Pergamon

Tetrahedron Vol. 50, No. 48, pp. 13801-13828, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00930-9

Hindered Organoboron Groups in Organic Chemistry. 28 The Solvolyses of Bis(2,6-dimethyl-4-methoxyphenyl)organylboranes, $(DMP)_2BR$

Andrew Pelter* and Robert Drake

Department of Chemistry, University College of Swansea, Singleton Park, Swansea, SA2 8PP, UK.

Abstract. Mineral acid catalysed methanolysis of *bis* (2,6-dimethyl-4-methoxyphenyl)organylboranes $(DMP)_2BR$, (1), is much faster than that of the corresponding dimesitylorganylboranes, Mes_2BR. This allows for the release of organyl groups from 'overhindered' boranes. It also provides a link between $(DMP)_2BR$, from which α-carbanions can be produced, and $RB(OMe)_2$ which do not yield α-carbanions. Solvolyses can be enhanced by the use of glycol, which renders even acetic acid on effective solvolysis catalyst.

Introduction. We have previously used a steric approach to solve the problem of producing boron stabilised carbanions. For this purpose we have introduced *bis*(2,4,6-trimethylphenyl)organylboranes (dimesitylorganylboranes, Mes_2BR)[1-7] and *bis*(2,4,6-triisopropylphenyl)organylboranes, (ditripylorganylboranes, $Trip_2BR$)[8-10] each containing two 2,6-disubstituted aryl groups. Both series of compounds give rise to highly hindered products such as $Mes_2BCR^1R^2R^3$ or $Trip_2BCR^1R^2R^3$, which we term 'overhindered boranes', from which it has been difficult or impossible to liberate the organyl groups even using normally efficient reactions such as alkaline hydrogen peroxide oxidation. Two examples[11,12] are shown in equations (1) and (2).

$$(Me)(Et)(Pr^n)CBMes_2 \xrightarrow[Bu_4NHSO_4,\ 60^oC,\ 24h]{70\%H_2O_2\ /\ NaOH} (Me)(Et)(Pr^n)COH(30\%) \qquad (1)$$

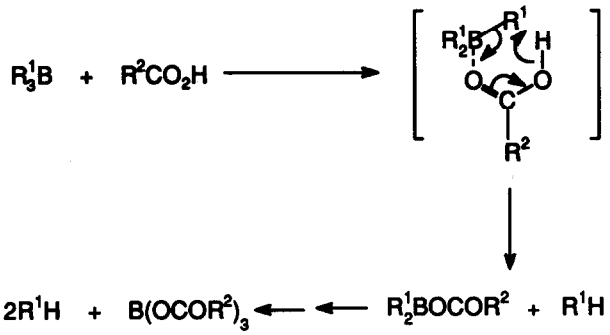
$$Trip_2BOct^n \xrightarrow{30\%H_2O_2\ /\ NaOH} \text{no reaction} \qquad (2)$$

In order to maximise the utility of reactions involving boron stabilised carbanions, it is important to have the capability of efficiently cleaving the organyl groups from the product boranes. However, most such cleavage reactions proceed by initial attack of the reagent *on boron*, and such reactions are strongly inhibited by steric hindrance around the boron atom.[13,14] It would therefore be advantageous to produce diarylorganylboranes, in which the aryl groups retained the 2,6-disubstitution patterns of the dimesityl- and ditripyl-boranes but which readily underwent electrophilic attack on the aryl groups leading to cleavage of the Ar-B bonds. Presumably reactions directly on the aromatic rings would not be so greatly influenced by the steric hindrance around the boron atom.[15]

In this approach we were encouraged by early reports[16,17] that hydrolysis[16] and brominolysis[17] of dihydroxyphenylborane proceed by electrophilic attack on the phenyl ring. By contrast, trialkylboranes are resistant to attack by water[18] and most mineral acids.[19] Thus trimethylborane undergoes 87% loss of *one* methyl group after heating with water for 9h at 215°C.[18] Loss of two methyl groups only occurs at 310°C, and other tri-*n*-alkylboranes are only slightly more reactive.[20]

Hydrogen chloride requires a temperature of 110°C to remove one *n*-butyl group from tri-*n*butylborane, and even at 180°-210°C two *n*-butyl groups are not completely removed.[21] Aqueous hydrogen bromide removes one *n*-butyl group on refluxing for 1h.[22] Only anhydrous hydrogen fluoride readily cleaves tri-*n*-alkylboranes,[23] in part at least due to the high heat of formation of the B-F bond.[24]

The reactions of tri-*n*-alkylboranes with carboxylic acids proceed so that an *n*-alkyl group is readily removed at room temperature, the second is removed after a prolonged reaction time, and removal of the third alkyl group requires 130°-140°C.[25-27] The rates of protonolysis are *inversely* proportional to the pK_A of the carboxylic acids. Thus for the protonolysis of triethylborane by acetic acid, the rate constant is 4.7×10^{-3} mol.$^{-1}$ sec.$^{-1}$ whilst it is too low to measure for trifluoroacetic acid.[28] The reaction, which is first order in both components, proceeds with retention of configuration[29] and is sensitive to steric hindrance, particularly at the β -carbon atom.[30] The progressive lowering of the rates of protonolysis of the first, second and third alkyl groups shows that the Lewis acidity of the boron atom is an important factor in the rate of solvolysis. To explain these results a cyclic mechanism shown in Scheme 1 has been proposed.[31]



Scheme 1

In a preliminary experiment[32] we showed that the mesityl group was more susceptible to solvolysis by a carboxylic acid than a 1-alkenyl group (equation 3).

$$Mes_2BCH{=}CHHex^n \xrightarrow[65^oC,\ 24h]{6\ EtCO_2H} \underset{(80\%)}{MesH} + \underset{(14\%)}{CH_2{=}CHHex^n} + MesB(O_2CEt)CH{=}CHHex^n \qquad (3)$$

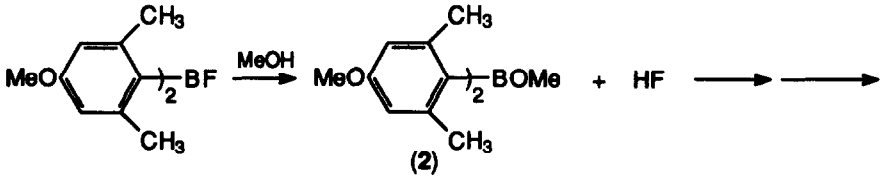
The 2,6-dimethyl-4-methoxyphenyl(DMP) group.[33] The 2,6-dimethyl-4-methoxyphenyl (DMP) group seemed worth investigating for three reasons. (i) 3,5-Dimethylphenol is cheap and readily available. (ii) 1-Boryl-DMP derivatives retain the 2,6-dialkylation pattern of the mesityl and tripyl series.
(iii) Replacement of the 4-alkyl group of the mesityl and tripyl series by a 4-methoxy group should aid electrophilic attack on the aromatic ring.

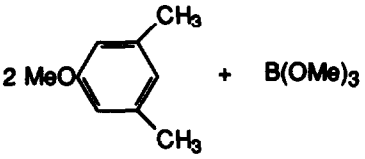
With regard to points (i) and (ii) we have, in the preceding paper[34], developed simple routes for the synthesis of $(DMP)_2BR$, (1), and demonstrated the ready production of α-carbanions from (1).[34] To support point (iii) we noted; (a), that anisole is more susceptible than toluene to electrophilic attack[35]; (b), that dihydroxy(4-methoxyphenyl)borane undergoes protonolysis[16] and brominolysis[17] much more readily than does dihydroxy(4-methylphenyl)borane; (c), trimethoxyborane is far more readily hydrolysed than is trimethylborane.[18] Hence the DMP group might well be readily released from an overhindered borane and the product should then be capable of oxidation according to equation 4.

$$(DMP)_2BCR^1R^2R^3 \xrightarrow{EH} (DMP)B(E)CR^1R^2R^3 \xrightarrow{EH} E_2BCR^1R^2R^3 \xrightarrow{[O]} HOCR^1R^2R^3 \qquad (4)$$

Methanolysis of $(DMP)_2BX$ with mineral acid catalysis.

(i) *Methanolysis of $(DMP)_2BF$.* A 0.259M solution of $(DMP)_2BF$ in THF containing hexadecane as an internal g.l.c. standard was divided into two portions. An equal volume of anhydrous methanol was added to each portion, one of which was held at 50°C and the other at 20°C. Samples were removed at various intervals, quenched and quantitatively analysed for 3,5-dimethoxybenzene (DMPH) (equation 5).





+ $B(OMe)_3$ (5)

The results (exact procedures for this and all succeeding studies are given in the Experimental section) showed that at 50°C, one equivalent of DMPH was produced in 1h, whilst removal of both groups took 8.5h (Figure 1). There was, however, no break in the curve. At 20°C, one DMP group was removed in 14h, but even after 75h reaction was incomplete.

