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A first one-pot synthesis, isomerization and synthetic utility of mono- and bis Morita–Baylis–Hillman adducts of 1,1′-ferrocenedialdehyde

Ponnusamy Shanmugam *, Suchithra Madhavan, Kodirajan Selvakumar, Vadivel Vaithiyanathan, Baby Viswambharan

Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), Thiruvananthapuram 695 019, Kerala, India

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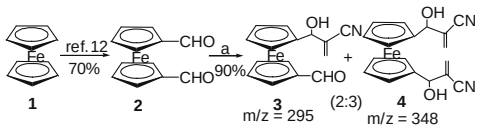
ABSTRACT

A one-pot synthesis of mono- and bis-Morita–Baylis–Hillman adducts of 1,1′-ferrocenedialdehyde has been achieved. These adducts undergo a facile and efficient stereoselective isomerization with a number of saturated, unsaturated, aromatic alcohols, phenols and thiophenol with a montmorillonite K10 clay catalyst to afford highly functionalized trisubstituted alkene derivatives of ferrocene. The synthetic utility of isomerized derivatives has been demonstrated by a ferrocene appended novel macrocycle synthesis, a ferrocenyl bis-triazole synthesis and an evaluation of the liquid crystalline property of a cholesterol derivative of ferrocene.

1. Introduction

The chemistry of ferrocene and its derivatives remains an important research area[1] due to its extensive applications in the development of novel materials,[2] catalysts for asymmetric synthesis[1e,3] and non-linear optical properties,[4] in biology[5] and in redox electrochemistry.[6] Among the various carbon-carbon bond forming reactions, Morita–Baylis–Hillman (MBH) adducts play an important role in synthetic chemistry, since they serve as versatile synthons in the construction of complex molecular frameworks.[7] The stereoselective construction of *E*- and *Z*-trisubstituted alkenes is very important in organic synthesis; however, only a limited number of methods are known[8] including the isomerization of acetates of MBH adducts with various catalysts.[9] The functionalization of ferrocene **1** under mild conditions remains, however, a difficult task, since multi-step rigorous reaction conditions are generally required for the purpose. Therefore, more simple and practical methods for its functionalization are still required. In continuation of our research on the novel synthetic applications of MBH adducts,[10] we have recently reported the isomerization of the MBH adducts of ferrocenealdehyde with various nucleophiles to afford functionalized *E*-trisubstituted alkenes stereoselectively.[11] In view of efficiency, the simultaneous functionalization of both the rings of ferrocene under mild reaction conditions is apparently more desirable. However, the functionalization of both the rings of ferrocene exploiting MBH chemistry is not known at present. Therefore, we investigated the functionalization of ferrocene by the use of MBH chemistry. The details of the one-pot synthesis, isomerization and synthetic utility of mono- and bis-MBH adducts of 1,1′-ferrocenedialdehyde are described in this Letter.

Dialdehyde **2**[12] with acrylonirile and a catalytic amount of DABCO afforded an inseparable mixture of mono- and bis-MBH adducts **3** and **4** in a 2:3 ratio with an excellent combined yield (Scheme 1). The ratio of the products was estimated from the ^{1}H NMR spectrum of the mixture of **3** and **4**. Fortunately, the bis adduct **4** could be isolated by simple crystallization. The ^{1}H NMR spectrum of **4** showed two multiplets at δ 5.98 and 5.05 for exocyclic methylene and methine protons, respectively, and ferrocenyl



Scheme 1. One-pot synthesis of mono- and bis-MBH adducts **3** and **4**.

* Corresponding author at present address: Organic Chemistry Division, Central Leather Research Institute (CLRI), Adyar, Chennai 600 020, India. Tel.: +91 44 24913289; fax: +91 44 24911589.
E-mail address: shanmu196@rediffmail.com (P. Shanmugam).

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protons appeared as a singlet at δ 4.47. The FAB mass spectrum showed a molecular ion peak at m/z 348 (M^+) which confirmed the symmetric nature of the bis-MBH adduct **4**. Final proof for the bis adduct structure was arrived at from single crystal X-ray analysis (Fig. 1). However, the synthesis of other MBH adducts of **2** with activated alkenes such as MVK, methyl acrylate, vinyl sulfone and acryl amide following the standard procedure failed to produce results.

