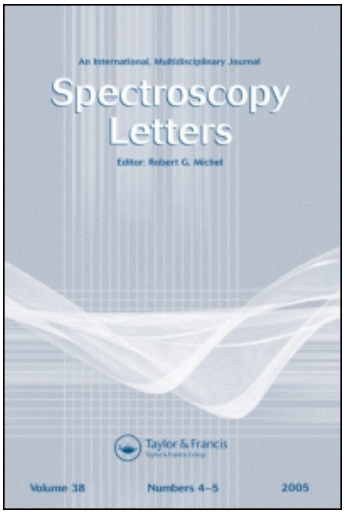

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COMPLETE ANALYSIS OF THE ^{1}H AND ^{13}C NMR SPECTRA OF 5-ISOPROPYLSULFONYL-2-NORBORNENES THROUGH THE APPLICATION OF TWO-DIMENSIONAL NMR TECHNIQUES

KEY WORDS : 5-isopropylsulfonyl-2-norbornenes, ^{1}H-^{1}H homonuclear and ^{1}H-^{13}C heteronuclear two-dimensional chemical shift correlations, ^{1}H NMR, ^{13}C NMR.

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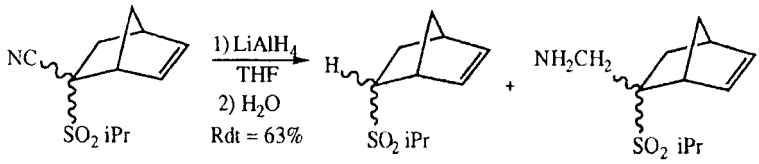
ABSTRACT

Total assignment of ^{13}C and ^{1}H NMR spectra of the 5-isopropylsulfonyl-2-norbornenes **2** was achieved using the concerted application of two-dimensional homonuclear and heteronuclear chemical shift correlations. The stereochemistry of both the diastereoisomers endo **2a** and exo **2b** have been established using the magnitude of the proton coupling constants.



1 **2** (50%) **3** (50%)

1a/1b = 92/8 **2a/2b** = 16/84 **3a/3b** = 92/8

FIG. 1 Reduction reaction of the 5-cyano-5-isopropylsulfonyl-2-norbornenes **1. a** and **b** refer respectively to endo and exo isomers (position of the sulfonyl group).

INTRODUCTION

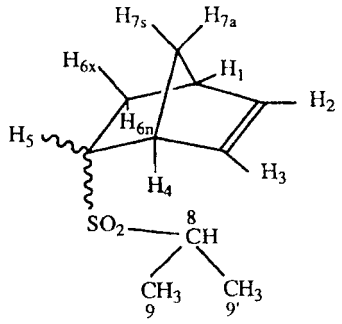
During the reduction of 5-cyano-5-isopropylsulfonyl-2-norbornene **1** with $LiAlH_4$, an unexpected C-CN bond cleavage was observed.[1] Indeed, starting from **1**, a mixture of the amine **3** and the reduced product **2** was obtained (figure 1).

A possible mechanism for this substitution of the cyano group by an hydrogen atom could involve an electron transfer[2] from the metal hydride to the nitrile. In order to explore this hypothesis, it is necessary to know the **2a/2b** ratio in the crude product of the reduction reaction, since a mechanistic pathway involving a free radical would lead to a racemization at the 5-C centre. From this point of view, the ^1H NMR is an efficient tool provided that the chemical shifts of significant hydrogens of the isomers are different and unambigously assigned.

In this paper the total assignment of the ^1H and ^{13}C chemical shifts were achieved using concerted application of two-dimensional experiments. As a consequence the stereochemistry of both isomers was unequivocally established.

EXPERIMENTAL

Both compounds **2a** and **2b** were isolated as pure product and characterized by mass spectrometry and centesimal analysis.



2

FIG.2 Structure and numbering of the 5-isopropylsulfonyl-2-norbornenes **2** (the indices n, x, s and a represent endo, exo, syn and anti respectively).

Proton, carbon-13 and ^{1}H- ^{1}H homonuclear two-dimensional chemical shift correlations were recorded on a Bruker AM-200 spectrometer, while ^{13}C-^{1}H heteronuclear diagrams were obtained on a Bruker AM-400X apparatus. The NMR spectra were measured as solutions in chloroform-d and tetramethylsilane was used as standard in both measurements. Proton-proton coupling constants were extracted from resolution-enhanced ^{1}H spectra using the gaussian multiplication technique.[3]

Resonance multiplicities for ^{13}C were established via the acquisition of DEPT spectra; for the DEPT sequence,[4] the width of a ^{13}C 90° pulse was 13 μs, the width of a ^{1}H 90° pulse was 29 μs and the $(2J)^{-1}$ delay was set equal to 3.7 ms.

