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Charge transfer complex enabled mechanochemical synthesis of chalcogenoacetylenes *via* alkynyl radicals†

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Mechanochemistry has become an appealing strategy to enable numerous organic transformations. While significant advancements have been achieved, radical coupling reactions under mechanochemical conditions are still in their infancy. In this study, a charge transfer complex enabled mechanochemical generation of alkynyl radicals from alkynyl sulfonium salts is reported. This method provides a convenient pathway to achieve alkynyl selenides and alkynyl tellurides under much simpler conditions, without inert gas protection.

Introduction

In the past decades, mechanochemistry has emerged as a powerful technique with significance across a range of multi-scale applications in chemical synthesis and materials science.[1] The solvent-free properties and mechanical activation mode not only make this technique compatible with the concept of green chemistry,[2] but more importantly, can also provide higher and even completely new reactivities compared to solution-based methods. Recently, mechanochemistry has come to be considered a valuable potential synthetic technology for various synthetically important bond formations.[3] However, the application of mechanochemical processes in radical chemistry is quite limited due to the inherent unpredictable nature of highly reactive radical intermediates.[4] Only recently, seminal studies using piezoelectric materials[5] as ideal photoredox catalyst mimics have been accomplished by the groups of Ito and Bolm,[6] opening up new avenues for the generation of radicals (Fig. 1A). Since then, several radical transformations have been reported under ball milling conditions.[7] However, most of them employed diazonium salts as aryl radical precursors.[7b,e,l,m] Recently, Mandal, Bhunia, and co-workers developed an interesting solid-state method for the generation of the super electron donor phenlenyl anion under ball milling conditions for the single electron reduction of aryl halides (Fig. 1B).[8] Compared with these developed alkyl and aryl radicals under mechanochemical conditions, radical reactions involving alkynyl radicals under ball milling conditions remain unexplored. Given the importance of the alkyne func-

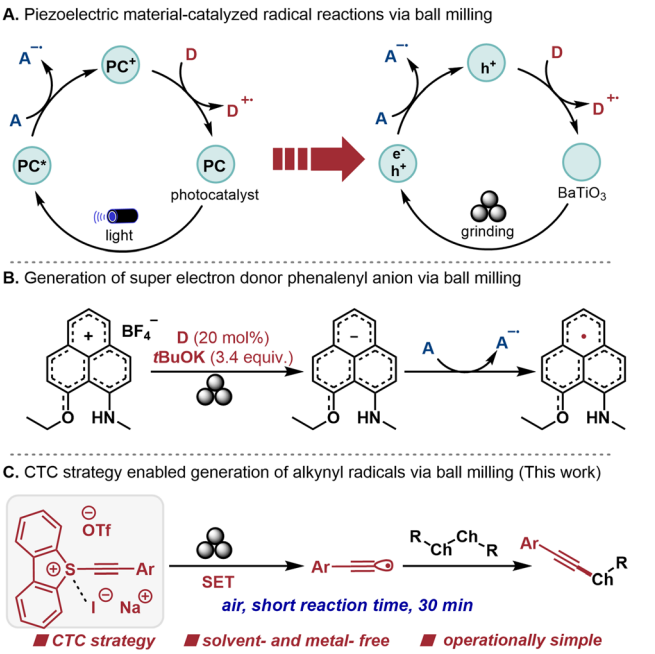

Fig. 1 (A) Piezoelectric material-catalyzed radical reactions *via* ball milling, (B) generation of the super electron donor phenlenyl anion *via* ball milling, and (C) this work: charge transfer complex enabled radical alkynylations *via* ball milling.

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tionalities in organic synthesis[9] and the inherent advantages of mechanical techniques, investigating new mechanochemistry strategies for the generation of alkynyl radicals is imperative.

