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One-Pot Processes

Interception of Cobalt-Based Carbene Radicals with α-Aminoalkyl Radicals: A Tandem Reaction for the Construction of β-Ester-γ-amino Ketones**

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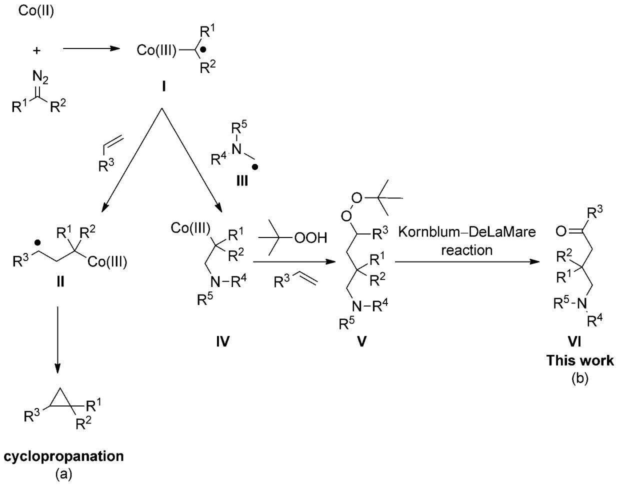
Abstract: *The interception of cobalt-based carbene radicals with α-aminoalkyl radicals was combined with the Kornblum–DeLaMare reaction and provides β-ester-γ-amino ketones, which are otherwise difficult to obtain in high chemoselectivity. Mechanistically, this transformation is an interplay of cobalt-based carbene radicals, organoradicals, and ionic intermediates and involves the construction of two C−C bonds and one C=O bond in a one-pot process. The reaction also features a wide substrate scope and is highly efficient and insensitive to moisture and air.*



Scheme 1. Interception of cobalt-based carbene radicals with olefins and α-aminoalkyl radicals.

The metal–carbon bond in transition-metal carbene complexes, such as those of Cu, Ru, Rh, Pd, or Au, is generally considered as a double bond.[1] In sharp contrast, cobalt carbene complexes are of a fundamentally different type; their metal–carbon bonds display a strong single-bond character, and these complexes thus behave as carbene radicals.[2] This special property has been exploited by synthetic chemists on numerous occasions to create cyclopropane moieties from olefins and diazo compounds. Since the pioneering studies by the groups of Nakamura, Yamada, and Katsuki, who disclosed that cobalt carbene complexes are capable of olefin cyclopropanation reactions,[3] the current state-of-the-art reactions have been developed by the groups of Zhang and de Bruin.[4] Unlike cyclopropanations catalyzed by other metals,[5] Co-based cyclopropanation reactions are distinguished by their wide substrate scopes, tolerating both electron-rich and electron-poor alkenes and several classes of diazo compounds, as well as their simpler operation procedures as the diazo compounds do not need to be added slowly to minimize undesirable carbene dimerization processes. Mechanistic studies generally support a reaction model that involves an unusual cobalt-based carbene radical intermediate, which undergoes sequential radical addition and substitution (Scheme 1 a).[2] Aside from the cyclopropanation reactions of olefins, alkynes and carbon monoxide could also be used as the acceptors of cobalt-based carbene radicals to construct β-lactams[4h] and 2*H*-chromenes.[4i]

Even though cobalt-based carbene radicals have already been used for a wide range of applications, particularly in the area of cyclopropanation, their synthetic utility is still far from being fully explored. Recently, radical tandem reactions[4h,i,6] have attracted significant interest as a synthetic strategy of considerable untapped potential. Thus, we envisaged that once the cobalt-based carbene radical intermediate is generated, instead of adding to an olefin, alkyne, or CO, it can alternatively be intercepted by another radical species, which could open up a range of new opportunities for synthetic chemistry. We recently developed an oxidative cyanation reaction of tertiary amines involving the in situ generation of α-aminoalkyl radicals.[7a] On the other hand, we previously succeeded in combining the addition of organocobalt species to olefins and the Kornblum–DeLaMare reaction[8] for the construction of 1,4-dicarbonyl compounds using *tert*-butyl hydroperoxide (TBHP) as the primary oxidant.[7b] Based on these results, we hypothesized that incorporating a tertiary amine and TBHP into the Co-catalyzed cyclopropanation system might trigger a novel reaction pathway. As shown in Scheme 1 b, rather than adding to an olefin, cobalt carbene radical **I** can be intercepted by α-aminoalkyl radical **III**, which is generated in situ from the tertiary amine, to form organocobalt species **IV**, which can then be coupled with the olefin

