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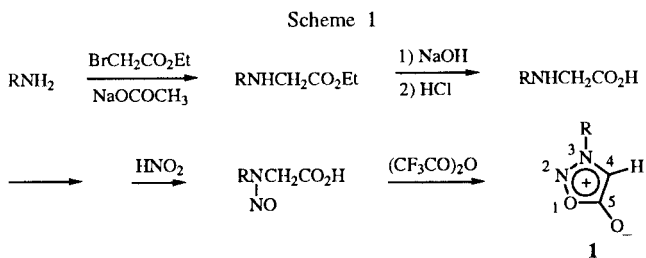
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Exclusive aryl ring nitration of a series of 3-arylsydnone **1** with electron donors (di- or tri-methyl) on the aryl ring is reported.

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Sydnone, *cf.* **1** undergo electrophilic aromatic substitution reactions with an ease apparently similar to that of furan [1] and, in general, 3-arylsydnone **1** (R = Ar) react with electrophiles to give the corresponding 4-substituted derivatives. In the case of 3-arylsydnone, where one could conceive of a competition between substitution on the aryl or sydnone rings, the exclusivity of sydnone ring substitution with the vast majority of electrophiles is attributable to the deactivation of the aryl substituent by the electron-withdrawing effect of the sydnone ring nitrogen (the N-3 position bears a substantial fractional positive charge [2]). Competitive aryl ring substitution has been observed both on bromination of aminoarylsydnone [3] and on nitration of some slightly activated arylsydnone [4] unsubstituted at the 4-position. The latter results are of considerable interest since they represent the only *general* examples of aryl ring substitution in competition with the sydnone ring. It is surprising that the parameters affecting concomitant or exclusive substitution on the aryl ring are unknown and, accordingly, in order to probe these aspects further, we have subjected a series of 3-arylsydnone with electron donors on the aryl ring to nitration under standard conditions.

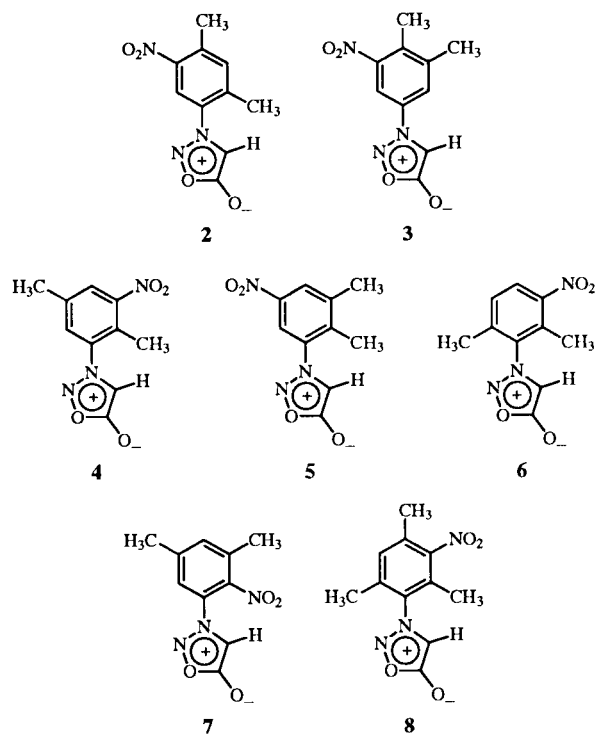
The compounds chosen for study were all six of the possible 3-(dimethylphenyl)sydnone **1a-f** and 3-(2,4,6-trimethylphenyl)sydnone **1g**, all of which were available in our laboratory from our previous examination of the bromination of such species [5]. The preparative scheme to **1a-g** is shown in Scheme 1.



a) R = 2,4-Me₂C₆H₃ b) R = 3,4-Me₂C₆H₃ c) R = 2,5-Me₂C₆H₃ d) R = 2,3-Me₂C₆H₃
e) R = 2,6-Me₂C₆H₃ f) R = 3,5-Me₂C₆H₃ g) R = 2,4,6-Me₃C₆H₂

