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DIMESITYLBORYL COMPOUNDS. PART III.* OXYGEN DERIVATIVES

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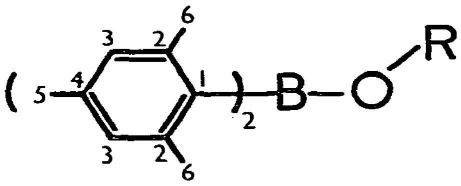
Summary

A series of alkoxy and aryloxydimesitylboranes (Mes_2BOR) has been synthesised, characterised and their ^1H, ^{11}B and ^{13}C NMR data recorded The corresponding data for fluorodimesitylborane is reported. As has been found for other dimesitylboryl systems, the mesityl ^{13}C chemical shifts remain virtually unchanged with change in R.

It is concluded that there is no B-aryl π backbonding in Mes_2BX systems and that B-X π bonding increases in the order N>O>F>C.

Introduction

This paper reports the synthesis and properties of a series of alkoxy and aryloxydimesitylboranes Mes_2BOR (I). The work is part of a systematic study of derivatives of the dimesitylboryl group outlined in Part II of this series [1].



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* For Part II see ref.1

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Results

The resistance of dimesitylborinic acid (R=H) to the normally observed dehydration reaction (equation A), which makes isolation of pure borinic acids difficult [2], has been known for some time [3]. The only other borinic acid showing like behaviour is the similarly sterically crowded compound $[\{(CH_3)_3Si\}_2CH]_2BOH$[4]. The mechanism of reaction (A) is not known but it must differ significantly from that of the esterification reaction (equation B) since this has proved to be the synthetic method of choice for the borinic acid esters reported here [5].

$$2R'_2BOH \rightarrow (R'_2O)_2B + H_2O \qquad (A)$$

$$Mes_2BOH + ROH \rightarrow Mes_2BOR + H_2O \qquad (B)$$

Attempts to prepare the t-butoxy derivative by this method failed. However less convenient alternative methods do yield products containing this ester but because of the inherent reactivity of the latter a pure sample has not so far been obtained.

The esters reported here are all air stable colourless, crystalline solids with the exception of Mes_2BOBu^n which is an oil at room temperature. They are readily soluble in most organic solvents but once dissolved are prone to slow atmospheric oxidation. It is assumed that these compounds, like bis (2,6-dimethylphenyl)methoxy borane [6], are monomeric in solution. This view is supported by the ^{11}B chemical shift data.

^1H Spectra

As is the case with the alkyl [7] and amino [1] derivatives the ^1H spectra of the mesityl groups in these compounds are not very informative. They all show a fairly broad singlet in the aromatic region (in the range δ 6.60-6.76 in CCl_4) and a solvent and substituent dependent signal ca. δ 2.20, due to the methyl groups. This signal is usually two singlets (ratio 2:1) but can be a singlet in certain cases.

^{11}B Spectra

The results are given in Table 1. These fairly broad signals occur in the range δ 51±2ppm which is similar to that observed for alkoxydialkylboranes. They are ca. 6ppm downfield from the value for ethoxydiphenylborane [8].

Table 1. The chemical shifts $\delta^{13}C$ and $\delta^{11}B$ of compounds (I)

		$\delta^{13}C$						$\delta^{11}B$
No.	R	1	2	3	4	5	6	
1	H	136.9	141.0	128.3	138.8	21.1	22.4	50.5
2	Me	136.2	141.1	128.2	138.3	21.1	22.4	51.0
3	Et	136.3	141.0	128.2	138.3	21.1	22.4	51.0
4	Pr^n	136.2	141.0	128.2	138.2	21.1	22.4	50.0
5	Pr^i	136.6	141.0	128.2	138.1	21.1	22.5	49.0
6	Bu^n	136.5	141.0	128.2	138.2	21.1	22.4	51.5
7	$CH_2CH{=}CH_2$	136.2	141.1	128.2	138.4	21.1	22.4	51.0
8	$CH_2C\equiv CH$	135.3	141.4	128.3	138.8	21.1	22.4	51.0
9	CH_2Ph	135.9	141.0	128.2	138.5	21.1	22.4	51.0
10	Ph	135.7	141.1	128.2	138.9	21.1	22.4	53.0
11	$p\text{-}Bu^t\text{-}C_6H_4$	135.9	141.1	128.2	138.8	21.1	22.4	53.5
12	$p\text{-}Cl\text{-}C_6H_4$	135.2	141.2	128.4	139.2	21.2	22.4	53.0
13	$p\text{-}MeO\text{-}C_6H_4$	135.9	141.2	128.2	138.8	21.2	22.4	53.0

