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Diels-Alder Reactions of 1,3-Dienylborate Salts with Activated Dienophiles

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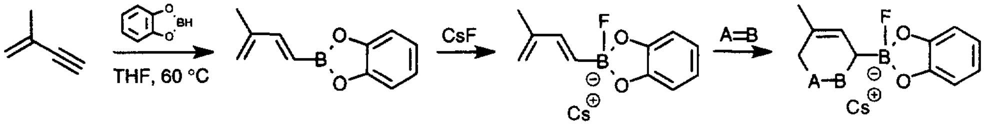
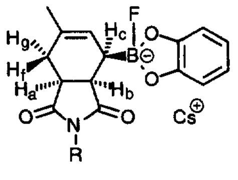
Abstract: 1,3-Dienylborate **3** is found to be a very reactive diene for the Diels-Alder reaction to produce functionalized cyclic allylborates in good yields. Copyright © 1996 Published by Elsevier Science Ltd

The large number of readily available diene and dienophile synthetic equivalents make the intermolecular Diels-Alder reaction a highly important synthetic tool. For exemple, 3-borylpropenoic acid derivatives are efficient synthetic equivalents of *E*-*β*-hydroxyacrylic acid and *E*-*β*-hydroxyvinylamine.[1] Several years ago, we described a stereoselective tandem reaction involving Diels-Alder reaction of a 1,3-dienylboronate followed by the condensation with an aldehyde on the resulting allylic boronate.[2,3] We disclose here that 1,3-dienylborates are exceptionally reactive and stereoselective dienes, being far more reactive than boronic esters in Diels-Alder reactions and significantly the reaction can be carried out in aqueous medium in some cases.

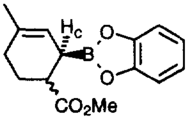
1,3-Dienylboronate **2** was easily prepared through direct and quantitative hydroboration of enyne **1** with catecholborane.[2a] Since catechol ester of arylboronic acids are known to undergo *stable* ate complexes derived from fluoride salts,[4] **3** was prepared quantitatively by addition of a stoichiometric amount of CsF to a THF solution of **2**. The ^{11}B-NMR spectrum (DMSO) of **3** at room temperature with BF_3-ether as external standard shows a single signal at $\delta = 9.7$, which means a shift of $\Delta\delta = 21.7$ to higher field compared with the signal of the uncomplexed compound **2** ($CDCl_3$, $\delta = 31.4$). This is characteristic of compounds with tetracoordinated boron.[5] The ^{19}F-NMR ($\delta = -131.9$; $CFCl_3$ as external standard) and the ^{1}H-NMR spectrum are also consistent with structure **3**.



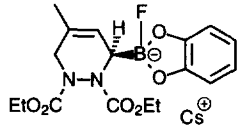
1 **2** **3** **4b-7b**



4b R = Ph
5b R = Me



6a,a'(*cis/trans* = 90:10)



7b

The 1,3-dienylborate **3** was directly treated with common dienophiles **8-11** affording the adducts **4b**, **5b** and **7b** (Table 1). In these reactions, the formation of the Diels-Alder adducts appears to be quantitative by NMR before workup. The donation of electrons from fluorine to boron activates the diene. As a consequence, the rate of the reaction of borate **3** with **8-11** is greatly accelerated. Remarkably, the reaction proceeds even at room temperature to produce adducts **4b** and **5b** derived from an *endo* transition state, as suggested by previous work[2a,b] and confirmed by the following coupling constants for **4b**: $J_{H_bH_c}$ 7, $J_{H_aH_b}$ 9, $J_{H_aH_f}$ 4, and $J_{H_aH_g}$ 8 Hz. Condensation of *N*-phenylmaleimide with borate **3** proceeds equally in toluene, MeOH, and even in a mixture of H_2O/MeOH (90:10) giving rise to the Diels-Alder adduct **4b** in good yields (entries 2-4). Whereas the reaction of **2** with methyl acrylate proved to be regioselective and quite *endo* selective when performed without solvent at 79 °C (**6a,a'**, entry 6), the reaction of borate **3** resulted in the polymerization of the alkene. Reaction of 1,3-dienylborate **3** with diethylazodicarboxylate **11** at ambient temperature afforded the 1,2,3,6-tetrahydropyridazine **7b** (85%).

Table 1. Diels-Alder Reaction of 2 and 3 with Activated Dienophiles

Entry	Dienophile	Solvent/T (°C)/*t* (h)		Yield (%) (*endo*:*exo*)[e]	
		2	**3**	**2**[f]	**3**[g]
1	**8**[a]	C_6H_6/60/6	THF/25/1	**4a** (> 95:5)[h]	**4b** (97) (> 95:5)
2	**8**[a]	-	$C_6H_5CH_3$/25/2	-	**4b** (63) (> 95:5)
3	**8**[a]	-	MeOH/25/1	-	**4b** (70) (> 95:5)
4	**8**[a]	-	H_2O:MeOH[i]/25/1	-	**4b** (85) (> 95:5)
5	**9**[b]	-	THF/25/1	-	**5b** (92) (> 95:5)
6	**10**[c]	80/12[j]	80/6[j]	**6a,a'** (90:10)[k]	**6b** (0)[l]
7	**11**[d]	C_6H_6/60/12	THF/0/1	**7a** (0)[h]	**7b** (85)

[a] *N*-Phenylmaleimide. [b] *N*-Methylmaleimide. [c] Methylacrylate. [d] diethylazodicarboxylate. [e] Ratio determined by ^{1}H-NMR. [f] Overall yields for the tandem Diels-Alder reaction-aldehyde condensation were determined. See references 2a,b. [g] Isolated yields. [h] Reference 2a. [i] H_2O:MeOH 90:10. [j] Without solvent. [k] Reference 2b. The reaction of 1,3-dienylpinacolboronate with methylacrylate using toluene as solvent at 100 °C showed almost no *endo*/*exo* selectivity (65:35, 69%, reference 2a). [l] Polymerisation of the alkene.

The reaction conditions for cycloaddition are sufficiently mild and allow scope for structural variations. The synthetic applications of this work[3a] are now under active investigation.

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