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Stereospecific Olefin-Forming Elimination Reactions of β-Hydroxyalkylsilanes

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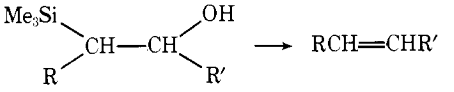
Abstract: In order to study the stereochemistry of elimination reactions of β-hydroxyalkylsilanes, 5-trimethylsilyl-4-octanol (**2**) was prepared by two routes, and the cis:trans ratios of the 4-octenes formed in the β-elimination reactions were examined. Addition of ethyllithium to vinyltrimethylsilane, followed by reaction with butyraldehyde, gave **2** as a 2:1 mixture of diastereomers. Reduction of 5-trimethylsilyl-4-octanone (**5**) with diisobutylaluminum hydride (DIBAL) at −120° gave predominantly one diastereomer of **2** (presumably threo); β-elimination reactions with sodium hydride or potassium hydride gave predominantly *trans*-4-octene, while β-elimination reactions under a variety of acidic conditions gave predominantly *cis*-4-octene. Thus, by a choice of conditions for the elimination reaction, either cis or trans olefin can be prepared from a single precursor.

The need for methods for the stereospecific synthesis of olefins has become increasingly apparent in recent years,[2] in part because of the discovery of many olefinic natural products, particularly the insect hormones and pheromones,[3] and in part because of the many recent advances in the use of polyolefins in nonenzymic biogenetic-like cyclizations to form polycyclic compounds.[4]

We have been interested in the possibility that the elimination reactions of β-hydroxyalkylsilanes could be used for the stereospecific synthesis of olefins.[5] These elimination reactions have been known for almost 3 decades,[6] and have been shown to occur under both acidic[6] and basic[7-9] conditions. A number of synthetic applications have appeared recently,[8-15] beginning with the work of Peterson;[8] normally mixtures of cis and trans olefins have been obtained. Since the precursor β-hydroxysilanes in these reactions may have been mixtures of diastereomers, a definitive statement regarding the stereochemistry of the olefin-forming step was not possible.



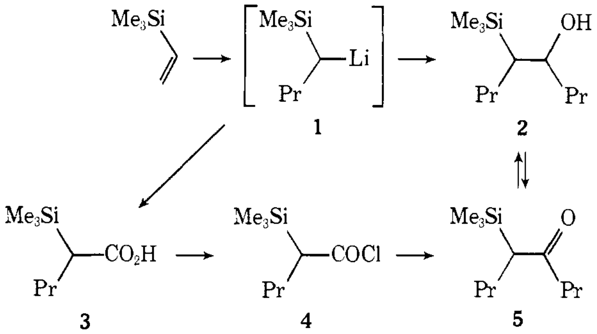
We wish to report here the selective synthesis of one diastereomer of a β-hydroxyalkylsilane and the demonstration that the elimination reactions are stereospecific and can be controlled to proceed in either a syn or an anti manner; thus, either a cis or a trans olefin can be formed from a single β-hydroxysilane.

Results and Discussion

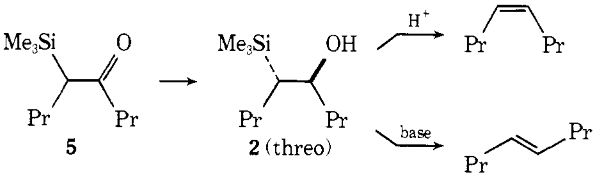
To determine the stereochemistry of the elimination reactions of β-hydroxyalkylsilanes, we have examined the cis:trans ratio of the 4-octenes produced by the elimination of 5-trimethylsilyl-4-octanol (**2**) prepared by two different routes. Compound **2** was first prepared by addition of ethyllithium to vinyltrimethylsilane, followed by reaction[16] with butyraldehyde. On treatment of **2** with acids, mixtures of *cis*- and *trans*-4-octene were formed. In one experiment, the absence of the isomeric 3-octenes in the product was demonstrated by ozonolysis.

Initially, we hoped to use an intermediate sulfonate derivative as a substrate for elimination reactions under mild conditions. Treatment of **2** with methanesulfonyl chloride and triethylamine[17] produced 4-octene directly in a 2:1 cis:trans ratio. Treatment of **2** with sodium hydride in hexamethylphosphoric triamide (HMPA) followed by *p*-toluenesulfonyl chloride and tetraethylammonium fluoride produced 4-octene in a 1:2 cis:trans ratio. Attempts to isolate the tosylate were unsuccessful; moreover, omission of the *p*-toluenesulfonyl chloride and the tetraethylammonium fluoride from the reaction mixture resulted in a similar mixture of octenes. The reversal of stereochemistry in these two reactions suggested that the β-hydroxyalkylsilane **2** had been formed as a mixture of diastereomers, and that the elimination reaction was syn under one set of conditions and anti under the other. We therefore sought to prepare one diastereomer of **2**.

