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Sulfur-Based Protecting Groups for Pyrroles and the Facile Deprotection of 2-(2,4-Dinitrobenzene)sulfinyl and Sulfonyl Pyrroles

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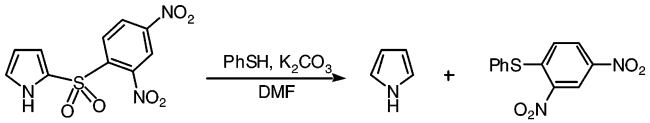

Stabilized pyrrole

The effectiveness of simple sulfinyl and sulfonyl groups as electron-withdrawing protecting groups for pyrroles has been analyzed using ^{13}C NMR spectroscopy and confirmed by consideration of X-ray crystal structures. Additionally, the 2,4-dinitrobenzenesulfinyl and sulfonyl groups are shown to be effective electron-withdrawing protecting groups for pyrroles, and they can be removed by treatment with benzene thiol or thiolate under mild and specific conditions.

Pyrrole constitutes the central unit of a wide range of compounds including natural and synthetic products with biological activities[1,2] and porphyrinogenic macrocycles with useful optical and medicinal properties.[3−7] However, the synthesis of specifically functionalized pyrroles is a challenging and specialized field in which there is heavy reliance on traditional reactions. Success in synthetic pyrrole chemistry often relies upon the delicate control of the nucleophilicity of the electron-rich pyrrolic core, since overcontrol inhibits desired nucleophilic reactions while undercontrol allows rampant nucleophilic reaction and polymerization to give unwelcome tars. Such control is usually effected by electron-withdrawing protecting groups at the 2-position, with 2-carboxylate groups being the most common.[4,6,8,9] The 2-carboxylate group acts as an electron-withdrawing group (EWG), essentially a protecting group, for the electron-rich pyrrolic core through resonance with the doubly vinylogous carbamate (Figure 1),[6] thereby preventing unwanted pyrrole polymerization and other electrophilic addition reactions.

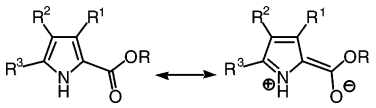

FIGURE 1. Resonance stabilization of 2-carboxylatepyrroles.

Typically, the derivatization of pyrroles and functional group interconversions are conducted with the 2-carboxylate group in place until another EWG is introduced onto the ring, whereby the carboxylate can then be removed. However, removal of the 2-carboxylate group from functionalized pyrroles is often problematic, despite it being one of the most widely used reactions in pyrrole and porphyrin chemistry. Harsh, basic conditions are typically required to effect hydrolysis and decarboxylation in one pot, and low yields often result.[8,10] The removal of *tert*-butyl esters can be achieved using trifluoroacetic acid at room temperature (acid-catalyzed decarboxylation), but such conditions are not always suitable for use with acid-sensitive pyrroles.[8] The use of benzyl esters allows for facile hydrogenolysis to give the corresponding 2-carboxylic acid, but subsequent decarboxylation still requires harsh acidic, basic, or thermal conditions.[8]

As part of a new project to identify alternative protection/deprotection strategies for pyrroles, we sought functional groups that would act as efficient EWGs, thereby stabilizing the pyrrolic core, and that would be facile to remove under specific conditions. Amines are often protected or derivitized as the corresponding sulfinamides and sulfonamides,[11] and so we investigated the utility of sulfinyl and sulfonyl groups as protecting groups for pyrroles, bearing in mind that the nucleophility of pyrroles originates with the lone pair of electrons on the *N*-atom. Several groups have reported on 1-sulfonyl pyrroles,[12−15] and there are a few reports on the synthesis and reactions of 2-sulfinyl and 2-sulfonylpyrroles.[16−29]

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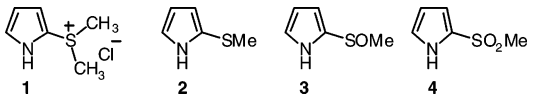
TABLE 1. ^{13}C NMR δ_C ($CDCl_3$) Chemical Shifts (ppm) for Pyrroles 1−4

