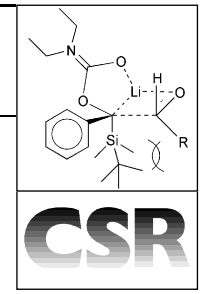
# New developments in the Peterson olefination reaction



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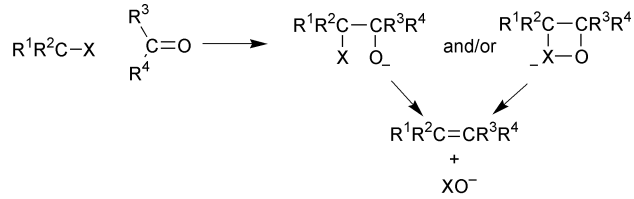
**Noteworthy developments of the Peterson olefination reaction are reviewed. Evidence for both concerted and stepwise mechanisms for the Peterson olefination reaction is presented. The strong affinity of the oxygen anion for the silyl moiety is emphasised when the Peterson olefination reaction takes preference over both the Julia and Wittig reactions in the presence of *S*- and *P*-stabilised silyl carbanions. Cerium-mediated Peterson methylenation reactions are discussed.**

## 1 Introduction

The Peterson olefination is considered to be the silicon variation of the Wittig-type reactions (Scheme 1),[1] which involve the addition of α-heteroatom stabilised carbanions to aldehydes and ketones.




**Scheme 1**

One advantage of the Peterson olefination is that the disiloxane ($R_3SiOSiR_3$) by-product is usually volatile and thus

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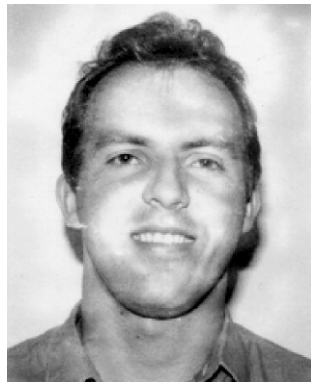
**Frances van Staden**

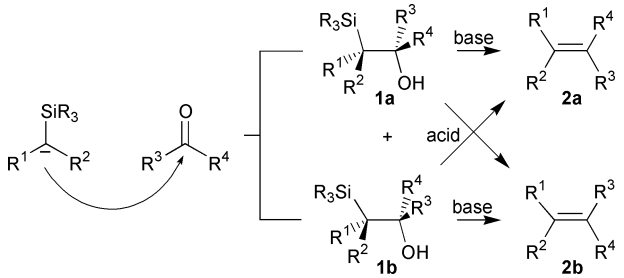


**David Gravestock**

**David Ager**

readily removed in comparison to the involatile triphenylphosphine oxide by-product of the Wittig reaction.[2]

The Peterson olefination is the reaction of an α-silyl carbanion with an aldehyde or ketone to afford the β-hydroxysilyl intermediates **1a** and **1b**, that can be treated with either acid or base to afford the desired olefins stereoselectively (Scheme 2).[3]




**Scheme 2**

An important feature of the Peterson olefination is that both the *E*- and *Z*-isomers **2** can be obtained from a single diastereoisomer; *e.g.* treatment of the *erythro* β-hydroxysilane with acid would favour the formation of the *E*-isomer, whereas the *Z*-isomer would be formed under basic conditions.[4] Another attribute of this reaction is that the *E*-isomer, like the *Z*-isomer, can be prepared stereoselectively from both stereoisomers of the β-hydroxysilane. Therefore, the Peterson olefination is considered to be an attractive alternative to Wittig reactions.[5] In the instance when a carbanion stabilising group is present *alpha* to the carbanion, *e.g.* $R^2 = C_6H_5$ or $CO_2R$ (Scheme 2), the olefins (**2a** and **2b**) are isolated directly.

