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Reference Data

^{13}C Nuclear Magnetic Resonance Studies on 1,3-Diphenylprop-2-enones

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The ^{13}C NMR spectra of 48 differently substituted chalcones (1,3-diphenylprop-2 enones) have been recorded and the results are discussed. The data will be useful in the identification of new/natural chalcones.

KEY WORDS Chalcones 1,3-Diphenylprop-2- enones ^{13}C NMR chemical shifts

INTRODUCTION

Chalcones (1,3-diphenylprop-2- enones) constitute an important group of natural products and some have been found to possess a wide range of biological activities.[1–6] They are useful in the production of nematic liquid crystals[7] and photosensitive polymers[8] and in the biosynthesis and synthesis of different classes of flavonoids. The ^{13}C NMR spectra of some chalcones have been studied previously,[9–17] but no detailed discussion has been provided; in addition, they were of compounds that are not analogues of naturally occurring chalcones. The object of this work was to extend this range, and we now report on the structures and chemical shifts of 48 differently substituted chalcones of which some are found in nature. Chalcones often occur in minute amounts in nature, and it is important to provide comparable data in one solvent ($CDCl_3$) from which it is easy to recover the chalcone.

EXPERIMENTAL

Chalcones **1–48** (Table 1) were synthesized by the base-catalysed Claisen–Schmidt reaction of the appropriate benzaldehyde and acetophenone. The purities of all the compounds were checked from their melting points and spectral data. The ^{13}C NMR spectra were recorded on a Bruker AM-250 FT 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 μs pulse, 2-*s* repetition time, 1000–5000 transients, 32K data points used in each measurement, 142 85 Hz spectral width and 0.9 Hz per point digital resolution. Both ^{13}C proton-coupled and decoupled spectra were measured.

RESULTS AND DISCUSSION

The carbon chemical shifts in chalcones **1–48** (Table 1) are summarized in Tables 2 and 3. The proton noise decoupled spectra show the carbonyl carbon resonance in the range δ 186.95–193.86 ppm (Table 3), identifiable by its characteristic peak; C-α absorbs between δ 117.65 and 130.45 ppm and C-β between δ 137.90 and 145.77 ppm (Table 3). The low-field shift of C-β compared with that of C-α in all the compounds may be due to the electron-withdrawing benzoyl group attached to the neighbouring carbon atom.

The effect of oxygenated functions (—OH, $—OCH_3$, $—OCH_2O—$, $—OCH_2C_6H_5$) on the aromatic rings is characteristic in that the resulting quaternary carbon moves *ca* 20–35 ppm downfield. The carbon atoms *ortho* or *para* to the oxygenated carbon move upfield (by 5–15 ppm) whereas those at *meta* positions do not show any appreciable change.

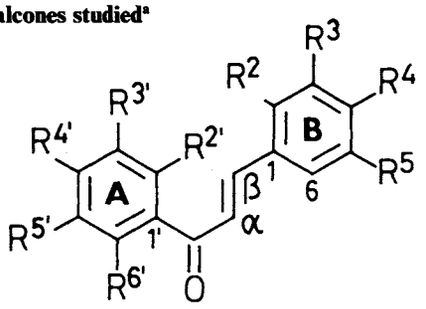
The C-1′ signal in **1–25**, having C-2′ oxygenation, appeared between δ 105.80 and 123.92 ppm; the large difference in these C-1′ δ values is due to the different oxygenation patterns in ring A. The C-1′ signal in **26–48**, lacking a substituent at C-2′ and having substituents at C-3′ and C-4′, appeared between δ 130.54 and 133.42 ppm. The C-5′ signal in **1** was at δ 123.03 ppm and in **2–5**, having only C-2′ and C-4′ oxygenation, at δ 105.07–107.63 ppm. Compounds **11–16**, having C-2′, C-4′ and C-6′ oxygenation, had a C-5′ signal between δ 91.04 and 91.93 ppm. In **6–10** (having a C-2, C-3′ and C-4′ oxygenation pattern), however, the C-5′ signal appeared between δ 102.46 and 104.55 ppm. In **22** (having a C-2′, C-3′, C-4′ and C-6′ oxygenation pattern), the signal was upfield at δ 87.22 ppm, and in **26–48** (having a C-3′ and C-4′ oxygenation pattern) was between δ 106.49 and 113.62 ppm. The C-6′ signal in **1–10**, which lacked a C-6′ substituent, appeared between δ 125.43 and 132.67 ppm and in **26–48** between δ 110.61 and 124.23 ppm. In **17** and **18**, lacking substitution at C-6′ but having oxygenated substituents at C-2′, C-4′ and C-5′, C-6′ absorbed at δ 112.64 and 110.98 ppm, respectively.

