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Base-Induced Reactions of α-Methylene-β-hydroxysilanes. Formation of Allenes

Paul F. Hudrlik,* Amude M. Kassim, E. L. O. Agwaramgbo,[1] Kofi A. Doonquah,
Ralph R. Roberts, and Anne M. Hudrlik

Department of Chemistry, Howard University, Washington, D.C. 20059

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Summary: α-Methylene-β-hydroxysilanes react with NaH in octane to give predominantly allenes resulting from β-elimination. The corresponding reactions in more polar solvents or with KH give mixtures of products from β-elimination and desilylation, with desilylation predominant in the more polar systems.

Although simple (saturated) β-hydroxysilanes readily undergo base-induced β-elimination reactions to give olefins,[2] β-hydroxysilanes which are also vinylsilanes (α-alkylidene-β-hydroxysilanes) are relatively unreactive to some of these conditions.[3] Treatment of such compounds with fluoride has led to allylic alcohols[4] from desilylation,[5] and treatment with metal hydrides has led to allylic alcohols[4d,j,6b] or the corresponding silyl ethers.[4d,6a,c,d] Compared to the saturated systems, the β-elimination reactions in the unsaturated systems are disfavored, presumably because they would lead to relatively strained allenes, and the desilylation reactions are favored by the greater stability of vinyl anions over the analogous alkyl anions.

The base-induced β-elimination reactions of the saturated β-hydroxysilanes are typically carried out with KH in an ethereal solvent such as ether or tetrahydrofuran (THF), or with NaH in a more polar solvent such as dimethylformamide.[2] We have previously shown that simple (saturated) β-hydroxysilanes react with bases such as KOtBu or KOH in a highly polar solvent such as Me_2SO (particularly in the presence of a proton source such as H_2O) to give predominantly products of desilylation rather than β-elimination.[7] Since very polar conditions appeared to favor the desilylation reaction with the saturated β-hydroxysilanes, we felt the use of very nonpolar conditions might favor β-elimination (allene formation) with α-alkylidene-β-hydroxysilanes.

We have previously suggested that desilylation reactions of saturated β-hydroxysilanes involve a homo-Brook rearrangement followed by hydrolysis or cleavage of the resulting silyl ethers,[7a] and we have shown that the base-induced β-elimination reactions of simple β-hydroxysilanes take place in a syn manner.[2c] Thus, probable reaction pathways for the β-elimination and desilylation reactions of α-alkylidene-β-hydroxysilanes are shown in Scheme I. The fluoride-induced desilylations may also take place by this pathway.

We have studied the reactions of α-methylene-β-hydroxysilanes with bases in different solvents to help determine the factors influencing desilylation versus β-elimination. We were especially interested in finding conditions which favor β-elimination, enabling these reactions to be used for the synthesis of allenes. Allenes have previously been prepared from α-alkylidene-β-hydroxysilanes by a two-step procedure involving conversion of the hydroxyl to a better leaving group followed by treatment of the product with fluoride.[3,4h,i,8]

As substrates for these reactions, we have prepared the α-methylene-β-hydroxysilanes **1** and **5** by reaction of 1-(trimethylsilyl)vinyllithium with cyclohexanone (90% yield) and 2-decanone (77–84% yield), respectively. We have treated substrate **1** with NaH and with KH in a variety of solvents, and with NaH/18-crown-6 (catalytic) in a few solvents. In most cases, allene **2** and silyl ether **4** were the only products observed; with NaH in Me_2SO, the allylic alcohol **3** was observed. Typical results are shown in Table I. Reaction times shown are those for complete or nearly complete consumption of substrate **1**.

As can be seen from Table I, the relative amount of β-elimination (giving **2**) was highest with nonpolar conditions. With NaH in heptane or octane, no reaction occurred at room temperature, but at reflux, the allene **2** was by far the major product observed. (With hexane or cyclohexane as the solvent, reaction was very slow, and somewhat more of the desilylation product **4** was observed.)

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[1] Current address: Tougaloo College, Tougaloo, MS 39174.