Very few preparations of diastereomerically pure β-hydroxysilanes are reported.[18] We decided to investigate the reduction of the β-ketosilane **5**[20] as a possible route to one diastereomer of the β-hydroxyalkylsilane **2**. We first prepared the β-ketosilane **5** by treating the acid chloride **4**[21] with an organocuprate reagent.[22] The precursor acid **3** was obtained from vinyltrimethylsilane by the addition of ethyllithium followed by carbonation.[23] The ketosilane **5** was more conveniently prepared by CrO_3–pyridine[24,25] oxidation of the β-hydroxyalkylsilane **2** prepared above.[27]



The β-ketosilane **5** could be reduced cleanly to the hydroxysilane **2** by treatment with lithium aluminum hydride,[28] aluminum hydride, or diisobutylaluminum hydride (DIBAL). A number of other reducing agents were studied; many of these gave mixtures consisting predominantly of 4-octanol and 4-octanone with loss of the trimethylsilyl group.[29] Although we were unable to directly determine the diastereomeric composition of the β-hydroxyalkylsilane **2** formed in the reductions, the composition was inferred from the cis:trans ratios of the olefins obtained in the elimination reactions. Reductions with lithium aluminum hydride or with aluminum hydride, followed by elimination, gave variable ratios of cis and trans olefins. DIBAL gave consistent results and was the most selective reducing agent we investigated. Reduction of **5** in ether at −78° followed by elimination gave a 7:3 isomeric ratio of olefins. Reduction with DIBAL in pentane at −120° evidently formed one diastereomer of **2** quite selectively; the elimination reactions on the product gave either *cis*- or *trans*-4-octene in up to 95% stereochemical purity. The elimination reactions could be effected under a number of mild conditions; the results are given in Table I.



The above results demonstrate that the elimination reactions of β-hydroxyalkylsilanes are stereospecific, and that the acid- and base-promoted reactions take the opposite stereochemical course. The acid-promoted reactions are almost certainly anti by analogy to several related solvolytic β-elimination reactions.[32] The base-promoted elimination reactions must then be syn, which is in accord with early speculation[7,8] and with more recent calculations.[33]

In our initial preparation of the β-hydroxyalkylsilane **2** by reaction of the intermediate **1** with butyraldehyde, the olefin mixture obtained after elimination suggests that **2** was formed in a threo:erythro ratio of 2:1.[34] We found reduction of the β-ketosilane **5** to be a much more selective way to form the β-hydroxysilane; the threo:erythro ratio was evidently about 15:1. The predominant formation of the threo isomer in the reduction of **5** is in accord with Cram's rule,[35] if the trimethylsilyl group is taken to be larger than the *n*-propyl group.

Table I. Elimination Reactions of 5-Trimethylsilyl-4-octanol (2)[a]

Conditions	% yield of 4-octene[b]	Ratio Cis	Ratio Trans
KH–THF, room temp, 1 hr	96	5	95
NaH–HMPA, room temp, 20 hr	85	7	93
H_2SO_4–THF, room temp, 10 hr	99	92	8
$BF_3 \cdot Et_2O$–CH_2Cl_2, 0°, 1 hr	99	94	6
MsCl, Et_3N–pentane, 0°, 20 min	80	89	11
NaOAc, Ac_2O–DMSO, room temp, 12 hr	81	87	13
NaOAc, HOAc, 50°, 30 min	85	98	2

[a] Prepared from 5 by reduction (DIBAL) at −120°. [b] Yield determined by VPC using an internal standard.

Conditions previously employed for the elimination reactions of β-hydroxyalkylsilanes include sulfuric acid,[6,8] acetic acid,[11,12] sodium hydride,[8] and potassium hydride.[8] In agreement with an earlier report,[8] we found that the elimination reaction using sodium hydride in tetrahydrofuran (THF) was very slow at room temperature (1% of 4-octene after 20 hr), while the use of potassium hydride in THF resulted in a facile elimination reaction. In the more highly solvating medium HMPA, we found the elimination reaction with sodium hydride proceeded at a synthetically useful rate.

Elimination reactions using methanesulfonyl chloride-triethylamine or using sodium acetate and acetic anhydride in dimethyl sulfoxide always produced 4-octene less stereospecifically than did the other conditions. With methanesulfonyl chloride-triethylamine and with sodium acetate in acetic acid, the yields were sometimes variable. Sulfuric acid in THF and boron trifluoride etherate in CH_2Cl_2 consistently gave excellent results. From this study, it is clear that a variety of mild conditions can accomplish the β-elimination reaction.