Subsequently, the isomerization of **3** and **4** (Scheme 2) with various oxygen and sulfur nucleophiles was examined. Thus, the isomerization of a mixture of **3** and **4** with an excess of propargyl alcohol and 100% w/w montmorillonite K10 clay at reflux for 12 h afforded the corresponding mono **5** and bis-isomerized adduct **17** in 65% and 68% yields, respectively (Table 1, entry 1). The yields were calculated based on the ratio of **3** and **4**. The compounds **5** and **17** were separated by silica gel column chromatography and characterized by spectroscopic studies. Thus, the ^{1}H NMR spectrum of **5** showed two singlets at δ 9.91 and δ 6.89 due to aldehyde and olefin protons. A triplet at δ 2.52 and a doublet at δ 4.27 (J = 2.3 Hz) confirm terminal alkyne and methylene protons. A multiplet of eight protons at δ 4.94–4.53 represents ferrocenyl protons. The FAB mass spectrum showed a molecular ion peak at m/z 333.54 (M^+) and confirms structure **5**. The ^{1}H NMR spectrum of **17** showed a singlet at δ 6.9 for the *E*-olefin proton, two singlets at δ 4.86, 4.89 and a doublet at 4.09 (J = 3.0 Hz) due to ferrocene and $-CH_2$ protons. A singlet at δ 2.51 represents the terminal alkyne protons. The final proof on the symmetric nature of **17** was achieved based on the FAB mass spectrum as it showed a molecular ion peak at m/z 424.75 (M^+). The ^{13}C NMR spectrum showed peaks at δ 146.55 and 118.58 due to olefinic and nitrile carbons, respectively. The E-geometry of products **5** and **17** was assigned based on the literature analogy.[8,9,11]

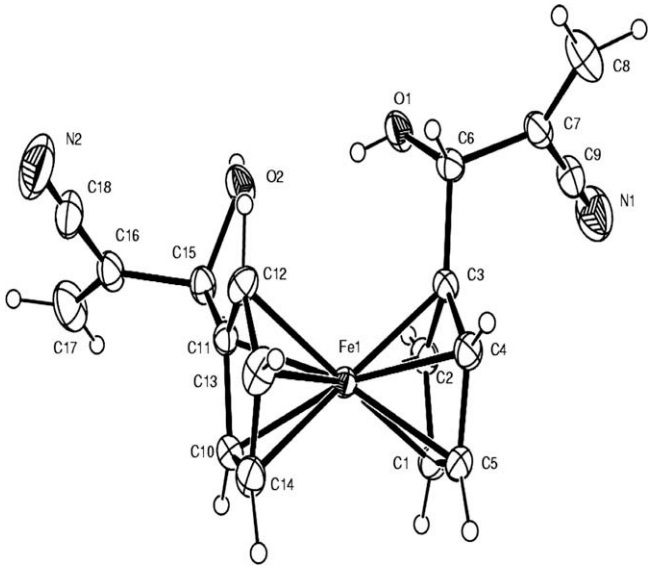
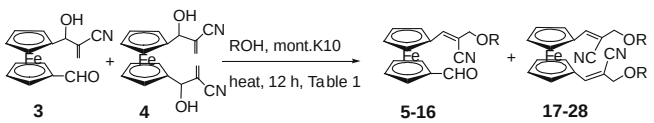


Figure 1. X-ray crystal structure of bis MBH adduct **4**.



R = propargyl, Me, Bn, allyl, p-cresol, 2-naphthyl, 4-methylthiophenol, homopropargyl, cholesterol, ethane-1,2-diol, propane-1,3-diol, but-2-yne-1,4-diol

Scheme 2. One-pot isomerization of mono- and bis-MBH adducts **3** and **4** into alkene derivatives **5**–**28**.