A decade ago, the major drawbacks of the Peterson olefination reaction were considered to be (i) the difficulties experienced in producing α-silyl carbanions and (ii) the poor diastereoselectivities obtained during the preparation of the β-hydroxysilane intermediates **1** (Scheme 2). Consequently, much of the research efforts this decade has centred around the development of stereoselective β-hydroxysilane preparations, since this was believed to be pivotal to the increased application of the Peterson olefination in synthesis.[3,6]

This overview of the Peterson olefination highlights some of the noteworthy and unexpected findings published between 1987 and 1999, *i.e.* subsequent to the last review published in 1990,[3] and our discussions are limited to reactions under basic conditions.

## 2 Mechanism of the Peterson olefination reaction

Evidence that the reaction mechanism of the Peterson olefination involves the formation of a four membered intermediate corroborates the theory that this olefination is the silyl variation of the Wittig reaction. Another school of thought believes that the Peterson olefination proceeds in a stepwise manner (Scheme 3). Therefore the statement published by Ager in 1990 still applies;[3] "At present, the exact mechanism of the Peterson reaction is not clear."

The following sections will show that there exists experimental evidence in support of both a stepwise (Steps 1–3, Scheme 3; Sections 2.1 and 2.2) and concerted mechanism, *i.e.* where Steps 1 and 2A proceed simultaneously to form the oxasiletanide intermediate (Scheme 3; Section 2.3). It is assumed that the elimination of the silanoxide moiety from an oxasiletanide intermediate (Step 3A, Scheme 3) would proceed in a concerted manner.

Pelter and co-workers[1] compared the short B–O and B–C bond lengths, to the P–O, P–C and Si–O, Si–C bond lengths, in the cyclic four membered transition states (Fig. 1). These

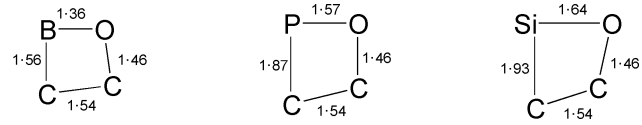


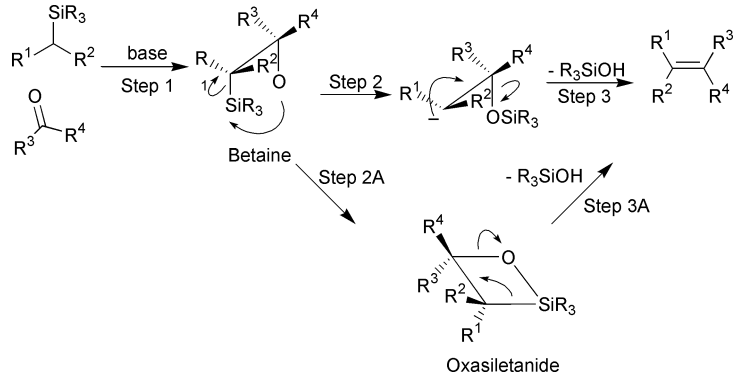

**Fig. 1**

authors attributed the excellent *E*-selectivities obtained when boron stabilised carbanions were reacted with aldehydes, to the closer proximity of the stereodifferentiating groups in the transition state. By analogy the closer proximity of the stereodifferentiating groups in the four membered transition state of the Wittig, compared with the Peterson olefination, might explain the good selectivity of the Wittig reaction, whilst prior to 1987 it was generally accepted that poor selectivity is obtained with the Peterson olefination.[7]

It is apparent from a comparison of these four membered transition states (Fig. 1), that as a consequence of the extreme polarisation, the Peterson olefination is least likely to proceed *via* a four membered intermediate (Scheme 3). It was proposed that the lability of the $C^{\delta-}$–$Si^{\delta+}$ bond, as a consequence of the extreme polarisation,[8] facilitates the rapid formation of the stronger O–Si bond (Scheme 3, step 2) and subsequent elimination of the silanol to afford the olefin.[9]