The homonuclear ^{1}H- ^{1}H shift correlated two-dimensional diagrams were obtained using the COSY-45[5] pulse sequence. The spectral widths were F_2 : 1500 Hz and F_1: +- 750 Hz allowing digital resolution of 1.47 Hz per point. The spectra were collected as 2048 x1024 blocks of data and were processed by sinusoïdal multiplication in each dimension by symmetrisation of the final data matrix. Other parameters were as follows : number of increments in t_1, 512; scans, 16; phase coupling, 16 and relaxation delay, 1s.

The heteronuclear two-dimensional ^{1}H-^{13}C chemical shift correlation experiments were obtained with proton decoupling in the F_1 dimension.[6] The

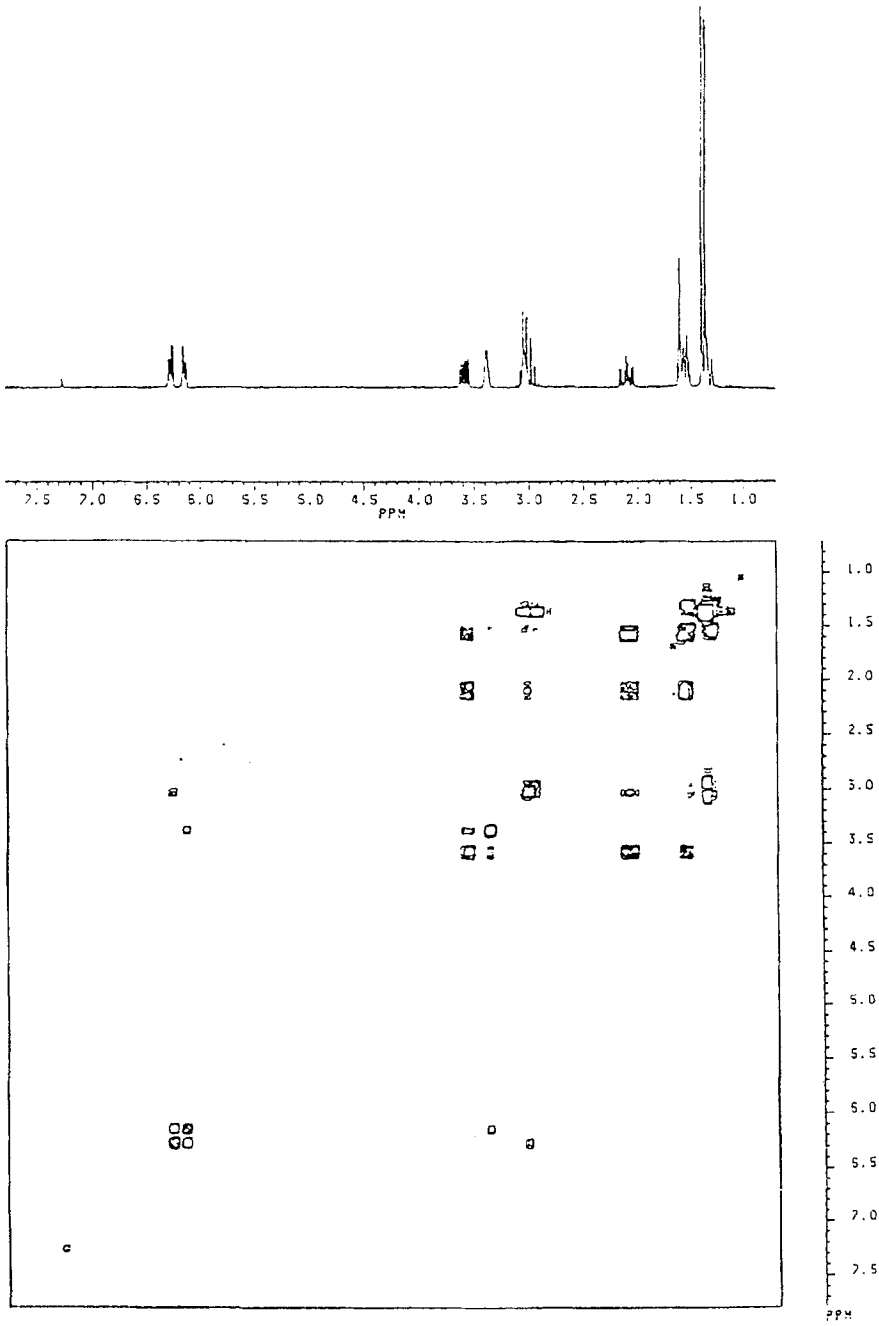


FIG. 3 Proton two-dimensional homonuclear chemical shift-correlated spectrum (COSY) of **2a**.

