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Copper-catalyzed oxidative cleavage of carbon–carbon double bond of enol ethers with molecular oxygen

Makoto Tokunaga *, Yuki Shirogane, Hiroshi Aoyama, Yasushi Obora, Yasushi Tsuji

Catalysis Research Center, Graduate School of Science, Hokkaido University and JST (Japan Science and Technology Corporation), Kita 21, Nishi 10, Kita-ku, Sapporo 001-0021, Japan

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Abstract

A novel C=C bond cleavage reaction of aromatic enol ethers (**1**) to give ketones (**2**) using molecular oxygen as oxidant is described. Among the examined catalysts (Cu(II), Pd(II), Ru(II), and H^+), $CuCl_2$ exhibited the highest activity. The reaction proceeded smoothly with several kinds of substrates.

Keywords: Copper catalysts; Oxidation; C=C cleavage; Molecular oxygen

1. Introduction

Oxidative cleavage of carbon–carbon double bond is an important functional group transformation. In particular, the reaction of enol ethers to give carbonyl compounds has been investigated employing ozone [1] or singlet oxygen [2] as oxidant. These methods are useful in organic synthesis, however, a special equipment such as an ozonizer or a photochemical apparatus is necessary to perform them. On the other hand, molecular oxygen is a convenient oxidizing agent and its utilization has been attracted considerable attention from the viewpoint of environmentally benign synthesis [3]. In this regard, transition metal catalysts have been employed for the C=C bond cleavage of alkenes with molecular oxygen [4]. Particularly for related substrates of enol ethers such as enamines, Kaneda et al. [4a] reported efficiency of Cu(II) catalysts in 1982, however, no further investigations and applications have been made after the work. We disclose here an unprecedented copper-catalyzed oxidative cleavage of enol ethers with molecular oxygen.

We found the C=C bond cleavage reaction unexpectedly. We have investigated hydrolysis of alkenyl ethers and esters and its application to asymmetric synthesis [5]. Several kinds of metals such as Pd(II), Pt(II), Hg(II), Ru(II), Co(III), Cu(II), and Sc(III) showed catalytic activity in the hydrolysis of benzyl vinyl ether to give benzyl alcohol and acetaldehyde. During the course of the study of the hydrolysis of chiral and prochiral alkenyl ethers, an aromatic enol ether **1a** gave the expected hydrolyzed product **3a** accompanied with an oxidatively cleaved product **2a**. Among the examined catalysts, Cu(II) complexes found to be most effective for the formation of **2a** (Table 1).

Under 1 atm molecular oxygen, **2a** was obtained in 86% yield without the formation of **3a** using 5 mol% $CuCl_2$ in the presence of H_2O (5 equiv.) in acetonitrile (entry 1). Molecular oxygen is essential for this reaction; the reaction under argon atmosphere did not afford **2a** at all, but gave **3a** in almost quantitative yield (entry 2). The reaction with lower catalyst loading (1 mol%) gave slightly lower yield of **2a** (entry 3). In the absence of H_2O, the reaction became sluggish; **2a** was obtained in 33% yield after 24 h (entry 4). The reactions in THF, 2-propanol, and methanol gave lower yields of

* Corresponding author. Tel.: +81117069158; fax: +81117069156.
E-mail address: tokunaga@cat.hokudai.ac.jp (M. Tokunaga).

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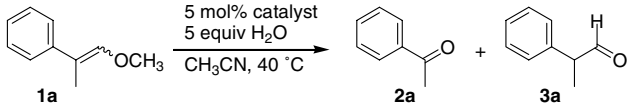
Table 1
Oxidative cleavage of C=C bond of **1a** with various catalysts



