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Hindered Organoboron Groups in Organic Chemistry. 25. The Condensation of Aliphatic Aldehydes with Dimesitylboryl Stabilised Carbanions to give Alkenes.[1,2]

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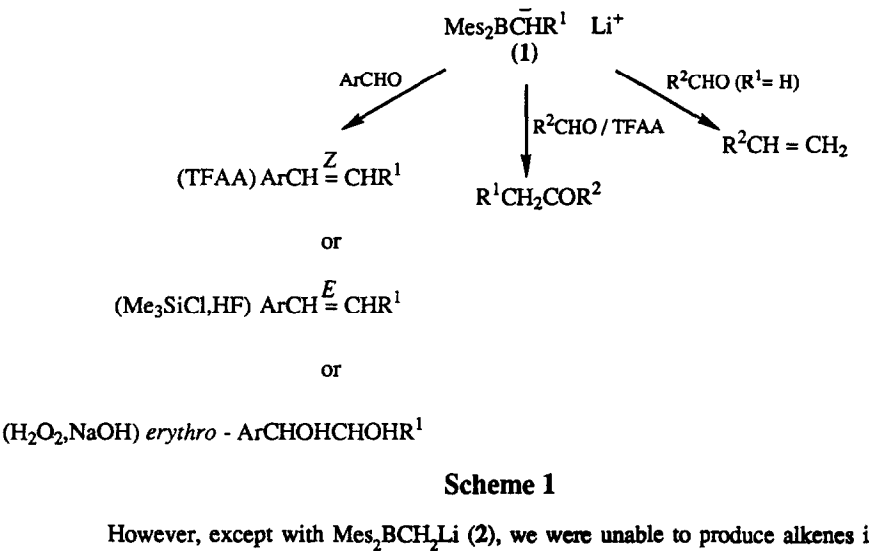
Abstract. In the presence of protic acids the condensation of aliphatic aldehydes with dimesitylboryl stabilised carbanions results in alkenes. In the presence of strong acids such as HCl or CF_3SO_3H, the products contain > 90% of *E*-alkenes in all cases tried. When acetic acid is used, then *Z*-alkenes may result predominantly, particularly in the cases of R^5CHO and R^1CHO.

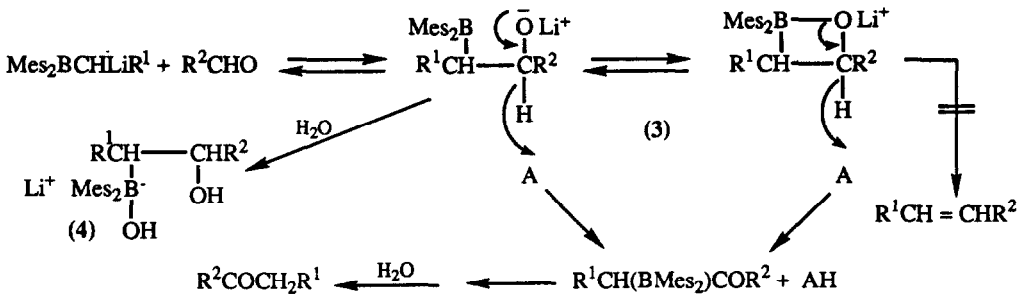
We have previously shown[1-5] that the condensation of dimesitylboryl stabilised carbanions with aldehydes is a versatile and useful process (Scheme 1).



Scheme 1

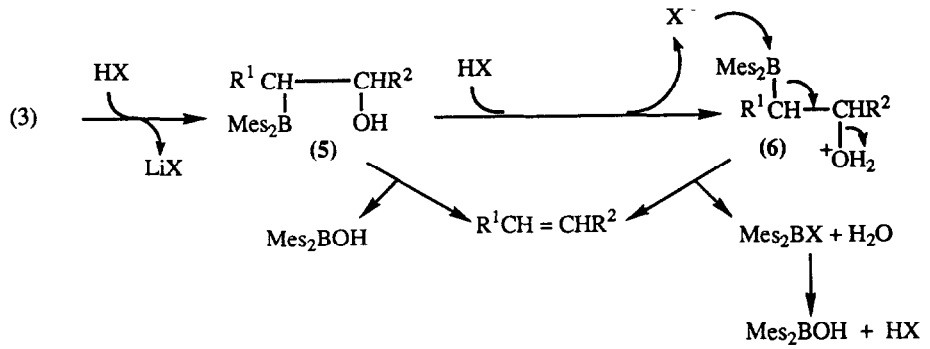
However, except with Mes_2BCH_2Li (2), we were unable to produce alkenes in good yields from the reactions of $Mes_2BCHLiR^1$ (1) with aliphatic aldehydes. In general, in the presence of a hydride receptor (A) such as trifluoroacetic anhydride (TFAA), N-chlorosuccinimide (NCS) or even starting aldehyde, a unique redox reaction occurs

that finally yields ketones. This process we have formulated as in Scheme 2.



Scheme 2

If Scheme 2 were correct, the electron rich nature of (3) would be the cause of the preference for hydride transfer, as compared with elimination to give alkenes. Therefore, neutralisation of (3) might encourage alkene formation. However, addition of Lewis acids did not achieve this end and neither did the addition of water.[1] The latter failure may have been due to the production of (4) from the lithium hydroxide evolved in the reaction of (3) with water. We therefore argued that the addition of aldehyde together with a protic acid, HX, might give rise to (5) or (6), either of which could readily give alkene (Scheme 3).



Scheme 3

The reaction of HX with (3) would give the neutral species (5) which could directly eliminate. Excess of (strong) acid might lead to further protonation to give (6) which could readily yield alkene. It should be noted that according to Scheme 3, only a catalytic excess of acid should be required. It may also be inferred that (6) will exist mainly in that conformer in which the two electron deficient centres are *anti* to each other, thus encouraging *anti* rather than *syn*-elimination.

