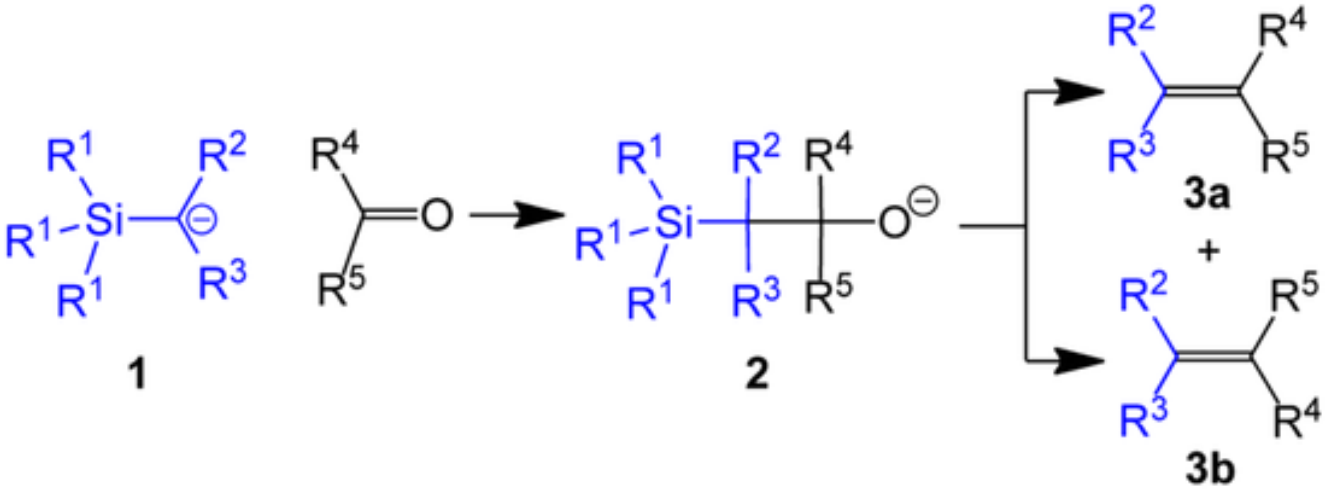
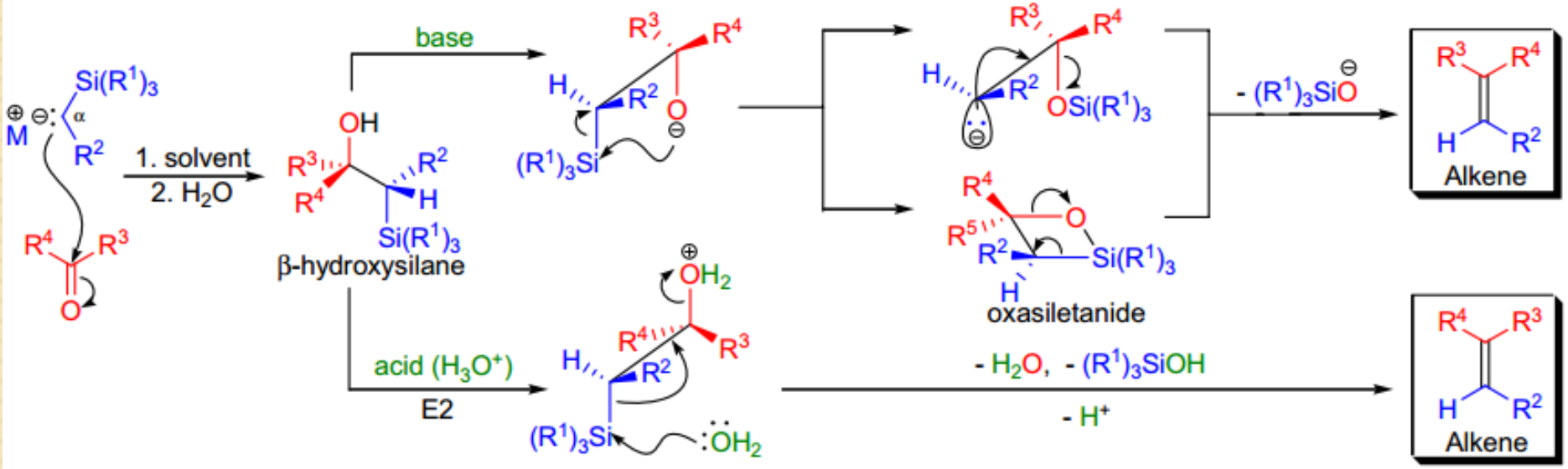
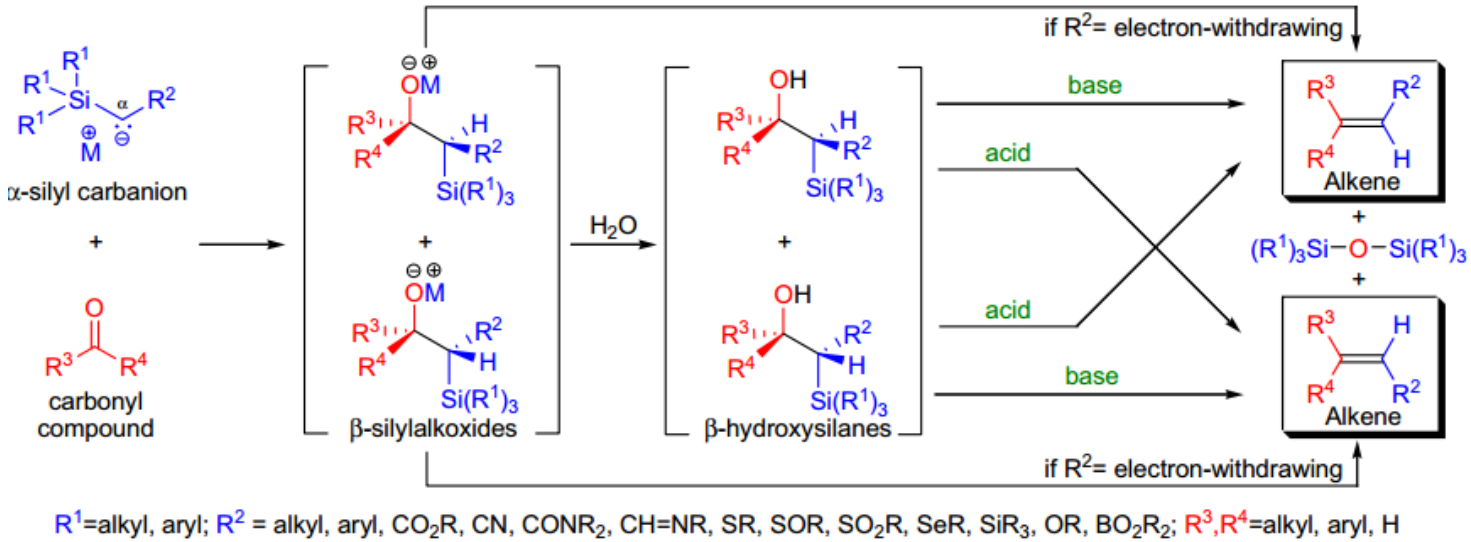
PETERSON OLEFINATION



