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Facile oxidative hydrolysis of acetals to esters using hypervalent iodine(III)/LiBr combination in water

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ABSTRACT

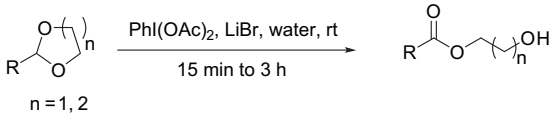
The combination of (diacetoxy)iodobenzene ($PhI(OAc)_2$, DIB) and lithium bromide (LiBr) efficiently oxidized cyclic and acyclic acetals to the corresponding hydroxyalkyl carboxylic esters and simple esters in good to excellent yields. The merits of this reaction are that it employs commercially available and non-explosive hypervalent iodine(III) reagent, water as the solvent, a short reaction time, and mild reaction conditions.

1. Introduction

In recent years, hypervalent iodine reagents have gained popularity in organic chemistry as reflected by the growing number of related communications, reports, and reviews.[1] The increasing interest in these nonmetallic oxidizing reagents is mainly due to their benign properties, chemoselectivity, mild reaction conditions, ease of handling, availability, and ready preparation from commercially available starting materials. In addition to serving as conventional oxidizing reagents,[2] the synthetic utilities of hypervalent iodine oxidants were employed to promote elegant oxidative transformations in the field of natural product synthesis and new synthetic methodologies due to their potential applications in the construction of carbon–carbon and carbon–heteroatom bonds.[3] Despite their intriguing utility in organic synthesis, broadly employed pentavalent iodine reagents, for example, Dess–Martin periodinane (DMP)[4] and *o*-iodoxybenzoic acid (IBX)[5] are thermally unstable and potentially explosive, respectively. As a result, it is highly desirable to employ the readily available and relatively stable hypervalent iodine(III) reagents in place of iodine(V) reagents.

Hydroxyalkyl carboxylic esters are of particular importance serving as cross-linking agents for polyesters and fungicides.[6] Direct conversion of cyclic acetals to their corresponding hydroxyalkyl carboxylic esters can be mediated by a variety of reagents, which include molecular oxygen–Co(II),[7] di-*tert*-butyl peroxide,[8] *tert*-butyl hydroperoxide in combination with transition metals,[9] *tert*-butyl hydroperoxide-pyridinium dichromate (PDC),[10] *tert*-butyl hydroperoxide-iodine(III) compounds,[11] potassium permanganate,[12] electrochemical oxidation,[13] ozonolysis,[14] electrophilic halogen,[15] *m*-chloroperbenzoic acid in the presence of 2,2′-bipyridinium chlorochromate (BPCC) or borontrifluoride etherate,[16] sodium perborate in acetic anhydride,[17] and oxone.[18]

In continuation of our ongoing research interest regarding the development of new synthetic applications of *o*-iodoxybenzoic acid (IBX),[19] we have recently disclosed a combined use of IBX and tetraethylammonium bromide in water for oxidative cleavage of acetals to their corresponding hydroxyalkyl esters and simple esters.[20] Encouraged by these results, we now report a practical and facile oxidative hydrolysis of cyclic acetals by (diacetoxy)iodobenzene ($PhI(OAc)_2$, DIB) in the presence of lithium bromide (LiBr) in water at room temperature to afford the corresponding hydroxyalkyl carboxylic esters (Scheme 1).



Scheme 1. DIB mediated oxidative cleavage of acetals.