The idea of adding an aldehyde together with a proton source to an anion is not readily acceptable. The process depends upon preferential reaction of the anion with the aldehyde rather than with the proton source which, particularly if it is an acid, rapidly discharges the anion. However, it has been shown previously that polycondensation of an aldehyde with an anion may be controlled with water,[6] and various aqueous work-ups of conjugate addition reactions have been spoiled by the water generating the ketone which reacted preferentially with excess organometallic reagent, *which has not been destroyed.*[7] Furthermore, subsequent to our work,[5] we found brief mention of the use of acetic acid to affect the stereochemistry of condensations of $(MeO)_2P(O)CH_2CO_2Me$/LDA.[8]

We therefore tried the low temperature (-127°C) addition of a mixture of aldehyde and acetic acid to $Mes_2BCHLiHept$, (7), as a representative dimesitylboryl stabilised carbanion. To our pleasure, ketone formation was completely inhibited and alkenes resulted. Thus, as a matter of some generality, and possible surprise, *aldehydes may be condensed with carbanions in the presence of protic acid.* The results of our initial study using acetic acid are given in Table 1.

Table 1

Reactions of $Mes_2BCHLiHept$ with RCHO/CH_3CO_2H (1 equiv)

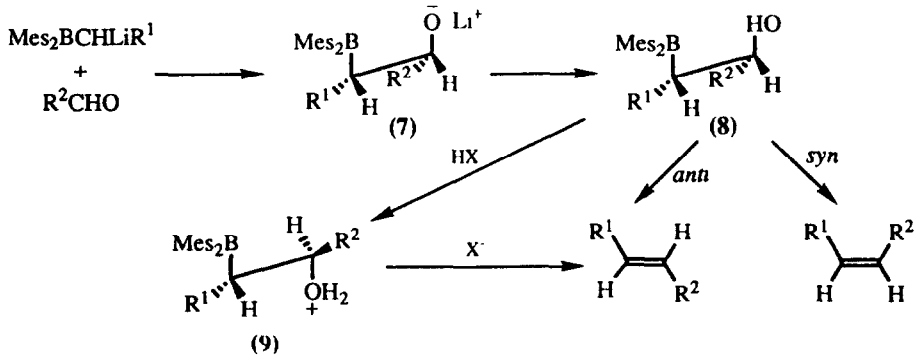
Exp.	R	Yield %[a]	*E*:*Z*[b]
1	Me	52	42:58
2	Et	75	49:51
3	Hept	77	65:35
4	Me_2CH	87	69:31
5	Bu^t	79	0:100
6	Chx[c]	83	10:90

[a]Yields are of isolated, purified RCH=CHHept. [b]Capillary g.c./i.r. [c]Chx=cyclohexyl.

The isolated yields (unoptimised) of alkenes are generally acceptable, but in most of the cases tried, the reaction was not stereoselective. However, more hindered aldehydes did give *Z*-alkene either exclusively (experiment 5) or as the major product (experiment 6), suggesting that, at least for these two cases, both the initial condensation and the elimination are under good stereochemical control. Clearly, for experiments 1-4, either the condensation or the elimination is not stereoselective.

In the reactions of aromatic aldehydes, the initial reaction was highly stereoselective[2,3] and it was the elimination that had to be controlled. We argued that if the condensation of aliphatic aldehydes followed the same route as that of aromatic aldehydes to give *erythro*-products (7) and then (8), an inference it must be stressed not backed by direct observation, then the presence of an excess of acid, particularly strong acid, might produce *E*-alkene, if the two electron deficient centres in (9) position themselves *anti* to each other

(Scheme 4). This had been the situation when the initial condensation products of aromatic aldehydes were trapped with chlorotrimethylsilane and then reacted with aq. HF.[2,3]



Scheme 4

The least stereoselective experiment in Table 1 is experiment 2, the condensation of propanal with (7), and we therefore chose to try to affect that experiment by variations in the quantity and type of protic acid used. The results are presented in Table 2.

Table 2

Condensation of EtCHO with (7) in the presence of acid to give EtCH=CHHept

Exp.	Acid	Equiv. of acid	% Yield[a]	*E*:*Z*[b]
2[c]	CH_3CO_2H	1 0	75	49:51
7	CH_3CO_2H	2.5	73	61:39
8	CF_3CO_2H	2.5	71	70:30
9	CF_3SO_3H	2.5	66	78:22
10	CF_3SO_3H	5.0	49	91:9
11	HCl[d]	2.5	68	84:16
12	HCl[d]	5.0	57	86:14

[a]Yield of isolated, purified alkene. [b]Ratio by g.c./i.r [c]From Table 1 for comparison. [d]As an ethereal solution.

The presence of even 2.5 equivalents of acid (experiments 7, 8, 9, 11) affects the yield very little but does, however, strongly enhance the proportion of *E*-undec-3-ene in the product. Use of five equivalents of strong acid does cause a lowering of yield (experiments 10, 12) but, in one case (experiment 10), gives alkene with strongly enhanced stereoselectivity. In fact, the excess acid should be needed only in catalytic quantities, and if our production of carbanion is less than quantitative, as is sure, then one equivalent of acid will always be effectively a small excess. In our general survey, presented in Table 3, this was our standard procedure in order not to lower yields, which were not, however, optimised.