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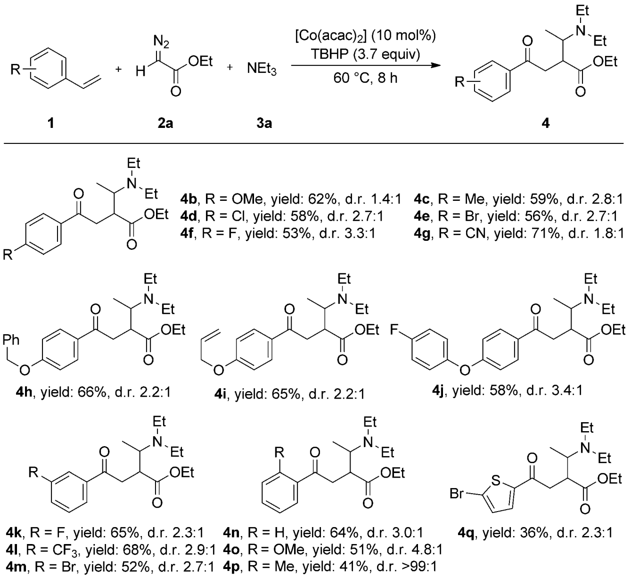
and TBHP to afford peroxide **V**. Subsequently, Kornblum–DeLaMare reaction of **V** delivers the desired product **VI**. Consequently, this reaction sequence combines a carbene radical, an organoradical, and an ionic Kornblum–DeLaMare reaction step into a single catalytic cycle, a strategy that has so far remained underexplored. Aside from its novel mechanism, this tandem process provides direct access to a variety of β-substituted γ-amino ketones, which are otherwise difficult to synthesize from easily available α-diazo esters, amines, and olefins.

The successful development of this one-pot multicomponent reaction, however, hinges on the resolution of two major challenges. The first technical difficulty concerns the high reactivity, and consequently, the instability of both carbene radical **I** and organoradical **III**, necessitating a careful choice of reagents and reaction conditions that can divert the intermediates towards the selective formation of organocobalt species **IV** instead of towards the well-studied and understood radical addition pathway (Scheme 1 a). The second, equally important challenge is the demand of this process for an oxidative environment, which is in stark contrast to the fact that Co-catalyzed reactions of olefins and diazo reagents usually require inert atmospheres.

As a start, we conducted a few pilot reactions using [Co(TPP)] (cobalt(II) *meso*-tetraphenylporphyrin),[4a] a common catalyst for olefin cyclopropanation, to evaluate the feasibility of the proposed coupling reaction. With TBHP as the oxidant, the reaction mixture containing 1-(*tert*-butyl)-4-vinylbenzene (**1a**), ethyl diazoacetate (**2a**), and triethylamine (**3a**) afforded the desired β-ester-γ-amino ketone **4a** in 32 % yield. To improve the efficiency of the process, we took a page from the [Co(acac)$_2$] catalyzed synthesis of 1,4-dicarbonyl compounds that we recently developed[7b] and found that switching to [Co(acac)$_2$] substantially increased the yield of **4a** to 72 % (acac = acetylacetonate; for detailed information on the optimization of the reaction conditions, see the Supporting Information, Table S1). This one-pot multicomponent reaction only requires mildly oxidative conditions, can even be performed in an open flask exposed to air, and can be conveniently scaled up to 10 mmol while still retaining a satisfactory yield of 67 %. Interestingly, oxygen had no significant effect on the efficiency, and a comparable yield was obtained under argon.