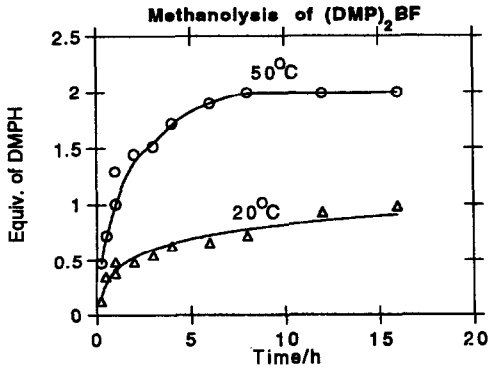


Fig. 1

Surprisingly, the ^{11}B nmr of the product mixture showed that both BF_3 and $B(OMe)_3$ were present, and in the case of the 20°C solvolyses there was also some $(DMP)B(OMe)_2$. Trifluoroborane could be produced by reaction (6) (though dismutations and exchange reactions could occur at all stages of the solvolytic pathway), which though unforseen is not unreasonable in view of the strength of the B-F bond[22] and the stability of the trifluoroborane-methanol complex.[36] Reaction (6) results in the loss of hydrogen fluoride and a possible slowing of solvolysis dependant on whether or not, and to what extent, trifluoroborane is itself a catalyst.

$$(MeO)_3B + 3HF \longrightarrow BF_3 + 3MeOH \qquad (6)$$

(ii) *Methanolysis of $(DMP)_2BOMe$ (2).* The results of some solvolyses of $(DMP)_2BOMe$ using one equivalent each of different acids in THF-MeOH (1:3) at 0.08M concentrations of (2) and acid at 50°C are shown in Figure 2.

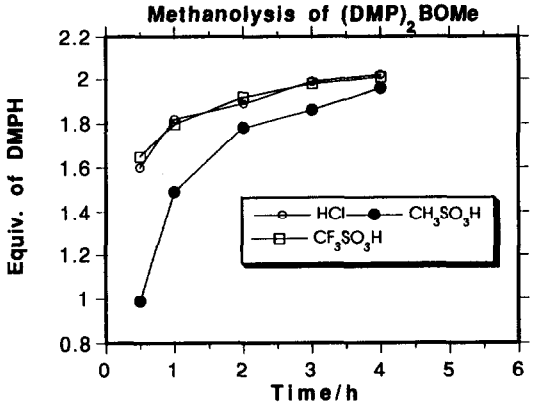


Fig. 2

In this case mineral acid effects the removal of both DMP groups in *ca.* 3h which contrasts with the methanolysis of $(DMP)_2BF$ in which the mineral acid is removed by equation (6). Acetic and trifluoroacetic acids were completely ineffective as acid catalysts for the removal of DMP groups. Ammonium chloride and sodium methoxide also did not function as catalysts and no protonolysis occurred with pure methanol.

It took *ca.* 3h for the removal of the DMP group from $(DMP)B(OMe)_2$ using hydrogen chloride, showing that *it is the second step in the methanolysis of $(DMP)_2BOMe$ that is the slow step.*

(iii) *The methanolysis of alkylbis(2,6-dimethyl-4-methoxyphenyl)boranes(1).*

For these experiments the same methodology was used as for the methanolysis of $(DMP)_2BOMe$ (2), with the overall results given in Table 1.

Table 1. Mineral acid catalysed methanolyses of hindered diarylorganylboranes, Ar_2BX

Exp.	Organoborane	Time(h) to remove 1 or 2 aryl groups					
		HCl		CF_3SO_3H		$MeSO_2H$	
		1	2	1	2	1	2
1	$(DMP)_2BMe$	0.10	1.05	0.10	1.05	0.10	1.05
2	Mes_2BMe	36.4	48(1.15)[a]	48.0(0.89)[a]	-	-	-
3	$(DMP)_2BEt$	0.22	1.7	0.22	1.7	0.48	3.60
4	$(DMP)_2BBu^n$	0.24	1.6	0.24	1.6	0.54	3.25
5	$(DMP)_2BOct^n$	0.30	3.2	0.50	4.0	-	-
6	$(DMP)_2BCH(Me)Pr^n$	1.0	17.2	1.0	17.2	-	-
7	$(DMP)_2BCH(Et)Pr^n$	4.2	56.8	4.2	56.8	-	-
8	$(DMP)_2BCH(Et)Hept^n$	6.2	136	6.4	150	-	-
9	$(DMP)_2BBu^t$	7.2	109	7.2	109	18	200(1.80)[a]
10	Mes_2BBu^t	190	200(1.01)[a]	200(0.9)[a]	-	-	-
11	$(DMP)_2BC(Me)(Et)(Bu^n)$	12.6	179	12.6	179	-	-
12	$(DMP)_2BCH_2CH{=}CH_2$[b]	0.20	2.9	0.47	4.5	0.9	5.6
13	$(DMP)_2BCH_2SiMe_3$	0.15	5.0	0.15	5.0	-	-
14	$(DMP)_2BCH{:}CHBu^n$	1.1	19.0	0.60	4.4	-	-
15	$(DMP)_2BC(Et){=}CHEt$	[101][c]	-	16.0	[99][c]	-	-
16	$(DMP)_3B$	No reaction		No reaction		No reaction	
17	$(DMP)_2BC{\equiv}CBu^n$[d]	0.80	12.2	0.16	4.4	-	-
18	$(DMP)_2BOMe$	3.1	-	3.1	-	-	-
19	$(DMP)B(OMe)_2$	0.16	3.0	0.16	3.0	-	-

[a] Reaction stopped at time shown, with mol. equiv. of DMPH present shown in brackets. [b] Allyl group also lost.

[c] Reaction stopped at 96h, time of reaction estimated graphically. [d] Hexynyl group also lost.

Clearly hydrogen chloride and trifluoromethanesulphonic acids are the most effective mineral acid catalysts for the removal of one or two DMP groups from $(DMP)_2BX$. Even these fail when the boron group is surrounded by 6-*ortho*-methyl groups (experiment 16), as found for the mesityl series[14], though the reason for the failure may be different in the two cases (*vide infra*).

Experiments (1) and (2) and experiments (9) and (10) illustrate that indeed *$(DMP)_2BR$ solvolyse faster than Mes_2BR in comparable conditions*. In all but two cases (experiments 12, 17), $RB(OMe)_2$ is produced, as

established by the peak at 31ppmm in the ^{11}B nmr and by oxidation to give ROH in > 95% yields. In certain cases (experiments 5, 8, 11) the analytical conditions were such that if any RH had been produced, it would have been detected but, in fact, the alkane was not seen. **Thus the link has been established between $(DMP)_2BR$, which yields α-carbanions and $(MeO)_2BR$ that do not.**

Lengthening of an *n*-alkyl chain has little effect on the rates of methanolysis (experiments 1, 3, 4, 5) but α-substitution particularly by an ethyl group led to lowering of the rates of methanolysis (experiments 6,7,8), enhanced by a lengthening of the main chain (experiment 8). α,α-Disubstitution led to a further lowering of the rate of methanolysis (experiments 9,11). *Nevertheless, even in these dilute kinetic conditions, both DMP groups were eventually removed for all $(DMP)_2BR$.*

When an alkenyl group was attached to boron the rate of methanolysis was lowered (compare experiments 4 and 14) and this effect was strongly increased by α-substitution of the alkene (experiment 15). An alkynyl group attached to boron had much the same effect as a CH=CHR group (compare experiments 14 and 17). For the solvolysis of alkenyl- or alkynyl-boranes the use of trifluoromethane sulphonic acid is advantageous, presumably because hydrogen chloride adds to the unsaturated systems.

The known ease of protonolysis of allyl-[37-39] and alkynyl-boranes[40-42] is in line with the loss of these organyl groups concomitantly with the DMP group (experiments 12, 17).

Concentration effects. For both practical and theoretical purposes it was necessary to examine the effects of concentrations of both acid and substrate. The acid used was HCl and $(DMP)_2BBu^t$ was chosen as a difficultly hydrolysable borane. The results (Table 2) are as expected and show that by increasing the concentrations, even $(DMP)_2BBu^t$ can be methanolysed with little trouble. The ease of loss of *one* DMP group is particularly important as this may be sufficient for further reactions, such as with alkaline hydrogen peroxide, to proceed rapidly (*vide infra*).

Table 2. Concentration effects on the methanolysis of $(DMP)_2BBu^t$

Exp.	Molarity of $(DMP)_2BBu^t$	Time(h) for removal of 1 or 2 DMP groups					
		0.5 equiv. HCl		1.0 equiv. HCl		2.0 equiv. HCl	
		1	2	1	2	1	2
20	0.073	21.4	192(1.45)[a]	7.2	109	4.9	77
21	0.089	-	-	-	-	3.1	67
22	0.145	-	-	2.8	50.5	-	-
23	0.178	-	-	2.0	41.6	-	-

[a] Reaction stopped at 192h; mol. equiv. of DMPH in brackets.

Solvent composition effects. The kinetic experiments used a 3 : 1, MeOH-THF mixture, which was the highest proportion of methanol that could be present and the reaction mixture remain homogeneous. In Table 3 are shown the results of some variations in the solvent composition of homogeneous methanolyses of $(DMP)_2BBu^t$.