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[5] Reactions in which silicon is replaced by hydrogen have been called "protiodesilylation" or "protodesilylation". However, according to IUPAC recommendations, this transformation should be called "hydrodesilylation" or "desilylation", unless it is necessary to make a distinction between the isotopes of hydrogen ("protiodesilylation", "deuteriodesilylation", etc.). See Jones, R. A. Y.; Bunnett, J. F. *Pure Appl. Chem.,* **1989,** *61,* 725–768, especially p 732. In this paper we have used "desilylation" to refer to both hydrodesilylation (*e.g.,* **1** → **3**) and homo-Brook rearrangement (*e.g.,* **1** → **4**).

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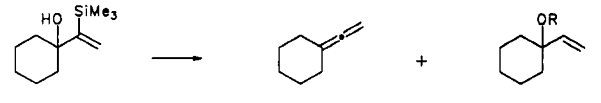
Table I. β-Elimination/Desilylation of 1 under Various Conditions

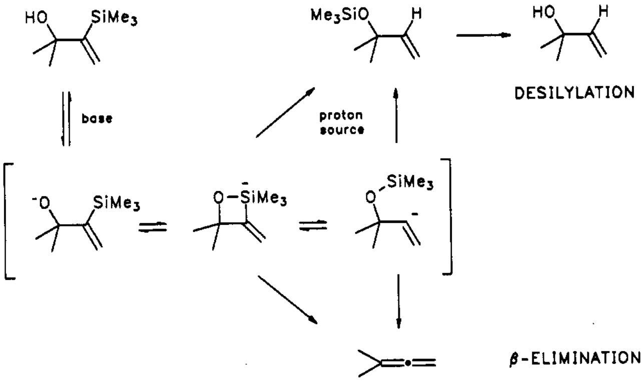


1 2 3 (R = H) 4 (R = SiMe$_3$)

	NaH		KH		NaH/18-crown-6	
solvent	time	2/4[a]	time[b]	2/4[a]	time[b]	2/4[a]
octane	1 day[c]	1:tr	3–5 days	1:1–2	1–4 days	tr:1
heptane	2–3 days[c]	>10:1	3–5 days	1–2:1		
toluene	1 day[c]	4:1	1 day	3:2	1 day	tr:1
Et_3N	6 h–1 day[c]	3:2	1–2 days	~1:1		
TMEDA	1–3 h[d]	1:10				
Et_2O	2 days[c]	NR	5 h	3:4		
dioxane	1 h[c]	1:2	1 h	1:2		
THF	1–2 days[b]	1:10	1 h	1:4		
DME	1–2 days[b]	tr:1	few min	tr:1		
Me_2SO	few minutes[b]	*e*				

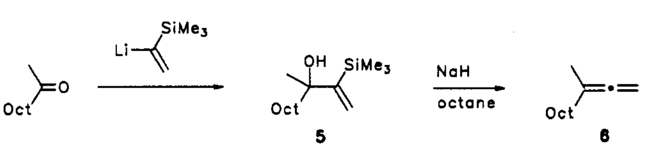
[a] Approximate GC ratios, not corrected for detector response; tr = trace; NR = no reaction. [b] At room temperature. [c] Twenty-four hours at room temperature followed by indicated number of hours at reflux. [d] At 100 °C. [e] Only the hydroxy compound 3 was detected.

Scheme I



On the other hand, with NaH/18-crown-6 in octane, reaction took place (slowly) at room temperature, and silyl ether 4 was essentially the only product. (In a preliminary experiment, a reaction of 1 with NaH/18-crown-6 in octane heated at reflux was complete within 1 h, and was less selective, giving a ratio of 2/4 of about 1:6.) Use of polar solvents for the reaction of 1 with NaH also led to only (or almost only) desilylation products (compound 4 using dimethoxyethane (DME), and, in preliminary experiments, using pyridine and acetonitrile, and alcohol 3 using Me_2SO). In general, reactions with NaH/18-crown-6 and with KH were faster (or proceeded at lower temperatures) than the analogous reactions with NaH, but resulted in more desilylation.

Preliminary experiments using ultrasound (Bransonic 220 ultrasound bath) did not indicate an improvement in the reaction. Treatment of substrate 5 with NaH in octane under sonication at 55 °C for 2 days resulted in little or no reaction, while similar treatment with NaH in THF resulted in a slow reaction yielding predominantly a compound tentatively identified by GC/MS as the silyl ether[9] (analogous to 4) together with a very small amount of allene 6. The lack of improvement in the reaction under sonication suggests that alkoxide formation with sodium hydride is not the slow step (which is perhaps not surprising).



