Synthesis and catalysed hydroboration of styryl sulfonamides[1]

Natalie A. Wynberg, Lisa J. Leger, Maren L. Conrad, Christopher M. Vogels, Andreas Decken, Stephen J. Duffy, and Stephen A. Westcott

Abstract: We have prepared the aryl sulfonamides 4,4′-R-$C_6H_4SO_2NHC_6H_4CH{=}CH_2$ (R = CH_3, **1a**; NO_2, **1b**) by addition of 2 equiv. of 4-vinylaniline to the corresponding sulfonyl chlorides. The disulfonamides 4,4,4′-(R-$C_6H_4SO_2)_2$-$NC_6H_4CH{=}CH_2$ (R = CH_3, **2a**; NO_2, **2b**) were also prepared using 4-vinylaniline and 2 equiv. of the sulfonyl chlorides in the presence of DMAP. Although hydroborations of sulfanilamide derivatives **1** suffered from competing hydrogenation reactions, judicious choice of the transition metal catalyst gave selective formation of either the primary or secondary boronate esters in hydroborations of **2a**.

Key words: boronate esters, catalysed hydroborations, sulfanilamides, vinylaniline.

Résumé : On a préparé les aryl sulfonamides, 4,4′-R-$C_6H_4SO_2NHC_6H_4CH{=}CH_2$ (R = CH_3, **1a**; NO_2, **1b**) par l'addition de deux équivalents de 4-vinylaniline aux chlorures de sulfonyle correspondants. On a aussi préparé les disulfonamides 4,4,4′-(R-$C_6H_4SO_2)_2NC_6H_4CH{=}CH_2$ (R = CH_3, **2a**; NO_2, **2b**) à partir de la 4-vinylaniline et de deux équivalents de chlorures de sulfonyle, en présence de DMAP. Quoique les réactions d'hydroboration des dérivés sulfanilamides **1** soient en compétition avec les réactions d'hydrogénation, un choix judicieux d'un catalyseur à base d'un métal de transition permet d'obtenir la formation sélective des boronates soit primaires ou secondaires lors des hydroborations du composé **2a**.

Mots clés : esters de l'acide boronique, hydroborations catalysées, sulfanilamides, vinylaniline.

[Traduit par la Rédaction]

Introduction

The hydroboration of alkenes and alkynes, which constitutes the addition of a B—H bond across a carbon—carbon multiple bond, is a remarkably important reaction in organic synthesis (1). Although simple boron hydride reagents such as borane ($H_3B{\cdot}X$, where X is a Lewis base) and 9-borabicyclo[3.3.1]nonane react readily with alkenes at room temperature, hydroborations with catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$) generally require elevated temperatures. The discovery that transition metals can be used to catalyse the addition of HBcat to substrates has become an important and well-established technique in organic synthesis (2–6). These reactions can have regio-, chemo-, or stereoselectivities complementary, or more remarkably, opposite to those from products obtained via the uncatalysed variant. For example, hydroborations of styrenes ($ArCH{=}CH_2$) with HBcat proceed to give selectively either the expected primary boronate ester ($ArCH_2CH_2Bcat$) or the secondary boronate ester ($ArCH(Bcat)CH_3$), depending upon the choice of catalyst used to affect this transformation (Scheme 1) (3). Rhodium-catalysed hydroborations are the most common and synthetically useful of these reactions. They are believed to proceed via initial oxidative addition of HBcat (7), followed by coordination of the alkene to the metal centre with subsequent insertion of the alkene into either the Rh—H (8) or the Rh—B bond (9) and reductive elimination to yield the desired product (10). The unusual secondary boronate ester product is believed to arise when the metal centre can best stabilize a benzylic intermediate during the catalytic cycle.

Although a considerable amount of research has focused on the catalysed hydroboration of simple unsaturated hydrocarbon systems, much less is known about analogous reactions with heteroatom-containing substrates (3, 11–17). For instance, catalysed hydroborations of pyrrolidinyl amides with HBcat gave, after oxidation, *syn* 1,3-hydroxy amides with high levels of regio- and stereochemical control (18). The remarkable selectivities observed in these reactions are believed to arise from a directing effect of the amide moiety. As part of our ongoing investigation into generating biologically active boron compounds (19) and, in an effort to expand the scope of metal-catalysed hydroborations, we de-

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Dedicated to Professor Howard Alper in recognition of his outstanding contributions in catalysis.