Reaction mechanism





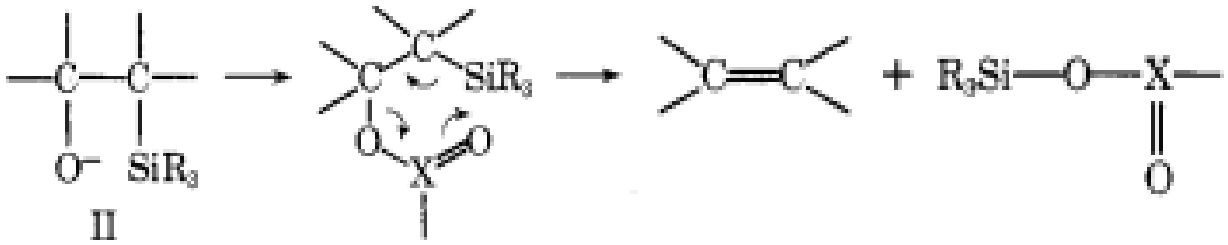
R^1=alkyl, aryl; R^2 = alkyl, aryl, CO_2R, CN, $CONR_2$, CH=NR, SR, SOR, SO_2R, SeR, SiR_3, OR, BO_2R_2; R^3,R^4=alkyl, aryl, H

- The addition of the α-silyl carbanions to carbonyl compounds gives rise to a mixture of diastereomeric β-silylcarbinols, which can be isolated and separated only if the R^2 substituent in the α-silyl carbanion is not electron-withdrawing;

- Upon treatment with base (NaH, KH, KOt-Bu), the β-silylcarbinols undergo a stereospecific syn-elimination, while treatment with dilute acid or a Lewisacid (AcOH, H_2SO_4, $BF_3{\cdot}OEt_2$) results in a stereospecific anti-elimination;

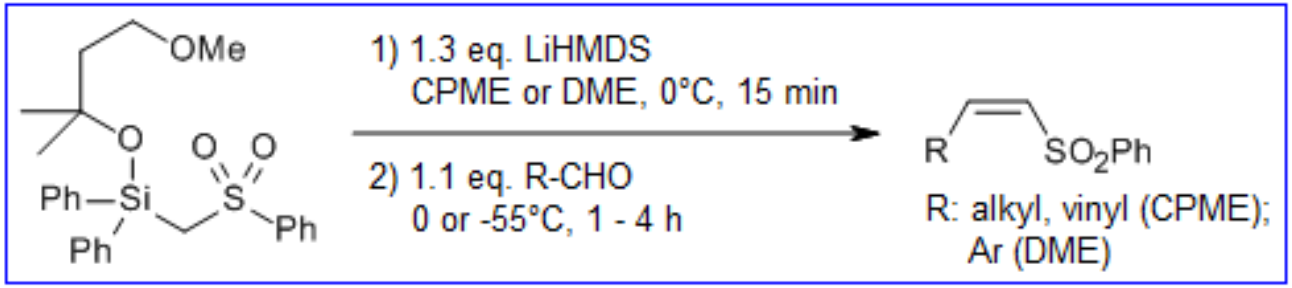
- The silicon group(SiR_3) has been replaced with groups containing other elements (SbR_2, AsR_2, SnR_3, HgR, etc.) also form alkenes, but usually the corresponding α-carbanions are harder to prepare and the elimination requires special and often harsh conditions.

