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Spiroborate catalyzed reductions with *N*,*N*-diethylaniline borane

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ABSTRACT

Reduction of esters, amides, and ketones by *N*,*N*-diethylaniline borane is accelerated by catalysts derived from spiroborate complexes. Esters are reduced at ambient temperature in less than 4 h with this amine borane and 5 mol % spiroborate 6. Functional group selectivity shows ketone and tertiary amide reduction is faster than ester or nitrile reduction.

A number of alumino- and borohydride reducing agents[1] are available for ester reduction but some reducing agents present significant limitations, either in selectivity or handling. Singaram has elegantly demonstrated the abilities of lithium aminoborohydrides in selective ester and amide reductions.[2] Late stage reduction of functional groups during the synthesis of drug candidates presents significant challenges due to the need for highly selective reagents. For example, in attempting the reduction of only the methyl ester in a multi-functional molecule during the synthesis of a viral RNA replication inhibitor, Agbodjan et al.[3] tried a number of reducing agents with limited success. In addition, substrates can be prone to epimerization;[4] therefore a non-basic reducing agent is desirable to minimize undesired by-product formation.

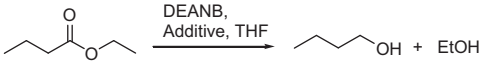
Borane-tetrahydrofuran complex (BTHF), borane-dimethyl sulfide (DMSB), and *N*,*N*-diethylaniline borane (DEANB) have all been widely used for selective reduction operating via an electrophilic mechanism.[5] An example of selective ester reduction using DMSB successfully produced (*S*)-3,4-dihydroxybutyric acid methyl ester from L-malic acid dimethylester.[6] In a multi-functional substrate, 2 equiv of DMSB in THF at reflux reduced a lactam to the amine (49% yield) in the presence of an ethyl ester, while applying 6 equiv reduced both the ester and the amide.[7] Reduction using boranes in THF at reflux can lead to ring opening of THF giving butyl borate, thus requiring an excess of borane for complete substrate reduction.

Development of selective reducing agents that are easily handled, stable, yet reactive enough to perform the desired reduction under mild conditions, that is, at ambient temperature, is a highly desirable goal to expand the organic chemist's toolbox.

DEANB exhibits low reactivity toward many substrates, however, the reactivity of DEANB toward ketone reduction is dramatically accelerated by utilizing oxazaborolidine catalysts.[8] For example, DEANB reduction of acetophenone required 6–8 h at reflux,[9] whereas when catalyzed by MeCBS (**1**) the reduction is complete within 15 min at ambient temperature.

Oxazaborolidine catalysts are envisioned to increase ketone reaction rates by two convergent mechanisms,[10] (1) carbonyl coordination of the substrate to a Lewis acidic boron to increase the electrophilic character of the carbon, coupled with (2) dynamic equilibrium of borane coordination to the Lewis basic nitrogen center of the catalyst to facilitate proximal interaction of the substrate with borane and to increase hydride nucleophilicity. Since oxazaborolidines have not been studied for accelerated reduction of ester or amide functional groups,[11] we embarked on a plan to investigate ester reduction. (*R*)-MeCBS (**1**, 5 mol %) was found to dramatically increase the rate of ester reduction by DEANB at ambient temperature when compared to long reaction times at elevated temperature required with DEANB alone, (Scheme 1, Table 1, entries 1 and 2). Screening of compounds with both Lewis acidic and Lewis basic sites, Figure 1, allowed catalyst structure optimization, see Table 1. Altering the oxazaborolidine structure by removal of the phenyl groups or methyl on boron decreased catalytic activity. Dialkylaminoborane or aminoborate derivatives, **4** and **5**, respectively, were ineffective.

Spiroborates with diverse structural and electronic environments were prepared by reaction of dialkylborane or dialkoxyborane and aminoalcohols. Compound **6** derived from *N*-methyl-2-aminoethanol and catecholborane showed excellent results compared to catalysts **7** and **8** prepared from 9-BBN and pinacolborane. The lower activity of **7** and **8** is possibly due to steric bulk around boron. On the other hand, the simplest spiroborate structure, **9**, was also ineffective. Changing the secondary amine to pyridine, primary amine or tertiary amine in the catalyst structure dramatically decreased activity (**10**, **11**, and **12** of Fig. 1). The chiral spiroborate of Ortiz-



Scheme 1. Ethyl butyrate reduction.

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Table 1
Ethyl butyrate reduction by DEANB:[a] catalyst screening

Entry	Additive	Temp (°C)	Time (h)
1	None	85, 50	9, 48[c]
2	5 mol % **1**	20	7
3	10 mol % **6**, **13**	20	5
4	10 mol % **2**, **3**[b], **7–9**	20	10–24
5	10 mol % **4**, **5**, **10–12**	20	>24[d]

[a] 1:1 ratio of ester: DEANB, borane added to ester and catalyst in THF.
[b] Catalyst formed in situ.
[c] 87% complete reduction.
[d] Incomplete reduction.

