

## Note

### A simple procedure for hydroboration using tetrabutylammonium borohydride

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Tetrabutylammonium borohydride hydroborates unsaturated systems in refluxing chloroform. With enynes, selectivity is observed for terminal unsaturation. However, selectivity is not observed with dienes.

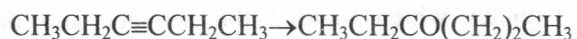
Hydroboration of alkenes and alkynes can generally be achieved by using electrophilic borane reagents like BMS<sup>1</sup>, Borane-THF<sup>1</sup> etc. which need extra care during their handling. Metal borohydrides have been shown to exhibit apparent electrophilicity in the presence of esters by Tandem reduction-hydroboration process. Thus lithium borohydride<sup>2</sup> and calcium borohydride<sup>3</sup> were reported to effect hydroboration in presence of esters. However, a solution of zinc borohydride in tetrahydrofuran was found to hydroborate unsaturated systems even in the absence of esters<sup>4</sup>. Herein we report hydroboration observed with tetrabutylammonium borohydride which is a solid reagent and hence can be conveniently handled. It can be prepared by the metathesis reaction of tetrabutylammonium salt with sodium borohydride and stored without the loss of hydride under nitrogen atmosphere for a fairly long period at room temperature<sup>5</sup>. However, we found that tetrabutylammonium borohydride was found to liberate diborane in chloro solvents like CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub> etc. as evidenced through <sup>11</sup>B NMR

which showed a multiplet centered around -26.4 ppm corresponding to B<sub>2</sub>H<sub>7</sub><sup>-</sup> (ref. 6). This prompted us to carry out hydroboration studies with this reagent in chloro solvents.

As there are a number of boron reagents available for hydroboration, for any new reagent, the important features to be considered in hydroboration reactions are stoichiometry and regio selectivity. This study would ensure the utility of the reagent for selective hydroboration. The stoichiometry was followed by performing the reaction at different olefin : borohydride ratio and studying the reaction mixture after subjecting to oxidation with alkaline H<sub>2</sub>O<sub>2</sub> using GC (Table I). The results indicated that tetrabutylammonium borohydride hydroborates only two equivalents of terminal olefins leading to the formation of dialkyl boron species. Hence taking 2 equivalents of alkene per borohydride a number of terminal alkenes have been converted to alcohols in good yields (Table II). Similarly internal and cyclic alkenes were also converted to the corresponding alcohols.

Terminal alkynes undergo dihydroboration with tetrabutylammonium borohydride resulting in the formation of a dibora adduct. Oxidative hydrolysis of dibora adduct with alkaline H<sub>2</sub>O<sub>2</sub> yielded 80% of the corresponding terminal alcohol (Table II).

The formation of dibora adduct could not be prevented even by using an excess of alkyne. Internal alkynes generally form vinyl boranes which on oxidation yield ketones as the major product. Thus, 3-hexyne yielded 3-hexanone.



However, diphenyl acetylene yielded 1,2-diphenylethanol as the major product indicating that dihydroboration had occurred. The dibora

Table I—Stoichiometry of hydroboration of alkene

Olefin* in mmole	BH <sub>4</sub> <sup>-</sup> in mmole	Olefin remaining in mmole	Primary alcohol in mmole	Secondary alcohol in mmole	Olefin reacted/ BH <sub>4</sub> <sup>-</sup> in mmole
5	1.25	2.25	2.25	0.5	2.2
5	2.5	0.75	3.7	0.55	1.7
7.5	2.5	2.1	4.8	0.6	2.1

\*Dodecene and decene were the olefins used.

Table II—Hydroboration studies with alkenes, alkynes and eneynes

Substrate	Product	Yield (%) <sup>c</sup>
Alkenes		
1-Decene	1-Decanol	90
1-Dodecene	1-Dodecanol	91
5-Decene	5-Dodecanol	92
Ethylidene cyclohexene	2-cyclohexyl ethanol	85
$\alpha$ -Pinene	3-Pinanol	75
$\beta$ -Pinene	Myrtanol	75
Cyclohexene	Cyclohexanol	80
Methyl-10-undecenoate	11-Hydroxy methyl-undecenoate	90
Alkynes		
1-Octyne	1-Octanol	87
1-Hexadecyne	1-Hexadecanol	90
3-Hexyne	3-Hexanol	90
Diphenylacetylene	1,2-Diphenylethanol	83
Methyl-10-undecynoate	11-Hydroxy methyl-undecanoate	75
Ene-yne		
1-Octene-4-yne	4-Octyne-1-ol	85
1-Nonene-4-yne	4-Nonyne-1-ol	86
1-Hexadecyne-11-ene	11-Hexadecene-1-ol	82

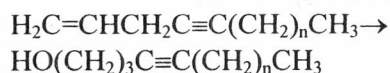
[Substrate] : [H] = 5 : 10,  
<sup>c</sup>Isolated yield per mmole of the substrate reacted.

adduct formation may be due to the better planarity and increased electrophilicity experienced by the alkyne during the course of the reaction. A similar observation was made in the reaction with silica gel supported zinc borohydride<sup>7</sup>.



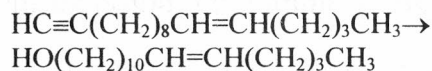
To study the regioselectivity of the reagent, hydroboration of dienes and eneynes were performed. There was no selectivity observed with 1,11-dienes which yielded the primary and the secondary alcohol in the ratio of 1:1.5.

However, with eneynes we observed a peculiar selectivity during hydroboration. Thus, 1-octene-4-yne and 1-nonene-4-yne yielded terminal alcohol as the major product showing the selectivity of the reagent towards terminal double bond (Table II).



where  $n = 2, 3$

But, in the case of 1-hexadecyne-4-ene, only the alkyne group has reacted indicating that the reagent has terminal selectivity.



This result was utilized in the synthesis of Z-11-alken-1-ol which are pheromone components of many insect species.

### Experimental Section

**Typical procedure for hydroboration.** To tetrabutylammonium borohydride ( $10\text{H}^-$ ) (2.5 mmole) in chloroform was added substrate (5 mmole) and the mixture refluxed for 5 hr. The excess hydride was quenched with dil.  $\text{H}_2\text{SO}_4$ . The reaction mixture was made alkaline by adding NaOH and the organoboron intermediate was oxidized with 30%  $\text{H}_2\text{O}_2$  at room temp. The organic layer was separated from the aq. layer, dried over anhyd.  $\text{Na}_2\text{SO}_4$  and the solvent removed at diminished pressure. Yields are given in the Table II.

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