Table 3

Condensation of $Mes_2BCHLiR^1$ with R^2CHO in the presence of HX to give $R^1CH=CHR^2$

Exp.	R^1	R^2	HX	Equiv. of HX	% Yield[a]	*E*:*Z*[b]
13	Me	$PhCH_2$	CH_3CO_2H	1.0	74	14:86
14	Me	$PhCH_2$	CF_3SO_3H	1.2	69	93:7[c]
15	Me	Chx	CH_3CO_2H	2.0	67	63:37
16	Me	Chx	HCl	1.2	72	97:3
17	Me	Bu(Et)CH	CH_3CO_2H	1.0	52	24:76
18	Me	Bu(Et)CH	CF_3SO_3H	1.0	57	95:5
19	Me	Oct	CH_3CO_2H	1.0	77	44:56
20	Me	Oct	CF_3SO_3H	1.0	48	90:10
21	Pr	Chx	CH_3CO_2H	1.0	61	17:83
22	Pr	Chx	HCl	1.0	64	95:5
23	Pr	Bu(Et)CH	CH_3CO_2H	1.0	74	4:96[d]
24	Pr	Bu(Et)CH	CF_3SO_3H	1.0	59	92:8[d]
5[e]	Hept	Bu^t	CH_3CO_2H	1.0	79	0:100
25	Hept	Bu^t	HCl	1.0	72	92:8
1[e]	Hept	Et	CH_3CO_2H	1.0	75	49:51
10[f]	Hept	Et	CF_3SO_3H	5.0	49	91:9
6[e]	Hept	Chx	CH_3CO_2H	1.0	83	10:90

[a] Yields of isolated, purified alkenes. [b] Capillary g.c./i.r. [c] The figures underlined are those with $\geq$ 90% of *E* or *Z*-alkenes. [d] Established by ^{13}C nmr/ir. [e] From Table 1 for comparison. [f] From Table 2 for comparison.

From Table 3 it is clear that *by use of strong acid, alkene products containing > 90% of* E*-alkenes were always obtained, and therefore our process complements the Wittig reaction.* Use of acetic acid can lead to mixtures of *Z*- and *E*-alkenes. However, when hindered aldehydes are used, then *Z*-alkenes predominate, often to the extent of 90% or more (experiments, 23, 5, 6). In three more cases *Z*-alkenes are present to the extent of 75% or more (exp. 13, 17, 21). There are some astonishing reversals of stereochemistry evident in Table 3 (experiments 23, 24; 5, 25) and in *all* cases strong acid gives much more of the *E*-alkene.

For comparison, we present, in Table 4, our results using [i], the standard Wittig reaction and [ii], the Schlosser[9] modification of the Wittig reactions[10] of $Ph_3\overset{+}{P}-\overset{-}{C}HHept$ (**8**).

Table 4

Ratios of E:Z alkenes from the condensations of $Ph_3PCH_2Hept\ Cl^-$ with R^2CHO to yield $HeptCH{=}CHR^2$

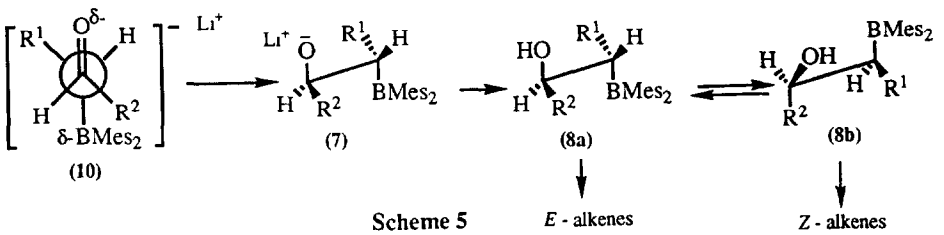
	Wittig reaction			Schlosser modification		
R^2	*Exp.*	E:Z[a,b]	*Yield %*[c]	*Exp.*	E:Z[a,d]	*Yield %*[c]
Me	27	34:66	67	28	77:23	42
Et	29	0:100[e]	73	30	100:0[e]	46
Hept	31	16:84	81	32	86:14	61
Me_2C	33	7:93	72	34	76:24	48
Bu^t	35	0:100	70	36	0:100	59
Chx	37	6:94	80	38	47:53	52

[a] 1 equivalent of PhLi. [b] Established by capillary g.c. [c] Isolated, purified product. [d] 2 equivalents of PhLi. [e] Established by ^{13}C nmr/ir.

The Wittig reaction is claimed to yield *Z*-alkenes from the condensation of non-stabilised ylids with aliphatic aldehydes. However, ylid (**8**) with a long alkyl chain gives *E, Z* mixtures, except in two cases (experiments 29, 35). Using the Schlosser-Wittig procedure the production of pure *E*-alkenes was achieved in only one case (experiment 30) and with pivaldehyde there was no reversal at all in the stereochemistry (experiments 35, 36). This is in great contrast with our procedure (Table 3, experiments 5, 25). In general, the Schlosser procedure gave > 90% of *E*-alkene in one case only, in further contrast to the present process which yields *E*-alkene as > 90% of the product in all cases.

Discussion.

As emphasised previously, we have no direct evidence of the stereochemistry of intermediate (**3**) (Scheme 3). However, our results indicate a highly stereoselective initial condensation in all cases. We suggest that, in the transition state, the negatively charged atoms, oxygen and boron, position themselves *anti*, as do the two alkyl groups R^1 and R^2, leading to a transition state resembling (**10**) (Scheme 5), which would yield the *erythro* alkoxide (**7**). This has close analogy with the reactions of aromatic aldehydes in which the intermediate has been shown to be *erythro* by direct examination. Protonation of (**7**) leads to neutral (**8**), elimination from which will depend on the conformer population. When R^2 is large, *e.g.* Bu^t, then the conformer (**8b**), with R^2 *anti* to $BMes_2$, will predominate, and undergo *syn*-elimination to give *Z*-alkenes. When R^2 is smaller, a greater contribution from conformer (**8a**) is possible, leading to increased proportions of *E*-alkenes.



