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A mechanochemical [2+2+2] cycloaddition facilitated by a cobalt(II) catalyst and piezoelectric materials†

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In this study, we present the first general mechanochemical protocol for the catalytic [2+2+2] cycloaddition of alkynes via a simple and inexpensive cobalt(II)-based catalytic system. The key to achieving the high efficiency of this mechanochemical transformation is the use of piezoelectric BaTiO₃ as a reductant in combination with an amine additive to facilitate the generation of a catalytically active low-valent cobalt species. This method is characterized by a broad substrate scope, short reaction times, solvent-less conditions, and the feasibility of reacting poorly soluble substrates. Thus, we provide a more efficient, broadly applicable, and sustainable alternative to existing solution-based protocols.

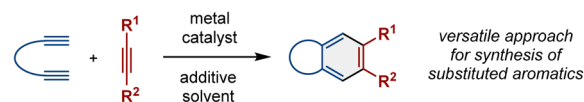
Introduction

Mechanochemistry, particularly when ball milling is used, has gained recognition as a sustainable and environmentally friendly alternative to traditional organic synthesis in solution.^{1–20} Ball milling eliminates the need for large amounts of harmful solvents in the reaction step and accelerates various organic transformations, making it more versatile, atom-efficient, energy-efficient, and environmentally beneficial than traditional solution-based methods. These advantages have been demonstrated in a variety of organic transformations that include synthetically important transition-metal-catalyzed processes such as cross-coupling reactions.^{1–20} Building on our recent success in leveraging ball-milling techniques to address challenges in traditional solution-based organic synthesis,^{21–33} we envisioned the development of a mechanochemical protocol for transition-metal-catalyzed [2+2+2] cycloadditions (Scheme 1A).^{34–38} Given the widespread use of the [2+2+2] cycloaddition in modern organic synthesis and materials science, we anticipate that such a mechanochemical approach would offer a more efficient and sustainable method that is complementary to existing solution-based methods. In 2016, Mack and co-workers have conducted a pioneering study describing the first attempt at a mechanochemical [2+2+2] cycloaddition of terminal alkynes using a nickel catalyst.³⁹ Interestingly, the ball-milling reaction gave [2+2+2+2]

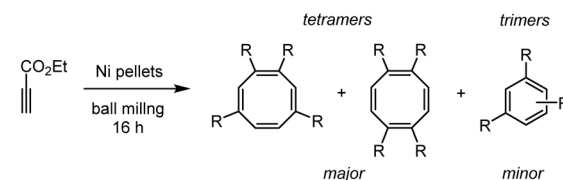
cycloadducts as the major products, while only a trace amount of the corresponding [2+2+2] products were obtained (Scheme 1B).³⁹ Thus, the synthetic potential of mechanochemical [2+2+2] cycloadditions remains to be explored further.

The transition-metal-catalyzed [2+2+2] cycloaddition can be catalyzed by a variety of different transition metals.^{34–38} Of these

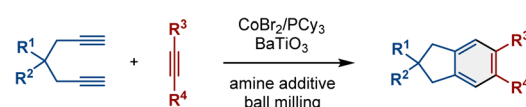
A. Transition-metal-catalyzed [2+2+2] cycloaddition



B. Previous attempt under mechanochemical conditions (ref. 39)



C. This work: the first general mechanochemical [2+2+2] cycloaddition



- key to success: use of piezoelectric BaTiO₃-amine system as reductant
- inexpensive, simple and abundant cobalt(II)-based catalytic system
- solvent-less • short reaction time • applicable to poorly soluble alkynes

Scheme 1 Development of a general, mechanochemical, catalytic [2+2+2] cycloaddition facilitated by piezoelectric BaTiO₃. (A) General scheme of catalytic [2+2+2] cycloaddition. (B) Previous attempt on mechanochemical cycloaddition of alkynes. (C) The first mechanochemical [2+2+2] cycloaddition using a cobalt(II) catalyst (this work).