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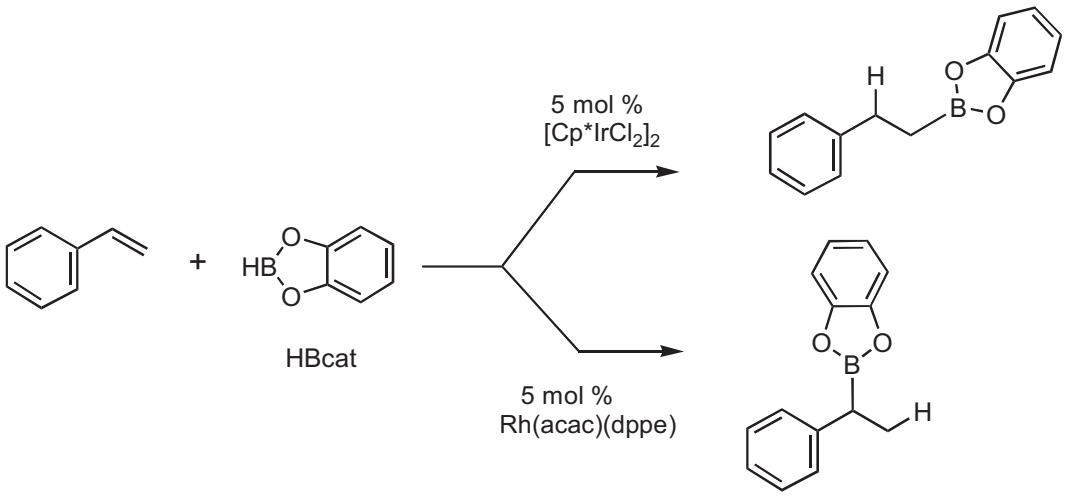
Scheme 1.



cided to examine the synthesis and hydroboration of sulfanilamide derivatives containing a pendant styryl moiety. Initial results are presented herein.

Experimental

Materials and methods

Reagents and solvents used were obtained from Aldrich Chemicals. $RhCl(PPh_3)_3$ (20), $Rh(acac)(coe)_2$ (21), and $[Cp^*IrCl_2]_2$ (22) were prepared as described elsewhere. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR spectrometer. ^{1}H NMR chemical shifts are reported in parts per million (ppm) and are referenced to residual protons in deuterated solvent at 270 MHz. ^{11}B NMR chemical shifts are referenced to external $BF_3{\cdot}OEt_2$ at 87 MHz. ^{13}C NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), and overlapping (ov). Infrared spectra were obtained using a Mattson Genesis II FT-IR spectrometer and are reported in cm^{-1}. Melting points were measured uncorrected with a Mel-Temp apparatus. GC-MS analyses were conducted using a Varian Saturn 2000 GC/MS/MS coupled to a CP-3800 GC. The GC was equipped with both the 1177 injection port with a CP-8410 liquid autoinjector connected to an SPB-1 (Supelco) fused silica column (30 m × 0.25 mm i.d. × 0.25 μm) and the 1079 solid injector chromatoprobe, attached to a 50 cm transfer line. The GC-MS spectrometer is controlled by the Saturn Workstation software, Version 5.51.

Synthesis

General synthesis of 1a and 1b

Under an atmosphere of dinitrogen, an Et_2O (2 mL) solution of 4-vinylaniline (2 equiv.) was added dropwise to a stirred Et_2O (5 mL) solution of the appropriate sulfonyl chloride. The mixture was allowed to stir for 18 h, at which point the resulting solid was removed by filtration and the filtrate stored at –30 °C for 2 days. Any subsequent precipitate was also removed by filtration and discarded. Compounds **1a** and **1b** were recovered upon removal of solvent under vacuum and washed with hexane (3 × 3 mL).

Compound 1a

Yield: 70%, mp 80–82 °C. ^{1}H NMR ($CDCl_3$) δ: 7.65 (d, J = 8 Hz, 2H, Ar), 7.26 (d, J = 8 Hz, 2H, Ar), 7.21 (d, J = 8 Hz, 2H, Ar), 7.01 (d, J = 8 Hz, 2H, Ar), 6.76 (br s, 1H, N*H*), 6.60 (d of d, J = 18, 10 Hz, 1H, C*H*=CH_2), 5.64 (d, J = 18 Hz, 1H, CH=C*H*H), 5.18 (d, J = 10 Hz, 1H, CH=CH*H*), 2.36 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 144.0, 136.1, 136.0, 135.9, 134.9, 129.7, 127.3, 127.2, 121.7, 113.8, 21.6. IR (Nujol): 3271, 2943, 2922, 1597, 1508, 1392, 1333, 1159, 1090, 906, 814, 681, 492. EI-MS *m*/*z* (relative intensity): 273 (73, $[M]^+$), 155 (5), 118 (100), 91 (58).