5 6

A mixture of the silyl ether (analogous to 4) and allene 6 was also observed in a preliminary experiment using KH in octane at room temperature (without sonication). Treatment of 5 with NaH in octane at reflux resulted in allene 6 together with several percent of the silyl ether.

The β-elimination reactions in octane at reflux may have some preparative value, since the allene is by far the major product. In a preparative experiment, treatment of 5 with NaH in octane at reflux (27 h) produced pure allene 6 in 54% yield after chromatography.

Experimental Section

General. All reactions were carried out under a nitrogen or argon atmosphere. The verb "concentrated" refers to removal of solvent under reduced pressure (water aspirator) using a rotary evaporator. ^1H NMR spectra were obtained on Nicolet NT-200 (200 MHz) or General Electric QE-300 (300 MHz) spectrometers, and ^{13}C NMR spectra (75.6 MHz) were obtained on the latter instrument. Chemical shifts are reported relative to $CHCl_3$ (δ 7.26) for ^1H spectra of compounds containing Me_3Si, to Me_4Si (δ 0.00) for ^1H spectra of compounds not containing Me_3Si, and to $CDCl_3$ (δ 77.0) for ^{13}C spectra. Mass spectra were obtained on a Finnigan MAT 4500 or a Hewlett-Packard 5890 Series II/5971A gas chromatography mass spectrometer (GC/MS) system. Gas chromatography (GC) analyses were carried out using a flame ionization detector on a Hewlett-Packard 5880 instrument using a 12.5-m crosslinked polymethyldisiloxane capillary column or on a Shimadzu GC-9A using a 2.1-m glass column packed with 3% OV-101 silicone on 100/120 mesh Supelcoport.

Octane, heptane, dioxane, and dimethyl sulfoxide were distilled from CaH_2. Toluene and 1,2-dimethoxyethane (DME) were distilled from sodium. Triethylamine and tetramethylethylenediamine (TMEDA) were distilled from BaO. Diethyl ether (anhydrous) and tetrahydrofuran (THF) were distilled from sodium and benzophenone.

1-[1-(Trimethylsilyl)vinyl]cyclohexanol (1)[4a,10] was prepared by treatment of cyclohexanone with 1-(trimethylsilyl)vinyllithium.[4a,6b,c,10] A comparison sample of ethenylidenecyclohexane (2)[3b,11] was prepared from 1 by treatment with trifluoroacetic anhydride/pyridine followed by n-$Bu_4NF{\cdot}3H_2O/Me_2SO$.[3b] A comparison sample of 1-vinylcyclohexanol (3)[12] was prepared by treatment of cyclohexanone with vinylmagnesium bromide. A comparison sample of the trimethylsilyl ether 4 of 1-vinylcyclohexanol was prepared by treatment of 3 with hexamethyldisilazane followed by trimethylsilyl chloride.[13]

General Procedure for Treatment of 1-[1-(Trimethylsilyl)vinyl]cyclohexanol (1) with Base (e.g. NaH). Sodium hydride (144 mg of a 50% dispersion in oil, 3 mmol) was washed with two 10-mL portions of pentane. To the residue was added 5 mL of the solvent followed by a solution of 99 mg (0.5 mmol) of compound 1 and about 40 mg of internal standard (dodecane; octanol when the solvent was Me_2SO) in 1 mL of the solvent.

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(9) Trimethylsilyl ether of 5: mass spectrum m/z (tentative assignment, rel inten) 256 (M^+, 0.07), 241 ($[M - Me]^+$, 9), 229 ($[M - CH{=}CH_2]^+$, 1.9), 143 ($[M - oct]^+$, 100), 75 (Me_2SiOH^+, 23), 73 (Me_3Si^+, 45).

