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REACTIONS OF THEXYLBORANE-N,N-DIETHYLANILINE (TBDA)

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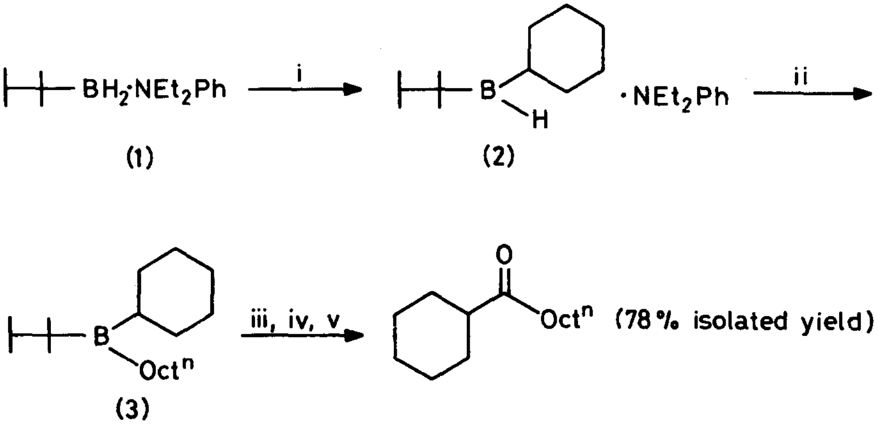
1, 1, 2-Trimethylborane-THF complex (thexylborane-THF) is a bifunctional hydroborating agent that has found many applications in reactions involving two migrations from boron to carbon[1,2]. However the complex undergoes slow isomerisation[2] and must be made in the cold immediately prior to use. Thexylborane may be stabilized as the triethylamine complex but hydroboration with the complex leads to the production of monoalkylborane-NEt$_3$ with displacement of the 2,3-dimethylbut-2-ene(thexene)[3].

We now report that thexylborane-PhNEt$_2$(TBDA) is a stable form of thexylborane that readily hydroborates alkenes without displacement of thexene and is also an active reducing agent.

Amine complexes of borane itself have found little place as synthetic reagents[4] due to their low activity as hydroborating and reducing agents. Thus borane-NEt$_3$ only hydroborates hex-2-ene at 200°C, at which temperature isomerisation occurs so that the sole product is tri-n-hexylborane[5]. Addition of Lewis acids to competitively complex the amine has met with some success, but the hydroboration of oct-1-ene with borane-pyridine in the presence of BF$_3$-Et$_2$O still requires 16h. at 75°C. Weakening of co-ordination either sterically[7] or by use of a poorly basic amine (particularly arylamines[8]) is more successful in enhancing reactivity.

TBDA (1) is a complex of a hindered borane with an amine of high steric requirements and low basicity and we anticipated that it would be an active hydroborating agent. Indeed TBDA reacts with two equiv. of oct-1-ene in THF at 0° in 2h. to yield di-n-octylthexylborane in quantitative yield. It also reacts smoothly with one equivalent of cyclohexene to yield (2) which reacts with oct-1-ene to give (3). In no case was thexene displaced. Moreover the presence of the amine does not inhibit the cyanoborate reaction[9].



i, Cyclohexene, THF, 0°C, 2h; ii, Oct-1-ene, THF, 0°C, 2h; iii, KCN;
iv, TFAA-78°C; v, H_2O_2 - NaOH.

TBDA is made by addition of diethylaniline to a THF solution of thexylborane produced as usual[1, 2]. The THF may be removed and the reagent used neat or another solvent may be added. TBDA is miscible with hexane, benzene, dichloromethane and all ethereal solvents. It is stable either neat or in THF for long periods at 0°. There was no isomerisation or loss of hydride activity over 2 months at 0°C, and hence TBDA is a useful store of thexylborane.

These observations prompted us to compare TBDA with thexylborane-THF in reduction reactions. For comparability the same conditions were used as in a previous study[10], i.e. 2.5 mmole of substrate were reacted with 5 mmole of TBDA in sufficient THF to give 10ml. of solution, 1.0M in hydride. Of course these conditions are not necessarily optimal for preparative reactions. Aliquots were withdrawn periodically for hydride analysis and products were identified by g.l.c. and i.r. comparison with authentic samples.

Alcohols and Thiols.

In view of the stability of TBDA it was surprising to find that it reacted with alcohols and thiols at a faster rate than thexylborane-THF (Table 1).

Table 1

Compound	Thexylborane-THF[10]		TBDA	
	Hydride used	Time	Hydride used*	Time
$PhCH_2OH$	1.00	0.5h	1.00	3.5m
PhOH	1.00	6h	1.00	6m
$C_6H_{13}SH$	0.00	10h	-	-
EtSH	-	-	1.00	3h
PhSH	0.92	24h	1.00	0.5h

*All hydride used in evolution of hydrogen, not in reduction.

Aldehydes and Ketones.

The reduction of aldehydes and ketones to the corresponding alcohols goes at rates comparable to those of thexylborane-THF. Cinnamaldehyde may be completely reduced, but it is noteworthy that 1 equiv. of TBDA at 0°for 15m. produces cinnamyl alcohol (80% isolated yield) as the sole product. Similarly only the aldehyde group of campholenic aldehyde is reduced to give the corresponding alcohol in 80% isolated yield.

Carboxylic acids.

Extended reflux of carboxylic acids with excess thexylborane-THF yields aldehydes[10]. In contrast TBDA at 0°C reduces aliphatic carboxyl acids to the corresponding alcohols. uncontaminated with aldehyde. Benzoic acid in THF is only reduced to the extent of 15% in 48h. whereas in benzene 1.98 equiv. of hydride are taken up in 2.5h. 10-Undecenoic acid reacts only at the double bond with one equivalent of TBDA at 0° in 15m. Hydrolysis of the intermediate organoborane gives undecanoic acid in 90% isolated yield. This highly selective reaction augurs well for the synthetic utility of TBDA.

Esters and Anhydrides.

Aliphatic and aromatic esters are slowly (10% in 24h. at 0°C) reduced by TBDA in THF. Aliphatic acyclic anhydrides gives the corresponding alcohols in 24h. but cyclic anhydrides react very slowly to give complex mixtures.

Tertiary amides.

Aliphatic and aromatic tertiary amides give the corresponding tertiary amines at a rate of at least ten times faster than thexylborane-THF (Table 2).

Table 2

Compound	Thexylborane-THF[10]		TBDA	
	Hydride used	Time (h)	Hydride used	Time (h)
$C_5H_{11}CONMe_2$	1.92	72	1.99	6
$PhCONMe_2$	1.99	48	2.01	3
$C_5H_{11}COCl$	0.20	48	1.48	96
PhCOCl	0.55	48	1.11	192
$C_5H_{11}CN$	0.62	24	-	-
C_4H_9CN	-	-	2.01	72
PhCN	0.32	24	0.68	120

Acid Chlorides.

These compounds are only slowly reduced by TBDA (Table 2) to give the corresponding alcohol containing traces of aldehyde.

Nitriles.

Aliphatic and aromatic nitriles are slowly reduced to the corresponding primary amine by TBDA at a rate comparable to that of thexylborane-THF. Hydrolysis gave no aldehyde from imine intermediates.

The use of amine complexes of borane and alkyl -and arylboranes remains an undeveloped area of organic chemistry. The gross differences in behaviour between the triethylamine and diethylaniline complexes of thexylborane indicates that, by judicious choice of amine, not only may many organoboranes be stabilized to dismutation and isomerisation, but also that series of reagents of graded reactivity could be produced.

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