Compound 1b

Yield: 60%, mp 182–184 °C. ^{1}H NMR (DMSO-d_6) δ: 10.68 (br s, 1H, N*H*), 8.37 (d, J = 8 Hz, 2H, Ar), 7.99 (d, J = 8 Hz, 2H, Ar), 7.36 (d, J = 8 Hz, 2H, Ar), 7.08 (d, J = 8 Hz, 2H, Ar), 6.58 (d of d, J = 18, 10 Hz, 1H, C*H*=CH_2), 5.71 (d, J = 18 Hz, 1H, CH=C*H*H), 5.17 (d, J = 10 Hz, 1H, CH=CH*H*). ^{13}C NMR (DMSO-d_6) δ: 150.4, 145.4, 137.0, 136.3, 134.3, 128.8, 127.7, 125.2, 121.2, 114.4. IR (Nujol): 3224, 2935, 2912, 1606, 1527, 1348, 1165, 1086, 924, 854, 735, 604, 542. EI-MS *m*/*z* (relative intensity): 304 (41, $[M]^+$), 118 (100).

Reaction of 1a with 1 equiv. of HBcat in the presence of $RhCl(PPh_3)_3$

Under an atmosphere of dinitrogen, a 0.5 mL C_6D_6 solution of HBcat (1 equiv.) was added to a mixture of **1a** and $RhCl(PPh_3)_3$ (0.05 equiv.) in 0.5 mL of C_6D_6. The reaction was allowed to proceed for 4 h, at which point NMR spectroscopic data was collected. ^{1}H NMR δ: 7.92 (d, J = 8 Hz, 2H, Ar), 7.00 (d, J = 8 Hz, 2H, Ar), 6.96–6.82 (ov m, 4H, Ar and Bcat), 6.70–6.64 (ov m, 4H, Ar and Bcat), 2.31 (q, J = 8 Hz, 2H, CH_2CH_3), 1.82 (s, 3H, CH_3), 0.94 (t, J = 8 Hz, 3H, CH_2CH_3). ^{11}B NMR δ: 24.8 ($ArSO_2N(Bcat)CH_2CH_3$).

Reaction of 1b with 1 equiv. of HBcat in the presence of $RhCl(PPh_3)_3$

Under an atmosphere of dinitrogen, a 0.5 mL $CDCl_3$ solu-

tion of HBcat (1 equiv.) was added to a suspension of **1b** and $RhCl(PPh_3)_3$ (0.05 equiv.) in 0.5 mL of $CDCl_3$. The reaction was allowed to proceed for 18 h, at which point spectroscopic NMR data of the resulting hydrogenation product ($ArN(Bcat)CH_2CH_3$, 98% by NMR spectroscopy) was collected. ^{1}H NMR δ: 8.21 (d, *J* = 8 Hz, 2H, Ar), 7.93 (d, *J* = 8 Hz, 2H, Ar), 7.24–7.04 (ov m, 8H, Ar and Bcat), 2.56 (q, *J* = 8 Hz, 2H, CH_2CH_3), 1.16 (t, *J* = 8 Hz, 3H, CH_2CH_3). ^{11}B NMR δ: 24.5 ($ArN(Bcat)CH_2CH_3$).

General synthesis of 2a and 2b

Under an atmosphere of dinitrogen, a toluene (2 mL) solution of 4-vinylaniline was added dropwise to a stirred toluene (5 mL) mixture of the appropriate sulfonyl chloride (2.5 equiv.) and 4-DMAP (2.5 equiv.). The mixture was heated at reflux for 2 days, at which point solvent was removed under vacuum, and the resultant white solid was washed with Et_2O (3 × 5 mL). The filtrate was collected, and the Et_2O was removed under vacuum. The resulting solid was then washed with EtOH (4 × 5 mL) to afford **2**.