Having established the optimized coupling conditions, we next assessed the substrate scope of the reaction with a representative selection of styrenes. As shown in Scheme 2, a variety of substituted styrenes could be selectively oxidized to the corresponding β-ester-γ-amino ketones in satisfactory yields and moderate diastereomeric ratios, attesting to the broad tolerance of the reaction for electron-withdrawing and -donating substituents, such as halide, ether, trifluoromethyl, or cyano groups, and benzylic C−H bonds. Notably, when the aryl ring of the styrene coupling partner was replaced with a bromothiophene moiety, **4q** was generated in moderate yield. Steric effects were responsible for the improved diastereomeric ratios observed for the syntheses of **4n**, **4o**, and **4p**. The relative configuration of the major stereoisomer of **4g** formed in the reaction was determined by single-crystal X-ray crystallography (Scheme S1, Table S2–3).

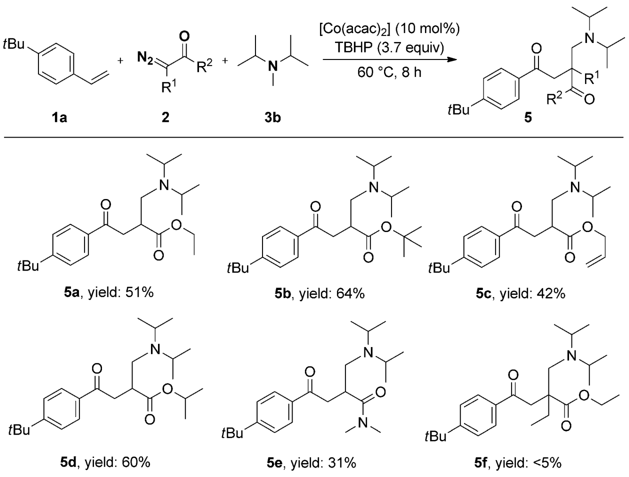


4b, R = OMe, yield: 62%, d.r. 1.4:1
4c, R = Me, yield: 59%, d.r. 2.8:1
4d, R = Cl, yield: 58%, d.r. 2.7:1
4e, R = Br, yield: 56%, d.r. 2.7:1
4f, R = F, yield: 53%, d.r. 3.3:1
4g, R = CN, yield: 71%, d.r. 1.8:1
4h, yield: 66%, d.r. 2.2:1
4i, yield: 65%, d.r. 2.2:1
4j, yield: 58%, d.r. 3.4:1
4k, R = F, yield: 65%, d.r. 2.3:1
4l, R = CF$_3$, yield: 68%, d.r. 2.9:1
4m, R = Br, yield: 52%, d.r. 2.7:1
4n, R = H, yield: 64%, d.r. 3.0:1
4o, R = OMe, yield: 51%, d.r. 4.8:1
4p, R = Me, yield: 41%, d.r. >99:1
4q, yield: 36%, d.r. 2.3:1

Scheme 2. Variation of the styrene. Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), **3a** (2.5 mmol), [Co(acac)$_2$] (0.05 mmol), TBHP (1.85 mmol), and 4 Å M.S. (200 mg) were stirred in 1,4-dioxane/CH$_2$Cl$_2$ (1.0 mL each) at 60 °C for 8 h. M.S. = molecular sieves.

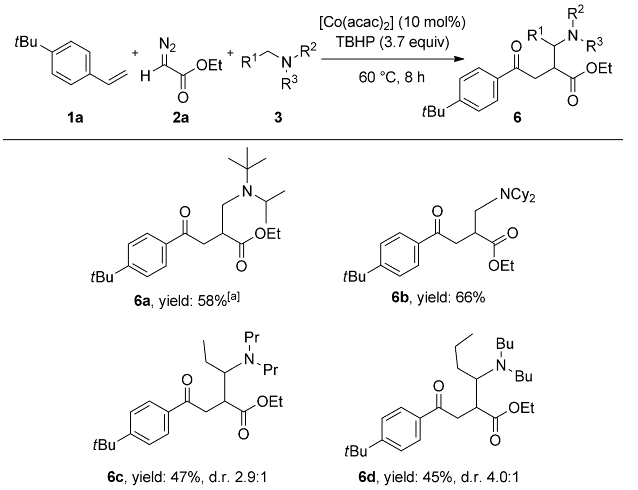
Similarly, our Co-catalyzed transformation was also shown to be compatible with a variety of diazo reagents (Scheme 3). A synthetically useful allyl group was well tolerated in the reaction, and **5c** was generated in moderate yield. Dimethyl diazoacetamide also proved to be an effective coupling partner and furnished product **5e** in 31 % yield. Unfortunately, only trace amounts of product **5f** were obtained when ethyl 2-diazobutanoate was used as the starting material.

