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THE HYDROBORATION-OXIDATION OF THE ISOMERIC TRIMETHYLSILYLCYCLOHEXENES AND THE ISOMERIC TRIMETHYLSILYLCYCLOPENTENES.

MILDRED DE JESUS, OSVALDO ROSARIO and GERALD L. LARSON*
Department of Chemistry, University of Puerto Rico, Río Piedras,
Puerto Rico 00931 (U.S.A.)

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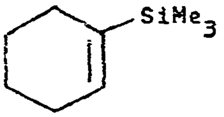
Summary

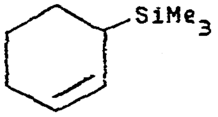
The isomeric trimethylsilyl substituted cyclohexenes, 1-trimethylsilylcyclohexene, 3-trimethylsilylcyclohexene, and 4-trimethylsilylcyclohexene and the analogous trimethylsilyl substituted cyclopentenes, 1-trimethylsilylcyclopentene, 3-trimethylsilylcyclopentene and 4-trimethylsilylcyclopentene have been hydroborated and oxidized under kinetic and thermodynamic conditions. The hydroborating agents used were borane and thexylborane in THF. The products of these reactions show a dependence on temperature and the hydroborating agent used and are a result of a rather facile migration of the boron atom around the ring. Some synthetically useful reactions are discussed as are the structures of various trimethylsilyl substituted cyclohexanols and cyclopentanols.

Introduction

The thermal isomerization of organoboranes is a well established process which usually requires heating the organoborane to temperatures above 100° in order to achieve reasonable rates [1]. It has been reported that the hydroboration of 1-methylcyclooctene results in a rapid isomerization of the intermediate organoboranes at temperatures as low as 0° [2]. The corresponding 1-substitued cyclopentenes and cyclohexenes, however, require higher temperatures before appreciable isomerization occurs. Musker and Larson [3] have noted a rather facile isomerization of the intermediate organoboranes obtained from the hydroboration of 1-trimethylsilylcyclohexene, I, with thexylborane. In conjunction with our interest in carbo-functional organosilanes we decided to undertake a detailed study of the hydroboration-oxidation of 1-trimethylsilyl substituted cyclohexenes and cyclopentenes. Thus we report here on the hydroboration-oxidation of 1-trimethylsilylcyclohexene, I, 3-trimethylsilylcyclohexene, II, 4-trimethylsilylcyclohexene, III, 1-trimethylsilylcyclopentene, IV, 3-trimethylsilylcyclopentene, V and 4-trimethylsilylcyclopentene, VI. These olefins were hydroborated with borane and thexylborane (2,3-dimethyl-2-butylborane) [4], in THF under kinetic and thermodynamic conditions, with the exception of III, which was only studied under kinetic conditions. The position of the boron atom in the intermediate organoboranes was determined by alkaline hydrogen peroxide oxidation [5].



I



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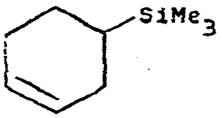

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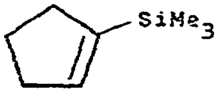
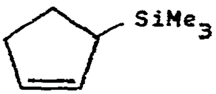
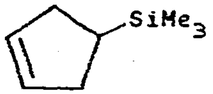


IV



V



VI

Results and discussion

Extent of Hydroboration

The reaction of 3 equivalents of I with 1 equivalent of borane in THF at 25° resulted in a rapid uptake of 1.5 equivalents of hydride (ca. 5 min) followed by a very slow uptake of hydride to form the dialkylborane derivative (48 h). Reaction beyond the formation of the dialkylborane did not occur. Compound I reacts slowly with thexylborane and is inert to 9-BBN [6] at 65° for 96 h. The isomer II is somewhat more reactive taking up 1.5 equivalents of hydride within 5 min and 2 equivalents after 4 h at 25°. The hydride uptake of this system did not exceed 2 equivalents even after several hours at 25°. Due to the small amounts of isomer III available, the extent of its reaction with borane was not investigated.

As expected the trimethylsilylcyclopentenes were more reactive towards borane. Isomer IV reacted rapidly with borane at 25° to take up 2 equivalents of hydride (5 min) followed by a slow reaction with the third equivalent of hydride to form the trialkylborane (24 h). Somewhat surprisingly the allyl isomer, V, reacted to form the dialkylborane in 2 h and the trialkylborane in 72 h at 25°, noticeably slower than the vinylsilane, IV. Again due to small amounts of sample, the extent of hydroboration of VI was not studied.

The hydroboration of the trimethylsilyl substituted cyclohexenes

A general description of the hydroboration of the three isomeric trimethylsilylcyclohexenes, I, II, and III is given in Scheme I. The results of the hydroboration-oxidation are given in Table I. The hydroboration of I with borane at -20° or 25° gives 1-trimethylsilylcyclohexanol, VII and trans-2-trimethylsilylcyclohexanol, VIII, as the only products in a ratio of 9:1 consistent with earlier work [7]. (entries 1 & 2) Raising the temperature of the hydroboration reaction to 65° (refluxing THF) for 24 h gives cis-3-trimethylsilylcyclohexanol, IX and trans-3-trimethylsilylcyclohexanol, X, with none of the isomers VII and VIII present. (entry 3) Thus, at 65° the intermediate organoboranes, XIII and XIV are unstable, undergoing dehydroboration rehydroboration to give the boranes XV and XVI which lead upon oxidation to alcohols IX and X, respectively. The use of thexylborane as the hydroborating agent results in a slower reaction, as expected, and alcohols VIII and X upon oxidation (entry 4) with complete loss

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Scheme I. The Hydroboration-Oxidation of the Trimethylsilylcyclohexenes, I, II and III. R= thexyl (2,3-dimethyl-2-butyl) or trimethylsilylcyclohexyl