Compound 2a

Yield: 70%, mp 176–178 °C. ^{1}H NMR ($CDCl_3$) δ: 7.81 (d, *J* = 8 Hz, 4H, Ar), 7.36 (d, *J* = 8 Hz, 2H, Ar), 7.32 (d, *J* = 8 Hz, 4H, Ar), 6.97 (d, *J* = 8 Hz, 2H, Ar), 6.69 (d of d, *J* = 18, 10 Hz, 1H, CH=CH_2), 5.77 (d, *J* = 18 Hz, 1H, CH=C*H*H), 5.33 (d, *J* = 10 Hz, 1H, CH=CH*H*), 2.45 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 145.1, 139.5, 136.7, 135.8, 133.6, 131.7, 129.7, 128.7, 127.0, 116.1, 21.8. IR (Nujol): 2970, 2951, 1595, 1462, 1377, 1167, 908, 806, 661, 550, 488. EI-MS *m*/*z* (relative intensity): 427 (98, $[M]^+$), 272 (53), 208 (100), 155 (13), 118 (16), 91 (20).

Compound 2b

Yield: 55%, mp 274 to 275 °C. ^{1}H NMR (DMSO-d_6) δ: 8.51 (d, *J* = 8 Hz, 4H, Ar), 8.12 (d, *J* = 8 Hz, 4H, Ar), 7.59 (d, *J* = 8 Hz, 2H, Ar), 7.10 (d, *J* = 8 Hz, 2H, Ar), 6.80 (d of d, *J* = 18, 10 Hz, 1H, CH=CH_2), 5.96 (d, *J* = 18 Hz, 1H, CH=C*H*H), 5.42 (d, *J* = 10 Hz, 1H, CH=CH*H*). ^{13}C NMR (DMSO-d_6) δ: 151.5, 143.6, 140.3, 135.8, 132.2, 132.1, 130.4, 128.1, 125.6, 117.9. IR (Nujol): 2935, 2902, 2863, 1710, 1531, 1462, 1377, 1169, 1082, 960, 920, 852, 733, 642, 602, 552. EI-MS *m*/*z* (relative intensity): 489 (2, $[M]^+$), 304 (57), 273 (3), 118 (100).

General procedure for the hydroboration of compounds 3 and 4

Under an atmosphere of dinitrogen, 1 equiv. of catecholborane in 0.5 mL of $CDCl_3$ was added to a 0.5 mL $CDCl_3$ solution of the appropriate catalyst and substrate. The reactions were allowed to proceed for 18 h, at which point NMR data were collected. Compounds **3** and **4** were isolated by recrystallization from a solution of $CDCl_3$:hexane (1:2) stored at –30 °C.

Compound 3

^{1}H NMR ($CDCl_3$) δ: 7.79 (d, *J* = 8 Hz, 4H, Ar), 7.29 (d, *J* = 8 Hz, 4H, Ar), 7.25–7.20 (ov m, 4H, Ar and Bcat), 7.08 (2nd order m, 2H, Bcat), 6.92 (d, *J* = 8 Hz, 2H, Ar), 2.99 (t, *J* = 8 Hz, 2H, CH_2CH_2Bcat), 2.44 (s, 6H, CH_3), 1.66 (t, *J* = 8 Hz, 2H, CH_2CH_2Bcat). ^{13}C NMR ($CDCl_3$) δ: 148.2, 146.0, 145.0, 136.8, 132.2, 131.5, 129.6, 128.8, 128.7, 122.7, 112.4, 29.4, 21.8, 12.1 (br, *C*-B). ^{11}B NMR ($CDCl_3$) δ: 34.8. EI-MS *m*/*z* (relative intensity): 547 (12, $[M]^+$), 429 (100), 273 (68), 155 (8), 118 (33).

Compound 4

^{1}H NMR ($CDCl_3$) δ: 7.81 (d, *J* = 8 Hz, 4H, Ar), 7.31 (d, *J* = 8 Hz, 4H, Ar), 7.30 (d, *J* = 8 Hz, 2H, Ar), 7.22 (2nd order m, 2H, Bcat), 7.09 (2nd order m, 2H, Bcat), 6.96 (d, *J* = 8 Hz, 2H, Ar), 3.01 (q, *J* = 8 Hz, 1H, $CH(Bcat)CH_3$), 2.45 (s, 6H, CH_3), 1.58 (d, *J* = 8 Hz, 3H, $CH(Bcat)CH_3$). ^{13}C NMR ($CDCl_3$) δ: 148.2, 145.7, 145.0, 136.9, 132.0, 131.6, 129.6, 128.7, 128.6, 122.9, 112.6, 24.8 (br, *C*-B), 21.8, 16.6. ^{11}B NMR ($CDCl_3$) δ: 34.1. EI-MS *m*/*z* (relative intensity): 547 (2, $[M]^+$), 428 (18), 246 (100), 155 (8), 118 (16).