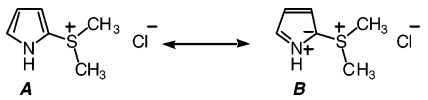
pyrrole	*C*2	*C*3	*C*4	*C*5	CH_3
1	103.6	121.0	110.1	130.2	31.0
2	121.3	115.1	110.0	120.0	21.9
3	128.1	113.5	108.8	124.6	49.0
4	127.1	115.2	111.0	123.7	45.6

However, the use of 2-sulfinyl- and 2-sulfonylpyrroles as general precursors[30,31] to functionalized pyrroles is unknown, and the controlled removal of such protecting groups remains largely uninvestigated.[17,29,32] Additionally, 2-sulfonyl-5-imino and 2-sulfonyl-5-vinylic pyrroles have been reported to exhibit second-order nonlinear optical effects,[33,34] and 3-sulfenylpyrroles have been investigated for their anti-inflammatory and analgesic activity, and therefore, sulfenyl- and sulfonyl-substituted pyrroles are useful target molecules in their own right.[35]



1 **2** **3** **4**

We prepared a series of pyrroles, **1**−**4**, substituted at the 2-position with sulfur-based groups. ^{13}C NMR spectroscopy has been used previously to assess the effectiveness of electron-withdrawing groups at the 2-position of pyrroles.[36−38] By analysis of Table 1,[39] which shows the assigned ^{13}C NMR chemical shifts for **1**−**4**, it is evident that the sulfinyl and sulfonyl groups in pyrroles **3** and **4**, respectively, effect similar electron withdrawal on the pyrrolic core as expected from their similar σ_m values of 0.52 and 0.60, respectively.[40] Of particular note are the *C*2 chemical shifts for **3** and **4** at 128.1 and 127.1 ppm, respectively, considerably downfield shifted compared to pyrrole itself which gives *C*2 at 118.0 ppm.[41] This deshielding at *C*2 is typical for pyrroles bearing good EWGs that stabilize, and therefore protect, the pyrrolic core (e.g., 2-methoxycarbonylpyrrole, *C*2 at 122.0 ppm).[36,42] The 2-sulfenyl group induces less of a deshielding effect, presumably due to the lower σ_m value (0.15) of the −SMe substituent.[40] Remarkably, pyrrole **1** gives a *C*2 chemical shift of 103.6 ppm. Although the σ_m value for $-S^+Me_2$ of 1.00 is indicative of pronounced electron-withdrawing ability, such a large effect on the chemical shifts for the pyrrole ring, based on this factor alone, is surprising. Additionally, the *C*5 chemical shift for **1** at 130.2 ppm is considerably deshielded compared to that of its analogues. Benzenedimethylsulfonium chloride has an ipso (α) ^{13}C shielding effect of −2.9 ppm and a para deshielding effect of +7.6 ppm, cf. benzene itself.[43] Evidently, pyrrole **1** shows a significant deviation from benzene in terms of the amplitude of the shielding with the dimethylsulfonium substituent. The N*H* ^{1}H NMR chemical shift for pyrrole **1** is at 13.90 ppm, rather downfield shifted compared to typical pyrroles which usually give N*H* chemical shifts in the 8−10.5 ppm range, depending on the substituents. This leads us to believe that pyrrole **1** exhibits significant ylide character as indicated by resonance form ***B*** (Figure 2), thus rationalizing the deshielding of *C*5 and N*H* and the shielding of *C*2.



A ⟷ ***B***

FIGURE 2. Resonance forms for 2-(methylsulfonium)pyrrole chloride.

Having affirmed that sulfinyl and sulfonyl groups can both act as stabilizing EWGs for pyrroles and cognizant of Fukuyama's 2- and 4-nitrobenzenesulfonamides (nosyl-protected amines) whereby protected amines are deprotected by reaction with PhSH and K_2CO_3 in DMF at room temperature,[44] we investigated the utility of the 2,4-dinitrobenzenesulfonyl group as an electron-withdrawing protecting group for pyrroles. 2-(2,4-Dinitrobenzenesulfenyl)pyrrole **(5)** was prepared by reaction of pyrrole with 2,4-dinitrobenzenesulfenyl chloride. 2-(2,4-Dinitrobenzenesulfinyl)pyrrole **(6)** and 2-(2,4-dinitrobenzenesulfonyl)-pyrrole **(7)** were prepared by oxidation of **5** (Scheme 1). The oxidation of **5** or **6** to the corresponding sulfone **7** proceeded in capricious and at best only very low yields, despite numerous attempts using *m*-CPBA, hydrogen peroxide, and Oxone under a variety of conditions. This is presumably due to the electron-poor nature of the sulfenyl group in **6**, since there are reports of facile oxidation of other 2-sulfenyl and 2-sulfinylpyrroles.[19,45] Nevertheless, this successful oxidation gave us the material that we needed to perform proof-of-principle reactions

