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HINDERED ORGANOBORON GROUPS IN ORGANIC SYNTHESIS. 12. THE BIS[2,6-DIMETHYL-4-METHOXYPHENYL]BORON [$(DMP)_2B$] GROUP, A NEW, READILY SOLVOLYSED CARBANION STABILISING GROUP

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Compounds $(DMP)_2BR$ are readily made and undergo proton abstraction to yield boron stabilised carbanions. Mineral acid solvolysis removes the DMP groups whilst leaving alkyl and alkenyl groups bonded to boron and thus oxidisable. The compounds provide an important link between diarylboranes and dialkoxyboranes.

The dimesityl boron group is now well established[2-9] as a group that allows deprotonation α- to boron whilst sterically inhibiting ate complex formation at boron.[2,10-12] A limit to the methodology of using such carbanions is reached when the products are so hindered that release of the organyl moiety becomes extremely difficult, even using normally facile reactions. This is because such reactions usually proceed by initial attack on boron,[13] which in these cases has been deliberately shielded (eq.1).

$$Mes_2BC(Me)(Et)C_4H_9 \xrightarrow[68^{o}C/24h]{70\%\ H_2O_2/NaOH} EtCH(Me)OHC_4H_9\ (30\%) \qquad (1)$$

To overcome this limitation we argued that attention should be switched to reagents that attack the aromatic group, as release of even one aromatic group would so relieve hindrance around boron that further reactions should be straightforward. Preliminary investigations showed that propionic acid released mesityl groups preferentially to alkenyl groups,[14] and indeed it is known that triarylboranes undergo solvolysis with alcohols faster than trialkylboranes.[15] We felt that replacement of the 4-Me group of the mesityl residue by a 4-OMe group might have several advantages as follows, (i) electrophilic attack, including protonation, on the 2,6-dimethyl-4-methoxyphenyl (DMP) group should be more ready than on the mesityl group itself. Thus, dihydroxy(4-methoxyphenyl)borane undergoes brominolysis much more readily than dihydroxy(4-methylphenyl)borane.[16] Anisole is more susceptible to electrophilic attack than is toluene[17] and trimethoxyborane is more readily hydrolysed than trimethylborane;[18] (ii) anion formation should be as ready as with the mesityl group, but with the advantage that deprotonation at the 4-methyl group is not possible;[19] (iii) 2,6-dimethyl-4-methoxybenzene is readily made[20] from the commercially available phenol.

We therefore set out to make a range of compounds (see Table 1) of generic formula $(DMP)_2BR$. The required compounds were made in three ways[20]. The first was the reaction of alkyl lithium reagents with $(DMP)_2BF$,[20] the second (equation 2) was by deprotonation-alkylation of $(DMP)_2BR$. This sequence proves that, in fact, deprotonation proceeds as expected and that the resultant anion reacts in the usual fashion. We shall report elsewhere on the alkylation and boron-Wittig reactions of these anions. The third method is by hydroboration of alkynes by $(DMP)_2BH$[20] in a fashion similar to Mes_2BH. This too will be reported separately.

$$(DMP)_2BCH_2R^1 \xrightarrow[2.\ R^2X]{1.\ MesLi} (DMP)_2BCHR^1R^2 \xrightarrow[2.\ R^3X]{1.\ MesLi} (DMP)_2BCR^1R^2R^3 \qquad (2)$$

The boranes were dissolved in MeOH/THF (3:1)[21] containing one mol equivalent of acid to give a solution that was 0.08M in both acid and $(DMP)_2BR$. The acids studied included HCl, CF_3SO_3H (TFMSA), CH_3SO_3H (MSA) and CH_3CO_2H. The solutions were held at $50^o \pm 0.5^oC$ and regularly and quantitatively monitored by g.c. for DMPH and RH (equation 3). Formation of $RB(OMe)_2$ was ascertained by ^1H and ^{11}B n.m.r. whilst oxidation gave ROH (or DMPOH) which were also measured. The results are shown in Table 1. Before considering these it must be noted that CF_3CO_2H (TFA) was also used as the acid catalyst. The results are not given in Table 1 as with this acid, no methanolysis at all was observed in any case!

$$(DMP)_2BR \xrightarrow{H^+/MeOH} DMPH + (DMP)B(OMe)R \xrightarrow{H^+/MeOH} DMPH + RB(OMe)_2 \qquad (3)$$

Table 1 shows clearly that mineral acid catalysed methanolysis of $(DMP)_2BR$ is much faster than equivalent solvolysis of Mes_2BR. The more hindered the borane the greater are the differences. It was not possible to remove both mesityl groups from Mes_2BMe or Mes_2BBu^t (entries 16, 17) whereas both DMP groups were readily removed (entries 1, 8). The differences using acetic acid are less marked (compare entries 1, 8 with 16, 17), betokening a different mechanism of methanolysis for carboxylic acids and mineral acids.

Methanolysis with HCl and TFMSA removes one DMP group from $(DMP)_2BR^p$ within 1 h (entries 1, 4), and from $(DMP)_2BR^s$ and $(DMP)_2BR^t$ within 5 h. Both DMP groups may be removed in all cases by allowing further reaction, though the time required varies with the structure of the alkyl group. The seemingly highly hindered $(DMP)_2BCH_2SiMe_3$ is also readily solvolysed. ***In no case was there any evidence that the alkyl group was cleaved from boron.*** We have therefore succeeded in carrying out the process outlined in equation (3). It is interesting that the strength of the mineral acid is of importance, so that MSA can be used, but is slower than HCl or TFMSA in its action.