X-ray data

Crystals of **3** were grown by slow evaporation using $CHCl_3$ at –30 °C. Crystals were coated with Paratone-N oil, mounted using a glass fibre, and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and with 90 s exposure times. The detector distance was 6 cm. The crystal was twinned, and the orientation matrixes for two components were determined (23, 24), and the data were reduced (25). The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL) (26) using all reflections. One of the ethyl linkages was disordered, and the site occupancy was determined using an isotropic model as 0.7 (C(41)—C(42)) and 0.3 (C(41′)—C(42′)) and was fixed in subsequent refinement cycles. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model.

Results and discussion

N-Aryl sulfonamides are an important class of compounds, particularly in pharmaceutical research (27), where a number of these compounds have been reported to act as class III antiarrhythmic agents (28), non-nucleotide reverse transcriptase inhibitors (29), and as HIV-1 protease inhibitors (30). We have recently undertaken a study to investigate the synthesis and biological activity of novel borosulfonamides (31, 32). Interest in compounds containing boronic acids ($RB(OH)_2$) or boronate esters ($RB(OR')_2$) arises from their remarkable versatility in organic synthesis (33), as well as from their potent biological activities (34–42). For instance, the boron compounds boromycin and aplasmomycin are powerful antibiotics, and *L*-4-borono-phenylalanine has found significant application in boron neutron capture therapy for the treatment of certain cancers (43). These properties, along with their ability to transport water-insoluble reagents through membranes (44), make boronate ester compounds useful carrier ligands for biologically active compounds.

In this study, we have prepared the novel aryl sulfonamides 4,4′-R-$C_6H_4SO_2NHC_6H_4CH$=CH_2 (R = CH_3, **1a**; NO_2, **1b**) (Fig. 1) by addition of 2 equiv. of 4-vinylaniline to the corresponding sulfonyl chlorides. Varying the physical

Scheme 2.

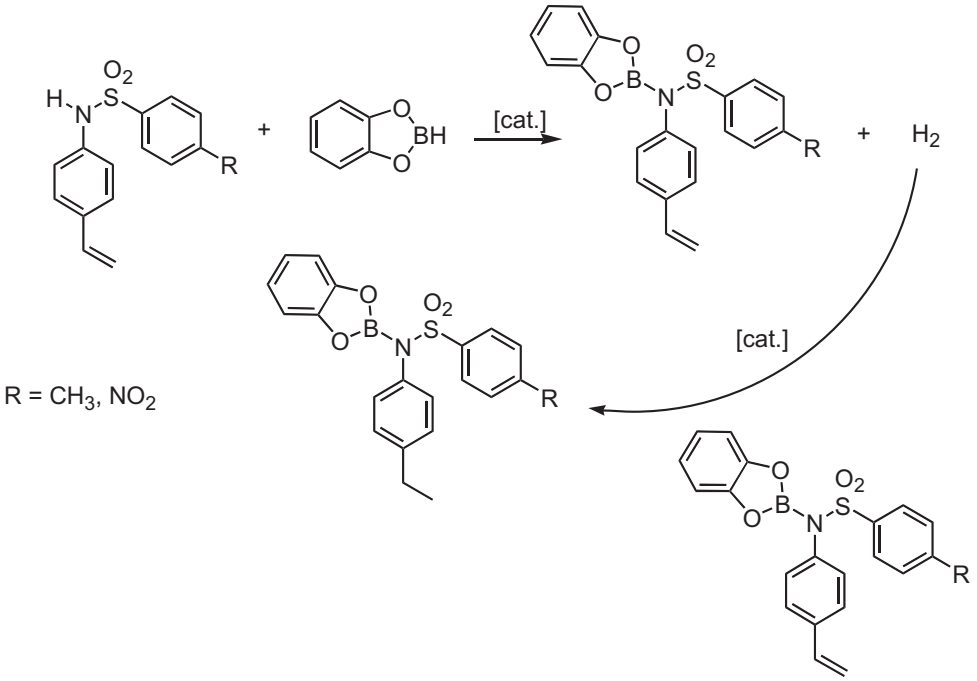
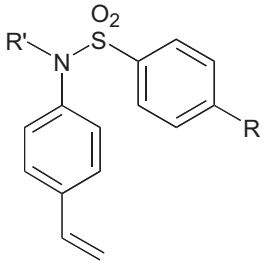