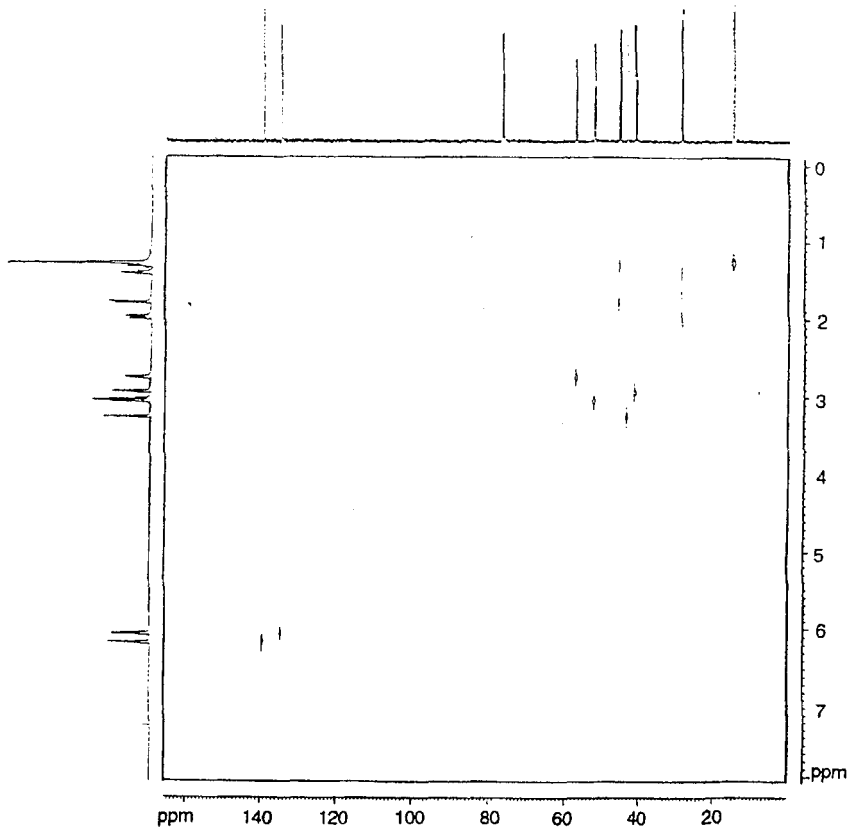
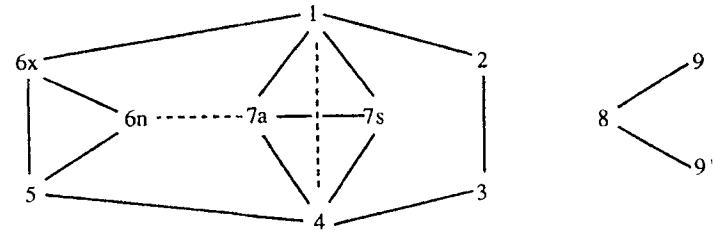
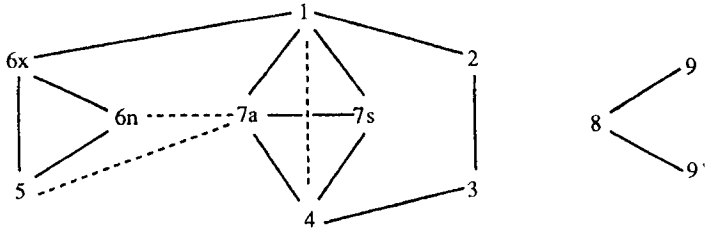


FIG. 4 ^{13}C-^{1}H two-dimensional heteronuclear shift-correlated spectrum of **2b**.

spectra were acquired with 4K x 256 data points and a data acquisition of 16 scans x 128 increments in t_1 and zero filling in the F_1 dimension. Spectral widths of 15000 and 3000 Hz were employed in the F_2 (^{13}C) and F_1 (^{1}H) domains respectively. The data were processed using sine bell functions for weighting in both dimensions. The refocusing delay was 2.5 ms, the mixing delay 3.7 ms, the relaxation delay 1s and 32 phase cycling steps were employed.



