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# Co-Catalyzed Synthesis of 1,4-Dicarbonyl Compounds Using TBHP Oxidant

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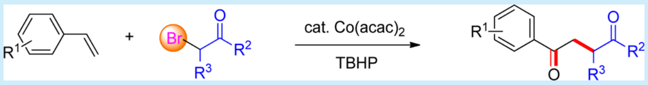
*Supporting Information*

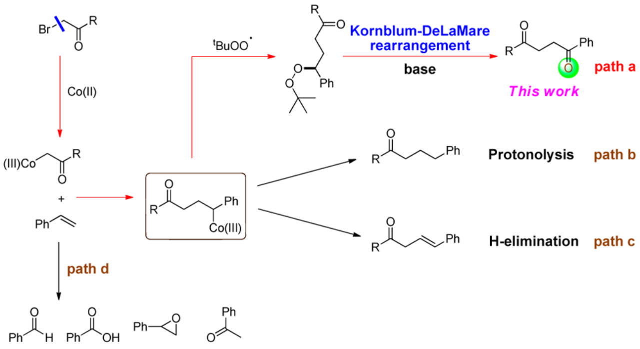
**ABSTRACT:** A Co-catalyzed reaction for the construction of 1,4-dicarbonyls has been reported in which cascade organocobalt addition/trapping/Kornblum–DeLaMare rearrangement were involved. In view of the easy availability of starting materials, wide substrate scope, high functionality tolerance, and operational simplicity, this protocol constituted a simple, practical, and powerful alternative compared with previous approaches.



1,4-Dicarbonyl compounds are versatile building blocks for the synthesis of various carbocyclic and heterocyclic compounds,[1] such as cyclopentenones, furan, thiophene, pyridazines, and pyrrole derivatives. As a result, significant efforts have been directed toward the synthesis of this highly valuable synthon. For example, the conjugate addition of acyl anion equivalents to Michael acceptors provided a powerful method for 1,4-dicarbonyl synthesis.[2] Other attractive approaches consist of nucleophilic substitution of $\alpha$-haloketones,[3] chain extension of 1,3-dicarbonyl compounds,[4] oxidative coupling of enolates[5] or alkenes,[6] and the addition of homoenolate equivalents to acid derivatives.[7] Recently, enolate heterocoupling has also emerged as a straightforward approach for the chemoselective formation of 1,4-dicarbonyl.[8] Despite the great successes achieved in this field, significant improvement is still in demand in terms of availability of starting materials, substrate scope, and functional group tolerance.

Current methods for 1,4-dicarbonyl synthesis have mainly relied on the reactions between two derivatives of carbonyl compounds. The cobalt-mediated radical reaction[9,10] has emerged as an attractive and powerful tool in the domain of synthetic organic chemistry. Recently, we developed several radical reactions using TBHP as an oxidant,[11a−h] in which the ${}^{t}$BuOO$^{\bullet}$ radical was generated *in situ* and served as a key intermediate. Combining the above two concepts, tandem addition of organocobalt to styrenes/interception by the ${}^{t}$BuOO$^{\bullet}$ radical was envisioned to afford a *tert*-butylperoxide compound, which could undergo Kornblum–DeLaMare rearrangement[12] to form the expected 1,4-dicarbonyl product (Scheme 1, path a). To the best of our knowledge, both the trapping of organocobalt with the ${}^{t}$BuOO$^{\bullet}$ radical and the combination of organocobalt chemistry and Kornblum–DeLaMare rearrangement are so far underexplored. From the synthetic point of view, this methodology is also intriguing due to its direct use of easily available styrenes and $\alpha$-bromocarbonyls.

**Scheme 1. Our Strategy for the Synthesis of 1,4-Dicarbonyls**



Many obstacles to the formation of 1,4-dicarbonyls remain in the hypothesis. One is how to trap the benzylcobalt by the ${}^{t}$BuOO$^{\bullet}$ radical in high chemoselectivity without the influence of competitive protonolysis[10d,e,k,m] (Scheme 1, path b) and $\beta$-H elimination[9c,e−g,i,10b,c,g,l] (Scheme 1, path c), both of which were well documented to be side reactions. Another noticeable side reaction is the oxidation of styrene in the presence of TBHP through oxidative cleavage,[13] epoxidation,[14] or Wacker oxidation[15] (Scheme 1, path d).

