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¹³C Nuclear Magnetic Resonance Studies on Pyrano- and Dihydropyrano-1,3diphenylprop-2-enones

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The ¹³C NMR spectra of 19 differently substituted pyrano- and dihydropyrano-1, 3-diphenylprop-2-enones were recorded and the results are discussed. The data will be useful in the identification of new and natural chalcones. 611 (1989).

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INTRODUCTION

In a previous study¹ we interpreted the ¹³C NMR spectra of a range of differently oxygenated chalcones. In order to extend this range we have synthesized a series of chromano-, chromeno- and chromanalochalcones, i.e. the cyclized analogues on ring A of 3-methylbut-2-enylated chalcones. Many





- 10 $R_1 = R_2 = H; R_3 = OH$
- 11 $R_1 = R_2 = H; R_3 = -OCH_2OCH_3$
- 12 $R_1 = R_2 = OCH_3$; $R_3 = H$
- 13 $R_1 = R_3 = OCH_3$; $R_2 = H$
- 14 $R_1 = H; R_2 = R_3 = OCH_3$



Ö 19

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of these chalcones have been synthesized for the first time. A large number of chalcones having this unit are known to occur in nature. Chalcones, as such, are important with respect to their physicochemical and biological activities, e.g. antibacterial,²⁻⁵ antifungal,^{2,5–9} anti-inflammatory,^{10,11} antimicrobial,^{10,12-16} antiulcer, 17,18 antianticancer^{20,21} tumour,19 and insect antifeedant²² and as binders for prostaglandins;²¹ many chalcones are also useful as antioxidants for oils.²³⁻²⁷ To our knowledge, a detailed systematic ¹³C NMR spectral study of such chromano- and chromenochalcones has not previously been made. We report here the ¹³C NMR chemical shifts for eight chromanochalcones (1-8), six chromenochalcones (9-14), four chromanalochalcones (16-19) and one furanochalcone (15).

EXPERIMENTAL

All the chalcones were synthesized by the base-catalysed $[Ba(OH)_2]^{28}$ Claisen–Schmidt reaction of the appropriate benzaldehyde and acetophenone. The purities of the compounds were checked from their melting points (Table 1) and/or spectral data.

The ¹³C NMR spectra were recorded on a Bruker AM-250 Fourier transform NMR spectrometer. The conditions were as follows: 297 K, 5 mm tube, 8% solution in $CDCl_3$ with TMS as internal standard, deuteriated solvent as internal lock, 90°/3.8 pulse, 2 s repetition time, 1000–5000 transients, 32K data points used in each measurement, 142–185 Hz spectral width and 0.9 Hz per point digital resolution. Both ¹³C proton coupled and decoupled spectra were recorded.

Reference Data

Compound	M.p. (°C)	Compound	M.p. (°C)
1	189	11	Oily
2	170-171	12	117
3	128-129	13	148
4	147	14	134
5	122-123	15	135–136
6	129	16	180-181
7	119	17	171
8	179–180	18	191
9	_	19	90
10	196–197		

RESULTS AND DISCUSSION

The chemical shift values for 1-19 are given in Tables 2 and 3. The assignments were made from the signal multiplicities and the spectral characteristics of model compounds, and by comparing measured and calculated chemical shifts.

The 13 C NMR spectral assignments of some chalcones have been published previously, ${}^{29-37}$ but without detailed discussion. Since these chalcones have a 3-methylbut-2-enyl unit with the hydroxyl group on the adjacent carbon forming the dihydropyran ring on ring A, it is worth analysing the chemical shifts of this moiety and its effect on the chemical shifts of the remainder of the molecule.

