Preparation of Sulfenyl Pyrroles

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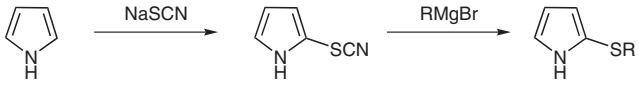
Abstract: Sulfenyl groups are attracting interest as masking/protecting groups for pyrroles. A facile one-step synthesis of sulfenyl pyrroles, involving the reaction of pyrroles with *N*-(aryl- and alkylthio)phthalimides in the presence of $MgBr_2$, is reported and the methodology extends to include sulfinyl pyrroles. The one-step procedure gives good yields and is more efficient and practical than current multistep protocols to sulfenyl pyrroles that involve thiocyanato pyrrolic intermediates. A convenient procedure for the synthesis of *N*-(aryl- and alkylthio)phthalimides is also reported.

Key words: pyrrole, thiophthalimide, magnesium bromide, sulfenylation, sulfinylation

The preparation and manipulation of functionalized pyrroles is of increasing importance,[1–6] with electronic, biological, and optical properties leading to their increasing incorporation into new materials and improved pharmaceuticals.[1,7–10] The synthesis of functionalized pyrroles is challenging[9,11,12] and traditionally involves high temperatures, excess reagents, and harsh conditions. Successful synthetic pyrrole chemistry is often achieved by the utilization of 2-carboxylate pyrroles, whereby the electron-withdrawing carboxylate group serves to temper the nucleophility of the pyrrolic core.[11] Recently, the sulfenyl group has been shown to effectively mask the 2-position of pyrroles,[13,14] and the utility of 2-sulfenyl pyrroles in acylation reactions, nitration reactions, and condensation reactions with various aldehydes has highlighted the sulfenyl group as a valuable pyrrole masking/protecting group that can be removed using Raney nickel.[14]

2-Sulfenyl pyrroles may be prepared by reaction of pyrrole with sulfenyl chlorides,[15] although such sulfenylating reagents are not ideal due to their limited stability. Alternatively, the reaction of pyrrole with thiocyanate salts gives 2-thiocyanato pyrrole[16–21] which may be reacted with various Grignard reagents[14,22] to give the corresponding 2-sulfenyl pyrroles (Scheme 1). We prepared 2-thiocyanato pyrrole using an iodine-catalyzed reaction of sodium thiocyanate and pyrrole in methanol.[21] The resulting 2-thiocyanato pyrrole decomposed and it was necessary that reactions using Grignard reagents were effected immediately,[23] with no purification of the thiocyanate. Furthermore, even traces of 2-thiocyanato pyrrole passed through multiple layers of latex gloves and caused stains and discomfort of the skin,[13] as noted previously[18] for



Scheme 1 2-Sulfenyl pyrroles via 2-thiocyanato pyrrole

3-thiocyanato pyrrole. These impracticalities prompted our search for an improved, generalized route to a variety of sulfenyl pyrroles.

3-Sulfenyl indoles may be prepared[24] by reacting indoles with thiols, in the presence of Selectfluor,™ which presumably acts to fluorinate the thiol and thus generate an electrophilic sulfenylating agent. Furthermore, *N*-(phenylthio)phthalimide,[25–27] which has been used with enolates, enamines, and oximes,[28,29] has recently been utilized in the preparation of 3-sulfenyl indoles.[30] In this reaction, catalytic amounts of $MgBr_2$ (or alternative halide sources) activate the reagent to generate the corresponding sulfenyl bromide in situ, a process driven by concomitant loss of the phthalimide anion. Thus, *N*-(phenylthio)phthalimide is a stable and essentially odorless sulfenylating agent that is activated, only upon demand, through halide catalysis.

Given the practical difficulties that we encountered using 2-thiocyanato pyrrole, we sought to investigate the utility of phthalimide-based sulfenylating reagents for the preparation of 2-sulfenyl pyrroles. We thus prepared a variety of *N*-(aryl- and alkylthio)phthalimides and subsequently reacted these sulfenylating reagents with several α- and β-unsubstituted pyrroles to accordingly prepare a range of 2- and 3-sulfenyl pyrroles.

