Stereochemistry of the Thermal Decomposition of 2-Trimethylsilyl Alcohols and Derivatives

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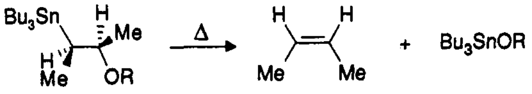
Received October 8, 1993

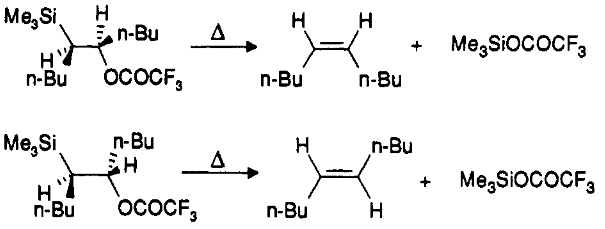
Peterson olefination has proven to be a very useful synthetic reaction in organic chemistry, as an alkene of either configuration can be stereospecifically obtained from a β-silylated alcohol of a given stereochemistry, depending on whether the reaction conditions are basic or acidic.[1] Another way to obtain alkenes from β-silylated alcohols is through the thermolysis of the corresponding esters in solution. This thermally induced decomposition is complicated by the concurrent elimination of acid. It can be partially driven to the elimination of a silyl ester leading to the alkene, however, by using a polar medium or, to a smaller extent, by varying the nature of the leaving group (e.g. trifluoroacetoxy instead of acetoxy), as the concurrent eliminations respond differently to solvent polarity and substituent changes.[2] While the stereochemical course of the acidic and basic decompositions of β-silylated alcohols have been thorougly investigated, the stereochemistry of thermal eliminations in β-silylated alcohols, ethers, and esters has not been studied. It has only been postulated that, as with the pyrolysis of esters, the thermolysis of β-silylated esters,[3,4] alcohols,[5] or ethers[5] was a syn elimination. Recently, studies on the stereochemical course of the thermal decomposition of (2-(acyloxy)alkyl)trialkylstannanes[6] and (2-hydroxyalkyl)trialkylstannanes[7] have been reported. Surprisingly, they showed that the decompositions were clean anti eliminations of stannyl carboxylates or hydroxides. Compared to the pyrolysis of esters, which is a syn elimination,[8] the introduction of a trialkylstannyl group β to an acyloxyl group induced a dramatic change in the course of the elimination.



$R = H, COCH_3$

A stereochemical study of the thermal decomposition of β-silylated esters, ether, and alcohols has been undertaken to check whether silicon has the same directing effects as tin in these eliminations. β-Trimethylsilylated alcohols were stereospecifically prepared by the method described by Hudrlik .[9] β-Silylated esters could not be prepared by the same routes which led to β-stannylated esters.[6] Under standard conditions in the presence of pyridine, the desired esters are not formed from acetyl, isobutyroyl, or pivaloyl chlorides. This lack of reactivity can be attributed either to a steric bulkiness of a trimethylsilyl group higher than that of a tributylstannyl group (the tin–carbon bond is longer than the silicon–carbon bond) or to some electronic effect of the silicon on the hydroxyl,[10] lowering its reactivity. Reactive trifluoroacetic anhydride led to the expected trifluoroacetates, and esterifications with DCC allowed the preparation of the requisite acetates in decent yields.[11]

These esters were then subjected to thermolysis. With trifluoroacetates, thermal conditions were quite mild, as 24 h at 0 °C was sufficient for a complete decomposition. *threo*-6-(Trimethylsilyl)-5-decyl trifluoroacetate led to (*Z*)-5-decene (entry 1), while *erythro*-6-(trimethylsilyl)-5-decyl trifluoroacetate gave (*E*)-5-decene (entry 2). The decompositions were thus highly stereoselective anti eliminations of trimethylsilyl trifluoroacetate, analogous to what was recorded with β-stannylated esters,[6] and not a syn elimination as it was postulated up to now.[3,4] They were also highly selective as no elimination of trifluoroacetic acid, which would have given 4-(trimethylsilyl)-4-decene, could be detected. In contrast, the thermolysis of 1-(*m*-chlorophenyl)-2-(trimethylsilyl)ethyl trifluoroacetate in xylene at 202 °C in the presence of 1.1 equiv of 2,6-lutidine was not chemoselective.[2] It led to a mixture of 67% (*m*-chlorophenyl)ethylene and 33% 1-(*m*-chlorophenyl)-2-(trimethylsilyl)ethene.