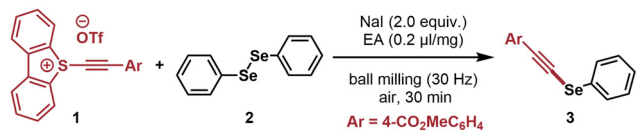
Recently, the photoactive charge transfer complex (CTC) strategy has emerged as an additional approach to photoredox catalysis, eliminating the need for photocatalysts.[10] However, the applications of this strategy under ball milling conditions remain underdeveloped. In 2022, we discovered that alkynyl sulfonium salts could generate alkynyl radicals by a single electron transfer (SET) process *via* chalcogen bonding under blue light irradiation.[11] Based on these results, we wondered whether the CTC strategy could be applied in mechanochemistry to generate alkynyl radicals under much simpler conditions without inert gas protection (Fig. 1C).

Results and discussion

To test our hypothesis, initial experiments were conducted with the alkynyl sulfonium salt **1** [12] and diphenyl diselenide **2**. We were pleased to find that NaI as the electron donor and ethyl acetate (EA) as the liquid-assisted grinding (LAG) additive afforded alkynyl selenide **3** [13] in 95% yield, as determined by GC-MS using *n*-hexadecane as the internal standard (Table 1, entry 1). Screening LAG additives showed that EA was the best choice (entries 2–4). Control experiments demonstrated the importance of the electron donor and the LAG additive (entries 5–7).

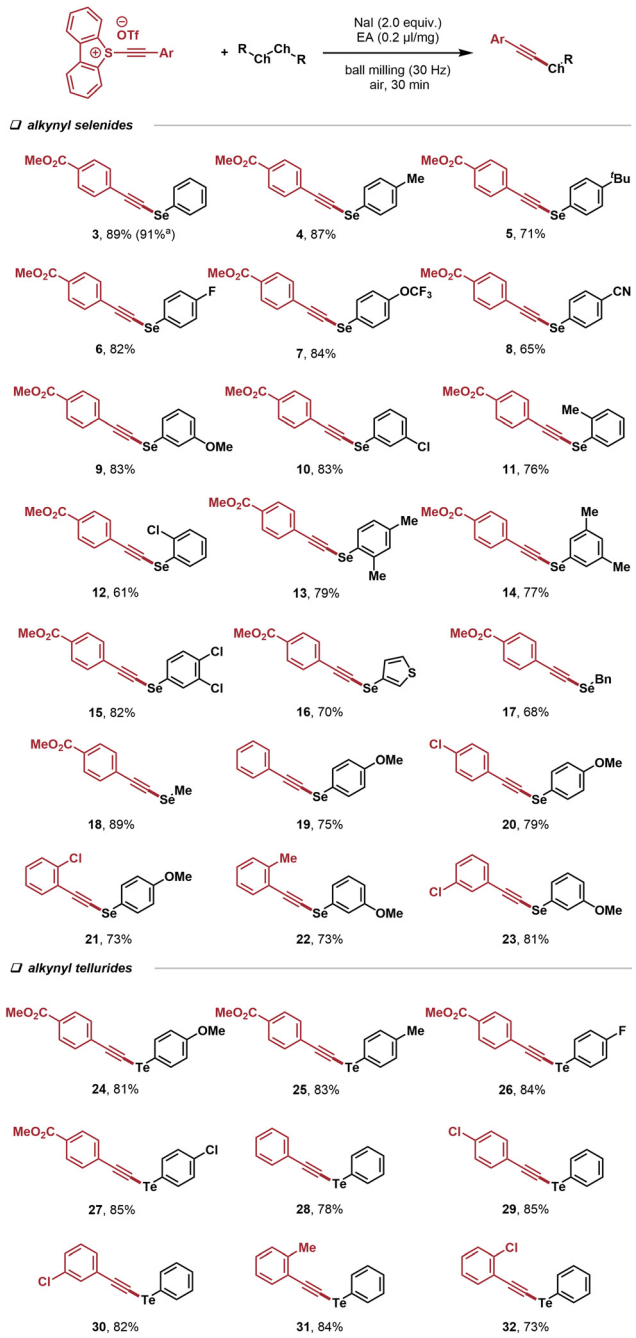
With the optimal conditions in hand, we first evaluated the substrate scope of various diphenyl diselenides. As shown in Scheme 1, diphenyl diselenides with both electron-donating (4-Me and 4-*t*Bu) and electron-withdrawing (4-F, 4-OCF_3, and 4-CN) groups on the aryl ring were suitable for this transformation, giving the corresponding products **4–8** in good to high yields. Moreover, the reaction was compatible with substrates containing –OMe, –Cl, and –Me at the *meta*-position and the *ortho*-position, providing **9–12** in 61–83% yields. The di-substituted substrates also reacted smoothly, giving products