C-1 in compounds lacking a substituent at C-2 absorbed between δ 126.65 and 135.44 ppm and in **35–37** and **45–47**, having a C-2 and C-3 oxygenation pattern, in the range δ 121.28–129.53 ppm. In compounds having only C-2 and C-4 substituents, the C-1 signal was between δ 116.91 and 117.69 ppm. The C-6 signal was in the range δ 113.46–132.48 ppm; the large difference in its chemical shift in these compounds is due to the different oxygenation patterns in ring B.

Appropriate chemical shift values for the methoxy, methylenedioxy and benzylic carbons can be found in Table 2.

Reference Data

Table 1. Structures of the chalcones studied[a]



Compound	$R_{2'}$	$R_{3'}$	$R_{4'}$	$R_{5'}$	$R_{6'}$	R_2	R_3	R_4	R_5
1	OH	H	H	H	H	H	OH	OCH_3	H
2	OH	H	OCH_3	H	H	H	H	H	H
3	OH	H	OCH_3	H	H	H	OCH_3	OCH_3	H
4	OH	H	OCH_3	H	H	H	—OCH_2O—		H
5	OCH_3	H	OCH_3	H	H	H	—OCH_2O—		H
6	OH	OCH_3	OCH_3	H	H	H	H	OCH_3	H
7	OH	OCH_3	OBz	H	H	H	—OCH_2O—		H
8	OH	—OCH_2O—		H	H	H	H	OCH_3	H
9	OH	—OCH_2O—		H	H	H	OCH_3	OCH_3	H
10	OH	OCH_3	OCH_3	H	H	OCH_3	H	OCH_3	H
11	OH	H	OCH_3	H	OCH_3	H	H	H	H
12	OH	H	OH	H	OCH_3	OCH_3	H	OCH_3	H
13	OH	H	OCH_3	H	OCH_3	OCH_3	H	OCH_3	H
14	OH	H	OCH_3	H	OCH_3	H	H	OCH_3	H
15	OH	H	OCH_3	H	OCH_3	H	OCH_3	OCH_3	H
16	OH	H	OCH_3	H	OCH_3	H	—OCH_2O—		H
17	OH	H	OCH_3	OCH_3	H	H	OCH_3	OCH_3	H
18	OH	H	OCH_3	OCH_3	H	H	—OCH_2O—		H
19	OH	H	OCH_3	OCH_3	OCH_3	H	H	H	H
20	OH	H	OCH_3	OBz	OCH_3	H	OCH_3	OCH_3	H
21	OH	H	OCH_3	OBz	OCH_3	H	OCH_3	OBz	H
22	OH	OCH_3	OCH_3	H	OCH_3	H	H	OCH_3	H
23	OH	OCH_3	OCH_3	OCH_3	OCH_3	H	H	H	H
24	OCH_3	OH	OCH_3	OCH_3	OCH_3	H	H	H	H
25	OCH_3	OCH_3	OCH_3	OCH_3	OCH_3	H	H	H	H
26	H	OBz	OBz	H	H	H	H	H	H
27	H	OBz	OBz	H	H	H	H	OCH_3	H
28	H	OBz	OBz	H	H	OCH_3	H	H	H
29	H	OBz	OBz	H	H	H	OCH_3	OCH_3	H
30	H	OBz	OBz	H	H	H	OBz	OCH_3	H
31	H	OBz	OBz	H	H	H	—OCH_2O—		H
32	H	OBz	OBz	H	H	OCH_3	H	OCH_3	H
33	H	OBz	OBz	H	H	OCH_3	H	OBz	H
34	H	OBz	OBz	H	H	OBz	H	OBz	H
35	H	OBz	OBz	H	H	OH	OCH_3	H	H
36	H	OBz	OBz	H	H	OCH_3	OCH_3	H	H
37	H	OBz	OBz	H	H	OBz	OCH_3	H	H
38	H	OBz	OBz	H	H	OCH_3	H	H	OCH_3
39	H	—OCH_2O—		H	H	H	H	H	H
40	H	—OCH_2O—		H	H	H	H	OCH_3	H
41	H	—OCH_2O—		H	H	H	OCH_3	OBz	H
42	H	—OCH_2O—		H	H	H	—OCH_2O—		H
43	H	—OCH_2O—		H	H	OCH_3	H	OCH_3	H
44	H	—OCH_2O—		H	H	OCH_3	H	OBz	H
45	H	—OCH_2O—		H	H	OCH_3	OCH_3	H	H
46	H	—OCH_2O—		H	H	OBz	OCH_3	H	H
47	H	—OCH_2O—		H	H	OH	OCH_3	H	H
48	H	—OCH_2O—		H	H	OCH_3	H	H	OCH_3

[a] Bz = $OCH_2C_6H_5$.