### 2.1 Stepwise reaction mechanism

There appears to be overwhelming evidence in support of a stepwise mechanism (Scheme 3),[3,10] which involves the addition of the carbanion to the carbonyl compound (Step 1), followed by the rapid formation of the O–Si bond (Step 2) and elimination of the silanol group (Step 3).[5,10*b*,11] In some cases, elimination of the silanol is so rapid that no rotation about the C–C bond is observed during Steps 2 and 3 (Scheme 3), giving the same outcome as a concerted elimination from the betaine. The observed selectivities can be explained using the following




**Scheme 3**

literature models, which attempt to predict how the carbanion and carbonyl compound orientate themselves relative to one another.

The approach control model proposed by Bassindale and co-workers[12] assumes the absence of chelation control. The stereoselectivity of the reaction is the result of the carbanion attacking the carbonyl at an angle greater than 90° (*ca.* 109°, Fig. 2). The priorities of the substituents are based on their relative steric bulk and the stereochemical outcome of the reaction is a result of the steric effects depicted in Fig. 2.

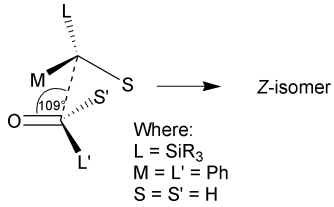
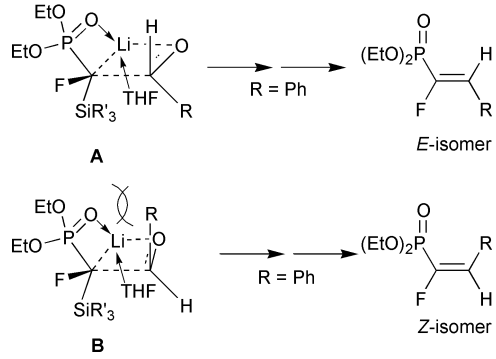



**Fig. 2**

Independent researchers have reported that the model proposed by Bassindale and co-workers[12] predict the outcome of the Peterson olefination accurately.[6b,13] Furthermore, if the Bassindale model[12] is correct, steric factors would have a marked effect on the stereoselectivity of the reaction.

## 2.2 'Butterfly' transition states

The approach control model proposed by Bassindale and co-workers[12] applies to systems where chelation control is absent. Washbüsch and co-workers[14] presented additional evidence for a stepwise mechanism and proposed the formation of a 'butterfly' transition state in the presence of a chelating α-stabilising phosphonate moiety. The formation of a closed four-centred transition state, analogous to that of the Wittig–Horner reaction, was assumed (Scheme 4).

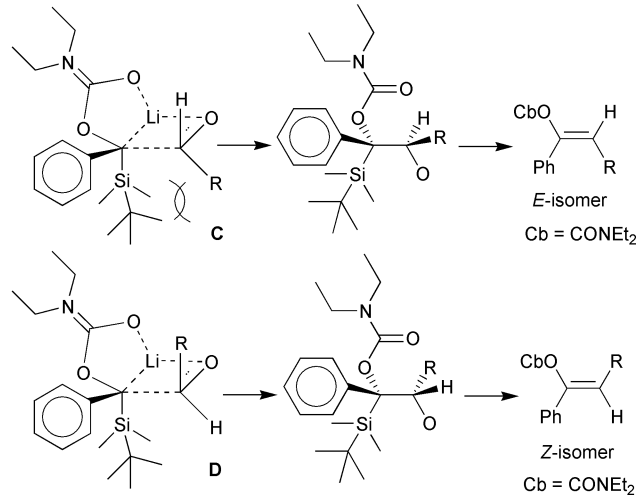



**Scheme 4**

The *E*-isomer (transition state **A**) is favoured on steric grounds. The 'butterfly' transition state (Scheme 4) illustrates how this selectivity might be influenced by the steric bulk of the axially orientated silyl moiety (transition state **A**) explaining the observed decrease in *E*:*Z* ratio with increasing silyl bulk.

