The Mechanism of the Peterson Reaction. Part 2.[1] The Effect of Reaction Conditions, and a New Model for the Addition of Carbanions to Carbonyl Derivatives in the Absence of Chelation Control

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The stereochemistry of the Peterson olefination reaction between $PhC\bar{H}SiMe_3$ and PhCHO has been studied under a wide variety of conditions with excellent reproducibility and extremely high yields. The effects of counterion, solvent, added salts, variation of the carbanion-forming base, and temperature have been investigated. The product stereochemistry is remarkably insensitive to the reaction conditions. The results lead to a new method of analysis of steric approach control based on the angle of approach as defined by Dunitz and Baldwin. The method involves analysis of 'primary' and 'secondary' transition-state interactions. This analysis should be generally applicable to carbanion additions in which chelation is insignificant.

The Peterson olefination reaction[2] is analogous to the Wittig reaction and provides a versatile method for the synthesis of alkenes and functionalised alkenes. The general reaction is shown in equation (1). The reaction has been reviewed recently

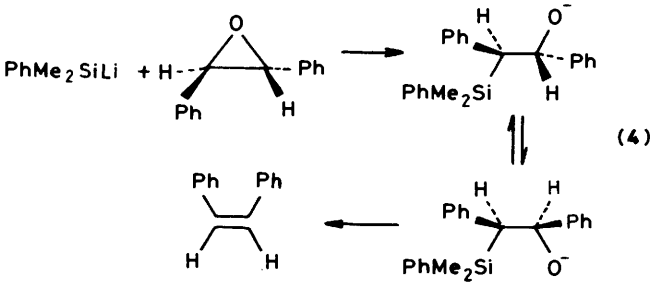
$$R'CHO + R\bar{C}HSiMe_3 \longrightarrow R'CH{=}CHR + Me_3SiO^- \quad (1)$$

by Ager,[3] and it is clear that relatively little is known of the factors affecting the overall stereochemistry. The generally accepted mechanism is given in equations (2) and (3).

$$R'CHO + R\bar{C}HSiMe_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R'-\underset{H}{\overset{O^-}{C}}-\underset{H}{\overset{SiMe_3}{C}}-R \quad (2)$$

$$R'-\underset{H}{\overset{O^-}{C}}-\underset{H}{\overset{SiMe_3}{C}}-R \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R'CH{=}CHR + Me_3SiO^- \quad (3)$$

The second step of the reaction has been shown to be stereospecific.[3] Hudrlik[4] demonstrated that diastereoisomerically pure β-hydroxysilanes undergo *syn*-elimination in the presence of 1 equiv. of base, and *anti*-elimination under acidic conditions. Similarly,[5,6] silyl carbanions produce alkenes stereospecifically from epoxides. Reetz[6] treated *trans*-stilbene oxide with dimethylphenylsilyl-lithium to give *cis*-stilbene as the only product [equation (4)].



(4)

These, and other,[3] experiments all lead to the conclusion that the first step in the Peterson reaction (the addition of the silyl carbanion to the carbonyl compound) determines the ratio of *cis* to *trans* alkenes formed. This represents a major departure from the Wittig reaction mechanism. In an early experiment, closely related to that of Reetz,[6] Trippett[7] isolated mixtures of *cis*- and *trans*-stilbene from the reaction of sodium diphenylphosphide with pure *trans*-styrene oxide. The first addition step of the Wittig reaction is reversible[7] and 'stereochemical drift,' with particular reference to oxaphosphetane intermediates, has recently been elegantly studied by n.m.r. spectroscopy.[8]

There are numerous applications of the Peterson reaction in the literature;[1-3,9-14] the stereochemistry of a selection of these is shown in Table 1. Typically, approximately equal amounts of diastereoisomeric alkenes are formed, with, in some examples, a slight bias towards the *cis*-alkene. This is particularly true where chelation control is possible, and also in the case of $Bu^tMe_2Si\bar{C}HCN$ with hexanal.[9]

If the Peterson reaction is to find wide use in synthesis, the stereoselectivity must be improved. This study is one of a series[1] designed to probe the mechanism of the reaction and to improve its stereoselectivity. The aim was to study the effect of reaction conditions on stereoselectivity and to produce a conceptual model for the addition of the α-silyl carbanion to the carbonyl compound.