Table 3. Solvent composition effects on the methanolysis of $(DMP)_2BBu^t$

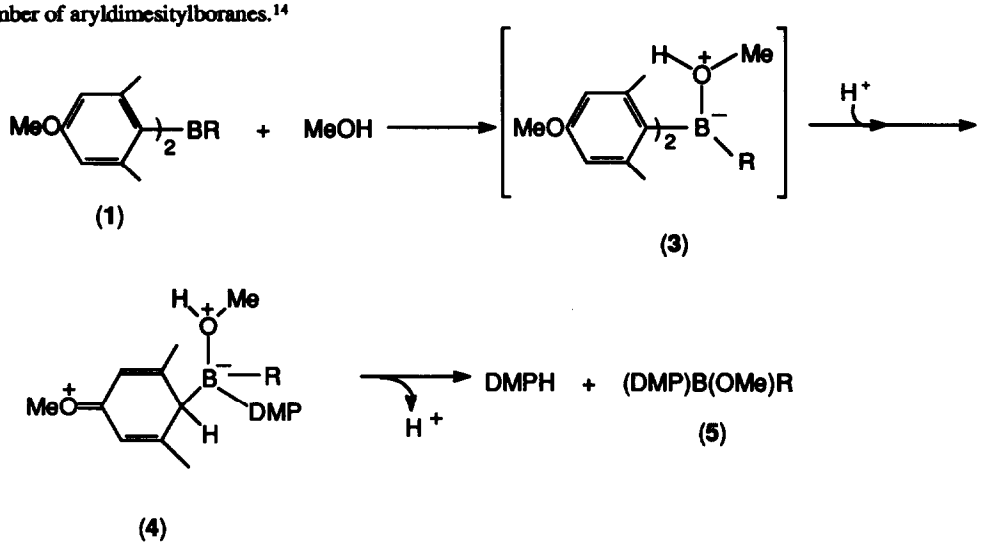
Exp.	Solvent MeOH : THF	Conc. of borane (M)	Time(h) for removal of 1 or 2 DMP groups 1	2
24	2.70 : 1.0	0.073	7.2	108
25	0.38 : 1.0	0.073	3.9	192 (1.45)[a]
26	2.70 : 1.0	0.17	2.0	41.6
27	0.70 : 1.0	0.17	1.4	44.0

[a] Reaction stopped at time shown, with mol. equiv. of DMPH present shown in brackets.

Most interestingly, lowering the amount of methanol present led to an *increase* in the rate of removal of the first DMP group and a *decrease* in the rate of removal of the second group, in both comparison experiments (24, 25 and 26, 27).

Mechanism of the mineral acid catalysed solvolysis of $(DMP)_2BR$

Scheme 2 shows a possible mechanism for the methanolysis of (1) which is similar to a proposal for a number of aryldimesitylboranes.[14]



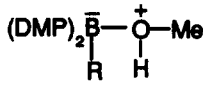
Scheme 2

The initial step in this possible pathway, is the complexation of methanol to (1) to give (3). This is then protonated to give (4), which rapidly breaks down to DMPH and (5).

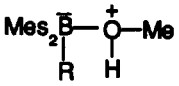
If this mechanism were correct, then the enhanced rates of methanolysis of $(DMP)_2BR$ compared with Mes_2BR would be due to either the first or second step. For both series, the steric situation around boron, for any given alkyl group, is the same. Therefore the rates of complexation of methanol would depend on the relative Lewis acidity of the boron atoms. ^{11}B nmr[34] indicates that the Lewis acidity of the boron of $(DMP)_2BR$ may be lowered relative to Mes_2BR, whilst the ^{13}C nmr shows that it is about the same, and

certainly not increased. Therefore an increase in the rate of complexation cannot explain the increased rate of methanolysis of $(DMP)_2BR$.

In the second step a proton adds to complex (3) to give (4). In both (3) and the comparable species (6) the aromatic groups are attached to a negatively charged tetracoordinate boron atom. This will offset any electron release from the methoxy group, and given the same steric situation, it is difficult to see why (3) should be protonated faster than (6). Hence the mechanism given in Scheme 2 seems unlikely for the methanolysis of (1).

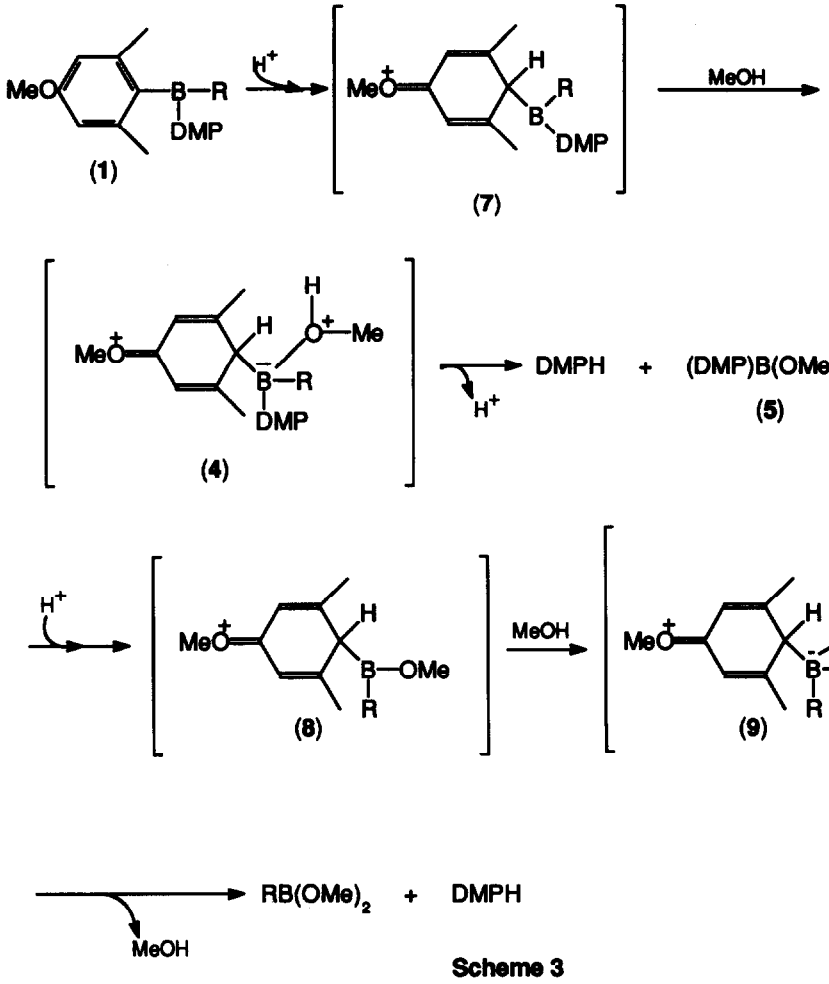


(3)



(6)

An analogous mechanism (Scheme 3) to that proposed[16] for the protodeboronation of aryldihydroxyboranes with concentrated mineral acids seems the most probably route for the methanolysis of (1).



Scheme 3

In this pathway the *uncomplexed* borane (1) is protonated to give (7). The mesityl group is less susceptible to direct protonolysis than the DMP group, in the same way that toluene is less susceptible to electrophilic attack than anisole. Hence the mesityl group may be cleaved by a mechanism akin to that given in Scheme 2. The Lewis acidity of the boron atom in the positively charged species (7), will be strongly enhanced as compared with (1), and complexation with methanol made correspondingly easier. This yields (4) which rapidly breaks down to the cleavage product, DMPH and (5).

The direct protonation of (1), should not be particularly dependant on the alkyl group and therefore the dependance exhibited in Table 1 is most probably due to the complexation of methanol with (7) to give (4), in the second step of the process.

Hydrogen chloride is virtually dissociated in methanol[43] and this will presumably be true also for trifluoromethanesulphonic acid by virtue of its greater acidity.[44] In both cases the proton donating species will be oxonium ions derived from THF and methanol, explaining the similar rates of reactions in comparable mixtures of these solvents. Methanesulphonic acid is a weaker acid and in the same conditions will produce a lower concentration of oxonium ions. This would lower the rate of reaction, as would attack by the molecular acid.

The much slower removal of the second aryl group may be the result of more than one factor. In the intermediate (8), the Lewis acidity at boron is lowered relative to (7), by virtue of the oxygen atom attached to boron. Hence production of (9) will be greatly slowed relative to the production of (4). The retarding effect of a methoxy group attached to boron is illustrated by comparison of experiments 1 and 18 and also comparison of experiments 18 and 19. Another possible factor is that collapse of (4) will proceed with a greater relief of steric strain than with the breakdown of (9).

The lowering of the rate of methanolysis of $(DMP)_2BCH{=}CHBu^n$ (experiment 14) or $(DMP)_2BC(Et){=}CHEt$ (experiment 15) would be due to an electronic overlap of the alkenyl group and the boron atom. Thus the ^{11}B nmr of $(DMP)_2BBu^n$ has a signal at 78.1 compared with that of $(DMP)_2BCH{=}CHBu^n$ at 64.4[34] The very great effect on the rate of methanolysis produced by the substitution of an α-ethyl group (experiment 15) must be due to a steric factor. This may be partly due to the β-substituent effect noted for trialkylboranes[30] together with the planarity of the unsaturated system, leading to a highly encumbered boron atom, which would find great difficulty in proceeding from (7) to (4).

The solvent effects are of particular interest. The increase in the rate of methanolysis of (1) with an increase of the amount of THF present, reflects the increase in the quantity of $[THFH]^+$ present as compared with $[MeOH_2]^+$. The rate of removal of the second DMP group is lowered by an increase in the proportion of THF in the solvent mix. Removal of the second DMP group involves a difficult complexation of methanol in going from (8) to (9) and a lowering in the proportion of methanol present would have an adverse effect on this step.