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2. Results and discussion

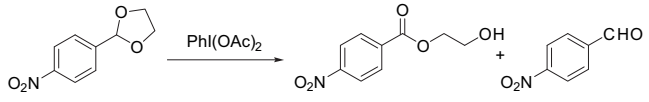
To identify suitable reaction conditions, we screened several reaction parameters using the 1,3-dioxolane **1a** derived from 4-nitrobenzaldehyde as a model substrate and the results are summarized in Table 1. Our previous study prompted us to initially carry out the reaction in water.[20] In the absence of additive and despite prolonged reaction time (3 h), no reaction took place and mostly **1a** was recovered (entry 1). The addition of bromide salts such as KBr, NaBr, LiBr, and Et_4NBr promoted the reaction to afford **2a** in moderate to excellent conversion (entries 2–5); LiBr gave the best conversion (91%).[21–23] At this point, we chose LiBr as an additive for this reaction and further explored other reaction parameters. Improved conversion was observed when running the reaction for 45 min. (99% conversion, entry 6). The type of halide anion has a significant effect on this conversion and bromide anion was found indispensable for the conversion of **1a** to **2a**. Mostly **1a** was recovered when the reaction was conducted in the presence of either NaCl or LiI (entries 7 and 8). We have also briefly examined the solvent effect and found that most frequently used organic solvents gave inferior results (entries 9–13). It is worth noting that extensive hydrolysis was observed when the reaction was carried out using molecular bromine as a reagent in the absence of $PhI(OAc)_2$: % conversion; **2a** (32%) and **3a** (47%). Overall, the optimum conditions comprised carrying out the reaction in water (0.25 M) in the presence of $PhI(OAc)_2$ (1.25 equiv) and LiBr (0.25 equiv) at room temperature.

In order to demonstrate the scope and the generality of the present reaction, the oxidative hydrolysis of a variety of acetals was examined under the optimized reaction conditions. The results are summarized in Table 2. The reaction was allowed to proceed until complete consumption of acetal was observed as judged by TLC monitoring. In general, the reactions went to completion within 15 min providing the corresponding hydroxyalkyl carboxylic esters in moderate to excellent yields (46–94%). Among the substrates tested, the nitro-substituted aromatic dioxolanes and dioxanes underwent oxidative hydrolysis at slower rate therefore this required longer reaction times (45–180 min) or excess amounts of reagents (entries 1–4). It is worth noting that the oxidative hydrolysis of **1b** and **1d** under our previously established conditions (IBX (1.1 equiv)/Et_4NBr (0.5 equiv)/H_2O/65 °C) gave inferior results; **2b** was isolated in 50% yield after 3 h and no reaction in case of **1d**.[20] Oxidation of cyclic acetals derived from bromo-, chloro-, fluoro-, and methyl-substituted aromatic dioxolanes and dioxanes gave the corresponding esters in moderate to excellent yields (entries 5–12). Furthermore, cyclic acetals derived from aliphatic aldehydes generally afforded the corresponding esters in good yields (entries 13–22). High yields were also obtained with the cyclic acetals derived from α-disubstituted aldehydes (entries 23–26). Finally, the oxidative hydrolysis of acyclic dialkyl acetals **4a** and **4b** proceeded readily, affording the corresponding simple esters **5a** and **5b** in moderate yields (entries 27 and 28).

Under similar reaction conditions, the reaction of unsymmetrical cyclic acetals was also briefly examined. It was found that the reaction proceeded readily but without selectivity. After chromatographic purification, a mixture of inseparable isomeric hydroxyalkyl carboxylic esters and an over-oxidized keto-ester were isolated. The results are summarized in Table 3.

While no detailed mechanistic studies have been carried out for an explanation of the reaction mechanism, a probable mechanistic pathway was assumed based on the experimental results and literature precedents on similar acetal cleavage and $PhI(OAc)_2$/bromide anion mediated reactions.[15,22] Displacement of the acetate ligand of $PhI(OAc)_2$ with bromide anion gave reactive intermediate **6**. The intermediate **6** reacted with acetal **1** through an electron transfer process, furnishing stabilized acetal carbocation **7**.

