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THE HYDROBORATION OF TRIMETHYLSILYL ENOL ETHERS

GERALD L. LARSON*, DAVID HERNANDEZ** and ANTONIO HERNANDEZ
Department of Chemistry, University of Puerto Rico, Rio Piedras 00931 (Puerto Rico)
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Summary

The hydroboration—oxidation of a variety of trimethylsilyl enol ethers has been investigated. The trimethylsiloxy group exerts a strong directive effect on the reaction to place the boron atom predominantly on the β carbon. The resulting β boryl intermediates undergo a facile elimination in the acyclic systems, but are much more stable in the cyclic systems. The reaction of the trimethylsilyl enol ethers of cyclic ketones gives either *trans*-1,2 diols or monosilylated *trans*-1,2 diols depending upon the work-up procedure.

Introduction

The hydroboration of vinyl substituted alkenes has been the subject of a number of papers. Among the systems that have been studied are vinyl chlorides [1—4], vinyl bromides [3], ethyl enol ethers [4, 5], enolate anions [6], trimethylsilyl enol ethers [6], enol acetates [4, 7], thio enols [8] and enamines [9, 10].

The work of Brown and Sharp [4] on the hydroboration of ethyl enol ethers, which showed that the ethoxy group has a strong directive effect placing the boron atom exclusively on the β carbon and that the resulting β boryl intermediates from these reactions are quite stable to elimination prompted us to investigate the hydroboration of trimethylsilyl enol ethers in some detail. It seemed to us that the trimethylsiloxy group should also have a strong directive effect on the incoming boron atom and that it might undergo a β elimination reaction with boron only reluctantly. Two other advantages in the use of trimethylsilyl enol ethers are their availability [11] and their ready hydrolysis to alcohols. The possibility of a 1,2 diol synthesis thus seemed realizable via this route. Indeed, Klein and coworkers [6] have reported that the hydroboration—oxidation of two trimethylsilyl enol ethers, those of cyclohexanone and 4-methylcyclohexanone give *trans*-1,2 diols in good yield.

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* Address correspondence to this author.

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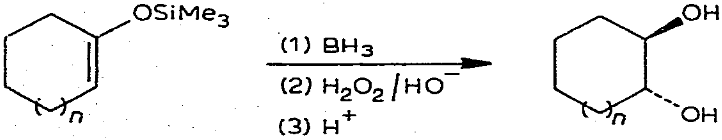
We wish to report here the results of our study of the hydroboration—oxidation of a number of trimethylsilyl enol ethers.

Results and discussion

Trimethylsilyl enol ethers of cyclopentanone, cyclohexanone and cycloheptanone

The hydroboration of these enol ethers was carried out using one equivalent of borane in THF for one hour at 0°. The reaction mixture was oxidized with a solution of alkaline hydrogen peroxide. In order to get the best yields of diols it was necessary to wash the organic layer with two or three portions of 10% HCl during work-up. If this step is omitted the major product is the monosilylated diol (see later). The reaction is rapid as evidenced by TLC analysis. The results of the reaction are given in Table 1. The reaction is illustrated by eqn. 1.



(1)

(Ia) $n = 0$
(Ib) $n = 1$
(Ic) $n = 2$

(IIa) $n = 0$
(IIb) $n = 1$
(IIc) $n = 2$

The lack of any ketone in the product mixture strongly implies that the reaction is quantitative and that the boron atom goes exclusively to the β carbon in these systems. The presence of a small amount of monool in the products, however, does not allow us to completely rule out the possibility of a small amount of an α boryl intermediate being formed. An α boryl intermediate could lead to monool in two ways; an α elimination of trimethylsiloxyborane could occur to give a carbene, which would give an alkene, hydroboration—oxidation of which would give the monool, or an α transfer reaction [12] could occur to give trimethylsiloxycyclohexylborane, which would be oxidized to the monool. The fact that

