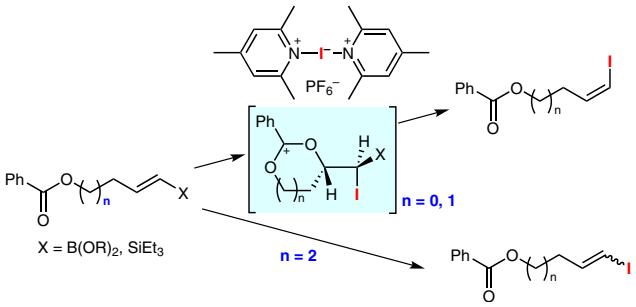
Synthesis M. Fujita et al. Special Topic

E/*Z*-Selectivity Controlled by Participation of Internal Oxy Group During Electrophilic Substitution of Alk-1-enylboronate with Bis(2,4,6-trimethylpyridine)iodonium Salt

Morifumi Fujita*
Hee Jin Lee
Chisaki Ichihara
Takashi Sugimura

Graduate School of Material Science, University of Hyogo, Kohto, Kamigori, Hyogo 678-1297, Japan
fuji@sci.u-hyogo.ac.jp



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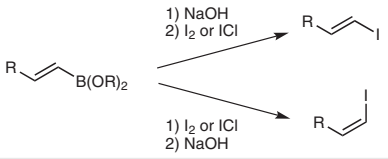
Abstract Stereospecific inversion of configuration was observed in electrophilic iodo-substitution of 4-benzoyloxybut-1-enylboronate using bis(2,4,6-trimethylpyridine)iodine(I) salt, rationalized by participation of the internal benzoyloxy group.

Key words alkenylboronate, iodoalkene, neighboring group participation, *E*/*Z*-selectivity, iodonium

Alk-1-enyl iodides are important synthetic intermediates, especially for stereoselective alkene and polyene synthesis.[1] Alkenylboronic acids and alkenylboronates are stereoselectively converted to alkenyl iodides via electrophilic substitution.[2] The *E*/*Z* stereoselectivity in iodo-substitution is controlled by the order of addition of the base and iodine source (I_2 or ICl), as shown in Scheme 1.[3–5]



Scheme 1 Iodo-substitution of alkenylboronate

Iodine-substitution in the presence of NaOH proceeds with retention of configuration. In contrast, inversion of configuration takes place in the absence of NaOH, when it is added after the reaction. Sodium hydroxide has been considered to react at the boron atom position to make a tetrahedral boronate complex. Electrophilic substitution of the tetrahedral boronate complex proceeds rapidly with retention of configuration via a simple addition–elimination mechanism. Boronates and boronic acids with less reactivity towards the elimination lead to *anti*-addition–*anti*-elimination, resulting in inversion of configuration.

In this communication, we report neighboring group participation control of the *E*/*Z* selectivity in iodo-substitution of alk-1-enylboronate pinacol ester using bis(2,4,6-trimethylpyridine)iodine(I) hexafluorophosphate (BTMPI).[6] BTMPI is a commercially available iodination reagent with high level of electrophilicity owing to the cationic character, and liberates weak nucleophiles during iodination.[6a] These properties may be suitable for highlighting the intramolecular nucleophilic participation.

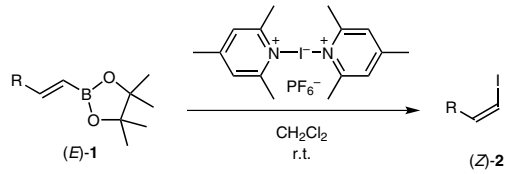
The *E*-isomers of alkenylboronate pinacol ester, (*E*)-**1a–e**, were prepared by conventional hydroboration of alkynes,[7] while the *Z*-isomers (*Z*)-**1b–e** were prepared by rhodium-catalyzed hydroboration.[8] The pinacol esters are relatively stable against hydrolysis, and tolerate purification by silica gel column chromatography.

The reaction of (*E*)-**1a–e** with BTMPI was carried out in dichloromethane at room temperature and gave alkenyl iodide **2**, as summarized in Table 1. The reactions of (*E*)-3-benzoyloxyprop-1-enylboronate (*E*)-**1a** and (*E*)-4-benzoyloxybut-1-enylboronate (*E*)-**1b** preferentially yield the corresponding (*Z*)-alk-1-enyl iodide, (*Z*)-**2** (Table 1, entries 1 and 2). In contrast, substrate (*E*)-**1c** with a longer pentenyl group led to a *Z*/*E* mixture of alkenyl iodide (entry 4). High *Z*-selectivity was observed in the reaction of (*E*)-**1d**, with the same pentenyl chain as **1c**, however, the oxy functional group is benzyloxy (entry 7). The *Z*-selectivity in reactions of (*E*)-**1a**, (*E*)-**1b**, and (*E*)-**1d** is in contrast with the *Z*/*E* mixture obtained from simple dec-1-enylboronate (*E*)-**1e** (entry 9). The reactions in diethy ether/dichloromethane (entries 3 and 5) or under dilute conditions (entries 6 and 8) slightly affected the stereoselectivity and improved the chemical yield.