Table 1
Optimization of reagents and reaction conditions for the conversion of **1a** to **2a**[a]

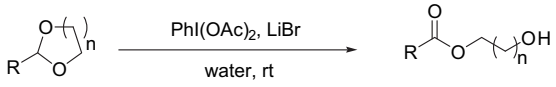


1a **2a** **3a**

Entry	Additive	Solvent	Time (min)	Conversion (%)[b]	
				2a	**3a**
1	None	H_2O	120	0	0
2	KBr	H_2O	30	70	0
3	NaBr	H_2O	30	46	1
4	LiBr	H_2O	30	91	1
5	Et_4NBr	H_2O	30	82	3
6	LiBr	H_2O	45	99	1
7	NaCl	H_2O	45	0	0
8	LiI	H_2O	45	4	3
9	LiBr	CH_2Cl_2	60	78[c]	0
10	LiBr	CH_3CN	60	51[c]	0
11	LiBr	THF	60	[d]	0
12	LiBr	Acetone	60	82	2
13	LiBr	CH_3OH	60	13	0

[a] Reagents and conditions: **1a** (0.5 mmol), $PhI(OAc)_2$ (1.25 equiv), additive (0.25 equiv), solvent (2 mL), room temperature.
[b] Calculated from ^1H NMR (300 MHz) integration.
[c] Diester and bromoalkyl carboxylic ester were obtained as by-products.
[d] Complex mixture.

Table 2
Oxidation of acetals with $PhI(OAc)_2$/LiBr in water[a]

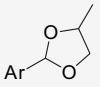
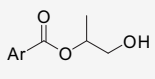
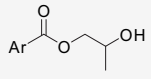
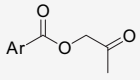


1 **2**

Entry	Acetal	R=	*n*	Time (min)	**2**	Yield[b] (%)
1	**1a**	4-$O_2NC_6H_4$	1	45	**2a**	85
2	**1b**		2	45	**2b**	76
3[c]	**1c**	2-$O_2NC_6H_4$	1	120	**2c**	82
4	**1d**		2	180	**2d**	81
5	**1e**	4-BrC_6H_4	1	15	**2e**	94
6	**1f**		2	15	**2f**	81
7	**1g**	3-ClC_6H_4	1	15	**2g**	79
8	**1h**		2	15	**2h**	80
9	**1i**	4-FC_6H_4	1	15	**2i**	46
10	**1j**		2	15	**2j**	90
11	**1k**	4-$CH_3C_6H_4$	1	15	**2k**	46
12	**1l**		2	15	**2l**	86
13	**1m**	$C_6H_5CH_2$	1	15	**2m**	70
14	**1n**		2	15	**2n**	80
15	**1o**	*n*-C_5H_{11}	1	15	**2o**	84
16	**1p**		2	15	**2p**	90
17	**1q**	*n*-C_6H_{13}	1	15	**2q**	92
18	**1r**		2	15	**2r**	90
19	**1s**	*n*-C_8H_{17}	1	15	**2s**	87
20	**1t**		2	15	**2t**	92
21	**1u**	*n*-$C_{13}H_{27}$	1	15	**2u**	72
22	**1v**		2	15	**2v**	85
23	**1w**	Cyclohexyl	1	15	**2w**	81
24	**1x**		2	15	**2x**	71
25	**1y**	$Ph(CH_3)CH$	1	15	**2y**	83
26	**1z**		2	15	**2z**	79
27	**4a**[d]			15	**5a**	67
28	**4b**[d]			15	**5b**	65

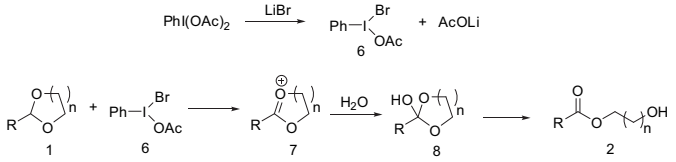
[a] Reagents and conditions: acetal (0.5 mmol), $PhI(OAc)_2$ (1.25 equiv), LiBr (0.25 equiv), H_2O (2 mL), room temperature.
[b] Isolated yields after purification by column chromatography.
[c] The reaction employed $PhI(OAc)_2$ (1.5 equiv) and LiBr (0.5 equiv).
[d] Phenylacetaldehyde dimethyl acetal (**4a**); 2-phenylpropanal dimethyl acetal (**4b**); methyl phenylacetate (**5a**); methyl 2-phenylpropanoate (**5b**).

