

## Carbon-13 NMR Spectra of some 11-Membered Ketolactones and the Related 2,2-Dialkyldimedones

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Neste trabalho são analisados os espectros de  $^{13}\text{C}$  de algumas cetolactonas sintéticas de 11-membros (6-alkil-3,3-dimetil-5-oxo-8,9-benzodecenolídeos, **1**; 6-alkil-3,3-dimetil-5,9-dioxodecanolídeos, **2a**, e monocetais correspondentes, **2b**) bem como de suas precursoras 2,2- dialquildimedonas (**3a - g**).

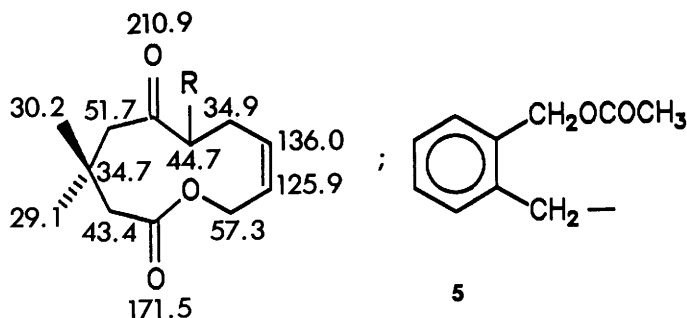
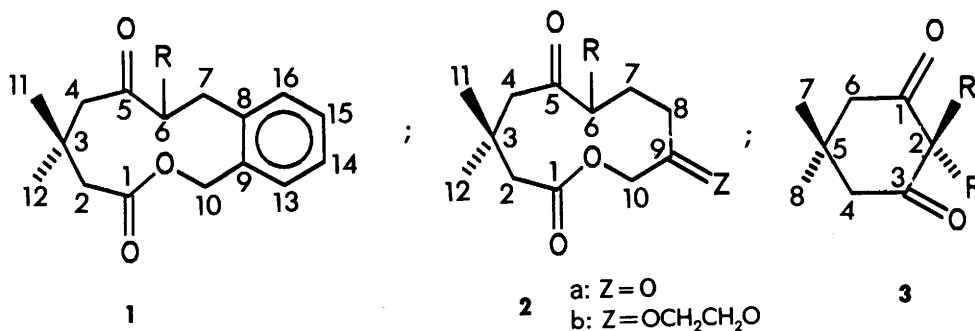
$^{13}\text{C}$  chemical shifts in the synthetic 11-membered ketolactones (6-alkyl-3,3-dimethyl-5-oxo-8,9-benzodecenolides, **1**; 6-alkyl-3,3-dimethyl-5,9-dioxodecanolides, **2a**, and the corresponding 9-ketals, **2b**) as well as the related 2,2- dialkyldimedones (**3a - g**) have been assigned.

**Key words:** ketolactones,  $^{13}\text{C}$  NMR spectra, dimedones, 2,2-dialkyl; cyclohexanediones.

### Introduction

Some years ago, we described the carbon-13 NMR spectra of several 9 to 16-membered ketolactones and the related 2,2-dialkyl-5,5-dimethylcyclohexane-1,3-diones (**2**,

2-dialkyldimedones)<sup>1,2</sup>. We now report the  $^{13}\text{C}$  chemical shifts of some new members of the title compounds (**1-3**), synthesized earlier in our laboratories<sup>3,4</sup>.



R = CH<sub>3</sub>(16.8): **4**

**Table 1.**  $^{13}\text{C}$  chemical shifts of 6-alkyl-3, 3-dimethyl-5-oxo-8, 9-benzo-decenolides (1)

Carbon, *	Substituent (R)		
	Methyl	Allyl	Benzyl
			38.30, CH <sub>2</sub>
			139.83, C-1
		H <sub>2</sub> C 	36.53, C-2
	18,08	HC 	136.00, C-3
	CH <sub>3</sub> , q	H <sub>2</sub> C	117.34, C-4
C - 1, s	171.22		171.29
C - 2, qAB	43.59		43.65
C - 3, s	33.82		33.78
C - 4, t	51.84		52.76
C - 5, s	211.04		210.36
C - 6, d	49.20		54.91
C - 7, t	37.92		35.12
C - 8, s (143.1), (141.1)	141.02		141.14
C - 9, s (140.1), (135.5)	133.88		133.90
C - 10, t	64.35		64.38
C - 11, q	30.26		30.26
C - 12, q	28.80		28.65
C - 13, d (127.5)	130.17		130.08
C - 14, d (125.9)	126.34		126.31
C - 15, d (127.5)	129.31		129.36
C - 16, d (128.1)	131.63		131.58

\* s, d, t, q and qAB denote singlet, doublet, triplet, quartet and AB type quartet, respectively, as observed in SFORD spectra; calculated values in parenthesis (see text).