The *Z*-isomers of alkenylboronates were also employed for the iodo-substitution reaction with BTMPI (Table 2). The reaction of (*Z*)-4-benzoyloxybut-1-enylboronate (*Z*)-**1b** selectively gave (*E*)-**2b** with inversion of configuration (Table 2, entry 1). Taking the result of (*E*)-**1b** into consideration, the substitution of 4-benzoyloxybut-1-enylboronate (**1b**) stereospecifically proceeds with inversion of configuration. A decrease in the *E*/*Z* selectivity was observed in the reaction of (*Z*)-5-benzoyloxypent-1-enylboronate (*Z*)-**1c** (entries 2 and 3), as with (*E*)-**1c**. The benzyloxy substrate of **1d** led to stereospecific substitution with inversion of configuration (entry 4).

Stereospecific inversion of configuration was observed in the reactions of **1a**, **1b**, and **1d**. The stereospecifity decreased in the reaction of **1c** and **1e**. These results are rationalized with a reaction mechanism that involves neighboring group participation, as illustrated in Scheme 2. The benzoyloxy group of **1a** and **1b** nucleophilically attacks the olefin moiety giving five- and six-membered oxonium cation intermediate, respectively, during the electrophilic substitution. Initial *anti*-addition is likely followed by *anti*-elimination to yield alkenyl iodide **2** with inversion of configuration. The decrease in *E*/*Z* selectivity in the reaction of **1c** may be attributed to the less favorable seven-membered oxonium cation. The benzyloxy substrate **1d** is able to form the five-membered oxolanyl cation during the electrophilic substitution. The five-membered oxolanyl cation generated from the benzoyloxy substrate **1c** must be unstable owing to the electron-withdrawing benzoyl group on the oxonium.

Table 1 Reaction of (*E*)-**1** with BTMPI[a]

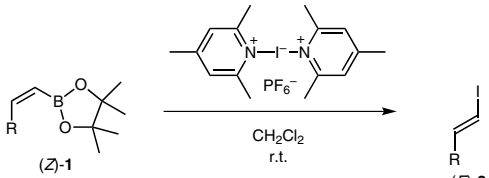


(*E*)-**1** (*Z*)-**2**

Entry	Substrate	R	Yield of **2** (%)	*Z*/*E*
1	(*E*)-**1a**	$PhCO_2CH_2$	60	89:11
2	(*E*)-**1b**	$PhCO_2(CH_2)_2$	59	91:9
3[b]	(*E*)-**1b**	$PhCO_2(CH_2)_2$	71	96:4
4	(*E*)-**1c**	$PhCO_2(CH_2)_3$	39	55:45
5[b]	(*E*)-**1c**	$PhCO_2(CH_2)_3$	46	71:29
6[c]	(*E*)-**1c**	$PhCO_2(CH_2)_3$	61	40:60
7	(*E*)-**1d**	$PhCH_2O(CH_2)_3$	55	93:7
8[c]	(*E*)-**1d**	$PhCH_2O(CH_2)_3$	68	>98:2
9	(*E*)-**1e**	$Me(CH_2)_7$	63	68:32

[a] The reaction was typically carried out in CH_2Cl_2 (1 mL) containing **1** (0.17 mmol) and BTMPI (0.22 mmol) at 25 °C for 2–6 h.
[b] Reaction was carried out in Et_2O/CH_2Cl_2 = 1:1 (v/v).
[c] The reaction was carried out in dilute solution. The concentrations of the substrate and reagent were one fifth of those under the typical conditions.

