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The title reaction involves metal free TEAB-catalyzed S-S bond cleavage, C-S bond formation and C-C bond formation; it uses readily available disulfides and alkynes as substrates, environmentally TEAB as catalyst to synthesize useful benzothiophene derivatives. This process has a broad substrate scope, and various benzothiophenes were obtained in good to excellent yields, even on gram scale. TEAB=Tetraethylammonium Bromide.
Metal-free \( n\text{-Et}_4\text{NBr}\)-catalyzed radical cyclization of disulfides and alkynes leading to benzothiophenes under mild conditions †

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† DOI: 10.1039/b000000x

A novel \( n\text{-Et}_4\text{NBr}\)-catalyzed method for the synthesis of benzothiophene derivatives via cascade reactions of substituted disulfides with alkynes through S-S bond cleavage and alkynyl radical cyclization reactions has been developed. The reaction has a high functional-group tolerance. The new method is environmental and practical, and the starting materials are readily available. These advantages, relative to previous methods, provide an opportunity for the construction of diverse and useful benzothiophene motifs.

Introduction

Heterocycles widely occur in natural products and biologically active molecules. Especially, they have often been assigned as privileged structures in drug development. Consequently, developing new, versatile and efficient approaches for the synthesis of heterocycles is of high ongoing interest. Benzothiophene derivatives are important heterocycles which have attracted much attention for their frequent occurrence in natural products and their wide range of biological and physiological activities and are also widespread in material chemistry. For example, they are often used as antimitotic, antifungal agents (1) and they are also found in numerous clinically important drugs, such as clopidogrel, zileuton, arzoxifene and raloxifene (Scheme 1). Thus, development of novel and efficient methods for the synthesis of these compounds will be valuable for the screening of novel biologically active molecules. However, investigations on the synthetic methods for the formation of benzothiophene motifs are rather limited. The conventional methods for the synthesis of these important compounds typically involve two approaches. One is the electrophilic cyclization of o-alkynyl thioanisoles. The second approach mainly involves transition-metal catalyzed or strong base enhanced cyclization of o-haloalkynylbenzenes with various thiol surrogates. Despite some great advantages of these reactions, there are still certain limitations including harsh reaction conditions, the easily available precursors and metal salt catalytic conditions. In 1973, Undheim and Lie attempted the direct conversion of thiophenols and alkynes to benzothiophene motifs under metal-free conditions, unfortunately, long time (5-22 days) were required, and the resulting yields were low. Very recently, Li and co-workers developed an elegant work for the synthesis of benzothiophenes via intermolecular oxidative cyclization between thiophenols and alkynes using Mn(OAc)\(_2\) as the catalyst.

Scheme 1 Popular drugs containing the benzothiophene motif

Disulfides are very stable in air and easily prepared from readily available thiols. Recently, using disulfides as the starting materials to construct sulfur-based compounds via S-S bond cleavage have caught considerable attention. Moreover, there are increasing demands for metal-free reactions owing to trace-metal impurities can be avoided in the end products. In particular, direct and straightforward formation of various functional groups from inert C-H bonds meets the requirement of atom-economy and has emerged as a powerful tool for organic synthesis. In this respect, lots of examples of direct sp\(^2\) C-H functionalization via the radical pathway for the synthesis of heterocycles have been significantly disclosed by us and other research groups. Herein, we report a simple and practical metal-free approach to benzothiophenes via alkynyl radical cyclization reactions under mild conditions (eq 1).

\[
\text{R}_1\text{S} = \text{C OSCO}_2 \xrightarrow{S-S \text{bond cleavage}} \text{R}_3\text{C=O} \xrightarrow{\text{radical cyclization}} \text{R}_1\text{R}_2\text{R}_3\text{COSCO}_2
\]
Results and Discussion

