¹H and ¹³C NMR Spectra of Some 2-Substituted 4,5-Dimethylfurans

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¹H and ¹³C NMR spectra of 22 2substituted 4,5-dimethylfurans are reported. The J(C,H) values were used for signal assignments and for the identification of geometrical isomers of some derivatives.

KEY WORDS 2-Substituted 4,5-dimethylfurans ¹H and ¹³C NMR spectra

INTRODUCTION

Derivatives of 2,3-dimethylfuran are important intermediates in the synthesis of antibiotics, analgetics, natural compounds and pheromones. They also serve as precursors for the synthesis of aromatic and heteroaromatic compounds. In an earlier paper¹ we described a simple and facile synthesis and the utilization of 2,3-dimethylfuran (1) and the preparation of some of the compounds now reported. No systematic study of the NMR spectra of 2-substituted-4,5-dimethylfurans has, to our knowledge, been previously published.

RESULTS

Table 1 lists the ¹H NMR spectra and Tables 2 and 3 give the ¹³C chemical shifts and the J(C,H) values, respectively. The assignments of the carbon signals were based on the characteristic splittings of signals and the values of long-range J(C,H) coupling constants in proton-coupled ¹³C NMR spectra. In some cases, selective heteronuclear decoupling and the DEPT pulse sequence were used for signal assignment.

Substituents in position 2 of the furan ring influence the chemical shifts of H-3, C-3, C-4 and C-5.² The deshielding of H-3 in 19–22 can be accounted for by their stereochemistry, and indicates a preferred *s-cis* conformation of the furan ring with respect to the double bond in position 2. Such a preference has also been observed in analogous compounds, viz. the products of Knoevenagel condensation of 2-furaldehyde and Meldrum's acid.³ The ³J(C,H) values (Table 3) were used for the assignment of the functional group carbons attached to the double bond (derivatives 8, 19-22), and for the determination of the geometrical isomers of the trisubstituted ethylenes. Compounds 9-12 and 18 were identified as E isomers and 13 and 23 as Z isomers. The measured coupling constants are comparable to those of other 2-furylethylene derivatives.^{4,5} The fact that 12 is an E isomer was established from the value of the vicinal coupling constant ${}^{3}J(C-8)$, H-6) = 6.1 Hz, and from analogous compounds where the data for both corresponding isomers were measured.⁴ The decreased value of the ³J(CH₃',H) trans coupling constant has been explained^{6,7} by the effects of structural factors such as the electronegativity of substituents and steric interactions.

EXPERIMENTAL

¹H NMR spectra were recorded at 298 K on a Tesla BS 587 Fourier transform spectrometer operating at 80 MHz, in either CDCl₃ or DMSO- d_6 (see Table 2), with tetramethylsilane as internal standard. The ¹³C NMR spectra were recorded using the same spectrometer' and solvents and the following conditions were used: 20.18 MHz; tube diameter, 10 mm; concentration, 0.5 mol dm⁻³ or saturated solutions; internal stan-

Table 1. ¹H NMR spectra (δ , ppm; J, Hz) of 2-substituted 4,5-dimethylfurans^a

Compound	H-3	5-Me	4-Me	R	J(H,H)
1	6.13	2.18	1.93	7.17 (H-2)	J(2,3) = 1.7
2	7.06	2.32	2.02	9.45 (CHO)	
3	6.98	2.30	1.99	2.39 (CH ₃)	
4	7.12	2.31	1.99	12.06 (COOH)	
5	5.72	2.19	1.87	2.14 (CH ₃)	
6	6.46	2.26	1.95	7.40 (H-6), 6.36 (H-7), 9.90 (COOH)	J(6,7) = 15.1
7	6.69	2.29	1.98	7.68 (H-6), 7.40, (H-7)	J(6,7) = 13.2
8	7.18	2.38	2.04	7.32 (H-6)	
9	7.24	2.36	2.03	7.87 (H-6), 3.88 (COOCH ₃)	
10	7.22	2.32	1.99	7.80 (H-6), 9.80 (COOH)	
11	7.27	2.37	2.04	7.79 (H-6), 2.49 (COCH ₃)	
12	6.62	2.30	1.99	7.75 (H-6), 2.54 (CH ₃)	
13	6.92	2.24	1.98	6.78 (H-6), 4.31 (OCH ₂), 1.35 (CH ₃)	
14	7.31	2.37	2.04	2.48 (CH ₃)	
15	6.68	2.32	1.98	8.40 (H-6), 3.73 (NH ₂)	
16	6.16	2.23	1.92	7.07 (H-6), 2.91 [N(CH ₃) ₂]	
17	7.21	2.32	2.00	8.88 (H-6), 3.42 [N(CH ₃) ₃]	
18	6.29	2.21	1.92	7.27 (H-6), 6.17 (H-7), 4.15 (CH)	J(6,7) = 14.9
				1.19 [(CH ₃) ₂], 5.68 (NH)	
19	8.36	2.39	2.07	8.22 (H-6), 1.75 (CH ₃) ₂	
20	8.37	2.38	2.04	8.19 (H-6), 1.25–2.00 [(CH ₂) ₅]	
21	8.32	2.38	2.07	8.18 (H-6), 1.70–2.25 [(CH ₂) ₄]	
22	8.38	2.38	2.05	7.91 (H-6), 11.17 (NH)	
23	6.98	2.31	1.97	7.33 (H-6) ^ь	
* For solve	nts, see T	able 2.			

