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External Oxidant-Free Oxidative Tandem Cyclization: NaI-Catalyzed Thiolation for the Synthesis of 3-Thiosubstituted Pyrroles

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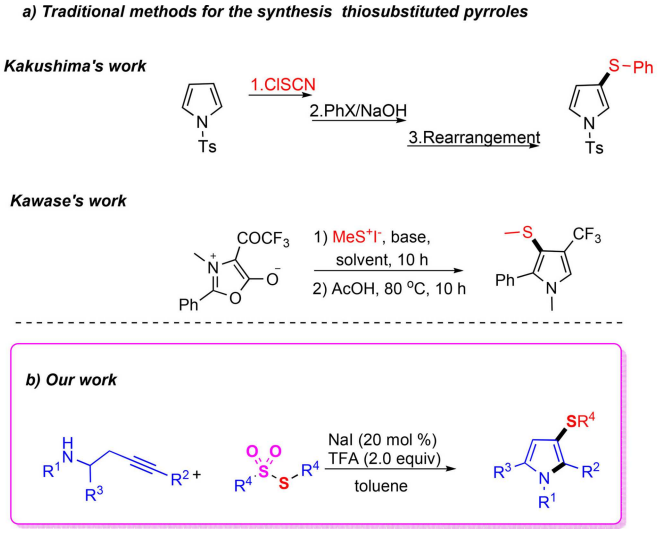
Abstract: A simple method for the synthesis of 3-thiosubstituted pyrroles from homopropargylic amines and thiosulfonates via a tandem sulfenylation/cyclization has been developed. The thiosulfonates are used both as substrates and oxidants in this transformation. This procedure exhibits good functional group tolerance and a series of 3-thiosubstituted pyrrole derivatives was obtained in moderate to good yields.

Keywords: 3-Thiosubstituted pyrroles; Homopropargylic amines; Thiosulfonates; Tandem sulfenylation/cyclization

Organic sulfides are widely used in materials, natural products, pesticides, and medicine.[1] Therefore, it is crucial to choose the suitable sulfur source to synthesize various sulfides. In previous research, a variety of sulfur sources were explored to synthesize useful sulfides such as sodium sulfinates,[2] phenylsulfinic acid,[3] sulfonyl hydrazide,[4] sulfonyl chloride,[5] sodium thiosulfate, thiosulfonate,[6] and dimethyl sulfoxide.[7] Among them, thiosulfonate is one of the most useful sulfur sources and is worthy to explore. Fujiki's group reported that thiosulfonates were employed as the sulfur source to generate thiocyanides with potassium cyanide in the absence of solvent.[8] Adimurthy's group developed a metal-free and organic-solvent-free sulfenylation method for the synthesis of imidazo[1,2-*a*]pyridines with thiosulfonates.[9]

Pyrrole is an important nitrogen heterocyclic compound, and it plays a vital role in the construction of biologically active molecules and organic nitrogen heterocyclic framework.[10] Moreover, the thiosubstituted pyrroles also play a significant role in organic synthesis and medicinal chemistry.[11] Although the uses of thiosubstituted pyrroles have been explored in recent years, there are very few reports on the synthesis of 3-thiosubstituted pyrroles. Simple synthetic method to form 3-thiosubstituted pyrroles still remains a great challenge.[12] Kakushima's group has reported the synthesis of 3-thiosubstituted pyrroles from readily available *N*-tosyl-2-pyrrole through a tedious process.[13] Recently, a two-step synthesis of 3-thiosubstituted pyrroles using 4-trifluoroacetyl-1,3-oxazolium-5-olates and trimethylsulfonium iodide via oxidative arylation has been reported by Kawase's group.[14] To date, there are no reports using simple substrates to efficiently synthesize 3-thiosubstituted pyrroles. Herein, we report a simple method for the synthesis of 3-thiosubstituted pyrroles from the homopropargylic amines and thiosulfonates via tandem sulfenylation/cyclization (Scheme 1).

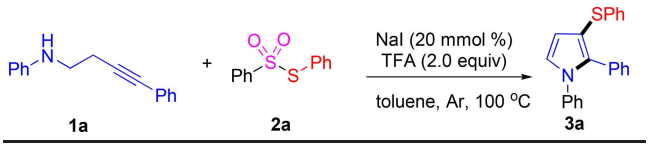
Initially, *N*-(4-phenylbut-3-yn-1-yl) aniline (**1a**) and *S*-phenyl benzenethiosulfonate (**2a**) were chosen as the reactants and were treated with I_2 in toluene at 100 °C under argon atmosphere. The desired 1,2-diphenyl-3-(phenylthio)-1*H*-pyrrole (**3a**) was isolated in 33% yield (see Supporting Information (SI), Table S1, entry 1). The structure of the isolated product was determined by X-ray crystallographic analysis. The reaction temperature was varied to evaluate the effect on the yield and it was found that any change of the temperature would decrease the yield of **3a** (Table S1, entries 2–3). Once the optimum temperature was established, various solvents were examined,



Scheme 1. Reactions for the synthesis of thiosubstituted pyrroles.