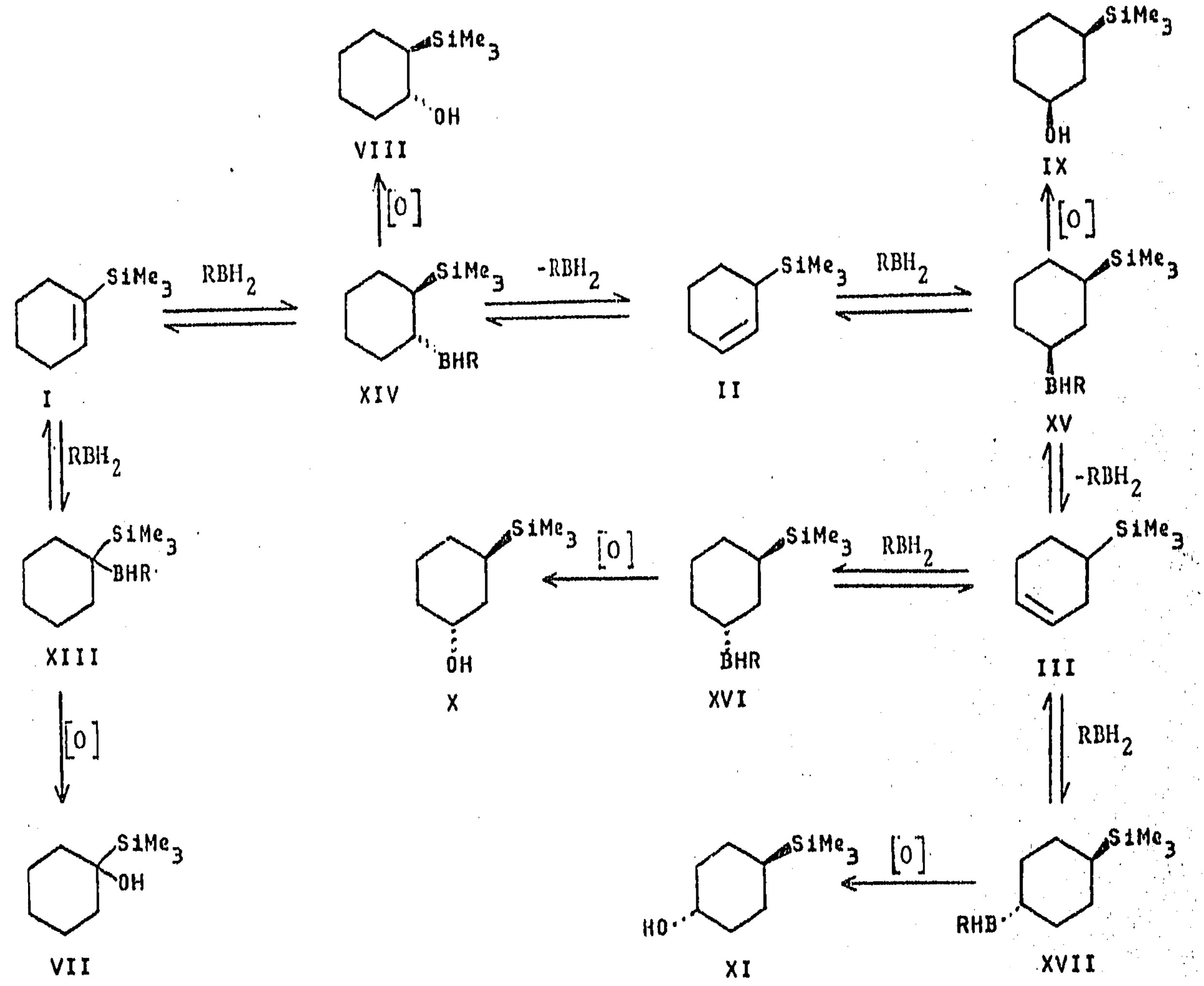

Table I. Products of the Hydroboration-Oxidation of the Trimethylsilylcyclohexenes.

Entry	Olefin	Hydroborating Agent	Conditions	VII	VIII	IX	X	XII	Yield
1	I	BH_3	-20°/15 min	92	8	--	--	--	
2	I	BH_3	25°/2 h	90	10	--	--	--	45%
3	I	BH_3	65°/24 h	--	--	93	7	--	
4	I	RBH_2[a]	25°/8 h	--	83	--	17	--	
5	I	RBH_2	25°/28 d	--	trace	74	26	--	50%
6	I	RBH_2	65°/26 h	--	--	92	8	--	70%
7	II	BH_3	-20°/1 h	--	24	17	59	--	
8	II	BH_3	25°/1 h	--	3	6	91	--	64%
9	II	BH_3	25°/7 d	--	6	71	23	--	
10	II	RBH_2	25°/5 d	--	--	74	26	trace	
11	III	BH_3	0°/1 h	--	--	24	49	25	
12	III	RBH_2	0°/1 h	--	--	24	52	24	

a. RBH_2 = thexylborane. b. Isolated yield of isomeric mixture.

of VIII and foramtion of IX when the hydroboration is allowed to proceed for several days at 25° (entry 5) or 26 h at 65° (entry 6).

