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A gentle and efficient route for the deoxygenation of sulfoxides using catecholborane (HBcat; cat = 1,2-$O_2C_6H_4$)

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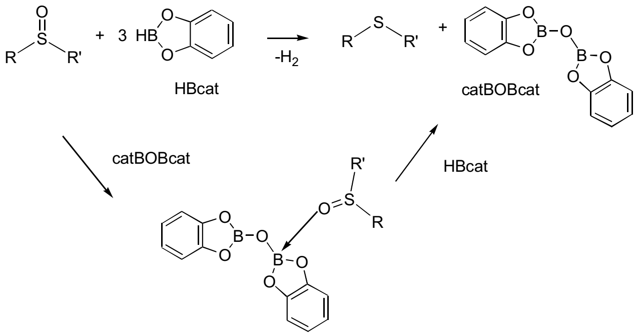
Abstract—The addition of catecholborane (HBcat; cat = 1,2-$O_2C_6H_4$) to a wide range of sulfoxides affords the corresponding sulfides, dihydrogen, and catBOBcat. The diboron compound catBOBcat acts like a Lewis acid and will coordinate one molecule of the starting sulfoxide. Although deoxygenations with bulky or electron withdrawing sulfoxides are slow, these reactions can be greatly accelerated with the use of excess HBcat or by employing a rhodium catalyst.

The reduction of sulfoxides to the corresponding sulfides is an important reaction that has found considerable utility in organic synthesis[1] and in biochemical reactions.[2] While numerous methods are available for the deoxygenation of sulfoxides, they often suffer from serious disadvantages, such as the use of expensive reagents that are difficult to handle, functional group incompatibility, difficult work-up procedures or harsh reaction conditions (i.e., low pH, high temperatures, or long reaction times).[3] For instance, a recent report describes the reduction of sulfoxides using 2,6-dihydropyridine; however, reactions must be carried out at elevated temperatures and for the case of diphenyl sulfoxide, tetramethylene sulfone must be used as a solvent to ensure complete conversion.[4]

Although a number of borane reagents, such as thexylchloroborane-methyl sulfide[5] and BBr_3[6] have also been used for these deoxygenation reactions, the difficulty in handling these highly reactive reagents makes their use somewhat impractical. In this study, however, we report that catecholborane (HBcat; cat = 1,2-$O_2C_6H_4$),[7] which is a more stable and easily handled dialkoxyborane, can be used for the gentle and efficient deoxygenation of a wide range of sulfoxides.[8]

We have found that reactions can be carried out at room temperature using 3 equiv of HBcat to give the corresponding sulfide in quantitative yield along with dihydrogen and the diboron compound catBOBcat (Scheme 1).[9] Related chelating diborane derivatives have found recent utility as co-initiators in the polymerization of isobutene and other boronic anhydrides derived from the hydrolysis of B–X (X = H or Cl) have



Scheme 1. Deoxygenation of sulfoxides using catecholborane.

Keywords: Catalysis; Catecholborane; Deoxygenation; Lewis acid; Sulfoxides.

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Table 1. Deoxygenation of sulfoxides using 3 HBcat in C_6D_6

Entry	R	R′	Time (h)	^{11}B NMR[a]
1	CH_3	CH_3	48	14.8
2	$–(CH_2)_4$		0.25	14.8
3	$PhCH_2$	CH_3	0.5	16.2
4	Ph	CH_3	150	17.5
5	$4\text{-}CH_3C_6H_4$	CH_3	150	17.9
6	Ph	Ph	>500	18.4
7	Ph	$CH{=}CH_2$	—	18.9
8	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	>500	20.8
9	$4\text{-}O_2NC_6H_4$	$4\text{-}CH_3C_6H_4$	>500	21.3
10	CF_3CH_2	CH_2Ph	>500	21.4

[a] ^{11}B NMR of catBOBcat·OSRR′ adduct in ppm, which could also be obtained by independent 1:1 reaction of catBOBcat with sulfoxide.

