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Methodology: Hydroboration Amination to Yield Alkylamines

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Kenyon College Dept. Of Chemistry, Summer Science 2006

Goal

Development of an efficient hydroboration amination methodology for terminal olefins.

Approach

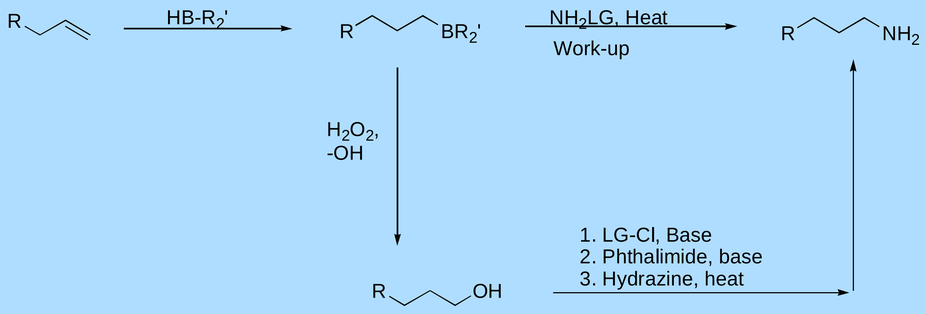
•A well-established but lengthy synthetic method for transforming terminal olefins to primary amines is the Gabriel amine synthesis (Scheme 1).

•This is a three-step process that uses an organoborane, which is then oxidized. After oxidation, a cocktail of reagents is added to produce the terminal amine.

•A direct approach has been described that uses the hydroboration amination process, although reported yields are modest. The protocol has not found widespread application. We plan to explore a number of potential leaving groups and conditions to improve its efficacy. The goal approach is outlined in Scheme 1.

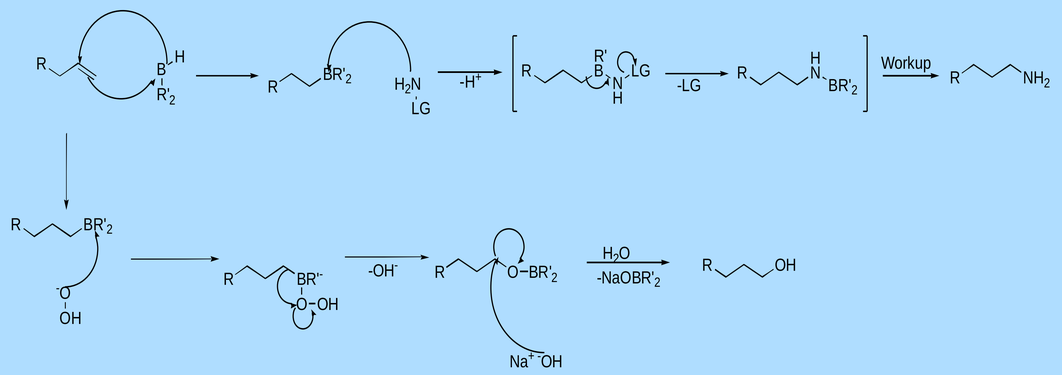
•Instead of using the Gabriel amine synthesis, a borane (such as BH_3 or 9-BBN) attacks the olefin's terminus. The resulting organoborane is treated with a nitrogen-containing group followed by an acid work-up.

Scheme 1. Comparative synthetic methods for the synthesis of terminal amines from terminal olefins. Top: hydroboration amination method to be tested. Bottom: Gabriel amine synthesis.



Experimental Details

Scheme 2. Mechanistic overview of the hydroboration amination reaction (Top), and the hydroboration oxidation reaction (Bottom).



•Scheme 2 outlines the mechanisms of reactions preformed and studied this summer.

•Using the amination reaction in Scheme 2 as a model, the direct amination of 1-octene was pursued.

•BH_3 and 9-BBN were used for hydroboration.

•Nitrogen containing groups tested were NaN_3[1] and NH_2Cl[2], and the presence of 1-octylamine was verified using ^{1}HNMR and GC/MS, and yields are outlined in Table 1.

•The hydroboration step was tested using the known synthetic method of hydroboration oxidation[3], whose mechanism is outlined in Scheme 2.

•Both BH_3 and 9-BBN were tested, and the presence of 1-octanol was verified using ^{1}HNMR and GC/MS, and yields are outlined in Table 2.

Results and Observations

Table 1. Summary of hydroboration amination results in relation to leaving groups with BH_3 as the borating agent.

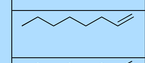
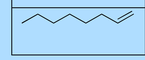
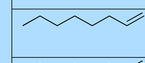
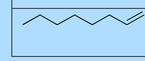
Starting Material	Product	Nitrogen Group	Experimental % Yield	Literature % Yield
		NaN_3	4%	79%
		NH_3Cl	5%	90%

Table 2. Summary of hydroboration oxidation results with BH_3 and 9-BBN as the borating agents.

Starting Material	Product	Hydroborating Agent	Experimental % Yield
		BH_3	92%
		9-BBN	75%

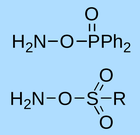
•The summer was spent problem solving. The method attempted first utilized BH_3 and NH_2Cl, which gave the meager 5% yield.

•No product was synthesized when attempting this method with 9-BBN in the hydroboration step. That is when the actual hydroboration step was tested using hydroboration oxidation.

•With the confirmation of the hydroboration step's functionality, the NaN_3 synthetic method was attempted, again producing a low 4% yield.

•The NH_2Cl method did not work as well as the in the literature, and it could be the result of the degradation of reagents used to synthesize NH_2Cl. The hydroboration step worked, as shown by the hydroboration oxidation reaction preformed previously. Yet yields were still low, showing that something was wrong with the NH_2Cl synthesis.

•There are a number of other nitrogen reagents with potential leaving groups that can be tried in the future, as shown in Scheme 3.



Scheme 3. Ammonia derived compounds to be tested in the future using the hydroboration amination reaction.

R= p-tol, Me, OH, CF_3

Acknowledgements

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Works Cited

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3. Mayo, et. al. *Microscale Organic Laboratory*. 4th ed. John Wiley and Sons, Inc.: NY. 1987. 223-229.