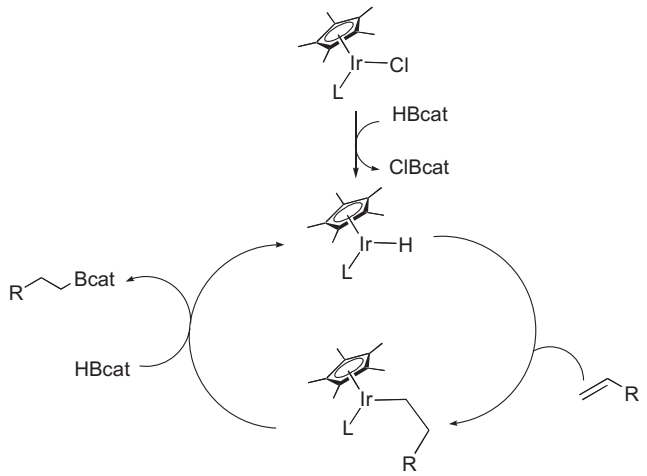
Fig. 1. Styryl sulfanilamides.



1a: R = CH_3, R' = H
1b: R = NO_2, R' = H
2a: R = CH_3, R' =4-$SO_2C_6H_4CH_3$
2b: R = NO_2, R' =4-$SO_2C_6H_4NO_2$

and electronic properties of the sulfonyl chlorides will allow for the general synthesis of a wide variety of styryl sulfanilamide derivatives. Unfortunately, we have found that metal-catalysed addition of 1.1 equiv. of HBcat to styryl sulfonamides **1a** and **1b** gave significant amounts (>95% by ^{1}H NMR spectroscopy) of hydrogenation products R-$C_6H_4SO_2N$(Bcat)$C_6H_4CH_2CH_3$ (R = CH_3 or NO_2). These products presumably arise as a result of an initial interaction of the borane with the sulfonamide N—H bond to generate a new N—Bcat bond while liberating dihydrogen, which can subsequently add to the styryl group in the presence of a catalyst (Scheme 2). Indeed, a new N—B resonance is observed in the ^{11}B NMR spectra at 25 ppm. Furthermore, reactions with excess HBcat gave a complicated mixture of products arising from competing hydrogenation and (or) hydroboration reactions, regardless of the catalyst used to affect these transformations. We therefore investigated the analogous reactions of sulfonamides **2**, which do not contain an active N—H bond.

Scheme 3.



The novel disulfonamides 4,4,4′-(R-$C_6H_4SO_2)_2NC_6H_4$-CH=CH_2 (R = CH_3, **2a**; NO_2, **2b**) could be prepared in moderate to good yields using 4-vinylaniline and 2.5 equiv. of the sulfonyl chlorides in the presence of excess DMAP. However, the introduction of a second nitrobenzene group in **2b** made this sulfonamide derivative insoluble in non-coordinating organic solvents, and as a result, hydroboration studies could not be conducted on this substrate. Addition of HBcat to **2a** using the iridium catalyst [Cp*$IrCl_2]_2$ (45) proceeded smoothly to give the expected primary boronate ester product **3** in high yields (by multinuclear NMR spectroscopy), along with minor amounts (<5%) of the corresponding hydrogenation product. A small amount of hydrogenated alkene, arising from the degradation of HBcat, is almost always observed in reactions using a late metal catalyst (46). Although it is possible that reactions using this catalyst precursor proceed via an oxidative addition mechanism, similar

Scheme 4.