N-(Phenylthio)phthalimide (**1a**) is commercially available and may also be readily prepared by the reaction of phenylsulfenyl chloride (prepared in situ from thiophenol and chlorine gas) and phthalimide,[25,27] whereby varying the thiol allows access to other *N*-(aryl- and alkylthio)phthalimides. An alternative route to sulfenyl chlorides involves the reaction of thiols or disulfides with sulfuryl chloride.[31,32] This approach permits the stoichiometry of the reaction to be easily controlled, without the need for time-consuming titrations that are required to ensure the desired stoichiometry when using thiols and chlorine gas.[25]

Our initial efforts focused on the synthesis of **1a** following a similar procedure established using chlorine gas.[27] Phenylsulfenyl chloride was thus prepared by the reaction of thiophenol with sulfuryl chloride in dichloromethane at 0 °C for 10 minutes (Scheme 2). The resulting solution was then added dropwise to a solution of phthalimide and tri-

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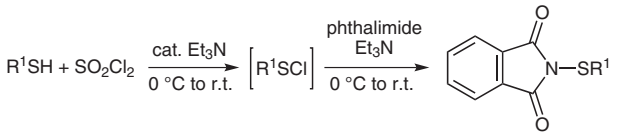


1a, R^1 = Ph, 83%
1b, R^1 = Bn, 30%
1c, R^1 = Et, 63%
1d, R^1 = decyl, 70%
1e, R^1 = *t*-Bu, 22%
1f, R^1 = 4-$MeOC_6H_4$, 70%

Scheme 2 Synthesis of *N*-(aryl- and alkylthio)phthalimides

ethylamine in dichloromethane to effect an exothermic reaction, and a mixture of products resulted. Repeating the reaction at 0 °C gave **1a** in only 22% yield, as compared to 69% yield reported using chlorine gas.[27] Similar results were obtained when attempting to prepare *N*-(benzylthio)phthalimide (**1b**)[25] and *N*-(ethylthio)phthalimide (**1c**).[25] The problem seemed to lie in the synthesis of the sulfenyl chloride and, as noted by others,[31,32] the addition of catalytic amounts of triethylamine improved the production of phenylsulfenyl chloride and made a significant overall improvement to provide **1a–d** in good yields (Scheme 2). However, both **1e**[25] and **1f** were inaccessible via this procedure but changing the solvents to hexanes for the preparation of the sulfenyl chloride and DMF in the second step provided **1e** and **1f** in acceptable yields. Equally important, in order to facilitate successful purifications using recrystallization, unreacted phthalimide was easily removed by treatment of a dichloromethane solution of the crude material with 1 M NaOH. While these yields are somewhat lower than those involving chlorine gas, this procedure offers a rapid and convenient access to a variety of *N*-(aryl- and alkylthio)phthalimides in reasonable quantities (e.g., 50 mmol) and acceptable yields with minimal effort. Furthermore, unlike the sulfenyl chlorides, all examples were crystalline and displayed no sign of decomposition after more than six months of storage in a sealed bottle (in air) at room temperature.