Then *threo*- and *erythro*-6-(trimethylsilyl)-5-decyl acetates were thermolyzed. The *threo* isomer led to (*E*)-5-(trimethylsilyl)-5-decene contaminated with a mixture of (*E*)- and (*Z*)-5-decene (entry 3), and the *erythro* isomer gave a mixture of (*Z*)-5-(trimethylsilyl)-5-decene and (*Z*)- and (*E*)-4-decene (entry 4). A complete change in the course of the reaction was observed, as the elimination of

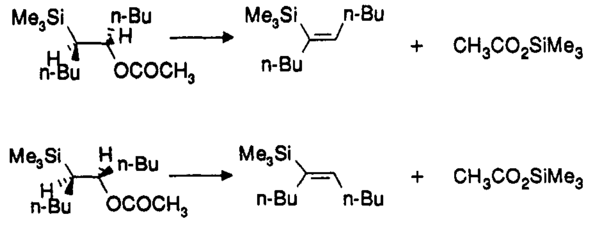


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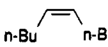
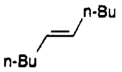
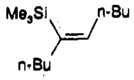
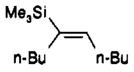
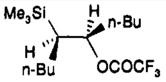
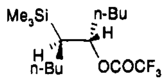
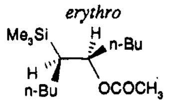
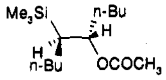
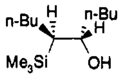
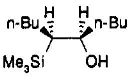
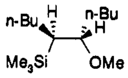
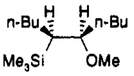
Table 1. Thermolysis of 2-Trimethylsilyl Alcohols, Ethers, and Esters

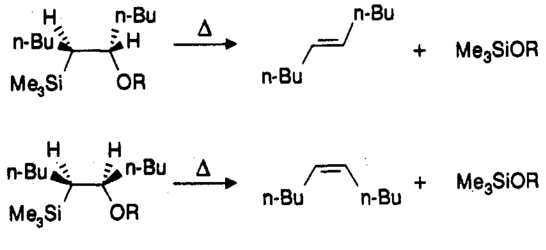
			yield and product ratio			yield and product ratio		
entry		temp (°C)						
1	 *threo*	0	100%[a]	99 (anti)	1	0%		
2	 *erythro*	0	100%	3	97 (anti)	0%		
3	 *threo*	250	9%	59 (anti)	41	91%	0	100 (syn)
		550	30%	80 (anti)	20	70%	14	86 (syn)
		650	57%	97 (anti)	3	43%	18	82 (syn)
4	 *erythro*	250	2%	42	58 (anti)	98%	89 (syn)	11
		350	7%	38	62 (anti)	93%	88 (syn)	12
		450	12%	34	66 (anti)	88%	80 (syn)	20
		550	42%	26	74 (anti)	58%	64 (syn)	36
5	 *threo*	450	100%	7	93 (syn)	0%		
6	 *erythro*	450	100%	94 (syn)	6	0%		
7	 *threo*	450	100%	9	91 (syn)	0%		
8	 *erythro*	450	100%	96 (syn)	4	0%		

[a] Isolated yields of decomposition products were superior to 85%.

trimethylsilyl acetate was almost inhibited. A similar behavior, but less clean, was recorded in the thermolysis of β-silylated carbamates and methanesulfonates.[4] The selectivity of the concurrent elimination of trimethylsilyl acetate was not as good as the elimination of trimethylsilyl trifluoroacetate suggesting that two different mechanisms were operating. Nevertheless, it showed a clear anti preference at high temperature. The results of the thermolysis were sensitive to temperature, which was varied from 250 to 550 °C. Low temperatures favored acetic acid elimination and decreased its selectivity, while high temperature favored trimethylsilyl acetate elimination and increased its selectivity.

The thermolysis of *threo*- (entry 5) and *erythro*- (entry 6) 6-(trimethylsilyl)-5-decanol was conducted at 450 °C. It led to (*E*)- and (*Z*)-dec-5-ene, respectively, with high yields. That was indicative of a clean syn elimination of trimethylsilanol. With equivalent β-stannylated alcohols, an anti elimination was recorded at a low temperature (100 °C), and a syn elimination occurred when the temperature was raised.

When thermolyzed, *threo*- (entry 7) and *erythro*- (entry 8) 5-methoxy-6-(trimethylsilyl)decanes led to (*E*)- and (*Z*)-dec-5-ene, respectively, which indicated a syn elimination.



R = H, Me

The reaction occurred at temperature higher than with the corresponding alcohols but was still quite selective as the purity of the produced olefin was better than 90% in each case.

