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DIELS-ALDER CYCLOADDITION OF 3-BORYLPROPENOIC ACID DERIVATIVES AND THEIR USE AS SYNTHETIC EQUIVALENTS OF E-β-HYDROXY ACRYLIC ACID AND E-β-HYDROXY VINYLAMINE.

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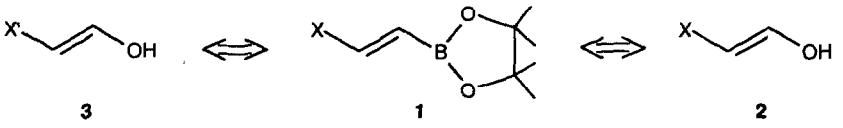
Abstract : Cycloadditions of E-vinylboronic esters **1a-c** bearing an electron withdrawing group in β position to the boronic function with 1,3-butadiene and 2,3-dimethylbutadiene give smoothly the corresponding Diels-Alder adducts. Functional group manipulations such as oxidation of the carbon-boron bond leads to the corresponding alcohol with retention of configuration. The transformation of the carboxylic acid group into an NH-Boc is possible in the presence of the boronic ester leading to trans-β-amino boronic acid derivative **5g** which oxidation and deprotection give the trans-β-amino alcohol **5i**. This shows that 3-borylpropenoic acid derivatives may be interesting synthetic equivalents of E-β-hydroxy acrylic acid and E-β-hydroxy vinylamine.

Introduction

The idea of activation of dienophiles by a trivalent boron atom with its empty p orbital is synthetically attractive because the Diels-Alder adducts can be transformed into alcohols, ketones, amines and several other functional groups, none of which can usually be produced by a direct Diels-Alder reaction. A special feature of using vinylboranes as dienophiles is the potential for control of their properties based on variation of the substitution on the boron. However, a literature survey reveals that Diels-Alder cycloadditions on vinylboranes are scarce. It was not until recently that Singleton et al [(1)] have reported that dialkylvinylboranes react with a variety of dienes from room temperature to 50°C. These omniphilic dienophiles display interesting reactivity and regioselectivity [(2)]. Vinyldichloroboranes were also shown to be reactive dienophiles and behave as synthetic equivalents of secondary enamines of defined stereochemistry in the sequence Diels-Alder cycloaddition - reductive alkylation of azides [(3)]. A drawback of these dienophiles is their sensitivity to oxidation and moisture. Vinylboronic esters are more stable and those derived from pinacol, 3,3-dimethylpropanediol or pinanediol can even be purified by column chromatography. Nevertheless, they were shown to be poorly reactive toward 1,3-dienes [(4)] and a temperature as high as 200°C was required for the reaction of dibutylvinylboronic ester with cyclohexa-1,3-diene to occur [(5)]. We therefore thought that the reactivity of vinylboronic esters could be substantially increased by adding an electron withdrawing group on the double bond β to the boryl group. We have prepared a variety of these new electron poor olefins [(6)]. Since the Diels-Alder reaction is a ring forming reaction of prime importance, we have studied the reactivity of the electron poor olefins **1a-d** toward 1,3-butadiene and 2,3-dimethyl-1,3-butadiene with a double goal : one was to learn about the reactivity of these olefins and second to show their possible use as synthetic equivalents of β-functionalized enols **2** and **3** with defined stereochemistry where X' in **3** is the result of a chemical transformation of X (scheme 1).



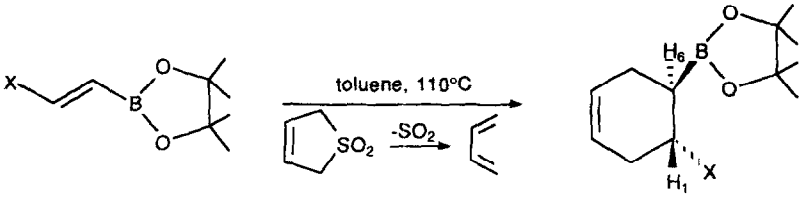
Scheme 1

The absence of direct methods for Diels-Alder reaction on vinyl alcohols and vinyl amines makes practical and reactive synthetic equivalents of these species highly desirable. Some work is being done along these lines which makes vinyldialkylboranes [1] and vinyldichloroboranes [3] emerging reagents. The work on the olefins **1** reported in this paper is an addition to this growing area [9].

Results and discussion

Diels-Alder cycloadditions :

1,3-butadiene, thermally generated "in situ" from sulfolene [7] in toluene at 110°C in a sealed tube reacted with olefins **1a-c** [6b] for 24 hours to give the adducts **4a-c** (scheme 2).

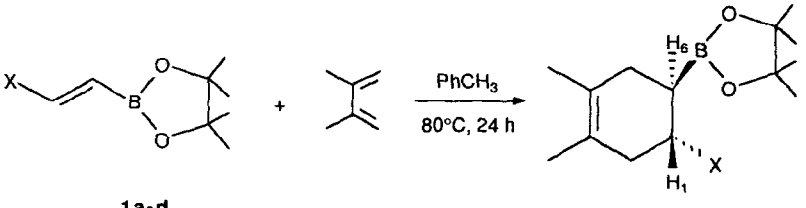


1a : X = $SO_2C_6H_4CH_3$
1b : X = CO_2CH_3
1c : X = CO_2H
1d : X = COCl

4a-c

Scheme 2

The same reaction was observed when 2,3-dimethyl-1,3-butadiene was used at 80°C in toluene according to scheme 3.



1a-d

5a-d

Scheme 3

Reaction times were not optimized except for the acid chloride **5d** where 4 hours at 80°C were necessary for the reaction to go to completion. Results are reported in table 1.

Table 1

1,3-butadiene and 2,3-dimethyl-1,3-butadiene Diels-Alder cycloaddition with vinylboronates **1a-d**.

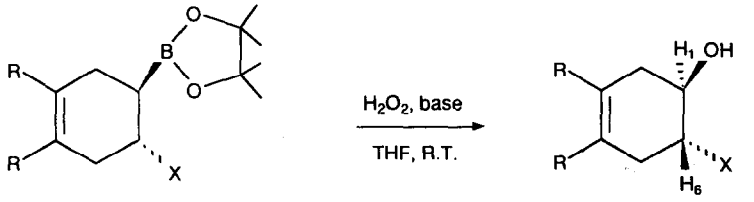
N°	X	Diene	$^3JH_1H_6$ (Hz)	Yields % [a]
				
4a	$SO_2C_6H_4CH_3$		9.0	73
4b	CO_2CH_3	"	9.3	75
4c	CO_2H	"	10.6	86
4d	COCl	"	9.1	83 [b]
				
5a	$SO_2C_6H_4CH_3$		10.8	89
5b	CO_2CH_3	"	11.2	81
5c	CO_2H	"	10.8	95
5d	COCl	"	9.8	76[c] ; 96 [d]

[a] Yields are for isolated pure compounds. [b] Yield obtained in the reaction of **4c** with $SOCl_2$ at 0°C for 30 minutes. [c] Yield obtained in the Diels-Alder cycloaddition. [d] Yield obtained from **5c** when treated with $SOCl_2$.