We first chose 1,2-diphenyldisulfane \(\text{1a}\) and dimethyl but-2-yne-dioioate \(\text{2a}\) as the model substrates to optimize the catalysis conditions, which include oxidants, catalysts and solvents under nitrogen atmosphere. As shown in Table 1, several oxidants, \(\text{Phl(OAc)}_2\), \(\text{O}_2\), \(\text{TBHP}\), \(\text{H}_2\text{O}_2\) and \(\text{K}_2\text{S}_2\text{O}_8\) (10 mol % catalytic amount relative to 1,2-diphenyldisulfane) were tested in DCE (entries 1-5) by using TEAB as the catalyst, and \(\text{K}_2\text{S}_2\text{O}_8\) was the most effective oxidant. We attempted to use different catalysts, and TEAB was a suitable catalyst (entries 5-9 and 15). The effect of solvents (DCE, toluene, \(\text{CH}_3\text{CN}\), 1,4-dioxane) was also investigated (entries 5, 10-12), DCE provided the highest yield. Reaction temperature was also investigated, and the yield of the target product reached maximum at 90 °C. After the optimization process for catalysts, oxidants, solvent and temperature, the following cyclization reactions were performed under our standard conditions: 10 mol % TEAB as the catalyst, 2.2 equiv of \(\text{K}_2\text{S}_2\text{O}_8\) as the oxidant and DCE as the solvent at 90 °C under nitrogen atmosphere.

Table 1 Optimization of the reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Oxidant</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEAB</td>
<td>(\text{Phl(OAc)}_2)</td>
<td>DCE</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>TEAB</td>
<td>(\text{O}_2)</td>
<td>DCE</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>TEAB</td>
<td>TBHP</td>
<td>DCE</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>TEAB</td>
<td>(\text{H}_2\text{O}_2)</td>
<td>DCE</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>TEAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>DCE</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td>TBAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>DCE</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>TBAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>DCE</td>
<td>58</td>
</tr>
<tr>
<td>8</td>
<td>TBAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
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<td>55</td>
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<td>9</td>
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<td>DCE</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>TEAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>(\text{CH}_3\text{CN})</td>
<td>45</td>
</tr>
<tr>
<td>11</td>
<td>TEAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>toluene</td>
<td>40</td>
</tr>
<tr>
<td>12</td>
<td>TEAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>1,4-dioxane</td>
<td>38</td>
</tr>
<tr>
<td>13</td>
<td>TEAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>DCE</td>
<td>40</td>
</tr>
<tr>
<td>14</td>
<td>TEAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>DCE</td>
<td>62</td>
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<tr>
<td>15</td>
<td>TEAB</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>DCE</td>
<td>81</td>
</tr>
<tr>
<td>16</td>
<td>None</td>
<td>(\text{K}_2\text{S}_2\text{O}_8)</td>
<td>DCE</td>
<td>trace</td>
</tr>
</tbody>
</table>

*Reaction conditions: under nitrogen atmosphere, \(\text{1a}\) (0.5 mmol), \(\text{2a}\) (1.7 mmol), catalyst (0.05 mmol), oxidant (2.2 equiv), solvent (1.5 mL), 90°C and reaction time (24 h). TBAC=(n-Bu)\text{NCl}; TBAB=(n-Bu)\text{NBBr}; TBAI=(n-Bu)\text{NI}; TEAB=Et\text{NBBr}; TBHP=tert-butyl hydroperoxide solution 5.5M in decane; DCE=1,2-dichloroethane. Isolated yield (based on the amount of \(\text{1a}\)). 50°C, 60°C, 80°C.

The scope of TEAB-catalyzed cascade reactions of the substituted disulfides with alkynes was investigated under the optimized conditions. As shown in Table 2, the radical cyclization reactions could be performed for all the substrates examined, and the desired benzo[b]thiophene derivatives were obtained in good isolated yields. For substituted disulfides the substrates containing electron-donating groups exhibited higher reactivity than the others (products \(\text{3c, 3d, 3e, 3f, 3s, 3t, 3u and 3v}\)). For different alkynes, including symmetric or unsymmetrical alkynes their reactivity did not show obviously difference (products \(\text{3a-3r, 3s-3v}\)). Unfortunately, terminal alkyne, 1,2- diarylethyne and 1,2-dialkylethyne were the poor substrates in this transformation (products \(\text{3w-3z}\)). As expected, meta-substituted substrates gave a mixture of two regioselective products (products \(\text{3m/3n}\) and \(\text{3m/3n'}\)), which suggested that the existence of possible steric hindrance arising from the presence of a meta-substituent “COOMe” (see table 2, \(\text{3m and 3n}\)). Besides that, the more stability of intermediate C of \(\text{3m and 3n}\) as shown in Scheme 5 can not be excluded. The metal-free TEAB-catalyzed radical cyclization reactions could tolerate some functional groups including esters (products \(\text{3a-3v}\)), ethers (products \(\text{3c, 3d, 3m, 3o and 3t}\), C-Cl bond (products \(\text{3e, 3f and 3g}\) and C-Br bond (products \(\text{3h and 3i}\)), which could be used for further modifications at the substituted positions. The structure of \(\text{3b}\) was unambiguously confirmed by X-ray crystallographic analysis (Figure 1), (see Supporting Information for details). Interestingly, treatment of benzenethiol (\(\text{4a}\)) with dimethyl but-2-yne-dioioate (\(\text{2a}\)) under the optimized conditions produced dimethyl benzo[b]thiophene-2,3-dicarboxylate (\(\text{3a}\)) in a moderate yield (Scheme 2).