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metals, cobalt has proven to be an inexpensive and robust catalyst.^{40–48} In particular, catalytic systems using a cobalt(II) salt^{40–43,47,48} have been widely used as simpler alternatives to conventional more expensive and air-sensitive cobalt(I)-based catalysts, such as $\text{CpCo}(\text{CO})_2$ and $\text{CoCl}(\text{PPh}_3)_3$.^{44–46} In cobalt(II) catalytic methods, the efficient *in situ* reduction of cobalt(II) to low-valent cobalt species $[\text{Co}(\text{I})$ or $\text{Co}(0)]$ using a metal-based reductant such as zinc or manganese is important for achieving effective catalysis under mild conditions.^{40–43} Rovis and co-workers have demonstrated that an iridium-based photocatalyst can be used for reducing cobalt(II) to generate a catalytically active cobalt(0) species *in situ*, enabling efficient $[2+2+2]$ cycloaddition reactions.⁴⁷ It has also been reported that at high temperature ($>130^\circ\text{C}$), cobalt(II) can directly catalyze the cycloaddition in the absence of a reductant.⁴⁸ The reductant-free reaction presumably proceeds through a $\text{Co}(\text{II})/\text{Co}(\text{IV})$ catalytic cycle.⁴⁸ Despite recent advances in this area, these solution-based methods commonly require the use of substantial amounts of toxic solvents, high temperatures, and extended reaction times, all of which represent important disadvantages to solution-based approaches.^{40–48}

Herein, we report the first mechanochemical $[2+2+2]$ cycloaddition of alkynes achieved *via* a simple, inexpensive, and highly robust catalytic system based on cobalt(II) bromide, tricyclohexylphosphine (PCy_3), and piezoelectric BaTiO_3 (Scheme 1c). Notably, the use of piezoelectric BaTiO_3 ^{29–31,49–59} as a reductant in combination with *N,N*-diisopropylethylamine (DIPEA)

proved to be crucial for facilitating a highly efficient mechanochemical $[2+2+2]$ cycloaddition, as the efficiency was much lower under conditions where traditional metal reductants were used. The mechanochemical system presented here allows synthesizing a diverse range of substituted benzenes in short reaction times (~ 60 min), under mild conditions without the need for heating or reaction solvents, thereby complementing existing solution-based $[2+2+2]$ cycloaddition strategies. This work also demonstrates the effectiveness of using a unique reduction system that uses piezoelectricity to generate catalytically active low-valent metal species under mechanochemical conditions.^{31,49}

Results and discussion

Our study began with the optimization of the reaction conditions using diyne **1a** and ethynylbenzene **2a** as model substrates (Table 1). All mechanochemical reactions were conducted using a Retsch MM400 mill [stainless-steel (ss) milling jar (5 mL), 30 Hz; ss ball (10 mm diameter); (for details, see the ESI†)]. First, we conducted the reaction using cobalt(II) bromide (CoBr_2) in the presence of MeCN as a liquid-assisted-grinding (LAG) additive, and no product was formed (entry 1, Table 1). The desired product (**3a**) was obtained in 55% yield when tricyclohexylphosphine (PCy_3) was added as a ligand (entry 2, Table 1).⁴⁷ This was an unexpected result because the reaction had proceeded without a reductant under very mild conditions.⁴⁸

Table 1 Optimization of the reaction conditions^a

Entry	2a (equiv.)	Ligand (20 mol%)	Reductant (5.0 equiv.)	Additive (1.0 equiv.)	Yield ^b (%)
1	3	None	None	None	<1
2	3	PCy_3	None	None	55
3	3	PCy_3	Zn	None	60
4	3	PCy_3	Mn	None	66
5	3	PCy_3	BaTiO_3	None	61
6	3	PCy_3	BaTiO_3	DIPEA	96 (86 ^c)
7	3	PCy_3	None	DIPEA	54
8	3	PCy_3	Li_2TiO_3	DIPEA	32
9	3	PCy_3	ZnO	DIPEA	52
10	3	PCy_3	Li_2TaO_3	DIPEA	36
11	3	PCy_3	LiNbO_3	DIPEA	21
12	3	PCy_3	Al_2O_3	DIPEA	0
13	3	PCy_3	BaO	DIPEA	0
14	2	PCy_3	BaTiO_3	DIPEA	68
15	3	PPh_3	BaTiO_3	DIPEA	31
16	3	dppp^d	BaTiO_3	DIPEA	6
17	3	dppb^d	BaTiO_3	DIPEA	44

^a Reaction conditions: **1a** (0.20 mmol), ethynylbenzene **2a**, CoBr_2 (10 mol%), and DIPEA (1.0 equiv.) in a stainless-steel (ss) ball-milling jar (5 mL) with one ss ball (diameter: 10 mm), ball milling for 1 h. ^b Determined from the NMR spectrum of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. ^c Isolated yield. ^d 10 mol%.



