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Hindered Organoboron Groups in Organic Chemistry. 24. The Condensation of Aliphatic Aldehydes with Dimesitylboron Stabilised Carbanions to give Ketones.

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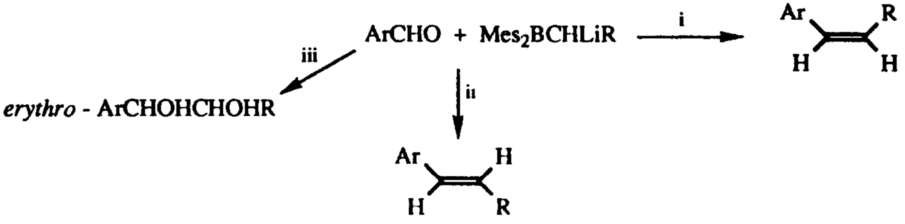
Abstract. The condensation of boron stabilised carbanions, $Mes_2BCHLiR^1$, ($R^1 \neq H$) with aliphatic aldehydes, R^2CHO, followed by treatment with trifluoroacetic anhydride (TFAA) or N-chlorosuccinimide (NCS) is an unique, broadly applicable redox process that yields ketones, $R^1CH_2COR^2$, directly and in high yields. The anion Mes_2BCH_2Li ($Mes_2BCHLiR^1$, R^1=H) gives high yields of alkenes, $R^2CH=CH_2$ in the same conditions.

We have, in the preceding paper[1] delineated the reactions of aromatic aldehydes with dimesitylboron stabilised carbanions to give *E* or *Z* alkenes or *erythro*-1,2-diols, dependant on the method of work up (Scheme 1).



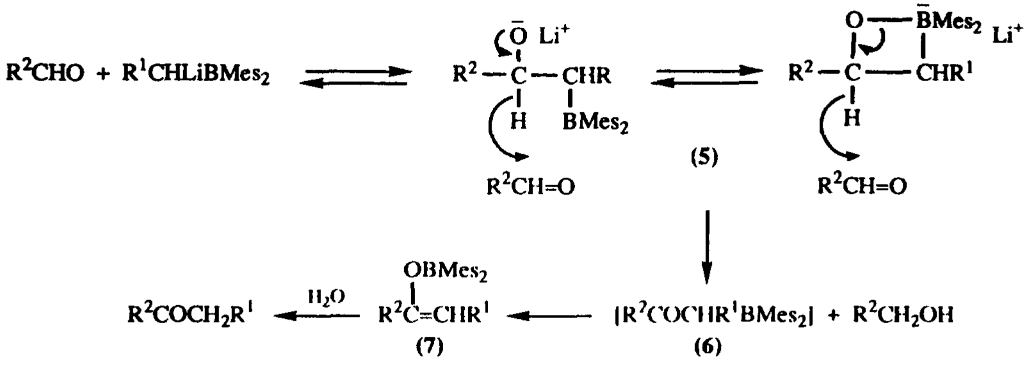
i) TFAA, -110°C ; ii) (a) Me_3SiCl, -110°C ; (b) aq. HF/CH_3CN ; (iii) NaOH, H_2O_2, -110°C

Scheme 1

We attempted to extend these results to aliphatic aldehydes, and a very preliminary result showed that low temperature condensation of Mes_2BCH_2Li (1) with octanal gave $HeptCH=CH_2$ in good yield.[2] This was a Wittig type condensation that we thought would be the norm. In this and the following paper we report the results of further investigations of this type of condensation, which we have presented in preliminary form.[3,4]

In order to generalise the process, we studied the reaction of $Mes_2BCHLiHept$ (2) with octanal. To our surprise, hexadecan-8-one (3) (18%) was the only characterisable product from the reaction at -78°C. The yield of (3) was raised to 36% by carrying out the reaction at -110°C but in both reactions none of the expected alkene, hexadec-8-ene (4), was observed.

We had previously[1] observed minor ketone products arising from similar reactions with aromatic aldehydes. The ketones must be the products of a redox reaction, which we ascribed to the reduction of aldehyde by the intermediate, in a Canizzaro-like process (Scheme 2). The aldehyde is present due to the initial condensation being reversible and, as one equivalent of aldehyde is consumed for each redox reaction, the overall yield of ketone can be 50% at most.



Scheme 2

For aromatic aldehydes the initial condensation gave intermediate (5) in the open chain form[1], but for aliphatic aldehydes the oxaboratetane form must be taken into account when considering the hydride transfer. The product, (6), following the hydride transfer, would rearrange to the vinyloxyborane (7)[5], hydrolysis of which would then yield ketone.

However, ketone (3) represented only a minor component of the total product under the conditions used and therefore a series of experiments was undertaken in order to understand and control the reactions leading to ketones and, possibly, to alkenes.

If (7) were an intermediate, then alkylation should provide an α-alkyl derivative. In practice, addition of methyl iodide to the reaction mixture after condensation did provide 9-methylhexadecan-8-one (8) as shown in equation (1), as well as (3).

$$\underset{(2)}{\mathrm{Mes_2BCHLiHept}} + \mathrm{HeptCHO} \rightarrow [\mathrm{X}] \xrightarrow{\mathrm{MeI}} \underset{(15\%)}{(3)} + \underset{(8)\,(21\%)}{\mathrm{HeptCOCH(Me)Hept}} \qquad (1)$$

Since ketone formation must result from an oxidation at some stage, addition of an external oxidant might be expected to increase the yield of this product. Indeed, addition of iodine as an electron acceptor raised the yield of (3) to 44%, but did not give the high yield of ketone expected from an external oxidant.

We hoped that addition of Lewis acids at low temperature (-115°C) might both enhance the susceptibility of the aldehydes to condensation and lower the anionic character of the intermediate (5) thereby reducing the likelihood of hydride transfer and therefore suppressing formation of ketone. In practice, addition of titanium tetrachloride or zinc chloride led to complex product mixtures containing neither alkene nor ketone. Dimethylaluminium chloride had little effect on the reaction and addition of one equivalent of boron trifluoride etherate gave a 1:1 mixture of alkene and ketone but in low yields (17% of each). In one case only was there good recovery of material. This was the condensation of pivaldehyde with (2) in the presence of one equivalent of $BF_3.OEt_2$, which gave 2,2-dimethyldecan-3-one (70%) and 2,2-dimethyldec-7-ene (13%).

We had previously used chlorotrimethylsilane (TMSCl) and trifluoroacetic anhydride (TFAA) to trap intermediates in condensations with aromatic aldehydes.[1] We anticipated that these reagents would react with (5) to discharge its anionic character and hence its ability to donate a hydride to an acceptor. On this reasoning we assumed that, using these additives, alkenes rather than ketones should result. Our findings are presented in Table 1.