Adducts **4a-c** and **5a-d** were isolated in good yields after purification by kügelrohr distillation or column chromatography on silica gel. The acid chloride **4d** could not be obtained from the direct reaction of 1,3-butadiene with **1d** which is not stable under these conditions (110°C in toluene). Nevertheless, **4d** was easily obtained by treatment of the carboxylic acid **4c** with $SOCl_2$ at 0°C in a 83 % yield. The stereochemistry of adducts **4** and **5** is secured by diagnostic values of the JH_1H_6 coupling constants ($9.0 \leq JH_1H_6 \leq 11.2$ Hz) characteristic of a 1.2 trans diaxial relationship [8].

Oxidation of adducts 4 and 5.

The lack of reactivity of vinyl alcohols as dienophiles and the need for the preparation of oxygen-functionalized Diels-Alder products urge the discovery of synthetic equivalents of enols. Vinylboranes are emerging as effective reagents in this context [9]. Thus the carbon-boron bond in boronates **4** and **5** was easily oxidized by 30 % hydrogen peroxide in THF at room temperature in the presence of a base (scheme 4).



4 : R = H

5 : R = Me

6 : R = H

7 : R = Me

Scheme 4

A phosphate buffer was used for **4** and **5** with X = $CH_3C_6H_4SO_2$ and X = CO_2CH_3 whereas 3N sodium hydroxide gave better results for **4c** and **5c**. Cyclohexenols **6** and **7** were obtained in good yields after purification by column chromatography or by recrystallisation (table 2).

Table 2 : Oxidation of boronates **4** and **5**.

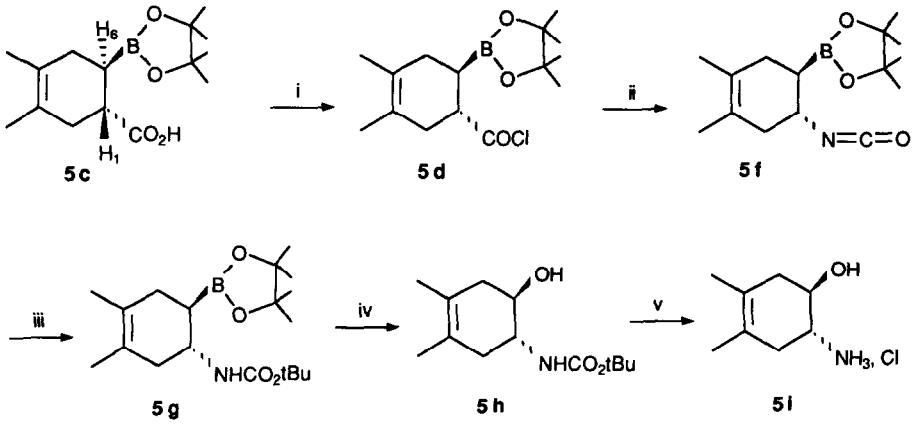
	R = H			R = Me		
X	Product	Yield(%)[a]	JH_1H_6(Hz)	Product	Yield(%)[a]	JH_1H_6(Hz)
$CH_3C_6H_4SO_2$	**6a**	57	10.2	**7a**	57	10.3
CO_2Me	**6b**	55	10.2	**7b**	68	9.9
CO_2H	**6c**	70	10.5	**7c**	68	9.8

[a] Yields are for isolated pure compounds.

Again, the JH_1H_6 coupling constant values $9.8 \leq JH_1H_6 \leq 10.5$ Hz are characteristic of a 1.2 trans diaxial relationship. This is in agreement with an oxidation process occuring with retention of configuration (10).

Fonctionnal group manipulations in 5c:

The presence of a sulfonyl, ester or carboxylic acid group in the cycloadducts **4** and **5** offers additional possibilities of functional group manipulation. This is illustrated by the transformation of **5c** into the trans aminoalcohol **5i** according to scheme 5.

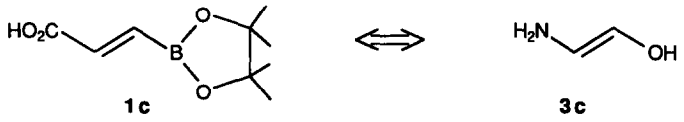


Scheme 5

i : $SOCl_2$, 0°C, 96 %. ii : $TMSN_3$, toluene, 90°C, 84 %. iii : tBuOH, TMSCl [11], 86 %. iv : H_2O_2, 3N NaOH, THF, 65 %. v : Et_2O, HCl, 65 %.

The acid chloride **5d** either obtained from the carboxylic acid **5c** or directly from **1d** was treated by 2 equivalents of azidotrimethylsilane in toluene at 90°C leading to the isocyanate **5f** isolated in a 84 % yield.

That the Curtius rearrangement occurs with retention of configuration is confirmed by a 9.3 Hz value for the JH_1H_6 coupling constant. **5f** was easily transformed into the BOC derivative **5g** which oxidation under the usual conditions led to the trans aminoalcohol derivative **5h**. Bubbling HCl gas through an etheral solution of **5h** led to the cristalline hydrochloride **5i**. All the derivatives mentionned above are trans as it is shown by the coupling constant values ($9.3 \leq JH_1H_6 \leq 10.2$ Hz). As the two key steps in this sequence, ie the Curtius rearrangement and the carbon-boron bond oxidation, occur with retention of configuration, the olefin **1c** can be considered as the synthetic equivalent of the E-enaminol **3c**.



1c **3c**

In conclusion, the addition of an electron withdrawing group in the β position of the boronate functionality makes the olefins **1** attractive dienophiles which are reactive enough toward simple dienes to give interesting functionalized Diels-Alder adducts. The carbon-boron bond in these cycloaddition products may be further transformed as it has been illustrated by their oxidation to cyclohexenols with conservation of stereochemistry. Therefore, 3-borylpropenoic acid **1c** is a synthetic equivalent of E-β-hydroxy acrylic acid. It has also been shown that **1c** could be an interesting synthetic equivalent of E-β-hydroxy vinylamine **3c**.