1a **2a** **3a**

Entry	Catalyst	Atmosphere	Time (h)	Yield of **2a** (%)[a]	Yield of **3a** (%)[a]
1	$CuCl_2$	O_2	1	86	0
2	$CuCl_2$	Ar	24	0	>99
3[b]	$CuCl_2$	O_2	3	68	0
4[c]	$CuCl_2$	O_2	24	33	0
5[d]	$CuCl_2$	O_2	18	14	0
6[e]	$CuCl_2$	O_2	13	75	0
7[f]	$CuCl_2$	O_2	4	70	0
8	$Cu(OTf)_2$	O_2	1	82	0
9	CuCl	O_2	3	78	0
10	$CuBr_2$	O_2	24	66	23
11	$PdCl_2(PhCN)_2$	O_2	32	67	9
12	$PdCl_2(PhCN)_2$	Ar	24	0	38
13	$[RuCl_2(p\text{-cymene})]_2$	O_2	1	11	0
14	HCl	O_2	1	0	93
15[g]	HCl	O_2	24	52	21
16	*p*-TsOH	O_2	24	64	11
17	*p*-TsOH	Ar	24	0	95
18	None	O_2	24	0	0

[a] GC yield.
[b] 1 mol% catalyst.
[c] In the absence of H_2O.
[d] THF was used as solvent.
[e] 2-Propanol was used as solvent.
[f] Methanol was used as solvent.
[g] 0.5 mol% catalyst.

2a without the formation of **3a** (entries 5–7). Other copper salts such as $Cu(OTf)_2$ and CuCl showed similar activity to $CuCl_2$ (entries 8 and 9), but $CuBr_2$ suffered from a lower rate and a poor selectivity of **2a** (entry 10).

In our previous work [5], $PdCl_2(PhCN)_2$ exhibited the highest activity for the hydrolysis reaction. This time, the Pd complex catalyzed the C=C cleavage reaction under oxygen atmosphere (entry 11), as well as hydrolysis reaction under argon atmosphere (entry 12). In both cases, the catalytic activity was lower than the copper complexes. A ruthenium complex, $[RuCl_2(p\text{-cymene})]_2$ showed also lower activity than copper complexes (entry 13).

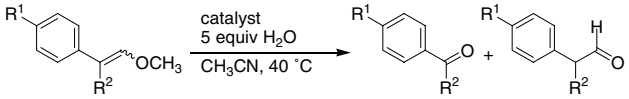
Interestingly, Brønsted acids also catalyzed the oxidation reaction though the activity was not high. When 5 mol% HCl was used as a catalyst, hydrolysis proceeded exclusively (entry 14). However, 0.5 mol% HCl catalyzed the oxidative cleavage reaction slowly and afforded a mixture of **2a** and **3a** (52% and 21%, entry 15). In addition, 5 mol% *p*-TsOH also gave a mixture of **2a** and **3a** (64% and 11%) under O_2 atmosphere (entry 16), but gave **3a** as sole product under argon atmosphere (entry 17). In the absence of a catalyst, the reaction did not proceed at all (entry 18).

The substrate generality was examined with various aromatic enol ethers **1b–h** (Table 2). All the substrates gave ketones **2b–h** in good yields in high selectivity. Electron donating substituents at the *para*-position of the aromatic ring made the reaction faster than electron withdrawing groups (entries 1–4). Ethyl, undecyl, and phenyl group as the R^2 substituent did not affect the reactivity (entries 5–7).

In order to investigate the fate of the ether moiety, the reaction with a dodecyl ether **1i** was carried out (Scheme 1). As a result, dodecyl formate (65%) was isolated together with **2a** (90%). In addition, from a cyclic enol ether **1j**, a formate **2j** (20%) was obtained as well as 2-acetylbenzaldehyde (**4**) (15%), which could be formed via oxidation of 2-acetylbenzylalcohol (see Scheme 2).

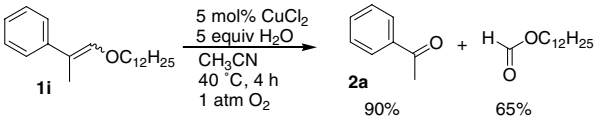
A possible mechanism is depicted in Fig. 1. Although detailed mechanism of the present copper catalyzed C=C bond cleavage reaction is unclear, it is likely that the reaction involves a radical cation of an enol ether and a dioxetane intermediate. Thus, the catalytic cycle starts with one-electron oxidation of a coordinated enol ether by Cu(II) (step a). The next step is electron transfer to a coordinated molecular oxygen (step b), followed by the formation of a dioxetane (step c). The final step is

