DIMESITYLBORYL COMPOUNDS

IV *. SULPHUR DERIVATIVES

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Summary

A series of hydrocarbylthiodimesitylboranes (Mes_2BSR) has been synthesized, characterised and their ^1H, ^{11}B and ^{13}C NMR data recorded. The steric hindrance induced by the four *ortho* methyl groups is insufficient to prevent rapid hydrolysis in the air of the B—S bonds in compounds where R = alkyl. However, with the bulkier R = aryl groups hydrolytic stability is achieved.

The existence of appreciable boron—sulphur π back-bonding in these compounds is shown by the presence of non-equivalent mesityl groups in the ambient temperature ^1H and ^{13}C NMR spectra. The mechanism which leads to removal of this non-equivalence has a free energy of activation $\Delta G^{\ddagger}_{77} = 76.9 \pm 0.4$ kJ mol^{-1} for R = Ph.

Introduction

This paper reports the preparation and properties of some hydrocarbylthiodimesitylboranes Mes_2BSR (I) as part of a systematic study of the properties of dimesitylboryl compounds.

Compared with boranes containing boron bonded to first row elements little is known about the chemical and physical properties of the phosphorus and sulphur analogues. The fact that the dimesitylboryl group imparts appreciable kinetic stability to Mes_2BX compounds has already been noted in earlier parts of this series. It was of interest to see if such effects operate in the corresponding sulphur compounds since B—S bonds are notoriously labile and are consequently of some synthetic utility [2]. In addition ^{13}C chemical shift data were required for comparison with those already obtained for dimesitylboryl
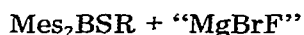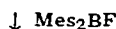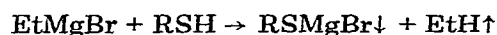
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derivatives of first row elements with a view to rationalising the electronic effects operating in such systems.

(I)
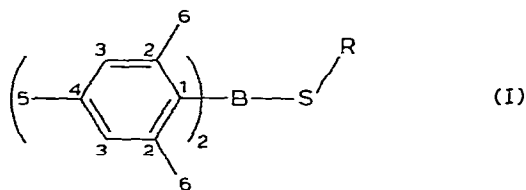
Results

The compounds were all made in high yields according to the following scheme:

$$EtMgBr + RSH \rightarrow RSMgBr\downarrow + EtH\uparrow$$

$$\downarrow Mes_2BF$$

$$Mes_2BSR + \text{``MgBrF''}$$

$$R = Me, Et, CH_2Ph, Ph, p\text{-}Me\text{-}C_6H_4.$$

Recrystallisation from pentane or pentane/ether mixtures gave white crystalline products which were characterised by ^1H and ^{11}B NMR and precise mass spectrometric measurements. The alkyl derivatives are moisture sensitive whereas the aryl derivatives are only slightly affected by atmospheric moisture after 12 h. All show good solubility in aprotic solvents. Their monomeric nature is confirmed by comparison of their ^{11}B chemical shift values (Table 1) with those of Me_2BSMe and Me_2BSPh (δ $^{11}B \sim 74$ ppm) [3] which are known to be monomers [4].

^1H spectra

Compared with the proton spectra of other compounds in this series the spectra of the compounds reported here (Table 1) prove revealing. The spec-

TABLE 1

THE CHEMICAL SHIFTS δ^1H AND $\delta^{11}B$ OF COMPOUNDS I

No.	R	δ^1H				$\delta^{11}B$
		o-CH_3	p-CH_3	m-H	others	
1	CH_3	2.24	2.31	6.73	CH_3, s, 2.07	70.0
2	C_2H_5	2.24	2.32	6.71	CH_2CH_3, t, 1.16 CH_2CH_3, q, 2.58	71.0
3	CH_2Ph	2.22	2.27	6.67 6.76	CH_2Ph, s, 3.78 CH_2Ph, m, 7.02	73.0
4	Ph	2.08 2.37	2.17 2.24	6.57 6.76	Ph, s, 7.05	73.5
5	p-MeC_6H_4	2.09 2.37	2.19 2.26	6.52 6.69	p-$CH_3C_6H_4$, s, 2.26 p-$CH_3C_6H_4$, s, 6.83	73.0

trum of 1 is of a routine nature and requires no further comment. The signal due to the four *meta* protons is a broad singlet for 2 but is split into two poorly separated singlets (1 : 1) in the case of 3. The signals for the *para* methyl protons are singlets in both cases, those due to the *ortho* methyl groups are also singlets but are reduced in intensity with concomitant shoulders. In both cases the total methyl signals are equivalent to eighteen protons.