We began our condition optimization with the use of $Et_3N$ as the solvent, as it could promote Kornblum–DeLaMare rearrangement and, meanwhile, suppress proton abstraction.[16] A high yield of 86% was obtained by treating the reaction of 1-(*tert*-butyl)-4-vinylbenzene and ethyl 2-bromopropanoate with 10 mol % $Co(acac)_2$ and 4.0 equiv of TBHP at 100 °C for 24 h under an air atmosphere (Table S1, entry 1; see Supporting Information). Co-catalyzed reductive coupling has been well developed in the past decades.[9e−h] Herein, we demonstrate a rare example of Co-catalyzed oxidative coupling,[17] in which both a C–C single bond and C=O double bond were constructed selectively in one pot. Remarkably, a similar result was obtained under an inert atmosphere, implying that molecular oxygen did not act as an oxidant for this

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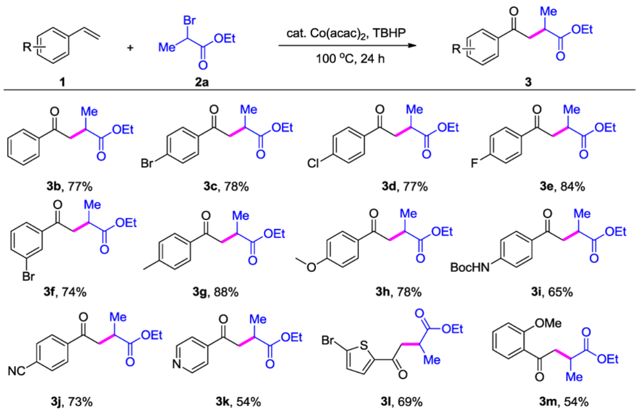
transformation. This is in sharp contrast with the reported synthesis of 1,4-dicarbonyl via a radical process[6] (Table S1, entry 20).

With the optimized reaction conditions in hand, we next evaluated a wide range of substituted styrenes. As shown in Scheme 2, the reaction demonstrated a broad tolerance toward a variety of functional groups such as halide (**3c**−**3f**, **3l**), nitrile (**3j**), ether (**3h**, **3m**), benzylic C−H bond (**3g**), and BocNH (**3i**). Substitution at all *ortho* (**3m**), *meta* (**3f**), and *para* (**3c**−**3e**, **3g**−**3j**) positions are compatible. Heterocyclics such as 4-vinylpyridine and 2-vinylthiophene are suitable substrates, albeit resulting in slightly lower yields (products **3k** and **3l**). When aliphatic alkenes were subjected to the reaction, no significant amount of the corresponding 1,4-dicarbonyls were obtained under standard conditions.

**Scheme 2. Scope of Styrenes**[a]

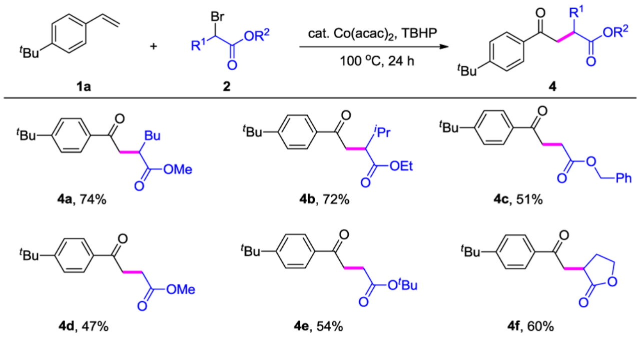


[a]0.5 mmol of **1**, 1.5 mmol of **2a**, 0.05 mol of Co(acac)$_2$, 2.0 mmol of TBHP, 2.0 mL of Et$_3$N, at 100 °C for 24 h in a sealed tube.

With 4-*tert*-butylstyrene (**1a**) as the coupling partner, *α*-bromoesters carrying different substituents all reacted smoothly generating the desired products in moderate to high yields (Scheme 3). Notably, *γ*-butyrolactone was also apt, furnishing **4f** in 60% yield.