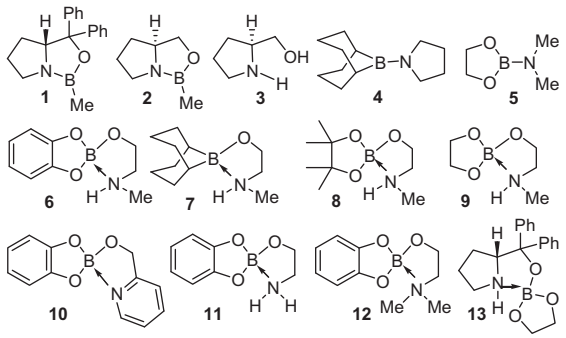


Figure 1. Compounds tested in ester reduction with DEANB.

Mercales[12] **13**, similar in steric bulk to (*R*)-MeCBS, also gave excellent results. In view of the fact that an ester reduction does not generate a chiral center, the chiral catalysts, **1**, **2**, **3**, and **13**, were not selected for further study due to their chirality adding superfluous cost and complexity.

Further evaluation with a formulation of DEANB with 10 mol % **6** (dubbed SpiroCAT) added to ethyl butyrate in THF showed even higher catalytic activity, Table 2 entry 1, compared to addition of DEANB to the ester/catalyst mixture. By adding the ester into the DEANB/SpiroCAT formulation, reduction was quite exothermic and complete within 30 min. Catalyst loading at 5 mol % SpiroCAT in DEANB required 4 h for ester reduction regardless of formulation age, entry 2. Reduction in methyl *t*-butyl ether was complete in 3.5 h, while toluene required 6 h compared to 4 h in THF, entry 3.

Table 2
Catalyzed ester reduction by DEANB and SpiroCAT at rt

Entry	Substrate[a]	Mol % **6**	Time (h)	Conversion[b] (yield)[c]
1	Ethyl butyrate	10	2.5	100 (64)
2	Ethyl butyrate	5	4, 4[d]	100
3	Ethyl butyrate	5	3.5[e], 6[f]	100
4	Ethyl isobutyrate	10	2.5	100
5	Ethyl benzoate	10	>72	90 (83)[g]
6	*t*-Butyl acetate	10	>72	95[h]
7	*i*-Propyl acetate	10	4.8	100
8	*i*-Propyl butyrate	5	3.3	100 (41)
9	*t*-Butyl propionate	5	48	86
10	Ethyl 3-Br-benzoate	5	24[i]	90 (90)
11	Methyl (*S*)-mandelate	5	24[j]	85 (83)

[a] 1:1 ratio of ester: DEANB, DEANB/SpiroCAT added to ester in THF.
[b] Conversion monitored by ReactIR.
[c] Unoptimized isolated yield.
[d] Using formulation aged one year.
[e] Reaction in *t*-butyl methyl ether.
[f] Reaction in toluene.
[g] 26 h at 50 °C with 5 mol % SpiroCAT.
[h] Reaction 50% conversion in 9 h by ReactIR, and 95% in 72 h by GC.
[i] 24 h at 50 °C, yield adjusted for 8% ester recovered.
[j] Plus 4 h at 50 °C, yield adjusted for 15% ester recovered.

Probing the structure of the ester demonstrated a relationship between reduction rate and ester structure and electronics, Table 2, entries 4–10. Ethyl *n*-butyrate and ethyl *i*-butyrate were reduced rapidly while ethyl benzoate reduction was slowly reduced. *t*-Butyl esters are reduced much more slowly compared to *i*-propyl esters, entries 6 and 9 versus entries 7 and 8. Therefore, alkyl esters can be reduced selectivity in the presence of these less-reactive esters. For example, reduction of a 1:1 mixture of ethyl butyrate and ethyl benzoate resulted in 90% reduction of ethyl butyrate but only 1% reduction of the benzoate at 20 °C. In contrast to lithium aminoborohydride, a stronger reducing agent, which rapidly reduced both aliphatic and aromatic esters at 0 °C, DEANB/5 mol % SpiroCAT selectively reduced the aliphatic ester.

Reduction of ethyl benzoates can be pushed to completion by extended reaction time at 50 °C, entries 5 and 10. Reduction of ethyl 3-bromobenzoate at 50 °C delivered 3-bromobenzyl alcohol with no loss of the halogen, entry 10. The reduction of methyl (*S*)-mandelate was slower than expected but the chiral center of the diol product was unaffected by the reduction conditions.