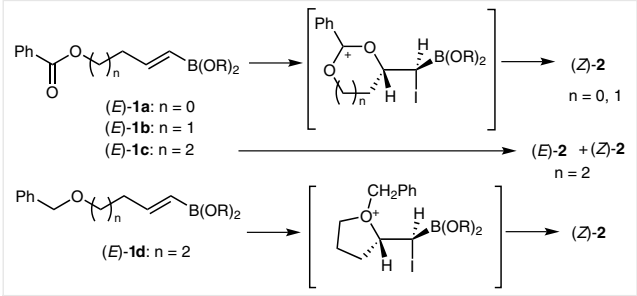
Table 2 Reaction of (*Z*)-**1** with BTMPI[a]



(*Z*)-**1** (*E*)-**2**

Entry	Substrate	R	Yield of **2** (%)	*E*/*Z*
1	(*Z*)-**1b**	$PhCO_2(CH_2)_2$	65	>98:2
2	(*Z*)-**1c**	$PhCO_2(CH_2)_3$	57	84:16
3[b]	(*Z*)-**1c**	$PhCO_2(CH_2)_3$	69	66:34
4[b]	(*Z*)-**1d**	$PhCH_2O(CH_2)_3$	69	92:8
5[b]	(*Z*)-**1e**[c]	$Me(CH_2)_7$	71	82:18

[a] The reaction was typically carried out in CH_2Cl_2 (1 mL) containing **1** (0.17 mmol) and BTMPI (0.22 mmol) at 25 °C for 2–6 h.
[b] The reaction was carried out in dilute solution. The concentrations of the substrate and reagent were one fifth of those under the typical conditions.
[c] The sample was a mixture of (*Z*)-**1e** and (*E*)-**1e** (87:13).

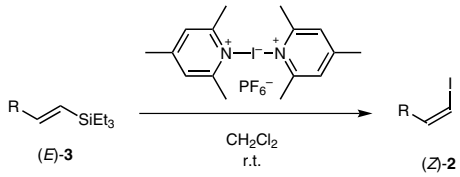


Scheme 2 Plausible mechanism for inversion of configuration

Participation of the carbonyl oxygen in iodo-substitution has been discussed for the reaction of acyloxyprop-1-enyl(trimethyl)silane with *N*-iodosuccinimide (NIS).[9] For comparison, 4-benzoyloxybut-1-enylsilane (**3b**) and 5-benzoyloxypent-1-enylsilane (**3c**) were subjected to iodo-substitution with BTMPI as summarized in Table 3. In the literature,[9] the reaction of both (*E*)- and (*Z*)-3-acyloxyprop-1-enyl(trimethyl)silane with NIS preferentially yielded *Z*-iodide resulting from the thermodynamic stability of the cationic intermediate. A similar tendency was observed in the reaction of **3b** with BTMPI (Table 3, entries 1 and 2). The *Z*-isomer of iodide (*Z*)-**2b** was preferentially obtained. The difference in the selectivity between the boronates **1** and the silanes **3** can be explained by the difference of reactivity of the elimination step. A difference in the elimination reactivity was also observed in reactions with (diacetoxyiodo)benzene under acidic conditions.[10]

Retention of configuration was observed for the iodo-substitution of alkenylzirconium[1a,11] and alkenylindium[12]

Table 3 Reaction of Alk-1-enylsilane **3** with BTMPI[a]



Entry	Substrate	R	Yield of **2** (%)	*Z*/*E*
1	(*E*)-**3b**	$PhCO_2(CH_2)_2$	45	>98:2
2	(*Z*)-**3b**	$PhCO_2(CH_2)_2$	88	69:31
3	(*E*)-**3c**	$PhCO_2(CH_2)_3$	61	35:65

[a] Reaction was typically carried out in CH_2Cl_2 (1 mL) containing **3** (0.17 mmol) and BTMPI (0.34 mmol) at 25 °C for 7–17 h.

intermediates, even in the case of 4-benzoyloxybut-1-enyl and 5-benzyloxypent-1-enyl species. These results suggest that the internal oxy group does not participate in the reaction of a strong electrofuge.

In summary, we have demonstrated that stereospecific inversion of configuration is achieved in idodo-substitution of alk-1-enylboronate through participation of an internal benzoyloxy group.

Major reagents and solvents were obtained from commercial sources and were used without further purification, unless otherwise noted. CH_2Cl_2 was purified by distillation over CaH_2. Column chromatography was performed on silica gel 60 (0.063–0.200 mm) from Merck. ^1H and ^{13}C NMR spectra were recorded on a Jeol ECA-600 spectrometer as solutions in $CDCl_3$. ^1H NMR spectra were recorded using the residual $CHCl_3$ as an internal reference (7.24 ppm) and ^{13}C NMR using $CDCl_3$ as an internal reference (77.00 ppm). Jeol JMS-T100LC spectrometer was used for mass spectra measurements. IR spectra were recorded on a Jasco FT/IR-410 spectrometer.

