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Metal catalyzed deoxygenation by carbon monoxide of *o*-substituted nitrobenzenes. Synthesis of 1,4-dihydro-2*H*-3,1-benzoxazin-2-one derivatives *

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Abstract

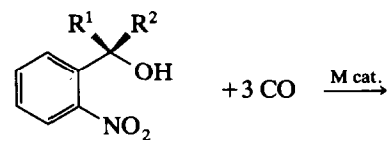
The reductive carbonylation of *o*-nitrobenzylalcohols, *o*-$NO_2C_6H_4CR^1R^2OH$ [$R^1 = R^2 = H$ (**1**); $R^1 = R^2 = CH_3$ (**2**); $R^1 = H$, $R^2 = CH_3$ (**3**); $R^1 = H$, $R^2 = C_6H_5$ (**4**)], catalyzed by ruthenium and palladium-based catalytic systems gives the corresponding 1,4-dihydro-2*H*-3,1-benzoxazin-2-one derivatives, **1a**–**4a**. Reaction conditions used were 20–60 atm of carbon monoxide and 100–170°C. The palladium catalyst has been shown to be by far superior to the ruthenium catalyst in this reaction as far as selectivity is concerned. By carbonylation of *o*-nitrophenethylalcohol (**5**) with the palladium system as catalyst a mixture of the monomeric **5a** and dimeric **5b** cyclic carbamates has been obtained.

1. Introduction

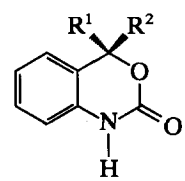
The transition-metal-catalyzed synthesis of *N*-heterocycles, *via* the reductive carbonylation with carbon monoxide of *o*-substituted nitrobenzenes, is a well-established method.

Many catalytic systems have been reported, yielding different types of heterocycle, sometimes with good selectivity [1].

Previously, we have reported the synthesis of indoles [2], carbazole [3], benzotriazoles [4], and benzimidazoles [5] by this route. We report here, the catalytic synthesis of 1,4-dihydro-2*H*-3,1-benzoxazin-2-one derivatives by reductive carbonylation of *o*-nitrobenzylalcohols (eqn. (1)).



$R^1 = R^2 = H$ (**1**)
$R^1 = R^2 = CH_3$ (**2**)
$R^1 = H$, $R^2 = CH_3$ (**3**)
$R^1 = H$, $R^2 = C_6H_5$ (**4**)



(1)

$R^1 = R^2 = H$ (**1a**)
$R^1 = R^2 = CH_3$ (**2a**)
$R^1 = H$, $R^2 = CH_3$ (**3a**)
$R^1 = H$, $R^2 = C_6H_5$ (**4a**)

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TABLE 1. Conversion and selectivity of the $[Ru_3(CO)_{12}]$-catalyzed carbonylation of *o*-nitrobenzylalcohol (**1**) [a]

Run	Cocatalyst	Solvent	Time (h)	Conversion (%)	Yield (%) [b]		
					1a	**1b**	**1c**
1	$[Et_4N]Cl$	*o*-$C_6H_4Cl_2$	0.125	32	13	24	61
2	$[Et_4N]Cl$	*o*-$C_6H_4Cl_2$	0.25	83	43	30	26
3	$[Et_4N]Cl$	*o*-$C_6H_4Cl_2$	0.5	98	45	31	22
4	$[Et_4N]Cl$	*o*-$C_6H_4Cl_2$	1	99	51	22	17
5	$[Et_4N]Cl$	*o*-$C_6H_4Cl_2$	3	99	51	3	5
6	$[Et_4N]Cl$	C_6H_5Cl	0.5	87	23	50	26
7	$[n\text{-}Hex_4N]Cl$	C_6H_5Cl	0.5	35	17	41	39
8	$[Et_4N]Cl$	C_6F_6	0.5	30	10	3	5
9	$[n\text{-}Hex_4N]Cl$	C_6F_6	0.5	40	10	6	8
10	$[Et_4N]Cl$	THF	1	99	51	21	18
11	$[Et_4N]Cl$	CH_3CN	1	99	24	45	9
12	–	$C_6H_5CH_3$	3	42	0	35	36

[a] All catalytic reactions were carried out at $P_{CO} = 60$ atm, $T = 170°C$. [nitro compound 1] = 0.1 mol/l, catalyst $[Ru_3(CO)_{12}]$, nitro compound 1/catalyst molar ratio = 100, co-catalyst/catalyst molar ratio = 7. [b] Calculated with respect to converted nitrocompound 1.