Results obtained with different tertiary amines are summarized in Scheme 4. In all cases, the expected β-ester-γ-amino ketones were obtained in satisfactory yields. Inter-



5a, yield: 51%
5b, yield: 64%
5c, yield: 42%
5d, yield: 60%
5e, yield: 31%
5f, yield: <5%

Scheme 3. Variation of the diazo reagent. Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), **3b** (2.5 mmol), [Co(acac)$_2$] (0.05 mmol), TBHP (1.85 mmol), and 4 Å M.S. (200 mg) were stirred in 1,4-dioxane/CH$_2$Cl$_2$ (1.0 mL each) at 60 °C for 8 h.

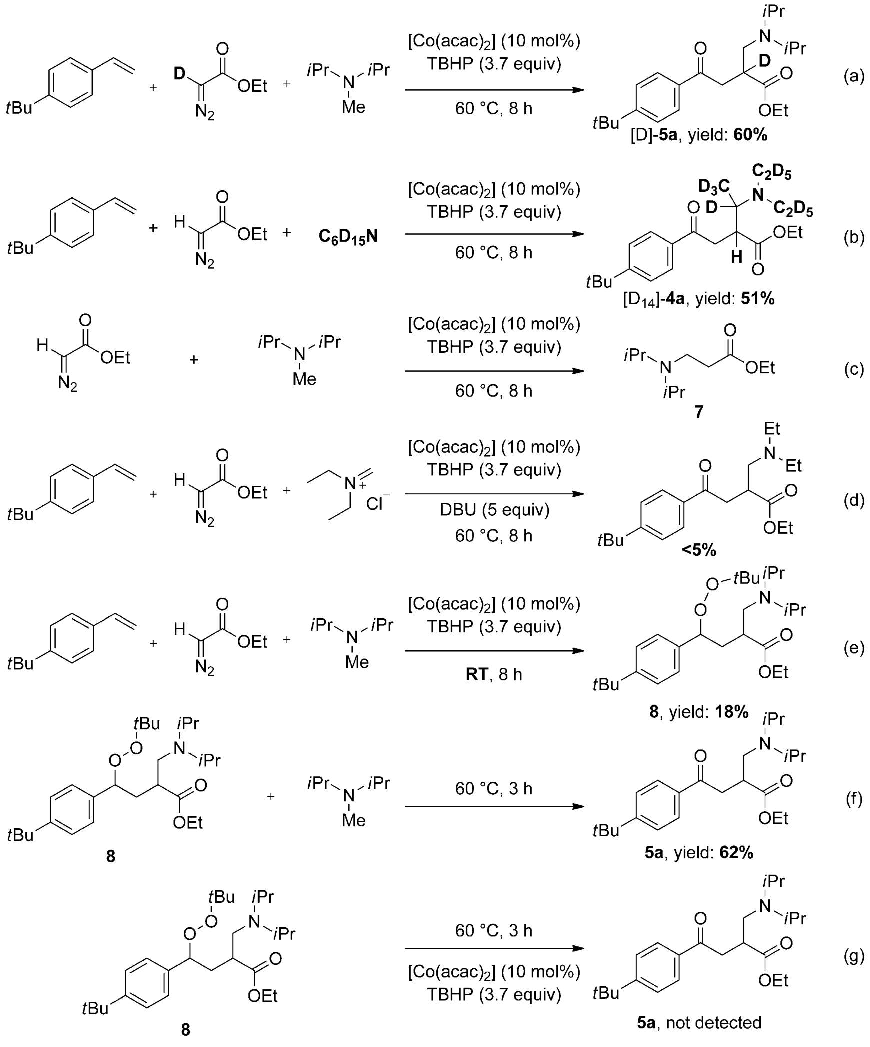


Scheme 4. Variation of the tertiary amine. Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), **3** (2.5 mmol), [Co(acac)$_2$] (0.05 mmol), TBHP (1.85 mmol), and 4 Å M.S. (200 mg) were stirred in 1,4-dioxane/CH$_2$Cl$_2$ (1.0 mL each) at 60 °C for 8 h. [a] 80 °C.