C-4" of the dihydropyranochalcones 1–7 absorbed between δ 21.64 and 21.84 ppm, but in 8 the signal shifted upfield to δ 17.09 ppm, which may be due to the presence of the methoxy group at the neighbouring C-4' position. In the pyranochalcones 9-14, C-4" absorbed between δ 118.09 and 121.18 ppm because of the presence of the double bond. The exceptionally low value of δ 107.09 ppm for 15 may be due to the presence of a furan ring. C-4" in the 5"-hydroxy- dihydropyranochalcones 16–19 absorbed in the range δ 20.69-22.04 ppm. C-5" of the dihydropyranochalcones absorbed between δ 31.68 and 32.83 ppm, but in 16-19 its signal was between δ 68.83 and 69.49 ppm owing to the presence of the hydroxyl group at C-5". In the pyranochalcones the C-5" signal was in the range δ 126.83–127.90 ppm, and in the furanochalcone 15 it appeared at δ 144.85 ppm. The C-6" carbon in all the compounds having a pyran or dihydropyran ring absorbed between δ 70.61 and 79.52 ppm. The chemical shift values of the two gemdimethyl carbons in 16-19 differed by about 2-4 ppm because of their different stereochemical positions, absorbed in the range δ 24.91-30.60 ppm. The two gem-dimethyl

Table 2. ¹³C chemical shifts (ppm) of the carbon atoms of ring B and the α , β -unsaturated carbonyl moiety of the chalcones studied

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-a	C-β	c=0	OMe
1	131.06	128.87	128.39	128.76	128.3 9	128.87	120.51	143.89	191.59	
2	131.28	130.30	116.17	161.49	116.17	130.30	117.39	142.60	192.14	
3	131.04	130.17	116.67	161.40	116.67	130.17	118.67	143.67	191.73	56.18
4	127.60	130.18	114.33	164.03	114.33	130.18	118.00	143.73	191.64	55.31
5	129.07	153.17	148.89	122.17	114.07	124.08	119.76	138.77	191.99	55.81, 61.21
6	117.16	161.98	98.36	160.34	105.68	130.64	118.45	139.50	192.27	55.40, 55.51
7	128.00	111.26	149.29	152.80	114.28	123.10	118.37	144.19	191.68	56.03, 56.10
8	129.60	129.60	114.21	164.00	114.21	129.60	125.63	140.12	192.80	55.25, 55.50
9	136.10	128.83	127.35	129.31	127.35	128.83	123.77	144.36	191.63	
10	127.90	127.66	115.49	160.30	115.49	127.66	124.59	144.65	192.24	
11	127.69	130.25	116.60	160.00	116.60	130.25	118.46	144.03	191.69	56.20
12	128.98	153.30	149.70	121.94	114.19	124.09	119.81	139.15	192.60	55.82, 61.21
13	117.08	160.42	98.39	160.12	105.49	130.85	121.22	139.92	192.23	55.41, 55.51
14	127.86	110.53	149.31	151.61	111.22	123.22	121.14	144.52	191.59	56.01, 56.01
15	135.70	128.62	127.16	132.08	127.16	128.62	97.97	184.32	186.14	61.76
16	135.43	12 9 .19	128.99	130.73	128.99	129.19	121.37	143.96	191.84	
17	128.96	148.92	148.92	114.19	119.80	124.11	121.96	129.21	1 92 .07	55.82, 61.24
18	117.02	159.59	98.35	160.40	105.47	130.81	118.19	139.96	192.32	55.41, 55.51
19	129.00	129.71	128.76	130.22	128.76	129.71	127.87	140.85	190.17	56.04