Table 3
Oxidation of unsymmetrical acetals with $PhI(OAc)_2$/LiBr in water

Entry	Acetal; Ar=	Yield[a] (%)			
					
1[b]	4-$O_2NC_6H_4$	85 (1:1.5)		12	
2[c]	2-$O_2NC_6H_4$	81 (2:1)		7	

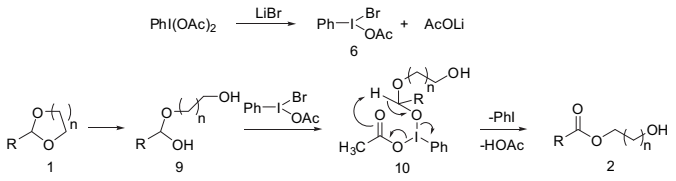
[a] Isolated yields after purification by column chromatography.
[b] The reaction employed $PhI(OAc)_2$ (1.25 equiv) and LiBr (0.25 equiv) for 45 min.
[c] The reaction employed $PhI(OAc)_2$ (1.5 equiv) and LiBr (0.5 equiv) for 90 min.

Nucleophilic attack by water, leading to hemiorthoester **8**, followed by ring opening eventually gave hydroxyalkyl carboxylic ester **2** (Scheme 2).



Scheme 2. Proposed mechanistic pathway for $PhI(OAc)_2$/LiBr mediated oxidative hydrolysis of acetals.

An alternative mechanism includes formation of hemiacetal **9** and the reactive intermediate **6** under the reaction conditions. Displacement of the polarized bromine atom of **6** by the hydroxyl group at the hemiacetal carbon provided intermediate **10**, which readily decomposed with the elimination of iodobenzene and acetic acid to give hydroxyalkyl carboxylic ester **2** (Scheme 3).



Scheme 3. Alternative mechanistic pathway for $PhI(OAc)_2$/LiBr mediated oxidative hydrolysis of acetals.

3. Conclusion

In summary, we have demonstrated the facile aqueous oxidative hydrolysis of acetal **1** to hydroxyalkyl carboxylic esters **2** using a combination of environmentally benign (diacetoxy)iodobenzene ($PhI(OAc)_2$, DIB) as oxidant and LiBr. The present system showed broad generality, tolerating a range of substrate structures. In comparison with our previously reported procedure, the apparent merits of the present protocol include use of a commercially available and non-explosive reagent, superior efficiency, mild reaction conditions (room temperature), and short reaction time.

4. Experimental

4.1. General

Reagents were obtained from commercial suppliers and used without prior purification. Analytical thin layer chromatography (TLC) plates were purchased from Merck (silica gel 60 F_{254}). Column chromatography was carried out using silica gel 60 (0.063–0.200 mm). Known compounds were characterized by ^1H and ^{13}C NMR, IR, and mass spectroscopy, and their spectroscopic data were identical to those previously reported in the literature; (**2a**),[24] (**2b**, **2e**, **2g**–**2j**, **2m**, **2n**, **2s**–**2v**, **2y**, **2z**, **5b**),[20] (**2c**),[25] (**2f**),[7b] (**2k**),[9c,16b] (**2l**),[16b] (**2w**),[25] (**5a**).[26] All new compounds were characterized by ^1H and ^{13}C NMR, IR, and high-resolution mass spectroscopy. ^1H NMR and ^{13}C spectra were recorded on a Bruker DPX-300 and Bruker Avance 500 spectrometers. Infrared spectra were recorded on a Perkin Elmer GX FT-IR System spectrometer. High-resolution mass spectra (HRMS) were determined using Bruker micro TOF spectrometer.

4.2. General procedure for the synthesis of hydroxyalkyl carboxylic esters 2

$PhI(OAc)_2$ (0.625 mmol, 201.3 mg) was added to a suspension of acetal (0.5 mmol) and LiBr (10.7 mg, 0.25 mmol) in water (2 mL) and the reaction mixture was vigorously stirred at room temperature for a given time as shown in Table 3. Upon completion of the reaction (TLC monitoring), the reaction mixture was quenched by addition of saturated aqueous sodium thiosulfate (5 mL), basified with saturated aqueous sodium hydrogen carbonate (5 mL), followed by stirring, and extracted with EtOAc (3×5 mL). The combined organic extracts were washed with water (10 mL), brine (10 mL), dried ($MgSO_4$), filtered, and concentrated (rotary evaporator). The residue was purified by column chromatography (silica gel) to furnish the analytically pure product.

