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Metal catalysed hydroboration of vinyl sulfides, sulfoxides, sulfones, and sulfonates

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Abstract

The hydroboration of phenyl vinyl sulfide with catecholborane (HBcat) and pinacolborane (HBpin) has been examined with a number of rhodium complexes, all of which proceed with excellent regiocontrol in favour of the branched product $PhSCH(B(OR)_2)CH_3$. The corresponding linear product can be obtained exclusively in reactions employing $[Cp^*IrCl_2]_2$ and HBcat. Catalysed hydroborations of (*E*)-2-(*p*-toluenethio)styrene with HBcat using Rh(acac)(dppp) gave predominant formation of one product while reactions using HBpin afforded several products arising from a competing C–S bond cleavage (acac = acetylacetonato, dppp = 1,3-bis(diphenylphosphino)propane). Although reactions of phenyl vinyl sulfoxide were complicated by a competing deoxygenation reaction, hydroborations of phenyl vinyl sulfone using HBcat once again gave regioselective formation of either the branched or linear products, depending on the choice of catalyst used to effect this transformation. Catalysed hydroborations of phenyl vinyl sulfonate were less chemo- and regioselective, yielding hydrogenation and diboration products in addition to the two hydroboration product isomers.

Keywords: Boronate esters; Catalysis; Hydroboration; Regioselectivity; Vinyl sulfides

1. 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-, and stereoselectivities that are complementary, or more remarkably, opposite to those obtained *via* the uncatalysed variant. For example, hydroboration of vinyl arenes ($ArCH{=}CH_2$) with HBcat give selectively either the expected linear boronate ester products ($ArCH_2CH_2Bcat$) or the branched boronate ester products ($ArCH(Bcat)CH_3$), depending upon the choice of catalyst used in these reactions (Scheme 1) [3]. While many transition metals can be used to catalyse these reactions, rhodium complexes are the most common and synthetically useful. A plausible mechanism for these reactions involves 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

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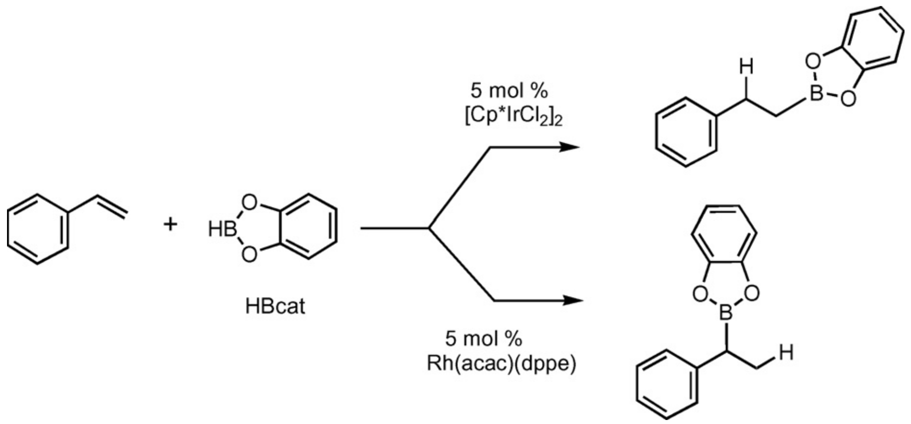


Scheme 1. The hydroboration of styrene with HBcat.

elimination to yield the desired product [10]. The branched boronate ester product is believed to arise when the metal centre can best stabilise a benzylic intermediate during the catalytic cycle.

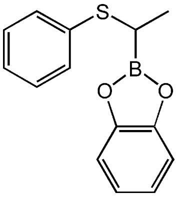
Although a considerable amount of research has focused on the catalysed hydroboration of simple unsaturated hydrocarbon systems, much less is known about analogous reactions with heteroatom-containing substrates [3,11–17]. For instance, catalysed hydroborations of pyrrolidinyl amides with HBcat gave, after oxidation, *syn* 1,3-hydroxy amides with high levels of regio- and stereochemical control. The remarkable selectivities observed in these reactions are believed to arise from a directing effect of the amide moiety [18]. In a similar study, Dai and co-workers found that rhodium catalysed hydroborations of allyl sulfones gave the branched boronate ester, where the directing effect of the sulfone oxygen is believed to be responsible for the regiocontrol in these reactions [17]. As part of our ongoing investigation into generating biologically active boron compounds [19], we have examined the catalysed hydroboration of vinyl sulfides, sulfoxides, sulfones, and sulfonates in an effort to expand the scope of these reactions and to see what effect different oxidation states of sulfur had on product selectivities. A preliminary account of this work has been published [16].

2. Experimental

Reagents and solvents used were purchased from Aldrich Chemicals and HBcat was distilled prior to use. NMR spectra were recorded on a JEOL JNM-GSX270 FT spectrometer. ^{1}H NMR chemical shifts are reported in ppm and referenced to residual solvent protons in deuterated solvent at 270 MHz. ^{13}C NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz and are reported in ppm. ^{11}B NMR chemical shifts are reported in ppm and are referenced to $BF_3{\cdot}OEt_2$ as an external standard at 87 MHz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), and overlapping (ov). All reactions were performed under an atmosphere of dinitrogen. 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.

2.1. Preparation of **1a**

A solution of HBcat (22 mg, 0.18 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of phenyl vinyl sulfide (20 mg, 0.15 mmol) and $RhCl(PPh_3)_3$ (7 mg, 0.010 mmol) in C_6D_6 (0.5 mL). The reaction was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. ^{1}H NMR δ 1.38 (d, $J = 7.2$ Hz, 3H, CH_3), 2.93 (q, $J = 7.2$ Hz, 1H, CHB), 6.70 (m, 2H, Ar), 6.89–6.97 (ov m, 5H, Ar), 7.30 (m, 2H, Ar); $^{13}C\{^1H\}$ NMR δ 16.6, 24.1 (br, CB), 112.7, 122.9, 126.9, 129.0, 131.6, 135.6, 148.3; ^{11}B NMR δ 33.5 (br).



2.2. Preparation of **2a**

A solution of HBcat (60 mg, 0.50 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of phenyl vinyl sulfide (62 mg, 0.46 mmol) and $[Cp^*IrCl_2]_2$ (9 mg, 0.010 mmol) in C_6D_6 (0.5 mL). The reaction was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. ^{1}H NMR δ 1.41 (t, $J = 7.9$ Hz, 2H, CH_2B), 2.94 (t, $J = 7.9$ Hz, 2H, CH_2), 6.80 (m, 2H, Ar), 6.90–7.05 (ov m, 5H, Ar), 7.25 (m, 2H, Ar); $^{13}C\{^1H\}$ NMR δ 11.6 (br, CB), 28.6, 112.4, 122.7, 126.0, 129.0, 129.7, 134.2, 148.5; ^{11}B NMR δ 34.2 (br).