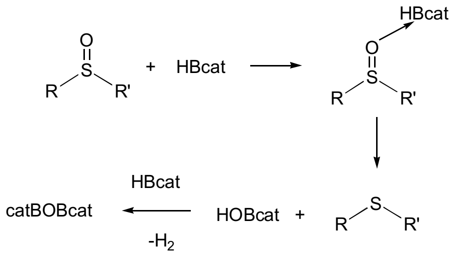
also been reported.[10] The formation of two B–O bonds provides an enormous enthalpic driving force (ΔH 180 kcal/mol) for these deoxygenations.[11] Not surprising is that reactions of sulfoxides containing bulky (Table 1, entries 6, 8, and 9) or electron withdrawing groups (entries 9 and 10) take considerably longer for complete conversion. Reactions with phenyl vinyl sulfoxide (entry 7) are complicated by competing addition of HBcat to the activated alkene.

With a slight excess of HBcat, reactions proceed initially to give varying amounts of deoxygenation product along with catBOBcat (by ^{1}H NMR spectroscopy). However, the formation of this latter species significantly retards reaction rates as it forms a relatively stable Lewis acid–base bond with any unreacted sulfoxide. For instance, with 3 equiv of HBcat, complete conversion of dimethyl sulfoxide (dmso) to dimethyl sulfide occurs in 48 h (entry 1). Presumably the long reaction time is due to strong adduct formation with the small and basic dmso substrate and the diboron compound. Interestingly, no adduct formation is observed between the softer sulfide and HBcat, or catBOBcat. At higher HBcat concentrations, however, the hydroborating reagent is presumably able to compete with catBOBcat and form a more reactive Lewis acid–base adduct, which then goes on to rapidly deoxygenate the sulfoxide. For instance, the reaction with dmso is complete within 10 min, if 6 equiv of HBcat are used to facilitate the deoxygenation. This rate increase with excess HBcat is observed in all reactions, including those involving the bulky and sluggish aryl sulfoxides (entries 6, 8, and 9).

Deoxygenations of sulfoxides with boranes and substituted boranes (R_2BH) are believed to proceed via initial Lewis acid–base adduct formation followed by loss of the desired sulfide along with the R_2BOH species (Scheme 2).[5,6] This latter transient species reacts rapidly with another equivalent of the hydroborating agent to give dihydrogen and R_2BOBR_2.

A single crystal X-ray diffraction study was conducted on the dmso catBOBcat adduct, the molecular structure of which is shown in Figure 1.[12] The diboron catBOBcat acts like a Lewis acid and coordinates with the sulfoxide through the basic oxygen atom to only one of the boron atoms. Related compounds of diborane(4) have been reported where mono-adduct formation with strong nucleophiles, such as pyridine, occurs rapidly but bis-adduct formation is slow on the NMR time scale.[13] Previous studies have also shown that trivalent catBOBcat shows slow binding with PMe_2Ph to afford an adduct which undergoes rapid intramolecular phosphine exchange on the NMR time scale.[11] The ^{11}B NMR data for this latter species shows a time average peak at 16.5 ppm, indicative of both three and four coordinate boron atoms.[14] In contrast, a peak at 21.6 ppm is observed for the uncoordinated catBOBcat. The ^{11}B NMR chemical shifts of the adducts formed in this study are shown in Table 1. Similar data are observed from the independent 1:1 addition of sulfoxide to preformed catBOBcat. The electron rich dmso and tetramethylene sulfoxide derivatives, have time averaged peaks at 14.8 ppm. The boron chemical shifts and sulfoxide deoxygenation rates are consistent with known basicities of the sulfoxides.[15] As expected, the bulky aryl and electron withdrawing sulfoxides show resonances in a continuum between three coordinate and four coordinate species.

