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Hindered Organoboron Groups in Organic Chemistry. 23. The Interactions of Dimesitylboron Stabilised Carbanions with Aromatic Ketones and Aldehydes to give Alkenes.[1]

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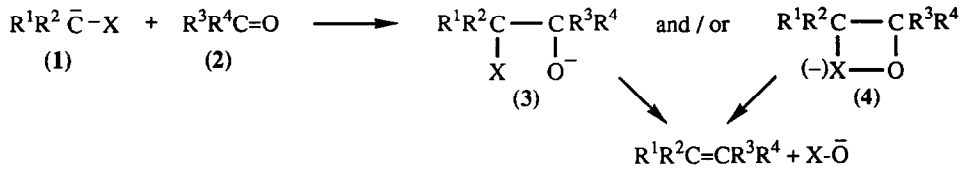
Abstract. Dimesitylboron stabilised carbanions react with diarylketones to give the corresponding alkenes in mild conditions with good yields. Reactions with aromatic aldehydes are more complex, but in all cases *E*-alkenes are available in good yields by trapping the intermediates with chlorotrimethylsilane followed by treatment with aq. HF/CH_3CN. Treatment of the same intermediates with trifluoroacetic anhydride gives mainly the *Z*-alkenes. The design and mechanisms of these important processes are considered.

Introduction. The Wittig reaction,[2,3] exemplified by equation 1, is a reaction central to much organic synthesis.

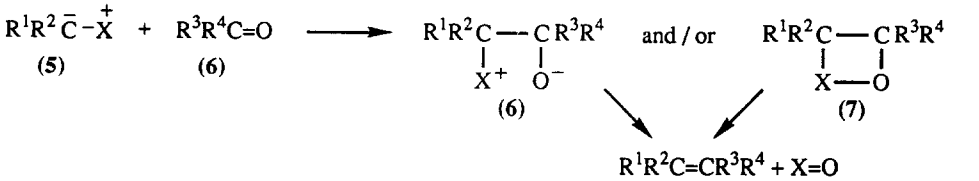
$$R^1R^2C{=}O + R^3R^4\bar{C}\text{-}\overset{+}{P}R^5_3 \rightarrow R^1R^2C{=}CR^3R^4 + R^5_3P{=}O \qquad (1)$$

Since its discovery, the factors influencing the stereochemistry of the reaction have received much attention,[4-8] and recent work has been comprehensively reviewed.[9] In particular, curiosity about the reasons for the stereoselectivity of the condensation of unstabilised triphenylphosphonium ylids with aldehydes to give *Z*-alkenes has been a great incentive to detailed studies, which have shown that the stereochemistry of the alkene products depends on a host of factors. Thus it is influenced by the organyl groups on phosphorus,[6,7,10] the presence or absence of lithium salts,[11] the structure of the aldehyde being condensed and, in particular, whether it contains groups that can stabilise a negative charge[12] or has an oxido group,[13,14] concentration effects[15] and temperature.[15,16] The question of whether or not a betaine intermediate is involved in the condensation has been discussed at length[9] and it seems most likely that betaines are not involved in most Wittig reactions.[9,17] Instead, 1,2-oxaphosphetanes are formed directly[7,9,18] as the kinetic products, and stereochemical drift by reversion of the oxaphosphetane to its components has been experimentally verified as the cause for lack of stereoselectivity.

The Wittig reaction is but one of a whole class of reactions that are summarised in Schemes 1 and 2.



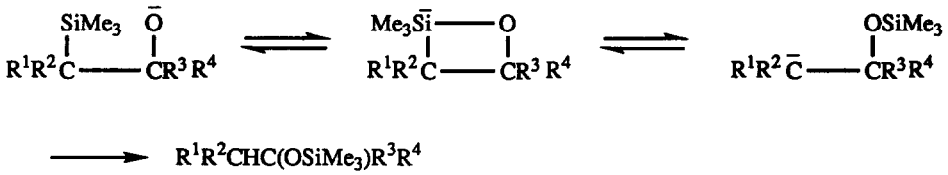
Scheme 1



Scheme 2

The Wittig reaction (X = PR_3) is an example of Scheme 2 whilst its variants, the Horner reaction (X=P(O)R_2)[19,20] and the Horner-Wadsworth-Emmons (HWE) reaction[21] (X=P(O)$(OR)_2$) fit into Scheme 1. The interactions shown in Schemes 1 and 2 have been reviewed.[22,23] Examples of the heteroatoms involved are sulphur[24,25], silicon[26,27], selenium[28], tin[29], lead[29], antimony[30], arsenic[31], bismuth[32], germanium[33], tellurium[34], aluminium[35], magnesium[36,37], zinc[38], transition metals[39] and boron.[40] In some of these reactions, for example those with sulphur and arsenic, instead of alkene product, the group X is expelled from the intermediate to give epoxides.

Other than the Wittig reaction, the most studied of these reactions is the Peterson reaction[41] (Scheme 1, X=$SiMe_3$). In this case the initial condensation is not stereoselective and the intermediate (3) (X=SiR_3) is formed as a roughly 1:1 mixture of *erythro* and *threo*-isomers[26] which can be remarkably invariant to variations in solvent, added salts, initial base and temperature.[27] However, the intermediate (3) (X=SiR_3) may be converted to the hydroxy compound which undergoes *anti*-elimination with acid and *syn*-elimination with base.[26,42,43] In order to obtain stereoselectivity the *erythro*- and *threo*-isomers must first be separated and then separately subjected to the appropriate conditions. There have been suggestions that anionic siloxetanes (4, X=SiR_3) may be involved in this reaction, and also in protiodesilylation[45] (equation 2).



$$\longrightarrow \quad R^1R^2CHC(OSiMe_3)R^3R^4 \qquad (2)$$

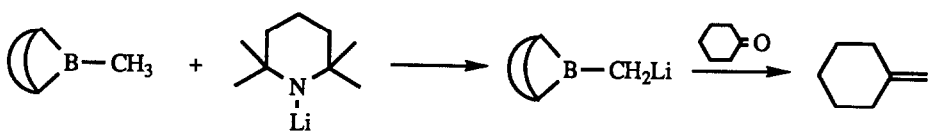
Of the many other reactions which are encompassed in Schemes 1 and 2, very little mechanistically is known.

Background to the reactions of boron stabilised carbanions with ketones and aldehydes

The first demonstration of the production of boron stabilised carbanions also reported the first condensations of such anions with aldehydes and ketones[40] (equation 3). Some interesting effects of temperature upon yields and stereoselectivities were given, but the work was never followed up.

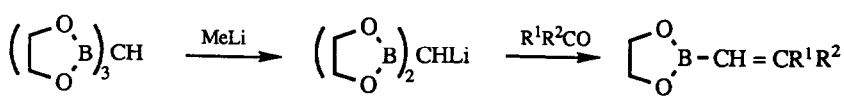
$$R^1CH_2CH(BR^2_2)_2 \xrightarrow{BuLi} R^1CH_2CHLiBR^2_2 \xrightarrow{R^3R^4CO} R^1CH_2CH{=}CR^3R^4 \qquad (3)$$

A further case of the condensation was given by Rathke,[46] who used a hindered base, lithium 2,2,6,6-tetramethylpiperidide (LTMPD) to abstract a proton from B-methyl-9-BBN and condensed the resulting anion with cyclohexanone as in equation (4). However, the yields with derivatives of 9-BBN other than the methyl, were very poor and in our hands this process could not be induced with B-hexyl-9-BBN using LTMPD, mesityllithium or tripyllithium (tripyl=2,4,6-triisopropylphenyl).[47]



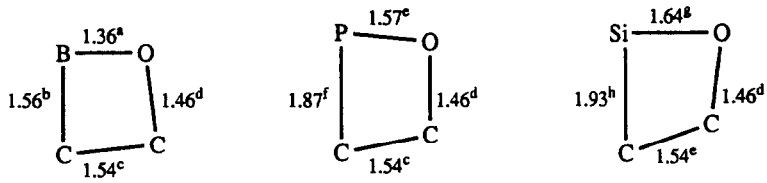
(4)

Boronic esters, in which there are more than one boron atom/carbon, have also been shown to undergo condensations with carbonyl compounds to yield alkenes (equation 5).[49,50]



(5)

Having made readily available a variety of dimesitylboron stabilised carbanions[51], we decided to systematically investigate their interactions with ketones and aldehydes. It further seemed possible that if the reaction proceeded through a boratoxetane intermediate, then the short B-O and B-C bond lengths as compared with P-O, P-C and Si-O, Si-C (Scheme 3)[54] would make the reaction more stereoselective than either the Wittig or Peterson reactions. This would therefore be a useful example of Scheme 1 (X=$BMes_2$).



a) in $B(OH)_3$, $B(OMe)_3$; b) in Me_3B ; c) in CH_3-CH_3 ; d) in oxetane ;
e) in $(HO)_3P=O$; f) in Me_3P ; g) in $(Me_3Si)_2O$, h) in Me_4Si.
All bond lengths in Å units, roughly to scale.

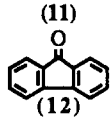
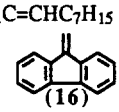
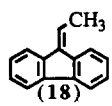
Scheme 3

Reactions of dimesitylboron stabilised carbanions with aromatic ketones

For our first experiments symmetrical, diaromatic ketones were used in order to avoid questions of stereochemistry and the possibility of enolate production by proton-lithium exchange. We used Mes_2BCH_2Li (8), $Mes_2BCHLiCH_3$ (9), and $Mes_2BCHLiHept^n$ (10) as representative boron stabilised carbanions. Our results are given in Table 1.[52]

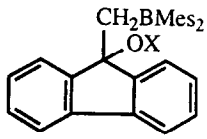
Table 1

The reactions of $Mes_2BCHLiR$ with aromatic ketones

Experiment	Ketone	R	Alkene Product [a]	Conditions	Yield(%)[b]
1	Ph_2CO(11)	H	$Ph_2C=CH_2$ (12)	24h, 20°C	75(95)
2	(11)	CH_3	$Ph_2C=CHCH_3$ (14)	1h, 0°C; 12h, 20°C [c]	70(90)
3	(11)	C_7H_{15}	$Ph_2C=CHC_7H_{15}$ (15)	1h, 0°C; 12h, 20°C [d]	70(90)
4	 (12)	H	 (16)	12h ; 20°C [c]	80
5	(12)	CH_3	 (18)	1h, 0°C ; 12h, 20°C [c]	90

a) Alkenes either compared directly with authentic samples or fully characterised. b) Isolated yields of purified products (g.c. yields) c) Initial product stirred in $CHCl_3$ for 12h / 20°C.
d) Initial product stirred in $CHCl_3$ for 3h / 20°C.