Table 1 Optimization of the reaction conditions[a]



Entry	Variation from standard conditions	Yield[b] (%)
1	None	89
2	DMF instead of EA	63
3	DCM instead of EA	76
4	THF instead of EA	72
5	Without NaI	Trace
6	Without EA	47
7	Without NaI and EA	Trace

[a] Reaction conditions: **1** (0.4 mmol, 2.0 equiv.), **2** (0.2 mmol), NaI (0.4 mmol, 2.0 equiv.), and EA (0.2 μL mg^{-1}) were added to a stainless-steel jar (5 mL) with nine stainless steel balls (each stainless steel ball had a diameter of 5 mm and weighed *ca.* 0.6 g) under air and milled at 30 Hz for 30 min. [b] GC-MS yields with *n*-hexadecane as the internal standard.



Scheme 1 Reaction scope. Reaction conditions: alkynyl sulfonium salts (0.4 mmol, 2.0 equiv.), diselenides or ditellurides (0.2 mmol), NaI (0.4 mmol, 2.0 equiv.), and EA (0.2 μL mg^{-1}) were added to a stainless steel jar (5 mL) with nine stainless steel balls (each stainless steel ball had a diameter of 5 mm and weighed *ca.* 0.6 g) under air conditions and milled at 30 Hz for 30 min. Yields of the isolated products are given beside the desired products; trace amounts of diynes were detected as by-products. [a] 1.0 mmol.

13–15 in moderate to high yields. Notably, 1,2-di(thiophen-3-yl) diselane was also compatible and provided **16** in 70% yield. Based on the success with diphenyl diselenides, we attempted to apply this strategy to alkyl diselenide substrates. It was found that dibenzyl diselenide and dimethyl diselenide underwent smooth transformation to give the corresponding products **17** and **18** in 68% and 89% yields, respectively. Then, various alkynyl sulfonium salts were examined and all of them performed admirably (**19–23**).

Considering the medical applications of tellurides,[14] we further evaluated the corresponding tellurylation reactions under the same reaction conditions. The ditellurides containing electron-donating or electron-withdrawing substituents attached to the phenyl ring, such as 4-methoxyl, 4-methyl, 4-fluro, and 4-chloro, all reacted well with **1** to produce the corresponding products **24–27** in high to excellent yields. In addition, several alkynyl sulfonium salts were examined as well, and all reactions proceeded well, affording the corresponding products **28–32** in high yields.

To obtain a deeper insight into the mechanism of this transformation, a series of mechanistic experiments were carried out, and the results are shown in Fig. 2. First, the alkynyl sulfonium salts containing an iodide anion instead of a trifluoromethanesulfonate anion reacted well with diphenyl diselenide **2** in the absence of NaI, affording product **3** in 89% yield (Fig. 2A, top), which demonstrated the importance of the iodide anion as the electron donor. Then, the reaction was performed in the absence of diphenyl diselenide **2**, leading to iodoethynylbenzene **34** in a yield of 59%; meanwhile, the dimer of phenylacetylene **35** was detected by GC-MS (Fig. 2, middle), which indicated the generation of the alkynyl radical. Next, iodoethynylbenzene **34** and diphenyl diselenide **2** were milled under the standard reaction conditions and product **3** was not detected, which ruled out the possible pathway between the iodoethynylbenzene and diselenide (Fig. 2A, bottom). Moreover, the radical pathway of this reaction was further confirmed by a radical inhibition experiment. When 5.0 equiv. of 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was subjected to the standard reaction conditions, product formation was inhibited (product **3** was not detected) and iodoethynylbenzene **34** was also not formed (Fig. 2B). These results suggested that radicals may be involved in the process.