The mild conditions, the high yields, the stereospecificity, and the stereochemical control in being able to prepare either a cis or a trans olefin from a single precursor in these elimination reactions[36] illustrate their considerable potential value in synthetic organic chemistry, if efficient methods to prepare diastereomerically pure β-hydroxyalkylsilanes become available. Such methods are being developed in our laboratory and will be the subject of future reports.

Experimental Section

Commercially available compounds were used without further purification unless otherwise noted. Pentane was shaken with concentrated H_2SO_4, dried over anhydrous K_2CO_3, and distilled. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride, triethylamine and pyridine were distilled from barium oxide, and hexamethylphosphoric triamide (HMPA) and dimethyl sulfoxide (DMSO) were distilled under reduced pressure from calcium hydride. Acetic anhydride, butyraldehyde, and methanesulfonyl chloride (MsCl) were distilled. Chromium trioxide was washed with CH_2Cl_2, then dried under oil-pump vacuum over P_2O_5. Diisobutylaluminum hydride (DIBAL) (0.96 *M* solution in hexane) and sodium hydride (57% dispersion in mineral oil) were obtained from Alfa Inorganics, Beverly, Mass. Potassium hydride was obtained as a slurry in mineral oil from Research Organic/Inorganic Chemical Corp., Belleville, N.J. Ethyllithium and *n*-propyllithium were prepared from the corresponding alkyl bromides.[37]

All reactions were carried out under a nitrogen atmosphere unless otherwise indicated, and liquids were transferred with nitrogen-flushed syringes. The use of the verb "concentrated" refers to evaporation of solvent under reduced pressure (water aspirator) using a rotary evaporator. The use of the term "evaporative distillation" refers to a short-path (bulb-to-bulb) distillation in a Kugelrohr apparatus under oil-pump vacuum.

Vapor phase chromatographic (VPC) analyses were performed on a Varian Aerograph Model 90-P instrument using helium as the carrier gas at a flow rate of 100 ml/min.[38,39] Infrared (ir) spectra were obtained using a Perkin-Elmer Model 137 spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained using a Varian T-60 or a JEOL MH-100 spectrometer; chemical shifts are reported in parts per million, using $CHCl_3$ (δ 7.28) as the internal reference. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-7 instrument. Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

5-Trimethylsilyl-4-octanol (2) by Reaction of 1 with Butyraldehyde. A solution of 0.679 g (6.77 mmol) of vinyltrimethylsilane in 15 ml of THF[40] was cooled to −78°, and 7.65 ml (8.8 mmol) of ethyllithium (1.15 *M* in ether) was added. The mixture was stirred for 2 hr at −78°, warmed over 1 hr to −30°, and cooled again to −78°. A 0.66-ml (0.54 g, 7.5 mmol) sample of butyraldehyde was added, and the reaction mixture was warmed to room temperature over 1 hr and was stirred an additional 2 hr. The reaction mixture was poured into saturated NaCl overlaid with ether. The ether layer was dried ($MgSO_4$), concentrated, and evaporatively distilled (oven temperature 120°) yielding 1.272 g (93%) of **2**: ir (film) 2.9, 3.4, 8.0, 11.9 μ; NMR ($CHCl_3$) δ 0.00 (s, 9 H), 0.7-1.1 (broad, 7 H), 1.1-1.8 (broad, 10 H), 2.1-2.4 (m, 1 H), 3.85 (broad, 1.4 H); mass spectrum[41] *m/e* 184 $(M - H_2O)^+$, 169, 159, 147, 145, 112, 110, 83, 75, 73. VPC analysis (SE-30, 120°)[38a] showed the major peak (97% of peak area) at 6.08 min; the retention time of dodecane under these conditions was 4.21 min.

A sample of comparable purity from a separate but similar experiment was purified by preparative VPC followed by evaporative distillation.

Anal. Calcd for $C_{11}H_{26}OSi$: C, 65.27; H, 12.94. Found: C, 65.10; H, 13.16.

Elimination Reaction with $BF_3 \cdot Et_2O$ in CH_2Cl_2. To a solution of 154.4 mg (0.76 mmol) of **2** (from reaction of **1** with butyraldehyde) in 10 ml of CH_2Cl_2 was added 0.5 ml of boron trifluoride etherate, and the resulting solution was stirred for 1 hr at room temperature. The mixture was added to saturated $NaHCO_3$ overlaid with pentane; the organic layer was washed with two additional portions of saturated $NaHCO_3$ and was dried ($MgSO_4$). VPC analysis (no internal standard)[39a] indicated a 64:36 ratio of *cis-* to *trans*-4-octene had been formed. The solvent was removed by distillation; the NMR ($CHCl_3$) and ir (film) of the residue were very similar to those of a mixture of authentic *cis-* and *trans*-4-octene.