For 4 the *meta* proton signal consits of two well separated singlets (1 : 1). The methyl region consists of four singlets (2 : 1 : 1 : 2). This spectrum is virtually identical in appearance to the high temperature spectrum of (2,6-dimethylanilino)dimestylborane depicted by Glowgowski et al. [5] if the amino and methyl proton resonances of the anilino group are omitted. The spectrum of 5 is very similar to that of 4 except that the *p*-tolyl methyl group has the same chemical shift as one of the *para* methyl mesityl groups and the spectrum in the methyl region is therefore a 2 : 2 : 1 : 2 set of singlets. These results indicate the presence of two non-equivalent mesityl ligands, the magnetically anisotropic aryl groups in 4 and 5 being responsible for the good resolution observed in the spectra of these two compounds.

^{11}B spectra

The chemical shift values are given in Table 1. Reasonable signals were observed in the range associated with R_2BSR' compounds [3].

^{13}C spectra

The chemical shift data for the mesityl carbons, obtained from fully proton noise decoupled spectra, are given in Table 2. In all compounds two sets of signals are observed with the exception of the C(1) and C(5) carbons for which only one signal is seen. The C(1) resonances appear as very broad low intensity signals due to the quadrupolar nature of the directly bonded boron atom. This effectively masks the chemical shift differences of the two non-equivalent C(1) carbons in each compound. The chemical shift differences in the case of C(5)

TABLE 2

THE CHEMICAL SHIFTS $\delta^{13}C$ OF THE MESITYL CARBONS IN COMPOUNDS I

No.	R	$\delta^{13}C$					
		1 [a]	2	3	4	5 [a]	6
1	CH_3	137.5	141.1 138.8	128.8 128.1	138.6 137.8	21.1	23.7 22.2
2	C_2H_5	137.6	141.1 138.6	128.8 128.1	138.5 137.7	21.1	23.7 22.4
3	CH_2Ph	138.0	141.2 138.8	128.8 128.3	139.4 138.0	21.1	23.6 22.3
4	Ph	137.6	140.8 139.4	128.8 128.2	138.8 138.1	21.0	23.5 22.4
5	p-MeC$_6$H$_4$	137.7	140.8 139.4	128.7 127.9	138.7 138.0	21.1	23.5 22.5

[a] No chemical shift differences discernable. See text for explanation.

carbons are too small to be observable. These effects have also been seen for some Mes$_2$BNHR compounds [6].

## Discussion

The fact that when R = alkyl hydrolysis takes place readily in air indicates that the four *ortho* methyl groups of the mesityl ligands provide insufficient bulk to prevent nucleophilic attack. Bulky R groups, such as aryls, are apparently also needed before resistance to hydrolysis by atmospheric moisture is achieved. This is presumably due to the longer boron—sulphur bond compared with systems where boron is bonded to carbon, oxygen or nitrogen substituents.

The surprising observation that the mesityl ligands are non-equivalent, under the experimental conditions used, is due to restricted rotation about the boron—sulphur bonds in these compounds. It is analogous to the well documented situation in aminoboranes [7]. To our knowledge this is the first time similar π back-bonding effects have been observed in organylthioboranes.

Variable temperature ^{1}H NMR measurements on 4 permitted the measurement of coalescence temperature for the sets of *meta* hydrogens (84°C) and *para* methyl (69°C) signals. Use of the equation $\Delta G_c^{\ddagger} = T_c[190.9 + 19.1 \log(T_c/\Delta\nu)]$ J mol^{-1} [7,8] gave a mean value of $\Delta G_{77}^{\ddagger} = 76.9 \pm 0.4$ kJ mol^{-1} for the process. Such effects imply that, in order to maximise π back-bonding, the planar conformation A is the most stable in solution at ambient temperatures. There is compelling structural evidence to support this view. Electron diffraction studies by Seip et al. on a series of six boron-sulphur compounds have shown that all are virtually planar in the gas phase [9].

By analogy with *syn-anti* isomerism of imines (II) two limiting mechanisms for the process are possible [10]. The first involves a 90° rotation about the B—S bond in planar conformer A to give the perpendicular conformer B. The second involves linear inversion (lateral shift) of the phenyl group to the linear conformation C.