The reaction of (8)[55] with benzophenone (11) (Table 1, exp. 1) was carried out both by adding the ketone to the anion and by reverse addition. In each case reaction was exothermic and instantaneous and gave a g.c. yield of 1,1-diphenylethene (12) of *ca.* 95%. When (12) was purified by chromatography rather than direct distillation, a small amount (~ 5%) of $Mes_2BCH_2C(OH)Ph_2$ (13) was also isolated. We frequently observed at least some of the alkoxides derived from intermediates analogous to (13) and also that they readily decomposed in chloroform (or $CDCl_3$ whilst taking nmr spectra), and we therefore left the initial alkoxide/alkene reaction products in chloroform as a standard part of our procedure, This was used in experiments (2) and (3), with no attempt to isolate intermediates. When anion (8) was condensed with fluorenone (12) there was an immediate exothermic reaction, the solution turned deep red and in 5 min a white solid precipitated. After 20h at 20°C, analysis of the supernatent showed that there was only a 10% yield of dibenzofulvene (16). The solid was therefore filtered and a portion of it carefully neutralised. Examination of its nmr spectra showed it to be (17b), which was reasonably stable in chloroform but, on standing in chloroform, slowly gave dibenzofulvene. The initial solid, which we assume to be the lithium alkoxide (17a) was insoluble in THF, ether or light petroleum but soluble in acetone, in which it was stable, and in chloroform, in which it rapidly decomposed to give (16). Chromatography gave (16) in 80% yield of pure product, that polymerised on standing.[56] A similar reaction (Table 1, exp. 5) was carried out with anion (9) to give (18), m.p. 102-103°C.



17(a) X = Li
(b) X = H

Clearly the condensation of dimesitylboron stabilised carbanions with aromatic ketones is a useful synthetic reaction.*

Condensations with aromatic aldehydes to give E-alkenes.

In order to discover firstly whether or not dimesitylboron stabilised carbanions condense with aromatic aldehydes to give alkenes and then secondly the stereochemistry of the reaction, we decided on preliminary studies of the reactions of benzaldehyde with carbanions $Mes_2BCHLiCH_3$ (9) and $Mes_2BCHLiHept$ (10). The preliminary results are presented in Tables 2 and 3.

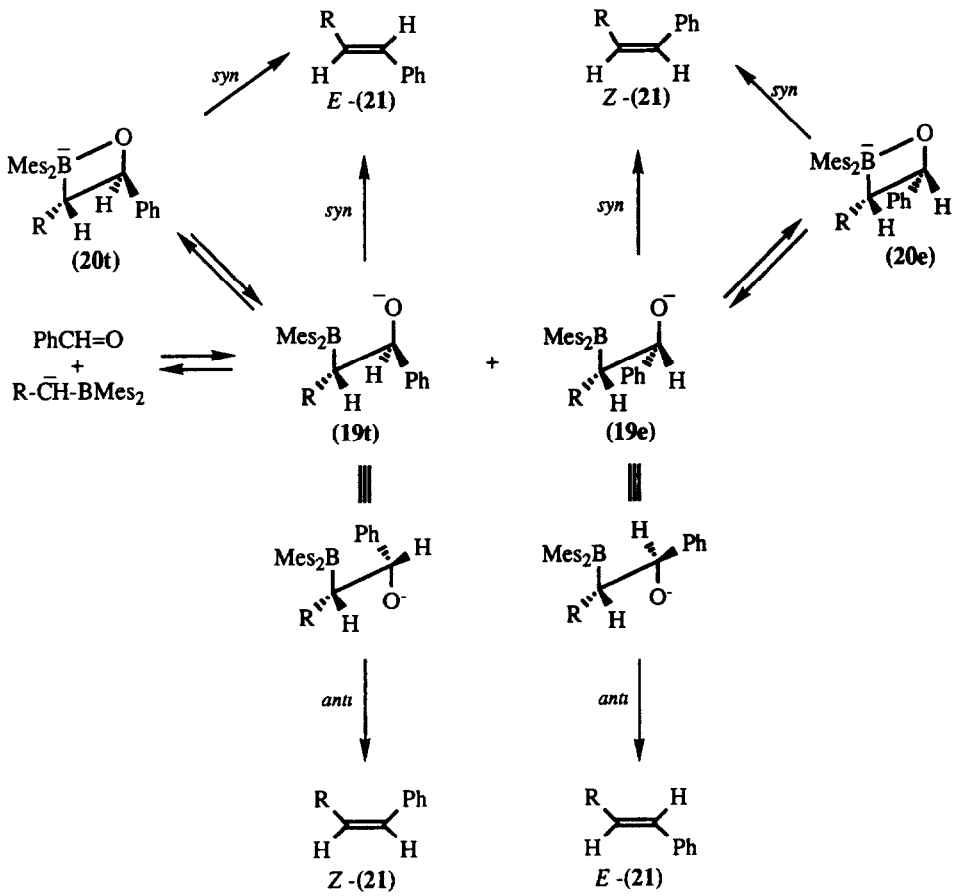
*We thank Dr. J. W. Wilson for helpful discussions on this part of this paper.

Table 2

Reactions of $Mes_2BCHLiCH_3$ (9) with PhCHO in THF at -78°C for 1h.

Experiment	Work-up	Products (%)[a]				
		$PhCH{:}CHCH_3$	$PhCHOHCH_2CH_3$	$PhCOCH_2CH_3$	$PhCH_2OH$	Other
6	$CHCl_3$, reflux	0	43	19(32)	13	0
7	H_2O, -78°C 25°C, 16h	0	22(23)	22(23)	16	0
8	Me_3SiCl, -78°C, 1h 25°C, 16h	0	0	22	0	$Mes_2BCH(CH_3)CH(Ph)OH$ 50
9	$NaOH,H_2O_2$, -78°C	0	0	0	0	$PhCHOHCHOHCH_3$[b] 50

a) *Isolated (g.c.) yields* b) *Erythro:threo = 12:1.*



Scheme 4

Table 3

Reactions of $Mes_2BCHLiHept^a$ (10) with PhCHO in THF

Exp.	Conditions	Work-up	Yields of Products (%)[a]				
			E-PhCHCHHept	$PhCHOHCH_2Hept$	$PhCOCH_2Hept$	$PhCH_2OH$	$PhCH_2OCOPh$
10[b]	25°C, 1h	$CHCl_3$, reflux	6	0	18	68	8
11[c]	-78°C, 1h	$CHCl_3$, reflux	(50)	(5)	d	0	d
	25°C, 15h						
12	-78°C, 1h	$NaOH/H_2O_2$	(16)	(3)	e	0	e
	25°C, 15h	25°C, 25h					
13	-78°C, 1h	aq. HCl	(33)	(5)	f	0	f
	25°C, 15h	25°C, 15h					
14	-78°C, 1h	Diglyme	(19)	(5)	7	0	0[g]
	25°C, 15h	reflux					
15	-110°C, 3h	THF	24(24)	0(5)	12(24)	28	0[g]
	25°C, 2h	reflux					
16	-110°C, 3h	aq. HCl	(44)	(5)	(33)	0	0[g]
	25°C, 2h	25°C, 15h					
17	-110°C, 3h	$CHCl_3$	(44)	(5)	(36)	0	0[g]
	25°C, 2h	reflux					
18	-110°C, 3h	NaOMe	(41)	(5)	(30)	0	0[g]
	25°C, 2h	25°C, 72h					
19	-110°C, 3h	HCl/Et_2O	(44)	(5)	(30)	0	0[g]
	25°C, 2h	25°C, 72h					

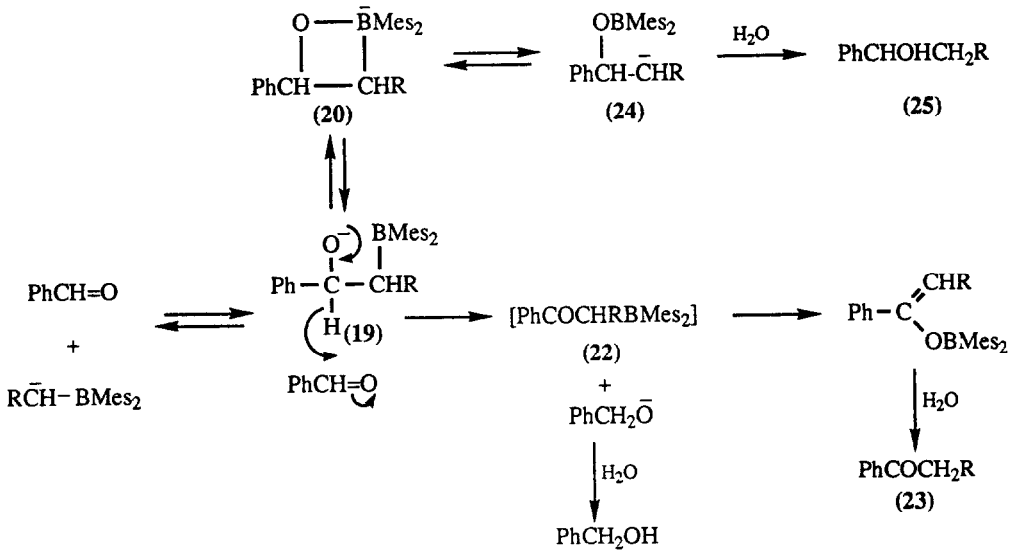
[a] Isolated (g.c.) yields. [b] Mes_2BOH (51%) isolated. [c] $PhCO_2H$ (19%) isolated. [d] Same retention times, 25% combined. [e] 13% combined. [f] 15% combined.

[g] Not present by i.r. and t.l.c. of crude product.

Before discussing these results, in Scheme 4 are presented possible pathways for alkene production. Initial condensation could yield either (**19t***) or (**19e***) or both. These could cyclise to boratoxetanes (**20e**) and (**20t**), which could also be formed directly. The boratoxetanes would then decompose to alkenes (**21**) by *syn*-elimination so that *E*-alkenes would arise from the *threo*-isomer. The oxyanions (**19**) could undergo either *syn*- or *anti*-elimination. In the latter case, *E*-(**21**) would be produced from *erythro*-(**19**).

It seemed likely that, due to the interactions between the negatively charged oxygen and the electron deficient boron atom, the boratoxetanes (**20**) would be favoured. However, the boron atom is extremely hindered, and in the boratoxetanes there are severe eclipsing interactions, so that the attractive forces tending to (**20**) are offset by strong steric influences. The oxyanions (**19**) might undergo *syn*-elimination or *anti*-elimination (though the mechanism of the latter must involve other molecules of (**19**). Thermodynamically (**20t**) would be favoured, as would (**19e**).

We were surprised to find that, using conditions most favourable for alkene formation from aromatic ketones, the condensation of benzaldehyde with (**9**) gave no alkene at all. Instead, there was a large amount of product ($PhCHOHCH_2CH_3$) due to protiodeboronation, (akin to protiodesilylation[45], eq. 2) and the ketone, $PhCOCH_2CH_3$, arising from a redox reaction (Table 2, experiment 6). To explain these findings another reaction grid (Scheme 5) related to Scheme 4, is presented.



Scheme 5

*(**19t**) = *threo*-**19**); (**19e**) = *erythro*-(**19**).

In Scheme 5, the initial condensation is reversible, which allows for a variable quantity of benzaldehyde to be present as well as accounting for any stereochemical drift.[9] Either (20) or (19), but particularly the latter, could act as a hydride donor in a Canizzaro type reaction with benzaldehyde to give (22) and eventually (23) as work-up. A shift of the boron atom from carbon to oxygen, possibly *via* (20) then gives (24) in a protiodeboronation reaction, which yields alcohols (25). *The ketone product (23) is produced in all reactions*, except those involving low temperature oxidations, and it is particularly important in the reactions of aliphatic aldehydes with aliphatic aldehydes (next paper and ref. 57).