Elimination Reaction with H_2SO_4 in CH_2Cl_2. To a solution of 102.6 mg (0.507 mmol) of **2** (from the same batch used in the previous experiment) in 20 ml of CH_2Cl_2 were added 0.050 ml of *n*-octane (internal standard) and 2 drops of concentrated H_2SO_4. After being stirred for 4 days at room temperature, the mixture was added to saturated $NaHCO_3$, and the organic layer was separated and dried ($MgSO_4$). VPC analysis[39a] indicated a 63:37 ratio of *cis-* to *trans*-4-octene was formed in 89% yield.

A CH_2Cl_2 solution resulting from a similar experiment was treated with ozone at −78°. Dimethyl sulfide (1 ml) was added, and the mixture was allowed to warm to room temperature overnight. VPC analysis (DC-550, 50°)[38b] indicated that butyraldehyde was present, but valeraldehyde was not detectable.

Elimination Reaction with MsCl and Et_3N. To an ice-cooled solution of 111.5 mg (0.55 mmol) of **2** (from reaction of **1** with butyraldehyde) in 10 ml of pentane was added 0.154 ml (1.11 mmol) of triethylamine. Methanesulfonyl chloride (0.064 ml, 0.83 mmol) was added dropwise. *n*-Butylbenzene (91.1 mg) was added, and the reaction mixture was stirred for 20 min at 0°, then added to 1 *N* HCl overlaid with ether. The layers were separated, and the ether layer was washed with saturated $NaHCO_3$ and was dried ($MgSO_4$). VPC analysis[39b] indicated that a 63:37 ratio of *cis-* to *trans*-4-octene was formed in 87% yield.

A number of different batches of **2** were prepared by minor modifications of the procedure given above; similar elimination reactions on the products gave similar ratios of *cis-* and *trans*-4-octene, occasionally varying up to 10% in either direction.

Elimination Reaction with NaH in HMPA. Sodium hydride (27.2 mg of a 57% dispersion in oil, 0.65 mmol) was stirred with 5 ml of pentane, and the liquid was removed with a pipet. To the residue was added a solution of 100.7 mg (0.497 mmol) of **2** (from the same batch used in the previous experiment) in 4 ml of HMPA, and the mixture was stirred for 3 hr at room temperature. *p*-Toluenesulfonyl chloride (190 mg, 1.0 mmol) was added, and the mixture was stirred an additional 3 hr, then 222 mg (1.5 mmol) of tetraethylammonium fluoride and 90.1 mg of *n*-butylbenzene were added. The resulting mixture was stirred at room temperature for 18 hr, then added to saturated $NaHCO_3$ overlaid with ether, and the organic layer was separated and dried ($MgSO_4$). VPC analysis[39b] indicated that a 36:64 ratio of *cis-* to *trans*-4-octene was formed in 84% yield. Later experiments showed that similar yields and isomer ratios were obtained when the *p*-toluenesulfonyl chloride and the tetraethylammonium fluoride were omitted.

2-Trimethylsilylvaleric Acid (3). A solution of 1.0378 g (10.35 mmol) of vinyltrimethylsilane in 50 ml of THF[40] was cooled to −78°, and 8.25 ml (13.4 mmol) of ethyllithium (1.63 *M* in ether) was added. The reaction mixture was stirred at −78° for 10 hr, warmed to 0° over 1 hr, and cooled again to −78°. The mixture was added to an excess of crushed Dry Ice in pentane; as soon as the excess Dry Ice evaporated, the resulting mixture was added to cold 6 *N* HCl, forming a slurry containing ice. As soon as the ice melted, the mixture was shaken in a separatory funnel, and the organic layer was separated, dried ($MgSO_4$), concentrated, and evaporatively distilled (oven temperature 150°) giving 1.515 g (84%) of **3** as a liquid which solidified below room temperature: ir (film) 2.8-4.0, 5.93, 8,0, 11.8 μ; NMR (CCl_4) δ 0.00 (s, 2 H, impurity), 0.10 (s, 9 H), 0.8-1.1 (broad, 3 H), 1.1-1.8 (broad, 5 H), 1.8-2.1 (m, 1 H); mass spectrum *m/e* 159 $(M - CH_3)^+$, 156, 147, 145, 129, 75, 73. VPC analysis (SE-30, 145°)[38a] showed the major peak (95% of peak area) at 1.72 min; the retention time of tetradecane under these conditions was 3.97 min.