The hydroboration of II follows a similar pattern as that of I. At -20° with borane, II gives after oxidation the alcohols VIII, IX and X (entry 7). Increasing the temperature of the reaction to 25° leads to these same alcohols, but with the alcohol, X, predominating (entry 8). The hydroboration of allyltrimethylsilane with borane gives only 3-trimethylsilyl-1-propanol as the product of oxidation [8,9] This has been explained as a possible consequence of the electronic effect of the trimethylsilylmethyl group on the hydroboration reaction [8]. Similar arguments applied to the hydroboration of II would lead to XV and XVI as the favored boranes. Of these two boranes, XVI would be favored kinetically and XV thermodynamically. The results of entries 8 and 9 are consistent with this argument as are the entries 4 and 5. Stereochemical arguments also support this line of thinking since in the borane, XVI one of the groups, either the trimethylsilyl or the boryl group will occupy an axial position, whereas in the borane, XV, both the trimethylsilyl and the boryl groups can occupy equatorial positions. The hydroboration of II with thexylborane at 25° for 5 d (entry 10) gives after oxidation alcohols IX and X in the same 76:24 ratio as that observed in the hydroboration of I with thexylborane (entry 5), consistent with the argument that the hydroboration of I goes through olefin II under thermodynamic conditions.

For comparison purposes, the hydroboration-oxidation of 3-tert-butylcyclohexene was briefly studied. Pasto and Klein [10] have reported that the hydroboration-oxidation of this olefin with an excess of borane for 30 min at 0° gives all four possible isomeric alcohols, <u>cis</u> and <u>trans</u>-2 and <u>cis</u> and <u>trans</u>-3-tert-butylcyclohexanol in a ratio of 1.4:43.3:1.7:53.6 Freppel and coworkers [11] reported the same alcohols in a similar ratio, but the conditions of the hydroboration reaction were not stated. We found that hydroboration with borane under thermodynamic conditions (65°/48 h) leads to <u>cis</u>-3 and trans-3-tert-butylcyclohexanol in a ratio of 67:33. Thus, this tert-butyl system also undergoes an isomerization process at relatively mild temperatures.

The olefin, III, was only briefly investigated under kinetic conditions giving the results shown in entries 11 and 12. It is of interest to note that no cis-4-trimethylsilylcyclohexanol, XII, could be detected, though several GLC columns and conditions were tried in addition to column chromatogrpahy on alumina. Pasto and Klein [10] have reported that the hydroboration of 4-tert-butylcyclohexene with borane gives all four possible isomeric alcohols upon oxidation.

The hydroboration of the trimethylsilylcyclopentenes

The hydroboration-oxidation of the isomeric trimethylsilylcyclopentenes, IV, V and VI is more straight-forward that that of the cyclohexene series. The results of this study are shown in Scheme II and tabulated in Table II. The hydroboration-oxidation of IV with borane under kinetic conditions gives 1-trimethylsilylcyclopentanol, XVIII, and trans-2-trimethylsilylcyclopentanol, XIX, as the only oxidation products in a ratio of 87:13 (entry 1). Carrying out the hydroboration at 25° for 48 h, however, leads to only alcohol XIX after oxidation (entry 2). Thus, the intermediate borane, XXII, is thermodynamically unstable at 25°, but the borane, XXIII is stable at 25°. Hydroboration of IV with thexylborane under kinetic conditions (0°/2 h) gives only alcohol XIX (entry 3) whereas under thermodynamic conditions (25°/48 h) only 7-9% of XIX is obtained and 91-93% of trans-3-trimethylsilylcyclopentanol, XX. The borane, XXIII (R= thexyl) is therefore, not stable at 25°.

Hydroboration-oxidation of olefin V with borane under kinetic conditions gives only alcohol XX (entry 5). Hydroboration with thexylborane, on the other hand, gave both XIX and XX as oxidation products in a ratio of 15:85 (entry 6). The hydroboration of isomer VI with either borane or thexylborane under kinetic or thermodynamic conditions gave only alcohol XX as the oxidation product. Thus, the hydroboration

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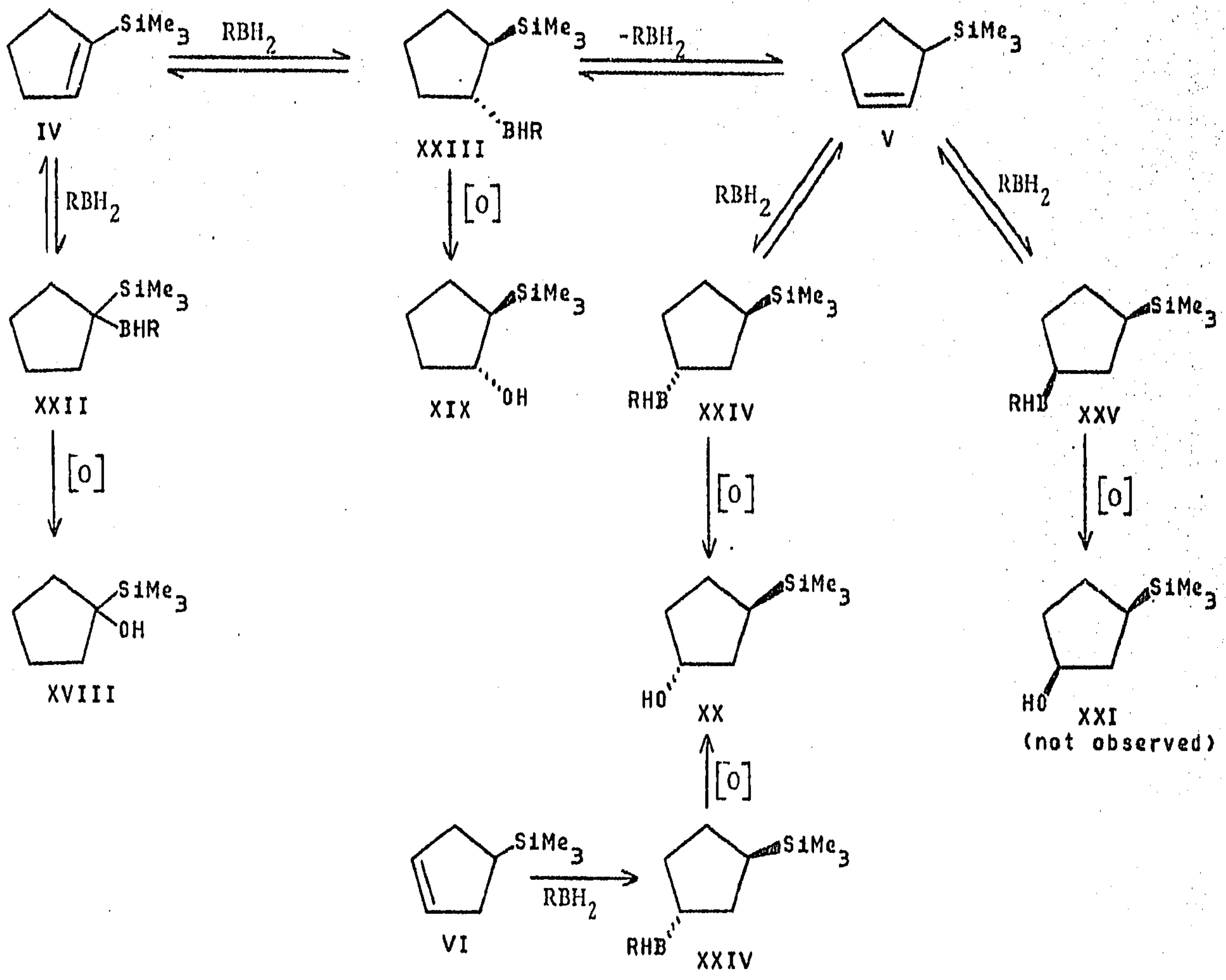
Table II. Products of the Hydroboration-Oxidation of the Trimethylsilylcyclopentenes

