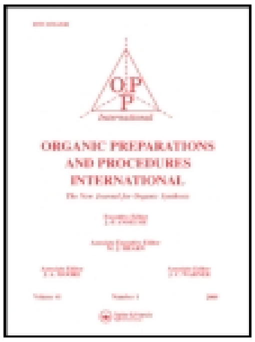

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Reaction of 4-Iodo-3-(2-iodoaryl)sydnones with Sodium Sulfite and Sodium Borohydride

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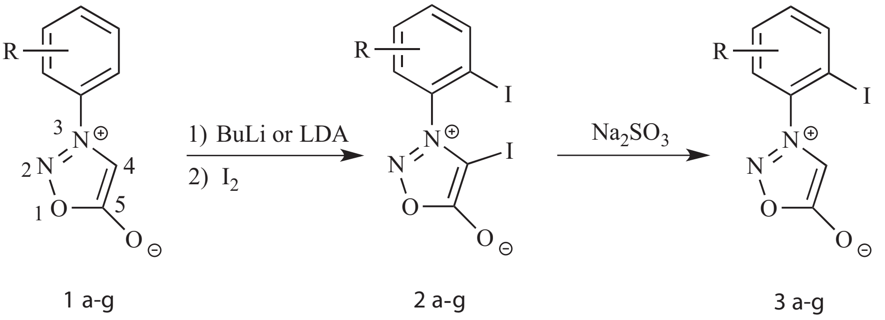
Sydnones (*e. g.* **1**) are members of the class of compounds known as mesoionic[1] and they have been studied extensively.[2] Previous results from our group demonstrated that the debromination of 4-bromo-3-arylsydnones to 3-arylsydnones may be effected using sodium borohydride,[3] sodium dithionite[4] or sodium sulfite.[5] More recently, we have extended the utility of the latter reagent to the selective removal of an iodine attached to the C4 carbon of the sydnone ring in the presence of an *o*-aryl-attached iodine (*e. g.* **2a** to **3a**).[6] The present article is a further extension of this protocol and related ones.



a, R = H; b, R = 4-Br; c, R = 3-Cl; d, R = 4-Cl; e, R = 4-CH_3; f, R = 4-CH_3O; g, R = 3,5-diCH_3O

To examine the deiodination of the diiodo species, it was necessary to prepare several substituted analogs **2b–g**. It was anticipated that the latter would be available *via* modifications of our previously reported dilithiation protocol[7] involving treatment of the parent sydnone **1a** with ^{n}BuLi at low temperature followed by addition of I_2 to give **2a**. However, it was anticipated that this approach might be problematic for any sydnone bearing a bromine atom on the aryl ring (*e. g.* **1b**), wherein competitive metal-halogen exchange could occur, and we were aware that the chloro-containing species (*cf.* **1c** and **1d**) might suffer a similar fate. Further, for those sydnones containing at least one methoxy group (*e. g.* **1f** and **1g**), directed lithiation, especially of the latter com-

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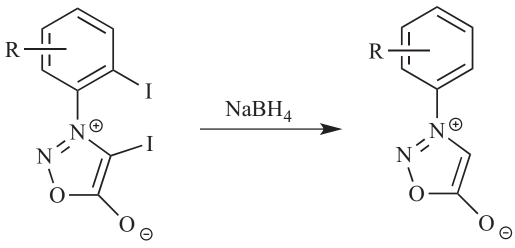
pound (**1g**), might result in arylsydnones with different substitution patterns from the compounds targeted.