With Schemes 4 and 5 in mind, it is possible to rationalise the preliminary results presented in Tables 2 and 3. The protiodeboronation and redox condensation products of experiment 6 show that the required intermediates (19) and/or (20) are being formed to at least 70% extent but are not undergoing elimination. Attempts to neutralise (19), (20) with water (experiment 7) or trimethylsilane (experiment 8) also did not yield alkene. However, from the latter experiment, attempts to isolate products by chromatography on silica gave $PhCH(OH)CH(CH_3)BMes_2$ (26) as crystals, m.p. 90°C in 50% yield, and J=10Hz for PhC*H*(OH). A repeat experiment, using a shorter time for chromatography gave (26) plus 16% of (27), $PhCH(OSiMe_3)CH(CH_3)BMes_2$, m.p. 86-88°C as a single isomer with J=9Hz for PhC*H*($OSiMe_3$). The instability of (26) and (27) precluded X-ray analysis and we turned to conformational arguments to assign stereochemistry. In general, when there are no strong attractive interactions between the groups on C-1 and C-2, then the *anti*-conformation with the most favourable gauche interactions will be most populated, as in Figure 1. For the *erythro*-isomer this will be conformer (i) with a large J_{AB} coupling constant of *ca.* 10Hz and for the *threo*-isomer, this will be conformer (ii) with a much smaller coupling constant. Many examples are known.[23,58,59]

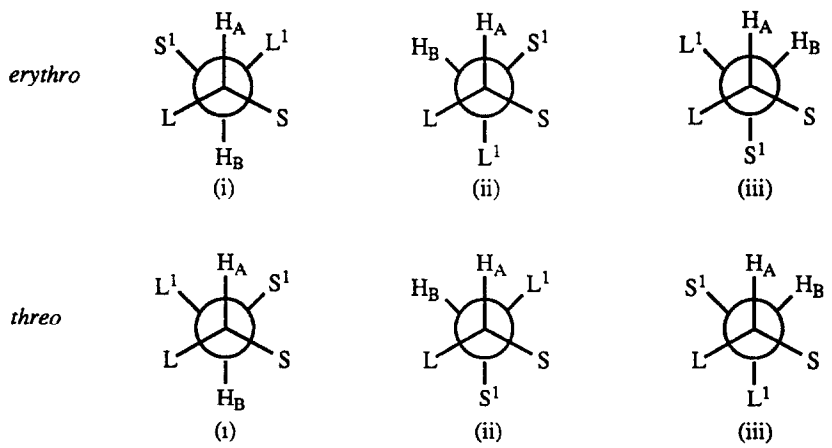
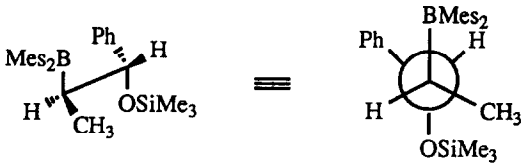


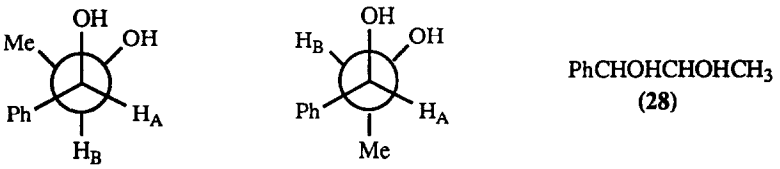
Figure 1

In (27) the $BMes_2$ group is very large, as is the $OSiMe_3$, and models indicate that these would have to be *anti-* in the most favoured conformation. In that case only the *erythro*-isomer (27e) would give rise to a J_{AB} of 10Hz. A similar argument can be given for (26).



(27e)

Using such an argument it is best to have both isomers to hand, but if there are large distinctions between the "large" and "small" groups as in (27), then a prediction based on the coupling constant of one isomer, is reasonable. Strong hydrogen bonding can, however, stabilise some otherwise unfavourable gauche conformers.[60,61] Both isomers of 1,2-dihydroxy-1-phenylpropane (28) are known and fully characterised.[58,62,63] In each case the conformer that gives rise to good hydrogen bonding is favoured, as shown in Figure 2.



(28e) (28t) (28)

Figure 2

For (28t), H_A is reported at *ca.* δ 4.3, J_{AB}=7.6Hz and for (28e), H_A is at 4.7, J_{AB}=3.6Hz.

A low temperature oxidation of the reaction mixture from (9) and benzaldehyde was carried out (experiment 9) and furnished (28) in 50% yield as a 12:1 mixture of (28e) PhC*H*OH at δ 4.75, J_{AB}=3.4 and (28t), PhC*H*OH at δ 4.35, J_{AB}=7.2. As the oxidation of organoboranes proceeds without exception with retention of configuration,[64] (28c) must have come from (26e), in accord with the conformation assignment. *Thus the initial condensation appears to be highly stereoselective,* the small amount of (28t) possibly arising from stereochemical drift during the oxidation.

The situation with regard to condensations involving carbanion (10) (Table 3) was somewhat different. Reaction at 25°C/1h gave a large amount of benzyl alcohol, and very little condensation products, presumably due to reversion to components followed by Canizzaro reaction, at 25°C (experiment 10). Dropping the temperature with the same work-up gave 50% of 1-phenylnon-1-ene (29), and this was entirely the *E*-isomer by ^1H, ^{13}C nmr and g.c. analysis. Attempts to reduce the amount of redox products by oxidation at 25°C (experiment 12), adding

aqueous acid (experiment 13) and refluxing in various solvents (experiments 14,15) were unsuccessful in terms of alkene yield. Most interestingly, when the initial condensation was done at -110°, the product mixture was almost invariant, regardless of the work-up (experiments 16-19) and the redox product $PhCOCH_2Hept$ (30) figured largely together with *E*-(29). Indeed, the results of condensation accounted for *ca.* 80% of the weight of the components and for 100% of product, a great contrast with experiment 10. Therefore, at -110°C, reversion of the intermediates to components is very slow in comparison with elimination, redox and protiodeboronation reactions.

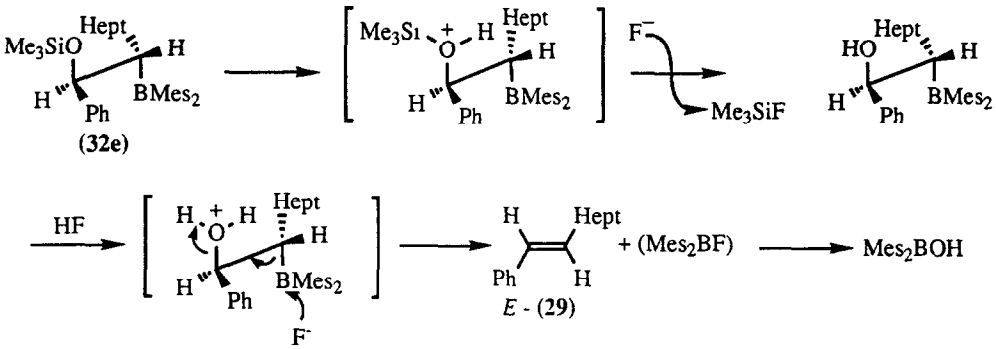
With these pieces of information to hand, it remained to control the reaction to give alkene stereospecifically and in good yields. The redox reactions and protiodeboronation of intermediates (19) and (20), if the analysis in Scheme 5 is correct, are caused by the anionic nature of the intermediates. Reversion of (19) and (20) is lowered by using low temperatures. Therefore, condensation and conversion of the intermediates to neutral substances at low temperatures was indicated. Attempted trapping by a variety of reagents, *e.g.* PhCOCl, Bu^tSiMe_2Cl was unsuccessful, but when a reaction between benzaldehyde and (10) at -78°C was reacted with trimethylchlorosilane also at -78°C, a 78% yield of $PhCH(OSiMe_3)CH(Hept^n)BMes_2$ (31) was isolated, and proved to be remarkably stable. It could be crystallised from hot methanol, handled in air and purified on alumina, and analysis by the usual physical methods showed that it was isomerically pure, as well as confirming the structure. The coupling constant for the PhC*H*O proton was 10Hz, showing that it was pure *erythro*-isomer. The structure of the intermediate was proven by carrying out an experiment in two portions and working one up by careful low temperature oxidation with $NaOH/H_2O_2$ and the other by silylation. The latter gave (31e), isomerically pure in 85% yield, whilst the oxidation gave the diol, $PhCHOHCHOHHept^n$, (32) in 80% yield. The latter was a 93:7 mixture of (32e) (J_{AB}=4Hz) and (32t) (J_{AB}=10Hz) respectively. The generalisation of this unique condensation (equation 6) to yield *erythro*-1,2-diols has been reported in a preliminary note[65] and will be the subject of a full paper in this series.

$$ArCHO + RCHLiBMes_2 \xrightarrow[2.\ -78°C,\ NaOH/H_2O_2]{1.\ -78°C,\ THF} \textit{erythro}\text{-}ArCHOHCHOHR \qquad (6)$$

Two major conclusions can be drawn at this stage. (1) *The condensation of both (9) and (10) with benzaldehyde is highly stereoselective and proceeds in good yields to give* erythro-*intermediates. (2) Because* E-*alkene is produced, the elimination is an* anti-*elimination from (19e) and does not involve a boratoxetane.*

Because the silylated intermediate (**32e**) was produced as one isomer in 85% yield, it seemed worth studying to see whether or not it would yield alkene. With TBAF at -78°C, only products characteristic of the lithio intermediate (**19e**, R=Hept^n) were isolated, *e.g.* PhCH=CHHept^n (**29**) (46% >98:2 of *E*:*Z*), PhCOCH$_2$Hept^n (17%) (**30**), PhCHOHCH$_2$Hept (8%) and PhCH$_2$OH (15%). Pyrolysis of (**32e**) at 150°C/2mm Hg gave 60% of alkene (**29**) as a mixture of 55*E*:45*Z* isomers. This was the first time that an appreciable amount of *Z*-alkene was produced in this study, and clearly on pyrolysis, both *syn* and *anti*-eliminations were occurring. Direct oxidation of (**32e**) by refluxing NaOH/H$_2$O$_2$ (gentler conditions were unsuccessful) gave all possible condensation products, *e.g.* *E*-(**29**), 26%, (**30**), (30%), PhCHOHOct^n, (16%) and (**28e**) (24%).

Thus, either pyrolysis or the conversion of (**32e**) back to its anion were non-productive. We therefore looked for acid conditions, hoping to encourage *anti*-elimination by generating a protonated hydroxyl group which would position itself *anti* to the electron deficient boron atom and undergo *anti*-elimination according to Scheme 6. In the event, reaction of (**32e**) with a solution of aqueous HF in acetonitrile was complete in 10 min at -78°C and yielded alkene in 95% yield (*E*:*Z* =84:16).