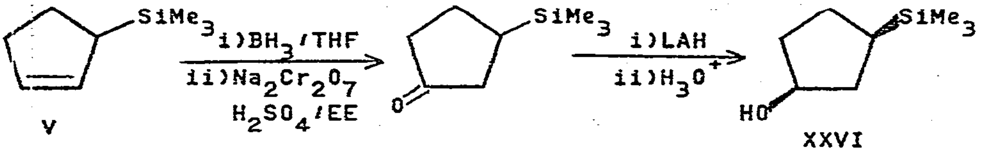
Entry	Olefin	Hydroborating Agent	Conditions	XVIII	XIX	XXII	XXIV	Yield
1	IV	BH_3	0°/30 min	87	13	--	--	76%
2	IV	BH_3	25°/48 h	--	100	--	--	
3	IV	RBH_2[a]	0°/2 h	--	100	--	--	
4	IV	RBH_2	25°/48 h	--	7-9	91-93	--	55%
5	V	BH_3	0°/30 min	--	--	100	--	70%
6	V	RBH_2	0°/2 h	--	15	85	--	
7	VI	BH_3	0°/30 min	--	--	100	--	
8	VI	RBH_2	0°/1 h	--	--	100	--	
9	VI	RBH_2	25°/7 d	--	--	100	--	

a. RBH_2 = thexylborane. b. Isolated yield of isomeric mixture.

Scheme II. The Hydroboration-Oxidation of the Trimethylsilylcyclopentenes, IV, V and VI. R= thexyl (2,3-dimethyl-2-butyl) or trimethylsilylcyclopentyl



of the trimethylsilylcyclopentenes, IV, V and VI leads only to placement of the boron atom trans to the trimethylsilyl group. For purposes of comparison an authentic sample of cis-3-trimethylsilylcyclopentanol, XXVI, was prepared according to eqn. 1. The lithium aluminum hydride reduction of 3-trimethylsilylcyclopentanone would be expected to give the cis isomer based on Ashby's results with 3-methylcyclopentanone [12].



(1)

Synthetically useful reactions

In the course of this work some useful reactions in the synthesis of carbo-functional organosilanes emerged. Among these are the conversion of I to the tertiary alcohol, VII (entry 1 Table I). This reaction is made more attractive by the fact that the alcohol, VIII, is easily removed from the reaction mixture by treatment with dilute acid [13]. The conversion of either I or II to a mixture of alcohols IX and X represents an improvement over the published procedure for the preparation of these compounds, which requires a sensitive hydrogenation of m-trimethylsilylpehnol [14]. Chromic acid oxidation of the intermediate boranes, XV and XVI gives rise to 3-trimethylsilylcyclohexanone in 50% yield. A recent synthesis of derivatives of 3-trimethylsilylcyclohexanones has been reported [15]. In the cyclopentyl series hydroboration provides entries to alcohols XVIII, XIX and XX. Chromic acid oxidation of the organoborane, XXIV, gives rise to 3-trimethylsilylcyclopentanone in 52% yield.

Table III. Some Physical and Spectral Properties of Trimethylsilyl Substituted Cyclohexanols and Trimethylsilyl Substituted Cyclopentanols.

Alcohol	bp/mmHg[a]	mp(°C)	n_D (T°C)	δ C$\underline{H}$OH	Ring	$(C\underline{H}_3)_3Si$	%m/e73[b]	%m/e75[c]
VII	63-7/2	--	1.4691(20)	--	1.45	-0.07	90	87
VIII	46-8/1	47-48	--	3.37	1.08-1.70	0.0	63	100
d	46-8/1	59-60	--	4.12	1.55	0.0	46	100
IX	70-5/2	--	1.4669(25)[e]	3.42	0.5-2.05	-0.07	100	90
X	70-5/2	--	1.4672(25)[f]	3.96	1.51	-0.07	100	65
XII	--	66-8[g]	--	3.40	1.45	-0.10	100	36
XVIII	62-5/8	--	1.4592(20)	--	1.67	0.03	100	91
XIX	75-85/10	--	1.4558(20)	4.13	1.67	0.0	100	83
XXII	--	--	1.4532(20)	4.27	1.57	-0.03	100	36
XXIV	107-110/25	--	1.4576(23)	4.23	1.52	-0.06	100	51

a. These often were distilled as a mixture of isomers. b. corresponds to $(CH_3)_3Si^+$. c. corresponds to $(CH_3)_2SiOH^+$. d. Cis-2-trimethylsilylcyclohexanol. e. Reference 9 gives n_D^{24} 1.4685. f. Reference 9 gives n_D^{24} 1.4702. g. Reference 9 gives mp 66-67.