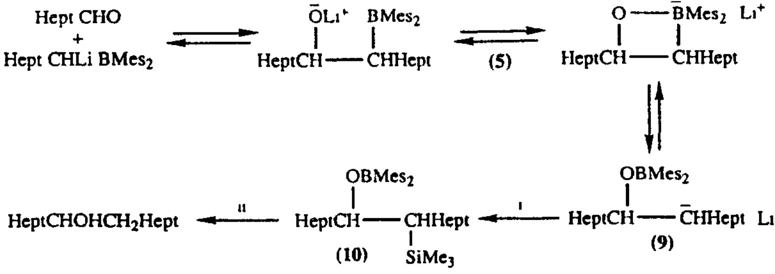
Table 1

Reactions of MesBCHLiHept with HeptCHO

Expt.	Conditions	Yields (%)[a] of Products		
		HeptCOOct	HeptCH=CHHept	HeptCHOHOct
1	Me_3SiCl, -78°C	85	14	0
2	Me_3SiCl ,-115°C; aq HF/CH_3CN	20	9	55
3	TFAA, -78°C	54	4	0
4	TFAA, -115°C	90	0	0
5	TFAA, -115°C, then reflux	(70)	(17)	0
6	TFAA, -115°C, 5MHCl/5h/60°C	(60)	0	0
7	TFAA, -115°C, $NaOH/H_2O_2$	(100)	0	0

[a]) Yields are of isolated materials, except those in parentheses, which are g.c. yields.

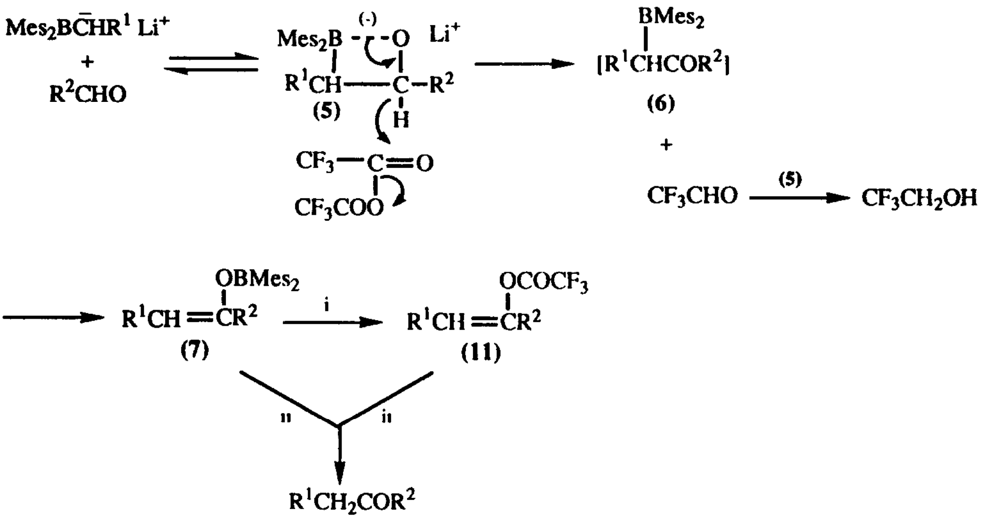
Clearly the expected switch from ketone to alkene had not occurred. On the contrary, in experiment 1, TMSCl appeared to be acting as a hydride acceptor at -78°C and for the first time a yield of ketone well in excess of 50% was achieved. At a lower temperature (experiment 2) the redox reaction did not occur and (5) appeared to undergo rearrangement[1], similar to that observed in the analogous condensation with silicon stabilised carbanions[6], to yield (9), (Scheme 3) which appeared to undergo an irreversible reaction to give (10). Subsequent treatment of (10) with aqueous HF/CH_3CN would then yield hexadecan-8-ol, as in Scheme 3. This was the only experiment to give an alcohol product.



i, Me_3SiCl , ii, aq HF/CH_3CN.

Scheme 3

When pre-cooled TFAA was added at low temperatures (experiments 3-7) a single product with the same retention time as alkene (4) was initially observed. However when, for isolation purposes, the reaction mixture was passed down a silica column, the product obtained was not alkene but, instead, was ketone (3) with a totally different retention time from the intermediate and from (4). The ketone was identified by direct comparison, and the initial product was shown to be (11, R^1=R^2=Hept) (Scheme 4) by isolation and direct comparison with an authentic sample. Our proposal for the reactions occurring is shown in Scheme 4, an adaption of Scheme 2. In this, the added TFAA acts as a hydride acceptor from (5) to give (6) and CF_3CHO. Trifluoroacetaldehyde acts preferentially as a hydride acceptor to give finally CF_3CH_2OH. As 1.2 equiv. of TFAA are normally used, then following the hydride transfers and production of (7)[5], there will be 0.7 equivalent left. This can then convert some of (7) into the enol trifluoroacetate (11) which, being far more volatile than (7), is the intermediate observed by g.c. Hydrolysis of the mixture gives the product ketone, (3).



i, TFAA ; ii, H_2O

Scheme 4

Experiments 4 and 7 showed that high yields of ketone can be achieved using TFAA and we chose the simple procedure of experiment 4 as our preferred general procedure. Reactions of several boron-stabilised anions were carried out at -127°C with a range of aldehydes and were worked-up without isolation of intermediates. Our results are presented in Table 2.

Table 2

Condensation of $Mes_2BCHLiR^1$ and R^2CHO in the presence of TFAA

Exp.	R^1	R^2	Yield %[a]	
			$R^1COCH_2R^2$	$R^1CH=CHR^2$
8	Hept	Me	71	0
9	Hept	Et	72	0
10	Hept	Hept	76	0
11	Hept	Bu(Et)CH	85	0
12	Hept	Bu^t	92	0
13	Hept	Cp[b]	89	0
14	Hept	Chx[c]	78	0
15	Pr	$PhCH_2$	75	0
16	Pr	Bu(Et)CH	87	0
17	Pr	Chx	82	0
18	Et	$PhCH_2$	41	0
19	Et	Bu(Et)CH	(41)	0
20	Me	Hept	d	d
21	H	Hept	0	91
22	H	Hept	0	81
23	H	Nonyl	0	74
24	H	Chx	0	(76)

a) Yields are of isolated, purified, fully characterised compounds, except for g.c. yields given in parentheses.
b) Cp=cyclopentyl. c) Chx=cyclohexyl. d) No product is predominant.