Methanolysis of $(DMP)_2BR$, using carboxylic acid catalysis.

These reactions were studied in the same way as the mineral acid catalysed methanolyses of $(DMP)_2BR$. The results are given in Table 4.

Table 4. Carboxylic acid catalysed methanolyses of hindered diarylorganylboranes

Exp.	Borane	Time(h) for removal of one or two aryl groups			
		CH_3CO_2H		CF_3CO_2H	
		1	2	1	2
28	$(DMP)_2BMe$	7.0	48(1.38)[a]	No reaction	
29	Mes_2BMe	8.0	34	-	
30	$(DMP)_2BEt$	8.6	99	No reaction	
31	$(DMP)_2BBu^n$	4.0	48(1.45)[a]	-	
32	$(DMP)_2BOct^n$	17.2	48(1.50)[a]	-	
33	$(DMP)_2BCH(Me)Pr^n$	32.8	96(1.0)[a]	-	
34	$(DMP)_2BCH(Et)Pr^n$	43.2	96(1.26)[a]	-	
35	$(DMP)_2BCH(Et)Hept^n$	170	200(1.0)	-	
36	$(DMP)_2BBu^t$ [b]	33	96(1.0)[a]	No reaction	
37	Mes_2BBu^t	200(0.79)[a]	-	-	
38	$(DMP)_2BC(Me)(Et)(Pr^n)$	96(0.75)[a]	-	-	
39	$(DMP)_2BCH{=}CHBu^n$	96(0.91)	-	-	
40	$(DMP)_2BC(Et){=}CHEt$	No reaction		-	
41	$(DMP)_3B$	No reaction		No reaction	
42	$(DMP)_2BCH_2CH{=}CH_2$	1.9	48(1.0)[a,c]	No reaction	
43	$(DMP)_2BOMe$	No reaction		-	
44	$(DMP)B(OMe)_2$	No reaction		-	

[a] Reaction stopped at time given with mol. equiv. of DMPH present given in brackets.

[b] Pivalic acid gave 1 mol. equiv. of DMPH after 28h and 1.3 mol. equiv. after 48h. [c] Allyl group also lost.

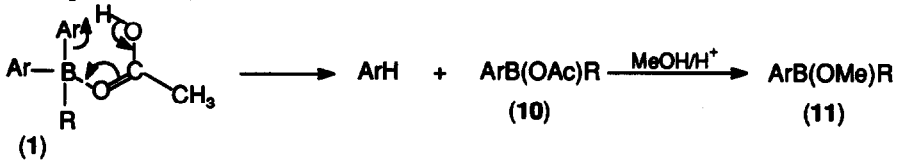
Acetic acid (and pivalic acid, experiment 36) is able to remove one aryl group from many Ar_2BR, though the reactions may be very slow (experiments 37, 38). For $(DMP)_2BMe$, the acetic acid catalysed reaction is *slower* than the corresponding reaction with Mes_2BMe (experiments 28, 29) though the reaction with $(DMP)_2BBu^t$ is considerably faster than with Mes_2BBu^t, (experiments 36, 37).

The electron availability at boron considerably affects the ability of acetic acid to catalyse methanolysis, and even one oxygen atom bonded to boron completely inhibits the reaction (experiment 43). This is in accord with the difficulty found in removing the second DMP group from compounds (1) using acetic acid catalysis (experiments 28, 31-41).

Substitution α to the boron atom inhibits acetic acid catalysed solvolysis of even one DMP group (experiments 33-36, 38, 40) and totally stops removal of a second DMP group in all cases.

Trifluoroacetic acid, though a considerably stronger acid than acetic acid, does not catalyse methanolysis in any of the cases tried (experiments 28, 30, 36, 41, 42, 43). Although solvolyses with acetic acid were also ineffective in the cases of experiments 41 and 43, experiments 28, 30 and 42 are the easiest acetic acid catalysed methanolyses.

These data are compatible with the acetic acid catalysed solvolyses proceeding by initial complexation followed by a cyclic proton transfer in the fashion (Scheme 1) accepted for carboxylic acid catalysed protonolyses of trialkylboranes. The acetoxyboranes, (**10**) produced, are converted to methoxyboranes, (**11**) in a separate step (Scheme 4).



Scheme 4

Displacement of the first aryl group may be aided by the great relief in steric strain caused by its loss, and by the greater migratory aptitude, aided by the 4-methoxy group in the case of the DMP group, of an aryl group as compared with an alkyl group. The Lewis acidity of either (**10**) or (**11**) is much reduced relative to (**1**)[45] and solvolysis by initial complexation is therefore inhibited, as shown by experiment 43. An additional factor may be that the release of steric strain by expulsion of ArH from (**10**) or (**11**) is less than it is from (**1**).

Allyl*bis*(2,6-dimethyl-4-methoxyphenyl)borane, like allyldimesitylborane[46] is not methanolysed on heating with methanol alone, the normally ready reaction being sterically inhibited. In the presence of acetic acid ***one DMP is cleanly removed***, and only subsequent to this does removal of the allyl group occur to give $(DMP)B(OMe)_2$ (experiment 42).

The lowering of reactivity of $(DMP)_2BCH{=}CHBu^n$ (compare experiments 31 and 39) may, as previously, be due to π bonding of the alkenyl group to the boron atom. This lack of reactivity is sterically reinforced in the case of α-substitution (experiment 40).

The ineffectiveness of trifluoroacetic acid (TFA) helps to confirm the proposed mechanism. Apparently TFA is not a sufficiently strong acid to react in the same way as hydrogen chloride or trifluoromethanesulphonic acid with (**1**). However, the basicity of the carbonyl group is lowered compared with acetic acid and therefore it cannot complex with the organoborane in order to initiate the cyclic protonolysis process.

The glycolysis of $(DMP)_2BR$, (1).

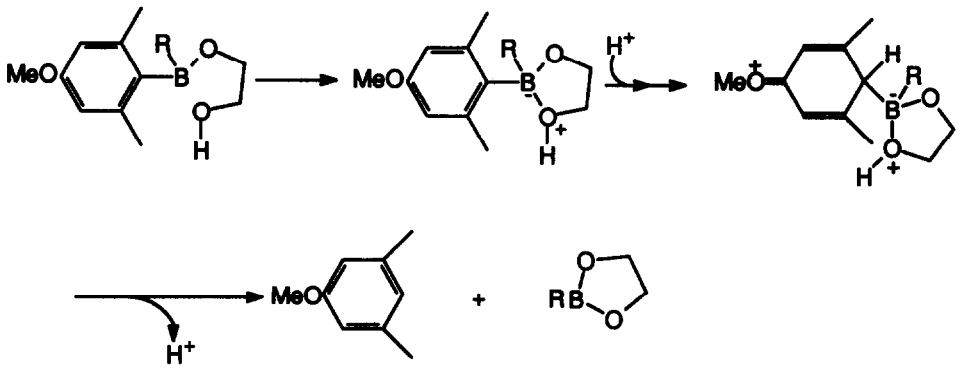
Some preliminary experiments were carried out using glycol for solvolysis of (**1**), in the hope that the complexation step required to initiate expulsion of the second DMP group would be intramolecular and that this would aid the solvolysis. Reactions were carried out as before, except that in order to keep the medium homogeneous a 1 : 1 ratio of glycol to THF had to be used. One equivalent each of borane to acid was used at the same concentrations as for methanolysis. Two difficultly solvolysable boranes were used, with the results given in Table 5.

Table 5. Comparisons of methanolyses and glycolyses of $(DMP)_2BR$

Exp.	Borane	Acid	Alcohol	Time(h) for alcoholysis of 1 and 2 DMP	
				1	2
45	$(DMP)_2BBu^t$	HCl	$(CH_2OH)_2$	0.1	10.3
46	$(DMP)_2BC(Me)(Et)(Pr^n)$	HCl	$(CH_2OH)_2$	1.6	26.4
47	$(DMP)_2BBu^t$	AcOH	$(CH_2OH)_2$	3.3	12.6
9	$(DMP)_2BBu^t$	HCl	MeOH	7.2	109[a]
11	$(DMP)_2BC(Me)(Et)(Pr^n)$	HCl	MeOH	12.6	179[a]
36	$(DMP)_2BBu^t$	AcOH	MeOH	33	96(1.0)[a]

a) Results from Tables 1 and 4 are given here for ready comparison.

For the hydrogen chloride reactions we were pleased to record very useful accelerations of the displacement of the second DMP group by the use of glycol in place of methanol. This can be explained as in Scheme 5.



Scheme 5

The increase in the rate of the glycolysis of the first DMP group compared with methanolysis (experiments 45, 9 and 46, 10) may be due to several factors. One is the different ratio of alcohol to THF in the experiments shown. When the ratio of methanol to THF was lowered from 3 : 1 to 0.7 : 1, then the rate of methanolysis of the first DMP group of $(DMP)_2BBut$ was somewhat increased (experiment 27, Table 2). The increased polarity of ethylene glycol compared with methanol may also be a contributory cause.