Scheme 6

There would appear to be salt effects, as in this case isolated (**32e**) gave a 97:3 mixture of *E*-(**29**) and *Z*-(**29**). We therefore examined two experimental processes. Procedure A is a one pot reaction at -78°C/1h with Me$_3$SiCl followed by addition of aqueous HF in acetonitrile without isolation of the intermediate. Procedure B involved isolation of the intermediate followed by its decomposition in a separate step. The results are presented in Table 4.

Table 4

The synthesis of alkenes by the condensation of $Mes_2BCHLiR$ with ArCHO

Expt.	Ar	R	Yield (%)[a]		E:Z ratios[b]	
			A	B	A	B
20	Ph	Hept	95	84	84:6	97:3
21	4-MeC_6H_4	Hept	86	83	89:11	95:5
22	4-ClC_6H_4	Hept	87	84	74:26	97:3
23	4-$MeOC_6H_4$	Hept	84	-	100:0	-
24	4-$NO_2C_6H_4$	Hept	65	74	93:7	98:2
25	Mesityl	Hept	80	-	100:0	-
26	Ph	Me	93[c]	78[c]	86:16	98:2

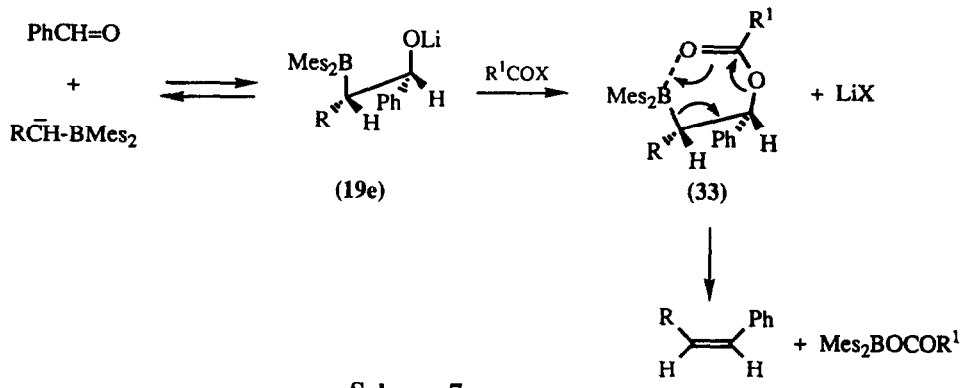
[a] Yields are of isolated, characterised products, based on aldehyde. [b] Determined by g.c. and nmr.

[c] G.c. yield using pure *trans*-2-methylstyrene for comparison.

Isolated chemical yields are generally acceptable and it was particularly gratifying that by this process anion (**9**), which had previously given no alkene, now (exp. 26) gave yields comparable with anion (**10**). Using either procedure A or procedure B it was always possible to obtain between 95-100% of *E*-alkene, regardless of whether the aromatic ring contains an electron donating (experiments 21, 23, 25) group, an electron withdrawing group (experiment 24), or a halogen (experiment 22), or no substituents (experiment 20). The process is under very strong steric control and *we suggest that the transition state resembles the* anti-*conformation of (19e). The reaction is dominated by the very bulky dimesitylboron group, enhanced by the short B-C bond length.*

Attempts to synthesise Z-alkenes.

It would be very desirable if a *syn*-elimination could be selectively induced to lead intermediates (**19e**) to *Z*-alkenes, thus allowing both *Z*- and *E*-alkenes to be made from the same intermediates. Possible acylation of (**19e**) would give (**33**) which might undergo a novel E_i elimination involving boron but akin to an ester elimination.[66] The required conformation might be encouraged by an attractive interaction between the basic carbonyl oxygen and the electron deficient boron atom (Scheme 7). However, the presence of LiX could well induce *anti*-elimination by attack of X^- on boron, the importance of this pathway being dependant on a number of factors, including the polarity of the solvent and the nature of X.



Scheme 7

One example of an attempt to trap an intermediate in a Peterson reaction was an acetylation that gave a 35% yield of acetyl derivative, which in turn underwent non-stereoselective elimination.[67]

We first used acetyl chloride at -78°C to react with (**19e**, R=Hept) produced, as usual, by condensation between benzaldehyde and $Mes_2BCHLiHept$ (**10**). The reaction gave a complex mixture containing (g.c.) 12% of 1-phenylnon-1-ene (**29**) as an *E:Z* mixture in the ratio of 1:1. The nmr spectra of the crude reaction product showed that the acetyl chloride had been converted to ketene and diketene, from which various products were formed.

To avoid ketene formation, benzoyl chloride was next tried. The reagent was sluggish and a long reaction time was required. Work-up and purification gave 17% of *E*-(**29**) and *Z*-(**29**) in the ratio of 39:61, with no trace of (**33**, R=Ph). It was encouraging that *Z*-alkene was the major isomer, for the first time.

We had previously used trifluoroacetic anhydride (TFAA) as a reactive acylating reagent lacking an α-proton[68] and accordingly used it in an attempt to trap (**19e**). Work-up of the reaction gave an isolated yield of 50% of a mixture of *E*-(**29**) and *Z*-(**29**) in a ratio of 13:87. In addition, PhCOOct (**30**) (11%) and PhCHOHOct (8%) were isolated. Despite the unsatisfactory yield, the high proportion of *Z*-alkene was encouraging and some preliminary experiments were carried out (Table 5).

Table 5

Investigation of the production of Z-PhCH=CHHept using TFAA work-up

Exp.	Reactant Ratios			Temp. (°C)	Yield (%)[a]	E:Z ratio[b]
	PhCHO	(10)	TFAA			
27	1.0	1.34	1.28	-78	56	13:87
28	1.0	1.40	3.15	-78	85	45:55
29	1.0	1.43	1.13	-110	60	3:97
30	1.0	1.32	1.32	-78	79	20:80
31	1.0	1.17	1.17	-78	77	10:90
32	1.0	1.01	1.02	-78	54	21:79

[a] Isolated yield, based on PhCHO. [b] Determined by g.c. and ^{1}H nmr.

Experiment 28 made it particularly clear that the *Z:E* ratios were very sensitive to the amount of TFAA used. Thus in experiment 28, use of a large excess of TFAA gave a better yield of alkene but with almost total loss of stereoselectivity. Experiments (27), (30) and (31) all use a ratio of (10) to PhCHO of 1.2-1.4 which we had already established as being necessary for high yield production of (19e), and in these experiments there is a definite trend to higher selectivity with less TFAA excess. The apparent exception, experiment 32, used only a 1:1 ratio of aldehyde to anion, which produces less (19e) and gives an effective excess of TFAA. Experiment 29 established that dropping the temperature strongly enhances the *Z:E* ratio of alkene. We could never detect (33, R^1=CF_3, R=Hept), and the results indicate that it is formed and decomposes even at -110°C, *syn*-elimination being preferentially favoured at this temperature. We then carried out a series of condensations at -110°C using exactly 20% excess of anion and TFAA compared with the aldehyde. It must be emphasised that exact control of the TFAA used is vital for production of *Z*-alkene. Our results are presented in Table 6.

Table 6

The production of Z-alkenes from ArCHO and $Mes_2BCHLiR$

Exp.	Ar	R	Yield (%),[a] (h)[b]	*E:Z*[c]
33	4-MeC_6H_4	Hept	74(2)	4:96
34	4-ClC_6H_4	Hept	73(1.5)	20:80
35	4-$MeOC_6H_4$	Hept	76(6)	9:91
36	4-$O_2NC_6H_4$	Hept	72(7)	69:31
37	Mesityl	Hept	75(6)	7:93
38	Ph	Me	77[d](2)	7:93

[a] isolated, characterised products. [b] reaction time at -110°C. [c] determined by g.c. and ^{1}H nmr.
[d] g.c. yield.

Experiments 29 (Table 5), 33, 35, 37 and 38 (Table 6) show an astonishing inversion of the *E*:*Z* ratios using TFAA work-up as compared with the chlorotrimethylsilane work-up reported in Table 4. In all cases the isolated yields are acceptable, even using a hindered aldehyde (experiment 37) or anion (9) (experiment 38). In two cases the reaction failed to give good stereoselectivity for *Z*-alkene, although its proportion was strongly enhanced. Both of these experiments (34, 36) involved aldehydes with *para*-electron withdrawing groups, the least selective reaction (experiment 36) having the most powerful electron withdrawing group. It may be that such groups lower any weak attractive forces required to encourage *syn*-elimination.

Summary

The condensations of diaryl ketones with dimesitylboron stabilised carbanions gives good yields of alkenes. The condensation of a wide variety of aromatic aldehydes with dimesitylboron stabilised carbanions with work-up with chlorotrimethylsilane followed by aqueous HF gives *E*-alkenes in excellent yields and very high stereoselectivities. An alternative work-up using TFAA gives good yields of Z-alkenes except when the aromatic aldehyde has an electron withdrawing group in the *para*-position. These processes are unique and offer new opportunities in synthesis.

Experimental

Technical Information. Infra-red spectra were recorded on a Pye Unicam SP1050 infra-red spectrometer using NaCl cells with neat liquids or solutions and KBr disks with solids. The polystyrene absorbances at 1603 cm^{-1} and 1494 cm^{-1} were used as references. Proton nmr were recorded on a Hitachi Perkin-Elmer R-24B spectrometer at 60MHz, a Varian HA-100 spectrometer at 100MHz and a Bruker WM-250 spectrometer at 250MHz using $CDCl_3$ as solvent and Me_4Si as reference, except where stated. Carbon (^{13}C) nmr were recorded on a Varian XL100 or a Bruker WM-250 Fourier transform nmr spectrometer, using $CDCl_3$ as a solvent and Me_4Si as an internal standard, except where stated. Low resolution mass spectra and accurate mass measurement were recorded on an AEI MS9 or a CG12-253 mass spectrometer.

Melting points were recorded on a Gallenkamp Hot Stage apparatus and were uncorrected. Boiling points were determined by Kugelrohr distillation and the temperature given is that of the Kugelrohr oven. Boiling points of alkenes are of *E, Z* mixtures. Thin layer chromatography was performed on silica gel (Merck) mounted on aluminium cards with fluorescent indicator (254 nm). Hplc were recorded using an LDC (Milton Roy constametric spectromonitor and C1-10 recorder apparatus using hypersil 5μ columns with efficiency N=55,580 plates/metre. Short flash chromatography was carried out on Keselgel 60G silica (Merck) on a 2' x 1" sintered (Grade 4) column using diethyl ether/petroleum mixtures under water vacuum pressure. Spinning chromatography (Chromatotron) separations used a circular plate of 2mm silica gel (with $CaSO_4$. $0.5H_2O$, Type 60 TLC, Merck) or neutral alumina impregnated with a fluorescent indicator. G.l.c. were recorded on a Varian-Vista with a Varian CDS 401 recorder, using 6' x $^1/_4$" steel columns with 5% SE30 with 5% OV-17 on diatomite 100-200 mesh, except where stated. Microanalyses were by Mr. O. Hughes (U.C. Swansea) using a Carbo Erba Strumentazione Elemental Analyser. Those liquid products that proved difficult to analyse had the molecular formula determined by high resolution m.s.

