A SYNTHESIS OF OLEFINS *via* HYDROBORATION OF CYCLIC TRIMETHYLSILYL ENOL ETHERS[1]

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The reductive dehydration of ketones to form olefins has been accomplished in a variety of ways with generally only moderate success.[3] Among the more recent and better ways to make this conversion are those involving hydroboration or hydroalumination of a functional olefin derived from the ketone. Thus, olefins have been prepared from the hydroboration of enamines[4] or enol acetates[5] when the intermediate organoborane is treated with acid or *via* the hydroalumination of enamines[6] or enol ethers[7] where the elimination occurs spontaneously.

We have shown that the hydroboration of trimethylsilyl enol ethers occurs to place the boron atom on the β carbon of the double bond.[8] In acyclic systems the resulting β-trimethylsiloxy organoborane is not stable undergoing a rapid elimination to form olefin, which is then hydroborated.[8,9] The *trans*-β-trimethylsiloxy organoboranes that result from the hydroboration of cyclic trimethylsilyl enol ethers are much more stable, however. We wish to report here that these intermediate boranes can be readily converted to cyclic olefins upon treatment with an acid catalyst. Thus, conversion of cyclic ketones to olefins is possible according to the sequence in Scheme I.

Scheme I
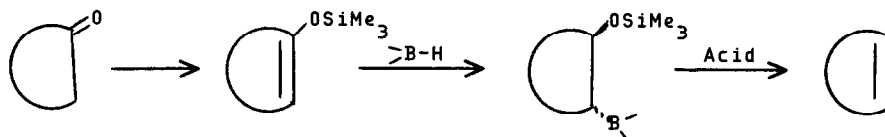
We have found that a variety of acids will catalyze the elimination reaction, including carboxylic acids, boron trifluoride-ethyl etherate or simply aqueous HCl. We have used aqueous HCl as the most convenient. The results are shown in Table I. The lower yield for the cyclooctanone system can be attributed to the fact that the intermediate organoborane undergoes an elimination before the addition of the acid and that the resulting cyclooctene is then hydroborated. Indeed, if the reaction mixture is oxidized rather than treated with acid, cyclooctanol is obtained in good yield.

It can be noted that the reaction serves very well for those systems which are symmetrical and would work well for those systems in which the trimethyl-silyl enol ether could either be selectively prepared or readily separated from its isomer. One such unsymmetrical system has been investigated, namely 2-methylcyclohexanone. Thus, formation of the trimethylsilyl enol ether of 2-methylcyclohexanone under thermodynamic conditions[10] gave an 80:20 mixture of 1-trimethylsiloxy-2-methylcyclohexene, I and 2-trimethylsiloxy-3-methylcyclo-hexene, II. The enol ether, I, was easily separated from II by distillation through a spinning band column. Hydroboration-elimination of the pure I gave 1-methylcyclohexene in 65% yield. Treatment of 2-methylcyclohexanone with the hindered base lithium diisopropylamide in THF followed by quenching of the anion with trimethylchlorosilane gave the enol ether, II.[10] Hydroboration-elimination of II gave 3-methylcyclohexene in 90% yield. Thus, the stereospecific synthesis of unsymmetrical cyclic olefins is only dependent upon the availability of single isomers of the trimethylsilyl enol ethers.[11]

<div align="center">Scheme II</div>
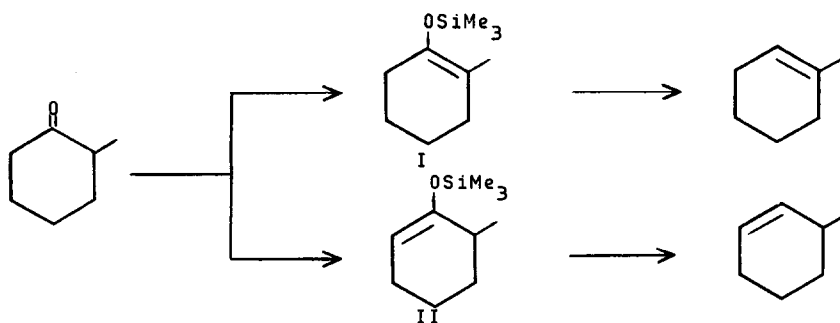
We are currently investigating the use of hindered hydroborating agents as a route to the stereospecific synthesis of cyclic olefins from a mixture of silyl enol ethers.

The preparation of cyclohexene is representative of the procedure. Into a 50 ml, round bottom flask was placed 4.25 g (25 mmol) of 1-trimethylsiloxy-cyclohexene, toluene (internal standard) and 10 ml of dry THF. To this was added 14.6 ml (25 mmol) of 1.71 $\underline{M}$ borane in THF[12] at 0°. The solution was stirred at 25° for 1 h and a few drops of water added to destroy the excess hydride present. This was followed by the addition of 15 ml of 10% HCl and refluxing for 4 h. The aqueous layer was extracted with ether and the combined organic layers washed with $NaHCO_3$ and water, dried and the solution subjected to GLC analysis. Careful distillation gave the pure cyclohexene.

Table I Formation of Olefins *via* the Hydroboration of Trimethylsilyl Enol Ethers

Ketone	Olefin	% Yield[a]
Cyclopentanone	Cyclopentene	75
Cyclohexanone	Cyclohexene	76
Cycloheptanone	Cycloheptene	90
Cyclooctanone	Cyclooctene	26
4-Methylcyclohexanone	4-Methylcyclohexene	76
4-^{t}Butylcyclohexanone	4-^{t}Butylcyclohexene	56
2-Methylcyclohexanone	1-Methylcyclohéxene[b]	65
2-Methylcyclohexanone	3-Methylcyclohexene[c]	90

a) GLC yield using toluene as internal standard, calculated from the trimethyl-silyl enol ether.

b) 1-Trimethylsiloxy-2-methylcyclohexene prepared under thermodynamic control according to the procedure of House, et al.[10]

c) 2-Trimethylsiloxy-3-methylcyclohexene prepared under kinetic control.[11]

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