The catalytic, reductive carbonylation of *o*-nitrophenol to benzoxazolone has been already described [1f,g].

We have compared the catalytic activity and selectivity of two systems: one based on $[Ru_3(CO)_{12}]$ in the presence of $[NEt_4]Cl$ as co-catalyst, which is very good for the conversion of nitrobenzene derivatives to carbamates [6], and the other based on $[Pd(O_2CR)_2]$ in the presence of chelating nitrogen ligands and 2,4,6-trimethylbenzoic acid (TMBA), which is very active and selective for the conversion of nitrobenzene to phenylisocyanate [7] and carbamate [8].

The benzoxazin-2-one derivatives, which have several uses as pharmaceuticals, can be obtained by various reactions including that of *o*-aminobenzylalcohols with phosgene [9]. However, this synthesis poses the same problems as the synthesis of isocyanates by reaction of amines with phosgene [10].

2. Results and discussion

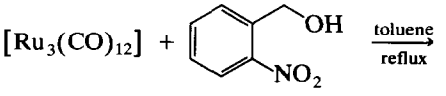
2.1. $[Ru_3(CO)_{12}]$ / $[NEt_4]Cl$ as a catalytic system

The results of the conversion of **1** to **1a** are shown in Table 1. By-products in this reaction are *o*-$NH_2C_6H_4CH_2OH$ (**1b**) and *o*-$NH_2C_6H_4CHO$ (**1c**).

With a substrate/catalyst ratio of 100, 1 h of reaction time is required to achieve a nearly complete conversion at 170°C (runs 1–5). However, we have already demonstrated that with this catalyst, catalytic activity begins only at 130–140°C, and this requires about 0.5 h with our heating system [6].

The nature of the solvent is important and this is probably related to the solubility of the ammonium salt in the reaction medium. The best solvents are *o*-$Cl_2C_6H_4$ and THF (runs 4, 5, 10), while an increase in the length of the organic substituent of the ammonium salt (runs 7 and 9) did not give better results than the use of $[NEt_4]Cl$. The co-catalyst (run 12) was in any case important for the synthesis of the cyclic carbamate, as it was for the synthesis of the linear carbamates [6]. In the latter case, toluene was used as the solvent of the catalytic reactions. However, even under the best conditions, the selectivity for the catalytic synthesis of **1a** was not satisfactory, and we explored the use of other catalytic systems (see later).

Being also interested in the isolation of possible intermediates in the reductive carbonylations of the organic nitro-derivatives under the action of transition metal carbonyls [3,11], we have also investigated the stoichiometric reaction between $[Ru_3(CO)_{12}]$ and **1** (eqn. (2)).



$$[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)] + CH_2O + 2\,CO_2 + CO \quad (2)$$

To our great surprise, a by-product of the reaction (up to now we have been unable to grow crystals suitable for an X-ray structural investigation of the main product of the reaction), is the known cluster $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu\text{-}NPh)]$ [12,13*]. To the best of our knowledge, this is the first report of a dealkylation of this type mediated by a transition metal cluster carbonyl. The formation of this hydride can explain in part the large amount of *o*-$NH_2C_6H_4CH_2OH$ (**1b**) formed during the catalytic reactions. This compound has been in fact considered a key intermediate, in the catalytic hydrogenation of nitrobenzene to aniline [12b]

* Reference with asterisk indicates a note in the list of references.

and is formed by reaction of $[Ru_3(CO)_{10}(\mu_3\text{-NPh})]$ with molecular hydrogen.