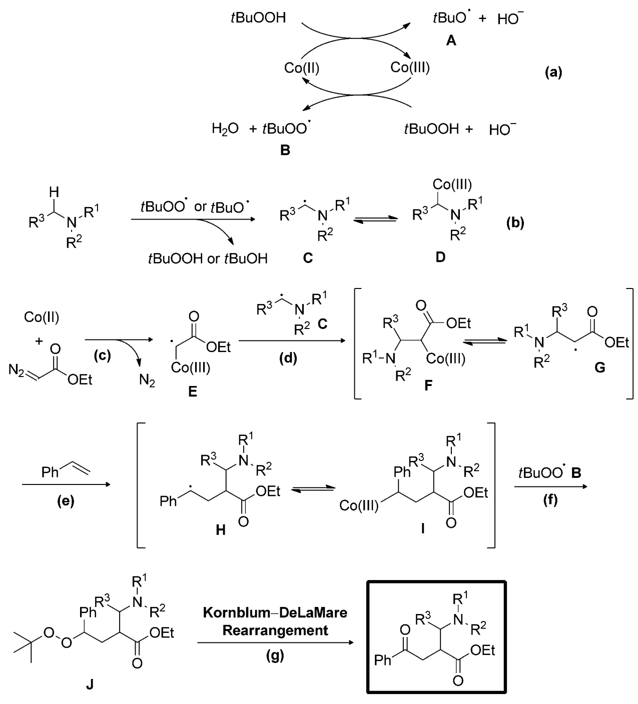
estingly, bulky substituents on the nitrogen atom of the amine had no significant impact on its reactivity. When unsymmetric tertiary amines were used, functionalization occurred preferentially on the primary C(sp^3)–H bond (**5a–e**, **6a–b**), presumably because of steric effects.

When the reaction was conducted using [D]-**2a**, the product [D]-**5a** was generated in 60% yield (Scheme 5a). The presence of deuterium in the product constitutes direct evidence against a plausible alternative mechanism, which attributes the origin of the diazo-derived radical intermediate to α-hydrogen abstraction. On the other hand, the use of deuterated Et$_3$N in place of its non-deuterated counterpart led to [D$_{14}$]-**4a** in satisfactory yield (Scheme 5b). This result indicates that a cross-coupling between the Co-based carbene radical and the α-aminoalkyl radical has occurred; this mechanism is distinct from those of C–H functionalization processes with the widely studied dirhodium- and copper-based carbene systems.[1c,e–h] When the model reaction was conducted in the absence of an olefin, a small amount of compound **7** was detected by GC analysis, which further confirmed that the process occurred by cross-coupling of the Co-based carbene radical and the α-aminoalkyl radical (Scheme 5c). To determine whether the tertiary amine could have participated in the reaction by forming a reactive iminium cation, we employed an iminium salt instead of the tertiary amine and did not observe the formation of the desired β-ester-γ-amino ketone, thereby effectively ruling out the hypothesis that the iminium ion is an intermediate of this transformation (Scheme 5d). Repeating the standard reaction at room temperature led to the isolation of peroxide **8** in 18% yield (Scheme 5e). When a reaction mixture containing **8** but no [Co(acac)$_2$] or TBHP was heated to 60 °C, the desired product **5a** was formed in 62% yield (Scheme 5f). However, **5a** could not be detected in the absence of amine **3b** (Scheme 5g), which indicates that the reaction proceeds by the in situ formation of a peroxide intermediate and a subsequent Kornblum–DeLaMare reaction.

Combining the above results and literature precedents, we propose a plausible mechanism (Scheme 6). The reaction begins with cobalt(II)-promoted homolytic decomposition of TBHP to yield *t*BuO$^•$ (**A**) and *t*BuOO$^•$ (**B**; step a).[7b,9] Both radical intermediates are capable of abstracting an α-hydrogen atom from the tertiary amine to form α-aminoalkyl radical **C** (b).[7a] In the meantime, activation of the diazo



Scheme 5. Mechanistic investigations.



