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Vinylboronates β-substituted by an electron withdrawing group : synthesis and Diels-Alder reactivity of a new type of electron deficient olefins

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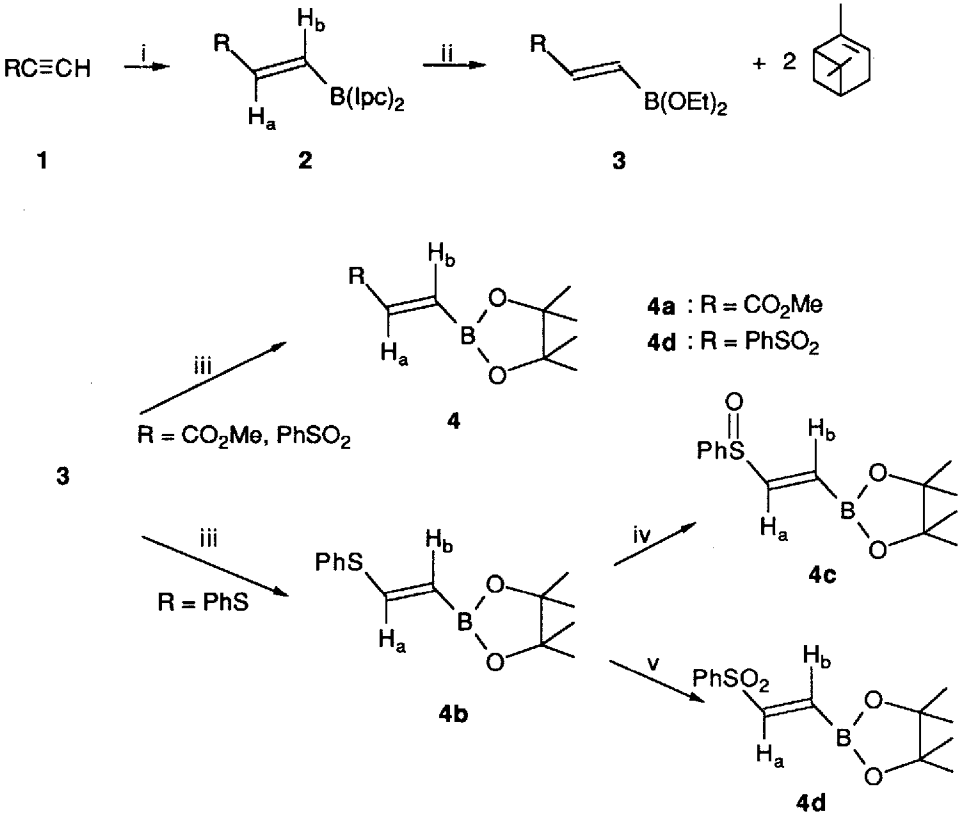
Abstract - The synthesis of E-vinylboronates β-substituted by an electron withdrawing group is described. This new type of electron-deficient olefins undergoes a clean Diels-Alder cycloaddition to typical 1,3-dienes.

Vinylboranes are easily accessible and widely used species for the synthesis of a host of unsaturated molecules (1). Surprisingly little has been done concerning their utility as partners in pericyclic reactions except for some scattered examples of 1,3 dipolar cycloadditions (2) and Diels-Alder reactions with simple vinylboronates (3). Temperatures as high as 200°C were required in certain cases thus showing the lack of reactivity of such species (4). In this note we report the synthesis of vinylboronates β-substituted by an electron withdrawing group and their Diels-Alder cycloaddition to typical 1,3-dienes.

The olefins were prepared according to the sequence depicted in the scheme I. The addition of one equivalent of the ethynyl derivatives **1a**, **1b** (5) and **1d** (6) to a THF suspension of one equivalent of diisopinocampheylborane (7,8) at low temperature led to the E-vinylboranes **2** exclusively (9) as shown by the ^{1}H NMR of the reaction mixture in THF (for example, **2a** : δH_a = 7.73 (d) ; δH_b = 6.15 (d) ; JH_aH_b = 18.4 Hz). An excess of acetaldehyde (10 eq.) was then added at 0°C and warming up of the reaction mixture to 40°C led to the moisture sensitive boronates **3** which were treated "in situ" by one equivalent of pinacol thus giving **4** isolated with good yields either by distillation or recristallisation. Furthermore, the oxydation of **4b** by one or two equivalents of mCpBA occurred non evently giving respectively the sulfoxyde **4c** or the sulfone **4d**. The results are summarised in table I.

Scheme I



Reagents and conditions : i (IpC)$_2$BH, THF, -35 → 0°C ; ii CH$_3$CHO (10 eq.), 0 → 40°C ; iii pinacol (1 eq.), R.T., then kugelrohr purification ; iv mCpBA (1 eq), CH$_2$Cl$_2$, 0°C ; v mCpBA (2 eq.), CH$_2$Cl$_2$, 0°C → R.T.