**Table 2.**  $^{13}\text{C}$  chemical shifts of 6-alkyl-3, 3-dimethyl-5, 9-dioxodecanolides (2a) and the 9-ketal (2b)

Carbon, *	Substituent (R)							
	Allyl		Benzyl		Allyl		Benzyl	
	H <sub>2</sub> C 	33.76	CH <sub>2</sub>	35.55	CH <sub>2</sub> 	33.72	CH <sub>2</sub> , 	35.81
	HC 	134.91	C-1,	138.81	HC 	135.73	C-1, 	139.66
	H <sub>2</sub> C	117.33	C-2,	128.76	CH <sub>2</sub>	116.64	C-2, 	128.82
			C-3,	128.63			C-3, 	128.43
			C-4,	126.56			C-4, 	126.18
	Z = O		O		(OCH <sub>2</sub> ) <sub>2</sub>	64.67	(OCH <sub>2</sub> ) <sub>2</sub>	64.47
C - 1, s	170.67		170.64			171.44		171.39
C - 2, qAB	43.36		43.34			43.48		43.69
C - 3, s	33.06		32.97			33.23		33.22
C - 4	49.45, ~t		49.97, qAB			49.16, t		50.17, qAB
C - 5, s	210.23		210.34			210.23		210.54
C - 6, d	51.44		53.26			51.79		53.68
C - 7, t	25.18		25.05			24.60		24.55
C - 8, t	34.89		34.81			29.72		29.98
C - 9, s	207.91		207.70			109.49		109.85
C - 10, t	67.20		67.12			64.53		64.68
C - 11, q	30.47		30.44			30.38		30.60
C - 12, q	29.72		29.51			29.12		28.69

\* Multiplicity observed in SFORD spectra.

Table 3. <sup>13</sup>C chemical shifts of 2,2-dialkyldimedones (3a - g)

N°	Substituents (R, R')*											
3a	CH <sub>3</sub> (20.44) 2-(Acetoxymethyl) benzyl (5): CH <sub>2</sub> (39.37), C-1/C-2 (135.19), C-3 (130.32), C-4 (127.47), C-5 (128.28), C-6 (130.92), H <sub>2</sub> C-O (63.86), CO <sub>2</sub> R (170.52), CH <sub>3</sub> (20.92).											
3b	H <sub>2</sub> C — CH = CH <sub>2</sub>		H <sub>2</sub> C — CH <sub>2</sub> — CO — CH <sub>2</sub> — OCO — CH <sub>3</sub>									
	39.75	131.67	119.81	26.05	33.76	202.72	67.85	170.08	20.39			
3c	Benzyl: CH <sub>2</sub> (41.92), C-1 (135.46), C-2 (130.77), C-3 (128.23), C-4 (127.20).											
			H <sub>2</sub> C — CH <sub>2</sub> — CO — CH <sub>2</sub> — OCO — CH <sub>3</sub>									
			27.46				33.82	202.57	67.81	170.04	20.35	
3d	H <sub>2</sub> C — CH = CH <sub>2</sub>		H <sub>2</sub> C — CH <sub>2</sub> — CO — CH <sub>2</sub>									
	40.50	131.31	119.92	25.58	33.39	208.61	67.97					
3e	H <sub>2</sub> C — CH = CH <sub>2</sub>		H <sub>2</sub> C — CH <sub>2</sub> — C(OCH <sub>2</sub> ) <sub>2</sub> — CH <sub>2</sub> OH									
	38.41	132.49	119.32	28.06	28.59	109.94	65.43	64.91				
3f	Benzyl: CH <sub>2</sub> (41.25), C-1 (136.27), C-2 (131.03), C-3 (128.06), C-4 (126.93).											
			H <sub>2</sub> C — CH <sub>2</sub> — C(OCH <sub>2</sub> ) <sub>2</sub> — CH <sub>2</sub> OH									
			28.27				28.97	109.93	65.48	64.99		
3g	Benzyl: CH <sub>2</sub> (41.05), C-1 (136.34), C-2 (131.06), C-3 (128.05), C-4 (126.91).											
			H <sub>2</sub> C — CH <sub>2</sub> — C(OCH <sub>2</sub> ) <sub>2</sub> — CH <sub>2</sub> — OCO — CH <sub>3</sub>									
			28.21				29.03	108.29	65.41	64.85	170.41	20.83
N°	C-1,3, s	C-2 s	C-4,6, t	C-5, s	C-7, q	C-8, q						
3a	210.65	64.51	52.87	30.20	29.50	28.04						
3b	208.51	67.42	51.56	30.69	29.12	28.16						
3c	209.30	68.18	52.22	30.32	28.69	28.38						
3d	208.45	67.54	51.47	30.70	29.40	27.88						
3e	208.87	67.86	51.61	30.65	29.12	28.75						
3f	209.74	68.72	52.43	30.21	29.66	29.44						
3g	209.54	68.48	52.47	30.15	29.93	29.59						

\* For the sake of simplicity, the observed multiplicity (SFORD) is omitted for the substituents.