A portion of the product was purified by preparative VPC followed by evaporative distillation. The elemental analysis (in two attempts) was unsatisfactory.

Anal. Calcd for $C_{18}H_{18}O_2Si$: C, 55.12; H, 10.41. Found: C, 56.69; H, 10.56.

5-Trimethylsilyl-4-octanone (5) from 3. To a solution of 0.396 g (2.27 mmol) of the acid **3** in 15 ml of hexane was added 0.58 ml (0.86 g, 6.8 mmol) of oxalyl chloride. (The reaction mixture was protected from the atmosphere with a drying tube.) The mixture was stirred for 2 hr at room temperature, then placed under aspirator vacuum, leaving the crude acid chloride **4** which was used without purification in the following sequence.

A mixture of 1.30 g (6.8 mmol) of CuI in 10 ml of anhydrous ether was cooled to 0°, and 11.2 ml (13.8 mmol) of *n*-propyllithium (1.23 *M* in ether) was added. After being stirred at 0° for 15 min, the reaction mixture was cooled to −78° and taken up in a syringe, then added to a cooled (−78°) solution of the above acid chloride in 15 ml of anhydrous ether. The resulting mixture was stirred for 1 hr at −78°, for 1 hr with warming to 0°, and for 30 min at 0°; then the mixture was poured into 10% NH_4Cl overlaid with ether. The organic layer was separated, dried ($MgSO_4$), concentrated, and evaporatively distilled (oven temperature 150°) yielding 0.293 g (64%) of **5**: ir (film) 3.4, 5.92, 8.0, 11.9 μ; NMR ($CHCl_3$) δ 0.00 (s, 9 H), 0.7-1.9 (broad, 14.5 H), 2.0-2.5 (m, 3 H).

On treatment with aqueous alcoholic base (5 ml of 0.1 *N* NaOH with 5 ml of isopropyl alcohol), the ketosilane **5** was hydrolyzed to 4-octanone within 1 hr at room temperature. The β-hydroxysilane **2** and the acid **3** were completely stable to similar conditions.

5-Trimethylsilyl-4-octanone (5) by Oxidation of 2. To 150 ml of CH_2Cl_2 was added 12 ml (149 mmol) of pyridine followed by 7.45 g (74.5 mmol) of CrO_3.[24] The mixture was stirred for 1 hr at room temperature, then a solution of 2.153 g (10.6 mmol) of the alcohol **2** (from reaction of **1** with butyraldehyde) in 7 ml of CH_2Cl_2 was added slowly. The reaction mixture was allowed to stand at room temperature for 10 min and was then filtered through dried (1-3 hr at 110°) Filtercel. The filtrate was poured into 10% NH_4Cl overlaid with ether; the ether layer was washed with two additional portions of 10% NH_4Cl, one portion of 2 *N* HCl, and finally, three portions of saturated $NaHCO_3$. The ether solution was dried ($MgSO_4$), concentrated, and evaporatively distilled (oven temperature 170°) yielding 1.4907 g (70%) of **5**. The ir and NMR spectra were essentially identical with those of the sample of **5** prepared from **3**; the mass spectrum[41] showed *m/e* 200 (M^+), 185, 171, 157, 130, 75, 73. VPC analysis (SE-30, 100°)[38c] showed the major peak (98% of peak area) at 4.50 min; the retention time of dodecane under these conditions was 4.27 min.

5-Trimethylsilyl-4-octanol (2) by Reduction of 5 with DIBAL. In one side of a two-bottomed flask were placed 26.2 ml (25.2 mmol) of DIBAL (0.96 *M* in hexane) and 10 ml of pentane; in the other side were placed 1.679 g (8.38 mmol) of the ketone **5** (from oxidation of **2** with CrO_3-pyridine) and 20 ml of pentane. The flask was immersed in a liquid nitrogen-ethanol bath (−120°) for 1 hr (to allow the temperature to equilibrate), then tipped to mix the contents of the two sides. The resulting mixture was kept at −120° for 3 hr, and then slowly warmed to −20° overnight. The mixture was poured into 2 *N* HCl overlaid with ether, and the organic layer was separated, washed with saturated $NaHCO_3$, dried ($MgSO_4$), concentrated, and evaporatively distilled (oven temperature 160°) giving 1.6540 g (98%) of the alcohol **2**. The ir and NMR spectra were very similar to those of the sample of **2** prepared by condensation of **1** with butyraldehyde (above). VPC analysis (SE-30, 105°)[38c] showed the major peak (99% of peak area) at 3.01 min; dodecane under these conditions had a retention time of 2.80 min.