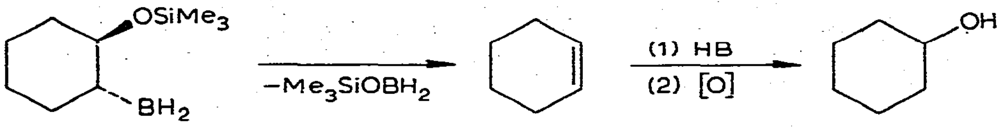
TABLE 1

HYDROBORATION OF CYCLIC TRIMETHYLSILYL ENOL ETHERS

Enol ether	Products	Yield
Ia	*trans*-1,2-Cyclopentanediol	63 [a]
	Cyclopentanol	4 [b]
	Cyclopentene	trace
Ib	*trans*-1,2-Cyclohexanediol	75 [a]
	Cyclohexanol	trace [b]
Ic	*trans*-1,2-Cycloheptanediol	49 [a]
	Cycloheptanol	trace [b]
III	4-t-Butyl-*trans*-1-*cis*-2-cyclohexanediol	56 [a]
	4-t-Butyl-*cis*-1-*trans*-2-cyclohexanediol	17 [a]
IV	1-Phenyl-*trans*-1,2-cyclohexanediol	50 [a]
	1-Phenyl-*trans*-2-trimethylsiloxy-1-cyclohexanol	14 [a]
	trans-2-Phenylcyclohexanol	4 [b]
V	α-Tetralol	92 [b]
	β-Tetralol	8 [b]
	1,2-Dihydronaphthalene	trace [b]

[a] Isolated yield. [b] GLC analysis.

no norcarane could be detected in the reaction mixture from Ic is evidence against an α elimination process as the resulting carbene should give some norcarane [3]. Evidence against an α transfer reaction will be given later in this paper. We favor a β elimination process from a β boryl intermediate to account for the small amounts of monools found in these reactions (eqn. 2). The somewhat greater

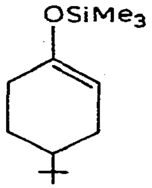


(2)

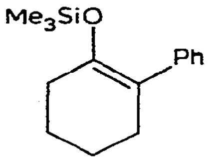
amount of cyclopentanol as opposed to cyclohexanol is consistent with the findings of Brown and Sharp [4] in the hydroboration of 1-ethoxycyclopentene and 1-ethoxycyclohexene.

Trimethylsilyl enol ethers of substituted cyclohexanones

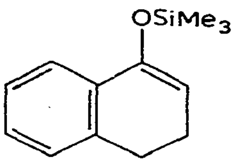
The hydroboration—oxidation of the trimethylsilyl enol ethers of 4-t-butylcyclohexanone (III), 2-phenylcyclohexanone (the 1-trimethylsiloxy-2-phenylcyclohexene isomer only) (IV), and α-tetralone (V) were studied. The enol



(III)

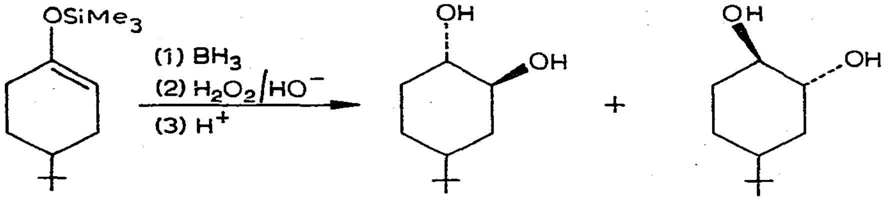


(IV)



(V)

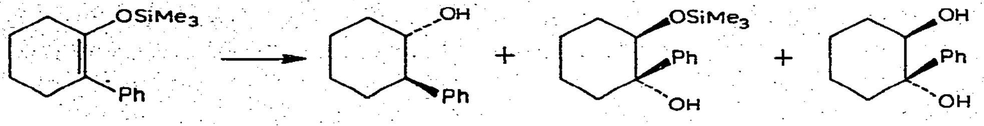
ethers, III and V, reacted within one hour at 0°, but IV required about five hours at 25° for complete reaction. The results of these reactions are given in Table 1. The enol ether, III, gave only two products (GLC), 4-t-butyl-*trans*-1-*cis*-2-cyclohexanediol (VI) and 4-t-butyl-*cis*-1-*trans*-2-cyclohexanediol (VII) in a ratio of 3/1 and in a 73% isolated, overall yield (eqn. 3). The isomers were separated by careful crystallization from pentane ether. Thexylborane (2,3-dimethyl-2-butylborane) [13] proved somewhat more selective giving a ratio of VI to VII of 88/12.