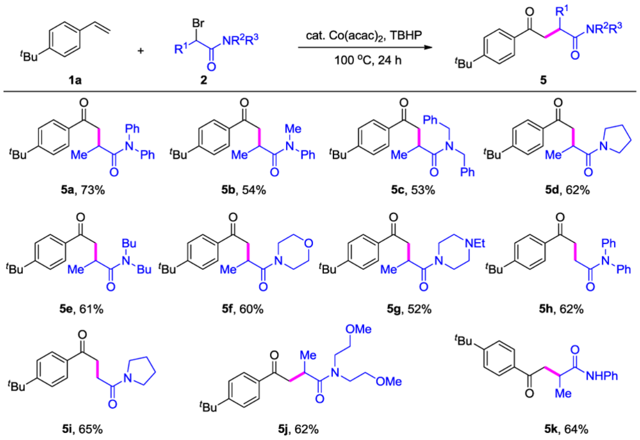
Apart from *α*-bromoesters, *α*-bromoamides are also examined (Scheme 4). Broad functionality tolerance was once again observed for various substituents including benzyl (**5c**), ether (**5f**, **5j**), amine (**5g**), and even an active HNCOPh group (**5k**), to give moderate to high yields. Either cyclic or acyclic amides are compatible with the reaction conditions.

**Scheme 3. Scope of *α*-Bromoesters**[a]



[a]0.5 mmol of **1a**, 1.5 mmol of **2**, 0.05 mol of Co(acac)$_2$, 2.0 mmol of TBHP, 2.0 mL of Et$_3$N, at 100 °C for 24 h in a sealed tube.

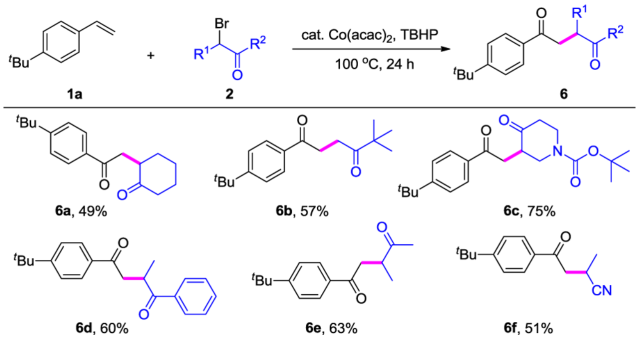
**Scheme 4. Scope of *α*-Bromoamides**[a]



[a]1.5 mmol of **1a**, 0.5 mmol of **2**, 0.05 mol of Co(acac)$_2$, 2.0 mmol of TBHP, 2.0 mL of Et$_3$N, at 100 °C for 24 h in a sealed tube.

An array of *α*-bromoketones were also investigated as starting materials. As shown in Scheme 5, yields for these transformations varied from 49% to 75%. Cyclic (**6a**, **6c**), acyclic (**6b**, **6e**), and aromatic ketones (**6d**) could all be accepted. It is noteworthy that *α*-bromonitrile also proved to be a compatible reaction partner, leading to the synthetically useful *β*-nitrile ketone **6f** in moderate yield.

**Scheme 5. Scope of *α*-Bromoketones**[a]



[a]0.5 mmol of **1a**, 1.5 mmol of **2**, 0.05 mol of Co(acac)$_2$, 2.0 mmol TBHP, 2.0 mL of Et$_3$N, at 100 °C for 24 h in a sealed tube.

A reaction of 4-*tert*-butylstyrene and 2-bromo-*N*,*N*-diphenylacetamide under optimized conditions was performed for 0.5 h. Trace amounts of byproducts **7** and **8** from protonolysis and a *β*-H elimination reaction of a benzylcobalt intermediate were found in the crude product by means of LC-MS (Figure 1). When the radical trap BHT (3,5-di-*tert*-butyl-4-hydroxytoluene) was added, the corresponding adducts **9** and **10** were observed in this reaction mixture. The detection of **9** and

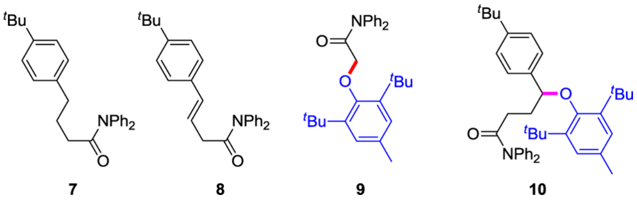
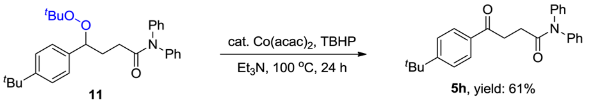


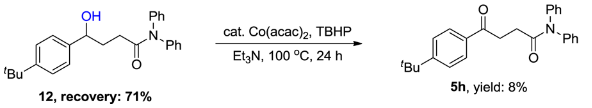
**Figure 1.** Investigation of reaction mechanism.

