenol dearomatization reactions using an external oxygenating source. Future work will focus on the use of other chiral iodobiarenes to additionally examine the potential of this reaction and to challenge the mechanistic and stereochemical control models proposed herein.

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