(3)

(III) (VI) (VII)

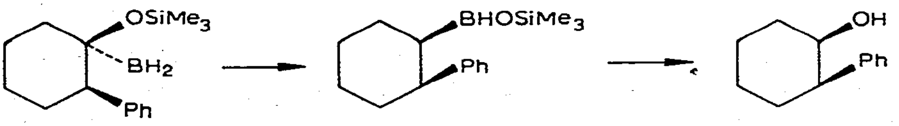
The reaction with 1-trimethylsiloxy-2-phenylcyclohexene (IV) gives the products shown in eqn. 4. It should be noted that no 2-phenylcyclohexanone nor



(IV)

(4)

cis-2-phenylcyclohexanol were observed. The absence of *cis*-2-phenylcyclohexanol rules out an α transfer reaction in this system and probably in the other systems as well, since Pasto and Hickman [12] have shown that the alpha transfer reaction occurs with inversion at carbon (eqn. 5). It is thus possible to say that in this system the boron atom goes exclusively to the β carbon. The small amount of *trans*-2-phenylcyclohexanol comes from a beta elimination process. The hydroboration—oxidation of 1-phenylcyclohexene has been shown to give only *trans*-2-phenylcyclohexanol [14].



(5)

Enol ether V gave as products only α and β tetralol with a trace of 1,2-dihydronaphthalene (GLC) and a trace of 1,2,3,4-tetrahydro-*trans*-1,2-naphthalenediol. Distillation gave an 81% yield of the combined isomeric monools. No alpha tetralone was observed. To check the postulate that the monools arise from the hydroboration of 1,2-dihydronaphthalene, this compound was made and hydroborated. Both the hydroboration of V and of 1,2-dihydronaphthalene gave α and β tetralol in a ratio of 92/8, consistent with the postulate that the monools arise from a beta elimination of an intermediate β boro system to give 1,2-dihydronaphthalene, which is then hydroborated and oxidized.

Trimethylsilyl enol ethers of acyclic ketones and aldehydes

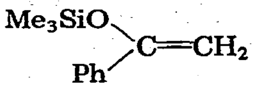
The trimethylsilyl enol ethers of acetophenone (VIII), butyraldehyde (IX) and isobutyraldehyde (X) were hydroborated for one hour at 0° with one equivalent of borane in THF or ether. The results are summarized in Table 2. In all cases the boron atom adds predominantly to the β carbon. Unfortunately, the

TABLE 2

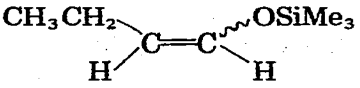
HYDROBORATION OF ACYCLIC TRIMETHYLSILYL ENOL ETHERS

Enol ether	Products	Yield [a] (THF)	Yield [a] (ether)
VIII	2-Phenylethanol	72	55
	1-Phenylethanol	18	14
	2-Phenyl-1-trimethylsiloxyethane	5	14
	1-Phenyl-1,2-ethanediol	3	2
IX	1-Butanol	63	28
	2-Butanol	3	
	1,2-Butanediol	3	5
	1-Trimethylsiloxy-2-butanol		15
X	Isobutanol	28	
	Isobutyraldehyde	6	
	1,2-Isobutanediol	3	

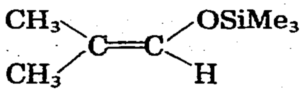
[a] GLC analysis.