Scheme 6. Proposed mechanism for the formation of β-ester-γ-amino ketones.

compound by the cobalt(II) complex leads to cobalt-based carbene radical **E** (c),[2] which is immediately trapped by **C** to afford organocobalt intermediate **F** (d). Notably, the high-resolution mass spectrum features a peak at *m/z* 344.0698, which corresponds to the organocobalt species **E**–**H**, which are generated in situ by hydrogen abstraction from cobalt-based carbene radical **E** (for details, see the Supporting Information). Next, the addition of radical **G**, which is formed by the reversible homolytic cleavage of **F**, to styrene generates the more stabilized benzyl radical **H** (e), which can then be selectively coupled with *t*BuOO**·** (**B**) to produce peroxide intermediate **J** (f). Finally, peroxide intermediate **J** undergoes a Kornblum–DeLaMare reaction[8] to give the desired β-ester-γ-amino ketone (g). Because of the well-established carbophilicity of cobalt, these carbon-centered radicals could be reversibly trapped by Co^{II} to form organocobalt intermediates.[10]

Several model studies were designed to better understand the mechanism of this transformation (Scheme S2). α-Bromoester **9**, which can serve as a precursor to an organoradical intermediate, was shown to be a suitable replacement for the diazo substrate, and the reaction afforded product **10** in good yield under the standard conditions (Scheme S2 a). In contrast, when β-amino ester **11** was used as the coupling partner, the corresponding product was not detected (Scheme S2 b). Similarly, the fact that compound **12** (a precursor to an organoradical species) was also a poor choice of substrate (Scheme S2 c) indicated that the β-ester-γ-amino ketone is not formed by the reaction of the α-diazo reagent with the olefin followed by coupling with the amine. *N*-Methyl-*N*-phenylmethacrylamide (**13**), an efficient radical acceptor for the construction of oxindoles by homolytic aromatic substitution,[11] was subjected to the standard conditions, and the corresponding oxindole **14** could be isolated, albeit in a low yield of 15 %, which indicated that the cobalt carbene radical had been intercepted with an α-aminoalkyl radical (Scheme S2d).

The involvement of reactive radical intermediates was also validated by the finding that the addition of radical traps, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT), could halt the formation of the β-ester-γ-amino ketones (Scheme S3). Four radical adducts whose formation was predicted by our proposed mechanism could be detected from the resulting reaction mixture, including those of the cobalt-based carbene radical **E** with radicals **C, G**, or **H**. As expected, when [D]-**2a** was used instead of **2a**, the corresponding deuterated adducts of radicals **E**, **G**, and **H** were also detected.

In summary, we have developed an unprecedented tandem process that features a cobalt-based carbene radical and involves radical and ionic reactions. The interception of the cobalt-based carbene radical with an α-aminoalkyl radical, followed by the Kornblum–DeLaMare reaction, allowed the efficient synthesis of various highly functionalized β-ester-γ-amino ketones. During this one-pot process, two C–C bonds and one C=O bond are constructed. Future research will focus on further studies of the unique reactivity of the cobalt-based carbene radicals through the development of more interception reactions.

Experimental Section

Cobalt(II) acetylacetonate (0.05 mmol) and 4 Å M.S. (200 mg) were added to a test tube. 1,4-Dioxane (1.0 mL), dichloromethane (1.0 mL), the alkene (0.5 mmol), amine (2.5 mmol), diazoacetic ester (1.0 mmol), and TBHP, (1.85 mmol, 0.25 mL, 70 % solution in water) were added by syringe. A balloon was put on the test tube. The reaction mixture was stirred at 60 °C for 8 h. It was then quenched (to consume residual TBHP) with a saturated Na_2SO_3 solution and extracted with ethyl acetate. The organic layers were combined and dried with Na_2SO_4. Removal of the solvents followed by flash column chromatography (petroleum/ethyl acetate) on silica gel afforded the desired product.

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Keywords: carbene radicals · cobalt · Kornblum–DeLaMare reaction · radical reactions · tandem reactions

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