Experimental

The reactions requiring an atmosphere of dry nitrogen were performed in flame dried glassware and were stirred magnetically. Toluene and dichloromethane were dried immediately prior to use by distillation under nitrogen from sodium benzophenone ketyl and P_2O_5, respectively. 2,3-Dimethyl-1,3-butadiene was dried on calcium hydride. Azido- and chlorotrimethylsilane were distilled prior to use. Melting points were taken on a Kofler apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 1420 model and samples examined as liquid film or nujol suspension. Frequencies ν are expressed in cm^{-1}. NMR spectra were measured in $CDCl_3$ solutions (except when another solvent is precised) on a Bruker AC 300 (300 MHz for ^1H and 75,5 MHz for ^{13}C). Chemical shifts, δ, are expressed in ppm downfield from internal tetramethylsilane. High resolution mass spectra were obtained on a Varian MAT 311 (Centre Régional de Mesures Physiques, Université de Rennes I). Microanalysis were performed at the Central Laboratory for Analysis, CNRS, Lyon (France). Thin layer chromatography was performed on aluminum plates coated with a 0.02 mm layer of silica gel 60F-254 purchased from Merck wheras column chromatography purifications were performed on silica gel (70-230 mesh) purchased from Merck.

1,3-butadiene adducts : general procedure for the preparation of compounds 4

The vinylboronate 1 (10 mmol) and the 3-sulfolene (1.78 g ; 15 mmol) were introduced in a tube together with 2 mL of toluene. The tube was sealed and the reaction mixture was heated to 110°C for 24 hours. It was then allowed to cool to room temperature and was opened. After removing the toluene under vacuum, the crude product was solubilized in pentane and filtered so as to remove sulfolene in excess. After removal of pentane under vacuum, the product was purified either by Kügelrohr distillation or by column chromatography on silica gel.

4a (isolated by column chromatography) : 2.65 g, 73 %.

TLC : diethyl ether/hexane : 8/2, Rf = 0.7.

IR, ν cm^{-1} : 1590 (C=C) ; 1370 and 1140 (SO_2).

^1H NMR, δ : 1.30 (s, 12H, $C(CH_3)_2$) ; 1.53 (dt, $J_{6,1} = 9.0$, $J_{6,5'} = 9.0$, $J_{6,5} = 6.3$, H_6) ; 2.10 - 2.40 (m, 4H, H_2, $H_{2'}$, H_5, $H_{5'}$) ; 2.44 (s, 3H, =C-CH_3) ; 3.42 (ddd, $J_{1,6} = 9.0$, $J_{1,2'} = 8.2$, $J_{1,2} = 6.2$, H_1) ; 5.50 - 5.80 (m, 2H, H_3, H_4) ; 7.30 - 7.40 (m, 2H, =C-H) ; 7.70 - 7.80 (m, 2H, =C-H).

^{13}C NMR, δ : 17.3 (dm, $^{1}J_{CH}$ ~120, C_6) ; 21.6 (qm, $^{1}J_{CH}$ = 127, =C-$\underline{C}H_3$) ; 24.6 (tm, $^{1}J_{CH}$ = 129, C_5) ; 24.7 (qm, $^{1}J_{CH}$ = 126, C($\underline{C}H_3$)2) ; 24.9 (qm, $^{1}J_{CH}$ = 126, C($\underline{C}H_3$)2) ; 25.6 (tm, $^{1}J_{CH}$ = 126, C_2) ; 61.2 (dm, $^{1}J_{CH}$ = 138, C_1) ; 83.7 (m, $\underline{C}(CH_3)_2$) ; 122.9 (dm, $^{1}J_{CH}$ = 158, C_3 or C_4) ; 126.7 (dm, $^{1}J_{CH}$ = 156, C_3 or C_4) ; 129.2 (dm, $^{1}J_{CH}$ = 165) ; 129.6 (dm, $^{1}J_{CH}$ = 161) ; 134.4 (m) ; 144.4 (m), aromatic carbons.

HRMS : calculated for $C_{16}H_{21}O_3S^{11}B$ $[M\text{-}CH_3COCH_3]^+$: 304.130, found : 304.130.

4b : $Eb_{0.02}$ = 65-70°C ; 2.0 g, 75 %.

IR, ν cm^{-1} : 1720 (C=O).

^{1}H NMR, δ : 1.22 (s, 6H, C(CH_3)2) ; 1.24 (s, 6H, C(CH_3)2) ; 1.40 (dt, $J_{6,1}$ = 9.3, $J_{6,5}$ = 9.3, $J_{6,5'}$ = 5.6, H_6) ; 1.90 - 2.20 (m, 3H, $H_{2'}$, $H_{5'}$, H_5) ; 2.33 (dm, $J_{2,2'}$ = 16.9, H_2) ; 2.64 (dt, $J_{1,6}$ = 9.3, $J_{1,2'}$ = 9.3, $J_{1,2}$ = 5.5, H_1) ; 3.67 (3H, s, O-CH_3) ; 5.60 - 5.80 (m, 2H, H_3, H_4).

^{13}C NMR, δ : 20.2 (dm, $^{1}J_{CH}$ ~120, C_6) ; 24.7 (qm, $^{1}J_{CH}$ = 127, C($\underline{C}H_3$)2) ; 24.8 (qm, $^{1}J_{CH}$ = 127, C($\underline{C}H_3$)2) ; 25.8 (tm, $^{1}J_{CH}$ = 127, C_5) ; 28.1 (tm, $^{1}J_{CH}$ = 128, C2) ; 40.6 (dm, $^{1}J_{CH}$ = 132, C_1) ; 51.5 (qm, $^{1}J_{CH}$ = 146, O-$\underline{C}H_3$) ; 83.1 (m, $\underline{C}(CH_3)_2$) ; 125.1 (dm, $^{1}J_{CH}$ = 151, C_3 or C_4) ; 127.0 (dm, $^{1}J_{CH}$ = 149, C_3 or C_4) ; 176.6 (m, $\underline{C}$=O).

Anal. $C_{14}H_{23}O_4B$: calc. % : C 63.18 ; H, 8.71. Found : C 63.2 ; H 8.8.

4c : $Eb_{0.02}$ = 105-110°C ; 2.17 g, 86 %.

IR, ν cm^{-1} : 3160 (br, OH) ; 1720 (C=O).

^{1}H NMR, δ : 1.23 (s, 6H, CH_3) ; 1.26 (s, 6H, CH_3) ; 1.39 (dt, $J_{6,1}$ = 10.6, $J_{6,5}$ = 10.6, $J_{6,5'}$ = 5.6, H_6) ; 1.95 - 2.25 (m, 3H, $H_{2'}$, H_5, $H_{5'}$) ; 2.39 (dm, $J_{2,2'}$ = 17.0, H_2) ; 2.70 (dt, $J_{1,6}$ = 10.6, $J_{1,2'}$ = 10.6, $J_{1,2}$ = 5.5, H_1) ; 5.60 - 5.80 (m, 2H, H_3, H_4) ; 10.75 (br s, COOH).