Structure determination of the trimethylsilylcyclohexanols

The structures of the isomeric trimethylsilylcyclohexanols, VII, VIII, IX, X and cis-2-trimethylsilylcyclohexanol (prepared via oxymercuration of I [3]) are based primarily on their PMR spectra, their chemical reactivity and comparison with authentic samples and literature data. All of the alcohols except VII were subjected to 90 MHz NMR analysis of the C_1 proton. Assuming that the trimethylsilyl group occupies an equatorial position this gives the stereochemistry of the OH group [16].

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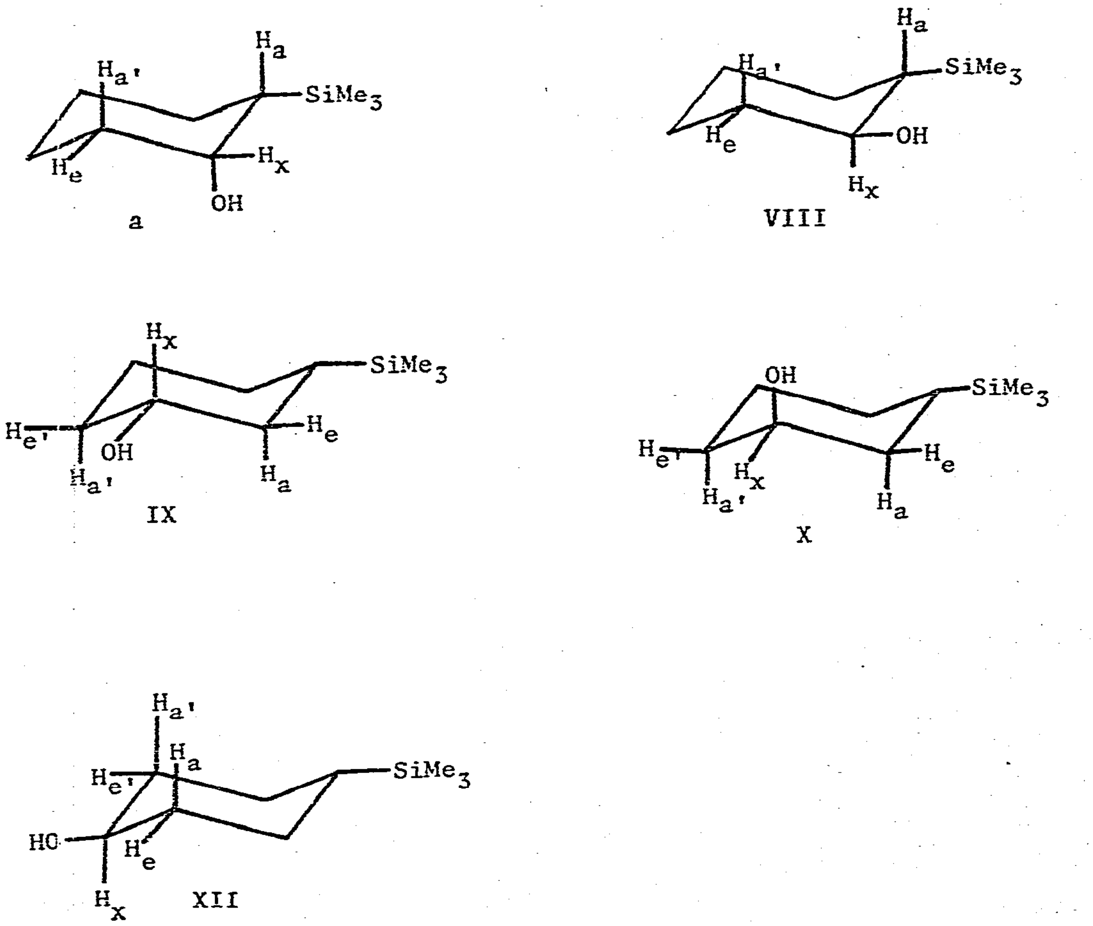

Figure 1 Conformational structures of the various trimethylsilylcyclohexanols. a is cis-2-trimethylsilylcyclohexanol.