Elimination Reaction with KH in THF.[8] Potassium hydride (0.10 g of a 50% slurry in oil, ~1.25 mmol) was stirred with 4 ml of pentane, and the liquid was removed by pipet. To the residue were added 5 ml of THF, 76.5 mg (0.378 mmol) of **2** (from reduction of **5** with DIBAL at −120°), and 98.8 mg of *n*-butylbenzene. After being stirred for 1 hr at room temperature,[42] the reaction mixture was added to cold 10% NH_4Cl overlaid with ether. The ether layer was separated and dried ($MgSO_4$). VPC analysis[39b] indicated that a 5:95 ratio of *cis*- to *trans*-4-octene was formed in 96% yield.

Elimination Reaction with NaH in HMPA. Sodium hydride (18.5 mg of a 57% dispersion in oil, 0.44 mmol) was stirred with 3 ml of pentane, and the liquid was removed by pipet. To the residue were added 11 ml of HMPA, 67.8 mg (0.335 mmol) of **2** (from reduction of **5** with DIBAL at −120°), and 83.0 mg of *n*-butylbenzene. After being stirred for 20 hr at room temperature,[43] the reaction mixture was added to 10% NH_4Cl overlaid with ether. The ether layer was separated and dried ($MgSO_4$). VPC analysis[39b] indicated that a 7:93 ratio of *cis*- to *trans*-4-octene was formed in 85% yield.

Elimination Reaction with H_2SO_4 in THF.[8] To a solution of 128.0 mg (0.632 mmol) of **2** (from reduction of **5** with DIBAL at −120°) and 131.6 mg of *n*-butylbenzene in 10 ml of THF was added 2 drops of concentrated H_2SO_4. The mixture was stirred at room temperature for 10 hr. A 5-ml aliquot was added to saturated $NaHCO_3$ overlaid with ether; the ether layer was separated and dried ($MgSO_4$). VPC analysis[39b] indicated that a 92:8 ratio of *cis*- to *trans*-4-octene was formed in 99% yield.

Elimination Reaction with $BF_3 \cdot Et_2O$ in CH_2Cl_2. To an ice-cooled solution of 65.7 mg (0.325 mmol) of **2** (from reduction of **5** with DIBAL at −120°) and 79.0 mg of *n*-butylbenzene in 10 ml of CH_2Cl_2 was added 0.50 ml (4.0 mmol) of boron trifluoride etherate. The mixture was stirred for 1 hr at 0°, then added to saturated $NaHCO_3$ overlaid with ether. The ether layer was separated and dried ($MgSO_4$). VPC analysis[39b] indicated that a 94:6 ratio of *cis*- to *trans*-4-octene was formed in 99% yield.

Elimination Reaction with MsCl and Et_3N. To an ice-cooled solution of 70.0 mg (0.346 mmol) of **2** (from reduction of **5** with DIBAL at −120°) in 10 ml of pentane were added 68.4 mg of *n*-butylbenzene and 0.145 ml (0.105 g, 1.04 mmol) of triethylamine. Methanesulfonyl chloride (0.088 ml, 130 mg, 1.14 mmol) was added, and the reaction mixture was stirred for 20 min at 0°, then added to 2 *N* HCl overlaid with ether. The layers were separated, and the ether layer was washed with saturated $NaHCO_3$ and was dried ($MgSO_4$). VPC analysis[39b] indicated that a 89:11 ratio of *cis*- to *trans*-4-octene was formed in 80% yield.

Elimination Reaction with NaOAc and Ac_2O in DMSO. To a solution of 26.9 mg (0.133 mmol) of **2** (from reduction of **5** with DIBAL at −120°) and 107.4 mg of *n*-butylbenzene in 10 ml of DMSO were added 0.5 g of sodium acetate and 2.0 ml of acetic anhydride. The reaction mixture was stirred for 12 hr at room temperature, and a 5-ml aliquot was added to saturated NaCl overlaid with ether. The layers were separated, and the ether layer was washed with saturated $NaHCO_3$ and was dried ($MgSO_4$). VPC analysis[39b] indicated that a 87:13 ratio of *cis*- to *trans*-4-octene was formed in 81% yield.

Elimination Reaction with NaOAc in HOAc.[12] To 15 ml of glacial acetic acid saturated with sodium acetate at 50° were added 98.1 mg (0.485 mmol) of **2** (from reduction of **5** with DIBAL at −120°) and 110 mg of *n*-butylbenzene. The reaction mixture was stirred at 50° for 30 min, cooled to room temperature, and poured into saturated $NaHCO_3$ overlaid with pentane. The layers were separated, and the pentane layer was washed with saturated $NaHCO_3$ and was dried ($MgSO_4$). VPC analysis[39b] indicated that a 98:2 ratio of *cis*- to *trans*-4-octene was formed in 85% yield.