^{13}C NMR, δ : 19.7 (dm, $^{1}J_{CH}$ ~120, C_6) ; 24.5 (qm, $^{1}J_{CH}$ = 127, $\underline{C}H_3$) ; 24.7 (qm, $^{1}J_{CH}$ = 126, $\underline{C}H_3$) ; 25.6 (tm, $^{1}J_{CH}$ = 125, C_5) ; 27.8 (tm, $^{1}J_{CH}$ = 129, C_2) ; 40.4 (dm, $^{1}J_{CH}$ = 129, C_1) ; 83.2 (m, $\underline{C}(CH_3)_2$) ; 125.0 (dm, $^{1}J_{CH}$ = 158, C_3 or C_4) ; 127.1 (dm, $^{1}J_{CH}$ = 157, C_3 or C_4) ; 182.6 (m, $\underline{C}$OOH).

Anal. $C_{13}H_{21}O_4B$: calc. % : C 61.93 ; H 8.40. Found : C 61.9 ; H 8.6.

Access to acid chlorides 4d and 5d from acids 4c and 5c.

Under a nitrogen atmosphere and at 0°C, 3 mL of freshly distilled thionyl chloride were added to the carboxylic acid (2 mmol). The mixture was stirred at 0°C for 30 minutes and then allowed to reach room temperature. After removing the excess thionyl chloride under vacuum, the crude oil was purified by Kügelrohr distillation.

4d : $Eb_{0.01}$= 75 - 80°C ; 0.45 g, 83 %.

IR, ν cm^{-1} : 1780 (C=O) ; 1650 (C=C).

^{1}H NMR, δ : 1.22 (s, 6H, CH_3) ; 1.26 (s, 6H, CH_3) ; 1.60 (dt, $J_{6,1}$ = 9.1, $J_{6,5}$ = 9.1, $J_{6,5'}$ = 6.0, H_6) ; 2.00 - 2.30 (m, 3H, $H_{2'}$, H_5, $H_{5'}$) ; 2.52 (dm, $J_{2,2'}$ = 17.3 , H_2) ; 3.12 (dt, $J_{1,6}$ = 9.1, $J_{1,2'}$ = 9.1, $J_{1,2}$ = 5.6, H_1) ; 5.60 - 5.80 (m, 2H, H_3, H_4).

^{13}C NMR, δ : 20.1 (dm, $^{1}J_{CH}$ ~130, C_6) ; 24.5 (qm, $^{1}J_{CH}$ = 127, $\underline{C}H_3$) ; 24.7 (qm, $^{1}J_{CH}$ = 126, $\underline{C}H_3$) ; 24.8 (tm, $^{1}J_{CH}$ = 128, C_5) ; 27.7 (tm, $^{1}J_{CH}$ = 128, C_2) ; 52.4 (dm, $^{1}J_{CH}$ = 135, C_1) ; 83.7 (m, $\underline{C}(CH_3)_2$) ; 124.0 (dm, $^{1}J_{CH}$ = 157, C_3 or C_4) ; 127.1 (dm, $^{1}J_{CH}$ = 158 C_3 or C_4) ; 177.3 (m, $\underline{C}$OCl).

HRMS : calculated for $C_{12}H_{17}O_3{}^{11}BCl$ $[M\text{-}CH_3]^+$: 255.096, found : 255.095. Calculated for $C_{13}H_{19}O_3{}^{11}B$ $[M\text{-}HCl]^+$: 234.143, found : 234.142. Calculated for $C_{12}H_{19}O_2{}^{11}B$ $[M\text{-}CO\text{-}HCl]^+$: 206.148, found : 206.147.

5d : $Eb_{0.001}$ = 95 - 100°C ; 0.57 g, 96 %.

IR, ν cm^{-1} : 1790 (C=O).

^{1}H NMR, $CDCl_3$, δ : 1.16 (s, 6H, C(CH_3)2) ; 1.18 (s,6H, C(CH_3)2) ; 1.48 (dt, $J_{6,1}$ = 9.8, $J_{6,5}$ = 9.8, $J_{6,5'}$ = 6.3, H_6) ; 1.50 - 1.60 (m, 6H, =C-CH_3) ; 1.80 - 2.10 (m, 2H, H_5, $H_{5'}$) ; 2.11 (dd, $J_{2',2}$ = 16.5, $J_{2',1}$ = 9.8, $H_{2'}$) ; 2.31 (dd, $J_{2,2'}$ = 16.5, $J_{2,1}$ = 5.6, H_2) ; 3.06 (dt, $J_{1,6}$ = 9.8, $J_{1,2'}$ = 9.8, $J_{1,2}$ = 5.6, H_1).

^{13}C NMR, δ : 18.7 (qm, $^{1}J_{CH}$ = 126, =C-CH3) ; 18.8 (qm, $^{1}J_{CH}$ = 126, =C-CH3) ; 21.7 (dm, $^{1}J_{CH}$ ~130, C_6) ; 24.4 (qm, $^{1}J_{CH}$ = 127, C(CH3)2) ; 24.7 (qm, $^{1}J_{CH}$ = 127, C(CH3)2) ; 31.5 (tm, $^{1}J_{CH}$ = 129, C_5) ; 34.0 (tm, $^{1}J_{CH}$ = 130, C_2) ; 53.5 (dm, $^{1}J_{CH}$ = 135, C_1) ; 83.6 (m, C(CH3)2) ; 122.9 (m, =C-CH3) ; 126.0 (m, =C-CH3) ; 177.4 (m, COCl).

HRMS : calculated for $C_{15}H_{24}O_3{}^{11}B^{35}Cl$ $[M]^+$: 298.150, found : 298.151.

Cycloaddition of 2,3-Dimethyl-1,3-butadiene.

Under a nitrogen atmosphere, the vinylboronate **1** (10 mmol) and freshly distilled 2,3-dimethyl-1,3-butadiene (3.4 mL ; 30 mmol) were diluted with 30 mL of anhydrous toluene. The reaction mixture was maintained at 80°C for 4 hours (**5d**) or for 24 hours (**5a-c**). After removing the toluene and the diene in excessunder vacuum, the crude product was either purified by kügelrohr distillation or recrystallized.

5a : mp = 132-134°C (hexane/diethyl ether 9/1) ; 3.47 g, 89 %.