With these caveats in mind, we first examined the dilithiation/iodination of 3-(4-tolyl)sydnone (**1e**). Gratifyingly, reaction of **1e** with ^{n}BuLi (3.4 eq) at −78°C, followed by treatment with iodine (2.2 eq), gave the corresponding diiodo species **2e** in 75% yield. Extension of the protocol to the *para*-chloro analog **1d** afforded **2d** in 54% yield. Similar conversions of **1f** (to **2f**) and **1g** (to **2g**) were accomplished in 88% and 86% yield, respectively, using three equivalents of both ^{n}BuLi and iodine at −45°C. As mentioned above, for the *meta*-chloro species **1c** the use of ^{n}BuLi appeared imprudent; it was hoped that the acidity of the aryl hydrogen flanked by both the chlorine and the sydnone ring might be increased sufficiently to allow the removal of that proton by a non-nucleophilic base such as lithium diisopropylamide (LDA) without inducing metal-halogen exchange. In the event, treatment of **1c** with LDA (2.2 eq.) at −78°C followed by the addition of iodine (2.2 eq.) afforded the diiodo compound **2c** in 75% yield. Unfortunately but not surprisingly, extension of the LDA/I_2 protocol to the *para*-bromo sydnone **1b** was considerably less successful; the resultant product mixture had to be subjected to multiple column chromatography to afford the desired product **2b** in only 35% yield.

With the diiodosydnones in hand, the generality of the selective removal of the sydnone-attached iodine using sodium sulfite in methanol was explored first. We had employed sodium sulfite previously as a reagent for the conversion of diiodosydnone **2a** to monoiodo sydnone **3a**.[6] In all cases, treatment of the diiodosydnones **2b**-**2g** with aqueous sodium sulfite in methanol afforded the corresponding *ortho*-iodoaryl sydnones **3b**-**3g** in good to high yields (75–95%) and high purity. The identity of the products was confirmed by satisfactory combustion analyses, the presence of the sydnone C=O stretching vibration at $\sim$1750 cm^{-1} and the expected chemical shifts and splitting patterns in their proton and carbon NMR spectra. For the latter, the most telling observation was the shift in the position of the sydnone C-4 position from *ca*. 54 ppm (δ) to *ca*. 95 ppm (δ), indicating the loss of an iodine from that position.

This reductive approach allows the preparation of species **3a–g**, which would be difficult to prepare by other methods and, since the *ortho*-iodo species **3a** has proven to be an attractive template for iterative Sonogashira coupling procedures, leading to sydnone-containing oligomeric areneynes as ligands for potential non-linear optical materials,[6] we anticipate that the present extension will greatly facilitate the preparation of the latter species.

Further, since we had employed sodium borohydride previously as a reagent for the facile removal of a C-sydnone-attached bromine,[3] it was of interest to determine if selective deiodination could be effected with this reagent as well. Surprisingly, when diiodosydnone **2a** was treated with sodium borohydride in methanol at room temperature, rapid (TLC evidence) removal of *both* iodine atoms occurred to afford 3-phenylsydnone (**1a**) in 73% yield. The procedure proved to be rather general and exposure of diiodosydnones **2d–2g** to the reagent under the same conditions gave the corresponding deiodinated compounds **1d–1g** in 86–92% yields. While the lability of groups attached to the sydnone 4-position is well known[4,5], to the best of our knowledge this is the first example of removal of an *o*-aryl attached group (in a 3-arylsydnone) by a nucleophilic reducing agent. It is reasonable to assume that the strong electron-withdrawing effect of the sydnone N-3 position activates the *ortho*-position to nucleophilic displacement, but confirmation of this speculation will require further mechanistic studies.



2 a, d-g 1 a, d-g

a, R = H; d, R = 4-Cl; e, R = 4-CH_3; f, R = 4-CH_3O; g, R = 3,5-diCH_3O

In conclusion, the sydnone dilithiation/iodination approach[7] has been extended and modified for the preparation of a number of aryl substituted diiodosydnones **2a**–**g**. Selective deiodination of the latter (to yield the *ortho*-iodo species **3a**–**g**) may be achieved in high yields under mild conditions. A novel, complete deiodination of **2a,d**–**g** to **1a,d–g** has been developed.