Table 2
Oxidative cleavage of C=C bond of various enol ethers **1b**–**h** catalyzed by $CuCl_2$ under O_2 atmosphere

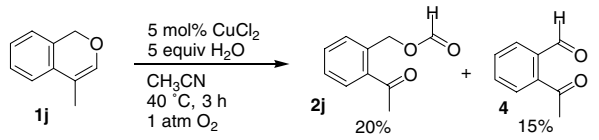


Entry	Substrate	R^1	R^2	Cat. (mol%)	Time (h)	Yield of **2** (%)	Yield of **3** (%)
1	**1b**	OCH_3	CH_3	1	2	76[a]	0
2	**1c**	CH_3	CH_3	1	2	87[a]	0
3	**1d**	Cl	CH_3	1	4	68[a]	0
4	**1e**	F	CH_3	1	3	63[a]	0
5	**1f**	H	C_2H_5	5	2	74[b]	0
6	**1g**	H	$C_{11}H_{23}$	5	5	88[b]	0
7	**1h**	H	Ph	5	3	92[b]	0

[a] GC yield.
[b] Isolated yield.



Scheme 1. Oxidative cleavage of C=C bond of **1i**.



Scheme 2. Oxidative cleavage of C=C bond of a cyclic enol ether (**1j**).

decomposition of the dioxetane to give a ketone and a formate ester (step d). A similar mechanism involving radical cations and dioxetanes is also proposed in oxidative C=C cleavage of enamines with Cu complexes by Kaneda et al. [4a]. An alternative route, oxidative cleavage of the aldehydes **3** to the ketones **2** (via enolization) is unlikely as shown in Scheme 3. The conversion of **3a** to the ketone **2a** under the standard condition found to be very slow (5% after 52 h).

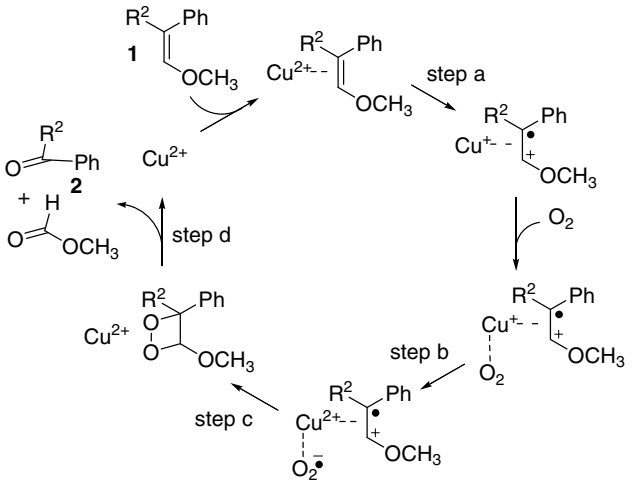
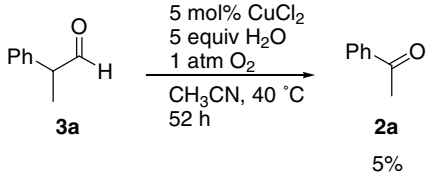


Fig. 1. A possible mechanism of Cu-catalyzed oxidaive cleavage of C=C bond.



Scheme 3. Oxidation of **3a** to **2a** under the standard condition.

It is known that enol ether radical cations are readily produced by chemical or electrochemical oxidations and non-oxidative heterolytic fragmentations [6], and play important role in DNA oxidations [6b].

Dioxetane intermediates and their decomposition into ketones and esters are common in the reactions using singlet oxygen [2]. Participation of the copper catalyst in the decomposition step can be presumed because the processes without the metals are known to be slow. In fact, high catalytic activity of $CuCl_2 \cdot 2H_2O$ in the decomposition of dioxetanes was reported [7]. The observed rate was more than 100 times faster than other metal complexes. Faster rate in protic solvents was also described [7], which may explain the acceleration effect of H_2O in our oxidative cleavage (entry 4 in Table 1).

With regard to the Brønsted acids catalyzed reactions, although the origin of the catalysis is rather ambiguous, it also seems to involve a radical cation and a dioxetane intermediate. A radical chain mechanism involves these intermediates is also proposed in a metal-free (heat assisted) C=C bond cleavage reaction [3b].