The model system chosen for the investigation was the addition of the phenyl(silyl)methanide anion, $PhC\bar{H}SiMe_3\overset{+}{M}$ (M = Li, Na, K, or Mg) to benzaldehyde, to give *cis*- and *trans*-stilbene. A method was developed whereby the yield of stilbenes, relative to the α-silyl carbanion, was measured by carefully calibrated g.l.c. columns to be 100 ± 3% with high reproducibility. The phenyl(silyl)methanide anion was generated quantitatively by desilylation of bis(trimethylsilyl)phenylmethane with alkoxide, usually in dipolar aprotic solvents [equation (5)]. Excess of benzaldehyde was used in the reaction,

$$PhCH(SiMe_3)_2 + RO^- \longrightarrow PhC\bar{H}SiMe_3 + ROSiMe_3 \quad (5)$$

$$PhC\bar{H}SiMe_3 + PhCHO \longrightarrow PhCH{=}CHPh + Me_3SiO^- \quad (6)$$

and a complete mass balance, as measured by g.l.c., was achieved [equation (6)]. It was established that there was no interconversion of *cis*-and *trans*-stilbenes under either the reaction or work-up conditions.

Table 1. Review of the stereochemistry of the Peterson reaction

α-Silylcarbanion	Carbonyl compound	Alkene (*cis*-to-*trans* ratio)	Yield (%)
$Me_3Si\bar{C}HC{\equiv}CSiMe_3$	$CH_3[CH_2]_4CHO$	$CH_3[CH_2]_4CH{=}CHC{\equiv}CSiMe_3$ (3:1)	77 (ref. 9)
$Ph_3Si\bar{C}H[CH_2]_2CH_3$	PhCHO	$CH_3[CH_2]_2CH{=}CHPh$ (1:1)	50 (ref. 10)
$Me_3Si\bar{C}HCO_2Et$	PhCHO	$PhCH{=}CHCO_2Et$ (3:1)	84 (ref. 11)
$Me_3Si\bar{C}HCO_2Et$	CH_3COPh	$Ph(CH_3)C{=}CHCO_2Et$ (2:1)	63 (ref. 11)
$Me_3Si\bar{C}HCO_2Et$	$CH_3[CH_2]_7CHO$	$CH_3[CH_2]_7CH{=}CHCO_2Et$ (1:1)	81 (ref. 12)
$Me_3Si\bar{C}HCN$	PhCHO	PhCH=CHCN (1:1)	77 (ref. 13)
$Bu^tMe_2Si\bar{C}HCN$	$CH_3[CH_2]_4CHO$	$CH_3[CH_2]_4CH{=}CHCN$ (3:1)	62 (ref. 9)
$Me_3Si\bar{C}HPh$	PhCHO	PhCH=CHPh (1:1)	50 (ref. 2)
$Me_3Si\bar{C}HCO_2^-$	PhCHO	$PhCH{=}CHCO_2^-$ (1:1)	88 (ref. 14)
$Me_3Si\bar{C}HCO_2^-$	$CH_3[CH_2]_4CHO$	$CH_3[CH_2]_4CH{=}CHCO_2^-$ (3:2)	90 (ref. 14)

Table 2. Effect of varying the alkoxide, ROM, on the stereochemical outcome of the Peterson reaction of $Ph\bar{C}HSiMe_3$ with PhCHO

ROM	Ratio of stilbenes produced (*cis*-to-*trans*)	Yield (%)[a]
MeONa	1:1.32	99
PrONa	1:1.33	100
Me_3SiONa	1:1.30	100

[a] The yields in this and all subsequent Tables refer to g.l.c. determinations.