Experimental Section

3-Phenylsydnone (**1a**) was synthesized from *N*-phenylglycine using a literature procedure.[8] The other starting sydnones, 3-(4-bromophenyl)sydnone (**1b**),[9] 3-(3-chlorophenyl) sydnone (**1c**),[10] 3-(4-chlorophenyl)sydnone (**1d**),[11] 3-(4-tolyl)sydnone (**1e**),[11] 3-(4-methoxyphenyl)-sydnone (**1f**)[12] and 3-(3,5-dimethoxyphenyl)sydnone (**1g**)[13] were prepared according to the reported procedure.[13] 4-Iodo-3-(2-iodophenyl)sydnone (**2a**) was prepared from 3-phenylsydnone.[7] All other starting materials and reagents were purchased commercially and used without purification unless otherwise noted. Melting points were determined on a Mel-Temp melting point device and are uncorrected. The infrared spectra were taken as KBr pellets on a Nicolet 6700 FTIR. NMR spectra were obtained on a Bruker Avance 300 MHz NMR and are reported relative to tetramethylsilane (TMS) as an internal standard. Elemental analyses were carried out by Midwest Microlab LLC, Indianapolis, IN 46250.

3-(4-Bromo-2-iodophenyl)-4-iodosydnone (2b)

To a stirred solution of 3-(4-bromophenyl)sydnone (**1b**, [0.10 g, 0.42 mmol]) in dry THF (40 mL) under an atmosphere of dry nitrogen at −40°C LDA (1.07 M, 1.00 mL, 1.00 mmol) was added dropwise. After 0.5 h, iodine (0.224 g, 0.88 mmol) was added in one portion and, after an additional 2.0 h, the mixture was allowed to warm to 0°C whereupon it was quenched with saturated brine (70 mL) then extracted with CH_2Cl_2 (2 × 50 mL). The combined layers were washed with aqueous sodium sulfite (5%, 2 × 50 mL), dried ($MgSO_4$) and evaporated *in vacuo* to yield an oil, which was purified by column chromatography (SiO_2, CH_2Cl_2 as eluent) to afford **2b** as colorless crystals (0.071 g, 35%), mp. 170–172°C. IR: 1745, 1726 (sydnone C=O), 1566, 1471 cm^{-1}. ^1H-NMR (DMSO-d_6): δ 8.46 (s, 1 H), 7.99 (d, 1 H), 7.82 (d, 1 H). ^{13}C-NMR (DMSO-d_6): δ 168.77 (sydnone C=O), 141.71, 137.26, 133.02, 129.41, 126.64, 97.79, 59.70 (sydnone C-4).

Anal. Calcd. for $C_8H_3BrI_2N_2O_2$: C, 19.50; H, 0.61; N, 5.68. Found: C, 19.39; H, 0.56; N, 5.45.

3-(3-Chloro-2-iodophenyl)-4-iodosydnone (2c)

To a stirred solution of 3-(3-chlorophenyl)sydnone **1c** [0.20 g, 1.02 mmol] in dry THF (30 mL) under an atmosphere of dry nitrogen at −78°C was added LDA (1.50 mL, 1.49 M, 2.24 mmol) dropwise. After 0.5 h, iodine (0.568 g, 2.24 mmol) was added and, after 3 h in total, the reaction was warmed to 0°C, quenched with saturated brine (70 mL) then extracted with CH_2Cl_2 (2 × 50 mL). The combined layers were dried ($MgSO_4$) and evaporated *in vacuo* to yield an oil, which afforded light yellow crystals upon trituration with diethyl ether. Further purification by column chromatography (SiO_2, CH_2Cl_2 as eluent) gave **2c** as colorless crystals (0.343 g, 75%), mp. 156–157°C. IR: 1722 (sydnone C=O), 1455, 1192 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 7.80 (m, 2 H), 7.99 (d, 1 H). ^{13}C-NMR (DMSO-d_6): δ 169.55 (sydnone C = O), 102.99, 47.05 (arom C), 140.58, 133.60, 131.91, 127.32 (arom C-H), 60.81 (sydnone C-4).

Anal. Calcd. for $C_8H_3ClI_2N_2O_2$: C, 21.44; H, 0.67; N, 6.25. Found: C, 21.53; H, 0.65; N, 6.05.