Nitration of the sydnone was effected by treatment of **1** with one equivalent of potassium nitrate in the presence of sulfuric acid at -7°. For all of the sydnone studied,

nitration under these conditions gave nitroaryl products **2-8**, from **1a-g**, respectively. In no case was there evidence for nitration on the sydnone ring, in line with Weintraub and Bambury's original observations with activated arylsydnone [4]. The identities of the nitroaryl sydnone **2-8** were established *via* satisfactory elemental analyses, the presence of both sydnone CH and NO₂ stretching absorptions in the infrared spectra (approximately 3120 and 1530 and 1350 cm⁻¹, respectively) and sydnone ring proton absorption in their proton nuclear magnetic resonance spectra (approximately δ 6.3-6.9). In the latter, the splitting patterns for the aryl protons [*ortho*-coupling, J = ~8 Hz for **6**, *meta*-coupling, J = ~2 Hz for **3-5**, **7** or *para*-coupling, J = ~1 Hz for **2**] were appropriate for the structures shown, **2-8**. In addition, in their carbon nuclear magnetic resonance spectra, the C-4 position appeared at ~95-9 ppm, in line with known values (95.1 [6]) for sydnone unsubstituted at the 4-position rather than that for a sydnone bearing a nitro group (121.7 [6]).



Surprisingly, in all of the reactions explored, the products shown, **2-8** were either obtained exclusively or were by far the major products. In general, it is apparent that the sydnone ring acts to direct incoming electrophiles to positions *meta* to itself and, where the two attached methyl groups do not activate the same positions on the aryl ring, this, coupled with a desire to avoid attachment between two groups, is the overriding feature. Where attachment between two groups was inevitable, as in **1f**, a preference for substitution between a methyl group and the sydnone moiety to form **7** was observed; a result congruent to that observed upon bromination of 3-(3,5-dimethoxyphenyl)sydnone [5].

Overall, we have shown that nitration of di- and trimethylphenylsydnones, *cf.* **1a-g**, occurs exclusively on the aryl ring with considerable regioselection therein. We intend to explore the utility of this process for the preparation of uniquely substituted heterocycles.

EXPERIMENTAL [7]

Nitration of Activated Arylsydnones: Representative Procedure.

The sydnone **1** was dissolved in concentrated sulfuric acid (~3 ml/mmol) and stirred at -7° to -8°. Crushed potassium nitrate (1.1 molar equivalents) was added over a fifteen minute period and after an additional 1.5 hours, the mixture was poured slowly into ice. The precipitate was removed by filtration, washed with aqueous sodium bicarbonate (10 ml), then with water (3 x 10 ml), dried and recrystallized from ethanol or isopropanol to yield the corresponding nitrosydnone, **2-8**.

3-(5-Nitro-2,4-dimethylphenyl)sydnone (**2**).

Using 3-(2,4-dimethylphenyl)sydnone (**1a**) [0.30 g, 1.6 mmoles] in the representative procedure gave **2** as light tan crystals, 0.23 g (62% yield), mp 123.5-125°; ir (potassium bromide): 3117 (sydnone C-H str), 1774 (sydnone C=O str), 1528 and 1355 (NO₂ str), 938, 727 cm⁻¹; ¹H-nmr (deuteriodimethyl sulfoxide): δ 8.16 (s, 1H, aromatic), 7.46 (s, 1H, aromatic), 6.54 (s, 1H, sydnone CH), 2.70 (s, 3H, CH₃), 2.40 (s, 3H, CH₃); ¹³C-nmr (deuteriodimethyl sulfoxide): 167.7 (sydnone C=O), 146.6, 138.4, 137.7, 131.6 (aromatic C), 136.0, 121.5 (aromatic CH), 96.4 (sydnone CH), 20.1 (CH₃), 16.6 (CH₃) ppm.

Anal. Calcd. for C₁₀H₉N₃O₄: C, 51.06; H, 3.83; N, 17.87. Found: C, 50.84; H, 3.87; N, 17.54.

3-(5-Nitro-3,4-dimethylphenyl)sydnone (**3**).