Scheme 5

Conclusion.

The versatility of the condensation of dimesitylboryl stabilised carbanions with aldehydes was initially illustrated in Scheme 1. To this can now be added the stereoselective production of *E*-alkenes from all aliphatic aldehydes tried and of *Z*-alkenes from R^1CHO and R^2CHO.

Experimental

Instrumentation.

Infra-red spectra were recorded on a Unicam SP1050 i.r. spectrometer using the polystyrene absorbances at 1602 cm^{-1} and 1495 cm^{-1} as references. Ultra violet spectra were recorded on a Perkin-Elmer 402 spectrometer using 10mm cells. ^1H nmr spectra were recorded on a Hitachi Perkin-Elmer R-24 B spectrometer at 60 MHz, a Varian HA-100 spectrometer at 100 MHz and a Bruker WM-250 spectrometer at 250 MHz, using deuteriochloroform as solvent and tetramethylsilane as internal reference. ^{13}C nmr were recorded on a Varian XL-100 nmr spectrometer, using deuterochloroform as solvent and TMS as internal standard. Low resolution mass spectra were recorded on a VG12-250J mass spectrometer or an AEI MS9 mass spectrometer. High resolution mass spectra were recorded on a VG ZAB-E mass spectrometer or an AE1 MS9 mass spectrometer. Boiling points were determined by Kugelrohr distillation apparatus, and the temperature given is that of the Kugelrohr oven, or by using a micro-boiling point apparatus (Siwoloboff's method). Boiling points of alkenes were determined on *E*-/*Z*-mixtures. The mixtures of *E*- and *Z*-alkenes were analysed on a Perkin-Elmer 8500 gas chromatograph with a GP-100 graphics printer using a 25m SGE capillary column with bonded phase aluminium clad. The various temperature programs used for each analysis are given in the appropriate place. G.c. estimations of the reaction yields were made by adding a known weight of a standard to the reaction mixture and determining the detector response factor for each component to be examined. Typical standards were straight chain hydrocarbons such as dodecane and tridecane. Where possible, products were identified by co-injection of authentic samples. Preparative chromatographic separations were achieved using silica or alumina as adsorbents in a glass column, with uv detection. Hplc was performed on a LDC/Milton Roy constametric spectromonitor with C1-10 recorder apparatus, using a 5μ Hypersil column. Microanalyses were determined using a Carlo Erba Strumentazione Elemental Analyser.

Reagents. All the reactions involving B-alkyldimesitylboranes and their derived carbanions used purified anhydrous reagents unless otherwise stated. Reactions were carried out under 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 has been described.[11]

THF was purified by passage through a column of dry neutral alumina under nitrogen. It was then refluxed in a solvent still under nitrogen with sodium (2g/l) and

benzophenone (8g/l) until the characteristic purple colour of the ketyl formed. This was followed by distillation. Diethyl ether and light petroleum were passed through an alumina column, stirred for 16 hours with calcium hydride, and distilled under nitrogen.[12] Chloroform was purified by distillation from phosphorus pentoxide. Benzene was purified by shaking with concentrated H_2SO_4, then with water, diluted NaOH and water, followed by drying with P_2O_5 and distillation under nitrogen from sodium metal. Acids were distilled immediately before use. Hydrogen chloride was generated, passed into dry ether, estimated and used at once.

Solutions of *n*-butyllithium and *t*-butyllithium in hexane 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.[13] Aliphatic aldehydes and acids were distilled immediately before use.

Purified solvents and reagents were stored under standard conditions for use in reactions involving air-sensitive compounds. These conditions have been extensively described.[11] B-Alkyldimesitylboranes were prepared as described previously[14] and stored in an active desiccator.

Procedures. The equipment and techniques involved in laboratory operations with air sensitive substances have been surveyed.[11] All glassware was oven dried (typically >12 hours at 120°C), assembled hot, and allowed to cool under a stream of nitrogen or argon introduced *via* hypodermic needles inserted through septum capped inlets with outlets protected by inert oil bubblers. 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. The reaction apparatus consisted of a septum capped flask equipped with a spiral inlet arm which is wholly immersed in the cooling bath.[15] The flask contains a coated magnetic follower to enable stirring of the reaction mixture *via* an external magnetic stirrer. A bleed needle to the nitrogen line was inserted through the cap to account for any change in the pressure within the vessel during reaction.

1. **Preparation of carbanions from B-alkyldimesitylboranes, Mes_2BR[1]**

All the boron stabilised carbanions were produced in the following way. Dry bromomesitylene (1g, 5mmol) was made up to a 1M solution in dry THF in a nitrogen flushed reaction flask (150ml) containing a magnetic follower and sealed with a septum cap. The solution was cooled to -78°C and stirred whilst *tert*-butyllithium (2.1M in hexane, 4.75ml, 10mmol) was added dropwise. The mixture was stirred for 15 min at -78°C and allowed to warm to room temperature over 15 min. A solution of the alkyldimesitylborane (Mes_2BR) (5mmol) in THF (10ml) at 25°C was added *via* a double-ended needle and the mixture stirred for 1h (R=Me, Et) or 2h (R=Pr, Bu, Oct). The resulting solution of the carbanion was ready for use.

2. **Preparation of alkenes for comparison purposes.**

2.1 General procedure for the preparation of alkenes by the Wittig method[16]

Triphenylphosphine (52.3g, 0.2mmol) and octyl bromide (40.5g, 0.2mol) were mixed in chlorobenzene (50ml) and heated under reflux for 48h. The chlorobenzene was removed

under vacuum (19mm Hg then 0.1mm Hg) to leave $Ph_3PCH_2Hept\ Br^-$ as a very viscous oil (92.6g, ~ 100%).