^b NH signal not observed.

Reference Data

Reference Data

Table 2. ¹³ C chemical shifts (ppm relative to TMS) of 2-substituted 4,5-dimethylfurans*								
Compound	C-2	C-3	C-4	C-5	5-Me	4-CH3	R	
1	139.6	112.9	113.8	147.4	11.2	9.8		
2	150.7	125.7	118.4	155.9	12.0	9.6	176.7 (CHO)	
3	150.3	121.3	117.7	153.7	11.9	9.7	185.7 (CO), 25.5 (CH ₃)	
4	140.9	123.6	117.7	154.5	11.9	9.6	163.9 (COOH)	
5	145.3	108.7	114.4	148.9	11.1	9.8	13.3 (CH ₃)	
6	148.1	111.7	117.7	152.0	11.8	9.7	133.0 (C-6), 112.4 (C-7), 172.4 (COOH)	
7	143.9	125.2	119.1	154.5	11.7	9.2	132.4 (C-6), 126.0 (C-7)	
8	146.0	127.2	121.2	158.5	12.4	9.6	142.0 (C-6), 73.6 (C-7), 114.7 (C-8′), 113.4 (C-8)	
9	146.4	125.8	120.4	156.8	12.2	9.7	139.1 (C-6), 94.7 (C-7), 163.8 (CO), 115.9 (CN), 53.0 (COOCH ₃)	
10	146.0	125.1	119.3	1 5 5.1	11.7	9.2	136.7 (C-6), 98.4 (C-7), 164.3 (CO), 116.8 (CN)	
11	146.6	126.7	120.7	157.4	12.3	9.7	136.8 (C-6), 102.4 (C-7), 191.3 (CO), 27.7 (CH ₃)	
12	145.4	123.4	118.6	153.5	12.0	9.6	120.8 (C-6), 142.4 (C-7), 14.0 (CH ₃)	
13	146.8	119.1	117.9	150.4	11.7	9.8	114.0 (C-6), 120.8 (C-7), 163.4 (CO), 61.9 (CH ₂), 14.2 (CH ₃)	
14	147.1	124.4	120.5	156.7	12.2	9.7	155.1 (C-6), 73.7 (C-7), 114.3 (CN), 114.2 (CN), 19.0 (CH ₃)	
15	146.9	120.9	117.6	152.6	11.9	9.7	150.0 (C-6)	
16	147.5	111.4	115.8	149.2	11.9	9.8	124.5 (C-6), 42.9 [N(CH ₃) ₂]	
17	142.5	126.8	118.3	155.1	11.6	9.2	151.0 (C-6), 55.2 [Ň(CH ₃) ₃]	
18	148.7	117.4	117.1	150.0	11.6	9.7	127.8 (C-6), 116.7 (C-7), 165.5 (C-8), 41.5 (C-9), 22.9 [(CH ₃) ₂]	
19	148.3	132.5	122.5	160.2	12.6	9.9	140.3 (C-6), 103.9 (C-7), 163.8 (C-8′), 160.7 (C-8), 104.1 (C-9), 27.5 [(CH ₃) ₂]	
20	148.4	132.3	122.4	160.0	12.6	10.0	140.2 (C-6), 104.9 (C-7), 163.9 (C-8'), 160.8 (C-8), 104.7 (C-9), 36.5 (C-10.10'), 22.4 (C-11.11'), 24.4 (C-12)	
21	148.2	132.5	122.5	160.1	12.6	9.9	140.3 (C-6), 104.6 (C-7), 164.4 (C-8), 161.4 (C-8), 113.3 (C-9), 38.3 (C-10.10'), 23.3 (C-11.11')	
22	148.0	120.7	121.5	159.3	11.9	9.4	136.3 (C-6), 109.6 (C-7), 163.4 (C-8'), 162.1 (C-8), 150.1 (C-9)	
23	146.9	123.6	119.1	154.4	11.7	9.3	117.5 (C-6), 120.1 (C-7), 196.4 (CS), 168.9 (CO)	
^a Solvents: compounds 7, 10, 17, 22 and 23 in DMSO- d_{6} , the others in CDCl ₃ .								