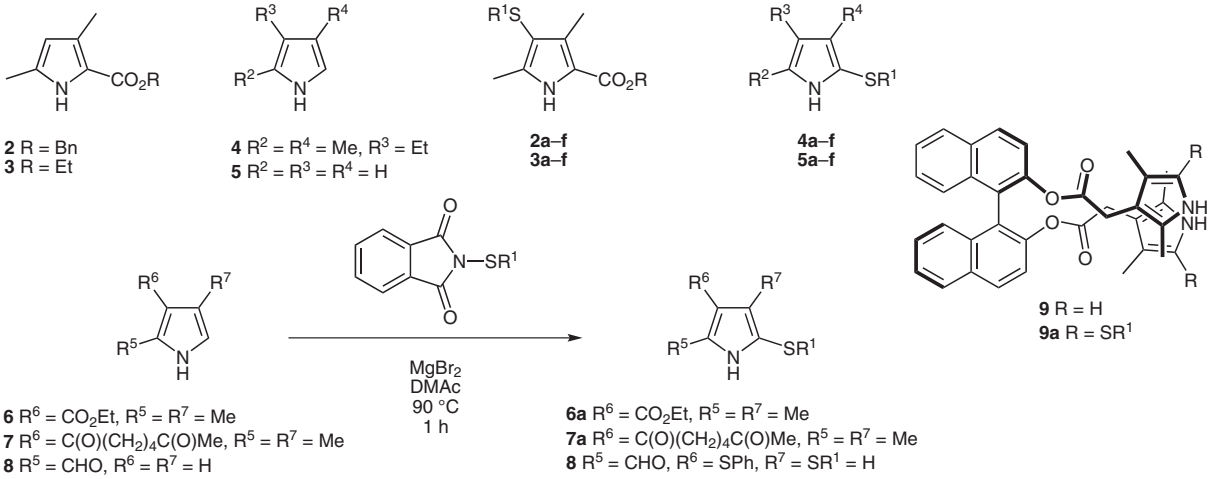
With a range of *N*-(aryl- and alkylthio)phthalimides in hand, we investigated the sulfenylation of benzyl 3,5-dimethyl-pyrrole-2-carboxylate (**2**), ethyl 3,5-dimethyl-pyrrole-2-carboxylate (**3**), kryptopyrrole (**4**), pyrrole (**5**), ethyl 2,4-dimethyl-1*H*-pyrrole-3-carboxylate (**6**), diketopyrrole (**7**), 1*H*-pyrrole-2-carbaldehyde (**8**), and (*R*)-BINOL ester pyrrole (**9**). The earlier method described for the isolation of 3-sulfenyl indoles,[30] prepared using **1a**, involved precipitation upon the addition of water. We adopted a basic aqueous workup procedure whereby the reaction mixture was diluted with ethyl acetate and washed several times with 1 M NaOH. This treatment gave improved yields of the sulfenylated pyrrole over precipitation, and allowed for the removal of the unreacted *N*-(aryl- and alkylthio)phthalimide, via hydrolysis, permitting chromatographic purification.

For *N*-(arylthio)phthalimides **1a** and **1f**, sulfenylation of electron-deficient pyrroles (**2** and **3**) and electron-rich pyrroles (**4** and **5**) proceeded smoothly to give 2-arylsulfenyl pyrroles **2a–5a** and **2f–5f**, respectively, in excellent yields (Table 1, entries 1–4 and 15–18). Solvent and temperature optimizations were conducted for the reaction of **1a** with pyrroles **2** and **3**. The use of DMAc[30] gave higher yields over DMF, and the optimal temperature for the reaction was 90 °C with full conversion in one hour, compared with 50% conversion in one hour at 50 °C. For the reactions of **1a** and **1f** with pyrrole **5**, the 2,5-bis-sulfenylated $\mathbf{5a_2}$ and $\mathbf{5f_2}$ (ca. 10% isolated yield for each; see Supporting Information for details) were also observed and decreasing the stoichiometry of *N*-(phenylthio)phthalimide **1a** in the reaction with **5** did not improve the yield of **5a** (Table 1, entry 4).