A portion (1.44g, 3.4mmol) of the phosphonium bromide was dissolved in THF (50ml) and stirred at 0°C. Bu^nLi (5mmol, 2ml of 2.5M) was added and the solution stirred at room temperature for 2h, on which it became blood red. The ylid solution was cooled to -78°C and a solution of aliphatic aldehyde (6.8mmol) in THF (5ml) was added with stirring. The reaction was allowed to reach room temperature, then stirred for 30 min. Water (25ml) was added, the mixture stirred for 1h, and the organic layer removed, dried ($MgSO_4$), filtered and concentrated. The crude product was placed on a silica gel column packed under light petroleum and then eluted with light petroleum. The alkene eluted rapidly and was analysed by SGE capillary g.c. to find the *E*:*Z* ratio. The following alkenes were made in this way. *Dec-2-ene* (0.32g, 67%), *E*:*Z* = 34:66. *Undec-3-ene* (0.38g, 73%), *E*:*Z* = 0:100 (^{13}C nmr, ν_{max} 725 cm^{-1}). *Hexadec-8-ene* (0.62g, 81%), *E*:*Z* = 16:84. *2-Methylundec-3-ene* (0.41g, 72%), *E*:*Z* = 7:93. *2,2-Dimethyldec-3-ene* (0.43g, 70%), *E Z* = 0:100 by g c. and ^{13}C nmr, ν_{max} 725 cm^{-1}. *1-Cyclohexylnon-1-ene* (0.56g, 80%), *E*.*Z* = 6:94. (Yields based on phosphonium salt).

2.2 Preparation of alkenes by the Schlosser modification of the Wittig reaction[17]

Octyltriphenylphosphonium bromide (1.44g, 3.4mmol) was suspended in a mixture of THF (25ml) and ether (15ml). Phenyllithium (3.4mmol) was added, and the solution was stirred for 10 min at room temperature and then cooled to -78°C. Freshly distilled aldehyde (3.4mmol) in ether (10ml) was then added with good stirring. Decolourisation was complete after 5 min at -70° to -40°C, after which more phenyllithium (3.4mmol) was added and the mixture stirred at -30°C for 5 min. Ethereal hydrogen chloride (3.5mmol) was added, followed by potassium *t*-butoxide (5.5mmol), 1:1 complex with *t*-butanol). The mixture was stirred at room temperature for 2h, after which solvent was removed under vacuum. The crude product was dissolved in ether (40ml), washed with water (3 x 20ml), dried ($MgSO_4$) and filtered. The products were isolated and analysed as in Section 2.1.

The following alkenes were produced in this way. *Dec-2-ene* (0.2g, 42%), *E*:*Z* = 77:23. *Undec-3-ene* (0.24g, 46%). *E*:*Z* = 100:0. *Hexadec-8-ene* (0.46g, 61%), *E*:*Z* = 86:14. *2-Methylundec-3-ene* (0.27g, 48%), *E*:*Z* = 76:24. *2,2-Dimethylundec-3-ene* (0.365g, 59%), *E*:*Z* = 0:100. *1-Cyclohexylnon-1-ene* (0.368g, 52%), *E*:*Z* = 6:94.

2.3 General procedure for the reaction of $Mes_2BCHLiR^1$ (1) with R^2CHO in the presence of protic acids.

A solution of (1) (5mmol) (Section 1) (R^1 = Me or Et or Hept) was cooled to -127°C under nitrogen and stirred. A solution of freshly distilled aldehyde (5mmol) and purified, dry acid (5mmol) in THF (8ml) pre-cooled to -78°C was added slowly down the spiral side arm, and the flask and the double-ended needle flushed with cold THF (2ml). The reaction mixture was stirred at -127°C for 1h, the cooling bath removed, and the mixture stirred at room temperature for 16h. Solvents were removed under vacuum, ether (30ml) added and the etheral extract washed with water (3 x 15ml), dried ($MgSO_4$), filtered and evaporated. The alkenes were isolated by chromatography on silica gel as in Section 2.1, and distilled.

2.3.1. Preparation of alkenes from the reaction of $Mes_2BCHLiHept$ with aliphatic aldehydes in the presence of acetic acid (Table 1).

Procedure 2.3 was used to give the following alkenes.

Dec-2-ene (0.365g, 52%), b.p. 168°C/750mm Hg (lit.[18] 170.5°C/760mm). M^+, 140.1598; $C_{10}H_{20}$ requires 140.1565. G.c. (50°C-100°C at 30°C/min; 100°C-150°C at 2°C/min) gives *E*:*Z* = 42.58. Retention time of the *Z*-isomer = 10.2min, and of the *E*-isomer = 10.58 min. δ_H, 0.89(3H, *t*, J=5Hz, H-10), 1.28(10H, s, H-5 to H-0), 1.62(3H, d, J=5Hz, H-1), 1.9-2.1(2H, m, H-4), 5.38-5.5(2H, m, H-2 and H-3). δ_C 12.72(C-10), 14.12(C-1), 22.74(C-9), 26.91(C-4), 29.3, 29.71, 31.96, 32.66(C-5 to C-8), 123.58(C-2, *Z*), 124.5(C-2, *E*), 130.94(C-3, *Z*), 131.75(C-3, *E*). ν_{max} 2910, 1470, 1380, 970, 725cm^{-1}.