Reference Data

Table 2. ^{13}C chemical shifts of the carbon atoms of ring B and of the methoxy, benzyloxy and methylenedioxy groups in the chalcones studied

Compound	C-1	C-2	C-3	C-4	C-5	C-6	$-OCH_3$	$-O-CH_2-O-$	$-OCH_2C_6H_5$
1	128.23	113.37	147.12	150.41	111.84	118.79	56.16		
2	134.79	128.94	128.48	130.63	128.48	128.92	55.60		
3	127.90	110.48	149.35	151.67	111.26	123.29	55.60, 55.02, 56.02		
4	129.96	107.62	148.50	150.01	108.73	125.36	55.57	101.71	
5	129.64	106.50	148.13	149.27	108.30	125.27	55.64, 55.40	98.55	
6	127.65	130.39	114.60	162.03	114.60	130.39	55.43, 56.16 60.59		
7	128.56	108.60	148.36	150.02	106.56	125.41	60.48		70.63
8	127.26	130.33	114.38	163.91	114.38	130.33	55.31	101.51	
9	127.58	110.25	148.01	149.27	111.13	123.38	55.95, 55.95	101.55	
10	116.91	161.61	98.74	163.04	105.82	131.31	55.55, 56.19, 55.69, 60.66		
11	134.63	128.87	128.35	129.65	128.35	128.87	55.57, 55.89		
12	117.37	160.55	98.44	163.43	106.30	130.51	55.20, 55.41, 55.60		
13	117.69	160.13	98.30	162.36	105.38	130.32	55.35, 55.35, 55.35, 55.60		
14	128.74	130.04	114.38	166.05	114.38	130.04	55.37, 55.37, 55.76		
15	129.28	111.47	149.84	151.77	111.97	122.92	55.66, 55.97, 56.21, 56.21		
16	130.17	106.45	148.10	150.69	106.71	124.91	55.50, 55.83	101.54	
17	128.19	111.45	149.70	152.10	111.74	123.05	56.14, 56.14, 56.31, 57.61		
18	129.21	106.66	148.38	149.99	106.63	125.34	56.09, 56.91	100.71	
19	135.44	128.94	128.42	130.24	128.42	128.94	56.09, 61.22 61.87		
20	128.27	109.33	150.33	153.50	112.35	122.51	55.98, 55.98 61.92		64.28
21	126.65	110.67	149.33	150.62	112.23	124.02	55.89, 55.89 61.90		70.80 70.80
22	128.22	130.17	114.38	161.50	114.38	130.17	55.37, 56.02 56.02, 60.70		
23	135.37	129.07	128.55	130.50	128.55	129.07	61.02, 61.35 61.61, 62.13		
24	134.47	128.94	128.61	130.63	128.61	128.94	61.15, 61.35 62.00, 62.26		
25	134.42	128.75	128.39	130.45	128.39	128.75	62.00, 62.00 61.30, 61.50		
26	134.94	128.77	128.22	130.20	128.22	128.77			71.09 70.72
27	127.65	129.97	114.24	161.39	114.24	129.97	55.25		71.09, 70.72
28	130.13	158.58	114.27	128.95	120.61	122.37	55.39		71.05, 70.70
29	128.01	114.53	149.28	151.34	113.10	121.32	56.00, 56.00		71.31, 70.90
30	128.51	113.09	149.83	150.46	111.00	123.21	56.11		71.27, 70.88 70.88
31	129.39	108.46	149.83	150.46	106.45	123.00		101.43	71.09, 70.72
32	117.16	162.73	98.31	160.16	105.24	130.60	55.31, 55.37		71.07, 70.72
33	117.27	161.78	99.11	160.04	105.97	130.48	55.29		70.93, 70.58 69.97
34	117.61	161.59	100.41	159.45	106.38	132.48			70.91, 70.70 70.43, 70.09
35	121.28	146.70	145.61	131.69	111.65	123.36	55.99		70.97, 70.67
36	129.04	153.00	148.61	123.14	114.27	124.89	55.64, 60.98		71.00, 70.63
37	129.53	153.13	148.61	123.20	113.88	124.10	55.76		75.20, 70.97 70.65