3-(4-Chloro-2-iodophenyl)-4-iodosydnone (2d)

To a stirred solution of 3-(4-chlorophenyl)sydnone (**1d**) [0.10 g, 0.51 mmol) in dry THF (50mL) under an atmosphere of dry nitrogen at −78°C was added ^{n}BuLi (1.6 M in hexane, 1.1 mL, 1.71 mmol) dropwise. After an additional 1 h, iodine (0.324 g, 1.28 mmol) was added in one portion. The reaction was left overnight after which time the contents were poured into saturated brine (100 mL) and, after the residual THF had evaporated, the mixture was extracted with dichloromethane (3 × 50 mL). The combined layers were washed with aqueous sodium sulfite (50 mL, 5%), dried ($MgSO_4$), filtered and evaporated *in vacuo* to yield an oil which was subjected to column chromatography (SiO_2, dichloromethane as eluent) and recrystallized from dichloromethane / hexanes to yield **2d** as colorless crystals (0.122 g, 54%), mp.145–146°C. IR: 2915, 1714 (C=O), 1589 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 8.03 (s, 1 H), 7.55 (d, 1 H), 7.31 (d, 1 H). ^{13}C-NMR ($CDCl_3$): δ 168.38 (sydnone C=O), 140.28, 139.45, 136.65, 130.13, 128.16, 94.51, 52.96 (sydnone C-4).

Anal. Calcd. for $C_8H_3ClI_2N_2O_2$: C, 21.44; H, 0.67; N, 6.25. Found: C, 21.39; H, 0.76; N, 5.94.

4-Iodo-3-(2-iodo-4-methylphenyl)sydnone (2e)

To a stirred solution of 3-(4-methylphenyl)sydnone (**1e**) [0.10 g, 0.57 mmol] in dry THF (50 mL) under an atmosphere of dry nitrogen at −78°C was added ^{n}BuLi (1.6 M in hexane, 1.2 mL, 1.94 mmol) dropwise. After 1 h, iodine (dried over P_2O_5, 0.324 g, 1.28 mmol) was added. After an additional 12 h, during which time the mixture was allowed to warm to room temperature, the mixture was poured into saturated brine (100 mL) and, after the residual THF had evaporated, the mixture was extracted with dichloromethane (3 ×100 mL). The combined layers were washed with aqueous sodium sulfite (50 mL, 5%), dried ($MgSO_4$), filtered and evaporated *in vacuo* to yield an oil, which upon crystallization from dichloromethane / hexanes afforded **2e** as colorless crystals (0.182 g, 75%), mp.188–190°C. IR: 2922, 1708 (sydnone C=O), 1570, 1474 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.89 (s, 1 H), 7.43 (d, 1 H), 7.23 (d, 1 H), 2.40 (s, 3 H). ^{13}C-NMR

($CDCl_3$): δ 168.60 (sydnone C = O), 144.84, 141.06, 130.43, 127.01, 124.79, 93.51, 53.03 (sydnone C-4), 21.04.

Anal. Calcd. for $C_9H_6I_2N_2O_2$: C, 25.26; H, 1.41; N, 6.55. Found: C, 25.56; H, 1.66; N, 6.34.

4-Iodo-3-(2-iodo-4-methoxyphenyl)sydnone (2f)

To a stirred solution of 3-(4-methoxyphenyl)sydnone (**1f**) [0.15 g, 0.77 mmol] in dry THF (50 mL) under an atmosphere of dry nitrogen at −45°C was added ^{n}BuLi (1.6 M in hexane, 1.5 mL, 2.31 mmol) dropwise. After 0.5 h, iodine (dried over P_2O_5, 0.586 g, 2.31 mmol) was added. After an additional 1 h, the mixture was allowed to warm to 0°C whereupon it was quenched with saturated brine (50 mL) then extracted with CH_2Cl_2 (3 × 40 mL). The combined layers were washed with aqueous sodium sulfite (200 mL, 5%), dried ($MgSO_4$), filtered and evaporated *in vacuo* to yield an oil, which was purified by column chromato-graphy (SiO_2, CH_2Cl_2 as eluent). Recrystallization from dichloromethane / hexane afforded **2f** as colorless crystals (0.304 g, 88%), mp. 128–130°C. IR: 2916, 1745 (sydnone C=O), 1589, 1494 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.50 (d, 1 H), 7.30 (t, 1 H), 7.10 (d, 1 H), 3.90 (s, 3 H). ^{13}C-NMR ($CDCl_3$): δ 169.0 (sydnone C = O), 162.0, 131.0, 128.0, 122.0, 115, 94.0, 56.0, 54.0 (sydnone C-4).