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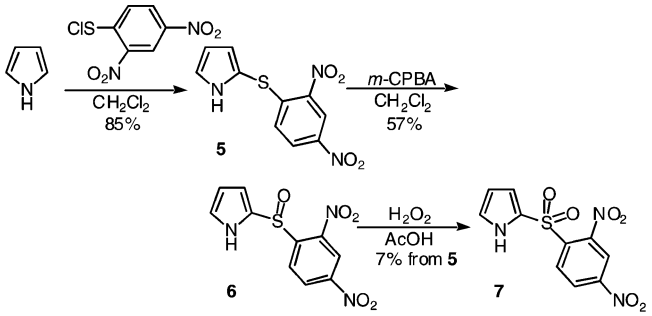
SCHEME 1. Synthesis of 5−7



for deprotection of 2-(2,4-dinitrobenzenesulfonyl)pyrrole (**7**). Our attempts to react pyrrole with 2,4-dinitrobenzenesulfonyl chloride were unsuccessful. The ^{13}C NMR chemical shifts for **6** and **7** confirm the effective electron-withdrawing ability of the 2,4-dinitrobenzenesulfinyl and 2,4-dinitrobenzenesulfonyl protecting groups for pyrroles.[46]

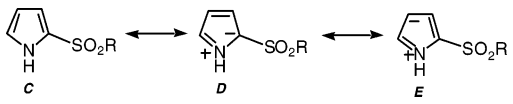
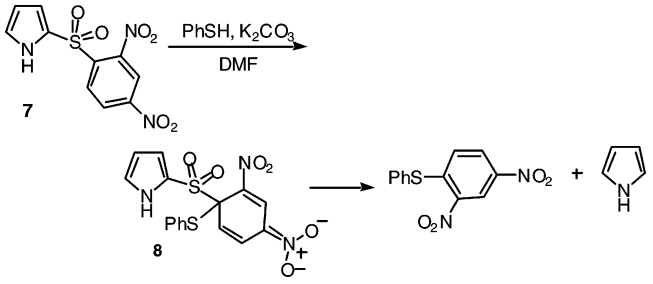


FIGURE 3. Major resonance forms of 2-sulfonylpyrroles.

Sulfonylpyrroles are formally vinylogous sulfonamides (Figure 3). The electron-withdrawing properties and ability of the sulfonyl group[47,48] to stabilize α-anions should render resonance form ***D*** to be significant, and thus, stabilizaton of the electron-rich pyrrolic core should occur.[37] This concept is supported by analysis of the X-ray crystal structure[46] of **7** as the N(1)−C(4) and C(2)−C(3) bonds in **7** (1.347(4) and 1.389(5) Å, respectively) are significantly shorter than the analogous bond lengths of 1.370(6) and 1.417(6) Å, respectively, obtained for pyrrole itself using microwave spectroscopy.[36,37,49] The C(1)−S(1) bond length in **7** (1.712(3) Å) is significantly shorter than the equivalent bond length of 1.748(4) Å in 2,4-dinitrophenyl phenyl sulfone,[50] again supportive of the significance of resonance form ***D***; X-ray crystal structures of **1**, **4**, and **5** all support the general trend that these sulfur-based substituents act as efficient EWGs for pyrroles.[46]

Rearrangements of sulfonium-,[23] sulfenyl-,[19] and sulfinyl-substituted[27] pyrroles have been reported to occur under acidic conditions. Indeed, the initial position of electrophilic attack on pyrroles has also been investigated.[20] Throughout our work only 2-substituted pyrroles were observed, as confirmed using ^{13}C NMR spectroscopy and X-ray crystallography; under no circumstances were rearrangement products observed under our reaction conditions. This is crucial to the use of the dinitrobenzenesulfur-based groups as protecting groups for pyrroles.

