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DIMESITYLBORYL COMPOUNDS. PART I. ALKYL DERIVATIVES

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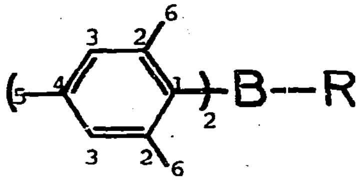
Summary

^{13}C and ^{11}B NMR data for a series of nine alkyldimesitylboranes are reported and discussed. The mesityl ring carbon atoms are insensitive to the character of the alkyl substituent. Sequential replacement of the methyl hydrogens in dimesitylmethylborane by methyl groups gives rise to an "α effect" whereas the chemical shift of the α carbon in benzyldimesitylborane is found to be insensitive to replacement of hydrogen by methyl groups.

Introduction

The recognition that boron stabilised carbanions can be readily synthesised in good yields from easily prepared air stable alkyldimesitylboranes has recently been reported [1]. Since these carbanions are potentially of synthetic utility it is desirable to have a thorough knowledge of the spectroscopic properties of the alkyldimesitylborane starting materials themselves. Furthermore application of ^{13}C NMR studies to organoboranes is still largely undeveloped and, as has been pointed out elsewhere [2], little is known in particular about substituent effects for saturated carbon atoms attached to boron. In this respect the study of a systematically related series of compounds has obvious advantages.

Consequently ^{13}C and ^{11}B NMR data have been obtained from a series of substituted dimesitylmethylboranes (I) to augment the ^{1}H data already available [1]. The new data are now reported here.



(I)

Results and Discussion

^{13}C Spectra

Assignment of resonances in the proton noise fully decoupled spectra was usually straightforward. Ambiguities were resolved by off-resonance or single frequency ^{13}C-{^{1}H} experiments. For compound 9 a completely undecoupled spectrum (run with retention of the NOE) was necessary in order to complete the assignment of all the resonances observed in the aromatic region.

The carbon atoms bound directly to boron appear as relatively broad, low intensity signals at the probe temperature (~ 35°) in $CDCl_3$. Their detection was found to be straightforward provided excitation pulses giving moderate flip angles were used (typically $\alpha = 30^\circ$) with a pulse interval of 2-3 seconds.

In all cases only one signal is observed for the ortho carbons and one for the meta carbons in the mesityl rings. Similarly, where R contains phenyl(s) only one signal for each set of ortho and meta carbons is observed.

In the case of compound 5 it was not obvious from the three methyl signals observed which of the two low field signals corresponded to that of the t-butyl methyls. This ambiguity arises because, while the para mesityl methyl signal is found to change very little with changes in R the ortho mesityl methyls in 5 are found to be deshielded in comparison with other members of the series.

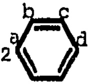
The same effect was also observed in the corresponding ^{1}H spectrum where the ortho methyl protons were found to be deshielded by about 0.14 ppm [1]. The problem was solved by a single frequency $^{13}C-\{^{1}H\}$ decoupling experiment with the proton frequency set at that of the t-butyl protons. The resultant spectrum showed conclusively that the ^{13}C signal at 25.6 ppm is due to the t-butyl methyl carbons.

For compounds 6-9 the phenyl resonances were assigned by comparison with each other and with the known ^{13}C chemical shift behaviour of alkylbenzenes [3]. In monoalkylbenzene systems the aryl carbon C(a), appears at lowest field and the chemical shift increases with increase in the size of the substituent whilst C(d) appears at highest field and is virtually independent of the substituent. C(c) is also substituent independent. The chemical shift of C(b) is substituent dependent and varies rather irregularly with substituent size. For compounds 7 and 8 both C(b) and C(c) are found in the range 127.7 ± 0.2 ppm. The lower value has been arbitrarily assigned to C(b) by comparison with monoalkylbenzenes carrying large substituents. The complete set of assignments are given in the table.

The results show that none of the mesityl ring carbons are sensitive to a change in R. This is to be expected since none of the R groups can interact with the boron via a π mechanism. The possible exception is compound 1 where a hyperconjugative interaction may be responsible for the slight deshielding of the C(1) carbons.

Sequential replacement by methyl groups of the hydrogen atoms on C(7) in compound 1 causes a deshielding "α effect" as observed in alkane series [3]. The presence of a phenyl group on C(7) causes a deshielding of 23 ppm and at the same time renders C(7) insensitive to further substitution by methyl groups. A second phenyl group however, causes an additional deshielding of 19 ppm. Further work with a wider range of substituents is obviously required before such effects are more fully understood.

