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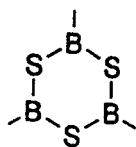
SYNTHESIS OF *B*-ARYL BORON-SULPHUR HETEROCYCLES FROM ARYLBORONDIBROMIDES

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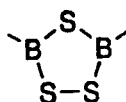
Abstract The synthesis and characterization of some aryl-substituted boron-sulphur heterocycles ($\text{Ar}_2\text{B}_2\text{S}_3$ and $\text{Ar}_3\text{B}_3\text{S}_3$) from ArBBr_2 ($\text{Ar} = \text{Ph}$, 2-MeC₆H₄, 3-MeC₆H₄, 4-MeC₆H₄, 4-EtC₆H₄, 3,5-Me₂C₆H₃, 2,4,6-Me₃C₆H₂) and sulphur containing reagents $(\text{Me}_3\text{C})_2\text{S}_2$, $(\text{Me}_3\text{Si})_2\text{S}$ and HgS are described.

INTRODUCTION

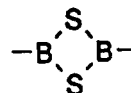
We have become interested in the syntheses of *B*-aryl boron-sulphur heterocycles with the aim of exploring their coordination chemistry. The heterocyclic systems that interest us are 1,2,3-trithia-2,4,6-triborinanes (structure 1), 1,2,4-trithia-3,5-diborolanes (structure 2), and 1,2-dithia-2,4-diboretanes (structure 3). Literature reports^{1,2} in this area are restricted to the *B*-phenyl derivatives (of structures 1, 2, and 3), the *B*-*p*-tolyl derivative (of structure 2), and to group 6 metal carbonyl complexes of $\text{Ph}_3\text{B}_3\text{S}_3$.



(1)



(2)



(3)

RESULTS AND DISCUSSION

The syntheses of $\text{Ar}_3\text{B}_3\text{S}_3$ and $\text{Ar}_2\text{B}_2\text{S}_3$ ($\text{Ar} = 2\text{-MeC}_6\text{H}_4$, 3-MeC₆H₄, 4-MeC₆H₄, 4-EtC₆H₄, 3,5-Me₂C₆H₃, 2,4,6-Me₃C₆H₂) were achieved by methods reported^{3,4} for the phenyl derivatives by reaction of ArBBr_2 and either HgS or $^t\text{Bu}_2\text{S}_2$ in refluxing

toluene respectively. ArBBr_2 derivatives were prepared by standard methods from either ArHgBr or ArSiMe_3 with BBr_3 . Attempts to prepare the 4-membered ring derivatives, $\text{Ar}_2\text{B}_2\text{S}_2$, by a route reported⁵ for $\text{Ph}_2\text{B}_2\text{S}_2$ using $(\text{Me}_3\text{Si})_2\text{S}$ and ArBBr_2 were unsuccessful; however, these reactions cleanly yielded the corresponding $\text{Ar}_3\text{B}_3\text{S}_3$ 6-membered rings. The new heterocycles have been characterized by NMR (^{11}B , ^1H , ^{13}C), IR and MS. Boron-11 chemical shift data are given in Table 1. Full details of the synthesis and characterization of these *B*-aryl boron-sulphur heterocycles are reported elsewhere.^{6,7}

TABLE I Boron-11 NMR data (δ/ppm , C_6D_6 solution) for triarylborathiins and diaryltrithiadiborolanes.

Aryl group	$\text{Ar}_3\text{B}_3\text{S}_3$	$\text{Ar}_2\text{B}_2\text{S}_3$
3-MeC ₆ H ₄	+60.4	+65.1
4-MeC ₆ H ₄	+59.9	+65.7
4-EtC ₆ H ₄	+59.7	+66.1
3,5-Me ₂ C ₆ H ₃	+60.4	+65.4
2-MeC ₆ H ₄	+62.2	+64.8
2,4,6-Me ₃ C ₆ H ₂	+65.4	+63.7

The syntheses and characterization of these heterocyclic compounds has been hampered by their extreme water/air sensitivity, and in air all compounds are rapidly hydrolysed to the related boroxine/boronic acid. We are currently investigating the reactions of these diaryltrithiadiborolanes and triarylborathiins with the following transition metal reagents ($[\text{M}(\text{CO})_3(\text{C}_7\text{H}_8)]$, $\text{M} = \text{Cr}, \text{Mo}$; $[\text{Fe}_2(\text{CO})_9]$; $[\text{Fe}(\text{CO})_3(\text{PhCH}:\text{CHCOMe})]$; $[\text{Pt}(\text{PPh}_3)_n]$, $n = 3, 4$; $[\text{Co}_2(\text{CO})_8]$; $[\text{Co}(\text{CO})_2(\text{C}_5\text{H}_5)]$; $[\{\text{Rh}(\text{COD})\text{Cl}\}_2]$; $[\text{MCl}(\text{PPh}_3)_3]$, $\text{M} = \text{Rh}, \text{Ir}$) and plan to report these results at a later date.

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