Table 3. Effect of varying the counterion, M, on the stereochemical outcome of the Peterson reaction between $Ph\bar{C}HSiMe_3M^+$ and PhCHO

Alkoxide ROM	Ratio of stilbenes produced (*cis*:*trans*)	Yield (%)
$LiOBu^t$	1:1.43	100
NaOMe	1:1.32	99
$KOBu^t$	1:1.30	100
$KOBu^t$–MgI_2	1:1.85	56

Table 4. Effect of added salts on the stereochemical outcome of the Peterson reaction between $Ph\bar{C}HSiMe_3$ and PhCHO

Salt	Mol. equiv. of salt added[a]	Alkoxide	Ratio of stilbenes produced (*cis*:*trans*)	Yield (%)
LiI	0.0	NaOMe	1:1.32	98
	0.34		1:1.31	103
	0.91		1:1.45	72
$LiClO_4$	0.0	$LiOBu^t$	1:1.43	100
	0.95		1:1.42	90
	1.98		1:1.45	71
	3.96		1:1.47	53
$NaBPh_4$	0.0	NaOMe	1:1.32	98
	0.31		1:1.20	94
	0.9		1:1.16	96
	1.76		1:1.13	98

[a] Relative to $PhCH(SiMe_3)_2$.

Results and Discussion

The reaction conditions under which the carbanion was formed, and the conditions of anion addition to benzaldehyde, were varied in a systematic manner. A range of alkoxides, ROM, can be used to generate the α-silyl carbanion, according to equation (5). The yields of stilbenes, and their diastereoisomeric ratios, for M = Na, in hexamethylphosphoramide (HMPA) solution, were independent of the nature of R, as shown in Table 2. The effect of counterion, M, on the diastereoisomeric ratio of *cis*- to *trans*-stilbene was measurable and reproducible, but very small, as shown in Table 3. The relative proportion of *trans*-stilbene produced falls in the order Mg > Li > Na ~ K. This conflicts somewhat with the results of Yamakado,[9] who found that in the addition of the ambident silyl carbanion $Me_3SiCH{=}C{=}\bar{C}SiMe_3$ to benzaldehyde the *cis*-to-*trans* ratio of products was 1:1 with lithium as counterion but 3:1 in the presence of magnesium. A direct comparison of this work with that of Yamakado[9] is difficult owing to the very different natures of the α-silyl carbanions involved, and the possibility of chelation control in the latter example. Our results suggest that the α-silyl carbanion behaves as a free carbanion, or more likely as a very loose ion-pair. A recent n.m.r. study[15] showed that benzyl-lithium in several solvents is tight-ion-paired but, under the same conditions, substitution of an α-hydrogen atom by an alkyl group tends to diminish ion-pairing. Phenylmethanide anions with bulky α-alkyl groups behave as loose ion-pairs. The phenyl(silyl)methanide anion, by analogy, would be expected to be loose-ion-paired, or approaching the free ions, as there is greater charge delocalisation in this ion, and HMPA is a powerful ionising solvent. Therefore, in our system, a relative insensitivity to counterion, M^+, is not unexpected. It is also clear from the insensitivity to RO^- in the carbanion-forming step that the α-silyl carbanion is essentially completely formed before addition to the carbonyl group takes place.

The study of addition of ionic salts to the reaction mixture (Table 4) provided some evidence for loose ion-pairing in the α-silyl carbanion. The effect of adding lithium perchlorate to the reaction mixture had an immeasurably small effect on the *cis*-to-*trans* stilbene ratio. However, when lithium iodide was added to $Ph\bar{C}HSiMe_3Na^+$ the *cis*-to-*trans* stilbene ratio increased steadily; on addition of 1 equiv. of LiI the ratio was the same as that for addition of $Ph\bar{C}HSiMe_3Li^+$ to benzaldehyde. It is highly unlikely that a simple salt effect is operating here as the addition of sodium tetraphenylborate to the $Ph\bar{C}HSiMe_3Na^+$ reaction mixture had a slightly opposite effect, with the amount of *cis*-stilbene slightly increased at the expense of the *trans*-isomer.

Once again these results point to the first step in the Peterson reaction being that in which the product ratio is determined. The Wittig reaction, in which the first step is reversible, is highly susceptible to salt effects.