Using 3-(3,4-dimethylphenyl)sydnone (**1b**) [0.25 g, 1.31 mmoles] in the representative procedure gave **3** as tan crystals, 0.19 g (61% yield), mp 133-134°; ir (potassium bromide): 3122 (sydnone C-H str), 1736 (sydnone C=O str), 1534 and 1364 (NO₂ str), 1179, 970, 894, 723 cm⁻¹; ¹H-nmr (deuteriodimethyl sulfoxide): δ 8.33 (d, 1H, aromatic) [J = 2 Hz], 8.14 (d, 1H, aromatic) [J = 2 Hz], 7.84 (s, 1H, sydnone CH), 2.48 (s, 3H, CH₃), 2.40 (s, 3H, CH₃); ¹³C-nmr (deuteriodimethyl sulfoxide): 168.2 (sydnone C=O), 150.6, 142.4, 134.4, 131.9 (aromatic C), 125.5,

114.5 (aromatic CH), 95.1 (sydnone CH), 20.0 (CH₃), 14.9 (CH₃) ppm.

Anal. Calcd. for C₁₀H₉N₃O₄: C, 51.06; H, 3.83; N, 17.87. Found: C, 50.88; H, 3.92; N, 17.57.

3-(3-Nitro-2,5-dimethylphenyl)sydnone (**4**).

Using 3-(2,5-dimethylphenyl)sydnone (**1c**) [0.30 g, 1.6 mmoles] in the representative procedure gave a mixture of three products which was separated by column chromatography (silica gel, dichloromethane/acetone [10:1] as eluant) to yield the major component **4** as a colorless solid, 0.22 g (60% yield), mp 192-194°; ir (potassium bromide): 3138 (sydnone C-H str), 1750 (sydnone C=O str), 1538 and 1343 (NO₂ str), 936, 732 cm⁻¹; ¹H-nmr (deuteriodimethyl sulfoxide): δ 8.17 (s, 1H, aromatic), 7.96 (s, 1H, aromatic), 7.59 (s, 1H, sydnone CH), 2.47 (s, 3H, CH₃), 2.28 (s, 3H, CH₃); ¹³C-nmr (deuteriodimethyl sulfoxide): 168.3 (sydnone C=O), 150.4, 139.2, 135.1, 125.4 (aromatic C), 131.1, 127.9 (aromatic CH), 99.1 (sydnone CH), 19.8 (CH₃), 12.8 (CH₃) ppm.

Anal. Calcd. for C₁₀H₉N₃O₄: C, 51.06; H, 3.83; N, 17.87. Found: C, 50.70; H, 3.79; N, 17.51.

3-(5-Nitro-2,3-dimethylphenyl)sydnone (**5**).

Using 3-(2,3-dimethylphenyl)sydnone (**1d**) [0.30 g, 1.6 mmoles] in the representative procedure gave **5** as light tan crystals, 0.23 g (62% yield), mp 170-171°; ir (potassium bromide): 3100 (sydnone C-H str), 1789 (sydnone C=O str), 1526 and 1352 (NO₂ str), 1146, 1071, 957, 926, 730 cm⁻¹; ¹H-nmr (deuteriodimethyl sulfoxide): δ 8.33 (d, 1H, aromatic, J = 2 Hz), 8.20 (d, 1H, aromatic, J = 2 Hz), 6.56 (s, 1H, sydnone CH), 2.55 (s, 3H, CH₃), 2.31 (s, 3H, CH₃); ¹³C-nmr (deuteriodimethyl sulfoxide): 168.2 (sydnone C=O), 145.9, 141.9, 139.9, 134.5 (aromatic C), 127.5, 118.6 (aromatic CH), 97.4 (sydnone CH), 20.7 (CH₃), 14.8 (CH₃).

Anal. Calcd. for C₁₀H₉N₃O₄: C, 51.06; H, 3.83; N, 17.87. Found: C, 50.80; H, 3.72; N, 17.71.

3-(3-Nitro-2,6-dimethylphenyl)sydnone (**6**).