## Experimental

The proton noise-decoupled and the single-frequency off-resonance decoupled (SFORD) <sup>13</sup>C NMR spectra of 0.5 - 1.0 molar solutions in CDCl<sub>3</sub>, containing 10% TMS (v/v), were recorded on a Bruker HFX-10 spectrometer at 22,63 MHz, using standard parameters, a pulse width of 12 μs, acquisition time of 0.82s, and without any pulse delay. The line positions and intensities were obtained relative to internal TMS. The reported values (δ p.p.m.) have been rounded to the nearest second decimal place.

## Results and Discussion

6-Alkyl-3,3-dimethyl-5-oxo-8,9-benzodecenolides (1: R = CH<sub>3</sub>, CH<sub>2</sub>-CH = CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>)<sup>3</sup>: The <sup>13</sup>C chemical shifts of three ketolactones examined in this series could be readily assigned (Table 1) on the basis of chemical shift rules, aided by the multiplicity observed in the SFORD spectra, and by comparison with the <sup>13</sup>C chemical shifts already described for the three analogous 8-decenolides 4 (R = CH<sub>3</sub>, CH<sub>2</sub> = CH-CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>)<sup>1</sup>. As expected, the most affected positions are α or β to the benzo- group, while the rest of the C-atoms absorb at almost identical

positions in both series. For a quick inspection, the <sup>13</sup>C chemical shifts for the 6-methyl analogue are shown along with the structure 4 (R = CH<sub>3</sub>)<sup>1</sup>. Moreover, comparison of these chemical shifts (Table 1) with those of the related dimedones (3; Table 3) reveals that the changes observed on lactonization are consistent with the conversion of a ketonic function into the lactonic one as well as the consequent alterations in the pattern of substitution; for instance, compare the values for C-4/6 in the dimedones with the values of C-2 and C-4 in the lactones.

Due to the lack of shielding parameters for the appropriate substituents on the benzo-group, the figures shown in parenthesis (Table 1) were obtained by using the values for ethyl and the hydroxymethyl groups<sup>5</sup>. The second calculated figures take into account the shielding of C-8 by the γ-carbonyl group (-2 p.p.m.) and that of C-9 due to the acylation of the hydroxymethyl group; for the latter case, compare the quaternary C-atoms in benzyl alcohol (δ140.8 p.p.m.) and benzyl acetate (δ136.2 p.p.m.)<sup>6</sup>. In spite of the *ortho*-substitution in the present series, the agreement between the calculated and the observed values is very satisfactory.

6-Alkyl-3,3-dimethyl-5,9-dioxodecanolides (2a) and the 9-Ketals (2b)<sup>4</sup> (Table 2): <sup>13</sup>C chemical shifts of four ketolactones examined in this group were also easily assigned with the help of noise-decoupled and SFORD spectra. The comparison of these values (Table 2) with those of the dimedones (Table 3) bears out again the arguments developed in the previous case. For instance, the tetrasubstituted C-2 in the dimedones ( $\delta$  67.5 - 68.5 p.p.m.), flanked by two carbonyl groups, becomes a methine in the lactones and absorbs at  $\sim$  15 p.p.m. upfield, as revealed by a doublet in the SFORD spectra.

The <sup>13</sup>C chemical shifts of 2,2 dialkyldimedones (3) are shown in Table 3. The availability of previous <sup>13</sup>C data, for several related dimedones<sup>2</sup>, was very helpful in the present case. The only point worth mentioning concerns the very closely spaced signals due to side-chain methylenes and the 5,5-dimethyl groups in compounds 3e, f, g; this rendered their SFORD spectra rather equivocal for a definite assignment. However, the first four entries (3a - d) being unambiguous, the trends established in these examples were followed in the case of the last three compounds.

Finally, we would like to point out the second-order effects observed in the SFORD spectra of compounds examined in the present study<sup>7</sup>. Thus, the allylic groups and, to a smaller extent, the benzylic carbons showed a further fine splitting or broadening of the expected multiplets, which was helpful in their assignment. Furthermore, in both the sets of ketolactones (1, 2a, 2b), C-2 was split as an AB type quartet (qAB), while C-4 showed this type of quartet only in a few cases, as indicated in Table 2.

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