Certain striking features emerge from Table 2. Experiments 8 to 17 show that with R^1=Pr and higher, excellent yields of ketones are isolated, regardless of whether the borane is condensed with R^pCHO, R^sCHO or R^tCHO. No alkene products were observed in any of these experiments. When R^1=Et, (experiments 18,19) the yields of ketones were lowered and when R^1=Me (experiment 20), a plethora of products resulted, amongst which only mesitylene could be identified by g.c. When R^1=H (experiments 21-24), the reactions became clean once more, but the products were alkenes. *Indeed, this is an excellent method for the methylenation of aldehydes* (equation 2).

$$RCHO + Mes_2BCH_2Li \rightarrow RCH=CH_2 \qquad (2)$$

It is clear that there is a fine balance between redox and elimination reactions which is affected by the length of the chain of the group attached to boron. We do not know why this is so, and the point requires further experimentation. It may be that the balance between the oxaboratetane and open chain forms of (5) is an important factor. In any case, it seemed that ketone production might be favoured by the presence of a hydride acceptor more efficient than TFAA, itself not noted as an oxidant.

After some experiments using iodine, phenyliodonium diacetate, NBS, and excess of aldehyde[7], it was found the N-chlorosuccinimide (NCS) was compatible with the reactants, intermediates and products, and that use of four equivalents of NCS gave acceptable yields of ketones from $Mes_2BCHLiMe$ and $Mes_2BCHLiEt$ (Table 3, experiments 25-30). However, although (1) did give some ketone under these conditions, the major product remained alkene (Table 3).

Table 3

Condensation of $Mes_2BCHLiR^1$ with R^2CHO in the presence of NCS

Expt.	R^1	R^2	Product	Yield (%)[a]
25	Hept	Hept	HeptCOOct	73
26	Et	$PhCH_2$	$PhCH_2COPr$	72
27	Et	Bu(Et)CH	Bu(Et)CHCOPr	79
28	Me	Hept	HeptCOEt	72
29	Me	$PhCH_2$	$PhCH_2COEt$	57
30	Me	Bu(Et)CH	Bu(Et)CHCOEt	68
31	H	Hept	$HeptCOCH_3$	(28)[b]
32	H	Bu(Et)CH	$Bu(Et)CHCOCH_3$	21[c]
33	H	Chx	$ChxCOCH_3$	(29)[b]
34	H	$PhCH_2$	$PhCH_2COCH_3$	44[d]

[a]) Yields of isolated, purified, fully characterised product. G.c. yields in parentheses. [b]) The rest of the product was alkene by g.c. [c]) Corresponding alkene (0.524g, 72%) was isolated. [d]) NCS-dimethyl sulfide used.

Thus, with the exception of R^1=H, the process shown in equation (3) is a unique and general method for the direct conversion of aldehydes to ketones.

$$Mes_2BCHLiR^1 + R^2CHO \xrightarrow{\text{TFAA or NCS}} R^1CH_2COR^2 \qquad (3)$$

When R^1=H, then the general methylenation process shown in equation (2) results.

Experimental

Instrumentation. Infra-red spectra were recorded on a Unicam SP1050 infra-red 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 10 mm 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 $CDCl_3$ as solvent and Me_4Si as internal reference. ^{11}B nmr were recorded on a Varian XL-100 nmr spectrometer, using boron trifluoride etherate in a co-axial cell as external standard, and quartz nmr tubes. Signals downfield from the boron trifluoride etherate (*i.e.* deshielded) were recorded as positive and chemical shifts are in ppm. ^{13}C nmr were recorded on a Varian XL-100 nmr or a Bruker WH-250 spectrometer, using deuterochloroform as solvent and TMS as internal standard. Low resolution mass spectra were recorded on a VG12-250J mass spectrometer or an AE1 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 a microboiling point apparatus (Siwoloboff's method). Melting points were recorded on a Gallenkamp hot stage apparatus and are uncorrected.

Gas liquid chromatography was performed on a Varian Vista Series 6000 chromatograph with a Varian CDS-401 data system as integrator and plotter. Reaction mixtures were analysed on a 6" x 1/4" stainless steel column packed with 5% OV-17 on diatomite 100-200 mesh. Tlc analyses were performed on either silica gel (Merck), on alumina (Fluka), plastic or aluminium backed plates, with a fluorescent indicator (254 nm). Preparative chromatographic separations were achieved using silica or alumina as adsorbents in a glass column.

Microanalyses were determined using a Carlo Erba Strumentazione Elemental Analyser. Some liquid products proved difficult to analyse and in these cases the molecular formula was determined by high resolution mass spectrometry on a sample which was pure by glc or hplc.

Reagents. All 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.[8]

THF was purified by passage through a column of dry alumina (neutral) 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.[9] 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. Trifluoroacetic anhydride and the alkyl halides were distilled from P_2O_5 immediately before use. 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.[10] 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.[8]

Experimental Procedures. The equipment and techniques involved in laboratory operations with air sensitive substances have been surveyed.[8]

All glassware was oven dried (typically >3 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 bubbles. 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 reaction apparatus consisted of a septum capped flask equipped with a spiral inlet arm which was wholly immersed in the cooling bath.[11] The flask contained 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 starting materials, alkenes and ketones used for comparison purposes.

1.1 Boranes

The boranes Mes_2BMe, Mes_2BEt, Mes_2BPr, Mes_2BBu and Mes_2Oct were all made and purified as described in Part 18 of this series.[12]

1.2 Carbanions

All the boron stabilised carbanions were produced in the following way. Dry bromomesitylene (1.00g, 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 (10 ml) 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.

1.3 Standard Ketones.

These were made by oxidation of the corresponding alcohols, themselves produced by reaction of the corresponding aldehyde with the appropriate Grignard reagent. A typical procedure is given below for *hexadecan-8-one* (3).

A solution of Jones reagent was prepared by the slow addition of conc. H_2SO_4 (8.7ml) to a solution of chromium trioxide (10.3g) in water (30ml). This solution was diluted to 10mmol CrO_3/10ml of solution. Hexadecan-8-ol (103g, 30mmol) was dissolved in acetone (30ml) and the solution cooled to 5°C in an ice bath. Jones reagent (20ml, 20mmol) was added over 2h to the stirred solution, and then for a further 0.5h at 5°C. The mixture was then diluted with water to 250ml, the organic material taken into ether (4 x 30ml), the ether extract dried ($MgSO_4$), filtered and concentrated. The product was purified by elution from a silica column with 1% ether in light petroleum to give pure *hexadecan-8-one* (3) (8.77g, 87%). The analytical data for this and other ketones prepared by this method were compared with those made *via* the boron stabilised carbanion route, and are given in that Section. Ketones made by the above method were: *2,2-dimethylundecan-3-one* (Bu^tCOOct) (90%); *cyclohexyl octyl ketone* (89%); *9-methylhexadecan-8-one* (8) (83%) and *nonan-2-one* (92%). Other available ketones were purchased.