In conclusion, we have performed copper-catalyzed oxidative C=C bond cleavage of aromatic enol ethers. The reaction employs rather mild condition compared with known methods in other alkenes using molecular oxygen ([3b] and references sited therein). Further investigation on the mechanism and synthetic applications are now in progress.

2. Experimental

2.1. Preparation and characterization of the substrates

Enol ethers **1** were synthesized by the procedures as described below and determination of *E*/*Z* stereochemistry were carried out by ^{1}H NMR, DPFGSE-NOE method [8] (double pulse field gradient spin echo), which gives nearly identical results to a conventional NOE difference experiment with better S/N ratio. Assignment of ^{1}H and ^{13}C chemical shifts was based on HMQC and HMBC experiments.

1-Methoxy-2-phenylpropene (**1a**) was synthesized from 2-phenylpropionaldehyde by a literature method [9a]. A mixture of 2-phenylpropionaldehyde (1.34 g, 10 mmol), trimethyl orthoformate (1.38 g, 13 mmol), and *p*-toluenesulfonic acid (19 mg, 0.10 mmol) was stirred at 70 °C for 3h. Then heated to 140 °C for 12 h, evolved methanol and trimethyl orthoformate was removed by distillation take off head. The mixture was distilled under reduced pressure and purified by silica-gel column chromatography (hexane/ether 10:1) to give **1a** [9b] (0.90 g, 6.1 mmol, 61%, *E*/*Z* = 3.3:1). ^{1}H NMR (C_6D_6, 400 MHz): (*E*)-isomer; δ 2.04 (3H, s), 3.11 (3H, s), 6.17 (1H, s), 7.00–7.25 (5H, m), (*Z*)-isomer; δ 1.76 (3H, s), 3.03 (3H, s), 5.72 (1H, s), 7.00–7.25 (3H, m), 7.73–7.77 (2H, m).

The substrates **1b**–**h** were prepared from corresponding ketones by Wittig reaction [1b].

1-Methoxy-2-(*p*-methoxyphenyl)propene (**1b**) (*E*/*Z* = 1:1.2). ^{1}H NMR (C_6D_6, 400 MHz): (*E*)-isomer; δ 2.07 (3H, s), 3.15 (3H, s), 3.30 (3H, s), 6.15 (1H, s), 6.75–6.79 (2H, m), 7.12–7.17 (2H, m), (*Z*)-isomer; δ 1.79 (3H, s), 3.08 (3H, s), 3.27 (3H, s), 5.73 (1H, s), 6.83–6.87 (2H, m), 7.71–7.74 (2H, m). ^{13}C NMR (C_6D_6, 100 MHz): (*E*)-isomer; δ 12.9, 54.5, 59.0, 113.9 (2C), 114.0, 126.1(2C), 133.3, 144.2, 158.4, (*Z*)-isomer; δ 18.2, 54.4, 59.2, 110.2, 113.4 (2C), 128.9 (2C), 131.2, 143.7, 158.1; EI-MS: $C_{11}H_{14}O_2^+$ requires *m*/*z* = 178.0994, found: 178.0991.

1-Methoxy-2-(*p*-tolyl)propene (**1c**) [9c] (*E*/*Z* = 1:1.2). ^{1}H NMR ($CDCl_3$, 400 MHz): (*E*)-isomer; δ 1.98 (3H, s), 2.34 (3H, s), 3.71 (3H, s), 6.38 (1H, s), 7.08–7.15 (4H, m), (*Z*)-isomer; δ 1.90 (3H, s), 2.34 (3H, s), 3.66 (3H, s), 6.08 (1H, s), 7.18–7.21 (2H, m), 7.48–7.74 (2H, m).