Although the mechanism of the reductant-free cycloaddition is still unclear at present, we think that the reaction might proceed through a phosphine-assisted Co(II)/Co(IV) catalytic cycle due to the generation of hot spots during ball milling.⁶⁰ Moreover, a mechanism where thermal disproportionation generates low-valent cobalt species cannot be ruled out unequivocally.^{34,47} In order to promote the [2+2+2] cycloaddition, the addition of metal-based reductants was investigated (entries 3 and 4, Table 1). When zinc was used, the yield of **3a** slightly improved to 60% (entry 3, Table 1). Performing the reaction with manganese did not significantly improve the yield of **3a** (66%, entry 4, Table 1). These results indicate that traditional metal-based reductants are unable to effectively generate catalytically active low-valent cobalt species under mechanochemical conditions. To overcome this challenge, we turned our attention to piezoelectric materials.^{29–31,49–58} Our group first reported that piezoelectric BaTiO₃ can act as a charge-transfer catalyst under ball-milling conditions to enable force-induced redox reactions.²⁹ Thus, we anticipated that piezoelectric BaTiO₃ could be used as a unique and highly efficient reductant to promote the [2+2+2] cycloaddition. However, when BaTiO₃ was used as a reductant in our reaction the desired product (**3a**) was obtained in a yield comparable to those obtained with the traditional metal-based reductants (61%, entry 5, Table 1). Nevertheless, we discovered that the addition of DIPEA as an additive in the presence of BaTiO₃ dramatically increased the yield (96%, entry 6, Table 1). On the other hand, the same reaction in the absence of BaTiO₃ gave **3a** in a much lower yield (54%, entry 7, Table 1). Importantly, the combination of the traditional metal reductants (zinc and manganese) and the amine additive did not improve the yield of **3a** (for details, see the ESI†). These results suggest that the combination of BaTiO₃ and the amine additive is essential to achieve a high yield with this mechanochemical protocol. We explored other

piezoelectric materials, such as lithium titanate (Li₂TiO₃), zinc oxide (ZnO), lithium tantalate (Li₂TaO₃), and lithium niobate (LiNbO₃), in the presence of DIPEA. These materials produced lower yields of **3a** (21–52%, entries 8–11, Table 1). Non-piezoelectric materials such as aluminum oxide (Al₂O₃) and barium oxide (BaO) did not yield **3a** (entries 12 and 13, Table 1). Reducing the amount of **2a** resulted in a lower yield of **3a** (68%, entry 14, Table 1). Finally, we screened other phosphine ligands, such as triphenylphosphine (PPh₃), 1,3-bis(diphenylphosphino)propane (dppp), and 1,4-bis(diphenylphosphino)butane (dppb), and found that PCy₃ was still the most effective (entries 15–17, Table 1).

To highlight the importance of the mechanical impact caused by ball milling for the effectiveness of the catalysis in the presence of piezoelectric BaTiO₃, we conducted the reaction using different ball-milling frequencies. Interestingly, when the reaction was performed at 15 Hz, only a trace amount of the product was obtained (entry 1, Table 2A). However, increasing the milling frequency to 20, 25, and 30 Hz resulted in dramatically improved yields of 51%, 71%, and 96%, respectively (entries 2–4, Table 2A). This result clearly demonstrates that the reaction efficiency is proportional to the amount of force applied through ball milling, which is consistent with a piezoelectrically induced acceleration mechanism.^{29–31,49–58} Furthermore, we conducted a solution-based version of the reaction using MeCN as the solvent in a sealed tube under argon with BaTiO₃ (Table 2B). After 1 hour, we only recovered the starting materials, and **3a** was not obtained (Table 2B). This result further supports the notion that the reaction with BaTiO₃ specifically requires ball-milling conditions.