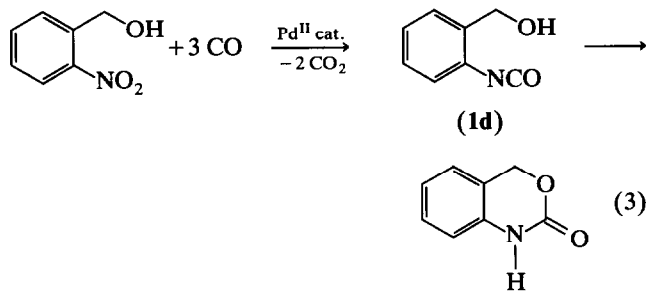
Finally, the formation of $o\text{-}NH_2C_6H_4CHO$ (**1c**) during the catalytic reaction could be due to an internal hydrogen transfer from the alcoholic group to nitrogen, in an intermediate nitrene species.

The necessity for the alkylammonium salt in the catalytic reaction confirms our previous results in the catalytic synthesis of linear carbamates [6]. The action of the halide on the intermediate nitrene ruthenium complex under carbon monoxide has been recently clarified [14].

2.2. *$[Pd(O_2CR)_2]$ ($R = CH_3$; 2,4,6-$(CH_3)_3$-C_6H_2) / chelating nitrogen ligands / 2,4,6-trimethyl benzoic acid (TMBA) as a catalytic system*

It has been shown previously that Pd^{II}-carboxylate, in the presence of chelating nitrogen donors such as phenanthroline and a hindered acid such as 2,4,6-trimethyl benzoic acid (TMBA), is a very selective catalyst for the conversion of nitrobenzene to phenylisocyanate [7] or carbamate [8].

Obviously the intermediate catalytic synthesis of *o*-isocyanatobenzylalcohol (**1d**) from **1** should lead readily to the cyclic carbamate **1a**, as in one of the routes employed in the organic synthesis of this derivative [9] (eqn. (3)).



(3)

Indeed, the catalytic synthesis of **1a** from **1** by using $[Pd(OAc)_2]$, 3,4,7,8-tetramethyl-1,10-phenanthroline (TMPhen) and 2,4,6-trimethyl benzoic acid as catalyst is very selective (Table 2, runs 1–4), the best conditions being $P_{CO} = 40$ atm, $T = 140$°C, ligand/palladium = 2 and acid/palladium = 24. The only by-product detected in the catalytic synthesis of **1a** was $o\text{-}NH_2C_6H_4CHO$ (**1c**). By increasing the temperature

TABLE 2. Conversion and selectivity of the $[Pd(O_2CR)_2]$/chelating nitrogen ligands (L)/2,4,6-trimethyl benzoic acid (TMBA) catalyzed carbonylation of *o*-nitrobenzyl alcohol (**1**) [a]

Run	L/Pd	TMBA/Pd	Time (h)	Temp. (°C)	PCO (atm)	Conversion (%)	Yield [b] (%)
Catalytic system $[Pd(OAc)_2]$ + 3,4,7,8-tetramethyl-1,10-phenanthroline							
1	2	24	2	180	40	100	99
2	2	24	2	140	40	100	99
3	2	24	2	130	40	77	87
4	2	24	2	120	40	55	90
5	2	24	2	100	40	22	50
6	2	24	1	140	40	73	96
7	2	24	4	120	40	84	89
8	2	24	3	100	40	25	60
9	2	24	4	100	40	43	48
10	2	24	2	130	20	99	83
11	2	24	2	130	60	76	89
12	2	24	2	100	20	18	78
13	2	24	2	100	60	21	55
14	2	0	2	180	40	100	20
15	2	0	2	140	40	48	49
Catalytic system $[Pd(TMB)_2]$ + 3,4,7,8-tetramethyl-1,10-phenanthroline							
16	2	0	2	140	40	54	45
Catalytic system $Pd(OAc)_2$ + 1,10-phenanthroline							
17	4	24	2	140	40	100	99
Catalytic system $[Pd(OAc)_2]$ + 2,2'-bipyridine							
18	4	24	2	140	40	9	0
19	6	24	2	140	40	28	0

[a] All catalytic reactions were carried out in toluene; TMBA is 2,4,6 trimethyl benzoic acid, the substrate **1** is *o*-nitrobenzylalcohol, the substrate **1**/catalyst molar ratio = 100, [nitro compound **1**] = 0.4 mol/l. [b] Yield of **1a** calculated with respect to converted nitrocompound **1**; the only by-product detected was $o\text{-}NH_2C_6H_4CHO$ (**1c**).

from 100 to 140°C, both conversions and selectivities increase (runs 2–5), while at 130°C with CO pressure increased from 20 to 60 atm, we observe an increase in the selectivity, but a decrease in the conversion (runs 10 and 11). This trend is rather common in this type of catalysis, and can be attributed to the requirement of a vacant site on the catalyst in the catalytic cycle [10].