Acidic elimination conditions are sometimes not feasible as the acid also promotes double bond isomerization. Additionally, elimination using sodium or potassium hydride may not be feasible due to incompatible functional groups. Chan et al. have found that acylation of the intermediate silylcarbinol with either acetyl chloride or thionyl chloride gives a β-silyl ester that will eliminate spontaneously at 25 ° C giving the desired alkene.

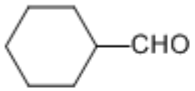
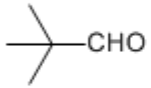
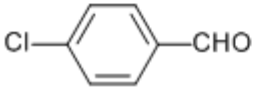


T. H. Chan, E. Chang., *J. Org. Chem.* **1974**, *39*, 3264–3268.

Peterson reagents

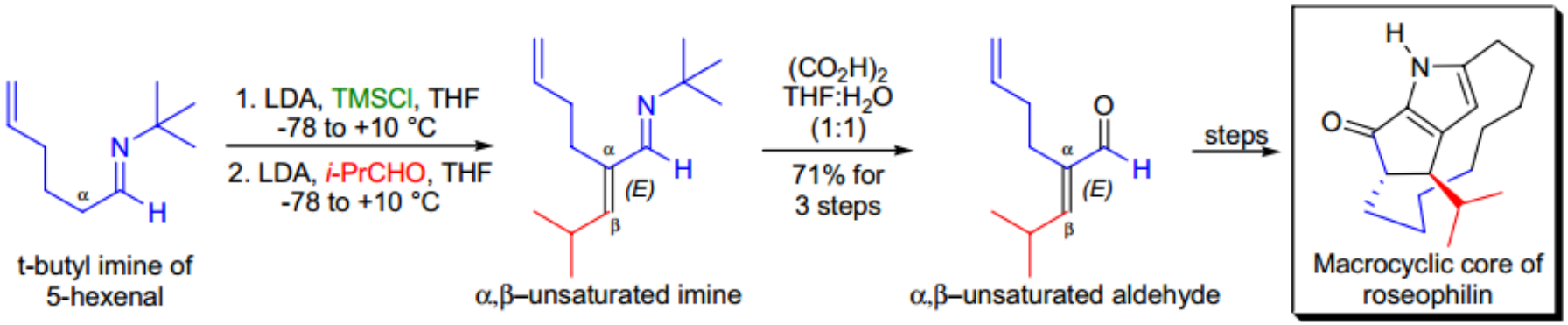


Peterson reagents, in which alkyloxy groups on the silicon atom fix the conformation of the anion after treatment with Li-base, were reacted with a variety of aldehydes to give *Z*-α,β-unsaturated sulfones with high *Z*-selectivity in very good yields.

aldehyde	T (°C)	t (h)	yield (%, isol.)	*Z*:*E*
$H_{15}C_7$—CHO	-78	2	85	97:3
	0	2	97	99:1
	0	2	79	88:12
	0	2	90	92:8
Ph—CHO	-55	3	90	94:6
	-55	3	67	93:7
	-55	4	64	87:13

K. Ando, T. Wada, M. Okumura, H. Sumida, *Org. Lett.*, **2015**, *17*, 6026-6029.

M.A. Tius et al. reported a formal total synthesis of the macrocyclic core of roseophilin.[52] The aliphatic five-membered ring of this core was prepared *via* a variant of the *Nazarov cyclization*. The precursor for this cyclopentannelation reaction is an (*E*)-α,β-unsaturated aldehyde, which was prepared using the *Peterson olefination* on the *t*-butylimine of 5-hexenal. First the α-TMS derivative of the imine was generated; then after a second deprotonation, the additon of isobutyraldehyde gave the (*E*)-α,β-unsaturated imine upon aqueous work-up. Acidic hydrolysis of this imine gave the desired (*E*)-α,β-unsaturated aldehyde in good yield.



In the final stages of the total synthesis of (+)-brasilenyne by S.E. Denmark and co-workers, the introduction of the (*Z*)-enyne side chain was accomplished with the *Peterson olefination*.[53] The aldehyde was treated with lithiated 1,3-*bis*(triisopropylsilyl)propyne at low temperature followed by slow warming of the reaction mixture to ambient temperature to give a 6:1 (*Z*:*E*) ratio of the desired enyne.