Alkenylboronate pinacol esters, (*E*)-**1b**,[10a] (*Z*)-**1b**,[10a] (*E*)-**1c**,[10a] (*E*)-**1d**,[10a] (*Z*)-**1d**,[10a] and (*Z*)-**1e**[8] were prepared as reported previously. Preparation of alkenylsilanes, (*E*)-**3b**, (*Z*)-**3b**, and (*E*)-**3c** were reported previously.[10b]

(*E*)-3-Benzoyloxyprop-1-enylboronate Pinacol Ester [(*E*)-1a][13]

Following the literature procedure,[13] the reaction of 3-benzoyloxyprop-1-yne (2.5 g, 15.8 mmol) with pinacolborane (3.4 mL, 24 mmol) in the presence of dicyclohexylborane (5.0 mmol) for 20 h at r.t. gave (*E*)-**1a** (3.05 g, 10.6 mmol, 67%) after column chromatography (SiO_2, eluent: 30% EtOAc in hexane); colorless oil.

IR (film): 2979, 1722, 1270, 1145, 712 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 8.06 (d, *J* = 7.6 Hz, 2 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 6.71 (dt, *J* = 18.6, 4.8 Hz, 1 H), 5.78 (d, *J* = 18.6 Hz, 1 H), 4.90 (m, 2 H), 1.25 (s, 12 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 166.04, 145.94, 132.99, 130.03, 129.67, 128.33, 83.43, 65.71, 24.75.

HRMS (ESI+): *m*/*z* calcd for $C_{16}H_{21}BO_4Na$ (M + Na): 311.1431; found: 311.1465.

(*Z*)-5-Benzoyloxypent-1-enylboronate Pinacol Ester [(*Z*)-1c)]

Bis(1,5-cyclooctadiene)-μ,μ′-dichlorodirhodium (10.8 mg, 0.022 mmol), tricylopentylphosphine (25 μL, 0.086 mmol), Et_3N (1.0 mL, 7.2 mmol), and pinacolborane (0.2 mL, 1.4 mmol) were successively mixed in cyclohexane (3 mL) under N_2. After stirring for 30 min, 5-benzoyloxypent-1-yne (0.50 g, 2.9 mmol) was added. The mixture was stirred overnight at r.t., and then purified by silica gel column chromatography (eluent: 10% EtOAc in hexane) to give (*Z*)-**1c** (100 mg, 0.32 mmol, 23%); colorless oil.

IR (film): 2979, 1720, 1274, 1145, 713 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 8.04 (d, *J* = 7.6 Hz, 2 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 6.45 (dt, *J* = 13.1, 6.9 Hz, 1 H), 5.38 (d, *J* = 13.1 Hz, 1 H), 4.32 (t, *J* = 6.9 Hz, 2 H), 2.56 (q, *J* = 6.9 Hz, 2 H), 1.85 (quint, *J* = 6.9 Hz, 2 H), 1.21 (s, 12 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 166.57, 153.30, 132.73, 130.54, 129.55, 128.24, 82.86, 64.61, 28.86, 28.63, 24.76.

HRMS (ESI+): *m*/*z* calcd for $C_{18}H_{25}BO_4Na$ (M + Na): 339.1744; found: 339.1782.

(*E*)-Dec-1-enylboronate Pinacol Ester [(*E*)-1e][14]

Following the literature procedure,[14] the reaction of dec-1-yne (0.9 mL, 5 mmol) with pinacolborane (0.8 mL, 5.5 mmol) in the presence of dicyclohexylborane (0.62 mmol) for 1 h at r.t. gave (*E*)-**1e** (0.98 g, 3.7 mmol, 73%) after column chromatography (SiO_2, eluent: 30% EtOAc in hexane). ^1H NMR spectrum of the product agreed well with the reported values.[14]

Iodo-Substitution; (*E*)- and (*Z*)-3-Iodoprop-2-enyl Benzoate (2a);[1b] Typical Procedure

To a solution of (*E*)-**1a** (50 mg, 0.17 mmol) in CH_2Cl_2 (1 mL) was added BTMPI (113 mg, 0.22 mmol) at r.t. After stirring at r.t. for 3.5 h, the reaction mixture was quenched with H_2O, and extracted with CH_2Cl_2. The organic phase was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, eluent: 10% EtOAc in hexane) to yield **2a** (31 mg, 0.11 mmol, 60%) as an 89:11 mixture of *Z*/*E*; R_f = 0.5 (hexane/EtOAc, 9:1); oil.

^1H NMR ($CDCl_3$, 600 MHz): δ (*Z*-isomer) = 8.04 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 6.60–6.53 (m, 2 H), 4.88 (d, *J* = 4.8 Hz, 2 H).