SCHEME 2. Deprotection of 7



Satisfied that the 2,4-dinitrobenzenesulfinyl and sulfonyl groups stabilize the electron-rich pyrrolic core, we sought to establish the ease with which such groups may be removed from pyrroles. We were delighted to observe that treatment of **7** with benzenethiol under basic conditions resulted in complete removal of the 2,4-dinitrobenzenesulfonyl group within 5 min. 2,4-Dinitro-1-(phenylthio)benzene[51] was recovered in quantitative yield after workup and purification (Scheme 2), and pyrrole was observed by HPLC in low yield (3%, confirmed by spiking). Such low recovery of pyrrole is expected, given its propensity to polymerize. Presumably, deprotection occurs via the Meisenheimer intermediate **8**;[44] in the absence of thiol, the basic conditions alone were unsuccessful in effecting deprotection. The deprotection of 2-(2,4-dinitrobenzenesulfinyl)pyrrole (**6**) also proceeded well, also giving 2,4-dinitro-1-(phenylthio)benzene in quantitative yield within 5 min. The deprotections were also successful in the absence of K_2CO_3, again giving quantitative yields of 2,4-dinitro-1-(phenylthio)benzene, but the reactions were significantly slower, requiring overnight stirring at room temperature for completion.

The mononitro analogues **9**−**11** were also prepared. Since the corresponding sulfonamides are used to protect amines,[11] and may be easily deprotected, we expected similar behavior for the pyrrole derivatives given our success with deprotection of the 2,4-dinitrosulfenyl- and sulfonylbenzene pyrroles. Oxidation of **9** or **10** to give the sulfone **11** proceeded in good yield, unlike the dinitro derivative discussed above, supporting the hypothesis that the electron-poor sulfinyl moiety in **6** considerably inhibits oxidation. Pyrroles **10** and **11** were exposed to standard deprotection conditions of benzene thiol (1.2 equiv) and K_2CO_3 (3.0 equiv) in DMF. In both cases, the required deprotection product 4-nitro-1-(phenylthio)benzene[52] was isolated but in only 30 and 38% yield, respectively. The remainder of the material consisted of the sulfenyl compound **9**, a consequence of reduction. For the mononitro derivatives, presumably reduction of the sulfinyl and sulfonyl pyrroles competes with nucleophilic attack at the ipso-position of the nitrobenzene ring. Given the electron-rich nature of the pyrrolic core and the necessity for considerable electrophility at the ipso-position on the nitrobenzene ring in order for the desired Meisenheimer intermediate to be formed, competitive reduction is reasonable. This rationale is also consistent

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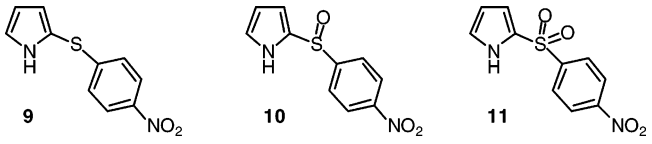
with the observation that oxidation of **10** to give **11** proceeds readily but that oxidation of **6** to give **7** proceeds extremely sluggishly.



This research shows that alternative protecting groups to carboxylates may be considered for pyrroles, thus expanding the synthetic scope of pyrrole chemistry. Our proof-of-principle studies show that 2,4-dinitrobenzenesulfinyl and sulfonyl groups are sufficiently electron-withdrawing to effectively stabilize pyrroles and that they may be efficiently removed using thiols and thiolates. The mononitrobenzenesulfinyl and sulfonyl pyrroles also stabilize the pyrrole ring, but deprotection of these functional groups is accompanied by reduction. Our research is now focusing on the efficient synthesis, from acyclic materials, of functionalized pyrroles with 2,4-dinitrobenzenesulfonyl protecting groups in the 2-position and assessing the robustness of these functionalized pyrroles.