Anal. Calcd. for $C_9H_6I_2N_2O_3$: C, 24.35; H, 1.36; N, 6.31. Found: C, 24.28; H, 1.40; N, 6.16.

4-Iodo-3-(2-iodo-3,5-dimethoxyphenyl)sydnone (2g)

To a stirred solution of 3-(3,5-dimethoxyphenyl)sydnone (**1g**, 0.10 g, 0.45 mmol) in dry THF (40 mL) under an atmosphere of dry nitrogen at −45 °C was added ^{n}BuLi (1.6 M in hexane, 0.8 mL, 1.35 mmol) dropwise. After 0.5 h, iodine (dried over P_2O_5, 0.343 g, 1.35 mmol) was added. After an additional 1 h, the mixture was allowed to warm to 0°C whereupon it was quenched with saturated brine (50 mL) then extracted with CH_2Cl_2 (3 × 40 mL). The combined layers were washed with aqueous sodium sulfite (150 mL, 5%), dried ($MgSO_4$) and evaporated *in vacuo* to yield an oil, which was purified by column chromatography (SiO_2, CH_2Cl_2 as eluent). Recrystallization from dichloromethane / hexane afforded **2g** as colorless crystals (0.183g, 86%), mp. 231–233°C. IR: 1738 (sydnone C=O), 1576, 1452 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 6.90 (d, 1 H), 7.20 (d, 1 H), 4.00 (s, 3 H), 3.90 (s, 3 H). ^{13}C-NMR (DMSO-d_6): δ 169.0 (sydnone C=O), 161.0, 160.0, 139.0, 106.0, 102.0, 77.0, 59.0 (sydnone C-4), 57.0, 56.0.

Anal. Calcd. for $C_{10}H_8I_2N_2O_4$: C, 25.34; H, 1.70; N, 5.91. Found: C, 25.44; H, 1.59; N, 5.79.

Reaction of Diiodosydnones 2b–g with Sodium Sulfite. General Procedure

To a solution of diiodinated sydnone (0.12–0.45 mmol) in methanol (2–4 mL) was added a solution of sodium sulfite (0.06–0.23 g, 0.48–1.8 mmol) in water (2–4 mL). The progress of the reaction was monitored by TLC and after all the starting material had reacted (usually 0.5 h to 1 h), the methanol was removed under a stream of air. The residual aqueous suspension was extracted with dichloromethane (3×10 mL) and the combined extract was washed with water (50 mL), dried over magnesium sulfate and evaporated *in vacuo*. The crude products were then purified, either by column chromatography (SiO_2, dichlorometha-ne/hexanes) or recrystallization from dichloromethane/hexanes.

3-(4-Bromo-2-iodophenyl)sydnone (3b)

3-(4-Bromo-2-iodophenyl)-4-iodosydnone (**2b**, 0.10 g, 0.20 mmol) using the general procedure gave, after recrystallization, **3b** as colorless crystals (0.055 g, 75%), mp. 183–184°C. IR: 1726 (sydnone C=O), 1576, 1483 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$): δ 8.40 (s, 1 H), 7.94 (d, 1 H), 7.82 (d, 1 H), 7.58 (s, 1 H). ^{13}C-NMR (DMSO-d$_6$): δ 168.2 (sydnone C=O), 141.7, 136.9, 132.7, 128.7, 126.3, 98.9 (sydnone C-4), 96.4.

Anal. Calcd. for $C_8H_4BrIN_2O_2$: C, 26.19; H, 1.10; N, 7.63. Found: C, 25.99; H, 1.14; N, 7.35.