1.4 Standard alkenes.

These were purchased when available, or made by the Wittig reaction. A typical procedure is given for *hexadec-8-ene*.

Triphenylphosphine (52.3g, 0.2mole) and octyl bromide (40.5g, 0.1mole) were dissolved in chlorobenzene (50ml) and the mixture heated under reflux for 48h. The chlorobenzene was removed on a rotary exaporator, followed by pumping at 0.1mm Hg, leaving the phosphonium salt (92.6g, ~100%) as a very viscous yellow oil.

A portion of the salt (1.44g, 3.4mmol) was dissolved in THF (50ml) and the solution cooled to 0°C. *n*-Butyllithium (2.0ml of a 2.5M hexane solution, 5mmol) was added and the mixture stirred at room temperature for 2h to give a blood red solution. The reaction mixture was cooled to -78°C and octanal (1.1ml, 6.8mmol) was added *via* a double-ended needle. The reaction was allowed to warm to room temperature and then stirred for a further 3 min. Water (25ml) was then added and the mixture stirred until the red colour disappeared, after which it was transferred to a separating funnel and the two phases separated. The organic layer was dried ($MgSO_4$), filtered and concentrated. The product was then purified by silica gel chromatography using light petroleum to give ***hexadec-8-ene*** (0.53g, 70%). δ_H 0.84(6H, t, J=4Hz, C*H*, t, J=4Hz, CH_3), 1.22(20H, br.s.H-2 to H-6), 1.95(4H, m, H-7), 5.30(2H, m, CH_2C*H*=). δ_C 14.2(CH_3), 22.8(C-7), 27.4-32.1(C-2 to C-6), 129.9(*C*H=). m/z.* 224(21), 83(66), 69(77), 55(100), 41(73). ν_{max} 3020, 2870, 1470, 1380 cm^{-1}. G.c. indicated that this was a 7*E*:93*Z* mixture.

***Z*-2,2-Dimethylundec-3-ene** (0.69g, 94%) was made in a similar way. δ_H 0.87(3H, t, J=6Hz, H-11), 1.08(9H, s, C(CH_3)$_3$), 1.27(10H, br.s. H-6 to H-10), 2.15(2H, m, H-5), 4.96-5.36 (2H, m, C*H*=C*H*). δ_C 14.1(C-1, C-11), 22.7(C-2), 28.4-33.1(C-5 to C-10), 129.1(C-4), 139.6 (C-3). m/z, 182(6), 83(100), 70(32), 69(75), 55(67), 41(63), ν_{max} 2970, 2940, 2870, 1470, 1365 cm^{-1}.

2. General procedure for the preparation of ketones by the condensation of $Mes_2BCHLiR^1$ with R^2CHO in the present of TFAA.

2.1 A solution of carbanion, prepared as above (Section 1.2) from 5mmol of the borane, was cooled to -127°C under a static pressure of nitrogen and stirred. A solution of freshly distilled aldehyde (5mmol) in THF (5ml) precooled to -78°C was slowly added by double-ended needle down the spiral arm of the reaction flask. The reaction was stirred for 1h at -127°C and then a solution of dry TFAA (1.26g, 6mmol) in THF (10ml) at -78°C was added in the same way. The mixture was stirred at -127°C for 1h, allowed to warm to room temperature and stirred for 18h. Solvents were removed under vacuum and ether (30ml) added. The solution was washed with water (3 x 20ml), dried ($MgSO_4$), filtered and concentrated. The crude product was placed on a silica gel (230-400 mesh) column and eluted first with light petroleum and then with 1% CH_2Cl_2 : 99% light petroleum which gave almost pure ketones. The ketones were further purified by distillation.

The ketones produced in this way were as follows.

2.2 Ketones from $Mes_2BCHLiHept$

2.2.1 Decan-2-one (0.554g, 71%) (Table 2, exp. 8) was isolated as an oil, b.p. 209°C/760mm lit.[13] 92°C/10mmHg). Found, C, 76.83%; H, 12.78%, M^+, 156.1512. $C_{10}H_{20}O$ requires C, 76.92%; H, 12.82%, M, 156.15141. δ_H 0.84(3H, t, J 6Hz, H-10), 1.0 to 1.65(12H, m, H-4 to H-9), 2.1(3H, s, H-1), 2.4(2H, t, J=8Hz, H-3). δ_C 14.07(C-10), 22.63(C-9), 23.88(C-8), 23.93(C-7), 29.10(C-6), 29.19(C-5), 29.8(C-4), 31.71(C-1), 43.84(C-3), 209.2(C-2). m/z 156(29) 77(100), 50(74). ν_{max} (film), 2940, 2870, 1725, 1470, 1364, 1165 cm^{-1}.

2.2.2 Undecan-3-one (0.612g, 72%) (Table 2, exp. 9) was isolated as an oil, b.p. 226°C/760mm (lit.[14], 227°C). Found, C, 77.63%; H, 12.91%, M^+ 170.1676. $C_{11}H_{22}O$ requires C, 77.57%; H, 12.93%, M, 170.1671. δ_H 1.01(3H, t, J=7Hz, H-1) and (3H, t, J=4Hz, H-11), 1.14-1.7 (12H, m, H-5 to H-10), 2.2-2.54(4H, m, H-2 and H-4). δ_C 7.8 (C-11), 14.09(C-1), 22.69(C-10), 24.02(C-9), 29.19(C-8), 29.37(C-7), 29.42(C-6), 31.88(C-5), 35.87(C-2), 44.48(C-4), 211.82(C-3). m/z, 170(5), 141(50), 72(100), 71(68), 69(15), 57(92), 55(28). ν_{max} (film, 2950, 1720, 1475, 1420, 1385, 1145, 1116 cm^1.

2.2.3 Hexadecan-8-one (0.912g, 76%) (Table 2, exp. 9) was isolated as a white solid, m.p. 42°C. Found, C, 79.97% H, 13.3%, M+ NH_4^+, 258.2787; $C_{16}H_{32}O$ requires C, 80.07%, H, 13.33%, M + NH_4^+, 258.2796. δ_H 0.86(6H, t, J=6Hz, H-1 and H-16), 1.1-1.7 (22H, H-2 to H-8 and H-10 to H-15), 2.2-2.46(4H, m, H-7 and H-9). δ_C 14.09(C-1, C-16)), 22.67, 22.76(C-2, C-15, C-14), 23.96(C-3, C-13), 29.17, 29.32, 29.43, 31.74, 31.86, 31.88(C-4, 5, 6, 10, 11,12), 42.86(C-7, C-9), 211.59(C-8). m/z 241(M + 1) (6), 141(27), 127(36), 113(8), 96(10), 71(69), 57(100). ν_{max} (KBr), 2940, 2865, 1720, 1470, 1220 and 1155 cm^{-1}.

