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Lewis Acids Based on Sulfur Containing Boron Heterocycles and Trialkylthioboranes

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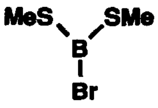
Abstract: The use of trialkyl- and aryl- thioboranes, along with 2-substituted 1,3,2-dithioborolans as Lewis acids has not previously been explored. The article describes the use of four such compounds in the Lewis acid catalysed Diels-Alder reactions of cyclopentadiene with crotonaldehyde, methacrolein, methylvinyl ketone and methylmethacrylate.

Chemically, little is known about trialkyl- and aryl-thioboranes and the 1,3,2-dithioborolans. To-date there has been no work carried out on these boron-sulfur systems as Lewis acids. Fortunately, a large amount of research has been directed towards the preparation, isolation and characterisation of boron-sulfur compounds.[1] The interest in these compounds as Lewis acids stems from the fact that consistently there is no evidence for association of trialkylthioboranes in solution.[2] It has also been noted that the bisalkylthioborane **1** is a monomer.[1] This lack of association should enhance the study of boron based Lewis acid systems because it is simpler to study a monomer than an aggregate. However, it has been observed that trialkythioboranes have no tendency for complex formation with triethylamine,[2] which might indicate that this type of thioborane has only weak Lewis acid properties. The boron-sulfur compounds, **2** to **5**, that have been used in these experiments are representative of the range available. To allow comparisons with other work in the Lewis acid area the Diels-Alder systems we have chosen are ones widely used in the determination of both reactivities and endo : exo selectivity enhancements by Lewis acids.[3]



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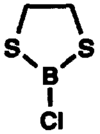

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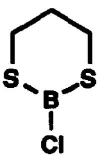

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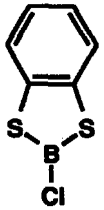

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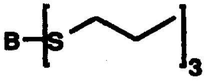

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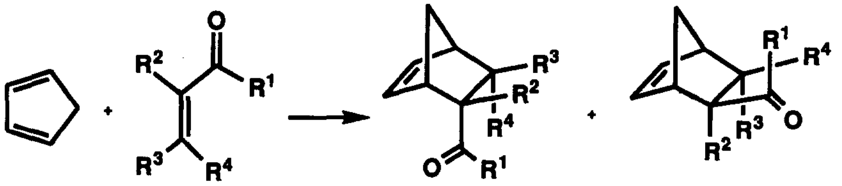
The boron-sulfur compounds **2** to **4** were prepared following the procedure of Finch and Pearn.[4] The dithiol (1.2 equivalents) was added dropwise to boron trichloride (1.0 equivalents) in dichloromethane under nitrogen at -78°C. The reaction mixture was warmed slowly to room temperature with the evolution of HCl. Removal of the dichloromethane by distillation and further distillation of the resulting clear yellow oil yielded the corresponding 2-chloro-1,3,2-dithioborolan. The trialkylborane **5** was prepared by a similar method but using 3.5 equivalents of propanethiol. The general reactions in which these boron-sulfur compounds were tested as Lewis acids are given in Scheme 1.



6 $R^1, R^2, R^4 = H, R^3 = Me$ **7** $R^1, R^3, R^4 = H\ R^2 = Me$ **8** $R^2, R^3, R^4 = H, R^1 = Me$
9 $R^3, R^4 = H, R^2, Me, R^1 = OMe$

Scheme 1

Table 1. Results for Simple Diels-Alder Reactions Catalysed by Compounds **2**, **3**, **4** and **5**.

Dienophile	**Boron-sulfur compound**			
	2	3	4	5
6 Crotonaldehyde	1h† 72%* 87:13#	1h 70% 88:12	14h 65% 95:5	3h 70% 89:11
7 Methacrolein	1h 58% 8:92	1h 90% 6:94	14h 65% 12:88	3h 78% 9:91
8 Methylvinyl ketone	1h 71% 90:10	1h 89% 76:24	14h 71% 97:3	3h 58% 88:12
9 Methylmethacrylate	1h 57% 30:70	1h 46% 25:75	14h no reaction	3h no reaction

Note: †reaction time, *yield, #endo:exo. **Reaction conditions:** Cyclopentadiene (5.0eq.), Boron-sulfur compound (0.2eq.), dienophile (1.0eq.), -78°C, dichloromethane, stirred under N_2. Reaction between cyclopentadiene and dienophiles **6** to **9** did not occur under the above conditions without the catalyst.

The results show clearly that simple sulfur containing boron heterocycles and trialkylthioboranes act as Lewis acids. It can be seen by comparison that compounds **2** and **3** are excellent Lewis acids, compound **5** is intermediate and **4** is relatively weak. Further investigations are being undertaken to establish the extent to which these Lewis acids can be used in synthetic processes and the nature of their interaction.

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