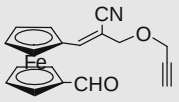
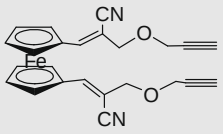
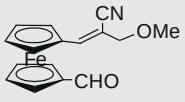
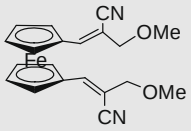
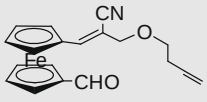
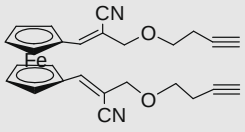
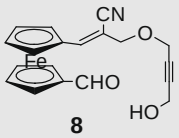
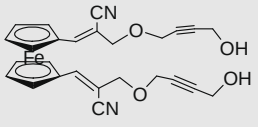
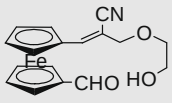
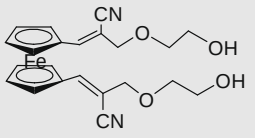
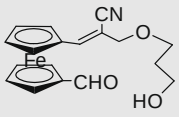
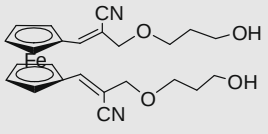
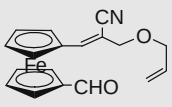
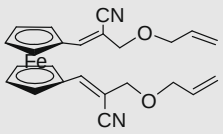
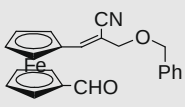
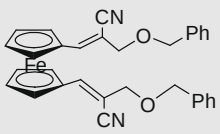
In order to demonstrate the applicability and generality of the isomerization of **3** and **4**, reactions with simple aliphatic alcohols, unsaturated alcohols, aromatic alcohols, phenols and thiophenol were examined. Accordingly, adducts **3** and **4** with unsaturated alcohols such as homopropargyl alcohol, but-2-yne-1,4-diol and allyl alcohol underwent isomerization smoothly to afford highly functionalized mono- and bis isomerized products in excellent yields (Table 1, entries 3, 4 and 7). Similarly, with saturated 1,2- and 1,3-diols, the corresponding isomerized products were obtained in excellent yields (Table 1, entries 5 and 6). The reactions with aromatic alcohols and phenols also afforded the corresponding isomerized products (Table 1, entries 8, 9 and 11). The isomerization with thiophenol was examined and thioacetal **14** was isolated as evidenced from its spectroscopic analysis (Table 1, entry 10). It is noteworthy that the mono **16** and bis cholesterol derivative **28** of the MBH adduct of 1,1′-ferrocenedialdehyde were prepared in excellent yield by the isomerization of adducts **3** and **4** with cholesterol, respectively (Table 1, entry 12). The liquid crystalline (LC) properties of the dicholesteryl derivative **28** were evaluated from its TG, DSC and POM analyses. It should be noted that the compounds reported herein are highly functionalized and can be used for further manipulation. The results are summarized in Table 1. All the new compounds were thoroughly characterized by spectroscopic methods (FTIR, ^{1}H, ^{13}C NMR and FAB-mass spectra).

To demonstrate the synthetic use of the products obtained, an Eglinton[13] coupling reaction of propargyl derivatives **5** and **17** afforded the corresponding highly functionalized novel diyne ether derivative **29** and 36-member macrocycle diyne ether derivative **30** in 46% and 43% yields, respectively (Scheme 3). An attempt to increase the yield of macrocycle **30** by Hay[14] coupling was unsuccessful (32%). The structure of the macrocycle **30** was assigned based on spectroscopic and FAB mass spectrum as it showed a molecular ion peak at m/z 844 (M^+). It should be noted that the ferrocene-derived macrocycles are important as they act as redox responsive ligands.[15] Furthermore synthetic utility was demonstrated by the synthesis of medicinally important ferrocenyl alkenylether bis-triazole[16] derivative **31** and was prepared in water: *t*-butanol medium from ferrocenyl bis propargyl derivative **17** exploiting 'Click' chemistry.[17] The bis allyl derivative of ferrocene underwent a ring closing metathesis by Grubbs II generation catalyst to form ferrocenophane[1d] **32** in 40% yield (see Scheme 4).