IR (Nujol), ν cm^{-1} : 1590 (C=O) ; 1370 and 1140 (SO_2).

^{1}H NMR, δ : 1.31 (s, 12H, C(CH3)2) ; 1.40 (ddd, $J_{6,1}$ = 10.8, $J_{6,5'}$ = 8.3, $J_{6,5}$ = 7.3, H_6) ; 1.50 - 1.60 (m, 6H, =C-CH3) ; 1.90 - 2.30 (m, 4H, H_2, $H_{2'}$, H_5, $H_{5'}$) ; 2.43 (s, 3H, $SO_2C_6H_4CH_3$) ; 3.40 (ddd, $J_{1,6}$ = 10.8, $J_{1,2'}$ = 9.8, $J_{1,2}$ = 6.5, H_1) ; 7.30 - 7.40 (m, 2H, =C-H) ; 7.80 - 7.90 (m, 2H, =C-H).

^{13}C NMR, δ : 18.5 (dm, $^{1}J_{CH}$ ~125, C_6) ; 18.6 (qm, $^{1}J_{CH}$ = 125, =C-CH3) ; 18.9 (qm, $^{1}J_{CH}$ = 125, =C-CH3) ; 21.6 (qm, $^{1}J_{CH}$ = 127, $SO_2C_6H_4CH_3$) ; 24.8 (qm, $^{1}J_{CH}$ = 127, C(CH3)2) ; 24.9 (qm, $^{1}J_{CH}$ = 127, C(CH3)2) ; 30.9 (tm, $^{1}J_{CH}$ = 128, C_5) ; 32.4 (tm, $^{1}J_{CH}$ = 127, C_2) ; 62.5 (dm, $^{1}J_{CH}$ = 142, C_1) ; 83.6 (m, C(CH3)2) ; 121.9 (m, =C-CH3) ; 125.5 (m, =C-CH3) ; 129.4 (dm, $^{1}J_{CH}$ = 165) ; 129.6 (dm, $^{1}J_{CH}$ = 165, =C-H) ; 134.3 (m) ; 144.3 (m), aromatic carbons.

Anal. : $C_{21}H_{31}O_4SB$: calc. % : C 64.62 ; H 8.00 ; found : C 64.1 ; H 7.9.

5b : $Eb_{0.001}$ = 65-70°C ; 2.38 g, 81 %.

IR, ν cm^{-1} : 1740 (C=O).

^{1}H NMR, δ : 1.21 (s, 6H, C(CH3)2) ; 1.24 (s, 6H, C(CH3)2) ; 1.34 (dt, $J_{6,1}$ = 11.2, $J_{6,5'}$ = 8.6, $J_{6,5}$ = 8.6, H_6) ; 1.55 - 1.65 (m, 6H, =C-CH3) ; 1.94 (dd, $J_{5,5'}$ = 17.4, $J_{5,6}$ = 8.6, H_5) ; 2.02 (dd, $J_{5',5}$ = 17.4, $J_{5',6}$ = 8.6, $H_{5'}$) ; 2.09 (dd, $J_{2',2}$ = 19.2, $J_{2',1}$ = 10.8, $H_{2'}$) ; 2.19 (dd, $J_{2,2'}$ = 19.2, $J_{2,1}$ = 5.6, H_2) ; 2.60 (ddd, $J_{1,6}$ = 11.2, $J_{1,2'}$ = 10.8, $J_{1,2}$ = 5.6, H_1) ; 3.66 (s, 3H, O-CH3).

^{13}C NMR, δ : 18.7 (qm, $^{1}J_{CH}$ = 125, =C-CH3) ; 19.0 (qm, $^{1}J_{CH}$ = 126, =C-CH3) ; 21.0 (dm, $^{1}J_{CH}$ ~140, C_6) ; 24.5 (qm, $^{1}J_{CH}$ = 126, C(CH3)2) ; 24.8 (qm, $^{1}J_{CH}$ = 126, C(CH3)2) ; 32.5 (tm, $^{1}J_{CH}$ = 126, C_5) ; 34.6 (tm, $^{1}J_{CH}$ = 129, C_2) ; 41.8 (dm, $^{1}J_{CH}$ = 129, C_1) ; 51.5 (qm, $^{1}J_{CH}$ = 147, O-CH3) ; 83.1 (m, C(CH3)2) ; 123.8 (m, =C-CH3) ; 125.7 (m, =C-CH3) ; 176.6 (m, C=O).

HRMS : calculated for $C_{16}H_{27}O_4{}^{11}B$ $[M]^+$: 294.200 ; found : 294.201.

5c : mp = 142-144°C (hexane) ; 2.66 g, 95 %.

IR (Nujol), ν cm^{-1} : 1690 (C=O).

^{1}H NMR, δ : 1.21 (s, 6H, C(CH3)2) ; 1.23 (s, 6H, C(CH3)2) ; 1.33 (ddd, $J_{6,1}$ = 10.8, $J_{6,5'}$ = 8.0, $J_{6,5}$ = 11.2, H_6) ; 1.55 - 1.65 (m, 6H, =C-CH3) ; 1.90 - 2.05 (m, 2H, H_5, $H_{5'}$) ; 2.11 (dd, $J_{2',2}$ = 16.9, $J_{2',1}$ = 10.8, $H_{2'}$) ; 2.24 (dd, $J_{2,2'}$ = 16.9, $J_{2,1}$ = 5.6, H_2) ; 2.64 (dt, $J_{1,6}$ = 10.8, $J_{1,2'}$ = 10.8, $J_{1,2}$ = 5.6, H_1) ; 11.40 (br s, COOH).

^{13}C NMR, δ : 18.7 (qm, $^{1}J_{CH}$ = 125, =C-CH3) ; 19.0 (qm, $^{1}J_{CH}$ = 125, =C-CH3) ; 20.7 (dm, $^{1}J_{CH}$ ~130, C_6) ; 24.5 (qm, $^{1}J_{CH}$ = 127, C(CH3)2) ; 24.7 (qm, $^{1}J_{CH}$ = 127, C(CH3)2) ; 32.3 (tm, $^{1}J_{CH}$ = 126, C_5) ; 34.2 (tm, $^{1}J_{CH}$ = 130, C_2) ; 41.6 (dm, $^{1}J_{CH}$ = 129, C_1) ; 83.2 (m, C(CH3)2) ; 123.8 (m, =C-CH3) ; 125.7 (m, =C-CH3) ; 182.8 (d, $^{2}J_{CH}$ = 6, COOH).

Anal. : $C_{15}H_{25}O_4B$: calc. % : C 64.31 ; H 8.99 ; found : C 64.4 ; H 9.2.