(VIII)



(IX)

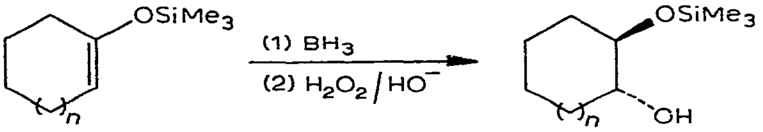


(X)

intermediate β substituted organoboranes are unstable with respect to elimination. Thus, they undergo a facile β elimination of trimethylsiloxyborane to give an alkene, which is subsequently hydroborated and oxidized to a monool. Thus, VIII gives 2-phenylethanol and 1-phenylethanol in a ratio of 81/19 (styrene gives a ratio of 81/19 [15]), IX gives mainly 1-butanol and 2-butanol in a ratio of 95/5 (1-butene gives a ratio of 94/6 [15]) and X gives mostly isobutanol. The small amount of isobutyraldehyde from X probably arises from unreacted enol ether. The use of diethyl ether solvent in the reaction gave slightly higher yields of monosilylated diols in these systems, the hydrolysis of the trimethylsilyl group being slower with the more water insoluble ether. The fact that a slightly better yield of the monosilylated diol is obtained in the reaction using diethyl ether solvent may be due to a lesser amount of β elimination reaction in the ether solvent during the hydroboration reaction or during the alkaline work-up.

Synthesis of monosilylated diols

The hydroboration of the enol ethers, Ia, Ib, and Ic, followed by simple alkaline hydrogen peroxide oxidation gave rise to monosilylated diols (eqn. 6). Whereas the compounds XIa, XIb and XIc could be obtained in THF, the compound XIc was best obtained in diethyl ether solvent. The results of these reactions are shown in Table 3. The properties of the monosilylated diols are given in the experimental section. Klein and coworkers [6] did not report the formation of monosilylated diols in the hydroboration of the trimethylsilyl enol ethers of cyclohexanone and 4-methylcyclohexanone. The difference in their results from



(6)

(Ia) $n = 0$
(Ib) $n = 1$
(Ic) $n = 2$

(XIa) $n = 0$
(XIb) $n = 1$
(XIc) $n = 2$

TABLE 3

PREPARATION OF MONOSILYLATED DIOLS

Enol ether	Product	Yield [a]
Ia	*trans*-2-Trimethylsiloxycyclopentanol	50
Ib	*trans*-2-Trimethylsiloxycyclohexanol	59
Ic	*trans*-2-Trimethylsiloxycycloheptanol	30 [b]

[a] Isolated yields. [b] Diethyl ether solvent.

ours is probably due to a difference in the time and/or temperature of the oxidation step. These monosilylated diols have potential use in stereochemical studies.

Conclusions

Clearly the trimethylsiloxy group in trimethylsilyl enol ethers directs the boron atom predominantly, if not exclusively to the β carbon of the enol ether. The resulting β boryl intermediate is stable to elimination only in cyclic systems, with the notable exception of the trimethylsilyl enol ether of α-tetralone. In acyclic systems the β boryl intermediate is unstable, undergoing a facile elimination reaction to give trimethylsiloxyborane and an alkene. Thus, the trimethylsilyl enol ethers of cyclic ketones are very good precursors to *trans*-1,2 diols via hydroboration, but the acyclic trimethylsilyl enol ethers are undesirable precursors for the synthesis of 1,2 diols via hydroboration.

Experimental

Instrumentation

Melting points are corrected. Infrared spectra were recorded on a Perkin—Elmer 237 spectrometer, PMR spectra on a Varian T60 spectrometer using internal tetramethylsilane as a standard, and mass spectra on a Hitachi—Perkin—Elmer RMS-4 mass spectrometer. Gas chromatographic analyses were run on a Perkin—Elmer 820 or 990 gas chromatograph using 20% DEGS, 5% SE-30 and 10% carbowax 20 M columns of 6 feet.

Materials

The trimethylsilyl enol ethers were prepared according to the procedure of House et al. [11] and were clean of any ketone or other impurities as evidenced by GLC immediately prior to use. Tetrahydrofuran, diglyme and ether were distilled from sodium benzophenone prior to use. All ketones and aldehydes were distilled prior to use. Boron trifluoride etherate was distilled from calcium hydride. A 2.05 *M* solution of borane in THF was prepared according to Brown and Sharp [4]. The external generation of diborane for the reactions in diethyl ether was carried out according to Brown [16] with the added precaution that a sodium borohydride in diglyme trap was placed in the system to trap any unreacted boron trifluoride. 1,2-Dihydronaphthalene was prepared from α-tetralol according to the procedure of Nystrom and Brown [17].

