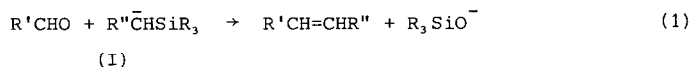THE PETERSON REACTION, PART I, THE EFFECT
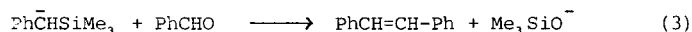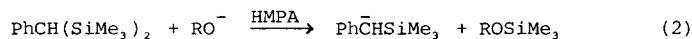
OF REACTION CONDITIONS AND STERIC CROWDING

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Summary: _The diastereoisomeric ratio of stilbenes formed in the Peterson reaction of_ $Ph\bar{C}HSiR_3$ _with PhCHO is shown to be insensitive to medium effects and temperature, but varies significantly as the bulk of_ SiR_3 _increases._

The Peterson reaction[1] is a versatile carbonyl olefination reaction that can be used as an alternative to the Wittig reaction[2]

$$R'CHO + R''\bar{C}HSiR_3 \rightarrow R'CH=CHR'' + R_3SiO^- \qquad (1)$$
$$(I)$$

Two major drawbacks to the extensive use of the Peterson reaction have been difficulty of obtaining the α-silyl carbanion (I), particularly in high yield[3], and the relative lack of stereoselectivity, when unsymmetrical α-silyl carbanions and carbonyl compounds are employed.[2] The work reported here is part of a systematic investigation of the mechanism of the Peterson reaction. The model system chosen for this initial study was the reaction of $Ph\bar{C}HSiMe_3\overset{+}{M}$ (M = Li, Na, K, Mg)with PhCHO, to give a mixture of _cis_ and _trans_-stilbenes. The stilbenes were formed by the addition of excess alkoxide (4 mmol) to a mixture of bis(trisubstitutedsilyl)phenylmethane (2 mmol) and benzaldehyde (17 mmol) in anhydrous hexamethylphophoramide (25 cm³) under an atmosphere of nitrogen, equations 2 and 3[4]

$$PhCH(SiMe_3)_2 + RO^- \xrightarrow{HMPA} Ph\bar{C}HSiMe_3 + ROSiMe_3 \qquad (2)$$

$$Ph\bar{C}HSiMe_3 + PhCHO \longrightarrow PhCH=CH-Ph + Me_3SiO^- \qquad (3)$$

After quenching with water, analysis of the products by glc indicated a stilbene yield of 100 ± 3% relative to the silane. Separate experiments showed that there was no interconversion of _cis_ and _trans_-stilbene under the reaction or work-up conditions. The ratio of _cis_ and _trans_ stilbene formed in this reaction was insensitive to the type of alkoxide used to generate the initial α-silyl carbanion confirming that in this system a free carbanion is generated.[5]

In contrast to the Wittig reaction,[6] the effect of varying the counterions and adding inert salts on the diastereoisomeric ratio of stilbenes obtained from the reaction of PhC̄HSiMe₃ with PhCHO was very small indeed (Tables I and II).

Table I

The effect of varying the counterion on the diastereoisomeric ratio of stilbenes produced by the Peterson Reaction

| alkoxide used in anion formation	cis/trans-stilbene	% Yield [a]
LiOBu^t	1:1.43	100
NaOMe	1:1.32	99
KOBu^t	1:1.30	100
NaOSiMe₃/MgI₂	1:1.81	50

[a]yield by g.l.c.

Table II

The effect of adding inert salts on the diastereoisomeric ratio of stilbenes produced by the Peterson Reaction

[LiClO₄]/mol l^{-1}[a]	cis/trans-stilbenes
0.000	1:1.43
0.074	1:1.43
0.150	1:1.45[b]
0.300	1:1.47[c]

[a][PhC̄HSiMe₃,Li⁺] = 0.084 mol l^{-1} [c]yield of stilbenes 53%

[b]yield of stilbenes 71%

In a related study of the Peterson reaction[7] it was shown that the reaction between Me₃SiCH=C̄SiMe₃ and PhCHO gave a 1:1 mixture of cis and trans products with lithium as the counterion, but with magnesium ion present, the ratio changed to 3:1. However, no such dramatic effect was observed in this study; the ratio moving slightly in the opposite direction. Again unlike the Wittig reaction the diastereoisomeric ratio of the Peterson reaction was found to be relatively insensitive to changes in the temperature from 5°C to 79°C and varying the solvent (HMPA; 1:4 mixture of HMPA and THF; DMSO and DMF). The variability of the cis:trans ratio in the Wittig reaction are frequently a result of the reversible formation of the intermediate oxaphosphetan/betaine. The consistency of the cis:trans ratio in the Peterson reaction of