2.2.4 5-Ethyltetradecan-6-one (1.02g, 85%) (Table 2, exp. 11), b.p. 278°C/760mm, (lit.[15] 90^0-93°C/0.8mm Hg). Found, C, 79.83%; H, 13.25%, M^+, 240.2451. $C_{16}H_{32}O$ requires C, 79.95%, H, 13.25%, M, 240.2433. δ_H 0.6-1.02(9H, m, H-1, H-14 and H-5''), 1.04-1.7(21H, m, H-2 to H-5, H-8 to H-13, H-5'), 2.36(2H, t, J=7Hz, H-7. δ_C 11.92(C-14), 13.93(C-1), 14.08(C-16), 22.68(C-13), 22.88(C-12), 23.56(C-11), 24.73(C-10), 29.19, 31.11, 31.88(C-3, C-4,

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

C-5′, C-8, C-9), 42.36(C-7), 53.94(C-5), 215.01(C-6). m/z 240(46), 141(37), 86(22), 71(31), 57(100). ν_{max} (film), 2940, 1723, 1472, 1388 cm^{-1}.

2.2.5 *2,2-Dimethylundecan-3-one* (0.91g, 92%) (Table 2, exp. 12) was isolated as an oil, b.p. 263°-264°C/750mm. M$^{\cdot+}$ 198.19817, $C_{13}H_{26}O$ requires 198.19836. δ_H 0.78-0.96(3H, m, H-11), 1.08(9H, s, C(C*H*$_3$)$_3$, 1.16-1.7(12H, m, H-5 to H-10), 2.44(2H, t, J=8Hz, H-4). δ_C 14.09(C-11), 22.69(C-10), 24.01(C-9), 26.45(C.(*C*H$_3$)$_3$), 29.23(C-8), 29.41(C-7), 29.76(C-6), 31.89(C-5), 36.47(C-4), 44.13(C-2), 215.99(C-3). m/z 141(38), 85(11), 71(51), 57(100), 55(29), 43(50). ν_{max} (film), 2920, 1720, 1475, 1373, 1130, 800, 722 cm^{-1}.

2.2.6 *Cyclopentyl octyl ketone* (1.03g, 89%) (Table 2, exp. 13) was isolated as a colourless oil, b.p. 81°C/0.1mm Hg. Found, C, 79.98%; H, 12.39%, M$^+$ 210.1998. $C_{14}H_{26}O$ requires C, 79.92%; H, 12.36%, M, 210.1984. δ_H 0.84(3H, t, J=5Hz, H-9)[a], 0.98-1.95(20H, m, H-3 to H-8 and H-2′, 3′), 2.4(2H, t, J=8Hz, H-2), 2.65-2.98(1H, m, H-1′). δ_C 14.13(C-9), 22.7(C-8), 24.0(C-7), 26.12(C-6), 29.02, 29.56, 29.51, 29.3, 31.98(C-3, C-4, C-5, C-2′, C-3′), 41.89(C-2), 51.45(C-1′), 213.1(C-1).

2.2.7 *Cyclohexyl octyl ketone* (0.87g, 78%) (Table 2, exp. 14) was isolated as a colourless oil, b.p. 139°C/5mm Hg. Calculated for $C_{15}H_{28}O$ is 224.2140, observed was 224.2140. δ_H 0.85(3H, t, J=6Hz, H-9)[b], 1.02-2.26(22H, m, H-3 to H-8, H-2′, 3′), 2.38(2H, t, J=8Hz, H-2). δ_C 14.68(C-9), 22.68(C-8), 23.81(C-7), 25.53, 25.77, 25.94, 28.57, 29.2, 29.42(C-3, 4, 5, 6, 2′, 3′), 40.7(C-2), 50.88(C-1′), 214.4(C-1). m/z, 244(4), 141(27), 111(37), 83(100), 71(32), 57(27), 55(52), 42(43). ν_{max} (film) 2960, 2880, 1725, 1460, 1380 cm^{-1}.

2.3 Ketones produced from $Mes_2BCHLiPr$

2.3.1 *1-Phenylhexan-2-one* (0.66g, 75%) (Table 2, exp. 15) was isolated as a clear oil, b.p. 84°C/0.5mm Hg. M$^{\cdot+}$ 176.12001, calculated for $C_{12}H_{16}O_4$ is 176.12011. δ_H 0.85(3H, t, J=7.35Hz, H-6)[c], 1.17-1.32(2H, m, H-5), 1.46-1.58(2H, m, H-4), 2.43(2H, t, J=7.25Hz, H-3), 3.66(2H, s, H-1), 7.17-7.44(5H, m, Ar-*H*). m/z 176(8), 105(7), 91(75), 85(81), 77(12), 65(30), 57(100), 41(29). ν_{max} (film) 3020, 2910, 1730, 1380, 1229, 1072, 770, 720 cm^{-1}.

2.3.2 *6-Ethyldecan-5-one* (0.8g, 87%) (Table 2, exp. 16) was isolated as a clear oil, b.p. 214°-216°C/750mm Hg. (M+1)$^+$ 185.1926, calculated for $C_{12}H_{25}$(M+1) is 185.1905. δ_H 0.81-0.93(9H, m, H-1, H-10, H-6″)[d], 1.18-1.6(12H, m, H-7 to H-9, H-2, H-3, H-6′), 2.25-2.43(3H, m, H-4, H-6). δ_C 10.82(C-10). 12.88(C-1), 21.49(C-2), 21.93(C-9), 23.77(C-3), 24.7(C-12), 28.78, 28.79(C-7, C-8), 30.17(C-11), 41.11(C-4), 52.87(C-6), 213.16(C-5). m/z 184(3), 128(18), 99(10), 85(58), 57(100), 41(28). ν_{max} (film), 2960, 2880, 1720, 1469, 1382, 1260 cm^{-1}.

2.3.3 *Cyclohexyl butyl ketone* (0.689g, 82%) (Table 2, exp. 17) was isolated as a clear oil, b.p. 234°C/750mm Hg. Found, C, 78.13%; H, 11.72%; M$^+$, 168.1511. $C_{11}H_{20}O$ requires C, 78.52%; H, 11.89%; M, 168.1514. δ_H 0.90(3H, t, J=7.25Hz, H-5)[e], 1.21-1.84(14H, m, H-3, H-4 and Chx-*H*), 2.25-2.37(1H, m, H-1′), 2.43(2H, t, J=7.1Hz, H-2). δ_C 13.5(C-5), 22.64(C-4), 25.93(C-3′), 26.02(C-4′), 26.2(C-3), 28.74(C-2′), 40.37(C-2), 50.87(C-1′), 213.25(C-1) m/z 168(26), 111(27), 85(42), 83(100), 57(52), 55(66), 41(26). ν_{max} (film) 2940, 2865, 1715, 1450, 1380, 1146 cm^{-1}.