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(1) Johnson and Johnson Fellow, 1973–1974.

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(3) For example, see (a) C. E. Berkoff, *Q. Rev., Chem. Soc.*, **23**, 372 (1969); (b) D. A. Evans and C. L. Green, *Chem. Soc. Rev.*, **2**, 75 (1973); (c) M. Jacobson, "Insect Sex Pheromones," Academic Press, New York, N.Y., 1972.

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(18) Both *cis*- and *trans*-2-trimethylsilylcyclohexanol have been prepared from cyclohexenyltrimethylsilane;[19a] although the thermal and acid-catalyzed β-elimination reactions of the related methyl ethers were studied,[19b] the β-elimination reactions of the alcohols were not reported. *trans*-2-Triphenylsilylcyclohexanol is known;[19c,d] treatment with P_2O_5 was reported to give cyclohexenyltriphenylsilane in 33% yield.[19c]

(19) (a) W. K. Musker and G. L. Larson, *Tetrahedron Lett.*, 3481 (1968); (b) *J. Am. Chem. Soc.*, **91**, 514 (1969); (c) H. Gilman, D. Aoki, and D. Wittenberg, *ibid.*, **81**, 1107 (1959); (d) G. J. D. Peddle, *J. Organomet. Chem.*, **14**, 115 (1968).

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(25) A number of other reagents were unsuccessful. Jones reagent[26a] gave only 4-octanone; two-phase dichromate oxidation[26b] or DMSO–DCC–CF_3CO_2H[26c] gave mixtures of 4-octanone and ketosilane **5**; DMSO–Cl_2 reagent[26d] gave a mixture containing none of the ketosilane **5**, the major component had ir and NMR spectra consistent with 5-chloro-4-octanone.

(26) (a) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); (b) H. C. Brown, C. P. Garg, and K.-T. Liu, *J. Org. Chem.*, **36**, 387 (1971); (c) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 5670 (1965); (d) E. J. Corey and C. U. Kim, *Tetrahedron Lett.*, 919 (1973).

(27) A few oxidations of β-hydroxyalkyl*triaryl*silanes to β-ketosilanes have been reported; see ref 19d and 20.

(28) Compare I. F. Lutsenko, Yu. I. Baukov, O. V. Dudukina, and E. N. Kramarova, *J. Organomet. Chem.*, **11**, 35 (1968).

(29) Loss of the trimethylsilyl group was the predominant result with $NaBH_4$ in HMPA or isopropyl alcohol, with $NaBH_2S_3$,[30a] or with LiB(*sec*-

Bu)$_3$H.[30b] No reaction was observed with NaBH$_4$ in glyme (75°, 1.5 hr); only low yields of **2** resulted from reactions with Zn(BH$_4$)$_2$ or LiAl(O-*t*-1=)$_3$H. Treatment of ketosilane **5** with triisobutylaluminum (TIBAL)[30c] in pentane gave only 4-octanone and isobutyltrimethylsilane after work-up; when the reaction was quenched with acetic anhydride before aqueous work-up, a mixture of enol acetates was formed, suggesting that an aluminum enolate had been formed.[31]

(30) (a) J. M. Lalancette and A. Freche, *Can. J. Chem.*, **48**, 2366 (1970); (b) H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **94**, 7159 (1972); (c) TIBAL has been shown to be a very selective reducing agent for acyclic α-ketols; see J. A. Katzenellenbogen and S. B. Bowlus, *J. Org. Chem.*, **38**, 627 (1973).

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(32) (a) (RO)$_2$B–C–C–Br, D. S. Matteson and J. D. Liedtke, *J. Am. Chem. Soc.*, **87**, 1526 (1965); (b) XHg–C–C–OR, W. Kitching, *Organomet. Chem. Rev.*, **3**, 61 (1968), and references cited therein; (c) Me$_3$Si–C–C–Br, A. W. P. Jarvie, A. Holt, and J. Thompson, *J. Chem. Soc. B*, 852 (1969); see also R. B. Miller and T. Reichenbach, *Tetrahedron Lett.*, 543 (1974); (d) Me$_3$Si–C–C–OMe, see ref 19b; (e) Ph$_3$Sn–C–C–OH, D. D. Davis and C. E. Gray, *J. Org. Chem.*, **35**, 1303 (1970).

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(38) The following columns were used for VPC analysis: (a) 5% SE-30 on Chromosorb W, 5 ft × 0.25 in.; (b) 10% DC-550 on Chromosorb W, 10 ft × 0.25 in.; (c) 3% SE-30 on Varaport 30, 5 ft × 0.25 in.