Table 2 TEAB-catalyzed Synthesis of benzo[b]thiophene derivatives via radical cyclization of disulfides with alkynes

<table>
<thead>
<tr>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CO}_2\text{H})</td>
<td>(\text{CO}_2\text{H})</td>
<td>80%</td>
</tr>
<tr>
<td>(\text{Me})</td>
<td>(\text{Me})</td>
<td>70%</td>
</tr>
<tr>
<td>(\text{Me})</td>
<td>(\text{Me})</td>
<td>80%</td>
</tr>
<tr>
<td>(\text{Me})</td>
<td>(\text{Me})</td>
<td>70%</td>
</tr>
<tr>
<td>(\text{Me})</td>
<td>(\text{Me})</td>
<td>90%</td>
</tr>
</tbody>
</table>

*Reaction conditions: under nitrogen atmosphere, substituted diphenyldisulfane (0.5 mmol), alkynes (1.7 mmol), TEAB (0.05 mmol), \(\text{K}_2\text{S}_2\text{O}_8\) (1.1 mmol), DCE (1.5 mL). Isolated yield (based on the amount of \(\text{1a}\)). Reaction time (24 h).
Scheme 2 Synthesis of 3a using benzenethiol (4a) and dimethyl but-2-ynedioate (2a) as starting materials under standard conditions.

Further, we explored the synthetic applicability of the method. As shown in Scheme 3, the gram-scale reaction was performed in the usual laboratory setup with a one-neck round-bottomed flask fitted with a nitrogen balloon, and the reaction afforded 3a in 93% yield. This example clearly demonstrates the practical aspect of this newly developed method.

Scheme 3 Synthesis of 3b on gram scale

To understand the mechanism further, the reaction of 1a was tested in the presence of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, a well-known radical inhibitor) as a radical scavenger. The formation of 2a was completely inhibited in the reactions (eqs 1. Scheme 4), demonstrating that a radical process may be involved in this reaction. Moreover, control experiments were conducted to elucidate the mechanism of this radical cyclization reaction. The intermolecular kinetic isotope effects (KIE) were investigated, and no kinetic isotope effect (KIE\(\delta_\text{H}/\delta_\text{D} = 1.0\)) was observed, which indicates that C-H bond cleavage might not be the rate-determining step (eqs 2. Scheme 4).

Scheme 4 Control experiments

On the basis of these preliminary results and reports in the literature, a possible mechanism for TEAB-catalyzed radical cyclization reactions for the synthesis of benzothiophene derivatives is suggested in Scheme 5. Reaction of tetraethylammonium bromide with peroxydisulfate produced tetraethylammonium sulfate radical anions, followed by the tetraethylammonium sulfate radical reacts with the disulfides to form an thyl radical A. The addition of thyl radical A to alkyne 2a affords the alkenyl radical intermediate B, which further undergoes intramolecular radical substitution reaction to give intermediate C. Finally, hydrogen abstraction of radical intermediate C by tetraethylammonium sulfate radical anions leads to the benzothiophene derivatives. Further investigations on the more detailed mechanism are ongoing in our laboratory.

Scheme 5 A proposed mechanism for the direct transformation.

Experimental Section

General experimental procedures

All reagents and solvents were obtained from commercial suppliers and used without further purification. Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer. Flash chromatography was performed on silica gel (200 ~ 300 mesh). \(^1\)H and \(^13\)C NMR data were recorded at 400 and 100 MHz on a BRUKER 400 spectrometer. Chemical shifts (\(\delta\)) are expressed in parts per million (ppm) coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (\(^1\)H NMR and \(^13\)C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl\(_3\) as the internal standard (\(^1\)H NMR: TMS at 0.00 ppm, CDCl\(_3\) at 7.28 ppm; \(^13\)C NMR: CDCl\(_3\) at 77.0 ppm).