Next, we explored the scope of functional group reductions with the DEANB/5 mol % SpiroCAT formulation. Amides are commonly reduced with DMSB[13] or BTHF; for example, a peptide amide was successfully reduced selectively in the presence of an ester using BTHF at −20 °C.[14] However, borane derivatives of dialkylanilines and sterically hindered amines are significantly less reactive than BTHF and require prolonged heating at elevated temperatures to drive a *tert*-amide reduction to completion.[15]

With DEANB/5 mol % SpiroCAT, several tertiary amides were successfully reduced, see Table 3. While aliphatic amides were reduced easily at ambient temperature, the benzamide reduction benefited from higher reaction temperature (50 °C, entry 6). The amine product from reduction of Weinreb amide retained the *N*-methoxy group.

Unfortunately, butyramide (2.33 equiv of DEANB) and *N*-methylproprionamide (2 equiv of DEANB) were not rapidly reduced under these reaction conditions. In fact, the secondary amide appears to inhibit the catalytic activity of **6**. For example, addition of 10 mol % of *N*-methylpropionamide to an ethyl butyrate reduction using DEANB with 5 mol % **6** showed only 92% ester reduction in 21 h. Likewise, dimethylacetamide reduction was significantly slower in the presence of 10 mol % of *N*-methylpropionamide. In addition, ester reduction at rt required 24 h in the presence of 1 equiv of nitrile. Understanding this inhibition phenomenon is the subject of further work.

Further investigation of the activity and selectivity of the DEANB/5% SpiroCAT system showed ketones are rapidly reduced in less than 1 h at 20 °C. On the other hand, the nitrile reduction rate with the formulation was only slightly increased over DEANB alone. In contrast, Singaram has shown diisopropylaminoborane in the presence of $LiBH_4$ catalysis as an effective reducing agent for nitriles at rt, however lithium aminoborohydrides do not reduce nitriles at rt.[16]

Table 3
Amide reduction by DEANB and 5 mol % SpiroCAT, **6**

Entry	Substrate[a]	Temp (°C)	Time[b] (h); (isolated yield)
1	*N*,*N*-Dimethylacetamide	50[c]	6
2	*N*,*N*-Dimethylacetamide	20	2
3	*N*,*N*-Dimethylisobutylamide	20	3.3
4	*N*-Methoxy-*N*-methylacetamide	20	8
5	*N*-Methylcaprolactam	20	4 (82)
6	*N*,*N*-Dimethylbenzamide	50	3.5 (76)

[a] 1:1.67 ratio of amide: DEANB, formulation added to amide in THF.
[b] Time to 100% conversion by ReactIR.
[c] Without SpiroCAT.

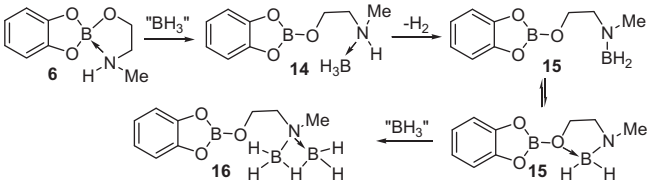
Based on Brown's work, amides were reduced by borane complexes in preference to ester, nitrile and nitro groups.[17] Reductions to probe the selectivity of functional groups with this new reagent formulation were conducted with a deficit (relative to total substrate amount) of DEANB/SpiroCAT at rt or slightly elevated temperatures, Table 4. The results show the selective reduction of dialkylamides in the presence of nitriles or esters and aliphatic esters in the presence of aliphatic nitrile or benzoate functionalities.

Carboxylic acids are rapidly reduced by DEANB without additives but SpiroCAT did not appear to increase the reduction rate. When a mixture of ethyl butyrate and benzoic acid were reduced with a slight excess of borane, the acid was reduced preferentially, with only a minor amount of ester reduction due to the presence of excess borane. Thus, the activity of SpiroCAT was not affected by the presence of carboxylic acid.

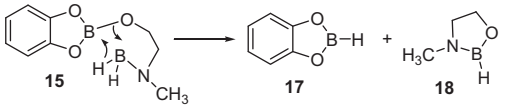
Further investigation of the DEANB/SpiroCAT formulation has revealed that 1 equiv of hydrogen evolves from reaction of borane and SpiroCAT. Neither aminoborane (**15**) nor bis(dialkylamino)diborane with bridging amine groups was seen in the region of the ^{11}B NMR spectrum between 0–2 and 3–6 ppm, respectively.[18] Subsequent interaction of the intermediate with another borane generates an aminodiborane, **16**, observed in the ^{11}B NMR spectrum as a broadened triplet at −18 ppm, Scheme 2. In one case, the peak was resolved as a dt; J = 130, 30 Hz. It is not known at this time if **16** is the active catalyst or the resting state of the catalyst. Dimethylaminodiborane[19] and morpholinodiborane, independently prepared for comparison of the ^{11}B NMR spectra, were ineffective catalysts for ester reduction by DEANB.

