Metal- and base-free tandem sulfonylation/cyclization of 1,5-dienes with aryldiazonium salts \textit{via} the insertion of sulfur dioxide†

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A metal- and base-free 5-endo-trig sulfonylative cyclization between 1,5-dienes, aryldiazonium salts and \( \text{SO}_2 \) (from SOgen) is presented. This method could successfully produce sulfonylated pyrrolin-2-ones in one pot with excellent regioselectivity and good-to-excellent yields. This strategy features mild reaction conditions and broad substrate scope. Moreover, a scale-up reaction and three synthetic applications demonstrate the practicality of this method. Lastly, control experiments indicate that the 5-endo-trig sulfonylative cyclization may proceed in a radical pathway.

Introduction

Pyrrolin-2-ones and their N-heterocyclic compound derivatives, widely exist in natural plants,\(^1\) pharmaceuticals\(^2\) and bioactive molecules.\(^3\) Similarly, sulfonyl groups are frequently found in pharmaceuticals\(^4\) and photoelectric materials\(^5\) due to their unique chemical properties. Numerous studies have indicated that the incorporation of sulfonyl groups into heterocycles could enhance their pharmacological activity.\(^6\) Therefore, great efforts have been devoted to explore efficient and straightforward methods to build sulfone-containing N-heterocyclic frameworks.

Radical cascade cyclization reactions represent a powerful strategy for the synthesis of functionalized cyclic structure, characterized by multiple C-C/C-X bond-forming in one step.\(^7\) The incorporation of sulfonyl group into heterocycles by radical cascade cyclization reactions has aroused extensive interest among scientists.\(^8\) In recent years, many sulfone-containing heterocyclic frameworks have been constructed by radical cascade cyclization reactions, such as sulfonylindoles,\(^9\) sulfonylindolinols,\(^10\) sulfonylated pyrrolidines,\(^11\) sulfonylated phenanthridines,\(^12\) sulfonylated benzofurans,\(^13\) sulfonated oxazolines,\(^14\) sulfonylated spirocycles\(^15\) and others.\(^16\) In 2021, sulfonylated pyrrolinones were synthesized via sulfonylation/cyclization of 1,5-dienes with sulfonyl chlorides or sodium sulfinates by Wang and co-workers (Fig. 1a and b).\(^17\) However, due to the limited accessibility of sulfonyl chlorides and sodium sulfinates, these two methods suffered from a narrow range of substrates. Besides, transition metal (Cu and Ag), base and elevated temperature were essential in these transformations.

On the other hand, direct insertion of sulfur dioxide (\( \text{SO}_2 \)) provides an alternative and efficient approach to introduce sulfonyl moiety into molecules.\(^18,19\) Recently, a cheap and bench-stable \( \text{SO}_2 \) surrogate (SOgen) has been developed by our group, which has been successfully applied in several sulfonylation reactions.\(^20\) Inspired by Wang’s work and our continuous...
interests in SO₂ chemistry, we herein attempt to construct sulfonylated pyrrolinones using SOgen as SO₂ surrogate (Fig. 1c). This transformation features metal- and base-free conditions and could proceed smoothly at room temperature to form sulfonylated pyrrolinones with excellent regioselectivity and good to excellent yields.

## Results and discussion

We started the studies by evaluating the reaction between 1,5-diene (1a), 4-methylbenzenediazonium tetrafluoroborate (2a) and SO₂ gas (from SOgen) under metal- and base-free conditions. Pleasently, when the reaction was carried out in NMP at room temperature for 24 h, desired product 3a was successfully obtained in 91% yield with excellent regioselectivity (Table 1, entry 1).

Then we explored the influence of other solvents on this reaction, the target product (3a) was not obtained in most solvents, such as THF, MeCN, DCM, toluene and MeOH (Table 1, entries 2–6). When the solvent was DMA, DMF and DMSO, 3a was formed in only poor yields (Table 1, entries 7–9). Next, the amount of SO₂ (from 2.5 equiv. to 4.0 equiv.) was investigated, and the results indicated that 4.0 equiv. was the best choice (Table 1, entries 10–12). Although this reaction could work under an air atmosphere, argon atmosphere proved to be more beneficial for the transformation (Table 1, entry 13). Finally, other sulfur dioxide surrogates were examined. The use of DABSO and inorganic SO₂ surrogates (Na₂S₂O₅ and K₂S₂O₇) could both lead to the formation of product 3a but with lower yields (Table 1, entries 14–16). Unfortunately, rongalite reagent (HOCH₂SO₂Na·H₂O) would hamper the reaction (Table 1, entry 17).

After determining the optimal reaction conditions, we began to explore the substrate scope of this reaction, and the results are summarized in Scheme 1. We first investigated the functional group compatibility of aryldiazenium tetrafluoroborates in the transformation. Alkyl substituted aryldiazenium tetrafluoroborates at the meta- or para-position of the phenyl ring proceeded well and afforded corresponding products 3b–3d in good yields (83–93%). While a methyl substituent at the ortho-position could lead to a lower yield (67%, 3e), possibly due to the steric hindrance. In addition, substrates with methoxy or phenoxo group delivered desired products 3f and 3g in 83% and 86% yield, respectively. Substrates bearing a biphenyl or 2-naphthyl group showed good reactivity, producing expected products (3h and 3i) in excellent yields. Notably, halogen groups were found to be well tolerated under the standard conditions (3j–3q). Moreover, substrates with electron-withdrawing groups such as MeC(O)₂, PhC(O)₂, CF₃C(O)₂, MeSO₂C(O)₂ were subject to the reaction conditions, and gave corresponding products (3r–3v) in good yields. In addition, heterocyclic diazonium salt was found to be compatible in the transformation (3w). Finally, aryldiazenium tetrafluoroborates with complicated substituent structures could also work smoothly to afford 3x and 3y in 92% and 90% yield, respectively.