All other reagents were obtained commercially and used without further purification.

Hydroboration—oxidation of trimethylsilyl enol ethers in THF

A solution of the trimethylsilyl enol ether (25 mmol) in THF (25 ml) was placed in a 100 ml round bottom flask. The system was cooled to between 0 and 5° with an ice bath and a solution of borane in THF (25 mmol) was added with a syringe. The reaction mixture was stirred for 1 h at about 0° and a mixture of 8 ml of 3 *N* sodium hydroxide and 8 ml of 30% hydrogen peroxide was added over 15 min using caution with the first few drops until the excess hydride is reacted. The resulting two phase system was stirred for 1 h at 35°, solid potassium carbonate added and the aqueous layer extracted with ether (2 × 25 ml). The combined organic layers were washed with 10% HCl (3 × 20 ml) and dried over anhydrous magnesium sulfate. The products were analyzed and isolated by GLC, distillation or crystallization.

Preparation of monosilylated diols

The procedure for the preparation of the monosilylated diols is the same as that for the hydroboration—oxidation of the trimethylsilyl enol ethers except that the acid washing of the organic phase during work-up is omitted. The physical and spectral properties of these systems are given below.

trans-2-Trimethylsiloxycyclopentanol. B.p. 70—74° (2 mm); n_D^{20} 1.4256; IR ($CHCl_3$) 3450 and 3610 (OH), 1250 and 840 cm^{-1} (Me_3Si); PMR (CCl_4) δ 0.12 (s, 9, CH_3Si), 1.68 (m, 6, CH_2), 3.70 ppm (m, 2, CHO), variable on dilution (s, 1, OH); mass spectrum (70 eV) *m/e* (rel. int.) 174 (1), 75 (100), and 73 (58).

trans-2-Trimethylsiloxycyclohexanol. B.p. 79—81° (1.2 mm); n_D^{20} 1.4506; IR (neat) 3500 (OH), 1250 and 840 cm^{-1} (Me_3Si); PMR (CCl_4) δ 0.12 (s, 9, CH_3Si), 1.70 (m, 8, CH_2), 3.22 ppm (m, 2, CHO), and variable on dilution (s, 1, OH); mass spectrum (70 eV) *m/e* (rel. int.) 188 (1), 75 (100) and 73 (92).

trans-2-Trimethylsiloxycycloheptanol. B.p. 78—79° (1.0 mm); n_D^{20} 1.4596; IR (neat) 3450 (OH), 1250 and 840 cm^{-1} (Me_3Si); PMR (CCl_4) δ 0.08 (s, 9, CH_3Si), 1.52 (m, 10, CH_2), 3.42 ppm (m, 2, CH—O), and variable on dilution (s, 1, OH); mass spectrum (70 eV) *m/e* (rel. int.) 202 (1), 75 (52) and 73 (100).

1-Phenyl-trans-2-trimethylsiloxy-1-cyclohexanol. (Obtained as a side product in the hydroboration of IV.) B.p. not determined, n_D^{20} 1.5096; IR (neat) 3550 (OH), 1250 and 840 cm^{-1} (Me_3Si); PMR (neat) δ —0.12 (s, 9, CH_3Si), 1.75 (m, 8, CH_2), 3.80 (m, 1, CH—O), 7.55 ppm (m, 5, aromatic), and variable on dilution (s, 1, OH); a mass spectrum was not obtained.

Hydroboration of 1,2-dihydronaphthalene

Into a 100 ml flask was placed 4.5 g (35 mmol) of 1,2-dihydronaphthalene and 35 ml of THF. A solution of borane in THF (35 mmol) was added at 0° over a 5 min period. After 90 min of reaction at 0° the reaction mixture was oxidized with 12 ml of 3 *N* sodium hydroxide and 12 ml of 30% hydrogen peroxide for 1 h at 35°. Gas chromatography of the dried ($MgSO_4$) organic layer showed a quantitative yield of a mixture of α-tetralol and β-tetralol in a ratio of 92/8.

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