PhMe was more efficient than1,4-dioxane, DCE, THF, CH_3CN, DMF and DMSO (Table S1, entries 4–9). Catalyst screening revealed that NaI gave better performance compared to CuI, KI, TBAI, NIS, and I_2 (Table S1, entry 11). Further optimization of the reaction properties showed that the reaction afforded a higher yield with trifluoroacetic acid (84% yield) than CF_3SO_3H, $BF_3{\cdot}OEt_2$, AcOH (Table 1, entries 1–4). When this reaction was performed in air, **3a** was afforded in only 52% yield, which was more than 30% lower than when using an argon atmosphere (Table 1, entry 5). Only trace amounts of desired product were detected without NaI (Table 1, entry 6). After varying each of these reaction conditions, the standard conditions were found that gave the best reaction yield (Table 1, entry 1).

Table 1. Optimization of Reaction Conditions [a].



1a 2a 3a

Entry	Variation from "standard conditions"	Yield of **3a** (%) [b]
1	**standard conditions**	**84**
2	CF_3SO_3H instead of TFA	66
3	$BF_3{\cdot}OEt_2$ instead of TFA	68
4	AcOH instead of TFA	74
5	Air instead of Ar	52
6	Without NaI	trace

[a] Standard conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), NaI (0.06 mmol), TFA (0.6 mmol) in 2 mL toluene at 100 °C under Ar.
[b] Isolated yields.

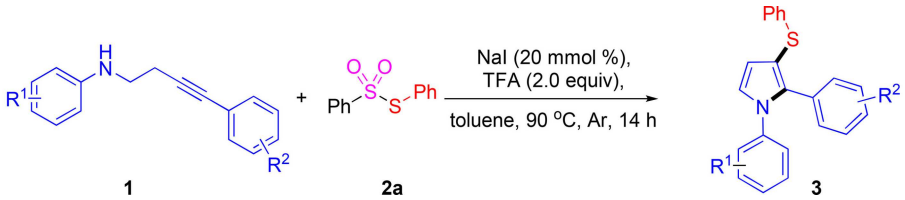
Under the optimized conditions, the scope and generality of this reaction were investigated and the results were shown in Table 2. A series of homopropargylic amines with electron-donating or -withdrawing groups on the benzene rings were reacted with *S*-phenyl benzenethiosulfonate efficiently, and the desired corresponding products were obtained in good yields (**3a–3i**, **3k–3q**). The reaction was insensitive to the steric effect of the *ortho*-, *meta*- and *para*-positions and the corresponding products **3b**, **3c** and **3d** were obtained in 66%, 68% and 68% yields, respectively.

Performing the reaction with substrate **1j** did not form the desired product **3j**. The standard conditions were also tolerated the heteroarene homopropargylic amines with thienyl and naphthyl substituents, and the corresponding products were obtained in 55% and 71% yields, respectively.

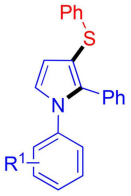
More challenging substrates were also evaluated in this reaction and the results were illustrated in Table 2. When *N*-(but-3-yn-1-yl)aniline and *N*-(1,4-diphenyl-but-3-yn-1-yl)aniline were used with the standard conditions, the corresponding products **3u** and **3v** were isolated in 10% and 63% yield, respectively.

Having successfully achieved the thiosubstituted pyrroles with homopropargylic amines, attention was shifted to explore the scope of the reactant **2** and the results were shown in Table 3. *S*-phenyl thiosulfonates bearing substituents such as –*t*Bu, –F, –Cl, –Br (**4a–4f**) on the phenyl ring gave the corresponding products in high yields. Naphthalen-1-yl sulfonate was also a suitable substrate for this process, giving the product **4g** with 51% yield. In particular, the standard conditions were also suitable for *S*-alkyl thiosulfonates, such as methyl and propyl, and the corresponding products were obtained in 83% and 82% yields.

Table 2. Scope of Homopropargylic Amines [a].