To evaluate the spectro-electrochemical properties of macrocyclic compound **30**, the UV–Vis spectrum showed a very strong absorption band at 297 nm, which is assigned to a high energy $\pi-\pi$ electronic transition, and a lower-energy weak band at 479 nm, corresponding to a metal-ligand charge transfer (CT) process ($\delta-\pi$).[18] Such spectral characteristics confer a dark red colour on the compound. The electrochemical property of the redox active ferrocene moiety has been studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The CV showed a reversible redox couple of ferrocene/ferrocenium at $E_{1/2}$ = 0.735 V as shown in Figure 2. Here we find a remarkable cathodic shift (225 mV) when compared with unsubstituted ferrocene ($E_{Fc+/Fc}$ = 0.51 V).[19] Repetitive scan rates from 0.1to 1 V prove that the compound is very stable. An increase in potential value is generally associated with an electron-acceptor property of the substituent.[20] Ferrocene derivatives substituted with macrocyclic ligands are prototype molecules which have proved to be versatile elegant ion-sensors .[21]

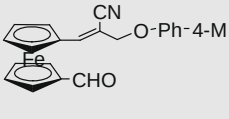
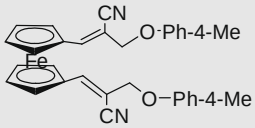
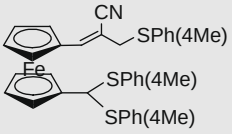
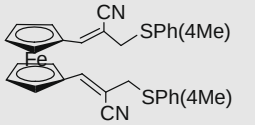
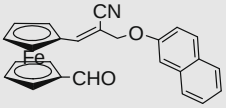
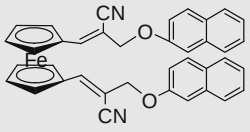
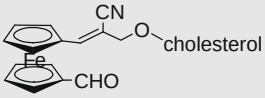
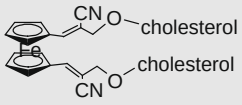
In conclusion, we have demonstrated a facile, efficient and first one-pot synthesis, isomerization and synthetic utility of mono- and bis-MBH adducts of 1,1′-ferrocenedialdehyde. The synthetic utility of the products has been demonstrated by macrocycle

Table 1
Isomerization of MBH adducts **3** and **4** into olefines **5**–**28**

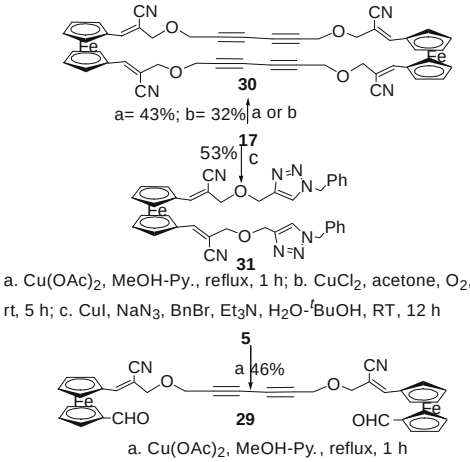
Entry	Alcohol	Products		Yields (%)	
		A	B	A	B
1	Propargyl alcohol[a]	 **5**	 **17**	65	68
2	Trimethyl ortho formate[b]	 **6**	 **18**	42	80
3	Homopropargyl alcohol[a]	 **7**	 **19**	62	70
4	But-2-yne-1,4-diol[c]	 **8**	 **20**	44	80
5	Ethane-1,2-diol[b]	 **9**	 **21**	62	60
6	Propane-1,3-diol[c]	 **10**	 **22**	64	60
7	Allyl alcohol[b]	 **11**	 **23**	65	68
8	Benzyl alcohol[b]	 **12**	 **24**	69	71

(*continued on next page*)

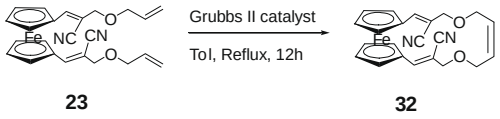
Table 1 (*continued*)

Entry	Alcohol	Products		Yields (%)	
		A	B	A	B
9	*p*-Cresol[b]	 **13**	 **25**	62	70
10	4-Methyl thiophenol[b]	 **14**	 **26**	55	68
11	2-Naphthol[b]	 **15**	 **27**	40	70
12	Cholesterol[c]	 **16**	 **28**	45	78

[a] Montmorillonite K10, 12 h, heat.
[b] CH_3CN, montmorillonite K10, 6 h, heat.
[c] CH_3CN, montmorillonite K10, 8 h, heat.



