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^{1}H and ^{13}C NMR Study of 2,3-Dicarboxymethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene Derivatives

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^{13}C and ^{1}H NMR spectral assignments have been obtained for 2,3-dicarboxymethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene and 19 of its derivatives. The use of a combination of one-dimensional and two-dimensional NMR techniques allowed the unambiguous assignments of all ^{13}C resonances of the bicyclic framework.

KEY WORDS ^{1}H NMR ^{13}C NMR XHCORR INADEQUATE oxanorbornadiene derivatives

INTRODUCTION

Norbornadienes, which can be photochemically transformed into quadricyclanes, are useful compounds with which to realize the storage and release of solar energy.[1,2] The best results have been obtained with derivatives simultaneously bearing electron-attracting and electron-withdrawing groups.[3] We have synthesized various 2,3-dicarboxymethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene derivatives (oxanorbornadienes) to establish whether they can be used in the same way, and describe here the ^{1}H and ^{13}C spectra of 20 oxanorbornadienes with various substituents on carbon 1, 4 or 6 (Fig. 1). To our knowledge only a few NMR spectra of such compounds have been reported previously, and no complete assignment of the carbon chemical shifts has been made.[4–7]. We used two-dimensional NMR techniques to determine such assignments.

EXPERIMENTAL

Oxanorbornadienes **1**–**20** were prepared by Diels–Alder reactions between equimolecular amounts of the furan derivative and dimethylacetylenedicarboxylate (DMAD). The temperature and reaction time were adjusted to obtain complete disappearance of the diene and DMAD.

All spectra were recorded on a Bruker WP 200 SY spectrometer operating at 200.132 MHz for ^{1}H and 50.323 MHz for ^{13}C, in deuteriated chloroform (one-dimensional NMR) or hexadeuteriated benzene (two-dimensional NMR), with all shifts referenced to tetramethylsilane (TMS).

Carbon-13 NMR and ^{1}H NMR spectra were recorded with the following parameters, respectively: pulse angle (PW) 3.2 μs (flip angle 45°) and 2 μs (flip angle 25°); acquisition time 1.3 and 2.3 s for a 32 and 16K data table with spectral widths (SW) of 230 and 13 ppm. Carbon-13 spectra were recorded with broadband decoupling.

The following parameters were used for spin-echo experiments (JMODXH): PW (90°) 6.4 μs; relaxation delay 4 s; $1/J(\mathrm{C,H})$ delay = 7.0 ms; SW 12 500 Hz.

The two-dimensional NMR spectra were recorded using the standard Bruker microprograms XHCORR[8] and INADEQUATE.[9] The proton–carbon chemical shift correlation utilized the XHCORR sequence with delays optimized for $J(\mathrm{C,H})$ values of 140 Hz. The spectra were acquired with 2K × 256 data points and a data acquisition of 64 × 256 increments in t_1 and zero filling in the F_1 dimension. The correlation experiments were applied using various F_2 spectral widths ranging from 3 to 7 kHz. The proton F_1 spectral width was 1500 Hz. The fixed delays were a 4.0 s relaxation delay, 3.5 ms polarization transfer delay and 1.75 ms refocusing delay. The carbon–carbon correlated two-dimensional spectra (INAD2D) were acquired with a spectral width of 6500 Hz in the F_2 domain and a 32-step phase cycling and data acquisition of 128 × 256 increments of t_1 to provide, after zero filling in the F_1 dimension, a matrix of 2048 × 512. Data files were processed using an unshifted sine-bell function in both dimensions before Fourier transformation. The delay for the creation of double quantum coherence was 6.5 ms and the relaxation delay was 10 s.