While reasonable reaction rates can be achieved using a large excess of the borane, this incurs a considerable amount of waste and would prove to be an expensive procedure for the deoxygenation of sulfoxides. More remarkable, however, is the observation that a catalytic amount of a rhodium complex (usually $RhCl(PPh_3)_3$ or Rh(acac)(dppe),[16] where acac = acetylacetonato and



Scheme 2. Possible mechanistic pathway for the deoxygenation of sulfoxides using HBcat.

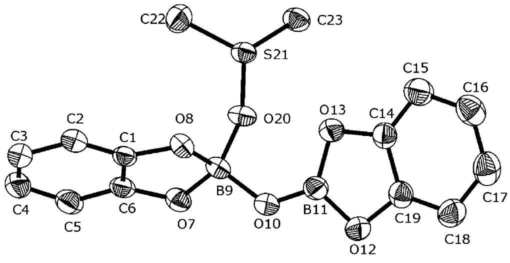


Figure 1. Molecular structure of catBOBcat dmso, with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: B(9)–O(7) 1.464(3); B(9)–O(8) 1.469(3); B(9)–O(10) 1.430(3); B(9)–(20) 1.534(3); B(11)–O(10) 1.324(3); B(11)–O(12) 1.393(3); B(11)–O(13) 1.400(3).

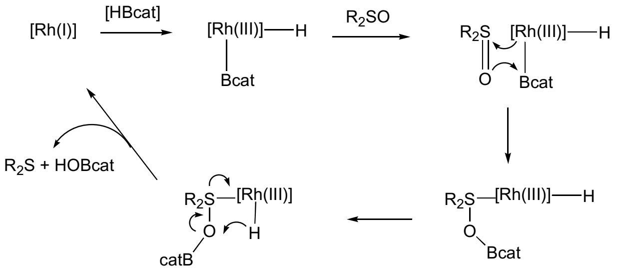


Figure 2. Rhodium-catalyzed deoxygenation of sulfoxides using HBcat.

dppe = 1,2-bis(diphenylphosphino)ethane) can be used to facilitate this addition using only 2 equiv of HBcat.[17] Reactions proceed cleanly at room temperature to give the desired product and are usually complete within 1 h. Unfortunately, reactions with phenyl vinyl sulfoxide are also complicated by a competing catalyzed hydroboration of the vinyl group.

The proposed reaction pathway for these rhodium-catalyzed deoxygenations involves initial oxidative addition of HBcat to the metal center,[18,19] followed by insertion of the basic oxygen into the rhodium boron bond (Fig. 2). Reductive extrusion would afford the transient catBOH species, which would react with another equivalent of HBcat to give dihydrogen and catBOBcat. Unfortunately, we were not able to observe the formation of HOBcat in these reactions using multinuclear NMR spectroscopy, even at −80 °C. Further work in this area will examine the use of HBcat for the deoxygenation of other heteroatom oxides and will be reported in due course.

In summary, catecholborane can be used as a gentle, efficient, and selective reagent for the deoxygenation of a wide range of sulfoxides. Although excess HBcat is required for bulky sulfoxides or sulfoxides containing electron withdrawing groups, the use of a rhodium catalyst greatly accelerates these reactions while allowing a minimal loading of borane.

Acknowledgements

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Supplementary data

Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.09.068.

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12. X-ray diffraction data were collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and ϕ scans with a scan width of 0.3° and 30 s exposure times. The detector distance was 5 cm. The data were reduced and corrected for absorption. The structure was solved by direct methods and refined by full-matrix least squares on F^2. All nonhydrogen atoms were refined anisotropically. $C_{14}H_{14}B_2O_6S$; $M_w = 331.93$; monoclinic, space group $P2(1)/c$, $a = 7.5684(8)$, $b = 8.9369(9)$, $c = 22.318(2)$ Å;

$\beta = 91.856(2)°$; $V = 1508.8(3)$ Å^3, $Z = 4$, $D_c = 1.461$ g/cm^3, $R_1 = 0.0404$, w$R_2 = 0.1060$, GoF = 1.076 for 3386 reflections with $I > 2\sigma(I)$. CCDC 233800.

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