Reference Data

Table 3.	¹³ C chemic	al shifts (p	pm) of the	carbon at	oms of ring	g A and the	e cyclized i	sopentenyl	ring			
Compound	C-1′	C-2'	C-3′	C-4'	C-5′	C-6′	C-4"	C-5"	C-6″	СН3	СН3	OCH ₂ /OCH ₂ O
1	112.63	164.11	104.84	161.48	114.12	130.41	21.71	32.69	75.89	26.89	26.89	
2	114.19	163.80	104.58	162.79	113.06	128.42	21.64	32.67	74.26	26.91	26.91	
3	112.64	164.17	104.92	163.07	114.28	128.76	21.83	32.83	75.93	26.99	26.99	94.43
4	112.49	161.90	104.80	161.23	114.17	130.90	21.72	32.71	75.79	26.88	29.59	
5	112.57	164.09	104.80	161.38	114.20	131.13	21.70	32.69	75.85	26.88	26.88	
6	112.20	164.00	104.75	163.03	114.37	130.95	21.77	32.7 7	75.68	26.89	26.89	
7	112.64	164.16	104.88	161.39	114.28	131.02	21.84	32.82	75.91	27.00	27.00	
8	109.83	161.20	109.83	161.18	101.65	129.99	17.09	31.68	74.77	26.79	26.79	
9	113.49	166.59	104.74	160.56	114.22	128.99	121.14	126.83	78.03	28.61	28.61	
10	113.29	165.99	104.34	163.48	113.51	128.11	120.71	127.90	79.23	28.28	28.28	
11	113.63	166.60	104.80	165.50	116.32	128.84	121.18	127.41	79.52	28.61	29.37	94.28
12	113.40	166.51	104.66	160.80	114.19	128.73	121.03	127.46	77.87	28.50	28.50	
13	113.23	166.42	104.64	163.13	114.38	128.54	118.25	127.38	77.71	28.47	28.47	
14	113.47	166.55	104.76	160.48	114.25	128.81	118.09	127.37	77.93	28.58	28.58	
15	119.60	158.78	122.18	152.78	105.00	126.59	107.09	144.85	70.61	24.96	25.44	
16		167.65	104.12	167.52	114.00	132.76	20.71	68.98	70.61	24.91	25.44	
17	110.31	164.26	104.98	160.00	114.19	131.95	22.04	69.43	78.21	25.09	30.54	
18	117.02	164.14	104.90	163.20	115.12	131.77	22.03	69.49	78.08	25.08	30.60	
19	110.14	154.86	113.16	162.10	102.85	130.22	20.69	68.83	78.64	25.80	27.18	

1 2

in 1–14 having a pyran/ carbons dihydropyran ring absorbed in a similar region, i.e. δ 26.79-29.59 ppm.

The carbonyl carbon absorbed between δ 186.14 and 192.80 ppm and was identifiable by its characteristic peak. The α -carbon absorbed at δ 117.39–127.87 ppm, except for 15 where its signal was at δ 97.97 ppm owing to the presence of the hydroxyl group at C- β . Owing to this hydroxyl group C- β itself absorbed downfield at δ 184.32 ppm, whereas for the other compounds its range was δ 138.77-144.65 ppm; this large difference is due to the diferent oxygenation pattern in ring B.

The carbon in ring A having the cyclized isopentenyl unit undergoes a low-field shift of about 5-6 ppm. The substituted C-3' in 8, 15 and 19 absorbed between δ 109.83 and 122.18 ppm, whereas an unsubstituted C-3' signal was between δ 104.12 and 104.98 ppm. Similarly, the signal for a substituted C-5' was between δ 113.06 and 116.32 ppm, but an unsubstituted C-5' absorbed between δ 101.50 and 105.00 ppm. C-2' and C-4' have oxygenated functions and absorbed between δ 152.78 and 166.60 ppm. The large-range for the C-1' signals, δ 110.14–119.60 ppm, is due to the different substitution pattern in ring A. C-6' is unsubstituted in all compounds and absorbed between δ 126.59–132.76 ppm.

C-1 in 1-4, 7, 9-11, 15 and 19 which lack an ortho substituent at C-2/C-6 absorbed at δ 127.60-136.10 ppm, and at δ 128.96-129.07 in 5, 12 and 17 having ortho and meta substituents. In 6, 13 and 18, the C-1 signal was between δ 117.02 and 117.16 ppm. Compounds having a meta and para substitution pattern (7 and 14) had the C-1 signal at δ 128.00 and 127.86 ppm, respectively, whereas the para-substituted compounds 2-4, 10 and 11) showed the C-1 signal between δ 127.60 and 131.28 ppm. All methoxy signals (Table 3) absorbed at 55-56 ppm, with the exception of 5, 12, 15 and 17, where one was downfield, around 61 ppm, because of the different oxygenation pattern. It is known³² that in the ortho-disubstituted anisoles the methoxy carbon signals are shifted downfield compared with anisole, and thus the low-field signals can be assigned to the C-2 (or C-2') methoxy carbon in 5, 12, 15 and 17.

These results should be useful in the identification of new and natural pyrano- and furanochalcones.