^{13}C Spectra

Assignment of the mesityl signals in the fully proton noise decoupled spectra was straightforward. The C_1 resonances, observed as fairly broad lines of low intensity, are the sharpest of any C_1 signals

Table 2. Mean chemical shift values $\delta^{13}C$ and $\delta^{11}B$ for compounds Mes_2BX

	$\delta^{13}C$						$\delta^{11}B$
X	1	2	3	4	5	6	
alkyl[a]	142.4	138.8	128.5	138.1[b]	21.0[b]	23.0[b]	84.4[c]
Ph[d]	141.7	140.7	128.2	138.6	21.2	23.4	79.3
Mes[d]	144.1	140.5	128.6	139.0	21.2	22.8	79.2
NR_2[e]	138.9	140.6	128.0	137.0	21.0	22.6	44.4
OR[f]	136.1	141.1	128.2	138.6	21.1	22.4	51.4
F	134.3	142.4[g]	128.6	140.5	21.3	22.3	53.0

a. mean of values reported in Part I

b. excluding values for the t-butyl and 2-phenyl-2-propyl derivatives where steric effects are operative

c. excluding the value for the diphenylmethyl derivative

d. full details for these compounds will be given in a future paper on unsaturated hydrocarbon derivatives

e. mean of values reported in Part II

f. mean of values reported in Table 1

g. $^3J(^{19}FBC^{13}C) = 4.4Hz$

yet observed in this series of compounds. These data are given in Table 1. Like the alkyl and nitrogen derivatives very narrow chemical shift ranges for the different carbons are observed.

Discussion

Numerous monophenylboranes have now been prepared and studied by ^{13}C magnetic resonance spectroscopy [9]. As explained elsewhere [9d] any mesomeric interaction between the phenyl ring and the boron atom is expected to show itself most clearly in the chemical shift of the *para* aromatic carbon atom. Results from a diverse series of phenylboranes indicate that the *para* carbon is deshielded in the following order; halogens > organyls > OR > SR > NR_2 and this has been correlated with decreasing B-phenyl π interactions. The chemical shift range observed for this series is ca. 8ppm and is approximately six times smaller than that observed for the isostructural and isoelectronic carbocations [9d]. This reduced range is in accord with the expectation that trigonal boron is a good σ donor and poor π acceptor, whereas the opposite is true for the central carbon of the carbocations [10].

Hitherto only a few diphenylboranes have been subjected to similar studies. No obvious chemical shift relationships could be detected [9b,c,d]. Of crucial importance to the interpretation of diarylborane chemical shift data is the structure of such compounds in solution. The following observations are thus pertinent to the discussion. X-ray structure data have shown that triphenylborane [11] and trimesitylborane [12] adopt a propellor conformation in the ground state in which the sense of twist of all three groups is the same. The angles of twist of the aryl rings out of the plane defined by the boron atom and the three carbons bonded to it are ~30° and ~50° respectively. Similarly, an X-ray analysis of $Mes_2BN{=}CPh_2$ shown the mesityl rings are rotated out of the C_1-B-C_1 plane with angles of twist ~50° [13].

The results of low temperature ^1H NMR studies on trimesitylborane and related compounds are consistent with the propeller-like geometry of these compounds persisting in solution [12]. This led these authors to suggest that "- in contrast to (aryl) carbonium ions, where conjugative effects seem to play a major role, the barriers to rotation in arylboranes are mainly steric in origin". Furthermore in the same work a negligible substituent effect on the rotational barrier in both dimesityl-9-anthryl and 9(10-methoxyanthryl)borane derivatives was observed. Similar dynamic NMR studies on several alkoxy-orthosubstituted diarylboranes [6] have been interpreted in terms of three alternative solution structures, two of which involve a propeller conformation for the three ligands. In the third a perpendicular conformation is defined in which one of the aryl groups is at right angles to the plane containing the boron, the two carbons and the oxygen bonded to it, with the second ring lying in this plane. This perpendicular conformation has been used to rationalise the ^1H solution spectra of a series of sterically crowded _para_ and _meta_-substituted aryl-n-butoxy(2,4,6-tri--tert-butyl-phenyl)boranes [14]. The significant point from this latter study is that the rotational barrier about the B-aryl bond shows only a slight _para_-substituent effect. Since the barrier to rotation about the B-aryl bond in these alkoxydiarylboranes is very similar ($\Delta G^{\ddagger}$ lies in the range 48 to 57 kJ mol^{-1}) it is concluded that in these compounds too, the rotational barrier is primarily due to steric effects with B-aryl π bonding being of only minor significance.