5d : $Eb_{0.001}$ = 95-100°C ; 2.27 g, 76 %. Spectroscopic data are given in the preceeding section.

Oxidation of sulfones 4a, 5a and esters 4b, 5b.

A phosphate buffer solution (7 mL) was added to a solution of adduct (5 mmol) in 20 mL of THF and at 0°C. 2.5 ml of a 30 % H_2O_2 solution (20 mmol) were then added dropwise. The reaction mixture was allowed to reach room temperature and was vigorously stirred for 12 hours. 40 mL of a saturated solution of ammonium chloride were added and the aqueous phase was

extracted with 3 x 100 mL of diethyl ether. The organic phase was then washed with 3 x 10 mL of water to remove most of the pinacol generated during the oxidation. The extract was dried ($MgSO_4$), filtered and purified either by recrystallization or by column chromatography on silica gel.

6a : mp = 103-105°C (CCl_4) ; 0.72 g, 57 %.

IR (Nujol), ν cm^{-1} : 3400 (br, OH) ; 1370 and 1140 (SO_2).

^1H NMR, δ : 2.10 - 2.30 (m, 3H, H_2/H_2', H_5, H_5') ; 2.47 (s, 3H, CH_3) ; 2.50 - 2.70 (m, 1H, H_2/H_2') ; 3.29 (dt, $J_{6,1}$ = 10.2, $J_{6,5}$ = 10.2, $J_{6,5'}$ = 6.7, H_6) ; 4.17 (ddd, $J_{1,6}$ = 10.2, $J_{1,2'}$ = 7.6, $J_{1,2}$ = 6.2, H_1) ; 4.17 (br s, OH) ; 5.40 - 5.60 (m, 2H, H_3, H_4) ; 7.35 - 7.45 (m, 2H) ; 7.75 - 7.85 (m, 2H).

^{13}C NMR, δ : 21.7 ($SO_2C_6H_4\underline{C}H_3$) ; 26.0 ($C_5$) ; 34.0 ($C_2$) ; 65.0 ($C_1$ or C_6) ; 65.7 (C_1 or C_6) ; 122.8 (C_3 or C_4) ; 124.5 (C_3 or C_4) ; 128.9 ; 129.9 ; 134.1 ; 145.3 aromatic carbons.

Anal. $C_{13}H_{16}O_3S$: calc. % : C 61.88 ; H 6.39 ; found : C 61.7 ; H 6.2.

7a : mp = 114-116°C (CCl_4) ; 0.8 g, 57 %.

IR (Nujol), ν cm^{-1} : 3540 (br s, OH) ; 1370 and 1140 (SO_2).

^1H NMR, δ : 1.50 - 1.60 (m, 6H, =C-CH_3) ; 2.00 - 2.30 (m, 3H) ; 2.30 - 2.50 (m, 1H) ; 2.46 (s, 3H, $SO_2C_6H_4$ CH_3) ; 3.28 (dt, $J_{6,1}$ = 10.3, $J_{6,5}$ = 10.3, $J_{6,5'}$ = 6.8, H_6) ; 4.0 (br s, OH) ; 4.11 (ddd, $J_{1,6}$ = 10.3, $J_{1,2'}$ = 9.0, $J_{1,2}$ = 6.3, H_1) ; 7.30 - 7.40 (m, 2H) ; 7.75 - 7.85 (m, 2H).

^{13}C NMR, δ : 18.2 (qm, $^1J_{CH}$ = 126, =C-$\underline{C}H_3$) ; 18.5 (qm, $^1J_{CH}$ = 126, =C-$\underline{C}H_3$) ; 21.7 (qm, $^1J_{CH}$ = 127, $SO_2C_6H_4\underline{C}H_3$) ; 31.7 (tm, $^1J_{CH}$ = 130, C_5) ; 40.2 (tm, $^1J_{CH}$ = 128, C_2) ; 65.7 (dm, $^1J_{CH}$ = 140, C_6) ; 66.0 (dm, $^1J_{CH}$ = 147, C_1) ; 121.9 (m, =$\underline{C}$-CH_3) ; 123.8 (m, =$\underline{C}$-CH_3) ; 129.0 (dm, $^1J_{CH}$ = 165, =$\underline{C}$-H) ; 129.9 (dm, $^1J_{CH}$ = 161) ; 134.0 (m) ; 145.2 (m), aromatic carbons.

Anal. $C_{15}H_{20}O_3S$: calc. % : C 64.26 ; H 7.19 ; found : C 64.6 ; H 7.3.

6b (isolated by column chromatography on silica gel) : 0.43 g, yield 55 %.

TLC : Diethyl ether/heptane/ethyl alcohol : 90/9/1, Rf = 0.7.

IR, ν cm^{-1} : 3440 (br, OH) ; 1720 (C=O).

^1H NMR, δ : 2.00 - 2.10 (m, 1H, H_5/H_5') ; 2.20 - 2.30 (m, 1H, H_5/H_5') ; 2.30 - 2.50 (m, 2H, H_2, H_2') ; 2.61 (dt, 1H, $J_{6,1}$ = 10.2, $J_{6,5}$ = 10.2, $J_{6,5'}$ = 5.6, H_6) ; 3.48 (br s, OH) ; 3.73 (s, 3H, CH_3) ; 4.06 (dt, 1H, $J_{1,6}$ = 10.2, $J_{1,2'}$ = 10.2, $J_{1,2}$ = 5.7, H_1) ; 5.50 - 5.70 (m, 2H, H_3, H_4).

^{13}C NMR, δ : 28.5 (tm, $^1J_{CH}$ = 129, C_5) ; 33.3 (tm, $^1J_{CH}$ = 128, C_2) ; 47.3 (dm, $^1J_{CH}$ = 129, C_6) ; 51.9 (qm, $^1J_{CH}$ = 147, O-$\underline{C}H_3$) ; 67.8 (dm, $^1J_{CH}$ = 159, C_1) ; 124.6 (dm, $^1J_{CH}$ = 159, C_3 or C_4) ; 124.7 (dm, $^1J_{CH}$ = 159, C_3 or C_4) ; 175.6 (m, $\underline{C}$=O).

HRMS : calculated for $C_8H_{12}O_3$ $[M]^+$: 156.079, found : 156.079.

7b (isolated by column chromatography on silica gel) : 0.63 g, yield 68 %.

TLC : hexane/diethyl ether 7/3, Rf = 0.2.

IR, ν cm^{-1} : 3430 (br, OH) ; 1720 (C=O).