Reagents. All reactions involving organoboranes were carried out using purified anhydrous reagents, unless otherwise stated. Reactions involving the use and production of air and water sensitive compounds were carried out under a static pressure of argon or nitrogen used directly from the cylinder through a glass line directly connected *via* a three-way tap to a vacuum pump. The preparation and purification of reagents for use in reactions of organoboron compounds have

been reviewed.[69] Solvents were treated as follows.[70] THF was purified first by passing through dry, neutral alumina under nitrogen or agon. Sodium (2g per litre) and benzophenone (8g per litre) were then added to the THF in a still and the mix stirred under argon to give a purple solution of the sodium benzophenone ketyl. The THF was then distilled from the ketyl, under argon, as required. Glyme, diethyl ether, petroleum ether and cyclohexane were passed through an alumina column, stirred for 16 hours with calcium hydride and distilled from calcium hydride under nitrogen or argon. Carbon tetrachloride and ethyl acetate were purified by distillation from phosphorus pentoxide. Methanol was dried and purified by distillation from magnesium methoxide. Chloroform was distilled from phosphorus pentoxide. Acetonitrile was BDH analytical grade. Chlorotrimethylsilane was distilled and stored under argon over 3A molecular sieves. Acetyl chloride and benzoyl chloride were distilled under argon just before use. Trifluoroacetic anhydride (TFAA) was distilled from P_2O_5 immediately before use. Benzaldehyde was distilled immediately before use. 4-Chlorobenzaldehyde and mesityl aldehyde were dried in a vacuum oven at 40°C/1mm Hg for 24h and 4-nitrobenzaldehyde was sublimed at 60°C/0.1mm Hg before use. Mesityl bromide was distilled under nitrogen, at reduced pressure, prior to use. Solutions of *n*- and *t*-butyllithium in hexanes and methyllithium in ether were obtained from Aldrich and standardised every three to four weeks by direct titration of the carbon-lithium bond with butan-2-ol using 1,10-phenanthroline as indicator.[71] B-Methyl- and B-ethyl- and B-octyl dimesitylborane[55] were kept in a desiccator and dried in a drying pistil at 35°C/2mm Hg for 2h prior to use. Purified solvents and reagents were stored under standard conditions for use in reactions involving air sensitive compounds.

Experimental Procedures The equipment and techniques involved in laboratory operations with air sensitive substances have been surveyed.[69] All glassware was oven dried (typically >24 hours at 120°C) assembled hot, and allowed to cool under a stream of nitrogen or argon introduced *via* needles inserted through serum capped inlets with outlets protected by inert oil bubble. Manipulation of liquids was carried out under an inert atmosphere, using syringes and double-ended needle techniques. Syringes and double-ended needles were flushed with nitrogen as they cooled. Solids were transferred, either in air without delay and flushed with nitrogen prior to reaction, or by using a dry box.

Unless otherwise stated, the apparatus for reactions at room temperature or below consisted of a septum capped flask containing a coated magnetic follower to enable stirring of the reaction mixture *via* an external magnetic stirrer. A bleed needle to an argon line was inserted through the cap to allow for any changes in the pressure within the vessel during reaction.

1) **Procedure for the preparation of anions (8), (9) and (10) derived from Mes_2BMe, Mes_2BEt and Mes_2BHept respectively[55]**

Bromomesitylene (1.0.5g, 5.5mmol) was made up to a 0.5M solution in a round-bottomed flask by addition of THF (11ml). The flask was cooled to -78°C and Bu^tLi (2 equiv. of a freshly standardised solution, normally about 1.8-2.0M in hexane), was added with stirring. The solution became pale yellow and a white solid precipitated. The mixture was stirred for 15 min at -78°C, then placed in a bath at 25°C for 15 min, during which the precipitate dissolved. The reaction mixture containing MesLi (5.5mmol) was transferred *via* a double-ended needle to the previously weighed out B-alkyldimesitylborane (5mmol) in THF (15 ml) at 25°C, the mixture stirred for 1h for (**8**) and (**9**) and 2h for (**10**) and then used for further reaction.

2) **Condensation of boron stabilised carbanions with aromatic ketones.**

1,1-Diphenylethene (12).

A solution of anion (**8**) was prepared from B-methyldimesitylborane (1.38g, 5.15mmol) as in Section 1, and the solution was divided into two equal portions.

(a) Benzophenone (2.6ml of 1M solution in THF) was added at 20°C with stirring to one portion. There was an exothermic reaction and the resultant pink solution was then stirred for 24h at room temperature and quenched by addition of water. G.c., (10% SE 30, 6′ column) analysis indicated a 95% yield of (**12**). Solvent was removed at 12mm Hg and light petroleum (40°C-60°C, 15ml) was added. A precipitate of Mes_2BOH (0.56g, 80%) was collected and the solution was concentrated and distilled to give (**12**) (0.31g, 65%), b.p. 137°-139°C/12mm Hg; (lit.[72], 134°C/10mm Hg).

(b) The second portion of the solution of (8) was added to benzophenone (0.47g, 2.6mmol) with stirring. An exothermic reaction occurred, the carbanion colour was discharged and after 30 min. the solution became a dark pink. After 1h, g.c. analysis showed *ca.* 95% yield of (12). The reaction was quenched with water, the organic phase separated and the aqueous phase extracted with ether (3 x 10ml). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. Light petroleum (40°C-60°C) was added, as before, and the Mes_2BOH that precipitated was filtered off. The residue was placed on a silica column (4cm x 2cm) and eluted with petrol. The first 40ml fraction gave (12) (0.35g, 75%). δ_H, 7.23 (10H), 5.40(2H), M^+ 180. Further elution with $CHCl_3$ gave the unstable $Mes_2BCH_2C(OH)Ph_2$ (0.07g ~6%), from which it was not possible to obtain a clear m.p., mass spectrum or analysis. It had δ_H 7.24 (10H, 2 x C_6H_5), 6.79 (4H, 2 x $C_6H_2Me_3$), 2.27 (18H, Ar-CH_3), 1.88 (CH_2-B), ν_{max} (KBr), 3618, 1614cm^{-1}.

1,1-Diphenylprop-1-ene (14).

Benzophenone (3.7ml of 1M in THF) was added at 0°C to a stirred solution of anion (9), prepared as in Section 1, from B-ethyldimesitylborane (1.04g, 3.74mmol), and the solution stirred for a further 1h at 0°C, and then at room temperature for 12h. Solvent was removed at 12mm Hg, the residue dissolved in $CHCl_3$ (10ml) and left for 12h at room temperature, after which time g.c. analysis of a quenched aliquot indicated >95% formation of (14). The chloroform was removed at the pump and the product purified by elution with light petroleum from a silica gel 60 column (4cm x 3cm). The first 3ml contained almost all the mesitylene whilst the next 30ml contained product. Recrystallisation from light petroleum gave (14) as crystals (0.51g, 70%), m.p. 52°-53°C (lit.[73] 52°-53°C). Found C, 92.86%; H, 7.32%. $C_{15}H_{14}$ requires C, 92.86%; H, 7.14%. δ_H 1.72 (3H, d, J=7Hz, C=CHCH_3), 6.14(1H, q, J=7Hz, C=CHCH$_3$), 6.9-7.5 (10H, m, Ar-H).

1,1-Diphenylnon-1-ene (15).

Benzophenone (1.8ml of 1M in THF, 1.8mmol) was added to a stirred solution of carbanion (10), prepared in the usual way from B-octyldimesitylborane (0.69g, 1.9mmol), at 0°C. After 1h at 0°C the colour had changed to violet and after a further 12h at room temperature it had become pale orange. The solvent was removed at 12mm Hg, the residue dissolved in $CHCl_3$, stirred at 20°C for 3h, then concentrated. Elution from a silica column with light petroleum gave 1,1-diphenylnon-1-ene (14) (0.35g, 70%) identical in all respects (g.c. co-injection, ^{1}H nmr, i.r.) with an authentic sample.[74]

9-Methylenefluorene, Dibenzofulvene (16).

Fluorene (1.5ml of 2M solution in THF, 3.0mmol) was added in a dropwise fashion at 20°C to a stirred solution of anion (8) prepared from B-methyldimesitylborane (0.8g, 3.0mmol). The reaction was exothermic, the solution became deep red and after 5 min a white solid precipitated. After 16h at 20°C, the solid was allowed to settle and an analysis (g.c. 10% SE 30, 6') of the supernatent gave a yield of 10% of (15). The solid, which was insoluble in ether, THF, light petroleum, soluble in acetone and unstable in $CHCl_3$, was filtered off, washed with ether and dried (1.2g). The ^{1}H nmr indicated that it was lithium 1-(dimesitylborylmethyl)-1-hydroxyfluorene. δ_H 6.8-7.7 (8H, m, fluorene protons), 6.62 (4H, s, mesityl Ar-H), 2.18s, 2.05s(18H, Ar-CH_3) 1.72(B-CH_2). ν_{max} (KBr) 3100-3540, 1612, 1454cm^{-1}. Neutralisation of a small portion gave the parent alcohol m.p. 70°-72°C, which was also unstable and could not be kept. The solid lithium salt (1.0g) was dissolved in $CHCl_3$ and set aside for 16h at 20°C, after which t.l.c. indicated its complete decomposition. The chloroform was removed by low temperature evaporation and Mes_2BOH(Li) removed by dilution with light petroleum. Flash chromatography on neutral silica using light petroleum gave (16) (0.42g, 80%) as the product from the first 40ml eluted. Although (16) rapidly polymerised at room temperature[56] it was possible to obtain a g.c. comparison with an authentic sample,[56] and a ^{1}H nmr with peaks at δ 5.90(2H, s, C=CH_2), 6.8-7.35(4H, m, ArH), 7.4-7.8(4H, m, Ar-H).

9-Ethylidenefluorene (18).

Fluorenone (3.4ml, 1M in THF, 3.4mmol) was added to a stirred solution of anion (9) (from B-ethylmesitylene (0.96g, 3.45mmol)) at 0°C. Stirring was continued at 0°C for 1h, and then at 20°C for 12h. The solvent was removed at 12mm Hg at < 25°C, the residue dissolved in $CHCl_3$ (10ml) and stood for 12h at room temperature. Chloroform was removed under reduced pressure

and (18) was isolated by chromatography on silica get 60 (4cm x 3cm) using light petroleum. The product came in the first 30ml and was purified by recrystallisation from light petroleum as crystals m.p. 102-103°C (0.46g, 70%) (lit.[75] m.p. 104°C). Found C, 93.7%; H, 6.47%. $C_{15}H_{12}$ requires C, 93.7%; H, 6.3%. δ_H 2.30(2H, d, J=7Hz, C=CH-C*H*$_3$), 6.76(1H, q, J=7Hz, C=C*H*-CH$_3$) 7.1-7.4(4H, m, H-1, H-4), 7.45-7.9(4H, m, H-2, H-3).