*4.2.1. 3-Hydroxypropyl 2-nitrobenzoate (**2d**).* Compound **1d** (104.5 mg, 0.5 mmol). Column chromatography (silica gel, 13×2 cm; hexanes–EtOAc, 4:1 to 1:1) gave the title compound. Yield: 91.2 mg (81%); yellow liquid; R_f=0.15 (hexanes–EtOAc, 3:2). IR (neat, cm^{-1}): ν_{max} 3419, O–H; 1732, C=O. ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (dd, J=7.4, 1.8 Hz, 1H), 7.76 (dd, J=7.4, 1.8 Hz, 1H), 7.74–7.59 (m, 2H), 4.49 (t, J=6.1 Hz, 2H), 3.75 (td, J=6.1, 5.4 Hz, 2H), 2.11 (t, J=5.4 Hz, 1H), 1.98 (quin, J=6.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 165.3, 132.9, 131.8, 129.9, 127.5, 123.9, 63.0, 60.8, 27.7. HRMS (ESI-TOF) calcd for $C_{10}H_{11}NO_5Na$ [$(M+Na)^+$]: 248.0535; found: 248.0564.

*4.2.2. 2-Hydroxyethyl hexanoate (**2o**).* Compound **1o** (72.0 mg, 0.5 mmol). Column chromatography (silica gel, 13×2 cm; hexanes–EtOAc, 9:1 to 7:3) gave the title compound. Yield: 67.2 mg (84%); colorless liquid; R_f=0.30 (hexanes–EtOAc, 7:3). IR (neat, cm^{-1}): ν_{max} 3417, O–H; 1736, C=O. ^1H NMR (300 MHz, $CDCl_3$): δ 4.20 (t, J=4.7 Hz, 2H), 3.82 (t, J=4.7 Hz, 2H), 3.71–2.92 (br, 1H), 2.34 (t, J=7.5 Hz, 2H), 1.64 (quin, J=7.5 Hz, 2H), 1.38–1.25 (m, 4H), 0.89 (t, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.3, 65.8, 61.1, 34.1, 31.2, 24.5, 22.2, 13.8. HRMS (ESI-TOF) calcd for $C_8H_{16}O_3Na$ [$(M+Na)^+$]: 183.0997; found: 183.1008.

*4.2.3. 3-Hydroxypropyl hexanoate (**2p**).* Compound **1p** (79.0 mg, 0.5 mmol). Column chromatography (silica gel, 13×2 cm; hexanes–EtOAc, 9:1 to 7:3) gave the title compound. Yield: 78.3 mg (90%); pale yellow liquid; R_f=0.23 (hexanes–EtOAc, 7:3). IR (neat, cm^{-1}): ν_{max} 3418, O–H; 1738, C=O. ^1H NMR (300 MHz, $CDCl_3$): δ 4.21 (t, J=6.2 Hz, 2H), 3.67 (t, J=6.2 Hz, 2H), 2.49 (br s, 1H), 2.30 (t, J=7.5 Hz, 2H), 1.85 (quin, J=6.2 Hz, 2H), 1.61 (quin, J=7.5 Hz, 2H), 1.40–1.15 (m, 4H), 0.88 (t, J=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.2, 61.1, 59.0, 34.1, 31.6, 31.1, 24.5, 22.1, 13.7. HRMS (ESI-TOF) calcd for $C_9H_{18}O_3Na$ [$(M+Na)^+$]: 197.1154; found: 197.1146.