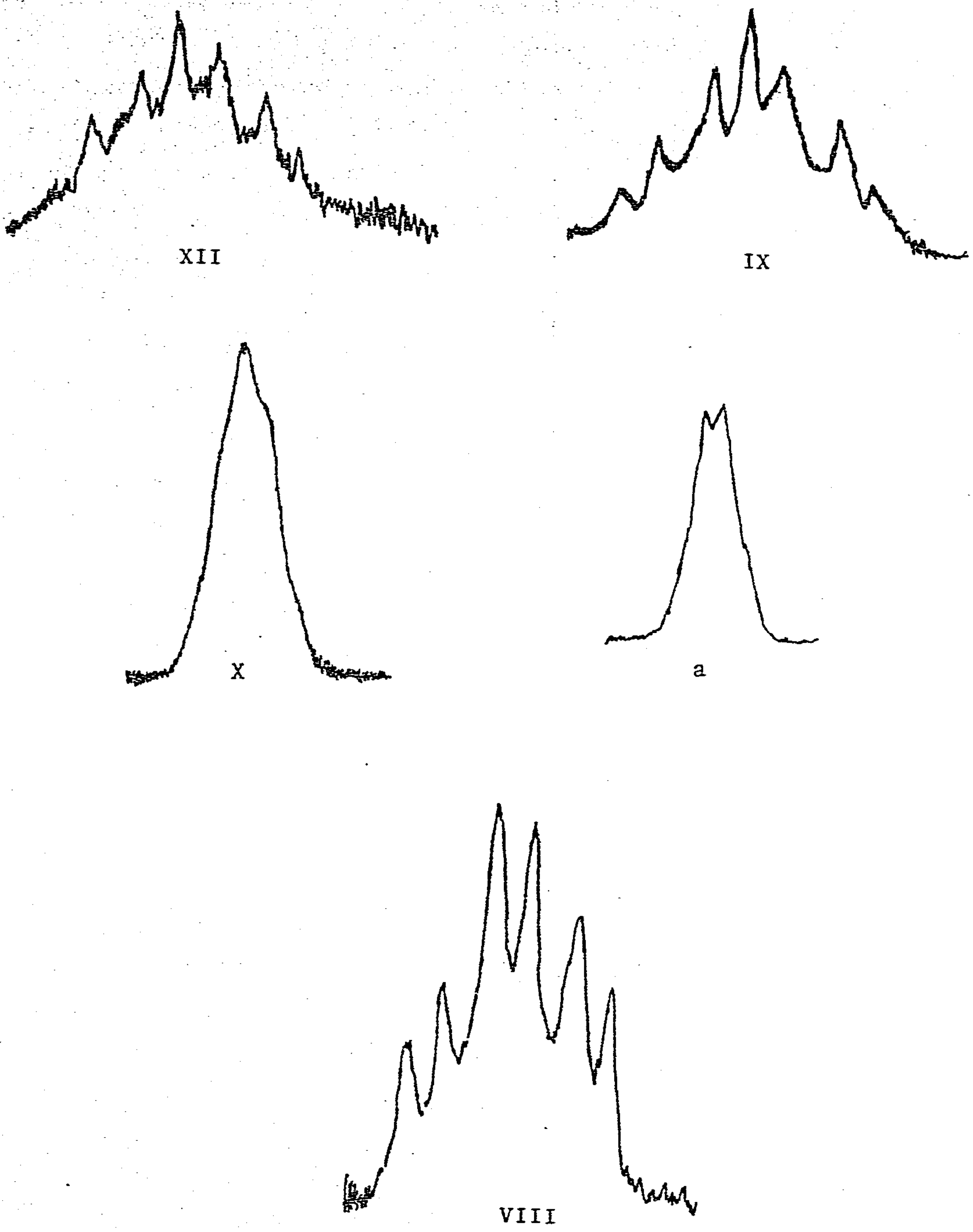

Figure 2. 90 MHz PMR spectra of the C_1 proton of the various trimethylsilylcyclohexanols. a is *cis*-2-trimethylsilylcyclohexanol.

The tertiary alcohol, VII, showed no resonance for a proton attached to a carbon bearing oxygen in the PMR spectrum. It showed PMR and IR spectra identical to those of an authentic sample [13]. The mass spectrum of this alcohol showed peaks at m/e 67 (100%), 73 (90%) and 75 (87%). The trans-2-trimethylsilylcyclohexanol, VIII, showed a broad resonance at δ 3.39 for the axial C_1 proton. The 90 MHz PMR spectrum showed this proton to be a sextet (doublet of triplets) with Ja,x = Ja',x = 10 Hz and Je,x = 4 Hz, consistent with an axial proton [16]. (figure 2) The mass spectrum of this material showed peaks at m/e 73 (62%) and 75 (100%). Treatment of VIII with a dilute solution of p-toluenesulfonic acid in benzene gave cyclohexene and hexamethyldisiloxane. The cis-2-trimethylsilylcyclohexanol showed a narrow multiplet at δ 4.12 for the C_1 proton for an equatorial proton. The 90 MHz PMR spectrum showing a narrow band for this proton with small coupling constants between Ha, Ha', He and Hx [16]. The mass spectrum of this compound showed peaks at m/e 67(52%), 73 (46%) and 75 (100%). This isomer did not react with dilute acid.

The trans-3-isomer, X, showed a narrow band in the PMR spectrum at δ 3.96 for the equatorial C_1 proton. (figure 2) In addition the PMR and IR spectra were identical to those of an authentic sample. The mass spectrum showed peaks at m/e 73 (100%) and 75 (65%). The cis isomer, IX, showed a broad resonance in the PMR spectrum for the axial C_1 proton. This proton appeared as a heptet (triplet of triplets in the 90 MHz PMR spectrum with Ja,x = Ja',x = 10 Hz and Je,x = Je',x = 4 Hz. The mass spectrum showed peaks at m/e 73 (100%) and 75 (90%). It is interesting to note that the peak at m/e 75 corresponding to the Me_2SiOH^+ ion is greater in the cis isomers than in the trans isomers and can be used as a test of the isomers when both are available.

Trans-4-trimethylsilylcyclohexanol, XII, showed a melting point and spectral data identical to those reported by Fessenden and coworkers [14]. The 90 MHz PMR spectrum confirmed this assignment showing a broad resonance, appearing as a septet (triplet of triplets) centered at δ 3.42 for the axial C_1 proton with Ja,x = Ja',x = 10 Hz and Je,x = Je',x = 4.5 Hz.

Structure determination of the trimethylsilylcyclopentanols

Of the five possible isomeric trimethylsilylcyclopentanols, XVIII, XIX, XX, XXI and <u>cis</u>-2-trimethylsilylcyclopentanol, only alcohols XVIII, XIX and XX were obtained in the hydroboration studies. Isomer XXI was prepared by reduction of 3-trimethylsilylcyclohexanone. Attempts to prepare an authentic sample of <u>cis</u>-2-trimethylsilylcyclopentanol via oxymercuration of IV failed.