Next, the substrate scope of 1,5-dienes was investigated. The results showed that halogen groups (–Cl, –Br and –I) on 1,5-dienes had little effect on the reaction, and the corresponding products 3z–3ae were formed in 80–93% yields. Notably, 1,5-diene with a strongly electron-withdrawing group (–NO₂) could deliver desired products 3af in an excellent yield (90%). Meanwhile, the one with an electron-donating group (–Me) could also give products 3ag in a similar yield (91%). Naphthalene ring was well tolerated, achieving 3ah in 92% yield and the configuration of compound 3ah was confirmed by X-ray crystallography. Pyridine moiety was also adapted to the reaction conditions and generated 3ai in 80% yield. In addition, it was found that benzodioxole moiety (3aj) could be well tolerated under the standard conditions. When R₂ group was replaced by other substituents, such as benzyl, phenyl, n-butyl and –CH₂COOEt, desired products (3ak–3ap) could still be made in good-to-excellent yields. When R₃ group was alkyl, the sulfonylation reaction could still proceed, demonstrated by two successful examples (3aq and 3ar). It was worth noting that compound 3ar contained two isomers (3ar-1 : 3ar-2 = 1 : 1).

The practicality of this methodology was successfully illustrated by the production of 3a with 90% yield in a scale-up reaction (Scheme 2(1)). To further demonstrate the synthetic utility of this method, 3a was then applied in subsequent transformations. In the presence of diethylamine, the acetyl group on the nitrogen atom could be easily removed in a quantitative yield (Scheme 2(2)). Then, different substituents could be introduced on the N atom. For example, N–H could be

| Entry | Variation from std conditions | Yield of 3a (%) |
|-------|-------------------------------|-----------------|
| 1     | None                          | 91 (87)         |
| 2     | THF instead of NMP             | 0               |
| 3     | MeCN instead of NMP            | 0               |
| 4     | MeCN instead of NMP            | 0               |
| 5     | Toluene instead of NMP         | 0               |
| 6     | MeOH instead of NMP            | 0               |
| 7     | DMSO instead of NMP            | 21              |
| 8     | DMF instead of NMP             | 20              |
| 9     | DMA instead of NMP             | 56              |
| 10    | 3.5 equiv. of SO₂              | 86              |
| 11    | 3.0 equiv. of SO₂              | 80              |
| 12    | 2.5 equiv. of SO₂              | 74              |
| 13    | Air instead of Ar              | 54              |
| 14    | DABSO as SO₂ surrogate         | 71              |
| 15    | Na₂S₂O₅ as SO₂ surrogate       | 53              |
| 16    | K₂S₂O₇ as SO₂ surrogate        | 52              |
| 17    | HOCH₂SO₂Na·H₂O as SO₂ surrogate| 0               |

* Standard conditions: chamber A, SOgen (0.80 mmol), 1-methyl-4-vinylbenzene (0.81 mmol), tetradecane (1.0 mL), at 100 °C for 10 min; chamber B, 1a (0.2 mmol, 1.0 equiv.), 2a (0.44 mmol, 2.2 equiv.), NMP (1.0 mL), at room temperature for 24 h under argon atmosphere. Yields were determined by ¹H-NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in the parentheses. The reaction was set up in a 4 mL vial.
transferred to N–Me (5) in 90% yield in a mixture of sodium hydride and iodomethane (Scheme 2(3)). In addition, the amide moiety of 3a could be reduced to hydroxy amine (6) via ring-opening by NaBH₄ in excellent yield (Scheme 2(4)).

In order to understand the mechanism of this reaction, three control experiments with radical scavengers were carried out. Firstly, in the presence of radical scavenger (TEMPO), the desired product (3a) was totally quenched and TEMPO adduct 7

Scheme 1 Substrate scope. Reaction conditions: chamber A, SOgen (0.80 mmol), 1-methyl-4-vinylbenzene (0.81 mmol), tetradecane (1.0 mL), at 100 °C for 10 min; chamber B, 1 (0.2 mmol, 1.0 equiv.), 2 (0.44 mmol, 2.2 equiv.), NMP (1.0 mL), at rt for 24 h under argon atmosphere. All yields are isolated yields.
was identified by LC-MS (Scheme 3a(1)). Secondly, when 1,1-diphenylethylene or BHT was added, the reaction showed similar result and corresponding aryl radicals adduct (8) or (10) sulfonyl radicals adduct (9) or (11) were identified, respectively (Scheme 3(2) and (3)). These results indicated that this transformation might proceed through a radical pathway.

Base on the control experiments and literature, a plausible reaction mechanism is proposed herein (Scheme 3b). One of lone-pair electrons on the N atom of 1,5-diene is transferred to aryl diazonium tetrafluoroborate, which leads to the formation of nitrogen radical cation species (A) and aryl radical. Then aryl radical is trapped by sulfur dioxide and gives aryl sulfone radical (B). Sulfonyl radical (B) selectively adds to the double bond of 1,5-diene and produces alkyl radical species (C). Subsequently, intramolecular 5-endotrig cyclization produces intermediate (D), which has an equilibrium with (E). Finally, the desired product (3) is produced via tautomerization from (E).

Conclusions

In conclusion, a metal- and base-free sulfonylative cyclization of 1,5-dienes with aryl diazonium salts via the insertion of SO\(_2\) (from SO\(_2\)gen) has been developed. This method can work under mild conditions and provide the desired products in good yields with excellent regioselectivity. In addition, this approach greatly expands the substrates scope compared with previous reported work. Preliminary mechanism studies indicate that this 5-endotrig sulfonylative cyclization may proceed in a radical pathway.

Conflicts of interest

There are no conflicts to declare.

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