Wittig reactions are similarly highly solvent-dependent, being particularly sensitive to protic solvents.[7] In the case of the Peterson reaction, protic solvents cannot be used, as they rapidly quench the α-silyl carbanion. Despite this limitation we

Table 5. Effect of adding tetrahydrofuran to the hexamethylphosphoramide solvent in the Peterson reaction of $PhCHSiMe_3$ and PhCHO

Alkoxide	% THF by volume	Ratio of stilbenes produced (*cis*:*trans*)	Yield (%)
LiOBu^t	0	1:1.43	100
	20	1:1.33	98
	40	1:1.27	58
NaOMe	0	1:1.32	98
	20	1:1.30	103
	40	1:1.36	99
	50	1:1.48	98
	70	1:1.52	70
KOBu^t	0	1:1.28	100
	20	1:1.31	98
	40	1:1.32	98
	60	1:1.29	97
	80	1:1.33	96

Table 6. Effect of varying the solvent in the Peterson reaction of $PhCHSiMe_3$ with PhCHO

Solvent	Alkoxide	Ratio of stilbenes produced (*cis*:*trans*)	Yield (%)
Dimethylformamide	$NaOSiMe_3$	1:1.14	96
	NaOPr	1:1.13	88
Dimethyl sulphoxide	$NaOSiMe_3$	1:1.20	99
	KOBu^t	1:1.32	97
Tetrahydrofuran	KOMe[a]	1:1.44	88

[a] Plus 1 equiv. of 18-crown-6.

Table 7. Effect of temperature on the Peterson reaction of $PhCHSiMe_3$ with PhCHO in HMPA

Temperature (°C)	Ratio of stilbenes produced (*cis*-to-*trans*)	Yield (%)
5	1:1.25	97
26	1:1.32	99
46	1:1.33	98
76	1:1.39	90

studied the effect of solvent on the product ratio, within the range available. Again, only small changes were observed as the solvent was varied. The addition of $PhCHSiMe_3M^+$ to benzaldehyde in HMPA–THF mixtures was studied, as shown in Table 5. With KOBu^t as base there was no significant change in the *cis*-to-*trans* ratio of stilbenes in solvent mixtures containing up to 80% THF. When NaOMe was the base the relative amount of *trans*-stilbene increased slowly, but consistently, as the amount of THF increased. These results seem to be consistent with an increased amount of ion-pairing for sodium salts in the less polar medium, whereas the more electropositive potassium salts remain as free ions, or very loose ion-pairs. Similarly, the amount of *trans*-stilbene might be expected to increase with the lithium counterion although in our experiments there was a small decrease as the amount of THF increased. These results with $PhCHSiMe_3Li^+$ were frustrated by poor solubility and usually low yields of stilbenes, and are considered unreliable. Some other solvent systems are shown in Table 6; the results are in accord with our interpretation of the other systems.

The effect of temperature on the *cis*-to-*trans* ratio is shown in Table 7. There was very little change either in yield or in *cis*-to-*trans* stilbene ratio as the temperature was raised from 5 to 76 °C.

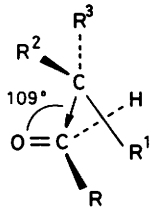


Figure 1. The approach of a carbanion $R^1R^2R^3C^-$ to an aldehyde RCHO

Individually, the foregoing results are not useful in increasing the stereoselectivity of the Peterson reaction, but they have allowed us to propose a model for the crucial first addition of the α-silyl carbanion to the carbonyl compound.