Table 2. (Continued)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	$-OCH_3$	$-O-CH_2-O-$	$-OCH_2C_6H_5$
38	124.49	153.30	112.23	116.68	148.54	113.59	55.59, 55.86		70.96, 70.59
39	134.74	128.69	128.14	130.16	128.14	128.69		101.65	
40	127.46	129.90	114.15	161.33	114.15	129.90	55.14	101.60	
41	128.08	113.23	150.23	151.29	110.54	122.54	55.82	101.69	70.59
42	129.32	108.50	148.12	151.43	108.26	124.35		101.47 101.70	
43	117.05	162.76	98.29	160.18	105.24	130.78	55.31, 55.37	101.58	
44	117.27	161.86	99.18	160.14	106.01	130.71	55.37	101.57	70.05
45	128.91	152.98	148.65	122.99	113.87	124.44	55.64, 61.05	101.63	
46	129.31	153.03	151.25	123.24	113.88	124.22	55.59	101.55	75.10
47	121.31	151.37	146.75	121.77	111.72	124.58	56.13	101.67	
48	124.32	153.20	112.12	116.69	152.95	113.46	55.45, 55.74	101.55	

Table 3. ^{13}C chemical shifts of the carbon atoms of ring A 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-α	C-β	C=(O)
1	114.67	163.72	118.67	136.14	123.03	129.63	118.52	145.42	192.23
2	114.12	165.98	101.12	166.70	107.63	131.21	120.30	144.28	191.78
3	114.19	166.14	101.12	166.63	107.56	131.15	118.09	144.58	191.73
4	114.19	165.99	101.12	166.70	106.78	131.15	118.35	144.28	191.70
5	121.05	163.95	101.35	164.05	105.07	132.67	124.63	141.60	190.26
6	115.89	158.51	137.26	158.41	103.08	125.82	118.03	144.57	187.33
7	115.66	158.48	136.21	157.45	104.55	125.52	118.04	144.45	192.21
8	117.22	161.83	134.57	153.75	102.46	125.43	117.65	144.70	192.58
9	117.30	153.82	127.58	151.68	102.52	125.47	117.93	145.06	192.54
10	115.68	158.10	137.36	160.63	102.91	125.80	118.63	140.54	186.95
11	106.71	162.71	93.97	168.45	91.93	166.31	127.18	142.26	191.00
12	105.80	163.57	96.37	168.36	91.51	164.91	125.34	137.90	192.85
13	106.40	162.70	93.72	168.22	91.04	165.69	125.28	138.14	192.93
14	106.29	161.43	93.97	168.39	91.25	162.54	125.23	142.39	192.63
15	106.90	162.71	94.40	168.82	91.64	166.54	126.06	142.87	188.02
16	106.60	162.53	93.98	168.38	91.25	166.05	124.78	142.32	188.39
17	112.38	161.99	101.11	156.31	142.13	112.64	118.58	144.67	188.41
18	111.73	161.65	101.61	156.93	141.66	110.98	118.23	144.28	191.28
19	108.79	162.80	96.64	160.26	128.42	155.07	126.60	143.11	192.90
20	109.09	162.71	96.54	160.07	128.22	155.24	122.78	143.59	192.11
21	111.07	162.70	96.54	160.33	128.23	153.50	124.31	143.42	190.78
22	106.91	158.25	130.95	158.57	87.22	159.42	125.11	142.78	193.27
23	111.31	151.04	128.55	138.62	137.45	155.07	126.73	143.69	193.86
24	113.60	163.03	135.14	137.00	137.63	157.83	128.61	145.77	192.30
25	123.92	153.84	142.99	143.21	140.08	143.27	130.45	142.69	
26	131.47	114.25	148.67	152.99	112.89	121.69	123.19	143.81	
27	131.75	114.24	148.62	152.79	112.91	119.26	123.01	143.67	188.43
28	131.39	111.08	148.61	152.76	110.97	122.99	123.15	139.38	188.98
29	131.91	111.20	148.85	153.03	110.31	119.71	122.94	144.16	188.60
30	131.89	114.48	148.84	153.00	113.62	119.83	122.65	144.05	188.51
31	131.65	114.28	148.84	153.00	112.93	110.61	124.86	143.59	188.18
32	132.13	114.31	148.58	152.58	112.94	122.97	119.91	139.50	189.03
33	131.99	114.14	148.49	152.50	112.79	122.92	119.87	139.32	188.86
34	132.02	113.91	148.61	152.45	112.87	122.95	120.57	139.87	188.87
35	131.69	114.17	148.53	152.77	112.81	123.20	122.95	139.13	189.03
36	130.54	113.91	148.71	152.88	112.88	119.44	123.89	138.54	188.50
37	131.50	114.04	152.72	153.07	112.81	120.11	123.33	139.18	188.73
38	131.62	114.15	152.74	153.04	112.78	122.50	123.13	139.06	188.77
39	132.69	108.16	148.05	151.47	107.66	121.43	124.44	143.93	187.88
40	132.98	108.15	147.99	151.28	107.62	119.08	124.23	143.79	187.93
41	132.92	108.15	149.53	147.99	107.62	119.46	124.27	144.08	187.92
42	133.00	107.73	148.25	151.44	106.49	119.58	124.91	143.92	187.93
43	133.42	108.30	147.95	151.11	107.65	124.22	119.85	139.78	188.72
44	133.39	108.29	147.95	151.12	107.50	124.23	119.96	139.70	188.67
45	132.84	108.18	148.04	151.41	107.67	119.33	123.95	138.75	188.25
46	132.74	108.14	147.94	147.21	107.53	120.05	124.44	139.34	188.37
47	133.18	108.43	145.67	148.08	107.75	119.58	123.18	139.44	188.84
48	132.86	108.15	147.91	151.23	107.53	122.23	124.23	139.14	188.25