Experimental Section

Dimethyl(2-pyrrolyl)sulfonium chloride and 2-(methylthio)-pyrrole were prepared as previously reported.[28] 2-(Methylsulfinyl)pyrrole[21] was prepared according to the method used by Carmona et al.[27] for the synthesis of 2-(butylsulfinyl)pyrrole. 2-(Methylsulfonyl)pyrrole[21] was prepared from 2-(methylthio)-pyrrole according to the method used by Beveridge and Harris[45] for the synthesis of 2-(2-nitrobenzenesulfonyl)pyrrole.

2-(2,4-Dinitrobenzenesulfenyl)pyrrole (5).[26] Freshly distilled pyrrole (4.0 mL, 57.7 mmol) was added to a solution of 2-(2,4-dinitrobenzene)sulfenyl chloride (12.91 g, 55.0 mmol) in dry CH_2Cl_2 (500 mL), under nitrogen. The reaction mixture was stirred for 16 h at room temperature and then the solvent removed in vacuo. The crude product was then purified by column chromatography (dry-loaded) eluting with 2:3 CH_2Cl_2/hexanes, followed by crystallization from CH_2Cl_2 and hexanes, giving the title compound as a yellow crystalline solid (10.2 g, 70%): mp 149−150 °C; R_f (4:1 CH_2Cl_2/hexanes) 0.37; δ_H ($CDCl_3$) 6.44−6.48 (1H, m, *H*4), 6.70−6.74 (1H, m, *H*3), 6.92 (1H, d, *J* 10, Ar*H*), 7.34−7.39 (1H, m, *H*5), 8.29 (1H, dd, *J* 10, 2, Ar*H*), 8.45 (1H, br s, N*H*), 9.15 (1H, d, *J* 2, Ar*H*); δ_C ($CDCl_3$) 111.8 (*C*4), 112.2 (*C*2), 120.8 (*C*3), 121.3, 127.2, 124.0 (*C*5), 128.9, 143.7, 144.7, 149.2; *m/z* 265 (M^+, 12), 82 (100) (found M^+, 265.0142, $C_{10}H_7N_3SO_4$ requires 265.0157).

2-(2,4-Dinitrobenzenesulfinyl)pyrrole (6). 2-(2,4-Dinitrobenzenesulfenyl)pyrrole (**5**) (2.0 g, 7.5 mmol) was dissolved in CH_2Cl_2. A solution of 50% *m*-CPBA (2.85 g, 8.25 mmol) was added and the reaction mixture stirred for 2 h. The precipitate was then filtered off and purified by column chromatography (dry loaded) eluting with 1:49 MeOH/CH_2Cl_2 to give the title compound as green/yellow solid (1.20 g, 57%): mp 157−158 °C dec; R_f (1:19 MeOH/CH_2Cl_2) 0.24; δ_H ($CDCl_3$) 6.21−6.23 (1H, m, *H*4), 6.56−6.58 (1H, m, *H*3), 6.92−6.94 (1H, m, *H*5), 8.67 (1H, d, *J* 10, Ar*H*), 8.72 (1H, dd, *J* 10, 2, Ar*H*), 8.92 (1H, br s, N*H*), 9.03 (1H, d, *J* 2, Ar*H*); δ_C($CDCl_3$) 111.0 (*C*4), 113.0 (*C*3), 120.9, 123.1 (*C*5), 127.4, 129.3, 127.2, 145.1, 147.2, 151.1; δ_C (DMSO-d_6) 109.8, 113.6, 121.2, 124.4, 128.7, 130.0, 130.2, 145.2, 149.1, 149.6; *m/z* 281 (M^+, 100), 82 (23).