For *N*-(alkylthio)phthalimides **1b–e**, sulfenylation of electron-deficient pyrroles (**2** and **3**) and electron-rich pyrroles (**4** and **5**) proceeded, but with noticeable differences across the series. For example, reaction of **4** with **1b–d** occurred in excellent yield (Table 1, entries 7, 11, and 14), but no reaction occurred with the more steric demanding **1e**. Furthermore, **1b** reacted smoothly with pyrroles **4** and **5** (Table 1, entries 7 and 8), **1c** with **3** and **4** (Table 1, entries 9 and 10), and **1d** with **3** and **4** (Table 1, entries 13 and 14); however, reactions of **1b** with **2** or **3**, and **1c** and **1d** with **2** proceeded with incomplete conversions (Table 1, entries 5, 6, 9, and 12). Even when using a procedure developed for sluggish reactions and/or utilizing longer reaction times,[30] incomplete conversions were observed. In addition, reactions of **1c** and **1d** with **5** gave a mixture of products sulfenylated at the 2-, 3-, and/or 5-positions (see Supporting Information for details). In order to investigate the functional group tolerability of this approach, pyrroles **6–9** were reacted with *N*-(phenylthio)phthalimide (**1a**). Pyrroles **6**, **7**, and **9** reacted smoothly to provide the corresponding sulfenylated products in good to excellent isolated yields (Table 1, entries 19, 20, and 22); however, pyrrole **8** (Table 1, entry 21) provided only 36% yield of 3-sulfenylated pyrrole **8a**.

Compared to the preparation of sulfenyl pyrroles via derivatization of thiocyanato pyrroles with Grignard reagents, the method reported here gives clean products, with facile workup and isolation procedures, that would otherwise be difficult to attain. In particular, in our hands **5a** prepared using 2-thiocyanato pyrrole and phenylmagnesium bromide is unstable in air, even after extensive chromatographic purification, and must be either used immediately or N-protected with an electron-withdrawing group.[23] In contrast, **5a** prepared via the phthalimide route described herein is bench-stable, with no sign of decomposition after more than three months. The reaction of pyrrole with *N*-(phenylthio)phthalimide was performed on a large scale to produce 6.3 mmol of **5a** in 62% isolated yield. With direct access to large quantities of sulfenyl pyrroles, this method should find several applications in other synthetic endeavors.

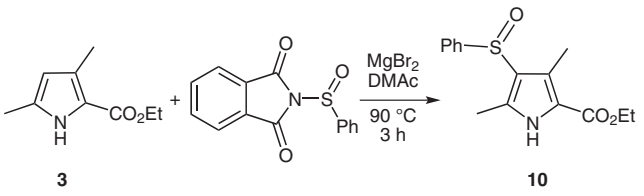
Table 1 Sulfenylation of Pyrroles



Entry[a]	Pyrrole	R^1	Product	Yield (%)
1	**2**	Ph	**2a**	>95
2	**3**	Ph	**3a**	>95
3	**4**	Ph	**4a**	>95
4	**5**	Ph	**5a**[14,22]	62[b,c]
5	**2**	Bn	**2b**	41[d,e]
6	**3**	Bn	**3b**	71[d,f]
7	**4**	Bn	**4b**	89
8	**5**	Bn	**5b**	40[g]
9	**2**	Et	**2c**	56[h,i]
10	**3**	Et	**3c**	93
11	**4**	Et	**4c**	90
12	**2**	decyl	**2d**	54[d,j,k]
13	**3**	decyl	**3d**	>95[l]
14	**4**	decyl	**4d**	95
15	**3**	4-$MeOC_6H_4$	**2f**	89
16	**3**	4-$MeOC_6H_4$	**3f**	>95
17	**4**	4-$MeOC_6H_4$	**4f**	>95
18	**5**	4-$MeOC_6H_4$	**5f**	62
19	**6**	Ph	**6a**	88
20	**7**	Ph	**7a**	>95
21	**8**	Ph	**8a**	36
22	**9**	Ph	**9a**	67

[a] Unless otherwise noted, all reactions were conducted using 0.44 mmol of the pyrrole with 1.0 equiv of the thiophthalimide reagent and 0.01 equiv of $MgBr_2$.
[b] Conditions: 10 mmol of pyrrole.
[c] The amounts of 0.75 or 1.0 equiv of thiophthalimide reagent gave similar results.
[d] Conditions: 1.6 equiv of thiophthalimide, 0.7 equiv of Et_3N and 0.5 equiv of $MgBr_2$; reaction stirred for 3 d.
[e] Conversion: 43%.
[f] Conversion: 73%.
[g] Isolated as a 2.2:1 inseparable mixture of **5b** (40%) and 2,5-bis-sulfenylated material **5b$_2$** (18%).
[h] Conversion: 60%.
[i] Isolated as a 1.5:1 inseparable mixture of **2c** (56%) and starting material **2** (37%).
[j] Conversion: 57%.
[k] Reaction stirred for 6 h.
[l] Reaction stirred for 3 h.