Evidence from the work reported here suggests that this may be a general conclusion for all $aryl_2BX$ systems. Table 2 lists the mean ^{13}C chemical shifts of the mesityl groups in the series of compounds studied to date. Included, for comparison, are data for Mes_2BF (which completes the Mes_2BX series for first row elements), trimesitylborane and dimesitylphenylborane. In the latter compound the δ ^{13}C values for the phenyl carbons are: C_1, 145.9(144.1); o, 136.2(138.6); m, 127.9(127.4); p, 131.9(131.3). The values in parenthesis are the mean of two independent measurements [9a,9d,15] of the corresponding carbons in triphenylborane.

The close similarity between the chemical shift data for all these compounds, for some of which convincing crystal and solution structure data is known, implies that B-aryl π bonding is insignificant in all dimesityl and triarylborane derivatives.

It is clearly seen from the data listed that in the absence of steric effects other than those associated with the mesityl moities there is virtually no variation of δ C_3 and δ C_6 both of which are deshielded with respect to the corresponding carbons in mesitylene itself, measured under the same experimental conditions (δ $\underline{C}(CH_3)$,137.6; δ $\underline{C}(H)$,127.0; δ $\underline{C}H_3$,21.2). The chemical shifts of C_5 are constant and equal to that of a methyl group in mesitylene. The C_2 and C_4 carbons show slight but inconsistent variation. We believe therefore, that whilst minor B-aryl π delocalisation effects in these systems cannot be unambiguously ruled out at present, slight concentration effects, solvent shifts and steric differences between substituents separately or in combination are responsible for the range of ~3.5ppm observed for the <u>ortho</u> and <u>para</u> carbon chemical shifts. For example, it has been shown that going from the neat liquid to a 30% $CDCl_3$ solution can cause a shift of ~1ppm in the phenyl carbon resonances of phenylboranes [9c]. We have also observed similar shifts for the C_2 and C_4 carbons on changing the solvent from $CDCl_3$ to CS_2 or $(CD_3)_2SO$. The fact that additional steric effects are operative is seen from the data of the amino and alkyl compounds. In the amino derivatives[1]significant changes in the C_2, C_3 and C_4 chemical shifts take place on changing R from H to alkyl or aryl and also in changing the size of the alkyl group [7]. In the alkyl series, increasing the size of R causes a shielding of C_4 of ca. 1.3ppm on going from methyl to a tertiary carbon substituent with a large concomitant deshielding of the C_6 carbons.

The increase in shielding of C_1 (~8ppm) with increase in electronegativity and/or decrease in size of X is the one simple consistent trend observed. This effect has also been observed in phenylboranes [9d]. As pointed out by Nöth et al [9d] strong electronegative groups attached to aryl substituents do not necessarily cause a deshielding of C_1. The origin of this effect is not obvious but it would appear that the bond angles at the boron atom may in some way be influential [9d,15]. These are of course, affected by the size and shape of X. The boron chemical shifts follow the pattern observed for R_2BX systems when R is hydrocarbyl. The mean δ ^{11}Bppm(X) values for R_2BX systems are: 86,(CR'_3); 47,(NR'_2); 53,(OR'); and 60,(F); when R = alkyl and when R = phenyl the values are 71, 43, 45 and 47, respectively [8]. These values can be rationalised with an increasing B-X π backbonding order of N>O>F>C. It is assumed for the systems studied here there is no such π backbonding when X = hydrocarbyl. This order is consistent with theoretical studies on H_2BX systems [10] and the semi-empirical approach to ^{11}B chemical shifts of Nöth and Wrackmeyer [8]. It is also in accord with dynamic PMR studies which indicate that $\Delta G^{\ddagger}$ for the barrier to rotation about the B-X bond is > 70 kJ mol^{-1} in monoaminoboranes [16] and ca. 50 kJ mol^{-1} for alkoxydiarylboranes [6]. In the absence of steric effects these values can be correlated with the degree of B-X π bonding [16].