2a



2b

FIG. 5 Proton connectivities found in the COSY spectra of **2a** and **2b**. The bold and dotted lines indicate connectivities via ^{2}J or ^{3}J and ^{4}J couplings respectively.

RESULTS AND DISCUSSION

The ^{1}H and ^{13}C NMR spectral parameters for **2a** and **2b** were deduced from the concerted application of 2D-homonuclear and heteronuclear chemical shift correlations. ^{1}H-^{1}H homonuclear diagram (figure 3) establishes proton connectivity from the evidence of proton-proton couplings. Then these proton assignments were correlated with the ^{13}C spectrum using the 2D-heteronuclear experiment (figure 4).

TABLE 1

^1H and ^{13}C NMR Chemical Shifts and ^1H-^1H Coupling Constants for the 5-(endo)-Isopropylsulfonyl-2-Norbornene **2a**.

	^{13}C	^1H	
Assignment[a]	δ[b]	δ[a,b]	Coupling constants[c]
1	42.90	3.03	^3J1-2 : 3.1; ^4J1-4 : 0.8; ^3J1-6x : 3.7;
2	137.31	6.26	^3J2-3 : 5.7; ^3J3-4 : 2.8; ^3J4-5 : 3.2;
3	131.53	6.15	^3J4-7a : 1.5; ^3J4-7s : 1.5; ^3J5-6x : 9.2;
4	45.14	3.38	^3J5-6n : 4.7; ^2J6n-6x : -12.0;
5	58.56	3.58	^4J6n-7a : 2.7; ^2J7a-7s : -8.4; ^3J8-9 : 6.9
6	29.65	2.10 (x) and 1.60 (n)	
7	49.74	1.54 (s) and 1.32 (a)	
8	53.92	3.00	
9	15.22	1.38	
9'	15.65	1.35	

[a] Determined from 2D measurements

[b] In ppm from TMS

[c] In Hz

A convenient starting point for this analysis is provided by the most deshielded ethylenic protons which display cross-peaks with the bridgehead resonances. Then H-1 can be easily assigned since this signal is correlated with one proton of methylene group CH_2-6. Figure 5 shows the complete ^1H intercoupling network found for **2a** and **2b**. Complete stereochemical assignment of 5-isopropylsulfonyl-2-norbornenes **2** follows from the close examination of the vicinal and long-range (ω) coupling constant values. Using the previous results for the well-documented norbornane derivates,[7] the clear-cut differences between

TABLE 2

^{1}H and ^{13}C NMR Chemical Shifts and ^{1}H-^{1}H Coupling Constants for the 5-(exo)-Isopropylsulfonyl-2-Norbornene **2b**.

	^{13}C	^{1}H	
Assignment[a]	δ^{b}	$\delta^{a,b}$	Coupling constants[c]
1	41.55	3.04	$^{3}J1\text{-}2$: 2.9; $^{4}J1\text{-}4$: 1.5; $^{3}J1\text{-}7a$:1.3;
2	139.87	6.27	$^{3}J1\text{-}7s$: 1.3; $^{3}J1\text{-}6x$: 3.4; $^{3}J2\text{-}3$: 5.6;
3	135.32	6.16	$^{3}J3\text{-}4$: 3.1; $^{3}J4\text{-}7a$: 1.5; $^{3}J4\text{-}7s$: 1.5;
4	43.82	3.38	$^{3}J5\text{-}6x$: 4.9; $^{3}J5\text{-}6n$: 8.6; $^{4}J5\text{-}7a$: 1.3;
5	57.61	2.85	$^{2}J6n\text{-}6x$: -11.9; $^{4}J6n\text{-}7a$: 2.6;
			$^{2}J7a\text{-}7s$: -8.8; $^{3}J8\text{-}9$: 6.9
6	28.45	2.10 (x) and 1.51 (n)	
7	45.97	1.91 (s) and 1.43 (a)	
8	52.80	3.14	
9	15.04	1.38	
9'	15.47	1.37	

[a] Determined from 2D measurements

[b] In ppm from TMS

[c] In Hz

^{3}J H-5n, H-4 and ^{3}J H-5x, H-4 allow differentiation between endo **2a** and exo **2b** derivatives (tables 1 and 2).

From these results, it is possible to determine the **2a/2b** ratio (16/84) directly on the reaction mixture by integration measurements of 5-endo and exo protons.

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