This approach to pyrroles substituted with sulfur-containing moieties was extended to include the preparation of sulfoxide-substituted pyrroles (Scheme 3). For example, reaction of *N*-(phenylsulfinyl)phthalimide[27,33] with pyrrole **3** in the presence of $MgBr_2$ provided **10** in 25% unoptimized isolated yield (70% yield based on recovered starting material).



Scheme 3 Sulfinylation of **3**

In summary, *N*-(aryl- and alkylthio)phthalimides may be used for the sulfenylation and sulfinylation of pyrroles. Furthermore, we have optimized the workup procedure for the sulfenylation reaction such that the current route to sulfenyl pyrroles is amenable to scale-up and gives products that are not susceptible to degradation, unlike the route involving thiocyanato pyrrole.

General Procedures and Representative Data

Sulfenylating Reagents 1a–d

Sulfuryl chloride (1.0 equiv; ca. 5 M in CH_2Cl_2) was added dropwise via a dropping funnel to a solution of thiol (0.05 mol; ca. 1 M in CH_2Cl_2) and Et_3N (0.1 mL) at 0 °C. After stirring for 15 min, the mixture was warmed to r.t. for 30 min and then cooled to 0 °C. The resulting solution was transferred dropwise via cannula to a solution of phthalimide (1.0 equiv; ca. 1 M in CH_2Cl_2) and Et_3N (1.3 equiv) at 0 °C, and the mixture was then warmed to r.t. over 1 h. The solution was diluted with H_2O, extracted with CH_2Cl_2 (3×) before being dried over Na_2SO_4, and then concentrated to give crude product that was purified using recrystallization. For samples with appreciable amounts of phthalimide present, the crude was dissolved with CH_2Cl_2, diluted with 1 M NaOH, extracted with CH_2Cl_2 (3×) before being dried over Na_2SO_4, then concentrated before being purified by recrystallization.

2-(Phenylthio)isoindoline-1,3-dione (1a)[25–27]

Recrystallization from EtOH gave the title compound as a yellow solid (9.6 g, 83%); mp 163–164 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (2 H, dd, *J* = 3.0, 5.5 Hz), 7.78 (2 H, dd, *J* = 3.0, 5.5 Hz), 7.62–7.58 (2 H, m), 7.33–7.25 (3 H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.9 (2 × s), 135.3 (s), 134.9 (2 × d), 132.2 (2 × s), 131.2 (2 × d), 129.5 (3 × d), 124.3 (2 × d). HRMS (ESI$^+$): *m/z* calcd for $C_{14}H_9NO_2S$: 255.0354 {278.0252 for [M + Na]}; found: 278.0246.

Sulfenylating Reagents 1e and 1f

Sulfuryl chloride (1.0 equiv; ca. 5 M in hexanes) was added dropwise via a dropping funnel to a solution of thiol (0.05 mol; ca. 1 M in hexanes) and Et_3N (0.1 mL) at 0 °C. After stirring for 15 min, the mixture was warmed to r.t. for 30 min and then cooled to 0 °C. The resulting solution was transferred dropwise via cannula to a solution of phthalimide (1.0 equiv; ca. 1 M in DMF) and Et_3N (1.3 equiv), and stirring was continued at r.t. for 1 h. The solution was transferred to a beaker containing ice-cold water, the resulting suspension was filtered, and then washed with ice-cold water before being dried to give crude product that was purified by recrystallization. For samples with appreciable amounts of phthalimide present, the crude was treated as previously described (vide supra).