The presence of a metal β to oxygen reduces the stability of the corresponding ester or alcohol: 35 min were necessary to decompose 6-(trimethylsilyl)-5-decyl acetate while no appreciable decomposition was noticed when 5-decyl acetate was heated under the same conditions. The replacement of a tin by a silicon induced a marked increase in the stability of β-metalated esters and alcohols. For instance, 5-acetoxy-6-(trimethylsilyl)decanes were stable at 0 °C while 2-acetoxy-3-(tributylstannyl)butanes decomposed within a few hours at the same temperature. That confirmed results reported by Lambert on solvolysis of β-stannylated[12] and β-silylated alcohols[13] where considerably higher reaction rates were recorded with stannylated alcohols than with silylated alcohols. This change did not perturb the stereochemistry of the elimination in β-metalated esters when a good leaving group (trifluoroacetate) compensated the weaker stabilizing effect of the metal (Si). However, with a poorer leaving group (acetate), the course of the thermolysis was modified. The elimination of trimethylsilyl acetate only occurred at higher temperatures, but, under these conditions, the concurrent elimination of acetic acid was preponderant. The silicon induced a very high stereoselectivity, which is quite rare in such ester thermolysis, in the side elimination of trimethylsilyl acetate which showed an anti preference. This behavior, varying with the nature of the leaving group, has already been discussed in terms of the basicity of the leaving group[4] and the charge distribution, on the basis of a syn elimination.[3] An explanation based on the observed anti elimination could be as follows: with a good leaving group, a partial charge greater than with a poor leaving group would be developed during the transition state.[3] Its antiperiplanar delocalization on the silicon would make the silicon–carbon bond weaker and then would allow the elimination of trimethylsilyl ester to proceed at a low temperature. When a poor leaving group is used, the charge developed during the transition state would be weaker. Its delocalization on silicon would also be weak, which would make the silicon–carbon bond stronger and would allow the concurrent elimination of acid to occur. This stabilization would be important enough, however, to impose an antiperiplanar arrangement of the silicon and the leaving group, and thus to allow the reaction to show an unusually high stereoselectivity.

In the case of β-silylated alcohols, a third reaction, the clean syn elimination of trimethylsilanol, occurred.[5] The replacement of a tin by a silicon did not allow the anti elimination[7] to proceed at a low temperature because of the decrease of the stabilization effect of the metal. Instead, when the temperature was increased, a nucleophilic attack of oxygen on the silicon induced a stereospecific syn elimination of trimethylsilanol. The same reaction occurred with β-silylated ethers. Kinetic studies of the thermolysis of 1-methoxy-2-(trimethylsilyl)ethane showed that there was a strong evidence that it decomposed via a four-membered cyclic transition state.[5,14] The present study confirmed this hypothesis, as a syn elimination of methoxytrimethylsilane was observed with substituted β-silylated ethers.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. THF and diethyl ether were distilled from sodium benzophenone ketyl prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer, and ^{29}Si NMR spectra on a Bruker AC 200 (solvent $CDCl_3$, internal reference Me_4Si). The compounds to be pyrolyzed (3 mmol) were dropped onto an electric-heated column packed with quartz helicies at a rate of about one drop every 5 s, under a stream of N_2. The receiver at the bottom of the column was kept at -50 °C. No starting material was recovered in the products. Yields of decomposition products were superior to 85%. They were analyzed by GLC and identified by comparison with authentic samples, and by ^{1}H and ^{13}C NMR spectra.

***threo*-6-(trimethylsilyl)-5-decanol.** Prepared as described for *threo*-5-(trimethylsilyl)-4-octanol:[9] ^{1}H NMR δ 0, 0.86, 1.2–1.78, 3.74, 4.9; ^{13}C NMR δ -0.88, 13.92, 22.58, 22.98, 26.53, 28.71, 32.23, 36.01, 34.65, 73. Anal. Calcd for $C_{13}H_{30}SiO$: C, 67.75; H, 13.12. Found: C, 67.31; H, 13.48. ***erythro*-6-(trimethylsilyl)-5-decanol.** Prepared as described for *erythro*-5-(trimethylsilyl)-4-octanol:[9] ^{1}H NMR δ 0, 0.85, 1.24–1.44, 3.72, 4.8; ^{13}C NMR δ -1.13, 13.97, 22.60, 23.12, 24.79, 28.73, 30.61, 36.25, 32.57, 72.99. Anal. Calcd for $C_{13}H_{30}SiO$: C, 67.75; H, 13.12. Found: C, 67.56; H, 13.49.