2-(2,4-Dinitrobenzenesulfonyl)pyrrole (7). To glacial acetic acid (10 mL) at 40 °C was added 2-(2,4-dinitrobenzenesulfenyl)pyrrole (**6**) (100 mg, 0.377 mmol). After 10 min, 30% hydrogen peroxide (0.500 mL, 4.41 mmol) was added to the reaction flask. The reaction mixture was stirred for 27 h and then poured into distilled water, followed by the addition of satd $NaHCO_3$. The aqueous reaction mixture was then washed twice with ethyl acetate. The combined organic layers were dried over $MgSO_4$, and then the solvent was removed in vacuo to yield the crude product as an oily yellow residue. Careful crystallization from CH_2Cl_2 and hexanes gave the title product as a bright yellow crystalline solid (8 mg, 7%): mp 132−134 °C; R_f (1:19 EtOAc/hexanes) 0.24; δ_H ($CDCl_3$) 6.38−6.40 (1H, m, *H*4), 7.08−7.10 (1H, m, *H*3), 7.16−7.18 (1H, m, *H*5), 8.45 (1H, d, *J* 10), 8.52−8.55 (2 H, m), 9.49 (1H, br s, N*H*); δ_C ($CDCl_3$) 112.0 (*C*4), 119.4 (*C*3), 120.2, 125.3 (*C*2), 126.2 (*C*5), 127.2, 132.8, 141.3, 148.7, 150.2; *m/z* 297 (M^+, 100), 82 (53) (found M^+, 297.0064, $C_{10}H_7N_3SO_6$ requires 297.0055).

2-(4-Nitrobenzenesulfenyl)pyrrole (9). Following the procedure for the preparation of 2-(2,4-dinitrobenzenesulfenyl)-pyrrole **(5)**, the title compound (57%) was prepared as a yellow crystalline solid from pyrrole and 2-(4-nitrobenzene)sulfenyl chloride: mp 76−77 °C; R_f (1:1 hexanes/CH_2Cl_2) 0.24; δ_H ($CDCl_3$) 6.38−6.40 (1H, m, *H*4), 6.61−6.63 (1H, m, *H*3), 7.01 (1H, d, *J* 10), 7.04−7.06 (1H, m, *H*5), 7.99 (1H, d, *J* 10), 8.37 (1H, br s, N*H*); δ_C ($CDCl_3$) 111.3 (*C*4), 112.7 (*C*2), 119.9 (*C*3), 123.2 (*C*5), 124.2, 125.1, 145.4, 149.9; *m/z* EI+ 220 (M^+, trace); *m/z* APCI+ 221 (MH^+, 100), 205 (16).

2-(4-Nitrobenzenesulfinyl)pyrrole (10). Following the procedure for the preparation of 2-(2,4-dinitrobenzenesulfinyl)-pyrrole, the title compound (88%) was prepared as a light yellow crystalline solid from 2-(4-nitrobenzenesulfenyl)pyrrole: mp 154 °C; R_f (1:1 EtOAc/CH_2Cl_2) 0.17; δ_H ($CDCl_3$) 6.32−6.33 (1H, m, *H*4), 6.78−6.80 (1H, m, *H*3), 7.02−7.04 (1H, m, *H*5), 7.81 (1H, d, *J* 10), 8.36 (1H, d, *J* 10), 9.42 (1H, br s, N*H*); δ_C ($CDCl_3$) 110.2 (*C*4), 115.9 (*C*3), 124.2, 125.2 (*C*5), 125.9, 128.2 (*C*2), 149.4, 151.2; *m/z* APCI+ 237 (MH^+, 100), 220 (37).

2-(4-Nitrobenzenesulfonyl)pyrrole (11). Following the procedure for the preparation of 2-(2,4-dinitrobenzenesulfinyl)-pyrrole, the title compound (84%) was prepared as a very pale yellow crystalline solid from 2-(4-nitrobenzenesulfenyl)pyrrole and excess *m*-CPBA: mp 271−272 °C; R_f (1:1 EtOAc/CH_2Cl_2) 0.90; δ_H ($CDCl_3$) 6.40−6.42 (1H, m, *H*4), 6.99−7.01 (1H, m, *H*3), 7.09−7.11 (1H, m, *H*5), 8.12 (1H, d, *J* 10), 8.36 (1H, d, *J* 10), 9.15 (1H, br s, NH); δ_C ($CDCl_3$) 112.3 (*C*4), 117.2 (*C*3), 124.7, 124.8 (*C*5), 126.6 (*C*2), 128.2, 148.3, 150.3; *m/z* APCI+ 253 (100), 156 (18).

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Supporting Information Available: X-ray crystallographic data and ORTEP diagrams for **1**, **4**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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