(II)

(A)

(B)

(C)
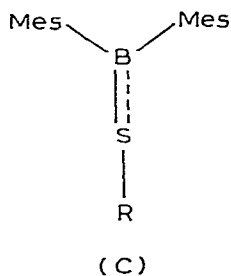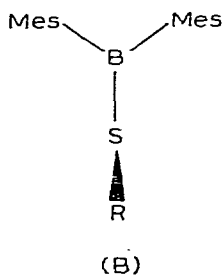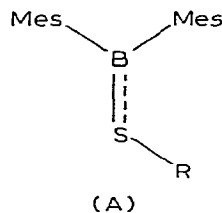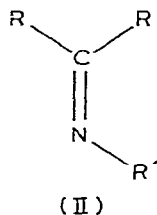
The activation energy is identifiable with steric and B—S π bonding effects in the rotational mechanism whilst for inversion it is identified with "rehybridisation" changes of the sulphur atom. Ab initio molecular orbital calculations provide evidence to support the rotational mechanism. Studies on H_2BOH have shown that rotation is more favoured than inversion by 20 kJ mol^{-1} [11] and the value of ~84 kJ mol^{-1} for rigid rotation about the B—S bond in H_2BSH is close to the value of 76.9 kJ mol^{-1} found for the coalescence process in 4 [12]. In the latter study steric and π bonding effects were found to contribute almost equally to the barrier. If the mechanism is in fact rotational then knowledge of possible steric effects operating in such compounds will lead to values which reflect the degree of B—X π bonding present in these systems. To this end comprehensive dynamic ^{13}C NMR studies are planned on the sulphur compounds reported here, on Mes_2BOR systems where the PMR variable temperature results of Mislow et al. [13] for alkoxydiarylboranes are very relevant and on Mes_2BNHR systems where the rotational mechanism must unquestionably apply.

The mesityl ^{13}C chemical shift values show similar behaviour to those observed for other systems in this series in that for each type of carbon atom very little variation in its chemical shift value occurs on changing R. The mean value for C(1) carbons (137.7) does not fit into the trend of increase in shielding with increase in electronegativity and/or decrease in size of X observed for first row elements [1]. These results would seem to suggest that mesityl carbon ^{13}C chemical shift values are of little use as aids to understanding the electronic effects of the B—X bonds in these systems. Large steric effects, as would be expected, are readily detectable [14].

Experimental

^{13}C and ^{11}B NMR spectra were recorded under the same conditions used in earlier studies [1]. Routine ^1H spectra were recorded on a Perkin Elmer R12A instrument in CCl_4 with internal TMS as reference. The variable temperature results on 4, using hexachlorobutadiene as solvent, were obtained using a Perkin Elmer R32 (90 MHz) instrument. Temperatures were checked by the glycol calibration method. A coalscence temperature for the two *ortho* methyl signals could not be obtained since near the coalescence point the two signals were hidden by the singlet resulting from the coalescence of the two *para* methyl signals. Syntheses were carried out under dry nitrogen atmospheres using anhydrous oxygen-free solvents. All manipulations involving the compounds were carried out in a dry nitrogen-filled glove box or in modified Schlenk tubes. NMR samples were prepared under these conditions and the tubes closed with tightly fitting caps. The synthesis of all five compounds followed the same procedure. The parent thiol (usually 0.01 mol) in ether (20 ml) was added dropwise to a stirred solution of the stoichiometric amount of ethyl magnesium bromide (methyl magnesium iodide in the case of R = Me) in ether (30 ml) at 0°C. A white suspension of the magnesium thiolate was produced during the addition accompanied by gas evolution. The mixture was stirred for 2 h at room temperature for R = alkyl or under reflux for R = aryl. A solution of the stoichiometric amount of fluorodimesitylborane in ether

(20 ml) was added dropwise to the stirred suspension of the magnesium thiolate at room temperature. The flocculent thiolate suspension was slowly replaced (30 min for R = alkyl, 2—3 h for R = aryl) by a denser precipitate of magnesium salts. The reaction mixture was stirred overnight and filtered through anhydrous $MgSO_4$. Removal of the solvent in vacuo gave a white solid which was triturated with a 50 : 50 pentane/ether mixture (70 ml) and refiltered. Removal of the solvent mixture gave the products in 85% yields or better. Recrystallisation from pentane or pentane/ether mixtures gave well formed crystalline materials. Uncorrected melting points, recorded in sealed capillaries, were as follows: 1, 99—102; 2, 102—104; 3, 76—79; 4, 106—108, 5, 94—96°C.

Acknowledgements

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