3-(3-Chloro-2-iodophenyl)sydnone (3c)

3-(3-Chloro-2-iodophenyl)-4-iodosydnone (**2c**, 0.20 g, 0.45 mmol) using the general procedure afforded, after recrystallization, **3c** as colorless crystals (0.135 g, 93%), mp. 237–239°C. IR: 1749 (sydnone C=O), 1562, 1475 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.77 (d, 1 H), 7.57 (t, 1 H), 7.42 (d, 1 H), 6.58 (s, 1 H). ^{13}C-NMR (CDCl$_3$): δ 168.5 (sydnone C=O), 141.9, 139.6, 132.8, 130.3, 124.9, 98.8, 97.7 (sydnone C-4).

Anal. Calcd. for $C_8H_4ClIN_2O_2$: C, 29.80; H, 1.25; N, 8.69. Found: C, 29.74; H, 1.25; N, 8.62.

3-(4-Chloro-2-iodophenyl)sydnone (3d)

3-(4-Chloro-2-iodophenyl)-4-iodosydnone (**2d**, 0.112 g, 0.25 mmol) using the general procedure yielded, after recrystallization, **3d** as colorless crystals (0.07 g, 87%), mp. 179–181°C. IR: 3139, 1727 (sydnone C=O), 1573, 1433 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$): δ 8.28 (s, 1 H), 7.94 (d, 1 H), 7.81 (d, 1 H), 7.58 (s, 1 H). ^{13}C-NMR (DMSO-d$_6$): δ 168.2 (sydnone C=O), 139.1, 137.5, 136.5, 129.7, 128.4, 98.9 (sydnone C-4), 96.1.

Anal. Calcd. for $C_8H_4ClIN_2O_2$: C, 29.80; H, 1.25; N, 8.69. Found: C, 29.82; H, 1.32; N, 8.44.

3-(2-Iodo-4-methylphenyl)sydnone (3e)

4-Iodo-3-(2-iodo-4-methylphenyl)sydnone (**2e**, 0.05 g, 0.12 mmol) using the general procedure gave, after column chromatography, **3e** as colorless crystals (0.03 g, 85%), mp. 134–135°C. IR: 3137, 1730 (sydnone C=O), 1590, 1447 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.87 (s, 1 H), 7.38 (d, 2 H), 7.28 (d, 2 H), 6.52 (s, 1 H), 2.45 (s, 3 H). ^{13}C-NMR (CDCl$_3$): δ 168.7 (sydnone C=O), 144.6, 141.3, 130.4, 127.0, 126.3, 97.7 (sydnone C-4), 91.6, 21.0.

Anal. Calcd. for $C_9H_7IN_2O_2$: C, 35.79; H, 2.34; N, 9.27. Found: C, 35.47; H, 2.60; N, 9.53.

3-(2-Iodo-4-methoxyphenyl)sydnone (3f)

4-Iodo-3-(2-iodo-4-methoxyphenyl)sydnone (**2f**, 0.056 g, 0.13 mmol) using the general procedure afforded, after recrystallization, **3f** as colorless crystals (0.036 g, 95%), mp. 139–141°C. IR: 3150, 1753 (sydnone C=O), 1490, 1365 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.5 (d, 1 H), 7.4 (d, 1 H), 7.1 (d, 1 H), 6.5 (s, 1 H), 3.9 (s, 3 H). ^{13}C-NMR (CDCl$_3$): δ 169 (sydnone C=O), 162, 131, 127, 126, 115, 98 (sydnone C-4), 92, 56.

Anal. Calcd. for $C_9H_7IN_2O_3$: C, 33.99; H, 2.22; N, 8.81. Found: C, 34.05; H, 2.16; N, 8.79.