*4.2.4. 2-Hydroxyethyl heptanoate (**2q**).* Compound **1q** (79.0 mg, 0.5 mmol). Column chromatography (silica gel, 13×2 cm; hexanes–EtOAc, 9:1 to 7:3) gave the title compound. Yield: 80.1 mg (92%); colorless liquid; R_f=0.33 (hexanes–EtOAc, 7:3). IR (neat, cm^{-1}): ν_{max} 3423, O–H; 1738, C=O. ^1H NMR (300 MHz, $CDCl_3$): δ 4.14

(t, J=4.5 Hz, 2H), 3.75 (t, J=4.5 Hz, 2H), 2.28 (t, J=7.2 Hz, 2H), 2.05 (br s, 1H), 1.54 (quin, J=7.2 Hz, 2H), 1.38–1.21 (m, 6H), 0.80 (t, J=6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 65.8, 61.2, 34.1, 31.4, 28.7, 24.8, 22.4, 13.9. HRMS (ESI-TOF) calcd for $C_9H_{18}O_3Na$ [$(M+Na)^+$]: 197.1154; found: 197.1142.

*4.2.5. 3-Hydroxypropyl heptanoate (**2r**).* Compound **1r** (86.0 mg, 0.5 mmol). Column chromatography (silica gel, 13×2 cm; hexanes–EtOAc, 9:1 to 7:3) gave the title compound. Yield: 84.6 mg (90%); pale yellow liquid; R_f=0.33 (hexanes–EtOAc, 7:3). IR (neat, cm^{-1}): ν_{max} 3419, O–H; 1738, C=O. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.23 (t, J=6.1 Hz, 2H), 3.69 (t, J=6.1 Hz, 2H), 2.44 (br s, 1H), 2.32 (t, J=7.5 Hz, 2H), 1.87 (quin, J=6.1 Hz, 2H), 1.62 (quin, J=7.5 Hz, 2H), 1.33–1.27 (m, 6H), 0.89 (t, J=6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3, 61.1, 59.0, 34.2, 31.7, 31.3, 28.7, 24.8, 22.4, 13.9. HRMS (ESI-TOF) calcd for $C_{10}H_{20}O_3Na$ [$(M+Na)^+$]: 189.1493; found: 189.1486.

*4.2.6. 2-Hydroxyethyl cyclohexanecarboxylate (**2w**).* Compound **1w** (78.1 mg, 0.5 mmol). Column chromatography (silica gel, 13×2 cm; hexanes–EtOAc, 9:1 to 3:2) gave the title compound. Yield: 69.7 mg (81%); colorless liquid; R_f=0.30 (hexanes–EtOAc, 7:3). IR (neat, cm^{-1}): ν_{max} 3443, O–H; 1732, C=O. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.23–4.18 (m, 2H), 3.82 (t, J=4.5 Hz, 2H), 2.35 (tt, J=11.4, 3.6 Hz, 1H), 2.28 (br s, 1H), 1.96–1.88 (m, 2H), 1.81–1.73 (m, 2H), 1.69–1.61 (m, 1H), 1.52–1.40 (m, 2H), 1.35–1.18 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.5, 65.8, 61.3, 43.1, 28.9 (2C), 25.6, 25.3 (2C). HRMS (ESI-TOF) calcd for $C_9H_{16}O_3Na$ [$(M+Na)^+$]: 195.0992; found: 195.1002.

*4.2.7. 3-Hydroxypropyl cyclohexanecarboxylate (**2x**).* Compound **1x** (85.0 mg, 0.5 mmol). Column chromatography (silica gel, 13×2 cm; hexanes–EtOAc, 9:1 to 3:2) gave the title compound. Yield: 66.1 mg (71%); colorless liquid; R_f=0.28 (hexanes–EtOAc, 7:3). IR (neat, cm^{-1}): ν_{max} 3419, O–H; 1732, C=O. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.23 (t, J=6.1 Hz, 2H), 3.68 (t, J=6.1 Hz, 2H), 2.31 (tt, J=11.2, 3.7 Hz, 1H), 2.13 (br s, 1H), 1.98–1.82 (m, 4H), 1.82–1.70 (m, 2H), 1.70–1.60 (br, 1H), 1.54–1.13 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.6, 61.0, 59.1, 43.2, 31.8, 29.0 (2C), 25.7, 25.4 (2C). HRMS (ESI-TOF) calcd for $C_{10}H_{18}O_3Na$ [$(M+Na)^+$]: 209.1154; found: 209.1180.

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