3. Condensation of boron stabilised carbanions with aromatic aldehydes.

3.1 Untrapped reaction between anion (10) and benzaldehyde.

A solution of carbanion (10), (3mmol) was cooled to -78°C under argon and stirred. Freshly distilled benzaldehyde (0.371g, 3.5mmol) was weighed into a dry argon flushed Wheaton bottle, sealed with a septum cap, and dissolved in THF (3ml). The benzaldehyde solution was cooled to -78°C, and added slowly to the stirred carbanion solution at -78°C *via* a cooled double ended needle, and flushed with cold THF (1ml). The carbanion colour disappeared at once and the reaction was stirred for 1h at -78°C and then at room temperature for 16h.

Solvents were removed under vacuum, dry redistilled $CHCl_3$ (15ml) added and the slurry heated under reflux for 16h. Removal of the chloroform was followed by addition of light petroleum (20ml) which caused precipitation. The organic layer was removed and the precipitate was washed with petrol (20ml) and the solvent removed from the combined extracts. The products were separated on a Kieselgel 60 column using gradient elutions of light petroleum and CH_2Cl_2, then CH_2Cl_2 and Et_2O. The following products were obtained.

(i) *E-1-Phenylnon-1-ene* (0.212g, 35%), b.p. 80°-82°C/0.1mm Hg (lit.[76] 122°-126°C/1mm Hg). Found C, 89.17%, H, 10.78%, M^{+} 202.1718 $C_{15}H_{22}$ requires C, 89.1%; H, 10.9% M, 202.1721. ν_{max} 3020, 2970, 2940, 2865, 1600, 965cm^{-1}. m/z 202(35), 118(12), 117(83), 115(17), 105(10), 104(100), 91(26). ^{1}H and ^{13}C nmr in Tables 7 and 9. The coupling constant of 16Hz shows the product is the *E*-isomer. The *E*-isomer had a retention time by g.c. of 19.6 min on a programme starting at 60°C to 25°C at 10°C/min, 5 min at 25°C, then 10°C/min to 245°C. On the same programme the *Z*-isomer has a retention time of 18.36 min.*

(ii) *1-Phenylnonan-1-one.* (0.36g, 55%) had ν_{max} 2936, 1700cm^{-1}; δ_H 0.85(3H, m, C*H*$_3$), 1.27(12H, m, H-2 to H-7), 2.87(2H, t, H-8), 7.22-7.5(3H, m, Ar*H*), 7.8-8.0(2H, m, Ar-*H*), δ_C 14.01(C-9) 22.72, 24.56, 29.28, 29.57, 31.91(C-2 to C-7), 38.61(C-8), 128.09, 128.54, 132.6, 137.74 (Aromatic carbons), 199.65(C=O); m/z 218(3.4), 133(10), 120(92), 105(100). The sample was identical in all respects with an authentic sample#, b.p. 100°C/0.2mm Hg (lit.[79], b.p. 298-300°C/760mm Hg).

(iii) *Benzyl Alcohol* (0.032g, 10%). This was identical in all respects to an authentic sample.

3.2 Representative investigation, as in Table 3, of the reaction between (10) and PhCHO.

Benzaldehyde (0.482g, 0.46ml, 4.55mmol) was slowly added to a stirred solution of anion (10) (from Mes_2BOct, 1.47g, 4.05mmol) held at -96°C. The solution was cooled to -110°C for 3h, during which the red colour of the anion faded, and then allowed to warm to room temperature over 2h. Dodecane was added to the solution as internal standard, the solution made up to 50ml and divided into five 10ml aliquots.

Aliquot 1 was heated under reflux in THF for 15h. G.C. analysis gave results as in Table 3, exp. 15. The reaction mixture was separated by column chromatography (silica gel, 100-200 mesh, 25 x 3.5cm column) using gradient elution and (1) petroleum ether, (2) $CHCl_3$ and (3) ether to give the results shown in Table 3, exp. 15.

To *aliquot 2*, 1.5.ml of 3M HCl was added and the reaction stirred at room temperature for 15h, then extracted with $CHCl_3$, washed with water, dried ($MgSO_4$), filtered and evaporated (Table 3, exp. 16).

The solvent was removed from *aliquot 3*, chloroform (10ml) was added and the mixture heated under reflux for 10h (Table 3, exp. 17).

* Pure Z-PhCH=CHC$_7$H$_{15}$ was made by hydrogenation of PhC≡CHC$_7$H$_5$ over Lindlar catalyst. The *E*-isomer was produced from the same alkyne by reduction with Na/NH$_3$.[77]

Pure PhCOC$_8$H$_{17}$ produced from PhCHOHC$_8$H$_{17}$, itself made from PhCHO and C$_8$H$_{17}$MgBr.[78]

Aliquot 4 was stirred with NaOMe (1 drop) for 3 days. The solution was neutralised with CH_3COOH, extracted into chloroform, washed with water, dried ($MgSO_4$), filtered and evaporated (Table 3, exp. 18).

The *fifth aliquot* was stirred at r.t. with HCl/Et_2O for 3 days. The usual work-up gave the results shown in Table 3, exp. 19.

3.3. Reactions of benzaldehyde with $Mes_2BCHLiCH_3$ (9) using various work-up conditions. A solution of anion (9) (10mmol) was made as in Section 1, using ethyldimesitylborane (2.78g,10mmol). n-Dodecane (508.6mg) was added and the solution was divided into four equal aliquots.

Aliquot 1. The anion solution was cooled to -78°C and benzaldehyde (2.5ml of 1M solution in THF, 2.5mmol) was added slowly with stirring. The mixture was stirred for 1h at -78°C and chlorotrimethylsilane (0.27g, 2.5mmol) added. The reaction mixture was stirred for 1h at -78°C, allowed to come to room temperature over 1h and then stirred for 16h. Solvents were removed, chloroform was added and filtered from the white precipitate. The chloroform was removed and the residue separated on Kieselgel 60, 100-200 mesh, using gradient elution between light petrol (40-60°C) and chloroform. The following compounds were isolated. (1) *Trimesitylborane*[82] (136mg, 14.8%); m.p. 190°C (lit.[82] 190.5-192.5°C)! (2) *$PhCH(OSiMe_3)CH(CH_3)BMes_2$, 1-phenyl-1-trimethylsilyloxy-2-dimesitylborylpropane* (144mg, 12.6%) as colourless crystals m.p. 86-88°C. This material is unstable and neither an analysis nor an accurate mass measurement of a molecular ion (not present in m.s.) could be obtained. The compound had δ_H -0.1(9H, s, $Si(CH_3)_3$), 1.21(3H, d, J=7Hz, CH_3-CH), 2.13(12H, s, Ar-CH_3), 2.28(6H, s, ArCH_3), 2.84(1H, m, CH_3CH-CH, J=8Hz), 4.98(1H, d, J=8Hz, PhCH-O), 4.73(4H, s, Mes-H), 6.8-7.2(5H, m, C_6H_5). δ_C 0.0($SiCH_3$), 12.28(CH_3-CH), 20.87, 23.17(Ar-CH_3), 44.6(C-2), 77.43(C-1), 126.39, 127.20(C-2", C-3", C-4"), 128.34(C-3'), 137.68(C-1'), 138.67(C-2', C-4'), 145(C-1"). All peaks were *single* peaks. m/z 324(0.4), 323(1.7), 281(2), 250(22), 249(100,Mes_2B), 248(23), 219(26), 218(35), 179(61, $PhCH{=}OSiMe_3$), 177(15), 118(8, $PhCH{=}CHCH_3$), 117(11).
(3) *1-Phenyl-1-hydroxy-2-dimesitylborylpropane, $PhCHOHCH(CH_3)BMes_2$* (102mg, 10.7%) as colourless crystals, m.p. 90°C. This was an unstable compound and no analysis, accurate molecular weight (no $M^{\cdot+}$) or ^{13}C nmr could be obtained due to its decomposition. It had δ_H 1.15(3H, d, J=7Hz CH_3-CH), 2.18(12H, s, Ar-CH_3), 2.22(6H, s, Ar-CH_3), 2.7(1H, m, B-CH-CH_3), 5.02(1H, d, J=8Hz, PhCH-O), 6.6-6.9(5H, m, Ar-H), 7.0-7.5(4H, m, Ar-H). m/z 249(100), 209(11), 121(12), 117(13).
(4) *Propiophenone* (35mg, 15%), identical with an authentic sample.
(5) *Benzyl benzoate* (12.5mg, 2.4%), identical with an authentic sample.
(6) *Dimesitylhydroxyborane* (120mg, 18.3%), identical with an authentic sample.
(7) *Benzyl alcohol* (*ca.* 15%, g.c.).

Aliquot 2. This was cooled to -78°C and benzaldehyde (2.5ml of 1M solution in THF, 2.5mmol) was added and the mixture stirred at -78°C for 1h. TFAA (2.5mmol) was added slowly, the reaction mixture stirred for 1h at -78°C, allowed to warm to room temperature over 1h, and then stirred for a further 16h. Solvents were removed, chloroform added, the liquid decanted from the precipitate and washed (H_2O), dried ($MgSO_4$) and filtered. The product was a complex mixture that contained no identifiable compounds such as $PhCH(OCOCF_3)CH_2CH_3$ or $PhCOCH_2CH_3$.

Aliquot 3. This was cooled to -78°C and benzaldehyde added as for aliquots 1 and 2. The mixture was stirred at -78°C for 1h and then oxidised, also at -78°C, by addition of 5M NaOH (5ml) and 50% H_2O_2 (5ml). The reaction was stirred for 1h at -78°C, allowed to warm to room temperature over 1h, then stirred for 16h. Solvents were removed, chloroform (10ml) was added and the extract washed with saturated sodium chloride, water, dried ($MgSO_4$) and evaporated. G.c. (5%, SE30 and carbowax) showed only MesH and MesOH. The residue was separated on silica gel, 100-200 mesh, (10g) by gradient elution using petroleum and chloroform. From this was isolated *1-phenyl-1,2-propanediol* [61-63] (152mg, 40%) m.p. 70°C, as a mixture of *erythro* and *threo*- isomers in the ratio of 10:1. The ratio was readily established as the *erythro* form had H-1 at δ 4.75, d, J=3.4Hz and the *threo* had H-1 at δ 4.35, d, J=7.2Hz in accord with

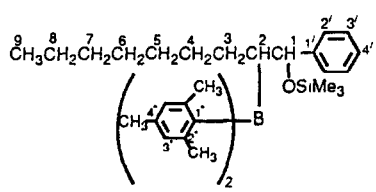
the literature. δ_H 1.03(3H, d, J=7Hz, C*H*$_3$-CH), 2.51(2H, s, O*H*), 3.96(1H, m, CH-C*H*-CH$_3$), 4.35(d, J=7.2Hz) < 10% and 4.75 (d, J=3.4Hz, PhC*H*CH$_3$) together one proton, 7.25(5H, s, C$_6$*H*$_5$). δ_C 16.7 (*C*H$_3$, *erythro*), 18.7(*C*H$_3$, *threo*-), 71.3(CH$_3$*C*HO, *erythro*), 72.2(CH$_3$*C*HO *threo*), 77.2 (PhC*H*O, *erythro*), 79.5(PhC*H*O, *threo*), 126-128 (Aromatic C), 140.5(C-1', *erythro*), 141.1(C-1', *threo*), m/z 108(91), 107(76), 79(100).