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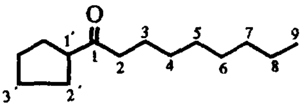

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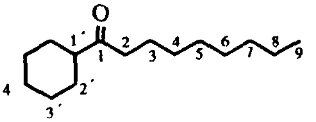

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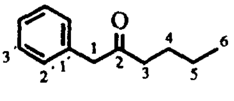

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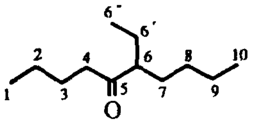

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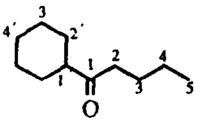


2.4 Ketones produced from $Mes_2BCHLiEt$

2.4.1 1-Phenylpentan-2-one (0.332g, 41%) (Table 2, exp. 18) was isolated as an oil, b.p. 114°C/4mm Hg. Found, C, 81.92%; H, 8.87%; M^+, 162.0999. $C_{11}H_{14}O$ requires 81.55%; H, 8.64%; M, 162.1045. δ_H 0.83(3H, t, J=7.4Hz, H-5),[a] 1.55(2H, sextet, J=7.5Hz, H-4), 2.38(2H, t, J=7.2Hz, H-3), 3.62(2H, s, H-1), 7.15-7.32(5H, m, Ar-*H*). δ_C 13.61(C-5), 17.15(C-4), 43.83(C-3), 50.08(C-1), 126.89, 128.66, 129.4(C-2', C-3', C-4'), 134.5(C-1'), 208.2(C-2). m/z 162(6), 91(58), 83(15), 77(5), 71(100), 65(29), 43(61). ν_{max} (film), 3025, 2850, 1720, 1450, 1364, 1120, 1090, 750, 690 cm^{-1}.

2.4.2 5-Ethylnonan-4-one (0.348g, 41%) (Table 2, exp. 19) was isolated as an oil, b.p. 97°C/10mm Hg. Found, $(M+1)^+$, 171.1725, $C_{11}H_{22}O$ requires M+1 = 171.1749. δ_H 0.81-0.93(9H, m, CH_2CH_3), 1.62-1.91(10H, m, H-2, H-6, H-7, H-8, H-5')[b], 2.36-2.42(3H, m, H-3, H-5). δ_C 11.93(C-9), 13.99, 14.02(C-1, C-5"), 17.11(C-8), 23.90, 24.90, 29.96, 31.31(C-2, C-6, C-7, C-10), 44.46(C-3), 53.96(C-5), 213.7(C-4). m/z 171(M+1)(3), 114(21), 99(16), 86(12), 71(68), 57(100), 43(46). ν_{max} (film) 2940, 1720, 1468, 1385, 1120, 1030, 730 cm^{-1}.

3. General procedure for the preparation of ketones by the condensation of $Mes_2BCHLiR^1$ with R^2CHO in the presence of NCS.

3.1 A solution of carbanion, $Mes_2BCHLiR^1$ (R^1=H, Me, Et, Hept) (5mmol) prepared as above (Section 1) was cooled to -127°C under nitrogen and stirred. A solution of freshly distilled aldehyde (5mmol) in THF (5ml), pre-cooled to -78°C was added, *via* a cooled double-ended needle, dropwise down the spiral side arm of the reaction flask.

The mixture was stirred at 127°C for 1h and then a solution of sublimed N-chlorosuccinimide (2.6g, 20mmol) in THF (65ml) at -78°C was added through a wide bore double-ended needle. The mixture was stirred at -127°C for 2h, allowed to warm to room temperature, at which it was stirred for 18h.

Solvents were removed under vacuum and then ether (50ml) added. The suspension was washed with water (4 x 20ml), dried ($MgSO_4$) and filtered. The crude product was purified by chromatography on a silica gel (230-400 mesh) column, the ketones being eluted with a 1% CH_2Cl_2 : 99% light petroleum mixture.

3.2 Ketones produced from $Mes_2BCHLiHept$

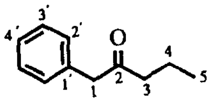
3.2.1 Hexadecan-8-one (0.876g, 73%) (Table 3, exp. 25) was isolated as a clear oil. It was identical in all respects with an authentic sample (Section 2).

3.3 Ketones produced from $Mes_2BCHLiEt$

3.3.1 1-Phenylpentan-2-one (72%)[16] (Table 3, exp. 26) was isolated with mesitylene and identified by comparison of its g.c. and ^1H nmr with an authentic sample. The yield was calculated by g.c. analysis using hexadecane as internal standard and a response factor of 1.0968.

3.3.2 5-Ethylnonan-4-one (79%) (Table 3, exp. 27) identical with authentic product by g.c. co-injection and g.c./m.s. The yield was calculated using hexadecane as an internal standard and a response factor of 1.1237.

a



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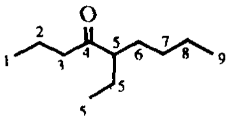


3.4 Ketones produced from $Mes_2BCHLiMe$

3.4.1 Decan-3-one (0.56g, 72%) (Table 3, exp. 28) was isolated as an oil, b.p. 211°C/758mm Hg (lit.[17] 203°C/754mm Hg). Found, C, 76.88%; H, 12.79%, $(M+NH_4)^{\cdot+}$, 174.1854. $C_{10}H_{20}O$ requires C, 76.87%; H, 12.81%, $(M+NH_4)^+$, 174.1858. δ_H 0.71(3H, t, J=5.8Hz, H-10), 0.88(3H, t, J=6.1Hz, H-1); 1.1(8H, s, H-6 to H-9), 1.37-1.43(2H, m, H-5), 2.20-2.29(4H, m, H-2 and H-4). δ_C 7.87(C-10), 14.1(C-1), 22.73, 24.1, 29.2, 29.4, 31.84(C-5 to C-9), 42.47(C-4), 211.41(C-3). m/z 156(1.3), 127(19), 85(8), 72(34), 57(100), 43(27), 41(18). ν_{max} (film), 2980, 2880, 1722, 1465, 1380, 1140, 1110 cm^{-1}.