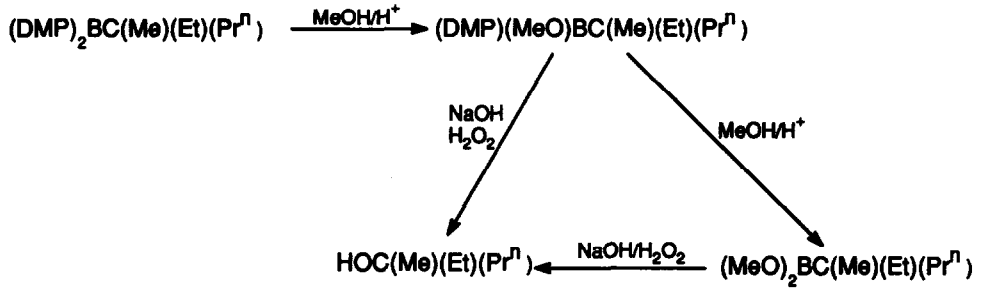
Entirely unexpected to us were the results of experiment 47. For glycolysis acetic acid functions as an effective catalyst for the removal of ***both*** DMP groups from $(DMP)_2BBu^t$ (experiment 47), in great contrast to methanolysis (experiment 36), in which removal of the first DMP group is slow, and the second DMP group is not touched. More work is required to explain these results. Glycol has a higher capacity for hydrogen bonding than methanol[47] (though see ref. 48) and this may influence the dissociation of acetic acid. More

particularly, although many solvent parameters (*e.g.* $E_T(30)$/(kcal.mol^{-1}) and E_T^N, are very similar for methanol and ethylene glycol[49a], the basities differ greatly with $B\gamma(MeOH) = 0.50$ and $B\gamma((CH_2OH)_2) = 0.84$.[49b, 50] Basity is a measure of the *cation* solvating power of a solvent, and glycol is far superior to methanol in this respect. The acities ($A\gamma$) of methanol and ethylene glycol are very similar at 0.75 and 0.78 respectively,[49b, 50] and so the difference between the two solvents in the function ($A\gamma + B\gamma$), ***which alone accounts for over 98% of the solvent effects in 77 solvent sensitive processes***[50], is due almost entirely to differences in $B\gamma$. Thus acetic acid may well function in ethylene glycol as an almost totally dissociated acid, like a mineral acid.

The second step will most probably be intramolecular and the solvolysis may again become more akin to the mineral acid catalysed reactions.

Use of preliminary methanolysis for the overall oxidation on an 'overhindered' borane

Our original objective was to release the organyl group of heavily hindered alkyldiarylboranes by first removing one or both of the aryl groups, so leaving the resulting borane sensitive to the usual degradation methods. To test whether or not this was feasible, as seemed probable given the results obtained with mineral acid catalysed methanolysis of $(DMP)_2BR$, we chose to study our most hindered borane $(DMP)_2BC(Me)(Et)(Pr^n)$. The analogous $Mes_2BC(Me)(Et)(Pr^n)$ had not previously been oxidisable in an efficient fashion.[11] We therefore tested the reactions set out in Scheme 6. Methanolysis was done under standard kinetic conditions and oxidations were with alkaline 30% H_2O_2. The results are given in Table 6.



Scheme 6

Table 6. Degradation of $(DMP)_2BC(Me)(Et)(Pr^n)$ by methanolysis then oxidation

	Exp. 48	Exp. 49	Exp. 50	Exp. 51
Time (h) of sample removal	0	4	16	180
Oxidation conditions	65°C/24h	65°C/24h	r.t., 3h	r.t., 3h
Yield (%) of $HOC(Me)(Et)(Pr^n)$	26	53	92	96
Total reaction time (h)	24	28	19	183

According to experiment 11 (Table 1) it takes 12.6h to fully remove one DMP group, and 179h to remove both DMP groups from $(DMP)_2B(Me)(Et)(Pr^n)$, in kinetic conditions, which were those used for

experiments 48-51. Table 6, experiment 50, shows that by removal of *one* DMP group followed by r.t. oxidation it was possible to get a 92% yield of HOC(Me)(Et)(Pr^n). Removal of the second DMP group (experiment 51) slightly improved the yield but this was not a convenient procedure, due to the long solvolysis time required. With no preliminary methanolysis, extended oxidation at 65°C gave only a low yield of the carbinol (experiment 48), which was improved, in line with the partial loss of one DMP group, on using a preliminary solvolysis of 4h (experiment 49).

Thus we have achieved our objective in that preliminary methanolysis of one DMP group from an overhindered diarylborane, followed by oxidation affords a convenient and efficient procedure for the release of the hindered organyl group (experiment 50) even under kinetic conditions. It will easily be possible to make the process yet more efficient by increasing the concentrations of the borane and acid (see Table 2) and by decreasing the proportion of methanol in the THF-MeOH reaction mixture (see Table 3). The discovery that glycolysis is a much more rapid process than methanolysis (only 1.6h for the release of one DMP group from $(DMP)_2B(Me)(Et)(Pr^n)$) points the way ahead for even more recalcitrant boranes, from which preliminary glycolysis, followed by oxidation, should readily release the organyl group.

EXPERIMENTAL

Technical Information

Boron (^{11}B) nmr were recorded on a Varian X-100F nmr spectrometer using $BF_3.OEt_2$ in a co-axial tube as external standard and quartz nmr tubes. Signals, in p.p.m., downfield from the standard are recorded as positive.

Gas liquid chromatography was performed on a Varian Vista Series 6000 chromatograph with a Varian CDS-401 data system as integrator and plotter. All mixtures were analysed on a 10' x $^1/_8$" stainless steel column packed with 5% SE30 on Chromsorb 9 packing, except where stated. The basis temperature programme for analysis of product mixtures was 120°C/2 min. then ramp to 240°C at 30°C/min., then held for 1 min. Modifications to this are noted in the relevant section. Glc estimations of yields were made by adding a known weight of a standard (*e.g.*dodecane, hexadecane) to the reaction mixture and determining the response factor for each component to be estimated. Coinjections were used to help identify products whenever possible.

All reactions were carried out under argon[51] using purified anhydrous reagents[52] unless otherwise stated. Tetrahydrofuran was given a preliminary purification by passing through dry neutral alumina under nitrogen or argon pressure. Sodium (2g/l) and benzophenone (8g/l) were then added to the THF in a still, and the mix stirred under argon until the purple colour of the benzophenone ketyl developed. The THF was then distilled from the ketyl as required. Methanol was dried and purified by distillation from magnesium methoxide. Ethylene glycol was distilled from dried 4Å molecular sieves and stored under argon over freshly dried 4Å molecular sieves.

Solutions of acid in alcohols were prepared by adding a known weight of the freshly distilled acid to the dry alcohol in a septum capped graduated flask. The solution was made up to the mark with dry alcohol and the resulting solution standardised by titration against standardised sodium hydroxide solution.

Bis(2,6-dimethyl-4-methoxyphenyl)boranes were prepared and handled as previously described.[34] The preparations of dimesitylboranes used have also been fully described.[1]

Experimental Procedures.

The equipment and techniques involved in laboratory operations with air sensitive substances have been surveyed.[48] In particular all glassware was dried at 120°C for > 4h (typically 24h), assembled hot and cooled under a stream of argon introduced and expelled through septum capped inlets and outlets using hypodermic needles. Manipulation of liquids under argon was achieved using oven dried syringes and double-ended needles cooled by flushing with argon. All operations involving solid $(DMP)_2BX$ were carried out in an argon flushed glove box.

Solvolyses were carried out in 25ml round-bottomed flasks modified with a built-in tap, the opening of which was protected by two rubber septum caps. ^{11}B nmr spectra of reaction mixtures were obtained by transferring a portion of the solution by double-ended needle to a dry, argon flushed septum capped 5mm nmr tube.

Methanolysis reactions.

The reactions of $(DMP)_2BF$ with methanol.

Bis(2,6-methyl-4-methoxyphenyl)fluoroborane (1.057g, 3.52mmol) and hexadecane (0.7871g) were dissolved in THF (6ml). Two 3ml portions were transferred into round-bottomed tap flasks and dry methanol (7ml) was then added to each flask. One flask was maintained at 50°C in a thermostatic bath, whilst the other was maintained at 20°C. Samples were removed at various times, quenched with solid sodium carbonate and analysed for 3,5-dimethylmethoxybenzene (DMPH) by g.l.c. using the standard conditions. The results as mole equivalents of DMPH are given in Table 7.

Table 7. Results of the methanolysis of $(DMP)_2BF$

Time/h	Mole Equivalents of DMPH present with time at given temperature	
	50°C	20°C
0.25	0.471	0.125
0.5	0.728	0.347
1.0	1.007	0.381
1.5	1.294	0.487
2.0	1.444	0.483
3.0	1.516	0.547
4.0	1.721	0.633
6.0	1.895	0.663
8.0	1.995	0.725
12.0	1.991	0.935
16.0	2.005	0.985
24.0	-	1.127
50.5	-	1.628
75.0	-	1.848

Acid catalysed methanolyses of organoboranes.

All these reactions were carried out by the same general method. A standard solution (~0.4M of the borane was prepared in dry THF, hexadecane (~0.6g/g borane) was added as an internal standard. Aliquots of this solution were then added to argon flushed round-bottomed tap flasks that had been charged with solutions of 0.1M acid in methanol, one equivalent of acid to the added borane being used. In all cases hydrogen chloride, trifluoromethanesulphonic acid and acetic acid were used as catalysts and in several cases trifluoroacetic acid, methanesulphonic acid and neat methanol were also used, this being specified with the results of the individual reactions, Tables 8 to 27.