Similarly, the chelating ability of the carbamate functionality is well documented[15] and corroborated by the observed stereoselectivity of the Peterson olefination with benzyl carbamates.[16a] The observed *Z*-selectivity is similarly explained by a 'butterfly' like transition state (transition state **D**, Scheme 5) which take these complex induced proximity effects into consideration. The simultaneous coordination of the amide oxygen anion and the carbonyl oxygen to the lithiated carbanion results in the formation of the proposed 'butterfly' like transition state (Scheme 5).

In this model, like the approach control model,[12] the orientation of the stereodifferentiating groups relative to one




**Scheme 5**

another in the 'butterfly' transition state determines the stereoselectivity of the reaction. The unfavourable steric repulsion between the bulky silyl group and the R-group in transition state **C** outweighs the steric repulsion experienced between the carbamate and R-group in transition state **D** (Scheme 5). Thus, an increase in the steric bulk of the silyl functionality leads to a decrease in the *E*:*Z* ratio of the vinyl carbamates. The 'butterfly' model explains the observed selectivities accurately and is thus considered to be most appropriate for the carbamate system, since the bridging effect of the carbamate functionality is taken into consideration.[16b]

Aggregation numbers of organolithium species have a marked effect on the course of reactions and are influenced and changed by the solvent, base and temperature employed.[17] The two-step ('butterfly') mechanism described here does not take into consideration aggregation effects.

## 2.3 Oxasiletanide intermediates and transition states

Okazaki's research group has performed elegant experiments to show, by crystallographic means, the existence of pentacoordinate 1,2-oxasiletanide[18] intermediates (Fig. 3), when β-hydroxysilanes are treated with base.

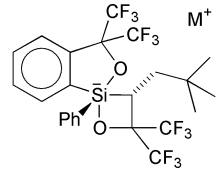



**Fig. 3**

It has been proposed that the stereoselectivity of the Peterson olefination is a delicate balance between steric and electronic factors in the transition state between the carbanion and electrophile.[19] In a more recent investigation, Bassindale's research group investigated the role of silicon–oxygen interactions in the determination of the stereochemical outcome of the Peterson olefination reaction.[20] The results of their investigations show that an increase in the silicon–oxygen interaction in this transition state between the carbanion and electrophile (Fig. 4 in contrast to Fig. 2), increases the *E*-selectivity.

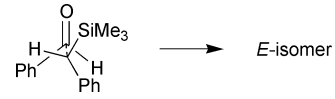
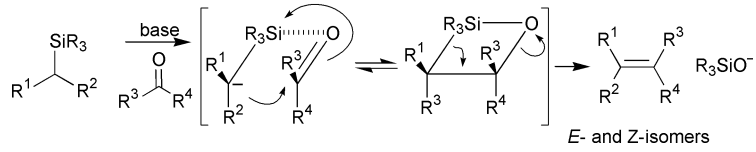



**Fig. 4**

According to this evidence the carbonyl compound approaches the planar anion in such a way that coordination



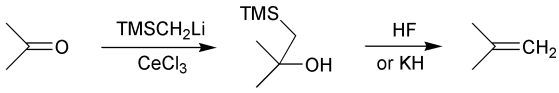

**Scheme 6**

between the oxophilic silyl moiety and the carbonyl oxygen is maximised (Scheme 6),[18] decreasing the dihedral angle between the oxygen and silicon (Fig. 4).[20] It is conceivable that steps 1 and 2A (Scheme 3) proceed simultaneously leading to the concerted formation of an oxasiletanide intermediate (Scheme 6). The other substituents on the substrate and electrophile would then align so that the steric interactions are minimised (Scheme 6). Thus, in contrast with the stepwise models, the bulk of the silyl moiety would not affect the selectivity and the relative orientations of the substituents would be fixed as a consequence of the Si–O coordination.