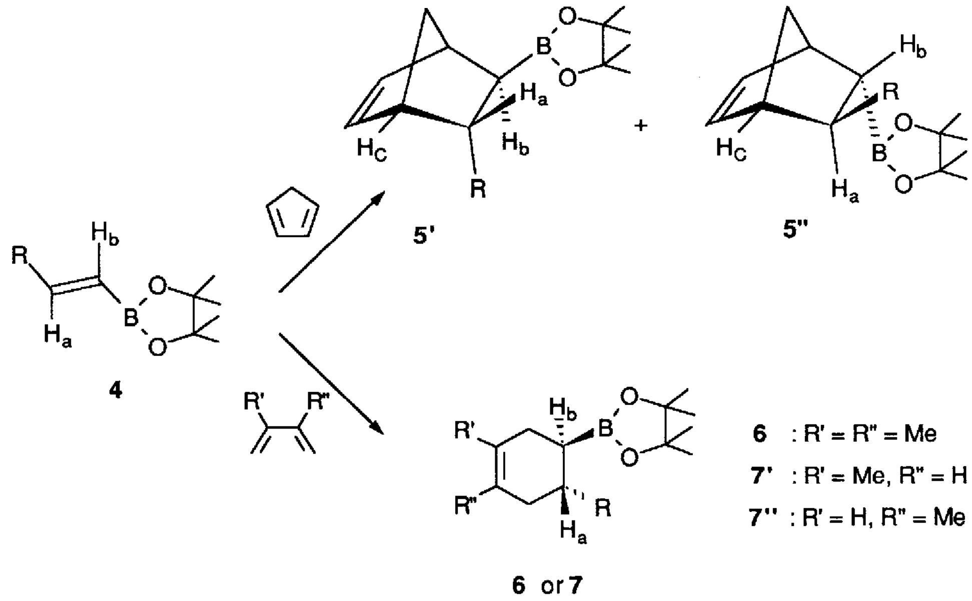
Table I - Synthesis of the vinylboronates **4** (10)

N°	R	$^3J_{HaHb}$ (Hz)	Eb°C/mm Hg or m.p. °C	Yield (%)
4a	CO$_2$Me	18.3	110-112/25	84(a)(b)
4b	PhS	17.4	105-110/0.05	95(a)(b)
4c	PhSO	17.2	124-125(c)	92(d)
4d	PhSO$_2$	17.5	113-114(c)	75(a), 63(d)

(a) Yield calculated from **1**. (b) This olefin contains about 5 % of impurities which could not be removed by distillation. (c) Recristallised from a 1/1 mixture of ether and hexane. (d) Yields calculated from **4b**.

The E stereochemistry of the double bond manifested itself in a large $^3J_{HH}$. The boronates **4a**, **4c** and **4d** reacted with cyclopentadiene, 1,3-dimethylbutadiene and isoprene according to scheme **II**.

Scheme II



The results and reaction conditions are indicated in table II.

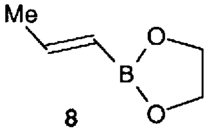
Table II - Diels-Alder cycloaddition of vinylboronates **4** (10).

Adduct	R	Solvent/t°C(a)	5'/5" or 7'/7"	B.p.°C/mm Hg or m.p. °C	Yield (%)(b)
5a	CO_2Me	toluene/110°C	70/30	80-85/0.005(c)	85
5b	PhS	"	-	-	N.R.
5c	PhSO	$CHCl_3$/65°C	81/19	153-154(d)	98
5d	$PhSO_2$	CH_2Cl_2/R.T.	86/14	135-136(d)	93
6a	CO_2Me	toluene/110°C	-	65-70/0.05	83
6d	$PhSO_2$	"	-	137-138	95
7'a + 7"a	CO_2Me	"(e)	55/45(f)	85-90/0.5(c)	86

(a) Reaction time : 12 h. (b) Values refer to isolated total yields. (c) Boiling point of the mixture of isomers (kugelrohr distillation, oven temperature given). (d) Melting point of the major diastereoisomer after recristallisation from ether. (e) The reaction was carried out in a sealed tube. (f) The ratio **7'a/7"a** may be reversed.

Several points are worthy of note. The yields are good except for **5b** which did not react(11). Two diastereoisomers were obtained with cyclopentadiene, the major one exhibiting the electron withdrawing group in the endo position. This was established on the basis of the ^{1}H NMR data and relies on the diagnostic $^3J_{HcHa}$ coupling of 3.8, 3.4 and 3.1 Hz in **5'a**, **5'c** and **5'd** respectively and ≈ 0 Hz in **5"** (12). **5c** was obtained as a mixture of only two diastereoisomers. The stereochemistry at the sulfur center was not established. Nevertheless, the treatment of **5c** with PCl_3 (13) (CH_2Cl_2, 0°C, 0.25 h, quantitative) gave a 80/20 mixture of **5'b** and **5"b** ($^3J_{HcHa}$ = 3.3

and 1.5 Hz) and thus giving an entry to these derivatives not directly accessible by the Diels-Alder reaction. The stereochemistry of the adducts **6a** and **6d** relies on a large $^3J_{HaHb}$ value (11.2 and 9.4 Hz respectively) typical of a trans diaxial arrangement of H_a and H_b. The reaction with isoprene showed no regioselectivity leading with good yield to an unseparable mixture of the trans regioisomers **7'a** and **7"a** ($^3J_{HaHb}$ = 10.7 and 10.9 Hz).



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Finally, it is interesting to compare the reactivity towards cyclopentadiene of **4a**, **4c**, **4d** and the E-vinylboronate **8**. **8** gave (170°C, 60 h, 100 %) a mixture of four diastereoisomers (3c). **4a** reacted in boiling toluene whereas the sulfonyl derivative **4d** gave the adducts at room temperature thus showing a large difference in reactivity.

In conclusion, the adjonction of an electron-withdrawing group on the double bond of a vinylboronate makes these olefins reactive dienophiles. These cycloaddition reactions associated with a subsequent fonctionnalisation of the boron-carbon bond should offer multiple synthetic possibilities in terms of using the olefins **4** as synthetic equivalents of many functionalities such as enols or primary and secondary enamines for example.

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