^1H NMR ($CDCl_3$, 600 MHz): δ (*E*-isomer) = 8.03 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 6.74 (dt, *J* = 14.4, 6.2 Hz, 1 H), 6.60–6.53 (m, 1 H), 4.72 (d, *J* = 6.2 Hz, 2 H).

(*E*)-4-Iodobut-3-enyl Benzoate [(*E*)-2b][11]

Yield: 32.5 mg, 0.11 mmol (65%); oil; from (*Z*)-**1b** (50 mg, 0.17 mmol).

IR (film): 2956, 1718, 1274, 1115, 711 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 8.01 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 6.58 (dt, *J* = 14.4, 6.9 Hz, 1 H), 6.21 (d, *J* = 14.4 Hz, 1 H), 4.34 (t, *J* = 6.9 Hz, 2 H), 2.51 (q, *J* = 6.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 166.39, 141.66, 133.04, 130.07, 129.58, 128.40, 77.51, 62.85, 35.32.

HRMS (ESI+): *m*/*z* calcd for $C_{11}H_{11}IO_2Na$ (M + Na): 324.9701; found: 324.9726.

(*Z*)-4-Iodobut-3-enyl Benzoate [(*Z*)-2b]

Yield: 71 mg, 0.235 mmol (71%); oil; from (*E*)-**1b** (100 mg, 0.33 mmol).

IR (film): 2955, 1718, 1274, 1114, 711 cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.03 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 6.39 (d, *J* = 6.9 Hz, 1 H), 6.31 (q, *J* = 6.9 Hz, 1 H), 4.39 (t, *J* = 6.9 Hz, 2 H), 2.62 (q, *J* = 6.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 166.51, 136.88, 132.99, 130.10, 129.65, 128.36, 85.15, 62.69, 34.49.

HRMS (ESI+): *m*/*z* calcd for $C_{11}H_{11}IO_2Na$ (M + Na): 324.9701; found: 324.9688.

5-Iodopent-4-enyl Benzoate (2c)

Yield: 29 mg, 0.092 mmol (57%); oil; from (*Z*)-**1c** (50 mg, 0.16 mmol).

^{1}H NMR ($CDCl_3$, 600 MHz): δ (*Z*-isomer) = 8.05 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 6.27 (d, *J* = 6.9 Hz, 1 H), 6.22 (q, *J* = 6.9 Hz, 1 H), 4.33 (t, *J* = 6.9 Hz, 2 H), 2.32 (q, *J* = 6.9 Hz, 2 H), 1.90 (quint, *J* = 6.9 Hz, 2 H).

^{1}H NMR ($CDCl_3$, 600 MHz): δ (*E*-isomer) = 8.02 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 6.54 (dt, *J* = 14.4, 7.6 Hz, 1 H), 6.07 (d, *J* = 14.4 Hz, 1 H), 4.31 (t, *J* = 6.9 Hz, 2 H), 2.22 (q, *J* = 7.6 Hz, 2 H), 1.87 (quint, *J* = 6.9 Hz, 2 H).

(*Z*)-5-Benzyloxy-1-iodopent-1-ene [(*Z*)-2d][12]

Yield: 68 mg, 0.225 mmol (68%); oil; from (*E*)-**1d** (100 mg, 0.33 mmol).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.35–7.31 (m, 4 H), 7.26 (m, 1 H), 6.21–6.15 (m, 2 H), 4.50 (s, 2 H), 3.49 (t, *J* = 6.9 Hz, 2 H), 2.23 (q, *J* = 6.9 Hz, 2 H), 1.74 (quint, *J* = 6.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 140.73, 138.48, 128.32, 127.59, 127.49, 82.71, 72.91, 69.47, 31.57, 28.07.

(*E*)-5-Benzyloxy-1-iodopent-1-ene [(*E*)-2d][1a]

Yield: 48 mg, 0.16 mmol (69%); oil; from (*Z*)-**1d** (70 mg, 0.23 mmol).

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.35–7.25 (m, 5 H), 6.49 (dt, *J* = 14.4, 6.9 Hz, 1 H), 5.97 (d, *J* = 14.4 Hz, 1 H), 4.47 (s, 2 H), 3.45 (t, *J* = 6.9 Hz, 2 H), 2.14 (q, *J* = 6.9 Hz, 2 H), 1.69 (quint, *J* = 6.9 Hz, 2 H).

(*E*) and (*Z*)-1-Iododec-1-ene (2e)

Yield: 50 mg, 0.19 mmol (71%); oil; from (*Z*)-**1e** (70 mg, 0.26 mmol).

The analytical and spectral data of the products were in accordance with the reported values.[15,16]

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1558967.

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