The rigorous application of chemical shift theory is of limited use for nuclei other than hydrogen [17]. This difficulty arises from the fact that the paramagnetic screening contribution to the observed chemical shifts cannot be properly evaluated without precise knowledge of appropriate excited state wavefunctions. In the absence of this information recourse is made therefore to pragmatic approaches based upon experience and chemical intuition. Neighbouring group anisotropies, π bonding and ring current effects are some of the explanations most frequently invoked. None of these effects can be properly quantified. For boron compounds π and σ bonding effects are usually used to correlate chemical shift variations of the magnitudes reported here. This approach is not without its difficulties. Although π backbonding explains the trend noted above, changing the boron substitution pattern in the series BR_nX_{3-n} (R = alkyl, n = 0,1,2) causes a complete reversal in the ^{11}B shielding order. For R_2BX compounds this order is N>O>F, for RBX_2 it becomes F=O>N (for all three types of compounds δ ^{11}B = 31±3ppm) and for BX_3 systems it is F>O>N [8]. This can be rationalised in terms of a synergism between inductive (σ bond polarisation) and conjugative (π backbonding) effects. A decrease in σ electron density at boron with increase in the number of X substituents is thus partially compensated for by π electron back donation. Since σ bond polarisation is assumed to increase with increase in electronegativity the nett effect of this behaviour would be expected to follow the order F>O>N. There is evidence to support this view from theoretical studies of BH_nF_{3-n} (n = 3,2,1,0) systems. It is found that occupation of the boron

2p π orbital rises with increase in fluorine substitution but that the combined inductive effect is greater and hence the boron becomes progressively more positively charged [18].

There are however inconsistencies which arise with this explanation. Increase in sigma bond polarisation with increase in electronegativity is expected to cause a deshielding of the boron nucleus [19]. This correlation appears to work for some tetravalent boron nuclei [19c]. However, recent data show that on replacing the alkyl groups of a trialkylborane with less electronegative substituents, which do not possess electron pairs capable of π back donation, causes a deshielding of the boron nucleus [20], vis:-

	BR_3	→	$R_2B\text{-}BR_2$	→	$R_2B\text{-}\underline{B}(SiR'_3)R$
δ ^{11}Bppm	~86		~105		127

This implies that an increase in σ bond polarisation causes a shielding effect. It may be that for trivalent boron compounds with NR'_2, OR' or F substituents occupancy of the boron 2p π orbital is the dominant factor in determining the ^{11}B chemical shifts observed. This is not the case however when the potential π donor is a heavier atom such as S, Se, Cl, Br or I. The ^{11}B chemical shift values of R_2BX compounds containing these substituents are virtually constant with a value of 79±5ppm [8]. The π electron donating ability of these ligands should vary appreciably, consequently other effects must play the dominant role in determining the ^{11}B chemical shifts in these compounds.

These observations, coupled with the problems posed by the ^{13}C chemical shift variations of carbon atoms bonded directly to boron, highlight the inadequacy of even the qualitative models cuurently in use, to interpret reliably, chemical shift effects for nuclei other than hydrogen.

Experimental

The compounds were prepared from dimesityl borinic acid and the corresponding alcohol using the azeotropic distillation method [5].

Where necessary a nitrogen atmosphere was used during the reaction. Compounds (2)→(5) and (7) were recrystallised from the parent alcohol, the remainder from hexane/diethyl ether mixtures. The yields after one recrystallisation were: compounds (7) and (12) ca. 60%, compounds (2)-(5), (8)-(11), (13) > 85%. Dimesityl borinic acid was made in quantitative yield by the hydrolysis of dimesitylfluoroborane [3]. The compounds were characterised by ^1H and ^{11}B N.M.R. and precise mass spectrometric measurements. They had the following uncorrected melting points: (1), 140-141°; (2), 75-76°; (3), 76-77°; (4), 42-44°; (5), 86-87° (7), 121-122°; (8), 82-83°; (9), 74-76°; (10), 135-136°; (11), 175-176°; (12), 100-101°; (13), 115-116°C.

^{13}C and ^{11}B NMR spectra were recorded in 10mm tubes at a probe temperature of ca. 35° on a Jeol FX90Q FT spectrometer using ca. 30% (w/v) solution in $CDCl_3$. Internal TMS and external BF_3 etherate were used as references for carbon and boron, respectively. The carbon spectra were recorded using a 10μ sec. pulse (tip angle ~30°) and a 2 or 3s pulse interval. The chemical shift convention for boron is the same as that for carbon i.e. downfield shifts from the reference are positive and quoted in ppm. The measurements are precise to ±0.1 ppm for ^{13}C and ±0.5 ppm for ^{11}B.

The chemical shift values for the ^1H and ^{13}C nuclei in the R groups are all of a routine nature and are therefore not reproduced here. A complete set of chemical shift data for all the Mes_2BX compounds studied to date is available on request.

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