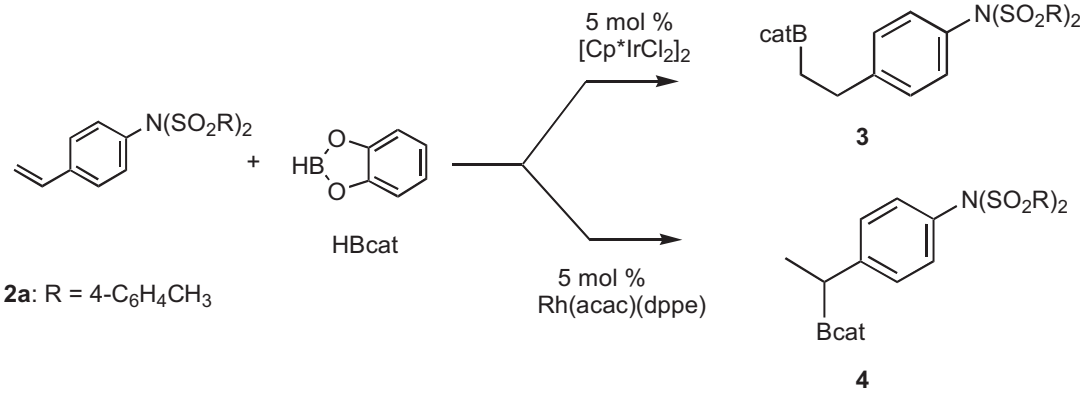
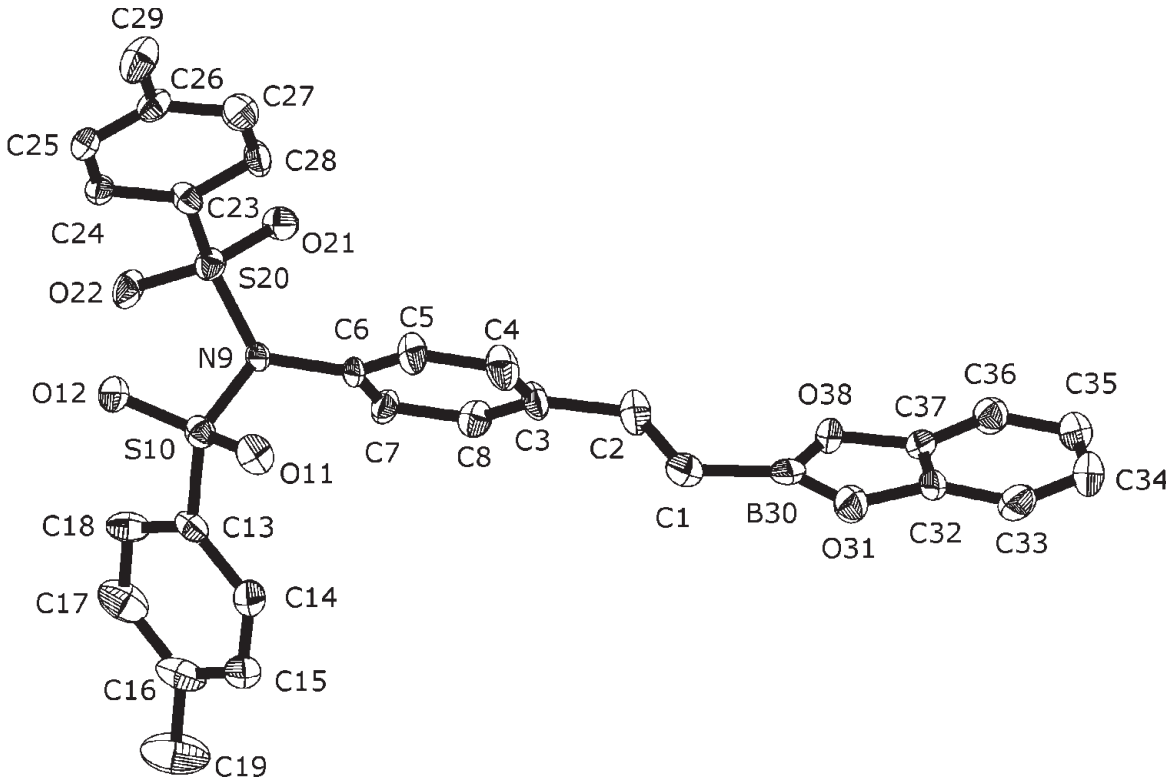


Fig. 2. Molecular structure of **3** with displacement ellipsoids drawn at the 30% probability level. Solvent molecule and hydrogen atoms omitted for clarity.



to those purported for reactions using rhodium-based catalysts, it is also possible that these reactions may be occurring via a σ-bond metathesis pathway to give **3** (Scheme 3). This reaction could proceed via initial metathesis of an Ir—Cl bond with HBcat to give a transient iridium hydride species. The formation of Ir-H species in hydroborations using HBcat has been reported previously (45). Subsequent insertion of the alkene into the Ir—H bond, followed by a σ-bond metathesis with HBcat would give the primary boronate ester while regenerating the active Ir-H catalyst. A similar mechanism has been proposed for reactions of HBcat using early metal and lanthanide catalysts (47). The iridium-catalysed hydroboration of alkenes using pinacolborane is also known to give the corresponding primary boronate ester products (48, 49).