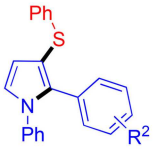


1 2a 3



3

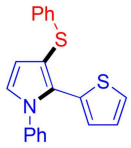
R^1= H, **3a** (84%),
2-Me, **3b** (66%),
3-Me, **3c** (68%),
4-Me, **3d** (68%),
2,5-*di*Me, **3e** (65%),
4-Et, **3f** (62%),
2-*i*Pr, **3g** (55%)
3-MeO, **3h** (50%)
4-F, **3i** (72%)



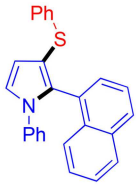
3

R^2 = 2-Me, **3k** (63%),
3-Me, **3l** (68%),
4-Me, **3m** (65%),
3,4-*di*Me, **3n** (64%),
4-MeO, **3o** (91%),
4-F, **3p** (50%),
4-Cl, **3q** (89%)

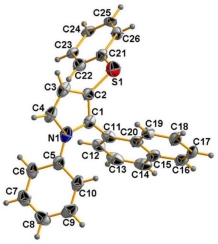
3j, (0%)



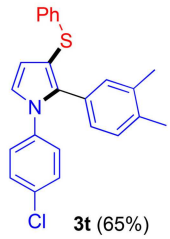
3r, (55%)



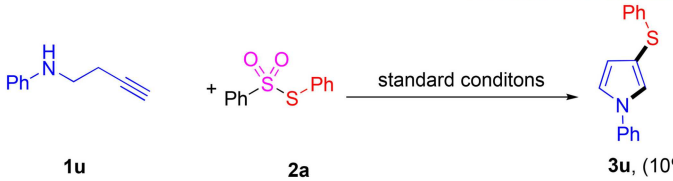
3s, (71%)



3s



3t (65%)



1u **2a** **3u**, (10%)

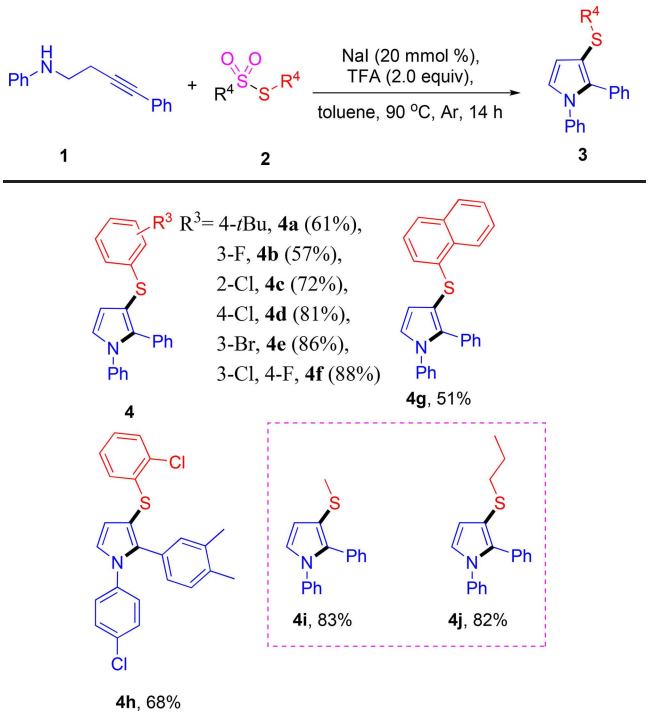
1v **2a** **3v**, (63%)

[a] Standard conditions: **1 a** (0.3 mmol), **2 a** (0.36 mmol), NaI (0.06 mmol), TFA (0.6 mmol) in 2 mL toluene at 100 °C under Ar.

In order to verify the mechanism, the following experiments were carried out (Scheme 2). The reaction was almost unaffected by the radical inhibitor 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylated hydroxytoluene (BHT), which suggest that a radical pathway can be excluded in this mechanism under the standard conditions. 1,2-Diphenyl-1*H*-pyrrole was used to determine the mechanism and no intermediate was detected. This result shows that 1,2-diphenyl-1*H*-pyrrole does not take part in the reaction. The nucleophile of 1-methyl-1*H*-indole **5** was also exposed to the standard conditions and the desired product **6** was isolated in 48% yield, which was also observed by GC-MS analysis (see SI). This result indicates the electrophile PhS^+ exists in this transformation.

Based on the experimental results, a plausible reaction mechanism is proposed in Scheme 3. Initially, *S*-phenyl benzenethiosulfonate **2 a** is converted to the corresponding cationic complex **A**[12b,15] and intermediate **B** in the presence of NaI and TFA. Subsequently, the thiiranium ion species **C**, which is formed through the addition of the cationic complex **A** and *N*-(4-phenylbut-3-yn-1-yl)aniline **1 a**, undergoes intramolecular nucleophilic attack and cyclization to generate the

Table 3. Scope of Thiosulfonates [a].



[a] Standard conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), NaI (0.06 mmol), TFA (0.6 mmol) in 2 mL toluene at 100 °C under Ar.