The structure of XVIII was determined by its lack of a resonance in the PMR spectrum for a proton on a carbon bearing oxygen and from its mass spectrum, which showed peaks at m/e 73 (100%) and 75 (91%). Its formation is also consistent with the hydroboration-oxidation of other vinylsilanes [17]. The isomer, XIX, showed a resonance at δ 4.13 for the C_1 proton. The mass spectrum showed peaks at m/e 73 (100%) and 75 (83%). Treatment of XIX with dilute acid resulted in the rapid formation of cyclopentene and hexamethyldisiloxane. The isomer, XX, showed a resonance at δ 4.27 for the C_1 proton and peaks in the mass spectrum at m/e 73 (100%) and 75 (36%). This isomer gave no reaction with dilute acid. Oxidation of the intermediate organoborane, which led to XX, with chromic acid gave 3-trimethylsilylcyclopentanone. Reduction of this ketone with lithium aluminum hydride gave an authentic sample of <u>cis</u>-3-trimethylsilylcyclopentanol, XXI, which showed a resonance in the PMR spectrum at δ 4.23 for the C_1 proton and peaks in the mass spectrum at m/e 73 (100%) and 75 (51%). The higher percentage of the m/e 75 peak in the <u>cis</u> isomers is again noted.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen. In the case of the hydroborations the nitrogen atmosphere was maintained until after the oxidation step was complete. All glassware was flame dried under a stream of nitrogen prior to use. All solvents were dried by distillation from sodium and benzophenone immediately prior to use. Borane in THF was prepared according to Brown and Sharp [18] and thexylborane according to Brown and Zweifel [19]. 1-Chlorocyclohexene and 1-chlorocyclopentene were prepared according to the procedure of Mausseron and Jacquer [20], 3-chlorocyclopentene according to Goering and coworkers [21] and 3-bromocyclohexene according to Kharasch and coworkers [22]. 4-Bromocyclohexene was prepared according to the procedure of Jensen and Bushweller [23]. All other materials were obtained from common sources and distilled prior to use. GLC analyses were carried out using a Perkin-Elmer 990 or Perkin-Elmer 820 gas chromatographs. Preparative GLC was accomplished with a Varian 90P gas chromatograph. Columns used were a 20'x1/4", 20% DEGS on chromosorb W 80/100 mesh, a 12'x1/4" carbowax 20M on chromosorb W 80/100 mesh, and a 12'x1/8" apiezon on chromosorb W 80/100 mesh. The PMR spectra were recorded with a Varian T60 NMR spectrometer and mass spectra with a CEC 21-104 mass spectrometer. The 90MHz PMR spectra were kindly supplied by Dr. Richard Fish of the University of California at Berkeley.

1-Trimethylsilylcyclohexene, I, was prepared in 91% yield from cyclohexenyllithium and trimethylchlorosilane in ether. It showed bp 78-81°/32mm; n_D^{20} 1.4626 (lit. [24] bp 74-5°/30mm; n_D^{20} 1.4628).
3-Trimethylsilylcyclohexene, II, was prepared in 67% yield by the slow addition (2.5 h) of 3-bromocyclohexene (0.27 mol) to a mixture of lithium wire (0.60 g-at) and trimethylchlorosilane (0.27 mol) in 250 ml of THF at -50° (reaction started at 0° and cooled to -50°). It showed bp 85-9°/40mm; n_D^{25} 1.4605.
4-Trimethylsilylcyclohexene, III, was prepared in 29% yield by the addition of 4-bromocyclohexene (20 mmol) to a mixture of lithium

(50 mg-at) and trimethylchlorosilane (30 mmol) in 75 ml of THF at 0°. This showed bp 75-85°/30mm; n_D^{22} 1.4578 (lit. [25] bp 175-6°/760mm; n_D^{20} 1.4600).

1-Trimethylsilylcyclopentene, IV, was prepared in 62% yield from cyclopentenyllithium and trimethylchlorosilane in ether. It showed bp 78-80°/94mm; n_D^{20} 1.4466.

3-Trimethylsilylcyclopentene, V, was prepared in 80% yield by the slow addition (5 h) of 3-chlorocyclopentene (0.15 mol) to a mixture of lithium (0.34 g-at) and trimethylchlorosilane (0.20 mol) in 200 ml of THF at -50° (reaction started at 0° and cooled to -50°). This showed bp 74-80°/100mm; n_D^{23} 1.4470.

4-Trimethylsilylcyclopentene, VI, was prepared in 18% yield by the addition of thionyl chloride to <u>trans</u>-3-trimethylsilylcyclopentanol at 0°. The product contained 10% of the isomer, V.

General Procedure for the Determination of Hydride Uptake.

A 100 ml, round-bottom flask was charged with 30 mmol of the olefin to be studied along with enough THF to make the total volume 54.5 ml. To this was added by means of a syringe 5.4 ml of a 1.86 <u>M</u> solution of borane in THF making the total solution 0.5 M in olefin. Aliqouts of 4 ml were taken at various time intervals and hydrolyzed using a 1:1 mixture of ethanol and THF, with the hydrogen evolved being measured in a gas buret [26].

General Procedure for Hydroboration with Borane in THF.

Into a 100 ml, 2-neck, round-bottom flask was placed 25 ml of the olefin and 25 ml of THF. To this solution was added 13.4 ml of a 1.86 <u>M</u> borane solution in THF (25 mmol) by means of a syringe, with ice bath cooling. The reaction was allowed to continue either at 0°, room temperature, or refluxing depending on the system and desired conditions. Aliquots were taken and oxidized by the addition of 3<u>N</u> NaOH and 30% hydrogen peroxide.