Scheme 3. Synthetic use of propargyl derivatives of mono- and bis-MBH adducts **5** and **17**.



Scheme 4. Synthetic use of the allyl derivative of bis-MBH adduct **23**.

synthesis and their electrochemical property was evaluated by CV studies. The synthesis of medicinally important ferrocenyl alkenyl-lether bis-triazole derivative has also been achieved. Further works on these compounds for the evaluation of ion-sensing, LC property and whether they can be used as catalytic ligands in organic synthesis are in progress.

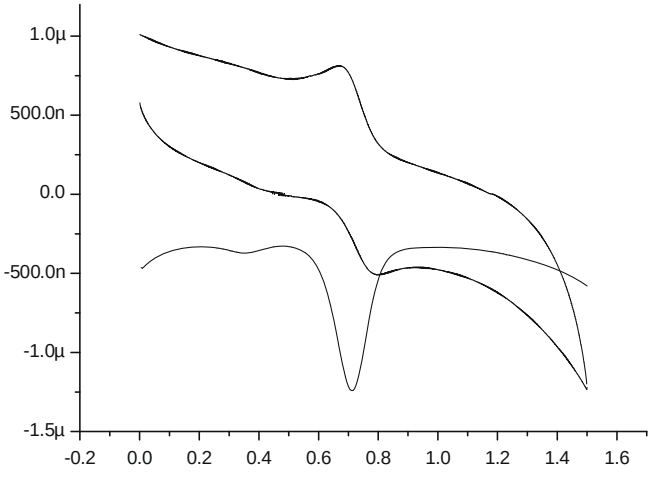


Figure 2. CV and DPV of compound **30**.

2. General experimental procedure

2.1. Preparation of mono- and bis-MBH adduct of 1,1′-ferrocenedialdehyde

A mixture of 1,1′-ferrocenedialdehyde (1 mmol), acrylonitrile (1.5 mmol) and DABCO (0.02 mmol) without any solvent was stirred at rt for 6 h (monitored by TLC). After the completion of the reaction; the evaporation of excess acrylonitrile under reduced pressure followed by purification by silica gel column chromatography using EtOAc/hexane (30:70) afforded a 2:3 mixture of mono- and bis-Morita–Baylis–Hillman adducts of 1,1′-ferrocenedialdehyde in an excellent combined yield (90%).

2.2. Isomerization

A mixture of mono and bis-Morita–Baylis–Hillman adducts of 1,1′-ferrocenedialdehydes 3 and 4 (1 mmol), 100% w/w Mont. K-10 clay and alcohols (2 equiv) in acetonitrile (0.5 mL) was allowed to reflux for 12 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, the crude mixture was purified by silica gel column chromatography using gradient elution with hexane and hexane: EtOAc to afford pure products in good yields (68–80%).

2.3. Eglinton coupling

A mixture of **17** (1 mmol) and 2 equiv of $Cu(OAc)_2{\cdot}H_2O$ (2 mmol) in pyridine–CH_3OH (1:1, 2 mL) was refluxed at 70 °C for 1 h. After the completion of the reaction, the solvent was removed under reduced pressure. The crude reaction mixture was diluted with ethyl acetate (50 mL) and washed successively with 2 N HCl, water, aqueous $NaHCO_3$ solution and brine. The organic layer was separated, dried (anhyd Na_2SO_4) and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography by elution with hexane–EtOAc mixture to afford pure 1, 3-diyne **30** (43%);

2.4. Hay coupling

A mixture of **17** (1 mmol), 2 equiv of $CuCl_2$ and a catalytic amount of TMEDA in acetone under O_2 atmosphere was stirred at rt for 5 h. After the reaction (TLC), the crude compound was directly subjected to silica gel column chromatography by elution with hexane-EtOAc mixture to afford compound **30** in 32% yield.