Based on the optimization results and control experiments, we would like to propose a plausible role for BaTiO₃ in this catalytic system (Scheme 2). Under ball-milling conditions, piezoelectric materials generate highly polarized particles

Table 2 Control experiments^a

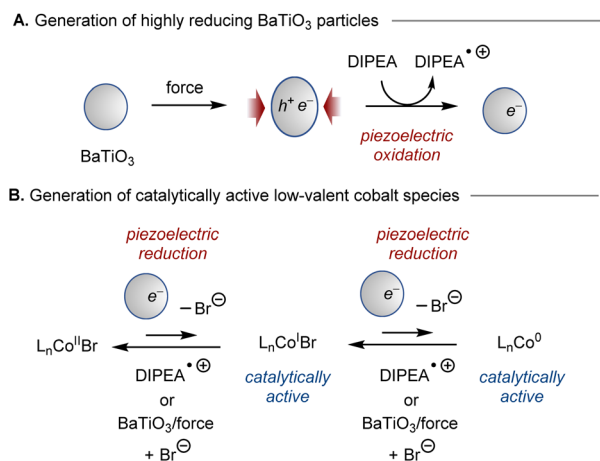
A. Effect of milling frequency

Entry	Frequency (Hz)	Yield (%)	
1	15	4	
2	20	51	
3	25	71	
4	30	96	

B. Solution-based reaction in a test tube

		<1% yield	
time = 0 h		time = 60 min	

^a Reaction conditions: **1a** (0.20 mmol), ethynylbenzene **2a** (3.0 equiv.), CoBr₂ (10 mol%), and DIPEA (1.0 equiv.) in a stainless-steel (ss) ball milling jar (5 mL) with one ss ball (diameter: 10 mm).



Scheme 2 Plausible mechanism for the piezoelectrically promoted generation of catalytically active cobalt species. (A) Activation of BaTiO₃. (B) Piezoelectric-induced reduction enabling the formation of low-valent cobalt species.

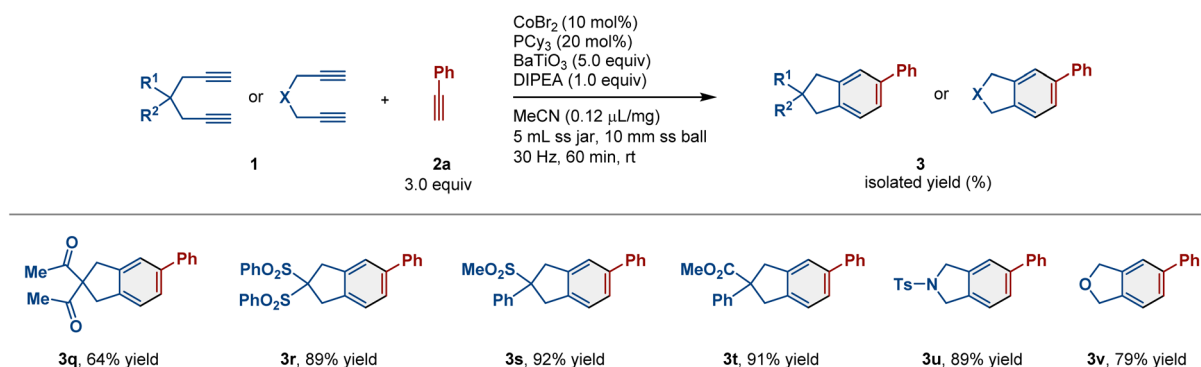
(Scheme 2A).^{2–31,49–58} These polarized particles could then oxidize DIPEA to generate highly reducing, negatively charged particles (Scheme 2A). Subsequently, the activated particles can be expected to reduce cobalt(II) to cobalt(I), which is a catalytically active species in the [2+2+2] cycloaddition reaction (Scheme 2B). A mechanism where the generation of cobalt(0) is followed by the [2+2+2] cycloaddition is also possible (Scheme 2B).⁴⁷ We speculate that the generated low-valent cobalt species are transient, as they can be readily oxidized by the tertiary amine radical cation or the polarized BaTiO₃ particles (Scheme 2B). Although further mechanistic investigations are necessary, we propose that the low-valent cobalt species undergoes oxidative cyclization, followed by alkyne insertion and reductive elimination to furnish the desired product (see ESI† for details).