**10** provided the proof of homolysis of the carbon−cobalt bond of the organocobalt intermediate (see path a in Scheme 1) in this oxidative process.

The above experiments provide evidence for the formation of organocobalt intermediates and their thermal homolysis to generate radicals during this 1,4-dicarbonyl formation reaction. Next, we try to investigate the role of *tert*-butylperoxide in this transformation. After careful examination, *tert*-butylperoxide **11** was observed in the reaction mixture. As further evidence, it could undergo Kornblum−DeLaMare rearrangement to afford the predicted $\gamma$-ketone amide **5h** in 61% yield (eq 1), implying it functions as a reaction intermediate in this transformation. It is worth noting that this result was different form Lei' report,[18] in which $\beta$-peroxy ketone was not directly involved in the generation of the desired $\alpha,\beta$-unsaturated ketone. Meanwhile, a very poor yield of **5h** was achieved when benzyl alcohol **12** was subjected to the same reaction system (eq 2), thereby ruling out the possibility of the latter's direct oxidation into the 1,4-dicarbonyl product.[19a−c]



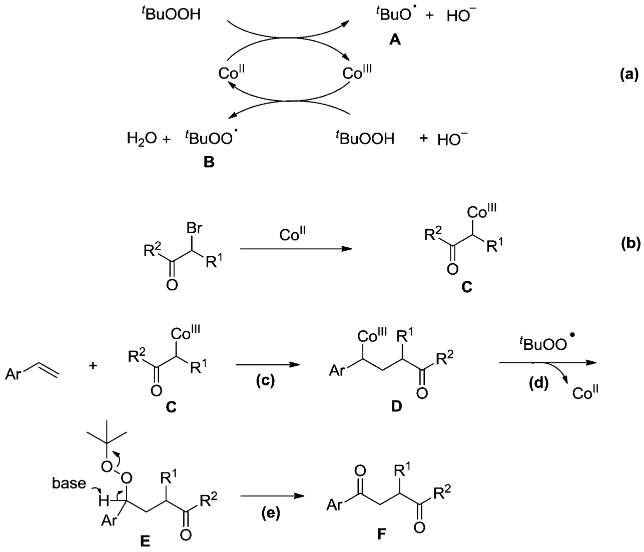
(1)



(2)

Based on the above-mentioned findings, a plausible mechanism is outlined in Scheme 6. The cobalt catalyst is hypothesized to promote both the decomposition of TBHP that generates $^t$BuO$^\bullet$ radical **A** and $^t$BuOO$^\bullet$ radical **B**[20] (Scheme 6a) and the reductive cleavage of the C−Br bond that converts the $\alpha$-bromoketone to the organocobalt **C** (Scheme 6b). **C** is trapped by styrene to form intermediate **D** (Scheme 6c), which can then selectively be displaced with $^t$BuOO$^\bullet$ **B** to afford the peroxide intermediate **E** (Scheme 6d). Finally, base-promoted Kornblum−DeLaMare rearrangement lead to the formation of the 1,4-dicarbonyl **F** (Scheme 6e). Noteworthily, free radical intermediates generated *in situ* from organocobalt complexes cannot be ruled out in this transformation.

**Scheme 6. Proposed Reaction Mechanism**



In summary, we have implemented a new termination mode of the carbon−cobalt bond by trapping with the $^t$BuOO$^\bullet$ radical, wherein the *in situ* generated *tert*-butylperoxide can then undergo Kornblum−DeLaMare rearrangement to furnish a range of 1,4-dicarbonyls. Our method utilizes easily available starting materials, offers operational simplicity, and enjoys a broad substrate scope as well as functionality tolerance. Currently, interception of an organocobalt by other radicals to develop a new methodology is in progress in our laboratory.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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