Undec-3-ene (0.58g, 75%), b.p. 165°C/750mm Hg (lit.[18] 73°C/10mm Hg), *E*:*Z* = 49:51 (g.c. 50°C-100°C at 30°C/min, 100°C-160°C at 1°C/min, retention time. *E* = 17.37 min, *Z* = 17.55 min). δ_H 0.8-1.02(6H, m, H-1 and H-11), 1.28(10H, s, H-6 to H-10), 1.86-2.14(4H, m, H-2 and H-5), 5.3-5.5(2H, m, H-3). δ_C 14.12, 14.39(C-1, C-11), 20.58, 25.68, 27.2, 29.33, 29.8, 31.99, 32.66(C-2, C-5 to C-10), 129.45, 129.40(C-4, *E* and *Z*), 131.55, 131.93(C-3, *E* and *Z*), m/z* 154(5), 97(7), 83(15), 70(51), 56(87), 43(70), 41(100).

Hexadec-8-ene (0.86g, 77%), b.p. 144-146°C/10mm Hg) (lit.[19] 118°-124°C/2.5mm Hg). Found C, 85.62%, H, 13.97%, M^+, 224.2507. $C_{16}H_{32}$ requires 85.71%, H, 14.29%, M, 224.2504. *E*:*Z* = 65:35 (g.c. 50°-100°C at 30°C/min., 100°C-180°C at 3°C/min, retention time *Z* = 30.33min; *E* = 30.59 min. δ_H 0.8(6H, t, J=7Hz, H-1, H-16), 2.29(20H, m, H-2 to H-6, H-11 to H-15), 1.84-2.14(4H, m, H-7, H-10), 5.3-5.5(2H, m, H-8, H-9). δ_C 14.11(C-1, C-16), 22.74, 27.29, 29.2, 29.7, 31.96, 32.67(C-2 to C-7 and C-10 to C-15), 129.95, 130.15, 130.4, 130.6(C-8, C-9, *E* and *Z*). m/z 224(2), 97(48), 83(64), 71(50), 69(82), 54(100), 43(70), 41(91). ν_{max} 2920, 1470, 1380, 970, 720 cm^{-1}.

2-Methylundec-3-ene (0.73g, 87%), b.p. 79°/80°C/10mm Hg. Found C, 85.83%; H, 14.12%; M^+, 168.1882. $C_{10}H_{20}$ requires C, 85.71%; H, 14.29%; M, 168.1878. *E*:*Z* = 69:31 (g.c. programme, 60°C-100°C at 24°C/min, 100°C-150°C at 2°C/min, 150°C-250°C at 30°C/min. Retention times were *E* = 10.39 min; *Z* = 10.72 min. δ_H 0.83-0.97(9H, m, H-1, H-2' and H-11), 1.27(10H, s, H-6 to H-10), 1.95-2.04(2H, m, H-5), 2.2-2.4(1H, m, H-2), 5.19-5.36(2H, m, H-3, H-4). δ_C 14.1(C-11), 22.69(C-1, C-2'), 23.2(C-2), 29.23, 29.31, 29.73, 31.02, 31.90, 32.58(C-5 to C-10), 127.24, 127.5(C-4, *E*, *Z*), 137.45, 137.5(C-3, *E*, *Z*). m/z 168(1), 69(61), 57(80), 55(100). ν_{max} (film), 2960, 2880, 1475, 1388, 975, 910, 740 cm^{-1}

2,2-Dimethylundec-3-ene (0.719g, 79%), b.p. 83°C/10mm Hg. M^+, 182.2034, $C_{13}H_{26}$ requires 182.2035. *E*:*Z* = 0:100 (g.c. programme, 50°C-110°C at 9°C/min, 110°C-150°C at 2°C/min, 150°C-200°C at 30°C/min. Retention time for the *Z* -isomer was 20.94 min and in an authentic *E*:*Z* mixture, that of the *E*-isomer was 22.1 min. δ_H 0.8-1.5(22H, m, H-1, H-6 to H-11), 2.04-2.28(2H, m, H-5), 5.01-5.44(2H, m, H-3, H-4). δ_C 14.1(C-11), 22.7, 28.4, 29.3, 29.4, 30.4, 31.9(C-5 to C-10), 31.2(C-1), 33.1(C-2), 129.15(C-4), 139.6(C-3). m/z 182(20), 181(13), 97(26), 84(31), 83(100), 70(27), 69(60), 55(32). ν_{max} (film) 2920, 1470, 1368, 1209, 725 cm^{-1}.

*All mass spectra given as m/z (relative abundance)

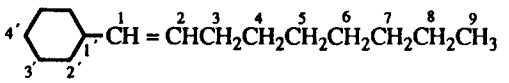
1-Cyclohexylnon-1-ene (0.86g, 83%), b.p. 120°C/10mm Hg (lit.[20] 209°C/760mm Hg). M^+, 208.2205, calculated for $C_{15}H_{28}$ is 208.2191. *E:Z* = 10:90 (g.c. programme 60°C-100°C at 24°C/min, 100°C-175°C at 3°C/min, 175°C to 230°C at 30°C/min. Retention of the *Z*-isomer = 28.45 min and of the *E*-isomer = 29.59 min. δ_H 0.87(3H, t, J=9Hz, H-9*), 1.02-1.50(20H, m, H-2' to H-4', H-4 to H-8), 1.48-1.84(2H, m, H-3), 2.82-3.2(1H, m, H-1'), 5.1-5.4(2H, m, H-1, H-2). δ_C 14.13(C-9), 22.8, 26.15, 26.24, 27.55, 29.37, 29.86, 30.13, 32.02, 33.54(C-3 to C-8, C-2' to C-4'), 36.44(C-1'), 127.84, 128.1(C-2, *E, Z*), 136.0, 136.4(C-1, *E, Z*), m/z 208(17), 109(48), 96(97), 81(100), 67(88), 55(72), 41(89). ν_{max} (film) 2900, 1455, 1380, 970, 890, 725 cm^{-1}.