***threo*-6-(trimethylsilyl)-5-decyl trifluoroacetate.** An amount of 2.87 g (12.5 mmol) of *threo* alcohol and 1.08 g (13.7 mmol) of pyridine in 20 mL of diethyl ether were placed in a three-necked flask at -20 °C. An amount of 2.87 g (13.7 mmol) of trifluoroacetic anhydride in 10 mL of anhydrous diethyl ether was added slowly. The resulting mixture was stirred at -20 °C for 30 min. The solid was filtered off, and the solution was washed with cold saturated aqueous $CuSO_4$ and 10% aqueous $NaHCO_3$ and was dried over $MgSO_4$ in the refrigerator. The solvent was evaporated (0 °C) to give the desired product (60%), 2.44 g of which was found to be too thermally unstable to be analyzed. The *erythro* isomer was prepared analogously and could be characterized at -40 °C by ^{1}H and ^{13}C NMR spectroscopy: ^{1}H NMR δ 0, 0.86, 1.25–1.39, 5.22; ^{13}C NMR δ -1.02, 22.44, 22.84, 26.17, 27.87, 31.61, 32.52, 32.81, 82.33, 114.60, 157.25.

***threo*-6-(trimethylsilyl)-5-decyl acetate.** An amount of 2.87 g (12.5 mmol) of alcohol and 0.82 g (13.7 mmol) of acetic acid in ether (10 mL) were placed in a three-necked flask and cooled at 0 °C. An amount of 3.22 g (15.6 mmol) of 1,3-dicyclohexylcarbodiimide (DCC) and 0.15 g (1.2 mmol) of 4-(dimethylamino)pyridine (DMAP) in 50 mL of ether were slowly added. The reaction mixture was stirred overnight. Ether (20 mL) was added and the mixture filtered. The organic layer was washed twice with 5% hydrochloric acid, once with aqueous $NaHCO_3$, and once with saturated aqueous NaCl and dried. The solvents were evaporated, and chromatography of the residue (alumina, petroleum ether) gave the *threo* ester (2.7 g, 80%): ^{1}H NMR δ 0, 0.84, 1.21–1.58, 1.96, 4.96; ^{13}C NMR δ -0.83, 14.01, 22.56, 22.87, 23.19, 25.76, 26.47, 31.62, 32.33, 33.19, 77.19, 170.94; ^{29}Si NMR 2.53. Anal. Calcd for $C_{15}H_{32}SiO_2$: C, 66.12; H, 11.84. Found: C, 65.58; H, 11.49.

***erythro*-6-(trimethylsilyl)-5-decyl acetate:** ^{1}H NMR δ 0, 0.86, 1.23–1.37, 1.96, 5.02; ^{13}C NMR δ -0.79, 14.01, 21.14, 22.44, 22.97, 25.39, 28.16, 32.66, 33.37, 33.77, 75.59, 170.24; ^{29}Si NMR δ 3.42. Anal. Calcd for $C_{15}H_{32}SiO_2$: C, 66.12; H, 11.84. Found: C, 66.83; H, 12.14.

***threo*-5-methoxy-6-(trimethylsilyl)decane.** In a dry three-necked flask were placed sodium hydride (25 mmol, 0.6 g) and dry tetrahydrofuran (10 mL). The flask was cooled at 0 °C with stirring, and methyl iodide (50 mmol, 7.1 g) was added. The *threo* alcohol (12.5 mmol, 2.9 g) in tetrahydrofuran (5 mL) was added dropwise. After 1 h, the reaction mixture was hydrolyzed by dropwise addition of sufficient water to dissolve any precipitate. The aqueous layer was separated and extracted twice with ether. Then the organic layer was washed with saturated NaCl and dried over $MgSO_4$. The solvents were evaporated, and the chromatography of the residue (alumina, petroleum ether) gave the *threo* ether (2.4 g, 80%): ^{1}H NMR δ 0, 0.85–1.57, 3.17–3.24; ^{13}C NMR δ -0.97, 14.13, 23.17, 23.72, 26.14, 28.09, 29.78, 33.79, 56.0, 83.60; ^{29}Si NMR δ 2.40. Anal. Calcd for $C_{14}H_{32}SiO$: C, 68.78; H, 13.19. Found: C, 68.21; H, 12.75. ***erythro*-5-methoxy-6-(trimethylsilyl)decane:** ^{1}H NMR δ 0, 0.85–1.47, 3.25; ^{13}C NMR δ -0.57, 14.01, 22.91, 25.52, 28.62, 28.76, 33.60, 34.01, 56.23, 81.89; ^{29}Si NMR δ 3.41. Anal. Calcd for $C_{14}H_{32}SiO$: C, 68.78; H, 13.19. Found: C, 68.34; H, 12.94.

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