The essential role of 2,4,6-trimethyl benzoic acid is shown by runs 14–16 (Table 2). On the other hand, the less basic donor 2,2'-bipyridine is practically inactive (runs 18 and 19), while with phenanthroline the ligand/palladium ratio must be increased to 4 (run 17) in order to obtain a good conversion and selectivity.

By using $[Pd(TMB)_2]$ (TMB = 2,4,6-trimethylbenzoate) [7] instead of $[Pd(OAc)_2]$ we discovered that the catalytic system is more robust with respect to decomposition to palladium metal. We have carried out some experiments adding fresh substrate to the same catalytic system, after the end of the first catalytic cycle (Table 3). For comparison, we also reported conversion and yield for a reaction carried out with a high substrate/catalyst ratio (run 1). A comparison of runs 2 and 5, and of runs 3 and 6, confirms this. Moreover, it appears that incomplete conversion of the substrate after the first cycle is useful in order to prevent the decomposition of the catalyst (runs 2–4). Finally, the catalytic systems do not suffer from contact with air during the second addition of the substrate (runs 2 and 3, runs 5 and 6).

TABLE 3. Effect of subsequent additions of substrate in the palladium-catalyzed carbonylation of *o*-nitrobenzylalcohol (**1**) [a]

Run	1/Pd	Time (h)	Conversion (%)		Yield [d] of **1a** (%)
			1st cycle	2nd cycle [c]	
Catalytic system $[Pd(OAc)_2]$ + 3,4,7,8-tetramethyl-1,10-phenanthroline					
1	410	2	81		77
2 [b]	100+	2+	100	–	
	100 [e]	2	–	67	74
3 [c]	100+	2+	100	–	
	100 [e]	2	–	68	75
4 [c]	100+	1+	73	–	
	70 [e]	1	–	87	78
Catalytic system $[Pd(TMB)_2]$ + 3,4,7,8-tetramethyl-1,10-phenanthroline					
5 [b]	100+	2+	100	–	
	100 [e]	2	–	96	79
6 [c]	100+	2+	100	–	
	100 [e]	2	–	79	72

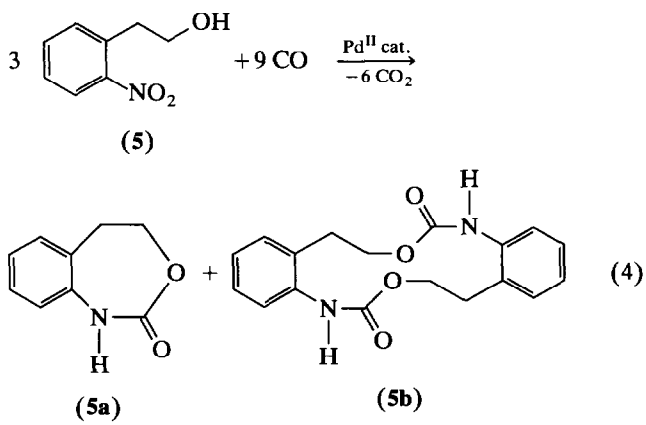
[a] All catalytic reactions were carried out at $PCO = 40$ atm, $T =$ 140°C; [nitro compound **1**] = 0,4 mol/l (except run 1, [**1**] = 1.8 mol/l), nitro compound as *o*-nitrobenzylalcohol **1**, ligand/Pd molar ratio = 2, TMBA/Pd molar ratio = 24. [b] Second addition of nitro compound **1a** in air. [c] Second addition of nitro compound **1a** under CO pressure. [d] Calculated with respect to converted nitrocompound **1**. [e] Nitro compound **1** added after the first cycle.