RESULTS AND DISCUSSION

The ^{13}C and ^{1}H NMR data are presented in Tables 1–3. The chemical shift assignment of protons and carbons is straightforward for

1 $R_1 = R_4 = R_6 = H$
2 $R_1 = CH_3$
3 $R_1 = CH_2CH_3$
4 $R_1 = (CH_2)_3CH_3$
5 $R_1 = (CH_2)_4CH_3$
6 $R_1 = (CH_2)_6CH_3$
7 $R_1 = CH_2OH$
8 $R_1 = CH_2SCH_3$
9 $R_1 = CH_2NCS$
10 $R_1 = CH(OCH_2CH_3)_2$
11 $R_1 = CHNN(CH_3)_2$
12 $R_1 = OCH_3$
13 $R_6 = CH_3$
14 $R_6 = CH_2OH$
15 $R_1 = R_4 = CH_3$
16 $R_1 = R_4 = CH_2OH$
17 $R_1 = CH_2OH,\ R_4 = CH_3$
18 $R_1 = CH_3,\ R_6 = CH_2OH$
19 $R_1 = CH_2OH,\ R_6 = CH_3$
20 $R_1 = R_4 = R_6 = CH_3$

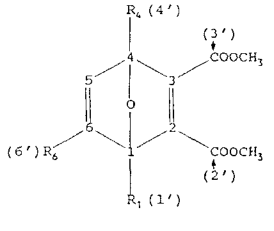

Figure 1. Structure of oxanorbornadienes.

Table 1. Carbon-13 chemical shifts

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′/C-3′	C-4′	C-6′	Methyls	Others
1	85.1	153.1	153.1	85.1	143.3	143.3		163.3			52.3	
2	94.0	156.6	151.4	83.5	144.7	146.1	15.2	162.9/165.0			52.3/52.3	
3	98.4	156.3	151.5	83.3	144.7	144.8	22.0	162.8/165.3			52.2/52.3	9.0
4	97.9	156.5	151.5	83.4	144.5	145.2	28.6	162.8/165.3			52.2/52.2	27.0 22.9 13.9
5	97.9	156.5	151.5	83.4	144.6	145.3	28.9	162.8/165.3			52.0/52.1	32.0 24.6 22.4 13.9
6	97.9	156.5	151.4	83.4	144.5	145.2	28.9	162.8/165.3			52.2/52.2	31.7 29.7 29.0 24.8 22.6 14.4
7	98.4	153.7	152.7	84.1	145.0	142.6	60.0	163.0/164.8			52.4/52.5	
8	99.0	154.4	152.1	83.9	144.7	144.4	33.0	162.7/164.7			52.3/52.4	17.2
9	95.5	154.4	150.8	84.3	145.8	141.9	44.3	162.6/163.6			52.5/52.6	135.1
10	98.8	156.5	149.3	83.8	144.2	142.6	98.4	162.4/165.3			52.2/52.2	63.8 15.2
11	96.6	156.6	149.9	83.5	144.4	144.0	122.9	162.7/165.3			52.1/52.2	42.3
12	118.5	153.3	151.5	78.5	146.5	140.9		162.2/164.3			52.4/52.4	55.0
13	88.4	152.5	153.8	85.8	134.1	155.4		163.4/163.6		14.2	52.3/52.4	
14	85.8	152.6	153.1	85.5	135.2	158.9		163.2/163.9		59.1	52.4/52.5	
15	92.1	154.4	154.4	92.1	147.3	147.3	15.4	164.4	15.4		52.0	
16	97.3	153.5	153.5	97.3	144.2	144.2	59.9	164.3	59.9		52.6	
17	96.4	150.5	158.1	92.9	147.5	144.1	60.2	164.6/164.6	15.1		52.3/52.3	
18	94.4	156.5	151.5	82.6	137.9	158.9	13.7	162.7/165.7		58.4	52.2/52.5	
19	99.0	153.9	152.7	83.2	136.4	153.9	59.2	163.0/164.8		13.1	52.3/52.4	
20	93.3	155.6	154.6	91.1	138.5	157.5	13.8	164.4/164.7	15.6	12.8	52.1/52.1	

Table 2. Assignment of proton NMR spectra. Chemical shifts (ppm)