General procedure for synthesis of substituted benzothiophenes: A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with TEAB (10.5 mg), potassium persulfate(1.1 mmol), substituted various disulfides (1) (0.5 mmol) and alkenes (2) (1.7 mmol). The tube was evacuated twice and backfilled with nitrogen, and DCE (1.5 mL) was added.
to the tube under nitrogen atmosphere. The tube was sealed with a balloon and then the mixture was allowed to stir under nitrogen atmosphere at 90 °C for 24 h. After completion of the reaction, the resulting solution was cooled to room temperature and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product (3).

**Dimethyl benzo[b]thiophene-2,3-dicarboxylate (3a):**

1. Eluent petroleum ether/ethyl acetate (30:1). White solid, mp 83-84 °C.
2. 1H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.92 (d, 1H, $J = 5.2$ Hz), 7.84 (d, 1H, $J = 5.6$ Hz), 7.50-7.55 (m, 2H), 4.02 (s, 3H), 3.94 (s, 3H).
3. 13C NMR (CDCl$_3$, 100 MHz, ppm) $\delta$ 164.9, 162.2, 140.3, 136.7, 133.2, 133.1, 127.5, 124.5, 122.6, 53.0, 50.9.
4. HRMS m/z calcd. for C$_{10}$H$_6$O$_2$S [M+Na$^+$]: 273.0197, found: 273.0191.

**Diethyl benzo[b]thiophene-2,3-dicarboxylate (3b):**

1. Eluent petroleum ether/ethyl acetate (30:1). White solid, mp 62-64 °C.
2. 1H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.95 (d, 1H, $J = 6.0$ Hz), 7.84 (d, 1H, $J = 6.0$ Hz), 7.48-7.45 (m, 2H), 4.52 (q, 2H, $J = 7.2$ Hz), 4.42 (q, 2H, $J = 7.2$ Hz), 1.45 (t, 3H, $J = 7.2$ Hz), 1.41 (t, 3H, $J = 8.0$ Hz). 13C NMR (CDCl$_3$, 100 MHz, ppm) $\delta$ 164.9, 162.8, 140.3, 136.9, 133.5, 133.3, 127.3, 125.6, 124.4, 122.5, 62.1, 14.17, 14.16. HRMS m/z calcd. for C$_{10}$H$_6$O$_2$S [M+Na$^+$]: 301.0510, found: 301.0511.

**Dimethyl 5-methoxybenzo[b]thiophene-2,3-dicarboxylate (3c):**

1. Eluent petroleum ether/ethyl acetate (30:1). White solid, mp 98-100 °C.
2. 1H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.71 (d, 1H, $J = 8.8$ Hz), 7.37 (s, 1H), 7.15 (d, 1H, $J = 9.2$ Hz), 4.10 (s, 3H), 3.95 (s, 3H), 3.89 (s, 3H). 13C NMR (CDCl$_3$, 100 MHz, ppm) $\delta$ 164.9, 162.8, 158.4, 139.7, 134.5, 132.9, 132.3, 123.2, 118.8, 105.3, 55.6, 53.0, 52.8. HRMS m/z calcd. for C$_{10}$H$_6$O$_2$S [M+Na$^+$]: 303.0303, found: 303.0303.

**Diethyl 5-methoxybenzo[b]thiophene-2,3-dicarboxylate (3d):**

1. Eluent petroleum ether/ethyl acetate (30:1). White solid, mp 59-61 °C.
2. 1H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.69 (d, 1H, $J = 9.2$ Hz), 7.38 (s, 1H), 7.13 (d, 1H, $J = 9.2$ Hz), 4.50 (q, 2H, $J = 8.0$ Hz), 4.41 (q, 2H, $J = 8.0$ Hz), 3.88 (s, 3H), 3.98 (s, 3H), 3.89 (s, 3H). 13C NMR (CDCl$_3$, 100 MHz, ppm) $\delta$ 164.5, 161.9, 158.3, 138.0, 134.9, 132.9, 123.3, 123.2, 118.6, 105.3, 62.1, 61.8, 55.5, 14.2, 14.1. HRMS m/z calcd. for C$_{10}$H$_6$O$_2$S [M+Na$^+$]: 331.0616, found: 331.0610.