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Reference Data

Table 3.	Coupling con	stants, <i>J</i> (C,F	I) (Hz), for	compound	s 1–23
	C-3,H-3	C-2,H-3	C-6,H-6		
Compound	(C-3,H-2)	(C-2,H-X)	(C-7,H-7)	C-8,H-6	C-8′,H-6
1	170.3	9.7			
	(13.4)	(200.2)*			
2	173.3	9.7	177.0		
		(31.2) ^b			
3	172.7	9.2			
4	173.9	9.2			
5	169.1	c			
6	174.2	9.7	160.2		5.9
			(161.2)		
7	175.1	9.1	195.1		
			(166.0)		
8	175.2	9.7	161.7	13.4	7.9
9	173.9	9.7	160.5	12.2	7.4
10	173.9	9.1	161.7	13.4	6.1
11	161.9	9.7	159.9	12.8	6.1
12	169.8	9.2	158.9	6.1	—
13	176.4	9.7	160.5	_	4.9
14	174.5	c			
15	173.9	9.2	164.2		
16	174.8	9.2	165.1		
17	175.7	9.7	167.8		
18	169.1	9.7	153.8		
			(152.6)		
19	180.4	9.7	153.8	11.6	7.3
20	180.2	9.4	153.0	11.0	7.2
21	180.2	9.4	153.2	11.2	7.3
22	180.0	9.5	152.0	10.3	7.3
23	177.0	9.3	164.2		6.1
ª C-2,H-2. ^b C-2,H-al ^c Unresolv	d. red.				

dard, TMS; spectral width, 5000 Hz; pulse width, 3 μ s; flip angle, 30°; pulse delay, 2 s; and digital resolution, 0.6 Hz per point.

Compounds 1-4 and 6 were prepared according to Ref. 1. Compounds 10-12, 16 and 19-23 were prepared from 2 and derivative 14 from 3 by condensation;⁸ derivative 17 was obtained by the reaction of 16 with methyl iodide in benzene and 13 was prepared according to Ref. 9.

Compounds 5 and 15: 24.8 g (0.2 mol) of 2 were dissolved in 125 ml of 1,2-dihydroxyethane and 85% hydrazine hydrate was added (15 ml) to the vigorously stirred solution, kept at 0 °C. For compound 15, this mixture was stirred for 3 h and yellow crystals separated: 15, m.p. 164–167 °C (decomp.), yield 85%. For compound 5, the reaction mixture was stirred for 30 min at 0 °C and then for 1 h at room temperature. Sodium hydroxide (4 g) was added and the reaction mixture was heated at 100 °C for 1 h. The volatile components were removed by distillation at 150–180 °C, the distillate was separated from the aqueous layer, dried with NaOH and distilled after about 1 g of sodium had been added. The product, 5, had b.p. 124–127 °C, yield 15.5 g (70%).

Compound 18: PCl₃ (30.5 g, 0.2 mol) was added to 2-aminopropane (59 g, 0.2 mol) in 300 ml of toluene at 10 °C. The reaction mixture was refluxed in an inert atmosphere for 2 h, 6 (33 g, 0.2 mol) was then added and refluxing was continued for 2 h. The mixture was poured on to ice (200 g) and the organic layer was separated and concentrated. The crude 18 was purified by crystallization from a mixture of toluene and hepane; m.p. 141– 143 °C, yield 20.7 g (50%).

Reference Data



- $H_{3}C \xrightarrow{4} 3$ $H_{3}C \xrightarrow{5} 0 R$
- $13 H = \frac{6}{C} = \frac{7}{C} + \frac{N_3}{C} = \frac{13}{C} + \frac{1$

$$14 \begin{array}{c} 6 \\ C = C \\ H_3 C \end{array} \begin{array}{c} 7 \\ C = C \\ C \\ C \\ C \\ C \\ C \\ N \end{array}$$

- 15 CH=N-NH₂
- 16 CH=N-N(CH₃)₂
- 17 CH=N-N*(CH₃)₃ Br⁻
- 6 7 8 9 18 CH=CH-CONH-CH(CH₃)₂



H⁶, S-CS H², CO-NH

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