2.4 Preparation of undec-3-ene from $Mes_2BCHLiHept$ and EtCHO in the presence of various protic acids (Table 2).

The procedure used was exactly that given in Section 2.3. The alkene product was isolated from a silica column eluted with light petroleum. Analysis for *E:Z* ratio was carried out on a SGE capillary column using the programme 50°C-100°C at 30°C/min, 100°C-160°C/min. *Z*-Undec-3-ene had a retention time of 17.55 min and the *E*-isomer had R_T = 17.37 min. *Acetic acid* (0.3g, 5mmol, 1 equiv) gave undec-3-ene (0.58g, 75%), *E:Z* = 49:51. *Acetic acid* (0.75g, 12.5mmol, 2.5 equiv) gave undec-3-ene (0.55g, 73%), *E:Z = 61:39. Trifluoroacetic acid* (1.48g, 12.5mmol, 2.5 equiv) gave undec-3-ene (0.53g, 71%), *E:Z* = 70:30). *Trifluoromethanesulfonic acid* (1.87g, 12.5mmol, 2.5 equiv) gave undec-3-ene (0.51g, 66%), *E:Z* = 78:22. *Trifluoromethanesulfonic acid* (3.75g, 25mmol, 5.0 equiv) gave undec-3-ene (0.38g, 49%), *E:Z* = 91:9. *Ethereal hydrogen chloride* (12.5mmol, 2.5 equiv) gave undec-3-ene, (0.525g, 68%) *E:Z* = 84:16 and the *same acid* (25mmol, 5.0 equiv) gave the alkene (0.44g, 57%), *E:Z* = 86:14.

2.5 Condensation of $Mes_2BCHLiR^1$ with R^2CHO in the presence of protic acids (Table 3).

In all cases the procedure followed was that of Section 2.3. *1-Phenylbut-2-ene* was obtained from the reaction between freshly distilled phenylacetaldehyde (0.6g, 5mmol) and $Mes_2BCHLiMe$ (5mmol, Section 1) as a colourless oil, b.p. 63-64°C/10mm Hg (lit.[21] 76°C/18mm Hg). The alkene was analysed for *E:Z* ratio using a temperature programme of 60°C-110°C at 10°C/min, 110°C-175°C at 3°C/min, 175°C-200°C at 30°C/min to give R_T, *E*-isomer = 9.66 min and Z-isomer = 10.10 min. δ_H 1.66-1.75(3H, m, H-4), 3.35(2H, dd, J=5Hz, J_2 = 12Hz, H-1), 5.44-5.64(2H, m, H-2, H-3), 7.13-7.29(5H, Ar-*H*). δ_C 17.85(C-4), 39.08(C-1), 124.8, 125.8, 125.3, 128.33, 128.47, 130.1(C-2, C-3, C-1', C-2', C-3', C-4'). m/z = 132(55), 131(16), 117(100), 115(46), 91(64), 77(21), 65(24), ν_{max} (film) 3040, 1940, 1500, 1450, 968, 910, 730, 690 cm^{-1}. The reaction gave the following results. (i) *AcOH* (0.30g, 5mmol) gave alkene (0.49g, 74%, *E:Z* = 14:86; (ii) *AcOH* (0.60g, 10mmol gave alkene (0.42g, 63%, *E:Z* = 21:79); (iii) CF_3CO_2H (0.57g, 5mmol) gave alkene (0.37g, 56%, *E:Z* = 41:59),(iv) *HCl-Et₂O* (5mmol) gave alkene (0.475g, 72% *E:Z* = 78:22); (v) CF_3SO_3H (0.748g, 5mmol) gave alkene (0.455g, 69%, *E:Z* = 93.7).

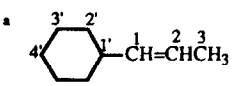


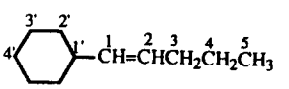
1-Cyclohexylprop-1-ene was obtained from ChxCHO (0.56g, 5mmol) and $Mes_2BCHLiCH_3$ (5mmol, Section 1) using the procedure in Section 2.3, as a colourless oil, b.p. 166-167°C/760mm Hg (lit.[22] 152°C/760mm Hg) M^+, 124.1267, C_9H_{16} requires 124.1252. The alkene was analysed for *E*:*Z* ratios using a temperature programme of 50°C-110°C at 9°C/min, 110°C-140°C at 2°C/min, 140°C-200°C at 40°C/min. R_T, *E* = 7.77 min, *Z* = 7.54 min. δ_H, 0.83-1.88(14H, m, H-3, H-1' H-2' H-3' H-4'[a]), 5.35-5.39(2H, m, H-1, H-2). δ_C 18.03C-3), 26.34(C-4'), 29.79(C-3'), 33.32(C-2'), 40.79(C-1'), 122.04(C-2), 137-74(C-1). m/z 124(11), 95(11), 85(67), 84(55), 83(100), 67(36), 49(59), 47(43). ν_{max} (film) 2940, 2880, 1450, 970, 730 cm^{-1}. *Acetic acid* (0.6g, 10mmol) gave alkene (0.42g, 67%, *E*:*Z* = 63:37), CF_3SO_3H (0.75g, 5mmol) gave alkene (0.37g, 59%, *E*:*Z* = 97:3).