**Dimethyl 5-chlorobenzo[b]thiophene-2,3-dicarboxylate (3e):**

1. Eluent petroleum ether/ethyl acetate (30:1). White solid, mp 105-107 °C.
2. 1H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.79 (s, 1H), 7.78 (d, 1H, $J = 8.0$ Hz), 7.45 (d, 1H, $J = 8.0$ Hz), 4.03 (s, 3H), 3.96 (s, 3H). 13C NMR (CDCl$_3$, 100 MHz, ppm) $\delta$ 164.2, 161.9, 138.2, 137.8, 135.6, 132.3, 131.9, 128.1, 124.2, 123.6, 53.2, 53.0. HRMS m/z calcd. for C$_{10}$H$_6$Cl$_2$O$_2$S [M+Na$^+$]: 306.9815, found: 306.9815.

**Diethyl 5-chlorobenzo[b]thiophene-2,3-dicarboxylate (3f):**

1. Eluent petroleum ether/ethyl acetate (30:1). White solid, mp 81-83 °C.
2. 1H NMR (CDCl$_3$, 400 MHz, ppm) $\delta$ 7.98 (s, 1H), 7.78 (d, 1H, $J = 8.0$ Hz), 7.45 (d, 1H, $J = 8.0$ Hz), 4.51 (q, 2H, $J = 8.0$ Hz), 4.17 (q, 2H, $J = 8.0$ Hz), 4.41 (q, 2H, $J = 8.0$ Hz), 1.48-1.40 (m, 6H). 13C NMR (CDCl$_3$, 100 MHz, ppm) $\delta$ 163.8, 161.5, 138.2, 137.9, 135.9, 132.1, 131.9, 127.9, 124.1, 123.6, 62.4, 62.1, 14.1. HRMS m/z calcd. for C$_{12}$H$_6$Cl$_2$O$_2$S [M+Na$^+$]: 335.0121, found: 335.0126.
Dimethyl 4-methoxybenzo[b]thiophene-2,3-dicarboxylate (3m): Eluent petroleum ether/ethyl acetate (40:1). White solid, mp 118-119 °C. 1H NMR (CDCl3, 400 MHz, ppm) δ 7.75-7.79 (m, 2H), 7.67 (d, 1H, J = 8.8 Hz), 7.48 (d, 1H, J = 8.8 Hz), 4.42 (q, 2H, J = 7.2 Hz), 4.30 (q, 2H, J = 7.2 Hz), 1.37-1.42 (m, 15H). 13C NMR (CDCl3, 100 MHz, ppm) δ 164.7, 149.0, 137.7, 136.9, 133.5, 133.3, 123.3, 121.3, 120.1, 62.0, 61.8, 31.3, 14.2. HRMS m/z calcd. for C16H16O5S [M+Na]+: 357.1136, found: 357.1137.

Dimethyl 5-tert-butylbenzo[b]thiophene-2,3-dicarboxylate (3o): Eluent petroleum ether/ethyl acetate (30:1). Pale yellow viscous liquid. 1H NMR (CDCl3, 400 MHz, ppm) δ 7.77 (s, 1H), 7.67 (d, 1H, J = 8.8 Hz), 7.46 (d, 1H, J = 8.8 Hz), 4.02 (q, 2H, J = 7.2 Hz), 4.00 (q, 2H, J = 7.2 Hz), 1.37-1.42 (m, 15H). 13C NMR (CDCl3, 100 MHz, ppm) δ 163.7, 161.4, 138.6, 138.3, 135.7, 131.8, 130.5, 127.2, 123.8, 119.8, 62.4, 62.1, 14.1 HRMS m/z calcd. for C14H13BrO3S [M+Na]+: 378.9616, found: 378.9615, 380.9588.

Ethyl 3-phenylbenzo[b]thiophene-2-carboxylate (3s): Eluent petroleum ether/ethyl acetate (30:1). Light yellow viscous liquid. 1H NMR (CDCl3, 400 MHz, ppm) δ 7.92 (d, 1H, J = 8.0 Hz), 7.58 (d, 1H, J = 8.0 Hz), 4.51 (q, 2H, J = 8.0 Hz), 4.43 (q, 2H, J = 8.0 Hz), 1.47-1.40 (m, 6H). 13C NMR (CDCl3, 100 MHz, ppm) δ 163.7, 161.4, 138.6, 138.3, 135.7, 131.8, 130.5, 127.3, 123.8, 119.8, 62.4, 62.1, 14.1 HRMS m/z calcd. for C14H13BrO3S [M+Na]+: 378.9615, found: 378.9615, 380.9588.