2.5. Synthesis of a bis triazole derivative of ferrocene

A mixture of **17**, 3 equiv of NaN_3, 3 equiv of benzyl bromide, 5.2 equiv triethyl amine and 5 mol % of CuI in *t*-BuOH–H_2O(1:1, 1 mL) mixture was stirred at rt for 6 h. After the reaction (TLC), the crude compound was dissolved in diethyl ether and passed through a Celite pad. The filtrate was washed with water, the organic layer washed with brine, dried (anhyd Na_2SO_4) and concentrated in vacuo. The crude reaction mixture was purified by silica gel column chromatography by elution with hexane-EtOAc mixture to afford compound **31** in 53% yield.

3. Spectral data for selected compounds

3.1. Compound 3

FTIR (CH_2Cl_2) δ_{max}: 3340, 2250, 1618, 1054 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 4.35–4.47 (m, 3H), 4.76–4.82 (m, 1H), 5.00–5.05 (m, 1H), 5.90–6.05(m, 2H); FAB mass: calcd for $C_{18}H_{16}FeN_2O_2$ is 348.17; Found: 348.38 (M^+).

3.2. Compound 28

FTIR (CH_2Cl_2): δ_{max}: 1222, 1459, 1469, 1614, 1723, 2951, 3027 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.81 (s, 3H), 3.43 (s, 1H), 3.50 (s, 1H), 4.37–4.39 (m, 2H), 4.64 (s, 2H), 6.50 (s, 1H), 6.39–7.05(m, 4H); ^{13}C NMR($CDCl_3$/TMS, 75.3 MHz): δ 18.6, 22.7, 24.2, 24.5, 24.8, 30.0, 30.2, 33.8, 37.8, 39.1, 41.53, 69.7, 71.0, 71.5, 71.7, 73.1, 78.2, 78.8, 79.2, 79.4, 106.2, 109.7, 110.5, 112.8, 113.6, 116.8, 121.1, 121.9, 123.8, 124.0, 140.4, 142.5, 145.8, 147.9, 186.5; FAB mass: calcd for $C_{72}H_{104}FeN_2O_2$ is 1085.45; Found: 1108.65 (M^++23).

3.3. Compound 30

FTIR (CH_2Cl_2): δ_{max}: 743, 1078, 1159, 1454, 1719, 2250 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 4.23–4.34 (m, 4H), 4.50 (s, 2H), 4.54 (s, 2H), 4.82 (s, 2H), 4.98 (s, 2H), 6.70 (s, 1H), 9.71 (s, 1H); FAB mass: calcd for $C_{36}H_{28}Fe_2N_2O_4$ is 664.30; Found: 664.09 (M^+).

3.4. Compound 31

FTIR (CH_2Cl_2): δ_{max} 1166, 1443, 1730, 2248, 2931, 3289 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 3.78–3.94 (m, 4H), 4.34–4.38 (m, 2H), 4.48 (s, 1H), 4.52–4.57 (d, 1H, J = 14.8 Hz), 4.74 (s, 1H), 4.91 (s, 1H), 5.00–5.05 (d, 1H, J = 14.9 Hz), 6.61 (s, 1H), 6.91–7.36 (m, 6H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 52.7, 62.7, 70.9, 71.0, 71.3, 71.5, 72.2, 77.9, 104.4, 118.1, 121.9, 128.0, 129.12, 129.16, 133.62, 144.6, 146.3; FAB mass: calcd for $C_{38}H_{32}$ FeN_8O_2 is 688.56.

3.5. Compound 32

^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 4.11–4.35 (m, 8H), 4.46 (s, 4H), 4.77 (s, 2H), 4.90 (s, 2H), 5.85 (s, 1H), 5.97 (s, 1H), 6.90 (s, 1H), 6.98 (s, 1H); FAB mass: Calcd for $C_{22}H_{20}FeN_2O_2$ is 400.34; Found: 400.89 (M^+).

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