1-Methoxy-2-(*p*-chlorophenyl)propene (**1d**) (*E*/*Z* = 1:1.1). ^{1}H NMR ($CDCl_3$, 400 MHz): (*E*)-isomer; δ 1.95 (3H, d, *J* = 1.4 Hz), 3.71 (3H, s), 6.39 (1H, d, *J* = 1.4 Hz), 7.19–7.28 (4H, m), (*Z*)-isomer; δ 1.88 (3H, d, *J* = 1.4 Hz), 3.67 (3H, s), 6.12 (1H, d, *J* = 1.4 Hz), 7.19–7.28 (2H, m), 7.51–7.56 (2H, m). ^{13}C NMR (C_6D_6, 100 MHz): (*E*)-isomer; δ 12.5, 60.1, 113.5, 126.2 (2C), 128.5 (2C), 131.5, 139.2, 145.5, (*Z*)-isomer; δ 18.2, 60.3, 109.7, 128.0 (2C), 128.8 (2C), 131.5, 136.8, 145.2; EI-MS: $C_{10}H_{11}ClO^+$ requires *m*/*z* = 182.0498, found: 182.0487.

1-Methoxy-2-(*p*-fluorophenyl)propene (**1e**) (*E*/*Z* = 1:1.1). ^{1}H NMR (C_6D_6, 400 MHz): (*E*)-isomer; δ 1.94 (3H, d, *J* = 1.4 Hz), 3.11 (3H, s), 6.00 (1H, d, *J* = 1.4 Hz), 6.75–6.94 (4H, m), (*Z*)-isomer; δ 1.65 (3H, d, *J* = 1.4 Hz), 3.00 (3H, s), 5.66 (1H, d, *J* = 1.4 Hz), 6.85–6.90 (2H, m), 7.52–7.56 (2H, m). ^{13}C NMR (C_6D_6, 100 MHz): (*E*)-isomer; δ 12.6, 59.0, 113.2, 115.0 (2C, d, *J* = 21 Hz) 126.5 (2C, d, *J* = 7.7 Hz), 134.6 (d, *J* = 2.9 Hz), 145.1, 161.6 (d, *J* = 244 Hz), (*Z*)-isomer; δ 18.0, 59.3, 109.4, 114.5 (2C, d, *J* = 21 Hz) 129.3 (2C, d, *J* = 7.7 Hz), 134.6 (d, *J* = 2.9 Hz), 144.5, 161.2 (d, *J* = 246 Hz); Anal. Calc. for $C_{10}H_{11}FO$: C, 72.27; H, 6.67. Found: C, 72.78; H, 6.80.

1-Methoxy-2-phenyl-1-butene (**1f**) [9d] (*E*/*Z* = 1.2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): (*E*)-isomer; δ 1.05 (3H, t, *J* = 7.3 Hz), 2.52 (2H, q, *J* = 7.3 Hz), 3.70 (3H, s), 6.27 (1H, s), 7.15–7.37 (5H, m), (*Z*)-isomer; δ 1.05 (3H, t, *J* = 7.3 Hz), 2.32 (2H, q, *J* = 7.3 Hz), 3.63 (3H, s), 6.08 (1H, s), 7.15–7.37 (3H, m), 7.46–7.50 (2H, m).

1-Methoxy-2-phenyl-1-tridecene (**1g**) (*E*/*Z* = 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): (*E*)-isomer; δ 0.92 (3H, t, *J* = 6.8 Hz), 1.22–1.46 (18H, m), 2.54 (2H, t, *J* = 6.8 Hz), 3.71 (3H, s), 6.31 (1H, s), 7.18–7.37 (5H, m), (*Z*)-isomer; δ 0.92 (3H, t, *J* = 6.8 Hz), 1.22–1.46 (16H, m), 2.32 (2H, t, *J* = 6.8 Hz), 3.65 (3H, s), 6.10 (1H, s), 7.18–7.37 (3H, m), 7.48–7.53 (2H, m). ^{13}C NMR (C_6D_6, 100 MHz): (*E*)-isomer; δ 14.2, 22.8, 27.0, 28.4–32.0 (8C), 59.9, 120.3, 125.9 (2C), 126.0, 128.4 (2C), 140.0, 145.3. (*Z*)-isomer; δ 14.2, 22.8, 28.4–32.0 (8C), 32.7, 60.1, 117.0, 126.1, 128.0 (2C), 128.3 (2C), 137.7, 144.1; EI-MS: $C_{20}H_{32}O^+$ requires *m*/*z* = 288.2453, found: 288.2460.