The resulting solutions were maintained in a thermostatic bath at 50 ± 0.5°C. Samples were removed at various times and quenched with solid sodium carbonate. In several cases it was initially found that the pure borane decomposed during g.l.c. analysis to give 3,5-dimethyl-1-methoxybenzene, so interfering with the analysis. This could be prevented by oxidising the removed sample by addition of solid 3-chloroperoxybenzoic acid and this was done in all cases. The samples were then analysed by g.l.c. for 3,5-dimethylmethoxybenzene and 2,6-dimethyl-4-methoxyphenol using the standard conditions, unless otherwise stated, so as to allow monitoring of any production of alkane. In no instance was any alkane observed. The results as mole equivalents of DMPH are given in Tables 8 to 27. At the end of the reaction the solutions were allowed to cool and analysed by ^{11}B nmr which showed that the organyl group was not removed from boron except as mentioned previously. When the alkyl group contained more than four carbons the product mixtures were also oxidised and analysed for resulting alcohol and in all cases this was obtained in better than 95% yield.

Table 8. Results of the methanolysis of $(DMP)_2BCH_3$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts[a]			
	HCl	CF_3SO_3H	CH_3SO_3H	CH_3CO_2H
0.25	1.53	1.59	1.02	-
0.5	1.95	1.90	1.89	0.30
1	2.03	2.00	2.05	0.56
2	1.97	2.00	1.96	0.79
4	2.01	1.99	1.99	0.91
8	-	-	-	0.98
16	-	-	-	1.11
24	-	-	-	1.24
48	-	-	-	1.34

[a] Trifluoroacetic acid and pure methanol also used, no reaction occurred.

The ^{11}B nmr showed peaks at 32.2δ due to $(MeO)_2BMe$ and at 54.4δ due to (DMP)B(OMe)Me in the acetic acid catalysed case.

Table 9. Results of the methanolysis of $(DMP)_2BEt$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts			
	HCl	CF_3SO_3H	CH_3SO_3H	CH_3CO_2H
0.25	1.17	1.12	0.59	-
0.5	1.57	1.49	1.00	-
1	1.82	1.93	1.55	0.35
2	2.06	1.95	1.85	0.74
4	2.01	1.98	1.98	0.91
8	1.98	2.00	2.01	1.06
24	2.06	2.01	2.06	1.33
48	-	-	-	1.67
96	-	-	-	1.94

The ^{11}B nmr showed a peak at 31.9δ due to $EtB(OMe)_2$ in all cases.

Table 10. Results of the methanolysis of $(DMP)_2BBu^n$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts[a]			
	HCl	CF_3SO_3H	CH_3SO_3H	CH_3CO_2H
0.5	1.44	1.38	0.90	0.34
1	1.81	1.88	1.52	0.58
2	2.01	2.00	1.71	0.78
4	1.97	2.06	2.08	0.90
8	-	-	2.05	1.16
16	2.01	1.97	1.98	1.23
24	-	-	-	1.28
48	-	-	-	1.44

[a] Trifluoroacetic acid and pure methanol also used, no reaction occurred.

The ^{11}B nmr showed a peak at 32.19δ due to $Bu^nB(OMe)_2$ in the HCl, CF_3SO_3H and CH_3SO_3H catalysed cases plus a peak at 53.97δ due to $(DMP)B(OMe)Bu^n$ in the acetic acid catalysed case.

Table 11. Results of the methanolysis of $(DMP)_2BOct^n$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
0.25	0.90	0.67	-
0.5	1.21	1.00	0.42
1	1.66	1.27	0.47
2	1.83	1.71	0.53
4	2.04	1.98	0.70
8	1.97	2.03	0.78
16	2.01	2.00	0.95
24	-	-	1.09
48	-	-	1.50
96	-	-	1.74

The ^{11}B nmr showed a peak at 31.9δ due to $Oct^nB(OMe)_2$ in the HCl and CF_3SO_3H catalysed cases plus a peak at 54.0δ due to $(DMP)B(OMe)Oct^n$ in the acetic acid catalysed case.

Glc showed no production of octane, the temperature programme being modified with an initial temperature of 90°C with a four minute hold. The product mixtures were oxidised and analysed for octanol. This gave yields of 98%, 97% and 95% of octanol with respect to borane for the HCl, CF_3SO_3H and CH_3CO_2H catalysed reactions respectively.

Table 12. Results of the methanolysis of $(DMP)_2BCH(Me)Pr^n$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
0.25	0.33	0.39	-
0.5	0.73	0.82	-
1	1.04	0.95	0.20
2	1.19	1.29	0.29
4	1.55	1.44	0.53
8	1.81	1.81	0.66
16	1.89	1.87	0.81
24	2.06	1.97	0.95
48	2.00	1.99	0.97
96	-	-	1.04

The ^{11}B nmr showed peaks at 31.4δ due to 2-PentB$(OMe)_2$ in the HCl and CF_3SO_3H catalysed cases and at 53.5δ due to (DMP)B(OMe)-2-Pent in the CH_3CO_2H catalysed case.

The product mixtures were oxidised and analysed for 2-pentanol. This gave yields of 98%, 99% and 96% of 2-pentanol with respect to borane for the HCl, CF_3SO_3H and CH_3CO_2H catalysed reactions respectively.

Table 13. Results of the methanolysis of $(DMP)_2BCH(Et)Pr^n$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
0.5	0.55	0.37	-
1	0.62	0.66	0.23
2	0.87	0.81	0.27
4	1.05	0.98	0.32
8	1.26	1.17	0.53
16	1.37	1.40	0.68
24	1.67	1.54	0.81
48	1.93	1.97	1.05
96	2.02	2.05	1.27

The ^{11}B nmr showed a peak at 31.5δ due to 3-HexB$(OMe)_2$ in the HCl and CF_3SO_3H catalysed cases, plus one at 53.4δ due to (DMP)B(OMe)-3-Hex in the CH_3CO_2H catalysed case.

The product mixtures were oxidised and analysed for 3-hexanol. This gave yields of 97%, 99% and 97% of 3-hexanol with respect to borane for the HCl, CF_3SO_3H and CF_3CO_2H catalysed reactions respectively.

Table 14. Results of the methanolysis of $(DMP)_2BCH(Et)Hept^n$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
0.5	0.50	0.42	-
1	0.60	0.56	-
2	0.73	0.71	-
4	0.89	0.85	0.13
8	1.13	1.08	0.18
16	1.29	1.27	0.22

Table 14. (Continued)

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
24	1.40	1.35	0.38
48	1.70	1.62	0.48
100	1.90	1.82	0.73
150	2.01	1.99	1.00
200	1.97	2.00	1.01

The ^{11}B nmr showed peaks at 31.1δ due to 3-DecB(OMe)$_2$ in the HCl and CF_3SO_3H catalysed cases and at 54.6δ due to (DMP)B(OMe)-3-Dec in the CF_3CO_2H catalysed case.

Glc using standard conditions showed no production of decane during the methanolysis. The product mixtures were oxidised and analysed for 3-decanol. This gave yields of 95%, 97% and 96% of 3-decanol with respect to borane for the HCl, CF_3SO_3H and CF_3CO_2H catalysed reactions respectively.

Table 15. Results of the methanolysis of (DMP)$_2$BBu^t

Time/h	Mole equivalents of DMPH present with time for various acid catalysts[a]			
	HCl	CF_3SO_3H	CH_3SO_3H	CH_3CO_2H
1	0.19	0.18	-	-
2	0.32	0.41	0.25	0.14
4	0.62	0.68	0.46	0.29
8	1.06	1.02	0.69	0.43
16	1.34	1.30	0.92	0.74
24	1.54	1.55	1.09	0.87
48	1.75	1.80	1.37	1.00
96	1.96	1.92	1.58	1.00
150	2.00	2.01	1.70	-
200	1.99	2.00	1.86	-

a) Trifluoroacetic acid and pure methanol were also used, but no reaction occurred.

The ^{11}B nmr showed peaks at 32.0δ due to Bu^{t}B(OMe)$_2$ in the HCl, CF_3SO_3H and CH_3SO_3H catalysed cases and at 55.7δ due to (DMP)B(OMe)Bu^t in the CH_3SO_3H and CH_3CO_2H catalysed cases.