We next investigated alkenyl groups attached to boron (entries 12, 13). In this case use of TFMSA is advantageous as it cannot be utilised by the double bond. The release of DMP groups is somewhat slower than the corresponding alkyl derivatives (compare entries 3, 4 with 12 and 6 with 13) but was efficient nonetheless. The most striking feature was ***the specific cleavage of the MDP groups compared with the alkenyl groups***, despite the known ease of solvolysis of alkenyl-boron bonds.[22]

In only one case did an aliphatic group compete with DMP groups for methanol, and that was the allyl group of $(DMP)_2BCH_2CH{:}CH_2$. This is not unexpected in view of the known ease of removal of allyl groups from boron by proton transfer using a cyclic mechanism.[13, 23]

TABLE 1 Methanolysis of hindered organoboranes

Exp.	Organoborane	Time (h) for removal of 1 or 2 aryl groups with acid							
		HCl		CF_3SO_3H		CH_3SO_3H		CH_3CO_2H	
		1	2	1	2	1	2	1	2
1	DMP_2BMe	0.10	1.05	0.10	1.05	0.10	1.05	7.0	48 (1.38)[a]
2	DMP_2BEt	0.22	1.7	0.22	1.7	0.48	3.60	8.6	99
3	DMP_2BBu^n	0.24	1.6	0.24	1.6	0.54	3.25	4.0	48 (1.45)[a]
4	DMP_2BOct^n	0.30	3.2	0.50	4.0	-	-	17.2	48 (1.50)[a]
5	DMP_2B-2-Pentyl	1.0	17.2	1.0	17.2	-	-	32.8	96 (1.0)[a]
6	DMP_2B-3-Hexyl	4.2	56.8	4.2	56.8	-	-	43.2	96 (1.26)[a]
7	DMP_2B-3-Decyl	6.2	136	6.4	150	-	-	170	200 (1.0)[a]
8	DMP_2BBu^t	0.4	23.0	0.4	23.0	1.20	37	33	96 (1.0)[a]
9	DMP_2B-3-Methyl-3-Hexyl	2.6	79.2	2.6	79.2	-	-	96(0.75)[a]	-
10	$DMP_2BCH_2CH{=}CH_2$[b]	0.20	2.9	0.47	4.5	0.9	5.6	1.9	48(1.0)[a]
11	$DMP_2BCH_2SiMe_3$	0.15	5.0	0.15	5.0	-	-	-	-
12	$DMP_2BCH{=}CHBu^n$	1.1	19	0.60	4.4	-	-	96(0.91)	-
13	$DMP_2BC(Et){=}CHEt$	[101][c]	-	16.0	[99][c]	-	-	No reaction	
14	DMP_2BOMe	0.16	3.0	0.16	3.0	0.42	5.0	No reaction	
15	$DMPB(OMe)_2$	3.1	-	3.1	-	-	-	No reaction	
16	Mes_2BMe	36.4	48(1.15)[a]	48(0.89)[a]	-	-	-	8	34
17	Mes_2BBu^t	190	200(1.05)[a]	200(0.90)[a]	-	-	-	200(0.79)[a]	-

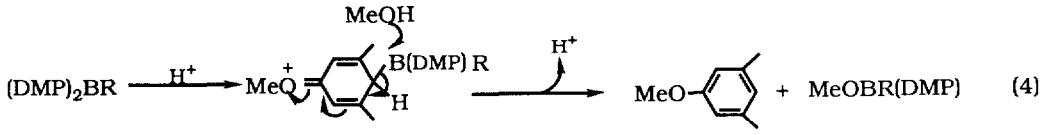
a) Reaction stopped after time shown. Mole equivalents of DMPH present given in brackets.

b) The allyl group is lost at about the same rate.

c) Reaction stopped after 96h, time of reaction estimated graphically.

Entries (14) and (15) are of some interest. Acetic acid gave no solvolysis at all, whereas mineral acids rapidly methanolyse the alkoxyborane substrates. Clearly electron demand at boron is paramount for acetic acid, emphasising that this reagent first co-ordinates at boron and then transfers a proton by a cyclic mechanism.[24] The reaction may be inhibited by steric hindrance around boron, by lowering the electrophilicity of the boron[25], or by lowering the nucleophilicity of the acid,[15, 24] as with TFA. The latter is apparently too weak on acid to protonate the aromatic groups and too poor a nucleophile to co-ordinate to the boron, so that it is completely ineffective as a catalyst. The strong mineral acids presumably readily protonate the aromatic rings.

The steric effects discernible are ascribed to the second reaction step of methanolysis of the protonated intermediate (equation 4). We have found that use of glycol accelerates the reaction, and will report this in our full paper.



(4)

Alkyldialkoxyboranes and alkenyldialkoxyboranes have a rich chemistry.[26] It is not possible to directly produce α-anions from $R^1B(OR^2)_2$ to carry out their manipulations. In this paper we have shown that $(DMP)_2BR$ not only are useful in their own right but provide an important link between boranes that produce stabilised carbanions and dialkoxyboranes that do not (equation 5).

$$(DMP)_2BCH_2R^1 \longrightarrow (DMP)_2B\bar{C}HR^1 \longrightarrow (DMP)_2BCHR^1R^2 \longrightarrow (MeO)_2BCHR^1R^2 \longleftarrow (MeO)_2BCH_2R^1 \quad (5)$$

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1. This title replaces that previously used. Reference 9 should be looked at as part 11 of this series.
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