2-(4-Methoxyphenyl)isoindoline-1,3-dione (1f)

Recrystallization from 75% EtOAc in hexanes gave the title compound as a yellow solid (7.4 g, 70%); mp 203–204 °C (75% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (2 H, dd, *J* = 3.0, 5.5 Hz), 7.76 (2 H, d, *J* = 9.0 Hz), 7.75–7.72 (2 H, dd, *J* = 3.0, 5.5 Hz), 6.84 (2 H, d, *J* = 9.0 Hz), 3.78 (3 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.0 (2 × s), 161.6 (s), 136.8 (2 × d), 134.7 (2 × d), 132.2 (2 × s), 125.7 (s), 124.0 (2 × d), 114.9 (2 × d), 55.6 (q). HRMS (ESI$^+$): *m/z* calcd for $C_{15}H_{11}NO_3S$: 285.0460 {308.0357 for [M + Na]}; found: 308.0352.

Sulfenylated Pyrroles 2a,c,f, 3a,c,d,f, 4a–d,f, 5a,a_2,b,b_2,c_2,c_2',c_3,d,d_2,d_2',d_3,f,f_2, 6a, 7a, 9a, 10

A stirred suspension of the pyrrole (0.44 mmol), thiophthalimide sulfenylating reagent (1.0 equiv), and $MgBr_2$ (0.01 equiv) in degassed *N*,*N*-dimethylacetamide (1 mL) was heated at 90 °C for 1 h. After cooling to r.t., the solution was diluted with EtOAc, extracted with 1 M NaOH (3×) before being dried over Na_2SO_4, and then concentrated to give crude product that was purified using flash column chromatography (FCC).

3-Ethyl-2,4-dimethyl-5-(phenylthio)-1*H*-pyrrole (4a)

Flash column chromatography (5% Et_2O in hexanes) gave the title compound as a purple solid (99 mg, >95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (1 H, br s), 7.21–7.17 (2 H, m), 7.08–7.05 (1 H, m), 6.96–6.95 (2 H, m), 2.43 (2 H, q, *J* = 7.0 Hz), 2.19 (3 H, s), 2.07 (3 H, s), 1.09 (3 H, t, *J* = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.2 (s), 129.1 (2 × d), 127.1 (s), 126.9 (s), 125.6 (2 × d), 125.0 (d), 122.7 (s), 109.1 (s), 18.2 (t), 15.7 (q), 11.6 (q), 10.1 (q). HRMS (ESI$^-$): *m/z* calcd for $C_{14}H_{17}NS$: 231.1082 {230.1003 for [M – H]}; found: 230.1009.

Sulfenylated Pyrroles 2b,d, 3b, 8a

A stirred suspension of the pyrrole (0.44 mmol), thiophthalimide sulfenylating reagent (1.6 equiv), Et_3N (0.7 equiv), and $MgBr_2$ (0.5 equiv) in degassed *N*,*N*-dimethylacetamide (1 mL) was heated at 90 °C for 1 d. After cooling to r.t., the solution was diluted with EtOAc, extracted with 1 M NaOH (3×) before being dried over Na_2SO_4, and then concentrated to give crude product that was purified using FCC or preparative thin-layer chromatography (PTLC).

Ethyl 4-(benzylthio)-3,5-dimethyl-1*H*-pyrrole-2-carboxylate (3b)

Reaction stirred for 3 d; FCC (70–100% CH_2Cl_2 in hexanes) gave the title compound as a beige solid (90 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.76 (1 H, br s), 7.22–7.16 (3 H, m), 7.00–6.96 (2 H, m), 4.30 (2 H, q, *J* = 7.0 Hz), 3.60 (2 H, s), 2.28 (3 H, s), 1.86 (3 H, s), 1.36 (3 H, t, *J* = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.7 (s), 139.0 (s), 138.4 (s), 132.6 (s), 129.2 (2 × d), 128.4 (2 × d), 126.9 (d), 117.9 (s), 111.8 (s), 60.2 (t), 41.0 (t), 14.8 (q), 11.6 (q), 11.3 (q). HRMS (ESI$^+$): *m/z* calcd for $C_{16}H_{19}NO_2S$: 289.1136 {312.1034 for [M + Na]}; found: 312.1029.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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