Further experiments, with BTHF and SpiroCAT to explore the intermediates also show formation of amine borane **14** followed by conversion to aminodiborane **16** in the presence of additional borane. The catalyst prepared from SpiroCAT and BTHF reduces ethyl butyrate in 4 h at rt with DEANB as the reducing agent.

Another mechanistic possibility is the formation of oxazaborolidine **18** and catecholborane (**17**) from the aminoalcohol moiety **15**, Scheme 3. The ^{11}B NMR spectrum of the DEANB-SpiroCAT formulation also displays a small doublet at 27.5 ppm (J = 190 Hz)[20] in lesser amount relative to the aminodiborane triplet at −18 ppm. Oxazaborolidine compounds with a B–H have been observed by ^{11}B NMR spectroscopy at 25–28 ppm (monomer)[21] and 7.6 (dimer)[22] while catechol borane is at 28 ppm (J = 190 Hz). Addition of catechol borane to the formulation increased the doublet at 27.5 ppm and the decoupled spectrum showed one resonance in this area.[23] In the DEANB-SpiroCAT formulation an oxazaborolidine would likely exist as the BH_3 adduct which is usually observed at −12 to −14 ppm as a quartet[24] or as a complex with coordinated *N*,*N*-diethylaniline. The ring-boron of oxazaborolidine-borane adducts with different substituents has been reported at 3.2 by Corey (no coupling given) and at 6 and 1.5 ppm by Contreras.[25] The absence of resonances in the region between 1–6 ppm suggests an absence of oxazaborolidine–borane adduct in the DEANB-SpiroCAT formulation.



Scheme 2. Proposed active catalyst in SpiroCAT reductions.



Scheme 3. Possible oxazaboroline catalyst.

N-Methylaminoethanol (5 mol %) and excess DEANB were heated together in an attempt to generate an oxazaborolidine catalyst in situ. The ^{11}B NMR spectral resonances were at 28 ppm (d, J = 158 Hz), 12 ppm (s, spiroborate) and as an unresolved shoulder on DEANB at −18 ppm. The doublet coupling constant of the peak at 28 ppm is closer to that of a dialkoxyborane than oxazaborolidine. Although this in situ catalyst showed peaks in the ^{11}B NMR spectrum similar to but not identical to those observed in the DEANB/SpiroCAT formulation, the catalytic activity of the in situ prepared catalyst was considerably less than observed using SpiroCAT in the ethyl butyrate reduction, 9.25 h versus 4 h. The exact nature of the active catalyst warrants further study.

Spiroborate **6**, used in a formulation with DEANB, was found to effectively accelerate the reduction of esters, tertiary amides, and several other functional groups. Esters, which are typically difficult to reduce with borane complexes, can be reduced at room temperature in less than 4 h.[26] Probing the selectivity of the catalyzed reductions has shown that tertiary amide reduction preferentially occurs in the presence of esters or nitriles. These results demonstrate the mild and selective nature of this catalyst system and indicate utility in reduction of selected functional groups of a multi-functional structure.

Table 4
Catalyzed selective reduction by DEANB and 5 mol % SpiroCAT, **6**

Entry	Substrate A; % reduced[a]	Substrate B; % reduced[a]	Substrate C; % reduced[a]	DEANB: total substrate ratio[b]	Reaction Temp (°C)	Reaction time
1	Ethyl butyrate; 90%	Ethylbenzoate; 1%	—	0.8:2	20	8
2	*N*,*N*-Dimethyl-acetamide; 99+%	Benzonitrile; 0%	—	1.66:2	20+[c]	2
3	*N*,*N*-Dimethyl-acetamide; 99+%	Heptane nitrile; 0%	—	1.66:2	20	6
4	*N*,*N*-Dimethyl-acetamide; 80%	Ethyl butyrate; 5%	—	1.68:2	20	3
5	*N*,*N*-Dimethyl-acetamide; 88%[d]	Benzonitrile: 0%	Ethyl benzoate; 0%	1.66:3	40–45	20
6	Ethyl butyrate; 99+%	Benzonitrile: 12%	—	1.33:2	50	4
7	Ethyl butyrate; 80%	Benzonitrile: 34%	—	0.8:2	20	20
8	Ethyl butyrate; 90%[e]	Heptane nitrile; 0%	—	1:2	20	6
9	Ethyl butyrate; 80%	Benzonitrile: 0%	Ethyl benzoate; 0%	1:3	20	17
10	Ethyl butyrate; 12%	Benzoic acid; 99%	—	1.35:2	20	4

[a] GC yield.
[b] DEANB/SpiroCAT added to substrate mixture.
[c] Reaction exothermed and gelled.
[d] Amide reduction 77% complete in 30 min.
[e] 100% at 24 h.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.09.022.

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