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THE STEREOCHEMISTRY OF THE β ELIMINATION OF β-TRIMETHYLSILOXY ORGANOBORANES*

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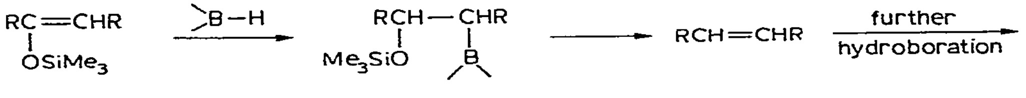
Summary

The stereochemistry of the β elimination of β-trimethylsiloxy organoboranes has been investigated by studying the β-methylstyrenes formed from the hydroboration of 1-phenyl-2-trimethylsiloxypropene. It is concluded that the major pathway for the elimination of a β-siloxy organoborane is a *cis* elimination even in the presence of boron trifluoride-ethyl etherate. The presence of pyridine in the reaction mixture slows down the elimination reaction.

Introduction

Eliminations of β functional organoboranes have been shown to occur via three possible mechanisms: (1) *Syn* elimination via a four-centered transition state, (2) *Anti* base catalyzed eliminations and (3) *Anti* acid catalyzed eliminations [1,2].

Recently, we have shown that the hydroboration of trimethylsilyl enol ethers proceeds by addition of the B atom on the β carbon of the double bond [3]. The resulting β-trimethylsiloxy organoboranes from cyclic enol ethers are stable, yielding *trans*-1,2 diols upon oxidation [3,4]. However, the intermediate β-trimethylsiloxy organoboranes from acyclic enol ethers are unstable, undergoing a facile β elimination of trimethylsiloxyborane [3]. We wish to report here on the stereochemistry of this β elimination (eqn. 1).



$$\underset{\text{OSiMe}_3}{\text{RC}}{=}\text{CHR} \xrightarrow{>\text{B}-\text{H}} \underset{\text{Me}_3\text{SiO}}{\text{RCH}}-\underset{\text{B}}{\text{CHR}} \longrightarrow \text{RCH}{=}\text{CHR} \xrightarrow[\text{hydroboration}]{\text{further}} \qquad (1)$$

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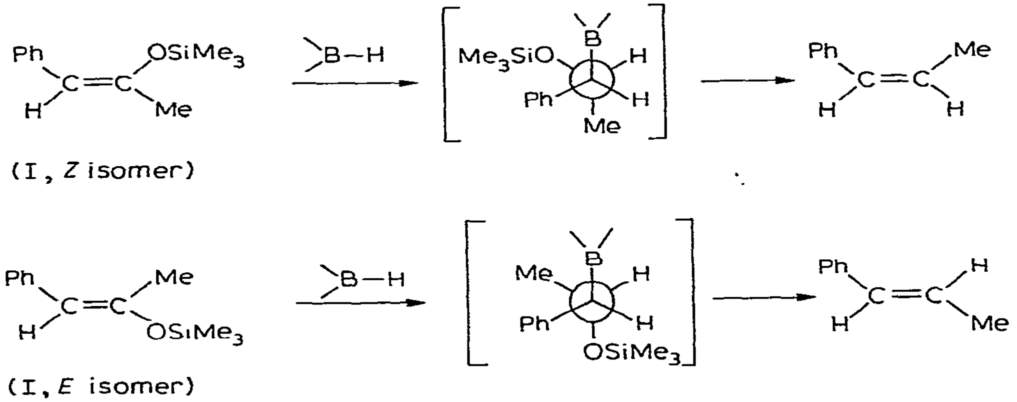
Results and discussion

Reaction of phenylacetone with trimethylchlorosilane in DMF in the presence of triethylamine according to House et al. [5], afforded a 75% yield of a mixture of *Z* and *E* 1-phenyl-2-trimethylsiloxypropene (I) in a *Z*/*E* ratio of 80/20. The ratio of isomers was determined by careful integration of the vinyl protons at 5.25 ppm and 5.75 ppm, corresponding to the *Z* and *E* isomers, respectively [5]. Hydroboration of a four-fold excess of I with borane or 2,3-dimethyl-2-butylborane (thexylborane) in THF gave the results shown in Table 1 (eqn. 2). An excess of the silyl enol ether was used in order to give a maximum amount of the β-methylstyrenes and to minimize problems due to the hydroboration of the β-methylstyrenes formed. The results of these reactions can only be interpreted in terms of *cis* elimination of trimethylsiloxyborane. The elimination when borane is used as the hydroborating agent is 100% *cis*, dropping to 91% when thexylborane is used as the hydroborating agent. The lower specificity of the elimination with thexylborane could be due to the larger size of the thexylborane, but is more likely a reflection of the fact that of the two product olefins, *cis*-β-methylstyrene would hydroborate faster than the *trans*-β-methylstyrene, thus giving the appearance of a less selective *cis* elimination. It has been shown that *cis* olefins undergo hydroboration faster than their *trans* isomers [6]. Hydro-



(2)

TABLE 1

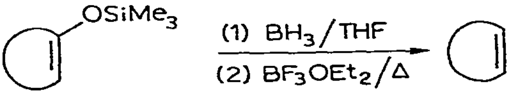
RATIO OF β-METHYLSTYRENES FORMED IN THE HYDROBORATION OF 1-PHENYL-2-TRIMETHYLSILOXYPROPENE.