PhC̄HSiMe$_3$ with PhCHO presumably reflects the irreversible formation of the competing *threo* and *erythro* β-silylalkoxides (scheme) which undergo stereospecific *syn*-eliminations to give the *trans* and *cis*-stilbenes respectivley.[8,9]

Scheme : The formation of *cis* and *trans* stilbene in the Peterson reaction
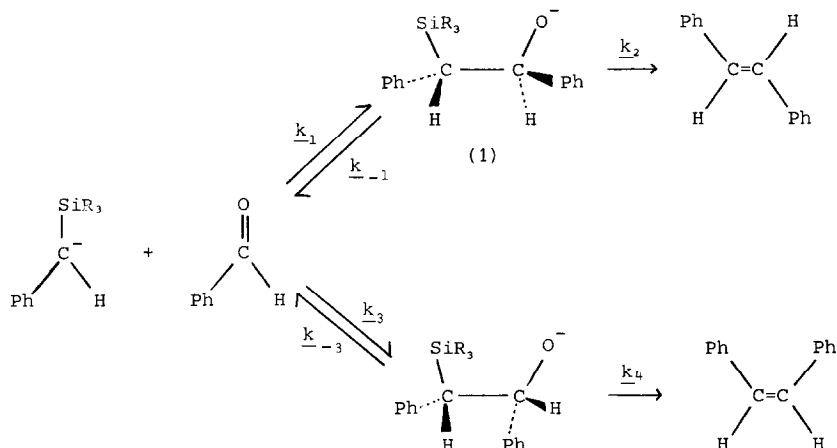
The only other variable in this system, that allows the isolation of *cis* and *trans*-stilbene, is the nature of the groups on silicon. We have synthesised a number of α-trisubstituted-α-trimethylsilyltoluenes which form the corresponding α-trisubstituted silylbenzyl carbanion on treatment with alkoxides. We have confirmed that the less sterically hindered trimethylsilyl group was always preferentially cleaved.

$$PhCH(SiMe_3)SiR_3 + R'O^- \rightarrow PhC\bar{H}SiR_3 + Me_3SiOR' \qquad (4)$$
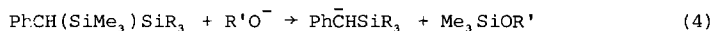
The effects of varying the steric size of the groups attached to the silicon on the *cis:trans* stilbene ratio obtained from the Peterson reaction are given in Table III.

Table III

The effect of varying the SiR$_3$ group on the ratio *cis:trans* stilbenes, obtained by the reaction of PhC̄HSiR$_3$ with PhCHO

R$_3$Si	*cis:trans*-stilbene ratio
Me$_3$Si	1:1.30
Et$_3$Si	1:1.24
Mecy$_2$Si[a]	1:1.14
Me$_2$Bu^{t}Si	1:1.04
Ph$_2$Bu^{t}Si	1:0.65
Ph$_3$Si	1:0.52

[a]methyldicyclohexylsilyl, yield 94%

The increase in the proportion of cis-stilbene is steady, but not monotonic, as the steric bulk of R_3Si increases. The triphenylsilyl group gives rise to the largest *cis:trans* ratio that we bave obtained; a diastereoisomeric excess of about 50%. A similar increase in the proportion of *cis*-isomer with increased steric bulk has been reported for the reaction of the ambident carbanion $R_3SiCH=C=\bar{C}SiMe_3$ with hexanal which always reacted at the end bearing the R_3Si substituent.[7] For that system the proportion of *cis*-isomer increased by a factor of seven on changing from $SiMe_3$ to $SiMe_2Bu^t$. An analogous study of the Wittig reaction[10] of $R_3\overset{+}{P}-\overset{-}{C}HPh$ with PhCHO showed that increasing the steric bulk at phosphorus favours *cis*-stilbene formation.

As the first step of the Peterson reaction, using semi-stabilised α-silyl carbanions, is irreversible[9] then the *cis:trans* ratio is controlled by the relative rates of the steps, $\underline{k}_3:\underline{k}_1$ (Scheme). It follows that any alteration of the *cis:trans*-stilbene ratio will be achieved by changing the relative energies of the related transition states leading to the *erythro* and *threo* β-silyl alkoxide intermediates. This is in contrast to the Wittig reaction where the *cis:trans* ratio can be accounted for by either, the mode of $2\pi + 2\pi$ cyclo-addition[10,11], cleavage of the P-C bond of the oxaphosphetan, followed by rotation and elimination[12,13], or the effect of phenyl groups on phosphorus on the direction of attack[14]. We believe that the results reported herein can be accommodated by postulating a delicate balance between steric and electronic factors in the two transition states leading to β-silyl alkoxides. This will be developed fully in subsequent papers.

References

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