Aliquot 4. This was treated with benzaldehyde at -78°C as for aliquots 1-3. The mixture was stirred at -78°C for 22h, allowed to come to room temperature over 1h, stirred for 16h and then solvents evaporated off. Chloroform (10ml) was added and the mixture heated under reflux for 12h. Chloroform was then removed and the residue separated on a silica gel, 100-200 mesh (25g) column (15 x 2.5cm) eluted with light petroleum/chloroform mixtures. From this was recovered only *PhCHOHEt* (84mg, 25%), identical with an authentic sample, *PhCOEt* (mixed with a little Mes$_2$BOEt from the ethanol in the AR chloroform) and Mes$_3$B (18.5%).

4. ***Synthesis of (31a) by the reaction of (10) with benzaldehyde followed by reaction with chlorotrimethylsilane.*** Benzaldehyde (0.2650g, 2.5mmol) and carbanion (**10**) (3mmol) were reacted together as in section 3.1. The reaction was stirred for 2h at -78°C and a solution of freshly distilled chlorotrimethylsilane (0.3368g, 3.1mmol) in THF (10ml) cooled to -78°C, was added under argon pressure through a cooled double-ended needle, followed by a further portion of THF (2ml) at -78°C from the same flask. The pink reaction mixture was stirred at -78°C for 1h, then at room temperature for 16h. The solvents were removed under pressure to leave a yellow slurry, to which was added light petroleum (30ml) to give a white precipitate and a yellow solution. The mixture was centrifuged, the petroleum layer removed and evaporated to give a yellow liquid (1.42g), which was separated on two 2mm alumina Chromatotron plates which were eluted with petroleum ether. This gave a colourless liquid (1.21g) which solidified, and on recrystallisation from light petroleum gave *erythro-1-phenyl-1-trimethylsilyloxy-2-dimesitylborylnonane,* (**31e**) (1.05g, 78%), m.p. 81-82°C. Found C, 80.21%, H, 9.95%; $C_{36}H_{53}SiOB$ requires C, 80.0%; H, 9.8%. δ_H -0.10(9H, s, Si(C*H*$_3$)$_3$, 0.86(3H, t, C*H*$_3$-CH$_2$), 1.10(10H, m, CH$_3$(C*H*$_2$)$_5$), 1.54(2H, m, C*H*$_2$-CH-B), 2.28(18H, s, Ar-C*H*$_3$), 2.70(1H, m, -C*H*BMes$_2$), 4.85(1H, d, J=11Hz, C*H*-OSiMe$_3$), 6.75(4H, s, Mes-*H*), 7.10(5H, m, C$_6$*H*$_5$). δ_C* 0.3(Si(*C*H$_3$)$_3$), 14.2(C-9), 21.5(C-5"), 22.8(C-8), 23.3(C-7), 29.0(C-6), 29.7(C-5), 31.9(C-4), 33.0(C-3), 50.1(C-2), 78.4(C-1), 126.6(C-4'), 127.4(C-3'), 127.6(C-2'), 128.5(C-3"), 137.8(C-2"), 139.1(C-4"), 142.3(C-1'), 145.9(C-1").

5. ***Reactions of (31e).*** (i) *Pyrolysis of (31e).* Compound (**31e**), (0.81g, 1.5mmol) was weighed into the end bulb of a Kugelrohr short path, bulb to bulb distillation apparatus, which was then evacuated to 0.1mm Hg and the temperature raised to 150°C. A clear liquid distilled over and this was taken into light petroleum and chromatographed on silica gel using light petroleum as eluent. *1-Phenylnon-1-ene* (0.182g, 60%) was isolated as a 55:45 mixture of *E*:*Z* isomers. (ii) *Oxidation of (31e).* Compound (**31e**) (0.2435g, 0.45mmol) was dissolved in THF (5ml) and the stirred solution held at 20°C whilst first 5M NaOH (0.7ml) then methanol (2ml) then hydrogen peroxide (60% w/v 0.6ml) were added dropwise and the mixture refluxed for 4h at 60°C. It was extracted with ether (30ml), the ether layer washed with water (3 x 10ml), dried (MgSO$_4$), filtered and evaporated to give crude product (0.1784g), which was separated by chromatography on silica gel with gradient elution from 100% petroleum ether to 100% ether. This gave E-*1-phenylnon-1-ene* (0.022g, 24%) pure by ^{1}H nmr and g.c., *1-phenylnonan-1-one* (0.0271g, 30%), *1-phenylnonan-1-ol* (0.0153g, 16%) identical with an authentic sample and *erythro-1-phenyl-1,2-dihydroxynonane* (0.235g, 24%). δ_H 0.86(3H, m, C*H*$_3$CH$_2$), 1.25(m, CH$_2$ of heptyl chain), 4.52(1H, d, J=4Hz, PhC*H*OH-), 7.2(5H, s, C$_6$*H*$_5$).

*Numbering as shown



(iii) *Reaction of (27) with tetra-n-butylammonium fluoride.*

A solution of Bu_4NF (stored over 3A molecular sieves under argon) (0.986M in THF, 4.1ml, 4mmol) was added to a stirred solution of (27) (0.108g, 2mmol) at -78°C, and the reaction stirred at -78°C for 1h. No reaction occurred and therefore the mixture was allowed to warm to room temperature and stood for 16h. Solvents were removed under reduced pressure and light petroleum (30ml) added. A white precipitate formed from which the petrol was decanted and concentrated to *ca.* 10ml. This was applied directly to a column of silica gel made up in petrol, and the column eluted with light petroleum, dichloromethane and ether. The following products were isolated: (i) *1-phenylnon-1-ene* (0.186g, 46%), *E*:*Z* was > 98: < 2 by g.c. analysis), (ii) *1-phenylnonan-1-one* (0.074g, 17% identical with an authentic sample), (iii) benzyl alcohol (0.032g, 15%) identical with an authentic sample, (iv) *1-phenylnonan-1-ol* (0.035g, 8%), identical by ^1H nmr and g.c. with an authentic sample.

6. Stereoselective syntheses of E-alkenes by reaction of (31) and analogues with aq.HF/CH_3CN.

6.1. Procedure A.

A solution of aromatic aldehyde (2.1mmol) in THF (3ml) in a Wheaton flask at -78°C was added to a stirred solution of the appropriate carbanion (3mmol) at -78°C using argon pressure and a cooled double-ended needle. The Wheaton flask and needle were flushed with THF (3ml) at -78°C and this was added to the reaction mixture. A solution of chlorotrimethylsilane (0.3368g, 3.1mmol) in THF (3ml) was made up in an argon flushed Wheaton bottle, sealed with a rubber septum and cooled to -78°C. The solution was added to the stirred reaction mixture at -78°C by means of a double-ended needle and washed through with cold THF (3ml). The reaction mixture was then stirred for 1h at -78°C after which the rubber septum was removed and a solution of aqueous HF (40%, 1ml) in acetonitrile (20ml), made up in a pvc beaker, was added dropwise with good stirring at -78°C. The reaction mixture decolourised at once and the cooling bath was removed. The reaction mixture was stirred at room temperature for 30 min then poured into light petroleum (30ml), the petrol solution was washed with water (3 x 15ml), dried ($MgSO_4$), filtered and evaporated to give crude product, normally as a yellow liquid. Alkene products were isolated using a silica Chromatotron from which the alkenes eluted with petrol except when the product contained a 4-nitro- or a 4-methoxyphenyl group for which a 90:10 mixture of petrol:dichloromethane was used. Mesitylene was removed from products by pumping for 16h at 1mm Hg.

The alkenes prepared by this process were as follows.

(i) *1-Phenylnon-1-ene* (0.403g, 95%) as a mixture of 84*E*:16*Z* (g.c.).

(ii) *1-(4-Chlorophenyl)non-1-ene* (0.432g, 87%) as a mixture of 76*E*:24*Z* (g.c.) (g.c. programme, 60° to 220°C at 10°C/min, 220°C for 20 min., 220°C to 245°C at 10°C/min, 245°C for 5 min. Retention times : *E*-isomer, 26.19 min, *Z*-isomer, 22.90min). Found, C, 76.0%; H, 8.8%, $C_{15}H_{21}Cl$ requires C, 76.1%; H, 8.9%. $M^{\cdot+}$, 236.1331; 238.1306. $C_{15}H_{21}{}^{35}Cl$ requires 236.1331; $C_{15}H_{21}{}^{37}Cl$ requires 238.1302. m/z 238(12), 236(39), 153(20), 151(67), 140(40), 138(100), 125(16), 116(23), 115(28). ν_{max} (film) 2980, 2940, 2860, 1495, 1095, 965 cm^{-1}. For ^1H, ^{13}C nmr spectra of the *E* -isomer see Tables 7 and 9, and for the *Z*-isomer see Tables 8 and 10.

(iii) *1-(4'-Methylphenyl)non-1-ene* (0.390g, 86%) as a 89*E*:11*Z* mixture (g.c. programme as for (ii), retention time of *the E* -isomer is 21.63 min and of the *Z* is 19.97 min). $M^{\cdot+}$, 216.1876, $C_{16}H_{24}$ requires 216.1878. m.s. 216(34), 132(13), 131(100), 118(62), 116(12), 105(15), 91(11), ν_{max} (film) 2980, 2940, 2882, 1470, 965 cm^{-1}. For the ^1H and ^{13}C nmr of the *E* -isomer see Tables 7 and 9, and for the *Z*-isomer see Tables 8 and 10.

(iv) *1-(4'-Methoxyphenyl)non-1-ene* (0.409g, 84%) as the *E* -isomer only by g.c. and ^1H nmr (g.c. programme as in (ii), retention time = 28.05 min). $M^{\cdot+}$ 232.1827, $C_{16}H_{24}O$ requires 232.1827. m/z 232(46), 148(12), 147(100), 134(17), 121(20), 115(9), 91(15). For ^1H and ^{13}C nmr see Tables 7 and 9.

(v) *1-(4'-Nitrophenyl)non-1-ene* (0.337g, 65%) was isolated as a yellow liquid, b.p. 121°C/0.1mm Hg as a 93*E* :7*Z* mixture (g.c. programme, 60°-245°C at 10°C/min, held at 245°C for 20 min, retention time of *E* -isomer was 33.16 min and of the *Z* was 28.46 min). $M^{\cdot+}$ 247.1566, $C_{15}H_{21}NO_2$ requires 247.1572. m/z 247(19), 147(100), 137(17), 116(51), 115(43), 91(14).