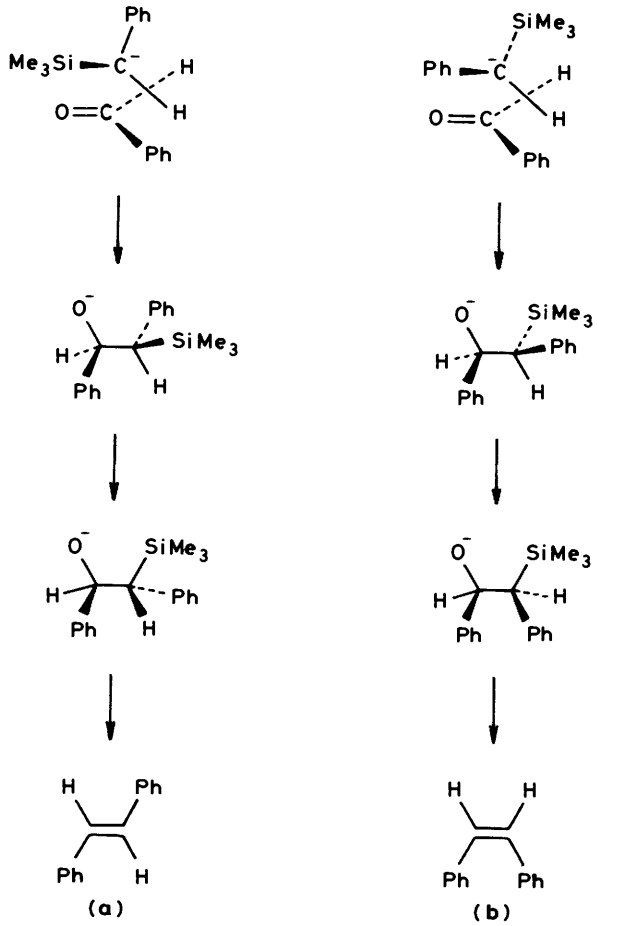
In the addition of enolate anions to carbonyl compounds chelation control[16] through chair-like transition states is considered to dominate the stereochemistry. In the case of our model Peterson reaction, and the addition of many other carbanions to carbonyl compounds, no such control is possible. A four-centre interaction between an ion-paired carbanion and the carbonyl compound is conceivable but our results suggest that this is most unlikely, or has a miniscule effect on the product stereochemistry.

For the addition of $PhCHSiMe_3$ to PhCHO we postulate an early, reactant-like transition state, as this is most consistent with the insensitivity of the product ratio to reaction conditions. The model that we are about to describe is most applicable to the initial stages of an addition where the approach angle is at least 109° and the deviation from planarity in the carbonyl compound is minimal. As the transition state becomes intermediate-like then the relative energies of possible intermediates assume a greater importance.

Previous models for the addition of non-enolate carbanions to carbonyl compounds have concentrated on the anion attacking at 90° to the carbonyl framework. This approach leads directly to a comparison of the stabilities of diastereoisomeric intermediates. The major problem with that model is that it completely fails to account for the so-called '*erythro*-selectivity'[17,18] of carbanion additions. The seminal work of Burgi and Dunitz[19] and Baldwin[20] has forced a reappraisal of any model for nucleophilic attack at carbonyl groups. It has been shown convincingly[19] that nucleophiles attack the carbonyl group approximately in the plane of the C–O π-bond and with a Nu–C–O angle of about 109°. It is therefore misleading simply to analyse conformations of intermediates. The *initial* steric interactions should be analysed, as shown in Figure 1.

We postulate that *one* interaction will be more important than the other two, *viz.* in Figure 1 the first, major, steric influence will result from interaction amongst R^1, R, and H. This *primary* steric influence is a direct consequence of the carbanion attacking at an angle greater than 90°. The most favoured orientation for attack will be that in which the primary steric influence is minimised. The steric outcome of the reaction is then determined by the relative extents of the *secondary* steric influences; the interaction of R^2 and R^3 with R.

If we apply this to the reaction between $PhCHSiMe_3$ and PhCHO, two transition states can be drawn, one leading to *cis*-stilbene and the other to *trans*-stilbene, as shown in Scheme 1. The primary steric influence is minimised by placing the anion α-hydrogen atom in the most hindered position, between the aldehyde phenyl group and hydrogen. The major secondary steric interactions are between (a) the benzaldehyde phenyl



Scheme 1. Steric approach control leading to (a) *trans*-stilbene and (b) *cis*-stilbene in the addition of $Ph\bar{C}HSiMe_3$ to PhCHO

group and the anion trimethylsilyl group, and (b) the two phenyl groups.

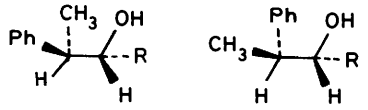
To account for the slight but consistent excess of *trans*-stilbene it must be postulated that trimethylsilyl group is, in this case, very slightly smaller than a phenyl group. This is not unreasonable as the long C–Si bonds (*ca.* 190 pm) separate the atoms in Me_3Si to a much greater extent than in the t-butyl group.*

Thus we suggest that our model for steric approach control is applicable to the Peterson reaction, and many other systems. In this, and subsequent papers we set out to provide theoretical and experimental justification for the model.