Selective formation of the unusual secondary boronate ester **4** could be achieved in these reactions using either $RhCl(PPh_3)_3$ or Rh(acac)(dppe) (acac = acetylacetonato, dppe = 1,2-bis(diphenylphosphino)ethane) as the catalyst precursor (Scheme 4). The latter is a very active and selective catalyst precursor for a wide range of alkenes, where the resting state of the catalytically active species is the zwitterionic complex, Rh(dppe)(η^6-catBcat) (50). Compounds **3** and **4** have been characterized using a number of physical techniques, including multinuclear NMR spectroscopy. A broad peak at approximately δ 30 ppm in the ^{11}B NMR spectra is

Table 1. Crystallographic data collection parameters for **3**.

Complex	**3**
Formula	$C_{28}H_{26}BNO_6S_2 \cdot 1/2CHCl_3$
Formula mass	607.11
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.291 5(12)
b (Å)	18.403(3)
c (Å)	19.051(3)
α (°)	80.093(2)
β (°)	87.942(2)
γ (°)	84.195(2)
V (Å^3)	2 848.5(7)
Z	4
ρ_{calcd} (mg m^{-3})	1.416
Crystal size (mm^3)	0.4 × 0.075 × 0.050
Temperature (K)	173(1)
Radiation	Mo Kα (λ = 0.710 73)
μ (mm^{-1})	0.372
Total reflections	18 974
Total unique reflections	18 974
No. of variables	752
Theta range (°)	1.43–25.00
Largest difference peak and hole (e Å^{-3})	1.104 and –0.725
S (GoF) on F^2	0.835
R_1[a] ($I > 2\sigma(I)$)	0.056 9
wR_2[b] (all data)	0.143 5

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0638P)^2]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (°) for **3**.

Bond lengths (Å)	
C(1)—C(2)	1.517(5)
C(1)—B(30)	1.562(6)
N(9)—S(10)	1.687(3)
N(9)—S(20)	1.688(3)
S(10)—O(12)	1.423(2)
S(10)—O(11)	1.434(2)
S(10)—C(13)	1.752(3)
S(20)—O(21)	1.432(2)
S(20)—O(22)	1.435(2)
S(20)—C(23)	1.756(3)
B(30)—O(31)	1.389(5)
B(30)—O(38)	1.402(5)
O(31)—C(32)	1.383(4)
O(38)—C(37)	1.399(4)
Bond angles (°)	
C(6)-N(9)-S(10)	117.4(2)
C(6)-N(9)-S(20)	120.1(2)
S(10)-N(9)-S(20)	122.46(16)
O(12)-S(10)-O(11)	119.98(15)
O(12)-S(10)-N(9)	106.00(15)
O(11)-S(10)-N(9)	106.47(15)
O(12)-S(10)-C(13)	109.98(15)
O(11)-S(10)-C(13)	108.24(16)
N(9)-S(10)-C(13)	105.14(16)
O(21)-S(20)-O(22)	119.64(17)
O(21)-S(20)-N(9)	104.04(14)
O(22)-S(20)-N(9)	108.98(14)
O(21)-S(20)-C(23)	109.36(15)
O(22)-S(20)-C(23)	109.81(16)
N(9)-S(20)-C(23)	103.72(16)
O(31)-B(30)-O(38)	111.2(3)
O(31)-B(30)-C(1)	125.9(4)
O(38)-B(30)-C(1)	122.8(4)
C(32)-O(31)-B(30)	104.7(3)
C(2)-C(1)-B(30)	113.4(4)

observed for both sulfonamides, indicating that the boron atom lies in a three-coordinate C-Bcat environment (51). Compound **3** has also been characterized by a single crystal diffraction study, and the molecular structure is shown in Fig. 2;[4] crystallographic data are given in Table 1, and selected bond distances and angles are shown in Table 2. The B—O bond distances (avg. = 1.3955(5) Å) are also typical for three-coordinate Bcat groups (52–55) and are significantly shorter than those observed in chelate complexes with diphenylborinic acid (ca. 1.5 Å), where the boron atom is four coordinate (56).

In summary, we have prepared novel sulfanilamide derivatives containing styryl groups and have examined metal-catalysed hydroborations of these substrates using HBcat. Judicious choice of the catalyst precursor used to affect these transformations allows for the selective generation of either the primary or secondary boronate ester. Preliminary work has shown that these reactions are general, as analogous compounds could be obtained in metal-catalysed hydroborations of thiophene sulfonamide derivatives. Future work will investigate the potential biological activities of a wide range of novel styryl sulfonamides and the corresponding boron-containing derivatives, the results of which will be presented in due course.

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[4] Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3675. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 256413 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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