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Aliquots were taken and worked up by adding to saturated NaHCO$_3$ overlaid with ether. The ether layers were removed by pipet, dried (MgSO$_4$), and analyzed by GC (Hewlett-Packard). When the reaction was found to have gone to completion, water was slowly added followed by ether. The aqueous layer was extracted twice with ether, and the combined organic layers were washed twice with saturated NaHCO$_3$, dried (MgSO$_4$), and analyzed by GC and GC/MS. Product assignments were confirmed by comparing the GC and GC/MS to those of the comparison samples.[14]

3-Methyl-2-(trimethylsilyl)-1-undecen-3-ol (5). To 2.99 mL (19.4 mmol) of (α-bromovinyl)trimethylsilane in 20 mL of anhydrous ether at −78 °C was added 25.5 mL of *tert*-butyllithium (1.6 M in pentane, 40.8 mmol) dropwise. The resulting mixture was stirred at −78 °C for 3 h after which 2.57 mL (13.6 mmol) of 2-decanone in 10 mL of anhydrous ether was added dropwise. The resulting mixture was stirred at −78 °C for 6 h. The cold bath was removed; the reaction mixture warmed to room temperature overnight and was poured into 100 mL of ice-cold 5% HCl. The aqueous layer was extracted with three portions of ether, and the combined organic layers were washed with three portions of saturated NaHCO$_3$, dried (MgSO$_4$), and concentrated. The residue was purified by flash chromatography on 40 g of silica gel using pentane/ether (10:1) giving 2.67 g (76.7%) of alcohol 5 (as a pale yellow liquid): IR (film) 3615, 3480, 3060, 2958, 2929, 2857, 1249, 856, 839 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.13 (s, 9 H), 0.86 (crude t, 3 H), 1.2–1.4 (m, including s at 1.28) and 1.4–1.65 (m)(total 18.7 H), 5.38 (d, J = 2 Hz, 1 H); 5.60 (d, J = 2 Hz, 1 H); ^{13}C NMR (CDCl$_3$) δ 0.57 (Me$_3$Si), 14.07 (CH$_3$CH$_2$), 22.64 (CH$_2$), 23.85 (CH$_2$), 29.28 (CH$_2$), 29.58 (CH$_2$), 30.04 (CH$_2$), 30.11 (CH$_3$), 31.87 (CH$_2$), 42.96 (*C*H$_2$-hept), 77.80 (C), 122.82 (vinyl CH$_2$), 159.66 (vinyl C) (assignments by means of ATP, DEPT 135, and 2D (^{1}H–^{13}C) studies); mass spectrum *m/z* (rel inten) 256 (M$^+$, very small), 241 ([M − Me]$^+$, 2.5), 225 (1.3), 157 (6.8), 143 (11.4), 127 (100), 75 (83), 73 (31). GC analysis (Hewlett-Packard) (50 °C for 5 min, then 10 °C/min to 250 °C, and 250 °C for 5 min) showed the major peak at 15.98 min (96.8%).

3-Methyl-1,2-undecadiene (6). To pentane-washed NaH (from 0.44 g of a 50% dispersion in oil, 9.2 mmol) was added 15 mL of octane and 0.4 g (1.6 mmol) of substrate 5, and the resulting mixture was heated at reflux for 27 h.[15] The mixture was cooled to room temperature and added to cold aqueous NaHCO$_3$ overlaid with pentane. The aqueous layer was extracted twice with pentane, and the combined organic layers were dried (MgSO$_4$), concentrated, and chromatographed on Florisil (pentane). Residual octane was removed from the product by vacuum (35 mm, several days at room temperature) to give 0.14 g (54%) of 6[16] as a colorless liquid: ^{1}H NMR (CDCl$_3$) δ 0.88 (crude t, 3 H), 1.27 (bs, 12 H), 1.67 (t, J = 3 Hz, 3 H), 1.92 (m, 2 H), 4.57 (sextet, J = 3 Hz, 2 H); mass spectrum *m/z* (rel inten) 166 (M$^+$, 0.1), 151 ([M − Me]$^+$, 0.4), 138 (0.4), 137 (0.4), 124 (0.7), 123 (0.9), 110 (5.2), 109 (4.2), 95 (12), 81 (15), 68 (100), 67 (46). The IR spectrum was consistent with that reported.[16a] GC analysis (Shimadzu) (70 °C for 5 min, then 10 °C/min to 200 °C, and 200 °C for 5 min) showed the major peak at 10.8 min (92.4%).

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[14] This method of analysis may not have distinguished between allene 2 and isomers (see ref 15).

[15] When less solvent was used for the reaction, or when some of the solvent accidently evaporated during the reaction, product mixtures, including isomers (by GC/MS) of allene 6, were formed.

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