4-Ethyloct-2-ene was prepared from 2-ethylhexanal (0.64g, 5mmol) and $Mes_2BCHLiMe$ (5mmol, Section 1), using the procedure in Section 2.3, as a colourless oil, b.p. 132°C/760mm. M^+, 140.1561, $C_{10}H_{20}$ requires 140.1565. The alkene was analysed for *E*:*Z* ratio using a temperature programme of 60°C-110°C at 10°C/min, 110°C-180°C at 2°C/min, 180°C-280°C at 40°C/min, giving R_T, *Z* = 6.26 min, *E*= 6.05 min. δ_H 0.79-1.58(14H, m, H-4', H-4", H-5 to H-8), 1.64(3H, d, J=6.4Hz, H-1), 1.67-1.8(1H, m, H-4), 4.97-5.39(2H, m, H-2, H-3). δ_C 11.76(C-8), 14.15(C-4"), 17.96(C-1), 28.23(C-7), 29.64(C-6), 34.96, 34.97(C-5, C-4'), 44.64(C-4), 123.45(-2, *Z*), 124.36(C-2, *E*), 135.97(C-3, *Z*), 136.12(C-3, *E*). m/z 140(5), 84(16), 83(44), 70(35), 69(85), 55(100), 43(32), 41(61). ν_{max} (film) 2920, 1465, 1380, 967, 905, 730 cm^{-1}. *Acetic acid* (0.3g, 5mmol) gave alkene (0.366g, 52%) as a 24:76, *E*:*Z* mixture). CF_3SO_3H (0.75g, 5mmol) gave alkene (0.40g, 57%) as a 95:5, *E*:*Z* mixture.

Undec-2-ene, b.p. 195°C-196°C/760mm (lit.[23] 78.5°C/13mm Hg), identical in all respects with an authentic sample, was obtained as usual from the condensation of nonanal (0.71g, 5mmol) and $Mes_2BCHLiMe$ (5mmol, Section 1). The same temperature programme as for 1-phenylbut-2-ene gave R_T, *E* = 10.14 min, and R_T, *Z* = 10.39 min. *Acetic acid* (0.3g, 5mmol) gave alkene as a 44:56, *E*:*Z* mixture. CF_3SO_3H (0.75g, 5mmol) gave undec-2-ene as a 90*E* :10*Z* mixture.

1-Cyclohexylpent-1-ene, b.p. 191°C/760mm (lit.[22] 196°C/760mm) was obtained from the reaction of cyclohexylcarboxaldehyde (0.56g, 5mmol) with $Mes_2BCHLiPr$ (5mmol, Section 1). The *E*:*Z* ratios were calculated using a temperature programme of 60°C-100°C at 24°C/min, 100°C-200°C at 3°C/min, 200°C at 30°C/min. The retention time of the *E*-isomer was 11.43 min and of the *Z* -isomer was 10.97 min. δ_H 0.90(3H, t, J=7.2Hz, H-5[b]), 1.01-2.05(14H, m, H-3, H-4, H-2', H-3' H-4'), 2.21-2.27(1H, m, H-1'), 5.15-5.34(2H, m, H-1, H-2). δ_C 13.85(C-5), 16.17(C-4'), 23.24, 26.29, 29.67(C-H, C-2', C-3'), 33.56(C-3), 36.46(C-1'), 127.56(C-2, *E*), 127.84(C-2, *Z*), 136.24(C-1, *Z*), 136.7(C-1, *E*). m/z 152(12), 109(33), 96(24), 81(53), 67(100), 55(36), 41(29). ν_{max} (film) 2960, 1465, 970, 730 cm^{-1}. *Trifluoroacetic acid* (0.57g, 5mmol) gave the alkene (0.46g, 61%) in an *E*:*Z* ratio of 49:51. *Acetic acid* (0.3g, 5mmol) gave the alkene (0.46g, 61%) in an *E*:*Z* ratio of 17:83. *Ethereal HCl* (5mmol) gave the alkene (0.483g, 64%) in an *E*:*Z* ratio of 95:5.

a 

b 

6-Ethyldec-4-ene, b.p. 90°C/760mm was obtained from the reaction of 2-ethylhexanal (0.64g, 5mmol) with $Mes_2BCHLiPr$ (5mmol, Section 1). M^+ 168.1878, $C_{12}H_{24}$ requires 168.1878. It was not possible to analyse the material by g.c. using various columns and programmes, and ^{13}C nmr backed with i.r. data was used instead. δ_H 0.81-0.93(9H, m, H-1, H-10, H-6"*), 1.06-1.45(10H, m, H-2, H-7, H-8, H-9, H-6'), 1.95-2.05(2H, m, H-3), 2.16-2.24(1H, m, H-6), 4.97-5.44(2H, m, H-4, H-5). δ_C 11.94(C-1, C-10, C-6"), 23.14, 23.28(C-8, C-9), 28.9, 29.87, 30.08(C-2, C-7, C-6'), 33.64(C-3),39.14(C-6), 129.77(C-4, *Z*), 135.12(C-5, *Z*), 135.17(C-5,*E*). m/z 168(9), 139(4), 111(15), 97(24), 83(44), 69(100), 55(84), 41(89). ν_{max} (film) 2940, 1470, 1380, 970(*E*), 725(*Z*). *Acetic acid* (0.3g, 5mmol) gave alkene (0.62g, 75%) as a 4:96 mixture of *E*:*Z* isomers. CF_3CO_2H (0.57g, 5mmol) gave alkene (0.56h, 67%) as a 34:66 mixture of *E*:*Z* isomers. CF_3SO_3H (0.75g, 5mmol) gave 6-ethyldec-4-ene (0.49g, 59%) in an *E*:*Z* ratio of 92:8.

2,2-Dimethylundec-3-ene (See Section 2.3.1 for the preparation of the alkene in the presence of acetic acid). The same preparation as in Section 2.3.1 but using ethereal HCl (5mmol) gave the identical alkene (0.682g, 75%) with an *E*:*Z* ratio of 92:8.

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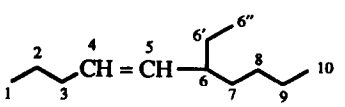
* 

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