	H—C-1	H—C-4	H—C-5	H—C-6	H—C-1′	H—C-4′	H—C-6′	Esters	Others
1	5.69	5.69	7.22	7.22				3.82	
2		5.60	7.17	6.98	1.70			3.75; 3.80	
3		5.65	7.19	7.00	2.21			3.78; 3.85	1.01
4		5.63	7.17	6.99	2.16			3.77; 3.84	1.39; 0.91
5		5.62	7.16	6.97	2.14			3.77; 3.82	1.34; 0.88
6		5.64	7.17	6.98	2.14			3.77; 3.84	1.27; 0.87
7		5.67	7.24	7.05	4.24; 4.32			3.80; 3.84	2.50
8		5.67	7.19	7.02	3.24; 3.35			3.79; 3.89	2.20
9		5.70	7.29	7.02	4.30; 4.40			3.82; 3.86	
10		5.71	7.18	7.18	5.17			3.75; 3.84	3.70; 1.24
11		5.66	7.25	7.27	6.63			3.81; 3.83	2.89
12		5.55	7.23	7.01				3.78; 3.87	3.58
13	5.36	5.60	6.60				2.02	3.82; 3.83	
14	5.57	5.66	6.85				4.43	3.80; 3.82	3.25
15			6.82	6.82	1.64	1.64		3.68	
16			7.08	7.08	4.23; 4.31	4.23; 4.31		3.81	
17			7.00	7.06	4.27	1.78		3.79; 3.83	
18		5.57	6.91		1.75		4.40	3.80; 3.84	
19		5.58	6.66		4.17; 4.31		1.96	3.80; 3.84	3.00
20			6.41		1.75	1.70	1.89	3.80	

compounds **1**, **15** and **16**, which are symmetrical molecules, and for **17** by analogy. For derivatives **2**–**14** and **18**–**20** only a few carbons could be assigned on the basis of their chemical shift values and spin-echo experiments.

For the monosubstituted derivatives **2**–**12**, the proton–carbon chemical shift correlation (XHCORR) allowed the unambiguous assignments of the resonances of C-5 and C-6 in all products as well as the carbon C-1′ of the side-chain in **5**, **6** and **7**. Carbons C-2 and C-3 are identified from the β substituent effect, the deshielding of C-2 being confirmed by carbon–carbon correlation for **2**, **3** and **7**.

The differentiation of the closely lying signals of the quaternary carbons in **13**, **18** and **20** could be solved only by INADEQUATE experiments. These assignments were then extended to **14** and **19**, except for C-1 and C-4 of the former which were differentiated by selective irradiation of the H—C-1, H—C-4 and H—C-5 hydrogens, followed by proton–carbon correlation experiments.

The introduction of substituents onto the bicyclic framework of the oxanorbornadiene derivatives led to the expected electronic and steric effects on the chemical shifts of neighbouring carbons. The β substituent effect is

Reference Data

Table 3. ^1H–^1H **coupling constants (Hz)**

Pair of protons	4,5	5,6	1,4	$1_a',1_b'$	5,6'
1	1.1				
2	2.0	5.2			
3	1.9	5.2			
4	2.0	5.2			
5	2.0	5.2			
6	2.0	5.2			
7	1.9	5.3		12.8	
8	1.8	5.2		13.5	
9	1.8	5.2		15.3	
10	1.6				
11	1.8	5.2			
12	2.0	5.4			
13	1.9		1.6		2.0
14	1.7		1.6		1.9
16				12.9	
17		5.2			
18	1.8				
19	1.6			12.0	1.8
20					1.8

observable on C-2 for **2**–**12** and, although small ($0.2 < \Delta\delta < 3.5$ ppm), the deshielding is larger than on C-6. The chemical shift of C-6, compared with **1**, at lower field for most compounds, but is at slightly higher field for **7**, **9**, **10** and **12** due to the heteroatom steric γ effect. The substituent chain is therefore oriented on the left side of the molecule. In some compounds the rotation around the C-1/C-1′ bond is restricted, as shown by the multiplicity of H—C-1′ (two doublets). In compound **12**, bearing a methoxy group, an important shielding (−6.6 ppm) is observed for C-4, in agreement with the γ antiperiplanar effect of the oxygen atom.

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News and Events

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