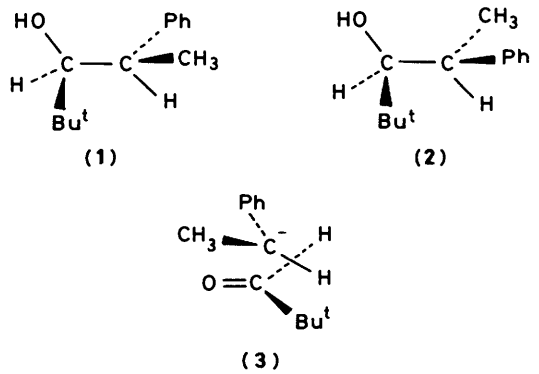
If our model for addition is reasonable, then the presence or absence of silyl groups in the anion is only important in determining the stereochemical outcome of the reaction insofar as it affects the steric demands in the transition state. We therefore carried out additions of analogous non-silylated carbanions to benzaldehyde and pivaldehyde. The results are shown in Table 8. Unfortunately there were problems associated with numbers of other systems tried. Bulky anions, such as $Ph\bar{C}HC(CH_3)_3$, induced Cannizarro reactions with aldehydes (further evidence that the steric demands of the $SiMe_3$ group are

* A referee has questioned this assumption. We have prepared[1] other α-silyl carbanions in which the SiR_3 group is undoubtedly larger than Ph, for example $SiPh_3$ where the *cis*-to-*trans* ratio changes to 1:0.52.

Table 8. The stereochemical outcome of the reaction of $Ph\bar{C}HCH_3$ with RCHO



R	(A):(B)	Overall yield (%)
$(CH_3)_3C$	3.13:1	91
Ph	1.22:1	89



Scheme 2.

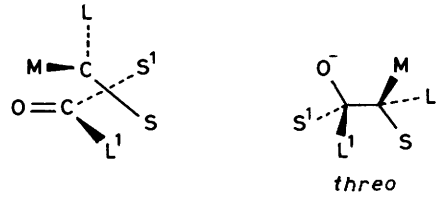


Figure 2. The general expression of the favoured approach of a carbanion $\bar{C}SML$ to a carbonyl compound $L^1S^1C{=}O$, in the absence of chelation control

not unduly large), and, with all anions, enolisable ketones underwent aldol condensations preferentially. The two reproducible and high-yield reactions support our model for steric control. The addition of $Ph\bar{C}HCH_3$ to $(CH_3)_3CCHO$ gave a 3:1 ratio of (**1**) to (**2**) (Scheme 2) with the transition state (**3**) being the one predicted to be most favoured (Ph > Me) and leading to (**1**). Similarly, the addition of $Ph\bar{C}HCH_3$ to PhCHO consistently gave an excess of the *threo*-isomer, as predicted by our model.

In summary, a general rule may be enunciated. Consider the irreversible addition of a carbanion $\bar{C}SML$ to a carbonyl compound $S^1L^1C{=}O$, where S, M, and L represent small, medium, and large groups, respectively. The stereochemical outcome of the reaction is determined by two steric influences, in the absence of chelation control. As a consequence of attack by the carbanion at 109° to the carbonyl compound the primary influence is such that the smallest carbanion ligand, S, is disposed between L^1 and S^1. The most favoured disposition of the remaining ligands is with M and L^1 and L and S^1 *gauche*. The favoured approach is illustrated in Figure 2. Experience

shows that chelation control, when possible, will dominate and this rule in those circumstances is invalid.

In a forthcoming paper we shall present further tests for the model and show how its application can significantly alter the *cis*-to-*trans* ratio in the Peterson reaction.

Experimental

I.r. spectra were obtained with a Pye Unicam SP 1050 instrument, and n.m.r. spectra with a JEOL FX90Q spectrometer. We thank Hoechst Pharmaceuticals Ltd., for mass spectra run on a Cresta MS30 spectrometer. Elemental analyses were obtained from Butterworth Ltd. G.l.c. analyses were performed with a Pye Unicam 204 chromatograph, using a flame ionisation detector, and coupled to a Laboratory Data Control computing integrator.