On the basis of the above experimental results and our previous studies,[15] we proposed a possible mechanism for this mechanochemical alkynylation of alkynyl sulfonium salts (Fig. 2C). After the formation of a charge transfer complex between the alkynyl sulfonium salt and NaI, the cleavage of the C–S bond occurred under ball milling conditions, leading to the generation of the alkynyl radical and the iodine radical; the former then reacts with diselenide to give the final product. Additionally, the alkynyl radical would be coupled with the iodine radical to give iodoethynylbenzene, which is supported by the results of the control experiment (Fig. 2A, middle).

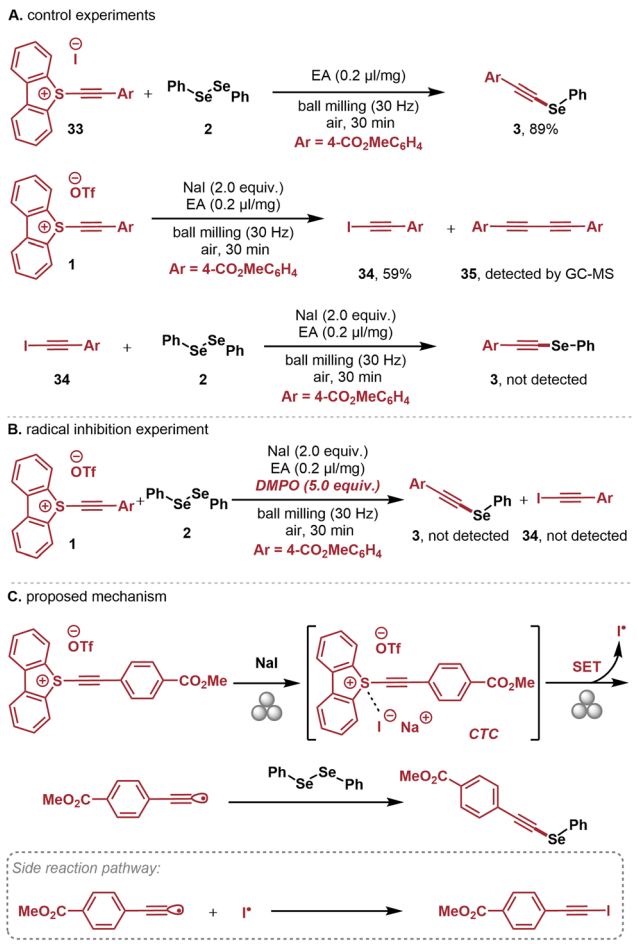


Fig. 2 (A) Control experiments, (B) radical inhibition experiment, and (C) proposed mechanism.

Conclusions

In summary, we have developed a new CTC strategy for synthesizing chalcogenoacetylenes from alkynyl sulfonium salts using NaI as the electron donor under mechanochemical conditions. The reactions are easy to perform, solvent- and metal-free, and proceed in a short reaction time (30 min) to provide products in good to excellent yields. The utilization of NaI as the electron donor and EA as the liquid-assisted grinding additive was identified as the key factor for this transformation. Further exploration on using the CTC strategy with mechanical techniques to develop new reaction modes is currently underway in our laboratory.

Data availability

The authors confirm that the data underlying this study are available within the article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

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