ν_{max} (film), 2983, 2940, 2881, 1600, 1520, 1345, 1110, 970, 955, 860 cm^{-1}. For ^1H, ^{13}C nmr of the *E* -isomer see Tables 7, 9, and for the *Z*-isomer see Tables 8 and 10.
(vi) *1-(2',4',6'-Trimethylphenyl)non-1-ene* (0.410g, 80%) was isolated as a colourless liquid b.p. 115°C/0.1mm Hg. The product was one isomer by g.c. (60° to 220°C at 10°C/min, 10 min at 220°C, 220°-245°C at 10°C/min, 10 min at 245°C) with a retention time of 25.10 min. The ^1H nmr (Table 7) and i.r. showed it to be the *E* -isomer. Found, C, 88.14%; H, 11.3%, $M^{\cdot+}$ 244.2202, $C_{18}H_{28}$ requires C, 88.5%; H, 11.5%, M, 244.2191. ν_{max} (film), 3020, 2960, 2940, 2860, 1614, 1470, 1380, 970, 850 cm^{-1}. (viii) *1-Phenylprop-1-ene* (0.249g, 93%) was identified by comparison of ^1H nmr and g.c. (60° to 115°C at 10°C for 8 min, 115°C to 180°C at 10°C/min, 180°C for 3 min, on a 5% carbowax 20M Chromosorb W AW/DMCS 100-200 mesh). The *E:Z* ratio was 84:16.

6.2. Procedure B. With isolation of silylated intermediates. *The process was exactly the same as procedure A (Section 6.1) up to and including the addition of chlorotrimethylsilane.* The reaction was stirred at -78°C for 1h, allowed to warm to room temperature and then stirred for 16h. Volatiles were removed at the pump, light petroleum (30ml) added and then decanted from the precipitate using a double-ended needle. The petroleum extract was concentrated and the crude product applied as a petrol solution to an *alumina* Chromatotron plate (2 runs on a 2mm plate) or alternatively to a column of neutral alumina deactivated by addition of 6% water by weight, made up in petrol, and the product eluted with petrol (Chromatotron) or petrol/dichloromethane, (90:10) (column). The product was cooled to -78°C in a 100ml r.b. flask containing a magnetic follower, and a solution of aq. hydrofluoric acid (40%, 1ml) in acetonitrile (20ml) was added and the mixture vigorously stirred. The cooling bath was removed, the solidified reaction mixture allowed to warm to room temperature and then stirred for 30 min. The reaction mixture was poured into petrol (30ml) and the lower layer removed and further extracted with petrol (3 x 20ml). The combined petrol extracts were washed with water (3 x 20ml), dried ($MgSO_4$), filtered and evaporated to give crude product. The alkene products were isolated by Chromatotron, as in procedure A. The following compounds were made by procedure B (characterisations previously given above).
(i) *1-Phenylnon-1-ene* (0.356g, 84%), *E:Z* = 97.3 (g.c.).
(ii) *1-(4-Chlorophenyl)non-1-ene* (0.417g, 84%), *E:Z* = 95:5 (g.c.)
(iii) *1-(4-Methylphenyl)non-1-ene* (0.374g, 83%), *E:Z* = 95:5 (g.c.).
(iv) *1-(4-Nitrophenyl)non-1-ene* (0.384g, 74%), *E:Z* = 98.2 (g.c.).
(v) *1-(Phenylprop-1-ene)* (0.169g, 78% calc. by g.c. of an authentic sample), *E:Z* = 98.2.

7. Stereoselective production of Z-alkenes by trapping with trifluoroacetic anhydride (TFAA).

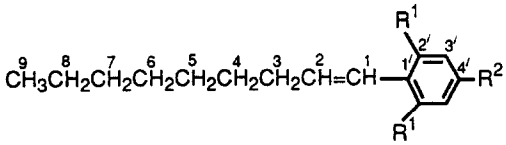
A solution of aromatic aldehyde (2.5mmol) in THF (3ml) at -78°C was added *via* a cooled double-ended needle under argon pressure to a well stirred solution of the carbanion (prepared as previously described) (3mmol) held at -110°C (liquid nitrogen-ether). The aldehyde flask and double-ended needle were flushed through with THF (3ml) at -78°C and stirred for the appropriate time (Table 4) at -110°C. A precooled solution of TFAA (0.6301g, 3mmol) in THF (3ml) was slowly added *via* a cooled double-ended needle under argon pressure to the stirred reaction mixture at -110°C, on which the colour changed from pink to yellow. The reaction mixture was stirred under argon at -110°C, at -78°C for 4h, and at room temperature for 16h. The volatiles were removed by pumping and light petroleum added to the residues. The petroleum solution was decanted and the alkene products isolated using a Chromatatron as described in Section 5, procedure A. Identification of the products was done by comparison with the characterised products obtained in section 5. The ^1H and ^{13}C nmr spectra of the *Z*- alkenes are given in Tables 8 and 10 and of the E-alkenes in Tables 7 and 9. The following products were obtained.
(i) *1-Phenylnon-1-ene* (0.389g, 77%), *Z:E* = 90:10 (g.c.).
(ii) *1-(4-Chlorophenyl)non-1-ene* (0.432g, 73%), *Z:E* = 80:20 (g.c.).
(iii) *1-(4-Methylphenyl)non-1-ene* (0.40g, 78%), *Z:E* = 96:4 (g.c.).
(iv) *1-(4-Methoxyphenyl)non-1-ene* (0.441g, 76%), *Z:E* = 91:9 (g.c.)
(v) *1-(4-Nitrophenyl)non-1-ene* (0.457g, 74%), *Z:E* = 31:69 (g.c.)
(vi) *1-(2',4',6'-Trimethylphenyl)non-1-ene* (0.458g, 75%), *Z:E* = 93:7 (g.c.)
(vii) *1-Phenylprop-1-ene* (0.227g, 77%, g.c. yield) *Z:E* = 93:7 (g.c.)

Table 7.

^1H nmr of product E*-alkenes*[a]

R^1	R^2	δ ppm, (multiplicity, J/Hz)							
		H-9	H-4-8	H-3	H-2	H-3	H-2′	H-3′	Other
H	H	0.86(t)	1.24(m)	2.14(m)	6.15(d.t.,16,6)	6.33(d,16)		7.20(m)[b]	-
H	Cl	0.86(t)	1.23(m)	2.14(m)	6.12(d.t.,16,6)	6.28(d,16)		7.15(s)	-
H	CH_3	0.86(t)	1.23(m)	2.10(m)	6.02(d.t.,16,6)	6.18(d,16)	6.94(d,8)	7.12(d,8)	2.20(s)[c]
H	OCH_3	0.86(t)	1.26(m)	2.17(m)	6.00(d.t.,16,6)	6.29(d,16)	6.77(d,8)	7.22(d,8)	3.70(s)[d]
H	NO_2	0.86(t)	1.28(m)	2.22(m)	6.40m		7.39(d,8)	8.10(d,8)	-
Me	Me	0.88(t)	1.29(m)	e	5.56(d.t.,16,6)	6.23(d,16)	-	6.77(s)	2.19(s)[e]

[a] In this and subsequent Tables of nmr data the numbering and nomenclature is as shown.



[b] Includes H-4′. [c] Ar-CH_3. [d] Ar-OCH_3. [e] Ar-CH_3.

Table 8.

^1H nmr of product Z*-alkenes.*

R^1	R^2	δ ppm, (multiplicity, J/Hz)							
		H-9	H-4-8	H-3	H-2	H-1	H-2′	H-3′	Other
H	H	0.85(t)	1.24(m)	2.29(m)	5.60(d.t.,12,7)	6.36(d.t.,12,7)	7.22(m)[a]		-
H	Cl	0.88(t)	1.28(m)	2.27(m)	5.69(d.t.,12,7)	6.36(d.t.,12,1)	7.28(m)		-
H	CH_3	0.88(t)	1.28(m)	2.28(m)	5.63(d.t.,12,7)	6.39(d.t.,12,1)	7.18(m)		2.35(s)[b]
H	OCH_3	0.85(m)	1.26(m)	2.24(m)	5.51(d.t.,12,7)	6.40m	6.73(d,9)	7.10(d,9)	3.70(s)[c]
H	NO_2[d]	0.85(t)	1.26(m)	2.25(m)	5.81(d.t.,12,7)	e	7.36(d,9)	8.14(d,9)	-
CH_3	CH_3	0.84(t)	1.23(m)	f	5.67(d.t.,12,7)	5.21(d.t.,12,0.5)	-	6.81	2.16,2.18[b]

[a] Includes H-4′. [b] Ar-CH_3. [c] Ar-OCH_3. [d] Taken from a 31:69 mixture of *Z*:*E* isomers.
[e] Masked by signal of *E*-isomer. [f] Masked by Ar-CH_3 signal.

Table 9

^{13}C nmr data for product E*-alkenes*

R^1	R^2	Chemical Shift (ppm)													
		C-9	C-8	C-7	C-6	C-5	C-4	C-3	C-2[a]	C-1[a]	C-1'[a]	C-2'[a]	C-3'[a]	C-4'[a]	R^1	R^2
H	H	14.13	22.77	29.33	29.33	29.53	31.96	33.16	131.06	129.92	138.08	128.46	126.08	126.76	-	-
H	Cl	14.13	22.77	29.34	29.34	29.83	31.96	33.13	131.87	130.03	136.55	128.60	127.14	132.41	-	-
H	CH_3	14.13	22.80	29.37	29.37	29.63	32.02	33.18	129.97	129.80	136.25	129.16	125.92	135.35	-	21.08
H	OCH_3	14.12	22.76	29.33	29.33	29.68	31.98	33.12	129.22	129.03	130.98	127.04	113.98	158.78	-	55.19
H	NO_2	14.10	22.71	29.10	29.22	29.22	31.87	33.28	128.16	136.71	144.56	126.35	123.93	146.52	-	-
CH_3	CH_3	14.13	22.83	29.34	29.34	29.75	32.08	33.57	127.50	135.58	134.91	135.72	128.50	135.42	20.88	20.88

[a]The assignment of these carbons was based on comparisons with the calculated[80] or reported[81] values in the corresponding styrenes $ArCH{=}CH_2$ and ArCH=CHR.

Table 10

^{13}C nmr data for product Z*-alkenes*

R^1	R^2	Chemical Shift (ppm)													
		C-9	C-8	C-7	C-6	C-5	C-4	C-3[a]	C-2[a]	C-1[a]	C-1'[a]	C-2'[a]	C-3'[a]	C-4'[a]	R^1	R^2
H	H	14.10	22.74	28.70	29.28	29.49	30.07	31.93	133.18	128.81	137.94	128.81	128.11	126.42	-	-
H	Cl	14.01	22.62	28.55	29.13	29.24	29.83	31.79	133.83	133.83	136.20	129.94	128.19	132.10	-	-
H	CH_3	14.10	22.71	28.75	29.28	29.42	30.12	31.93	132.51	132.51	135.99	128.81	128.72	135.88	-	21.13[b]
H	OCH_3	14.09	22.7	28.69	29.07	29.27	29.83	31.73	131.61	132.24	137.92	128.28	112.57	158.54	-	55.08[c]
H	NO_2[d]	14.10	22.71	e	e	e	e	e	128.66	137.21	144.52	127.06	123.49	146.49	-	-
CH_3	CH_3	14.10	22.71	28.72	29.25	29.25	29.78	31.90	128.43	133.33	134.03	135.90	127.84	135.73	20.26	20.96

[a]As note a, Table 9. [b]Ar-CH_3. [c]Ar-OCH_3. [d]Taken from an *E*:*Z* mixture, 69:31. [e]Signals very close to those of the *E*-isomer.

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