## 3 Cerium-mediated Peterson methylenation reactions

The Peterson olefination using silyllithium reagents such as $TMSCH_2Li$, unlike the analogous Tebbe[21] and Wittig olefinations, has not found wide application in methylenation reactions. This is a consequence of the fact that the above silyllithium reagents result in poor chemoselectivity due to their propensity to behave as strong bases.[22]

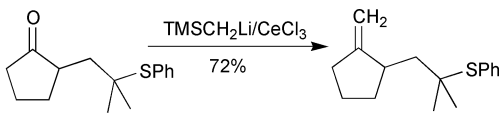
In 1987 Johnson and Tait[22] reported a cerium(III) chloride modified Peterson olefination that was particularly efficient for methylenation reactions (Scheme 7). Johnson and Tait[22]




**Scheme 7**

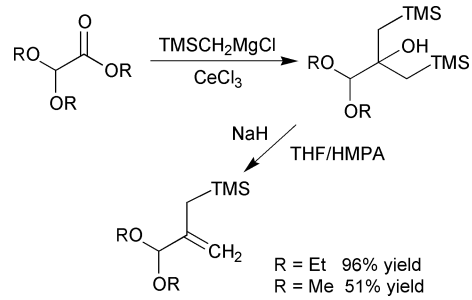
reported that the β-hydroxysilanes were prepared in very good yields when equimolar amounts of TMEDA and $CeCl_3$ were added to the reaction mixture, *i.e.* $TMSCH_2Li$ in THF was added to anhydrous $CeCl_3$ at −78 °C followed by the addition of the carbonyl compound. As usual, these β-hydroxysilanes were treated with either HF or KH to afford the olefins in good yields. A direct comparison of the β-hydroxysilane yields in the presence and absence of $CeCl_3$ proved the superiority of this method, even over Grignard reagents.[22]

The Johnson modification of the Peterson olefination has found application in the preparation of homoallyl phenyl sulfides[23] and bishomoallyl phenyl sulfides.[24] The enolisable cyclopentanone was methylenated successfully by this methodology (Scheme 8) in yields superior to those obtained with the analogous Wittig reactions.




**Scheme 8**

The silyl Grignard reagent, $TMSCH_2MgCl$, in conjunction with $CeCl_3$ is useful for the preparation of allyl silanes.[25] Two equivalents of reagent are added to an ester, which affords the β-hydroxysilane prior to a base-induced Peterson olefination reaction (Scheme 9).[25a] De Raadt and co-workers[26] employed an analogous strategy for the preparation of the carbohydrate allyl silanes, which were subsequently used to synthesise C-linked disaccharides. Fürstner and co-workers[27] reacted $TMSCH_2MgCl$ with acyl silanes to afford vinyl silanes.

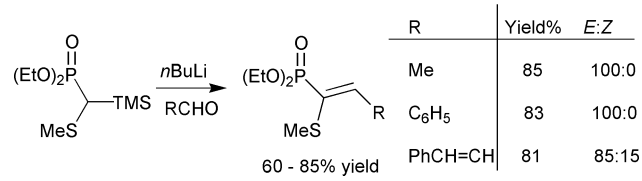



**Scheme 9**

## 4 Peterson *versus* Julia and Wittig olefination reactions

### 4.1 Competing Peterson and Wittig reactions

Contrary to reports that competing eliminations take place,[28] the sulfones and phosphonates (*vide infra*) are particularly good illustrations of the fact that the oxygen anion intermediate has a strong affinity for the silicon moiety and therefore, the Peterson olefination of these systems takes place in preference to the Julia and Wittig-type reactions. One of the most interesting systems used in the Peterson olefination is diethyl (methylthio-)(trimethylsilyl)methylphosphonate.[9a] It was reported that the Peterson olefination of the lithiated diethyl (methylthio-)(trimethylsilyl)methylphosphonate with aldehydes (including α,β-unsaturated aldehydes) proceeded *E*-selectively in good yields (Scheme 10).[9a]




| R | Yield% | *E*:*Z* |
|---|---|---|
| Me | 85 | 100:0 |
| $C_6H_5$ | 83 | 100:0 |
| PhCH=CH | 81 | 85:15 |