Table 16. Results of the methanolysis of $(DMP)_2BBu^t$. Effect of reagent concentrations

Time/h	Mole equivalents of DMPH present with time for various molar concentrations of borane/equivalents of acid					
	[0.073M]/0.5	[0.073M]/1	[0.073M]/2	[0.089M]/2	[0.145M]/1	[0.178M]/1
0.5	0.30	-	0.55	-	0.58	-
1	0.48	0.19	0.66	0.57	0.82	0.65
2	0.60	0.32	0.71	0.83	0.90	0.99
4	0.72	0.62	0.94	1.11	1.06	1.21
8	0.75	1.06	1.15	1.43	1.26	1.49
16	0.92	1.34	1.34	1.60	1.48	1.75
24	1.07	1.54	1.52	1.71	1.76	1.88
48	1.15	1.75	1.82	1.95	1.96	1.99
96	1.28	1.96	2.00	2.01	2.00	2.01
144	1.35	2.00	1.99	2.00	2.02	2.00
192	1.45	1.99	2.01	-	1.99	-

Table 17. Results of the methanolysis of $(DMP)_2BBu^t$. Effect of solvent composition

Time/h	Mole equivalents of DMPH present with time for various methanol to THF ratios/borane concentration			
	2.70 : 1 [0.073M]	0.38 : 1 [0.073M]	2.70 : 1 [0.17M]	0.70 : 1 [0.17M]
0.5	-	0.63	-	0.61
1	0.19	0.70	0.65	0.92
2	0.32	0.87	0.99	1.10
4	0.62	0.98	1.21	1.20
8	1.06	1.11	1.49	1.28
16	1.34	1.23	1.75	1.55
24	1.54	1.27	1.88	1.68
48	1.75	1.30	1.97	2.00
96	1.96	1.32	2.01	1.99
144	2.00	1.39	1.99	-
192	1.99	1.45	-	-

Table 18. Results of the methanolysis of $(DMP)_2BC(Me)(Et)(Pr^n)$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
1	0.20	0.17	-
2	0.32	0.33	-
4	0.52	0.50	-
8	0.80	0.87	0.17
16	1.09	1.02	0.27
24	1.16	1.23	0.46
48	1.51	1.51	0.59
96	1.79	1.82	0.75
150	1.96	1.95	a
200	2.01	2.00	-

a) Reaction stopped after ~110h due to accidental ingress of water.

The ^{11}B nmr showed peaks at 31.5δ due to 3-Me-3-HexB$(OMe)_2$ in the HCl and CF_3SO_3H catalysed cases and at 53.5δ and 76δ due to (DMP)B(OMe)-3-Me-3-Hex and $(DMP)_2$B-3-Me-3-Hex respectively in the CH_3CO_2H catalysed case. The product mixtures were oxidised and analysed for 3-methyl-3-hexanol. This gave yields of 96%, 95% and 96% of 3-methyl-3-hexanol with respect to borane for the HCl, CF_3SO_3H and CH_3CO_2H catalysed reactions.

Table 19. Results of the methanolysis of $(DMP)_2BCH_2CH{=}CH_2$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts[a]			
	HCl	CF_3SO_3H	CH_3SO_3H	CH_3CO_2H
0.25	1.05	0.62	0.43	0.52
0.5	1.43	1.04	0.74	0.82
1	1.61	1.46	1.04	0.93
2	1.93	1.72	1.49	1.07
4	1.99	1.94	1.88	0.97
8	2.06	1.98	2.01	1.05
24	2.01	2.03	2.00	0.99

a) Trifluoroacetic acid and pure methanol were also used, but no reaction occurred.

The ^{11}B nmr showed peaks at 30.7δ due to CH_2=$CHCH_2B(OMe)_2$ and at 18.8δ due to $B(OMe)_3$ in the HCl, CF_3SO_3H and CH_3SO_3H catalysed cases.

Use of peak areas gave the percentages of CH_2=$CHCH_2B(OMe)_2$ as 35%, 33% and 31% for the HCl, CF_3SO_3H and CH_3SO_3H cases respectively. In the acetic acid case a single peak at 30.0δ due to $(DMP)B(OMe)_2$ was observed. In the absence of catalyst only $(DMP)_2BCH_2CH$=CH_2 was observed.

Table 20. Results of the methanolysis of $(DMP)_2BCH_2SiMe_3$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts	
	HCl	CF_3SO_3H
0.25	1.48	1.61
0.5	1.76	1.75
1	1.88	1.85
2	1.93	1.95
4	1.97	1.95
8	2.01	1.99
16	2.00	2.01

The ^{11}B nmr showed a peak at 31.4δ due to $Me_3SiCH_2B(OMe)_2$ in both cases.

Table 21. Results of the methanolysis of $(DMP)_2BCH$=$CHBu^n$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
0.25	0.45	0.63	-
0.5	0.66	0.83	-
1	1.00	1.26	-
2	1.26	1.72	0.15
4	1.54	1.88	0.22
8	1.69	2.00	0.34
16	1.91	1.98	0.48
24	2.04	1.99	0.54
48	2.00	-	0.77
96	-	-	0.95

The ^{11}B nmr showed a peak at 27.0δ due to Bu^nCH=$CHB(OMe)_2$ in the HCl and CF_3SO_3H catalysed cases and at 46.9δ due to $(DMP)B(OMe)CH$=$CHBu^n$ in the acetic acid catalysed case.

The product mixtures were oxidised and analysed for hexanal by glc. This gave yields of hexanal as 97%, 98% and 97% with respect to borane for the HCl, CF_3SO_3H and CH_3CO_2H catalysed reactions respectively.

Table 22. Results of the methanolysis of $(DMP)_2BC(Et)=CHEt$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
1	0.15	0.31	0
2	0.26	0.37	0
4	0.31	0.58	0
8	0.47	0.67	0
16	0.71	0.94	0
24	0.74	1.23	0
48	0.85	1.57	0
96	0.97	1.98	0

The ^{11}B nmr showed a peak at 27.8δ due to $EtCH=C(Et)B(OMe)_2$ in the CF_3SO_3H catalysed case, at 47.6δ due to (DMP)B(OMe)C(Et)=CHEt in the HCl catalysed case, and at 70.0δ due to $(DMP)_2BC(Et)=CHEt$ in the acetic acid catalysed case.

Table 23. Results of the methanolysis of $(DMP)_2BC{\equiv}CBu^n$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts	
	HCl	CF_3SO_3H
0.25	0.60	0.96
0.5	0.88	1.51
1	1.10	1.71
2	1.36	1.87
4	1.67	1.98
8	1.84	1.99
26	1.99	2.03
48	2.03	2.00

The ^{11}B nmr of the product solutions showed a single peak at 18.7δ due to $(MeO)_3B$ in both cases.

Table 24. Results of the methanolysis of $(DMP)B(OMe)_2$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
0.25	0.50	0.57	0
0.5	0.75	0.70	0
1	0.87	0.85	0
2	0.96	0.93	0
4	1.00	0.99	0
8	1.00	1.01	0

The ^{11}B nmr showed a peak at 19.0δ due to $(MeO)_3B$ in the HCl and CF_3SO_3H catalysed cases.

Table 25. Results of the methanolysis of $(DMP)_2BOMe$

Time/h	Mole equivalents of DMPH present with time for various acid catalysts[a]			
	HCl	CF_3SO_3H	CH_3SO_3H	CH_3CO_2H
0.5	1.60	1.65	0.99	0
1	1.82	1.79	1.49	0
2	1.89	1.92	1.78	0
3	1.99	1.98	1.86	0
4	2.02	2.01	1.96	0
8	-	-	1.99	0
24	2.01	2.00	2.00	0

[a] Trifluoroacetic acid, ammonium chloride, sodium methoxide and pure methanol also used as catalysts, no reaction occurred in any case.

The ^{11}B nmr showed a peak at 19.0δ due to $(MeO)_3B$ in the HCl, CF_3SO_3H and CH_3SO_3H catalysed cases.

Table 26. Results of the methanolysis of Mes_2BMe

Time/h	Mole equivalents of MesH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
2	-	-	0.38
4	-	-	0.64
8	0.29	0.22	0.94
16	0.55	0.40	1.49
24	0.83	0.63	1.89
48	1.15	0.89	2.01

The ^{11}B nmr showed a peak at 31.9δ due to $MeB(OMe)_2$ in the acetic acid catalysed case plus a peak at 54.1δ due to MesB(OMe)Me in the HCl and CF_3SO_3H catalysed cases.

Table 27. Results of the methanolysis of Mes_2BBu^t

Time/h	Mole equivalents of DMPH present with time for various acid catalysts		
	HCl	CF_3SO_3H	CH_3CO_2H
12	0.20	0.14	-
25	0.35	0.25	0.21
50	0.53	0.47	0.35
100	0.75	0.64	0.60
200	1.01	0.90	0.79

The ^{11}B nmr showed a peak at 55.6δ due to $MesB(OMe)Bu^t$ plus a small peak due to Mes_2BBu^t in the CH_3CO_2H catalysed case.

Table 28. Results of the glycolysis of $(DMP)_2BR$

Time/h	Mole equivalents of DMPH present with time for various boranes andacid catalysts		
	$(DMP)_2BBu^t$		$(DMP)_2BC(Me)(Et)(Pr^n)$
	HCl	CH_3CO_2H	HCl
0.25	1.13	-	0.64
0.5	1.21	0.18	0.71
1	1.34	0.31	0.82
2	1.49	0.67	1.08
4	1.76	1.12	1.31
8	1.92	1.78	1.56
16	2.01	1.98	1.85
24	2.00	2.00	1.97
48	1.99	2.01	2.01

The ^{11}B nmr of the product solutions showed a single peak at 35.5δ due to $Bu^tB(O_2C_2H_4)$ or at 34.5δ due to 3-Me-3-HexB$(O_2C_2H_4)$.