Reaction conditions	*Z*/*E* Ratio of β-methystyrenes	% *cis*-Elimination
Borane in THF	81/19	100
Thexylborane in THF	73/27	91
9-BBN	none formed[a]	
Pyridine borane	none formed[b]	
Borane/BF_3[c]	77/23	96
Thexylborane/BF_3[c]	60/40	67

[a] The reaction of 9-BBN with the silyl enol ether is very slow. [b] The elimination is apparently very slow. The yield of diol upon oxidation was about 25%. [c] One equivalent of boron trifluoride-ethyl etherate was added per equivalent of borane or thexylborane.

boration of I with 9-BBN failed to yield any β-methylstyrene product.

In order to see if the elimination could be prompted to occur in a *trans* manner, the hydroboration reaction was carried out in the presence of one equivalent (per borane) of boron trifluoride-ethyl etherate. These results are shown in Table 1. The results show that even in the presence of the strong Lewis acid, boron trifluoride the elimination is predominantly *cis* being greater than 96% *cis* with borane and greater than 67% *cis* with thexylborane. This is a reflection of a weak interaction between the siloxy group and the boron trifluoride. Indeed, it has been shown that the siloxy oxygen is a weaker base then the ether oxygen [7], indicating that the siloxy group would be expected to compete unfavorably with the THF for the boron trifluoride-ethyl etherate. We have found, however, that a *trans* elimination of trimethylsiloxyborane may be accomplished in cyclic *trans*-2-trimethylsiloxy organoboranes using boron trifluoride-ethyl etherate as the catalyst (eqn. 3). This reaction is not spontaneous, however, requiring warming and several minutes for completion. Boron trifluoride has been shown to effectively catalyze *trans* eliminations in other β functional organoboranes [1].



(3)

(II)

The use of pyridine borane as the hydroborating agent resulted in only a small amount of β-methylstyrenes being formed. Oxidation of the reaction mixture showed the formation of 1-phenyl-2,3-propanediol in good yield indicating that prior complexation of the boron atom to pyridine slows down the elimination reaction greatly. Indeed, a base catalyzed *trans* elimination in these systems seems to be extremely difficult. Thus, a THF solution of II when hydroborated with borane and then refluxed with a 10% solution of sodium methoxide in methanol for several hours showed no formation of cyclohexane.

That the elimination occurs before the addition of water in the work-up is evidenced by the fact that upon oxidation of the reaction mixture products are obtained from the hydroboration of the olefins produced [3], and from the fact that the addition of water would be expected to give a *trans* elimination [8]. Control experiments showed that a mixture of borane and boron trifluoride-ethyl etherate in THF did not isomerize the trimethylsilyl enol ether (I) nor the β-methylstyrenes under the conditions of the reaction. Control experiments also showed that the rates of hydroboration of the *Z* and *E* isomers of I were not significantly different.

Experimental

Materials

All glassware was flame dried under a stream of nitrogen and all reactions were run under an atmosphere of dry nitrogen. THF was distilled from sodium and benzophenone prior to use. Standard borane—THF was prepared by the procedure of Brown and Sharp [9] and stored at 0°C. 2,3-Dimethyl-2-butylborane (thexylborane) was prepared according to Brown and Moerikofer [10] and was used immediately. 9-Borabicyclo[3.3.1]nonane (9-BNN) was prepared according to Brown and Knights [11] and was used immediately. Boron trifluoride-ethyl etherate was distilled from calcium hydride prior to use. The 1-phenyl-1-2-trimethylsiloxypropene (I) was prepared using the method of House et al. [5]. An authentic sample of *cis*-β-methylstyrene was prepared from 1-phenylpropyne according to the procedure of Zweifel and Brown [12]. An authentic sample of *trans*-β-methylstyrene, which contained about 10% of the *cis* isomer was prepared using the procedure of Nystrom and Brown [13].

Analyses

The analysis of the ratio of *cis*- and *trans*-β-methylstyrene was accomplished using a 15 foot, 20% DEGS column programmed from 75°C to 185°C at 3°/min on a Perkin—Elmer 990 Gas Chromatograph. Preparative GLC was carried out using a 6 foot, 20% DEGS column at 120°C on a Varian 90P Gas Chromatograph. The purified β-methylstyrenes were compared with authentic samples by their retention times, indices of refraction, IR and PMR spectra.

Hydroboration of 1-phenyl-2-trimethylsiloxypropene

Into a 100 ml, 2 neck flask was placed 8.24 g (40 mmol) of the trimethylsilyl enol ether (I) and 20 ml of THF. The system was cooled with an ice bath and 10 mmoles of borane (or thexylborane) were added. After stirring for 10 min the reaction mixture was hydrolyzed by the addition of 10 ml of water. The organic layer was washed with 1% potassium carbonate and saturated sodium chloride. The aqueous layer was extracted with ether and the combined organic layers dried over magnesium sulfate. GLC of the reaction mixture allowed the analysis of the ratio of *cis*- and *trans*-β-methylstyrene formed in the reaction. Preparative GLC gave the pure isomers, whose retention times, refractive indices, IR and PMR spectra were in complete accord with those of authentic samples and with literature values [14].

In the reaction with boron trifluoride-ethyl etherate added as catalyst, the silyl enol ether (I) was placed in the flask with 10 mmoles of boron trifluoride-ethyl etherate and the hydroboration carried out as above.

Control samples of the trimethylsilylenol ether (I) and of the β-methylstyrenes were subjected to the above reaction conditions with borane/boron trifluoride-ethyl etherate in THF and were found to undergo no change in their isomeric distribution.

Acknowledgements

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