1,5-diphenyl-4-(phenylthio)-2,3-dihydro-1*H*-pyrrole **D**. Finally, **D** is oxidized to create the desired product **3a**, the TFA in this reaction system leads to an increase in the yield and the TFA would increase the oxidizability of substrate **2**.[16]

In summary, we have reported the direct method for the synthesis of 3-thiosubstituted pyrroles from homopropargylic amines and thiosulfonates via tandem sulfenylation/cyclization reaction. This reaction constructs C–C/C–S bonds under mild conditions and a series of 3-thiosubstituted pyrroles are obtained in moderate to good yields.

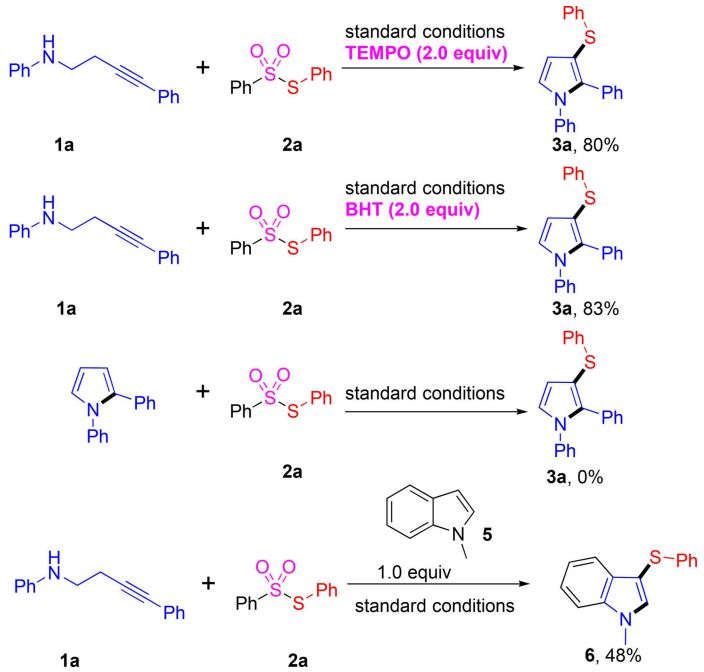
Experimental Section

Synthesis of 3-Thiosubstituted Pyrroles 3

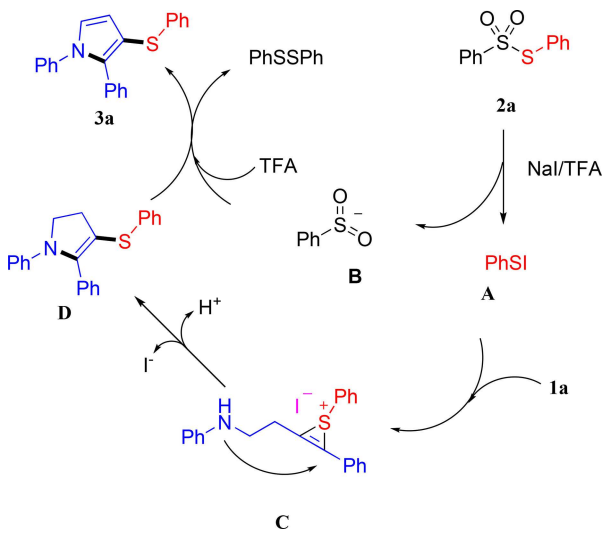
The alkynylamines **1** (1 equiv., 0.3 mmol), substituted thiosulfonates **2** (1.2 equiv., 0.36 mmol), NaI (0.2 equiv., 0.06 mmol), trifluoroacetic acid (2.0 equiv., 0.6 mmol) were mixed in toluene (2 mL) were stirred at 100 °C under argon for 14 h (TLC monitored). The reaction mixture was diluted with water and extracted with ethyl acetate for 3 times. Then the organic phase was combined and dried with anhydrous Na_2SO_4. The solvent was evaporated to in vacuo, the crude product was purified by column chromatography, eluting with petroleum ether/EtOAc (100:1) to afford the desired **3**.

X-Ray Crystallographic Data of 3s

CCDC-1908482 (**3s**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Scheme 2. Control Experiments.



Scheme 3. Proposed Mechanism.

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COMMUNICATIONS

External Oxidant-Free Oxidative Tandem Cyclization: NaI-Catalyzed Thiolation for the Synthesis of 3-Thiosubstituted Pyrroles

Adv. Synth. Catal. **2019**, *361*, 1 – 7

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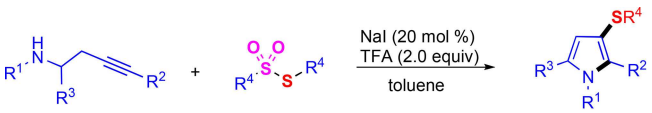

- Metal-free mild conditions
- Thiosulfonate used simultaneously as substrate and oxidant