The dried organic layers were subjected to analysis by GLC. In preparative procedures in which no aliqouts were taken, the reaction mixture was oxidized by the dropwise addition of 3N NaOH (7 ml) (carefully at first) followed by the dropwise addition of 30% hydrogen peroxide (7 ml). The resulting two phase system was heated to about 45° for 1 h , saturated with sodium chloride, the organic layer separated and the aqueous layer extracted with ether (25 ml). The combined organic layers were dried ($MgSO_4$) and the solvents removed by distillation followed by distillation of the products at reduced pressure.

General Procedure for the Hydroboration with Thexylborane.

Into a 100 ml, round-bottom flask equipped with sidearm was placed 2.10 g (25 mmol) of 2,3-dimethyl-2-butene and 25 ml of THF. This solution was cooled to 0°and 13.4 ml of a 1.86 M solution of borane in THF (25 mmol) was added by means of a syringe. The mixture was stirred for 1 h at 0°and 1 h at 25°after which time 25 mmoles of the olefin was added. The work-up procedure for these reactions was identical to that described above for the reactions with borane.

Preparation of Cis-3-Trimethylsilylcyclopentanol.

Into a 50 ml, 3 neck flask equipped with condenser,dropping funnel and magnetic stirrer was placed 15 ml of ether and 0.18 g (5 mmol) of lithium aluminum hydride. After stirring this solution for 15 min, 0.5 g (3mmol) of 3-trimethylsilylcyclopentanone was added slowly. The reaction mixture was stirred for 30 min after which time the excess hydride was destroyed by the addition of 10 ml of ethyl acetate at 0° The organic layer was washed with a 3 M sulfuric acid solution (15 ml) and the aqueous layer extraxted with ether (3x15 ml). The combined organic layers were washed with water (20 ml), dried (Na_2SO_4), filtered and the solvents removed by distillation yielding 0.35 g of crude product. Elution on an alumina column with hexane/ether (9:1) as eluent gave pure cis-3-trimethylsilylcyclopentanol,

n_D^{23} 1.4576. The original mixture contained about 6% of the *trans* isomer by GLC analysis.

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REFERENCES

1 H.C. Brown and B.C. Subba Rao, J. Org. Chem., 22 (1957) 1136.

2 H.C. Brown and G. Zweifel, J. Amer. Chem. Soc., 83 (1961) 2544.

3 W.K. Musker and G.L. Larson, Tetrahedron Lett., (1968) 3481.

4 E. Negishi and H.C. Brown, Synthesis, (1974) 77.

5 H.C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y. (1972) 321.

6 H.C. Brown, E.F. Knights and C.G. Scouten, J. Amer. Chem. Soc., 96 (1974) 7765.

7 G.L. Larson, Ph.D. thesis, University of California, Davis 1968.

8 D. Seyferth, H. Yamazaki and Y. Sato, Inorg. Chem., 2 (1963) 734.

9 P.R. Jones and J.K. Myers, J. Organometal. Chem., 34 (1972) C9.

10 D. J. Pasto and F.M. Klein, J. Org. Chem., 33 (1968) 1468.

11 C. Freppel, M.-A. Poirier, J.-C. Richer, Y. Maroni and G. Manuel, Can. J. Chem., 52 (1974) 4133.

12 E.C. Ashby and J.R. Boone, J. Org. Chem., 41 (1976) 2890.

13 See, for example, P.F. Hudrlik and D. Peterson, J. Amer. Chem. Soc., 97 (1975) 1464.

14 R.J. Fessenden, K. Seeler and M. Dagani, J. Org. Chem., 31 (1966) 2483.

15 M. Laguerre, J. Dunogues, N. Duffaut and R. Calas, J. Organometal. Chem., 120 (1976) 319. J.Dunogues, A. Ekouya, R. Calas, and N. Duffaut, *ibid*, 87 (1975) 151.

16 N.H. Bhacca and N.D. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden Day, San Francisco (1964) 78.
F. R. Jensen, V. Madan and D.H. Buchanan, J. Amer. Chem. Soc., 92 (1970) 1414.

17 D. Seyferth, J. Inorg. Nucl. Chem., 7 (1958) 152. D. Seyferth, J. Amer. Chem. Soc., 81 (1959) 1844. A.G. Brook and J.B. Pierce, J. Org. Chem., 30 (1965) 2566. M. Kumada, N. Imaki and K. Yamamoto, J. Organometal. Chem., 6 (1965) 490. G. Manuel, P. Mazerolles and J.C. Florence, ibid, 30 (1971) 5.

18 H.C. Brown and R.L. Sharp, J. Amer. Chem. Soc., 90 (1968) 2915.

19 G. Zweifel and H.C. Brown, ibid, 85 (1963) 2066.

20 M. Mausseron and R. Jacquer, Bull. Soc. Chim. France., (1950) 648.

21 H.L. Goering, R.L. Reeves and H.H. Espy, J. Amer. Chem. Soc., 78 (1956) 4926.

22 M.S. Kharasch, J.S. Sallo and W. Nudenberg, J. Org. Chem., 21 (1956) 129.

23 F.R. Jensen and C.H. Bushweller, J. Amer. Chem. Soc., 91 (1969) 577.

24 A.D. Petrov, V.F. Mirinov and V.G. Glukhovtsev, Zhurnal Obshei Khim., 27 (1957) 1535.

25 H.L. Goering, T.D. Nevitt and E.F. Silversmith, J. Amer. Chem. Soc., 77 (1955) 5026.

26 H.C. Brown, G.W. Kramer, A.B. Levy and M.M.Midland, "Organic Syntheses via Boranes", John Wiley and Sons, N.Y. (1975) 241.