Using 3-(2,6-dimethylphenyl)sydnone (**1e**) [0.30 g, 1.6 mmoles] in the representative procedure gave **6** as a colorless solid, 0.21 g (57% yield), mp 129-130°; ir (potassium bromide): 3160 (sydnone C-H str), 3100, 1755 (sydnone C=O str), 1535 and 1350 (NO₂ str), 1221, 942, 871, 852, 756 cm⁻¹; ¹H-nmr (deuteriodimethyl sulfoxide): δ 8.25 (d, 1H, aromatic) [J = 8.4 Hz], 7.68 (d, 1H, aromatic) [J = 8.4 Hz], 7.58 (s, 1H, sydnone CH), 2.28 (s, 6H, 2 CH₃); ¹³C-nmr (deuteriodimethyl sulfoxide): 168.2 (sydnone C=O), 148.1, 140.4, 134.3, 129.6 (aromatic C), 129.8, 127.5 (aromatic CH), 99.0 (sydnone C-H str), 16.8 (CH₃), 13.4 (CH₃) ppm.

Anal. Calcd. for C₁₀H₉N₃O₄: C, 51.06; H, 3.83; N, 17.87. Found: C, 51.08; H, 3.87; N, 17.80.

3-(2-Nitro-3,5-dimethylphenyl)sydnone (**7**).

Using 3-(3,5-dimethylphenyl)sydnone (**1f**) [0.34 g, 1.75 mmoles] in the representative procedure gave **7** as a pale yellow solid, 0.21 g (51% yield), mp 159-160°; ir (potassium bromide): 3116 (sydnone C-H str), 1759 (sydnone C=O str), 1533 and 1358 (NO₂ str), 1174, 958, 883, 842, 785, 738 cm⁻¹; ¹H-nmr (deuteriodimethyl sulfoxide): δ 7.49 (s, 1H, aromatic), 7.37 (s, 1H, aromatic), 6.68 (s, 1H, sydnone CH), 2.52 (s, 3H, CH₃), 2.47 (s, 3H, CH₃); ¹³C-nmr (deuteriodimethyl sulfoxide): 166.2 (sydnone C=O), 143.4, 142.7, 133.7, 126.8

(aromatic C), 136.3, 124.2 (aromatic CH), 97.1 (sydnone CH), 21.1 (CH₃), 17.9 (CH₃) ppm.

Anal. Calcd. for C₁₀H₉N₃O₄: C, 51.06; H, 3.83; N, 17.87. Found: C, 51.04; H, 3.81; N, 17.87.

3-(3-Nitro-2,4,6-trimethylphenyl)sydnone (**8**).

Using 3-(2,4,6-trimethylphenyl)sydnone (**1g**) [0.30 g, 1.5 mmoles] in the representative procedure gave **8** as a colorless solid, 0.27 g (73% yield), mp 182.5-183°; ir (potassium bromide): 3153 (sydnone C-H str), 3020, 1747 (sydnone C=O str), 1540 and 1383 (NO₂ str), 1177, 943, 862, 733 cm⁻¹; ¹H-nmr (deuteriodimethyl sulfoxide): δ 7.28 (s, 1H, aromatic), 6.52 (s, 1H, sydnone CH), 2.40 (s, 3H, CH₃), 2.28 (s, 3H, CH₃), 2.12 (s, 3H, CH₃); ¹³C-nmr (deuteriodimethyl sulfoxide): 169.7 (sydnone C=O), 165.2, 151.5, 137.8, 134.8, 127.9 (aromatic C), 132.7 (aromatic CH), 98.3 (sydnone C-H), 17.9 (CH₃), 13.5 (CH₃) ppm.

Anal. Calcd. for C₁₁H₁₁N₃O₄: C, 53.01; H, 4.42; N, 16.87. Found: C, 53.13; H, 4.59; N, 16.73.

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- [7] All melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra (potassium bromide) were measured on a Perkin Elmer 1600 Fourier transform (FT) instrument and nuclear magnetic resonance spectra (¹H and ¹³C) on an IBM NR/200 FTNMR at 200 MHz or 50 MHz, respectively, with tetramethylsilane as the internal standard, chemical shifts reported in ppm (δ). Combustion analyses were performed by Midwest Microlab, Indianapolis.