**Scheme 10**

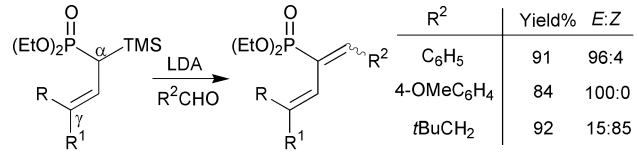
Three groups have investigated the Peterson olefination of α-silyl phosphorus stabilised carbanions. Savignac′s research group has demonstrated how this reaction can be used for the preparation of α-fluorovinylphosphonates[14,29] and 1-formylalkylphosphonates.[30] Initial investigations showed that a mixture of *E*- and *Z*-isomers were obtained.[29a] The reaction of the lithiated α-fluoro-α-trimethylsilylmethylphosphonate with aromatic aldehydes afforded the desired vinyl phosphonates *E*-selectively, whilst on reaction with ketones *Z*-selectivity was observed (Scheme 11).[14] Keeney and co-workers[31] employed an analogous strategy.

In a recent report the *Z*-alkylidene-3-oxobutylphosphonates were prepared *via* a Peterson olefination, whilst the Wittig–Horner reaction afforded the corresponding *E*-isomers.[32] The Collignon group have focused on the use of the silylated allyl phosphonates in the Peterson olefination for the preparation of vinyl phosphonate penta-1,3-dienes, which find application in

| $R^1$ | $R^2$ | Yield% | *E*:*Z* |
|---|---|---|---|
| $C_6H_5$ | H | 81 | 74:26 |
| *p*-$MeOC_6H_4$ | H | 91 | 70:30 |
| 2-furyl | H | 92 | 80:20 |
| 2-thienyl | H | 93 | 78:22 |
| 2-pyridinyl | H | 52 | 85:15 |
| (-)carvone | | 87 | 0:100 |
| 2-Me-*c*-$C_6H_9$ | | 62 | 0:100 |

**Scheme 11**

Diels–Alder reactions.[33] These authors have reported that typical of an allyl system[34] the nucleophilic addition can take place in either the α- or γ-position and that this depended on the bulk of the substituents at the γ-position and the nature (aldehyde, ketone or ester) of the reagent.[33b] When a phenyl substituent was present in the γ-position, the Peterson olefination afforded the dienes *E*-selectively with aromatic aldehydes and *Z*-selectively with aliphatic aldehydes (Scheme 12).[33c]



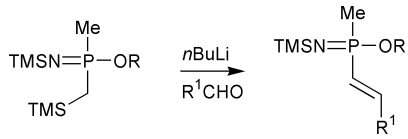
| $R^2$ | Yield% | *E*:*Z* |
|---|---|---|
| $C_6H_5$ | 91 | 96:4 |
| 4-$OMeC_6H_4$ | 84 | 100:0 |
| *t*$BuCH_2$ | 92 | 15:85 |

R = H and $R^1$ = Ph

**Scheme 12**

However, when the γ-dimethyl substituted α-silyl allyl phosphonates were reacted with alkyl formates ($R^2$ = OR′) the Peterson olefination afforded the 1-alkoxy-4-methylpenta-1,3-dienes *Z*-selectively (Scheme 12, R = $R^1$ = Me, $R^2$ = OR′).[33b]

The Peterson olefination of α-silyl phosphinimines was used to prepare *P*-vinyl substituted phosphazenes (Scheme 13).[35]



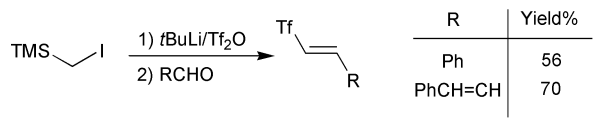
**Scheme 13**

These compounds were being prepared in an attempt to produce soluble, 'uncross-linked' precursors to a new class of poly(alkyl/arylphosphazenes) polymers, which could provide useful elastomers.