The chemical shifts[a] $\delta^{13}C$ and $\delta^{11}B$ of compounds (I)

No.	R	$\delta^{13}C$ 1	2	3	4	5	6	7	8	9	a	b	c	d	$\delta^{11}B$
1	$-\overset{7}{C}H_3$	143.7	139.1	128.5	138.5	21.1	22.9	19.4	-	-	-	-	-	-	82.0
2	$-\overset{7}{C}H_2\overset{8}{C}H_3$	142.6	138.9	128.4	138.1	21.1	22.6	26.3	9.2	-	-	-	-	-	84.9
3	$-\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_3$	142.9	138.9	128.3	138.1	21.1	22.6	37.3	19.1	17.5	-	-	-	-	84.7
4	$-\overset{7}{C}H(\overset{8}{C}H_3)_2$	142.2	138.6	128.4	137.6	21.0	23.3	31.0	18.9	-	-	-	-	-	87.8
5	$-\overset{7}{C}(\overset{8}{C}H_3)_3$	142.0	138.3	128.8	136.9	20.7	30.2	32.0	25.6	-	-	-	-	-	91.6
6	$-\overset{7}{C}H_2$ 	142.0	139.0	128.4	138.5	21.0	22.9	42.4	-	-	140.7	129.5	127.9	124.7	85
7	$-\overset{7}{C}H(\overset{8}{C}H_3)Ph$	142.0	138.8	128.4	138.0	21.0	23.3	42.6	15.0	-	145.0	127.5	127.9	124.5	87
8	$-\overset{7}{C}(\overset{8}{C}H_3)_2Ph$	142.0	139.0	128.8	137.3	20.8	25.2	42.0	29.9	-	150.0	127.6	127.8	124.9	82
9	$-\overset{7}{C}H(Ph)_2$	141.9	138.9	128.3	138.1	21.0	23.3	61.2	-	-	143.6	130.4	127.6	125.1	75

a. Spectra were recorded on ca. 30% (w/v) solutions in $CDCl_3$ which also provided the deuterium lock. $\delta^{13}C$ vs. TMS as internal standard, $\delta^{11}B$ vs. external BF_3 etherate.

When C(7) is fully substituted the ortho mesityl methyls are found to be deshielded, presumably due to steric repulsion by group R.

^{11}B Spectra

The boron consisted of a single peak which in the case of compounds 6-9 was very broad. The chemical shifts are in the range normally associated with trigonal boron bound to three saturated carbon atoms [4]. This implies that the boron atom in the compounds is not involved in π electron delocalisation with the aromatic rings to any significant extent. Such interactions have however been suggested to explain chemical shifts of para aromatic carbon atoms in phenylboranes [2].

The least sterically hindered compounds (1, 2 and 6) were found to slowly decompose in solution when in contact with air, as indicated by the slow growth, over several hours, of a second boron signal in the NMR spectra located at approximately 55 ppm. Preliminary investigations suggest this is due to oxidation of the alkyldimesitylborane to the corresponding alkoxyderivative Mes_2BOR. This process is very much slower in the solid state [1].

Experimental

Dimesitylpropylborane 3 was prepared in 80% yield by the established method [1,5] and characterised by ^1H NMR and high resolution mass spectroscopy, m.p. 69°. Dimesityldiphenylmethylborane 9 was prepared in 75% yield by the established method using diphenylmethyllithium. Recrystallisation from pentane gave well formed colourless crystals m.p. 179°. The ^1H NMR spectrum showed resonances at δ(TMS, $CDCl_3$), 2.05(12H, s, CH_3); 2.15(6H, s, CH_3); 4.95(1H, s, $CH(Ph)_2$); 6.60(4H, s, mesityl aromatics); 6.95(10H, m, phenyl aromatics). The mass spectrum showed the parent ion at $^m/_e$ 416. Anal. Calc. for $C_{31}H_{33}B$: C,89.42; H,7.99, found C,89.09; H,8.05%.

Spectra were recorded in 10 mm tubes at a probe temperature of ~308K on a Jeol FX90Q FT spectrometer using ca. 30% (w/v) solutions in

$CDCl_3$. Internal TMS and external BF_3 etherate (coaxial capillary) were used as references for carbon and boron, respectively. The carbon spectra were recorded using a pulse angle of 30° and a 2-3 s 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 ±0.2 ppm for ^{11}B with the exception of the boron values for compounds 6-9 where the estimated precision is ±0.5 ppm.

Acknowledgments

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