3-(2-Iodo-3,5-dimethoxyphenyl)sydnone (3g)

4-Iodo-3-(2-iodo-3,5-dimethoxyphenyl)sydnone (**2g**, 0.145 g, 0.30 mmol) using the general procedure yielded, after recrystallization, **3g** as colorless crystals (0.095 g, 91%), mp. 194–196°C. IR: 3145, 1597, 1454, 1327 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$): δ 7.5 (s, 1 H), 7.2 (s, 1 H), 7.1 (s, 1 H), 3.9 (s, 3 H), 3.8 (s, 3 H). ^{13}C-NMR (DMSO-d$_6$): δ 168 (sydnone C=O), 161, 160, 139, 105, 102, 96 (sydnone C-4), 76, 57, 56.

Anal. Calcd. for $C_{10}H_9IN_2O_4$: C, 34.50; H, 2.61; N, 8.05. Found: C, 34.44; H, 2.60; N, 7.88.

Reaction of Diiodosydnones 2a,d–g with Sodium Borohydride. General Procedure

To a stirred solution of the diiodinated sydnone **2a,d–g** (0.11–0.36 mmol) in methanol (1–3 mL) was added sodium borohydride (0.042–0.136 g, 1.1–3.6 mmol) in three portions over 15 min. The progress of the reaction was monitored by TLC and after all the starting material had reacted (usually <0.5 h), methanol was removed under a stream of air. The residue was treated with water (2–4 mL) and the resultant precipitate was collected *in vacuo* and dried to yield the nearly pure products **1a,d–g**.

3-Phenylsydnone (1a)

4-Iodo-3-(2-iodophenyl)sydnone (**2a**, 0.150 g, 0.362 mmol) using the general procedure afforded **1a** as colorless crystals (0.043 g, 73%), identical to an authentic sample.

3-(4-Chlorophenyl)sydnone (1d)

3-(4-Chloro-2-iodophenyl)-4-iodosydnone (**2d**, 0.104 g, 0.23 mmol) using the general procedure yielded **1d** as colorless crystals (0.039 g, 86%), identical to an authentic sample.

3-(4-Methylphenyl)sydnone (1e)

4-Iodo-3-(2-iodo-4-methylphenyl)sydnone (**2e**, 0.05 g, 0.117 mmol) using the general procedure gave **1e** as colorless crystals (0.018 g, 87%), identical to an authentic sample.

3-(4-Methoxyphenyl)sydnone (1f)

4-Iodo-3-(2-iodo-4-methoxyphenyl)sydnone (**2f**, 0.05 g, 0.11 mmol) using the general procedure yielded **1f** as colorless crystals (0.02 g, 92%), identical to an authentic sample.

3-(3,5-Dimethoxyphenyl)sydnone (1g)

Treatment of 4-iodo-3-(2-iodo-3,5-dimethoxyphenyl)sydnone (**2g**, 0.143 g, 0.30 mmol) using the general procedure led to **1g** as colorless crystals (0.062 g, 92%), identical to an authentic sample.

References

1. W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, 307 (**1949**).
2. D. L. Browne and J. P. A. Harrity, *Tetrahedron*, **66**, 553 (2010) and *loc. cit.*
3. K. Turnbull, *Synthesis*, 334 (**1986**).
4. K. Turnbull and M. Saljoughian, *Synth. Commun.*, **16**, 461 (1986).
5. K. L. McChord, S. A. Tullis and K. Turnbull, *Synth. Commun.*, **19**, 2249 (1989).
6. A. J. Weisner, T. M. Cooper and K.Turnbull, *Synth. Commun.*, **35**, 639 (2005).
7. K. Turnbull and D. M. Krein, *Tetrahedron Lett.*, **38**, 1165 (1997).
8. J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (**1935**).
9. R. A. Eade and J. C. Earl, *J. Chem. Soc.*, 2307 (**1948**).
10. Y. Ogata, A. Kawasaki and H. Kojoh, *J. Org. Chem.*, **39**, 3676 (1974).
11. W. Baker, W. D. Ollis, V. D. Poole, J. A. Barltrop, R. A. W. Hill and L. E. Sutton, *Nature*, **160**, 366 (1947).
12. R. A. Eade and J. C. Earl, *J. Chem. Soc.*, 591 (**1946**).
13. K. Turnbull, *J. Heterocycl. Chem.*, **22**, 965 (1985).