3.4.2 Benzyl ethyl ketone (Table 3, exp. 29) (1-Phenylbutan-2-one) (0.42g, 57%) was isolated as a clear oil, b.p. 229-230°C/750mm (lit.[16] 230°C/765 mmHg), M^+, 148.0931, $C_{10}H_{12}O$ requires 148.0888. δ_H 0.99 (3H, t, J=7.28Hz, H-4), 2.63(2H, q, J=7.23Hz, H-3), 3.63(2H, s, H-1), 7.16-7.32(5H, m, Ar-*H*). δ_C 7.74(C-4), 49.73(C-1), 126.9, 128.6, 129.4 (C-2′, C-3′, C-4′), 134.5(C-1′), 208.9(C-2). ν_{max} 3020, 2850, 1730, 1380, 1115, 917, 735, 690 cm^{-1}.

3.4.3 4-Ethyloctan-3-one (0.53g, 68%) (Table 3, exp. 30) was isolated as an oil, b.p. 189°C/760mm Hg. Found, C, 76.91%; H, 12.80%; $(M+1)^+$ 157.1607. $C_{10}H_{20}$ requires C, 76.87%; H, 12.81%; (M+1), 157.1593. δ_H 0.86(6H, q, J=7.1Hz, H-8, H-4")[a], 1.03(3H, t, J=7.25Hz, H-1), 1.17-1.67(8H, m, H-5, H-6, H-7, H-4′), 2.35-2.47(3H, m, H-2, H-4). δ_C 7.7(C-8), 11.94(C-4"), 13.97(C-1), 23.03(C-7), 25.03(C-6), 29.96(C-5), 31.44(C-4′), 35.61(C-2), 53.86(C-4), 214.7(C-3). m/z 156(1), 127(2), 100(26), 85(9), 71(7), 57(100), 43(25), 41(26). ν_{max} (film), 2980, 2895, 1470, 1385, 1110 cm^{-1}.

3.5 Ketones prepared from Mes_2BCH_2Li

3.5.1 Octan-2-one (0.199g, 28%) was isolated as an oil, b.p. 193°C/room pressure, (lit..[17]194-196°C/room pressure). Identical in all respects with an authentic sample.

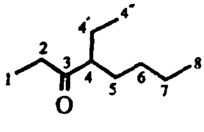
3.5.2 *3-Ethylheptan-2-one* (0.149g, 21%) was isolated as an oil, b.p. 164°C/756mm Hg, Lit.[18] (165-166°C/760 mm Hg. $(M+NH_4)^+$, 160.1703. $C_9H_{22}ON$ requires 160.1701. δ_H 0.87(6H, q, J=5.88Hz, H-7, H-3")[b], 1.19-1.67(5H, m, H-4 to H-6 and H-3′), 2.1(3H, s, H-1), 2.32-2.43(1H, m, H-3). δ_C 11.82(C-7), 13.36(C-3"), 22.96(C-6), 24.73(C-5), 28.75, 29.78, 31.11(C-8, C-4), C-1), 54.84(C-3), 210.12(C-2). m/z 142(3), 99(4), 86(49), 71(40), 57(100), 53(4), 43(69), 41(27). ν_{max} (film), 2980, 2895, 1475, 1385, 1113 cm^{-1}.

3.5.3 Cyclohexyl methyl ketone (0.18g, 29%) was isolated as an oil, b.p. 182°C (lit.[19] 180°C), M^+ 126.1048, $C_8H_{14}O$ requires 126.1045. δ_H 1.26-1.87(10H, m, H-2′ to H-4 ′)[c], 2.13(3H, s, H-2), 2.22-2.34(1H, m, H-1′), δ_C 25.7, 25.96(C-3′, C-4′), 27.84, 28.52(C-2, C-2′), 51.46(C-1′), 211.93(C-1). m/z 126(32), 111(16), 83(91), 71(46), 67(28), 55(100), 43(56), 41(33). ν_{max} (film) 2965, 2875, 1720, 1455, 1350, 887, 730 cm^{-1}.

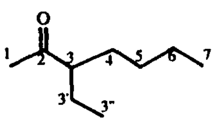
3.5.4 Preparation of benzyl methyl ketone by use of NCS-Me_2S

A solution of Mes_2BCH_2Li (5.68mmol) in THF made as in Section 2, was cooled to -78°C and transferred through a double-ended needle to a stirred solution of phenylacetaldehyde (0.68g, 5.68mmol) in THF (5ml) at -78°C. The reaction was allowed to stir for 1h at -78°C. *N*-Chlorosuccinimide (0.8g, 6mmol) in THF (30ml) was cooled to 0°C and dimethyl sulphide (0.37g, 0.437ml, 6mmol) was added dropwise by syringe. The resulting suspension was transferred *via* a wide bore, double-ended needle to the stirred reaction mixture at -78°C. Dry triethylamine (0.6g, 0.826ml, 6 mmol) was added by syringe and the reaction mixture was left stirring at -78°C for a further hour. The mixture was then stirred for 18h at room temperature. Solvents were removed under vacuum and ether (30ml) added. The solution was washed with 1M HCl (2 x 20ml), water (3 x 10ml), dried ($MgSO_4$), filtered and concentrated. The crude product (g.c. yield of ketone, 44%) was dissolved on a 230-400 mesh silica column and eluted with 1% CH_2Cl_2/99% light petroleum to give benzyl methyl ketone (0.282g, 37%), identical in every respect with an authentic sample.

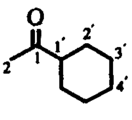
[a]



[b]



[c]



4. Alkenes produced from Mes_2BCH_2Li and RCHO in the presence of TFAA.

4.1 General procedure. The procedure used was exactly the same as the general procedure in Section 2. All product mixtures were analysed for ketones and alkenes by g.c. The alkenes were characterised by co-injection with authentic samples both by simple g.c. and by g.c./m.s. Isolation of alkenes was accomplished by slow elution of a long silica gel column (230-400 mesh) with light petroleum (40°-60°C). The alkenes ran before the mesitylene present.

In this way were prepared: (a) *oct-1-ene* (91%), g.c./m.s.); (b) *non-1-ene* (0.306g, 81%); (c) *undec-1-ene* (0.285g, 74%); *vinylcyclohexane* (76% g.c./m.s.).

5. Miscellaneous experiments

5.1 Isolation of 8-(trifluoroacetoxy)hexadec-8-ene from the condensation of $Mes_2BCHLiHept$ (2) and octanal in the presence of TFAA.

A solution of octanal (0.32g, 2.5mmol) in THF (3ml) at -115°C (Et_2O, liquid N_2) was added *via* a cooled double-ended needle to a stirred solution of carbanion (2) (3mmol, Section 1.2) at -115°C. The needle was washed through with cold THF (3ml) and the reaction mixture was stirred for 30 min at -115°C. A solution of TFAA (1.26g, 6mmol) in THF (3ml) at -78°C was then added, in the same fashion, to the stirred reaction mixture at -115°C. The reaction was then stirred for 1h at -115°C, for 3h at -78°C and for 16h at room temperature.