Hexamethylphosphoramide (Aldrich) was distilled from phosphorus pentaoxide and the sample boiling at 75–77 °C and 1 mmHg was collected and used immediately. Benzaldehyde (Aldrich) was distilled at 50—53 °C and 8 mmHg and stored under nitrogen. Tetrahydrofuran and diethyl ether were distilled from calcium hydride at atmospheric pressure immediately prior to use. All other commercially available materials were used without further purification. Bis(trimethylsilyl)-phenylmethane was prepared by the method of Dunogues[21] and was distilled at 38—39 °C and 1.5 mmHg (lit.,[21] b.p. 95 °C at 35 mmHg).

General Procedure for the Peterson Reaction.—Typically, bis(trimethylsilyl)phenylmethane (0.5 g, 2 mmol) was mixed at ambient temperature in a nitrogen-filled dry box with an excess of benzaldehyde (1.8 g, 17 mmol) in anhydrous hexamethylphosphoramide (25 cm^3). To this solution was added an excess of sodium methoxide (0.2 g, 4 mmol). The reaction was quenched after about 1—5 min with concentrated hydrochloric acid (100 cm^3), and the mixture extracted with dichloromethane (30—40 cm^3) containing a known quantity of phenanthrene (0.15 g) as internal g.l.c. standard. Each experiment was repeated, and duplicate samples from each experiment were injected into the g.l.c. instrument and analysed. The g.l.c. conditions were as follows: column packing 10% SE30 on Chromosorb W(80—100 mesh); 2.7 m column, i.d. 4 mm; nitrogen carrier gas, flow rate 30 cm^3 min^{-1}; injector temp 300 °C; column temperature 225 °C; detector temperature 350 °C; integrator settings; peak width 24, minimum data 500, threshold 100, noise 10, sampling 8, attenuation 64 × 10^3.

Other experiments followed the same procedure. When inorganic salts were used these were added and dissolved prior to alkoxide addition. When the alkoxide was varied the following quantities were used (other quantities were identical with those in the general procedure): potassium t-butoxide 0.2 g; lithium t-butoxide 0.18 g; sodium propoxide 0.25 g; sodium trimethylsilanolate 0.35 g. The results of these experiments are shown in Tables 2—7.

α-Methylbenzyl(trimethyl)silane.—A mixture of freshly distilled thionyl chloride (100 g, 0.84 mol) and 1-phenylethanol (41.1 g, 0.34 mol) was stirred overnight. Removal of the excess of thionyl chloride and distillation under reduced pressure gave (1-chloroethyl)benzene (27 g, 57.2%), b.p. 46 °C at 2 mmHg; δ($CDCl_3$) 1.83 (d, 3 H, CH_3), 5.07 (q, 1 H, CH), and 7.35 (s, 5 H, Ph).

(1-Chloroethyl)benzene (26.9 g, 0.192 mol) reacted with magnesium turnings (9.19 g, 0.383 mol) and chlorotrimethylsilane (41.58 g, 0.383 mol) in tetrahydrofuran (35 cm^3) to yield the crude *α-methylbenzyl(trimethyl)silane*, which was distilled under reduced pressure (yield 10.8 g, 32%), b.p. 36 °C at 0.5 mmHg, δ($CDCl_3$) 0 (s, 9 H, $SiMe_3$), 1.4 (d, 3 H, CH_3), 2.2 (q, 1 H, CH), and 7.15 (d, 5 H, Ph).

Diastereoisomeric Alcohols $PhCH(CH_3)CH(OH)R$ (R = Ph *or* Bu^t).—Sodium trimethylsilanolate was added to a known amount of α-methylbenzyl(trimethyl)silane and excess of aldehyde, RCHO, in anhydrous hexamethylphosphoramide at ambient temperature in a nitrogen-filled dry box. The reaction mixture was quenched after 1—5 min with dilute hydrochloric acid (2M), and extracted with dichloromethane (2 × 20 cm^3). The organic layer was washed with water, dried, and evaporated. The products were analysed by n.m.r. spectroscopy and g.l.c., with phenanthrene as internal standard. Each experiment was repeated, and duplicate g.l.c. injection was used. For R = Ph, the following quantities were used: $PhCH(CH_3)$-$SiMe_3$ 1.011 g, 5.68 mmol; PhCHO 1.25 g (excess); $NaOSiMe_3$ 0.637 g, 5.68 mmol; HMPA 50 cm^3; phenanthrene 0.2559 g. In this example stereochemical assignments were made by using the n.m.r. data of Ashby *et al.*[22]