### 4.2 Competing Peterson and Julia olefination reactions

The triflones are neutral, strong electron withdrawing groups, which can be used to stabilise an α-carbanion. Mahadevan and Fuchs[36] reported a convenient synthesis of the versatile functionalised methyl and vinyl triflone reagents. The substituted silyl methyl triflone was prepared from the (trimethylsilyl)methyl iodide previously employed in the Peterson olefination by Barrett and co-workers.[6a] The iodide was substituted for a triflone moiety and the α-silyl methyl triflone was subsequently reacted with an aldehyde to afford the vinyl triflones *E*-selectively in a one-pot Peterson olefination reaction (Scheme 14).[36] The analogous Wadsworth–Emmons reaction with a phosphonate reagent was, however, unsuccessful.

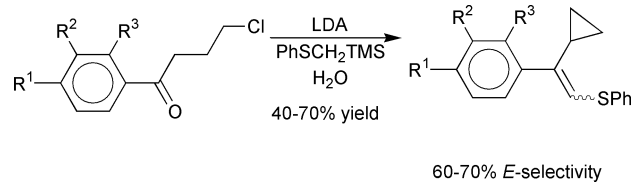
The highly stabilised silyl methyl sulfones have been used successfully in the Peterson olefination reaction. Such applications include the preparation of (*E*)-imidazo[1,2-*a*]pyridylvinyl sulfones as potential cardiovascular agents[37] and a new series of cyclopropyl vinyl sulfones,[38] which were of chemical and biological interest. The cyclopropyl vinyl sulfones were prepared in high yields, but both the *E*- and *Z*-isomers were obtained in equal amounts. Orita and co-workers[39] extended the carbon–carbon double bond formation further through the combination of a Peterson olefination–sulfone elimination strategy to afford acetylenes in a one-pot synthesis.



| R | Yield% |
|---|---|
| Ph | 56 |
| PhCH=CH | 70 |

**Scheme 14**

In an analogous preparation of the corresponding vinyl sulfides the *E*-selectivity was improved, but the moderate yields obtained were attributed to insufficient stabilisation of the lithiated α-silyl methyl sulfide carbanion (Scheme 15).[40] This



**Scheme 15**

approach has led to the preparation of a range of vinyl sulfides.[41] On reaction of the α-silyl methyl sulfide carbanion [PhSCH(Li)TMS] with acyl silanes (RCOTMS), Kang and co-workers[42] found that a mixture of both the Peterson olefination and Brook rearranged products were isolated.

## 5 Conclusions

It is apparent from the developments highlighted here that the Peterson olefination reaction has been studied extensively since 1990. Good selectivity has been achieved in the presence of a stabilising moiety, which results in the direct formation of the olefin products. Furthermore, the preferential formation of Peterson olefination rather than Wittig-type products in the presence of P- and S-stabilised silyl carbanions emphasizes the strong affinity of oxygen for silicon.

The results presented here lead to the conclusion that the mechanism of the Peterson olefination reaction is not generic, but is dependent on the reagents and functional groups employed. The evidence suggests that:

- the Peterson olefination reaction is less likely to proceed concertedly than the corresponding phosphorus-stabilised Wittig reactions;
- in the presence of chelation control the Peterson olefination reaction proceeds in a stepwise manner, through the formation of a "butterfly" transition state;
- a pentacoordinate 1,2-oxasiletanide intermediate is formed when certain β-hydroxysilanes are treated with base.

Today, the Peterson olefination reaction can be considered a useful reaction in the arsenal of the synthetic organic chemist. The stereoselectivities that can currently be achieved are comparable to those obtained with other Wittig-type olefinations.

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