1-Methoxy-2,2-diphenylethene (**1h**) [9e]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.19 (3H, s), 6.25 (1H, s), 7.15–7.37 (8H, m), 7.70–7.71 (2H, m).

The substrate **1i** was prepared from 2-phenylpropionaldehyde and 1-dodecanol by a similar procedure to **1a**.

1-Dodecyloxy-2-phenylpropene (**1i**) (*E*/*Z* = 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): (*E*)-isomer; δ 0.87 (3H, t, *J* = 7.2 Hz), 1.20–1.45 (18H, m), 1.62–1.72 (2H, m), 2.00 (3H, s), 3.84 (2H, t, *J* = 6.8 Hz), 6.47 (1H, s), 7.13–7.35 (5H, m), (*Z*)-isomer; δ 0.87 (3H, t, *J* = 7.2 Hz), 1.20–1.45 (18H, m), 1.62–1.72 (2H, m), 1.91 (3H, s), 3.81 (2H, t, *J* = 6.8 Hz), 6.18 (1H, s), 7.25–7.35 (3H, m), 7.63–7.67 (2H, m), ^{13}C NMR ($CDCl_3$, 100

MHz): (*E*)-isomer; δ 12.7, 14.3, 22.9, 26.1, 29.5–30.1 (7C), 32.1, 72.8, 114.2, 125.0 (2C), 125.8, 128.4 (2C), 141.0, 144.3, (*Z*)-isomer; δ 14.3, 18.4, 22.9, 26.2, 29.5–30.1 (7C), 32.1, 73.3, 110.1, 125.9, 127.5 (2C), 128.0 (2C), 138.6, 143.9; EI-MS: $C_{21}H_{34}O^+$ requires *m*/*z* = 302.2610, found: 302.2611.

The substrate **1j** was prepared from 2-iodobenzylalcohol by a literature method [9f].

4-Methyl-1*H*-2-benzopyran (**1j**) [9g]. ^{1}H NMR (C_6D_6, 400 MHz): δ 1.75 (3H, s), 4.86 (2H, s), 6.44 (1H, d, *J* = 1.2 Hz), 6.72 (1H, d, *J* = 7.6 Hz), 6.99 (1H, d, *J* = 7.6 Hz), 7.05 (1H, dt, *J* = 1.2 Hz, 7.6 Hz), 7.18 (1H, d, *J* = 7.6 Hz).

2.2. Typical procedure of the oxidative C=C bond cleavage reaction and characterization of the products

A 20 mL Schlenck flask was charged with $CuCl_2$ (6.7 mg, 0.050 mmol), acetonitrile (2 mL), **1a** (148 mg, 1.0 mmol), H_2O (90.1 mg, 5.00 mmol), and diglyme (internal standard for GC analysis, 26.8 mg, 0.20 mmol), and then the mixture was stirred at 40 °C under 1 atm O_2 for 1 h. The yield of the product **2a** was determined by GC analysis (Agilent HP-1 column, length 30 m, 0.32 mm ID).

The products **2a**–**h** and **3a** were characterized by GC, GC-MS, and ^{1}H NMR analysis by the comparison of commercially available authentic samples. Isolations of the products were carried out by silica-gel column chromatography.

2-Acetylbenzyl formate (**2j**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.61 (3H, s), 5.55 (2H, s), 7.39–7.45 (1H, m), 7.50–7.55 (2H, m), 7.80–7.84 (1H, m), 8.18 (1H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.9, 64.2, 128.0, 130.1, 132.4, 136.2 (2C), 160.7, 200.7; EI-MS: $C_{10}H_{10}O_3^+$ requires *m*/*z* = 178.0630, found: 178.0622.

2-Acetylbenzaldehyde (**4**) [9i]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.65 (3H, s), 7.61–7.74 (3H, m), 7.85–7.89 (1H, m), 10.23 (1H, s).

1-Dodecyl formate [9j]. ($CDCl_3$, 400 MHz): δ 0.87 (3H, t, *J* = 6.8 Hz), 1.20–1.40 (18H, m), 1.61–1.70 (2H, m), 4.15 (2H, t, *J* = 6.4 Hz), 8.05 (1H, s).

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