The solvents were removed under vacuum to give a residue which had one main peak (retention time = 30.7 min) in the g.c. (6', 5% OV 17; 60°-120°C(3°/min); 120°-250°C (5°/min), 250°C for 15 min). The residue was subjected to rapid flash chromatography on *neutral alumina.*

8-(Trifluoroacetoxy)hexadec-8-ene (150mg, 18%) eluted with hexane, before mesitylene and had the same g.c. retention time as the main peak of the crude product. The product is labile and could not be analysed nor did it give a molecular ion. The highest peak in the mass spectrum was at 223(17) ($M-CF_3CO_2$). δ_H 0.86(6H, t, J=7Hz, H-1, H-16), 1.90(22H, H-2 to H-6, H-10 to H-15), 2.22(2H, t, J=3Hz, H-7), 5.08(1H, t, J=7Hz, H-9). δ_C 23.0-33.1(C-1 to C-7, C-10 to C-16), 99.2, 110.4, 122.0, 133.8(CF_3), 118.2(C-9, *Z*-isomer), 130.3(C-9, *E*-isomer), 148.3(C-8), 158.0(C=O). ν_{max} (film) 2970, 2940, 2870, 1800, 1470, 1365, 1230 cm^{-1}.

5.2 Reactions of $Mes_2BCHLiHept$ (2) with HeptCHO in the presence of Me_3SiCl

5.2.1 To a stirred solution of (2) (2.2mmol, Section 1.2) at -78°C under argon was added a solution of octanal (0.18g, 0.14mmol) and chlorotrimethylsilane (0.436g, 4.2mmol) in THF (5ml), also at -78°C. The reaction mixture was stirred at -78°C for 3h, and then at room temperature for 16h. Solvents were removed under vacuum to give a residue with signals at 0.08 and -0.07ppm, suggesting silylated intermediates. G.c. analysis (6', 5% OV-17, on atomite 100-200 mesh, 60°-120°C (3°C/min), 120°-250°C (10°C/min), 250°C for 15 min) showed the presence of hexadec-8-ene (30.45 min), hexadecan-8-one (33.01 min) and an unidentified peak at 34.7 min.

The product mixture was dissolved in light petroleum (10ml), cooled to -78°C then stirred with aqueous hydrofluoric acid (1ml) in acetonitrile (20ml) for 30 min at -78°C. The mixture was allowed to warm to room temperature, the organic layer washed with water (4 x 20ml), dried ($MgSO_4$), filtered and examined by g.c. which showed that only hexadec-8-ene and hexadecan-8-one were present. Column chromatography on silica using hexane gave *hexadec-8-ene* (0.0439g, 14%) and with hexane/ether (99:1) *hexadecan-8-one* (0.286g, 85%) was isolated.

5.2.2 A solution of octanal (0.32g, 2.5mmol) in THF (5ml) was cooled to -78°C and added *via* a cooled double-ended needle to a stirred solution of (2) (3mmol, Section 1.2) at -115°C. The mixture was stirred at -115°C for 15 min, and then a solution of chlorotrimethylsilane (0.55g, 5mmol) at -78°C was slowly added. The mixture was stirred for a further 30 min at -115°C then allowed to warm to room temperature. Volatiles were removed at the pump, the residue was treated with aq. HF (1ml) in acetonitrile (20ml) for 30 min at -78°C and worked up as in Section 5.2.1. Chromatography on silica gel gave *hexadec-8-ene* (50mg, 9%), plus *hexadecan-8-one* (123mg, 20%) and *hexadecan-8-ol* (330mg, 55%), all identical with authentic samples.

5.2.3 Reaction of (2) with octanal followed by methylation.

A solution of octanal (0.16g, 1.3mmol) in THF (5ml) at -78°C was added *via* double-ended needle to a solution of anion (2) (1.56mmol) and the solution was stirred at -78°C for 20 min. A precooled solution of iodomethane (1.06g, 7.5mmol) in THF was added and the solution allowed to warm to room temperature. Solvents were removed at the pump and the product analysed by g.c. (6' carbowax 20M, 100°C for 2 min, 100° to 180°C at 10°C/min, 180°-220°C at 5°C/min, 220°C for 10 min), which showed peaks due to *hexadecan-8-one* (15%) at 11.94 min and *9-methylhexadecan-8-one* (21%) at 11.71 min, identical with authentic samples (Section 1.3) by co-injection.

5.2.4 Reaction of (2) with octanal followed by iodine.

Octanal (0.12g, 0.9mmol) in THF (3ml) at -78°C was added to a solution of (2) at -115°C. After 15 min stirring a solution of iodine (0.25g, 1.0mmol) in THF (3ml) at -78°C was added, the mixture stirred for 1h at -115°C, allowed to warm to room temperature and the volatiles removed at the pump. G.c. analysis gave only *hexadecan-8-one* (44%), identical with an authentic sample by coinjection.

5.2.5 Condensation of Mes_2BCH_2Li (1) with phenylacetaldehyde in the presence of phenyliodionium diacetate.

A solution of (1) (Section 1.2) (5mmol) was cooled to -127°C under argon and stirred. A solution of freshly distilled phenylacetaldehyde (0.6g, 5mmol) in THF (5ml) precooled to -78°C was added down the spiral side arm and the reaction mixture stirred for 1h. Phenyliodionium diacetate. (1.83g, 5.68mmol) in THF (2ml), MeOH (4ml) at -78°C was added and the mixture stirred for 1h at -127°C. It was then allowed to warm to room temperature (45 min) and stirred under nitrogen for 18h.

Solvents were removed under vacuum, the residue (8.1g) was dissolved in ether (50ml), washed with saturated aq. $NaHCO_3$ (15ml) and water (3 x 10ml), dried ($MgSO_4$) and filtered to give a yellow oil (4.3g). The yield of methyl benzyl ketone (24%) was calculated by g.c. (tridecane standard, response factor 1.1178) (5% OV-17, 50°-240°C (25°C/min), 240°-260°C (5°/min), 260°-280° (20°/min), 280°C (10 min).

5.2.6 Reaction of (2) with octanol in the presence of water.

A solution of (2) (2mmol, Section 1.2) was cooled to -78°C and a solution of octanal (0.23g, 1.75mmol) and water (0.04g, 3.15mmol) in THF (5ml) at -78°C was added with good stirring. The reaction mixture was stirred for 3h at -78°C, allowed to reach room temperature then stirred for 16h. Solvents were removed, and the residue was examined by g.c. Only one product, hexadecan-8-one (55%, based on octanal) could be detected.

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