With the optimized reaction conditions in hand, we explored the reaction scope by varying the alkyne substrate while keeping the diyne (**1a**) constant (Table 3). Unsubstituted phenylacetylene gave the desired cycloaddition product (**3a**) in excellent isolated yield (86%). We examined the electronic effects of

Table 3 Alkyne substrate scope^a

		CoBr ₂ (10 mol%) PCy ₃ (20 mol%) BaTiO ₃ (5.0 equiv) DIPEA (1.0 equiv) MeCN (0.12 μL/mg) 5 mL ss jar, 10 mm ss ball 30 Hz, 60 min, rt	 isolated yield (%)
1a	2 3.0 equiv		
3a , 86% yield	3b , 81% yield	3c , 75% yield	3d , 75% yield
3e , 86% yield	3f , 72% yield	3g , 67% yield	3h , 70% yield
3i , 66% yield	3j , 70% yield	3k , 82% yield	3l , 81% yield
3m , 80% yield	3n , 50% yield	3o , 44% yield	3p , 52% yield

^a Reaction conditions: diyne **1a** (0.20 mmol), alkyne **2** (3.0 equiv.), CoBr₂ (10 mol%), PCy₃ (20 mol%), DIPEA (1.0 equiv.), and MeCN (0.2 mL mg^{−1}) in a stainless-steel (ss) ball-milling jar (5 mL) with one ss ball (diameter: 10 mm) for 60 min, 30 Hz.

Table 4 Diyne substrate scope^a

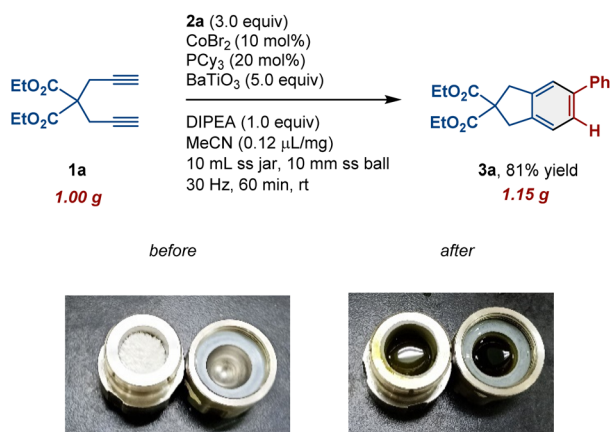
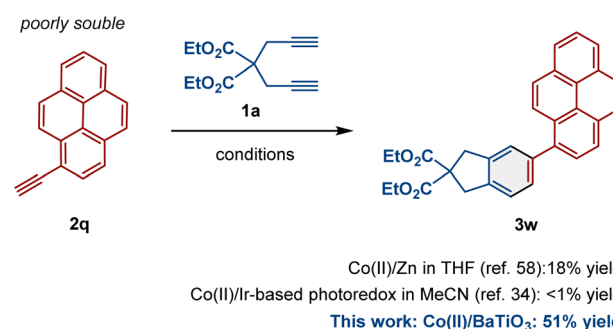
^a Reaction conditions: diyne **1** (0.20 mmol), alkyne **2a** (3.0 equiv.), CoBr_2 (10 mol%), PCy_3 (20 mol%), DIPEA (1.0 equiv.), and MeCN (0.2 mL mg^{-1}) in a stainless-steel (ss) ball milling jar (5 mL) with one ss ball (diameter: 10 mm) for 60 min, 30 Hz.