TABLE 4. Catalytic carbonylations of substituted *o*-nitrobenzylalcohols [a]; $[Pd(OAc)_2]$/TMPhen/TMBA as catalyst

Substrate	Conversion (%)	Yield (%) [b]
2-(Nitrophenyl)-2-propanol $o\text{-}NO_2C_6H_4C(CH_3)_2OH$ (**2**)	80	99 (**2a**)
1-(2-Nitrophenyl)-ethanol $o\text{-}NO_2C_6H_4CH(CH_3)OH$ (**3**)	100	99 (**3a**)
1-(2-Nitrophenyl)-benzylalcohol $o\text{-}NO_2C_6H_4CH(C_6H_5)OH$ (**4**)	80	87 (**4a**)
2-Nitrophenetylalcohol $o\text{-}NO_2C_6H_4CH_2CH_2OH$ (**5**)	100	60 (**5a**) [c]

[a] All catalytic reactions were carried out at $PCO = 40$ atm, $T =$ 140°C, [substrate] = 0.4 mol/l, catalytic system $[Pd(OAc)_2]$ + 3,4,7,8-tetramethyl-1,10-phenanthroline, ligand/Pd molar ratio = 2, TMBA/Pd molar ratio = 24, substrate/Pd molar ratio = 100, solvent toluene. The conversions and selectivities were qualitatively estimated. [b] Calculated with respect to converted nitrocompound; by-product is the corresponding amine. [c] By-product is the dimeric carbamate, **5b**.

The palladium catalytic system has also been tested with the substituted *o*-nitrobenzylalcohols (**2–4**) (Table 4). Even in this case, good conversions and selectivities have been observed. The use of *o*-nitrophenylethylalcohol (**5**) as substrate, gave about 60% of the monomeric cyclic carbamate, **5a**, while the dimeric carbamate, **5b**, was isolated as an insoluble product from the reaction mixture (eqn. (4)).



The carbonylation of **1** in methanol gave the cyclic carbamate (**1a**) as the predominant product (71%) compared to the linear carbamate, $o\text{-}MeO_2CNHC_6H_4CH_2OH$.

An interesting palladium metallocycle has recently been isolated from the conversion of nitrobenzene to phenylethylcarbamate carried out with this catalytic

system [15]. On the basis of the reactivity of this compound, a mechanism has been proposed that did not require the intermediate formation of any nitrene-palladium species. This could explain the much better selectivities observed with the palladium catalyst compared to ruthenium, for which the formation of an intermediate nitrene complex is likely [3,6,14]. It is known that nitrene complexes can be involved in a variety of different reactions [16].

3. Experimental details

IR spectra were recorded on Perkin-Elmer 1310 and Nicolet MX-1 FT-IR spectrophotometers. ^1H NMR spectra were recorded on a Bruker WP 80 SJ spectrometer with $SiMe_4$ as internal standard. MS was performed on a VG 7070 EQ machine.

Carbon monoxide was of high purity grade. Solvents were distilled before use; acetonitrile, chlorobenzene and *o*-dichlorobenzene over P_4O_{10}; toluene and tetrahydrofuran over sodium. Literature methods were used for the preparation of $[Ru_3(CO)_{12}]$ [17], $[Pd(O_2CR)_2]$ [7,18], compounds **2**, **3** [19], **4** [20], **1** and **5** were supplied by Aldrich. Reactions under high pressure were conducted in a glass liner inside a stainless steel autoclave. The air in the autoclave was replaced with dinitrogen by three freeze-pump-thaw cycles before the introduction of carbon monoxide at the desired pressure. The autoclave was heated by a thermoregulated silicone oil bath and magnetic stirring was applied. At the end of the reactions, the autoclave was rapidly cooled in an ice bath and the pressure then released.

In the case of solid compounds, the product present at the end of the reaction was filtered off and washed with toluene. Reaction solutions were quantitatively analyzed by HRGC on Carlo Erba Fractovap 4160 coupled with a Perkin-Elmer LCI-100 integrator, using hexamethylbenzene as internal standard. Selectivities were calculated on the amount of the starting material reacted.

Products of the reactions were identified by GC-MS, using a Hewlett Packard 5890 gas chromatograph coupled with a 5971A mass selective detector.