^1H NMR, δ : 1.50 - 1.70 (m, 6H, C=CH_3) ; 2.00 - 2.10 (m, 1H, H_5/H_5') ; 2.20 - 2.40 (m, 3H, H_5/H_5', H_2, H_2') ; 2.58 (dt, $J_{6,1}$ = 9.9, $J_{6,5}$ = 9.9, $J_{6,5'}$ = 6.5, H_6) ; 3.38 (br s, OH) ; 3.72 (s, 3H, O-CH_3) ; 4.02 (dt, $J_{1,6}$ = 9.9, $J_{1,2'}$ = 9.9, $J_{1,2}$ = 5.9, H_1).

^{13}C NMR, δ : 18.2 (qm, $^1J_{CH}$ = 126, =C-$\underline{C}H_3$) ; 18.8 (qm, $^1J_{CH}$ = 126, =C-$\underline{C}H_3$) ; 34.4 (tm, $^1J_{CH}$ = 129, C_5) ; 39.5 (tm, $^1J_{CH}$ = 126, C_2) ; 48.0 (dm, $^1J_{CH}$ = 131, C_6) ; 51.8 (qm, $^1J_{CH}$ = 147, O-$\underline{C}H_3$) ; 68.2 (dm, $^1J_{CH}$ = 144, C_1) ; 123.2 (m, =$\underline{C}$-CH_3) ; 123.8 (m, =$\underline{C}$-CH_3) ; 175.7 (m, $\underline{C}$=O).

HRMS : calculated for $C_{10}H_{16}O_3$ $[M]^+$: 184.110, found : 184.110.

Oxidation of acids 4c and 5c : general procedure.

An aqueous solution of 3N sodium hydroxide (7 mL ; 21 mmol) was added dropwise at 0°C to 5 mmol of the acids **4c** or **5c** in 20 mL of THF. 30 % hydrogen peroxide (2.5 mL ; 20 mmol) was then added to the reaction mixture which was then allowed to reach room temperature. After 12 hours, 40 mL of a saturated solution of ammonium chloride were added. The aqueous phase was washed with 2 x 100 ml of diethyl ether and then acidified to pH ~1 with HCl 3N. The product was extracted with 3 x 100 mL of diethyl ether. The organic phase was dried ($MgSO_4$) and filtered. After removing the solvents under vacuum, the crude product was recrystallized.

6c : mp = 98-100°C (CCl_4) ; 0.5 g, 70 %.

IR (Nujol), ν cm^{-1} : 3210 (br, OH, COOH) ; 1670 (C=O).

^1H NMR, $(CD_3)_2CO$, δ : 2.10 - 2.50 (m, 4H, H_2, H_2', H_5, H_5') ; 2.61 (dt, $J_{6,1}$ = 10.5, $J_{6,5}$ = 10.5, $J_{6,5'}$ = 5.6, H_6) ; 4.07 (dt, $J_{1,6}$ = 10.5, $J_{1,2'}$ = 10.5, $J_{1,2}$ = 5.7, H_1) ; 5.50 - 5.70 (m, 2H, H_3, H_4) ; 6.80 - 7.60 (brs, 2H, COOH and OH).

^{13}C NMR, $(CD_3)_2C=O$, δ : 28.4 (tm, $^1J_{CH}$ = 128, C_5) ; 33.5 (tm, $^1J_{CH}$ = 126, C_2) ; 47,1 (dm, $^1J_{CH}$ = 131, C_6) ; 67.9 (dm, $^1J_{CH}$ = 145, C_1) ; 124.7 (dm, $^1J_{CH}$ = 159, C_3 or C_4) ; 124.9 (dm, $^1J_{CH}$ = 159, C_3 or C_4) ; 177.7 (m, C=O).

Anal. $C_7H_{10}O_3$: calc. % : C 59.14 ; H, 7.09. Found : C 59.3 ; H 6.9.

7c : mp = 104-106°C (CCl_4) ; 0.58 g, 68 %.

IR (Nujol), ν cm^{-1} : 3410 (br, OH, COOH) ; 1690 (C=O).

^1H NMR, $(CD_3)_2C=O$, δ : 1.50 - 1.60 (m, 6H, CH_3) ; 2.10 - 2.30 (m, 4H, H_2, H_2', H_5, H_5') ; 2.50 (dt, $J_{6,1}$ = 9.8, $J_{6,5}$ = 9.8, $J_{6,5'}$ = 8.2, H_6) ; 3.96 (ddd, $J_{1,6}$ = 9.8, $J_{1,2'}$ = 9.4, $J_{1,2}$ = 5.7, H_1) ; 5.00 - 8.00 (br s, COOH and OH).

^{13}C NMR, $(CD_3)_2C=O$, δ : 18.3 (qm, $^1J_{CH}$ = 125, CH_3) ; 19.0 (qm, $^1J_{CH}$ = 125, CH_3) ; 35.1 (tm, $^1J_{CH}$ = 126, C_5) ; 40.7 (tm, $^1J_{CH}$ = 124, C_2) ; 48.8 (dm, $^1J_{CH}$ = 130, C_6) ; 68.7 (dm, $^1J_{CH}$ = 144, C_1) ; 124.1 (m, =C-CH_3) ; 124.2 (m, =C-CH_3) ; 176.7 (m, C=O).

HRMS calculated for $C_9H_{14}O_3$ $[M]^+$: 170.094, found : 170.094.

Synthesis of the hydrochloride 5i

Isocyanate 5f : To a solution of the acid chloride **5d** (1.49 g ; 5 mmol) in 20 mL of anhydrous toluene, was added azidotrimethylsilane (1.32 mL ; 10 mmol) at room temperature under a nitrogen atmosphere. After heating the reaction mixture at 90°C for 15 hours, toluene was removed under vacuum. The crude oil was purified by Kügelrohr distillation. This compound must be used immediately.

5f : $Eb_{0.001}$ = 80-85°C ; 1.16 g, 84 %.

IR, ν cm^{-1} : 2260 (N=C=O).

^1H NMR, δ : 1.25 (s, 12H, $C(CH_3)_2$) ; 1.41 (dm, $J_{6,1}$ = 9.3, H_6) ; 1.50 - 1.60 (m, 6H, =C-CH_3) ; 1.90 - 2.20 (m, 3H, H_2', H_5, H_5') ; 2.30 (dd, $J_{2,2'}$ = 16.8, $J_{2,1}$ = 5.3, H_2) ; 3.74 (ddd, $J_{1,6}$ = 9.3, $J_{1,2'}$ = 8.0, $J_{1,2}$ = 5.3, H_1).