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Tautomerism of 2-Benzothiazolylmalonates and 2-Oxobenzodihydrothiazol-3-yl-malonates

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The tautomerism of alkyl 2-benzothiazolylmalonates and 2-oxobenzodihydrothiazol-3-yl-malonates was studied by ¹H, ¹³C and ¹⁵N NMR spectroscopy. 2-Benzothiazolylmalonates isomerize in solution to the N—H tautomers with an intramolecular hydrogen bond between the N—H ··· O=C groups, whereas 2-oxobenzodihydrothiazol-3-yl-malonates are in the C—H forms. The complete Food Chem. 12, 205 (1983).

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assignments of the ¹³C NMR resonances are reported.

KEY WORDS CH-NH tautomerism of 2benzothiazolylmalonates 2-Oxobenzodihydrothiazol-3-yl-malonates ¹³C NMR ¹⁵N NMR

INTRODUCTION

The tautomerism of 2-benzothiazolylmethane derivatives has recently been studied by various spectroscopic techniques.^{1,2} An equilibrium between CH and NH tautomers was found to be affected by solvent and the C-substituent. We therefore examined 2-benzothiazolylmalonates (1) and 2-oxobenzodihydrothiazol-3-yl-malonates (2) with



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the aim of establishing which of the tautomeric forms is preferred.

RESULTS AND DISCUSSION

2-Oxobenzodihydrothiazol-3-yl-malonates (2) were used as model compounds for the CH tautomeric form. Signals corresponding to the methine proton (5.98-6.13 ppm) or the methine carbon (58.4-57.7 ppm, Table 2) were found in their ¹H or ¹³C NMR spectra which were absent in the spectra of 2benzothiazolylmalonates (1). A signal at 13.2 ppm was found in the ¹H NMR spectra of series 1 which does not depend on the solvents used (benzene, pyridine, dimethylsulphoxide. acetone. acetonitrile and chloroform). This is clear evidence for the presence of an intramolecular hydrogen bond. Three tautomeric forms can be envisaged for 2-benzothiazolylmalonates (1), with intramolecular $O - H \cdots N$ (a), $O - H \cdots$ O=C (b) or $N-H \cdots O=C$ (c) hydrogen bonds (Scheme 1).

The 13 C NMR spectra of series 1 were assigned (Table 1) in order to establish which of the tautomeric forms exists in solution. The resonances of the aromatic carbons of the benzothiazolyl group were assigned on the basis of literature data.^{3,4} The APT (attached proton test) experiment was used to identify methyl, methine and quaternary

Table 1. ¹³C chemical shifts (ppm) for alkyl 2-benzothiazolylmalonates (1)

R	C-2	C-3a	C-4	C-5	C-6	C-7	C.7a	C-2'	C-1'	C-3'	Others
CH ₃	170.2	138.3	112.7	126.8	123.6	121.7	128.1	85.5	169.3	167.9	51.7
C₂H₅	170.0	138.4	112.6	126.7	123.4	121.6	128.2	86.1	169.1	167.6	60.3, 14.4, 14.3
C ₃ H ₇	170.2	138.6	112.7	126.8	123.6	121.8	128.4	86.2	169.3	167.9	66.2, 22.3, 10.7
i-C ₃ H ₇	169.7	138.5	112.5	126.7	123.4	121.7	128.2	86.8	168.7	167.3	67.7, 67.6, 22.3, 22.2
i∼C₄H ₉	170.4	138.6	112.7	126.8	123.6	121.8	128.5	86.2	169.4	167.9	70.9, 70.8, 28.1, 19.4
CH ₂ CH=CH ₂	170.4	138.4	112.8	126.9	123.7	121.8	128.3	85.8	168.7	167.3	133.0, 132.7, 117.3, 65.1
CH₂Ph	170.4	138.4	112.8	126.9	123.7	121.8	128.4	85.8	168.7	167.4	136.8, 136.6, 128.4, 127.9, 127.7, 66.2
Cyclohexyl	169.9	138.6	112.5	126.6	123.3	121.7	128.3	86.9	168.7	167.4	72.6, 32.1, 31.9, 25.7, 23.9, 23.7