Preparation of 2,6-dimethyl-4-methoxyphenol

A 100ml round-bottomed flask was equipped with a magnetic stirrer and a pressure equalising dropping funnel. The flask was charged with *bis*(2,6-dimethyl-4-methoxyphenyl)hydroxyborane (1.63g, 5.5mmol) and dry chloroform (20ml) and cooled in an ice water bath. The funnel was charged with a solution of pure *m*-chloroperbenzoic acid (2.0g, 11.6mmol) in chloroform (50ml) which was added to the flask over an hour and the mix was stirred overnight at room temperature to complete the reaction. The mixture was washed with 1M $NaHCO_3$ solution (3 x 50ml) and water (2 x 50ml). The organic layer was separated, dried ($MgSO_4$), filtered and concentrated on a rotary evaporator to give an orange solid. Recrystallisation from 60°-80° petroleum spirit gave 2,6-dimethyl-4-methoxyphenol (1.42g, 85%) as pale orange needles m.p. 75°-76°C, (Lit.[53] 77°C).

δ_H, 2.20 (s, 6H, Ar-CH_3), 3.74 (s, 3H, OCH_3), 4.84 (s, 1H, O*H*), 6.56 (s, 2H, H-3). δ_C, 16.14 (q, Ar-CH_3), 55.58 (q, OCH_3), 113.8 (d, C-3), 127.4 (s, C-2), 146.19 (s, C-1), 152.90 (s, C-4). Low resolution e.i. mass spectroscopy gave peaks at m/z (intensity), 152(84.9), 137(100), 81(33.7), 79(30.8), 77(26.7), 53(29.7), 39(48.3). Low resolution c.i. mass spectroscopy gave a single peak at m/z 153.

REFERENCES

1. Pelter, A.; Singaram, B.; Warren, L.; Wilson, J. W., *Tetrahedron*, **1993**, *49*, 2965.
2. Wilson, J. W.; Pelter, A.; Garad, M.V.; Pardasani, R., *Tetrahedron*, **1993**, *49*, 2979.
3. Pelter, A.; Warren, L.; Wilson, J.W., *Tetrahedron*, **1993**, *49*, 2988.
4. Pelter, A.; Vaughan-Williams, G. F.; Rosser, R. M., *Tetrahedron*, **1993**, *49*, 3007.
5. Pelter, A.; Buss, D.; Colclough, E.; Singaram, B., *Tetrahedron*, **1993**, *49*, 7077.
6. Pelter, A.; Smith, K.; Elgendy, S.; Rowlands, M., *Tetrahedron*, **1993**, *49*, 7104.
7. Pelter, A.; Smith, K.; Elgendy, S., *Tetrahedron*, **1993**, *49*, 7119.
8. Pelter, A.; Smith, K.; Buss, D.; Norbury, A., *Tetrahedron Lett.*, **1991**, *32*, 6239.
9. Smith, K.; Pelter, A.; Norbury, A., *Tetrahedron Lett.*, **1991**, *32*, 6243.
10. Pelter, A.; Smith, K.; Buss, D.; Zhao-Jin, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 2249.
11. Williams, L., Ph.D. Thesis, University College of Swansea, 1983.
12. Norbury, A. M., Ph.D. Thesis, University College of Swansea, 1990.
13. Brown, H.C.; Dodson, V.H., *J. Am. Chem. Soc.*, **1957**, *79*, 2304.
14. Glogowski, M.E.; Zumblyadis, N.; Williams, J. L. R., *J. Organomet. Chem.*, **1982**, *231*, 97.
15. Staab, H.A.; Meissner, B. J., *Liebigs Ann.*, **1971**, *753*, 80; 92.
16. Kuivala, H. G.; Nahabedian, K. V., *J. Am. Chem. Soc.*, **1961**, *83*, 2159.
17. Kuivala, H. G.; Hendrickson, A. R., *J. Am. Chem. Soc.*, **1952**, *74*, 5068.
18. Ulmschneider, D.; Goubeau, J., *Chem Ber.*, **1957**, *90*, 2733.
19. Brown, H. C.; Herbert, M. C., *J. Organomet. Chem.*, **1983**, *255*, 135.
20. Mikhailov, B. M.; Vaver, V. A.; Bubnov, N. Yu., *Doklady. Akad. Nauk. S.S.S.R.*, **1959**, *126*, 575; *Chem. Abs. 54*, 261.
21. Booth, R. B.; Kraus, C. A., *J. Am. Chem. Soc.*, **1952**, *74*, 1415.
22. Johnson, J. R.; Snyder, H. R.; van Campen, M. G., *J. Am. Chem. Soc.*, **1938**, *60*, 115.
23. Olah, G. A.; Westerman, P. W.; Mo, Y. K.; Klopman, G., *J. Am. Chem. Soc.*, **1972**, *94*, 7859.

24. Greenwood, N. N.; Thomas, B.S., in 'Comprehensive Organic Chemistry' ed. J. C. Bailer, Pergamon Press, Oxford, U.K., 1973, Vol. 1, p.956.
25. Goubeau, J.; Lehman, H., *Z. anorg. allgem. Chem.*, **1963**, *322*, 224.
26. Brown, H. C.; Murray, K., *Tetrahedron*, **1986**, *42*, 5497.
27. Mikhailov, B. M.; Vaver, V. A., *Zhur. Obshch. Khim.*, **1961**, *31*, 574, c.f. Crighton, J.; Holliday, A. K.; Massey, A.G.; Thompson, N. R., *Chem. Ind.*, **1960**, 347.
28. Toporcer, L. H.; Dessey, R. E.; Green, S. I. E., *J. Am. Chem. Soc.*, **1965**, *87*, 1236.
29. Davies, A. G.; Roberts, B. P., *J. Chem. Soc., (C)*, **1968**, 1474.
30. Bigley, D. B.; Payling, D. W., *J. Inorg. Nucl. Chem.*, **1971**, *33*,1157.
31. Brown, H. C.; 'Hydroboration', W. A. Benjamin Inc., New York, **1962**, p.66.
32. Pelter, A.; Singaram, S.; Brown, H. C., Unpublished experiments, University College of Swansea.
33. Pelter, A.; Drake, R.; Stewart, M., *Tetrahedron Lett.*, **1989**, *30*, 3085.
34. Pelter, A., Drake, R., *Tetrahedron*, **1994**, *50*, preceding paper.
35. Brown, H. C.; Okamoto, Z., *J. Am. Chem. Soc.*, **1957**, *79*, 1913.
36. Beilstein, Vol. 1, 3rd ed^{n}, p.1184.
37. Soulié, J.; Cadiot, P., *Bull. Soc. Chim. Fr.*, **1964**, *12*, 3846.
38. Hartmann, H.; Birr, K.-H., *Z. anorg. Chem.*, **1959**, *299*, 174.
39. Negishi, E., in 'Comprehensive Organometallic Chemistry' ed. Wilkinson, J. and Stone, G., Pergamon, **1982**, Vol. 7, p.270.
40. Mikhailov, B. M.; Tutorskaya, F. B., *Dokl. Akad. Nauk. S.S.S.R.*, *1958*, *123*, 479. *Chem. Abs.*,*53*, 6990.
41. Topchiev, A. V.; Pauskin, Ya. M.; Prakorova, A. A.; Kurashev, M.V., *Dokl. Akad. Nauk. S.S.S.R.*, *1959*, 128, 110. *Chem. Abs.*, *54*, 1268.
42. Topchiev, A. V.; Pauskin, Ya. M.; Prakorova, A. A.; Frenkin, E. I.; Kurashev, M. V.; *Dokl. Akad. Nauk. S.S.S.R.*, *1960*, *134*, 364. *Chem. Abs.*, *54*, 1268i.
43. Bell, R. P., 'The Proton in Chemistry', Methuen and Co., London, 1973, Chapter 4.
44. Howells, R. D.; McCown, J. D.; *Chem. Rev.*, **1977**, *77*, 69.
45. Pelter, A.; Smith, K., in 'Comprehensive Organic Chemistry' ed. Barton, D. H. R.and Ollis, W. D., Pergamon Press, Oxford, Vol. 3, p.916.
46. Pelter, A.; Singaram, B.; Wilson, J. W.; *Tetrahedron Lett.*, **1983**, *24*, 631.
47. Wilkinson, S. G., in 'Comprehensive Organic Chemistry', ed. Barton, D. H. R.and Ollis, W. D., Pergamon Press, Oxford, Vol. 1, p.664.
48. Kamlet, M. J.; Abboud, J.-L.M.; Abraham, M. H.; Taft, R.W., *J. Org. Chem.*, **1983**, *48*, 2877.
49. Reichardt, 'Solvents and Solvent Effects in Organic Chemistry' 2nd Edition, VCH, Weinheim, Germany, 1988. (a) p366, 367; (b) p402.
50. Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S., *J. Am. Chem. Soc.*, **1983**, *105*, 502.
51. Kramer, G. W.; Levy, A. B.; Midland, M. M., in 'Organic Syntheses *via* Boranes', Brown, H. C., Wiley Interscience, New York, 1975.
52. Perrin, D. D., Armarego, W. L. F.; Perrin, D. R., 'Purification of Laboratory Chemicals', Pergamon Press, Oxford, 1980.
53. 'Dictionary of Organic Compounds', Chapman and Hall, 1982, Vol. 2, p.2079.

(*Received in UK* 27 *June* 1994; *revised* 14 *October* 1994; *accepted* 21 *October* 1994)