3.1. General conditions for all cyclisation reactions

All catalytic reactions with $[Ru_3(CO)_{12}]$ were carried out with a concentration of nitrocompound of 0.1 mol/l; nitrocompound/$[Ru_3(CO)_{12}]$, 100; $[Et_4N]Cl$/$[Ru_3(CO)_{12}]$, 7; $p_{CO} = 60$ atm, $T = 170°C$.

With $[Pd(O_2CR)_2]$ the concentration of nitrocompound was 0.4 mol/l; nitrocompound/$Pd(O_2CR)_2$, 100; ligand/$[Pd(O_2CR)_2]$, 2 unless otherwise stated; TMBA/$[Pd(O_2CR)_2]$, 24; $p_{CO} = 40$ atm; $T = 140°C$.

3.2. Reaction of $[Ru_3(CO)_{12}]$ with o-$NO_2C_6H_4CH_2OH$ (1)

$[Ru_3(CO)_{12}]$ (518 mg) was added to a solution of **1** (243 mg) in toluene (35 ml) under carbon monoxide. The solution was warmed to 110°C for 6 h. The solution was then evaporated to dryness under vacuum and the dark brown residue was washed with hexane (20 ml).

The hexane solution was concentrated to a small volume (5 ml) and stored overnight at 0°C. The precipitate of unreacted $[Ru_3(CO)_{12}]$ was filtered off.

On cooling the resulting solution at −20°C for 4 days, crystals of $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$ [12], suitable for an X-ray structural determination [13*] were obtained (6% yields).

3.3. Identification of organic compounds

Compound **1a**: IR (in Nujol): ν(N–H) 3240, 3158 and 3101 m; ν(C=O) 1716 cm^{-1}. MS (EI, 70 eV): *m/z* 149 (M^+, 20%), 104(100%), 91(56%), 77(34%). Anal. Found: C, 64.65; H, 4.75; N, 9.32. $C_8H_7NO_2$ calc.: C, 64.42; H, 4.73; N, 9.34%.

Compound **2a**: IR (in Nujol): ν(N–H) 3228, 3106m; ν(C=O) 1718 cm^{-1}. MS (EI, 70 eV): *m/z* 163 (M^+, 17%), 162(23%), 148(19%), 119(100%), 104(15%). Anal. Found: C, 65.57; H, 6.02; N, 8.43. $C_9H_9NO_2$ calc.: C, 65.85; H, 6.10; N, 8.54%.

Compound **3a**: IR (in Nujol): ν(N–H) 3230, 3152 m; ν(C=O) 1715 cm^{-1}. MS (EI, 70 eV): *m/z* 177 (M^+, 27%), 162(21%), 144(17%), 132(100%), 118(13%), 91(11%), 77(34%). Anal. Found: C, 67.69; H, 6.13; N, 7.83. $C_{10}H_{11}NO_2$ calc.: C, 67.8; H, 6.21; N, 7.91%.

Compound **4a**: IR (in Nujol): ν(N–H) 3225, 3150m; ν(C=O) 1710 cm^{-1}. MS (EI, 70 eV): *m/z* 225 (M^+, 17%), 180(23%), 164(18%), 152(15%), 146(100%), 119(18%), 105(24%), 91(12%), 77(33%). Anal. Found: C, 74.6; H, 4.84; N, 6.12. $C_{14}H_{11}NO_2$ calc.: C, 74.65; H, 4.92; N, 6.21%.

Compound **5a**: IR (in Nujol): ν(N–H), 3232, 3150 m; ν(C=O) 1718 cm^{-1}. MS (EI, 70 eV): *m/z* 163 (M^+, 20%), 132(21%), 118(100%), 106(33%), 91(16%), 77(30%). Anal. Found: C, 66.3; H, 5.6; N, 8.43. $C_9H_9NO_2$ calc.: C, 66.26; H, 5.52; N, 8.59%. ^1H NMR (in $CDCl_3$): δ 6.9–7.8 (m, 4H); 4.5 (t, 2H); 3.2 (t, 2H).

Compound **5b**: IR (in Nujol): ν(N–H) 3287m; ν(C=O) 1692 cm^{-1}. MS (EI, 70 eV): *m/z* 326 (M^+, 24%), 181(29%), 163(17%), 146(45%), 132(10%), 119(100%), 91(15%), 77(39%).

Acknowledgements

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