(39) In the elimination reactions, the ratios and yields of 4-octene were determined by VPC using an internal standard. Authentic samples of *cis*- and *trans*-4-octene for comparison were obtained from Chem Samples, Columbus, Ohio. (a) *n*-Octane was used as the internal standard, using a 20 ft × 0.25 in. column packed with 25% Carbowax 20M on Chromosorb W; typical retention times at 70° were 16.4 min (octane), 20.8 min (*trans*-4-octene), 22.7 min (*cis*-4-octene). (b) *n*-Butylbenzene was used as the internal standard; yields were determined on a 10 ft × 0.25 in. column packed with 10% SE-30 on Chromosorb W [typical retention times at 100°: 3.0 min (octenes), 12.3 min (*n*-butylbenzene)]; cis:trans ratios were determined on a 18 ft × 0.25 in. column packed with 15% Carbowax 20M on GCR [typical retention times at 75°: 10.35 min (*trans*-4-octene), 11.05 min (*cis*-4-octene)].

(40) A crystal of the indicator bipyridyl was present in this solution; in other similar experiments, the bipyridyl was omitted.

(41) This spectrum was taken of material of comparable purity from a separate but similar experiment.

(42) An aliquot taken after 5 min showed the reaction to be only 40% complete.

(43) An aliquot taken after 1 hr showed the reaction to be 79% complete.

Oxides of 1,3-Dithiane and 1,3,5-Trithiane. The Diamagnetic Anisotropy of Carbon–Sulfur Bonds

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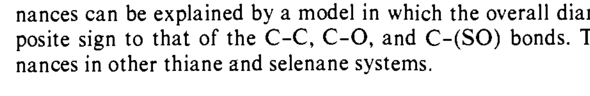
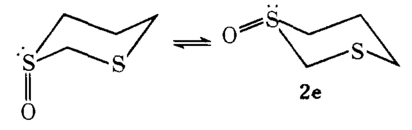
Abstract: The 270-MHz proton spectrum of 1,3-dithiane 1-oxide (**2**) reveals the presence of two isomers, in the ratio 84/16 at −81.5°. Configurational criteria developed in thiane systems confirm that the major isomer is the equatorial oxide. The activation parameters for ring reversal in 1,3-dithiane 1,1-dioxide (**3**) have been measured by the complete line-shape method: E_a = 11.2 kcal/mol, log A = 14.1, $\Delta H^\ddagger$ = 10.6 kcal/mol; $\Delta S^\ddagger$ = 3.8 gibbs, $\Delta G^\ddagger$ (−70.5°) = 9.8 kcal/mol. The proton spectrum of 1,3,5-trithiane 1-oxide (**7**) is invariant with temperature, so that only one isomer, probably with the oxide equatorial, must be present. The 90-MHz spectrum of the 2 protons of 1,3-dithiane *cis*-1,3-dioxide (**5**) changes from an AB quartet at room temperature to a broad singlet at −61°. This reversal of the usual direction of spectral changes is attributed to dimer formation at low temperature in the diequatorial form. Long-range zigzag couplings enable the axial and equatorial nature of the resonances to be identified for the 2 protons in all four of these molecules. The relative order of these resonances can be explained by a model in which the overall diamagnetic anisotropy of the C-S and C-(SO$_2$) bonds has the opposite sign to that of the C-C, C-O, and C-(SO) bonds. This model also explains the order of the axial-equatorial resonances in other thiane and selenane systems.

The conformational analysis of ring systems containing sulfur has been profitable not only because these heterocycles provide an interesting contrast to carbocyclic systems but also because of the widespread occurrence of sulfur heterocycles in nature. The present study is concerned with the conformational properties of the oxides of thiane systems that contain two or three sulfur atoms at alternate ring positions. 1,3-Dithiane (**1**) has one monoxide (**2**) and three dioxides (**3**–**5**). The monoxide (**2**), furthermore, has axial and equatorial modifications (eq 1). In the parent sulfide, thiane 1-oxide (**6**), the axial oxide form is favored at −90° by 175 cal/mol (62/38).[3] Equilibration methods[4] and comparison with the properties of materials whose configuration has been determined by crystallography[5] have indicated that this conformational preference is reversed in 1,3-dithiane 1-oxide and that the equatorial isomer (**2e**) is favored. The unsubstituted form (**2**), however, has not previously been studied.[6]



1 **2** **3** **4** **5**



2a **2e** (1)

The 1,1-dioxide (**3**) and the *trans*-1,3-dioxide (**4**) of 1,3-dithiane also undergo ring reversal, but by symmetry have an equilibrium constant of unity. The *cis*-1,3-dioxide (**5**)