^{13}C NMR, δ : 18.5 (qm, $^1J_{CH}$ = 126, =C-CH_3) ; 18.7 (qm, $^1J_{CH}$ = 126, =C-CH_3) ; 24.7 (qm, $^1J_{CH}$ = 127, $C(CH_3)_2$) ; 27.3 (dm, $^1J_{CH}$ ~120, C_6) ; 31.6 (tm, $^1J_{CH}$ = 130, C_5) ; 40.0 (tm, $^1J_{CH}$ = 127, C2) ; 52.5 (dm, $^1J_{CH}$ = 143, C_1) ; 83.5 (m, $C(CH_3)_2$) ; 122.5 (m, =C-CH_3) ; 122.6 (m, C=O) ; 125.6 (m, =C-CH_3).

HRMS calculated for $C_{15}H_{24}NO_3{}^{11}B$ $[M]^+$: 277.185 ; found : 277.185.

Carbamate 5g : To a solution of the isocyanate **5f** (1.39 g ; 5 mmol) in 20 mL of anhydrous dichloromethane, were added at room temperature under nitrogen, tBuOH (0.41 g, 5.5 mmol) and then chlorotrimethylsilane (0.32 mL ; 2.5 mmol). The reaction mixture was refluxed for 12 hours. The solvent and excess reactants were then removed under vacuum. The crude product was recrystallized.

5g : mp : 114-116°C (heptane) ; 1.5 g, 86 %.

IR (Nujol), ν cm^{-1} : 3330 (NH) ; 1670 (C=O).

^{1}H NMR, δ : 1.21 (s, 6H, C(CH$_3$)$_2$) ; 1.22 (s, 6H, C(CH$_3$)$_2$) ; 1.27 (dm, $J_{6,1}$ = 9.3, H$_6$) ; 1.43 (s, 9H, C(CH$_3$)$_3$) ; 1.50 - 1.70 (m, 6H, =C-CH$_3$) ; 1.70 - 1.85 (m, H$_2$') ; 2.02 (dd, $J_{5,5'}$ = 17.2, $J_{5,6}$ = 4.8, H$_5$) ; 2.17 (dd, $J_{5',5}$ = 17.2, $J_{5',6}$ = 8.8, H$_5$') ; 2.38 (dm, $J_{2,2'}$ = 15.9, H$_2$) ; 3.70-3.90 (m, H$_1$) ; 4.66 (br s, NH).

^{13}C NMR, CDCl$_3$, δ : 18.6 (=C-CH$_3$) ; 19.0 (=C-CH$_3$) ; 24.6 (C(CH$_3$)$_2$) ; 24.9 (C$_6$) ; 28.5 (C(CH$_3$)$_3$) ; 31.7 (C$_5$) ; 39.0 (C$_2$) ; 47.8 (C$_1$) ; 78.6 (C(CH$_3$)$_3$) ; 83.2 (C(CH$_3$)$_2$) ; 123.3 (=C-CH$_3$) ; 125.4 (=C-CH$_3$) ; 155.2 (C=O).

HRMS calculated for $C_{19}H_{34}NO_4{}^{11}B$ [M]$^+$: 351.258 ; found : 351.259.

Hydroxycarbamate 5h : **5g** (5 mmol) was oxidized by hydrogen peroxide in the presence of 3N sodium hydroxide, as described in the general procedure for acids **6c** and **7c**. **5h** is purified by column chromatography on silica gel.

5h : mp = 110-112°C. ; 0.79 g, 65 %.

TLC : diethyl ether/heptane/ethyl alcohol : 75/23/2, Rf = 0.5.

IR (CCl_4), ν cm^{-1} : 3600 (OH) ; 3440 (NH) ; 1670 (C=O).

^{1}H NMR, C_6D_6, δ : 1.09 (s, 3H, =C-CH$_3$) ; 1.13 (s, 3H, =C-CH$_3$) ; 1.16 (s, 9H, C(CH$_3$)$_3$) ; 1.50 - 1.70 (m, H$_5$') ; 1.90 - 2.10 (m, H$_2$) ; 2.10 - 2.25 (m, H$_5$) ; 2.20 - 2.30 (m, H$_2$') 2.80 (br s, OH) ; 3.40 - 3.60 (m, H$_1$) ; 3.60 - 3.80 (m, H$_6$) ; 4.45 (br s, NH).

^{13}C NMR, C_6D_6, δ : 18.5 (=C-CH$_3$) ; 18.7 (=C-CH$_3$) ; 28.4 (C(CH$_3$)$_3$) ; 37.3 (C$_2$ or C$_5$) ; 39.6 (C$_2$ or C$_5$) ; 52.7 (C$_6$) ; 70.5 (C$_1$) ; 79.7 (C(CH$_3$)$_3$) ; 123.2 (=C-CH$_3$) ; 123.6 (=C-CH$_3$) ; 156.8 (C=O).

Anal. $C_{13}H_{23}NO_3$: Calc. % C 64.70 ; H 9.61 ; N 5.80 ; Found : C 64.3 ; H 9.5 ; N 5.7.

Chlorhydrate 5i : A solution of the hydroxycarbamate **5h** (1.21 g ; 5 mmol) in 20 mL of diethyl ether was cooled to 0°C. HCl gas was bubbled in the solution until saturation. After 3 hours at 0°C, the precipitate was filtered and washed with diethyl ether. The product was recrystallized from a 8/2 mixture of ethyl alcohol and water.

5i : mp = 214-216°C ; 0.58 g, 65 %.

IR (hexachlorobutadiene), ν cm^{-1} : 3300 (NH_3) ; 3200 (OH).

^{1}H NMR, DMSO-d$_6$, δ : 1.55 (s, 6H, CH$_3$) ; 2.10 (dm, $J_{2,2'}$ = 17.1, H$_2$) ; 2.15 (dm, $J_{5',5}$ = 16.3, H$_5$') ; 2.28 (dd, $J_{5,5'}$ = 16.3, $J_{5,6}$ = 6.2, H$_5$) ; 2.42 (dd, $J_{2',2}$ = 17.1, $J_{2',1}$ = 6.3, H$_2$') ; 3.10 - 3.30 (m, H$_6$) ; 4.10 - 4.40 (m, H$_1$).

^{13}C NMR, DMSO-d$_6$, δ : 19.0 (CH$_3$) ; 19.3 (CH$_3$) ; 35.4 (C$_2$ or C$_5$) ; 37.8 (C$_2$ or C$_5$) ; 51.1 (C$_6$) ; 73.4 (C$_1$) ; 122.6 (=C-CH$_3$) ; 124.5 (=C-CH$_3$).

Anal. : $C_8H_{16}NOCl$: calc. % : C 54,08 ; H 9.08 ; N 7.88 ; Found : C 54.2 ; H 8.9 ; N 7.8.

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