For R = Bu^t the following quantities were used: PhCH(Me)-$SiMe_3$ 0.222 g, 1.25 mmol; Bu^{t}CHO 0.217 g (excess); $NaOSiMe_3$ 0.138 g, 1.23 mmol; HMPA 15 cm^3; phenanthrene 0.1539 g. In this example stereochemical assignments were made by using the data of Hirota,[23] Nishio,[24,25] and Zioudrou.[26] The results are given in Table 8.

References

1 Part, A. R. Bassindale, R. J. Ellis, and P. G. Taylor, *Tetrahedron Lett.*, 1984, **25**, 2705.
2 D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780.
3 D. J. Ager, *Synthesis*, 1984, 384.
4 P. F. Hudrlik and D. Peterson, *J. Org. Chem.*, 1975, **40**, 2263.
5 P. B. Dervan and M. A. Shippey, *J. Am. Chem. Soc.*, 1976, **98**, 1266.
6 M. T. Reetz and M. Placky, *Synthesis*, 1976, 199.
7 M. E. Jones and S. Trippett, *J. Chem. Soc. C*, 1966, 1090.
8 B. E. Maryanoff, A. B. Reitz, M. S. Mutter, R. R. Inners, and H. R. Almond, Jr., *J. Am. Chem. Soc.*, 1985, **107**, 1068.
9 Y. Yamakado, M. Ishiguro, N. Ibeda, and M. Yamamoto, *J. Am. Chem. Soc.*, 1981, **103**, 5568.
10 A. M. Van Heusen and J. F. Red, *Recl. Trav. Chim. Pays-Bas*, 1959, **55**, 78.
11 H. Taguchi, K. Shimoji, M. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2529.
12 K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, 1974, **96**, 1620.
13 I. Matsuda, S. Murata, and Y. Ishii, *J. Chem. Soc., Perkin Trans. 1*, 1979, 26.
14 P. A. Grieco, Chia-Lin, J. Wang, and S. D. Burk, *J. Chem. Soc., Chem. Commun.*, 1975, 537.
15 G. Fraenkel, M. J. Geckle, A. Kaylo, and D. W. Estes, *J. Organomet. Chem.*, 1980, **197**, 249.
16 D. Bergelson, L. I. Barsukof, and M. M. Shemyaker, *Tetrahedron*, 1967, **26**, 2709.
17 W. A. Kleselinck, C. T. Buse, and C. H. Heathcock, *J. Am. Chem. Soc.*, 1977, **99**, 247.
18 D. R. Williams, J. G. Phillips, and J. C. Huffman, *J. Org. Chem.*, 1981, **46**, 4103.
19 H. B. Bürgi and J. D. Dunitz, *Acc. Chem. Res.*, 1983, **16**, 161.
20 J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.
21 J. Dunogues, E. Jonseaues, and R. J. Calas, *J. Organomet. Chem.*, 1974, **71**, 393.
22 E. C. Ashby, G. F. Willard, and A. B. Joel, *J. Org. Chem.*, 1979, **44**, 1221.
23 M. Hirota, K. Abe, T. Sekiya, and H. Tashimo, *Chem. Lett.*, 1981, 685.
24 Y. Kodama, K. Nishihata, S. Zushi, M. Nishio, J. Ugawa, K. Sakamoto, and H. Iwamura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2661.
25 J. Uzawa, S. Zushi, Y. Kodama, Y. Fukuda, K. Nishihata, K. Umemura, M. Nishio, and M. Hirota, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 3623.
26 C. Zioudrou, I. Moustakali-Mavridio, P. Chrysochou, and G. J. Karabatsos, *Tetrahedron*, 1978, **34**, 3181.

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