different phenylacetylene substrates by introducing different electron-donating and -withdrawing groups at the *para* position of the benzene ring. A methoxy group at the 4-position provided the corresponding arene (**3b**) in 81% yield. Halides such as bromide, chloride, and fluoride were well tolerated under the applied reaction conditions, producing satisfactory yields of **3c** (75%), **3d** (75%), and **3e** (86%). Butyl and hexyl substituents at the *para* position were also well tolerated and furnished the corresponding products in good yield (**3f**: 72%; **3g**: 67%). An alkyne with an electron-withdrawing trifluoromethyl group also provided the corresponding product in good yield (**3h**: 70%). The reaction proceeded smoothly with a thiophene-substituted alkyne, resulting giving the heterocyclic biaryl compound **3j** in 70% yield. Alkyl-substituted alkynes were also investigated and gave the desired products in excellent yields (**3l**: 81%; **3m**: 80%). The use of an alkyne with a polyaromatic ring, phenanthrene, resulted in the efficient formation of arene **3k** in 82% yield. A trimethylsilyl (TMS)-substituted alkyne provided the corresponding product (**3n**) in 50% yield. Furthermore, this method proved to be efficient for internal alkynes, producing highly substituted arenes in moderate to good yields (**3o**: 44%; **3p**: 52%).

Next, we investigated the scope of different diynes (**1**) while ethenyl benzene (**2a**) was kept constant as a reaction counterpart (Table 4). Symmetrical diynes with diketone (**1b**), sulfonyl (**1c** and **1d**), ester (**1e**), *N*-tosylate (**1f**), and ether (**1g**) moieties furnished the expected products in good to moderate yields (**3q–3v**; 64–92%). This comprehensive study demonstrates the robustness and versatility of this mechanochemical [2+2] cycloaddition protocol. In our substrate scope studies, side products such as homocoupled products of the diynes were scarcely detected.

To demonstrate the scalability of our reaction, we conducted a gram-scale experiment (Scheme 3). Starting from 1.00 g of **1a**, we successfully obtained 1.15 g of **3a** in 81% yield without significant loss of yield compared to the small-scale reaction. This result showcases the practical utility of this mechanochemical protocol.

To further illustrate the advantages of our mechanochemical method over traditional solution-based techniques, we tested the reaction with alkyne **2q**, which is poorly soluble in common organic solvents (Scheme 4). For example, the solubility of **2q** in THF at room temperature is $1.7 \times 10^{-3} \text{ M}$, and in MeCN at room temperature $1.2 \times 10^{-2} \text{ M}$. Therefore, the previously reported solution-based reaction of **2q** using a cobalt(II)/zinc catalytic system in THF⁶¹ is slow, yielding only 18% of the desired

Scheme 3 Gram-scale synthesis of **3a**.Scheme 4 Reactions of poorly soluble alkyne **2q**; for the details of the reaction conditions, see the ESI.†

product (**3w**). We also tested a photoredox/cobalt(II) dual metallophotoredox system in MeCN,⁴⁷ albeit that the reaction did not afford **3w** (<1%). We confirmed that these reactions were carried out in slurry states, suggesting that the unsuccessful results were most likely due to the low solubility of **2q**. Another possibility is that the pyrene moiety of **2q** is capable of accepting excitation energy from the excited photocatalyst, thus suppressing the [2+2+2] cycloaddition.^{62–64} In contrast, under our mechanochemical conditions, the desired product (**3w**) was obtained in much higher yield (51%). These results demonstrate that the unique advantages of our mechanochemical approach will be able to expand the scope of [2+2+2] cycloadditions for poorly soluble alkynes and molecules capable of accepting excitation energy.

Conclusion

In summary, we have successfully developed the first general mechanochemical protocol for the [2+2+2] cycloaddition reaction of alkynes that employs a simple cobalt(II)-based catalyst. In this mechanochemical system, the modulation of the piezoelectrically induced oxidation state of the cobalt center is used to facilitate a highly efficient [2+2+2] cycloaddition. Importantly, the use of traditional metal reductants such as zinc and manganese resulted in low reactivity, highlighting the effectiveness of the piezoelectrically induced approach. This method is characterized by a broad substrate scope, short reaction times, and the use of an almost negligible quantity of solvent in the reaction step. Moreover, the mechanochemical approach can be readily scaled up to the gram scale and has proved advantageous for poorly soluble substrates, achieving yields unattainable by conventional solution-based methods. Beyond the practical utility of the mechanochemical [2+2+2] cycloaddition, this work showcases the great potential of our unique piezoelectric reduction system to generate catalytically active low-valent metal species, thus enabling highly efficient mechanochemical transformations.^{31,49}

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

KK and HI conceived and designed the study. KJ, KK and HI co-wrote the paper. KJ performed the chemical experiments and analysed the data. All authors discussed the results and the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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