Reference Data

References

1. O. G. deLima, J. F. deMello, J. S. C. deCoelho, F. D. deLyra, M. H. F. deAlbuquerque, G. B. Marini-Bettolo, G. D. Monache and F. D. Monache, *Farmaco, Ed. Sci.* **30**, 326 (1975); *Chem. Abstr.* **83**, 91495 (1975).
2. K. Kyogoku, K. Hatayama, S. Yokomori and T. Seki, *Jpn. Kokai* 75140430 (1975); *Chem. Abstr.* **84**, 121467 (1976).
3. M. Sasajima, S. Nakane, R. Saziki, H. Saotome, K. Hatayama, K. Kyogoku and I. Tanaka, *Nippon Yakurigaku Zasshi* **74**, 897 (1978); *Chem. Abstr.* **90** 197536 (1979).
4. K. Kyogoku, K. Hatayama, S. Yokomori, R. Saziki, S. Nakane, M. Sasajima, J. Sawada, M. Ohzeki and T. Tanaka, *Chem. Pharm. Bull.* **27**, 2943 (1979).
5. V. S. Kamat, F. Y. Chou, I. Kubo and K. Nakanishi, *Heterocycles* **15**, 1163 (1981).
6. D. S. Bhakuni and R. Chaturvedi, *J. Nat. Prod. (Lloydia)* **47**, 585 (1984).
7. K. Hanemann, H. Schubert, D. Demus and G. Pelzl, *East Ger. Pat.* 115283 (1975); *Chem. Abstr.* **87**, 76418 (1977).
8. M. Kato, M. Hasegawa and T. Ichijyo, *US Pat.* 3873500 (1975); *Chem. Abstr.* **83**, 29065 (1975).
9. E. Solčániová, Š. Toma and S. Gronowitz, *Org. Magn. Reson.* **8**, 439 (1976).
10. F. Membrey and J. P. Doucet, *J. Chim. Phys. Chim. Biol.* **73**, 1024 (1976).
11. K. R. Markham and B. Ternai, *Tetrahedron* **32**, 2607 (1976).
12. A. Pelter, R. S. Ward and T. I. Gray, *J. Chem. Soc., Perkin Trans. 1* 2475 (1976).
13. G. Musumarra and F. P. Ballistreri, *Org. Magn. Reson.* **14**, 384 (1980).
14. G. Musumarra, S. Wold and S. Gronowitz, *Org. Magn. Reson.* **17**, 118 (1981).
15. A. Patra, A. K. Mitra, A. Bhattacharya and N. Additya-Chaudhury, *Org. Magn. Reson.* **18**, 241 (1982).
16. M. Szajda, *Magn. Reson. Chem.* **27**, 399 (1989).
17. K. Hayamizu, M. Yanagisawa, T. Ishii, A. Yabe, O. Yamomoto, M. Nakayama and A. Hayashi, *Magn. Reson. Chem.* **27**, 899 (1989).

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