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STEREOSPECIFIC SYNTHESIS OF CIS OR TRANS OLEFINS FROM β-KETOSILANES

Paul F. Hudrlik and David Peterson

School of Chemistry, Rutgers University
New Brunswick, New Jersey 08903

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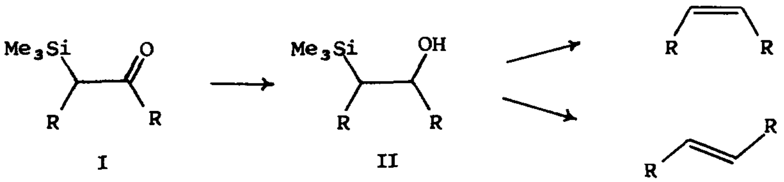
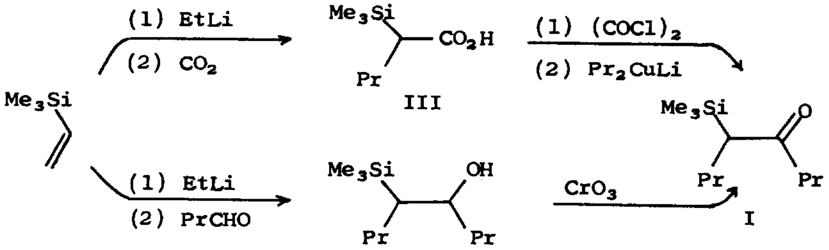
The synthesis of olefins by the acid[1] or base[2] catalyzed eliminations of β-hydroxysilanes has been an area of recent activity; however, the utility of this reaction has been hampered because mixtures of cis and trans isomers usually result. We wish to report that the β-ketosilane (I) (R = n-Pr) can be selectively reduced to one diasteromeric alcohol (II), which can be converted stereospecifically to either the cis or the trans olefin by proper choice of the conditions for the elimination.

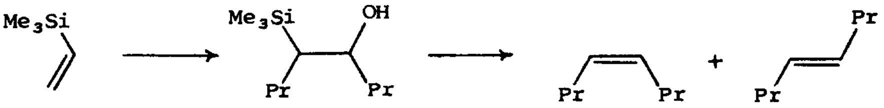


The synthesis of (I) has been completed via two routes. First, addition[3] of EtLi (1.3 equivalents) to $Me_3SiCH=CH_2$ at -78° in THF, followed by warming to 0°, and then carbonation with dry ice in pentane, gave upon workup with 6N HCl the silyl acid (III) in 81% yield.[5] Then (III) was converted to the acid chloride with oxalyl chloride and reacted with Pr_2CuLi[4] (3.0 equivalents) in ether at -78° to give (I) in 60% yield.[5]

A second synthesis started with the addition of EtLi (1.3 equivalents) to $Me_3SiCH=CH_2$, followed by addition of butyraldehyde (1.1 equivalents) at -78° to give the silyl alcohol in 91% yield.[5] The alcohol was oxidized with CrO_3-pyridine[6] at room temperature to give (I) in 68% yield.[5]



The silyl alcohol resulting from the condensation with butyraldehyde could be converted to 4-octene directly; however, a 72:28 mixture[7] of isomers was formed, with the predominant isomer dependent on the exact reaction conditions.



Elimination Conditions	Cis:Trans Ratio
$MsCl/Et_3N$/pentane/0°	72:28
NaH/HMPA/R.T.	28:72

These results suggest that the condensation with PrCHO gives a mixture of diasteromers, and that the elimination conditions are stereospecific. Therefore, if one diasteromer of the silyl alcohol could be formed exclusively, then either pure cis or pure trans olefin could be produced. Reduction of the ketone (I) with diisobutylaluminum hydride (DIBAL) (2.0 equivalents) in pentane at -120° gave the alcohol (II) in 97% yield.[5] Elimination of (II) under the conditions given in the Table gave specifically either cis or trans-4-octene[7] in good yields and in high isomeric purity.

The alcohol produced by reduction of (I) with DIBAL is presumably the threo isomer. This is in accord with the prediction of Cram's Rule[8], if Me_3Si is assumed to be larger than n-Pr. The eliminations with NaH and KH to give trans-4-octene are then syn, which is in accord with previous suggestions.[2b,9] The reactions which give cis olefin are then proceding via an anti elimination. A similar, acid catalyzed tin β-elimination was shown by Davis[10] to be anti.

TABLE

Conditions	yield of 4-octene[7]	cis	trans
KH/THF/R.T./1 hr.	96%	5%	95%
NaH/HMPA/R.T./20 hr.	85	7	93
H_2SO_4/THF/R.T./10 hr.	99	92	8
$BF_3 \cdot Et_2O/CH_2Cl_2$/0°/1 hr.	99	94	6
MsCl,Et_3N/Pentane/0°/15 min.	80	89	11
NaOAc,Ac_2O/DMSO/R.T./12 hr.	81	87	13

The mildness of these experimental conditions and the stereochemical control which is possible promise to make the elimination reactions of β-hydroxysilanes of increasing utility. It should be possible to extend this method to the synthesis of tri-substituted double bonds.[11]

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5. Yields refer to distilled compounds. Satisfactory IR, NMR, and mass spectra were obtained.

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7. Authentic samples of cis and trans 4-octene were available for comparison. Yields of octene were determined by VPC using an internal standard, and ratios were determined by VPC. In one experiment (H_2SO_4), the product of the elimination reaction was shown not to contain any 3-octene by ozonolysis. No valeraldehyde was detectable by VPC.

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